PHENYL AND PENTAFLUOROPHENYL SUBSTITUTED 1,3-DIOXOLAN 2,4-DIONES

by

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To my Mother.

I thank my parents for their encouragement during the early part of my education and their understanding during the latter part.

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SUMMARY

A series of phenyl and pentafluorophenyl substituted 1,3-dioxolan 2,4-diones (α-hydroxy carboxylic acid anhydrocarboxylates) has been prepared by the reaction of phosgene with the copper(II) salt of the appropriate α-hydroxy carboxylic acid and the potential use of such cyclic compounds as precursors in the synthesis of poly-α-esters investigated.

The kinetic behaviour during thermal decomposition of this anhydrocarboxylate series in non-hydroxylic solvents has been studied with particular reference to polymer formation. The reactivity of the anhydrocarboxylates to weak nucleophiles such as alcohols may be adequately explained in terms of the steric and electronic effects associated with both the anhydrocarboxylate and the attacking nucleophile. The solvent in this bimolecular reaction with alcohols exerts a considerable effect on the rate of reaction.

The effect of a pentafluorophenyl substituent on the reactivity and polymerisability of the cyclic monomer has been investigated. The results indicate that the effect of a fluoroaromatic substituent, unlike many other polymerisations, is to increase the polymerisability of the monomer.

The use of tertiary (aprotic) base initiators such as pyridine offers a low temperature synthetic route to poly-α-esters. The ease of polymerisation by this hitherto unexplored method is determined primarily by the size of the substituents on the monomer

and the extent to which those substituents may activate the ring to nucleophilic attack. The unusual kinetic behaviour exhibited by this type of reaction is explained in terms of the initial formation of a charge-transfer complex between monomer and initiator and subsequent decomposition to yield a polymerisable species.

A number of substituted poly-α-esters have been prepared, including the two optically active forms of the polymer in one case, and some physical properties briefly examined. The primary object of the work, however, was the elucidation of polymerisation mechanisms rather than the preparation of high molecular weight polymer.

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CHAPTER 1

1.1 Introduction

The study of polymeric compounds has during the last half century not only enabled many useful synthetic materials to become a direct benefit to society and act as a means of conserving natural resources but has also developed into a very interesting science in its own right. Numerous polymers are now marketed and these, with the exception of polytetrafluoroethylene and polyvinyl chloride and a handful of others, are exclusively hydrocarbon based.

The introduction of fluorine onto the polyethylene chain to produce polytetrafluoroethylene results in remarkedly improved thermal stability and extreme resistance to organic solvents. In addition the physical properties such as low solubility and coefficient of friction for this synthetic polymer are quite outstanding and the practical applications of polytetrafluoroethylene require no further discussion. The potential of highly fluorinated polymers was no doubt recognised by the unusual physical and chemical properties associated with highly fluorinated organic compounds and as a result considerable research has been expended in the development of fluorine-containing polymers. Recent work in this field has been reviewed by McLoughlin and Thrower,(1) Barson and Patrick,(2) and more extensively in a review edited by Wall.(3)

As a result of the extensive work on fluoroaliphatic polymers a number of commercially useful products have emerged. Polytetrafluoroethylene is probably the most important. The monomer, tetrafluoroethylene, is prepared commercially by the pyrolysis of chlorodifluoromethane using an alumina catalyst. Polymerisation is a strongly exothermic reaction and the monomer undergoes spontaneous photo-initiation when stored in glass containers in sunlight. Variations on copolymers of tetrafluoroethylene, chlorotrifluoroethylene, hexafluoropropylene and vinyl fluoride enable polymers to be manufactured whose properties for specific applications are superior to the homopolymers. The copolymerisation of tetrafluoroethylene and chlorotrifluoroethylene using Ziegler catalysts has produced polymers with a high degree of stereoregularity.

Acrylic acid may be grafted onto polytetrafluoroethylene to produce semipermeable membranes and recently developed electrochemical techniques enable the polymer to be plated with copper. Because of its high thermal and chemical stability coupled with a low coefficient of friction polytetrafluoroethylene is now used extensively for lining cooking utensils. Low molecular weight polymer has been used in the preparation of high-temperature lubricating greases and adhesives.

Whilst the chemical and physical properties of polyethylene and its commercial value are beyond question, this brief outline serves to demonstrate the great versatility of fluorine-substituted and perfluoro-substituted polymers of the type exemplified by polytetrafluoroethylene. Consequently, the field of fluorine-containing aliphatic polymers has been extensively and systematically studied. However, by comparison relatively little work has been carried out on systems containing perfluoroaromatic residues.

The latter polymers fall conveniently into two classes, the first in which the fluoroaromatic substituent is pendant to the main chain and secondly when the main chain is composed of fluoroaromatic units which are usually linked by bridging groups. Hydrocarbon polymers of the latter type show exceptional chemical and thermal stability, and it is not surprising that their fluorinated analogues have received comparatively more attention than pentafluorophenyl substituted polymers; they will, therefore, be considered first.

Relatively low molecular weights, ca. 1500, have been obtained in the synthesis of p-polyperfluorophenylenes, by heating para-dihalotetrafluorobenzene at 220°C with activated copper powder.(4) Somewhat higher molecular weights have been obtained by refluxing solutions of pentafluorophenylmagnesium bromide in tetrahydrofuran.(5) Pentafluorophenylmagnesium chloride spontaneously polymerises(6) in the same solvent at room temperature producing perfluorophenylenes of comparable molecular weight but containing residual amounts of chlorine. The thermal stability of p-polyperfluorophenylenes is comparable with the hydrocarbon analogue, but p-polyphenylene shows markedly better resistance to oxidation at temperatures up to 500°C.(7)

In order to incorporate some degree of flexibility into the rigid polyperfluorophenylene structure, various heteroatoms have been included in the chain as bridging groups. The incorporation of an oxygen atom between successive aromatic units produces polyperfluorophenylene ethers. A polymer of this type has been prepared by the reaction of potassium pentafluorophenoxide in excess pentafluorophenol; molecular weights of 1500-2000 were obtained. Successive melt polymerisations of the potassium salt of this low molecular weight polymer(8) enabled molecular weights of 12,500 to be achieved. Cross-linking of this latter polymer occurs by heating at 260°C for 18 hours, which finally produces a hard, brittle, insoluble glass which softens at 90°C and shows elastomeric characteristics up to 300°C. It is interesting to note that as the molecular weight increases, the polymer ranges from a soluble gum at room temperature, exhibiting rubbery behaviour from 40° to 70°C, to an insoluble cross-linked polymer with a higher softening temperature. The corresponding non-fluorinated aromatic model compound is considerably more thermally stable than the fluorinated analogue, and it would appear that in spite of the low molecular weights of the fluorinated polymer the introduction of fluorine results in a reduction in thermal stability but somewhat improved chemical stability. It has been suggested(1) that decomposition occurs at the C-O bond, which is lengthened and weakened by steric effects of ortho fluorine substituents.

Polyperfluorophenylenes linked by $-OCH_2-$ and -S- show very similar properties to their hydrocarbon counterparts(1) and in neither case do the ortho fluorines interfere with the bridging units.

The results of the investigation of polymers with tetrafluorophenylene units in the main chain have in general been disappointing even when allowance is made for the fact that high molecular weights are difficult to obtain. It is surprising, therefore, in view of the fact that poly(2,3,4,5,6-pentafluorostyrene), which possesses a pentafluorophenyl group pendant to the main chain, shows appreciably better thermal stability, oxidation resistance and U.V. resistance than does polystyrene,(9) that more systematic work has not been carried out on polymers containing pendant perfluoroaromatic groups.

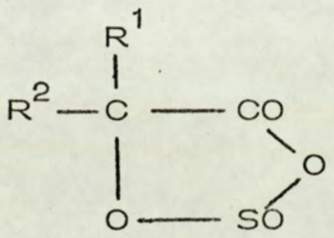
2,3,4,5,6-Pentafluorostyrene polymerises thermally at 60°C but at a somewhat slower rate than styrene. Anionic initiators have been used for other substituted 2,3,4,5,6-pentafluorostyrenes and U.V. radiation(10) has been found to initiate polymerisation. Poly-(2,3,4,5,6-pentafluorostyrene) is soluble in acetone and methyl ethyl ketone from which transparent flexible films have been cast.(1) The resistance of this polymer to γ-irradiation is comparable to polystyrene and is in marked constrast to fluoroaliphatic polymers in which degradation occurs much more readily.(1)

An interesting polymer structure which offers potential modifications with respect to the incorporation of fluorinated residues, is that possessing ester linkages. Little work has been carried out on the synthesis of fluorine-containing polyesters but initial reports demonstrate that the results obtained so far are encouraging.(12)

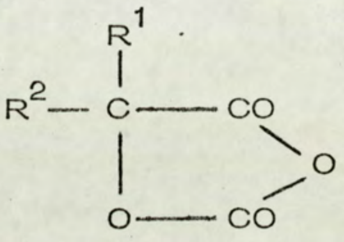
A rubber useful over the temperature range -50 to +150°C may be obtained by heating poly(hexafluoropentamethylene adipate) with peroxides.(11) Improved thermal stability in fluorine-containing polyesters as exemplified by poly(hexafluoropentamethylene oxybis-benzoate), which has a decomposition temperature in excess of 500°C, is expected; the reasons have been summarised by Trischler and Hollander.(12)

Probably the main reason for the limited number of synthetic routes is due to the instability of perfluorodiols and perfluorodicarboxylic acids.

Tighe et al$^{(13)}$ have reviewed a potential route to poly-α-esters containing fluorinated substituents via anhydrosulphites (I) derived from α-hydroxy carboxylic acids. A more general route to alkyl and spirocycloalkyl substituted poly-α-esters has been achieved by the same workers.$^{(14)-(18)}$ Results with phenyl substituted anhydrosulphites, however, have been poor.$^{(19)}$



(I)



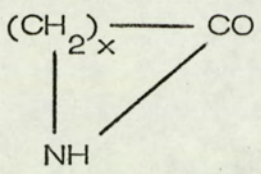
(II)

The work presented herein is concerned with the synthesis and polymerisation of anhydrocarboxylates (II) derived from α-hydroxy carboxylic acids containing aromatic and fluoroaromatic substituents. Polymerisation of the analogous anhydrosulphite occurs by the loss of sulphur dioxide and is essentially a ring-opening reaction.

Ring-opening polymerisation is a mode of polymer formation which offers distinct advantages over conventional addition and condensation polymerisations. In many ways this polymerisation may be classed as a condensation reaction since the polymer formed has the structural features of a condensation polymer. By way of contrast the polymer in a number of cases has the same composition as the monomer and the polymerisation takes place by a chain mechanism. In addition polymerisation, the monomer requires an active site and must be able to replicate the propagating species. Unfavourable equilibrium reactions between monomer, eliminated units and polymer are often encountered in condensation polymerisation and thus ring-opening polymerisation may be considered as combining the advantages of an addition type mechanism in the formation of a heterochain polymer.

A recent review(20) covers many aspects of ring-opening polymerisation. This mode of polymerisation may be conveniently divided into two types; firstly, when polymerisation results in the incorporation of all the elements included in the cyclic monomer and secondly when some elements are lost during polymerisation. The polymerisation of caprolactam resulting in the formation of a polyamide is an example of the former type, and the great industrial importance of this reaction emphasises that considerably more work has been carried out on this mode of polymerisation than on the latter. The monomer, caprolactam, may be polymerised by both anionic(20) and cationic(21) reactions although the mechanism of the latter has not been fully elucidated. The polymerisation of caprolactam in the presence of traces of water has been extensively studied by many workers but has the disadvantage of unfavourable equilibria.(22)

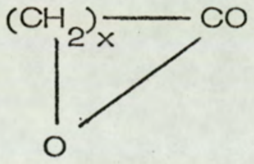
Factors affecting the polymerisability of these type of monomers include, ring size and ring strain, the size and number of substituents, and the polarity of the substituents. Carothers(23) has extensively studied the polymerisability of cyclic esters, although direct comparison of the different systems is difficult. Cyclic amides of general formula (III) vary considerably with respect to polymerisability as the size of the ring increases. The 5-membered lactam ring polymerises easily at low temperatures by an anionic mechanism but in contrast



(III)

no satisfactory method of polymerisation is available for the 6-membered ring. ϵ-caprolactam, having five methylene units in the ring, readily polymerises to give Nylon 6. Ring structures possessing in excess of six methylene units are fairly easily polymerised. Both aryl and alkyl substituents on the ring system diminish polymerisability.

The structure of lactones (IV) is analogous to cyclic amides and yet presents several fundamental differences in polymerisability of cyclic monomers. Correlations between polymerisability and ring strain in cyclic esters have not been totally successful. Whilst it may be argued that ring strain due to bond-angle distortion in three and four membered rings and ring strain due to bond opposition



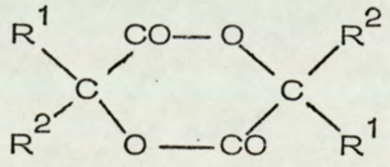
(IV)

forces in rings with seven or more units, would explain the polymerisability of these lactones, the argument would tend to suggest that the inadequacy of γ-butyrolactone to take part in a polymer forming reaction was due to the lack of ring strain within the molecule, but the infra red spectrum of γ-butyrolactone confirms a strained ring system.

It is interesting to note that the 6-membered lactone ring polymerises quite readily whereas the corresponding 6-membered lactam does not polymerise. Small(24) has suggested that the change in free energy for the hypothetical polymerisation of 5-membered lactones is at a maximum for this class of monomer, whilst in the case of lactams, the maximum occurs with the 6-membered ring.

The polarity of substituents on the ring has a considerable effect on the polymerisability of the ring. For example, the 4-membered β-propiolactone ring polymerises very rapidly and exothermically, whereas α,α-bischloromethyl propiolactone does not polymerise with such ease. The effect of electron withdrawing substituents is to stabilise the ring to polymerisation.

The 3-membered α-lactone ring does not result from the dehydration of glycollic acid; the dimeric six-membered cyclic ester (V; $R^1 = R^2 = H$), however is formed. The dimer formed from glycollic acid is known as glycollide and polymerises by the action of heat. The lactide obtained from lactic acid

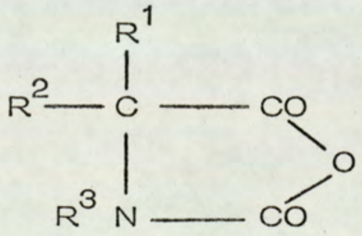


(V)

also polymerises smoothly as does the substituted glycollide derived from α-hydroxy butyric acid, but with formation of some non-polymeric products. Hall and Schneider(25) have reported that tetramethylglycollide is resistent to polymerisation. The size and number of substituents on the 6-membered cyclic dimer ester have a profound effect on the polymerisability of the ring.

General qualitative observations on the polymerisability of cyclic esters have been put forward by Hall and Schneider(25) and they suggest that four, seven and eight membered rings polymerise in all cases and that alkyl and aryl substituents on a ring always decrease polymerisability. They state that the polymerisability of five and six membered carbonyl containing cyclic monomers depends to a very great extent on the class of compound.

In contrast to the general qualitative observations of the effect of ring size and structure, and the effect of substituents on the polymerisability of lactams and lactones, ring-opening polymerisation of anhydrocarboxy derivatives of α-amino carboxylic acids (VI; N.C.A.), which results in the loss of some elements of the monomer ring, namely carbon dioxide, has been studied quantitatively and a more complete and sophisticated understanding of the effect of ring substituents has been achieved. The structural similarity of N.C.A.'s to anhydrocarboxy derivatives of α-hydroxy carboxylic acids necessitates a more detailed discussion of the modes of polymerisation of these monomers.



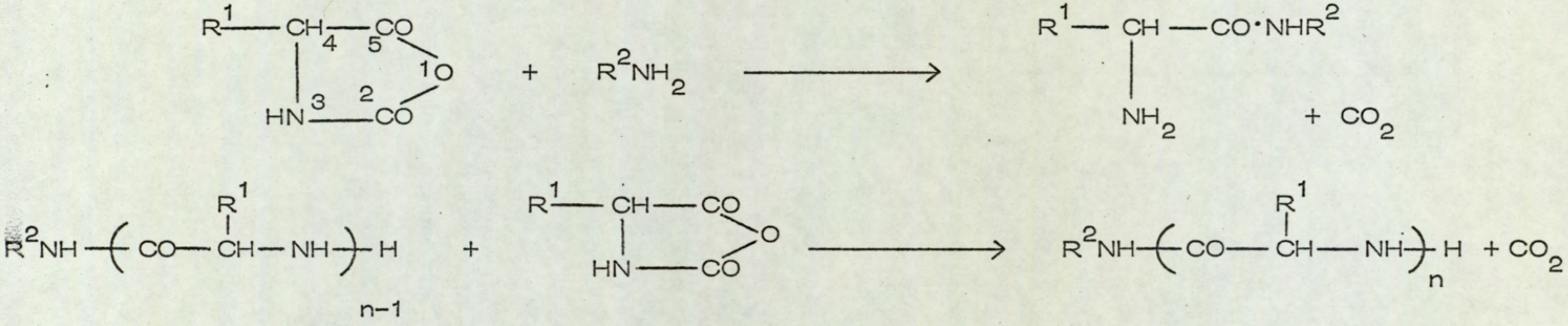
(VI)

The ability of N.C.A.'s to polymerise yielding polyamino acids, which are useful models of protein molecules and a potential route to synthetic silks, undoubtedly stimulated much interest in the synthesis and polymerisation of N.C.A.'s. A comprehensive discussion of N.C.A. polymerisation has been produced by Bamford(26) and more recently in a general review by Shalitin.(20)

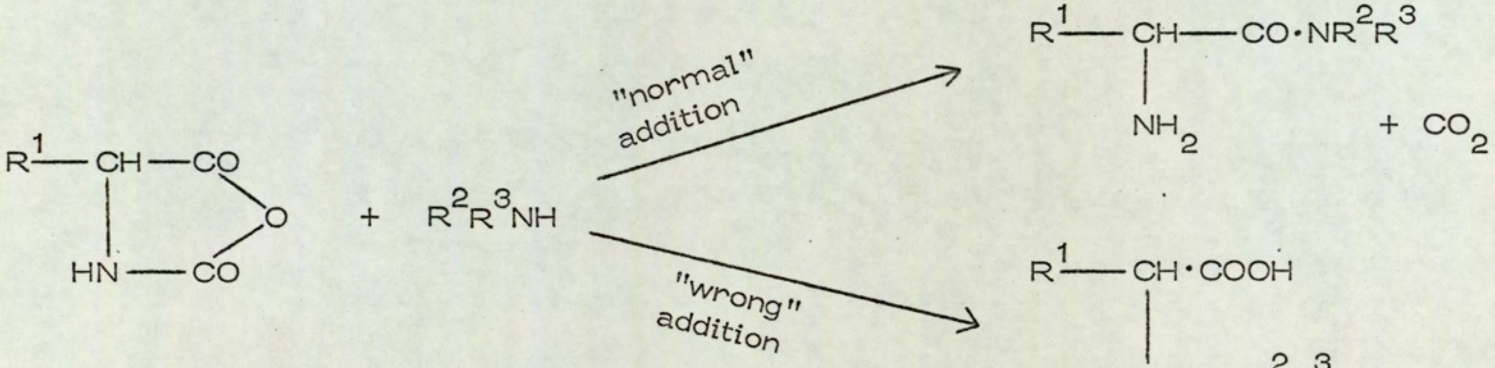
The predominant feature of this mode of polymerisation is that the chain growth process is irreversible and not subject to the limiting equilibria which are normally experienced with conventional condensation polymerisation.

The action of heat on the N.C.A.'s results in the formation of polymer. Rigorous exclusion of moisture in the preparation of the monomer still results in a bulk polymerisation, and it has, therefore, been suggested that the reaction is not catalysed by traces of water. It has been reported, however, that thermal polymerisation occurs via the open chain isomer of the N.C.A., the isocyanate,(27),(28) and polymerisation occurs by intermolecular interaction of the isocyanate with carboxylic groups. Substoichiometric amounts of primary or secondary amines serve to initiate polymerisation of the N.C.A. by direct attack of this nucleophile at the C (5) carbonyl as shown in scheme 1. Loss of carbon dioxide from this intermediate structure results in the formation of an α-amino acid amide. The propagation step involves the direct and continued attack of this regenerated amino group at the C(5) carbonyl of the monomer. The effect of substituents both on the N.C.A. and the initiator amine has been investigated in detail by Ballard and Bamford.(29) They concluded that the effect of a small substituent on the ring nitrogen has relatively little effect on the rate of polymerisation whereas the introduction of a second substituent at the C(4) carbon sterically

Scheme 1



Scheme 2



hinders the reaction pathway of the propagating nucleophile. This polymerisation is referred to as the "normal" amine addition. Trace amounts of water revert the N.C.A. to the parent α-amino acid and this so-formed amine group may also act as the propagating species and serve to initiate polymerisation. "Wrong" addition can occur at the C(2) carbonyl as shown in scheme 2 resulting in the formation of ureido acids. Glycine and phenylalanine show a tendency to form high yields of ureido acids with sterically hindered amines such as diethyl and tertiary butyl amines.(30)

Other polymerisation mechanisms of N.C.A.'s involve the use of tertiary amines, strong bases and metal salts. The latter involves the abstraction of the nitrogen proton by the base ion and subsequent anionic attack by the ring nitrogen on a second N.C.A. molecule. The polymer so formed is bifunctional and potentially capable of propagating from both ends and probably accounts for D.P. values in excess of the monomer to initiator ratio.

Different kinetic behaviour has been observed for initiation by strong bases and various mechanisms have been put forward. The most successful postulates are those by Idelson and Blout(31) and Szwarc's modification of the original mechanism put forward by Bamford and Block.(32)

The polymerisation of anhydrosulphites of α-hydroxy carboxylic acids (I) presents another interesting polymerisation resulting in the loss of some elements of the monomer ring system. Blaise and Montagne(33) first described methods of synthesis of anhydrosulphites derived from lactic and α-hydroxyisobutyric acids where $R^1 = CH_3$, $R^2 = H$ (I); and $R^1 = R^2 = CH_3$ (I) respectively. Alderson(34) reported molecular weights in the region of 100,000 from the thermal decomposition of α-hydroxyisobutyric anhydrosulphite (H.B.A.S.) in non-hydroxylic solvents. The ease with which H.B.A.S. polymerises is in direct contrast to the corresponding N.C.A. of α-amino isobutyric acid, which is resistant to polymerisation due to the repulsion between the methyl groups on the attacking chain end and the methyl substituents on the C(4) carbon.(29)

More recently extensive work has been carried out on synthesis(35) and polymerisation of other disubstituted(16)(17) and spirocycloalkyl(18)(36) substituted anhydrosulphites. A reaction mechanism has been put forward to account for the rapid formation of high molecular weight polymer by H.B.A.S.(37) and related anhydrosulphites. It is essentially a thermal extrusion reaction resulting in the elimination of sulphur dioxide to form a highly reactive α-lactone intermediate, which takes part in a rapid propagation step by reaction with the chain end hydroxyl group. A competitive polymerisation mechanism has been postulated which involves direct attack of the chain end hydroxyl group at the C(4) carbon. The latter mechanism has been shown to be insignificant in all cases except where at least one of the substituents at C(5) is a hydrogen.(38)

As the size of substituents on the anhydrosulphite ring increases, the rate of polymerisation increases. The limit to the use of anhydrosulphites as a means of preparing poly-α-esters appears to be in the successful purification of the monomer rather than the polymerisability of the anhydrosulphite. The molecular weight of the resultant polymer is determined principally by the monomer to impurity ratio. Parent acid impurity, which is formed by reaction of the anhydrosulphite with adventitious traces of moisture, limits the molecular weight which can be achieved as the concentration of hydroxyl groups essentially determines the number of active polymer chains taking part in the propagating reaction.

With large substituents such as phenyl groups, a secondary fragmentation process becomes appreciable. The combined presence of a phenyl and a hydrogen substituent results in a low yield of polymer and benzaldehyde as the principal fragmentation product. It has been stated(39) that any attempt to use mandelic acid anhydrosulphite (I, $R^1 = C_6H_5$; $R^2 = H$,) as an intermediate in the formation of the corresponding poly-α-ester must depend essentially upon a catalysed or initiated decomposition rather than the thermal decomposition route.

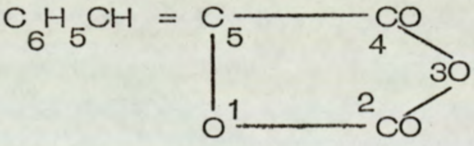
Initiated decomposition of anhydrosulphites has been reported(40) using such initiators as triethylamine, dimethylformamide and pyridine. Organometallic catalysts such as sodium methoxide, lithium butyl and zinc diethyl/water are also reported to polymerise anhydrosulphites. Yields of polymer are simply quoted as methanol insoluble fractions of the reaction mixture. The asymmetric selective polymerisation of α-hydroxy chloroisobutyric acid anhydrosulphite is claimed using the optically active tertiary amine brucine. This will be discussed in more detail in a subsequent chapter.

The anhydrocarboxy derivatives of α-hydroxy carboxylic acids have received remarkedly little attention in spite of the extensive studies on N.C.A.'s and the thermal polymerisation of anhydrosulphites.

Davies(41) first reported the synthesis of anhydrocarboxylates derived from glycollic, lactic and mandelic acids. Glycollic acid anhydrocarboxylate was reported to give the corresponding polymer on heating, while lactic acid anhydrocarboxylate remained largely unchanged. All anhydrocarboxylates were reported to react rapidly with water and amines with the evolution of carbon dioxide and the formation of limited amounts of oligomeric products.

Somewhat far removed from the use as a poly-α-ester precursor, lactic acid anhydrocarboxylate (II; $R^1 = H$, $R^2 = CH_3$) has been used in a dry beverage composition to act as an effervescing agent on mixing with water.(42)

5-Benzylidene 1,3-dioxolan 2,4-dione (VII) has been prepared(43) from phenyl pyruvic acid as a precursor to phenylpyruvoyl derivatives of peptides and amino acids. The authors report that the anhydrocarboxylate reacts with alcohols and amines without loss of



(VII)

carbon dioxide, principally by attack at the C(2) carbonyl to form α-(alkoxycarbonyloxy) cinnamic acids, whilst reaction with aniline results in the formation of the corresponding secondary amine derivative. The only reaction reported which resulted in the loss of carbon dioxide was that with the triethylamine salt of acetic acid; the enol acetate of phenyl pyruvic acid was formed.

The potential use of anhydrocarboxylates as precursors to poly-α-esters as typified by 5,5-dimethyl 1,3-dioxolan 2,4-dione has been discussed by Tighe.(44) The principal products of thermal decomposition were found to be carbon dioxide and isopropylidene carboxylate oligomers. Reaction with amines produced the corresponding amide by attack at the C(4) carbonyl and loss of carbon dioxide whereas decomposition in alcohols, although no increase in rate over non-hydroxylic solvents was observed, produced the corresponding α-hydroxy isobutyrate. Initiators such as lithium chloride, sodium methoxide and benzoyl peroxide produced little increase in the rate of decomposition. Strong Lewis acids were reported to accelerate the decomposition but did not yield polymer.

Although glycollic acid anhydrocarboxylate was reported to yield polymer by the action of heat,(41) the full potential of anhydrocarboxylates in the synthesis of poly-α-esters has remained dormant for two decades.

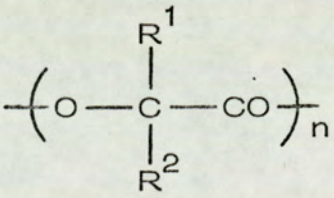
The use of polyesters as commercially viable synthetics has continually expanded since their formation became industrially feasible. The number of polyester compounds is far in excess of the number which have achieved commercial recognition. Probably the most important of these is poly(ethylene terephthalate) which typifies many physical properties of polyesters, although the chemical behaviour is characteristic of the constituents and structural features of the polymer rather than of the macromolecular state.

Polyesters are excellent fibre forming polymers and are resistent to many organic solvents and reagents, and as a textile fabric possess the inherent property of indifference to micro-organisms. In general they are resistant to oxidation and degradation by light.

The same combination of properties enables oriented films to be made which are becoming important for specialised applications such as electrical insulators for coils and transformers. Linear aliphatic polyesters have been used to obtain elastomeric fibres and plasticisers.(45)

Poly-α-esters have not been used extensively as commercial materials but are now becoming more important for specific uses. They are potentially useful in the field of surface coatings and have been processed into useful films and fibres. Poly(glycollic acid) and poly(lactic acid) have received notable attention in the field of absorbable surgical sutures.(46)

The synthesis of poly-α-esters with aromatic and fluoroaromatic substituents should result in a series of polymers whose physical and chemical properties differ markedly from polymers of simpler construction. The somewhat polar poly-α-ester backbone consisting of repeated ester linkages (VIII)offers a unique conformation of the chain



$$\left(O - \overset{R^1}{\underset{R^2}{C}} - CO \right)_n$$

(VIII)

when R^1 and R^2 differ substantially in size. The presence of electron withdrawing substituents such as phenyl and pentafluorophenyl groups is likely to enhance the polarity of the ester carbonyl and result in not only a coiled polymer chain, but also an increase in interchain adhesion.

Although poly(benzilic acid) (VIII, $R^1 = R^2 = C_6H_5$,) has been prepared by heating the sodium salt of α-chlorobenzilic acid,(47) yields are reported to be poor and molecular weights low and to date no satisfactory method of synthesis of such aromatic substituted poly-α-esters has been reported.

1.2 Scope and object of the present work

Anhydrocarboxylates have not been studied in as great detail as the analogous anhydrosulphites. Attempts to increase the series of polymerisable anhydrosulphites to include phenyl and pentafluorophenyl substituents and examine the thermal extrusion reaction yielding the α-lactone and subsequently polymer, has met with considerable difficulty.

The synthesis of pentafluorophenyl substituted anhydrosulphites produced a brown viscous oil which undoubtedly contained an appreciable amount of the desired product. The limitation of such anhydrosulphites lies in the thermal instability of the ring and in obtaining a successful low temperature, rapid purification technique. Anhydrocarboxylates possess the superficial property of being readily crystallisable solids. It was hoped that such a ring system containing the aforesaid substituents may have a favourable combination of thermal stability and electronic factors to enable poly-α-esters of the type described to be prepared.

The work presented in this thesis is primarily concerned with the synthesis of anhydrocarboxylates and an investigation of structure/reactivity relationships within the monomer molecule. Thermal polymerisation of these compounds is undesirable as a means of polymer synthesis, as long reaction times and high temperatures are required and the latter tends to result in an increased proportion of a secondary fragmentation process which is not polymer forming. A more desirable mode of polymerisation involves the use of initiators but requires special properties with regard to an active site in the monomer. A quantitative kinetic assessment of such required activity is essential in order to formulate possible initiated reactions. Low temperature polymerisations favour polymer chains possessing a high degree of tacticity. The formation of optically active polymers from optically active monomers, where R^1 and R^2 (VIII)are different may result in highly orientated chains.

A general synthetic route to phenyl and pentafluorophenyl substituted poly-α-esters will enable the effect of such substituents on the properties of the polymer to be ascertained.

It is hoped that the contents of this thesis will improve the present knowledge of ring opening reactions resulting in polymer formation and lay the foundations for a more generalised synthesis of phenyl, pentafluorophenyl and possibly perfluoroalkyl substituted poly-α-esters.

CHAPTER 2

Experimental Methods

Various instrumental techniques were employed for the characterisation of anhydrocarboxylates and monitoring the progressive synthetic steps from α-hydroxy acid to the copper (II) salt and finally the cyclic anhydrocarboxylate. Solvents and reagents required a particular degree of purity with regard to their anhydrous state and to the exclusion of trace quantities of more reactive species. The rates of decomposition and of polymer formation were measured by a number of methods including the rates of evolution of carbon dioxide and the appearance of an ester carbonyl absorption for the polymer in the infra red spectrum.

2.1 Instrumental Techniques

Infrared spectra.- A general purpose Perkin-Elmer Infrared grating spectrophotometer Model 457 was used to record spectra. All spectra unless otherwise stated were recorded with the sample in the form of a kBr disc. The reference cell used with all kBr samples was air.

Nuclear Magnetic Resonance Spectra.- Proton resonance spectra in the majority of cases were recorded using a Perkin-Elmer R14 spectrometer operating at 100 MHz and of ambient temperature 33.4°C. In some cases a Perkin-Elmer R10 spectrometer operating at 56.5 MHz was used. Fluorine resonance spectra were recorded on the latter instrument. An internal reference of tetramethylsilane was used for recording proton resonance spectra and deuterochloroform was found to be an ideal solvent. Details of solvents and concentrations are given with specific examples in the text.

Ultraviolet spectra.- A Perkin-Elmer 137 UV spectrophotometer was employed. All spectra were recorded using diethyl ether as a solvent. The 'MAR' grade of solvent was used as it possessed the required level of water content ($< 0.008\%$). The instrument used has the facility for a solvent blank which was employed throughout.

Mass spectrometry.- An AEI MS9 instrument was used for recording mass spectra. The instrument produces three spectra whose sensitivity varies in increments of ten enabling an accurate mass spectrum analysis to be made if desired.

Gas liquid Chromatography.- Traces were obtained using a Pye Gas Chromatograph Series 104 Katharometer. An E30 column consisting of silicone gum on firebrick was used and the carrier was helium.

Carbon/Hydrogen Analysis.- The instrument used was a Hewlett and Packard, F & M Scientific 185 Carbon, Hydrogen, Nitrogen Analyser. The operating furnace temperature was 1100°C.

Thermogravimetric Analysis (T.G.A.) and Differential Thermal Analysis (D.T.A.).- were carried out on a Du Pont Thermogravimetric Analyser 950 and a Du Pont Differential Thermal Analyser 900 respectively. The heating rates for various traces are given in the text. The analyses were carried out under an atmosphere of nitrogen.

Determination of Chlorine containing impurity.- The method employed was a modification of Ingram's(48) technique which enabled the concentration of ionisable chlorine to be determined potentiometrically.

Approximately 0.2 g. of material was weighed accurately and about 50 mls of a 3:1 (v/v) mixture of water/acetone added. A few drops of dilute nitric acid were added and the mixture heated to 65°C for two minutes and then allowed to cool to room temperature. The solution was titrated potentiometrically with standard 0.002M silver nitrate and the end point determined by graphical inspection.

An E.I.L. Model 23A pH meter was used with silver/silver, silver nitrate electrode system. The predominant chlorine containing impurity in the synthesis of anhydrocarboxylates is the α-chloro acid chloride. It has been shown(49) that the technique described determines both the alkyl and acyl chlorines present.

X-Ray Photographic Analysis.- X-Ray powder photographs were taken using a Phillips 11.46 cm diameter powder camera fitted with a 0.5 mm collimator. The samples were mounted in lithium beryllium borate tubes and the X-rays generated from a copper target at 40 kv using a nickel filter enabling only copper K_α radiation to be used. The film was processed after a one and a half hours exposure.

Dry Box Manipulations.- The manipulation of anhydrocarboxylates and dry solvents requires the use of a substantially dry atmosphere. This was achieved by the use of a Gallenkamp Model MA950 glove box. Atmospheric moisture was removed from the main chamber and entry chamber by circulating the air through two glass spirals immersed in a solid carbon dioxide/acetone cold trap, this was effected by the use of a circulation pump. In addition, to ensure that the glove box was always in a dry state evaporating dishes containing fresh phosphorus pentoxide were kept in both the main chamber and entry chamber. This enabled the glove box to be used for storing sealed containers of anhydrocarboxylate in a dry atmosphere.

2.2 Techniques of Kinetic Measurements

The decomposition of anhydrocarboxylates involves the loss of carbon dioxide. The rate of decomposition may, therefore, be empirically followed by recording the pressure of the evolved gas with time. A relationship between pressure of the gas and the concentration of monomer at any instant in time is derived in a later section.

The carbonyl absorption of the anhydrocarboxylate differs sufficiently from the ester carbonyl absorption of the polymer that the use of an infrared technique enables the concentration of monomer and of polymer to be followed simultaneously.

Gas Evolution Analysis

(i) Apparatus and cleaning procedure.- Two types of apparatus were used for following the rate of increase in pressure with time. Fig 2.1 and 2.2 show the types of apparatus employed. The apparatus shown in Fig 2.1 is a modification of the apparatus used by Ballard and Bamford.(50) This type of apparatus enabled the spiral section (A) minus the manometer to be dried in an oven prior to use, and then transferred to a dry box where the reactant solutions could be added. This type of apparatus was used for reactions involving an initiator which was placed in a small glass bucket hooked onto the stopper (B). After careful evacuation of the air from the joined spiral and manometer sections, the apparatus was isolated under reduced pressure by means of the tap on the vacuum line connecting tube (C). The apparatus was placed in a suitably thermostatted oil bath, Towson

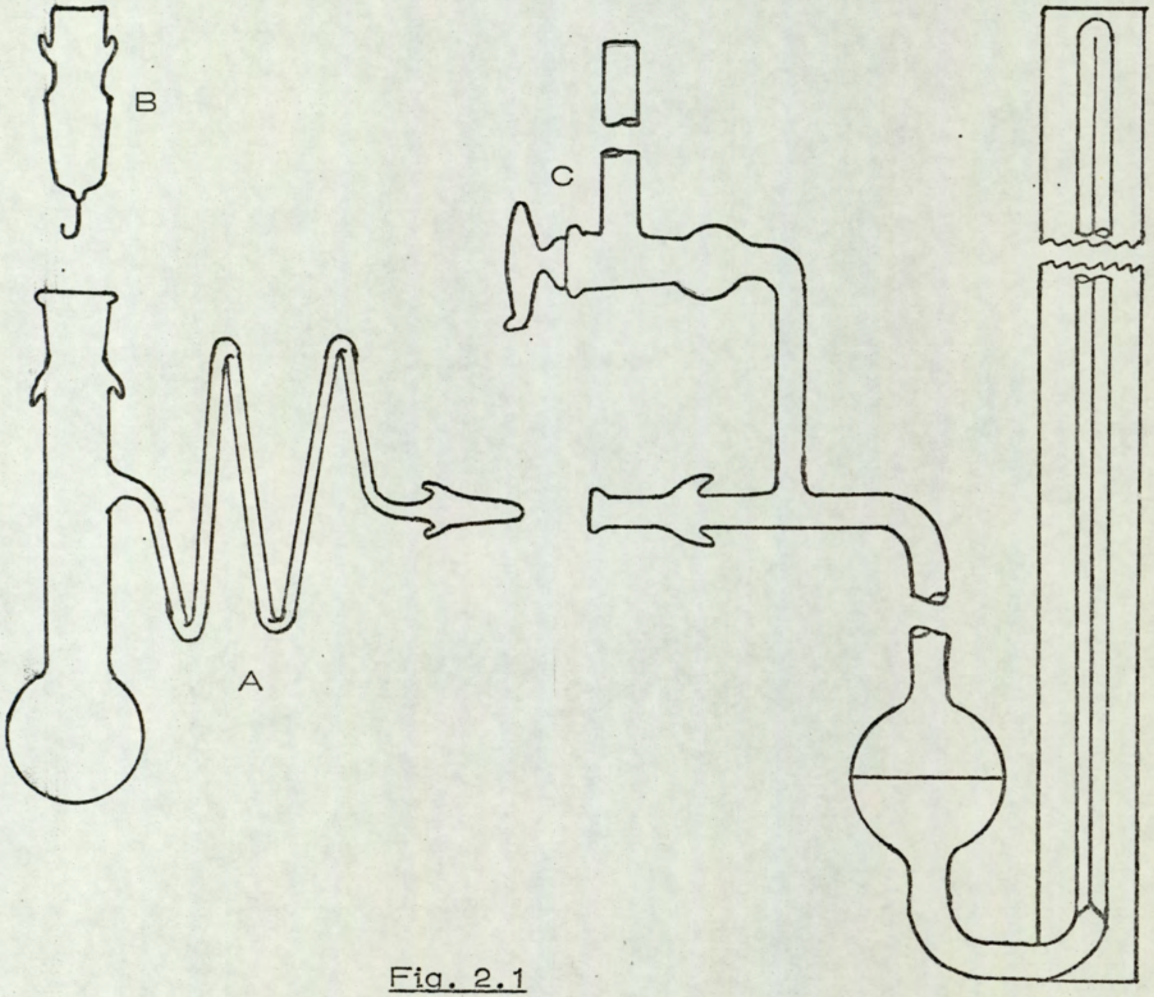


Fig. 2.1

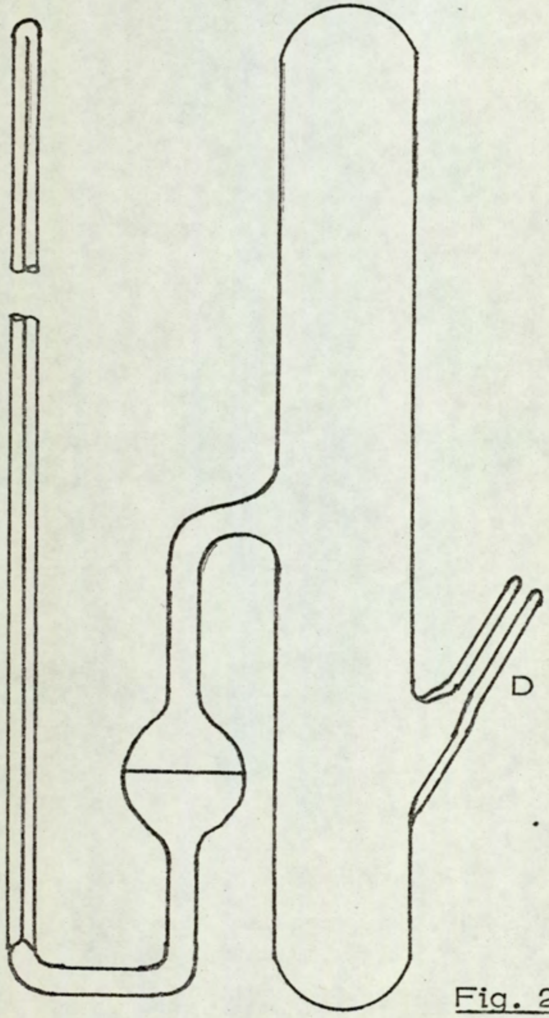


Fig. 2.2

and Mercer type, and the reaction started by knocking the suspended bucket containing the initiator into the base of the apparatus containing the solution of monomer.

This "initiator type" of equipment was only suitable for reactions to be carried out at temperatures below 50°C. Above this temperature considerable streaking of the grease used in the three Quickfit joints occurred and lead to the diffusion of bath liquid into the apparatus giving rise to erronious results.

The level of mercury in the manometer was followed by reference to a calibrated mirror scale attached to the reverse of the capillary section. This method of obtaining pressure readings was preferred over a cathetometer as the reactions carried out in this apparatus were rapid and did not allow time for the manipulation of a cathetometer between consecutive readings.

