SOME ASPECTS OF THE SYNTHESIS AND POLYMERISATION OF 1,3,2-DIOXATHIOLAN-4-ONE-2-OXIDES.

by

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SUMMARY

A number of 1,3,2-dioxathiolan-4-one-2-oxides (α-hydroxy carboxylic acid anhydrosulphites) have been prepared from disubstituted α -hydroxy-carboxylic acids and from α-hydroxy-cycloalkanoic acids. The thermal polymerisation of these compounds has been studied in a variety of solvents below 130°.

All of the derivatives show a general pattern of kinetic behaviour. In dry non-hydroxylic solvents the first order rate determining step in the sequence of reactions leading to polymer formation is a primary ring scission reaction in which a reactive intermediate is formed and sulphur dioxide eliminated. This intermediate, which is formally depicted as an α -lactone, then takes part in a very rapid chain propagation process, the individual steps of which govern the molecular weight distribution of the polymer.

Molecular weights of the polymers are controlled by adventitious traces of water and chlorinated by-products. The latter can be removed by a suitable combination of purification procedures such that in some cases a desirable level of monomer purity is reached.

An unusual feature of this polymerisation is the effect of ring substitution on the rate of polymerisation. In the dialkyl series the rate of polymer formation increases with increasing substituent size, whilst in the spirocycloalkyl series an additional substituent effect, conveyed ring strain, causes the cyclobutane derivative to decompose most rapidly. This compound deviates from the general reaction pattern in that the six membered glycollide as well as polymer is a principal product. In addition a bimolecular hydroxyl initiated decomposition is observed to occur.

An additional feature is the onset of a first order fragmentation

reaction which leads to carbon monoxide, sulphur dioxide and ketone formation. However, this reaction is not significant until temperatures in excess of 150°.

Several novel poly α-esters have been prepared and their crystalline and thermal behaviour briefly examined.

ACKNOWLEDGEMENTS

My sincere thanks go to Dr. B.J. Tighe for his advice and encouragement over the past three years.

I wish to acknowledge the help of technicians in the Chemistry Department for providing various service analysis.

In addition I thank my wife Jane for typing this thesis.

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G.P. BLACKBOURN

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CORRIGENDUM

Page 1, Second Paragraph, Line 3.

For :-

(for example, Penton and the β-polyester derived from 3,3-bischloromethyl substituted oxetane and propiolactone respectively).

Read :-

(for example, Penton from 3,3-bischloromethyl oxetane and the β-polyester from, α,α-bischloromethyl propiolactone).

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1. INTRODUCTION

The polymerisation of cyclic monomers has become increasingly important to large segments of the polymer and chemical industries. Nylon 6, a commercial fibre forming polymer, and polyformaldehyde, an engineering plastic, are derived from the cyclic monomers caprolactam and trioxan respectively, whilst polymers derived from 1,2-epoxide compounds have long had numerous uses in the plasticiser, surface coating and urethane foam, fields. A recent publication[1] covers many aspects of the ring-opening polymerisation of well established systems such as, epoxy compounds, lactones, lactams, formals, and N-carboxy-α-amino acid anhydrides.

This type of polymerisation provides an alternative route to many condensation polymers, and has realised some which otherwise have only been theoretical concepts (for example, Penton and the β-polyester derived from 3,3-bischloromethyl substituted oxetane and propiolactone respectively). The mode of polymer formation resembles addition rather than condensation polymerisation however, since addition of monomer (but never larger units) to the growing polymer chain occurs throughout the reaction. Thus problems associated with polycondensation, such as the non-attainment of high molecular weights because of chain end dilution and unfavourable condensation equilibria at high conversion, are not encountered, but unfortunately in some instances they are replaced by unfavourbale monomer, oligomer, and polymer equilibria.

Ring-opening polymerisation is observed to occur with two distinct types of cyclic monomer, inthat the whole, or alternatively only part of the ring is incorporated into the growing chain.

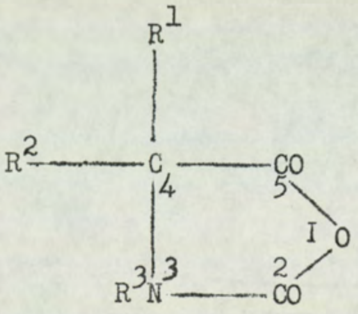
The majority of ring-opening polymerisations, including those commercial processes which have been referred to earlier, fall into the former category and have been widely studied. The work of Carothers[2] and Hall[3] provided a qualitative measure of polymerisability of cyclic carbonates, lactones, and lactams, in terms of ring size and substitution in or on the ring. A quantitative appraisal of these reversible systems by Dainton and Ivin[4] explained, in thermodynamic terms, concepts such as, the ceiling temperature, stabilisation of rings by alkyl substitution, and the fact that five and six membered rings are more stable than those containing three, four or seven members. Small[5] postulated that incorporation of hetero-groups such as (C—O—C) or (C—NH—C) does not significantly alter the internal energy of a ring system. Introduction of groups with bond lengths and angles which differ significantly from those of a ring methylene, for example (—O—CO—) or (—O—SO—) have a more marked effect, however, especially when dipole-dipole interactions occur. The ring is less stable because conformational rearrangement is required to minimise the overall contribution of bond strain, non-bonded interactions, and angle strain such that the resultant conformers are of higher energy.

Although the rate and mode of initiation and propagation are important in these systems, the prime factor which enables successful polymerisation is the choice of conditions in which the ring-chain equilibria lies in favour of polymer. As cyclic monomers of this type are fairly stable to heat, polymerisation by thermal methods alone are not often used, because the temperature required to achieve a reasonable polymerisation rate approaches the ceiling temperature. Ring systems which when opened concurrently lose a molecular fragment are not subject to such equilibrium conditions.

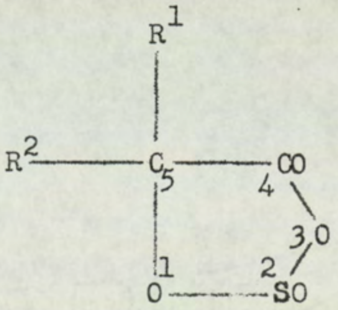
The application of heat alone is known to lead to ring-opening, and in some cases polymerisation, of both types of cyclic monomer. In such reactions the site of scission is made labile by bond stretching, bending, and/or polarisation, and although a functional group, such as a carbonyl, may increase the ease of ring-opening, it is because of the necessary conformational reorganisation into states of higher energy, and not chemical reactivity, that this occurs. Ring cleavage may occur without further fragmentation, as in the isomerisation of cyclopropane to propene[6], or eliminate a small inorganic fragment subsequent to bond scission, for example, sulphur dioxide from butadiene sulphone[7]. In special cases where ring contraction accompanies elimination, the reaction is termed an 'extrusion reaction'[8], and is typified by the pyrolysis of six membered ring sultones to a furan and sulphur dioxide[9].

In cases where ring-opening reactions are achieved by direct bimolecular attack, the role of alkyl substitution on the ring characteristics has received much attention. Thus a systematic study of, the hydrolysis of five membered ring sultones[10], the ethylene glycol initiated polymerisation of ε-caprolactones[11], and pivalate anion initiated polymerisation of β-lactones[12], has shown that an increase in ring substituent size, or number of substituents, is parallelled by increased ring stability. Steric factors contributing to increased stability in these cases are, obstruction of the reaction path, partial confinement of a large leaving group and restricted bond movements in intermediates formed as a result of ring cleavage. In cases where the reaction centre is several atoms away from the site of substitution, steric obstruction is greatly reduced and a measure of ring strain contributions is obtained. Searles[13] studied a series of β-dialkyl- and β-spirocycloalkyl-oxetanes and showed the latter to exert more strain on the oxetane ring. However, other workers[14,15] have shown that boron trifluoride catalysed polymerisation of dimethyl, spirocyclopropyl, and spirocyclohexyl β-substituted oxetanes occur at approximately the same rate. Electron density distribution is a more important feature in this polymerisation since bischloromethyl substitution reduces the basicity of the oxetane oxygen and lowers the rate of polymer formation by a factor of two hundred.

With the exception of anhydrocarboxy derivatives of α-aminocarboxylic acids (I; NCA's), ring chain polymerisation which involves elimination of a small inorganic fragment has not been studied in detail. NCA's received much attention in the 1950's because they were potential precursors for α-polypeptides. This class of polymer was considered potentially useful for synthetic silks. This thesis is primarily concerned with the synthesis and polymerisation of a related class of cyclic monomer expressed by the general formula (II).



(I)



(II)

1,3,2-dioxathiolan-4-one-2-oxides (II) are more widely known as α-hydroxycarboxylic acid anhydrosulphites, the name of the hydroxy acid being used as a prefix to identify individual members (for example, glycollic, lactic, and α-hydroxyisobutyric, acid anhydrosulphites, (II, $R^1 = R^2 = -H$; II, $R^1 = -H$, $R^2 = -CH_3$; II, $R^1 = R^2 = -CH_3$; respectively).

The unusual feature of polymerisation of monomers of types (I) and (II) is that the reactions are irreversible. Therefore polymerisability is not controlled by thermodynamic equilibria between monomer-oligomer-polymer. A clear recognition of this difference is not apparent in much of the literature. Thus generalisations which apply only to monomers which undergo reversible polymerisation have been applied to all ring-opening polymerisation reactions (for example, see reference 1, Introduction).

The polymerisation of NCA's has been reviewed in detail[1,16], and because they closely resemble anhydrosulphite structures, their kinetic behaviour is of interest, and useful for comparison. Polymerisation of NCA's in the presence of sub-stoichiometric amounts of primary or secondary amine (normal amine initiation) is a reaction which has been extensively studied[17,18]. The amine reacts directly with the anhydride at the C-5 carbonyl to form an intermediate which then undergoes bond scission and elimination to give α-aminoacid amide and carbon dioxide. The regenerated amino-group then reacts further with NCA to give dimer by means of which further propagation occurs. Structural variations on either the initiating amine or NCA were found to markedly affect the rate of initiation and/or polymerisation. Thus for a given initiator, alanine NCA (I; $R^1 = -CH_3$, $R^2 = -H$) is initiated much faster than that of α-aminoisobutyric acid (I; $R^1 = R^2 = -CH_3$), which has been attributed to steric interference in the latter[19]. As the amino-group is even more sterically hindered when it forms the terminal group of a polymer chain, subsequent propagation reactions involving the isobutyric derivative are infinitesimally slow.

Among several anomalies which have appeared during studies of normal amine NCA polymerisations are; carbon dioxide catalysis of sarcosine NCA polymerisation[18], attributed to carbamic acid formation, and 'wrong addition' to the C-2 carbonyl to form ureido acids, as evidenced in the decomposition of glycine NCA with basic amines[20].

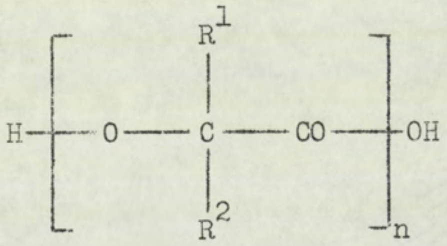
Initiation by tertiary amines, strong bases, or salts, involve different modes of mechanism. For example, in the first mentioned, hydrogen abstraction from the -NH- function gives an anionic species which is available to attack anhydride to form a dimeric anion, which in turn decarboxylates to give an amino-terminated dimer[21].

The preparation of anhydrosulphite derivatives (II) was first described by Blaise and Montagne[22] who detailed methods of their synthesis from glycollic, lactic, and α-hydroxyisobutyric acids. Further investigation showed that in the presence of nucleophilic reagents sulphur dioxide was liberated, alcohols, amines and water gave esters, anilides and parent hydroxy acid respectively. Under the action of heat alone sulphur dioxide was liberated leaving a polymeric gum.

Since this early work only eleven publications have described aspects of anhydrosulphite polymerisation.

Alderson[23], of Du Pont Limited, showed that controlled elimination of sulphur dioxide from α-hydroxyisobutyric acid anhydrosulphite (HBAS) in dry inert solvents, and in the absence of initiators, led to poly α-ester (III; $R^1 = R^2 = -CH_3$) of high molecular weight (M_n 108,000). The presence of moisture, however, drastically lowered molecular weight. Rose[24], of I.C.I. Limited, attempted to extend the series of anhydrosulphites using Alderson's techniques, but was not successful in obtaining good polymer from any but the HBAS system. Neither author proposed a polymerisation mechanism.

The industrial interest in the HBAS system presumably arose because of the economic viability of the precursor acid, which is available from acetone via the cyanohydrin, or by elemental addition of water to methyl methacrylate.



$$H-\left[O-\overset{R^1}{\underset{R^2}{C}}-CO\right]_n-OH$$

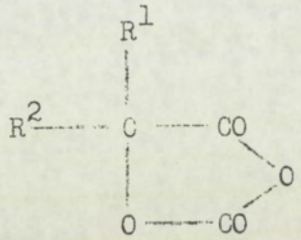
(III)

Ballard and Tighe[25,26] investigated the polymerisation of, HBAS, glycollic and lactic, acid anhydrosulphites (i.e. GAAS and LAAS), and proposed that two mechanisms could operate. In the first, ring-opening both at initiation and during propagation was accomplished by direct nucleophilic attack at the C-4 carbonyl of the anhydrosulphite ring, in a manner similar to normal amine initiation of NCA's. At temperatures below 60°steric interference was evidenced, since under the same conditions the order of polymerisability was GAAS > LAAS >> HBAS. At temperatures in the region of 100°, however, HBAS polymerised readily. A kinetic study of the HBAS reaction showed the rate determining step to be a thermal unimolecular process in which sulphur dioxide was eliminated. Subsequent initiation or propagation occured in a conventional way by rapid bimolecular nucleophilic attack on the residuum, which was proposed as an α -lactone ring. Polymerisation of HBAS therefore proceeds via a thermal extrusion reaction.

There are evidently two differences between the polymerisability of NCA's and anhydrosulphites. First the terminal group of the resultant polypeptide is of higher nucleophilicity than the terminal hydroxyl group of the poly α-ester, thus rendering direct attack on the anhydride by the former more effective. Secondly when direct bimolecular attack is greatly quenched by steric factors the architecture of the anhydrosulphite ring provides an alternative mode of polymerisation which is energetically feasible at workable temperatures.

Any other reports of thermal extrusion polymerisation are unknown, and although NCA's can be polymerised thermally, the reaction has been suggested to occur via an isomeric open chain isocyanate-carboxylic acid form[27].

The effect of substituents on thermal unimolecular ring-opening reactions is less fully reported than for bimolecular reactions, and there are few reports of alkyl substituted compounds. In this context it has been shown that propylene sulphite and 2,2-bis-chloromethyl propylene sulphite pyrolyse smoothly at 200 and 500° respectively whereas 2,2-dimethyl propylene sulphite resists pyrolysis even at 500°[28]. Heterolytic fission followed by electronic rearrangements are the proposed mechanisms operating in these reactions. Anhydrocarboxy derivatives of α-hydroxy acids (IV) show a similar trend. Thus the derivative of glycollic acid[29] decarboxylates to give polymer after 18 hours at 100° whilst that of α-hydroxyisobutyric acid[30] requires several weeks to fully convert to polymer at the same temperature. Methyl substituted butadiene sulphones exhibit varied stabilities when compared with the parent compound. β-Substitution stabilises the ring, but in contrast α-substitution enhances thermal dissociation because of electron release towards, and steric interaction with, the sulphone function[31].



(IV)

Recent papers from Japan claim room temperature polymerisation of HBaS using tertiary amines, tertiary amides, or dimethyl sulphoxide, but the products were of low molecular weight when compared with those obtained by thermal polymerisation. A mechanism involving ring-opening by direct attack at the C-4 carbonyl to form a zwitterion intermediate is proposed[32]. Asymmetric selective polymerisation is claimed if unsymmetrically substituted anhydrosulphites (for example, II; $R^1 = -CH_3$, $R^2 = -CH_2Cl$) are catalysed with optically active tertiary amines such as brucine, although the optically active polymers isolated were of low specific rotation[33].

Polymerisation of similar cyclic systems, such as anhydrocarboxy or anhydrosulphite derivatives of α-thioacids appear to have received little attention. The anhydrocarboxy derivatives of α-hydroxy acids have been investigated[29,30], but in general lack of suitable initiators, and their superior thermal stability does not lend them to polymer forming reactions.

Linear aliphatic polyesters have not enjoyed the wide application as a base material as have polyethylene terephthalate and unsaturated polyesters. As an ancillary material, however, theyhave found extensive uses as, polymeric plasticisers, and as intermediates in the preparation of polyurethanes for use as elastomers or spandex fibres. In general they have good oxidation and ozone resistance, but their resistance to alkaline hydrolysis is low and they are characterised by low melting points.

Carothers, in his early work studied many aspects of the preparation of aliphatic polyesters and the mechanisms involved therein. Only in the last fifteen years has this work been extended in any detail this being mainly due to the recent commercial availability of monomers such as ε-caprolactone and β-propiolactones.

Preparation of β-polyesters from the latter has received much industrial interest (I.C.I. Limited[34], Du Pont Limited[35], Royal Dutch Shell Limited[36]) since the properties of the polymers are far superior when compared with those having a larger aliphatic portion in the main chain. Thus polyα,α-dimethylβ-propiolactone can be melt spun at 280° to give hydrolysis resistant fibres of good dyeability and exceptional work recovery at low extension.

Polyα-esters (III) have similar potential since they are high melting, and when substituted, hydrolysis resistant[23]. Poly (oxyacetyl) (III; $R^1 = R^2 = -H$), and poly (oxy(methyl acetyl)) (III; $R^1 = -CH_3$, $R^2 = -H$), otherwise known as polyglycollide and polylactide respectively, have been described as potentially useful in the field of films, fibres, coatings, and surgical inserts[23,37,38].

The methods available for the preparation of polyα-esters are not numerous and often result in poor yields of polymer and/or low molecular weights. Methods such as self-condensation of acids or metal salts involve polymerisation in the melt at temperatures in the region of 200°, and are accompanied by degradation reactions and discolouration. The apparently attractive polymerisation of the appropriate glycollide by suitable catalysts, at low temperatures, is limited to simple derivatives monosubstituted at the 1, and 4 positions[3], although copolymers derived from monosubstituted, and a symmetrical disubstituted, glycollide may be prepared, providing that at least fifty mole per cent of the former is present[39]. Alternative routes via decomposition of the appropriate tertiary butyl per ester[40] or by oxygenation of the appropriate ketene[41] are limited by the feasibility of preparing the required intermediates.

The controlled thermal extrusion of sulphur dioxide from anhydrosulphites in solution, is potentially the best general method for the preparation of poly α-esters, particularly as the polymerisation (of HBaS) proceeds at convenient rates at temperatures below 100°.

1.1 Scope and Object of the Present Work

The chemistry and polymerisation of anhydrosulphites has not been extensively studied. Ballard and Tighe[25,26] have shown that thermal polymerisation of glycollic, lactic and α-hydroxyisobutyric acid, anhydrosulphites, is not controlled by a common mechanism, and that in the last case a thermal extrusion process predominates. The work to be presented herein investigates the possibility of extending studies of the alkyl substituted series of anhydrosulphites to higher members and providing a spirocycloalkyl series for comparison.

Other anhydrosulphites have been reported by Rose[24], but their purity was suspect, yields and polymerisability were poor. This may be due to the chemistry of the systems and/or experimental method. It is the first aim of this project to evaluate the synthetic feasibility of anhydrosulphites and their precursor materials, with particular reference to dialkyl and spiran derivatives. Realisation of impurities, a scheme for their removal and an appreciation of optimum conditions during preparation, purification, (and polymerisation), are prime requirements.

The bulk of the work here is concerned with the kinetic and mechanistic aspects of anhydrosulphite polymerisation. It is intended to concentrate on thermal polymerisation for several reasons. First, the literature indicates, and mechanistic considerations support, that higher molecular weight polymers are potentially obtained by this route. Secondly, as the decomposition modes of glycollic and α-hydroxy isobutyric derivatives are distinctly different, further structural modification may present alternative energetically favoured reactions. Thirdly, if thermal extrusion polymerisation predominates in other derivatives, as it is a hitherto unique process, a qualitative, and quantitative, assessment of substituent effects would be of interest.

Poly α-esters have potential application, and in addition because of their structural simplicity they provide an ideal system to study structure-property and structure-additive-property relationships. However a general method for their preparation is not known. It is hoped that the contents of this thesis will improve the present understanding of thermal extrusion polymerisation with specific reference to anhydrosulphite compounds, and that as a result several novel poly α-esters will become available.

2. EXPERIMENTAL METHODS

2.1 Apparatus and Technique

(i) Spectroscopy

Infra-red spectra were recorded using Perkin-Elmer spectrophotometers. For general purposes the Model 237 was adequate, but when higher resolution, or absorptions below 600 cm^{-1}, were required Model 225 was employed.

Ultra-Violet and Mass spectra were obtained using the Unicam SP 700 spectrophotometer and AEI MS 9 instruments respectively.

Nuclear Magnetic Resonance spectroscopy was carried out on Perkin-Elmer R 10 (60 Mc/s) and R 14 (100 Mc/s) spectrometers which were equipped with faculty for integration and variable temperature study. Tetramethyl silane was used as internal standard at all times. The R10 equipment was ideal for most systems studied, but for high resolution, or variation of sensitivity over a ten-fold range, the R 14 instrument was preferred.

Details of the state of the sample, cell dimensions, concentrations etc., are given with specific spectra in the text.

(ii) Gas Liquid Chromatography traces were obtained using Pye series 104 Model 24/34, or Varian Autoprep Model A 700, gas chromatographs. A thermal conductivity detector was used in both cases. For work involving anhydrosulphites a squalene on silocel column was preferred, otherwise a general purpose silicone gum on firebrick (SE 30) type was used. Invariably helium was used as a carrier gas at a flow rate of 50 mls. per minute.

Peak areas were measured with the Kent Chromalog digital integrator, or a fixed arm planimeter. In either case an average of several trace areas was taken.

(iii) Dry Box. For manipulations requiring a completely dry environment a Gallenkamp Model MA 950 glove box was used. The moisture was removed from the chamber by means of a circulating pump used in conjunction with two glass spiral cold traps (solid carbon dioxide/acetone). In addition two open beakers of sulphuric acid were kept within the box.

(iv) Trace Chloride Determination. A modification of Ingram's[42] method enabled ionisable chloride concentration to be determined potentiometrically.

To a weighed amount of material (approximately 0.1g.) was added a large excess of 3:1 (v/v) distilled water:acetone, and two drops of normal nitric acid. The solution was heated to 60° for three minutes, cooled, and titrated potentiometrically with 0.01 N silver nitrate. The end point was determined graphically.

A silver/silver:silver nitrate electrode system was used in conjunction with an E.I.L. Model 23A pH meter.

The principal use of this method was to determine the amount of α-chloroacid chloride impurity present in anhydrosulphite derivatives. Using the technique described an estimate of the ionisable chloride available in α-chloroacetyl chloride showed there to be 1.96 equivalents of chlorine per mole of the compound. Thus both alkyl and acyl chlorines are determined by this method.

(v) Distillation Techniques

Short path distillation, otherwise known as flash distillation, was employed to isolate crude anhydrosulphites from other reaction products. The material was agitated with a magnetic stirer, and distilled at reduced pressure through a preheated one foot column packed with raschig rings. The pot temperature was maintained at approximately 30° and the column 5°, in excess of the boiling point to ensure rapid distillation.

Fractional distillation. For quantities in excess of 100mls. the material was distilled through a two foot heated column packed with Dixon gauze rings. A variable take-off head allowed adjustment of the reflux ratio. Distillation at reduced pressure required incorporation of a Perkin triangle into the system to facilitate collection of fractions.

When volumes were small (5-100mls.), refined fractional distillation was carried out with the "Buchi" spinning band column.

Mechanical mixing of liquid and vapour accounts for the high efficiency of spinning band columns. The hold-up volume is low (approximately 1.5mls.) and in addition throughput rates and reflux ratios can be varied accurately. As far as distillation of anhydrosulphites is concerned this equipment is advantageous because the operation is achieved using the very minimum of heat input. A p.t.f.e. or stainless steel band were available, but the former preferred since it was inert to the systems under study.

The column efficiency was determined at atmospheric pressure using a 20:80 (v/v) binary mixture of n-heptane and methyl cyclohexane. Twenty mls. of the test mixture were charged to the pot and the column was held at total reflux for two hours before taking two distillate fractions at a reflux ratio of 30:1. The composition of distillate pot fractions was determined by refractive index and the number of theoretical plates was measured using a nomograph[43]. The efficiency was found to be twenty one theoretical plates, a value which was reduced when the instrument was operated under reduced pressure.

Vacuum sublimation. Conventional apparatus with a suitable coolant, usually carbon dioxide/acetone, in the cold finger was used.

Prepolymerisation. This proceedure was used as a final purification step for anhydrosulphite monomers. The material was held under vacuum at a temperature between 60-90° until approximately 30% of the product had decomposed. It was then removed from the oligomeric impurities by fractional distillation under reduced pressure.

(vi) Thermal Analysis

Differential thermal analysis (D.T.A.) traces were obtained using the Du Pont 900 thermal analyser in conjunction with a differential scanning calorimeter cell. The study was carried out in an atmosphere of nitrogen at a programmed heating rate.

Thermogravimetric analysis (T.G.A.) was carried out using the Du Pont 950 thermogravimetric analyser. A modular attachment, (consisting of a semi micro balance), to the basic 900 D.T.A. instrument enables weight loss to be measured in any atmosphere (usually nitrogen), either isothermally or at a given heating rate.

In preliminary D.T.A. and T.G.A. studies a heating rate of 10° per minute was used for non-isothermal work. In later experiments to obtain the precise position of peaks and weight losses a lower heating rate was employed.

(vii) Spherulite Formation

Optical microscopy was used to observe spherulite formation in polymer films. A Reichert hot stage microscope equipped with cross polars, and a magnification of 150, allowed spherulite characteristics to be observed in terms of change in birefringence. A modification at the eyepiece enabled a camera to be fitted, from which photographs of the spherulite patterns were obtained.

Depolarised light intensity measurements (D.L.I) provides an alternative and automated method of following rates of spherulite growth[44]. Essentially the equipment consists of a sample film placed between a polariser and an analyser of a hot stage microscope. The sample and its spherulite behaviour can be observed isothermally or at a given heating rate, the latter being accurately maintained by means of the D.T.A. programmer of the Du Pont thermal analyser. A photocell was incorporated in series with the microscope, and D.L.I. traces were obtained on an x-y recorder, the y-axis recording change in light intensity as measured by the photocell, and the x-axis recording the temperature (or time if isothermal) of the sample. The sample film was prepared by melting a few milligrammes of polymer on a glass cover slip and a second cover slip placed on top.

Solid crystalline materials, except those in the cubic crystalline system convert plane-polarised light into elliptically polarised light due to difference in refractive index along non-perpendicular and/or unequal crystal axes. At any transition temperature between ordered states, a change in the type of polarised light occurs. In addition to crystalline birefringence some materials exhibit form birefringence that depends on the ratio of amorphous to crystalline polymer, and provided that refractive indexes of the amorphous and crystalline material differ. The amount of translation of the transmitted light is a function of, the content of crystalline material, the size of crystalline regions, and the orientation of these regions. The exact effect, rotation of polarisation plane or translation to elliptical polarisation depends upon the system under study. These two processes as well as scattering will result in a change in light intensity at the photometer. The change in light intensity indicates that some physical change has occured in the molecular order in the sample.

(viii) Kinetic Measurements

All reactions were carried out in thermostatted eight litre Dewarvessel-baths equipped with efficient stirrers. Contact thermometer/relay/heater systems were used to control the temperature which fluctuated at most by ± 0.3°. Risella oil was used as a bath fluid up to 110°, and silicone oil utilised at higher temperatures.

Reactants were purified before use, and dried solvents were distilled just prior to requirement, the middle fraction only, being used. As anhydrosulphites react rapidly with trace moisture all manipulation of monomer solutions was carried out in a dry box.

Gas evolution analysis was carried out in two types of apparatus (Figure 1a and 1b). Model 1a, a modification of equipment designed by Ballard and Bamford[18], was used below 50° and enabled isolation of one of the reactants. Subsequent to evacuation and isolation of the system (by means of the vacuum tap) the reaction was started at will by knocking a small bucket containing the separate reactant to the base of the reaction vessel. Most anhydrosulphites studied were thermally stable at temperatures below 50°, consequently only a few reactions, usually in the presence of amines, were carried out in this apparatus. Above 50° the equipment described above was not suitable because grease used in the "Quickfit" joints streaked. An all in one type apparatus (Figure 1b), designed by Tighe, was therefore preferred. Evacuation was achieved by connecting the side arm to a vacuum line, and isolation by sealing the capillary tube by means of an oxygen/gas torch.

After baking in an oven the low temperature equipment (minus

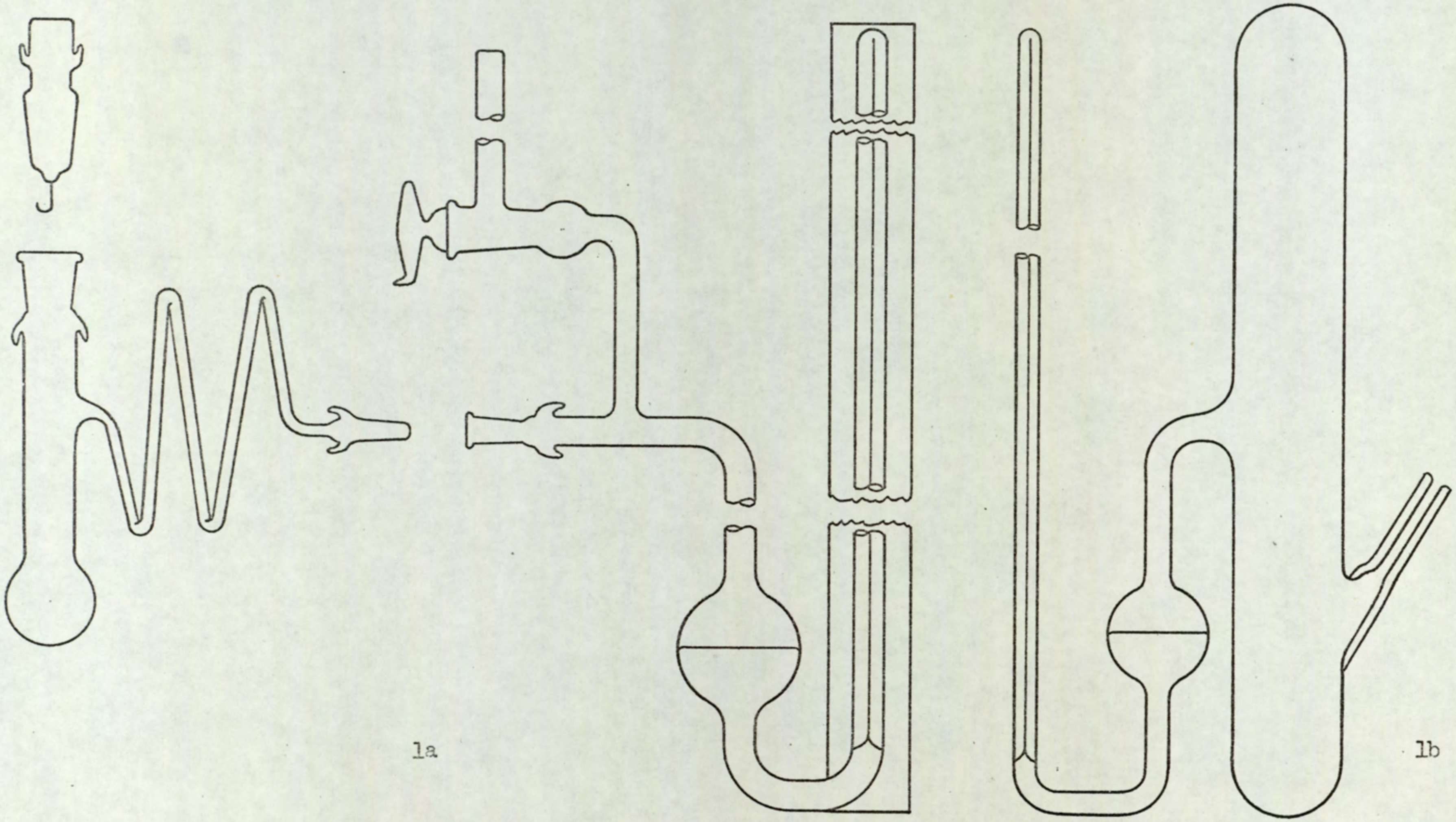


Figure 1. Gas evolution apparatus.

the manometer section) was introduced into the dry box, in which all the reactants were added. The high temperature apparatus was flamed out whilst under reduced pressure, allowed to cool, and purged with dry nitrogen. As the design did not allow entry into the glove box the reactant solutions were introduced by hypodermic syringe through the inert atmosphere.

Both models were then evacuated to low pressure, allowed to degas, and isolated by sealing the system. In those experiments where the reaction was to be studied over a particular range of sulphur dioxide pressure, after degassing and before isolation, sulphur dioxide was bled into the system until the desired **initial** pressure was reached. The apparatus was totally immersed in the oil bath, and changes in the manometric mercury level followed as a function of time, either by means of a cathetometer, or for more rapid reactions by reference to an attached calibrated mirror scale. Equilibration of the evolved sulphur dioxide between solution and vapour was achieved by agitating the equipment with a Pifco vibrator before a reading was taken. Failure to follow this procedure, or perform it efficiently, led to erronious results.

It is possible to derive a relationship between monomer concentration and gas pressure for the general case in which one mole of monomer decomposes to yield, interalia, one mole of gas, the initial monomer concentration $[M]_0$ being related to the monomer concentration at any instant $[M]$ and the concentration of gas the decomposition has produced $[G]$, by the equation:

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

If the reaction proceeds to completion:

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

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

$$P_\infty \propto [G]_\infty \qquad \ldots\ldots \qquad (3)$$

Introducing a proportionality constant

$$\pi P_\infty = [G]_\infty = [M]_0 \qquad \ldots\ldots \qquad (4)$$

If P is the pressure at any instant:

$$\pi P = [G] = [M]_0 - [M] \qquad \ldots\ldots \qquad (5)$$

Equations (4) and (5) combine to give:

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

Rearranging

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

Equations (6) and (7) are used frequently throughout the text to present rate data and evaluate kinetic parameters.

The equipment used here was designed such that the volume change over a complete reaction was very low (estimated as 0.01%), and so any change in pressure is related to a change in the number of moles in the vapour phase. Under the conditions of study sulphur dioxide, the major vapour component, behaves near to an ideal gas, and the associated laws can be applied. Thus at constant volume a change in pressure is directly related to a change in the number of moles of vapour. Complications due to volatility of other components in the system was allowed for, but usually only a small adjustment was required, (for example, the most volatile anhydrosulphite has a vapour pressure of approximately 15 mm. at 90°, which introduces an initial error of ± 4%). Solvents with a particular functional requirement were chosen where possible such that they had a very low vapour pressure at the temperature of study.

As sulphur dioxide is appreciably soluble in organic solvents the pressure as measured was only due to a fraction of the total concentration, but as Henry's law operates the concentration in the vapour was proportional to the total concentration. However, in cases where basic materials were present as reactants, or formed as products, their interactions with sulphur dioxide was anticipated and considered when anomalies arose. Finally, catalytic action, or inhibition, by the presence of mercury was not noted.

Infra-red techniques were also used in the kinetic study of anhydrosulphite polymerisation. A similar method has been used for a study of the polymerisation of NCA's by Idelson and Blout[45]. The most important advantage of this method is that it enables one to follow quantitatively and simultaneously the fate of more than one component of the system, in this case anhydrosulphite and polymer. This allows correlation of reactants or products with reaction rates, which are not necessarily the same. Requirements for success in this method are, homogeneity throughout the reaction, and selection of absorption bands such that no interference with solvent or other reaction components occurs.

To facilitate sampling the polymerisation was carried out under a bed of dry nitrogen, rather than at reduced pressure. Samples were taken by hypodermic syringe, quenched to 0°, and ran immediately on the infra-cord through the wave range 1950-1400 cm^{-1}. A quick operation was required at this point to prevent hydrolysis of the residual anhydrosulphite back to parent hydroxy acid. Several solvent peaks (nitrobenzene) were used as internal standards, although near to constant cell thickness was maintained using 0.025mm. p.t.f.e. spacers.

Since:

$$\log_{10} I = \epsilon cl$$

where I is the intensity of absorption, ϵ is a constant known as molal absorbivity, l is the path length (constant in this case), and c is the concentration (of monomer or polymer).

For anhydrosulphite monomer if the concentration at zero time is $[M]_o$ and the corresponding intensity of absorption I_o^m :

$$[M]_o = \xi \log I_o^m \qquad \ldots\ldots(9)$$

where ξ is a constant involving ϵ (monomer) and l.

If at any instant concentration of monomer $[M]$ has an intensity of absorption I^m:

$$[M] = \xi \log I^m \qquad \ldots\ldots(10)$$

and the amount of monomer decomposed at any instant is given by:

$$[M]_o - [M] = \xi \log I_o^m - \xi \log I^m \qquad \ldots\ldots(11)$$

The fraction of total monomer decomposed at any instant is thus:

$$\frac{[M]_o - [M]}{[M]_o} = \frac{\xi (\log I_o^m - \log I^m)}{\xi \log I_o^m} = \frac{\log I_o^m / I^m}{\log I_o^m} \qquad \ldots\ldots(12)$$

For polymer formation, at zero time the concentration of polymer is also zero. If at any instant the concentration of polymer [Pol] has a corresponding intensity of absorption I^p,:

$$[\text{Pol}] = \xi' \log I^p \qquad \ldots\ldots(13)$$

where ξ' is a constant involving ϵ (polymer) and l.

When the reaction is complete if the final polymer concentration $[\text{Pol}]_\infty$ has an intensity of absorption I_∞^p :

$$[\text{Pol}]_\infty = \xi' \log I_\infty^p \qquad \ldots\ldots(14)$$

and the fraction of total polymer formed at any instant is given by:

$$\frac{[\text{Pol}]}{[\text{Pol}]_\infty} = \frac{\xi' \log I^p}{\xi' \log I_\infty^p} = \frac{\log I^p}{\log I_\infty^p} \qquad \ldots\ldots(15)$$

If the monomer is consumed at the same rate as the polymer is formed the fraction of monomer remaining at any instant will be equal to, one minus the fraction of polymer formed. That is:

$$\frac{[M]_o - [M]}{[M]_o} = 1 - \frac{[Pol]}{[Pol]_\infty} = \frac{[Pol]_\infty - [Pol]}{[Pol]_\infty} \qquad \ldots\ldots(16)$$

or:

$$\frac{\log I_o^m / I^m}{\log I_o^m} = \frac{\log I_\infty^p / I^p}{\log I_\infty^p} \qquad \ldots\ldots(17)$$

Concentrations were related to the logarithm of intensity using the expressions above, but as a result of the close proximity of the peaks of anhydrosulphite (approximately 1810 cm^{-1}) and polymer (approximately 1740 cm^{-1}), error was introduced because the true base line was difficult to ascertain.

Gravimetry was a method also used to follow polymer formation. Known aliquots were taken from the reaction system at various times, quenched, pour~~r~~ed into an excess of methanol, and the precipitated polymer filtered quantitatively through a weighed glass sintered funnel. The residues were then dried to constant weight in a vacuum oven. However, the method was only successful at high rates of conversion and in systems where the resultant product was of high molecular weight. Error was introduced because oligomers present were not precipitated.

(ix) Molecular Weights

End group analysis. Hot micro titration, a modification of Pohl's[46] method for determining the molecular weight of polyethylene terephthalate, was required to determine carboxylic acid end groups of polyα-esters.

Accurately weighed polymer (0.04 - 0.05 g.) was stirred in 5.0 mls. of pure benzyl alcohol for three minutes at 160°. The solution was poured onto 10.0 mls. of distilled chloroform and the original vessel washed with a further 5.0 mls. of benzyl alcohol, which was then transferred to the polymer solution. Three drops of 0.1% phenol-red in ethanol were added and the whole stirred. Standardised benzyl alcoholic caustic soda was added from a microlitre syringe until the end point was reached. A blank run on solvents alone (10.0 mls. of benzyl alcohol plus 10.0 mls. of chloroform) gave a background titre which was subtracted from the subsequent values obtained when carboxylic end groups were determined. The solvents were not considered of sufficient purity until the blank titration was below ten microlitres of 0.1 N alcoholic sodium hydroxide.

Vapour pressure osmometry. The Mechrolab Model 301 A vapour pressure osmometer was employed in obtaining number average molecular weights below 20,000.

The method is an isopiestic one, in which differential mass transfer occurs between pure solvent, and polymer solution, droplets, in an atmosphere of pure solvent. The resultant temperature change as measured by a thermistor probe which supports each droplet, is dependant upon the concentration of polymer solution. Calibration of the instrument using benzil in the solvent of choice, and at varied concentrations, enabled the number of molecules of polymer in a given solution to be calculated.

Quantitative infra-red spectroscopy enables comparison of end group absorptions with an absorption band, usually that due to carbonyl stretching, or C-H bending, which occurs in the repeat unit.

The polymers were efficiently dried in a vacuum drying pistol before being run as ten per cent (w/w) potassium bromide discs. Exclusion of trace moisture was important as its position of absorption corresponds to that of the polymer end groups.

Nuclear magnetic resonance spectroscopy with integration provided an alternative spectroscopic method for comparing end group signals with those of the repeat unit. Spectra were recorded on the Perkin-Elmer R 14 instrument operating at 100 M/cs. By varying the sensitivity of the instrument the terminal group resonance signal was expanded, integrated, and compared with that of a substituent on the repeat unit. An error which became more apparent with high polymers was background noise. At high sensitivity this contributed significantly to the integral value for the terminal group resonance signal.

(x) X-ray Powder Photographs were taken with nickel filtered x-rays regenerated from a copper target at 40 Kv. The nickel filter ensured that only copper K_α radiation was used. The samples were mounted in lithium beryllium borate tubes in a Phillips 11.46 cm. diameter powder camera, fitted with a 0.5 mm. collimator. After one and a half hours exposure to the x-ray beam, the film was removed processed and examined.

2.2 Purification of Solvents and Reagents

Solvents and reagents were purified by modification of the recommended methods due to Weissberger[47] or Vogel[48]. If atmospheric distillation was required at any stage during the purification procedure, the system was vented to air through a calcium chloride tube to prevent entry of moisture. All materials were kept over a suitable drying agent, stored in a dry cabinet, and redistilled just prior to need, the middle fraction, only being used.

Nitrobenzene. Nitrobenzene was refluxed over phosphorous pentoxide for twenty four hours, and then fractionally distilled at atmospheric pressure through a two foot column packed with Dixon gauze rings. A variable take-off head was fitted to the top of the column and set such that a reflux ratio of approximately 10:1 was maintained. The fraction boiling at 210° was collected over previously baked barium oxide.

n_D^{20} 1.5523 (c.f. literature value[47] 1.5526)
Just prior to requirement the solvent was fractionally distilled under reduced pressure and the middle fraction of constant boiling point collected, (55° at 1.4 mm. Hg pressure).

p-Nitro~~benzene~~toluene. This solvent was purified in the same manner as nitrobenzene (boiling point 237° at atmospheric pressure).

Benzyl Alcohol was purified by fractional distillation at reduced pressure. The major fraction, boiling range 50-51° at 0.8 mm. Hg pressure, was collected over anhydrous calcium sulphate.
n_D^{21} 1.5397 (c.f. literature value[47] 1.5403)

Cyclohexanol. This was refluxed over barium oxide, and then fractionally distilled at reduced pressure. The middle fraction

(104° at 100 mm. Hg pressure) was collected. Its physical state at room temperature was taken as a guide to purity since it is a solid when free from contamination.

Dekalin. The solvent was washed three or four times with dilute (7% w/v) sulphuric acid, once with dilute (10% w/v) sodium hydroxide and, finally, three or four times with water. The washed material was dried over calcium sulphate, fractionally distilled under reduced pressure (62-63° at 6.0-6.5 mm. Hg pressure), and collected over fresh dessicant.

n_D^{20} 1.4760 (c.f. literature value[47] 1.4758)

Glycerol was refluxed over barium oxide under reduced pressure for ten hours and then fractionally distilled. The middle fraction (122° at 1.0 mm Hg pressure) was collected over fresh drying agent.

n_D^{25} 1.4734 (c.f. literature value[47] 1.4735)

Dioctyl phthalate. This was shaken with calcium chloride for two days, the suspension allowed to settle, and the required quantities removed by hypodermic syringe.

Chlorobenzene. The material was extracted with, sodium hydroxide, concentrated sulphuric acid, and then with water, dried over calcium chloride, and fractionally distilled at atmospheric pressure. The middle fraction (boiling point 132°) was collected over fresh calcium chloride.

Dimethyl sulphoxide. This solvent has an equilibrium moisture content of 10% at 20°. After refluxing over barium oxide the solvent was fractionally distilled at reduced pressure (boiling point 80° at 16 mm. Hg pressure), and collected over fresh drying agent.

Dimethyl formamide was purified by fractional distillation at atmospheric pressure. The fraction with a constant boiling point of 152° was collected over anhydrous calcium sulphate.
n_D^{20} 1.4310 (c.f. literature value[47] n_D^{25} 1.4269)

Pyridine. This was refluxed over sodium hydroxide pellets for twenty four hours, and then distilled at atmospheric pressure (boiling point 114.5°) onto fresh sodium hydroxide.

Benzylamine was allowed to stand over solid potasium hydroxide and fractionally distilled under reduced pressure. The middle fraction boiling at 100° under 45 mm. Hg pressure was collected over barium oxide.

Triethylamine. The material was treated with p-toluene sulphonyl chloride to remove any primary and secondary amines present. The reagent was then distilled at atmospheric pressure (boiling point 89°) and stored over previously baked barium oxide.
n_D^{21} 1.4015 (c.f. literature value[47] n_D^{20} 1.4010)

Diethyl ether. For anhydrosulphite synthesis or Grignard reactions ~~an~~ anhydrous grade of solvent (0.02% water), supplied by Fisons Scientific Apparatus Limited, was used.

Thionyl chloride was redistilled at atmospheric pressure just before use (boiling point 76.5°).

Silver oxide was supplied by British Drug Houses Limited. The material was dried in a vacuum oven at 80° and stored in a dessicator over calcium chloride.

n-Propyl bromide. The reagent was dried over calcium chloride and distilled at atmospheric pressure just prior to requirement (boiling point 70.5-71.0°).

n-Butyl bromide. This material was treated in a similar manner to n-propyl bromide (boiling point 100-102°).

Diethyl oxalate. After standing over anhydrous magnesium sulphate the reagent was fractionated at atmospheric pressure (boiling point 100-101.5°).

Diethyl ketone. This was dried over potasium carbonate and distilled at atmospheric pressure (boiling point 102°). Purity was assessed by gas liquid chromatography.

Cyclopentanone was purified as for diethyl ketone (boiling point 156.5° at atmospheric pressure).

Cycloheptanone. This was treated in a similar manner as diethyl ketone (boiling point 179.5° at atmospheric pressure).

2.3 Preparation of α-Hydroxy Acids

Those acids available commercially are listed below with appropriate supplier.

Glycollic acid:- Koch-Light Laboratories Limited.

Glycollic acid (aq.) solution 77.4% (w/v):- Hopkin and Williams Limited.

Copper (II) lactate:- British Drug Houses Limited.

α-Hydroxy isobutyric acid:- Koch-Light Laboratories Limited.

α-Hydroxy-α-methyl butyric acid:- Pfaltz and Bauer, Inc. New York.

Cyclopentanol-1-carboxylic acid:-
Cyclohexanol-1-carboxylic acid:- Newton Maine Limited.

The above acids were purified by recrystallisation from benzene or benzene-petroleum ether mixtures until a constant and sharp melting point was obtained. The usual synthetic route to α-hydroxy acids is from the appropriate ketone, via the cyanohydrin and its subsequent hydrolysis. However, when substituents on the α-carbon become large, or are cyclic structures in tension, the equilibrium reaction between acid and cyanohydrin is delicate, and often the former is preferred. In these cases an alternative method ofsynthesis was required.

α-Hydroxy-α-ethyl butyric acid. This acid was prepared from diethyl ketone via the cyanohydrin. Instead of water alone a tetrahydrofuran/water medium was preferred since all solids were dissolved and reaction occured at the liquid-liquid interface.

diethyl ketone	86.1 g.	≡ 106 mls.	1.0 M
sodium cyanide	80.0 g.		1.6 M
hydrochloric acid	164 mls.		
water	300 mls.		
tetrahydrofuran	200 mls.		

piperidine 6 drops

Hydrochloric acid was slowly added to the rest of the components in an efficiently stirred and cooled system. Total addition took 45 minutes, and the whole was then stirred for a further 12 hours, the temperature being maintained at 0-5° throughout the reaction. The two phases were separated and the aqueous fraction extracted with 3 x 100 mls. of diethyl ether. Organic fractions were combined, washed with sodium bicarbonate solution, and dried over anhydrous sodium sulphate. All volatile components, including THF (b.pt. 61°), were efficiently removed using a rotary evaporator at low pressure (10.0 mm.) and high temperature (80°). Residual crude cyanohydrin was shown by g.l.c. to be free from diethyl ketone, and approximately 95% pure.

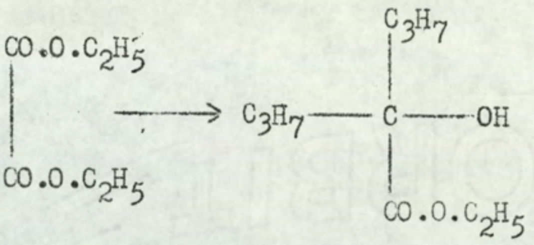
Hydrochloric acid (225 mls.) and the crude product from above were stirred as a one phase system at 80-103° for 48 hours, after which anhydrous sodium sulphate (75 g.) was added and the whole cooled, then filtered. The filtrate was extracted with 200 mls., then 3 x 100 mls. of diethyl ether, and finally dried over magnesium sulphate. Diethyl ether was stripped from the solution and the residual oil on cooling gave a solid. A benzene solution (100 mls.) of the crude product was purified with decolourising charcoal, passed through a short alumina column, and finally precipitated with petroleum-ether (800 mls.) to give a clean white product.

Yield 32.0 g. (25%) m.pt. 78-79°

Elemental analysis found: C, 54.3; H, 8.7; %

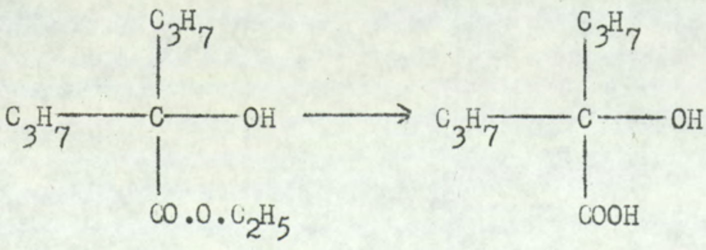
$C_6H_{12}O_3$ requires: C, 54.5; H, 9.1; %

α-Hydroxy-α-n-propyl pentanoic acid. Very low yields of cyanohydrin are obtained from di-n-propyl and higher ketones. The best route to this derivative was found to be a modification of that due to Hepworth[49], a selective attack of n-propyl magnesium bromide on diethyl oxalate.



n-propyl bromide	202 g. ≡	150 mls.	1.68 M
in anhydrous diethyl ether		100 mls.	
diethyl oxalate	98.0g. ≡	88 mls.	0.66 M
in anhydrous diethyl ether		300 mls.	
magnesium turnings (baked)	40.1 g.		1.68 M

A few mls. of ethereal n-propyl bromide were added to the slurry of magnesium turnings in ethereal diethyl oxalate. After an induction period of 20 minutes the reaction started. The n-propyl bromide solution was added over 3½ hours at such a rate that gentle reflux was maintained, and the whole then heated at 50° for a further 3 hours. To the cooled system was added water (500 mls.), and then 1:1 sulphuric acid (approximately 120 mls.) until complete solution was achieved. The solution was extracted with diethyl ether (4 x 250 mls.), the organic fractions combined and dried, and finally the ether stripped off, leaving as residue, the crude ethyl ester of the required α-hydroxy acid. Distillation of the ester at atmospheric pressure (b.pt.210-230°) gave 68.0 g. of pure material (54.8%).



ester	68.0 g.	0.36 M
sodium hydroxide	20.0 g.	0.5 M

The two components were stirred together for 8 hours at 120°, after which the system was cooled to 0° and 1:1 sulphuric acid (approximately 100 mls.) added. Extraction of the resultant slurry with diethyl ether (3 x 300 mls.), drying of the organic phase, and subsequent removal of volatiles gave the required crude product. A petroleum ether solution of the hydroxy acid was, decolourised with charcoal, taken through a short alumina column, and recrystallised at 0°.

Yield 35.2 g. (33% on diethyl oxalate) m.pt. 79° sharp

Elemental analysis found: C, 60.2; H, 10.0; %

$C_8H_{16}O_3$ requires: C, 60.0; H, 10.0; %

α-Hydroxy-α-n-butyl hexanoic acid. This acid was prepared in a manner similar to the di-n-propyl derivative.

n-butyl bromide	513 g. ≡	390 mls.	4.25 M
in diethyl ether	200 mls.		
diethyl oxalate	219 g. ≡	204 mls.	1.5 M
in diethyl ether	1 litre		
magnesium turnings	91 g.		4.25 M

The ethyl ester of the required hydroxy acid was distilled at atmospheric pressure (b.pt.240-246°).

Yield 267 g. (82.5%)

Hydrolysis of the ester:

ester	267.0 g.	1.24 M
sodium hydroxide	66.0 g.	1.65 M

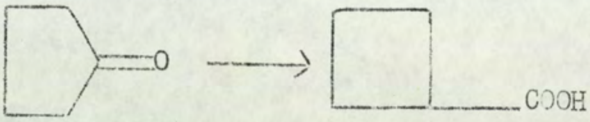
Yield of pure hydroxy acid 120 g. (42.5% on diethyl oxalate)

m.pt. 86.5-87.0°

Elemental analysis found: C, 64.3; H, 10.0; %

$C_{10}H_{20}O_3$ requires: C, 63.8; H, 10.6; %

Cyclobutanol-1-carboxylic acid. The α-hydroxy acid was prepared by α-bromination of cyclobutane carboxylic acid, and subsequent hydrolysis of the α-bromo acid. Cyclobutane carboxylic acid was best synthesised by the ring contraction and oxidation of cyclopentanone, a modification of the method used by Payne and Smith[50].



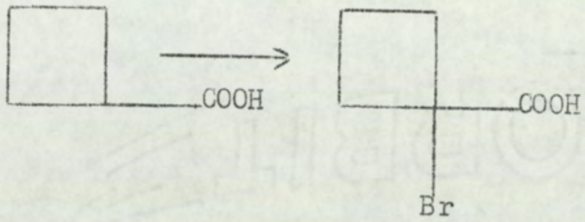
cyclopentanone	250 g.	≡ 266 mls.	3.0 M
hydrogen peroxide	320 g. (100 vols.)		
selenium dioxide	5.0 g.		
tertiary butanol	1.0 litre		

Cyclopentanone was added dropwise to the remainder of the constituents at 80° over approximately 1 hour. An exotherm was noted and some cooling required to keep the desired temperature. After a further 3 hours on a steam bath the reaction was cooled, left for several hours, and the aqueous tertiary butanol removed by rotary evaporation. The residue, an oil, was made up to approximately 1 litre by addition of diethyl ether and extracted with an aqueous potassium carbonate solution. In order to regenerate the free organic acid, to the cool aqueous phase was added a slight excess of 1:1 hydrochloric acid. Extraction with ether (6 x 300 mls.), and subsequent evaporation of volatiles isolated cyclobutane carboxylic acid. Fractional distillation of the crude product through a one foot column packed with Dixon gauze rings, at a reduced pressure of 0.35 mm. Hg pressure, gave a major fraction boiling at 57-58°.

Yield 47.0 g, (15.5% on cyclopentanone)

Equivalent weight by titration 105 (required 100).

N.M.R. multiplet centred at 2.22 p.p.m., quartet centred at 3.08 p.p.m. (c.f. literature values[51] multiplet 2.21 p.p.m. quartet 3.15 p.p.m.)



Method as used for the bromination of isobutyric acid[52].

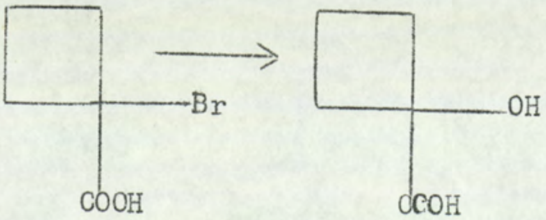
cyclobutane carboxylic acid	50 g.	0.5 M
red phosphorous	3.0 g.	0.1 M
bromine	150 g. ≡ 52.0 mls.	1.0 M

An exotherm accompanied the addition of bromine to cyclobutane carboxylic acid. The two components were heated for 6 hours at 100-110°, a cold surface condenser being required to prevent loss of bromine. Excess bromine and hydrobromic acid were then removed by evaporation at 60° under 90.0 mm. Hg pressure. Hydrolysis of the formed acyl bromide was effected by pouring the reaction into water (500 mls.), stirring, and leaving for several hours. The crude α-bromo acid was extracted from the aqueous system with diethyl ether (4 x 250 mls.), and isolated by rotary evaporation. Distillation at 0.4 mm. Hg pressure gave a large fraction boiling at 75-80°, which solidified to give white crystals when stored at 0°.

Yield 56.8 g. (62.6% on cyclobutane carboxylic acid)

Elemental analysis found: C, 35.0; H, 4.2; %

$C_5H_7O_2Br$ requires: C, 33.5; H, 3.9; %

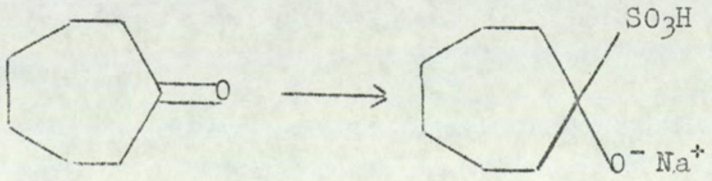


Method as Demjanov and Dojarenko[53].

bromocyclobutane-1-carboxylic acid	50.0 g.	0.28 M
potasium carbonate	55.2 g.	0.4 M
water	100 mls.	

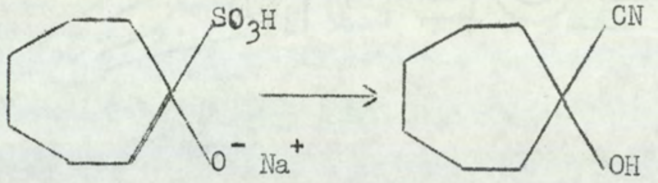
The molten acid was added to the alkaline solution (strong exotherm), refluxed for 6 hours, cooled in ice, and acidified with hydrochloric acid. Removal of the product from the aqueous phase was achieved by continuous ether extraction. The organic extract was dried, the volatiles removed, and the crude product distilled, the major fraction being taken at 120° under 0.5 mm. Hg. pressure. Yield 23.0 g. (70% on α-bromo acid; 6.9% on cyclopentanone). Infra-red, g.l.c., and elemental analysis showed the product to be an approximate 1:1 mixture of cyclobutanol-1-carboxylic acid and its derivative glycollide. This phenomenon has been noted previously and shown to be an equilibrium mixture[54].

Cycloheptanol-1-carboxylic acid. Cyanohydrin formation from cycloheptanone in the presence of hydrogen cyanide is not favoured since the bond angle reduction at the α-carbon (due to a change in bond hybridisation from sp^2 to sp^3) imposes increased ring strain. This problem was avoided by chosing an indirect route to cycloheptanone cyanohydrin,[55] which did not involve unfavourable equilibrium reactions.



cycloheptanone	56 g.	≡ 58.9 mls.	0.5 M
in diethyl ether		300 mls.	
sodium metabisulphite	150 g.		0.75 M
in water		200 mls.	

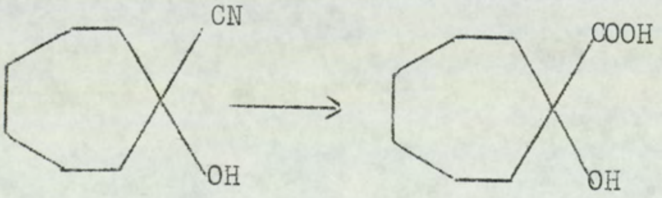
The whole was stirred for two hours, the product filtered and washed with ether.



bisulphite compound from above	
potassium cyanide	45 g.
water	500 mls.

After stirring the components for 6 hours the resultant oil was, extracted with ether, washed with, water (100 mls.), 1:1 sulphuric acid (100 mls.) and again with water (3 x 50 mls.), until neutral. The solution was dried over anhydrous magnesium sulphate and the volatiles stripped off by rotary evaporation. Distillation of the resultant oil at 0.8 mm. Hg pressure gave a major fraction boiling at 90-94°.

Yield 39.7 g. (56% on cycloheptanone).



cycloheptanone cyanohydrin	39.7 g.
hydrochloric acid	1 litre

Hydrolysis was carried out at 80-90° for 3 hours, after which the residual hydrochloric acid was stripped off on a steam bath under a slight reduced pressure. The residual slurry was extracted with benzene, and the resultant solution, dried, and decolourised with charcoal. The hydroxy acid recrystallised on storing at 0°.

Yield 32.1 g. (40.3% on cycloheptanone) m.pt. 76-78°.

Elemental Analysis found: C, 60.1; H, 9.1; %

$C_8H_{14}O_3$ requires: C, 60.7; H, 8.9: %

α-Hydroxy carboxylic acids are readily characterised by their infra-red spectra. Figure 2 shows the spectra obtained for α-hydroxy-α-n-butyl hexanoic acid in carbon tetrachloride at various concentrations. Absorptions due to hydroxyl stretching appear at 3560 cm^{-1} (sharp band) and 3300-2300 cm^{-1} (broad band), the former being assigned to alcoholic hydroxyl (intramolecular hydrogen bonded) and the latter to acid hydroxyl (intermolecular hydrogen bonded). At high dilution both monomeric and dimeric acid species are present as is evidenced in the hydroxyl stretching region and by the splitting of the carbonyl stretching absorption (1700 and 1750 cm^{-1}).

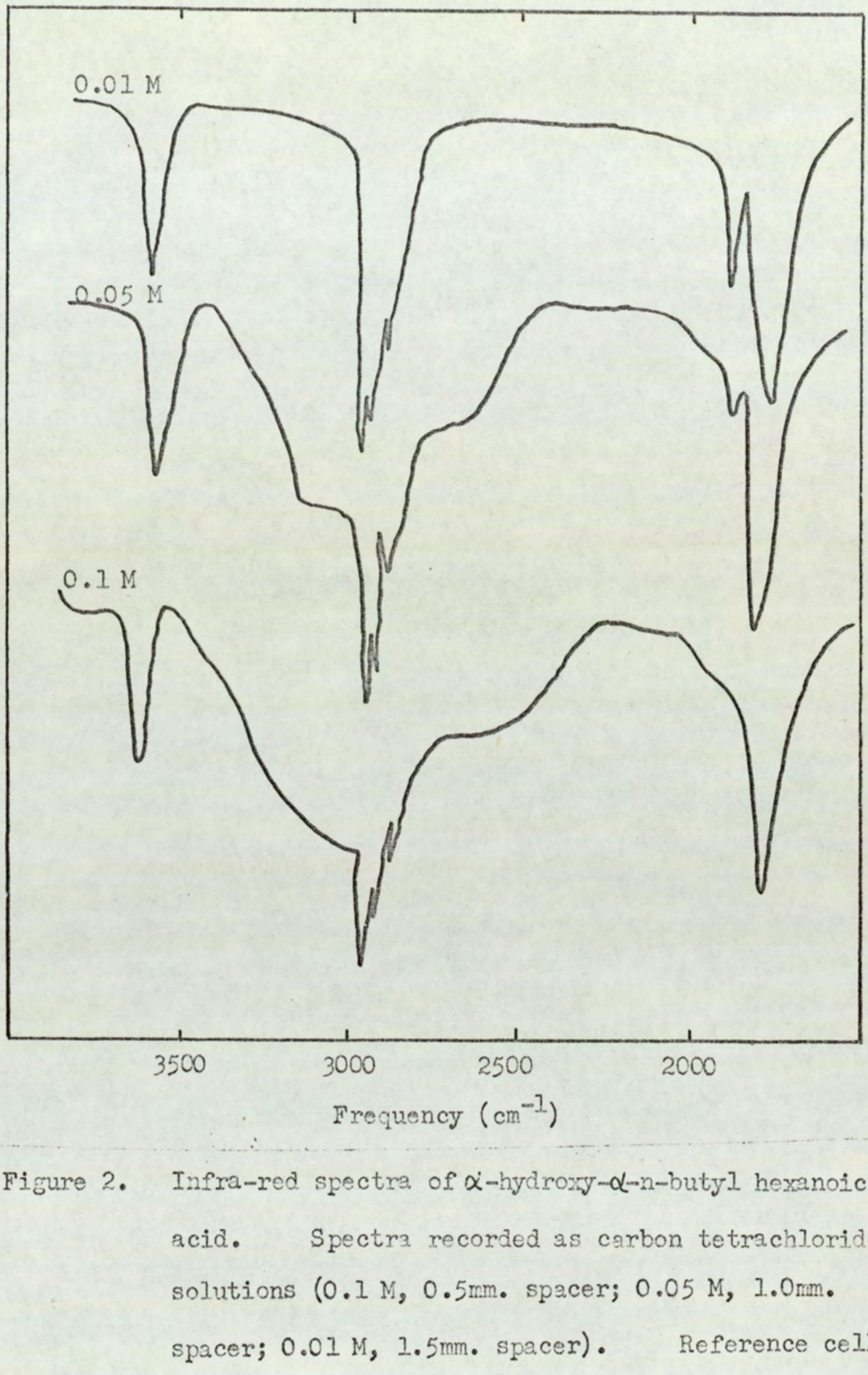


Figure 2. Infra-red spectra of α-hydroxy-α-n-butyl hexanoic acid. Spectra recorded as carbon tetrachloride solutions (0.1 M, 0.5mm. spacer; 0.05 M, 1.0mm. spacer; 0.01 M, 1.5mm. spacer). Reference cell carbon tetrachloride.

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

Copper (II) salts of α-hydroxy acids provide alternative anhydrous precursor materials for anhydrosulphite synthesis.

A 1.0 molar aqueous solution of free acid was neutralised with ammonium hydroxide and the solution heated to boiling point. Copper (II) chloride solution (0.5 molar) was slowly added to the system of aqueous ammonium salt. The mixture was cooled in ice to obtain the hydroxy acid salt as fine crystals. In some cases it was necessary to reduce the volume of solution before efficient precipitation occured.

The preparation of copper (II) glycollate using this method has been recently described by Thomas and Tighe[56]. Copper salts of diethyl and di-n-butyl hydroxy acids were readily prepared and in good yield (90±5%). The solubility of the latter in water was noticeably low, presumably because of the greater size of the organic radical.

Copper (II) α-hydroxy-α-ethyl butyrate

Elemental analysis found: C, 44.2; H, 5.9; %

$C_{12}H_{22}O_6Cu$ requires: C, 45.6; H, 6.3; %

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

Elemental analysis found: C, 53.4; H, 8.9; %

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

Neither of the above two compounds have been reported in the literature.

Attempts to prepare a copper salt from the mixture of cyclobutanol-1-carboxylic acid and its equilibrium component glycollide was only partially successful. A combination of acid, glycollide, and copper salt was always obtained.

The complete formation of the metal salt from free acid was readily recognised from the infra-red spectrum. A shift, and change in shape, in the hydroxyl stretching region is obtained and the carbonyl stretching frequency of the free acid is replaced by the carboxylate ion stretching band which occurs at a lower wave number (approximately 1630 cm^{-1}). Figure 3 illustrates a spectrum of copper (II) α-hydroxy-α- n-butyl hexanoate which should be compared with the parent acid (Figure 2).

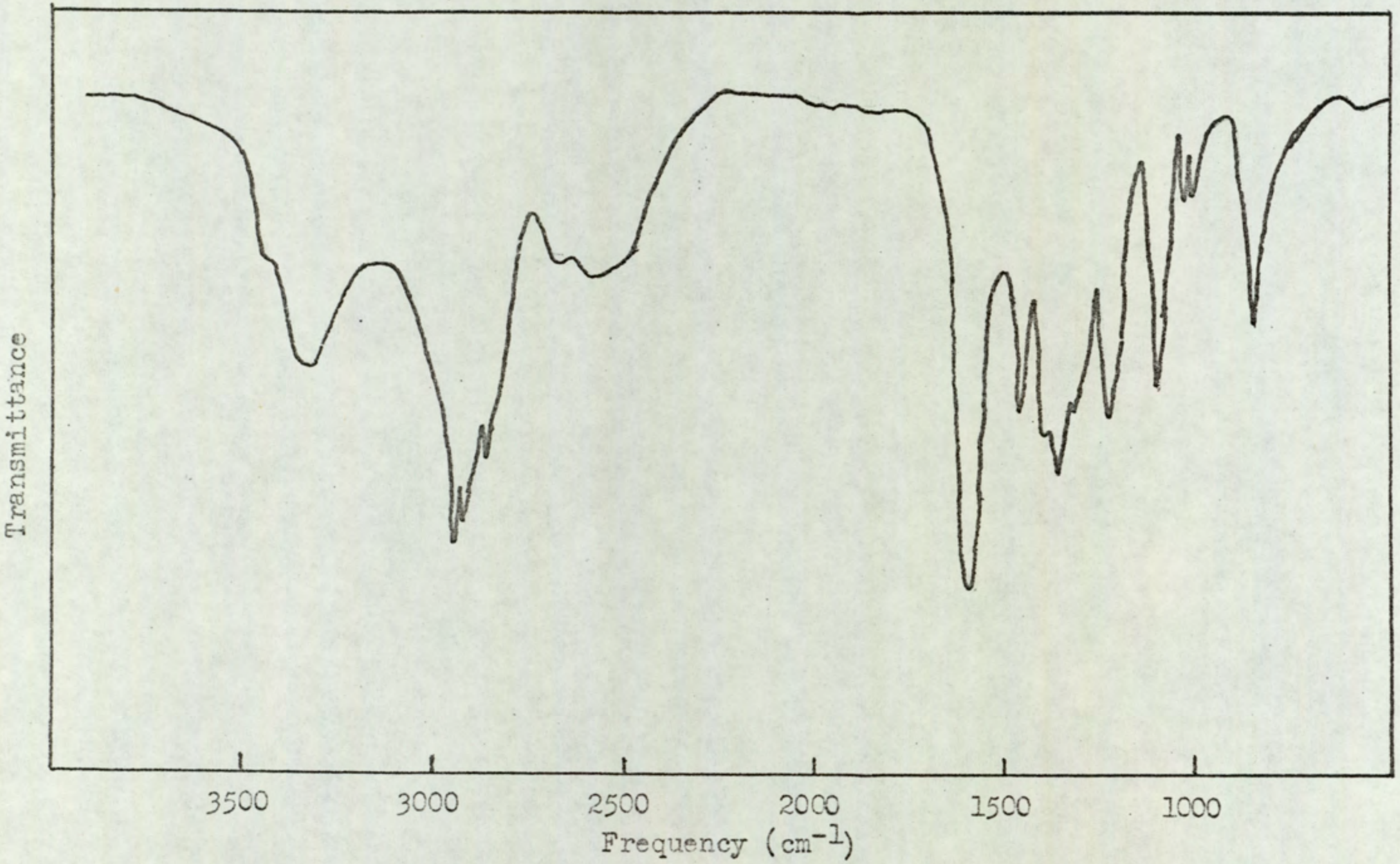


Figure 3. Infra-red spectrum of copper (II) α-hydroxy-α n-butyl hexanoate.

Spectrum obtained from KBr disc (10% w/w). Reference cell air.

2.5 Preparation of Anhydrosulphites.

Two routes were used; the action of thionyl chloride (a) on the appropriate α-hydroxy acid or (b) on its anhydrous copper (II) salt.

(a) Redistilled thionyl chloride (1.5 M) was added slowly to a stirred solution of the acid (1.0 M) in anhydrous ether (400 mls.) at -10° (solid carbon dioxide/acetone bath). The system was allowed to warm to 0° and stirred for 16-20 hours under reduced pressure (100-200 mm. Hg), followed by 2 hours at 20-30°. Finally, any residual ether and thionyl chloride was stripped off under reduced pressure (1.0-5.0 mm. Hg).

(b) To the dry anhydrous copper salt (1.0 M) slurried in dry ether (500 mls.) was added thionyl chloride (1.5 M) at 0°, and the mixture stirred for 20-30 minutes. The resultant precipitate of copper (II) chloride was filtered off and washed liberally with anhydrous ether to remove any occluded anhydrosulphite. The filtrate was then left for 1 hour under reduced pressure (100-200 mm. Hg) at room temperature and final traces of thionyl chloride stripped off as in (a).

The crude anhydrosulphite was obtained as a residual oil in both cases.

Purification was effected by a selection of the following methods.

Treatment with triethylamine. An equimolar amount (with respect to chlorine containing impurities) of pure triethylamine, was added dropwise as a 5% ethereal solution, to the crude anhydrosulphite, dissolved in ether at 0°. The precipitate was filtered off and ether stripped from the filtrate leaving substantially chlorine-free anhydrosulphite.

Treatment with silver oxide. An ethereal solution of anhydrosulphite was stirred with a two molar excess of silver oxide, (based on chlorine containing impurities), for 2 hours at 0°. The solid component was removed by centrifugation and the centrifugate evaporated at reduced pressure to leave substantially chlorine-free anhydrosulphite.

A combination of flash and fractional distillation, and prepolymerisation were also used to purify anhydrosulphites.

Both triethylamine and silver oxide treatments eliminate chlorine containing impurities. The latter was developed when it was found that triethylamine treatment was not suitable for higher homologues of the anhydrosulphite series.

A stepwise procedure for the purification of crude anhydrosulphite was as follows; (i) short path distillation, (ii) silver oxide treatment, (iii) fractional distillation employing the spinning band column, (iv) prepolymerisation, and subsequent fractional distillation into polymerisation or kinetic study vessels. In most cases it was necessary to repeat steps (ii) and (iii), until a desired level of purity was obtained.

Listed below are the anhydrosulphites prepared, together with any necessary deviations from the above purification scheme. Unless otherwise stated the preparation was by the action of thionyl chloride on free acid (method (a)). A detailed comparison of these systems and their synthetic feasibility is presented in Section 3.

<u>1,3,2-dioxathiolan-4-one-2-oxide</u>, GAAS, (glycollic acid anhydrosulphite). As commercially obtained glycollic acid contains impurities such as glycollide and glycollyl glycollate, the preferred route to the anhydrosulphite was via the copper (II) salt.

In addition, as the metal salt can be prepared from a technical grade aqueoussolution of acid the method is very much cheaper.
Yield 41%.

5-methyl-1,3,2-dioxathiolan-4-one-2-oxide, LAAS, (lactic acid anhydrosulphite). This was prepared in a manner similar to GAAS.
Yield 63.1%.

5,5-dimethyl-1,3,2-dioxathiolan-4-one-2-oxide, HBAS, (α-hydroxy-isobutyric acid anhydrosulphite).
Yield 68%.

5-methyl-5-ethyl-1,3,2-dioxathiolan-4-one-2-oxide, MEAS.
Yield 55%.

5,5-diethyl-1,3,2-dioxathiolan-4-one-2-oxide, DEAS.
Yield 80.4%.

5,5-di-n-propyl-1,3,2-dioxathiolan-4-one-2-oxide, DPAS.
Short path distillation of crude DPAS was accompanied by noticeable decomposition to oligomers. In addition, when the distillate was monitored by gas liqiud chromatography, di-n-propyl ketone was shown to be present as an impurity (1-2%). Fractional distillation, utilising the spinning band column gave anhydrosulphite distillate which was contaminated with only 0.05% ketone.
Yield 50.4%.

5,5-di-n-butyl-1,3,2-dioxathiolan-4-one-2-oxide, DBAS.
A relatively low crude product yield was obtained from the action of thionyl chloride on free acid and therefore the copper salt route was investigated. However, similar quantities of product were obtained in both cases. In a similar manner to DPAS, but to a greater degree, distillation of DBAS was accompanied by formation of ketone and decomposition to oligomers. Even careful manipulation

of the spinning band equipment resulted in 80-90% losses of the product, and the distillate was contaminated with a 10% minimum of di-n-butyl ketone.

A benzene solution of crude DBAS was passed through an acid alumina column which was continuously flushed with dry nitrogen at the entry and exit zones. This method met with little success however as it resulted in near total conversion back to the parent hydroxy acid. Attempts to vacuum sublime, or recrystallise the material at low temperature, were not successful either.
Yield 35% (crude); 2.1% (distilled).

1,3,2-dioxathiolan-4-one-2-oxide-5-spirocyclobutane, C'butAS, (cyclobutanol-1-carboxylic acid anhydrosulphite). The copper (II) salt route was preferred in the preparation of this derivative since less glycollide-1,4-dispirocyclobutane was present in the final product. A few minutes after total addition of thionyl chloride a white solid was precipitated, which was shown to be a mixture of the above glycollide and an unidentified acid. Attempted distillation of C'butAS was accompanied by drastic decomposition and therefore the crude product was only subjected to silver oxide treatment.
Yield 15% (crude).

Cyclopentane spiro-5-1,3,2-dioxathiolan-4-one-2-oxide, C'pentAS, (cyclopentanol-1-carboxylic acid anhydrosulphite). Short path distillation of the crude material was accompanied by trace ketone formation. As the reaction was essentially a clean one this stage was omitted.
Yield 74%.

Cyclohexane spiro-5-1,3,2-dioxathiolan-4-one-2-oxide, C'hexAS, (cyclohexanol-1-carboxylic acid anhydrosulphite). This derivative was synthesised and purified in a manner similar to C'pentAS.

Yield 69.5%.

Cycloheptane spiro-5-1,3,2-dioxathiolan-4-one-2-oxide, C'heptAS, (cycloheptanol-1-carboxylic acid anhydrosulphite). Purification methods involving distillation were not successful for C'heptAS since oligomer and ketone formation were considerable under these conditions. However, the crude product after silver oxide treatment was readily vacuum sublimed at temperatures in the region of 40°.

Yield 30% (vacuum sublimed); 4% (distilled).

2.6 Preparation of Polymers.

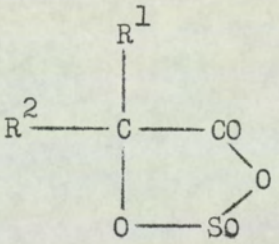
Anhydrosulphite polymerisation was carried out in Carius tubes under reduced pressure. The tubes were flamed out whilst connected to a vacuum line, cooled, and purged with dry nitrogen. Monomer solutions were prepared in the glove box, and introduced to the reaction vessel by hypodermic syringe in a dry inert atmosphere. Vacuum was applied, the system degassed, and then isolated by sealing with an oxygen/gas torch. When the polymerisation reaction was complete the tube was cooled in liquid nitrogen, opened, and the polymer precipitated from solution by maccerating with an excess of methanol.

3. ANHYDROSULPHITE SYNTHESIS AND CHARACTERISATION

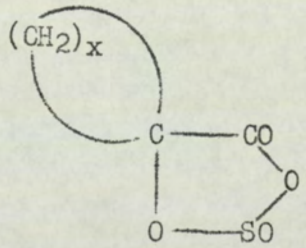
Results and Discussion

3.1 Synthesis

Competing reactions. Tables 1 and 2 list methods of purification, yields, purity and physical constants for an alkyl (I) and spirocycloalkyl (II) series of α-hydroxy carboxylic acid anhydrosulphites respectively.



(I)



(II)

Table 3 summarises yields of the various products obtained from the reaction of four α-hydroxy acids with a 50% molar excess of thionyl chloride in diethyl ether. The impurities formed are of three types: chlorine containing compounds, unconverted or regenerated α-hydroxy acid, and oligomeric residues. Preparative gas chromatography, infra-red and potentiometric chlorine estimations were methods used for the separation and identification of the chlorine containing impurity, which in most cases was shown to be the α-chloro acid chloride.

Because of the structural similarity of anhydrosulphites to organic sulphites the two classes of compounds show similar synthesis patterns. In both cases the initial step is the reaction of a hydroxyl function with thionyl chloride, a process

TABLE 1 – An alkyl series of α-hydroxycarboxylic acid anhydrosulphites: Synthesis purification and characterisations

	R^1	R^2	Purification techniques	Yield %	Chlorine content (moles/mole anhydrosulphite)		bp (°C/mm)	Refractive Index n_D^T	U.V.Spectra		I.R.Spectra		Sulphur dioxide evolved (% theoretical)
					Before purification	After purification			λ_{max}	$\log_{10}\varepsilon$	$\nu_{max}(C{=}O)$	$\nu_{max}(S{-}O)$	
GAAS	H	H	(a) or (b) (c), (d)	44.0	5×10^{-2}	5×10^{-3}	68-70/10	1.4750^{25}	210.5 291.5	2.091 3.0828	1825	1245	98 ± 2
LAAS	H	Me	(a),(c),(d)	63.1	6×10^{-2}	8×10^{-3}	70/12	-	-	-	1815	1235	97 ± 2
HBAS	Me	Me	(a) or (b) (c), (d)	68.0	1.54×10^{-2}	3.6×10^{-3}	56-7/12	1.4312^{20}	219.5 294.0	3.0017 1.2667	1825	1250	99 ± 2
MEAS	Me	Et	(b), (d)	55.0	7×10^{-2}	2.5×10^{-2}	29.5-30/1.4	1.4358^{23}	214.0 298.5	3.0319 1.3220	1812	1250	97 ± 2
DEAS	Et	Et	(b),(c),(d)	80.4	1.5×10^{-1}	2.8×10^{-3}	35-6/0.40	1.4423^{20}	208.5 283.0	3.1213 2.3410	1815	1255	99 ± 2
○DPAS	Pr	Pr	(b), (d)	50.4	1.0×10^{-1}	1.5×10^{-2}	63/0.7	1.4460^{21}	-	-	1805	1240	96 ± 2
○DBAS	Bu	Bu	(b), (d)	35.0[†] 2.1[‡]	3×10^{-1}	5×10^{-2}	84/1.2	1.4508^{20}	-	-	1810	1245	95 ± 2

Key to Table 1 see footnote of Table 2.

TABLE 2: A spirocycloalkyl series of α-hydroxycarboxylic acid anhydrosulphites: Synthesis purification and characterisation

	x	Purification techniques	Yield %	Chlorine content (moles/mole anhydrosulphite)		bp (°C/mm)	Refractive Index n_D^T	U.V. Spectra		I.R. Spectra		Sulphur dioxide evolved (% theoretical)
				Before purification	After purification			λmax	$\log_{10}\epsilon$	ν_{max}(C=O)	ν_{max}(S-C)	
○ C'butAS	3	(b)	15.0	2.6×10^{-1}	1.6×10^{-1}			211.0 292.0	3 1	1815	1225	80 ± 5
○ C'pentAS	4	(b), (d)	74.0	2.0×10^{-1}	1.4×10^{-3}	69-70/0.7	1.4700^{20}	211.5	3.0588	1818	1243	98 ± 2
C'hexAS	5	(b), (d)	69.5	5.0×10^{-2}	1.0×10^{-3}	67/0.4	1.4782^{20}	207.5 274.5	3.4842 1.7792	1810	1238	98 ± 2
○ C'heptAS	6	(b), (d)	30.1 † 4.0 ‡	8.0×10^{-2}	5×10^{-2}	(mp 7-9°)				1810	1235	93 ± 2

† not distilled

‡ distilled

○ compounds not previously reported in the literature

(a) Treatment with methylamine

(b) Treatment with silver oxide

(c) Flash distillation

(d) Fractional distillation using spinning band column

(e) Vacuum sublimation

which, in the formation of alkyl chlorides, has been shown to proceed via the S.N.$_i$ decomposition of an alkyl chlorosulphinate intermediate[58]. The chlorosulphinate can alternatively react with another alcoholic hydroxyl function to form an organic sulphite[59], or intramolecularly, with a carboxyl function to yield an anhydrosulphite. A scheme showing the reactions which compete with anhydrosulphite formation is presented in Figure 4.

Table 3

Products obtained from the reaction of various α-hydroxy acids with thionyl chloride (for reaction conditions see Section 2.5).