The second type of apparatus as shown in Fig 2.2 was designed by Tighe and contained both the reaction chamber and manometer section in one unit. This was used for reactions carried out at temperatures above 50°C, although it was suitable for reactions at lower temperatures in which the absolute initial rate of reaction was not required. Evacuation was effected by connecting the side arm (D) to a vacuum line and the apparatus isolated by sealing the 3mm capillary tube with an oxygen/gas torch.

The apparatus was cleansed by flaming out under reduced pressure and purging dry nitrogen into the vacuum line system to attain atmospheric pressure. The monomer solutions were introduced into the apparatus by means of a hypodermic syringe.

With both types of apparatus it is necessary to equilibriate the concentration of evolved carbon dioxide in solution and in the vapour phase. This was achieved by use of a Pifco vibrator, the solution was agitated immediately prior to taking a mercury level reading. Experience showed that this was an imperative procedure and if efficiently carried out produced more accurate results.

A useful relationship may be derived between the concentration of monomer and the pressure of carbon dioxide at any time during the decomposition. Nominally, one mole of monomer will decompose to give one mole of carbon dioxide and if $[M]_o$ is the initial concentration of monomer, $[M]$ is the concentration of monomer at any time and $[CO_2]$ is concentration of carbon dioxide produced by decomposition, the following relationship results;

$$[M]_o = [M] + [CO_2] \qquad \ldots\ldots\ldots \quad (1)$$

on completion of reaction the equation simplifies to;

$$[M]_o = [CO_2]_\infty \qquad \ldots\ldots\ldots \quad (2)$$

At constant temperature and volume for an ideal gas, the number of moles of CO_2 produced is directly proportional to the pressure of the gas;

$$P_\infty \propto [CO_2]_\infty \qquad \ldots\ldots\ldots \quad (3)$$

Therefore;

$$\pi P_\infty = [CO_2]_\infty = [M]_o \qquad \ldots\ldots\ldots \quad (4)$$

where π is a constant of proportionality. If the pressure at any instant is represented by P, equation (4) may be written as;

$$\pi P = [CO_2] = [M]_o - [M] \qquad \ldots\ldots\ldots \quad (5)$$

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

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

Further rearrangement gives;

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

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

There are three requirements for these equations to function accurately as applied to the system used herein. Constant temperature must be maintained throughout the reaction, the interior volume of the reaction vessel must remain constant and finally the gas, namely carbon dioxide, must be near to ideal.

The use of a contact thermometer/relay/heater system in controlling the oil bath temperature enabled an accurate temperature ($\pm 0.3^o$) to be maintained throughout. Both types of kinetic apparatus used involve the displacement of mercury from a reservoir as the pressure increases. However, this change in volume from initial to final state has been estimated as low as 0.01% of the total volume; the volume, therefore, remains effectively constant providing that wider bore manometer capillary tubes are avoided. Finally, low pressures are involved, up to 25 cm of mercury and carbon dioxide will behave near to an ideal gas. The vapour pressure of the solvent is effectively constant throughout the reaction and no error is introduced if sufficient time is allowed for the reaction vessel and its constituents to attain the working temperature of the oil bath before commencement of manometer readings.

Carbon dioxide is a weakly acidic gas and although possible interaction with some solvents was borne in mind no anomalies due to this effect nor catalysis or inhibition by mercury were observed under the conditions of measurement of reaction rates.

(ii) Sample manipulation.- All manipulations involving anhydrocarboxylates, solvents and reagents with the exception of pyridine and substituted pyridines, were carried out in a dry box. As the anhydrocarboxylates were in general solids, accurate concentrations of reactants were able to be made up. Solvents of various requirements were used, the principal solvent being nitrobenzene, enabling rates of decomposition to be measured at temperatures up to 130°C without any interfering increase in pressure due to the solvent. No difficulties resulting from the solubility of the anhydrocarboxylates were experienced.

(iii) Temperature controlled oil baths.- Three types of temperature controlled oil baths were used. The Townson and Mercer, Bridge control series II oil bath was used for initiated reactions below 50°C, requiring the apparatus shown in Fig 2.1. This model of temperature controlled oil bath had a facility for a forced cooling water jacket which enabled better temperature control to be achieved at temperatures around ambient conditions. A general purpose bath of 40 litre capacity was used for reactions to be carried out up to 80°C. The oil used was Risella and the bath had a fitted glass spiral for forced cooling. A boost-heater was incorporated for rapid temperature attainment and better temperature control at higher temperatures.

For temperatures in excess of 80°C a somewhat smaller

Dewar vessel of 8 litre capacity containing silicone oil was utilised. The latter two models had contact thermometer/relay/heater system for temperature control and were fitted with efficient stirrers.

Colorimetric Technique

In at least one case, the initiated decomposition of the anhydrocarboxylate in nitrobenzene resulted in the appearance of a deep reddish/brown colouration. The intensity of absorption of the colour in the visible region was recorded using a Perkin-Elmer 137 UV spectrophotometer and used as a means of following the rate of reaction.

The reaction was carried out under a bed of dry nitrogen rather than at reduced pressure to facilitate sample removal. Samples were removed at various time intervals and the reaction quenched in a carbon tetrachloride solution and maintained at 0°C until required (not longer than 1 hour). The colouration appeared to be coincident with loss of carbon dioxide, this phenomenon will be discussed in greater detail in Chapter 7, Section 7.1.

The intensity of absorption is given by;

$$\log_{10}\left(\frac{I_o}{I}\right) = \epsilon cl \qquad \ldots\ldots. \qquad (8)$$

where I_o is the intensity of the incident light, I is the intensity of transmitted light, ϵ is the molar absorptivity coefficient, l is the path length (constant in this case at 1 cm) and c is the concentration of absorbing species.

Most spectrophotometers record wavelength against absorbance which is given by;

$$A = \log_{10}\left(\frac{I_o}{I}\right) \qquad \ldots\ldots\ldots \qquad (9)$$

Equation 8 now reduces to;

$$C = A\,\epsilon^{1} \qquad \ldots\ldots\ldots \qquad (10)$$

where ϵ^{1} is a constant composed of ϵ and l, (i.e. $\epsilon^{1} = \frac{1}{\epsilon l}$).

At any instant during the reaction the following relationship applies;

$$[M]_o = [M] + [Pr] \qquad \ldots\ldots\ldots \qquad (11)$$

where [Pr] is the concentration of product. If the absorption is due to the product then at the end of the reaction;

$$[Pr]_{\infty} = [M]_o \qquad \ldots\ldots\ldots \qquad (12)$$

and thus,

$$[Pr]_{\infty} = A_{\infty}\,\epsilon^{1} = [M]_o \qquad \ldots\ldots\ldots \qquad (13)$$

The amount of monomer remaining at any time is given by;

$$[M] = A_{\infty}\epsilon^{1} - A_p\,\epsilon^{1} \qquad \ldots\ldots\ldots \qquad (14)$$

where A_p is the absorbance of product formed due to the decomposition of a concentration $[M]_o - [M]$ of monomer.

$$[M]_o - [M] = A_p\,\epsilon^{1} \qquad \ldots\ldots\ldots \qquad (15)$$

The fraction of total monomer decomposed at any time is thus;

$$\frac{[M]_o - [M]}{[M]_o} = \frac{A_p\,\epsilon^{1}}{A_{\infty}\,\epsilon^{1}} = \frac{A_p}{A_{\infty}} \qquad \ldots\ldots\ldots \qquad (16)$$

The spectra were obtained using matched cells; the reference cell contained the same initial concentration of carbon tetrachloride and nitrobenzene. The concentration of monomer was thus related to the ratio of absorbances as given by equation 16.

Infrared Techniques.-

The rate of polymerisation of some anhydrocarboxylates proceeds at a substantial rate when an initiator is used. The carbonyl absorption of the monomer in the infrared is sufficiently far removed from that of the polymer that the fate of both monomer and polymer may be monitored simultaneously by recording infrared spectra at various intervals of time. A similar method has been used by Idelson and Blout(51) in studying the polymerisation of N-carbonic anhydrides and also in the polymerisation of anhydrosulphites.(49)

The reaction is homogeneous throughout; no polymer precipitation occurs. The solvent used was tetrahydrofuran and no absorption of this solvent occurs in the region of study. However, a matched solvent blank cell was employed. Specific details of cell dimensions and monomer concentrations are given at relevant points in the text.

The intensity of absorption was measured as absorbance and thus equation 10 applies. That is;

$$C = A\,\epsilon^{1} \qquad \ldots\ldots\ldots \qquad (10)$$

If the concentration of monomer [M] at any instant has an absorbance A_m, then;

$$[M] = A_m\,\epsilon^{1} \qquad \ldots\ldots\ldots \qquad (17)$$

The concentration of monomer at zero time is $[M]_o$ and the absorbance is A_o, thus;

$$[M]_o = A_o\,\epsilon^{1} \qquad \ldots\ldots\ldots \qquad (18)$$

The fraction of the total monomer decomposed at any time is given by;

$$\frac{[M]_o - [M]}{[M]_o} = \frac{A_o\epsilon^1 - A_m\epsilon^1}{A_o\epsilon^1} = \frac{A_o - A_m}{A_o} \qquad \ldots\ldots\ldots \quad (19)$$

Considering the rate of polymer formation; this results in an equation similar to equation 16 in which the fraction of polymer formed at any instant is given by;

$$\frac{[\mathrm{Poly}]}{[\mathrm{Poly}]_\infty} = \frac{A_p}{A_\infty} \qquad \ldots\ldots\ldots \quad (20)$$

where $[\mathrm{Poly}]_\infty$ is the final concentration of polymer, [Poly] is the polymer concentration at any time during the reaction, A_p is the absorbance of the polymer during the reaction and A_∞ is the final absorbance of the polymer.

If the polymer is formed at the same rate as the monomer is consumed, then the fraction of monomer remaining will be related to the fraction of polymer formed by;

$$\frac{[M]}{[M]_o} = 1 - \frac{[\mathrm{Poly}]}{[\mathrm{Poly}]_\infty} = \frac{[\mathrm{Poly}]_\infty - [\mathrm{Poly}]}{[\mathrm{Poly}]_\infty} \qquad \ldots\ldots\ldots \quad (21)$$

In terms of absorbances, equation 21 becomes;

$$\frac{A_m}{A_o} = \frac{A_\infty - A_p}{A_\infty} \qquad \ldots\ldots\ldots \quad (22)$$

A linear relationship for equation 22 is indicative of polymer formation occurring at the same rate as monomer disappearance.

2.3 Purification of Solvents and Reagents

The main requirement for solvent purification was the exclusion of trace amounts of water. Solvent and reagents were

were purified essentially by the methods due to Weissberger(52) and Vogel(53) with adaptations according to the choice of internal drying agents for specific solvents. The distillations carried out at atmospheric pressure were vented to air through an anhydrous calcium chloride drying tube to prevent entry of atmospheric moisture.

Nitrobenzene.- Nitrobenzene was allowed to stand over phosphorus pentoxide for a period of forty eight hours. It was then fractionally distilled through a two foot column packed with Dixon gauze rings under reduced pressure using a dry nitrogen bleed system. The middle fraction was collected over previously baked barium oxide.

The solvent was again fractionally distilled under reduced pressure immediately prior to use. The middle fraction was collected at 70°C, 0.5 mm of mercury.

Chlorobenzene. - This solvent was shaken several times with anhydrous calcium sulphate and fractionally distilled onto baked barium oxide at atmospheric pressure. It was redistilled prior to use; the constant boiling fraction at 132°C was collected.

Benzyl alcohol.- The solvent was initially shaken with and allowed to stand over anhydrous magnesium sulphate. It was then fractionally distilled under reduced pressure onto baked barium oxide over which it was stored. The alcohol was redistilled under reduced pressure prior to use, the middle fraction was collected at 80°C, 5 mm pressure.

Alcohols.- The following drying and purification procedure was used for n-propanol, isopropanol, 2-methyl propanol and tertiary butanol.

The alcohol was shaken several times with anhydrous calcium sulphate and allowed to stand over this desiccant for several days. It was then fractionally distilled through a two foot fractionating column, the middle fraction was collected over fresh anhydrous calcium sulphate over which it was stored. The alcohols were redistilled prior to use.

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

Dimethyl sulphoxide.- Dimethyl sulphoxide was shaken several times with anhydrous calcium sulphate and then refluxed over baked barium oxide. It was fractionally distilled under reduced pressure and collected over fresh barium oxide and redistilled immediately prior to use.

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

Substituted Pyridines.- The following substituted pyridines were purified by a general procedure.

Pyridine	Supplier
2-methyl (α-picoline)	Hopkin & Williams Ltd
2,6-dimethyl (2,6 lutidine)	" "
4-methyl (γ -picoline)	" "
2-ethyl	Koch-Light Laboratories Ltd
2-methoxy	" "
2-n-propyl	Pfaltz & Bauer, inc.
4-tertiary-butyl	" "
2,6-dimethoxy	Ralph N. Emanuel Ltd.

The substituted pyridine was refluxed over sodium hydroxide pellets for twenty four hours with the stringent exclusion of atmospheric moisture. It was fractionally distilled onto baked barium oxide; the middle fraction was collected at atmospheric pressure.

Diethyl Ether.- The anhydrous grade of solvent (0.02% water) as supplied by Fison Scientific Apparatus Limited was used for Grignard reactions and anhydrocarboxylate syntheses.

For polymerisations carried out in diethyl ether the "MAR" grade of solvent was used as supplied by B.D.H. Chemicals Ltd., with a water content of 0.008%.

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

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

l-mandelic acid.- The α-hydroxy acid was obtained from Aldrich Chemicals Co., Inc.

d-mandelic acid. - supplied by Ralph N. Emanual Ltd.

Bromopentafluorobenzene.- Generous gifts of this chemical were obtained from the Imperial Smelting Corporation, Avonmouth.

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

α-hydroxy acids.- Mandelic, atrolactic and benzilic acids were commercially available. The anhydrocarboxylates prepared were derived from the corresponding D, L forms of the parent acid unless otherwise stated.

2.4 Synthesis of 2-Hydroxy 2(pentafluorophenyl) Propanoic Acid

Pentafluorophenylmagnesium bromide was prepared in the normal way(10) from bromopentafluorobenzene (1.0 mole) in anhydrous diethyl ether (1 litre). Pyruvic acid (1.0 mole) in diethyl ether (200 ml.) was slowly added to the stirred Grignard solution which was maintained below 5°C during the addition. The solution was allowed to warm to room temperature and stirred for 24 hours, after which it was hydrolysed with dilute hydrochloric acid (4N, 300 ml) and the ethereal layer separated. Removal of solvent, unreacted bromopentafluorobenzene and pentafluorobenzene, formed by hydrolysis of pentafluorophenylmagnesium bromide, left a brown solid of crude 2-hydroxy 2(pentafluorophenyl) propanoic acid. The crude hydroxy acid was conveniently purified by recrystallisation from benzene/petroleum-ether. The yield obtained was 85 g of the acid which had a characteristic melting point of 129°C.

2.5 General Synthesis of Phenyl and Pentafluorophenyl Substituted Anhydrocarboxylates

The anhydrocarboxylates were prepared by the action of phosgene on the anhydrous copper (II) salt of the corresponding α-hydroxy acid.

To the anhydrous copper (II) salt (1.0 mole) slurried in dry ether (3 litre) was added phosgene (2.0 moles) in dry ether (1.5 litre) and stirred for 4 days at room temperature. Anhydrous pyridine (1.8 moles) in dry ether (500 ml) was then added to remove the HCl formed in the cyclisation reaction. The precipitate of copper (II) chloride and pyridine hydrochloride was removed by filtration and washed with anhydrous ether to remove any remaining anhydrocarboxylate. The solvent, unreacted phosgene and hydrogen chloride were removed by evaporation and the solid remaining left under vacuum for 30 mins. to remove the final traces of volatile material.

With the exception of atrolactic acid anhydrocarboxylate (II, $R^1 = C_6H_5$, $R^2 = CH_3$) the crude product was obtained as a whitish solid. This, however, was isolated as a yellowish oil.

Further anhydrous ether was added to the crude anhydrocarboxylate and an amount of silver oxide equivalent to a 2 molar excess on the chloride containing impurity as determined by the previously described (section 2.1) modification of Ingram's(48) potentiometric technique. The mixture was stirred for 24 hours, the silver oxide removed by filtration and the ether removed by evaporation. The resulting anhydrocarboxylate contained no detectable traces of chloride impurity.

The anhydrocarboxylates were finally purified by vacuum sublimation at approximately 2° below their melting point. Ideal conditions for sublimation were found to be 0.5 mm pressure with a water cold trap temperature of 10–14°C. In the case of atrolactic acid anhydrocarboxylate a short-path flash distillation technique under vacuum was employed, the pure anhydrocarboxylate being isolated as a colourless viscous liquid.

CHAPTER 3

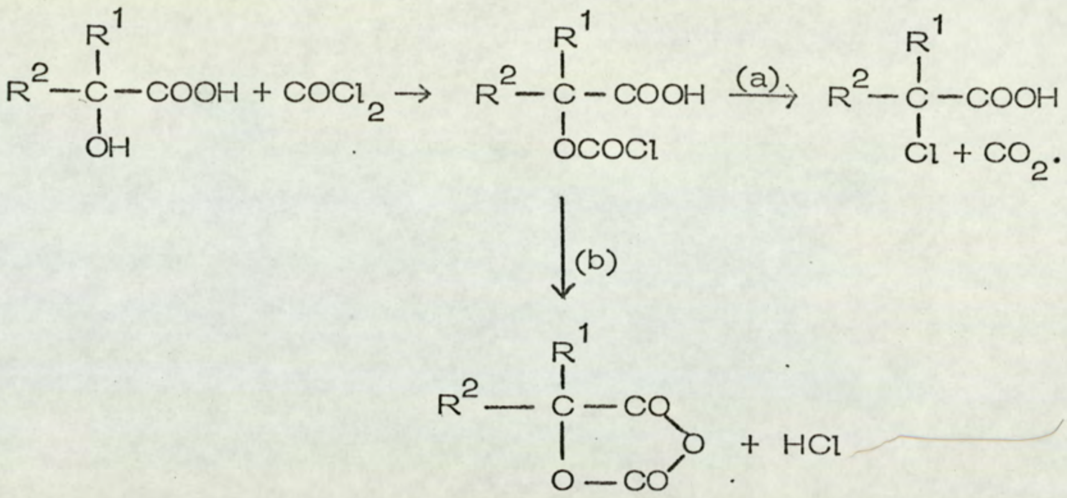
Synthesis and Characterisation

Phenyl and pentafluorophenyl substituted anhydrocarboxylates are isolated as white crystalline solids in the majority of cases. Their physical properties appear to follow a trend similar to that shown by the parent α-hydroxy acids.

3.1 Introduction

Previously reported methods of synthesis of substituted anhydrocarboxylates(41-44) have not been generally satisfactory. All methods have involved the addition of phosgene (carbonyl chloride), dissolved in a suitable solvent, to the appropriate α-hydroxy acid, and have been carried out in the region of 0°C. 5-Benzylidene 1,3-dioxolan 2,4-dione was prepared by the addition of redistilled phosgene to an ice-cool solution of enolic phenylpyruvic acid.(43) It was reported to be a colourless crystalline solid with a melting point of 155°C.

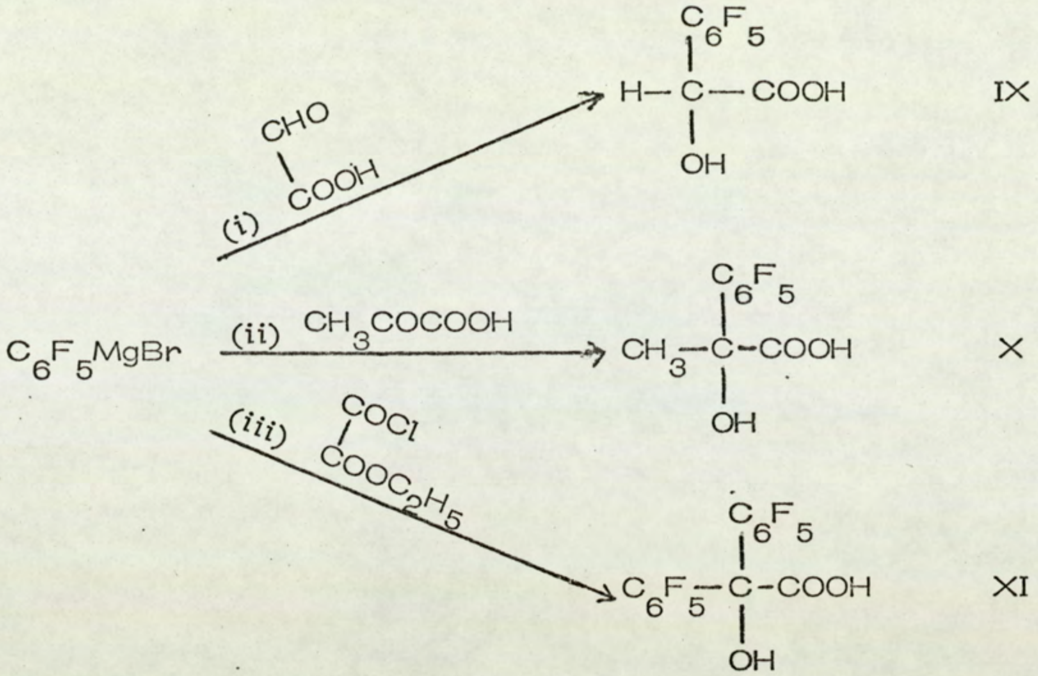
The reaction of phosgene with phenyl substituted α-hydroxy acids gives an appreciable quantity of α-chloro acid impurity. The unreacted parent acid is also present in substantial quantities. A suggested reaction scheme is given below and analysis of the reaction products has shown that when one of the substituents, R^1 or R^2, is a phenyl group, decomposition of the initial addition product proceeds predominantly by reaction (a) to yield the appropriate α-chloro acid.



An alternative method has been reported for the synthesis of the analogous anhydrosulphite derivatives of α-hydroxy acids.(39) This involves the addition of thionyl chloride to a slurry of the anhydrous copper(II) salt of the hydroxy acid in anhydrous ether; improved yields of phenyl substituted anhydrosulphites were reported. Use of anhydrous copper(II) salt enables the acid function to be obtained in dry state, and furthermore, in the subsequent reaction with phosgene the amount of unreacted parent acid is effectively reduced to zero.

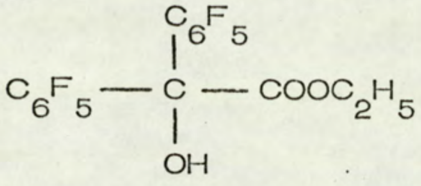
3.2 Pentafluorophenyl substituted α-hydroxy acids

The method of synthesis of fluorine containing α-hydroxy acids was essentially that reported by Tighe et al.,(13) and involved the addition of the Grignard reagent, pentafluorophenylmagnesium bromide to a solution of either (i) glyoxylic acid; (ii) pyruvic acid or (iii) ethyl oxalyl chloride, in anhydrous ether to give on hydrolysis the pentafluorophenyl substituted α-hydroxy acids as shown below.



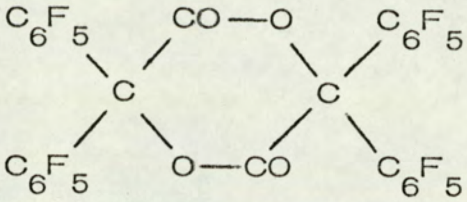
2-Hydroxy 2-(pentafluorophenyl) acetic (IX) and 2-hydroxy 2-(pentafluorophenyl) propanoic (X) acids were obtained as white crystalline solids with characteristic melting points, infra-red and n.m.r. spectra, after recrystallisation from benzene/ petroleum ether.

The white crystalline solid isolated from the acid hydrolysate in the reaction of the Grignard reagent with ethyl oxalyl chloride was not the required hydroxy acid. This was especially surprising since similar examination of the crude product indicated that the required α-hydroxy acid had been formed in good yield. Spectral examination showed it to be a mixture of possibly the ethyl ester of the required acid (XII) and the dehydrated dimeric structure (XIII) conventionally termed a substituted glycollide.



$(C_6F_5)_2C(OH)COOC_2H_5$

XII



XIII

Alkaline hydrolysis of the mixture using dilute potassium hydroxide and refluxing, resulted in the formation of oxalic acid, ethyl alcohol and pentafluorobenzene. This presumably occurs by hydrolysis of the ester function and cleavage of the pentafluorophenyl to carbon bond after hydroxide attack at the α-carbon. It would also appear that 2-hydroxy 2,2bis(pentafluorophenyl) acetic acid readily dehydrates in dry solvents with the formation of tetra (pentafluorophenyl) glycollide (XIII).

3.3 Copper (II) salts of α-hydroxy carboxylic acids

Phenyl substituted α-hydroxy acids were converted to their copper(II) salts via the ammonium salt. Ammonia solution was added to a solution of the hydroxy acid in distilled water, the excess ammonia removed by boiling. The aqueous solution of the ammonium salt was cooled and an excess of copper(II) chloride solution added until precipitation of the required salt was complete. The salt was separated by filtration, washed well with distilled water and diethyl ether, and finally dried in vacuo at 100°C.

The copper (II) salts of phenyl substituted hydroxy acids were obtained as pale green powders when anhydrous. The absence of any weight loss at around 100°C on the T.G.A. trace verified the anhydrous nature of the salts.

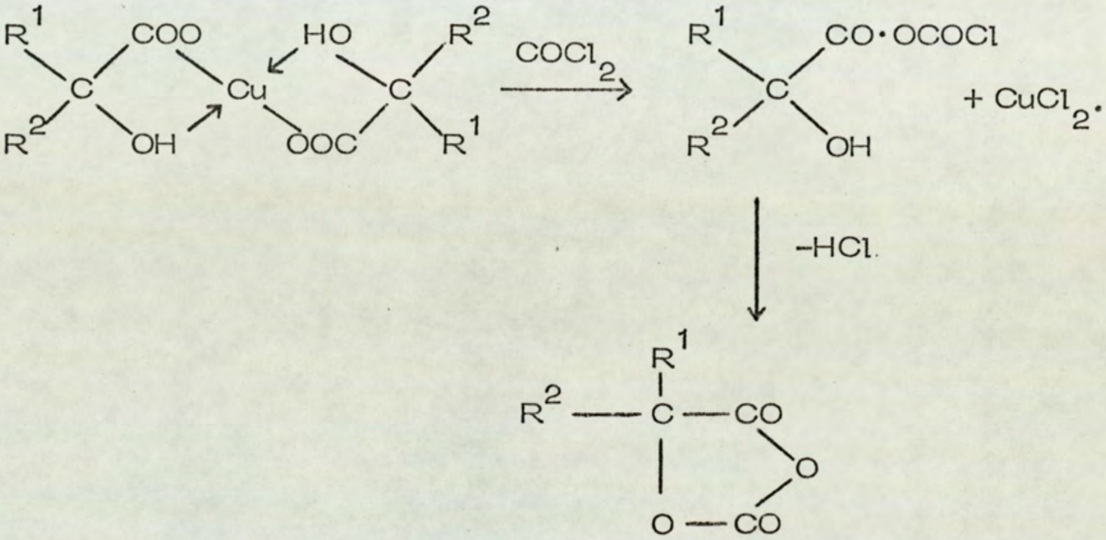
A slightly modified technique was used for the preparation of copper (II) salts derived from pentafluorophenyl substituted hydroxy acids. As was stated in Section 3.2, the refluxing of these acids in alkaline solution results in the cleavage of the pentafluorophenyl group from the α-carbon. For this reason the pH of the hydroxy acid solution was monitored instrumentally during the addition of ammonia in order to alleviate the necessity to boil off the excess ammonia to obtain a neutral solution of the ammonium salt. Subsequent addition of copper (II) chloride gave the required copper (II) salt.

3.4 Synthesis and Purification of Anhydrocarboxylates of α-hydroxy carboxylic acids

The anhydrocarboxylates were prepared by the action of phosgene on the anhydrous copper (II) salt of the corresponding α-hydroxy acid. Experimental details are given in Chapter 2, Section 2.5.

The use of the copper (II) salt in the synthesis has several advantages over the previously reported methods. Firstly, it may easily be obtained in an anhydrous state. Precautions for the rigorous exclusion of moisture effectively reduce the amount of parent acid impurity to a negligible amount as the acid is only generated by the reaction of the pre-formed anhydrocarboxylate with atmospheric moisture. It is for this reason that all reaction manipulations were carried out at room temperature in order to minimise the condensation of atmospheric moisture in the vicinity of the reaction medium.

The second advantage is that it enables half of the available chlorine impurity to be removed as a precipitate of anhydrous copper (II) chloride. Finally, use of the copper (II) salt promotes the formation of an acyl chloroformate by initial attack of the phosgene molecule at the carboxylate anion as depicted below.



The acyl chloroformate is inherently more stable than the alkyl chloroformate which is formed by phosgene addition at the hydroxyl centre in the reaction with an α-hydroxy acid. The latter intermediate species readily loses carbon dioxide to form the α-chloro acid by an S_{N_i} type reaction. Loss of HCl from the acyl chloroformate results in the formation of the cyclic anhydrocarboxylate.

The use of pyridine in the latter part of the synthesis not only effectively removes any hydrogen chloride eliminated during the cyclisation of the acyl chloroformate intermediate as pyridine hydrochloride, but also effects the loss of hydrogen chloride from the intermediate. The role of pyridine in promoting reactions by the removal of hydrogen chloride has been discussed by Gerrard in the reaction of alcohols with phosphorus trichloride,(54) and also the decomposition of alkyl chloroformates(55) in the presence of pyridine and pyridine hydrochloride. It is apparent from this observation that the so formed pyridine hydrochloride would promote a further decomposition of the acyl chloroformate to the corresponding ketone via the α-hydroxy acid chloride. However, this secondary decomposition is extremely slow and provided prolonged reaction times and elevated temperatures are avoided produces negligible amounts of ketone impurity.

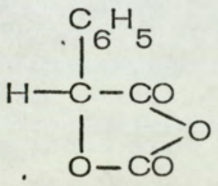
In the synthesis of atrolactic acid anhydrocarboxylate, acetophenone was detected as an impurity when temperatures of 50-60°C were used to remove the solvent after filtration of the etherial solution. A substantial reduction in the amount of ketone formed was observed when solvent was removed at room temperature.

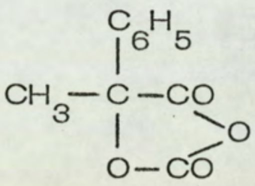
Purification by vacuum sublimation and flash distillation separated the anhydrocarboxylate from any trace amounts of acid and ketone. All manipulations of the anhydrocarboxylates were carried out in a dry box which was also used for storage purposes.

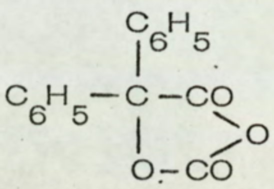
3.5 Anhydrocarboxylate Characterisation

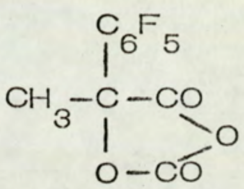
The formation of an anhydrocarboxylate, which may be considered as an intramolecular carboxy anhydride, from an α-hydroxy carboxylic acid presents several fundamental changes with respect to spectroscopic analysis. The most significant change is probably the absence of the acid O - H stretching absorption in the region 3000-3500 cm^{-1} of the infrared spectrum, on formation of the cyclic anhydrocarboxylate structure.

The anhydrocarboxylates which were principally used and to which direct reference will be made during the text are as follows;


XIV


XV


XVI


XVII

These structures are trivially named after the parent acid; for example, mandelic acid anhydrocarboxylate (XIV, $R^1 = H$; $R^2 = C_6H_5$), and will be referred to throughout the text according to the terminology which follows;

Parent Acid	R^1	R^2	Anhydrocarboxylate abbreviation
Mandelic	C_6H_5	H	MAAC
Atrolactic	C_6H_5	CH_3	AAAC
Benzilic	C_6H_5	C_6H_5	BAAC
2-hydroxy-2-pentafluorophenyl propanoic acid	C_6F_5	CH_3	PFAAC

Table 3.1 gives the physical properties of the prepared anhydrocarboxylates. The yields recorded were considered good as they were based on the purified material whereas previously reported yields were based on somewhat impure products. A rather low yield

Table 3.1

Physical properties of a series of phenyl substituted anhydrocarboxylates

Anhydro-carboxylate	Yield %	Melting Point Parent Acid(°C)	Melting Point Anhydro-carboxylate(°C)	CO_2 evolved % theoretical	%C - Found [%-required]	%H - Found [%-required]
MAAC	55	133 (a)	53.7 - 55.1	97 ± 2	61.9 [60.7]	3.3 [3.4]
AAAC	30	92(a)	<10	95 ± 2	60.7 [62.5]	3.6 [4.2]
BAAC	53	152 (a)	68.0 - 68.9	98 ± 2	73.0 [71.1]	3.7 [4.0]
PFAAC	62	129	63.8 - 65.3	99 ± 2	42.6 [42.6]	1.2 [1.1]

(a) from reference (56).

was recorded during the preparation of atrolactic acid anhydrocarboxylate (AAAC), this was principally attributed to the loss by decomposition during distillation and the fact that only the middle fraction was taken.

The melting points of the anhydrocarboxylates that have been studied appear to follow a trend similar to that shown by the parent acids rather than the order of molecular weights. It is not surprising, therefore, that AAAC is a viscous liquid at room temperature and has a melting point less than 10°C.

The percentage of the theoretical yield of carbon dioxide evolved during decomposition provided a useful and simple technique for assessing the anhydrocarboxylate purity. An accurately weighed quantity of anhydrocarboxylate (0.2–0.3 g) was dissolved in 4 mls of nitrobenzene and transferred to a kinetic apparatus of known dead-space volume of the type shown in Fig. 2.2 which was then sealed and transferred to an oil bath at the appropriate temperature (ca. 100°C). The amount of carbon dioxide evolved as measured by the pressure rise at that temperature, was determined as a percentage of the theoretical amount. The anhydrocarboxylate derived from 2-hydroxy-2-(pentafluorophenyl) propanoic acid, (PFAAC), was shown to be the most pure sample as ascertained by this method and was estimated to have less than 1% impurity.

The reproducibility of results obtained from elemental analysis was quite good when the fact that the samples were of relatively low melting point and volatility is taken into consideration. It is interesting to note that the more volatile sample AAAC gave the least reliable results, which was probably due to a combination of acetophenone impurity and volatilisation prior to ignition. However, the results obtained were well within the limits expected for this type of sample. Reconversion of the anhydrocarboxylate to the parent acid by hydrolysis in a moist atmosphere served as a useful preliminary tool in ascertaining the purity of the anhydrocarboxylate. The melting point of the resultant acid was found to be considerably lowered by such impurities as the corresponding ketone and α-chloro acid.

Infrared spectra were obtained with KBr discs and the spectrum of AAAC as a thin film (neat) between KBr plates. The predominant characteristic absorption of anhydrocarboxylates occurs in the carbonyl region. Two peaks are observed in this region, a strong absorption at 1810 ± 5 cm^{-1} and a medium strength absorption at 1890 ± 10 cm^{-1}, which may be attributed to the two distinct carbonyls in the cyclic system. A single peak is observed at 1720 ± 5 cm^{-1} for the carbonyl in the parent acid and the copper (II) salt shows a rather broad absorption at 1640 ± 5 cm^{-1}. The principal carbonyl absorptions of the anhydrocarboxylate differs substantially from that of the polymer and oligomeric species. These latter absorptions occur at around 1760 ± 15 cm^{-1} and are essentially ester carbonyl absorptions. The specific carbonyl absorptions of the anhydrocarboxylates studied are given in Table 3.2 and Fig. 3.1 shows a typical change in carbonyl frequency during the progressive synthetic steps from α-hydroxy acid to copper (II) salt and finally to the anhydrocarboxylate.

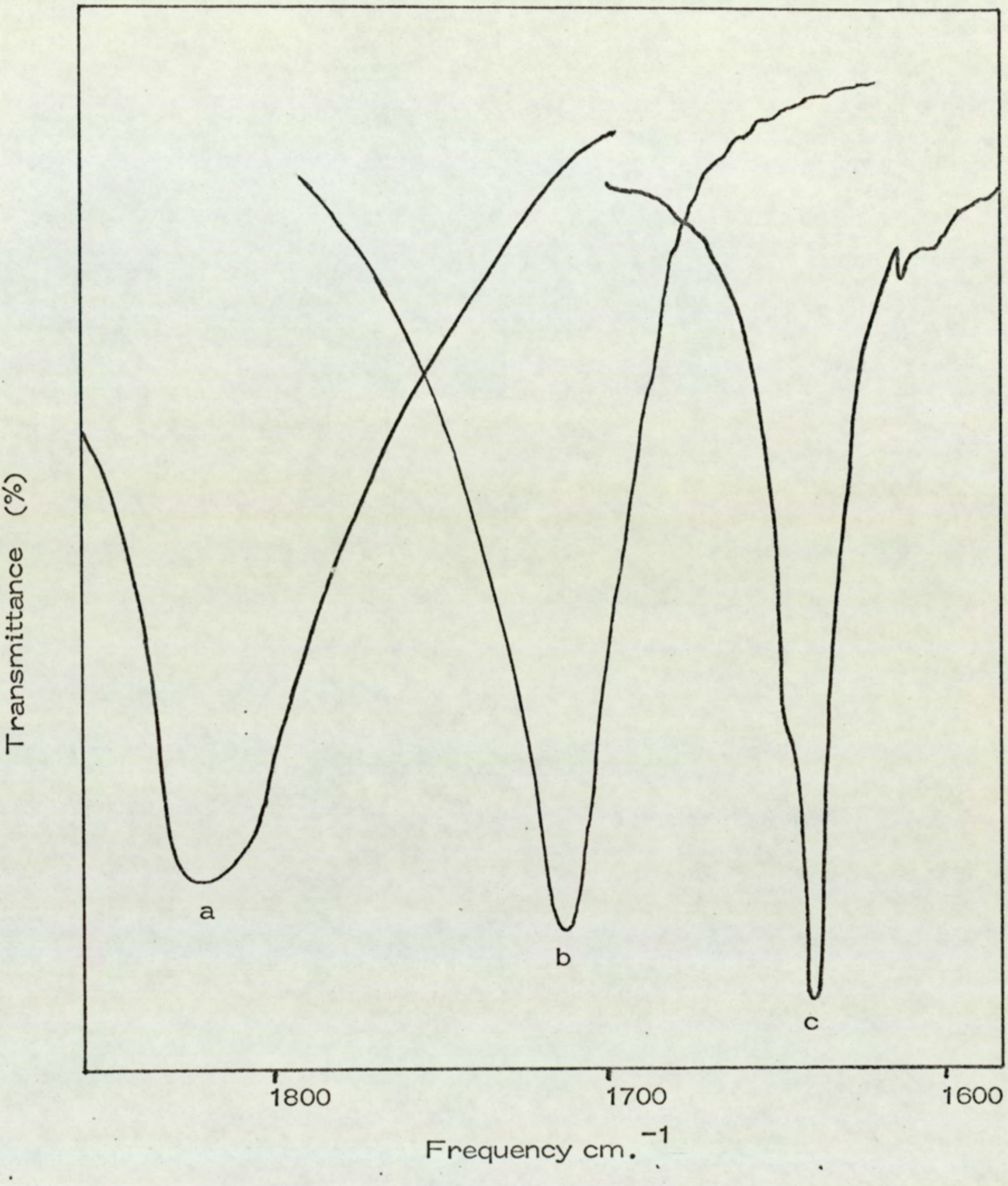


Fig. 3.1 Infra red spectra recorded as kBr discs of,

a) MAAC,

b) Mandelic acid,

c) Copper (II) salt of mandelic acid

showing the carbonyl absorption.

A spectrum of atrolactic acid anhydrocarboxylate (AAAC) is shown in Fig. 3.2.

Table 3.2

Carbonyl absorptions for phenyl substituted α-hydroxy acids, their copper (II) salts and the derived anhydrocarboxylates.

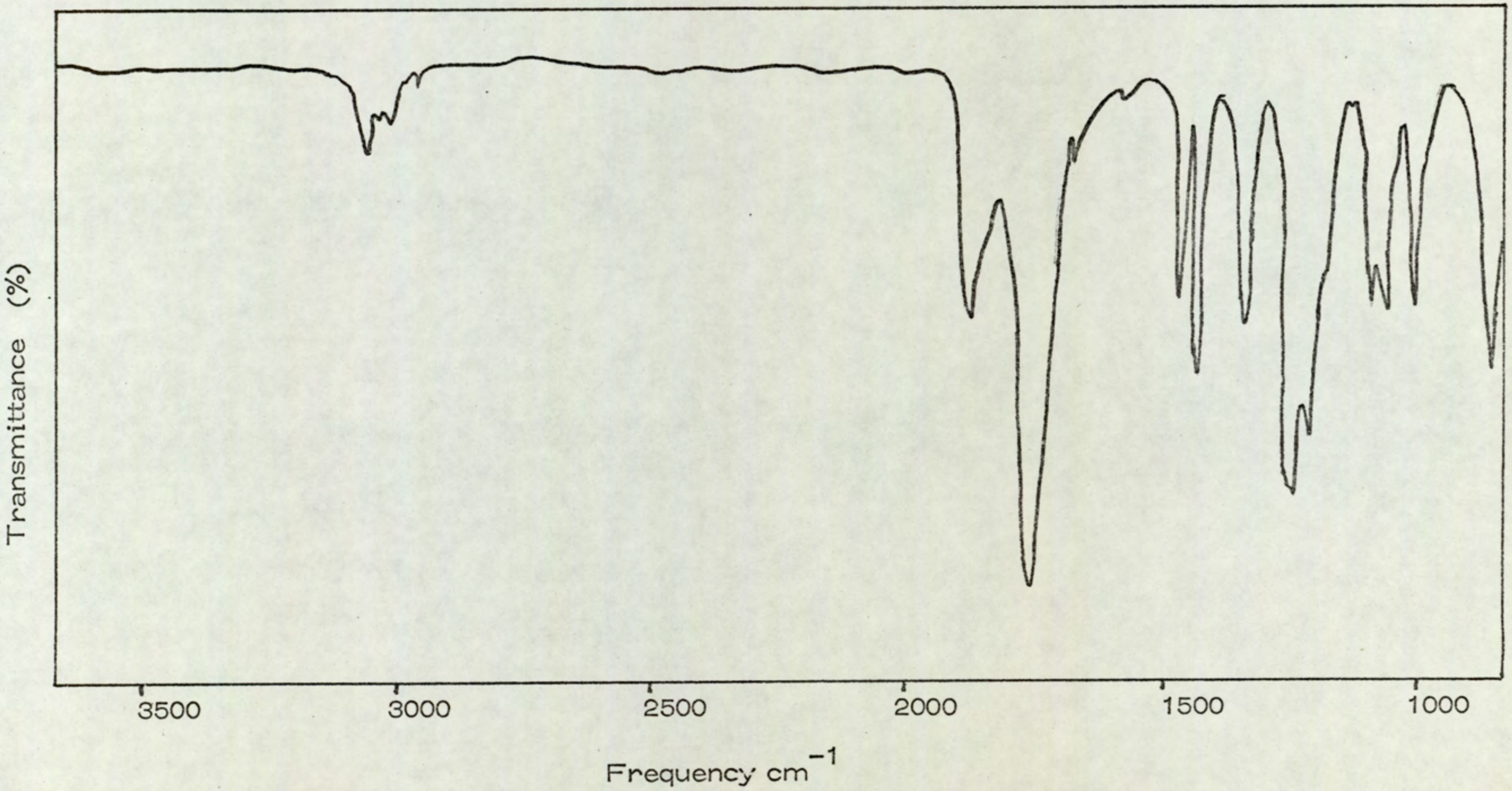
Parent acid	α-hydroxy acid (cm^{-1})	Copper (II) salt (cm^{-1})	Anhydrocarboxylate × (cm^{-1})
Mandelic	1712	1636	1813 (s) 1898 (m)
Atrolactic	1725	1633	1813 (s) 1885 (m)
Benzilic	1719	1648	1808 (s) 1895 (m)
2-hydroxy-2-pentafluoro-phenyl propanoic	1742	1650	1822 (s) 1881 (m)

× s - strong absorption
m - medium intensity absorption

Comparison of the frequency of the carbonyl absorptions for 2-hydroxy 2-(pentafluorophenyl) propanoic acid and the hydrocarbon analogue, atrolactic acid, and their corresponding copper(II) salts shows that the effect of the pentafluorophenyl substituent is to move the absorption to shorter wavelength. This effect is also observed for the strong carbonyl absorption in the anhydro-

Fig. 3.2

Infrared Spectrum of AAAC. The spectrum was recorded as a thin film using kBr plates, the reference cell was air.



carboxylates but by contrast the medium intensity absorption is moved to longer wavelength. Both carbonyl absorptions in the anhydrocarboxylate derivative of 2-hydroxy 2-(pentafluorophenyl) propanoic acid possess a shoulder peak. Characteristic C-F absorptions of the pentafluorophenyl group are shown at 1660 and 1532 cm^{-1}, both are of medium to strong intensity.(57)

High resolution nuclear magnetic resonance studies were carried out in 5-10% w/v solutions of the anhydrocarboxylate in deuterated chloroform. Actual chemical shifts of the parent acids and the formed anhydrocarboxylates are presented in Table 3.3. In the case of AAAC, the formation of the anhydrocarboxylate ring is accompanied by a deshielding of both the phenyl group protons and methyl protons. This effect is accentuated in the case of the single proton in mandelic acid and the corresponding anhydrocarboxylate.