Hydroxy acid	Reaction Products*				
	unreacted acid (%)	α-chloro acid (%)	α-chloro acid chloride (%)	anhydro-sulphite (%)	oligomers (%)
Lactic	20 ± 10	-	10	20 ± 10	20 ± 10
α-Hydroxy isobutyric	-	-	15 ± 10	70 ± 10	10
Cyclopentanol-1-carboxylic	-	-	20 ± 10	60 ± 15	10
Benzilic	80 ± 15	10	-	-	-

* Results include those observed by Tighe et al[25,26,57].

Decomposition of the chlorosulphinate to form anhydrosulphite was monitored by measurement of the residual chlorine content of the reaction mixture. The figures given below relate to the formation of DEAS:

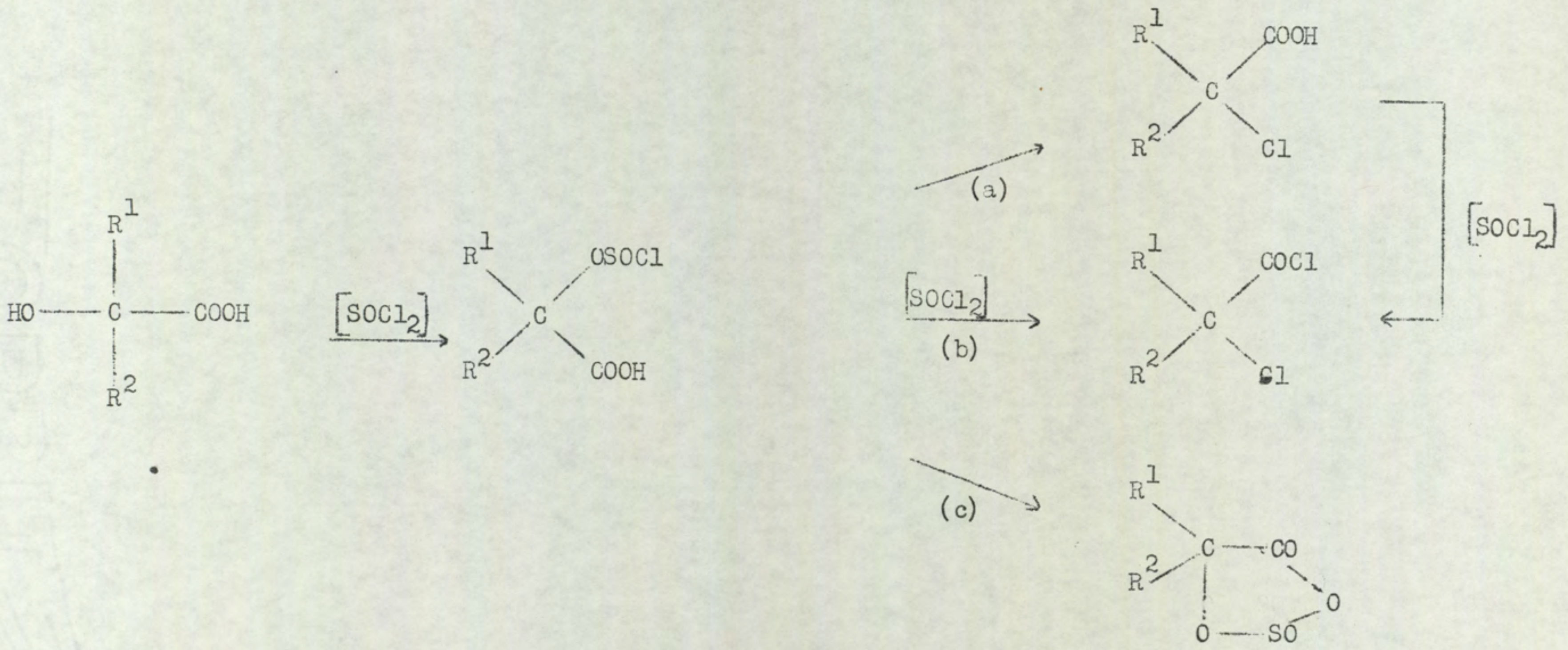


Figure 4. The reaction of α-hydroxy carboxylic acids with thionyl chloride

Reaction Stage (see Section 2.5)	Chloride Concentration (mole $^{-1}$)
(a) Before treatment at 30°	4.1
(b) After treatment at 30°	2.5

<u>Factors affecting chlorosulphinate formation</u>. The physical state of the acid and its solubility in the reaction medium are obviously important. Of the acids considered, all except lactic, and cyclobutanol-1-carboxylic acid were obtained in a high state of purity and although they were not always completely soluble in the reaction medium initially, total solution had occured before the addition of thionyl chloride was complete. In all the cases shown in Tables 1, and 2 a 50% molar excess of thionyl chloride was used and the reaction mixture maintained below 0° during the addition. Smaller amounts produced unconverted acid, whereas larger amounts or elevated temperatures resulted in higher yields of acid chloride by-products.

The reactivity of the parent α-hydroxy acids of the anhydrosulphite listed in Tables 1 and 2 to thionyl chloride can, to some extent, be estimated by the amount of unreacted acid remaining at the end of the reaction. This was most marked in the preparation of C'butAS and C'heptAS although some unreacted acid was isolated from the reaction products in GAAS, LAAS, and DBAS synthesis. Phenyl substituted α-hydroxy acids (for example, benzilic acid, Table 3) are much less reactive to thionyl chloride under the same conditions. The alcoholic hydroxyl-thionyl chloride reaction in non-polar media has been envisaged as nucleophilic attack of the hydroxyl oxygen upon sulphur. Electron withdrawing substituents would be expected to decrease the nucleophilicity of the hydroxyl group, and bulky groups impair its reactivity by steric hindrance. A case in which both electronic and steric effects apparently combined to inhibit the reactivity of an alcohol is 111,333-hexachloro-2-propanol which does not react directly with thionyl chloride[60].

Because of different pK values of the acids and the complicating effects of thionyl chloride on the polarity of the medium, electronic effects can not be accurately assessed. Steric effects are susceptible to more straightforward evaluation however and may be taken to influence the reactivity of the acid to some extent. Thus the lower reactivity of the parent acids of DBAS and C'heptAS, compared with lower homologues of the dialkyl and cycloalkyl series may be attributable to the steric hindrance of the relatively bulky dibutyl and cycloheptyl groups. The behaviour of glycollic, lactic and cyclobutanol-1-carboxylic acids is somewhat different. The last mentioned has impurity present due to an acid-glycollide equilibrium[54]; in addition the high degree of ring strain plays an important role. The composition of lactic acid has been discussed by several authors and shown to approach an equilibrium mixture of lactic acid, lactyl lactate, lactide, polylactyl lactic acids and water. Glycollic acid is similarly contaminated. The products of reaction are, in each case, more complex than the scheme shown in Figure 4 would suggest.

Factors affecting chlorosulphinate decomposition. Once formed, the chlorosulphinate can react further by three routes.

(i) Formation of an α-chloro acid by an SN_i type reaction (Figure 4a). This is a major product in the reaction of aromatic α-hydroxy acids with thionyl chloride.

(ii) Interaction (of either the α-chloroacid or the chlorosulphinate intermediate) with thionyl chloride to form an α-chloroacid chloride (Figure 4b).

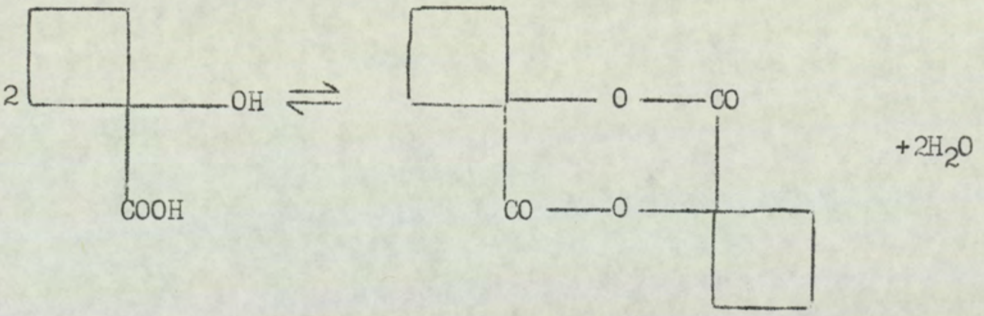
(iii) Ring closure via intra molecular elimination of hydrogen chloride to form an α-hydroxy carboxylic acid anhydrosulphite (Figure 4c).

Virtually all the chlorine containing impurity isolated in the preparation of each of the anhydrosulphites listed in Tables 1 and 2 was the appropriate α-chloroacid chloride. The substituents R^1 and R^2 influence the relative rates of reactions 4a, b, and c, and thus the extent of α-chloroacid chloride formation. Electron withdrawing substituents impose electropositive character on the α-carbon atom and thus facilitate the SN_i reaction. This is most marked in the case of α-phenyl-α-hydroxy acids[24,57], for example, benzilic acid (Table 3). Bulky substituents, on the other hand, restrict the mobility of the carboxyl and chlorosulphinate functions and, in extreme cases, render anhydrosulphite formation more difficult. Contributions from both effects are apparent in the reactions of α-phenyl-α-hydroxy carboxylic acids with thionyl chloride but for the alkyl and cycloalkyl series only steric effects are important. Although contribution from the slightly electron releasing alkyl substituents are favourable to anhydrosulphite formation the effect is insignificantly small. In the cases of DPAS, DBAS and CheptAS the large substituent size contributes towards reducing the yield of anhydrosulphite relative to α-chloroacid chloride.

Anhydrosulphite purification. The α-chloroacid chloride and anhydrosulphite have very similar physical properties and their separation by fractional distillation is only successful if the operation is repeated many times. Distillation techniques are completely effective for the removal of oligomeric residues which are formed as a result of the interaction of various impurities (α-chloro-acid chloride, α-hydroxy acid, etc.) with the anhydrosulphite or its decomposition products.

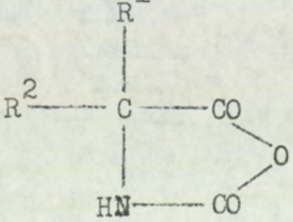
Thermal decomposition and consequent polymerisation is responsible in some cases, for low yields, since on ascending the homologous series boiling points are increased until they fall into the temperature range where thermal polymerisation occurs quite rapidly. Hence if the di-n-butyl anhydrosulphite (DBAS) is distilled (approximately 80° at 1.0 mm. Hg pressure), using a spinning band column, a purer sample is obtained, but only in very low yield, the remainder having polymerised. Instability due to ring strain can also lead to low yields as exemplified by DPAS and C'heptAS. These compounds have similar molecular formulae, but the di-n-propyl derivative can be distilled in fair yield whereas the cycloheptyl derivative is only obtained in 4% yield because of its higher rate of thermal breakdown. Detection of ketone in the short-path distillates of DPAS, DBAS, C'pentAS, C'hexAS and C'heptAS may be attributed to two effects. First the increase in boiling point temperature (a requirement of increasing molecular weight) might present conditions in which alternative decomposition modes become energetically competitive, and secondly, structural modifications may bring this competition into play at lower temperatures. The effects of ring strain and substituent size on the behaviour of anhydrosulphites will be discussed in later sections. Providing the system lends itself to distillation the anhydrosulphite is readily separated from any oligomers.

A modification of the synthesis procedure is to add thionyl chloride to the α-hydroxy carboxylate copper (II) salt. Of the anhydrosulphites in Tables 1 and 2 only GAAS, LAAS and C'butAS were preferably prepared by this method, some aryl substituted derivatives however, can only be prepared in this way[57]. For GAAS and LAAS the method is valuable because a pure anhydrous complex can be prepared from impure acid, hence yields are increased. In the case of C'butAS preparation, addition of thionyl chloride to free acid enhances glycollide formation (Equation 1) since water is efficiently scavenged.



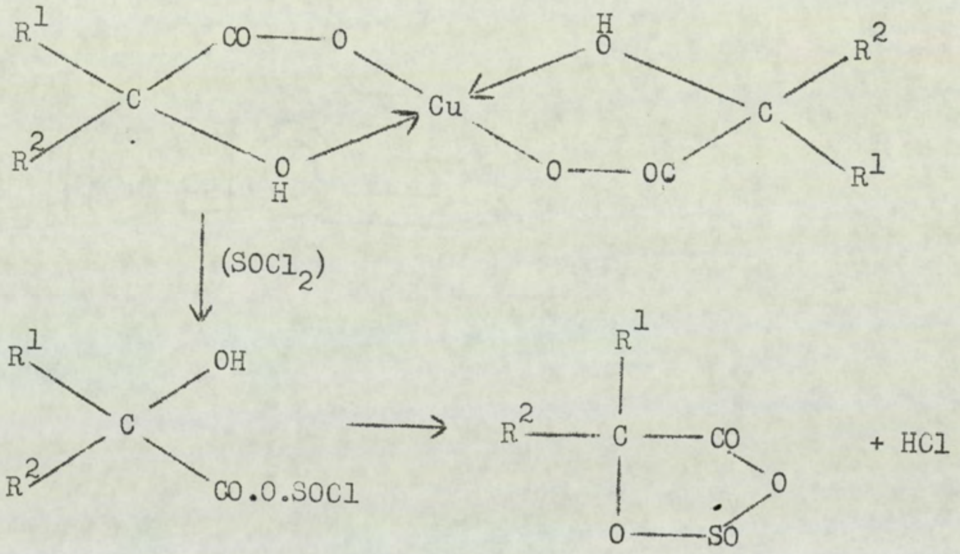
...... (1)

The metal salt route, however, quenches formation of this material. A recent report describes the preparation of N-carboxy α-amino acid anhydrides (III) by the action of phosgene on the copper (II) salt of



(III)

the appropriate α-amino acid[61]. The authors postulate that attack by phosgene occurs at the α-nitrogen, as it does in the free amino acid route. Since the complexing (donor) ability of oxygen and nitrogen differ, and the electrophilicity of phosgene and thionyl chloride is not the same, however, direct correlation is not possible. Major changes in by-product yields, and especially the very rapid rate of reaction, observed in anhydrosulphite formation, suggest a different mechanism, perhaps involving initial attack at the carboxylate anion to form an acyl chlorosulphinate, as formulated in Equation 2.



...... (2)

Efficient removal of impurities is imperative in polymerisation work since their presence drastically lowers the molecular weight of the resultant polymer. A suitable combination of purification procedures (mentioned in Section 2.5) is necessary to achieve the desired level of purity. Prepolymerisation and subsequent distillation adequately removes nucleophilic species (which take part in initiation processes), and oligomeric residues therby formed. The α -chloroacid chloride does not initiate the ring-opening process, but is incorporated throughout the polymerisation by termination and/ or transfer reactions.

Triethylamine and silver oxide proved most successful in removing chlorine containing impurities, the latter being preferred since it promotes less decomposition of the anhydrosulphite during the process. Once the level of chlorine impurity had been reduced to approximately one mole percent, fractional distillation through a spinning band column was able to reduce the level to around 0.2 mole percent. This instrument requires only a minimum input of heat to achieve distillation, thus keeping thermal degradation to a minimum. Tables 1 and 2 list chlorine present (a) in the crude anhydrosulphite after only flash distillation, and (b) in the anhydrosulphite after it had been treated by an appropriate combination of purification methods, but before final pre-polymerisation and distillation into a reaction vessel for rate studies. DBAS, C'butAS and C'heptAS were not obtained in the same degree of purity as the remainder because at their distillation temperatures mass decomposition occurs. The cycloheptyl derivative was finally purified by vacuum sublimation at 35°, but this technique gave relatively poor separation of the anhydrosulphite and α-chloroacid chloride. The dimethyl derivative (HBAS) is unique in that it can be obtained in a fairly high state of purity by distillation alone. This is reflected in earlier literature since this system is the only one from which high molecular weight polymers were obtained[23].

3.2 Characterisation

The assignment of anhydrosulphite structures was based on infra-red, ultra violet, nuclear magnetic resonance and mass spectra together with analytical results. It was found that the reproducibility of elemental analysis results was not good, probably because of the thermal instability of some members of the series and the ready hydrolysis of all by atmospheric moisture. A useful analytical procedure was devised which enabled all preliminary manipulation to be carried out in a dry box.

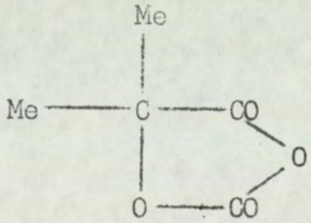
The anhydrosulphite was transferred to a kinetic apparatus of known deadspace volume, containing either nitrobenzene or aqueous acetone. Following thermal decomposition or hydrolysis, the resultant yield of sulphur dioxide was calculated and the solid derivative (polymer or parent acid) removed for analysis. Typical results are included in Tables 1 and 2. This technique, together with gas chromatography and elemental chlorine analysis enabled anhydrosulphite purity to be accurately assessed.

The anhydrosulphites, when pure, are colourless liquids and possess a characteristic pungent odour, they are non-flammable, soluble in most organic solvents and their densities are in the range 1.2-1.3 g. ml^{-1}. Earlier literature relating to the chemical properties of anhydrosulphites has been reviewed[62].

Infra-red spectra were obtained neat or as solutions in cyclohexane and carbon tetrachloride. Several absorptions can be assigned to the anhydrosulphite ring, two of which are listed in Tables 1 and 2. A single peak is observed in the carbonyl region (1815 ± 10 cm^{-1}), which differs substantially from the parent acid (1725 ± 5 cm^{-1}), the copper (II) salt (1625 cm^{-1}), and the oligomer

(1760 cm^{-1}), but unfortunately lies in the same region as that of the α-chloroacid chloride. The sulphoxide stretching frequency is found as a medium intensity sharp peak in the region of 1240 cm^{-1}, a higher frequency than is quoted for dialkyl sulphoxides (1050-1100 cm^{-1}) but nearer that for organic sulphites (1214 cm^{-1})[63]. Other absorptions which appear common to the ring system are found as medium intensity peaks at 1085 ± 15 cm^{-1} and 1045 ± 5 cm^{-1}. A spectrum, of C'hexAS in carbon tetrachloride (10% v/v) is given in Figure 5.

Ultra violet spectra were recorded as dilute cyclohexane solutions. The anhydrosulphites are characterised by two absorptions, the major appearing at a lower wavelength (214 ± 6 A). By analogy with dialkyl sulphoxides[64] it is probable that this absorption is due to promotion of the lone pair of electrons on the sulphur to a vacant 3d orbital, especially as 5,5-dimethyl 1,3-dioxalan-2,4-dione (IV) produces as similar spectra but the maximum extinction coefficient is much reduced ($\epsilon < 200$). Likely impurities such as α-chloroacid chloride and parent acid absorb at similar wavelengths but these compounds also have much lower molar extinction coefficients (ϵ approximately 200). The minor peak may be due to a carbonyl transition or possibly a ring-twist vibration as is observed in oxaspirane systems[13].



(IV)

The mass spectra of anhydrosulphites were examined. A

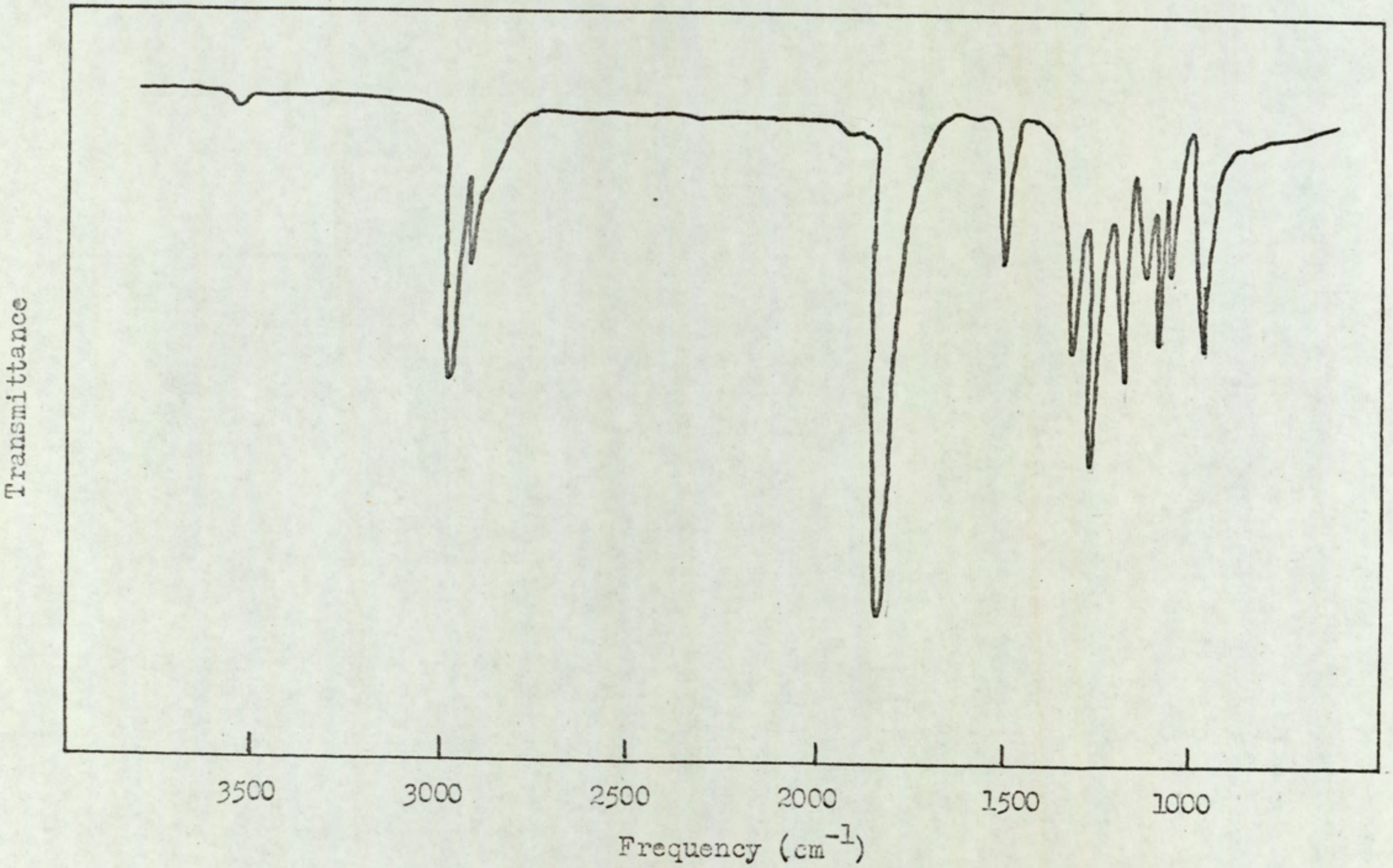


Figure 5. Infra-red spectrum of C'hexAS. Spectrum recorded as a carbon tetrachloride solution (10% v/v) using KBr plates and 0.025mm. spacer. Reference cell air.

characteristic set of main peaks corresponding to fragmentation of the anhydrosulphite ring was observed. The relative magnitude of these peaks appears to bear some relationship to the products of thermal decomposition of individual members, but for characterisation purposes the occurance together, of mass peaks (M - 64); (M - 92); (M - 108) and a much weaker peak at (M - 80), may be taken as typical of the anhydrosulphite ring.

Nuclear magnetic resonance studies were carried out on 10% (v/v) solutions of the anhydrosulphites in carbon tetrachloride or carbon disulphide. The anhydrosulphite ring deshields substituent protons with the result that chemically equivalent substituents are magnetically non-equivalent. This is illustrated in the simple case of HBAS (Figure 6a) where the splitting of the methyl substituent may be plainly seen (singlets at 8.25 τ and 8.41 τ). The same principle of non-equivalence extends to anhydrosulphites with other C-5 substituents, the complexity of the spectrum increasing as the series is ascended, due to a larger number of spin-spin interactions. This effect is illustrated in the spectrum of MEAS (Figure 6b). Signals due to the α-methyl (singlets at 8.23 τ and 8.39 τ) are similar to those of HBAS; in addition two triplets due to the β-methyl (centred at 9.2 τ and 8.92 τ J 7.0 cps) and two quartets due to the α-methylene group (centred at 8.05 τ and 7.93 τ, J 7.0 cps) are observed. Thus for characterisation purposes, the n.m.r. spectrum clearly distinguishes the anhydrosulphite on one hand and parent acid, oligomers and chlorine containing impurities on the other, since in all these latter cases chemically identical substituents are magnetically equivalent.

There is a striking difference between the n.m.r. spectra of

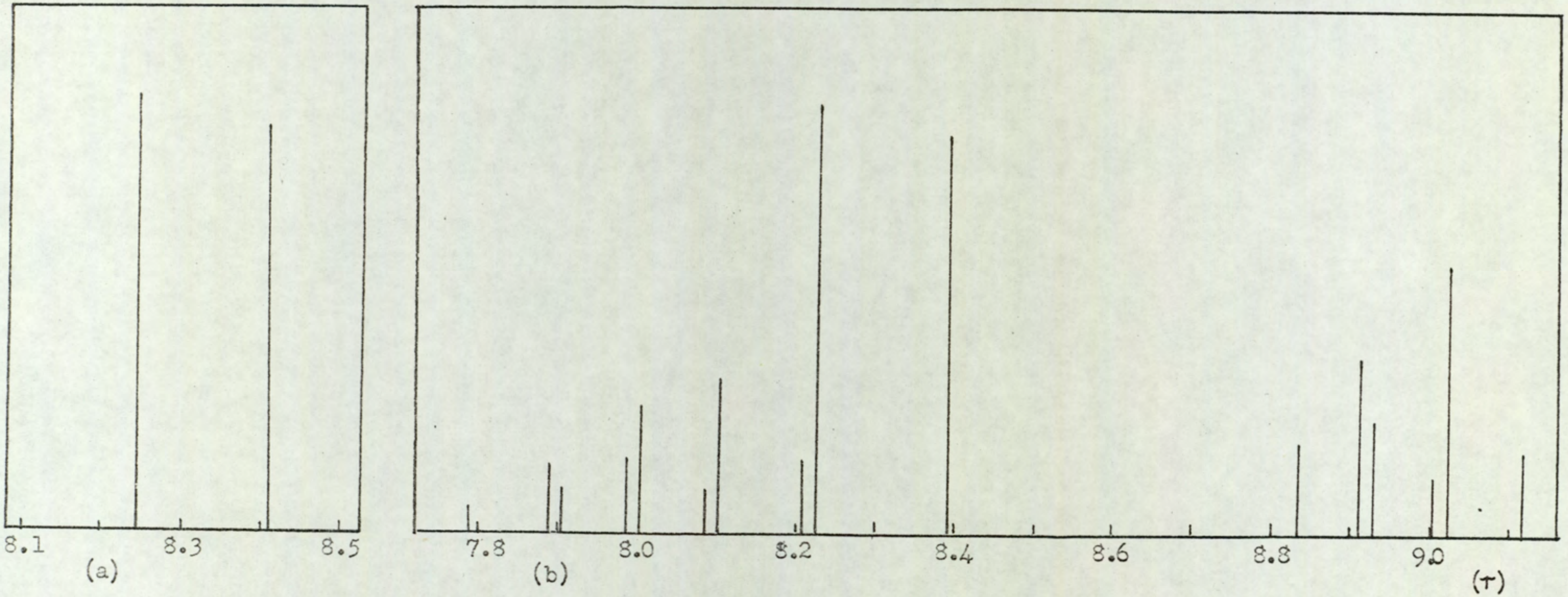
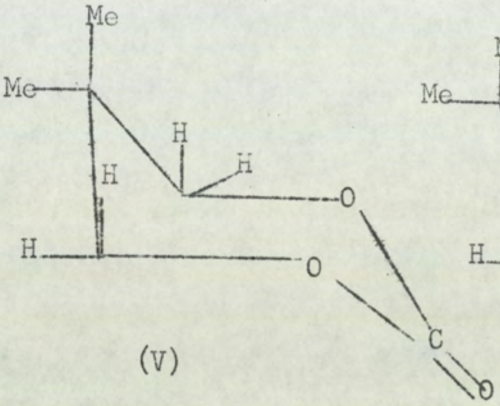
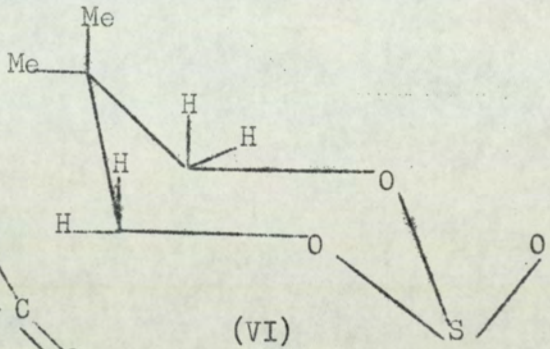


Figure 6. The nuclear magnetic resonance spectra of (a) HBAS (b) MEAS. Spectra recorded as carbon tetrachloride solutions (10% v/v), at 100 Mc/s.

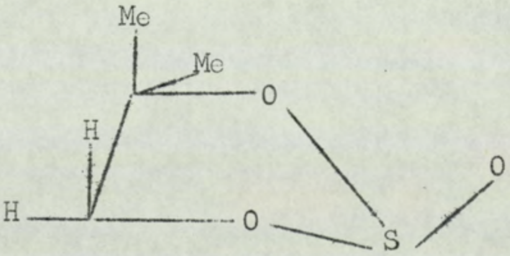
cyclic carbonates (V)[65] and cyclic sulphites (VIandVII)[65,66], which has been attributed to the planar and pyrimidal structures of the carbonate and sulphite moieties respectively.



(V)



(VI)



(VII)

The spectrum of the former simply consists of two singlets, one being assigned to methyl proton, and the other to ring proton resonance. Because of conformational differences, the latter are more complex, a split singlet being observed for methyl proton and a quartet, more correctly a converging doublet, for ring proton signals. That spectra of cyclic sulphites resemble those of HBAS and MEAS is presumably because they have similar structural features. By analogy with ethylene sulphite it would be anticipated that GAAS exhibits a coverging doublet, however, two such bands are observed centred at 4.76τ and 5.17τ (Figure 7). Similar behaviour is exhibited by LAAS. It would appear that in these two cases an

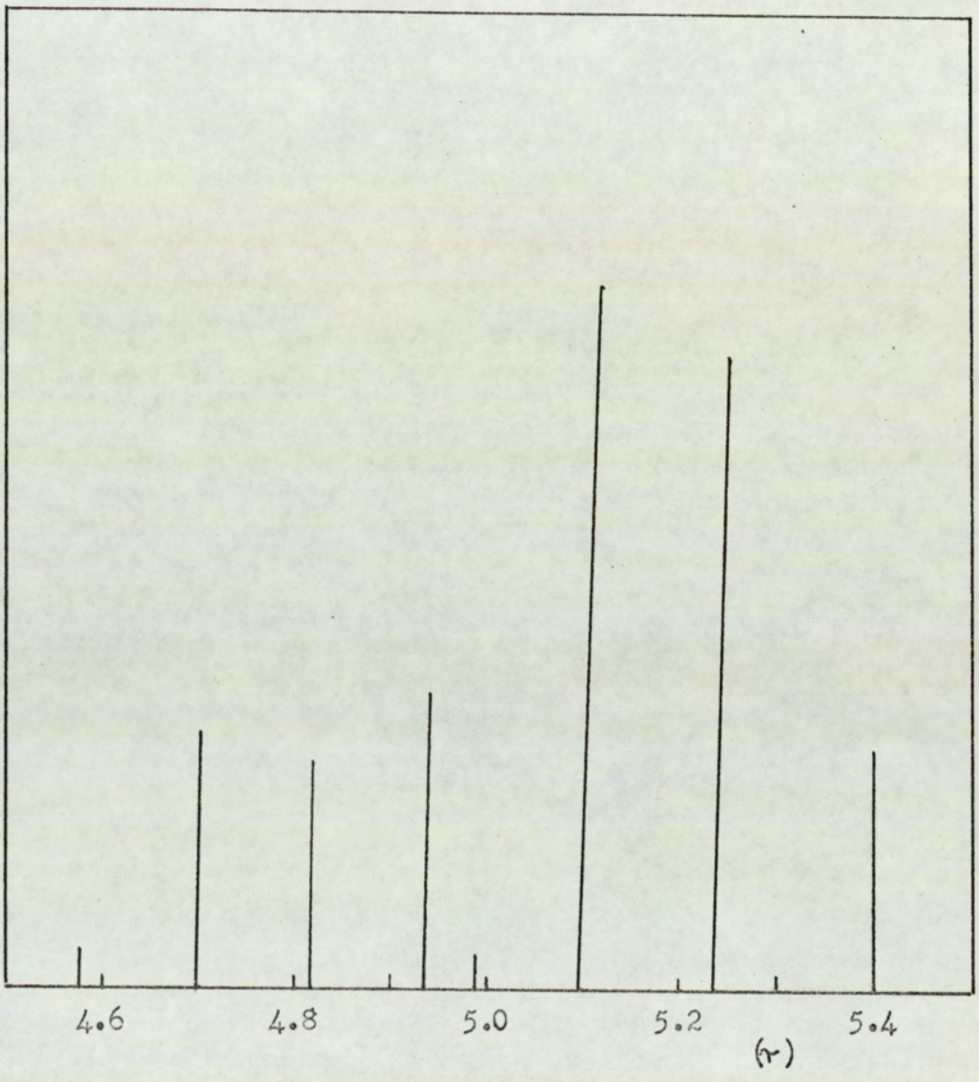
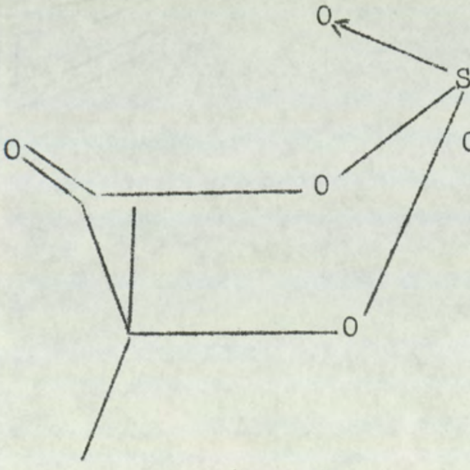


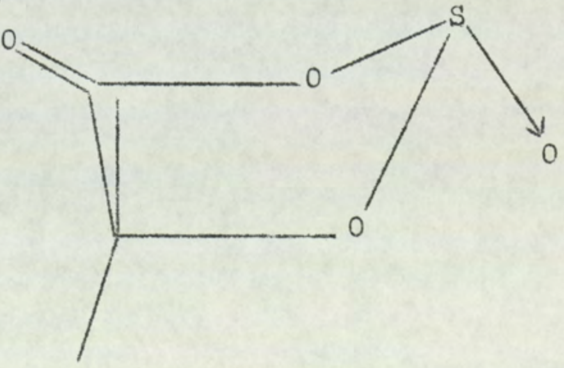
Figure 7. The nuclear magnetic resonance spectrum of GAAS. Spectrum obtained as carbon tetrachloride solution (10% v/v), operating frequency 100 Mc/s.

additional conformational difference requires further splitting.

This may be due to (a) a large conformational energy, such that under the conditions of study different forms are not interconvertable, (b) stereomutation about the sulphoxide group, and (c) a form stable in GAAS not allowed in higher homologues. The first two can be excluded since, any conformational energy effect would be more pronounced in substituted derivatives, and sulphur inversion is known to be a high energy process which usually occurs at temperatures in excess of 200°[67]. A plausible hypothesis based on (c) may be as follows. Two fixed conformations (VIIIa and b) are both present in GAAS as evidenced by two sets of converging doublets, whereas in HBAS, for example, a split singlet indicates only one form is present. Presumably in the latter case the form (VIIIa) is not favoured because of steric interaction between substituents and the sulphoxide oxygen. Before this postulate is established, however, further studies are required, especially as regards ring planarity, and the spectra of GAAS and HBAS at low and elevated temperatures.



(VIIIa)



(VIIIb)

4. THE POLYMERISATION OF 5,5-DIETHYL 1,3,2-DIOXATHIOLAN-4-ONE-2-OXIDE:-

Results and Discussion

The synthesis of 5,5-diethyl-1,3,2-dioxathiolan-4-one-2-oxide (I), hereinafter referred to as DEAS, was first reported by Rose[24]. In view of the methods of purification employed and the poor properties of products obtained in its attempted polymerisation the degree of purity was suspect. The work presented in this section compares the kinetic behaviour of pure DEAS during its decomposition (polymerisation) with that of HBAS.

4.1 Results

Thermal Polymerisation. The rates of appearance of polymer and disappearance of monomer were followed by gravimetry (or infra-red), and gas evolution techniques respectively. The rate of evolution of sulphur dioxide as a function of time was found, in dry non-hydroxylic solvents, to correspond directly to the rate of polymer formation. This type of behaviour, in which the ring-opening decomposition of the monomer represents the rate determining step in the sequence of reactionsleading to polymer formation was also observed with 5,5-dimethyl substituted monomer[25].

DEAS decomposition was measured in a range of solvents between 50 and 100°. Monomer decomposition was shown to be a first order process by computing the gas evolution data graphically in the form $\log ((p_\infty - p)/p_\infty)$ versus time. Typical examples are shown in Figure 8. The overall process can therefore be expressed by the equation:-

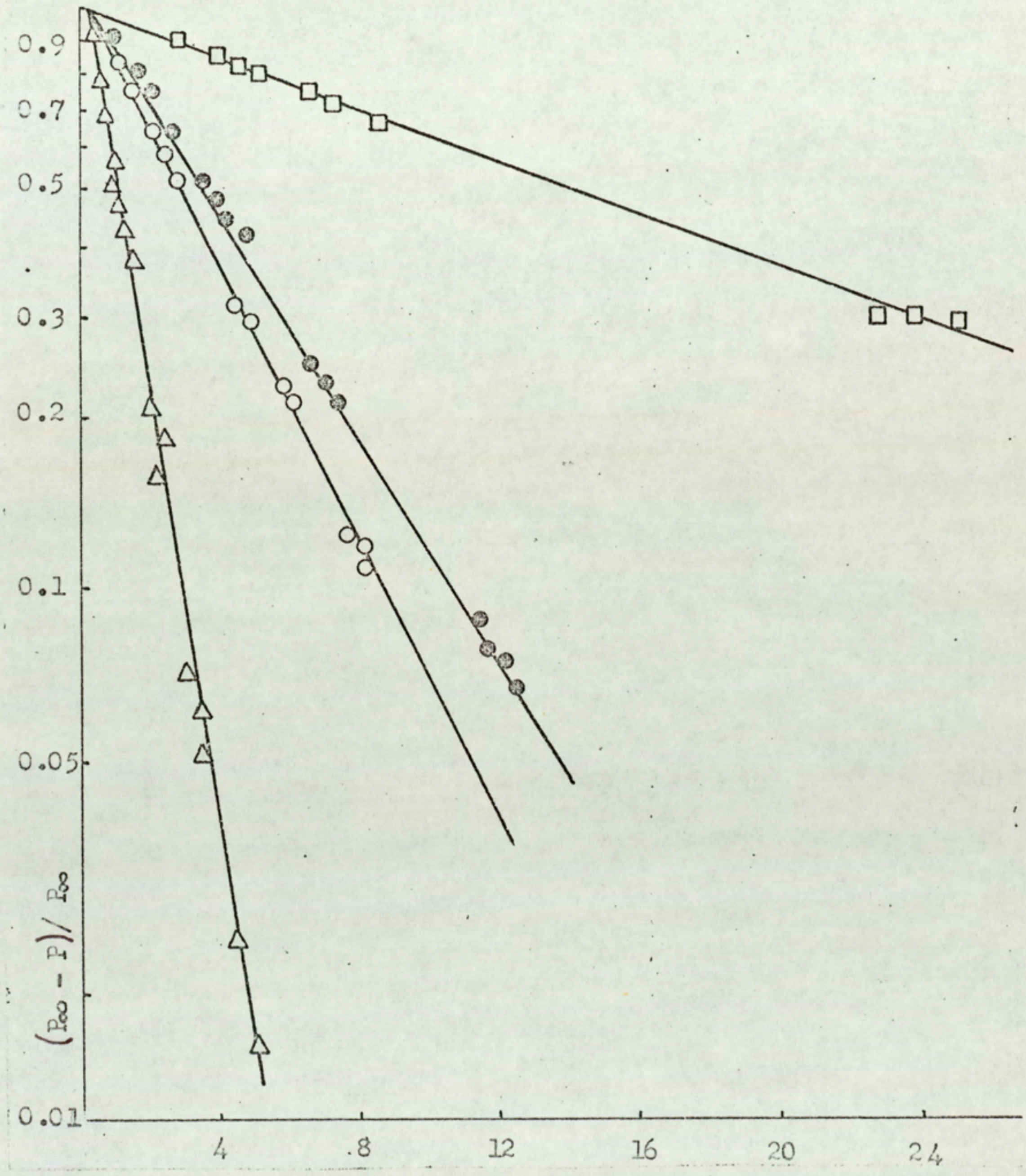


Figure 8. Semi logarithmic plot of $P_\infty - P / P_\infty$ versus time for the decomposition of DEAS in different solvents at 90°

△ nitrobenzene, ○ dioctyl phthalate

● chlorobenzene, □ dekalin

$$\frac{d[P]}{dt} = \frac{-d[DEAS]}{dt} = \frac{d[SO_2]}{dt} = k_1[DEAS] \quad \ldots\ldots \quad (1)$$

where $[P]$, $[DEAS]$ and $[SO_2]$ refer to the concentrations of polymer DEAS and sulphur dioxide respectively, and k_1 the first order rate. Changes in initial concentration and variations of sulphur dioxide pressure were investigated and did not significantly alter the measured values of k_1.

Table 4 presents the rate constants observed for the decomposition of DEAS in a series of solvents at temperatures in the region of 90°.

Table 4

First order rate constants (k_1) and half lives ($t_{\frac{1}{2}}$) for the decomposition of DEAS in various solvents. $[DEAS]_0 = 0.5$ mole litre^{-1}.

Solvent	Dielectric Constant at 90°	Temperature (°C)	$10^5 k_1$ (sec^{-1})	$t_{\frac{1}{2}}$ (min)
Dimethylsulphoxide	36	89.3	138	8.4
Glycerol	32	89.1	130	8.9
Nitrobenzene	25	90.0	20.1	57.5
p-nitrotoluene	17	88.1	10.5	110
Chlorobenzene	4.5	88.1	6.3	183
Dioctylphthalate	3.5	91.0	7.3	158
Dekalin	2.5	94.0	2.6	444

It is evident that in solvents of increasing dielectric constant there is a trend to faster reaction. Attempts to find a quantitative relationship between some function of rate and of dielectric were not altogether successful. Comparison of the figures in Table 4 with those presented elsewhere for HBAS[25] demonstrate that DEAS is more sensitive than HBAS to this change in solvent property.

Plots of conversion to polymer versus time for DEAS in nitrobenzene at various temperatures are given in Figure 9 and the derived rate constants and kinetic parameters shown in Table 5. The values obtained for activation energy (E), pre-exponential factor (A), and entropy of activation ($\Delta S\pm$) were derived from Arrhenius plots and are of the order expected for a genuine unimolecular process.

Table 5

First order rate constants (k_1), half lives ($t_{\frac{1}{2}}$), energy of activation (E), entropy of activation ($\Delta S\pm$) and frequency factor (A) for the polymerisation of DEAS in nitrobenzene.

$[DEAS]_o = 0.5$ mole litre^{-1}

	$10^5 k_1 (sec^{-1})$	$t_{\frac{1}{2}}$(min)
63^o	0.65	1777
82	5.67	203.7
90	20.1	57.5
96	37.0	31.2
E (kcal mole^{-1})	28.7	
A (sec^{-1})	4.2×10^{13}	
$\Delta S\pm$ (cal deg^{-1}mole^{-1})	+1.3	

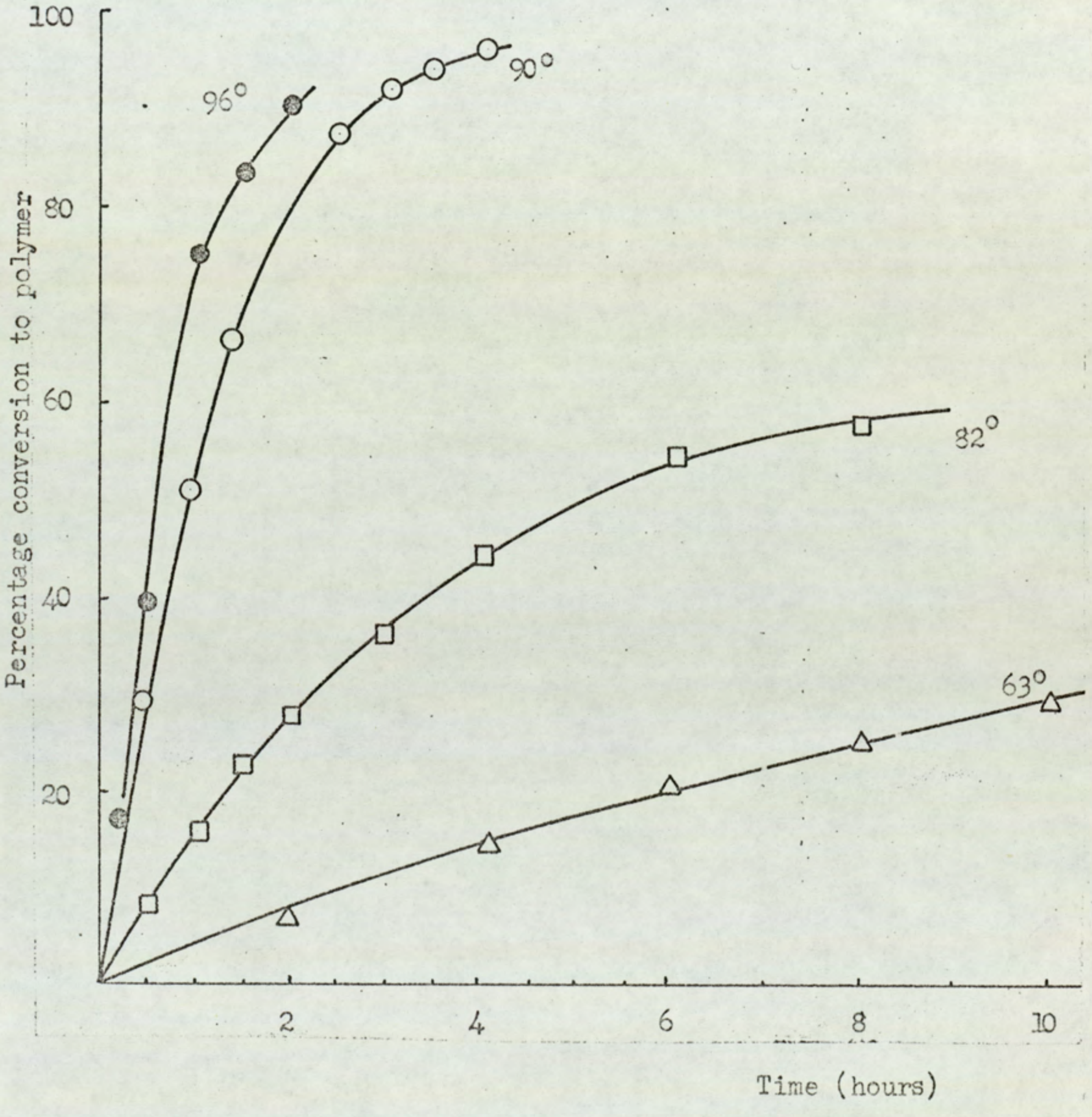
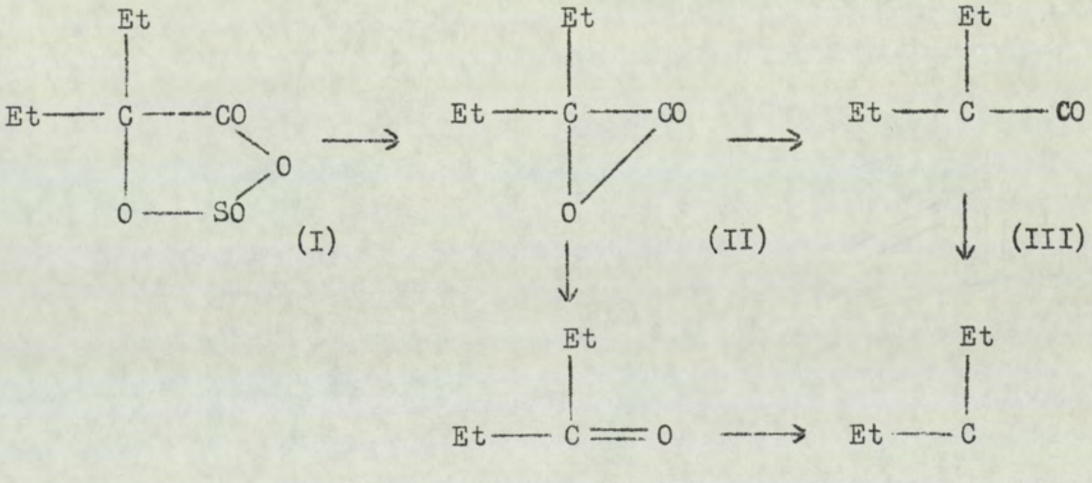


Figure 9. Polymerisation of DEAS in nitrobenzene at different temperatures. Plotted as percentage conversion to polymer versus time.

Transient formation of an α-lactone intermediate has been proposed to occur during the thermal decomposition of HBAS, further evidence for such species is found in the mass spectra of anhydrosulphites. As the sample attains temperatures above 200° in the instrument no parent peak is observed for DEAS, but the cracking pattern involved mass numbers of 114 (M-64), 98 (M-80), 86 (M-92) and 70 (M-108), which on consulting the whole spectrum can be assigned to the fragments (II), (III), (IV) and (V) respectively, of which signals for (II) and (IV) are particularly strong.



(I) (II) (III) (IV) (V)

Initiated Polymerisation. In certain cases[26] anhydrosulphites undergo a bimolecular ring-opening reaction in the presence of an alcohol, leading to regeneration of a hydroxyl group. The regenerated hydroxyl group can then take part in a bimolecular chain propagation reaction analogous to that observed to occur[16] with N-carboxy-α-amino acid anhydrides. The steric hindrance of the two C-5 methyl substituents in 5,5-dimethyl-1-3,2-dioxathiolan-4-one-2-oxide effectively prevents such a reaction occuring however. In order to determine the sensitivity of DEAS to hydroxyl group attack, rates of decomposition in nitrobenzene solution ($[M]_0$ = 0.5

moles/litre) containing various quantities of added benzyl alcohol ($[OH]_o$ = 0.1-0.5 moles/litre) were measured. The rate of DEAS decomposition was found to be independant of initial hydroxyl group concentration;

i.e. $$-\frac{d[DEAS]}{dt} = k_1[DEAS]^1[OH]^0 \qquad \ldots\ldots \quad (2)$$

Finally the decomposition of DEAS was examined in pure dry benzyl alcohol ([OH]approximately 8 moles/litre) at various temperatures. The value of the rate constants and derived kinetic parameters which are shown in Table 6, demonstrate that the decomposition of DEAS takes place less rapidly in benzyl alcohol than in nitrobenzene.

Table 6

First order rate constants(k_1), energy of activation (E), and frequency factor (A) for the decomposition of DEAS in benzyl alcohol. $[DEAS]_o$ = 0.5 moles/litre

	$10^6 k_1 (sec^{-1})$
79°	5.6
90	13.9
99	42.4
109	80.0
121	244.0
E (kcal $mole^{-1}$)	25.1
A (sec^{-1})	1.9×10^{10}

Arrhenius plots for DEAS decomposition in both benzyl alcohol and nitrobenzene are illustrated in Figure 10. The reaction product obtained in benzyl alcohol was not poly (oxy (diethyl acetyl)), (for explanation of nomenclature See Appendix 1), however, but benzyl-α-ethyl-α-hydroxybutyrate. For comparison, a similar study in cyclohexanol as medium gave a first order rate constant of 1.43 x 10^{-5} sec^{-1} at 90°, and a reaction product of cyclohexyl-α-ethyl-α-hydroxybutyrate.

More active nucleophiles were examined as potential initiators. Primary and secondary amines reacted very rapidly with an equimolar amount of DEAS to yield the appropriate amide. When substoichiometric amounts of amine were used a rapid reaction with approximately equimolar amount of DEAS again occured but the rate of the subsequent first order decomposition of DEAS was practically identical to that in the absence of amine. Similarly when substoichiometric amounts of amide were used, no evidence of initiated polymerisation was observed. Dimethyl sulphoxide when used as reaction medium has been observed (Table 2) to enhance rapid decomposition of DEAS. When used in less than equimolar quantities, however, no evidence of initiating or catalytic, activity was observed. Table 7 presents typical results obtained at 60°.

α-Chloroacid chloride impurity was not totally involved in the initial polymerisation steps, since the rate of DEAS decomposition was not significantly affected even when the impurity was present in concentrations as high as 15 mole per cent. Using chloride contaminated DEAS a polymerisation was allowed to proceed to approximately 50% conversion, and then residual monomer distilled out under reduced pressure. The recovered monomer when monitored for chlorine still contained a considerable fraction of impurity, Presence of α-chloroacid chloride drastically lowered the molecular

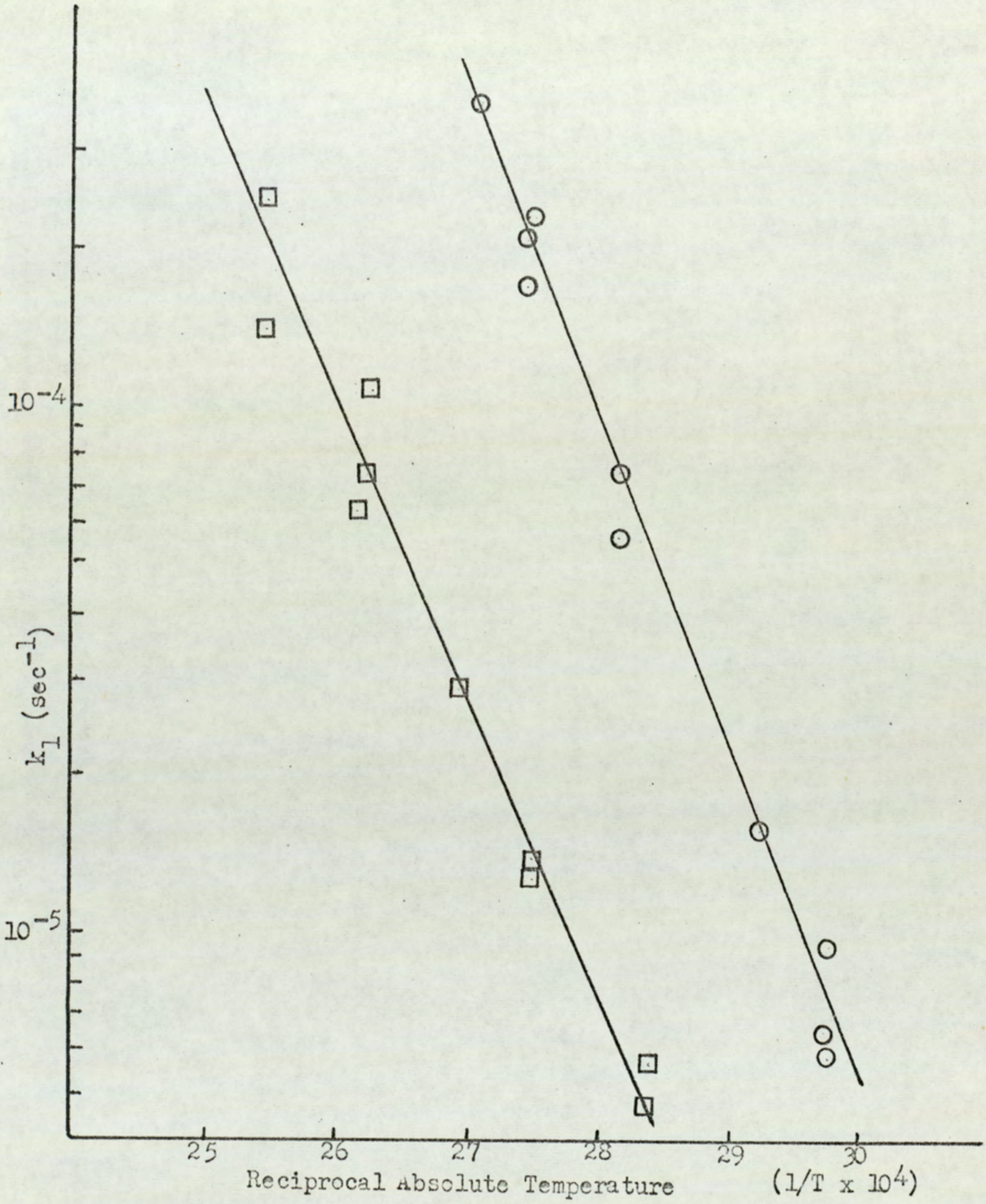


Figure 10. Arrhenius plots for the decomposition of DEAS in,

□ benzyl alcohol, and ○ nitrobenzene.

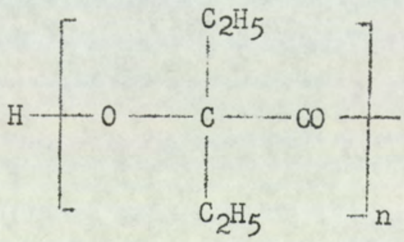
weight of the resultant product.

Table 7

The effect of additives [X] on the first order rate constant (k_1) for the decomposition of DEAS in nitrobenzene at 60°.

Additive	$[X]_o$ ($m.l^{-1}$)	$[DEAS]_o$ ($m.l^{-1}$)	$10^6 k_1$ (sec^{-1})
-	-	0.5	4.3
Dimethyl formamide	0.01	0.5	4.3
Dimethyl formamide	0.05	0.5	4.5
Dimethyl sulphoxide	0.01	0.5	4.4
Dimethyl sulphoxide	0.05	0.5	4.5

Examination of the polymers produced by the thermal decomposition of DEAS showed that they were linear poly α-esters, having the structure (VI).



$$\mathrm{H}\left[\mathrm{O}-\overset{\mathrm{C_2H_5}}{\underset{\mathrm{C_2H_5}}{\mathrm{C}}}-\mathrm{CO}\right]_n\mathrm{OH}$$

(VI)

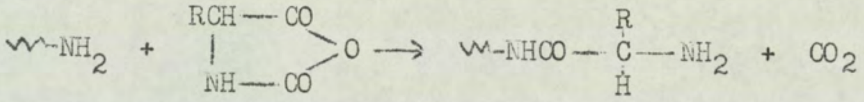
The value of n is governed, primarily, by the purity of the system. Thus if alcohols are added to the system, for example, although they do not react directly with DEAS, their presence lowers the molecular weight attainable and at the equimolar concentration level prevents polymer formation altogether. For any nucleophile (N) containing a labile hydrogen atom (for example, benzyl alcohol, benzylamine, and water) the degree of polymerisation (n) at complete conversion is given by the expression :-

$$n = \frac{[\mathrm{DEAS}]_0}{[\mathrm{N}]_0} \qquad \ldots\ldots (3)$$

In the absence of added nucleophiles adventitious traces of water control the molecular weight, and under these conditions each chain is terminated by one hydroxyl, and one carboxyl group.

4.2 Discussion

Ring-opening polymerisation reactions in which the propagation step consists of a bimolecular interaction between a terminal nucleophile and an active site within the ring are well known. Typical of this type of chain growth process is the amine initiated polymerisation of N-carboxy-α-amino acid anhydrides[16]. In this reaction a terminal (primary or secondary) amino group attacks an active carbonyl site. The resultant ring-opening and concurrent expulsion of carbon dioxide leads to chain extension (by one repeat unit) and regeneration of the terminal amino group (Equation 4).



$$\sim\!\sim NH_2 + \begin{array}{l} RCH - CO \\ | \qquad\quad > O \\ NH - CO \end{array} \longrightarrow \sim\!\sim NHCO - \underset{H}{\overset{R}{C}} - NH_2 + CO_2 \qquad \ldots\ldots \quad (4)$$

An analogous polymerisation mechanism has been shown to occur with those members of the anhydrosulphite series which contain at least one C-5 hydrogen atom. In this case the propagation species is a terminal hydroxyl group, attack takes place at the C-4 carbonyl group, sulphur dioxide is expelled and the polymer has a repeating ester rather than amide group. Both processes are characterised by second order kinetic behaviour, low activation energies (6-12 kcal mole^{-1}), very low frequency factors (10^2-10^5 litre mole^{-1}sec^{-1}) and pronounced sensitivity to reaction medium polarity.

The kinetic features associated with DEAS polymerisation are quite different from these and strongly resemble the observed behaviour of HBAS[25]. The reaction shows first order dependence on monomer concentration, zero order dependence on hydroxyl group concentration and yet the degree of polymerisation is controlled by initial concentration of hydroxyl groups. Furthermore in the presence of moisture the chains are carboxyl/hydroxyl terminated, and when monomer decomposition takes place in the presence of a molar excess of hydroxyl groups, the product is apparently formed by direct combination of the ring and attacking species. The values of activation energy (25-29 kcal mole^{-1}) and frequency factor (10^{12}-10^{13}sec^{-1}) associated with monomer decomposition, both in non-hydroxylic solvents to form polymer, and in alcohol to form esters, are typical of reactions in which thermal cleavage of a weak covalent bond is the rate determining step.

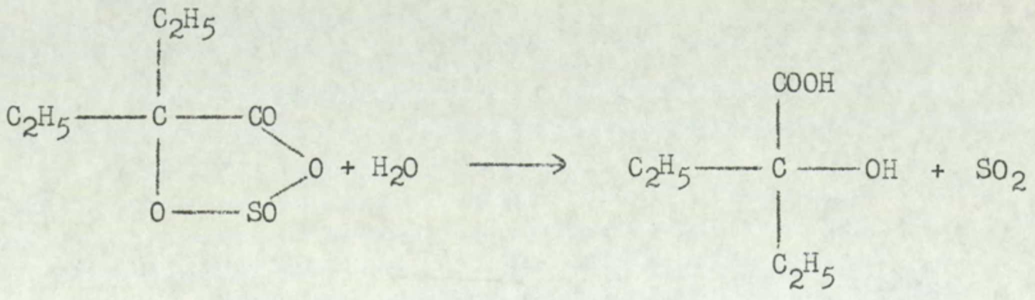
The sensitivity of DEAS to bimolecular hydroxyl group attack is conveniently assessed by comparing the first order rate constants in benzyl alcohol and nitrobenzene, but otherwise under identical conditions. Since the hydroxyl group concentration in benzyl alcohol is of the order of 8 moles/litre, direct attack by this species is readily detected. It is evident from the results presented earlier that a bimolecular mode of decomposition is insignificant under the conditions of study.

The fact that primary and secondary amines can attack DEAS directly is entirely consistent with the observed inter-relation of steric and electronic effects in this series[68]. The more powerful amine nucleophile overcomes the steric hindrance of the C-5 ethyl substituents, but the hydroxyl terminated product is unable to do this, thus no direct bimolecular chain propagation reaction is observed. Similarly tertiary amides are not able to act as chain propagating species, since in sub-stoichiometric amounts they do not sensibly alter the rate of monomer decomposition. Solvents of high polarity, or basicity, which do not contain a labile hydrogen atom, can markedly affect the rate of monomer decomposition, however, when used as reaction media. Other workers claim to have observed catalysed polymerisation of HBAS with such materials, but were unable to obtain high molecular weight polymer[32]. The ability of triethylamine to decompose anhydrosulphite monomers to oligomeric materials, even at 0°, was mentioned in section 3.1. In the light of present evidence polymerisation of DEAS by this route does not warrant favour, however, since the difficulty in purification, and the poorer products obtained, outweighs any possible advantage of faster reaction rates.

The behaviour of α-chloroacid chloride impurity is complex, as it is not involved in the initiation stages of the reaction. When present in concentrations below 15% no deviation in the decomposition rate was observed, a phenomenon which has also been noted with GAAS[56]. Since the impurity acts as an efficient molecular weight modifier it is probable that the compound plays a role in termination and/or transfer reactions.

The apparent inconsistencies in the behaviour of DEAS can be explained by a modification of the mechanism proposed for HBAS polymerisation.

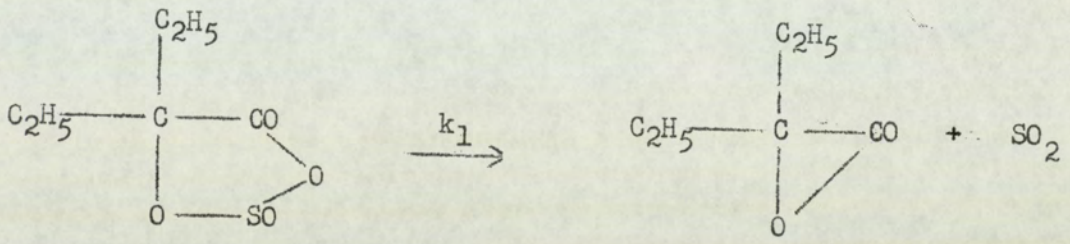
Adventitious traces of moisture will react with an equimolar quantity of DEAS to regenerate α-hydroxy-α-ethylbutyric acid (Equation 5). This is an extremely rapid reaction, even at room temperature.



(VII)

...... (5)

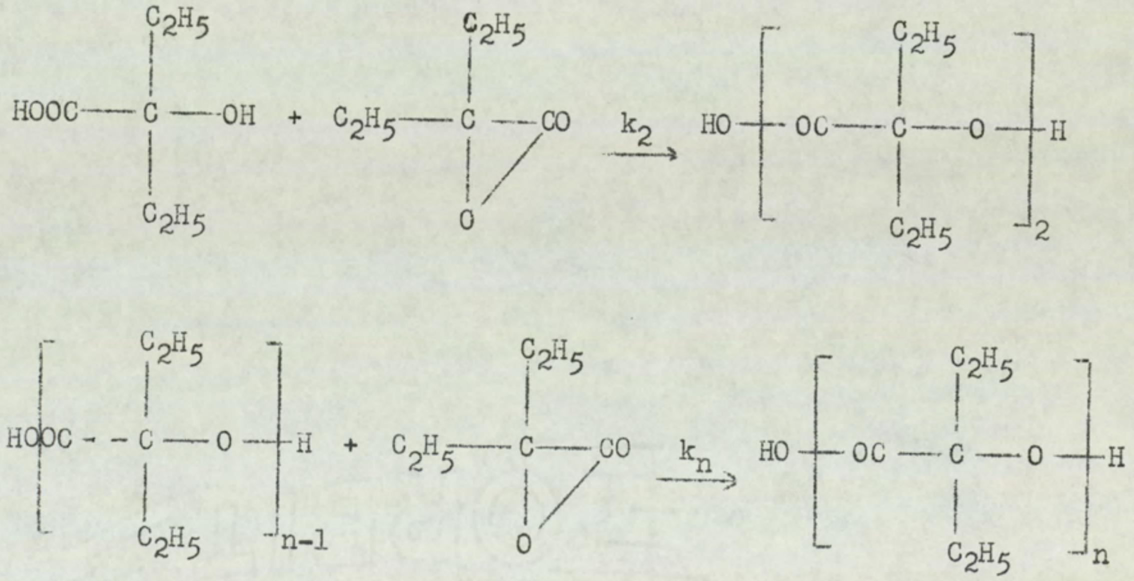
The rate determining step is the decomposition of DEAS to form a polymerisation intermediate with concurrent expulsion of sulphur dioxide (Equation 6). The intermediate which fulfills this requirement is considered, formally, to be an α-lactone (VIII).



(VIII)

......(6)

A rapid chain growth process then takes place as shown in Equation 7.



...... (7)

Since it is proposed that (VIII) is a very reactive species which can react rapidly with hydroxyl groups, k_2, k_3 ---- k_n are very much larger than k_1, and reaction (6) is rate determining. Therefore:-

$$k_1[\mathrm{DEAS}] = k_2[\mathrm{VIII}][X_1] + k_n[\mathrm{VIII}](\Sigma[X_{n-1}]) \qquad \ldots\ldots (8)$$

where, $[X_1]$ represents (VII) and $[X_n]$ represents structure (VI).

Thus sulphur dioxide evolution and polymer formation may be equated in the following way:-

$$\frac{d[SO_2]}{dt} = \frac{-d[DEAS]}{dt} = k_1[DEAS] = \frac{d[P]}{dt} \quad \ldots\ldots \quad (9)$$

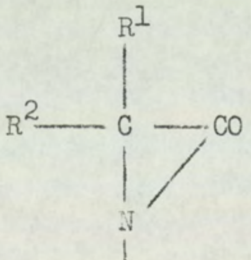
which is identical with Equation 1.

Radio tracer studies enabled values of k_n/k_2 to be obtained for the polymerisation of HBAS in different solvents. It was demonstrated that this ratio remained sensibly constant during the polymerisation and that its magnitude determines the molecular weight distribution in this type of polymerisation process. Although the value of k_n was somewhat greater than that of k_2, added quantities of parent α-hydroxy acid were always incorporated into the polymer before monomer decomposition was complete. Equation 3 demonstrates that this is also the case in DEAS polymerisation.

In the field of ionic reactions, α-lactone intermediates have been implicated in carboxylate-anion neighbouring group participation processes, (for example, the displacement of bromine from α-bromo-acids in alkaline solution[69]). Evidence for their formation has been found by following the stereochemistry of reaction products. These species have also been proposed in the radical decomposition of certain per-esters, for example, di-tertiary-butyl peroxy diphenylmalonate[40]. Decompsition of the latter in an excess of methanol gives monomeric α-methoxy diphenylacetic acid, which has been proposed as evidence for trapping the α-lactonic intermediate.

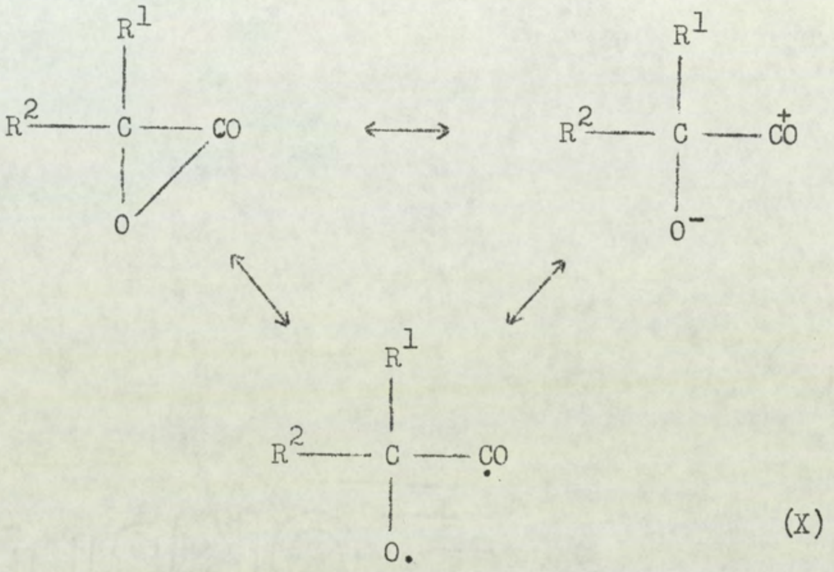
Similar behaviour is found with anhydrosulphites, since in the case of DEAS, its decomposition in excess benzyl alcohol at 90° yielded totally benzyl α-hydroxy-α-ethylbutyrate. This is not conclusive evidence for the transient existance of 3,3-diethyl acetolactone, however, since the same product is obtained by reaction, direct with the anhydrosulphite ring, or at some instant following primary scission but previous to sulphur dioxide expulsion. Of these alternative routes, direct attack on DEAS can be discounted since second order behaviour was not indicated in the rate data analysis. Also as expulsion of sulphur dioxide following primary scission is expected to be a concerted process, or nearly so, the complete intramolecular reorganisation occurs much more rapidly than any intermolecular action. In addition supporting evidence for diethyl acetolactone is found in the mass spectrum of DEAS, since under these conditions the primary electron induced fragment gives a strong signal and corresponds to the mass number of the lactone.

It is worth note that although α-lactones as such are very reactive and have never been isolated, even by low temperature trapping techniques, derivatives of α-lactams (IX) are known, and in some cases stable up to 100°[70].



(IX)

In the past there has been some controversy concerning the structure of α-lactones, as to whether they are covalent compounds or dipolar ions[40], however it would seem feasible to consider the third bond of the ring to be covalent but with a high degree of polarisation. Several resonating forms (X) may be expressed for the α-lactone:-



The precise nature of the intermediate in HBAS decompostion has been considered in detail[25]. Extreme polar or radical forms were discounted for several reasons; insensitivity to solvent polarity, inability of HBAS to drastically alter the rate of styrene polymerisation, inefficiency of radical scavengers to reduce HBAS decomposition rates and the failure to detect dimer-glycollide.

The rate of decomposition of DEAS is considerably more sensitive than that of HBAS, to the polarity of the reaction medium. On the other hand, HBAS, when freshly distilled, shows an intense violet colouration, which slowly disappears, and exhibits other radical characteristics, which are not apparent in the case of DEAS. It is likely, therefore, that theDEAS intermediate and reaction steps prior to its formation are more polar than those formed from HBAS.

The fact DEAS polymerisation in polar non-hydroxylic solvent occurs more rapidly than that of HBAS may be attributable to increased/ring strain due to the C-5 substituent size, and/or a greater charge donation by the ethyl substituents. In both cases polarisation of bonds within the anhydrosulphite ring is to be anticipated. This phenomenon is considered in more detail in the next section when the behaviour of other alkyl substituted derivatives is available.

Thus the first order rate constants for thermal polymerisation of symmetrically substituted 1,3,2-dioxathiolan-4-one-2-oxides at 90° in nitrobenzene are: 5,5-diethyl, $k_1 = 2 \times 10^{-4}$ sec^{-1}, and 5,5-dimethyl, $k_1 = 6 \times 10^{-5}$ sec^{-1}, whereas the unsubstituted ring is appreciably more stable ($k_1 = 5 \times 10^{-6}$ sec^{-1}).

5. THE POLYMERISATION OF OTHER ALKYL DISUBSTITUTED 1,3,2-DIOXATHIOLAN-4-ONE-2-OXIDES:-

Results and Discussion

Two previously unreported members of the symmetrical dialkyl series, 5,5-di-n-propyl and 5,5-di-n-butyl 1,3,2-dioxathiolan-4-one-2-oxides hereafter referred to as DPAS and DBAS respectively were synthesised. In addition an unsymmetrical derivative 5-methyl-5-ethyl-1,3,2-dioxathiolan-4-one-2-oxide, hereafter referred to as MEAS, was also prepared. Their chemical and kinetic behaviour is discussed in context with those other members of the series previously studied.

5.1 Results

Symmetrically Substituted Derivatives

General reactions. At room temperature both DPAS and DBAS reacted slowly with atmospheric moisture and much more rapidly in the presence of an excess of water. The decomposition of HBAS and DEAS by primary and secondary amines has been discussed in Section 4. With an excess of benzylamine in nitrobenzene at 30° both DPAS and DBAS reacted readily to form the appropriate secondary amide, the rate of attack being dependent upon substituent size. Thus Figure 11 shows the initial rates of decomposition of DBAS and BBAS in the presence of an excess of benzylamine at 30° in nitrobenzene. The rate of DBAS decomposed in dry nitrobenzene at the same temperature is included for comparison. It is evident that the rate of amine attack is reduced as substituent size increases.

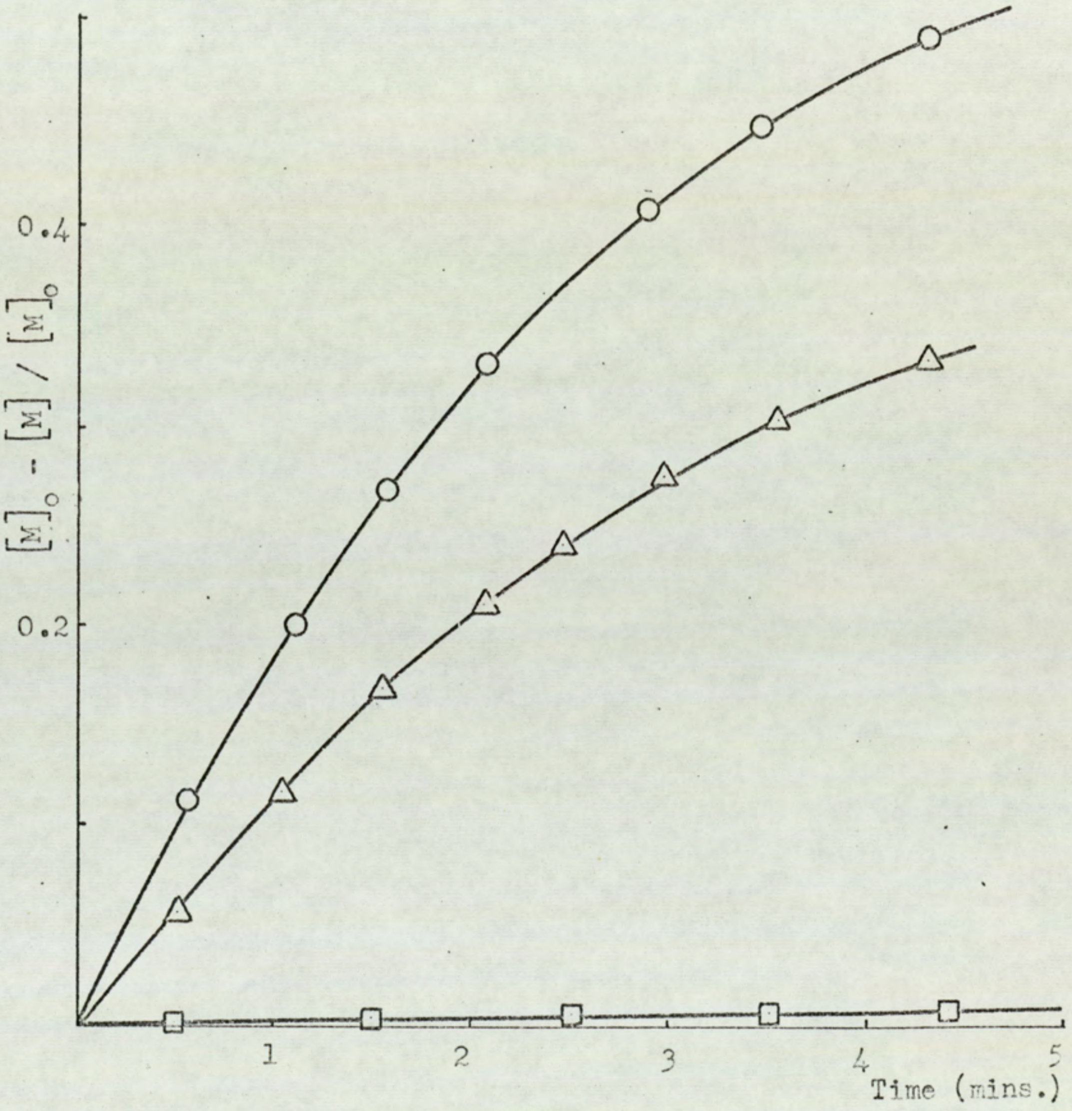


Figure 11. Initial rate curves for the decomposition of HBAS and DBAS (0.5 M) in nitrobenzene at 30°.

□ DBAS; △ DBAS + $Ph.CH_2 NH_2$ (2.0M).

○ HBAS + $Ph.CH_2 NH_2$ (2.0M).

Under similar conditions hydroxylic reagents, (for example benzyl alcohol) were not observed to react with either DPAS or DBAS, but since hydroxyl attack bears a special relationship to the chain propagation reaction during polymerisation, additional studies were carried out at temperatures corresponding to those employed for polymerisation in non-hydroxylic solvents.

Thermal decomposition of DPAS and DBAS were measured in non-hydroxylic solvents over a range of temperatures. The decomposition of each derivative was studied in nitrobenzene at temperatures between 65 and 95°. The rate of disappearance of anhydrosulphite, as monitored by sulphur dioxide evolution was found to correspond directly to the rate of product formed. Change of initial anhydrosulphite concentrations from 0.05 to 0.75 moles litre^{-1}, and variation of initial sulphur dioxide pressure did not alter the value of derived rate constants. All reactions showed first order dependence on monomer concentration (for example, Figure 12a) as did the decomposition of HBAS and DEAS. The rate constants measured in nitrobenzene at various temperatures together with derived kinetic parameters are presented in Table 8. The values obtained for frequency factor, energies, and entropies, of activation are of the order expected for genuine unimolecular processes. There is an obvious similarity between the thermal behaviour of HBAS, DEAS, DPAS, and DBAS since all show first order decomposition in non-nucleophilic solvents, which may be expressed in the form of a general rate equation:-

$$\frac{d[SO_2]}{dt} = \frac{-d[M]}{dt} = \frac{d[P]}{dt} = k_1[M] \qquad \text{......} \quad (1)$$

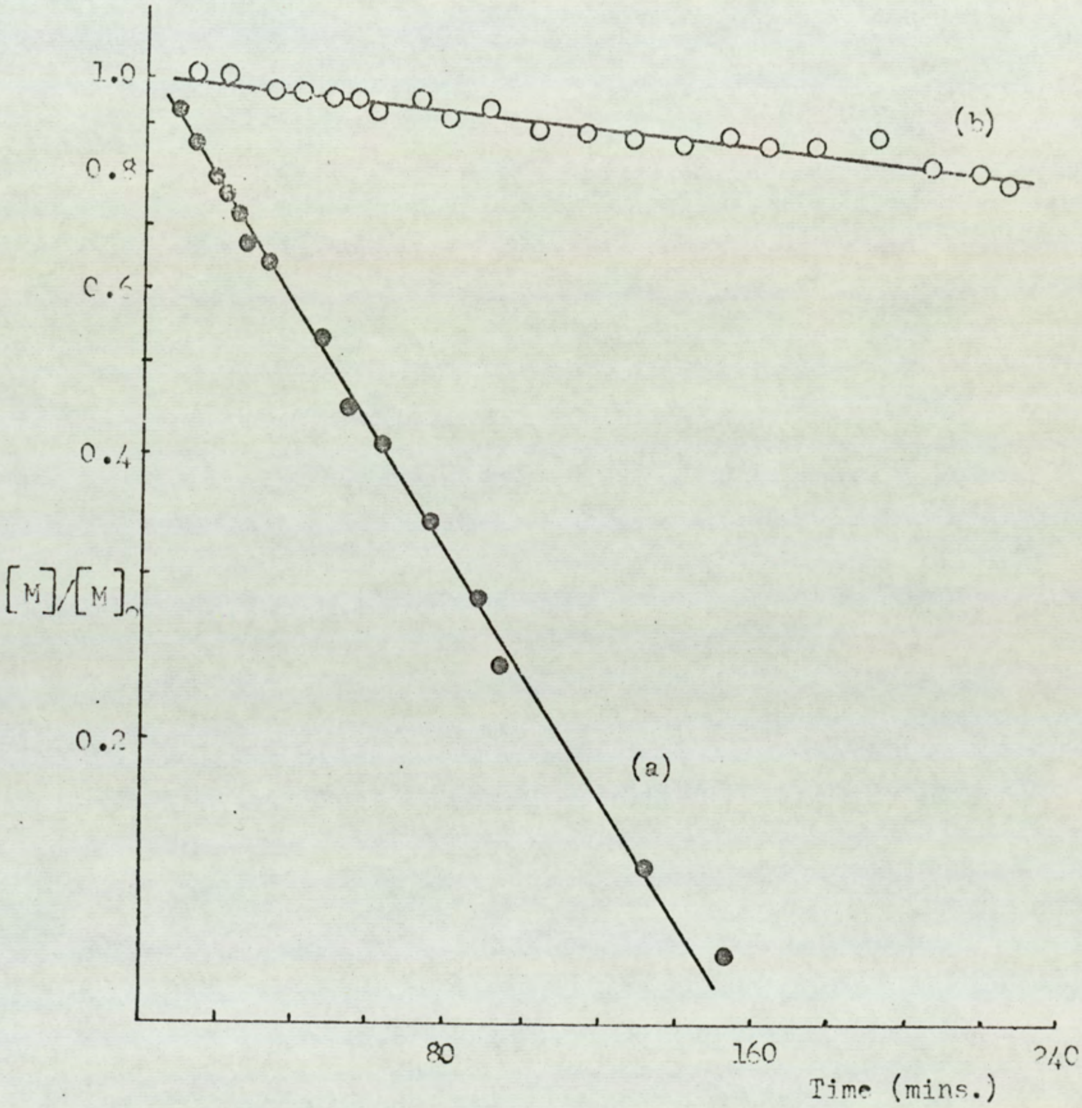


Figure 12. Decomposition reaction of DPAS at 90° in a) nitrobenzene, b) benzyl alcohol. $[DPAS]_o$ = 0.4 mole litre^{-1}. Semi logarithmic plot of DPAS against time.

where [M] refers to anhydrosulphite concentration and [P] the concentration of product (typically polymer).