The fluorine resonance spectra of 2-hydroxy 2-(pentafluorophenyl) propanoic acid and its anhydrocarboxylate were consistent with a pentafluoro substituted benzene ring. Fluorine-fluorine couplings of the distinct ortho, meta and para fluorines of the pentafluorophenyl group were observed and it is interesting to note that the proton resonance of the methyl groups in both the fluorinated acid and anhydrocarboxylate are moved to lower field frequency by the presence of a pentafluorophenyl substituent (cf. R^1 resonance of atrolactic acid). Also the methyl resonance occurs as a triplet whereas only a singlet is observed in the non-fluorinated compound. This is attributed to long range spin-spin coupling with the two ortho fluorine atoms on the pentafluorophenyl substituent.

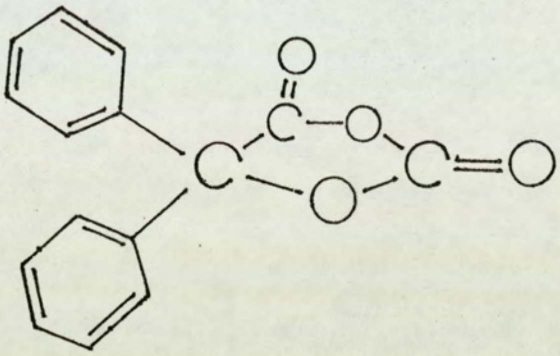
Table 3.3

Spectra recorded as deuterochloroform solutions, 10% w/v at 100 MHz. Reference T.M.S.

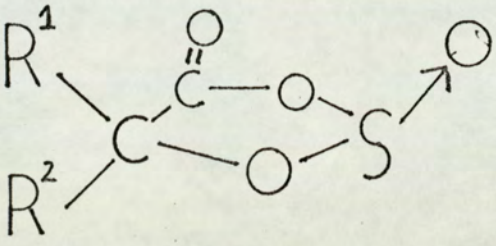
Parent Acid	α-hydroxy acid *	Anhydrocarboxylate *
Mandelic $R^1 = H$ $R^2 = C_6H_5$	4.70 (s) 2.50 (s)	3.98 (s) 2.49 (s)
Atrolactic $R^1 = CH_3$ $R^2 = C_6H_5$	8.18 (s)$^{+}$ 2.63 (m)	8.01 (s) 2.52 (m)
Benzilic $R^1 = C_6H_5$ $R^2 = C_6H_5$	} 2.54 (m)	} 2.44 (s)
2-hydroxy 2 pentafluoro-phenyl propanoic $R^1 = CH_3$ $R^2 = C_6F_5$	7.99 (t)$^{+}$ –	7.75 (t) –

* (s) – singlet + measured at 60 MHz.
(t) – triplet
(m) – multiplet.

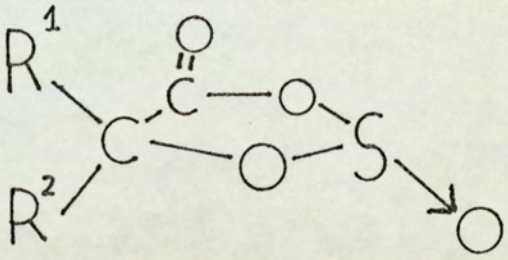
The anhydrocarboxylate presents an interesting case to which substituted anhydrosulphites may be compared. The anhydrocarboxylate ring is necessarily planar but could conceivably possess a degree of puckering or "pseudo-rotation." However, the signal obtained from a proton resonance is time averaged and therefore any rapid change in ring conformation would not be observed even though the phenyl substituents, for example, in benzilic acid anhydrocarboxylate are momentarily magnetically non-equivalent. The anhydrocarboxylate ring system may, therefore, be considered essentially planar, as shown below, in the absence of complicating factors.



In the case of anhydrosulphites, the 5-membered ring may also be considered planar in the absence of previously stated complicating factors. However, there is the possibility of two configurations about the ring sulphur/oxygen, (XVIII), (XIX), which results in two chemically equivalent substituents at C(5) becoming magnetically non-equivalent. In the two cases, $R^1 = R^2 = CH_3$ and $R^1 = R^2 = C_2H_5$, the n.m.r. spectrum has been resolved in terms of the two postulated ring sulphur configurations which produces two peaks of equal intensity in the case of dimethyl substitution and a somewhat more complicated spectrum in the diethyl case, in which proton-proton couplings of the methyl and the methylene groups are present. It must be pointed out that in the case of unsymmetrically substituted anhydrosulphites, for example when $R^1 = CH_3$, $R^2 = C_2H_5$, (XVIII), (XIX), there tends to be a weighting to one of the isomers; the ratio of the two isomers is about 2:1 in favour of XVIII, which is consistent with formation of the isomer presenting minimum steric repulsion between the sulphur-oxygen and the substituent groups R^1 and R^2.

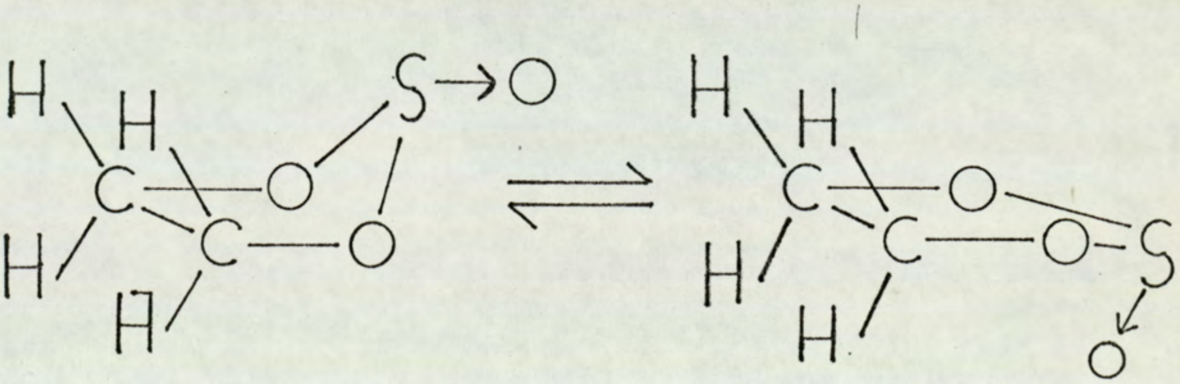


XVIII

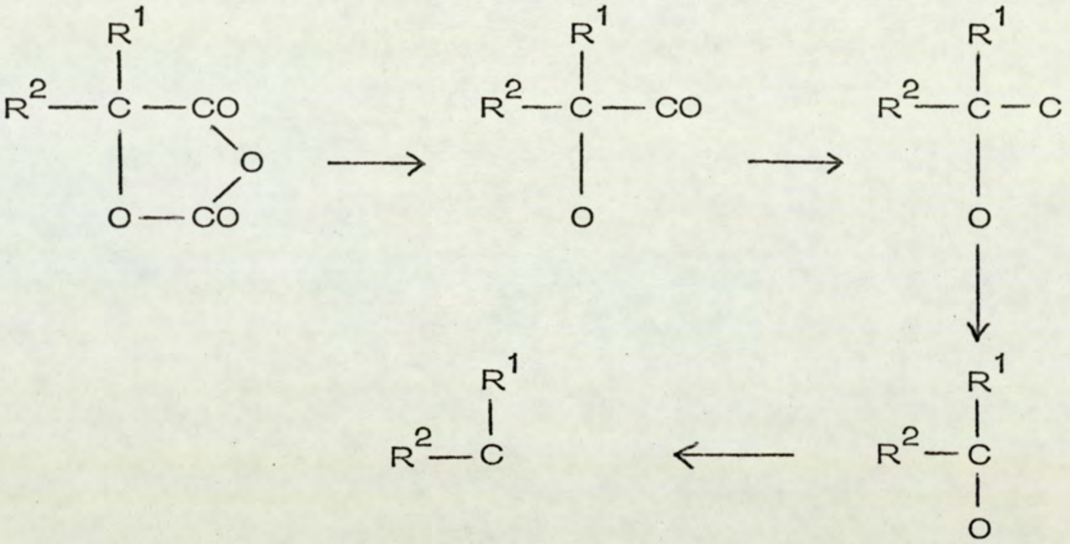


XIX

The difference in the proton resonance spectra of cyclic carbonates and cyclic sulphites has been explained(58)(59) by an envelope conformation with the sulphur atom above the plane of the ring. McNeal et al(60) have suggested the equilibrium shown below for the conformations of ethylene sulphite to explain the solvent dependence of the sulphur-oxygen absorption in the infra-red.



The mass spectra of anhydrocarboxylates presents an interesting feature in that top mass peaks are observed corresponding to the molecular weight of the anhydrocarboxylate. Principal ring fragmentation peaks are observed at (M - 44), (M - 60), (M-72) and (M - 88) which corresponds to the following fragmentation scheme;



These peaks appear to be typical of the anhydrocarboxylate ring and represent a stepwise fragmentation of the ring system. The fact that a top mass peak is observed is indicative of a degree of thermal stability greater than that shown by the analogous anhydrosulphite ring in which no such peak was found.(35)(49)

Ultraviolet spectra were recorded in diethyl ether. The results are presented in Table 3.4. The strong absorptions quoted are probably due to the K-bands of an aromatic system possessing chromophoric substitution in close proximity; in these cases the acid and anhydrocarboxylate carbonyls. High molar absorptivity coefficients, $\log_{10}\epsilon > 4.0$, are characteristic of this $\pi \rightarrow \pi^*$ transition. In the u.v. spectra of both the acid and anhydrocarboxylate, bands of lower molar absorptivity, ($\log_{10} \sim 4.2$), than the quoted band are present in the region 250–270mμ. These are probably due to the vibrational sublevels of the aromatic system, accompanying the electronic transition. In the case of

Table 3.4

Parent Acid	α-hydroxy acid		Anhydrocarboxylate	
	λ max	$\log_{10} \epsilon$	λ max	$\log_{10} \epsilon$
Mandelic	237.0	4.559	238.0	4.396
Atrolactic	237.5	4.524	235.5	3.234
Benzilic	235.5	5.034	240.5	5.221
2-hydroxy 2-pentafluorophenyl propanoic acid	234.5 [264.0]	4.783 [4.785]	233.0 [268.0]	4.756 [4.944]

2-hydroxy 2-(pentafluorophenyl) propanoic acid and the corresponding anhydrocarboxylate, these normally forbidden transitions occur as a broad absorption (Table 3.4, the values given in brackets) of high molar absorptivity and are probably due to the effect of a fully substituted benzene ring. It is relevant to note that the effect of a methyl group in atrolactic acid and the anhydrocarboxylate is to dampen the effect of the charge in electronic charge distribution occurring during excitation, although to a lesser extent in the parent acid.

In general, anhydrocarboxylates may be prepared by the direct reaction of phosgene on the copper (II) salt of the corresponding α-hydroxy carboxylic acid. Apparently the presence of electron withdrawing substituents such as phenyl groups, facilitate ring formation by both electronic factors and steric repulsion of the two substituents. The physical methods of characterisation employed herein clearly distinguish between the anhydrocarboxylate and the parent acid. The main chlorine containing impurity, namely the α-chloro acid, is effectively removed by chemical treatment and trace amounts of acid impurity are removed by vacuum sublimation.

The successful synthesis achieved may be considered as a general method of preparation of ring compounds of this type.

CHAPTER 4

The Thermal Decomposition of Phenyl Substituted 1,3-Dioxolan 2,4-Diones

The synthesis of 5-phenyl 1,3-dioxolan 2,4-dione, trivially known as mandelic acid anhydrocarboxylate (MAAC) was first reported by Davies(41) and after heating the compound at 120°C for 16 hours a viscous gum remained. To date, the syntheses of 5-methyl 5-phenyl 1,3-dioxolan 2,4-dione (AAAC) and 5,5-diphenyl 1,3-dioxolan 2,4-dione (BAAC) have not been reported. In this section the kinetic behaviour of these three anhydrocarboxylates during thermal decomposition is discussed, in order to establish a basis for the stability of the ring in the absence of other reacting species. The thermal stability of the series is compared with the analogous anhydrosulphite system and with 5,5-dimethyl 1,3-dioxolan 2,4-dione.

4.1 Results

Thermal decomposition of BAAC and AAAC

The rates of thermal decomposition of BAAC and AAAC were measured in nitrobenzene in the temperature range 90°-120°C. Gas evolution techniques using the kinetic apparatus discussed in Chapter 2, section 2.2, were employed to measure the rate of evolution of carbon dioxide and thus, by equation 6, the rate of disappearance of monomer was concurrently measured. The pressure of carbon dioxide was measured as a function of time and conversion of this data to a conventional first-order plot, $\ln[(P_\infty - P)/P_\infty]$ versus time, showed good straight line behaviour well into the second decade and indicated that the decomposition was first-order in monomer. Figure 4.1 shows typical first-order plots for the decomposition of BAAC and AAAC in nitrobenzene and dekalin.

In the absence of nucleophilic species such as hydroxyl groups, the overall thermal decomposition process may be expressed by equation 23, where $[CO_2]$ and $[M]$ are the concentrations of

$$\frac{d[CO_2]}{dt} = \frac{-d[M]}{dt} = k_1[M] \qquad \ldots\ldots (23)$$

carbon dioxide and monomer respectively and k_1 is the first-order rate constant. Variation of the initial concentration of monomer produced no observable change in the rate constant and no catalysis or inhibition by carbon dioxide was observed under the conditions of these experiments.

The percentage conversion of AAAC to polymer at various temperatures is shown as a function of time in Fig. 4.2. The derived first-order rate constants associated with the decomposition of AAAC are given in Table 4.1, with the corresponding half-lives ($t_{1/2}$). The activation energy (E), pre-exponential factor (A) and the entropy of activation ($\Delta S^{\ddagger}$) were obtained from a conventional Arrhenius plot. The values obtained were of the order expected for a first-order decomposition involving molecular scission of a co-

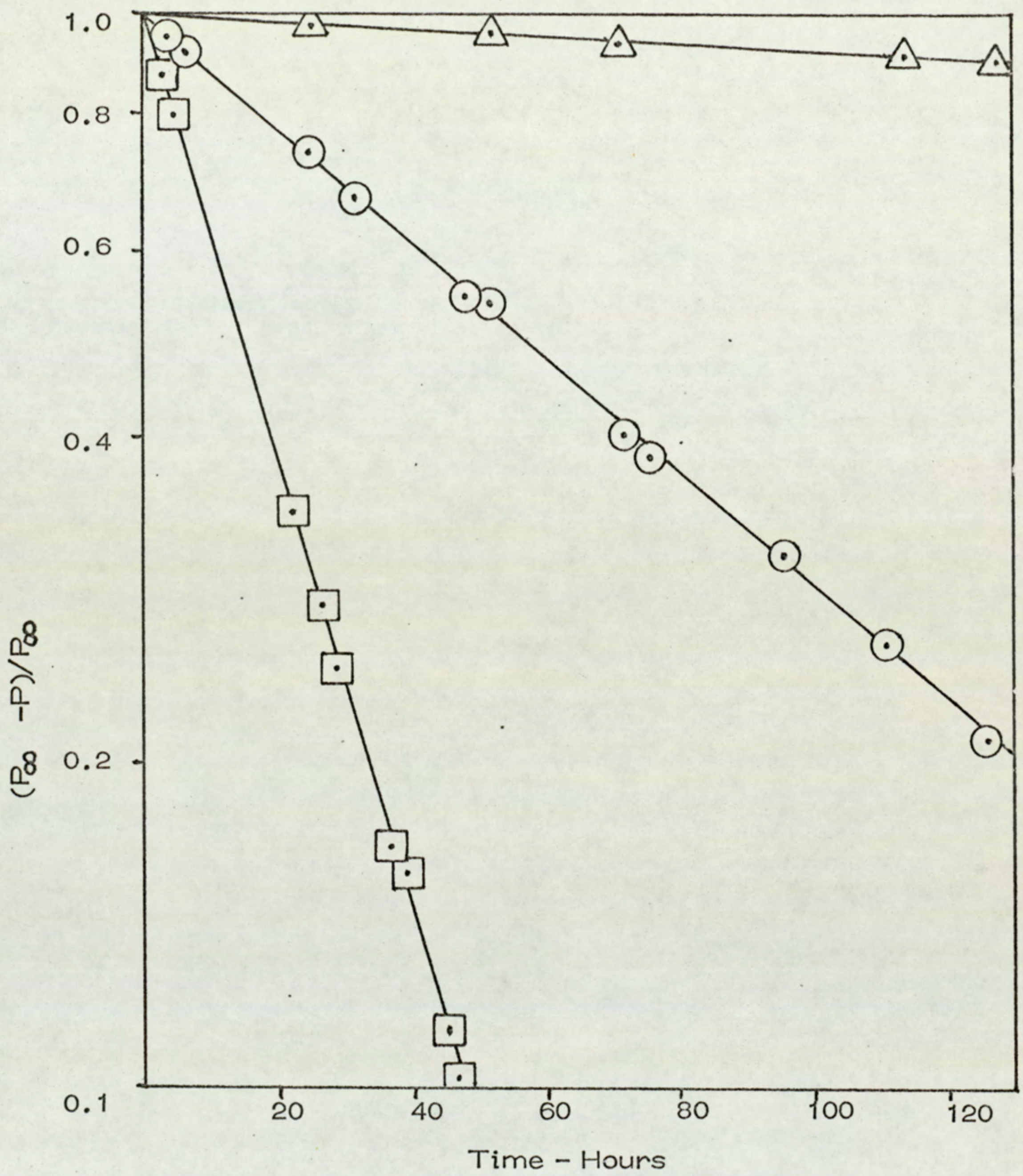


Fig. 4.1 Semi-logarithmic plot of $(P_\infty - P)/P_\infty$ versus time for the thermal decomposition of BAAC and AAAC.

⊡ BAAC in nitrobenzene at 90°C.

⊙ AAAC in nitrobenzene at 110.7°C.

△ BAAC in dekalin at 90°C.

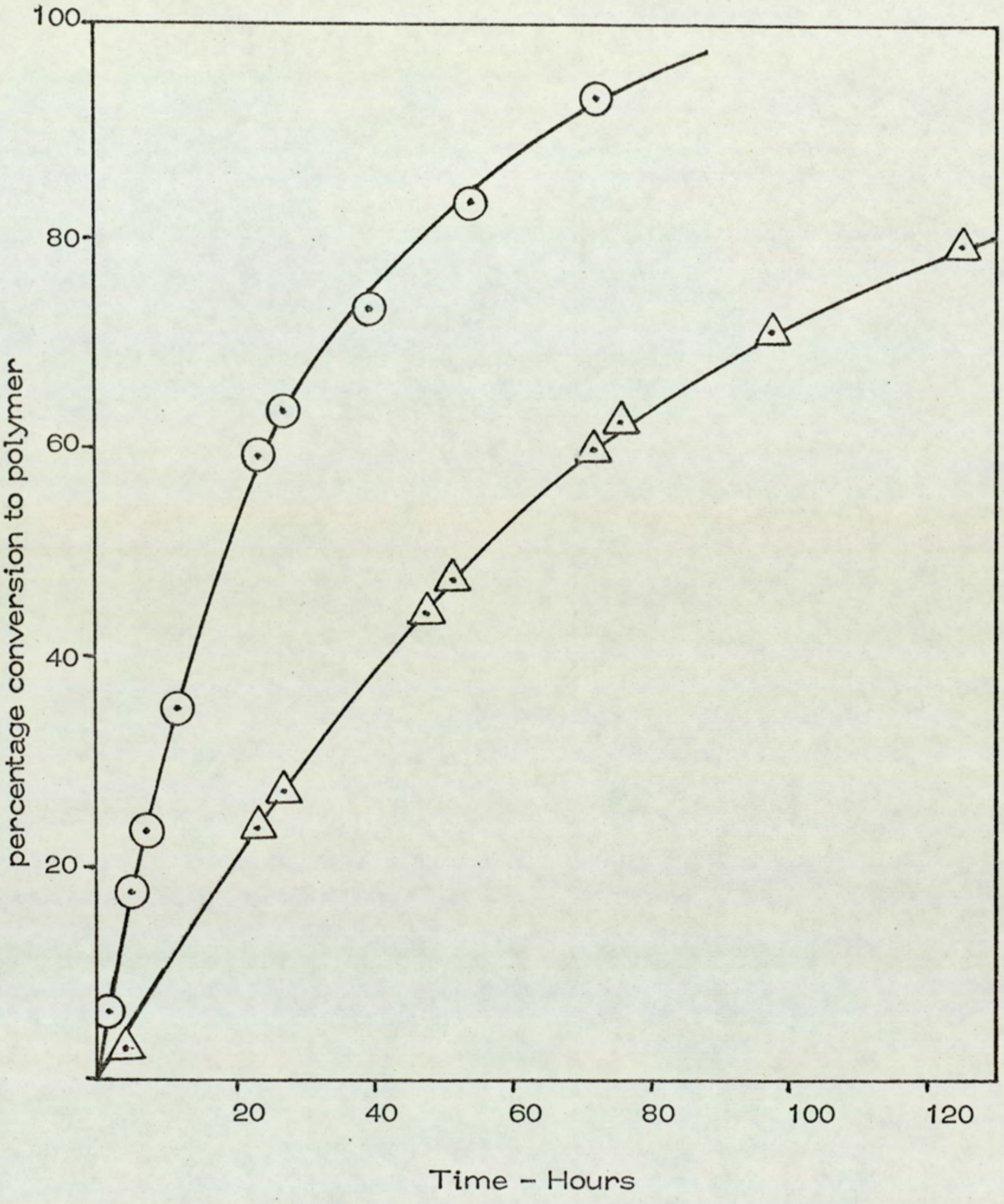


Fig 4.2 The polymerisation at AAAC in nitrobenzene at various temperature, plotted as percentage conversion to polymer against time.

⊙ at 121.6°C.

△ at 110.7°C.

valent bond in a strained ring system.

Table 4.1

First-order rate constants (k_1), half-lives ($t_{1/2}$), energy of activation (E), pre-exponential factor (A) and entropy of activation ($\Delta S^{\ddagger}$) for the thermal decomposition of AAAC in nitrobenzene.

$[AAAC]_o$ = 0.25 mol litre^{-1}.

Temp. °C	$10^6 k_1$(sec^{-1}.)	$t_{1/2}$ (hours)
96.1	0.84	230
102.2	1.54	125
110.7	3.35	57.5
121.6	10.5	18.3
E (kJ mol^{-1}.)	116.9	
A (sec^{-1}.)	2.6×10^{10}	
$\Delta S^{\ddagger}$ (J.K^{-1}mol^{-1}.)	-54.2	

The thermal decomposition of BAAC was studied under reaction conditions similar to those used for AAAC. The effect of a second phenyl substituent in place of a methyl substituent (ca. AAAC) has quite a marked effect on the thermal stability of the anhydrocarboxylate ring. At temperatures around 110°C, the first-order rate constant for the thermal decomposition of BAAC is some 30 times greater than the corresponding rate constant for AAAC. Table 4.2 tabulates the first-order rate constants, half-lives and the associated kinetic parameters for the thermal decomposition of BAAC at temperatures in the range 90° to 110°C. Arrhenius plots for both AAAC and BAAC showed good linear behaviour over the temperature range studied.

Although purified samples of the anhydrocarboxylates were used throughout for kinetic studies, it was observed that remarkably reproducible rate data were obtained even in the presence of small residual amounts of parent acid.

Table 4.2

First-order rate constants (k_1), half-lives ($t_{1/2}$) energy of activation (E), pre-exponential factor (A) and entropy of activation ($\Delta S^{\ddagger}$) for the thermal decomposition of BAAC in nitrobenzene.

$[BAAC]_o$ = 0.23 mol. litre^{-1}.

Temp. °C	$10^5 k_1$(sec^{-1}).	$t_{1/2}$ (mins.)
90	1.31	703
97.5	3.7	315
104.2	6.5	177
110	9.96	116
115.5	20.2	57
*90	0.013	8.7×10^4
E (kJ.mol^{-1})	143.7	
A (sec.$^{-1}$)	4.4×10^{15}	
$\Delta S^{\ddagger}$ (J.K^{-1}.mol^{-1})	+ 46.3	

* Measured in dekalin.

The value of the rate constant for the decomposition of BAAC in dekalin at 90°C is given in Table 4.2 for comparison with that obtained in nitrobenzene. The polarity of the solvent appears to have a pronounced effect on the rate of thermal decomposition of the anhydrocarboxylate ring.

Although the products of decomposition of BAAC were qualitatively similar to those obtained with AAAC, there were two significant differences. In the first place the polymer obtained was of much lower molecular weight ($\overline{M}n < 5,000$) and in the second it was contaminated with a ketonic impurity. The analysis of this product showed it to be benzophenone and the extent of its formation to be approximately 35% at 115°C.

Thermal decomposition of MAAC

The thermal decomposition of MAAC, unlike BAAC and AAAC, showed somewhat peculiar behaviour in that the reaction profile was markedly dependent upon the purity of the anhydrocarboxylate sample. Fig. 4.3 shows semi-logarithmic plots of $(P_\infty - P)/P_\infty$ versus time for the decomposition of samples of MAAC obtained at various stages of purification. The reaction of MAAC with a two molar excess of parent acid at 102°C showed good first-order behaviour with respect to monomer throughout 98% of the reaction. With reference to Fig. 4.3; (d) is a semi-logarithmic plot for the decomposition of MAAC, which had been vacuum sublimed immediately prior to use, in nitrobenzene at 90°C. With this exception

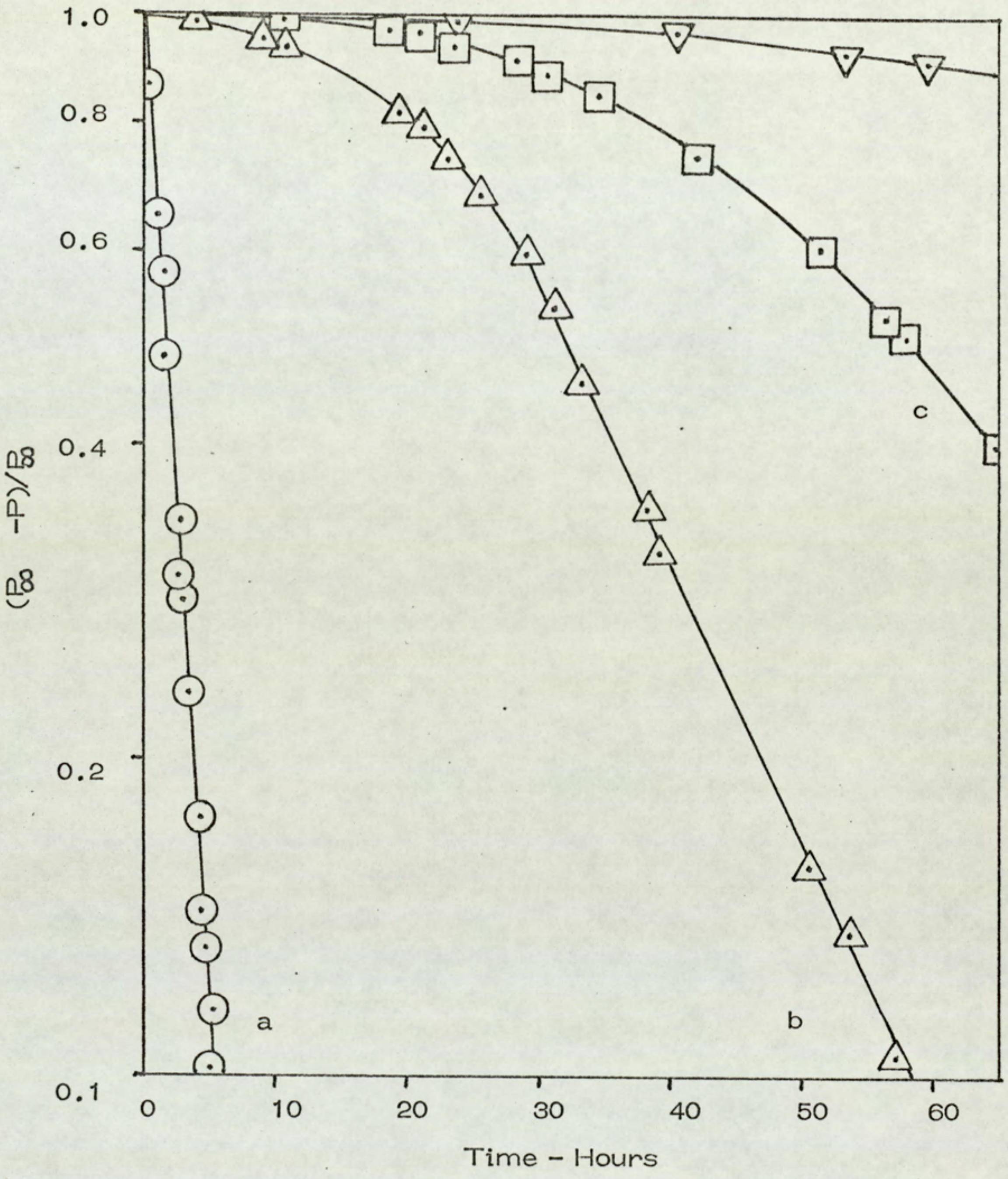


Fig. 4.3 Semi-logarithmic plot of $(P_\infty - P)/P_\infty$ versus time for the decomposition of MAAC in nitrobenzene. $[\mathrm{MAAC}]_o$ = 0.33 mol. litre^{-1}.

a) Vacuum sublimed MAAC with added parent acid at 102°C. $[\mathrm{Acid}]_o$ = 0.66 mol. litre^{-1}.

b) Recrystallised MAAC at 102°C.

c) Vacuum sublimed MAAC at 102°C.

d) Vacuum sublimed MAAC at 90°C.

other decompositions were carried out at 102°C.

The amount of chlorine containing impurity in both the recrystallised and vacuum sublimed samples was at an undetectably low concentration. The absolute exclusion of adventitious traces of moisture is not possible and thus in any sample of anhydrocarboxylate there will be a finite amount of the parent acid. It would appear from the results obtained that the presence of a trace amount of parent acid is responsible for the anomalous behaviour observed during the thermal decomposition of MAAC. The initial rate of decomposition of MAAC at 102°C is 5.2×10^{-7} sec^{-1} ($t_{1/2}$ = 343 hours); by comparison the rate of decomposition of AAAC at the same temperature is 1.54×10^{-6} sec^{-1}. In spite of the susceptibility of the reaction profile to parent acid impurity the purely thermal decomposition, which involves bond scission by a first-order process, occurs at a somewhat slower rate than for AAAC.

In this series of anhydrocarboxylates thermal stability appears to increase with decreasing ring substitution and it is evident that the monosubstituted ring (MAAC) shows a degree of thermal stability greater than that shown by phenyl substituted anhydrocarboxylates having a second substituent at C(5), but the overall reaction profile of the former is very much dependent upon the purity of the sample.

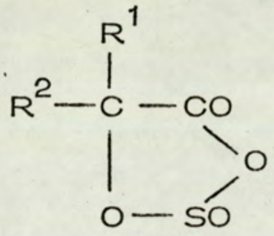
4.2 Discussion

By inspection of the relevant rate constants for the thermal decomposition of MAAC, BAAC and AAAC, the order of thermal stability is; MAAC $>$ AAAC $\gg$ BAAC. The rate constants measured in the case of AAAC and BAAC involve an apparently unimolecular decomposition and the overall process may be expressed by equation 23. The true rate constant for the decomposition of MAAC may in fact be considerably smaller than the estimate given as direct reaction of the parent acid with the anhydrocarboxylate ring may make a significant contribution to the observed rate even during the early stages of the reaction.

The energies of activation, pre-exponential factors and entropies of activation, Tables 4.1 and 4.2, are of an order consistent with a unimolecular process involving scission of a covalent bond. The presence of a second phenyl substituent at C(5) as in the case of BAAC, has a profound effect on the thermal stability of the ring.

In general at a given temperature, on the basis of previous experience with similar ring systems, the thermal stability of the anhydrocarboxylate ring will depend essentially upon three factors; the internal strain of the ring, the nature of the substituents at C(5) and the nature of the reaction medium. The two major contributing factors to ring strain are firstly, the inherent strain due to the actual nature of the ring and its composite parts, which is expected to be quite considerable by virtue of the heterocyclic structure. Bond angles are likely to vary considerably from their optimum value, ring puckering, however, would alleviate a part of this ring strain.

Secondly, the mutual repulsion of large substituents at C(5) will ultimately lead to compression of the internal carbon (5) bond angle. This latter phenomenon is known as the Thorpe-Ingold effect. Thus the incorporation of a second phenyl substituent as in BAAC gives rise to far greater ring strain than does a methyl substituent in AAAC. The thermal stability of alkyl and spirocycloalkyl substituted anhydrosulphites(49) has been explained in terms of the Thorpe-Ingold effect. Glycollic acid anhydrosulphite (I; $R^1 = R^2 = H$) has a first-order rate constant for thermal decomposition at 90°C in nitrobenzene, remarkedly similar to that for lactic acid anhydrosulphite (I; $R^1 = H$, $R^2 = CH_3$).



I

(ca. $k_1 = 5.9 \times 10^{-6}$ sec^{-1}. and $k_1 = 6.0 \times 10^{-6}$ sec^{-1}. respectively)(61) However, the incorporation of a second methyl substituent (I, $R^1 = R^2 = CH_3$) results in a ten-fold increase in the rate constant ($k_1 = 6.1 \times 10^{-5}$ sec^{-1}).(14) The replacement of a single C(5) hydrogen atom by a methyl substituent imparts very little extra strain to the ring, but the accommodation of two methyl substituents is more difficult and leads to a far greater decrease in ring stability.

A more direct ratification of this effect may be gained from the ring stability of spirocycloalkyl substituted anhydrosulphites. The degree of bond angle expansion or contraction at carbon (5) is very closely related to the degree of ring strain inherent in the spirocycloalkyl substituent. For example the first-order rate constants for thermal decomposition of spirocyclopentyl and spirocyclohexyl anhydrosulphites are 1.2×10^{-4} sec^{-1}. and 5.6×10^{-5} sec^{-1}. respectively.(36) The five membered spirocyclopentyl substituent imparts greater anhydrosulphite ring strain than does the virtually strain free spirocyclohexyl substituent. It is interesting to note that the presence of a substituent such as a spirocyclohexyl group shows somewhat greater thermal stability than the dimethyl substituted anhydrosulphite.

The observed order of thermal stability in the phenyl substituted anhydrocarboxylate series is consistent with enhanced ring strain imparted by the successive increase in size of the second substituent at C(5).

The ring opening reactions of dimethyl substituted anhydrocarboxylate in particular thermal decomposition have been tentatively reviewed by Tighe.(44) A value of $k_1 = 1.0 \times 10^{-7}$ sec^{-1}. was obtained for the first-order rate constant for thermal decomposition in nitrobenzene at 90°C. Replacement of one of the methyl substituents by a phenyl substituent would be expected to have a marked effect on the stability of the ring. The presence of a phenyl substituent increases the first-order rate constant by an estimated factor of four which is rather low when compared with thirty-fold increase over this value on incorporation of a second phenyl substituent.

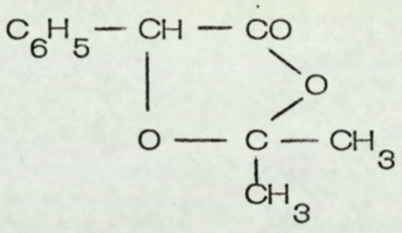
When assessing the relative stability of such ring systems it is necessary to consider the nature of the substituent, with regard to its electron donating or electron withdrawing power. Bischloromethyl substituted anhydrosulphite(62) shows greater thermal stability than the dimethyl derivative, although a more valid comparison would be with the diethyl substituted compound, in which substituent sizes are comparable and where the difference in stability is even more marked. The introduction of chloromethyl substituents on the anhydrosulphite ring leads to enhanced thermal stability due to the electron withdrawing property of the two chlorine atoms.

The phenyl group is regarded as mesomerically an electron donating substituent but inductively electron withdrawing. The opportunity of mesomeric transfer of electrons from the aromatic ring is not easily envisaged and thus the contribution to electron donation by this mode would be expected to be small. Electron withdrawal from the anhydrocarboxylate ring would be difficult to assess at this stage, but could conceivably explain, in conjunction with the relative lack of steric hindrance at the C(5) in MAAC, the peculiar behaviour of this monomer during thermal decomposition. The role of the phenyl group in this environment, as an electron withdrawing substituent, will be quantitatively discussed in the following chapter. In the case of the diphenyl substituted ring the overriding factor is the enhanced ring strain imparted by the increased opening of the phenyl-carbon-phenyl bond essentially due to the steric repulsion of two large polar groups.

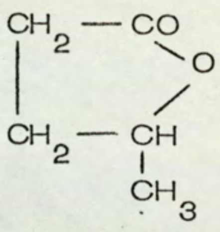
It is generally accepted that the nature of the reaction medium can have a profound effect on the rate of a reaction. A polar solvent facilitates solvolysis of polar species involved in a reaction and can ultimately result in an increase in the rate of reaction. The rate of decomposition of BAAC in nitrobenzene (dielectric constant at 90°C $\simeq$ 25) is 100 times faster than in dekalin (dielectric constant at 90°C $\simeq$ 2.5). While extensive work on the effect of solvent polarity on the rate of thermal decomposition has not been carried out, the results obtained would indicate that in the case of BAAC the use of a solvent of high dielectric constant promotes the formation of a transition state showing polar characteristics. The mechanism of decomposition and the nature of the intermediates will be discussed subsequently.

A similar trend in the magnitude of the rate constants in solvents of varying dielectric constant has been observed in anhydrosulphite systems but attempts to find a quantitative relationship between the first-order rate constants and dielectric constant were reported to be unsuccessful.(49)

The polymerisability of cyclic esters has been reviewed(25) and some generalised assessments of the factors affecting the polymerisability with regard to structure and substituents have been made. In no case was a 5-membered cyclic ester reported to polymerise to any degree and it was suggested that the polymerisability of 5- and 6- membered rings containing a single carbonyl function was very much dependent upon the class of compound involved. For example 2,2-dimethyl-4-phenyl 1,3-dioxolan 5-one (XX) was reported to be resistent to polymerisation as was γ -valerolactone (XXI). Cyclic compounds of this type having 4-, 7- and 8- membered rings polymerise but alkyl and aryl substituents tend to decrease polymerisability.



XX



XXI

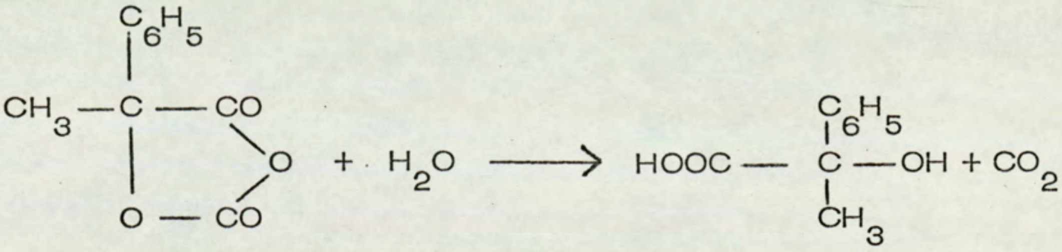
The thermal decomposition of AAAC produced a white amorphous solid the structure of which was consistent with a poly-α-ester.

The thermal decomposition of BAAC in nitrobenzene was unique in that it produced a deep red solution from which oligomeric products of a poly-α-ester were obtained. Polymer obtained from MAAC was difficult to isolate but nevertheless demonstrated that the decomposition of phenyl substituted anhydrocarboxylates at around 100°C was a polymer-forming reaction and emphasised the polymerisability of this class of ring compound. The rather disappointing yield of polymer from BAAC may seem superficially to give support to previously reported observations that aryl substituents decrease polymerisability,(25) but it is quite apparent that the presence of one phenyl group on the ring is essential in promoting the desired reactivity of the anhydrocarboxylate for polymer formation. This is exemplified by the fact that the dimethyl substituted anhydrocarboxylate is not a convenient precursor to the polymer.

The thermal polymerisation of anhydrosulphites has been proposed to occur by the thermal fragmentation of the ring to form a polymerisable intermediate, formally depicted as an α-lactone, and concurrent elimination of sulphur dioxide. Adventitious traces of moisture give rise to a corresponding quantity of parent α-hydroxy acid. The chain growth process involves a rapid bimolecular reaction of the α-lactone with, in the first instance the hydroxyl group of the parent acid, and subsequently with the hydroxyl group which forms the chain end.

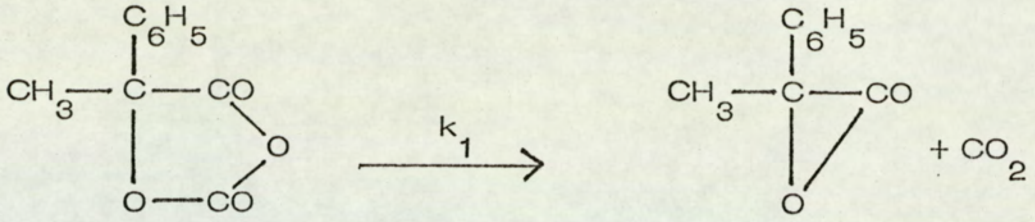
The kinetic observations of the polymerisation of AAAC and BAAC are identical to those of the analogous anhydrosulphite system. Thus a similar polymerisation sequence is proposed during the decomposition of these anhydrocarboxylates in nitrobenzene.

Trace amounts of parent acid are present due to the reaction of adventitious traces of moisture with an equimolar amount of anhydrocarboxylate, equation 24. The rate determining step of the polymerisation is considered to be



.... (24)

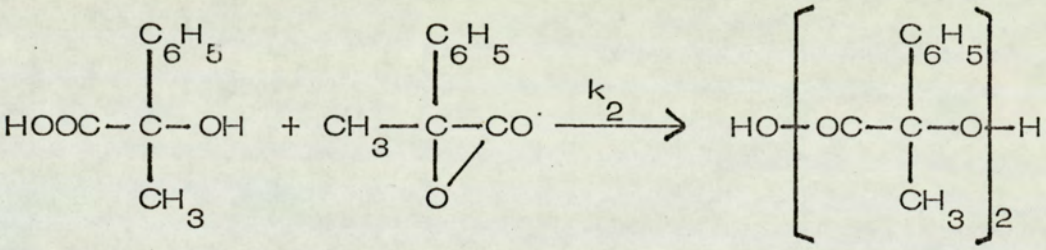
the decomposition of the anhydrocarboxylate to yield a postulated α-lactone intermediate (XXII) and loss of carbon dioxide, equation 25.



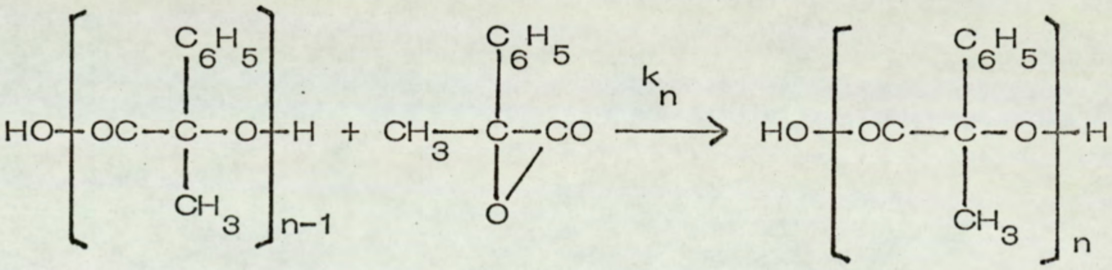
XXII

.... (25)

The chain growth process is qualitatively similar to that formulated in the case of anhydrosulphites and involves reaction of the α-lactone with the terminal hydroxyl group of the polymer chain as shown in equations 26 and 27.



.... (26)

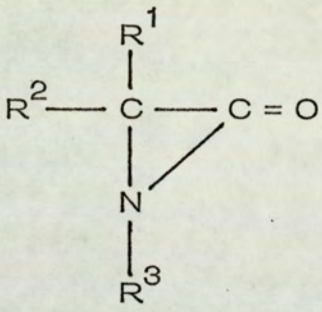


.... (27)

It is proposed that the α-lactone (XXII) is a very reactive species and that the rate constants associated with the propagation steps; k_2, k_3 ..... k_n etc., are very much larger than k_1.

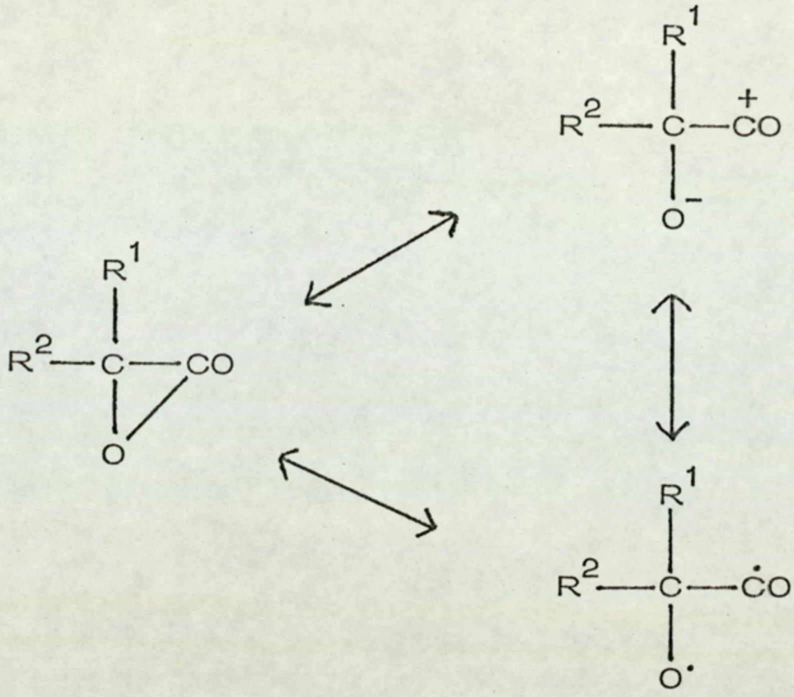
Supporting evidence for the existence of the α-lactone is found in the mass spectrum of anhydrocarboxylates. The thermal stability of the ring is such that a prominent top mass peak corresponding to the molecular weight is present. The initial loss of a CO_2 fragment gives rise to a (M-44) peak in the spectrum, of which the corresponding peak for AAAC is particularly strong. Similar fragmentation patterns have been observed in the anhydrosulphite series with the exception of a top mass peak.

The characterisation of α-lactones by conventional means has not been achieved although their transient existence is not doubted. Di-tert-butylacetolactone has been prepared in Freon 11 at -78°C, and reaction with ammonia yields di-tert-butylglycine.(63) In contrast the analogous α-lactam structure (XXIII) has been isolated and characterised and is in some cases stable above 120°C.(64)

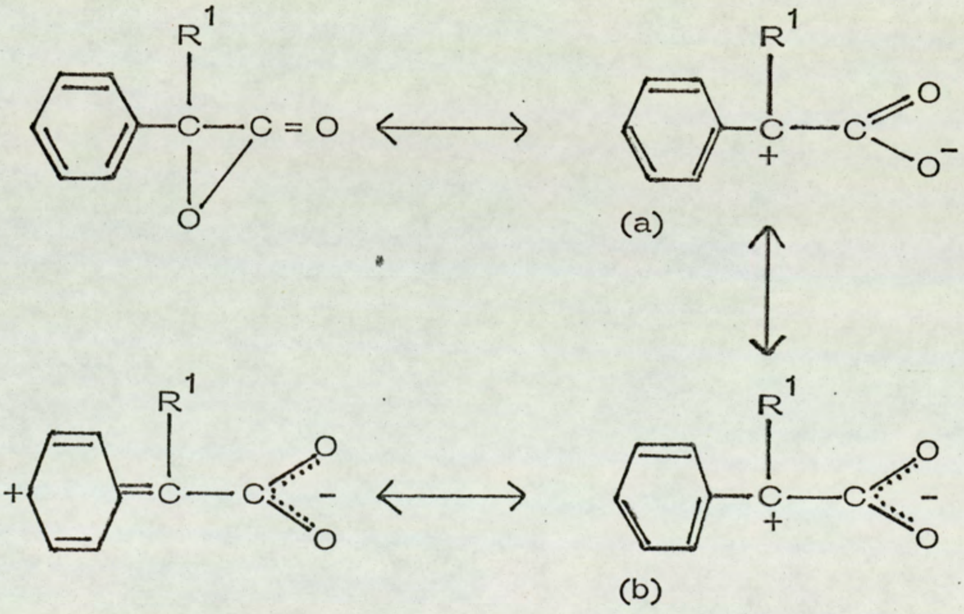


XXIII

The precise nature of the α-lactone has not been adequately ascertained; several resonance forms may be written (XXIV), from the purely covalent bonding to the extreme diradical and polar forms. In the case of alkyl substituted α-lactones the diradical or polar forms would not be expected to contribute greatly to the time averaged life of the intermediate. However, when one of the substituents is a phenyl group an entirely different mode of resonance stabilisation may occur as shown by XXV.



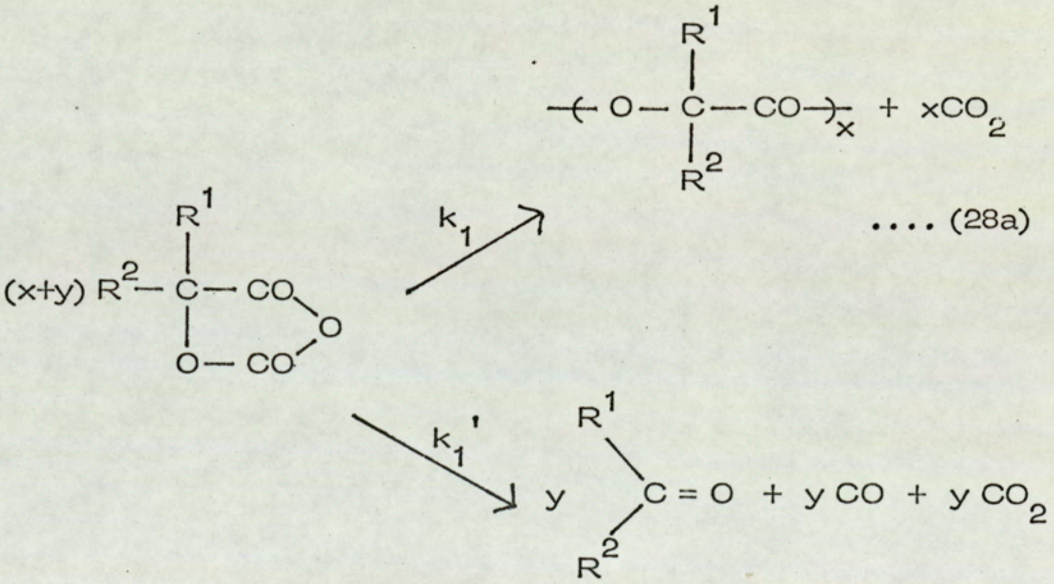
XXIV



XXV

Circumstantial evidence is presented for the existence of XXVa and XXVb in that the reaction of diphenylacetolactone with methanol results in the formation of α-methoxy benzilic acid and not the expected ester.(63) The α-lactone was formed by the reaction of diphenylketene with ozone at $-78^{\circ}C$, and the product of the reaction in the absence of methanol was reported to be the polyester of benzilic acid.

G.L.C. analysis of the reaction mixture from the thermal decomposition of BAAC at $115.5^{\circ}C$ showed that an amount of benzophenone corresponding to about 35% of the product was present. This secondary fragmentation to ketone has been observed to occur in anhydrosulphites.(49) The formation of ketone and polymer is controlled by two competing first-order reactions which may be conveniently represented by equations 23a and 28b.



.... (28a)

.... (28b)

The rate equation governing these two processes may be expressed as in equation 29

$$\frac{-d[M]}{dt} = \frac{d[P]}{dt} + \frac{d[K]}{dt} = (k_1 + k_1')[M] \qquad \text{.... (29)}$$

where [M], [P] and [K] are the concentrations of anhydrocarboxylate, polymer and ketone respectively. The values of k_1 and k_1' may be deduced from the relationship given in equation 30 from a consideration of the ratio of product formation; k is the overall observed rate constant.

$$k = k_1 + k_1' \qquad \text{.... (30)}$$

A detailed investigation of these two competing reactions has been carried out for 5,5-(bis-chloromethyl) anhydrosulphite.(62) Activation energies obtained for ketone formation were of the order of 150 kJ mol^{-1} ($\Delta S^{\ddagger} \sim + 40$ J.K.$^{-1}$ mol.$^{-1}$), whereas those for polymer formation were substantially lower, E = 120 kJ mol.$^{-1}$ ($\Delta S^{\ddagger} \sim - 30$ J.K.$^{-1}$ mol.$^{-1}$). This additional fragmentation process yielding ketone, which amounts to about 35% of the reaction, probably accounts for the unusually high activation energy obtained for the thermal decomposition of BAAC. It must also be noted that the entropy of activation has a positive value for this process, unlike the value obtained for the thermal decomposition of AAAC which is negative.

Ketone formation in the thermal decomposition of AAAC and MAAC was not detected using G.L.C., but by analogy with anhydrosulphite systems would be expected to be appreciable at temperatures in excess of 130°C.

The thermal decomposition of MAAC presents several anomalous features in that small concentrations of parent acid impurity present in normal samples of anhydrocarboxylate enhance the decomposition at temperatures in the region of 100°C, so that reaction times are considerably reduced. The effect of this is that the overall contribution of genuine unimolecular thermal decomposition of the ring is relatively small within the total time of reaction and for this reason little benzaldehyde would be expected to be formed.

With reference to Fig. 4.3, it would appear that the form of the reaction profile for MAAC is markedly dependent upon the purity of the anhydrocarboxylate with respect to parent acid impurity and that the acid is taking part in some additional reaction with the anhydrocarboxylate. In spite of the form of the reaction profile, the initial rate of decomposition of MAAC will approximate to the thermal fragmentation process and comparison of this value with corresponding values for AAAC and BAAC is instructive in that it may be demonstrated that the order of thermal stability is the same as the order of total substituent size at C(5). The rate constant for purely thermal decomposition of MAAC could be determined by carrying out the reaction at high temperatures at which the fragmentation process would swamp the effect of a small amount of impurity. But as previously discussed, higher temperatures tend to lead to an increase in the formation of ketone (or aldehyde), and thus the value of the rate constant would not reflect a true assessment of the polymer forming reaction.

The decomposition of phenyl substituted anhydrocarboxylates in the absence of added initiators at temperatures in the region $90^{\circ}-130^{\circ}C$ is not an altogether satisfactory method of polymer formation, with perhaps the exception of MAAC and AAAC, for a number of reasons. Firstly, the thermal stability is such that prolonged reaction times are required and in order to substantially reduce this time, higher temperatures must be used. Such reaction conditions increase the susceptibility of the monomer to a secondary fragmentation process yielding carbon monoxide and ketone (or aldehyde) which considerably reduces the yield of polymer. High temperatures are not favourable for the formation of polymers with a high degree of tacticity and thus the polymers so formed would tend to be amorphous and soluble in many organic solvents. High reaction temperatures also necessitate the use of high boiling point solvents such as nitrobenzene and unless a miscible cosolvent in which the polymer is insoluble is used, product isolation becomes difficult.

It is evident, therefore, that a more suitable mode of polymerisation would be by the use of an initiator. For this type of polymerisation, a necessary stipulation is that the monomer must contain an active site and be susceptible to attack by a regenerated species. In the subsequent chapter an assessment is made of the reactivity of the series of phenyl substituted anhydrocarboxylates to nucleophilic attack and to the extent they may lend themselves to an initiated mode of polymerisation.

CHAPTER 5

Steric, Electronic and Solvent Effects in the bimolecular reaction of Phenyl Substituted 1,3-Dioxolan 2,4-Diones with alcohols

The thermal polymerisation of phenyl substituted anhydrocarboxylates occurs essentially by the initial loss of carbon dioxide to form a postulated α-lactone intermediate which takes part in a rapid propagation step by reaction with a continually regenerated hydroxyl group, as expressed in equations 25-27. In any anhydrocarboxylate sample there will be a trace amount of parent acid resulting from the reaction of the anhydrocarboxylate with adventitious traces of moisture. Thus a mode of polymerisation which has not yet been considered, is that which occurs by direct attack of the terminal hydroxyl group at the C(4) carbonyl of the anhydrocarboxylate ring. The polymerisability of NCA derivatives is closely related to the reactivity of the ring with amine groups. By direct analogy with this system it would be expected that the polymerisability of anhydrocarboxylates would bear a similar relationship to the reaction of the ring with hydroxyl groups.

In this section structure/reactivity relationships within the monomer molecule are assessed by studying the kinetic behaviour of the anhydrocarboxylate in the bimolecular reaction with various alcohols. The relative magnitude of this bimolecular contribution during thermal polymerisation is discussed with particular reference to the attacking species and the reaction site, and the system as a whole compared with the anhydrosulphite system and the polymerisation of NCA derivatives.

The rate of reaction of the anhydrocarboxylate with benzyl alcohol was found to be very susceptible to changes in the solvent medium. The results obtained have been rationalised in terms of a solvent property parameter and the implications of these results are also discussed.

5.1 Results

Reaction with Benzyl Alcohol

The rates of decomposition of MAAC, AAAC and BAAC were measured in benzyl alcohol at temperatures between 35° and 80°C. Benzyl alcohol was chosen for a number of reasons; it has a high boiling point and is of reasonably high dielectric constant. In addition the general steric and electronic features associated with the nucleophile are similar to those of the terminal hydroxyl species. A useful comparison may also be made with the anhydrosulphite system. By maintaining the hydroxyl nucleophile constant important assessments may be made on the relative electronic and steric effects associated with this bimolecular reaction within the series of phenyl substituted anhydrocarboxylates.

Gas evolution techniques were used to follow the rate of reaction by measuring the pressure of the evolved carbon dioxide. Benzyl alcohol was used as the solvent medium and thus the concentration of hydroxyl groups remained virtually unchanged throughout the reaction. The variation of initial rates of CO_2 evolution with hydroxyl concentration demonstrated that the reaction was first-order with respect to hydroxyl concentration. A graphical presentation of $\ln[(P_{\infty}-P)/P_{\infty}]$ versus time gave a straight line plot and good first-order behaviour was observed to the end of the second decade. Fig. 5.1 shows typical plots for the reaction of MAAC and AAAC at 55°C and for BAAC at 60°C.

No CO_2 catalysis or inhibition was observed under the conditions of the experiment and variation of initial monomer concentration produce no significant change in the rate constant.

The reaction of anhydrocarboxylates with benzyl alcohol may be expressed by the following rate equation;

$$\frac{d\,[CO_2]}{dt} = \frac{-d\,[M]}{dt} = k_b[M]\,[OH] \qquad \ldots\ldots (30)$$

where $[CO_2]$, $[M]$ and $[OH]$ refer to the concentrations of carbon dioxide, monomer and benzyl alcohol respectively and k_b is the second-order rate constant. Equation 30 may be simplified to;

$$\frac{-d\,[M]}{dt} = k_b'\,[M] \qquad \ldots\ldots (31)$$

where k_b' is a pseudo first-order rate constant obtained from the graphical plot of $\ln[(P_{\infty}-P)/P_{\infty}]$ versus time, which enables k_b to be calculated from equation 32. The value of [OH] for benzyl alcohol is 9.6 mol. litre^{-1}.

$$k_b = \frac{k_b'}{[OH]} \qquad \ldots\ldots (32)$$

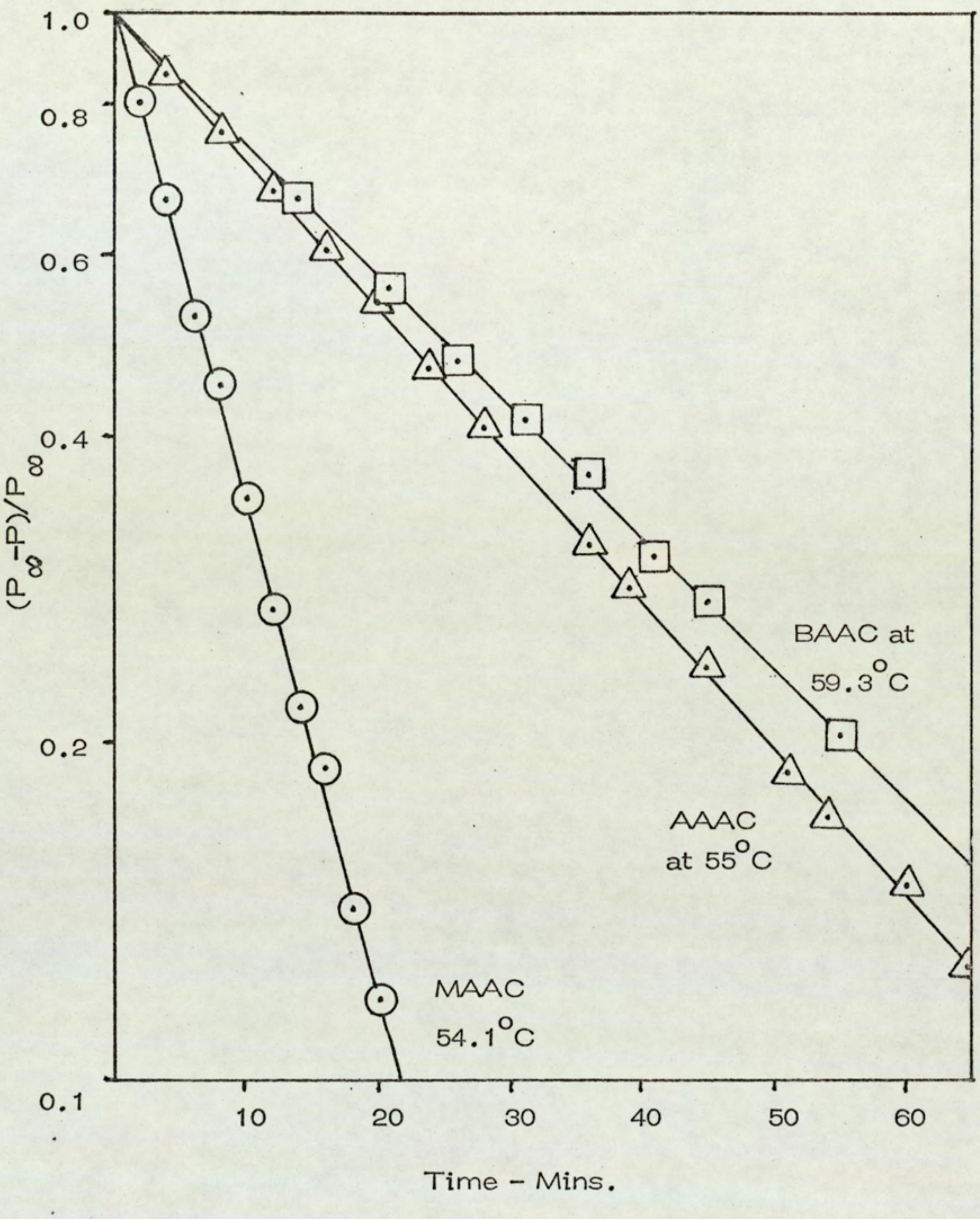


Fig. 5.1 Semi-logarithmic plot of $(P_\infty - P)/P_\infty$ versus time for the reaction of MAAC (⊙), AAAC (◬) and BAAC (⊡) with benzyl alcohol.

Table 5.1

Second-order rate constants (k_b), and the associated kinetic parameters for the reaction of MAAC with benzyl alcohol. $[MAAC]_o = 0.32$ mol. litre^{-1}.

Temp. ^oC	$10^4\ k_b$ l.mol.$^{-1}$sec.$^{-1}$
34.8	0.84
39.5	1.0
45.1	1.3
50	1.6
54.1	1.85
E (kJ. mol^{-1})	34.6
A (i.mol^{-1}sec^{-1})	83
$\Delta S^{\ddagger}$(J.K^{-1}mol^{-1})	-251

Equation 30 does not take into account the thermal decomposition of the anhydrocarboxylate. The full expression is given in equation 33.

$$\frac{-d[M]}{dt} = k_1[M] + k_b[M][OH] \qquad \ldots.(33)$$

Equation 33 may be written in the following form;

$$\frac{-d[M]}{dt} = (k_1 + k_b[OH])[M] \qquad \ldots.(34)$$

The rate constant, k_1, is for the purely thermal decomposition of the anhydrocarboxylate in a particular solvent. The actual rate of thermal decomposition in benzyl alcohol cannot be measured absolutely as the bimolecular reaction swamps the thermal rate. However, to a first approximation, this rate of thermal decomposition may be taken to be of a similar magnitude to that in nitrobenzene, but at the temperatures at which the investigation was carried out the thermal rate constant is insignificant compared with the rate constant for the bimolecular reaction. The ratio of the rate of reaction in benzyl alcohol to the rate in a non-hydroxylic solvent such as nitrobenzene serves as a useful quantity by which to assess the bimolecular contribution during thermal polymerisation. This quantity will be discussed in greater detail in the latter part of this section. For the purpose of assessing the reactivity of the series of anhydrocarboxylates to nucleophilic attack, the contribution by the thermal route to the decomposition may be ignored and hence equation 33 reduces to equation 30.

The derived second-order rate constants (k_b) for the reaction of MAAC, AAAC and BAAC are given in Tables 5.1, 5.2 and 5.3 respectively. The corresponding activation energies (E), pre-exponential factors (A) and the entropies of activation ($\Delta S^{\ddagger}$) were obtained from Arrhenius plots of the logarithm of the second-order rate constants versus the reciprocal of the absolute temperature. In all cases the Arrhenius plots showed good linear behaviour over the temperature range studied. Fig. 5.2 shows a typical Arrhenius plot for the reaction of AAAC with benzyl alcohol.

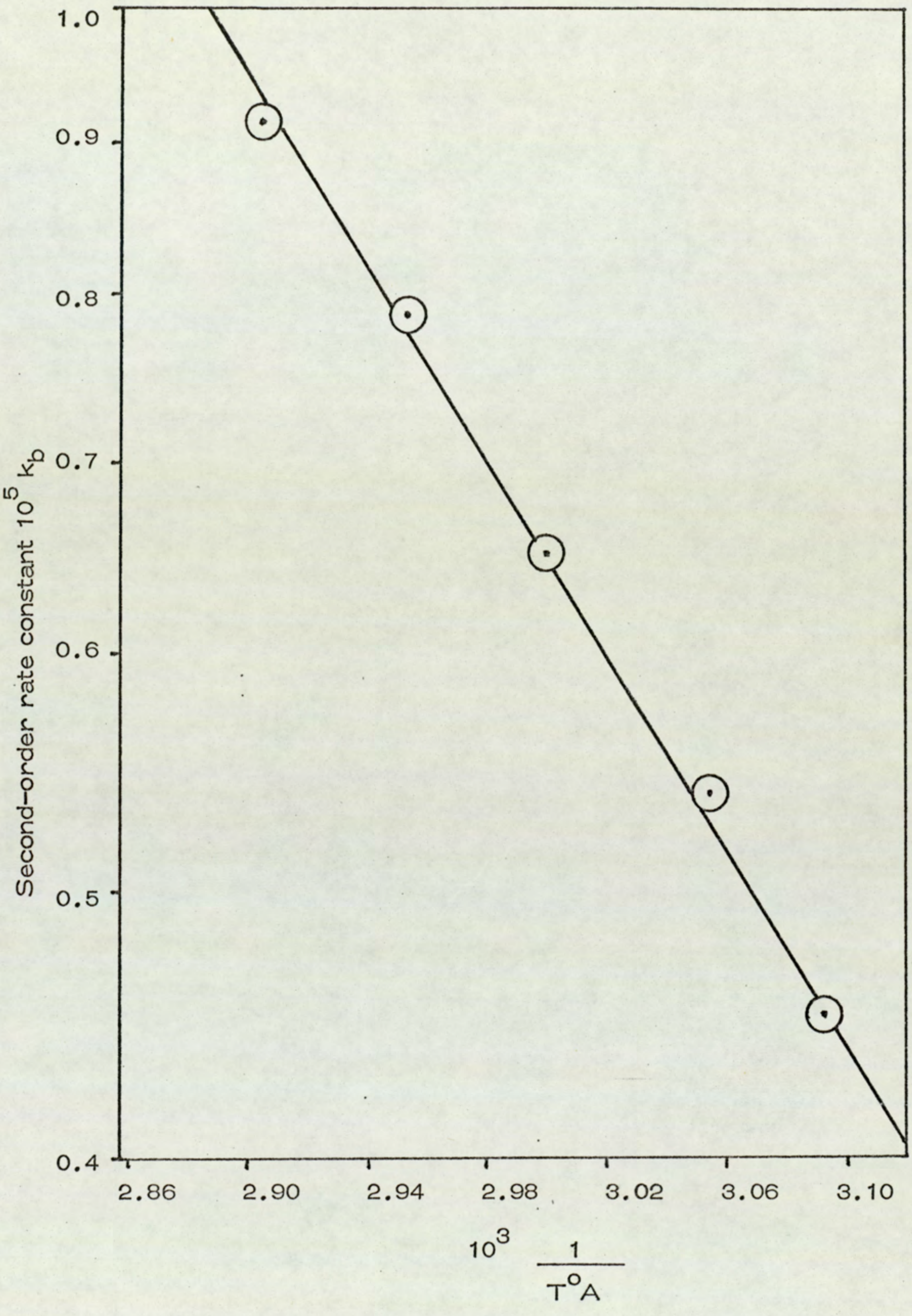


Fig. 5.2 Arrhenius plot of the second-order rate constants k_b versus the reciprocal of absolute temperature for the reaction of AAAC with benzyl alcohol. Temperature range $50^o - 70^oC$.

Table 5.2

Second-order rate constants (k_b) and the associated kinetic parameters for the reaction of AAAC with benzyl alcohol.

$[AAAC]_o = 0.31$ mol. litre.$^{-1}$

Temp. ^oC	$10^5 k_b$ l.mol.$^{-1}$ sec.$^{-1}$
49.8	4.4
55	5.4
60	6.5
65	7.9
70.1	9.1
E (kJ. mol.$^{-1}$)	34.4
A (l.mol.$^{-1}$sec.$^{-1}$)	16
$\Delta S^{\ddagger}$ (J.K^{-1}mol.$^{-1}$)	-262.5

Table 5.3

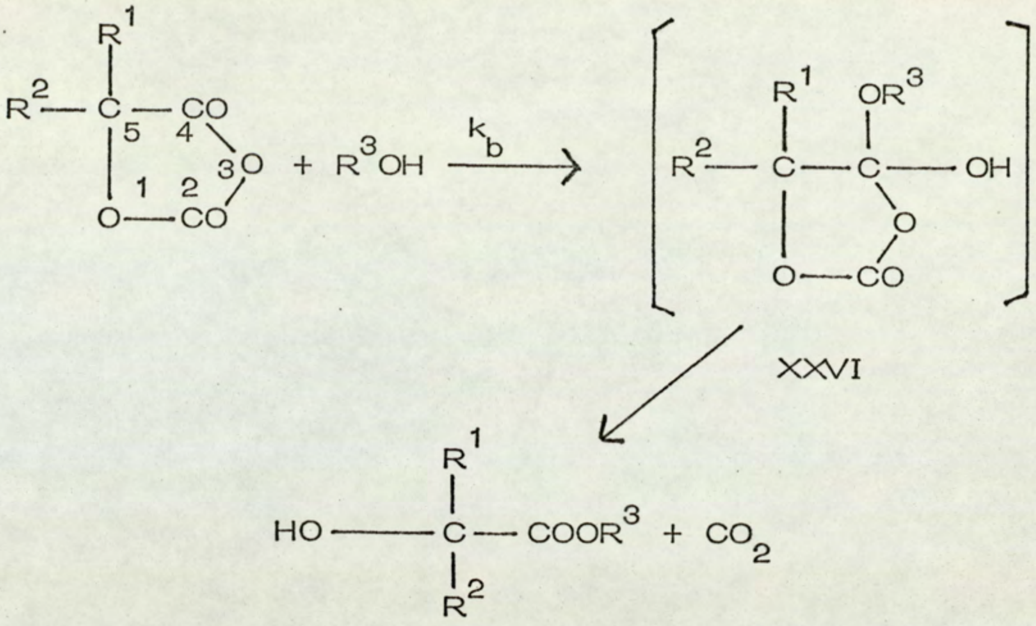
Second-order rate constants (k_b) and the associated kinetic parameters for the reaction of BAAC with benzyl alcohol. $[BAAC]_o$ = 0.28 mol. litre^{-1}.

Temp. ^oC	$10^5 k_b$ l. mol.$^{-1}$ sec.$^{-1}$
59.3	4.77
65	5.46
70.2	7.0
75	8.03
80.4	9.5
E (kJ. mol.$^{-1}$)	32.5
A (l. mol.$^{-1}$ sec.$^{-1}$)	5.9
$\Delta S^{\ddagger}$ (J.K.$^{-1}$mol.$^{-1}$)	-27

By inspection of Tables 5.1, 5.2 and 5.3 it can be clearly seen that the reactivity of a series of phenyl substituted anhydrocarboxylates with a given nucleophile, such as benzyl alcohol, bears no parallel relationship to the thermal stability of the anhydrocarboxylate. The results do indicate that the reactivity is closely related to the size of the second substituent at C(5) when one substituent remains constant at a phenyl group. The energies of activation are considerably lower than those encountered for thermal decomposition and are of the order to be expected for reactions involving nucleophilic attack at an activated site.

Calculated pre-exponential factors are low and the entropies of activation ($\Delta S^{\ddagger}$) are highly negative. This would suggest that the reaction path of the incoming nucleophile is sterically hindered and that the formation of the transition state results in a higher degree of order than that associated with the reactant state. When considering the order of reactivity of the series with benzyl alcohol, the observed order appears to be in good agreement with the order expected when considering substituent size and from a consideration of the kinetic parameters obtained.

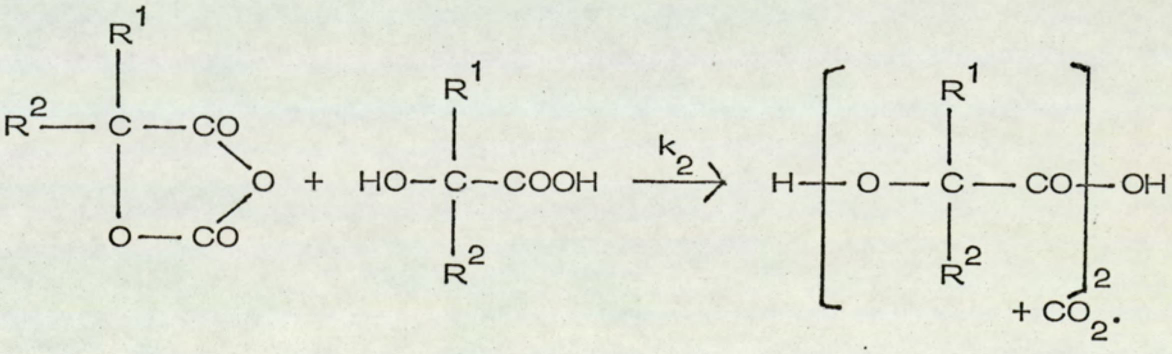
Reaction products were isolated and examined principally by G.L.C. and infrared spectroscopy and were separated by fractional distillation. In each case the product was the corresponding α-hydroxy carboxylic acid ester whose formation follows the general equation 35,



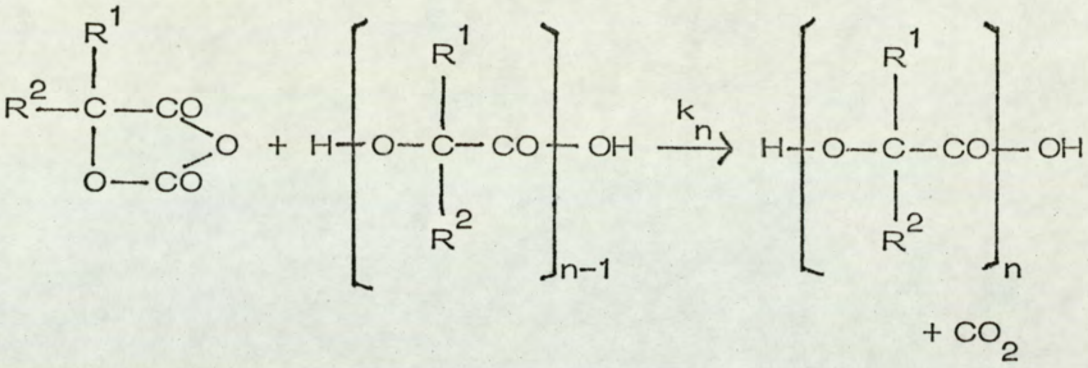
.... (35)

The addition of the alcohol to the C(4) carbonyl is envisaged as the rate determining step (k_b), with the loss of carbon dioxide and proton migration as the rapid decomposition of the intermediate (XXVI).

As previously mentioned there will in any thermal polymerisation of this type, be a bimolecular contribution to polymer formation, which involves the direct attack of a terminal hydroxyl group at the C(4) carbonyl, as shown in equations 36 and 37.



.... (36)



.... (37)

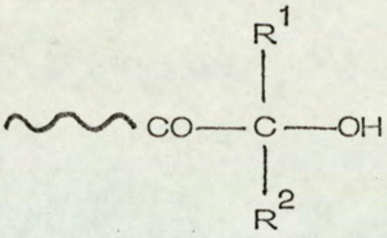
The value of the ratio of the rate of decomposition in benzyl alcohol and the rate in nitrobenzene; i.e. $(k_1 + k_b[OH])_{B.A.}/(k_1)_{N.}$, (where the subscripts B.A. and N. refer to benzyl alcohol and nitrobenzene respectively) enables an assessment to be made of the extent of this bimolecular contribution. For values of this ratio substantially greater than unity there is a significant bimolecular contribution as the value of $k_b[OH]$ becomes important. Table 5.4 gives the value of this ratio at 50°C with the corresponding second-order rate constants. The value of the ratio for MAAC is probably underestimated due to the fact that initial rates were taken to enable a rate constant for purely thermal decomposition to be obtained. The high values may be interpreted in terms of the opportunity for the bimolecular route to occur and the extent to which it does occur. In the case of BAAC there is a considerable degree of steric hindrance associated with the attacking nucleophile and for MAAC one side of the ring is relatively unsterically hindered. The nature of the propagating species (XXVII) during bimolecular polymerisation will affect the extent to which this process may occur.

Table 5.4

Second-order rate constants (k_b) for the decomposition of MAAC AAAC and BAAC in benzyl alcohol at 50°C and the corresponding values of the ratio $(k_1 + k_b[OH])_{B.A.}/(k_1)_N$.

Anhydrocarboxylate	$10^5\ k_b$ l.mol.$^{-1}$sec.$^{-1}$	$\frac{(k_1 + k_b[OH])_{B.A.}}{(k_1)_N}$
MAAC	16.0	$> 4.2 \times 10^5$
AAAC	4.4	1.12×10^5
BAAC	3.7 *	1.16×10^4

*calculated from Arrhenius plot.



$$\sim\sim\sim CO-\overset{\displaystyle R^1}{\underset{\displaystyle R^2}{C}}-OH$$

(XXVII)

The anhydrocarboxylate possessing two phenyl groups at C(5) will regenerate a propagating species (XXVII) where $R^1 = R^2 = C_6H_5$ and thus a sterically hindered monomer molecule will produce a sterically hindered propagating nucleophile and reduce the contribution of the bimolecular route in a two-fold manner.

The results indicate that the bimolecular route could contribute significantly but provided the concentration of terminal hydroxyl groups is sufficiently low, would not be the predominant mode of polymerisation during thermal decomposition.

Reaction with various Alcohols

The rates of decomposition of MAAC, AAAC and BAAC in a series of alcohols were measured in order to assess the effect of the structure of the attacking nucleophile for a given anhydrocarboxylate. The results showed good first-order behaviour in monomer and the decomposition obeyed the general rate equation expressed in equation 30. The decomposition of AAAC and BAAC was carried out using the alcohol as solvent and in the absence of a cosolvent. In the case of MAAC, however, the decomposition was carried out using nitrobenzene as a cosolvent in order to provide a control experiment in which to minimise the effect of the alcohol as reaction medium and to reduce the rate of reaction to a value which could be measured using the conventional sealed constant volume apparatus previously described. The results are presented in Tables 5.5 and 5.6. In all cases product isolation and characterisation showed that the corresponding ester had been formed according to equation 35.

Table 5.5

Second-order rate constants (k_b) for the decomposition of (i) AAAC at 45°C, $[AAAC]_o$ = 0.21 mol. litre^{-1}; and (ii) BAAC at 55.3°C, $[BAAC]_o$ = 0.19 mol. litre^{-1}, in a series of alcohols. Approximate dielectric constants are given.

Alcohol	Dielectric constant (approx.)	AAAC $10^4 k_b$ l.mol.$^{-1}$ sec.$^{-1}$	BAAC $10^4 k_b$ l.mol.$^{-1}$ sec.$^{-1}$
isopropanol	13	3.0	53.0
n-propanol	15	1.3	4.1
2-methyl propanol	13	0.8	1.8
benzyl alcohol	11	0.36	3.2
tert-butanol	10	0.34	1.0

Table 5.6

Second-order rate constants (k_b) for the decomposition of MAAC at 44.5°C in a series of alcohols, using nitrobenzene as a cosolvent. $[MAAC]_o = 0.39$ mol. litre^{-1}, $[\text{ØNO}_2] = 4.9$ mol. litre^{-1}. Approximate dielectric constants are given.

Alcohol	Dielectric constant (approx.)	[OH] mol. litre^{-1}	$10^4 k_b$ l.mol.$^{-1}$ sec.$^{-1}$
isopropanol	24	6.53	10.6
n-propanol	25	6.68	2.2
2-methylpropanol	25	5.41	1.3
benzyl alcohol	24	4.82	0.39
tert-butanol	23	5.32	0.25
benzyl alcohol*	11	9.63	1.3

*with no nitrobenzene as cosolvent.

It is apparent that the spread of activity observed on varying the structure of the anhydrocarboxylate to a given nucleophile is also reflected in the results obtained by varying the structure of the attacking nucleophile to a given anhydrocarboxylate ring. The reactivity of an anhydrocarboxylate to a series of alcohols will depend primarily on the nucleophilicity of the hydroxyl species, the steric hindrance associated with the reaction path of the incoming nucleophile and probably to a considerable extent, the nature of the solvent medium. With the exception of the reaction of

BAAC with 2-methyl propanol, the order of reactivity in the series of alcohols with the three anhydrocarboxylates is the same. It is interesting to note that there appears to be quite a fine balance between the steric and electronic effects associated with the attacking nucleophile. In all cases the reaction with isopropanol is by far the most rapid, and yet the introduction of a third methyl substituent in place of the secondary hydrogen results in a decrease in reactivity with the anhydrocarboxylate. The introduction of a methyl group on the n-propyl alcohol chain, displaced from the hydroxyl nucleophile by one methylene unit, to give 2-methyl propanol results in a decrease in the rate of reaction but which is by no means as great as in the latter case.