Table 8

First order rate constants (k_1, sec^{-1}), energies of activation (E, kcal. $mole^{-1}$), frequency factors (A, sec^{-1}), and entropies of activation (ΔS±, cal. $deg.^{-1} mole^{-1}$) for the decomposition of DPAS and DBAS in pure nitrobenzene. $[M]_0$ 0.4 mole $litre^{-1}$.

Anhydrosulphite	$k_1 \times 10^5$				E	10^{13}A	ΔS±
	69.5°	81.3°	89.6°	94.6°			
DPAS	1.87	9.3	23.9	27.4	30.5	52	+3.19
DBAS	2.73	11.4	25.6	46.7	28.3	3.5	+0.52

The decomposition of anhydrosulphites in solvents of varying dielectric , but at the same temperature and initial concentration was found to occur at different rates. Table 9 shows the first order rate constants for the decomposition of three anhydrosulphites in solvents of high and low dielectric constants at 90°. The sensitivity to polarity of reaction medium is apparently more marked in the higher members of the series.

The mass spectra of anhydrosulphites was reported earlier as providing supporting evidence for the proposed thermal decomposition mechanism, since mass peaks are observed at (M - 64) and (M - 92) and correspond to the largest molecular fragments. When considering the whole spectrum the two fragments can be assigned empirical formulae corresponding to α-lactone and ketone respectively. Relative intensities of these peaks, which may be expressed as the ratio of (M - 64) / (M - 92), show a trend in the series. The values obtained are; GAAS (0.1), DEAS (1.2), and DBAS (1.5).

Table 9

The effect of reaction medium on the rate constants (k_1) for the first order decomposition of various anhydrosulphites, at 90°.

Anhydrosulphite	Nitrobenzene $10^5 \times k_1$ (sec^{-1})	Dekalin $10^5 \times k_1$ (sec^{-1})
HBAS	6.1	2.2
DEAS	20.1	2.6*
DBAS	26.0	3.9

* 94°

Reaction with alcohols. Decomposition of DPAS and DBAS in benzyl alcohol at temperatures in the range 70-90° showed first order dependence on monomer concentration (Figure 12b). Since the observed rate constants (DPAS 1.24×10^{-5} sec^{-1}, and DBAS 2.7×10^{-5} sec^{-1}) are approximatley an order of ten below those in nitrobenzene it can be safely assumed that no bimolecular propagation reaction can effectively occur.

Although hydroxylic reagents would not react directly with higher members of the series an apparent initiation reaction was observed when a few mole per cent of a primary amine **were** added to anhydrosulphite in nitrobenzene. Following the initial rapid reaction between approximately equimolar quantities of amine and anhydrosulphite, however, the rate returned to that corresponding to the pure thermal process. In Figure 13 the rate of decomposition,

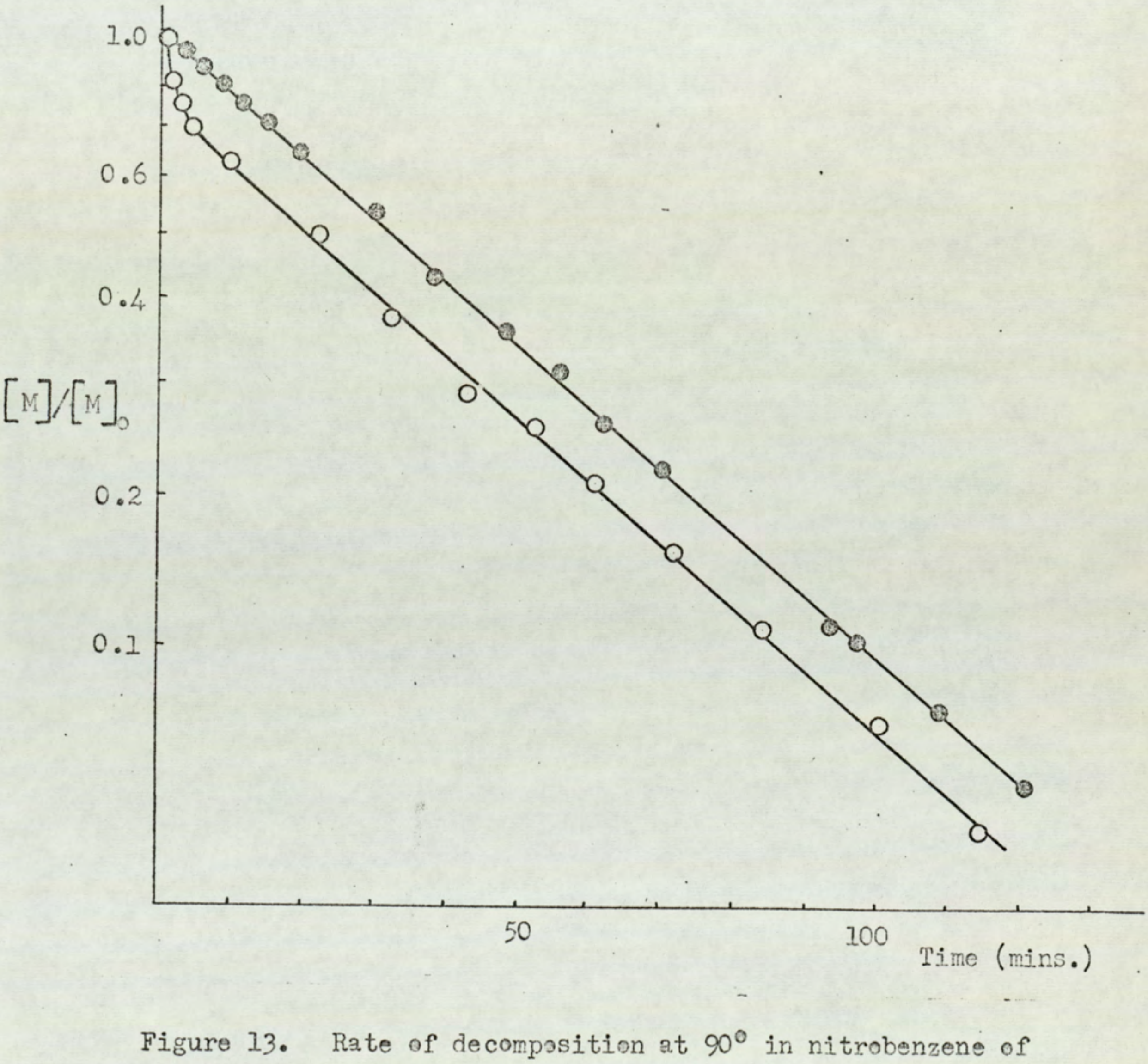


Figure 13. Rate of decomposition at 90° in nitrobenzene of

a) DBAS, ●; b) DBAS + 10 mole % benzylamine, ○.

[DBAS] $_o$ 0.4 mole litre^{-1}.

[Ph.CH$_2$ NH$_2$] 0.04 mole litre^{-1}.

Semi logarithmic plot of DBAS versus time.

at 90° of, (a) DBAS in nitrobenzene, and (b) DBAS plus 10 mole per cent of benzylamine in the same solvent, are shown. The polymers obtained from amine initiated systems were of lower molecular weight than those obtained from pure thermal polymerisation, and they showed an inverse proportionality to the concentration used when the initial anhydrosulphite concentration was kept constant (i.e. $M_n \propto 1/$ Amine).

5-Methyl-5-ethyl-1,3,2-dioxathiolan-4-one-2-oxide. The thermal decomposition of MEAS was studied in nitrobenzene over a range of temperatures. Rates were found to be first order and independent of initial concentrations. Velocity constants measured in nitrobenzene at various temperatures are given in Table 10.

Table 10

First order rate constants (k_1, sec^{-1}), energy of activation (E, kcal. $mole^{-1}$), frequency factor (A, sec^{-1}), and entropy of activation ($\Delta S \pm$, cal.deg.$^{-1}$mole^{-1}) for the decomposition of MEAS in pure nitrobenzene. $[M]_0$ 0.4 mole litre^{-1}.

Anhydrosulphite	10^5k_1 (sec^{-1})				E	10^{14}A	$\Delta S \pm$
	69.4°	78.0°	83.3°	89.6			
MEAS	0.94	2.38	4.72	10.3	29.9	1.2	+3.7

Figure 14 shows a typical rate curve for the decomposition of MEAS in nitrobenzene at 90°, together with similar curves for HBAS and DEAS, which are included for comparison. It is evident that MEAS exhibits thermal behaviour intermediate between HBAS and DEAS.

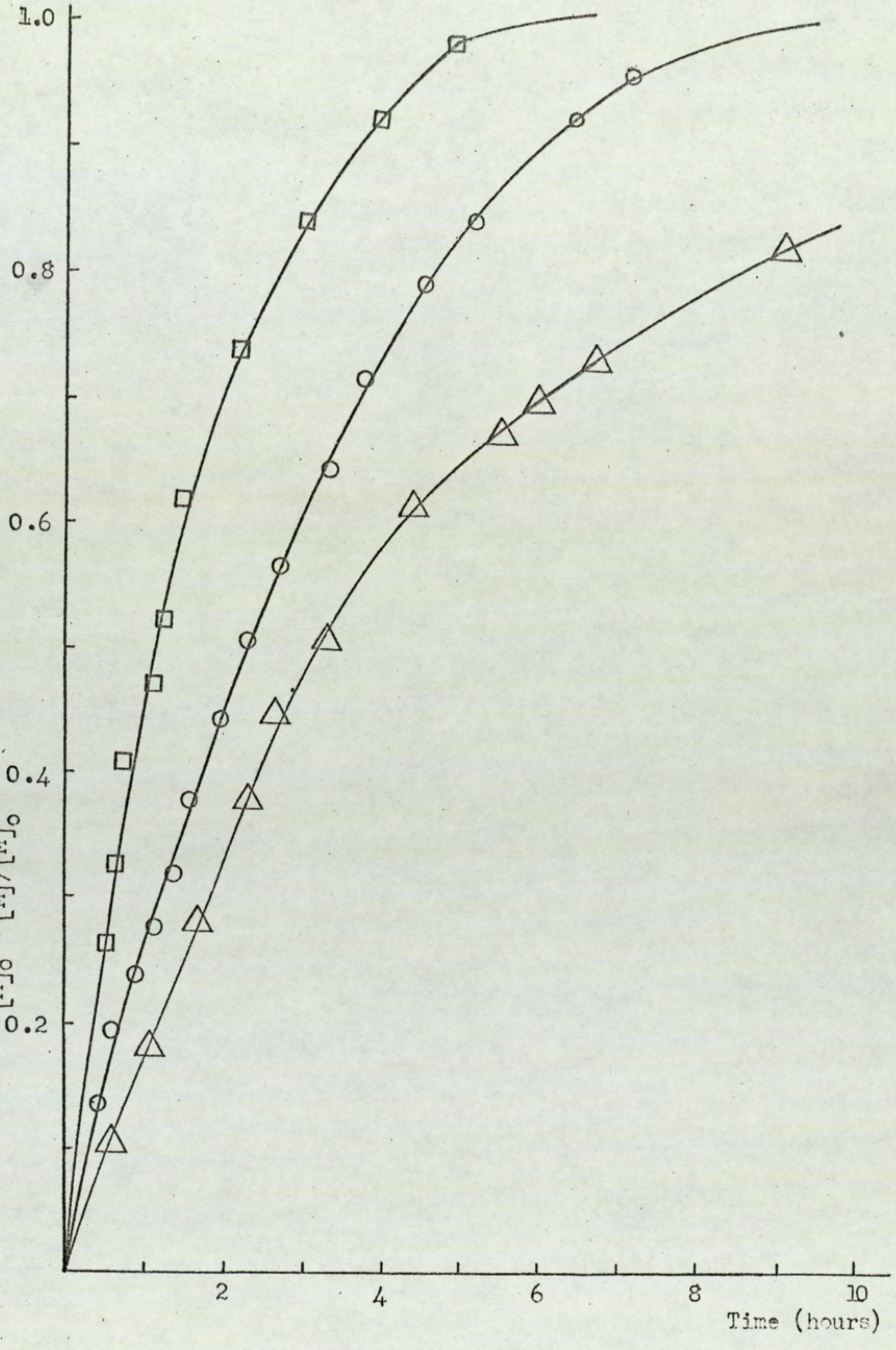


Figure 14. Rate curves for the decomposition of HBAS △, MEAS ○, and DEAS □, in nitrobenzene at 90°.

In benzyl alcohol as solvent the rate of MEAS decomposition was shown to be first order, ($k_1 = 3.3 \times 10^{-5}\text{sec}^{-1}$). As this value is considerably lower than that observed in nitrobenzene at the same temperature any contribution from bimolecular decomposition modes are insignificant and can be neglected in the reaction scheme.

Product Analysis. When the anhydrosulphites were decomposed in excess alcohol (benzyl alcohol) or amine (benzylamine) the products were shown to be the appropriate ester (benzyl ester) or amide (N-benzyl amide) respectively.

With the exception of poly DBAS all polymers in the series were obtained in near quantitative yield. Poly DBAS was obtained as poorly characterised low molecular weight material, and because of the solubility of trimers and tetramers etc. only a low yield of solid was isolated. Although DBAS has been shown to partially fragment to dibutyl ketone in distillation procedures, no ketone was detected in the products resulting from a polymerisation reaction. Poly MEAS was also difficult to obtain in high molecular weight, a reflection of the difficulty found in removing α-chloroacid chloride. The molecular weights of the prepared polymers are indicated in Table 11 and shown to depend upon the concentration of chloride impurity present in the monomer. Trace moisture is also an important molecular weight modifier but its concentration is difficult to estimate. A large batch process greatly reduces the mole fraction of trace moisture present, as is evident from reports of large scale polymerisation of HBAS to polymer having molecular weights in excess of 100,000[23].

Table 11

The effect of α-chloroacid chloride concentration (moles/mole of anhydrosulphite) on the molecular weight (M_n) of the resultant polymeric product.

Anhydrosulphite	Chloride x 10^3	M_n	$\overline{DP}$
HEAS	15.0	6000	70
	3.6	18000	210
MEAS	25.0	2400	24
DEAS	2.8	19000	165
DPAS	15.0	5600	34

5.2 Discussion

Reactivity with nucleophiles. Steric hindrance and nucleophilicity play an important role in direct attack on the anhydrosulphite ring, thus for the DPAS and DBAS systems over a temperature range of 20-90° alcohols are not reactive, whereas amines are. Investigations with amine were carried out below 40° because at these temperatures rates were more easily measured, and competition from the thermal scission process was insignificant. The possibility of nucleophilic attack on the sulphur of the anhydrosulphite ring was discounted since no sulphur containing products were observed, and all the experimental observations were consistent with the assumption that bimolecular attack took place at the C-4 carbonyl group. Rate of attack with a given amine at a particular temperature was reduced on ascending the series because of increased steric hindrance. Although the vacant orbital on the C-4 carbon lies essentially normal to the ring the approach of the attacking nucleophile is thought to be inclined to the ring along the (O-1) - (C-4) direction.

A method used throughout this work to assess contribution of bimolecular decomposition (or propagation) mechanisms, has been to compare the decomposition rate of a given anhydrosulphite in an inert polar medium (usually nitrobenzene), with that in a hydroxylic solvent (usually benzyl alcohol). A general rate equation for anhydrosulphite decomposition which involves both uni- and bimolecular modes of breakdown is given by:-

$$\frac{-d\,[\text{Anhydrosulphite}]}{dt} = (k_1 + k_2\,[\text{Nu}])\,[\text{Anhydrosulphite}] \qquad \ldots\ldots\ldots \quad (2)$$

where k_1 and k_2 describe the first and second order rate constants respectively, and [Nu] the total nucleophile concentration. If benzyl alcohol is used as reaction medium, [Nu] can be equated to the solvent concentration which is in the order of 8 moles litre^{-1}. Therefore if k_2 is at all significant its contribution is magnified in the overall rate expression ($k_1 + k_2$ [Nu]). Table 12 lists the rate constant in nitrobenzene (k_n) and the overall first order rate constant in benzyl alcohol (k_b), both at 90°, for the decomposition of the alkyl series of anhydrosulphites, and introduces the fraction k_b/k_n.

Table 12

The first order rate constants in nitrobenzene (k_n), and benzyl alcohol (k_b) for the decomposition of an alkyl series of anhydrosulphites at 90°. Values of the ratio of k_b/k_n for the same derivatives.

Anhydrosulphite	R^1	R^2	$10^5 k_n (sec^{-1})$	$10^5 k_b (sec^{-1})$	k_b/k_n
GAAS	H	H	0.59	37.0	627
LAAS	H	Me	0.6	8.5	141
HBAS	Me	Me	6.1	5.5	0.9
MEAS	Me	Et	10.3	3.3	0.3
DEAS	Et	Et	20.1	1.4	0.07
DPAS	Pr	Pr	24.0	1.2	0.05
DBAS	Bu	Bu	26.0	2.7	0.1
CMAS	CH_2Cl	CH_2Cl	0.22	1.9	9.0

The k_b/k_n ratio gives a quantitative measure of the uni- and bimolecular process contributions. Thus if GAAS is polymerised under conditions which ensure a degree of polymerisation of 600, then the contribution of each process will be approximately equal. It becomes evident that of the derivatives listed in Table 12 only GAAS, LAAS, and to a lesser extent CMAS[71], exhibit this double behaviour to any significant degree. If the k_b/k_n values for the series HBAS, MEAS, DEAS, DPAS, and DBAS, are compared it is clear that a levelling effect is not reached until DEAS, which indicates that exclusion of bimolecular propagation is not total in HBAS and MEAS as has been previously assumed. Another factor contributing here is the observed increased sensitivity of higher homologues in the series to changes in the polarity of the reaction medium. However, further evidence for some bimolecular contribution is found in comparing the relative stability of HBAS, MEAS, and DEAS in benzyl alcohol, with that in inert solvent systems. The order of stability is reversed. This is probably due to the contribution of an additional mechanism in the former case. Similar studies in cyclohexanol as reaction medium (Section 4.1) also gave low values for k_1, thus demonstrating that the phenomenon was not perculiar to benzyl alcohol alone.

Thermal decompsition. In contrast to the decrease in rate for bimolecular ring-opening, the rate of thermal ring-opening increases as the n-alkyl series is ascended, although Figure 15 would indicate that the limit of the effect is approached at DEAS. It is of interest that a plot of Tafts σ^* substituent constants[72] versus log thermal rate constant (Figure 16) gives a near-linear extrathermodynamic relationship which may indicate a more important contribution from inductive effects than has been previously suggested. The relatively high thermal stability

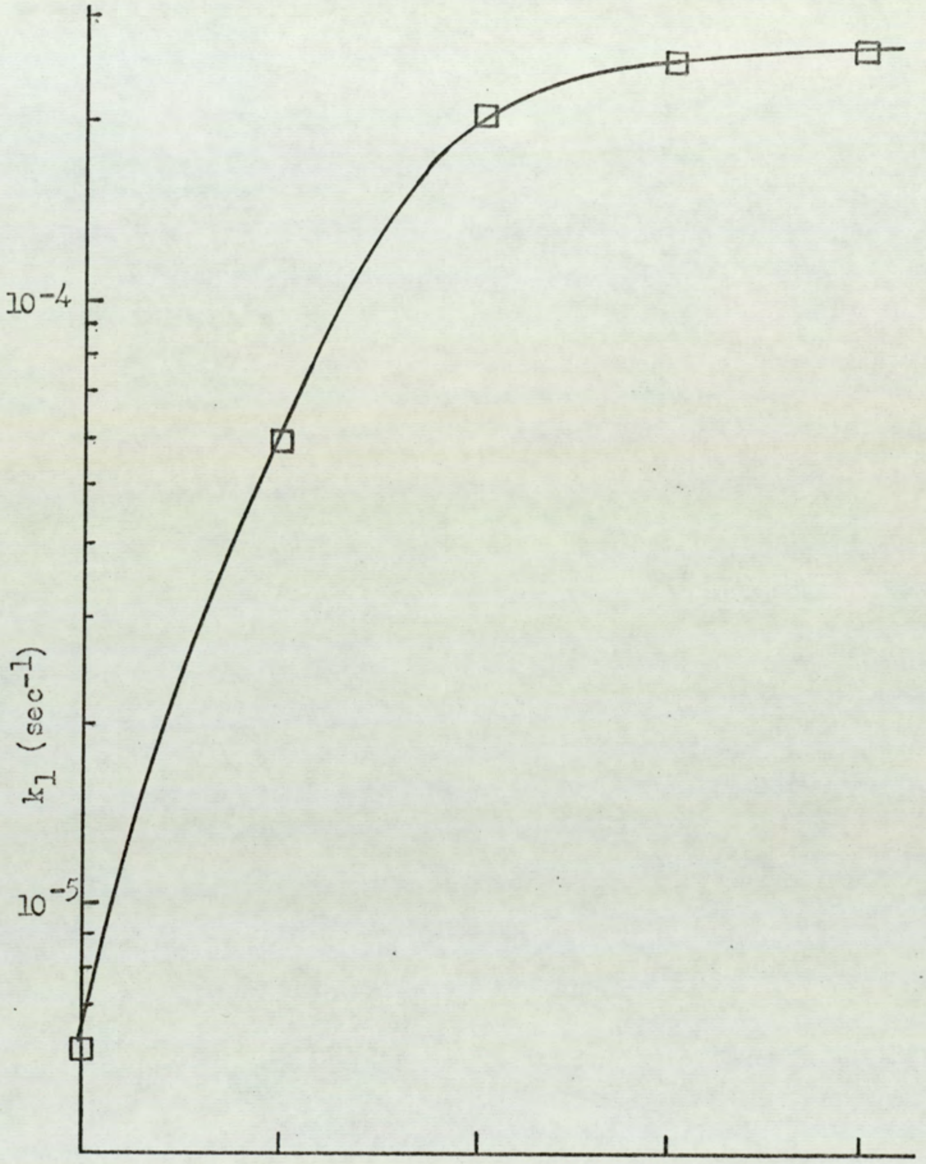


Figure 15. First order rate constants for the decomposition of various symmetrical dialkyl anhydrosulphites in nitrobenzene at 90° plotted as a function of the number of carbon atoms (n) in the substituents.

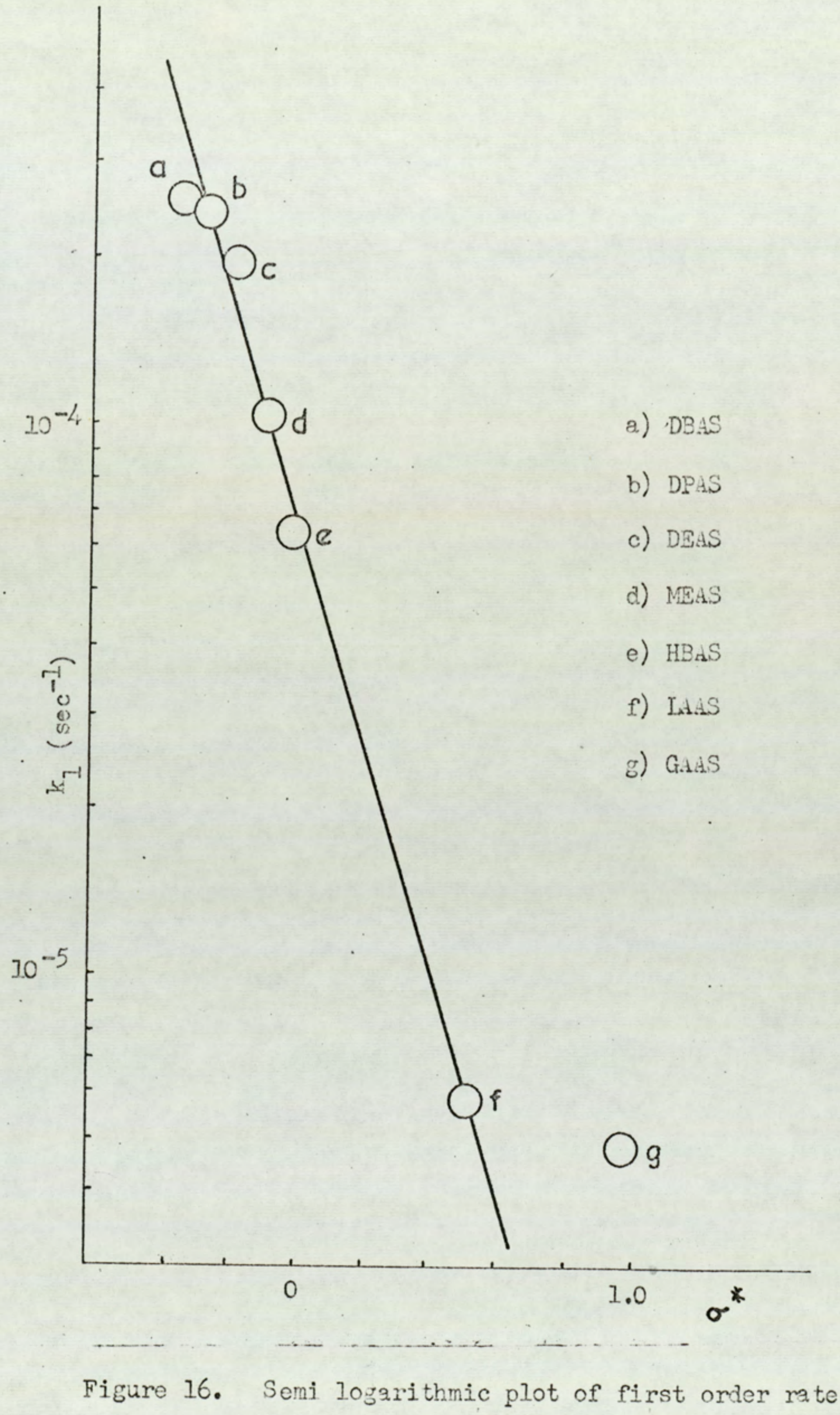
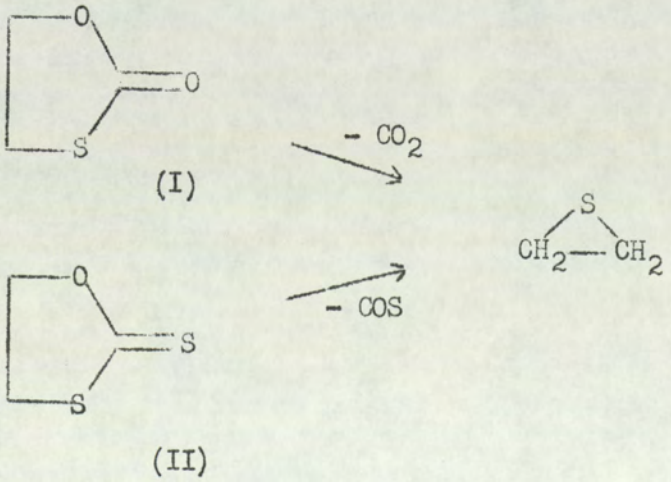


Figure 16. Semi logarithmic plot of first order rate constants for the decomposition of various anhydrosulphites in nitrobenzene at 90°, plotted as a function of Taft's σ^* substituent constants.

of CMaS[71] (k_1 2.2 x 10^{-6} sec^{-1} in nitrobenzene) is consistent with a contribution of this type since chloromethyl substituents, in contrast to alkyl groups, are electron withdrawing. Kinetic parameters derived from Arrhenius plots are of the order expected for a genuine unimolecular process and entirely consistent with a rate determining step which involves the thermal cleavage of a covalent bond in a strained ring system. The small positive entropies of activation may be attributed to the transition state being a loosened (excited) version of the reactant. Studies of the thermal decompostion of anhydrosulphites derived from, lactic[26], mandelic[57], and atrolactic[73], acids indicates that the activation energies for unsymmetrical derivatives are lower than those for the symmetrical series. However, the value obtained for MEaS shows that this phenomenon is specifically characteristic of monosubstituted derivatives and/or those containing an aryl substituent.

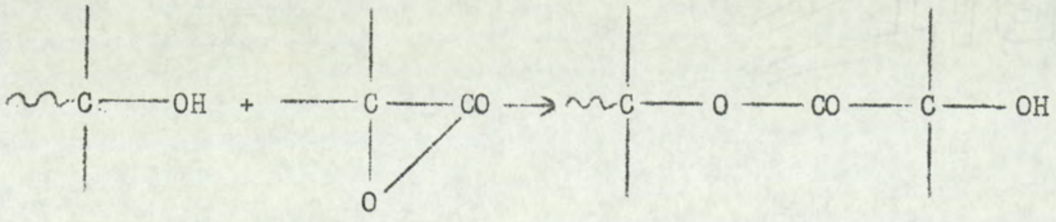
Estimation of bond energies in the ring and comparison with 1,3-oxathiolan-2-one (I) or -2-thione (II) which show an unambiguous scission pattern[74] (Equation 3), points to the initial scission taking place at the 1-2 or 3-4 bond.



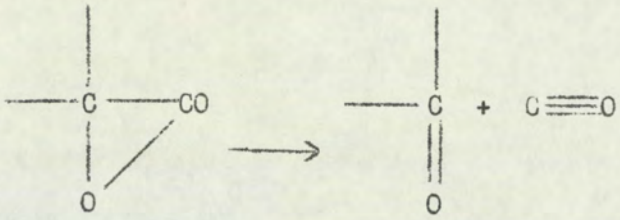
...... (3)

The relationship between nature and size of substituents and ease of polymerisation has been studied for many ring-opening polymerisation reactions. N-carboxy-α-amino acid anhydrides, which are typical of cyclic monomers that polymerise with concurrent elimination of a small gaseous molecule, polymerise less readily as substituent size is increased[19]. Ring-opening reactions of cyclic esters and other systems in which all the elements of the cyclic molecule are incorporated into the growing polymer chain are similarly sensitive to the presence of substituents in the ring. Hall[3] and his co-workers have summarised these effects showing that an increase in substituent size is parallelled by a decrease in ease of polymerisation.

The series of C-5, disubstituted anhydrosulphites described here present a unique situation. The rate of polymerisation is dependent upon the rate of primary ring scission, which involves concurrent expulsion of sulphur dioxide and formation of a reactive intermediate, formally expressed as a ring-contraction step. The α-lactone intermediate formed in this process takes part in a rapid chain propagation reaction (Equation 4) in which it shows some resemblance to larger ring analogues (for example β-lactone). Increased bulk and polarity of substituents would be expected to increase the stability of the intermediate and therefore reduce the rate of this chain growth reaction. The intermediate is so reactive and the rate of propagation so rapid, however, that this reaction remains sensibly spontaneous throughout the series studied.



...... (4)



...... (5)

The fact that the intensity the α-lactone peak relative to those of the ketone in the mass spectra of HBAS, DEAS, DPAS, and DBAS, increase in that order suggests increasing α-lactone stability under the conditions of reaction in the mass spectrometer. This may be taken as support for the view that ketone formation occurs by secondary fragmentation of the α-lactone (Equation 5) rather than a primary anhydrosulphite scission process. When competition exists between this secondary fragmentation of the α-lactone, and the chain propagation reaction, as for example in the thermal decomposition of anhydrosulphites at temperatures in the region of 100°, the chain propagation reaction is normally favoured to such an extent that no ketone formation is observed. As bulk or polarity of the substituent are increased however, propagation is apparently more drastically affected than the lactone fragmentation process and detectable or even large amounts of ketone may be formed[57,71]. In the series described here, however, ketone formation was only observed to occur to any degree with DBAS, and that at temperatures well above those required for polymerisation.

Interpretation of substituent effects in the polymerisation of anhydrosulphites must clearly be made on the basis of electronic as well as steric factors, although in the case of C-5 alkyl substituents the latter seem predominant. In passing along the series HBAS, MEAS, DEAS, DPAS, DBAS, the rate determining step in the series of reactions leading to polymer formation is seen to become more rapid. The effect becomes more marked as the dielectric constant of the reaction medium increases. The effect of increased dielectric, in the case of a given anhydrosulphite, is to increase the asymmetry of the electron distribution in the ring, thereby causing some lengthening and weakening of the bonds involved in the scission process. C-5 ethyl substituents would enhance this process (relative to C-5 methyl substituents) by increasing the electron density on the O-1 atom. The observed relationship between symmetrical C-5 substituents and the value of k_1 at 90° in nitrobenzene (Figure 15), which shows a relatively large change in passing from methyl to ethyl as compared to that between propyl to butyl, are consistent with, although not necessarily evidence for, a contribution of this type. The major (steric) contribution of increasing substituent size to ring instability is most readily understood in terms of the Thorpe-Ingold effect. Thus in order to accomodate larger substituents the bond angle co-joining them to the C-5 atom of the ring tends to increase, thereby transmitting a compressive strain to the anhydrosulphite ring.

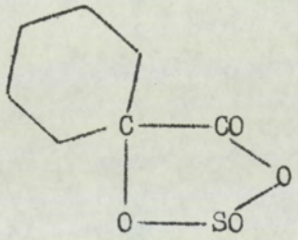
Although the effect of increasing alkyl substituent size does not sensibly affect the rate of polymerisation of the α-lactone intermediate, there is a detectable change in its polarity. HBAS shows some radical character in its thermal decomposition which DEAS does not; conversely DEAS in common with DPAS and DBAS apparently gives rise to more polar intermediates than does HBAS. This does not affect the general validity of the kinetic scheme proposed in Section 4, but may alter the relative rates of some of the processes involved. The incorporation of α-chloroacid chloride impurity into the polymer, for example, evidently takes place more efficiently with higher members of the series, and contributes to the difficulty experienced in obtaining high molecular weight polymers from these anhydrosulphites.

The limit of usefulness of the anhydrosulphite synthesis as a means of preparing poly α-esters appears to have been reached with DPAS although the difficulties experienced with DBAS were primarily associated with purification rather than polymerisation procedure.

6. THE POLYMERISATION OF CYCLOHEXANE SPIRO-5-1,3,2-DIOXATHIOLAN-4-ONE-2-OXIDE

Results and Discussion

Cyclohexane spiro-5-1,3,2-dioxathiolan-4-one-2-oxide (I), hereafter referred to as C'hexAS, was first synthesised by Rose[24], but in an impure state. Claims of rapid decomposition, even during purification, and formation of very low molecular weight polymer suggest the behaviour of C'hexAS may be quite different from that of HBAS. Using the procedures outlined in Section 3, a relatively pure sample of C'hexAS was prepared and its decomposition behaviour studied.



(I)

6.1 Results

Kinetics of Polymerisation. Rates of polymer formation were measured by sulphur dioxide gas evolution. That the variation of this parameter with time coincided with polymer formation was supported by infra-red evidence. The carbonyl absorptions of C'hexAS (1810 cm^{-1}) and poly C'hexAS (1742 cm^{-1}) were monitored as a function of time. Figure 17 shows the infra-red spectra (wave range 1950-1400 cm^{-1}) for a selection of samples taken at different times during the polymerisation. The reaction of

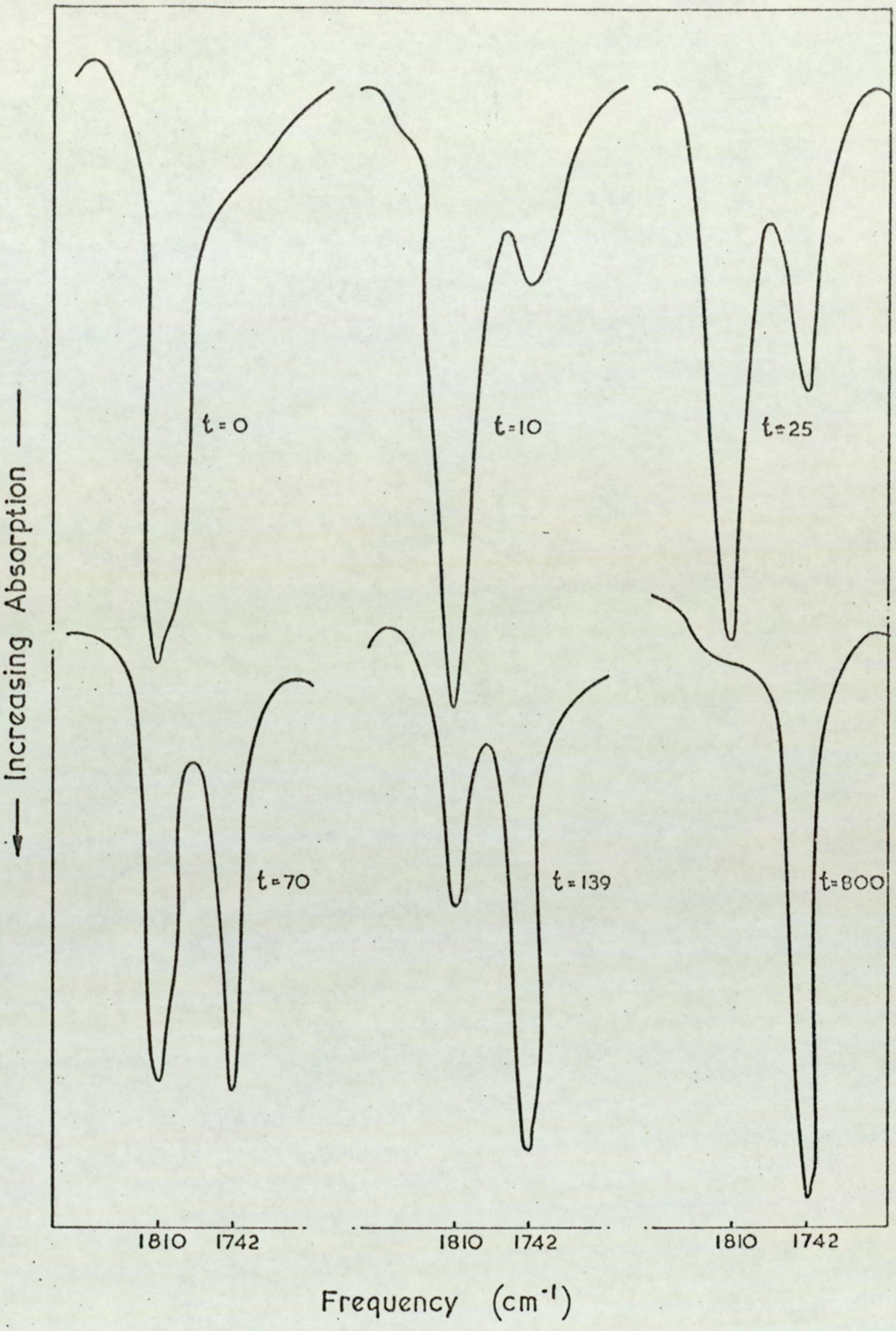


Figure 17. Infra-red spectra of samples taken at time (t, mins.) during the polymerisation of C'hexMS at 100° in nitrobenzene. Spectra recorded using Na Cl plates and 0.025 mm. p.t.f.e. spacers.

C'hexAS in nitrobenzene at 100° was followed by both gas evolution and infra-red analysis and both sets of data are presented in the form of first order plots in Figure 18. It is evident from these results that there is a direct relationship between the two processes, and that both are first order with respect to anhydrosulphite and polymer respectively. A tenfold change in initial concentration or variation of initial sulphur dioxide pressure did not significantly alter the value of the first order velocity coefficient. It follows that any stages leading to polymer formation, but subsequent to sulphur dioxide extrusion, occur faster than does C'hexAS decomposition. The reaction may be expressed in the form of Equation 1.

$$\frac{-d\,[\text{C'hexAS}]}{dt} = \frac{d\,[SO_2]}{dt} = \frac{d\,[P]}{dt} = k_1\,[\text{C'hexAS}] \qquad \ldots\ldots \quad (1)$$

where [C'hexAS], $[SO_2]$ and [P] represent the mole concentrations of C'hexAS, sulphur dioxide and polymer respectively, and k_1 the first order rate constant for the decomposition process. The effect of varying dielectric constant of solvent on the rate of reaction was investigated and the results are summarised in Table 13.

Plots of conversion to polymer versus time for C'hexAS in nitrobenzene at three temperatures are given in Figure 19 and for comparison similar curves for HBAS and DEAS in the same solvent at 90° are included. Table 14 lists rate constants together with other derived kinetic parameters for the decomposition of C'hexAS in nitrobenzene over a range of temperature.

The possibility of propagation by a bimolecular mechanism (as depicted in Equation 2) was investigated in the usual way by studying

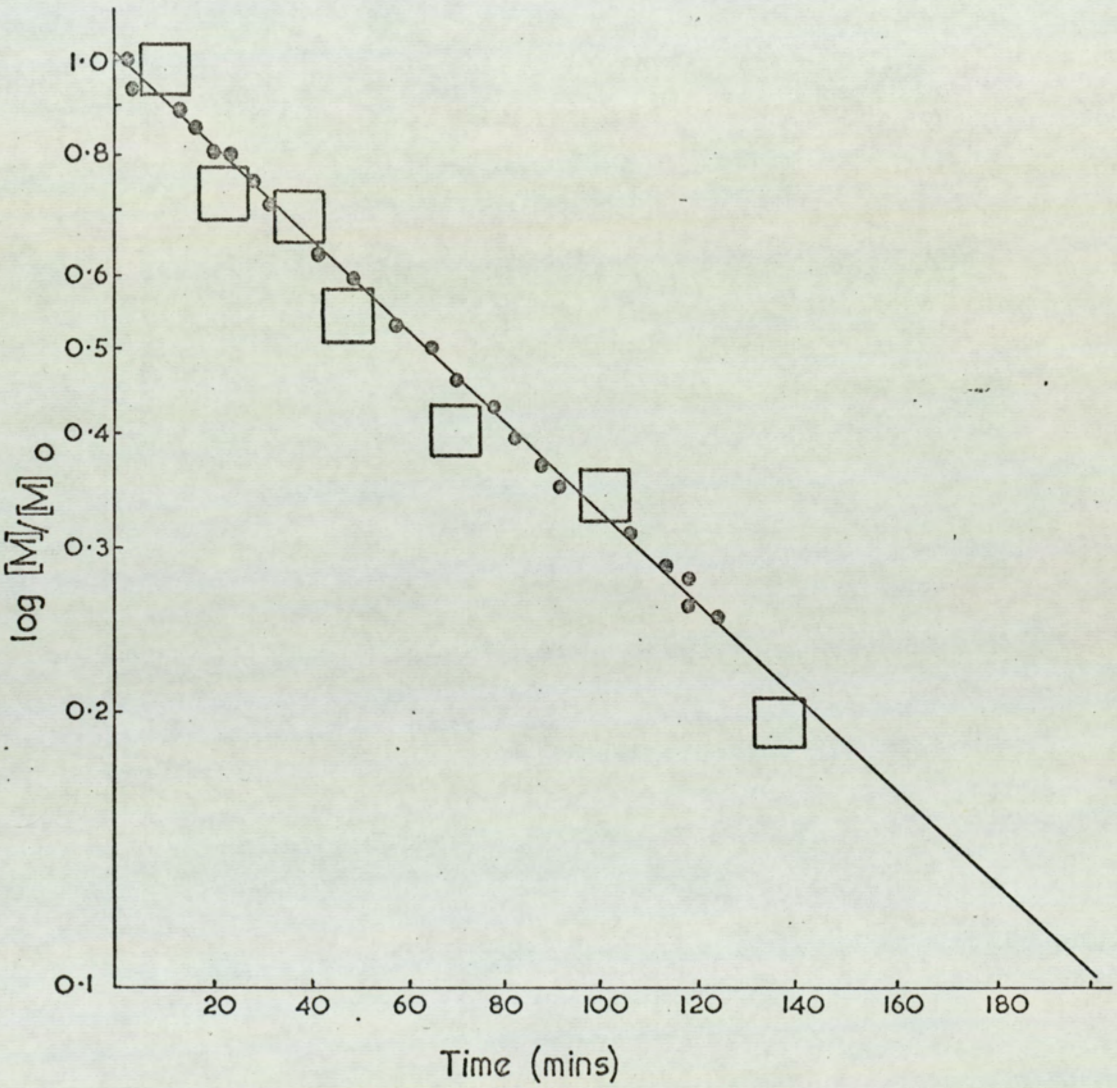


Figure 18. First order plots for the polymerisation of C'hexAS at 100° in nitrobenzene; gas evolution data ● , and infra-red data (polymer absorptions) ☐ . $[\text{C'hexAS}]_{o}$ 0.4 mole litre^{-1}.