Correlation of the relative magnitude of the steric effect and the electronic or polar effect of a substituent with the measured rate of a chemical reaction is difficult. The Taft $\rho^{*}\sigma^{*}$ Equation (38) permits the reaction rates of a large number of aliphatic reactions to be correlated with σ^{*}, which is considered as a polar substituent parameter; ρ^{*} is an empirical parameter dependent upon the nature of the reaction and on reaction conditions.

$$\log \frac{k}{k_o} = \rho^{*}\sigma^{*} \qquad \ldots.(38)$$

Deviations from equation 38 may be due to steric effects associated with the reaction and a second equation may be used, equation 39.

$$\log \frac{k}{k_o} = sE_s \qquad \ldots.(39)$$

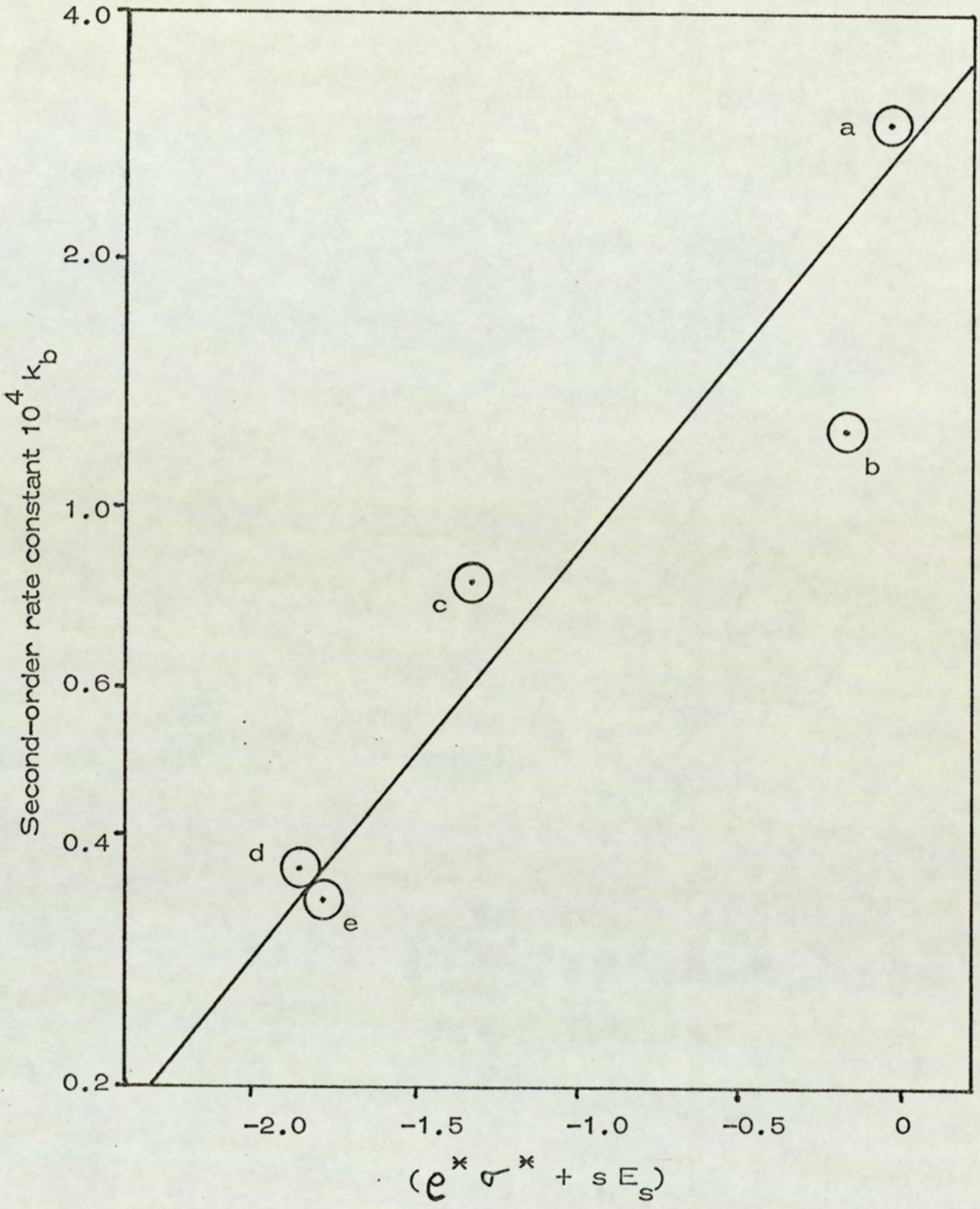
E_s may be identified as a steric parameter. The standard reaction used for the determination of relative steric effects is the acid catalysed hydrolysis of an ester in which the polar effects are comparatively small. For reactions in which the steric effects of substituents involve a similar mechanism to ester hydrolysis equation 40 is applicable.

$$\log \frac{k}{k_o} = \rho^{*}\sigma^{*} + sE_s \qquad \ldots . (40)$$

The values of ρ^{*} and s are determined empirically and may be considered as the relative magnitude of the polar and steric effects respectively. Equation 40 may be rewritten thus;

$$\log k = \rho^{*}\sigma^{*} + sE_s + C \qquad \ldots . (41)$$

where C is a constant dependent upon the standard model process but which does not interfere with the linearity of the relationship. A computer technique was used to determine the values of ρ^{*} and s. Values of these parameters were chosen to give the best straight line for equation 41. Fig. 5.3 is a plot of the logarithm of the second-order rate constant (k_b) versus the term ($\rho^{*}\sigma^{*} + sE_s$) for the reaction of AAAC with a series of alcohols. The results indicate that the rate may be correlated to a certain degree with the steric effect and the polar effect of the attacking nucleophile. The values obtained for ρ^{*} and s were -4.9 and +2.1 respectively, which suggests that the effect of the substituent in increasing the nucleophilicity of the hydroxyl group outweighs the steric effect. However, for a large substituent such as tert-butyl, in which the increase in nucleophilicity of the hydroxyl group would be expected to be greater than for an isopropyl derivative (this is reflected



<u>Fig. 5.3</u> A semi-logarithmic plot of the second-order rate constants (k_b) against the substituent factor ($\rho^* \sigma^* + s E_s$) for the reaction of AAAC with a series of alcohols.

a) isopropanol b) n-propanol c) 2-methyl propanol d) benzyl alcohol e) tert-butanol.

in polar substituent constants (σ^*) of -0.3 and -0.190 respectively), this effect is sufficiently balanced by a high steric substituent constant for tert-butyl of -1.54 (cf. isopropyl, -0.47).

Deviations from linearity in Fig. 5.3 may be due to the efficiency of the alcohol as a solvent in promoting and stabilising the transition state. Table 5.6 presents the second-order rate constants (k_b) for the decomposition of MAAC in a series of alcohols using nitrobenzene as a cosolvent, the approximate dielectric constant of the reaction medium is also given. The rate of decomposition in neat benzyl alcohol is given for comparison. The second-order rate constant in neat benzyl alcohol is some three times larger than the rate constant using nitrobenzene as a cosolvent in spite of the fact that the dielectric constant of the latter is considerably higher (which in the absence of other factors would tend to favour a reaction involving dipolar species). It is apparent that some solvent property other than dielectric constant affects the rate of reaction quite drastically.

Effect of Solvent Characteristics

In order to investigate the effect of the solvent on the bimolecular reaction of alcohols with anhydrocarboxylates and to gain a more precise knowledge of solvent parameters which most markedly affect the reaction, the reaction of MAAC with benzyl alcohol was investigated using various solvent mixtures. The concentration of benzyl alcohol was maintained constant at 4.82 mol. litre^{-1} for a series of reactions covering the full concentration ranges for the following pairs of solvents; nitrobenzene/anisole, nitrobenzene

/dimethyl sulphoxide (DMSO) and dimethyl sulphoxide/anisole. Maintaining the alcohol concentration constant enables the effect of varying the cosolvent property to be assessed without any complicating effect from the solvent characteristics of benzyl alcohol. The cosolvent pairs were chosen to enable the reaction to be studied over a fairly wide range of dielectric constants. The second-order rate constants (k_b) for the reaction using the various cosolvent pairs and the approximate dielectric constants are given in Table 5.7. In the case of the solvent pair nitrobenzene/anisole the rate of reaction tends to increase with decrease in dielectric and for the solvent pair anisole/DMSO the reaction increases with increase in dielectric. There is very little correlation between the reaction rate and solvent dielectric constant for the solvent pair nitrobenzene/DMSO.

A relationship which has been successfully used in a limited number of cases is a plot of the logarithm of the rate constant versus the dielectric function, $(\epsilon - 1)/(2\epsilon + 1)$, in which ϵ is the dielectric constant of the reaction medium. Fig. 5.4 shows a semi-logarithmic plot of the second-order rate constant (k_b) against $(\epsilon - 1)/(2\epsilon + 1)$ for the solvent pairs given in Table 5.7. There is some correlation between k_b and the dielectric function for a particular solvent pair but this does not extend to different cosolvent systems. It is apparent that any correlation must involve some other solvent property which can account for such a drastic increase in rate as experienced by changing the solvent from nitrobenzene to dimethyl sulphoxide.

Table 5.7

Second-order rate constants (k_b) for the reaction of MAAC with benzyl alcohol at 44.5°C, using various concentrations of solvent pairs. [OH] = 4.82 mol. litre^{-1}, $[MAAC]_o$ = 0.39 mol. litre^{-1}.

[ØNO$_2$] mol. litre^{-1}	[Anis] mol. litre^{-1}	[DMSO] mol. litre^{-1}	Dielectric constant (approx.)	$10^4 k_b$ l. mol.$^{-1}$ sec.$^{-1}$
4.86	-	-	24	0.39
3.18	1.61	-	19	0.45
2.45	2.30	-	17	0.47
1.71	3.00	-	14	0.49
-	4.61	-	9	0.47
-	3.00	2.47	19	2.16
-	2.30	3.50	23	3.2
-	1.61	4.58	27	3.5
-	-	7.05	34	3.9
1.71	-	4.58	31	3.3
2.45	-	3.50	30	4.04
3.18	-	2.47	28	1.93

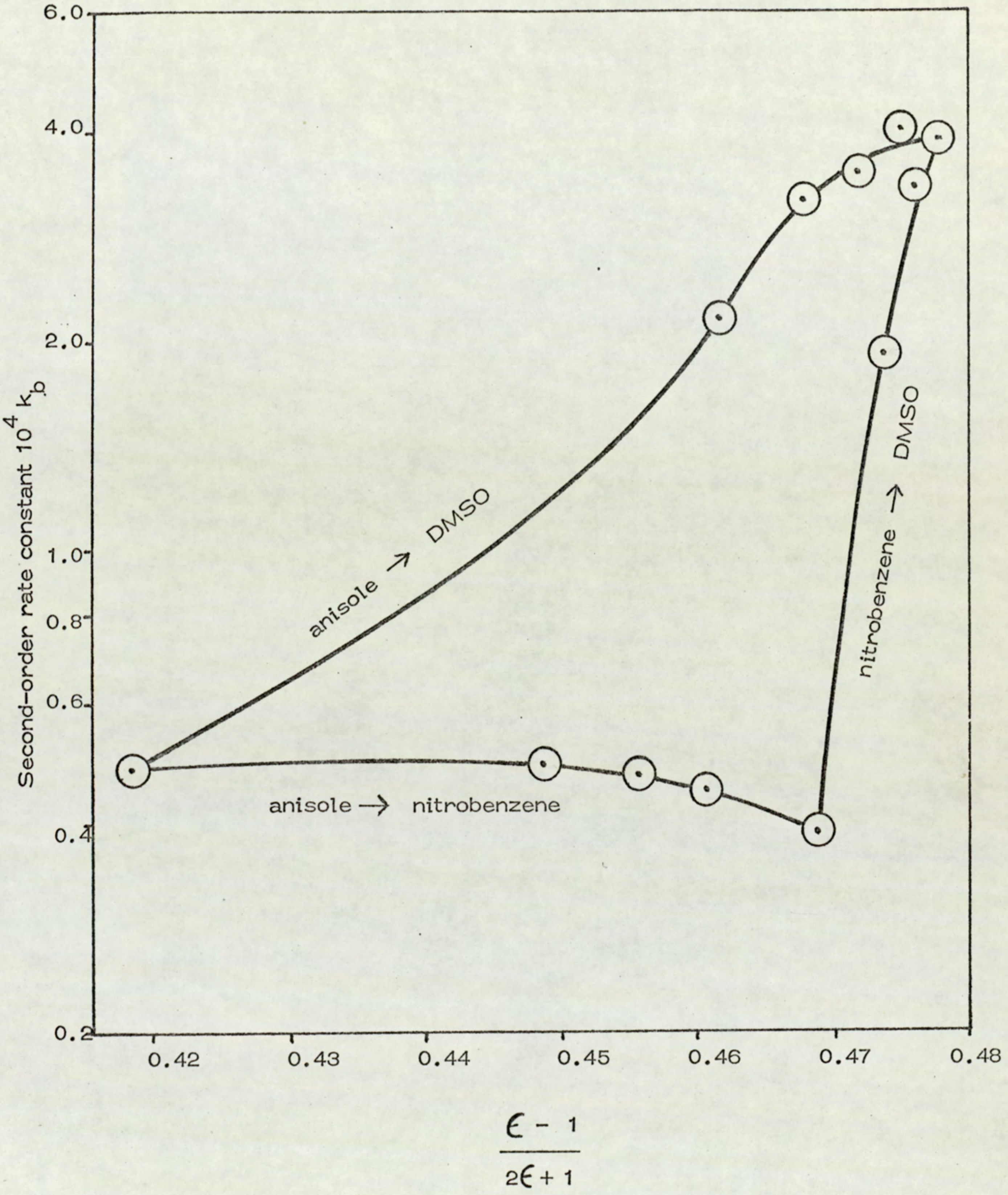


Fig. 5.4 Semi-logarithmic plot of the second-order rate constant (k_b) versus (ϵ - 1)/(2ϵ + 1) for various cosolvent pairs.

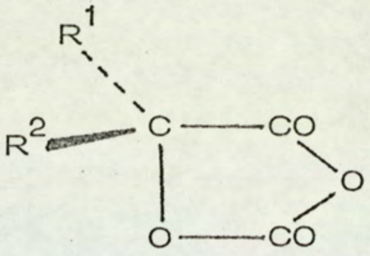
Various attempts have been made in producing a satisfactory relationship between solvent properties and the rate of reaction. Multi-correlation of spectroscopic properties and physical measurements with rates have been used to derive a satisfactory relationship in a limited number of specific cases but no general single solvent property has been effectively used. The use of a solvent property termed "donicity" in correlating the rate of this latter bimolecular reaction with the solvent system will be discussed in the following section.

5.2 Discussion

The choice of nucleophile by which to assess the reactivity of a given anhydrocarboxylate is determined primarily by the nature of the potential propagating species which is produced by that anhydrocarboxylate during a bimolecular polymerisation reaction. The substituents at C(5) of the anhydrocarboxylate become the substituents adjacent to the attacking nucleophile after each propagation step as attack at the C(4) carbonyl of the anhydrocarboxylate ring and subsequent loss of carbon dioxide is regarded as the propagation step. Under the conditions previously described, the reaction with benzyl alcohol involves only the first step in a propagation mechanism as the concentration of hydroxyl groups is some thirty times greater than that of the monomer. Thus any variation in the rate constants for successive propagation steps does not affect the observed rate. The comparison of rates with benzyl alcohol at a fixed temperature gives a genuine assessment of the order of reactivity of the series of anhydrocarboxylates with respect to the susceptibility of the C(4) carbonyl to nucleophilic attack. The nucleophile benzyl alcohol satisfies the requirements of a model propagating nucleophile, possessing a phenyl substituent on the carbon atom adjacent to the nucleophilic centre.

Specific activation of the C(4) carbonyl is primarily due to the inductively electron withdrawing power of the phenyl substituent at C(5). The presence of a second phenyl group in BAAC no doubt contributes additively to the activation of the carbonyl and yet presents considerable steric hindrance to an incoming nucleophile. Since a methyl group is an electron donating substituent, in AAAC we have the unusual situation of primary activation by the phenyl substituent and deactivation by the methyl group and in addition the methyl group presents a degree of steric hindrance to nucleophilic attack. In the case of MAAC there is activation of the carbonyl by the C(5) phenyl substituent and effectively no steric hindrance to attack from the side of the ring associated with the C(5) hydrogen substituent. This somewhat qualitative assessment of reactivity is in good agreement with the observed order of reactivity with benzyl alcohol.

Considering the configuration of substituents at C(5) (XXVIII),



XXVIII

then R^1 and R^2 will play a major part in both the activation of the C(4) carbonyl and the steric hindrance associated with the reaction path. As C(5) is directly bonded to the reaction site it will also play a significant part, however, the fourth substituent at C(5), namely O(1) will have a relatively small and constant contribution to both inhibition of the reaction path and activation of the C(4) carbonyl for a series of anhydrocarboxylates. Thus if polar and steric substituent constants are taken for the groups represented by $R^1 R^2 CH-$, where the hydrogen is considered as the non-interfering carbon-oxygen part of the molecule, then the rate of the reaction may be correlated with substituent parameters according to equation 40. Table 5.8 gives the relevant polar and steric substituent parameters. Taking a value of ρ^* = 3/2 and s = 1 results in equation 42, which adequately describes the relationship between the reaction rate and substituent parameters.

$$\log k = \frac{3\rho^*}{2} + E_s + C \qquad \dots . (42)$$

A semi-logarithmic plot of reaction rate against $(\frac{3\rho^*}{2} + E_s)$ is shown in Fig. 5.5, for the reaction with benzyl alcohol. The linearity of the plot indicates a good correlation of the rate with the substituent parameters and confirms that the two predominant

Table 5.8

Steric and Polar substituent parameters(65) for appropriate groups.

Substituent	σ^*	E_s	$\frac{3\sigma^*}{2} + E_s$
$C_6H_5CH_2$ (MAAC)	0.215	-0.38	-0.06
$C_6H_5(CH_3)CH$ (AAAC)	0.11	-1.19	-1.025
$(C_6H_5)_2CH$ (BAAC)	0.405	-1.76	-1.152

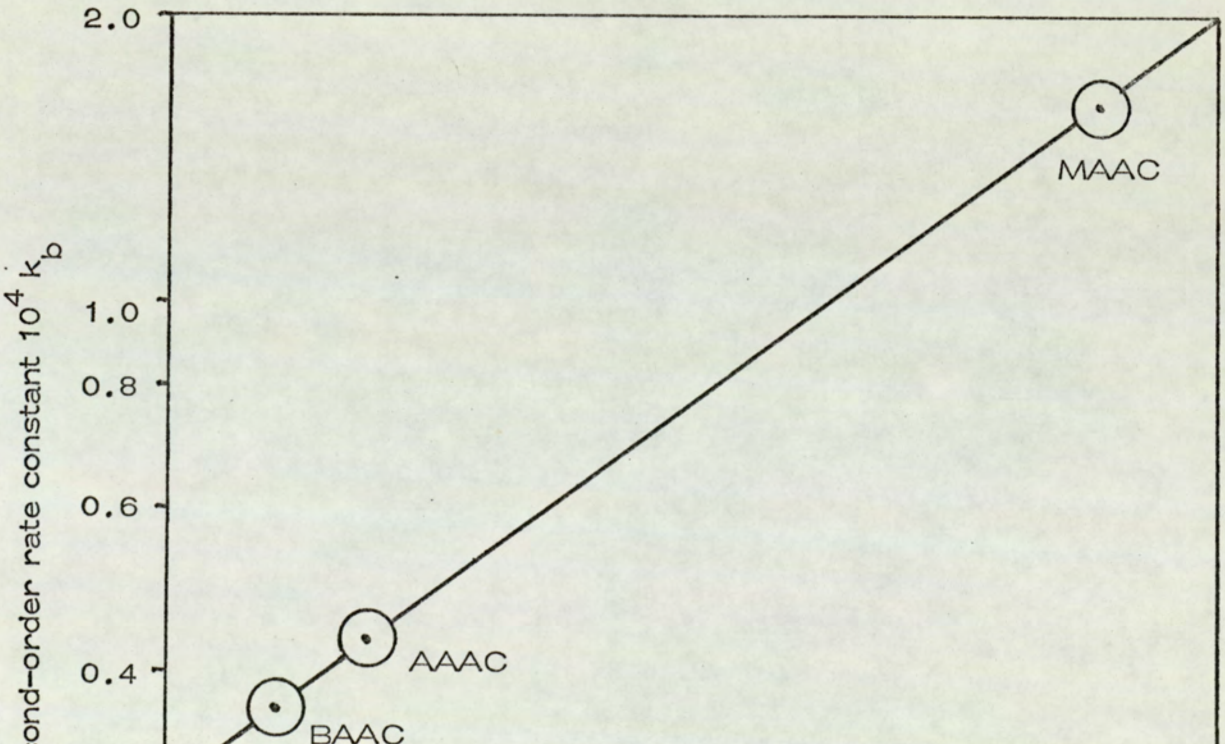


Fig. 5.5 Semi-logarithmic plot of the second-order rate against substituent parameter ($3\sigma^*/_2 + E_s$) for the reaction with benzyl alcohol at 50°C.

factors determining the rate of reaction of anhydrocarboxylates with a given nucleophile are essentially the activity of the carbonyl due to C(5) substituents and the steric hindrance associated with these substituents.

It is interesting to note that in the case of the dimethyl substituted anhydrocarboxylate (III, $R^1 = R^2 = CH_3$), no such reactivity of the C(4) carbonyl is observed. At 90°C in benzyl alcohol $k_b = 0.8 \times 10^{-8}$ l. mol.$^{-1}$ sec.$^{-1}$(44) (cf. nitrobenzene $k_1 = 1.0 \times 10^{-7}$ sec.$^{-1}$ at 90°C). It was suggested that the reason for such low reactivity was the nucleophilicity of the hydroxyl group being insufficient to overcome the steric hindrance of the ring C(5) substituents. Undoubtedly, the major factor is that the C(4) carbonyl is inactive to such an extent that bimolecular reaction does not occur and that the product, benzyl α-hydroxy isobutyrate is a result of reaction of the ring extrusion product, the α-lactone, with an hydroxyl group. Methyl substituents being inductively electron donating will ultimately cause deactivation of the C(4) carbonyl. It must be concluded that for such carbonyl reactivity, as experienced in this series of phenyl substituted anhydrocarboxylates a necessary requirement is for an inductively electron withdrawing substituent to be present on the C(5) carbon.

As a consequence of the C(4) carbonyl reactivity in phenyl substituted anhydrocarboxylates, a bimolecular polymerisation mode must be considered to be in competition with the thermal route. Adventitious traces of moisture reacting with the monomer to yield the parent α-hydroxy acid, presents the necessary propagating species. Two fundamental requirements for polymerisations of this type are that the monomer must contain an active site and secondly that the propagating species should be replicated as a result of attack on the monomer and its incorporation into the polymer chain. Reaction of the terminal hydroxyl group at the activated carbonyl is a potential mechanism for polymer formation. However, a contributing factor in the efficiency of this mode of polymerisation is in the size of the substituents at C(5), as these not only sterically hinder the reaction path of the propagating species but also determine the steric hindrance associated with this species. Thus a severely sterically hindered anhydrocarboxylate results in the formation of a sterically hindered propagating species and hence the opportunity for this bimolecular reaction is reduced in a two-fold manner. In the case of MAAC a situation is presented where there is a relatively unsterically hindered anhydrocarboxylate and propagating species. The anomalous behaviour observed in the kinetics of thermal decomposition of MAAC is due to a significant contribution of this bimolecular mode of polymerisation. The form of the reaction profile arises from the increase in magnitude of the rate constant for successive steps of propagation. After about four steps in polymerisation the rate constant for the reaction of polymer with monomer approximates to a constant value. This is considered in greater detail for a pentafluorophenyl substituted anhydrocarboxylate.

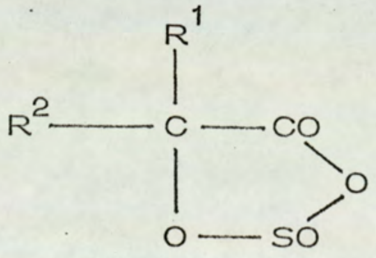
The ratio of the rate constant in benzyl alcohol to that in nitrobenzene is an indication of the extent of this bimolecular contribution. It must be emphasised that this ratio is derived from the reaction of the anhydrocarboxylate with a fixed nucleophile and does not take into account the steric hindrance or electronic properties associated with the different propagating species. Whilst the highly sterically hindered propagating species of BAAC has a severely restricted reaction path, it also experiences a considerable reduction in nucleophilicity due to the effect of two inductively electron withdrawing phenyl substituents on the carbon atom adjacent to the hydroxyl nucleophile.

As stated in section 5.1 of this chapter the ratio, $(k_1 + k_b [OH])_{B.A.}/(k_1)_N$, for MAAC may have been underestimated, however, the ratio does provide a tentatively qualitative assessment of the bimolecular contribution. The foregoing discussion suggests that the values ought to be considerably more spread to reflect the true probability of the process.

By way of summary of the modes of polymerisation in non-hydroxylic solvents at temperatures of the order 90^{o}-120^{o}C, AAAC and BAAC decompose predominantly by a unimolecular process to give a postulated α-lactone intermediate which then takes part in a rapid chain propagation reaction with a terminal hydroxyl group, polymerisation by a bimolecular route is thought to occur only to a very small extent. Decomposition of MAAC proceeds predominantly by a bimolecular process which involves direct attack of the terminal hydroxyl group at the C(4) carbonyl, the thermal stability is such that the unimolecular ring extrusion reaction to give the reactive α-lactone does not substantially contribute to the formation of polymer.

In both polymerisation modes the concentration of hydroxyl groups determines the degree of polymerisation since the α-lactone rapidly reacts with such groups as the propagating step, and in the bimolecular route attack of the hydroxyl group on the anhydrocarboxylate ring represents chain propagation. Where adventitious traces of moisture have reacted to produce a small concentration of parent acid prior to polymerisation, this impurity will limit the molecular weight of the resultant polymer and under these conditions each chain will be terminated by one carboxylic acid and one hydroxyl group.

In the analogous anhydrosulphite system (I) a similar situation is presented in which a bimolecular propagation reaction must be considered as a potential route to polymer.

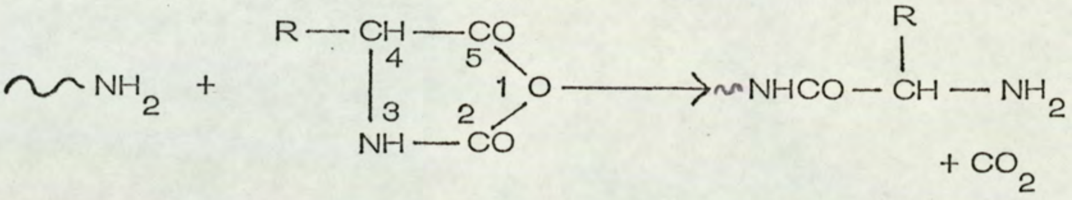


I

As already stated, the presence of an inductively electron withdrawing substituent at C(5), is necessary for activation of the C(4) carbonyl to nucleophilic attack and this requirement may be extended to anhydrosulphite systems. The ratio $(k_1 + k_b[OH])_{B.A.}/(k_1)_N$ acts as a semi-quantitative assessment of the relative reactivities of a series of such ring compounds to nucleophilic attack and in the series of anhydrosulphites (a) glycollic (I; $R^1 = R^2 = H$), (b) lactic (I; $R^1 = H$, $R^2 = CH_3$) and (c) mandelic (I; $R^1 = H$, $R^2 = C_6H_5$) the value of this ratio falls in a predictable order; (c) > (a) > (b). Neither mandelic nor glycollic acid anhydrosulphites possess an inductively electron donating substituent at C(5) and thus would be expected to have some reactivity towards benzyl alcohol; mandelic anhydrosulphite being more reactive due to the C(5) phenyl substituent. The presence of a methyl substituent considerably deactivates the C(4) carbonyl to nucleophilic attack as reflected in a low ratio of $(k_1 + k_b[OH])_{B.A.}/(k_1)_N$.(38) The importance of the electronic properties of C(5) substituents on the reactivity of the C(4) carbonyl is further exemplified by comparing the value of this ratio for diethyl and bischloromethyl substituted anhydrosulphites at 90°C. The diethyl derivative has a value of 0.07,(17) whereas the corresponding value for the bischloromethyl is of the order of 9.(38)

In general alkyl and spirocycloalkyl substituted anhydrosulphites have low values of $(k_1 + k_b[OH])_{B.A.}/(k_1)_N$ and do not, therefore, have a significant contribution to polymer formation by this bimolecular route. This is principally due to the fact that such substituents are inductively electron donating and thus lead to deactivation of the C(4) carbonyl to nucleophilic attack. In as much as anhydrocarboxylate are substantially more thermally stable than anhydrosulphites, they lend themselves to the accommodation of an inductively electron withdrawing phenyl substituent without undue loss of thermal stability.

The normal amine polymerisation of N.C.A.'s is dependent upon the reaction of a terminal amine group with the C(5) carbonyl of the ring as shown in equation 43.



.... (43)

The propagating species in this case is an amine group and whilst the kinetic features of this polymerisation process and the bi-molecular polymerisation of anhydrocarboxylates are similar in so far as they show second-order kinetic behaviour, low activation energies and low pre-exponential factors, the two reactions differ considerably in terms of the reacting species at the reaction site. The reactivity of the C(5) carbonyl would not be expected to be very different from the corresponding reaction site in anhydrocarboxylates in spite of the presence of a ring nitrogen (which may conceivably have an activating effect on the carbonyl). The electronic properties of the substituents at C(4) are likely to have a similar effect as on the anhydrocarboxylate ring. However, the nature of the propagating species, namely the amine group, in the case of N.C.A. derivatives is markedly different to the hydroxyl group. The amine group is a considerably stronger nucleophile and will therefore react rapidly with a somewhat deactivated carbonyl. Complications arise in the N.C.A. system when secondary amines and N-substituted rings are involved, in which case the propagating species is severely sterically hindered. Ballard and Bamford have carried out a detailed study of the effect of the size of the substituents on the polymerisation reaction involved.(29)

The similar polymerisation mode in anhydrocarboxylates involves a relatively weak hydroxyl nucleophile which requires an activated reaction site in order to contribute significantly to polymer formation. Amine nucleophiles such as benzylamine react extremely rapidly with anhydrocarboxylates to give the corresponding amide but polymerisation using amine initiators proceeds slowly as the terminal group becomes a hydroxyl species after the initial reaction with the anhydrocarboxylate. The use of tertiary amine bases to initiate polymerisation will be discussed in a subsequent chapter.

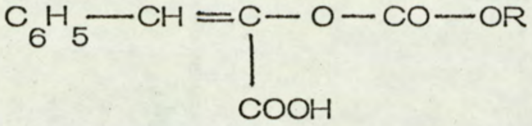
The polymerisation of β-propiolactone may be initiated by alcohols in the presence of base catalysts such as sodium hydroxide or sodium alkoxides.(66) The ring opens at the oxygen-carbonyl bond resulting in the formation of a hydroxyl terminated polyester; propagation occurs via this terminal hydroxyl group. The use of inorganic catalysts in the polymerisation of β-propiolactone has also been discussed by the same authors.(67) Various anionic catalysts have been used in the polymerisation of lactones. The types of catalysts used vary considerably in their effectiveness in forming high molecular weight polymer at reasonable rates. Metal alkyls and metal alkoxides appear to be the most effective in this respect. The mechanism which has been suggested for anionic polymerisation of lactones involves attack at the carbonyl by the anion and subsequent ring cleavage at the acyl-oxygen bond to yield an anionic terminated species which undergoes chain propagation by repeated attack at the active site in the monomer.

The use of such initiators in the polymerisation of anhydrocarboxylates may be considered feasible in view of the susceptibility of the C(4) carbonyl to nucleophilic attack. Polymerisation would be anticipated to proceed via a regenerated O(1) alkoxide anion which repeatedly reacts with the C(4) carbonyl during successive propagation steps. However, initial kinetic studies indicate that, whilst a rapid reaction takes place and the product is predominantly the corresponding polymer, propagation does not involve a regenerated alkoxide anion, but the polymerisation is a specific example of the general class of polymerisation initiated by aprotic bases which is considered in Chapters 7 and 8 of this thesis.

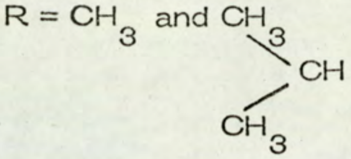
The reactivity of phenyl substituted anhydrocarboxylates to hydroxyl groups of varying nucleophilicity was assessed by carrying out the decomposition in different alcohols. However, caution must be taken in interpreting the results as very little is known about the way in which the solvent affects the rate of reaction. The concerted electron-releasing power of three methyl groups in tert-butanol effectively produces the strongest hydroxyl nucleophile of the series but it would appear that the steric hindrance associated with these substituents is sufficient to severely reduce the rate of reaction. Loss of a methyl group to give isopropanol results in a considerable increase in rate, whilst the effectiveness of an n-alkyl or 2-methyl substituted chain, presenting apparently little steric hindrance, appears to be less than this secondary alcohol. The decrease in rate on introducing a methyl substituent in the 2-position may be adequately explained in terms of the polar and steric substituent constants (σ^* and E_s respectively) for these groups. There is only a 10% increase in polar substituent constant on the introduction of this methyl group and yet there is almost a three-fold increase in the steric substituent constant; E_s = −0.36 for n-propyl and −0.93 for 2-methyl propyl.

The general order of reactivity of the series of alcohols is consistent for various anhydrocarboxylate structures. It is interesting to note that for a severely hindered reaction path as in the reaction with BAAC, benzyl alcohol, which would be anticipated to be a weaker nucleophile than 2-methyl propanol, is in fact more effective in attacking the C(4) carbonyl. The similarity of the steric substituent constants for benzyl and n-propyl groups probably accounts for the increase in rate over 2-methyl propanol for this sterically hindered reaction.

Products obtained from the reaction were the corresponding α-hydroxy carboxylic acid esters and carbon dioxide. In the case of the reaction of 5-benzylidene 1,3-dioxolan 2,4-dione with methanol and isopropanol,(43) the product is not, as might be expected by attack at the C(4) carbonyl, the corresponding ester, but the α-(alkoxy carbonyloxy) cinnamic acid (XXIX) resulting from nucleophilic attack at the C(2) carbonyl.



$C_6H_5—CH=C(COOH)—O—CO—OR$



$R = CH_3$ and $(CH_3)_2CH$

XXIX

This result is surprising when considering that the electronic effect of this vinyl substituent, as reflected in the polar substituent constant, is identical with that of two phenyl substituents. However, change in bond hybridisation from sp^3 to sp^2 at C(5) may have a pronounced effect on the susceptibility of the C(4) carbonyl to this form of attack as resonance forms involving electron donation to the anhydrocarboxylate ring may be written, which would result in a deactivation of the C(4) carboxyl.

Reaction of anhydrosulphites with alcohols presents a somewhat different situation. The spread of activity for a series of alcohols with a given anhydrocarboxylate is considerably greater than for the same alcohols with an anhydrosulphite. This is exemplified by the reaction of mandelic acid anhydrosulphite with a series of alcohols.(38) The remarkable point is that the order of reactivity of the alcohols is the reverse to that experienced with anhydrocarboxylates and falls in a sequence similar to the polar substituent constants for the appropriate alcohol functions.

The foregoing discussion must be considered as a somewhat tentative assessment of the reactivity of anhydrocarboxylates to alcohols. An important factor in determining the rate of a reaction is the characteristics associated with a particular solvent. As the reactions with alcohols were carried out using the alcohol as solvent, the effectiveness of the solvent in promoting the reaction may give rise to discrepancies in the direct correlation of reaction rate with a particular molecular structure. Energies associated with the solvolysis of the monomer and the transition state are extremely difficult to determine but may contribute substantially to the observed rate of reaction. As seen from Table 5.7 in the preceeding section there is very little correlation between the rate of reaction and the dielectric constant of the reaction medium. Some correlation may be observed for various solvent concentrations of a single solvent pair but the relationship breaks down when extended to different solvent pairs; Fig. 5.4. It is apparent that a more fundamental solvent property must be considered for a successful correlation.

In recent years a more comprehensive picture of solvent properties has emerged and in reactions of the type described here the most significant single property is apparently the "donicity" of the solvent. Kagiya et al(68) have made a quantitative study of the measurement of the electron donating nature and electron accepting nature of various organic solvents. The position of the O-D or C = O absorption band of a liquid compound which contained a small quantity of methanol-d or acetophenone was measured using infrared spectroscopy, and the perturbation which the solvent produced on these vibrational bands considered as a measure of the relative magnitude of the electron donating or electron accepting nature of the solvent. The electron donating power or electron accepting power is defined as the relative difference of the O-D or

C = O absorption band observed in the compound from that in benzene, counted as wave numbers. The electron donating power is measured with reference to the change in frequency of the O-D band and electron accepting power with reference to the C = O band. The electron donating power or donicity of a solvent appertains to the solvent as a medium rather than the molecular species involved, which probably accounts for the inadequacy of dielectric constants in correlating solvent properties as molecular polarisability and molecular dipole moments contribute to the dielectric phenomena.

Since donicity is measured by the perturbation of the O-D band in a particular solvent, values relating to alcohols cannot be measured by this spectroscopic technique. It is of considerable interest to have a more quantitative assessment of the role of alcohols, more in particular benzyl alcohol, as solvent in the bimolecular reaction with anhydrocarboxylates. More specifically, to choose a solvent whose properties enable a polymerisation to be carried out at a substantial rate either at lower temperatures or at lower concentrations of initiator, by seemingly unconventional routes.

In the reaction of MAAC with benzyl alcohol using the concentration ranges of three cosolvent pairs, the concentration of alcohol was kept constant in order to negate the effect of the alcohol with respect to its donicity. From a plot of the logarithm of the second-order rate constant (k_b) against cosolvent donicity, the value for the donicity of benzyl alcohol was determined by interpolation of the value of the rate constant in neat benzyl alcohol on this graph. The value obtained for the donicity of benzyl alcohol was 58.3; cf. nitrobenzene 21, anisole 26, dimethyl sulphoxide 141. This value enabled the total solvent donicity to be calculated and plotted against rate constant. Fig. 5.6 shows a plot of ln k_b versus total solvent donicity. Whilst the plot is not linear through its entirety, it shows good correlation between different cosolvent pairs.

It would appear, therefore, that for this type of reaction the donicity of the solvent is of primary importance and the dielectric constant of secondary importance. Combination of these two solvent properties as in equation 44 may give the required linear relationship between the observed rate of reaction and solvent properties. In equation 44 f' and f'' are some function of the total solvent donicity and dielectric respectively where $f' > f''$. Dn_i and ϵ_i are the donicity and dielectric of component i respectively for a multi-solvent system and m_i is the molar concentration of component i.

$$\log k = f' \frac{\sum_i m_i Dn_i}{\sum_i m_i} + f'' \frac{\sum_i m_i \epsilon_i}{\sum_i m_i} \qquad \ldots . (44)$$

Solvents of high donicity tend to increase the rate of this type of reaction and use of such solvents for initiated polymerisations would substantially reduce the reaction time. The choice of solvent with a reasonable high donicity value is severely restricted by the necessity to have an inert solvent. Solvents whose donicity

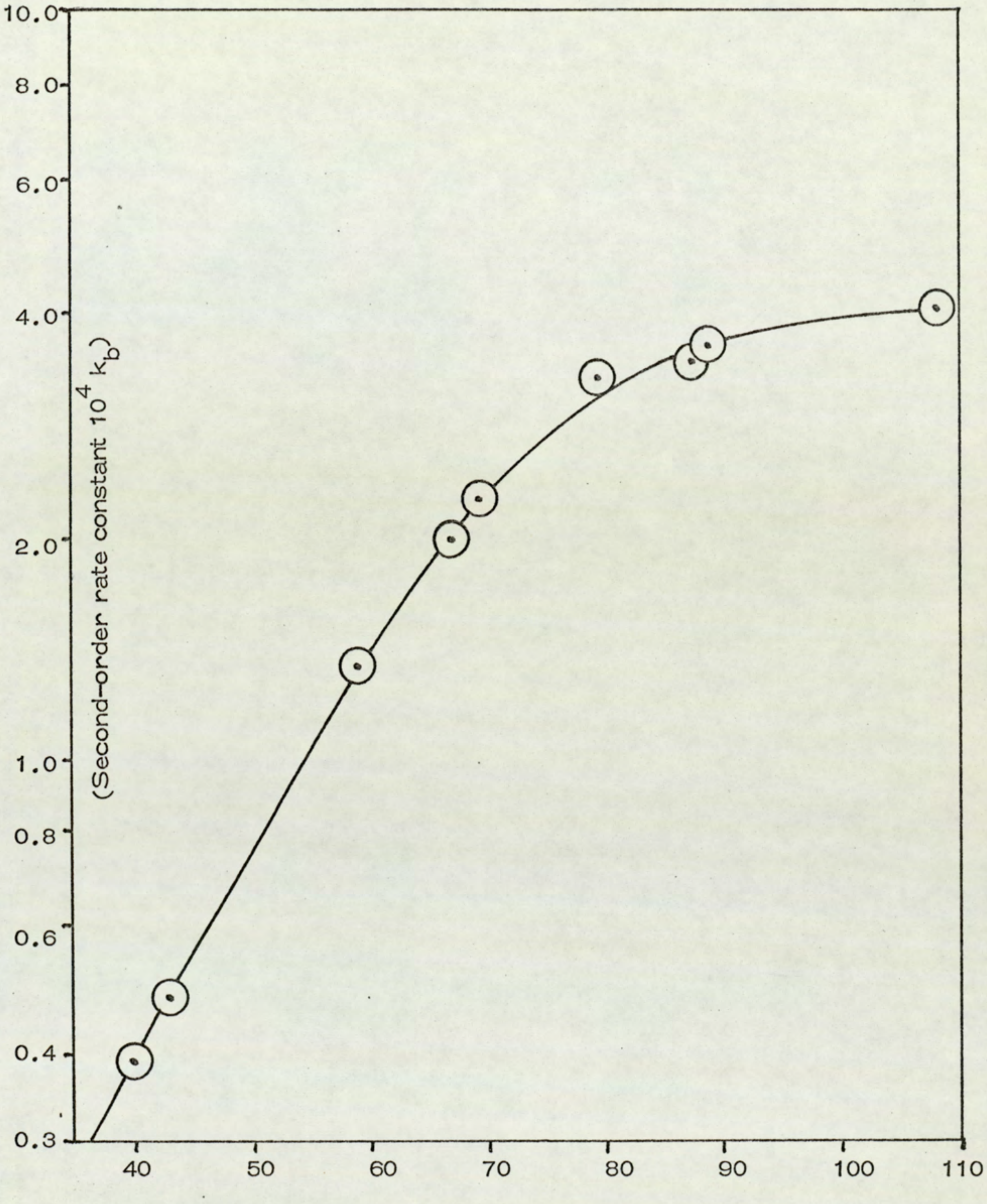


Fig. 5.6 Semi-logarithmic plot of the second-order rate constants (k_b) versus the total solvent donicity for the reaction of MAAC with benzyl alcohol with three cosolvent pairs.

values are greater than that for dimethyl sulphoxide tend to be alkyl amines which, as previously stated, react rapidly with anhydrocarboxylates. Thus dimethyl sulphoxide must be considered as the limiting solvent for this type of system.