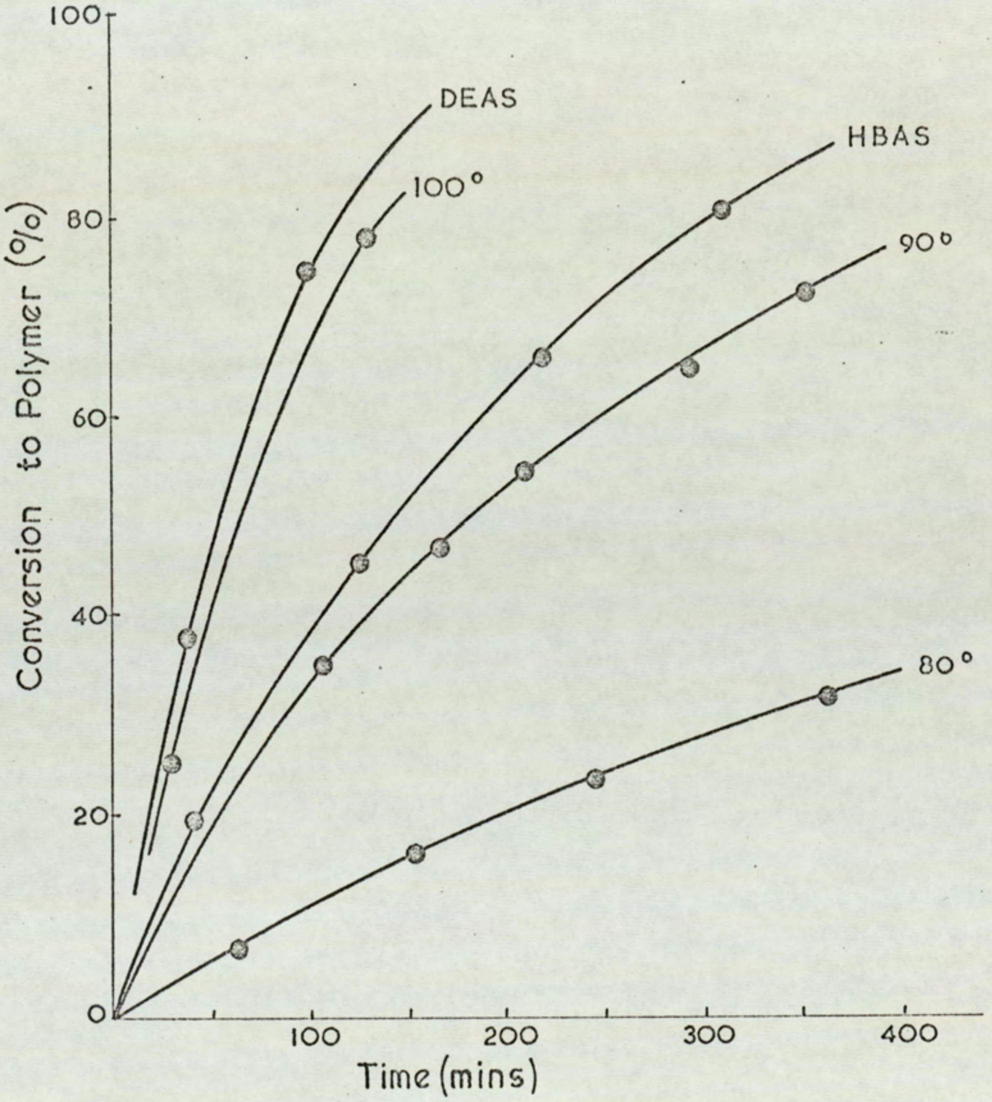
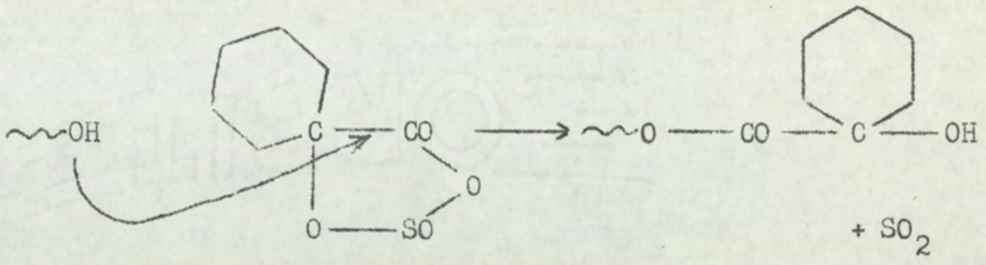


Figure 19. Conversion to polymer curves for the polymerisation of HBAS and DEAS at 90°, C'hexAS at 80, 90 and 100°, all in nitrobenzene as solvent.

the decomposition of C'hexAS in the presence of alcohols.



...... (2)

Table 13

Polymerisation of C'hexAS at 90°; effect of varying solvent polarity (dielectric constant).

Solvent	ε at 90°	10^5 k_1(sec^{-1})	$t_{\frac{1}{2}}$(mins)
Nitrobenzene	25	5.6	206
p-Nitrotoluene	17	5.07	221
Chlorobenzene	4.5	4.6	251
Di-octyl-phthalate	3.5	2.5	462
Dekalin	2.5	0.94	1229

Primary alcohols, over a range of concentration, did not affect the rate of decomposition of C'hexAS because of low nucleophilicity and steric protection of the carbonyl group by the cyclohexyl substituent. When benzyl alcohol was used as solvent then the observed rate constant was of the same order as that obtained in an inert solvent of similar dielectric constant. Hence at 90° in benzyl alcohol C'hexAS decomposed at a rate of 1.22 x 10^{-5} sec^{-1}, however, the principal products where benzyl-1-hydroxy cyclohexanoate and sulphur dioxide. The ratio of rates in benzyl alcohol (k_b) and nitrobenzene (k_n), at a given temperature, is a concept which has been described earlier and which is used to assess the contribution of mechanisms such as that given by Equation 2. For C'hexAS $k_b/k_n = 0.22$, a value which lies between that of EBAS (0.9) and DEAS (0.07).

Table 14

First order rate constants (k_1), half lives ($t_{\frac{1}{2}}$), energy of activation (E), entropy of activation ($\Delta S\pm$), and frequency factor (A) for the polymerisation of C'hexAS in nitrobenzene. $[\text{C'hexAS}]_o = 0.4$ mole litre^{-1}.

	$10^5\ k_1(\text{sec}^{-1})$	$t_{\frac{1}{2}}$(mins)
65.0°	0.21	5500
79.9	1.9	608
85.1	3.3	350
90.0	5.6	206
94.7	8.5	136
100.0	19.0	61
105.6	34.0	34
E(k.calmole^{-1})	32.57	
A(sec^{-1})	2.5×10^{15}	
$\Delta S\pm$(cal.deg^{-1}mole^{-1})	+9.5	

The mass spectrum of C'hexAS showed a fragmentation pattern characteristic of the anhydrosulphite series. Primary and secondary steps in the electron impact induced fragmentation were elimination of sulphur dioxide and carbon monoxide respectively.

(M - 64) and (M - 92) constituted the strongest peaks in the spectrum above m/e 98, and were assigned the structures of cyclohexane spriro-3-acetolactone and cyclohexanone respectively.

In the absence of added initiators, and in the presence of adventitious traces of moisture, polymers with molecular weight in the region of 12-14,000 were readily obtained.

Kinetics of Ketone Formation. Detection of cyclohexanone in the short-path distillate during the purification procedure of monomer, led to a quantitative examination of its formation in solution at temperatures between 150-200°.

An experimental determination of the rate of C'hexAS decomposition in nitrobenzene at 150° was in fair agreement with that predicted by extrapolation from the extended Arrhenius plot obtained from studies of the reaction at lower temperatures. This was taken as evidence for, no added complication to, or competition with, the primary scission process at temperatures in the region of 150°.

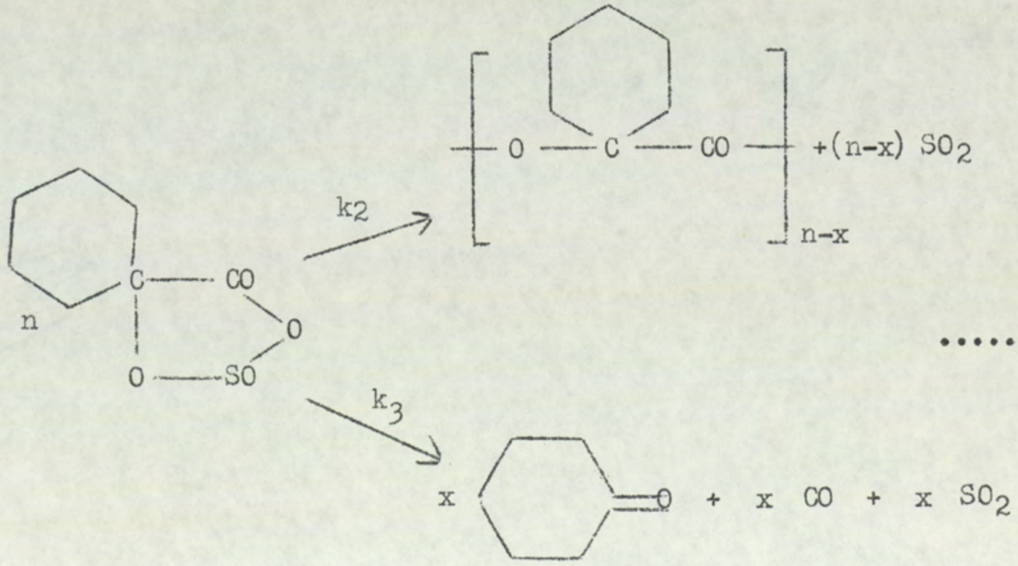
A standard aliquot was taken from stock solutions of C'hexAS in nitrobenzene and benzyl alcohol, sealed in evacuated Carius tubes, and subjected to temperatures of 151, 168, or 189° for at least eight estimated half lives. The solutions were analysed by g.l.c., and from calibration curves the amount of ketone formed was extrapolated. Table 15 expresses ketone formed (mole percentage of theoretical) as a function of temperature and solvent. Carbon monoxide, sulphur dioxide and cyclohexanone were detected by g.l.c. Poly C'hexAS the only other product formed in nitrobenzene precipitated on standing. It is evident from Table 15 that ketone formation occurs to a much lesser extent in benzyl alcohol, which together with other features may be used as evidence for ketone formation occurring as a result of secondary scission. The major product found in benzyl alcohol was benzyl cyclohexanol-1-carboxylate.

Table 15

Percentage of cyclohenanone formed when C'hexaS was decomposed at various temperatures in nitrobenzene and benzyl alcohol.

Temperature	Mole % Cyclohexanone	
	Nitrobenzene	Benzyl Alcohol
157°	2.6	0.20
168	3.6	-
189	5.4	0.24

The formation of ketone and polymer was found to be controlled by two competing first order reactions which may be conveniently represented by Equation 3.



...... (3)

If the concentrations of C'hexaS, cyclohenanone and poly C'hexaS are designated by [C'hexAS], [K] and [P] respectively then:

$$\frac{-d[\text{C'hexAS}]}{dt} = \frac{d[K]}{dt} + \frac{d[P]}{dt} = (k_2 + k_3)[\text{C'hexAS}] \qquad \ldots\ldots (4)$$

The fragmentation process leading to polymer formation (k_2) and ketone formation (k_3) can be related to the observed overall first order rate constant (k_1) by Equation 5:

$$k_1 = k_2 + k_3 \qquad \ldots\ldots (5)$$

and final concentrations of polymer and ketone in terms of k_2 and k_3 by Equation 6.

$$\frac{k_2}{k_3} = \frac{[P]_\infty}{[K]_\infty} \qquad \ldots\ldots (6)$$

For the three specific temperatures of reaction the overall rate constants (k_1) were extrapolated from the Arrhenius plot for the decomposition reaction, and polymer/ketone ratios were available from g.l.c. and gravimetry data. Values for k_2 and k_3 are presented in Table 16 together with derived frequency factors, energies and entropies of activation. Arrhenius plots for the three processes described by k_1, k_2 and k_3 are given in Figure 20.

There was no evidence for the presence of cyclohexanone affecting the rate of decomposition of C'hexAS, nor of its ability to modify the molecular weight of the polymeric product by chemical means.

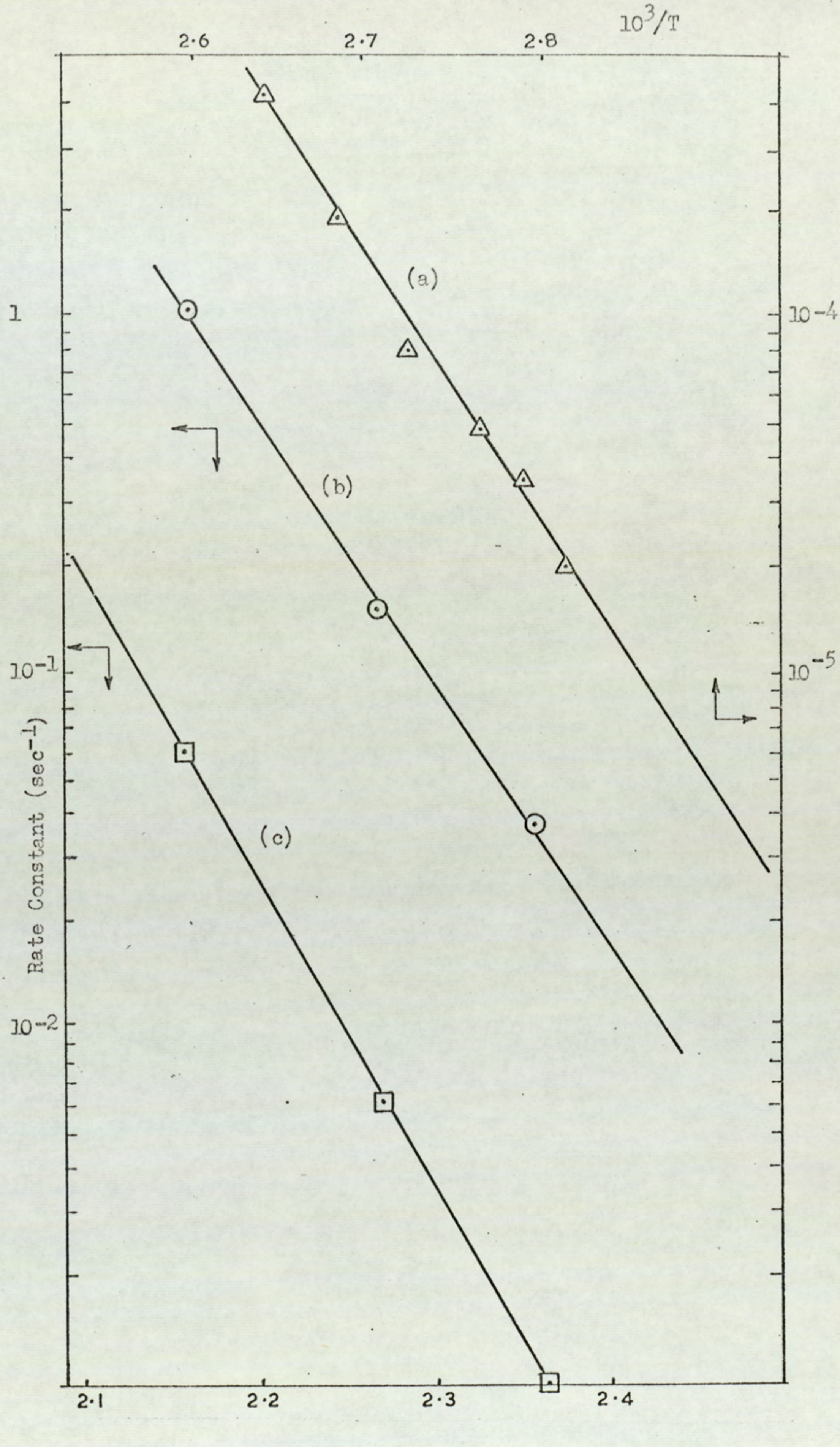


Figure 20. Arrnenius plots for those processes described by the rate constants a) k_1, b) k_2 and c) k_3.

Table 16

First order rate constants (k_2 and k_3), energies of activation (E), entropies of activation ($\Delta S\pm$), and frequency factors (A) for the thermal decomposition of C'hexAS in nitrobenzene.

$[C'hexAS]_0$ 0.53 mole litre^{-1}.

	k_2 (sec^{-1})	k_3 (sec^{-1})
151°	3.8×10^{-2}	1.0×10^{-3}
168	1.69×10^{-1}	6.2×10^{-3}
189	1.04	5.9×10^{-2}
A (sec^{-1})	2.0×10^{15}	5.2×10^{17}
E (k.cal.mole^{-1})	32.31	40.00
$\Delta S\pm$ (cal.deg^{-1}mole^{-1})	+9.0	+20.1

6.2 Discussion

Product analysis and rate data taken together with associate kinetic parameters for C'hexAS decomposition, below 100°, and in non-nucleophilic solvents, are consistent with the unimolecular thermal extrusion polymerisation scheme associated with those derivatives discussed in earlier sections. In common with other members of the anhydrosulphite series no evidence for sulphur dioxide catalysis, or inhibition, was found.

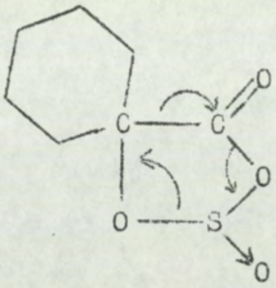
At the outset of work on this derivative the effect of a conjoined ring on the anhydrosulphite and α-lactone structures although unknown was anticipated to reduce their stability considerably. The work of Rose supports this view. There was no evidence for a change in type of intermediate or transition state, however, and although the polar and radical canonical forms of the lactonic intermediate (which do not require a third covalent bond in the lactone structure) seem energetically more feasible, a major contribution from either was not apparent in the experimental data. Although the substituents of DEAS and DPAS are more representative of a cyclohexane ring, C'hexAS is more thermally stable than either and resembles HBAS in its polymerisation behaviour (for example see Figure 19).

Thus both C'hexAS and cyclohexane spiro-3-acetolactone exhibit an unexpected degree of stability which can be related to the ability of a cyclohexane ring to relieve strain by puckering, and to undergo conformational changes without imposing strain on the partner ring of the spiran system. With respect to the anhydrosulphite ring the substituent α-carbons are therefore able to adopt a similar position relative to the 5-carbon as those of HBAS or 3,3-dimethyl acetolactone. In addition as the substituent has a ring structure individual bonds have less rotational degrees of freedom, and hence less steric influence when compared with two free ethyl or propyl substituents.

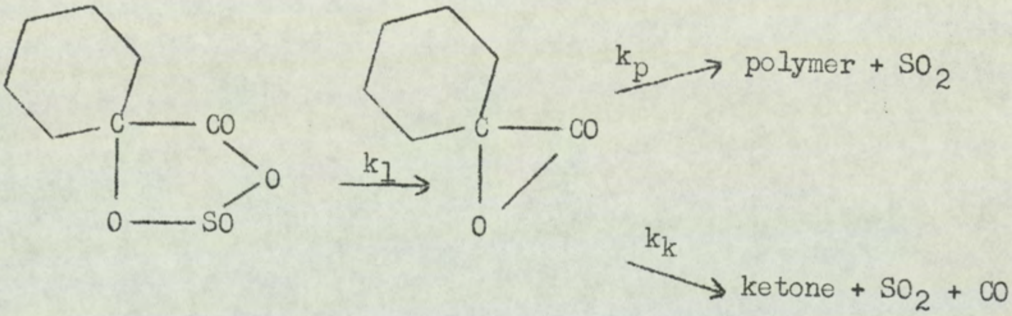
Ketone formation during bulk distillation is not a process unique to C'hexAS, it occurs to a greater extent with DBAS for example, and is partly responsible for distillation not being a suitable method of purification in this case. Although related, a study of the reaction in solution differs in that localised heating is prevented and the polarity of the reaction system is essentially governed by the solvent. At temperatures in excess of 150°, and in solution, C'hexAS decomposes, in part, to cyclohexanone. Similar behaviour has been observed with 5,5-diphenyl (BAAS)[57] and 5,5-bischloromethyl (CMAS)[71] 1,3,2-dioxathiolan-4-one-2-oxides, but the electron withdrawing nature of the substituents apparently requires that the reaction is competitive with normal polymerisation at lower temperatures. The 5-phenyl derivative (MAAS)[57] decomposes almost totally into benzaldehyde, but the kinetic parameters are not typical and suggest a modified scission mechanism.

First order behaviour was established for ketone as well as polymer formation. The reaction as represented by Equation 3 however, does not distinguish between primary scission (arising from electronic rearrangements in the sense depicted by (II)), and secondary scission (Equation 7), mechanisms. In the anhydrosulphite series, several qualitative observations point towards, but are not necessarily evidence for, ketonic products resulting from secondary fragmentation.

First, mass spectral data for the dialkyl series show that derivatives with strong α-lactone peaks correspond to those more liable to ketone formation (c.f. GaAS with DBaS; Section5).

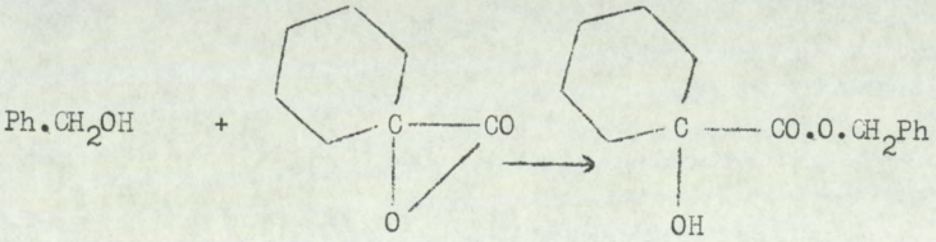


(II)



...... (7)

Secondly, rate constants determined at ketone forming temperatures fit an extension of the Arrhenius plot constructed from rate data obtained in the temperature range where polymer is the only product. Thirdly, much more cyclohexanone is formed in nitrobenzene than in benzyl alcohol, presumably because reaction of the intermediate with nucleophilic solvent (Equation 8) can compete with secondary scission.



...... (8)

That this is not a solvent dielectric effect is indicated by data regarding formation of syn-dichloroacetone from CMAS[71], which was shown to be favoured in low dielectric reaction media.

If cyclohexanone results from secondary scission (Equation 7) then the rate determinig step for both ketone and polymer forming reactions is the formation of α-lactone. Partial rate factors k_p and k_k (whose relative values are apparently dependant on hydroxyl concentration as well as temperature) will determine the amount of each product formed. The rate constants k_2 and k_3, which were evaluated in Section 6.1 are related to k_p and k_k by the expressions:

$$k_2 = \frac{k_p}{k_k + k_p} \times k_1 \qquad \text{...... (9)}$$

$$k_3 = \frac{k_k}{k_k + k_p} \times k_1 \qquad \text{...... (10)}$$

Although secondary scission is postulated here, more quantitative information is required for its justification, especially as regards the effect of; sub-stoichiometric amounts of alcohol in mixed solvent reactions,studies in high dielectric alcoholic solvents and mixed-anhydrosulphite alcohol reactions.

The high frequency factor associated with cyclohexanone formation arises from a high positive entropy of activation which is related to the looseness of certain vibrations in the activated complex. Special cases of reactions having high entropies of activation are known when a molecule decomposes by simultaneous breaking of two bonds (for example, mercury dialkyls[75]), and may apply here to the α-lactone (or primary scission step).

Strong nucleophiles, for example benzylamine react directly with C'hexAS, whereas potential but weaker nucleophiles for example benzyl alcohol, do not attack the 1,3,2-dioxathiolan-4-one-2-oxide ring, but rather the α-lactone. When either was present in substoichiometric amounts the resultant polymer had molecular weight inversely proportional to the nucleophile concentration. When C'hexAS is polymerised at temperatures between 60-180° in dry inert solvents the molecular weight of the resultant product is given by Equation 11:

$$M_n = \frac{[\text{C'hexAS}]_o - [K]_\infty}{[Nu]_o} \quad \ldots\ldots \quad (11)$$

where $[\text{C'hexAS}]_o$ refers to initial monomer concentration, $[K]_\infty$ final cyclohexanone concentration and $[Nu]_o$ total nucleophile concentration (i.e. trace adventitious moisture).

Thus although Rose[24] gives the impression that C'hexAS behaves quite differently from HBAS, and perhaps involves a different polymerisation mechanism, the work presented here shows that its thermal behaviour is quite typical of the series. Indeed, C'hexAS resembles HBAS more than any other anhydrosulphite so far studied. This becomes more evident in Section 7 when other spiran systems are discussed. In contrast to the oligomeric materials obtained by Rose.polymer obtained in this study was of reasonable molecular weight and by no means was its optimum value reached. The very limited success of other workers in producing pure monomer and high molecular weight polymer was evidently due to lack of appreciation of both the ketone forming reaction at high temperature and the ability of nucleophilic and α-chloroacid chloride impurities to drastically lower molecular weight.

7. THE POLYMERISATION OF OTHER CYCLOALKYL SPIRO SUBSTITUTED 1,3,2-DIOXATHIOLAN-4-ONE-2-OXIDES

Results and Discussion

1,3,2-dioxathiolan-4-one-2-oxide-5-spirocyclobutane, cyclopentane and cycloheptane spiro-5-1,3,2-dioxathiolan-4-one-2-oxides, hereafter referred to as C'butAS, C'pentAS and C'heptAS respectively, are systems which have not previously been reported in the literature. Their decomposition behaviour is discussed herein and a selection of results from the preceeding section relating to C'hexAS are included for comparison.

7.1 Results

Rates of decomposition were measured by following gas evolution and they were shown to occur at the same rate as polymer formation by infra-red analysis of time varied samples taken from the reaction system. Velocities of reaction were measured in nitrobenzene over a range of temperatures and found to be first order. As with most other anhydrosulphite systems studied a change in initial concentration did not alter the value of a given rate constant, nor was there any indication of sulphur dioxide catalysis or inhibition. Rates of decomposition in nitrobenzene at 90° are shown in Figure 21, and Figure 22 compares the Arrhenius plot of each derivative in the same solvent. Half lives and rate constants which are described by the rate curves in Figure 21 together with kinetic parameters derived from Figure 22 are given in Table 17.

The change of rate with solvent polarity was studied and all except C'butAS showed some dependence on variation of this parameter.

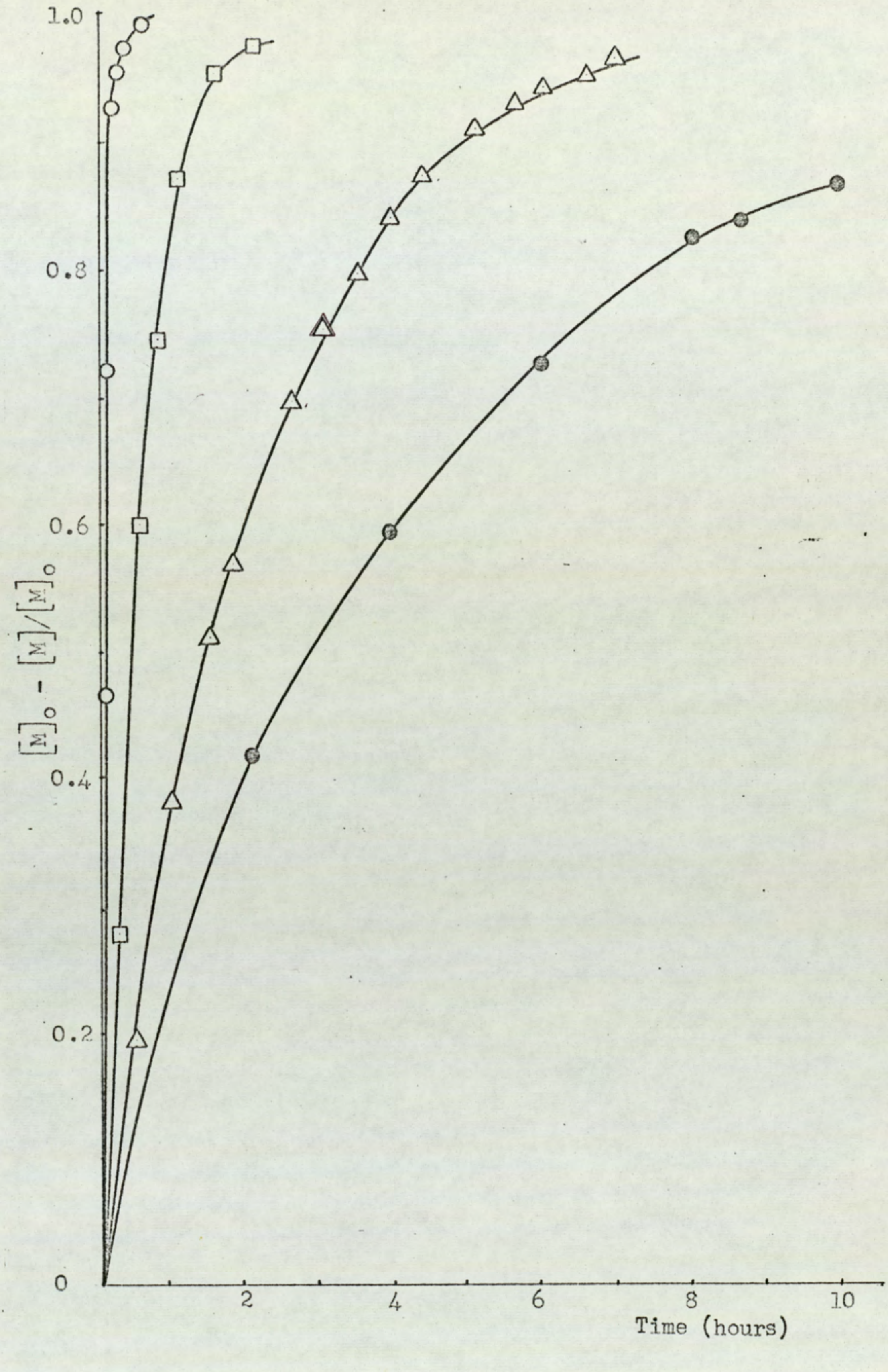


Figure 21. Rate curves for the decomposition of, ○ C'butAS, □ C'heptAS, △ C'pentAS and ● C'hexAS, in nitrobenzene at 90°.

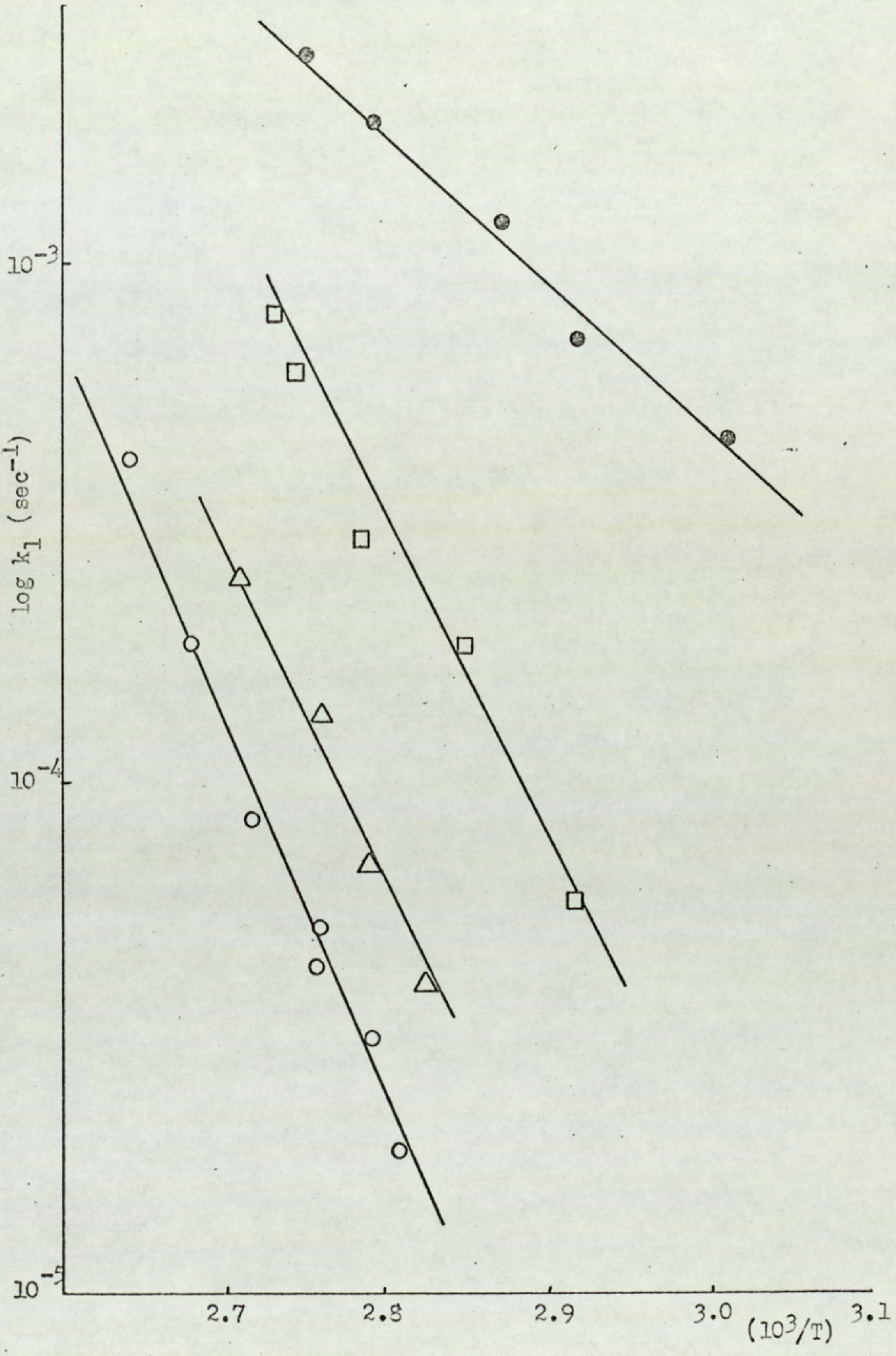


Figure 22. Semi logarithmic plot of first order velocity coefficient versus reciprocal of absolute temperature, for decomposition of the spiran series of anhydrosulphites. ● C'butAS, □ C'heptAS, △ C'pentAS and ○ C'hexAS.

C'but AS decomposed so rapidly at the temperature of study ($t_{\frac{1}{2}}$ approx. 5 mins.) that the method(s) used were not accurate enough to detect minor changes in the velocity coefficient. Decomposition rates in dekalin at 90° were:

C'pentAS $1.7 \times 10^{-5}sec^{-1}$

C'hexAS $9.4 \times 10^{-6}sec^{-1}$

C'heptAS $6.9 \times 10^{-5}sec^{-1}$

Table 17

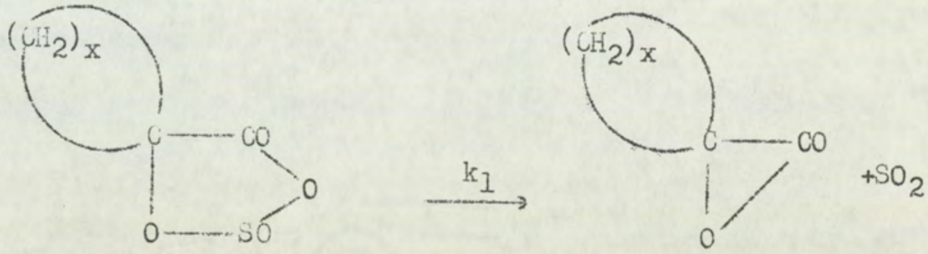
First order rate constants (k_1) and half lives ($t_{\frac{1}{2}}$), for the decomposition of C'butAS, C'pentAS, C'hexAS and C'heptAS in nitrobenzene at 90°, together with their energies of activation (E), entropies of activation ($\Delta S\pm$) and frequency factors (A) in the same solvent. [Anhydrosulphite]$_0$ = 0.4 mole litre^{-1}.

	C'butAS^x	C'pentAS	C'hexAS*	C'heptAS
$10^5k_1(sec^{-1})$	240.0	11.8	5.6	64.0
$t_{\frac{1}{2}}$(mins.)	4.8	96.0	206.3	16.1
E(k.cal.mole^{-1})	17 ± 2.5	28.5	32.6	28.5
$\Delta S\pm$(cal.deg.mole^{-1})	-25.8	0	+9.5	+3.2
A(sec^{-1})	4.44×10^7	1.95×10^{13}	3.42×10^{14}	1.06×10^{14}

* from Section 6.1

x an average value for E taken from those derived from two extreme Arrhenius slopes was employed to calculate A and $\Delta S\pm$.

The first order nature of these reactions together with the entropies and energies of activation were taken as typical of the established thermal scission process, which results in the synchronous extrusion of sulphur dioxide and formation of an α-lactone (Equation 1).



...... (1)

Mass spectra of all four members displayed a similar pattern, the primary fragment consisting of a strong peak corresponding to the α-lactone.

With the exception of C'butAS, decomposition in inert solvents below 100°, yielded the derivative poly α-ester as sole product. Oligomeric polyester (infra-red $\nu_{C=O}$ 1730 cm^{-1}) and the derivative glycollide ($\nu_{C=O}$ 1765 cm^{-1}), were shown to be the products of C'butAS decomposition, the latter being more predominant (approx. 70%).

Rates were studied in hydroxylic solvents (for example benzyl alcohol) because reaction with an alcoholic function is representative of rate determining bimolecular propagation during anhydrosulphite polymerisation. In the cases of C'pentAS, C'hexAS and C'heptAS the observed rate was considerably less than that in nitrobenzene, as might be expected on grounds of reduced solvent polarity. C'butAS, however, decomposed faster in benzyl alcohol indicating that both bimolecular and unimolecular decompositions were occuring. In addition no glycollide was detected in the products. A first order rate plot for the decomposition of C'butAS in benzyl alcohol at 60° is given in Figure 23 together with a similar plot in nitrobenzene. The overall first order rate constants obtained in benzyl alcohol at 90° for the

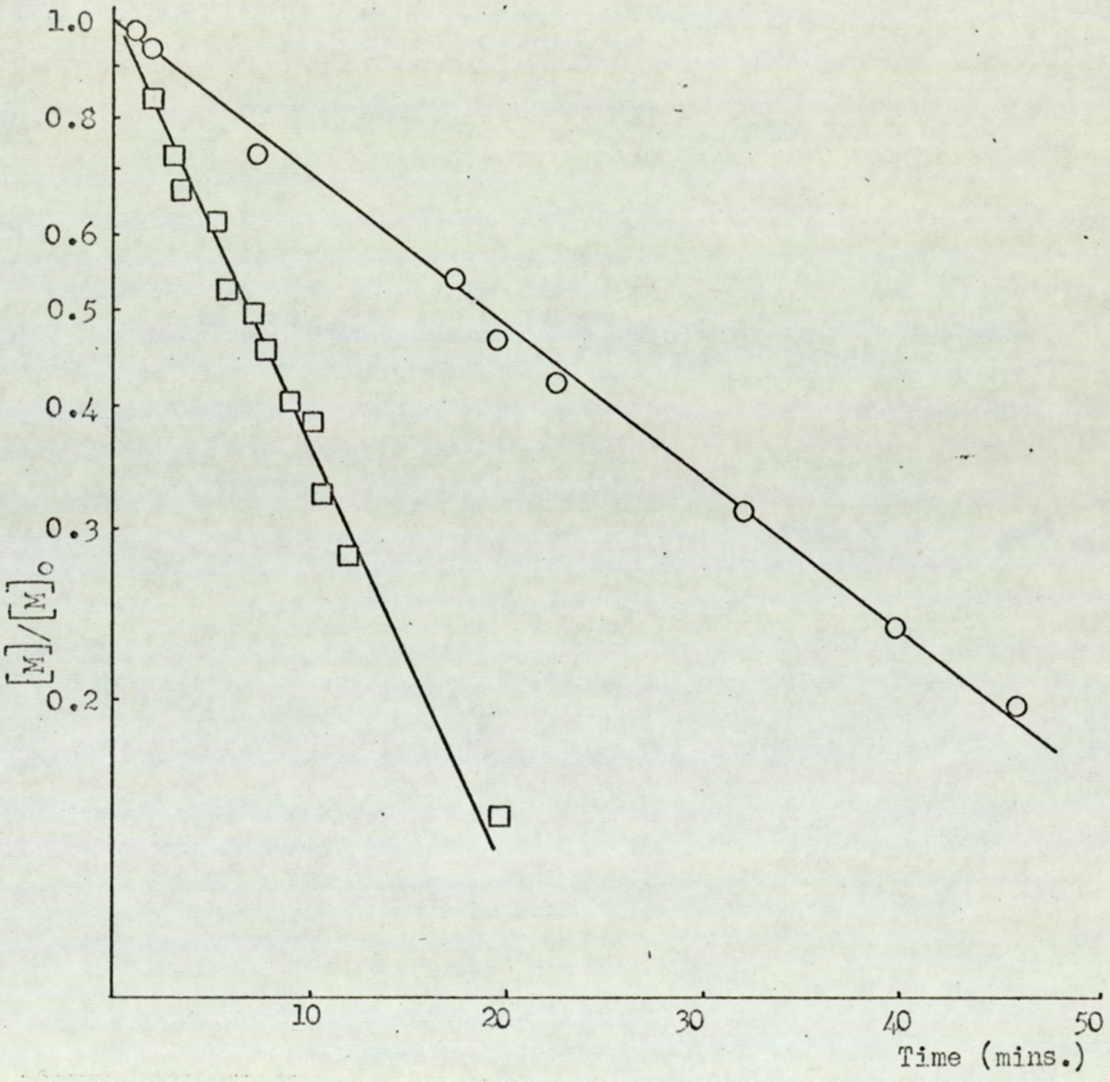


Figure 23. First order rate plot for the decomposition of C'butaS in; ○ nitrobenzene and □ benzyl alcohol, both at 60°.

decomposition of the spiran series, together with a comparison of the rate observed in nitrobenzene under the same conditions (k_b/k_n) are presented in Table 18

Table 18

Overall first order rate constants obtained in benzyl alcohol at 90° for the decomposition of the spiran series, and (k_b/k_n) ratios. $[\text{Anhydrosulphite}]_o$ 0.5 moles l^{-1}, $[PhCH_2OH]$ 8.75 moles l^{-1}.