The reaction of a series of phenyl substituted anhydrocarboxylates with a given hydroxyl group gives a good indication of the order of reactivity to nucleophilic attack. Steric and electronic factors associated with the substituents at C(5) determine the reactivity of the C(4) carbonyl of the ring compound, whilst the reactivity of a given anhydrocarboxylate to a series of alcohols depends not only on the aforementioned factors but also to a certain extent, the nature of the solvent medium. Investigation of the effect of the solvent medium on the rate of reaction of a specific alcohol with an anhydrocarboxylate indicates that the most significant single property is the donicity of the solvent system. Good correlation between different solvent pairs has been achieved using this solvent parameter.

CHAPTER 6

The Effect of Pentafluorophenyl Substitution on the Reactivity of the 1,3-Dioxolan 2,4-Dione Ring

In the two preceeding chapters an assessment of the relative reactivity of a series of phenyl substituted anhydrocarboxylates has been made. The most profound effect is the greatly increased susceptibility of the C(4) carbonyl to nucleophilic attack when a phenyl substituent is present at C(5). Enhanced electrophilicity of this carbonyl results from the introduction of a second phenyl substituent at C(5), but at the expense of accessibility of the C(4) reaction site due to increased steric hindrance. Hence, in the context of attack by a dipolar nucleophile an overall deactivation of 5,5-diphenyl 1,3-dioxolan 2,4-dione by comparison with 5-phenyl 1,3-dioxolan 2,4-dione results. One method of increasing the reactivity of the C(4) carbonyl to this form of attack is by the introduction of a pentafluorophenyl group whose inductively electron withdrawing power is considerably greater than its hydrocarbon analogue and yet presents very little increase in steric hindrance.

The peculiar behaviour of MAAC during thermal decomposition and the susceptibility of BAAC to ketone formation leave only a single choice in which to ideally study the comparative effects of a phenyl and a pentafluorophenyl group on the anhydrocarboxylate ring; that is a methyl and a pentafluorophenyl substituent at C(5).

In this section the effect of introducing a pentafluorophenyl substituent (as typified by 5-methyl, 5-pentafluorophenyl 1,3-dioxolan 2,4-dione, hereinafter referred to as PFAAC) on ring reactivity is discussed. Particular reference is paid to the polymerisability of the anhydrocarboxylate ring and its susceptibility to initiated polymerisation as discussed previously for the hydrocarbon analogue.

6.1 Results

Thermal decomposition

The thermal decomposition of PFAAC was carried out in nitrobenzene and the concentration of carbon dioxide evolved measured manometrically as a function of time. Both vacuum sublimed and recrystallised samples of PFAAC were used and the semi-logarithmic plot of $(P_\infty - P)/P_\infty$ versus time showed great similarity to the corresponding reaction profile obtained for the decomposition of MAAC in nitrobenzene at the same temperature. Fig. 6.1 shows the reaction profiles obtained for the thermal decomposition of vacuum sublimed and recrystallised PFAAC in nitrobenzene at 90° and 102°C and the decomposition of PFAAC in the presence of a two-fold molar excess of the parent α-hydroxy acid. The amount of chlorine containing impurity was monitored during the stages of the synthesis and found to be undetectably low in the vacuum sublimed and recrystallised samples. Parent acid is necessarily present as an impurity due to the reaction of the anhydrocarboxylate with adventitious traces of moisture during manipulation, in spite of the rigorous precautions of dry-box technique and solvent purification.

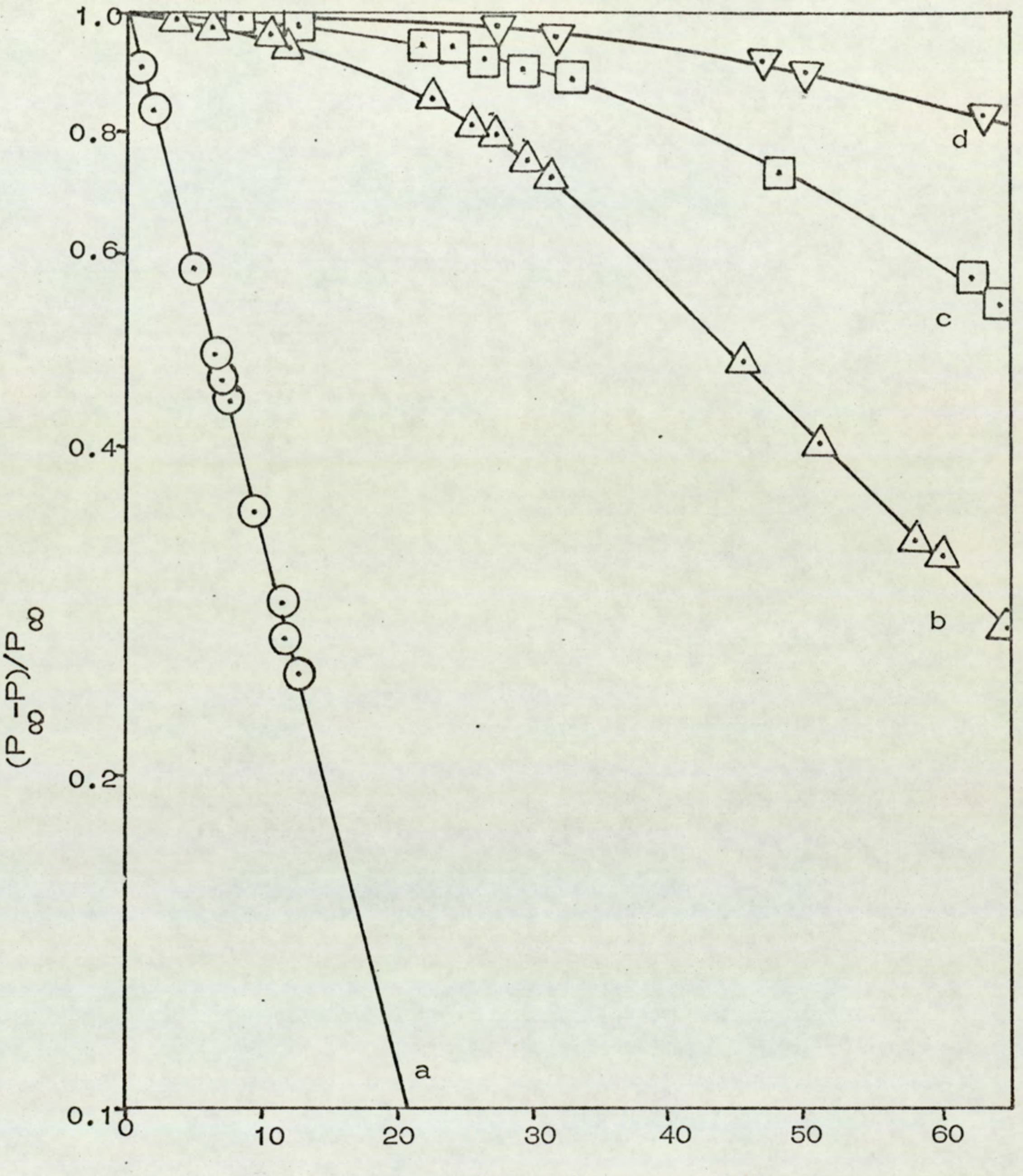


Fig. 6.1 Semi-logarithmic plot of $(P_\infty - P)/P_\infty$ versus time for the decomposition of PFAAC in nitrobenzene.

$[PFAAC]_o$ = 0.17 mol. litre^{-1}.

a) Vacuum sublimed PFAAC with added parent acid at 102°C. $[Acid]_o$ = 0.34 mol. litre^{-1}.

b) Recrystallised PFAAC at 102°C.

c) Vacuum sublimed PFAAC at 102°C.

d) Vacuum sublimed PFAAC at 90°C.

The reaction of PFAAC with a two-fold excess of parent acid gave a good first-order plot with respect to monomer concentration, throughout 95% of the reaction.

Comparison of the thermal behaviour of PFAAC with that of AAAC under identical conditions shows that the introduction of a pentafluorophenyl substituent in place of a phenyl group in the anhydrocarboxylate ring gives rise to an increase in susceptibility of the reaction profile to parent acid impurity. No anomalous kinetic behaviour is observed during the thermal decomposition of AAAC in nitrobenzene. The rate constant for purely thermal decomposition may be estimated by taking the initial rate of decomposition. The value obtained is of the order of 6.0×10^{-7} sec^{-1}. at $102^{o}C$ in nitrobenzene (cf. AAAC in nitrobenzene at $102.2^{o}C$, $k_1 = 1.54 \times 10^{-6}$ $sec.^{-1}$), but may be underestimated due to the effect of parent acid impurity. Fluoroaromatic substitution, therefore, gives rise to enhanced thermal stability of the anhydrocarboxylate ring.

The reaction profile is markedly dependent upon the purity of the anhydrocarboxylate as in the case of the thermal decomposition of MAAC. Decomposition of PFAAC in the presence of a two-molar excess of parent acid results in a good first-order plot of the extent of the reaction versus time. The reaction, however, is slower than for the analogous reaction of MAAC; this probably results from a combination of steric and electronic effects associated with both the anhydrocarboxylate and the reactivity of the parent acid.

The structure of

The product obtained from the decomposition of PFAAC at 102°C was consistent with a poly-α-ester although its solubility in nitrobenzene made isolation difficult. No ketonic secondary fragmentation product, acetopentafluorophenone, was detected by G.L.C. analysis of the reaction mixture. The absence of this product was probably due to a combination of greater thermal stability over the hydrocarbon analogues and the susceptibility of PFAAC to enhanced decomposition in the presence of residual amounts of parent acid impurity.

Reaction with Benzyl Alcohol

In the preceeding section the stability of PFAAC has been tentatively assessed in non-hydroxylic solvents. It would appear that the stability of this anhydrocarboxylate is markedly dependent upon small concentrations of residual parent acid. Such properties, which are very different from those of the hydrocarbon analogue, are to be expected on incorporation of such a highly electron withdrawing substituent as the pentafluorophenyl group on the anhydrocarboxylate ring. The reactivity of PFAAC to a given nucleophile was determined to enable a semi-quantitative assessment of the effect of the pentafluorophenyl group to be made.

The rates of decomposition of PFAAC were measured in benzyl alcohol in the temperature range 20° to 40°C. No anomalous behaviour in the use of benzyl alcohol has been observed with the hydrocarbon analogues and its chemical and physical properties are ideal for use both as reactant and reaction medium. Its use also enables a direct comparison to be made with other anhydrocarboxylate systems and with similar ring structures.

The rates of reaction were measured by gas evolution techniques; the pressure of carbon dioxide evolved was measured as a function of time. The use of benzyl alcohol as solvent medium enables the concentration of hydroxyl groups to be maintained considerably in excess of that of the monomer and to remain substantially constant throughout the reaction. As was the case with the hydrocarbon systems studied, no CO_2 catalysis or inhibition was observed with PFAAC and no significant change in the rate constant occurred on varying the initial concentration of the monomer. A semi-logarithmic plot of $(P\infty - P/P\infty)$ versus time showed good linear behaviour well into the second decade and indicated that the reaction was first-order in monomer. Fig. 6.2 shows typical first-order plots for the decomposition of PFAAC in benzyl alcohol at 20° and 40°C. Similar plots for the decomposition of AAAC at 50°C in benzyl alcohol and the thermal decomposition of PFAAC in nitrobenzene at 102°C are given for comparison of stability with the hydrocarbon analogue and in a non-hydroxylic solvent.

The decomposition of PFAAC in benzyl alcohol may be expressed by the rate equation 45, where k_1 and k_b are the rate constants, the first-order thermal decomposition and the second-order decomposition in benzyl alcohol respectively.

$$\frac{d[CO_2]}{dt} = k_1 [\mathrm{PFAAC}] + k_b [\mathrm{PFAAC}][\mathrm{OH}] \qquad \ldots . (45)$$

$[CO_2]$, [PFAAC] and [OH] refer to the concentrations of carbon

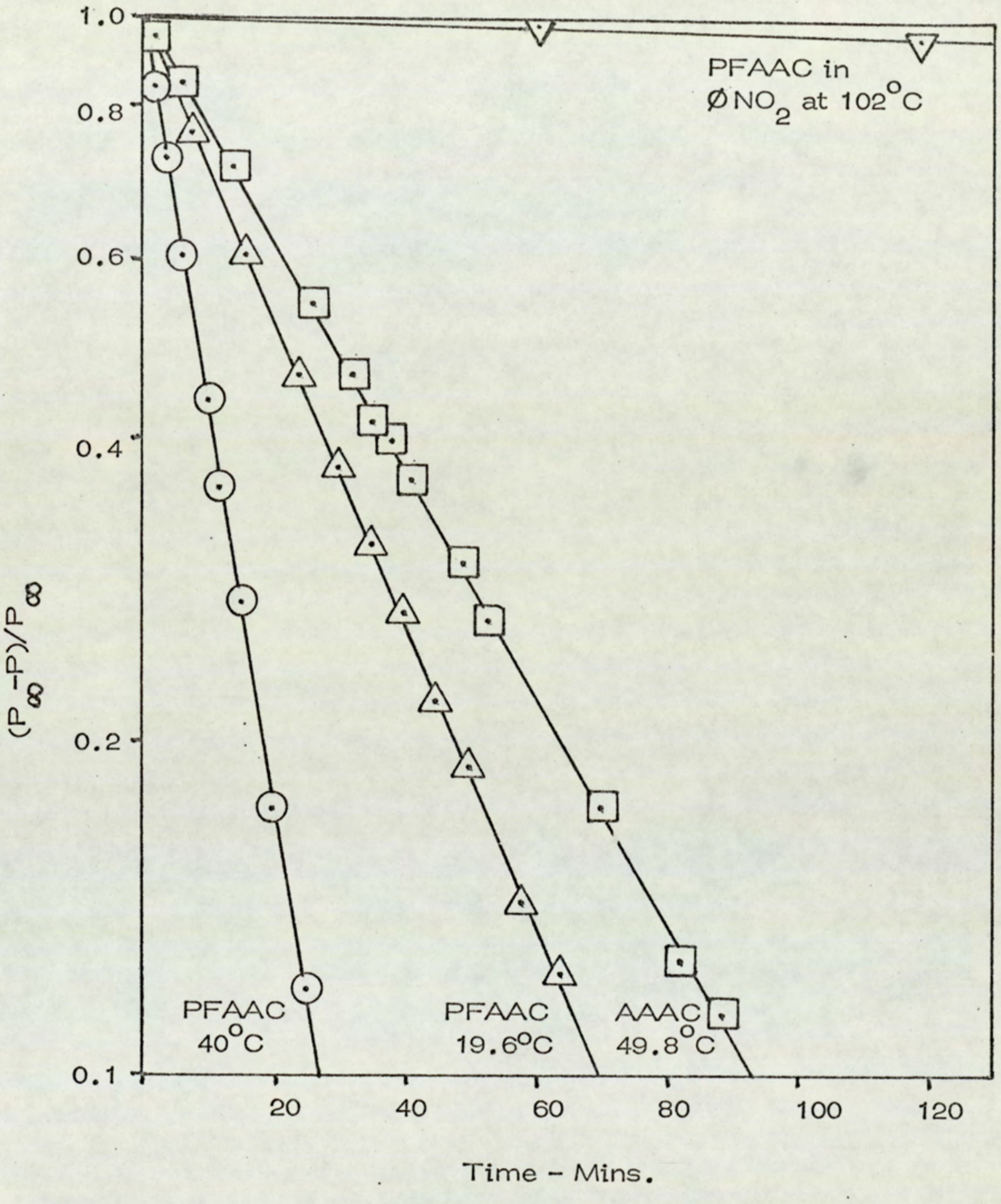


Fig. 6.2 Semi-logarithmic plot of $(P_\infty - P)/P_\infty$ versus time for the reaction of PFAAC (⊙, △) and AAAC (⊡) in benzyl alcohol and PFAAC in nitrobenzene (▽) at 102°C.

dioxide, the monomer and benzyl alcohol respectively. As may be seen from Fig. 6.2, the rate of thermal decomposition at 102°C is extremely slow compared with the rate of decomposition in benzyl alcohol at 20° and 40°C and thus the contribution of the thermal process at these lower temperatures will be considerably less than presented in Fig. 6.2. Thus equation 45 may be reduced to;

$$\frac{-d\,[\text{PFAAC}]}{dt} = k_b\,[\text{PFAAC}]\,[\text{OH}] \qquad \ldots.\ (46)$$

in which the thermal contribution is considered to be negligible.

The derived second-order rate constants (k_b) for the reaction of PFAAC with benzyl alcohol are given in Table 6.1. A conventional Arrhenius plot of these rate constants showed good linear behaviour over the temperature range studied; the associated kinetic parameters derived are given in Table 6.1. The results presented in Table 6.1 show that, as with the hydrocarbon series of anhydrocarboxylates, there is no direct correlation between the reactivity in benzyl alcohol and the thermal stability except it would appear that enhanced thermal stability leads to increased reactivity with benzyl alcohol as a result of electronic effects associated with the substituents at C(5). An electron withdrawing substituent leads to enhanced thermal stability but activates the C(4) carbonyl to nucleophilic attack.

The activation energy obtained for this reaction is some 10 kJ mol.$^{-1}$ greater than those obtained for the hydrocarbon analogues; the value of the pre-exponential factor and the entropy

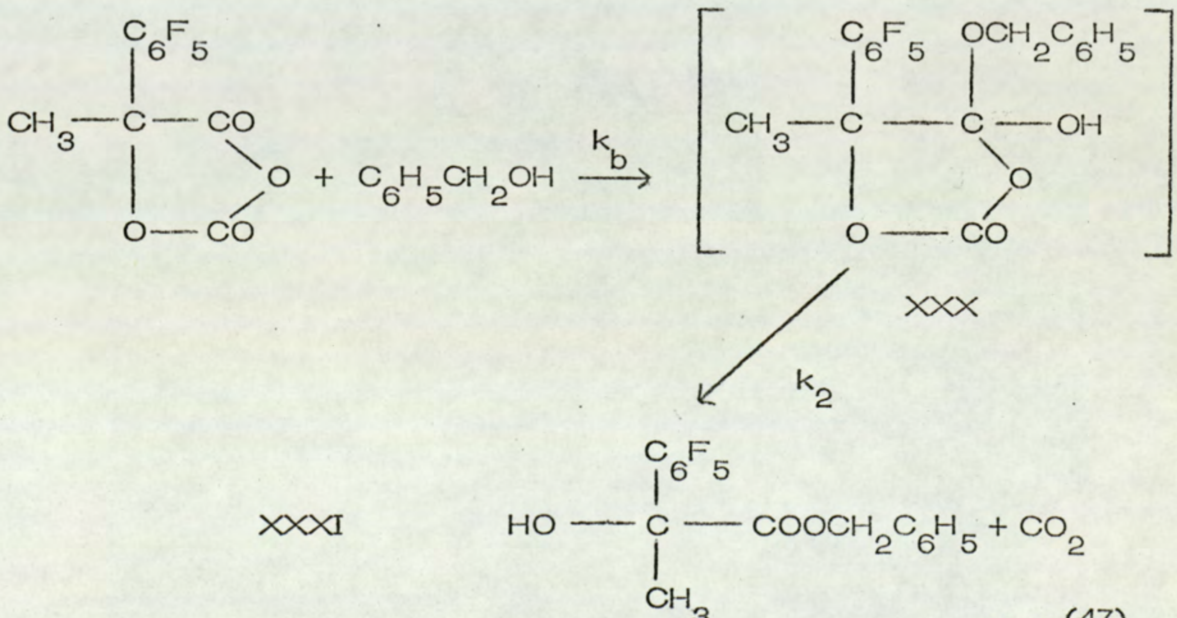
Table 6.1

Second-order rate constants (k_b), energy of activation (E), pre-exponential factor (A) and entropy of activation ($\Delta S^{\ddagger}$) for the reaction of PFAAC with benzyl alcohol. $[PFAAC]_o = 0.27$ mol. litre^{-1}.

Temp. ^oC	$10^5 k_b$ l.mol.$^{-1}$sec.$^{-1}$
19.6	4.55
24.8	6.35
29.7	9.5
31.9	9.5
34.8	13.0
40	14.7
E (kJ. mol.$^{-1}$)	43.5
A (l. mol.$^{-1}$ sec.$^{-1}$)	2.7×10^3
$\Delta S^{\ddagger}$ (J.K.$^{-1}$mol.$^{-1}$)	-222

of activation are also higher. This would tend to suggest, in the first instance, that although the reaction path of the incoming nucleophile is sterically hindered and the formation of the transition state results in a considerable degree of order over the reactant state, the situation is by no means as great as for the phenyl substituted anhydrocarboxylates. Secondly, it may also be inferred from the somewhat higher activation energy for PFAAC in this reaction, that the energy required for the formation of the transition state is higher than for the corresponding step in the hydrocarbon systems. However, the values of these kinetic parameters are of the order expected for nucleophilic attack at an activated site.

Isolation and characterisation of the reaction products showed that only a single product was formed and was consistent with attack of benzyl alcohol at the C(4) carbonyl resulting in the formation of the corresponding α-hydroxy acid ester (XXXI). Equation 47 shows the reaction process.



.... (47)

The rate determining step is envisaged as the addition of the alcohol at the C(4) carbonyl to yield the intermediate XXX which rapidly decomposes with the loss of carbon dioxide to give the ester.

In the previous chapter the use of the ratio of the rate of decomposition in benzyl alcohol and the rate in nitrobenzene; $(k_1 + k_b[OH])_{B.A.}/(k_1)_{N.}$, was used to assess the contribution of a bimolecular decomposition process during thermal decomposition which involves direct attack of the terminal hydroxyl group at the C(4) carbonyl. The value of this ratio, estimated at 50°C is 9.4×10^5 which is almost ten times greater than the value obtained for the hydrocarbon analogue, AAAC. It must be pointed out, however, that the true rate constant for thermal decomposition may in fact be smaller than that estimated from gas evolution measurements from Fig. 6.1, as direct reaction of the parent acid with the anhydrocarboxylate may make a significant contribution to the observed rate even in the early stages of the reaction. The high value obtained for this ratio suggests that there is a considerable bimolecular contribution to the rate of reaction during thermal decomposition and probably accounts for the somewhat anomalous kinetic behaviour observed. This is a direct result of the enhanced reactivity of the C(4) carbonyl to nucleophilic attack by the presence of the pentafluorophenyl substituent.

Reaction with various Alcohols

The effect of varying the structure of the attacking nucleophile was assessed by carrying out the decomposition of PFAAC in various alcohols. The decomposition was carried out in the same alcohols as for the previously studied hydrocarbon anhydrocarboxylates, using nitrobenzene as a cosolvent to enable rate constants to be obtained in a similar temperature range as other systems. The results showed good first-order behaviour in monomer well into the second decade and the decomposition obeyed the rate equation expressed in equation 46.

Fig. 6.3 shows rate curves for the decomposition of PFAAC in isopropanol, 2-methyl propanol and benzyl alcohol at 30°C. All reactions were carried out using nitrobenzene as a cosolvent. The second-order rate constants (k_b) for the decomposition of PFAAC in a series of alcohols are given in Table 6.2 with the dielectric constant of the medium. In all cases product isolation and characterisation showed that the corresponding ester of 2-hydroxy 2-pentafluorophenyl propanoic acid had been formed according to the specific equation 47 given for the reaction with benzyl alcohol.

By inspection of Table 6.2, it is apparent that the spread of activity of PFAAC with the series of alcohols is comparable to that observed with the hydrocarbon series. However, by comparison with the second-order rate constants presented in Table 5.5 for the reaction of AAAC with this series of alcohols, it may be seen that the specific activity observed with PFAAC is considerably greater than for AAAC. This would tend to suggest that relatively active nucleophiles more readily attack PFAAC at the C(4) carbonyl than AAAC. Little extra steric hindrance is presented in the case of PFAAC and further exemplification of the latter suggestion may be

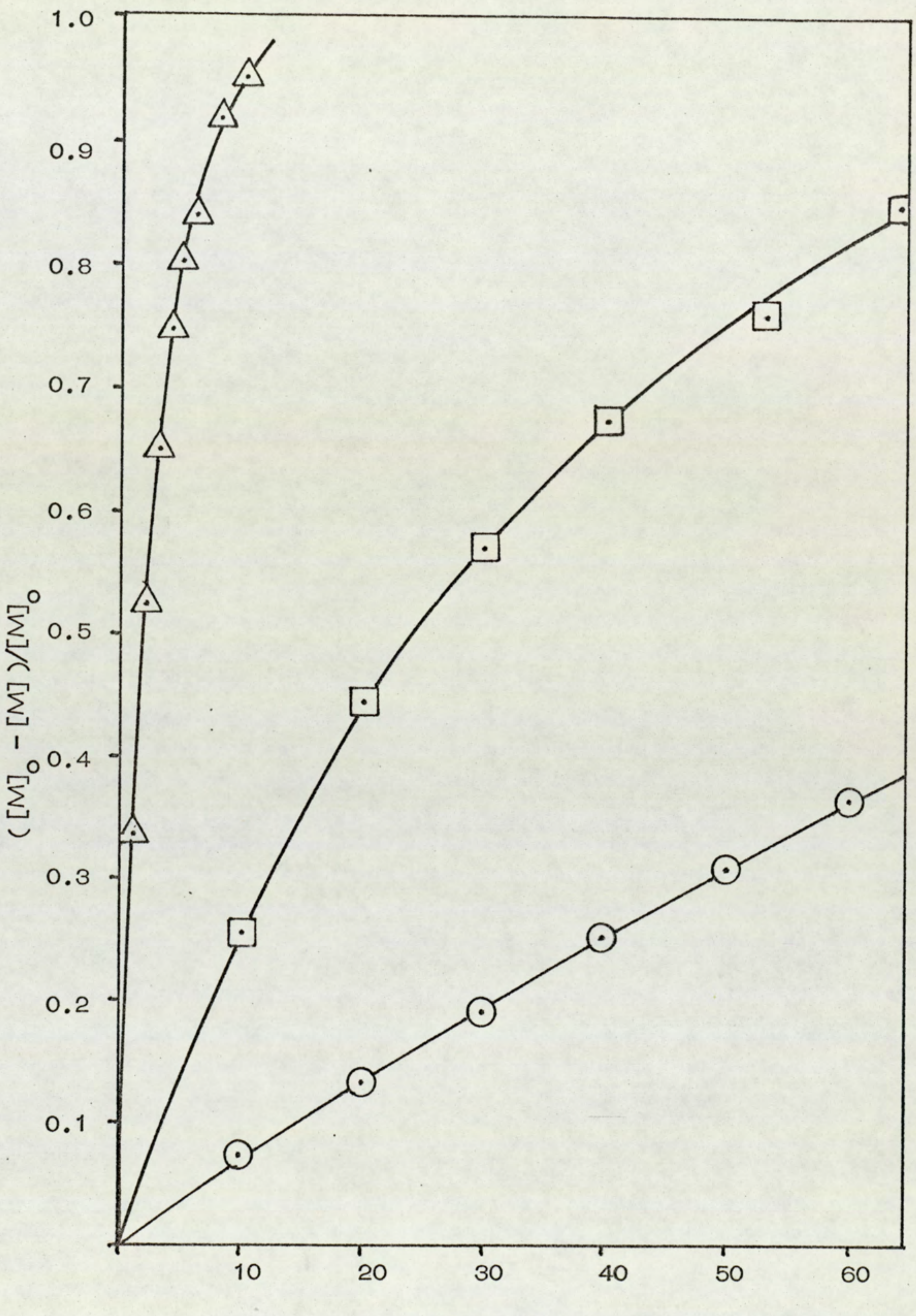


Fig. 6.3 Rate curves for the decomposition of PFAAC in isopropanol △ , 2-methyl propanol ⊡ and benzyl alcohol ⊙ , using nitrobenzene as cosolvent, at 30.0°C.

Table 6.2

Second-order rate constants (k_b) for the decomposition of PFAAC at 30°C in a series of alcohols, using nitrobenzene as a cosolvent. $[PFAAC]_o = 0.28$ mol. litre^{-1}, $[ØNO_2] = 4.9$ mol. litre^{-1}. Approximate dielectric constants are given.

Alcohol	Dielectric constant (approx.)	$[OH]_o$ mol. litre^{-1}	$10^5 k_b$ l.mol.$^{-1}$ sec.$^{-1}$
isopropanol	24	6.53	81.5
n-propanol	25	6.68	17.3
2-methylpropanol	25	5.41	8.6
tert-butanol	23	5.32	5.56
benzyl alcohol	24	4.82	2.65
benzyl alcohol*	11	9.63	9.5

*measured with no nitrobenzene as cosolvent.

gained from the fact that the most nucleophilic hydroxy compound, tert-butanol reacts more rapidly with PFAAC than does benzyl alcohol. It appears that the increased electrophilicity of the C(4) carbonyl in PFAAC enables to a certain extent the steric hindrance of the C(5) substituents to be overcome.

6.2 Discussion

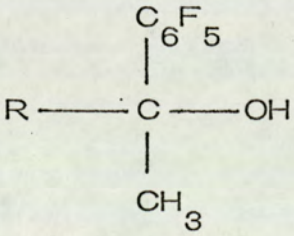
It is of great benefit to compare the thermal stability of a pentafluorophenyl substituted anhydrocarboxylate with its hydrocarbon analogue. Due to the unusual reaction profile experienced with PFAAC a direct comparison and assessment is not possible. However, a qualitative order of thermal stability may easily be produced and it is quite apparent that the effect of a pentafluorophenyl substituent markedly enhances the thermal stability of the ring. The thermal stability of PFAAC is of a comparable order to that observed for MAAC under the same conditions. In this environment the effect of a strongly electron withdrawing substituent is to increase the thermal stability of the ring. As discussed in Chapter 5, a direct analogy is the effect of chloromethyl substituents(62) on the anhydrosulphite ring leading to greater thermal stability over the hydrocarbon analogue. Ofthe four anhydrocarboxylates studied, pentafluorophenyl substitution possibly leads to the most thermally stable compound but as a result of such a substituent the susceptibility of the ring to enhanced decomposition in the presence of trace amounts of parent acid is greatly increased.

The linearity of the first-order plots obtained for the thermal decomposition of AAAC indicates that the presence of trace amounts of the parent acid does not sensibly affect the reaction profile. In contrast the reaction profile for PFAAC shows considerable curvature and a greatly increased rate of decomposition in the latter stages of the reaction. This will be discussed in more detail subsequently.

The effect of parent acid impurity may be overcome by carrying out the thermal decomposition at higher temperatures at which the first-order fragmentation of the anhydrocarboxylate ring would swamp this enhanced decomposition. The main disadvantage of high temperature decompositions is that the secondary fragmentation reaction, as in the case of the anhydrosulphites(49), becomes appreciable at temperatures in excess of 130°C, and thus reduces the proportion of polymeric products. The precise determination of the energy of activation and the associated kinetic parameters was not felt to be imperative as the work is primarily concerned with the polymerisability of the ring system.

Polymerisation of anhydrocarboxylates may occur in principle by two distinct mechanisms which may be considered to be in competition. The first involves a thermal extrusion reaction by a first-order process, resulting in the formation of a reactive α-lactone intermediate and loss of carbon dioxide. The α-lactone takes part in a rapid bimolecular reaction with hydroxyl groups present as trace amounts of impurity and arising in the first instance by reaction of the anhydrocarboxylate with moisture to give the parent α-hydroxy acid. Polymer formation occurs by repeated reaction of the terminal hydroxy group with the α-lactone. The second mechanism involves direct attack of the hydroxyl group at the C(4) carbonyl with subsequent loss of carbon dioxide and the formation of a further hydroxyl propagating species.

The magnitude of the ratio, $(k_1 + k_b[OH])_{B.A.}/(k_1)_{N.}$ may be considered as a semi-quantitative assessment of the extent of this bimolecular route. The value obtained for PFAAC (9.4×10^5 at 50°C) was considerably larger than those encountered for the hydrocarbon analogues and thus, coupled with the shape of the reaction profile, it is suggested that the bimolecular route is the predominant mode of polymerisation. Considering the nature of the propagating species; the nucleophilicity of the hydroxyl group, and hence the rate of attack at the C(4) carbonyl, is determined essentially by electronic effects of the other three substituents at the carbon to which the hydroxyl group is bonded. With reference to XXXII the first step of polymerisation is the reaction of the parent α-hydroxy acid with monomer, in which R = COOH.



$$R-\overset{\displaystyle C_6F_5}{\underset{\displaystyle CH_3}{C}}-OH$$

XXXII

The pentafluorophenyl and methyl groups will have a constant effect on nucleophilicity of the terminal hydroxyl group, however, the electron withdrawing carboxylic acid function will deactivate the hydroxyl nucleophile in the parent acid. The effect of this carboxylic acid group will diminish when displaced by one repeat unit from the hydroxyl group and thus the nucleophilicity of the propagating species may be considered to increase as the chain length increases. Thus $k_1 < k_2 < k_3$, but after some three or four propagating steps the carboxylic acid group is sufficiently far removed from the reaction site to have negligible effect on the hydroxyl group and the reaction proceeds at a substantially constant rate. With reference to Fig. 6.1, the semi-logarithmic plot for the decomposition of recrystallised PFAAC at 102°C; the graph shows good linearity for 70% of the reaction, this represents the limiting value of the rate constant for successive propagating steps.

The situation presented in the case of PFAAC is identical to the thermal decomposition of MAAC, however, in this latter case balance of steric and electronic effects leading to a significant bimolecular contribution are somewhat reversed. The nucleophilicity of the attacking hydroxyl group by comparison with that of PFAAC, is greater, but the C(4) carbonyl of MAAC is by no means as active to this form of attack. The determining factor in MAAC is the lack of a second substituent at C(5), which leads to a relatively unsterically hindered reaction path.

The anhydrosulphite ring is inherently less thermally stable than the anhydrocarboxylate ring, and whilst no work has been published on the effect of a pentafluorophenyl group on the anhydrosulphite ring a tentative assessment has been made.(69) The pentafluorophenyl/methyl anhydrosulphite appears to be less thermally stable than its hydrocarbon counterpart. By analogy with the anhydrocarboxylate system, it must be suggested that the observed rate of decomposition of this anhydrosulphite contains a significant contribution of the bimolecular route, whereas in the case of the hydrocarbon analogue the corresponding carbonyl is not sufficiently activated to nucleophilic attack for the steric hindrance of the two C(5) substituents to be overcome. Since the effect of an electron withdrawing substituent is to produce enhanced thermal stability and the size of the pentafluorophenyl group is comparable to that of a phenyl group, the pentafluorophenyl substituted anhydrosulphite would be expected to be more thermally stable than the hydrocarbon analogue.

The thermal decomposition of anhydrosulphites possessing small alkyl substituents at C(5) yields high molecular weight polymer with limitations arising due to the purity of the anhydrosulphite sample. The introduction of a phenyl or pentafluorophenyl substituent may be considered to decrease the polymerisability. Whilst the polymerisability of the phenyl substituted anhydrosulphite species is not questioned, the attainability of a purified sample of the monomer presents many synthetic problems and ultimately sets a limit on the use of anhydrosulphites as precursors in the synthesis of such substituted poly-α-esters.

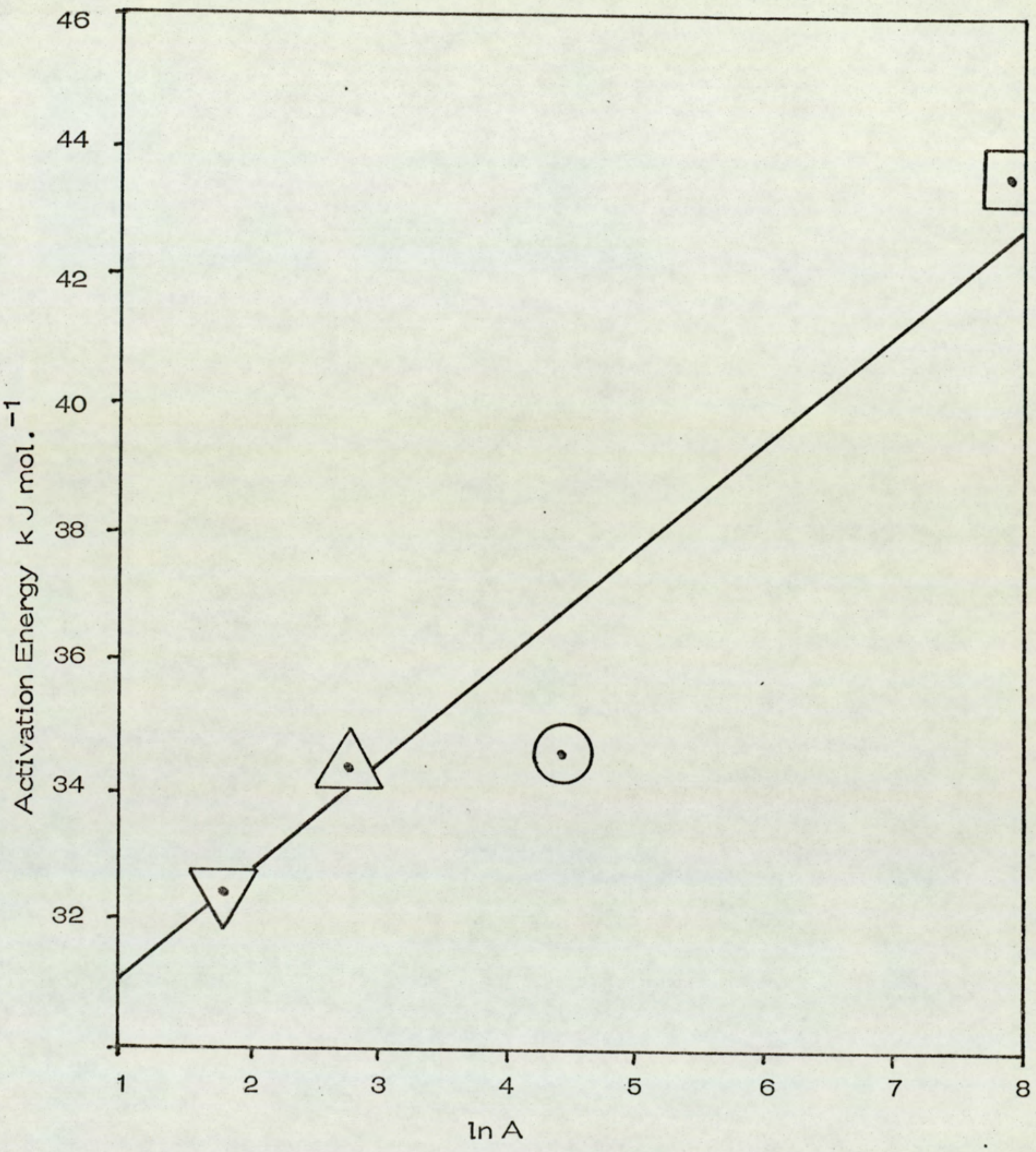
The inherent thermal stability of the anhydrocarboxylate ring sets a much higher limit from which the reactivity may be increased by various substituents. In spite of the enhanced thermal stability of PFAAC, the polymerisability of this species, in terms of rate of formation of polymer, is considerably increased over its hydrocarbon counterpart. This arises from the fact that the presence of a strongly electron withdrawing substituent such as the pentafluorophenyl group, offers an alternative mode of polymerisation, namely the bimolecular route. However, the effect of incorporating a large substituent is to decrease the stability of the anhydrocarboxylate ring to such an extent that thermal decomposition occurs at a sufficient rate for polymer to be formed. By way of summary, the predominant mode of polymerisation of AAAC is by the first-order thermal route via the α-lactone and for PFAAC, the bimolecular route involving terminal hydroxyl attack at the C-(4) carbonyl predominates.

By inspection of Table 6.1, it may be inferred that PFAAC is considerably more reactive than AAAC to attack by the nucleophile benzyl alcohol. The increase in activity of the C(4) carbonyl to this form of attack outweighs the steric effect of a second substituent at C(5), as evidenced by the somewhat slower rate of attack of MAAC over PFAAC. The higher values of the pre-exponential factor (A) and entropy of activation ($\Delta S^{\ddagger}$) for the reaction of PFAAC with benzyl alcohol, suggest that the formation of the transition state is considerably more efficient and is less ordered than for the hydrocarbon series. The nature of the attacking nucleophile is constant throughout but the C(4) carbonyl of PFAAC is considerably more electrophilic, thus the formation of the transition state would be expected to be more easily attained.

The values obtained for the energies of activation and the pre-exponential factors for the reaction of benzyl alcohol with a series of substituted anhydrocarboxylates may be rationalised in terms of an extrathermodynamic plot of these kinetic parameters. Fig. 6.4 shows such a plot. The linearity suggests that, in spite of a somewhat higher activation energy and pre-exponential factor, the reaction of this series of anhydrocarboxylates with benzyl alcohol is linked by a common mechanism.

PFAAC is considerably more reactive to benzyl alcohol than the phenyl substituted anhydrocarboxylates and it appears, therefore, that the predominant factor in determining the rate of reaction with a given nucleophile is the electrophilicity of the C(4) carbonyl, and that the size of the substituent at C(5), although of some importance, is a secondary factor. This is further emphasised by the fact that the dimethyl substituted anhydrocarboxylate does not react directly with benzyl alcohol to any significant extent.

In the previous chapter a relationship was obtained for the rate of reaction of the anhydrocarboxylates with benzyl alcohol at 50°C and the σ^* and E_s values for the C(5) entity and its substituents (Fig. 5.5, and Table 5.8). By interpolation of the estimated value of the second-order rate constant (from the Arrhenius plot), for the reaction of PFAAC with benzyl alcohol, a value of σ^* for the group $C_6F_5(CH_3)CH$ was found to be 0.9. The values of σ^* obtained for the group C_6H_5 and C_6F_5 are 0.6(65) and 1.1(70) respectively. The value for the group under discussion, therefore, is of an order expected. It is interesting to note that the increase in σ^* on the introduction of a single fluorine to a methyl group is



<u>Fig. 6.4</u> Extrathermodynamic Plot of the Activation Energy versus ln A for the reaction of benzyl alcohol with a series of anhydrocarboxylates.

▽ BAAC

△ AAAC

□ PFAAC

⊙ MAAC

1.1 units and for two fluorine atoms 2.05 units and yet the concerted effect of five fluorine in the C_6F_5 substituent results in an increase of only 0.5 units in the value of σ^*.

The reaction of PFAAC with a series of alcohols produced a similar spread of activity as observed with the hydrocarbon analogues. Table 6.2 gives the values of the second-order rate constants obtained for the reaction of PFAAC with benzyl alcohol using firstly nitrobenzene as cosolvent and secondly the alcohol as the only solvent. The rate constant for the reaction using a cosolvent is only 33% of that using neat benzyl alcohol. This value is comparable with that obtained for the reaction of MAAC with benzyl alcohol in which the rate constant in a cosolvent system was 28% of that in the pure alcohol.