	$10^5k_b(sec^{-1})$	k_b/k_n
C'butAS	1100	4.58
C'pentAS	1.65	0.14
C'hexAS	1.22	0.22
C'heptAS	5.7	0.09

For the specific decomposition of C'butAS in benzyl alcohol the observed overall rate constant (k_b) may be resolved into first and second order components as in Equation 2.

$$k_b = k_1 + k_2 \, [Ph.CH_2OH] \qquad \ldots\ldots (2)$$

Other members of the spiran series, however, simplify to $k_b = k_1$ since the second order component is negligible. An estimate of the bimolecular rate constant (k_2) was obtained by substituting the velocity coefficient value obtained in nitrobenzene at the same temperature for k_1, in Equation 2. The observed rate constants (k_b) together with the derived rate constants (k_2) and kinetic parameters for the bimolecular reaction of C'butAS with benzyl alcohol are given in Table 19.

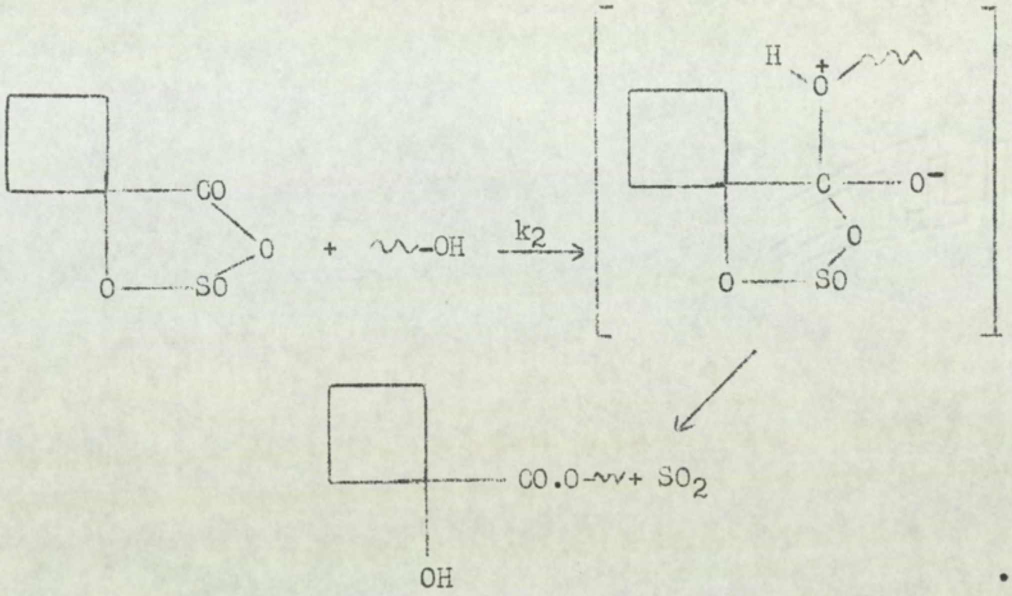
Table 19

Overall first order rate constants (k_b), and second order rate constants (k_2), for the reaction of C'butAS with benzyl alcohol in benzyl alcohol as solvent at various temperatures, together with energy and entropy of activation and frequency factor for the second order reaction.

$[\text{C'butAS}]_0$ 0.5 moles l^{-1}. $[\text{Ph.CH}_2\text{OH}]$ 8.75 moles l^{-1}.

	$10^4 k_b (\text{sec}^{-1})$	$10^5 k_2 (\text{l mole}^{-1}\text{sec}^{-1})$
49.4°	9.3	7.4
59.5	19.3	16.6
71.0	38.2	32.8
(E) k.cal.mole^{-1}		14.9
($\Delta S^{\pm}$) cal.deg^{-1},mole^{-1}		-35.3
(A) l. mole^{-1}sec^{-1}		1.01×10^6

The values of entropy and energy of activation together with the frequency factor are typical of a rate determining bimolecular process involving a transition state more polar than the reactants. Evidently the unimolecular reaction contributes significantly more than the bimolecular route at low hydroxyl function concentration. A similar competition of reaction modes is to be expected in the propagation reaction during polymerisation. Thus propagation by interaction between the terminal hydroxyl of a polymer chain and the α-lactone occurs more frequently than does direct bimolecular reaction with the anhydrosulphite ring (Equation 3).



...... (3)

The overall decomposition process can be represented by:

$$\frac{-d[C'butAS]}{dt} = \frac{d[SO_2]}{dt} = (k_1 + k_2[R\ OH])[C'butAS] \qquad \ldots\ldots (4)$$

where [C'butAS], and [SO_2], refer to the concentrations of C'butAS and sulphur dioxide and [R OH] to the total concentration of hydroxyl function.

In Section 6 decomposition of C'hexAS to cyclohexanone was shown to be a first order process of high activation energy, but even at temperatures in the region of 180° only 5% of ketone was formed. C'heptAS exhibited similar kinetic behaviour but for a given temperature was found to give a greater mole percentage of ketone. Cycloheptanone did not significantly interfere with polymerisation rate or polymer formation, even when present as a 20% contaminant.

With the exception of poly C'butAS, which was only obtained as oligomer, all polymers precipitated in good yield from the reaction solution on cooling. The molecular weights of products obtained were dependant upon the ease of monomer purification (that is, the mole ratio of α-chloroacid chloride impurity present in the polymerisation reaction) as is evidenced in Table 20.

Table 20

Purity of spiran monomers (expressed as moles of chlorine containing impurity per mole of anhydrosulphite), and molecular weight (M_n) of their derivative polymers.

Anhydrosulphite	Chloride x 10^3	M_n	DP
C'butAS	160	4-700	4-7
C'pentAS	1.4	9,260	83
C'hexaS	1.0	12,240	97
C'heptAS	50	1,760	12

7.2 Discussion

With the exception of C'butAS the spiran compounds were no more difficult to prepare than their equivalent dialkyl derivatives. C'butAS was difficult to synthesise and purify because of its high reactivity. Parent acid, glycollide-1,4-dispirocyclobutane and α-chlorocyclobutanoyl chloride, the major by-products did not interfere with the kinetic study, however, since remarkably constant results were obtained from several samples containing different ratios of each impurity.

Thermal decomposition. Simple di-n-alkyl substituted anhydrosulphites approach a limit to thermal instability as is shown in Figure 15. Their stability has been considered in terms of steric and electronic properties of the substituent. In the spiran series, ring strain, an additional substituent feature is introduced. As cycloalkyl groups exhibit an approximately equal but weak electron releasing effect[76], steric bulk and ring-strain are the predominant factors influencing the rate of thermal decomposition. The effect of substituent bulk on rate of thermal scission is of the same order as that observed for the eqivalent dialkyl compounds, but slightly less because the cyclic substituent has less freedom of movement. For the dialkyl series steric factors seemed reasonably constant for DEAS, DPAS, and DBAS and therefore ring-strain would appear to be the important variable in this spiran series.

Courtaulds models and n.m.r. spectra of anhydrosulphites together with an analogy with five membered cyclic organic sulphites indicate that there may be a slight deviation from planarity in the anhydrosulphite ring. Even so, because the constituent members of the ring impose rigidity there is no mechanism available to dissipate the strain conveyed by the other ring in the spiran system.

In general terms kinetic behaviour of spiran derivatives is substantially the same as that observed for the dialkyl series, and with the exception of C'butAS there was no deviation from the stoichiometry of the thermal decomposition reaction. The abnormal behaviour of C'butAS in this respect is attributable to the geometry of the molecule and will be discussed in more detail later.

In contrast to the general kinetic behaviour, the precise values of rate constants for thermal decomposition (Table 17) vary considerably. The contribution of ring-strain is best illustrated by comparison of spiro substituted anhydrosulphites with their equivalent open chain dialkyl derivatives, as demonstrated in Figure 24. It is immediately apparent that the conjoined ring has an effect and not merely due to physical size. Ring-strain contributions are superimposed on steric effects, and are of the order expected on grounds of accepted strain factors correlated from alicyclic hydrocarbon chemistry.

When considered in isolation the thermal behaviour of C'hexAS was unexpected and seemed odd, but its rate data is quite consistent if considered with the rest of the spiran series. It is apparent that the cyclohexyl substituent imposes little tension on the anhydrosulphite ring during its conformational movements since it has a thermal stability similar to that of HBAS. Further, C'hexAS shows a limited sensitivity to change in solvent polarity in common with HBAS, but in contrast to higher members of both the dialkyl and cycloalkyl series. Less polarisation about bonds in the α-lactone and transitions leading to it are suggested to explain this

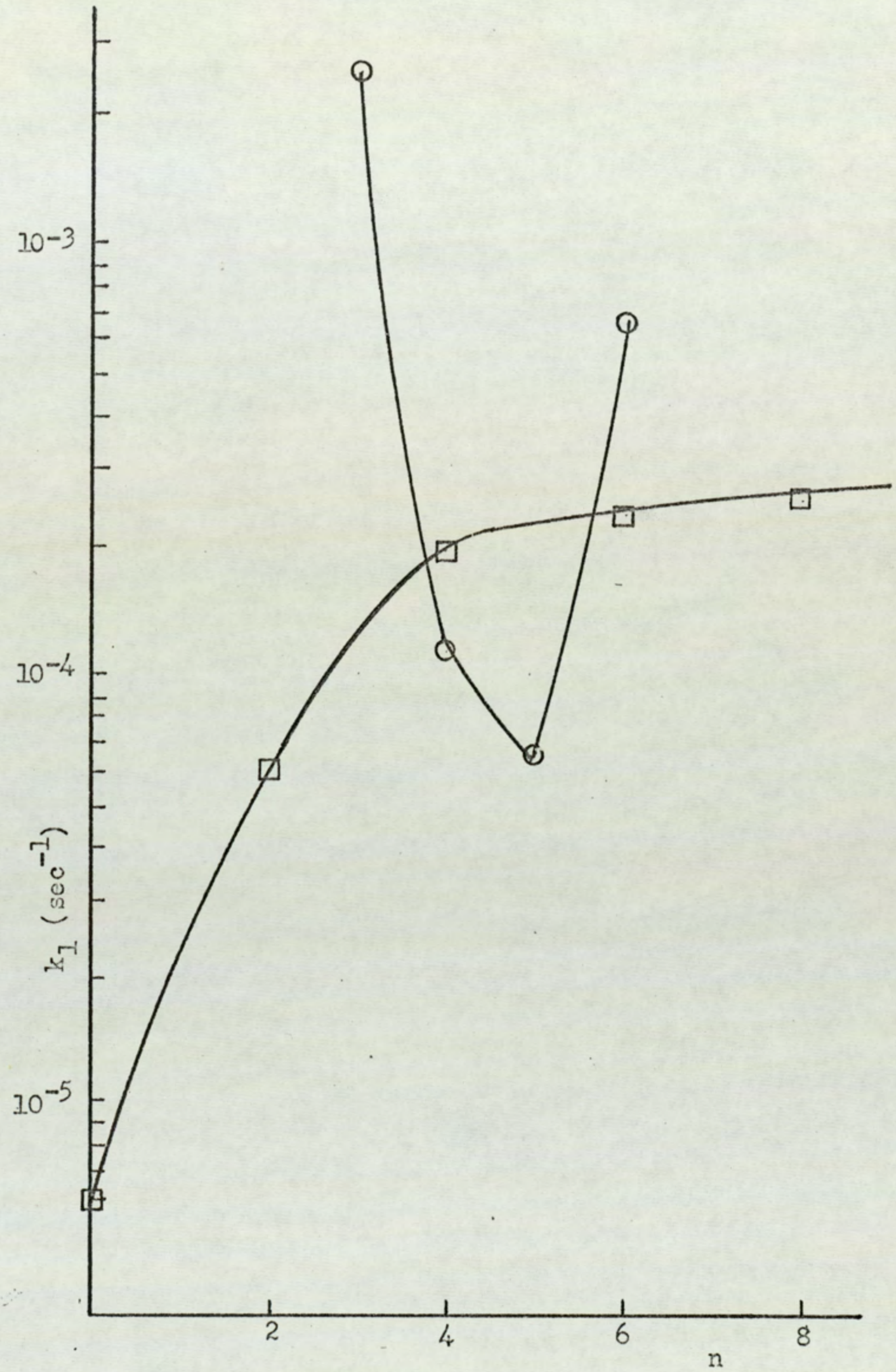


Figure 24. First order rate constants for the decomposition of various anhydrosulphites in nitrobenzene at 90°, plotted as a function of the number of carbon atoms (n) in the substituents. ☐ dialkyl series

○ spiran series

phenomenon.

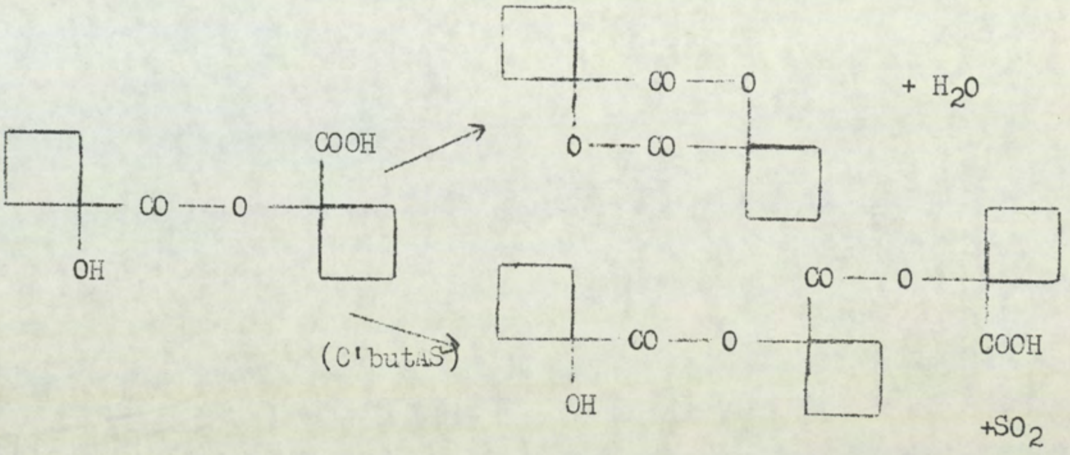
The cyclopentyl and diethyl compounds are similar to each other but more typical in their behaviour towards change in dielectric constant of the solvent medium. Again pseudo-rotation of the cyclopentane envelope conformation is able to occur with little imposed tension on the other ring. Cyclobutyl and cycloheptyl derivatives, however, exhibit marked signs of inflicted ring-strain since their rates of decomposition are considerably greater than the maximum plateau value (Figure 24) observed with the dialkyl series.

Attempts to relate observed rate constants with the shift of a given absorption in the infra-red are ultra-violet spectra of each anhydrosulphite, although qualitatively useful, were not successful when trying to derive an extrathermodynamic relationship.

It is difficult to seperate inductive, steric and ring-strain substituent effects in the anhydrosulphite compounds studied. Clearly, in dialkyl derivatives both inductive and steric contributions are important. Inductive effects in the spiran series are considered to be small and sensibly constant. Therefore differences between the curves illustrated in Figure 24 must be due to conveyed ring-strain by the spiro-substituents, since steric contributions for a given ring and its equivalent dialkyl group will be approximately the same. Both C'pentAS and C'heptAS exhibit quite marked rate-solvent polarity dependence as do DEAS, DPAS and DBAS. An induced degree of polarity in entities involved in the transition state appears to be responsible for this phenomenon. It seems likely that solvent sensitivity is derived from polarised bonds within the anhydrosulphite ring. Inductive effects donate charge to the ring, whereas steric and conveyed ring-strain contributions cause lengthening and bending of bonds from their favourite positions. In either event the result is to promote electronic asymmetry across the species, and particularly across the fragment to be extruded.

Glycollide formation is unique to C'butAS, however, Bocskin[54] has shown that for a series of 1-hydroxy cycloalkane carboxylic acids the cyclobutyl derivative has the best displaced bond angles to favour conversion to the glycollide. Energies and entropies of activation for the decomposition of C'butAS are not characteristic of the normal thermal ring cleavage observed for other spiro-anhydrosulphites. The reaction is abnormal in that the rate of decomposition is very high and polymer is not formed as the major product. A large and negative entropy of activation is indicative of a transition state more polar than the reactant, and the low energy of activation suggests a localised labile site for scission. Pronounced electron migrations, caused by high strain relayed to the anhydrosulphite ring, lengthening of bonds and induced polar character may be responsible for these kinetic anomalies.

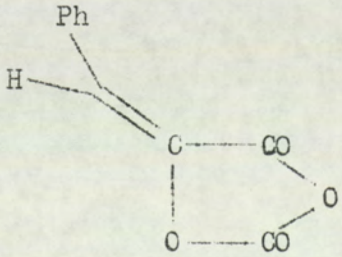
To allow glycollide formation by combination of two α-lactone units, the normal reaction with nucleophile must necessarily be quenched. There is no reason to support this view however, especially as glycollide products have not been observed in the polymerisation of other anhydrosulphite systems. The possibility of glycollide formation and subsequent polymerisation in these other systems can be discounted since Hall[3] has shown that tetra-substituted glycollides do not polymerise because of steric hindrance during the propagation reaction. A possible scheme which explains glycollide formation is presented in Equation 5. The dimer is shown to undergo either ring closure or propagation to form trimer. Considerations in earlier sections would indicate that formation and presence of water favours oligomeric products.



.....(5)

Thus the mechanism proposed is consistent with the obervations that only low molecular weight polymer is formed and that in benzyl alcohol as solvent glycollide formation is negligible. In the latter case the main product is monomeric benzyl ester and the dimer is not formed.

In the limit the smallest ring possible is a double bond. An example of ring-strain relayed by an olefinic bond is found with 5-benzylidene-1,3-dioxolan-2,4-dione (I)[77], which is a reactive compound when compared with the stable 5,5-dimethyl compound[30].



(I)

It is of interest that heating this compound gives the derivative glycollide in 80% yield. Evidently small ring spiro substituents favour glycollide formation in these types of cyclic monomer.

Ketone formation does not occur to any significant degree below 100°, and when present does not chemically interfere with the mode of polymerisation. That under the same conditions more ketone is obtained from C'heptAS than C'hexAS is a further consequence of ring strain, since the change in bond hybridisation from sp^3 to sp^2 at the C-5 carbon relieves compression in medium rings.

Hydroxyl initiated decomposition. Rate determining bimolecular propagation, involving anhydrosulphite molecules, can compete with the thermal extrusion reaction when structural features are favourable. Thus polymerisation of GAAS and LAAS proceeds along both reaction paths whereas HBAS (because of steric interference) only follows the extrusion route. Activation of the carbonyl carbon by bischloromethyl substitution, however, enables some bimolecular propagation to occur even though chloromethyl groups are more bulky than methyl substituents. The balance between steric and electronic factors is therefore delicate.

At the outset of this work it was thought that restricted freedom of movement in the substituent part of C'pentAS may just allow direct interaction between an approaching nucleophile (polymer end group) and the C-4 carbonyl to take place. Results in Table 18 demonstrate clearly that this is not the case. C'butAS, however, does decompose by both first and second order processes. The conformation of the cyclobutane ring pins back the α-methylene groups such that steric obstruction of potentially reactive bodies is not completely effective. Kinetic parameters associated with the second order process (Table 19) closely resemble those reported for 5-phenyl-1,3,2-dioxathiolan-4-one-2-oxide (MAAS)[68]. The second order rate constant for the reaction of C'butAS with benzyl alcohol is greater than that for GAAS (the non-substituted anhydrosulphite) under the same conditions, but when compared with the accompanying thermal scission process is not so significant. The increase in second order rate is taken as evidence for a puckered anhydrosulphite ring in which the carbonyl carbon is exposed more effectively in the reaction path.

Other spiran compounds are usually polymerised by ionic routes, the effect of substituent depending on its proximity to the reaction site. Thus the polymerisation of spiro β-propiolactones, initiated by the pivalate anion[12], show a marked decrease in rate as the size of the substituent increase, whilst boron trifluoride initiated polymerisation of cyclopropane and cyclohexane spiro-oxetanes[14,15] occur at approximately the same rate. In the former, the effect is steric since the equivalent open chain dialkyl analogues show similar behaviour, but in the latter the reaction centre is too far divorced from the substituent to be influenced by ring strain or steric bulk.

Spiran derivatives of α-aminoacid anhydrides[78] show enhanced thermal stability compared with open chain analogues (particularly monosubstituted), which is in contrast to anhydrosulphite behaviour. The rate of methoxide anion initiated polymerisation was found to depend upon the spiro-substituent, both in terms of ring-strain and steric obstruction. An additional feature, the conformational difficulty in incorporating a repeat unit into a polymer chain, was required to explain the low rate of polymerisation of the spiro-cyclopropyl derivative. As has been postulated earlier a similar phenomenon may be responsible for the low yield of polymer observed in the decomposition of C'butAS, however, this would not reflect in the rate constant derived from gas evolution data, since incorporation of additional units to the polymer chain occurs subsequent to the rate determining step in thermal polymerisation.

The kinetic study of C'butaS decomposition was hindered because a permanent equilibrium between cyclobutanol-1-carboxylic acid and its derivative glycollide together with a low thermal stability prevented adequate purification. To avoid ketone contamination of C'heptaS, vacuum sublimation was preferred to distillation in the purification procedure, however this process was less efficient in removing final traces of α-chlorocycloheptanoyl chloride impurity. These difficulties are reflected in the molecular weight of resultant polymeric products.

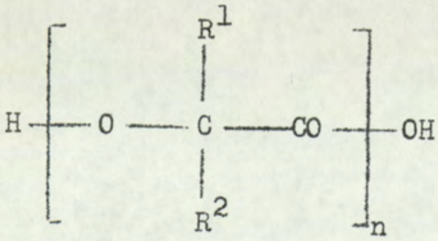
As with the dialkyl series, the limitations of anhydrosulphite polymerisation as a general method for preparing spiropoly α-esters are controlled by the synthetic feasibility of precursor materials. Extension of the spiran series by investigation of either the cyclopropyl or cyclo-octyl derivatives was considered although clearly from the present work both materials would be highly reactive and difficult to manipulate. It is doubtful whether either compound would provide high polymer when polymerised by the thermal route.

8. POLY α-ESTERS

Several systems of nomenclature have been used to describe individual polyα -esters (see Appendix I), however for simplicity, in this section the prefix poly- is used in front of the parent anhydrosulphite.

8.1 Characterisation

With the exception of DBAS and C'butAS, the thermal polymerisation of anhydrosulphites, in dry solvents, between 60-100°, gave near quantitative yields of white solid polymer. Some general properties of these polymers are given in Table 21. Soluble polymers were dissolved in deuterated chloroform (10% w/v) and studied using n.m.r. at 100 Mc/s. Increasing sensitivity of the instrument allowed location and integration of the terminal hydroxyl protons (singlet at 6.23τ). Infra-red spectroscopy in conjunction with n.m.r. was used to characterise the poly esters. Spectra were recorded from K Br discs (10% w/w) and the following absorptions are typical; 3450 cm^{-1} (ν_{O-H} polymeric hydroxyl); 1755 ± 10 cm^{-1} ($\nu_{C=O}$); 1095 ± 20, 1120 ± 20 cm^{-1} (both associated with ν_{C-O}); plus appropriate $-CH_2-$, and $-CH_3$ bands associated with the substituent(s). Elemental analysis taken together with spectral data is consistent with all the polymers having a linear poly α-ester structure (I).



$$H\left[O-\underset{R^2}{\overset{R^1}{C}}-CO\right]_n OH \qquad (I)$$

Table 21

Degree of polymerisation ($\bar{DP}$), melting and decomposition temperatures (T_m and T_d respectively), crystallinity (non-orientated) and solubility (in chloroform) of a selection of polyα-esters.

	$\bar{DP}$	T_m °C*	T_d °C*	Crystallinity	Solubility
polyHBAS	70	176	290	crystalline	sol.
	210	186	295	crystalline	insol.
	1162	190-220	-	crystalline	insol.
polyMEAS	24	-	270	amorphous	sol.
polyDEAS	165	194	240	crystalline	insol.
polyDPAS	34	195	227	crystalline	insol.
polyC'pentAS	83	-	274	amorphous	sol.
polyC'hexAS	97	-	256	amorphous	sol.
polyC'heptAS	12	-	230	amorphous	sol.

* As measured by D.T.A.; heating rate 5°/min., atmosphere nitrogen.

For polymers having n = 1-30, quantitative infra-red spectroscopy provides a fairly ready and convenient means of assessing molecular weight. A calibration graph based on the relative intensity of hydroxyl (approx. 3450 cm^{-1}) and ester carbonyl (approx. 1760 cm^{-1}) frequencies correlated fairly well with molecular weights assessed by other methods, but error due to presence of trace moisture (which absorbs in the hydroxyl region) was considerable for high polymer. N.M.R. can be used in a similar manner to compare end group resonance signals with those corresponding to the repeat unit, however because of a high signal/noise ratio at the hydroxyl resonance position, error was introduced for polymers with n in excess of 10. Vapour pressure osmometry, which proves valuable for poly HBAS[25] and poly LAAS[26], was of limited use due to the general insolubility of dialkyl polyα esters in organic solvents (such as for example; dekalin, benzene, chloroform, chlorobenzene, nitrobenzene, dimethyl formamide, dimethyl sulphoxide, dimethyl acetamide, bromopentafluorobenzene and perfluoroacetone). These polymers were soluble in hot substituted phenols or pyridine but these solvents are not ideally suitable because aliphatic poly esters exhibit instability in basic media.

The most successful method for obtaining reliable molecular weight data was found to be carboxyl end group titration, using a modification of Pohl's method[46]. Sources of error in the method were carefully investigated. Titrimetric precision was checked and found to be in the order of ± 5%, absorption of atmospheric carbon dioxide which could have drastic effects on alkaline titres of this order was efficiently prevented by the blanket of chloroform vapour above the polymer solution. Degradation (in hot benzyl alcohol necessary to achieve complete solution) was measured by end group carboxyl concentration and found to increase with time of dissolution,as demonstrated in Figure 25a for poly DEAS. Although lowering the temperature reduced degradation rate the time for complete solution is much longer and no improvement in total degradation was found. For poly DEAS at 160° the minimum time for complete solution is approximately 2 minutes whereas at temperatures below 100° dissolution is incomplete even after 15 minutes. In practice a dissolution temperature of 160° was used and a graphical correction applied to the result. Figure 25b shows on an arbitary scale the rates at which number of end groups increases with time for a series of poly α-esters. It is apparent that a substituent parameter

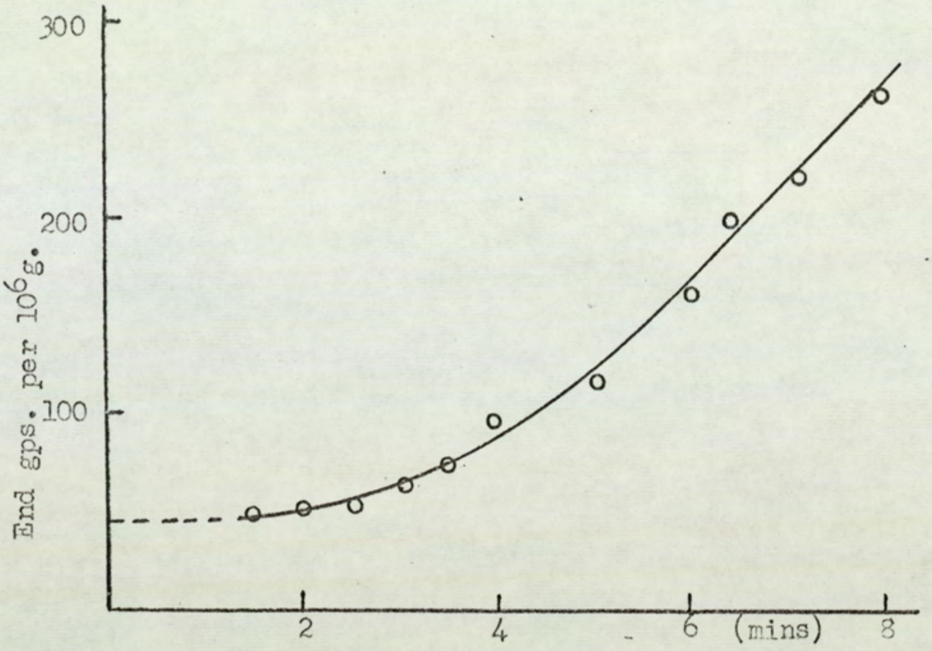


Figure 25a Dissolution of poly DEAS in benzyl alcohol at 159°.

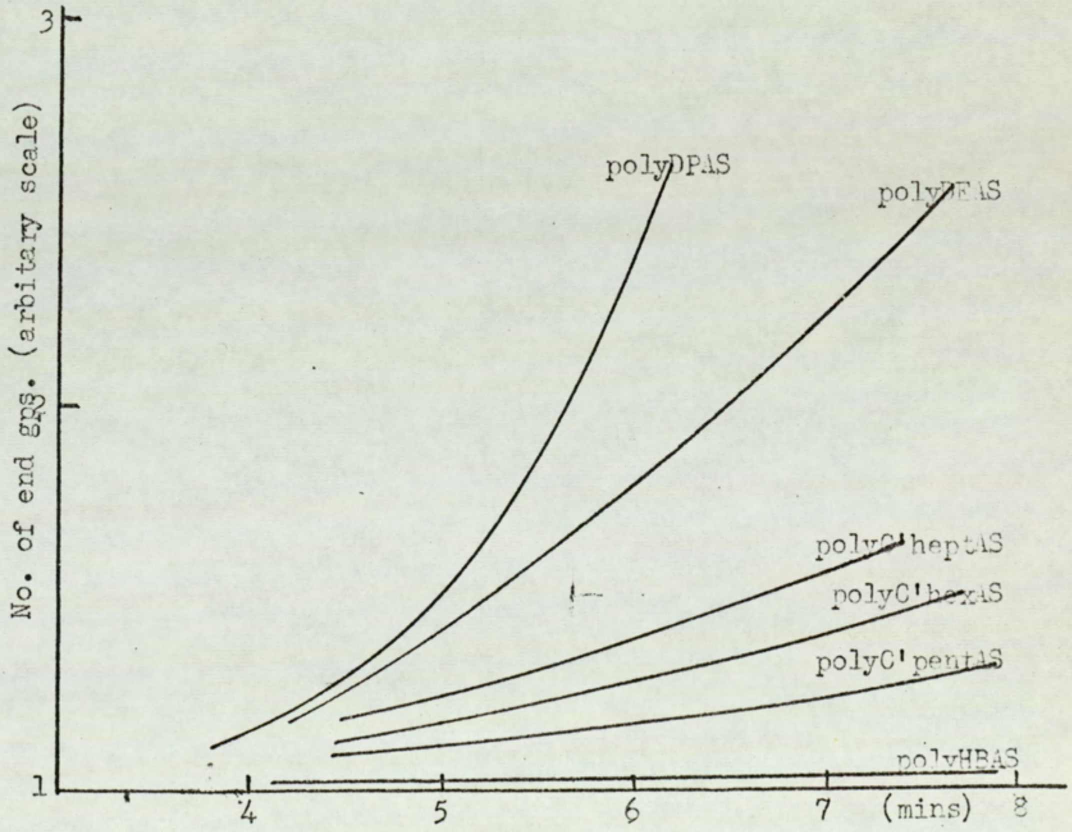


Figure 25b. Dissolution of various poly α-esters in benzyl alcohol at 159°.

affects the degradation process. Infra-red analysis of samples taken at various solution times for poly DEAS in cyclohexanol shows an absorption in the carbonyl stretching region (1703 cm^{-1}) which becomes larger with increasing time and is not present in the polymer initially. This band does not correspond to that observed for cyclohexyl-α-hydroxy-α-ethyl butyrate (1725 cm^{-1}).

Thermal stability. The thermal stability of this poly ester series, as measured by T_d (Table 21), demonstrates a trend since in both alkyl and spirocycloalkyl derivatives an increase in substituent size is accompanied by a lowering of degradation set in temperature. Melting temperatures of the crystalline poly α-esters on the other hand tend to increase, such that for higher derivatives the melt working temperature range is narrow. A comparison of stability based on data presented herein should be treated with caution because the molecular weights of individual polymers vary considerably and for this reason the effect of substituent structure on thermal behaviour is only assessed in the cases of poly HBAS, poly DEAS, poly C'pentAS and poly-C'hexAS.

A comparison of T.G.A. traces for poly HBAS, poly DEAS and poly-C'hexAS (Figure 26), all of similar molecular weight, demonstrates clearly that poly HBAS has a markedly superior stability. Poly-C'pentAS (not shown) gives a similar trace to poly C'hexAS but is displaced a few degrees towards higher temperature.

The degradation behaviour of poly HBAS has been studied in detail by Roberts[79], Sutton[80], Patterson[81] and O'Donnel[82]. Degradation rates followed by T.G.A.[80], thermovolatolisation analysis (T.V.A.)[80,81] and rheogoniometry[82] together with associated activation energies, show remarkable consistency even though the degradation parameter measured in each case is entirely different. All the processes

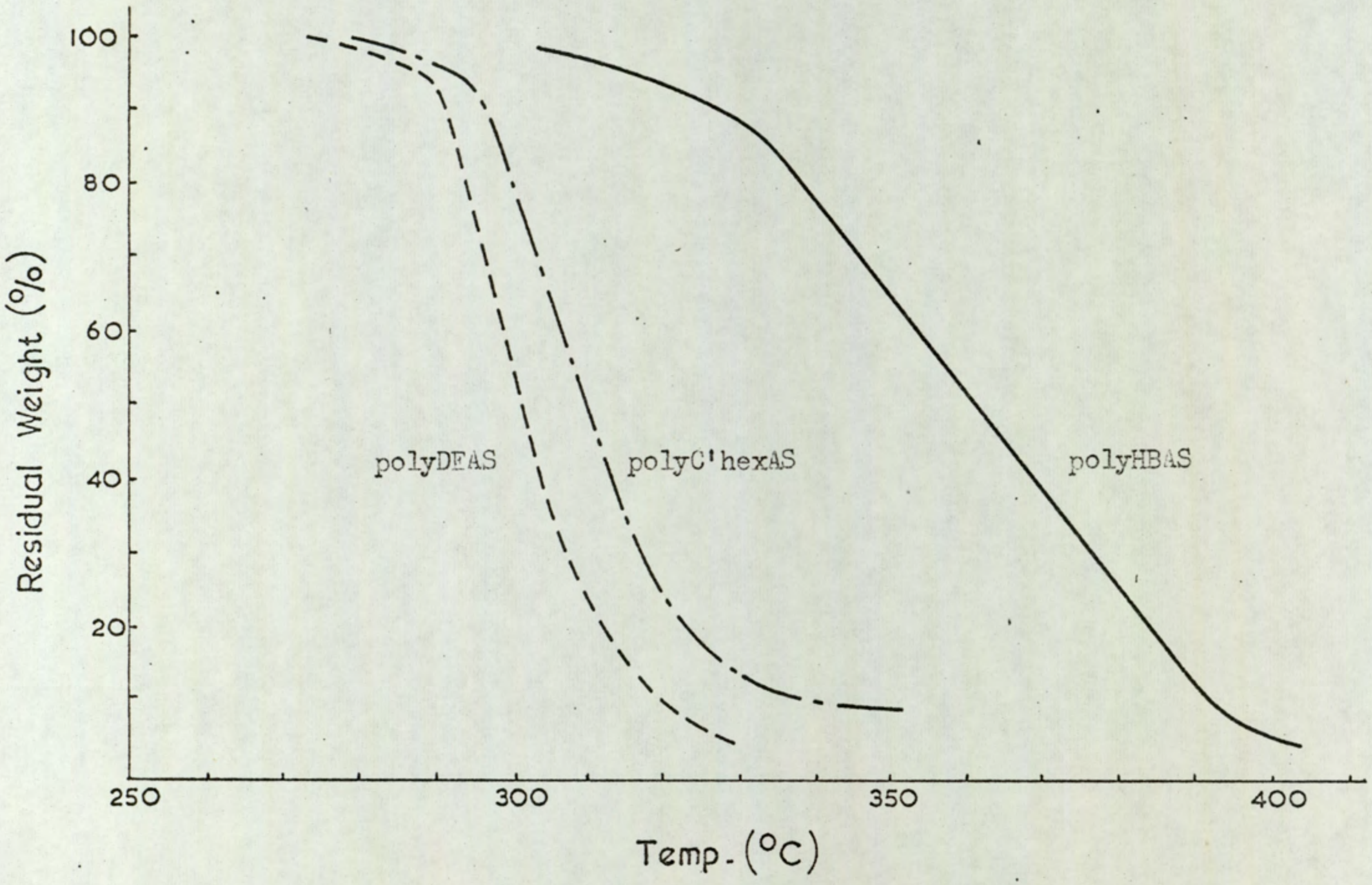
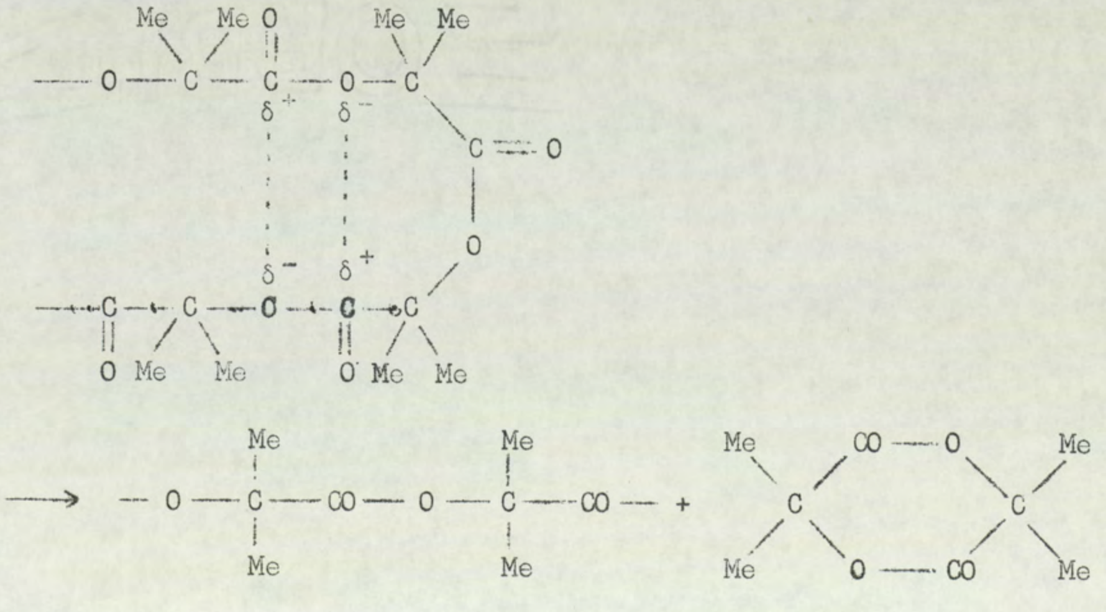


Figure 26. T.G.A. traces for poly DEAS, poly C'hexAS and poly HBAS (sample size approx. 5.0 mg.; heating rate 5° min^{-1}; atmosphere nitrogen).

measured showed first order dependence and product analysis by pyrolysis g.l.c. and gas evolution analysis[79] demonstrated that the only major product, below 400°, was tetramethyl glycollide. At temperatures between 400-600°, however, this compound behaves as a reaction intermediate and undergoes further decomposition to give carbon monoxide and acetone[79]. As the degradation process, followed by change in molecular weight of residual polymer, was shown to be first order and to possess similar rate constants as those obtained by T.G.A. and T.V.A., this provides good evidence that degradation does not take place by a random chain scission mechanism[82]. In addition Sutton has shown that chain end concentration (except at very low $\bar{DP}$) does not affect the decomposition rate. These facts, together with weight loss and appearance of volatiles both demonstrating first order dependence, point towards the principal degradation process being an intramolecular ester interchange reaction as expressed by Equation 1.



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Such reactions are known to occur during poly ester degradation[83].

This mechanism is in contrast to that proposed by Chujo[84], who for polyglycollide (poly GAAS) proposes an initial random scission mechanism followed by chain end unzipping reactions.

Analysis of isothermal T.G.A. traces for poly DEAS, poly C'pentAS and poly C'hexAS showed the degradation reaction to obey first order kinetics. Char residues of only a few percent appear to be a characteristic of the series. Rate constants together with activation energies derived from Arrhenius plots are given in Table 22.