The electronic and steric factors associated with the attacking nucleophile appear to be more finely balanced than do the same factors determining the reactivity of the C(4) carbonyl of the anhydrocarboxylate. Tertiary butanol is qualitatively the strongest nucleophile of the series but the reaction presents the most severely hindered reaction path. In the case of AAAC the steric hindrance is sufficient to reduce this alcohol to the least reactive of the series. However, for the more electrophilic C(4) carbonyl in PFAAC, the hydroxyl group of tertiary butanol is able to overcome a certain degree of steric hindrance associated with the reaction, which results in increased reactivity over a relatively unsterically hindered but weak nucleophile such as benzyl alcohol.

It is relevant to note that the least electrophilic C(4) carbonyl, AAAC, shows a far less spread in activity than does for example PFAAC, which possesses a more reactive reaction site.

With reference to the reactivity of the anhydrocarboxylates to a series of alcohols, it must be pointed out that the same factors contributing to high donicity of the solvent, namely the steric and electronic effects associated with the electron donating nucleophile, also affect the extent to which solvolysis of the transition state occurs. And whilst the steric and electronic effects associated with the attacking alcohol may be tentatively discussed, it would seem apparent that the more active nucleophile, when the species is used as the solvent medium, will give rise to an enhanced rate of reaction due to the aforementioned considerations. However, appreciating that the solvent medium will have an effect on promoting or retarding the reaction with a given nucleophile, the order of reactivity of the series of alcohols may be considered as a true representation of the susceptibility of the anhydrocarboxylates to reaction with various nucleophiles.

The relative effects of phenyl and pentafluorophenyl substituents on the reactivity of the anhydrocarboxylate ring may easily be understood in terms of the enhanced activity of the C(4) carbonyl. Electron donating substituents present at C(5), such as two methyl groups, result in ring system which shows considerable resistance to weak nucleophiles. Relatively strong nucleophiles by comparison to alcohols, such as primary amines result in a rapid decomposition of the anhydrocarboxylate to yield the corresponding amide but no polymeric products. The nature of the potential chain propagating species is necessarily an hydroxyl group and such alkyl substituents stabilise the ring to weak nucleophilic attack. The thermal stability of the anhydrocarboxylate with two methyl substituents is such that the thermal decomposition of this species is not a polymer forming reaction.

The incorporation of a single phenyl substituent in place of one of the methyl groups in the latter case reduces the thermal stability to an order which is compatible with polymer formation. Thus the thermal decomposition of AAAC results in an almost quantitative yield of the corresponding poly-α-ester. A second phenyl substituent, whilst undoubtedly reducing the thermal stability of the anhydrocarboxylate ring, unfortunately gives rise to a secondary fragmentation product, benzophenone, which ultimately decreases the yield of polymer. The effect of this second phenyl substituent is to decrease the polymerisability of the ring. The phenyl/hydrogen substituted anhydrocarboxylate may be considered to lie intermediate between the two previous cases, and although thermal decomposition is a polymer forming reaction, isolation of this unsymmetrical polymer from a solvent such as nitrobenzene becomes difficult.

The inductively electron withdrawing nature of the phenyl group results in an increase in the susceptibility of the C(4) carbonyl to nucleophilic attack. Pentafluorophenyl substitution considerably enhances the electrophilicity of this carbonyl. However, the bimolecular propagation reaction involving direct attack of the terminal hydroxyl group at the C(4) carbonyl proceeds at such a slow rate that it is an inconvenient method of producing polymers. A complicating factor also arises with this mode of polymerisation; the factors enhancing the susceptibility of the C(4) carbonyl to nucleophilic attack also decrease the nucleophilicity of the attacking hydroxyl group, which ultimately reduces the rate of polymerisation.

In spite of the difficulties experienced with the conventional methods of polymerisation of this type of ring compound, the enhanced electrophilicity of the C(4) carbonyl offers a potential site to be exploited in establishing a mode of polymerisation involving the use of a species which serves to initiate the decomposition of the anhydrocarboxylate ring and to subsequently form polymer.

CHAPTER 7

Tertiary Base Initiated Decomposition of Phenyl Substituted 1,3-Dioxolan 2,4-Diones

The susceptibility of the C(4) carbonyl of phenyl substituted anhydrocarboxylates to nucleophilic attack is such that it offers a potential site for initiated decomposition. The thermal decomposition of phenyl substituted anhydrocarboxylates, as discussed in the previous chapters, is a polymer forming reaction. In common with many other types of polymerisations, low temperature polymerisation favours the formation of more stereoregular polymer chains. In addition, choice of a suitable initiator would enable inconveniently long reaction times, as experienced with thermal polymerisation, to be avoided.

In the course of an examination of the effect of phenyl substituents on the general reactivity (and more specifically the search for other modes of initiated polymerisation), it was observed that in common with the dimethyl substituted anhydrocarboxylate, reaction with primary and secondary amines yielded the corresponding amides. Tertiary bases, however, lacking an available and transferable proton failed to form a direct bimolecular adduct, but were observed to give rise to a fairly rapid decomposition, which did not occur in the dimethyl case. The nature and products of this reaction were, therefore, examined in some detail.

In this section results are presented relating to the polymerisation of MAAC and BAAC using tertiary base initiators of the heteroaromatic type, namely pyridine and its derivatives. The two extremes of the phenyl substituted anhydrocarboxylate series were used in order to assess the potential use of this mode of polymerisation for the synthesis of phenyl substituted poly-α-esters.

7.1 Results

Initiated Decomposition of MAAC

The tertiary base initiated decomposition of MAAC was carried out in nitrobenzene, and the rate of decomposition measured by gas evolution techniques. The "initiator-type" constant volume kinetic apparatus as shown in Fig. 2.2 was used as temperatures in excess of 50°C were not required. The pressure of the evolved carbon dioxide was measured as a function of time, which, by equation 6 enables the rate of disappearance of monomer to be followed concurrently. Conversion of the CO_2 pressure data to a conventional first-order plot showed good straight line behaviour into the third decade. This indicated that the decomposition of MAAC using a tertiary base initiator was a first-order process with respect to monomer and that the effective concentration of active initiator remained constant throughout the reaction. Fig. 7.1 shows a typical first-order plot for the decomposition of MAAC at 25°C in the presence of approximately (a) 30% molar concentration of pyridine, and (b) 10% molar concentration of the same initiator. The curved plot (c) was obtained when the "bucket", containing a 10% molar quantity of pyridine in nitrobenzene, was not allowed to drop into the solution of monomer. It may be seen from this plot

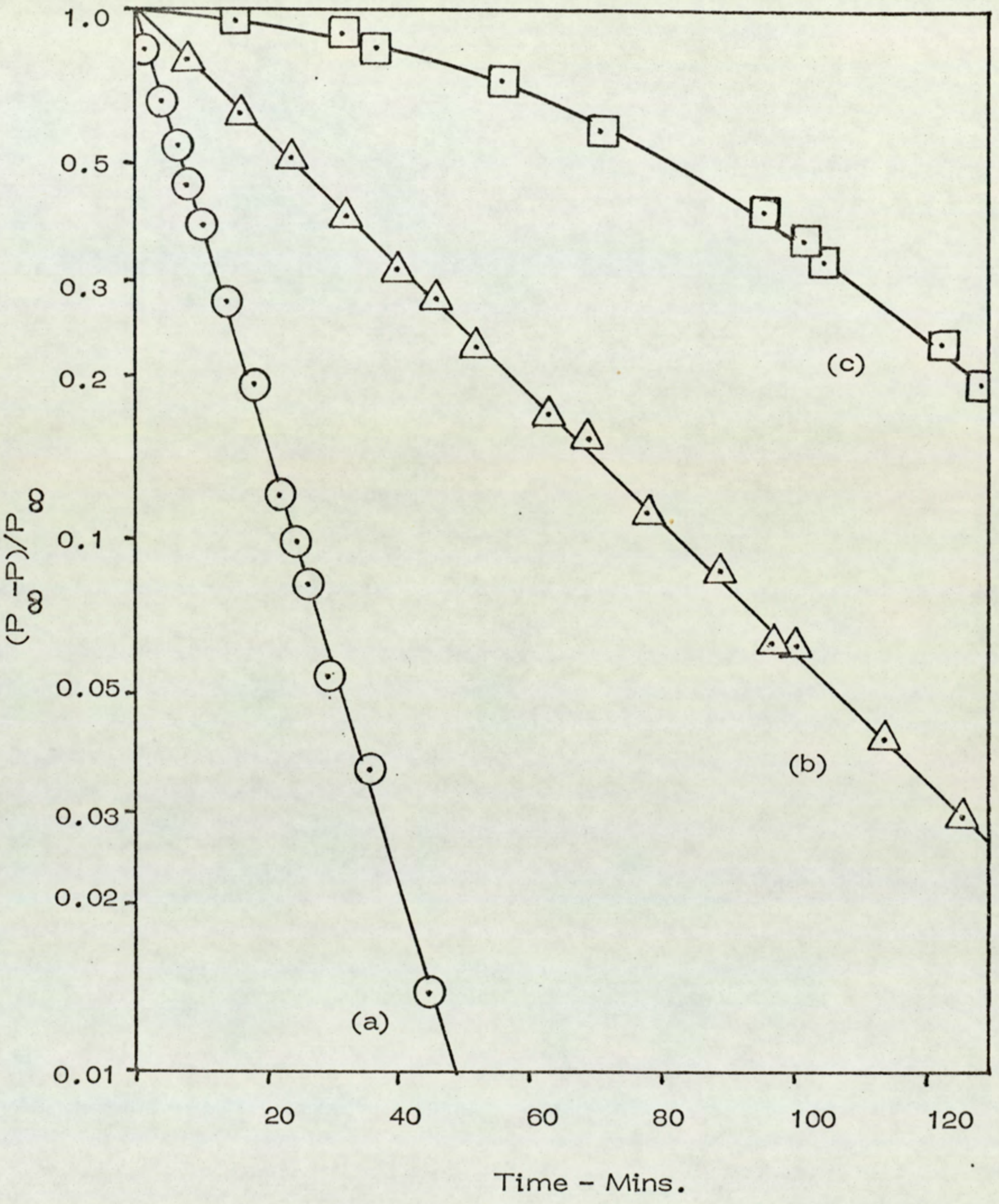


Fig. 7.1 First-order (semi-logarithmic) plots for the decomposition of MAAC in the presence of approximately,

⊙ 30% molar pyridine

△ 10% molar pyridine

⊡ vapour pressure of pyridine.

$[\text{MAAC}]_o = 0.33 \text{ mol.litre.}^{-1}$

that the decomposition of MAAC occurs at a substantial rate even in the presence of a very small concentration of pyridine; in this case the vapour pressure of pyridine at that temperature. The increase in rate is attributed to the equilibration of the initiator in the bucket and in the monomer solution.

Decomposition of MAAC in the presence of substoichiometric amounts of pyridine results in a greatly enhanced rate of decomposition. As may be seen from Fig. 7.1, the decomposition occurs even with a trace of pyridine and the rate appears to be dependent upon the concentration of pyridine used. Complete decomposition of MAAC occurs and thus it may be inferred that the pyridine initiator is not removed by chemical combination with the monomer.

Increase in initial concentration of pyridine resulted in a corresponding increase in the rate of reaction. The rate of reaction may, in general be expressed by equation 48;

$$\frac{-d[M]}{dt} = k_{obs.}[M][py]^x \qquad \text{.... (48)}$$

where [M], [py] and $k_{obs.}$ are the concentrations of MAAC, pyridine and the rate constant respectively, and x is the number of molecules of pyridine apparently involved in the rate determining step.

Equation 48 may be written in the form,

$$\frac{-d[M]}{dt} = k_{obs.}'[M] \qquad \text{.... (49)}$$

where,

$$k_{obs.}' = k_{obs.}[py]^x \qquad \text{.... (50)}$$

This is conveniently expressed in the logarithmic form,

$$\log_e k_{obs.}' = \log_e k_{obs.} + x \log_e[py] \qquad \ldots. (51)$$

Thus a plot of $\log_e k_{obs.}'$, the rate constant obtained from the first-order plot as in Fig. 7.1, versus $\log_e[py]$, enables $k_{obs.}$, the second-order rate constant for the process, and x, the order of dependence of the rate upon pyridine concentration to be easily determined.

Table 7.1 gives the first-order rate constants for the decomposition of MAAC with various concentrations of pyridine at 25°C and Fig. 7.2 shows a plot of $\log_e k_{obs.}'$ versus $\log_e[py]$ for this reaction.

Table 7.1

First-order rate constants obtained for the decomposition of MAAC with various concentrations of pyridine at 25°C. $[MAAC]_o = 0.33$ mol. litre^{-1}.

Pyridine concentration mol. litre^{-1}	$10^3 k_{obs.}'$ sec.$^{-1}$
0.0134	0.19
0.0266	0.42
0.0388	0.84
0.0528	1.2
0.0661	1.4
0.0792	1.6
0.2036	3.62

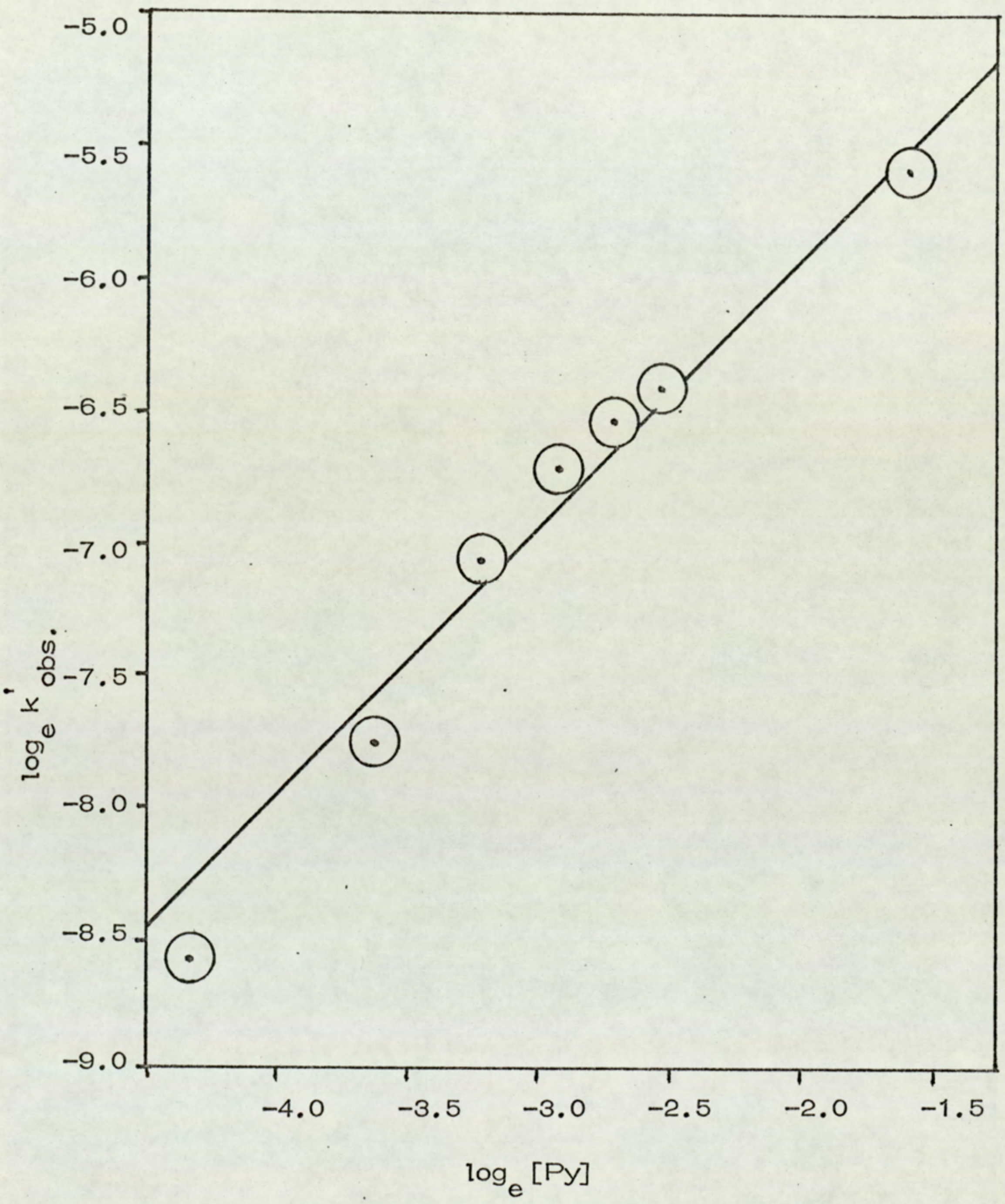


Fig. 7.2 Plot of $\log_e k'_{obs.}$ versus $\log_e$ [Py] for the decomposition of MAAC with pyridine at 25°C.

The gradient obtained is unity indicating that the reaction is first-order in pyridine. The equation expressing the overall rate of reaction may, therefore, be written;

$$\frac{-d[M]}{dt} = k_{obs.}[M][py] \qquad \ldots. (52)$$

where $k_{obs.}$ is the second-order rate constant for the process. The intercept at the point where the pyridine concentration corresponds to 1 mol. litre^{-1} enables $\log_e k_{obs.}$ to be determined and hence the second-order rate constant. The value of $k_{obs.}$ obtained by this graphical method ($k_{obs.} = 1.93 \times 10^{-2}$ l. mol.$^{-1}$ sec.$^{-1}$) is in good agreement with the value obtained by averaging the values of the rate constant according to equation 52 (1.91 $\times 10^{-2}$ l. mol. sec.$^{-1}$).

It must be emphasised that the first-order rate constant is independent of the monomer concentration at a particular temperature, but depends upon the concentration of pyridine present. Whilst approximately 10% molar concentration of pyridine has been used in one case the actual ratio of monomer to pyridine concentration is continually changing throughout the process of monomer decomposition and yet the reaction shows first-order dependence on residual monomer throughout.

The effect of temperature on the rate of decomposition of MAAC in the presence of a 10% molar concentration of pyridine was studied in the range 25° to 45°C. The derived second-order rate constants for this decomposition are given in Table 7.2.

Table 7.2

Second-order rate constant ($k_{obs.}$), energy of activation (E), pre-exponential factor (A) and entropy of activation ($\Delta S^{\ddagger}$) for the decomposition of MAAC in the presence of a 10% molar concentration of pyridine. $[MAAC]_o = 0.33$ mol.litre^{-1}, [py] = 0.033 mol. litre^{-1}.

Temperature °C	$10^2 k_{obs.}$ l.mol.$^{-1}$ sec.$^{-1}$
25.8	1.93
30.4	2.17
34.5	3.02
40.3	4.3
44.9	5.2
E (kJ mol.$^{-1}$)	48.3
A (l.mol.$^{-1}$sec.$^{-1}$)	4.3×10^6
$\Delta S^{\ddagger}$ (J.K.$^{-1}$mol.$^{-1}$)	-163

The activation energy (E), pre-exponential factor (A) and the entropy of activation ($\Delta S^{\ddagger}$) were obtained from a conventional Arrhenius plot. The value of the activation energy is somewhat higher than the value expected for nucleophilic attack at an activated site, and the values for A and the entropy of activation would suggest that the formation of the transition state requires a specific orientation of the reactants.

The decomposition of MAAC in the presence of pyridine presents several outstanding features in that decomposition results in the formation of polymer and no pyridine is associated with the polymer. There is also an unusual combination of activation energy, pre-exponential factor and entropy of activation; these lie intermediate in many respects between those parameters for nucleophilic attack and for scission of a covalent bond.

In order to ascertain the precise role of pyridine in the decomposition process a series of substituted pyridines were used. The nucleophilicity of the nitrogen in pyridine may be increased by the incorporation of alkyl groups as substituents on the pyridine ring. Thus the series; pyridine, α-picoline (2-methyl pyridine) and 2,6-lutidine (2,6-dimethyl pyridine) represents an increase in nucleophilicity of the nitrogen with increase in ring substitution. Figure 7.3 shows the initial rates for the decomposition of MAAC with a series of substituted pyridines and Table 7.3 tabulates the second-order rate constants for the process. The increase in nucleophilicity in passing from pyridine to α-picoline to 2,6-lutidine is also accompanied by an increase in the steric hindrance associated with the nitrogen nucleophile. It would, therefore, appear that the increase in rate due to the increase in nucleophilicity of the nitrogen is very nearly balanced by a decrease in reactivity due to the steric repulsion of the additional methyl groups. This is further emphasised by the somewhat drastic reduction in the rate constant when the base, 2-methoxy pyridine is used. In this case the steric hindrance of the substituent group is coupled with a decrease in nucleophilicity of the nitrogen by the inductively electron

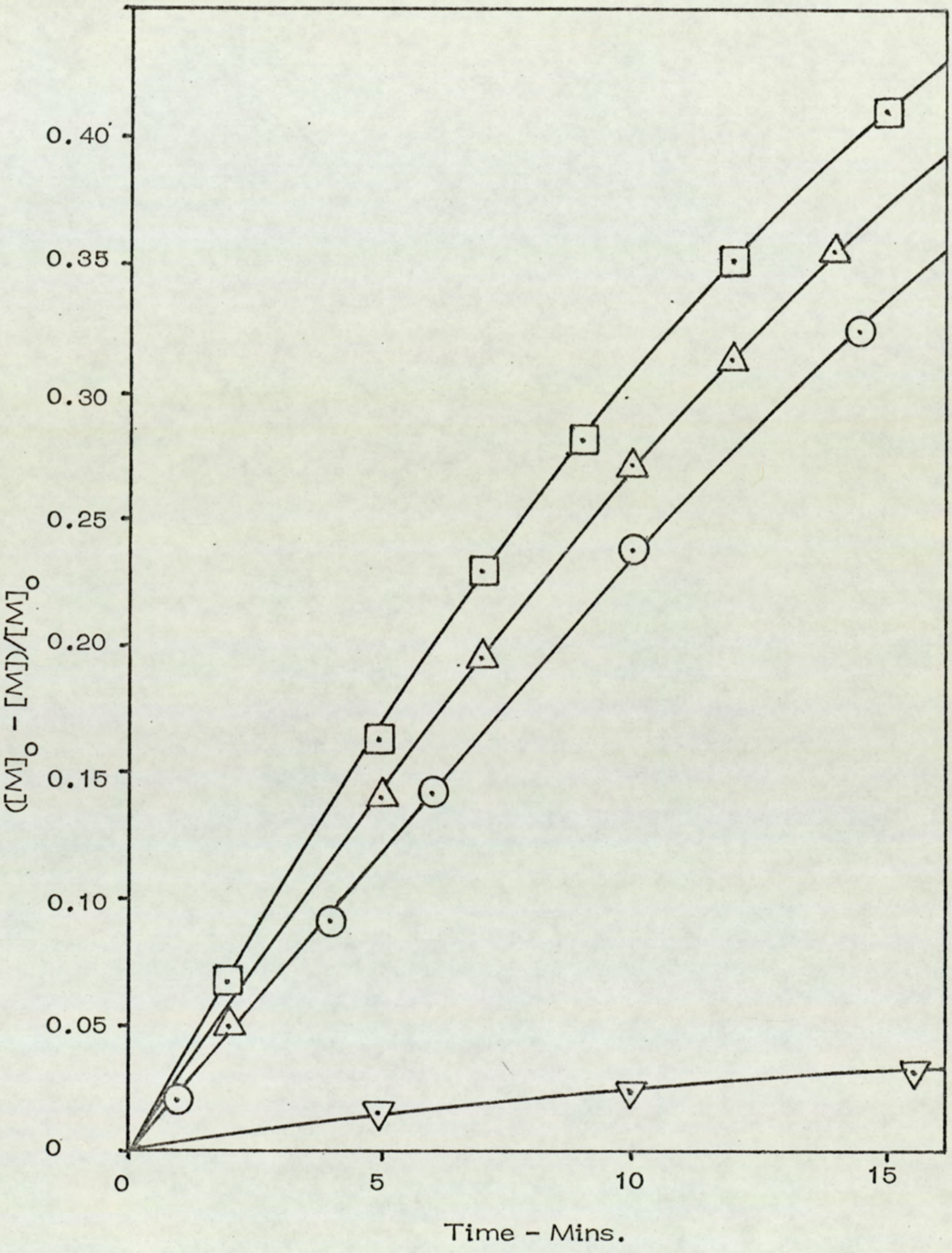


Fig. 7.3 Initial rate curves for the decomposition of MAAC with,

⊙ 10% molar concentration of pyridine
△ 10% molar concentration of α-picoline
⊡ 10% molar concentration of 2,6 -lutidine
▽ 50% molar concentration of 2-methoxy pyridine.

$[MAAC]_o = 0.33$ mol. litre^{-1}. Temp. 25.8^{o}C.

withdrawing methoxy substituent. The nucleophilicity of the nitrogen is reflected in the pKa values for the substituted pyridines and the results suggest that for an electron donating substituent, such as a methyl group, there is quite a fine balance between the steric and electronic effects associated with the heterocyclic base.

Table 7.3

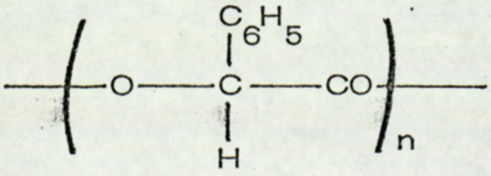
Second-order rate constants ($k_{obs.}$) for the decomposition of MAAC with a series of substituted pyridines at 25.8°C $[MAAC]_o$ = 0.33 $mol.litre.^{-1}$

Substituted Pyridine	pKa.	$10^2 k_{obs.}$ $l.mol.^{-1}$ $sec.^{-1}$
pyridine	5.17(a)	1.93
α-picoline	5.97(a)	2.07
2,6-lutidine	6.75(a)	2.33
2-methoxy pyridine	3.3(b)	0.00021

(a) obtained from reference (71)

(b) obtained from reference (72)

In all cases the decomposition of MAAC in the presence of pyridine and substituted pyridines resulted in the formation of a poly-α-ester (XXXIII).



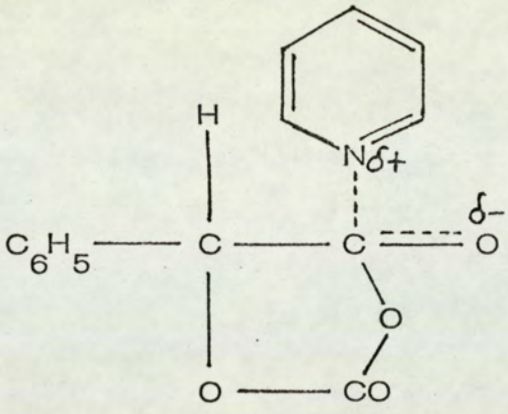
$$\left(-O-\overset{C_6H_5}{\underset{H}{C}}-CO- \right)_n$$

XXXIII

The type of mechanism which must be envisaged from a consideration of the results presented above, involves the formation of an intermediate between the monomer and base which rapidly decarboxylates to yield a species capable of taking part in a chain propagation process. The loss of pyridine may or may not be synchronous with the loss of carbon dioxide but the pyridine must at some stage be lost from the intermediate in order to take part in further decomposition reactions. Equation 53 depicts a possible sequence of reactions leading to the formation of products.

$$\begin{tikzcd}
\text{MAAC} + \text{Py} \arrow[r, shift left] & \text{[MAAC Py]} \arrow[l, shift left] \arrow[d] \\
\text{products} & \begin{matrix}\text{Polymerisable} \\ \text{species}\end{matrix} + CO_2 + \text{Py} \arrow[l]
\end{tikzcd} \quad \ldots . (53)$$

In the preceeding chapters, an assessment has been made of the susceptibility of the C(4) carbonyl of the anhydrocarboxylate ring to nucleophilic attack. No evidence was found for attack at the C(2) carbonyl, and, therefore, the intermediate suggested above may involve a form of a charge-transfer complex between the C(4) carbonyl and the pyridine molecule as in XXXIV. The strength of the charge-transfer bond will depend essentially upon the nucleophilicity of the nitrogen, the susceptibility of the C(4) carbonyl to this form of attack, and the steric hindrance associated with both the heterocyclic base and the substituents at C(5) of the anhydrocarboxylate.



XXXIV

Such complex formation of this type resulting in the enhanced polarisation of the C(4) carbonyl may conceivably be observed in the infrared spectrum in the region of a C = O stretching frequency. The ester carbonyl absorption of the polymer is sufficiently far removed from that of the anhydrocarboxylate, that this procedure is also a convenient way of monitoring the rate of disappearance of monomer and the rate of formation of polymer simultaneously. Tetrahydrofuran (T.H.F.) was found to be a suitable solvent for the anhydrocarboxylate and the polymer; no precipitation of the polymer occurred. The complete reaction was carried out in a liquid cell of thickness 0.025 cm., using a matched cell as a solvent blank. Fig. 7.4 shows a typical change in absorption of the monomer, MAAC, and polymer with time.

The decrease in intensity of the carbonyl absorption of the anhydrocarboxylate was indicative of the decomposition of monomer. It was hoped that a weak absorption in the region 1600–1800 cm^{-1} would be observed for the polarised C(4) carbonyl as depicted in XXXIV. However, the carbonyl absorptions for the monomer and polymer are sufficiently strong to overshadow the appearance of a

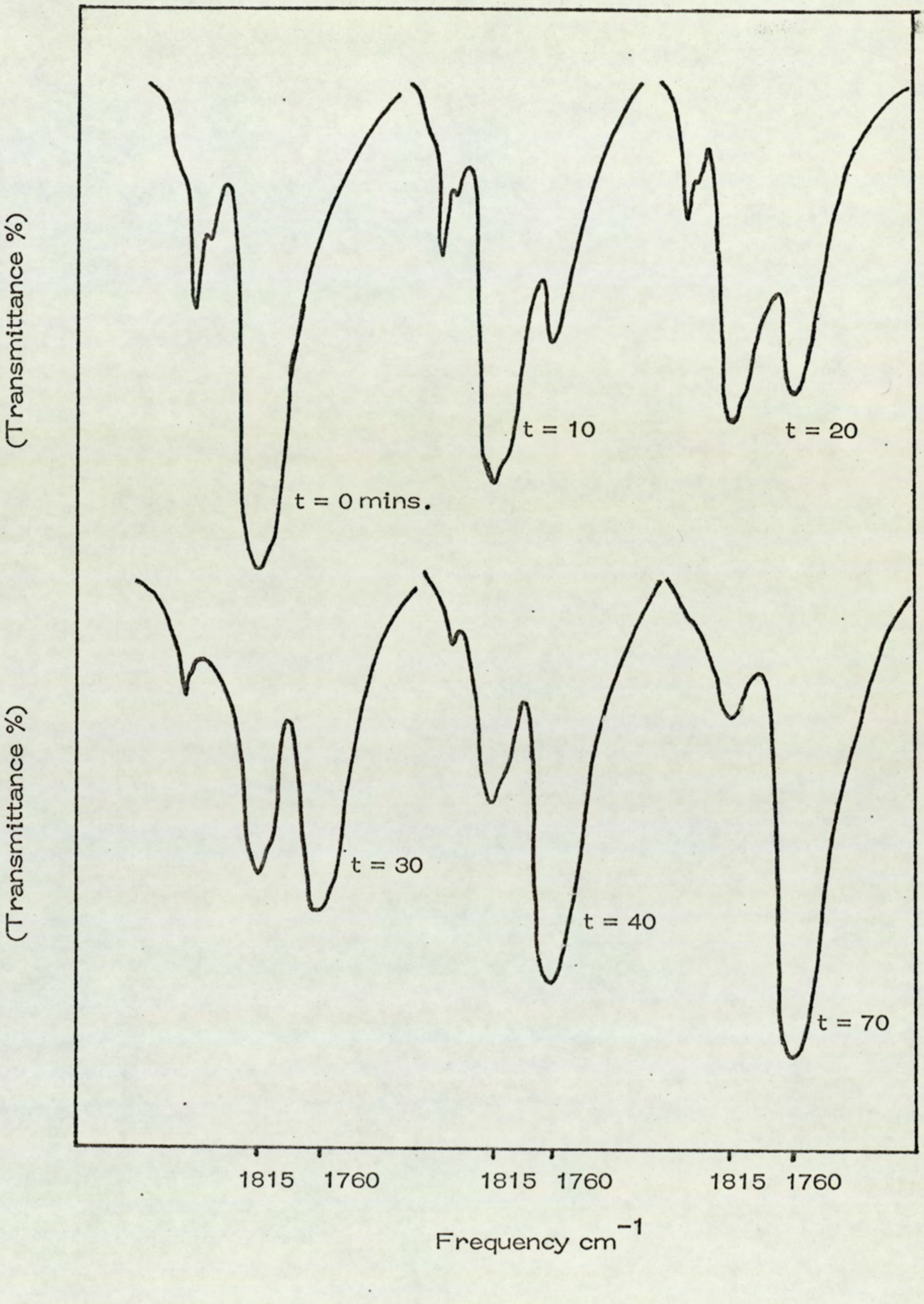


Fig. 7.4 Infrared spectra recorded during the polymerisation of MAAC using 10% molar concentration of pyridine as initiator. $[MAAC]_o$ = 0.9 mol. litre^{-1}, cell thickness 0.025 cm. Solvent; T.H.F. using a matched solvent blank.

weak addition carbonyl. If such a charge-transfer intermediate is formed during the decomposition then its maximum possible concentration will only be that of pyridine initiator. It is unlikely that all the pyridine is utilised in the formation of the intermediate, in which case the reverse reaction of the first stage equilibrium would be negligible compared with the forward reaction and the reaction profile would be considerably more complex.

Conversion of the absorbances for the monomer and polymer absorptions to conventional first-order plots according to equations 20 and 21 (section 2.2) enables the rate of monomer disappearance to be superimposed upon the rate of polymer formation. Fig. 7.5 shows first-order rate plots for the two processes. It is evident from the form of the linear behaviour of the two rates that the rate of formation of polymer is concurrent with the rate of disappearance of monomer.

The mechanism associated with the polymerisation of MAAC with pyridine will be discussed in section 7.2 of this chapter.

The absence of a hydrogen atom attached to the nucleophilic centre probably accounts for the fact that no pyridine-monomer product is formed. In the case of a relatively weak nucleophile such as benzyl alcohol, decomposition of the monomer in this solvent results in the formation of the corresponding α-hydroxy acid ester. The reaction with a strong nucleophile, benzylamine, gives the corresponding secondary amide and a quantity of the carbamate salt of the amine. The second-order rate constant for the reaction of MAAC with benzylamine is of the order of

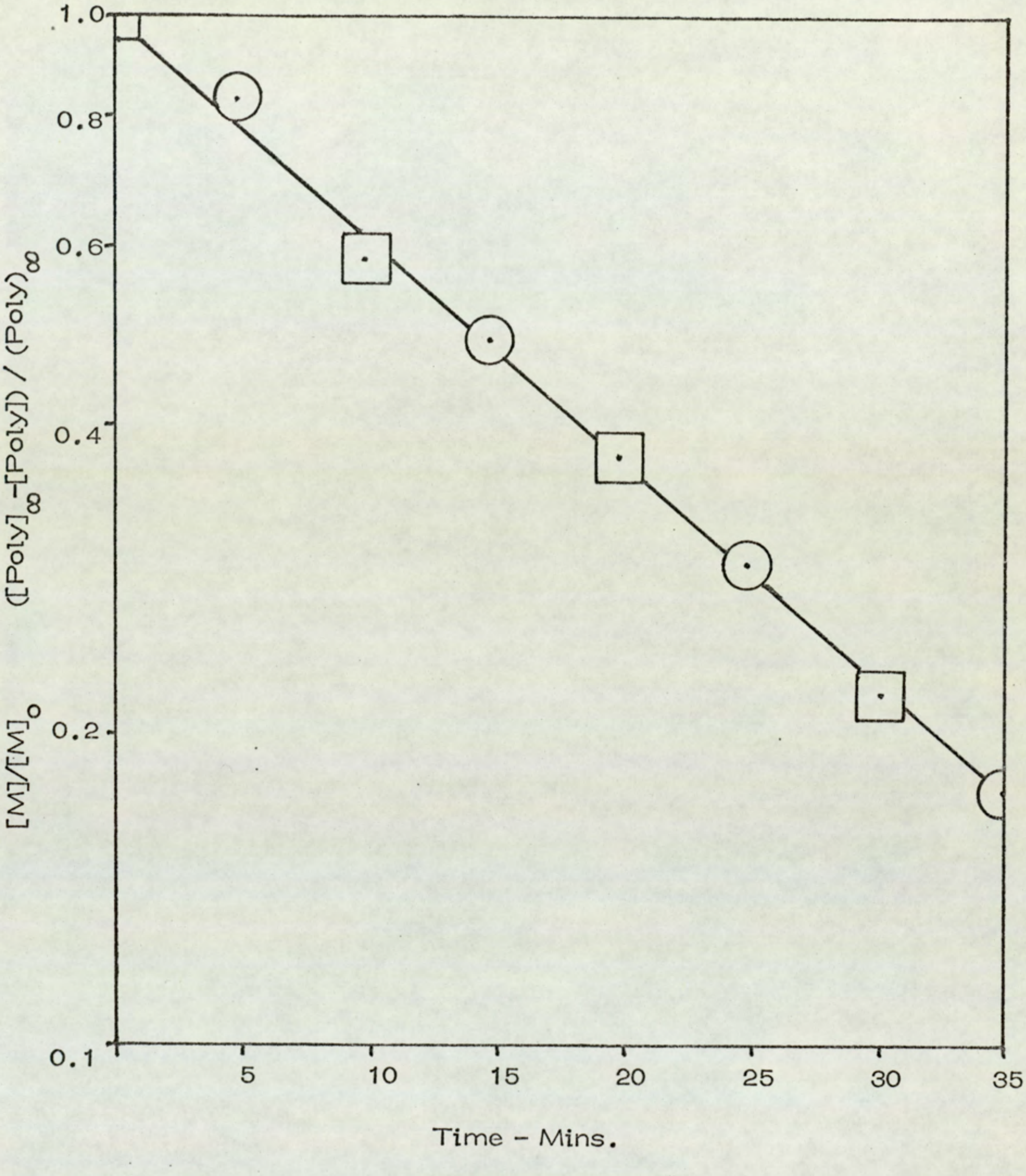


Fig. 7.5 First-order semi-logarithmic plot for the decomposition of MAAC with 10% molar pyridine in T.H.F.

⊙ disappearance of MAAC $[M]/[M]_o$

⊡ formation of polymer $([Poly]_\infty-[Poly])/[Poly]_\infty$

$[MAAC]_o = 0.9$ mol.litre^{-1}

Reaction carried out in a cell of 0.025 cm thickness and using a matched solvent cell blank.

$k = 1.0$ l.mol.$^{-1}$sec.$^{-1}$ at 35°C. This is a factor of 30 times greater than the corresponding decomposition with pyridine, and over 2×10^3 times greater than the reaction with benzyl alcohol.

Initiated Decomposition of BAAC

Preliminary investigations of the reaction of BAAC with pyridine showed that at room temperature the reaction proceeded at an extremely slow rate. Reactions using a ten-fold molar excess of pyridine in nitrobenzene resulted in a measurable rate of decomposition but the reaction was severely complicated by the solubility of carbon dioxide in high concentrations of pyridine in nitrobenzene. Increasing the temperature to 50°C resulted in a corresponding increase in rate of reaction. It was apparent that the incorporation of a second phenyl substituent at C(5) of the anhydrocarboxylate resulted in a drastic decrease in reactivity with pyridine in spite of an increase in the susceptibility of the C(4) carbonyl to nucleophilic attack.

In view of the inconveniently long reaction times involved at low temperatures which accentuated any leaks in the initiator-type kinetic apparatus, an assessment of the reactivity of BAAC with pyridine was carried out in the temperature range 60°-80°C using the sealed version of the kinetic apparatus, and using a pyridine concentration of about equimolar with respect to the monomer.

Essentially, the reaction of BAAC with an equimolar amount of pyridine in nitrobenzene over this temperature range was a rapid process and comparable to the reaction of MAAC with a 10%

molar concentration of initiator at room temperature. However, this rapid reaction in the case of BAAC was preceeded by quite a long induction period. Conversion of the pressure readings versus time for the decomposition, into a conventional first-order plot of $(P_\infty - P)/P_\infty$, resulted in a slow rate of reaction, but continually increasing for about the first 50% of the reaction. After this induction period the first-order plot showed good linear behaviour for the remainder of the reaction. Fig. 7.6 shows typical reaction profiles of first-order plots for the decomposition of BAAC with half-molar, equimolar and a two-molar excess (on monomer) of pyridine at 80°C. Calculation of the first-order rate constants for the latter part of the reaction and a plot of these values versus pyridine concentration according to equation 51 indicated that there was very little dependence of the rate of reaction on pyridine concentration. In fact the increase in rate constant with pyridine may indeed be due to the increase in donicity of the solvent medium, however, it is quite apparent that the presence of such amounts of pyridine do initiate the decomposition of BAAC.