Table 22

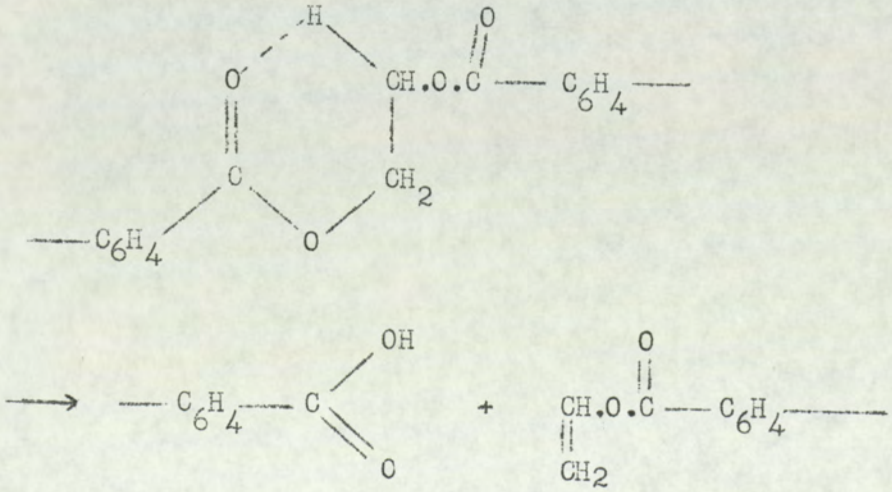
First order rate constants (k, sec^{-1}) for various polyα-esters obtained from isothermal T.G.A. traces, together with derived activation energies (E_{TGA}, k.cal. $mole^{-1}$). Activation energies obtained from T.V.A. analysis[81] are included for comparison.

Polymer	Temp. (°C)	k (sec^{-1})	E_{TGA}	E_{TVA} [81]
polyHBAS *	299	4.62×10^{-3}	31.1	30.2
	309	8.26×10^{-3}		
	315	1.57×10^{-2}		
polyDEAS	215	1.69×10^{-3}	42.5	44.0
	225	4.46×10^{-3}		
	235	1.32×10^{-2}		
polyC'pentAS	255	3.59×10^{-3}	40.5	39.0
	265	6.79×10^{-3}		
	275	1.22×10^{-2}		
polyC'hexAS	245	2.76×10^{-3}	42.1	-
	255	5.19×10^{-3}		
	265	1.90×10^{-2}		

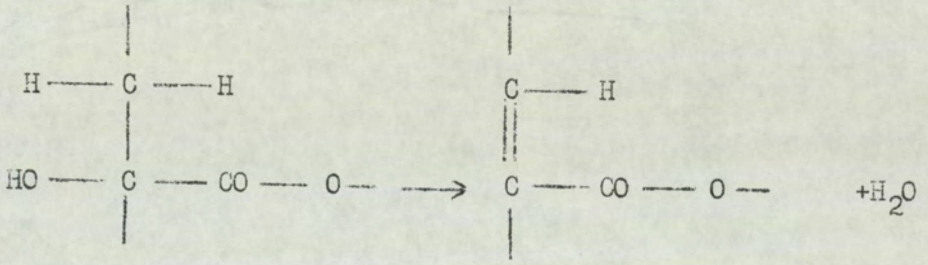
* Activation energy obtained from rheogoniometry[82] 33 k.cal. mole^{-1}.

It is possible that poly HBαS exhibits a superior thermal stability for two reasons. First, structural features of higher homologues enhance the intramolecular ester interchange process, and secondly, an alternative mechanism not favoured in the case of poly-HBαS comes into play at lower temperatures with other polyα-esters. The latter is considered more likely because; a) an increase in substituent size would be expected to reduce the ease of formation of the 4-centre transition state in ester interchange; b) a change in activation energy suggests a different or additional process is operating; and c) partially degraded polymers, with the exception of poly HBαS, show a degree of unsaturation in their structure.

A competition between ester interchange and depolymerisation involving olefinic compounds is well known in polyester degradation[83]. Pohl[85] has shown that for the latter process β-hydrogen atoms as well as the ester function are principal sites of weakness in the polymer chain. The degradation of polyethylene terephthalate (P.E.T.) has been considered in detail[86] and illustrates Pohl's observations.

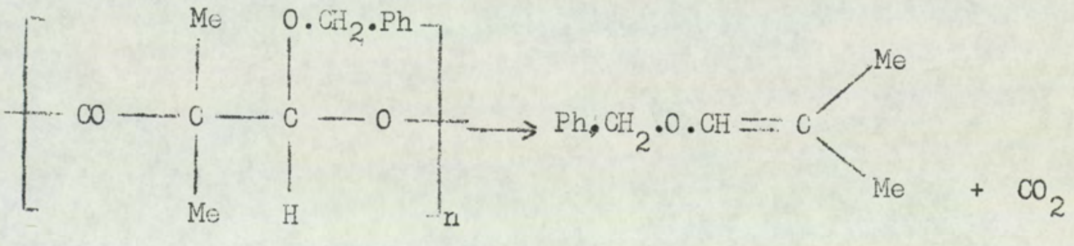


A similar type of degradation scheme may exist for polyα-esters but as poly HBaS contains β hydrogen atoms and does not apparently decompose by this route, a γ -hydrogen atom appears to be necessary for this reaction to occur. It is possible that when hydrogen atoms are only available in substituents pendant to the main chain, γ -hydrogens are those most suitably placed in order to provide close contact with the carbonyl oxygen thus aiding formation of the cyclic transition state. The relative rates of degradation of poly DEaS, poly C'pentaS and poly C'hexaS are consistent with a mechanism of this type since olefin formation in alicyclic compounds is more difficult than in acyclic compounds because of restricted bond movements. Other reactions which can lead to olefin formation include end group dehydration:



$$\mathrm{HO{-}\overset{\overset{|}{H-C-H}}{\underset{|}{C}}{-}CO{-}O{-}} \longrightarrow \mathrm{\overset{\overset{|}{C-H}}{\underset{|}{\overset{\|}{C}}}{-}CO{-}O{-}} \quad +\mathrm{H_2O}$$

and moleular abstraction of carbon dioxide as has been evidenced with dimethyl ketene copolymers[87].



$$\left[\mathrm{-CO-\overset{Me}{\underset{Me}{C}}-\overset{O.CH_2.Ph}{\underset{H}{C}}-O-} \right]_n \longrightarrow \mathrm{Ph.CH_2.O.CH{=}C}\begin{array}{l}\mathrm{Me}\\ \mathrm{Me}\end{array} + \mathrm{CO_2}$$

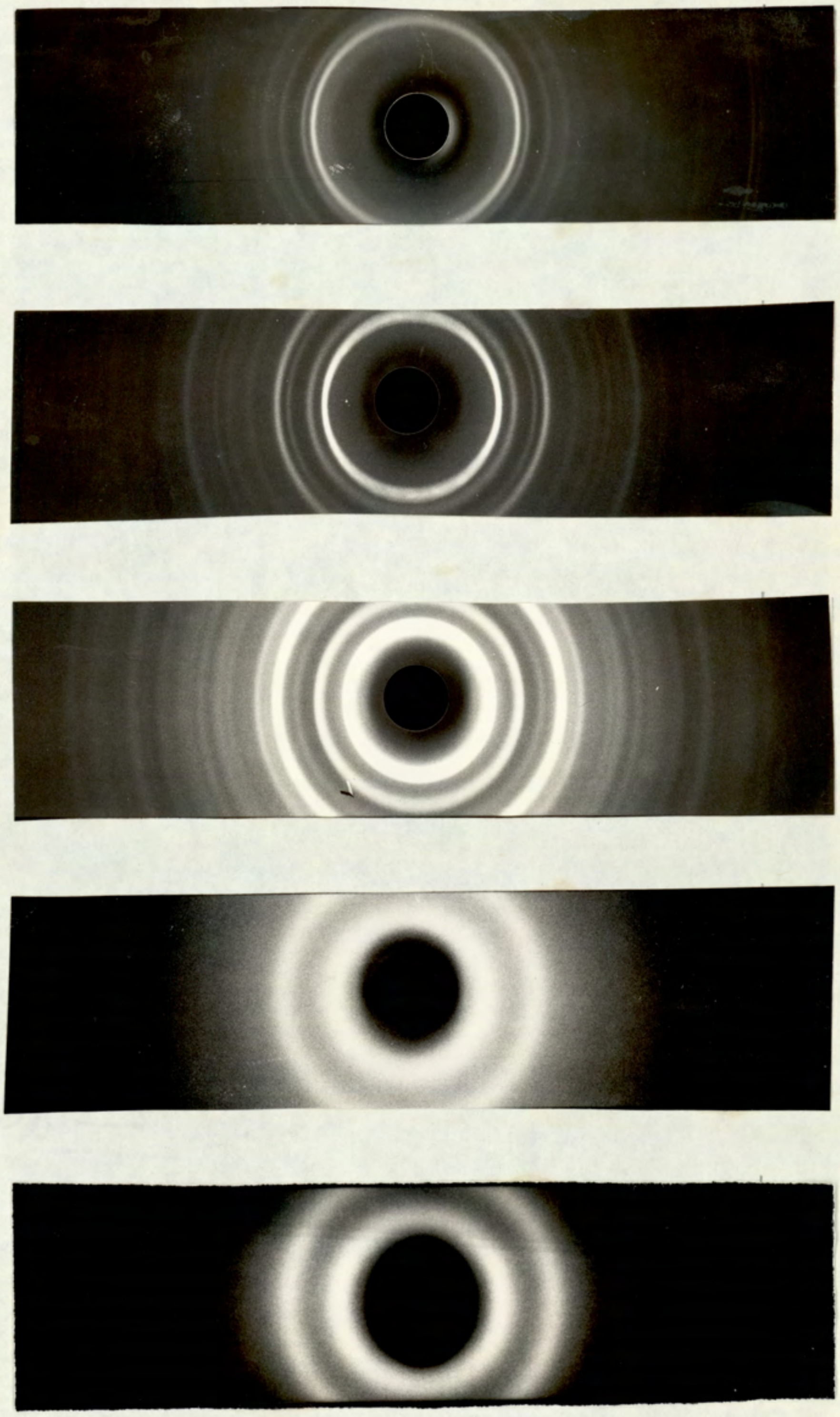
The variation of molecular weight with reaction time and a complete product analysis are required to justify anddifferentiate between any of the above mechanisms.

That relative rates of solution and melt degradation processes correlate well suggests a common substituent effect is operating in both cases.

Crystallinity. Of the polymers studied, in general, di-n-alkyl poly α-esters are crystalline materials whereas spirocycloalkyl derivatives are amorphous. X-ray powder photographs of poly HBAS, poly DEAS, poly DPAS, poly C'pentAS and poly C'hexAS, which are presented in Figure 27 illustrate this point.

A D.L.I. trace (full line) for poly DEAS is given in Figure 28, together with a D.T.A. trace (dotted line) for comparison. Under these conditions banded spherulites were observed (Figure 29), but similar analysis of other crystalline poly α-esters gave the more normal "maltese cross" type of spherulite. Large banded spherulites are not a common phenomenon although this type of crystallisation has been observed with other polymer systems including polyethylene, polyoxymethylene and P.E.T. No uniformly acceptable explanation of this behaviour has been proposed although some suggestions have been as to its origin[88]. It is of interest that there is a large difference between the T_m for poly DEAS and the onset of crystallisation temperature T_c (i.e. the temperature at which spherulites first appear) which infers that crystallisation occurs with some difficulty. A comparison of $T_m - T_c$ values obtained for various polyesters under identical conditions is shown in Table 23. During repeated melting and cooling the melting point was observed to rise by 10°, this being associated with removal of imperfections in the crystalline regions. As D.T.A. was performed on un-annealed polymer a slightly lower T_m was observed for this reason.

Structural features which favour polymer crystallinity include, chain polarity, linearity, molecular symmetry and regularity. Simple poly α-esters (for example poly GAAS, poly LAAS and poly HBAS) are crystalline because such requirements are satisfied primarily because of the high interchain cohesion consequent upon the highly



PolyHBAS

PolyDEAS

PolyDPAS

PolyC'pentAS

PolyC'hexAS

Figure 27. X-ray powder photographs of several poly α-esters.

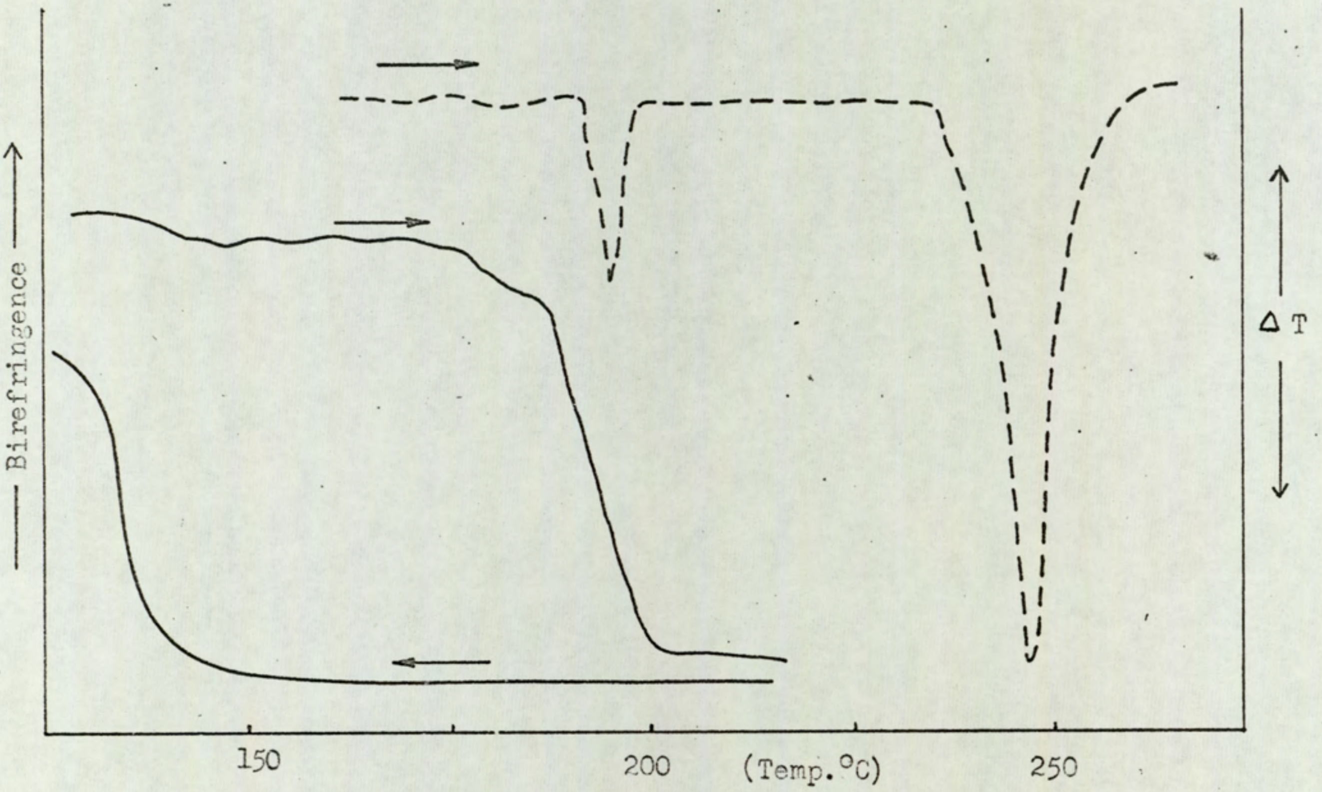


Figure 28. D.L.I. (full line) and D.T.A. (dotted line) traces for poly DEAS (heating rate 5° min^{-1}; cooling rate 2° min^{-1}).

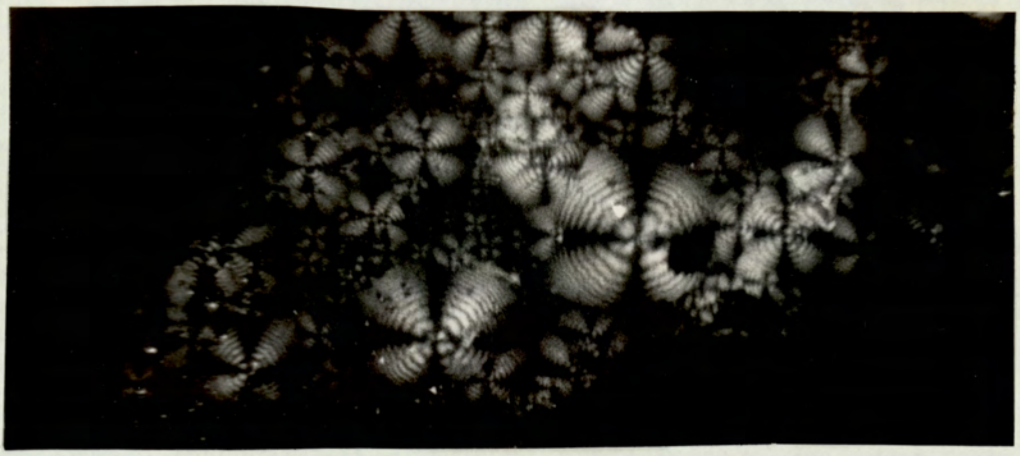


Figure 29. Banded spherulites observed for poly DEAS during D.L.I. analysis.

polar nature of the backbone.

Table 23

D.L.I. measurement of the onset of polyester crystallisation at a constant cooling rate of 10° min.$^{-1}$.

Polymer	$T_m - T_c$
poly(hexamethylene adipate)	8°[89]
P.E.T.	20°[89]
poly(tetramethylene terephthlate)	20°[89]
polyDEAS	58°

As the size of subsituent is increased in a given class of polymer, however, interchain cohesion is reduced and chain packing becomes more difficult. Thus if substituent groups larger than methyl are introduced the optimum interchain distances of approximately 5 A cannot be readily attained, and the crystallisation process is impeded. In light of this it is perhaps surprising that poly DEAS and poly DPAS are both crystalline. Their rate of crystallisation as monitored by D.L.I. measurements, is however very slow this being a consequence of chain packing difficulties.

Poly MEAS is unsymmetrically substituted and is amorphous because a degree of irregularity has been introduced. For similar reasons poly α-hydroxyisovalearate[90] (I; $R^1 = H$, $R^2 = iPr$) is also amorphous, but in contrast poly LAAS is crystalline[91]. In the case of poly LAAS since the substituent is small, helix formation is allowed to occur and interchain cohesion is strong.

The conformation of polymer chains is open to speculation since although those of poly LAAS are helical[91], and ability to form helical chains has been suggested as one requirement for banded spherulite formation, poly GAAS has been shown to exist in the extended planar zig-zag form[92]. It seems most probable however, that crystalline homologues higher than poly LAAS will crystallise in a helical conformation since in this manner bulky substituents can be most readily accommodated.

Poly (trimethylene oxides)[12] and poly β-esters[14] containing cyclic side groups which include a carbon atom of the main chain have been studied and found to provide a potential method of increasing the softening point whilst retaining or improving the degree of crystallinity for a given backbone chain. The rings are spread out from the main chain like the blades of a fan and because of conformational movements, provide an effectively thick pendant group which is likely to contact near neighbour atoms. Spirocycloalkyl poly α-esters in contrast to poly β -esters are amorphous, which is probably for two reasons. First, an odd-even effect, well known in aliphatic polyester systems, does not favour higher softening and crystalline properties for poly α-esters whereas it does for poly β-esters. Secondly as the cyclic substituent occurs more frequently per given length of polymer chain the required chain folding to provide crystalline regions is not allowed because of restricted bond movements and/or steric interaction.

The degree of crystallinity in poly α-esters governs, in part, the solubility of the material. Stronger intermolecular forces within crystalline regions make dissolution difficult and outside the range of most organic solvents.

8.2 Modification of Poly α -esters

Copolymerisation. The copolymerisability of HBAS and DEAS was bfiefly examined. Various comonomer ratios were prepared from stock solutions of HBAS and DEAS in nitrobenzene, and then polymerised in Carius tubes at reduced pressure. The polymers and a few of their properties are given in Table 24.

Table 24

Copolymers of HBAS and DEAS prepared in nitrobenzene at 90°. $[HBAS]_o + [DEAS]_o = 0.5$ mole litre^{-1}. Softening temperature (T_m) and decomposition aet in temperature (T_d) measured by D.T.A. (heating rate 5° min^{-1}; atmosphere nitrogen).

Code	Mole Ratio Initial		Relative consumption at time t. *		T_m °C	T_d °C	Remarks
	HBAS	DEAS	HBAS	DEAS			
A	1	-	1	-	185	315	crystalline
B	3	1	1	1	-	280	amorphous gum
C	30	1	10	1	165	290	crystalline
D	3	10	1	10	150	265	crystalline
E	1	10	1	30	165	235	crystalline
F	-	1	-	1	190	230	crystalline

* assessed assuming DEAS k_1 = 3HBAS k_1.

Evidence for genuine copolymer formation is given by thermal analysis. In Figure 30 D.T.A. and T.G.A. traces for copolymer D are compared with those for a physical mixture of homopolymers A and F.

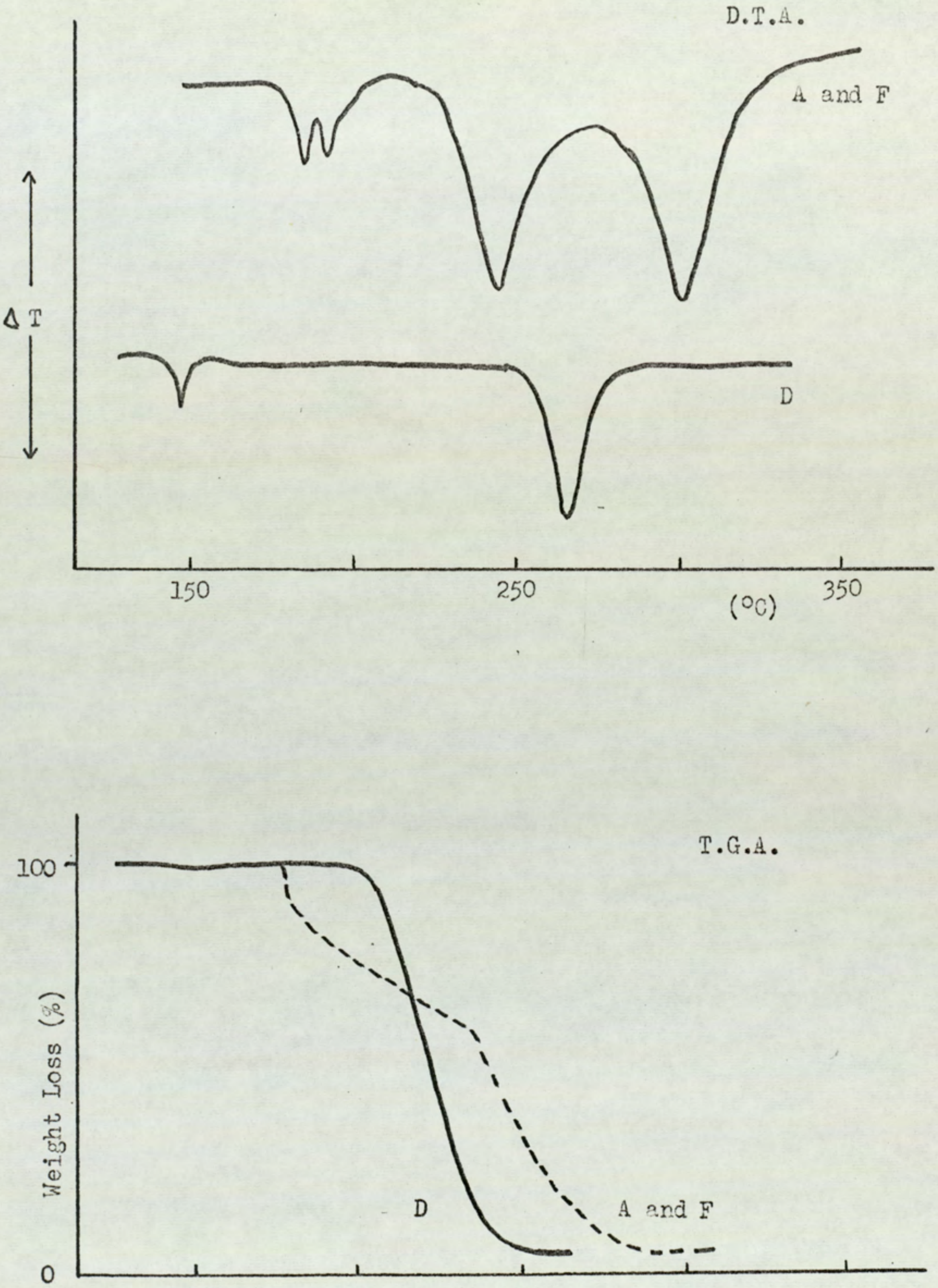


Figure 30. D.T.A. and T.G.A. traces for copolymer D and a physical mixture of homopolymers A and F (heating rate 5° min^{-1}; atmosphere nitrogen).

With the exception of copolymer B all the materials retained a degree of crystallinity as is demonstrated in the x-ray powder photographs given in Figure 31. This may indicate that poly HBAS and poly DEAS chains possess very similar conformations in their crystalline regions.

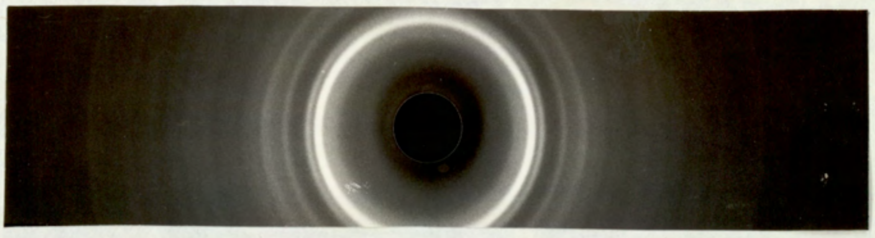
It is worth noting that incorporation of HBAS into DEAS homopolymers although reducing T_m is capable of elevating T_d by up to 35° (copolymer D) thereby widening the melt working range considerably.

Further studies are obviously required to determine whether these copolymers are block, random or alternating in kind. This will depend upon the relative reactivity of α-lactones with both types of polymer end group present.

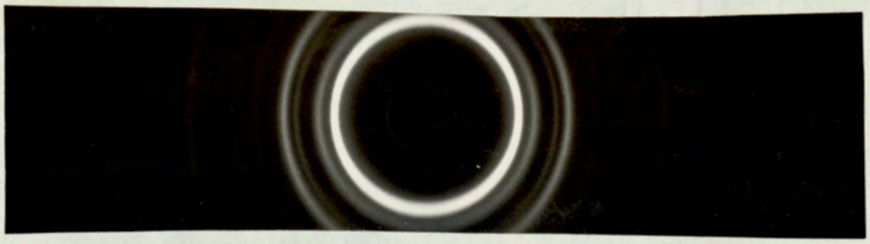
Chlorinated poly α-esters. Chloromethyl substitution is known to improve polymer properties. Penton, a commercial poly (2,2-bischloromethyl trimethylene oxide), illustrates this point since it has a T_m of 180° and is a flame, heat and chemical resistant material, which compares favourably with the equivalent dimethyl polymer, (T_m47°).

A monochloromethyl poly α-ester was successfully prepared from 5-chloromethyl-5-methyl-1,3,2-dioxathiolan-4-one-2-oxide by Rose[24]. On the other hand polymerisation of the bischloromethyl substituted anhydrosulphite is a slow process, gives low polymer and is accompanied by formation of considerable amounts of syn-dichloroacetone[71].

The majority of chlorinated polymers are derived from their parent chlorinated monomer, however, an alternative and potentially cheaper route is by chlorination of a hydrocarbon substituted polymer. A recent report[93] has claimed successful chlorination of several polyesters, particularly those that do not have hydrogen



Copolymer C



Copolymer D

Copolymer E

Figure 31. X-ray powder photographs of various copolymers derived from HBAS and DEAS.

atoms β - to the site of chlorination. In this way H Cl elimination, olefin formation and further degradation is prevented.

Since poly HBAS is structurally ideal for this treatment a preliminary investigation was carried out.

Chlorination of poly HBAS was achieved by passing chlorine gas through a mixture of partially dissolved polymer in chloroform, tetrachloroethane and water (1:2;4) for two hours at room temperature. The resultant polymer, which was precipitated with methanol had gained weight by an order of 70%. Elemental analysis showed the material to contain 52.8% chlorine, and although a fall in molecular weight was indicated, the polymer exhibited thermal stability which was superior to that of poly HBAS (T.G.A.; weight loss commences 360° levels out 450°).

An n.m.r. spectrum of a deuterated chloroform solution (Figure 32) was informative as regards the mode of chlorination. Clearly, random chlorination is indicated since signals due to $-CH_3$, $-CH_2Cl$ and $-CHCl_2$ are present in approximately equal abundance.

This method obviously has potential, since if high molecular weight poly HBAS is employed initially a drop in that of the final product could be tolerated. Variation of reaction conditions, addition of monitored amounts of chlorine and use of ultra-violet light may allow a more selective chlorination to occur.

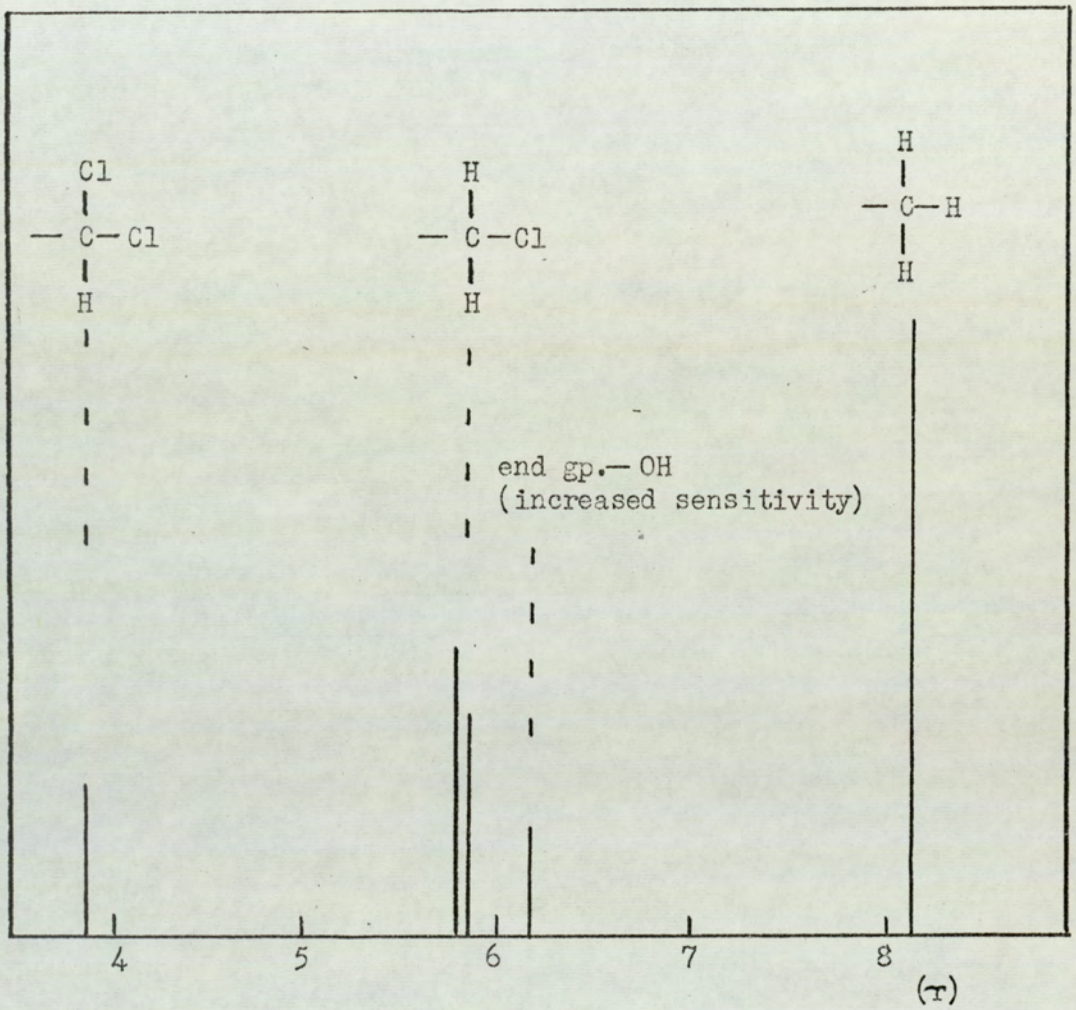


Figure 32. The n.m.r. spectrum of a chlorinated poly HBAS. Spectrum obtained as a deuterated chloroform solution (10% w/v), operating frequency 100 Mc/s.

9. CONCLUSIONS AND SUGGESTIONS FOR FURTHER WORK

9.1 Conclusions

The kinetics of anhydrosulphite polymerisation in the absence of initiators has been studied and applicability of the method as a general route to poly α-esters has been considered for a di-n-alkyl and spirocycloalkyl series.

Ease of monomer purification rather than polymerisability defines the useful limits of this polymerisation reaction. Although silver oxide treatment aids removal of chlorine containing by-products, subsequent fractional distillation is necessary to obtain monomer in the very high degree of purity required to give high polymer. As mass decomposition of C'butAS, C'heptAS and DBAS occurs at their distillation temperatures they were only obtained in a crude state and therefore until an efficient low temperature purification process is developed these compounds form the effective limits for the two series as far as high polymer forming reactions are concerned.

In general terms, the kinetics of thermal polymerisation followed a characteristic pattern for all the derivatives studied. The reactions are first order and of the thermal extrusion type previously suggested for HBAS[25]. Rate constants and kinetic parameters given within this text are therefore associated with monomer decomposition and not the chain growth process. At elevated temperatures (outside the range used for polymerisation) ketone formation competes with the normal polymer forming reaction.

C'butAS demonstrates several deviations from the general reaction pattern, this being a consequence of the geometry of the cyclobutane ring. Thus the derivative glycollide as well as polymer is a principal thermal decomposition product, and in addition a small but significant contribution of direct attack by polymer end groups on the anhydrosulphite ring takes place during propagation.

In contrast to the general uniformity of the reaction scheme the rate of thermal extrusion was found to vary considerably with change in substituent(s). In the dialkyl series an increase in steric and electron donating properties enhances the extrusion process although a limit is approached with diethyl and di-n-propyl substitution. The increase in rate which accompanies increase in substituent size presents a unique situation since in other ring-opening polymerisation reactions (for example NCA's) the opposite effect is observed. Conveyed ring strain, an additional feature, is introduced in the spirocycloalkyl series, the influence of which is most felt in the cases of C'butAS and C'heptAS. These two have decomposition rates well in excess of the limiting value found for the dialkyl series. These substituent effects are more pronounced in polar solvents because each is associated with producing electronic asymmetry across the anhydrosulphite ring.

The molecular weights of polymer obtained by thermal polymerisation are controlled by adventitious traces of water and α-chloroacid chloride impurity. As polymers discussed in this thesis were prepared on a small scale (approximately 0.01 M), transfer and purification losses were critical. As these factors are not so important in larger scale polymerisation it is considered that an improvement in apparatus design (particularly with respect to avoiding contact with air and moisture) would lead to polymers with higher molecular weight. In this way it is anticipated that molecular weights in the region of 40,000 could be obtained for poly-

DEAS, poly C'pentAS and poly C'hexAS.

The crystalline and thermal behaviour of a few poly α-esters has been examined. The highly polar backbone chain and the consequent strong interchain cohesion is responsible for the retention of a degree of crystallinity in some polymers which otherwise have unfavourable properties (such as steric bulk) for chain packing. Thermal degradation mechanisms associated with poly α-esters are simple and essentially primary processes, therefore thermal analysis techniques give valuable and unambiguous results. For this reason poly α-esters provide ideal model structures to study substituent and additive effects for more complex polyesters.

Anhydrosulphites readily copolymerise and provide a potential means of property modification of both poly α-ester and other polymer systems (for example those containing a terminal hydroxyl group). Chlorination of poly HBAS is a potentially attractive route to chlorinated poly α-esters.

9.2 Suggestions for Further Work

In order to expand the number of high molecular weight poly α - esters attainable three routes are open to investigation; low temperature anhydrosulphite purification, an alternative polymerisation route and ring-opening polymerisation of other but similar ring systems. The first of these must involve a kinetic and mechanistic study of the role of α -chloroacid chlorides during the thermal polymerisation reaction as well as an investigation of various chemical means for their removal. Claims of low temperature catalysed polymerisation of HBAS with tertiary bases[32] suggests that this may provide a competitive alternative route to poly α-esters, especially if monomer purity is not very critical. The obvious alternative precursor ring compound for polyα -ester is the anhydrocarboxy derivative of α -hydroxy acids, however in general at convenient workable temperatures they are thermally stable[29,30]. If aromatic substituent effects are parallel to those found in anhydrosulphite chemistry[57], however, decomposition rates may be enhanced to a suitable working level, thereby providing a source for aromatic substituted poly α-esters. Whilst these aromatic substituted polymers have potentially attractive properites, to date, they have only been obtained as oligomers[40,57,94]. Finally chlorination of attainable poly α-esters as a means of providing chlorinated polymers obviously warrants further investigation.

Monomers which might yield reasonable polymers using the techniques presently available, but which have not yet been prepared include, di-isopropyl, ethyl/hydrogen and propyl/hydrogen substituted derivatives. The first of these would give information regarding the effect of chain branching on the extrusion rate of monomer and crystallinity of polymer, whilst the remaining two are of interest because little change in order of either the first or second order propagation rates observed for LAAS (methyl/hydrogen) is to be expected. In addition as poly LAAS is crystalline and poly α-hydroxyisovalearate (isopropyl/hydrogen) is amorphous this property change must occur in either the ethyl or propyl derivative.

It is considered that the most friutful area for further work is in the field of copolymerisation. Although it is unlikely that homopoly α-esters will ever have extensive commercial application, monomeric, oligomeric or polymeric α-ester units may have useful modifying properties. In addition to copoly α-esters the following systems appear to be worth investigating.

A copolymer of α, α-dimethyl propiolactone and anhydrosulphite would be of interest because the homopolymer of the former exhibits very good work recovery[35] whilst those of the latter possess good tensile properties[92].

Block copolymers with butadiene may provide the requirement for a thermoplastic elastomer since it is probable that the polar polyα-ester and polybutadiene networks will be incompatible. As α, ω-dihydroxy polybutadienes (molecular weight approximately 4,000) are commercially available[95], the end groups of this polymer provide a site for anhydrosulphite propagation.

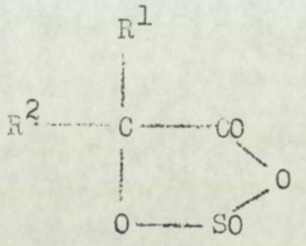
Inoue[96] has claimed successful copolymerisation of HBAS with certain olefins using radical catalysts systems. With acrylonitrile the polymers were shown to consist mainly of poly olefin grafted onto poly α-ester backbone. An alternative route to this type of polymer could be via anhydrosulphite monomer with unsaturation in the substituent (for example, cyclohexene spiro-5-1,3,2-dioxathiolan-4-one-2-oxide). Polymerisation or copolymerisation (with saturated anhydrosulphites) would give poly α-ester with a known site density for crosslinking or branching with polyolefin.

Polymers which have pendant nucleophilic groups (for example hydroxyl) possess suitable graft sites for poly α-esters. Thus poly vinyl alcohol and the cellulosics have ideal structure as have hydrogel polymers such as poly hydroxyethyl acrylate (Hydron; Smith and Nephew). The polymer obtained by controlled reduction of poly methyl methacrylate[97] (in the limit polymethallyl alcohol) provides an interesting material on which to graft anhydrosulphite, since by choice of reaction conditions the number of graft sites can be made available to specification.

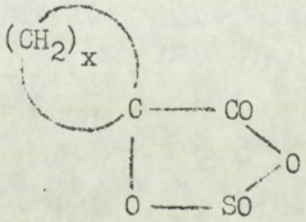
APPENDIX

Nomenclature

A major part of this thesis deals with the synthesis and polymerisation of compounds of the type (I) and (II).



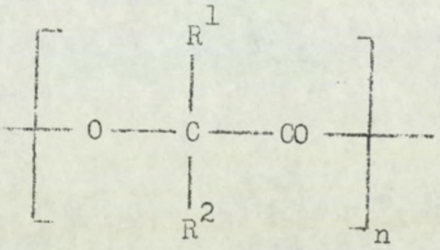
(I)



(II)

I.U.P.A.C. nomenclature[98] requires that the ring be called 1,3,2-dioxathiolan-4-one-2-oxide, but it is more commonly known as an α-hydroxy-carboxylic acid anhydrosulphite, the parent α-hydroxy acid being used as a prefix to identify individual members (e.g. lactic acid anhydrosulphite; R^1 = -H, R^2 = -Me). Trivial nomenclature becomes confusing for higher homologues and spiran systems (II), however, and the systematic nomenclature is to be preferred. Hence the anhydrosulphites derived from α-hydroxy-α-propyl pentanoic acid (I; $R^1 = R^2$ = -Pr) and cyclohexanol-l- carboxylic acid (II; x = 5) are referred to as 5,5-di-n-propyl-1,3,2-dioxathiolan-4-one-2-oxide and cyclohexane spiro-5-1,3,2-dioxathiolan-4-one-2-oxide respectively. A slight deviation from uniformity is necessary to describe the derivative of cyclobutanol-l-carboxylic acid(II, x = 3) since nomenclature requires that the larger ring is defined first in spiran compounds (i.e. 1,3,2-dioxathiolan-4-one-2-oxide-5-spirocyclobutane). To avoid lengthy repetition, each compound is a given an abbreviation which is clearly defined when an anhydrosulphite is introduced in the thesis.

It is common practice to refer to poly esters in terms of the systematic chemical names of the repeat unit (for example, polyethylene terephthalate and polytetramethylene adipate). Simple poly α-esters (III) have been known for some time and are often identified



$$\left[\; -O-\overset{R^1}{\underset{R^2}{C}}-CO- \;\right]_n \qquad \text{(III)}$$

in terms of the monomer or derivative acid (for example, polyglcollide or polyglycollic acid; III; $R^1 = R^2 = -H$). Higher homologues of this series however, do not have suitable euphonic names and the systematic I.U.P.A.C. nomenclature (for example, poly (isopropylidene carboxylate), III; $R^1 = R^2 = -Me$; and poly (3-pentylidene carboxylate), III; $R^1 = R^2 = Et$) is more explicit. The polymer chemistry division of the American Chemical Society[99] have recently suggested an alternative nomenclature for polyesters in which oxygen assumes seniority and which is particularly useful and brief for unambiguously defining spiran poly α-esters. Thus GAAS, DEAS and C'hexAS polymerise to give, poly (oxyacetyl), poly (oxy(diethylacetyl)) and poly (oxycyclohexanoyl). For the sake of brevity, throughout the text, poly α-esters are referred to by using the prefix poly- in front of the abbreviated form of the parent anhydrosulphite (for example, poly HBAS and poly C'heptAS).

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