Variation of the temperature had a more drastic effect on the rate of reaction than varying the pyridine concentration. Fig. 7.7 shows the reaction profiles for the decomposition of BAAC with an equimolar concentration of pyridine in nitrobenzene at temperatures in the range 60° to 80°C. Straight line behaviour is shown for the latter stages of the reaction, and whilst the validity of performing an Arrhenius plot and the relevance of the determined kinetic parameters may be questioned; parameters that are obtained do reflect

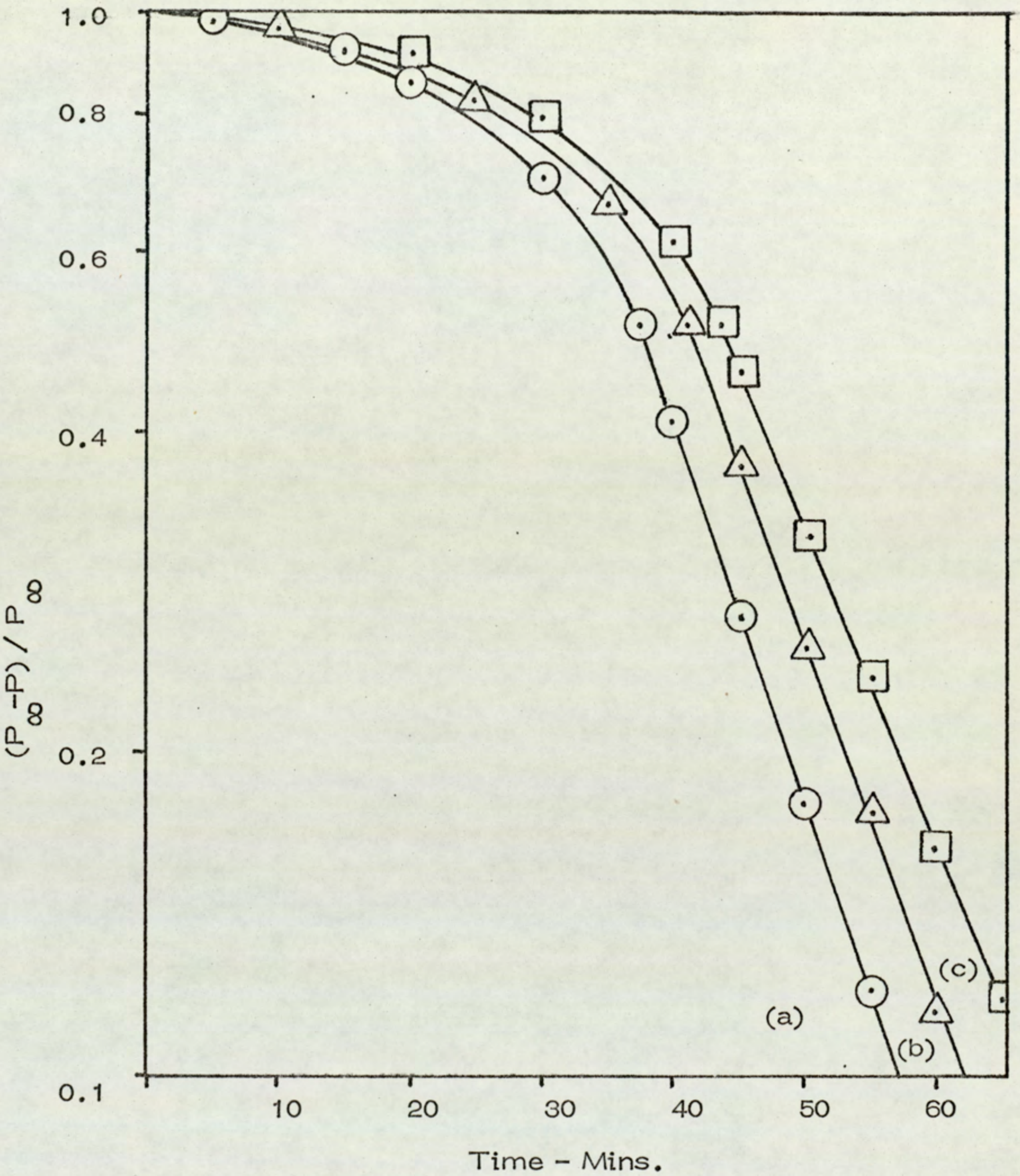


Fig. 7.6 Decomposition of BAAC with pyridine in nitrobenzene at 80.2°C. $[BAAC]_o$ = 0.30 mol. litre^{-1}.

(a) [pyridine] = 0.60 mol.litre^{-1}

(b) [pyridine] = 0.30 mol. litre^{-1}

(c) [pyridine] = 0.15 mol. litre^{-1}

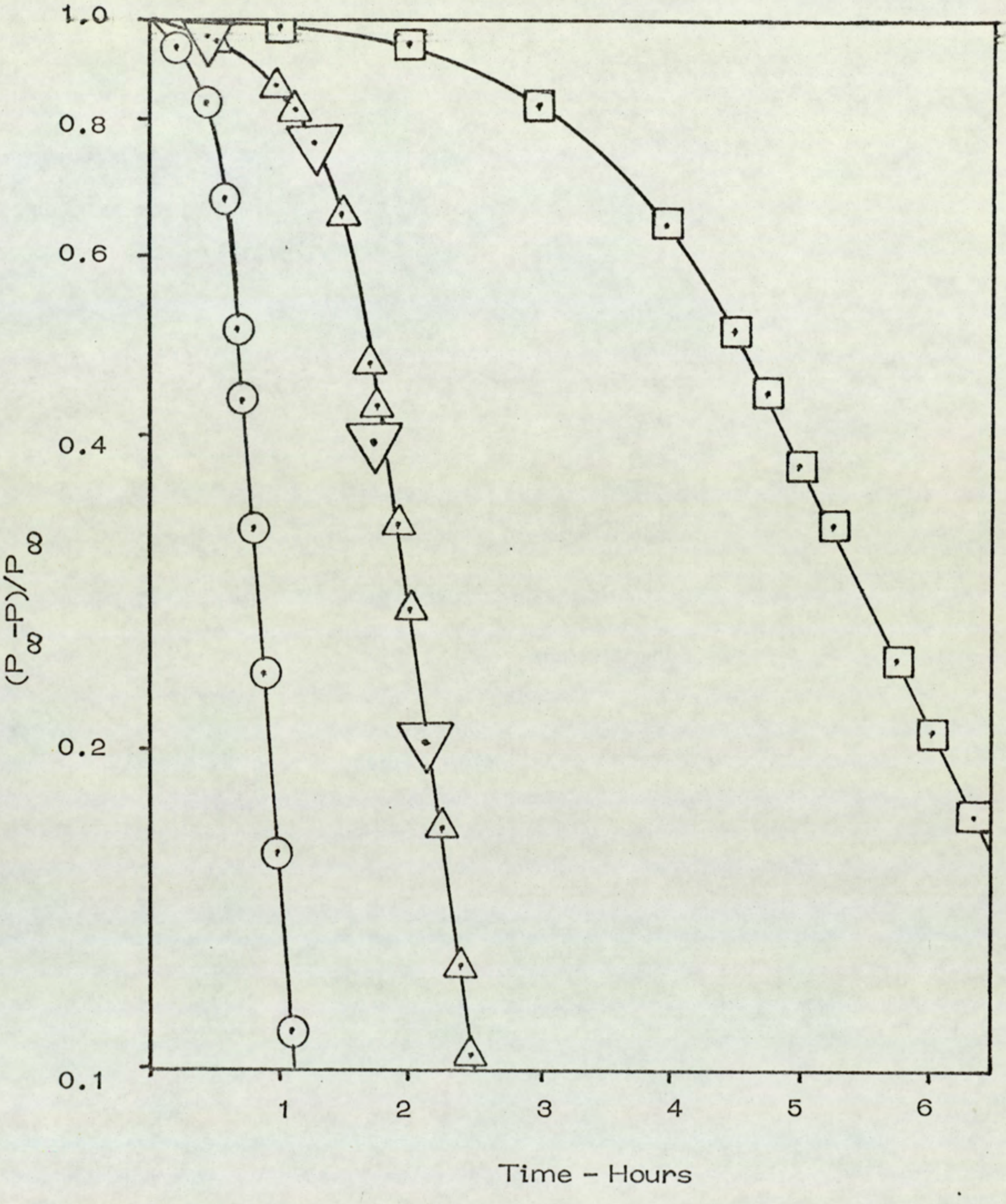


Fig. 7.7 Decomposition of BAAC with equimolar amounts of pyridine at,

⊙ 80.2°C; △ 70.2°C; ⊡ 60.3°C.

$[BAAC]_o = [Py] = 0.30$ mol.litre^{-1}

▽ the reaction followed colorimetrically.

the effect of temperature on the decomposition process, which over the latter stages obeys a first-order rate law with respect to residual monomer.

Table 7.4 gives the second-order rate constants and the derived activation energy for the decomposition of BAAC with an equimolar concentration of pyridine.

Table 7.4

Second-order rate constants ($k_{obs.}$), energy of activation (E), pre-exponential factor (A) and entropy of activation for the decomposition of BAAC with equimolar amounts of pyridine. $[BAAC]_o = [py] = 0.30$ mol.litre^{-1}.

Temperature ^oC	$10^3\, k_{obs.}$ l.mol.$^{-1}$sec.$^{-1}$
60.3	0.59
70.2	1.89
80.2	4.24
E (kJ mol.$^{-1}$)	87.7
A (l.mol.$^{-1}$sec.$^{-1}$)	3.8×10^{11}
$\Delta S^{\ddagger}$ (J.K.$^{-1}$mol.$^{-1}$)	-67.3

The value of the activation energy (E) obtained is somewhat higher than that obtained for the MAAC system. This may suggest that the charge-transfer complex, which is considered as an intermediate, does not possess the same degree of weakened bonds; this must ultimately be a result of the strength of the pyridine to carbonyl bond in the complex. Presumably the extent to which pyridine may initiate decomposition is also enhanced by the inherent ring strain of the anhydrocarboxylate. Thus, in the case of a strained ring system such as BAAC, once the intermediate has been formed the probability of decomposition of the anhydrocarboxylate is high.

In the case of MAAC it was apparent that the effect of increasing the nucleophilicity of the pyridine nitrogen by the presence of methyl substituents, was to a great extent offset by the steric hindrance of that substituent during some stage of the reaction. However, in BAAC the decomposition with α-picoline and 2,6-lutidine was considerably slower than for pyridine but the reaction profile retained its general form. Fig. 7.8 shows the decomposition of BAAC in the presence of equimolar amounts of pyridine, α-picoline and 2,6-lutidine. The results would suggest that for a sterically hindered anhydrocarboxylate, the steric effect of the substituted pyridine is more important than the nucleophilicity of the base in determining the rate of reaction.

The decomposition of BAAC with pyridine in nitrobenzene resulted, in all cases, in the solution turning a deep reddish brown colour. The rate of appearance of this colouration seemed to be coincident with the rate of decomposition as measured by the evolution of carbon dioxide. The rate of reaction was, therefore, followed by a colorimetric technique which involved measurement of the absorbance of the reaction solution in the visible region. The reaction was carried out at atmospheric pressure over a bed of dry nitrogen

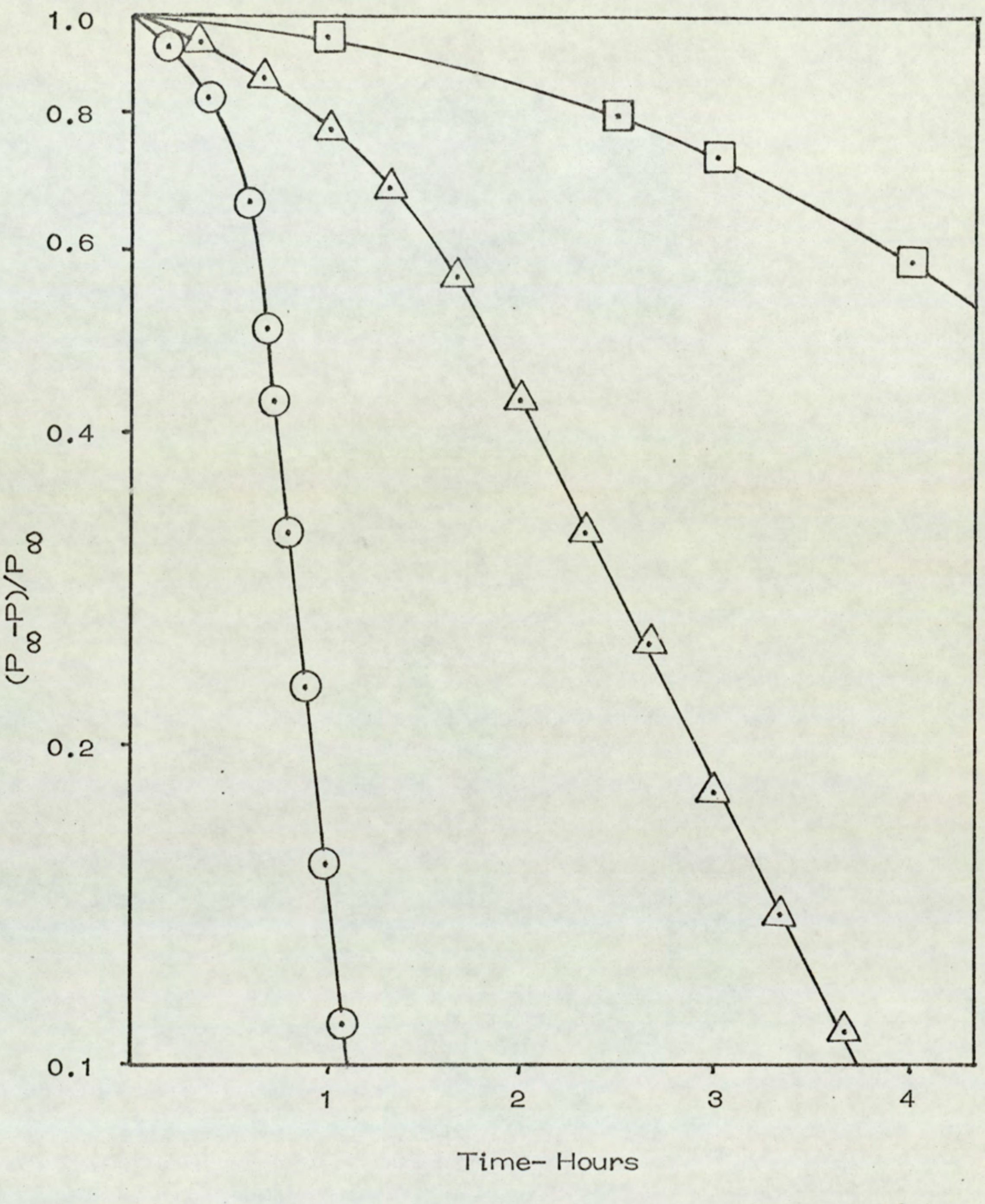


Fig. 7.8 The decomposition of BAAC in nitrobenzene at 80.2°C with equimolar;

⊙ pyridine

△ α-picoline

⊡ 2,6-lutidine

$[BAAC]_o = [Py] = 0.3$ mol. litre^{-1}.

at 70.2°C; samples were removed at intervals of time and the reaction quenched in carbon tetrachloride. A semi-logarithmic plot of $(A_{\infty} - A_p)/A_{\infty}$ versus time (see Fig. 7.7) where A_{∞} and A_p are the absorbances of the solution at the end of the reaction and during the reaction respectively, showed that the rate of appearance of the colour in the reaction mixture was indeed coincident with the rate of reaction as measured by gas evolution techniques, and demonstrates that the coloration is associated with product formation.

7.2 Discussion

The information to be discussed in this Chapter must be considered in the light of results to be presented in Chapter 9, and concerned with the structure of the polymers produced by tertiary base initiation. Thus, the polymers were observed to be hydroxyl/carboxyl terminated, to be completely free of pyridine residues, to possess relatively narrow molecular distributions and number average molecular weights which are independent of initial tertiary base concentration.

In spite of the thermal stability of MAAC this monomer is extremely sensitive to decomposition in the presence of small concentrations of pyridine. As demonstrated in Fig. 7.1, a vapour pressure concentration of pyridine is sufficient to drastically reduce its stability, and it is for this reason that substoichiometric amounts of pyridine are used during the synthesis of the monomer to ensure that no free pyridine is available for interaction with the formed monomer.

A semi-logarithmic plot of $(P_\infty - P)/P_\infty$, the function of which is related to the concentration of monomer by equation 6, versus time shows good straight line behaviour for over 98% of the reaction.

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

Variation of the initial monomer concentration produced no significant change in the rate constant. The observed rate of decomposition is, however, very much dependent upon the concentration of pyridine and increase in the pyridine concentration results in a corresponding increase in the rate of reaction. By graphical means the reaction has been shown to be first-order in pyridine concentration and the decomposition of MAAC with pyridine may be expressed by the simple rate equation 54, where [M] and $[CO_2]$ are the concentrations of monomer and carbon dioxide respectively at time t; $k_{obs.}$ and [py] are the observed second-order rate constant and the concentration of pyridine respectively.

$$\frac{-d\,[M]}{dt} = \frac{d\,[CO_2]}{dt} = k_{obs.}\,[M]\,[py] \qquad \ldots. \ (54)$$

A suggested mechanism for the decomposition of MAAC with pyridine involves an initial equilibrium reaction between monomer and pyridine and an intermediate, which is considered to be a charge-transfer complex, followed by the decomposition of this intermediate to yield a polymerisable species. Equation 55 outlines the scheme for the reaction,

$$M + Py \underset{k_{-b}}{\overset{k_f}{\rightleftharpoons}} [MPy^{*}] \xrightarrow{k_d} Prod + Py + CO_2 \quad \ldots (55)$$

where the charge-transfer complex is represented by $[MPy^{*}]$ and k_f, k_{-b} and k_d are the relevant rate constants for the processes as indicated. The equilibrium constant, K, is given by

$$K = \frac{k_f}{k_{-b}} \quad \ldots . (56)$$

The rate of formation of products may be written,

$$\frac{d\,[Prod]}{dt} = k_d\,[MPy^{*}] \quad \ldots . (57)$$

and the concentration of $[MPy^{*}]$ and reactants are related through the equilibrium constant, K, thus,

$$[MPy^{*}] = K\,[M]\,[Py] \quad \ldots . (58)$$

Equation 57 now becomes,

$$\frac{d\,[Prod]}{dt} = k_d\,K\,[M]\,[Py] \quad \ldots . (59)$$

assuming that the concentration of $[MPy^{*}]$ is small compared with [M], [Py] and [P]; that is, $[MPy^{*}]$ is a reactive intermediate. Equation 59 is similar in form to the observed rate equation 54, in which the observed rate constant is given by,

$$k_{obs.} = k_d K \quad \ldots . (60)$$

The measured rate constant $k_{obs.}$ is a product of the actual rate constant for the decomposition process and the equilibrium constant of the preceeding equilibrium. Thus the reaction appears first-order in spite of the complexity of the mechanism.

In the above treatment it has been assumed that the intermediate, $[MPy^{*}]$, is reactive and its concentration does not sensibly contribute to the stoichiometry of the overall reaction process. In view of this a conventional steady state treatment may be formulated, where the actual concentration of $[MPy^*]$ is assumed to be small and substantially constant. Thus the rate of formation of $[MPy^*]$ may be written as;

$$\frac{d\,[MPy^*]}{dt} = k_f\,[M]\,[Py] - k_{-b}\,[MPy^*] - k_d\,[MPy^*] \qquad \ldots. (61)$$

and is assumed to be a steady state concentration and the differential effectively equal to zero. From equation 61;

$$[MPy^*] = \frac{k_f\,[M]\,[Py]}{k_{-b} + k_d} \qquad \ldots. (62)$$

The observed rate of reaction is given by;

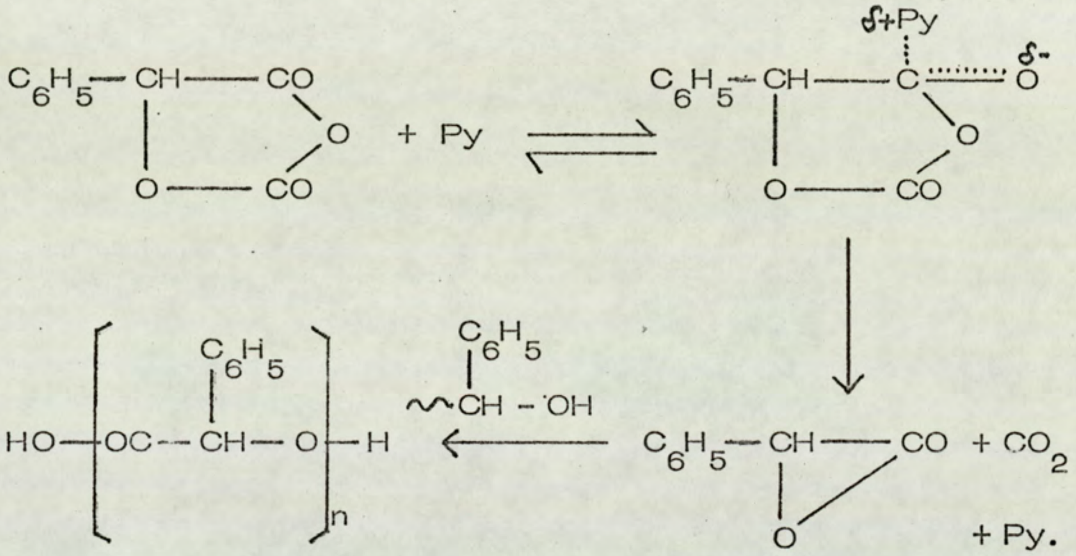
$$\frac{d\,[Prod]}{dt} = k_d\,[MPy^*] \qquad \ldots. (63)$$

which on combination with equation 62 results in the rate equation;

$$\frac{d\,[Prod]}{dt} = \frac{k_d k_f\,[M]\,[Py]}{k_{-b} + k_d} \qquad \ldots. (64)$$

The two treatments are not altogether independent, but it is interesting and instructive that if, from equation 64, $k_{-b} \gg k_d$, equation 64 reduces to a form identical to equation 59.

The sequence of reactions leading to the formation of polymer may now be formulated. The proposed mechanism involves the fragmentation of the anhydrocarboxylate ring in the charge-transfer complex and loss of carbon dioxide, with the formation of a species which is capable of taking part in a polymerisation reaction. The type of species envisaged after loss of carbon dioxide and in the absence of pyridine after monomer fragmentation is an α-lactone. The reaction sequence is shown in equation 65, in which the α-lactone takes part in a rapid chain propagation step with the terminal hydroxyl group of a polymer chain.



.... (65)

The loss of pyridine from the intermediate structure enables the initiating molecule to take part in further reactions. The role of pyridine may, therefore, be considered to greatly enhance the decomposition of the monomer to form a polymerisable intermediate, which is formally depicted as an α-lactone.

The Arrhenius plot, whilst instructive in assessing the effect of temperature upon the rate of reaction, does not reflect true values of the activation parameters associated with the rate-determining step. The actual step which involves bond breaking is governed by k_d, but the measured rate of reaction, $k_{obs.}$, is the product of k_d and the equilibrium constant, K, (equation 60). It may

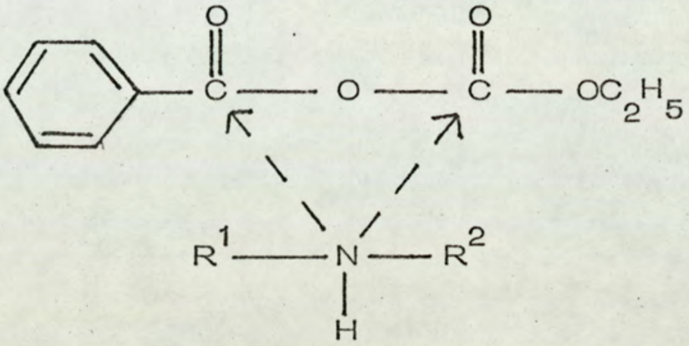
may be anticipated that the bond breaking step involving k_d would have a positive activation energy and the rate constant would increase with increase in temperature. In contrast, the equilibrium constant K, is likely to decrease with increase in temperature and, therefore, the activation energy obtained for the overal process (48.3 KJ. mol.$^{-1}$) is less than would be expected for the process involving k_d only.

The decomposition of MAAC in the presence of substituted pyridines leads in all cases, to the formation of polymer. Pyridine, α-picoline and 2,6-lutidine had a remarkedly similar effect on the decomposition of MAAC in that the observed rate constants, $k_{obs.}$, were comparable. The use of a weak base, 2-methoxy pyridine, resulted in a considerable reduction in the rate of reaction. The factors which affect the observed rate of decomposition are those which govern k_d and K. The decomposition of the intermediate is likely to be dependent upon the strength of the charge-transfer bond between the tertiary base and the C(4) carbonyl of the monomer and the ring strain associated with the anhydrocarboxylate. However, on increasing the nucleophilicity of the nitrogen by the incorporation of a methyl substituent also results in an increase in steric hindrance associated with the nucleophilic site, and the value of K will be very sensitive to the steric and electronic factors associated with the tertiary base. In the case of 2-methoxy pyridine, not only will k_d be considerably reduced due to a weaker charge-transfer bond, but the equilibrium constant (K) will also be much smaller due to the steric effect of the methoxy group and the relatively weak nucleophilic centre involved in the formation of the complex.

Many studies have been made on the ability of pyridine to form charge-transfer complexes. A well studied system is that of the pyridine-iodine complex and pyridine is of particular interest in that the molecule contains both n- and aromatic π -electrons. Charge-transfer complexes involving purely aromatic π -electron donors have relatively small association constants compared with the values which have been experienced for the pyridine-iodine system.(73) The association constants obtained for this latter system are comparable with those obtained for aliphatic amine complexes which must necessarily act as n-donors and, therefore, there is little doubt that predominant mode of charge-transfer complexing in pyridine, is by the n-donation of electrons of the tertiary nitrogen atom.

A stable complex has been reported between dimethylamine and sulphur dioxide.(74) The complex is described as a yellow oil with a melting point of 17°C. Complexes formed by n-donors are relatively strong and give support to the charge-transfer complex which is postulated during the decomposition of anhydrocarboxylates.

The susceptibility of a carbonyl function to attack by a nucleophile of the amine class may be easily understood by considering in the first place the nature of the attacking amine and secondly the nucleophilicity of the carbonyl group. The reaction of secondary amines with benzoic carbonic anhydride (XXXV) presents an interesting case in which a nitrogenous nucleophile is involved in the reaction at a carbonyl function.(75)



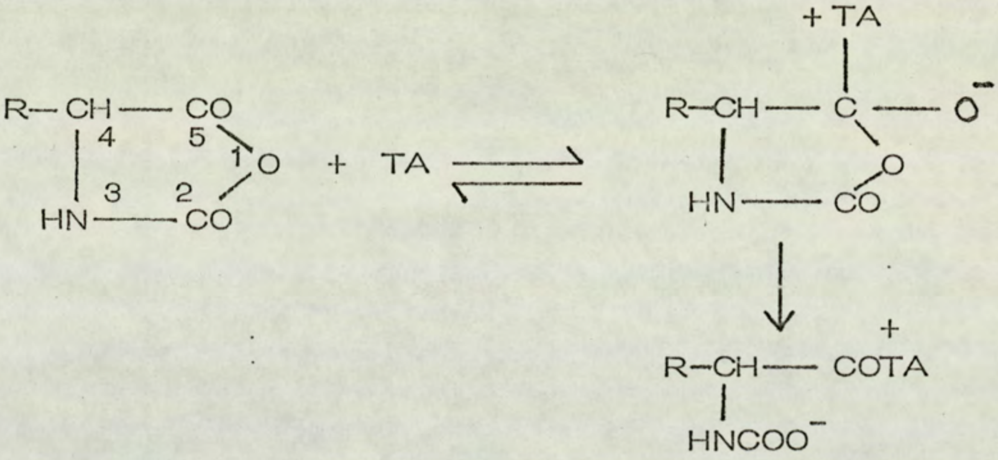
XXXV

In the cases where R^1 and R^2 are small alkyl substituents attack occurs at the more active carbonyl, adjacent to the phenyl group. Bond scission occurs and the loss of the hydrogen from the secondary amine results in the corresponding N-substituted benzamide being formed.

In the case of anhydrocarboxylates, the ring is a strained system and the attacking base possesses no labile hydrogen and thus no rearrangement and proton shift can occur after bond scission and loss of carbon dioxide. The role of pyridine is merely to enhance ring fragmentation to yield a polymerisable species.

The polymerisation of N.C.A. derivatives of α-amino carboxylic acids using tertiary amines presents an interesting case to which the polymerisation of anhydrocarboxylates with pyridine may be compared. It has long been known that N.C.A.'s undergo polymerisation when dissolved in pyridine and other tertiary amines, but to date no general mechanism is yet able to embrace all reported data. Several mechanisms are possible, each being predominant under special conditions, and of these, two require discussion.

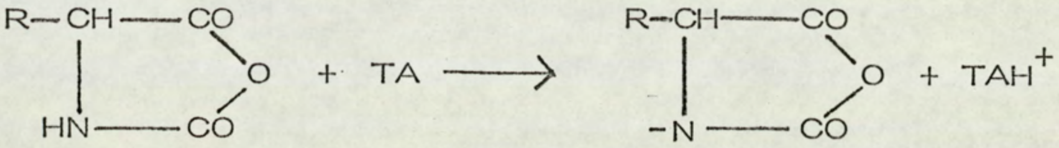
The molecular weights of the resultant polymers were found to be independent of the monomer to initiator ratio and to explain the tertiary amine initiation Wieland suggested a mechanism which is analogous to that existing for the reaction between amines and acid anhydrides.(76)(77) The amine nucleophile adds to the C(5) carbonyl to form an intermediate of the type shown in equation 66, which opens to form a Zwitterionic compound.



.... (66)

The propagation step was suggested to occur by reaction between the oppositely charged ends of the chain and subsequent loss of the tertiary amine (TA). This mechanism would account for formation of the cyclic dimers, but in practice no diketopiperazines were obtained.

More recently, Bamford and Block put forward a mechanism in which the role of the tertiary amine is to activate the N.C.A. monomer by abstracting a proton from the ring nitrogen, rather than as a nucleophile attacking the C(5) carbonyl. The nitrogen anion of the activated monomer attacks another N.C.A. molecule at the C(5) carbonyl, which after protonation and decarboxylation yields a species which possesses an active amino group at one end and an active N-carboxy anhydride at the other end. The general reaction scheme is given in equations 67 and 68.



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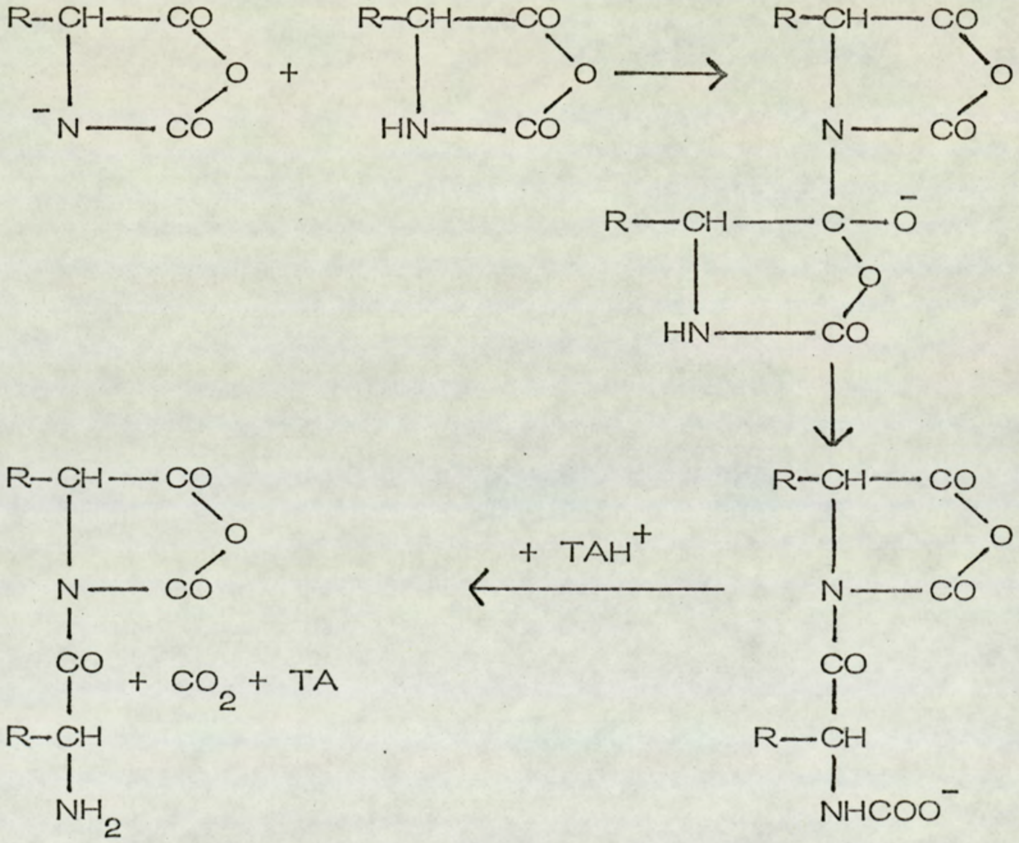


.... (68)

The ease of abstraction of the ring nitrogen proton will depend to a great extent upon the basicity of the tertiary amine and thus in the series pyridine, α-picoline and 2,6-lutidine, the more basic tertiary amine, 2,6-lutidine was found to be the most efficient initiator. The reverse situation would be anticipated if nucleophilic attack of the base were to occur at the C(5) carbonyl.

In the case of tertiary base initiated decomposition of anhydrocarboxylates several fundamental differences are apparent and do not, therefore, permit direct extrapolation of a common mechanism to essentially similar systems. In the first instance a Wieland-type mechanism would produce the analogous cyclic by-products of which none were detected as reaction products. The Bamford and Block mechanism would require proton abstraction from the monomer molecule as the primary step, and whilst a single hydrogen substituent is present at C(5) in MAAC, a mechanism involving loss of this hydrogen is not easily envisaged.

The fact that the molecular weight of the resultant polymer is independent of pyridine concentration and that increased initiator concentration gives rise to a corresponding increase in the rate of polymerisation, leads to the suggestion that the role of pyridine is not as a conventional initiator but as a means of promoting the decomposition of the anhydrocarboxylate to yield a polymerisable species.

The decomposition of BAAC in the presence of tertiary bases such as pyridine is more complicated than the MAAC system in that simple first-order kinetics are not observed. The reaction profile takes the form of a slow initial reaction which gradually accelerates and finally over the latter part of the reaction shows good first-order behaviour in residual monomer. Considering the steric and electronic effects associated with the monomer; BAAC possesses two rather bulky substituents at C(5) and yet has the necessary activated C(4) carbonyl for the formation of a charge-transfer complex. In view of the complications arising from the incorporation of a second phenyl substituent, it would be expected that the rate constants k_f, k_{-b} and k_d, as defined in equation 55, would vary considerably from the values experienced in the case of MAAC. The rate constants governing the forward and back reactions of the equilibrium, as deduced previously, will be larger than the decomposition of the charge-transfer complex, k_d. However, the magnitude of the rate constant governing the decomposition of this latter species must, in the first instance, be determined by the ring strain inherent in the monomer molecule. Thus even at room temperature the ratio of the values of k_d for BAAC and for MAAC is likely to be comparable with the corresponding ratio of the rate constants for thermal decomposition at a given temperature. The rate constant for thermal decomposition of BAAC is 100 times greater than the rate constant for thermal decomposition of MAAC. It may be inferred, therefore, that the value of k_d for BAAC will be greater than MAAC by a similar order of magnitude. However, the steric hindrance associated with the two phenyl substituents at C(5) results in a decrease in the rate of attainment of the equilibrium and necessitates the use of elevated temperatures in order to avoid inconveniently long reaction times. The true activation energy describing the bond scission process in the charge-transfer complex will probably not be very different from those experienced with purely thermal decompositions (i.e. $\sim$ 100 KJ mol.$^{-1}$). The high temperatures at which the rate of the decomposition of BAAC was measured will lead to values of k_d for BAAC, which are many orders of magnitude greater than those experienced with the analogous decomposition of MAAC at lower temperatures.

A situation is now presented where the value of k_d, at a given temperature is no longer small compared to k_{-b} and is becoming comparable to the value of k_f for the forward reaction of the equilibrium. Thus, the simplifying assumption made in equation 64, that $k_{-b} \gg k_d$, is no longer valid and simple first-order kinetics expressed in equation 59 are not observed. The reaction may now be considered to approximate to a series of first-order reaction of the type presented in equation 69. Reactions of this type are typified by an initial induction period of the form observed in the initiated decomposition of BAAC.

$$A \xrightarrow{k_A} B \xrightarrow{k_B} C \qquad \ldots. (69)$$

The opportunity for a reversible step during the first stage of the reaction serves to increase the time taken for attainment of the equilibrium and hence lengthen the induction period.

Increasing the pyridine concentration did not result in a corresponding increase in the observed rate of reaction of the order which was experienced with MAAC. This is not particularly surprising when considering the rather complicated kinetic description of the process and the relative rate constants describing the reaction. In the case of the initiated decomposition a MAAC, because of the relative magnitudes of k_f and k_{-b} compared to k_d, the decomposition step, increasing the pyridine concentration will result in a corresponding increase in the rate of formation of products. The rate of formation of products is given by equation 57,

$$\frac{d\,[\mathrm{Prod}]}{dt} \;=\; k_d\,[\mathrm{MPy}^{*}] \qquad \ldots.\ (57)$$

and thus an increase in the concentration of the intermediate ($[\mathrm{MPy}^{*}]$) gives rise to a corresponding increase in the observed rate of product formation even though the whole process is governed by a rate constant, k_d. Whereas for MAAC the actual concentration of intermediate is determined primarily, at a given temperature, by the ratio k_f/k_{-b} and the rate constant k_d is insignificant, the expression describing the concentration of intermediate in the initiated decomposition of BAAC involves k_d and the steady state approximation, which was used with confidence in the MAAC case, no longer applies. Thus a direct correlation of the observed reaction profile and initiator concentration is not to be expected.

Although the validity of the associated kinetic parameters obtained, as descriptions of the effect of temperature on the rate determining step, may be questioned, it is instructive to compare and contrast the values for BAAC during the latter stages of the reaction with those obtained for MAAC.

A somewhat higher energy of activation was obtained for BAAC. This is entirely consistent with a rate constant, governing a bond scission process, k_d, becoming more important than the equilibrium constant, which will decrease with increase in temperature, and whose effect will tend to outweigh the fragmentation process in MAAC. This is further exemplified by the high value of the pre-exponential factor obtained for BAAC, which is of the order expected for a process involving scission of a covalent bond.

Varying the structure of the tertiary base has a far more drastic effect on the reaction profile than was experienced during the initiated decomposition of MAAC. The limiting rate constants for the decomposition of BAAC with α-piodine and 2,6-lutidine over the latter stages of the reaction have not been calculated, but as may be seen from Fig. 7.8, the overriding factor, of those associated with the substituted pyridine, is the steric effect of the substituents at the 2- and 6- position. It may be anticipated from previous observations that the increased nucleophilicity of the base would increase the rate of reaction, and thus the form of the reaction profile obtained is an underestimated assessment of the steric effect of the methyl substituents.

Reaction products obtained from the decomposition of BAAC with pyridine at 80°C were qualitatively similar to those obtained during thermal decomposition, in that a quantity of benzophenone corresponding to about 30% of product was present. It would appear, therefore, that in the case of BAAC the initiated polymerisation, in the temperature range the study was carried out, is susceptible to the same competing and non-polymer forming reaction as was experienced during thermal polymerisation. It may be argued, in view of this observed secondary fragmentation process to ketone, that the monomer during initiated decomposition may go through a similar transition state to that during thermal decomposition. Thus the role of pyridine may be to activate the monomer molecule to an extent that "pseudo" thermal fragmentation of the anhydrocarboxylate can occur at considerably lower temperatures. The fragmentation of this activated ring is controlled by two competing first-order reactions similar to those described in Chapter 4, equations 28a and 28b, in which fragmentation leads to, in one case, the α-lactone and in the other, carbon monoxide and the ketone, benzophenone.

Initiated polymerisation has many advantages over polymerisation modes which require high temperatures as in the thermal decomposition of anhydrocarboxylates. In the first instance, lower temperatures may be used, which result in a more tactic formation of polymer chains. Secondly, competing non-polymer forming reactions tend to be minimised. Thus in the case of MAAC, polymerisation proceeds at a very convenient rate at room temperature and increasing initiator concentration, which does not affect the molecular weight, enables the rate of polymerisation to be increased and hence even lower temperatures may be used.

The initiated decomposition of BAAC presents a more complicated situation where the polymerisation, because of the necessity of higher temperatures, is subject to similar limitations as the thermal route. This is essentially due to the steric interference of the two C(5) phenyl substituents which inhibit the formation of the charge-transfer complex. However, by the use of strong, aprotic base initiators such as triethylamine and metal alkoxides, in which the alkoxide anion may act as a strong nucleophilic species, the necessary degree of reactivity to carry out the polymerisation at lower temperatures may be achieved. Whilst isolation of the polymer from BAAC was difficult the general method of initiating the decomposition of phenyl substituted anhydrocarboxylates to form a polymerisable species may, in general, be considered as a good synthetic route to polymers of this type.

CHAPTER 8

Tertiary Base Initiated Decomposition of 5-Methyl 5-Pentafluorophenyl 1,3-Dioxolan 2,4-Dione

In the previous chapter the initiated decomposition of MAAC and BAAC using tertiary bases of the pyridine type has been described. A necessary requirement for this mode of polymerisation is the activation of the C(4) carbonyl to attack by a nucleophile. An assessment has been made in Chapter 6, of the effect of a pentafluorophenyl substituent on the stability and reactivity of the anhydrocarboxylate ring to attack by nucleophiles. It may be inferred that 5-methyl 5-pentafluorophenyl 1,3-dioxolan 2,4-dione (PFAAC) may possess the necessary degree of reactivity for polymerisation similar to the tertiary base initiated mode previously described.

In this section, the reactivity of PFAAC with pyridine and a series of substituted pyridines is discussed. The general scheme of the polymerisation is considered to be similar to the one presented in the hydrocarbon case, but differs in that a simple correlation between the rate of reaction and initiator concentration is not found. The results may be explained in terms of a scheme similar to that for organic reactions involving charge-transfer complexes as intermediates, or in terms of restriction of the leaving group by solvolysis involving further initiating molecules. Superficial evidence is presented for the formation of a charge-transfer complex between the monomer and pyridine, and pre-formed polymer and pyridine. This gives support to the suggested reaction scheme.

8.1 Results

Decomposition of PFAAC in the presence of pyridine

Investigation of the decomposition of PFAAC in the presence of pyridine was carried out under similar reaction conditions to those for MAAC and BAAC. The temperature range giving convenient rates of reaction was found to be 40°-60°C, and for these reactions the sealed version of the constant volume kinetic apparatus was used. The decomposition was carried out in nitrobenzene using an equimolar concentration of pyridine with respect to monomer. The pressure of the carbon dioxide evolved during the reaction was measured as a function of time. A plot of $(P_\infty - P)/P_\infty$ versus time showed good linear behaviour well into the third decade and indicated that the reaction was first-order with respect to monomer, and that the concentration of active initiator remained effectively constant throughout the period of the reaction.

The initial rate of reaction was not measured as introduction of the pyridine into the solution of monomer was performed prior to sealing of the equipment and entry into the constant temperature oil bath. However, there was no evidence of an induction period as observed with BAAC during the initial measured stages of the decomposition. A semi-quantitative kinetic run using the "initiator-type" kinetic apparatus and a 5-molar excess of pyridine over monomer at 25°C also showed no evidence of an induction period.

Fig. 8.1 shows typical semi-logarithmic plots of $(P_\infty - P)/P_\infty$ versus time for the decomposition of PFAAC in the presence of an equimolar amount of pyridine, at various temperatures. The associated kinetic parameters were obtained from a conventional Arrhenius plot of the logarithm of the second-order rate constant versus the reciprocal of absolute temperature. The second-order rate constants ($k_{obs.}$) and the kinetic parameters obtained are given in Table 8.1.

Table 8.1

Second-order rate constants ($k_{obs.}$), energy of activation (E), pre-exponential factor (A) and the entropy of activation for the decomposition of PFAAC with an equimolar amount of pyridine. $[PFAAC]_o = [Py] = 0.25$ mol. litre.$^{-1}$

Temperature ^oC	$10^4 k_{obs.}$ l.mol.$^{-1}$ sec.$^{-1}$
40.0	2.86
45.2	4.19
50.2	6.85
55.2	8.58
60.3	14.3
E (KJ.mol.$^{-1}$)	62.5
A (l.mol.$^{-1}$sec.$^{-1}$)	6.9×10^6
$\Delta S^\ddagger$ (J.K^{-1} mol.$^{-1}$)	-157.3

The values of the pre-exponential factor (A) and the entropy

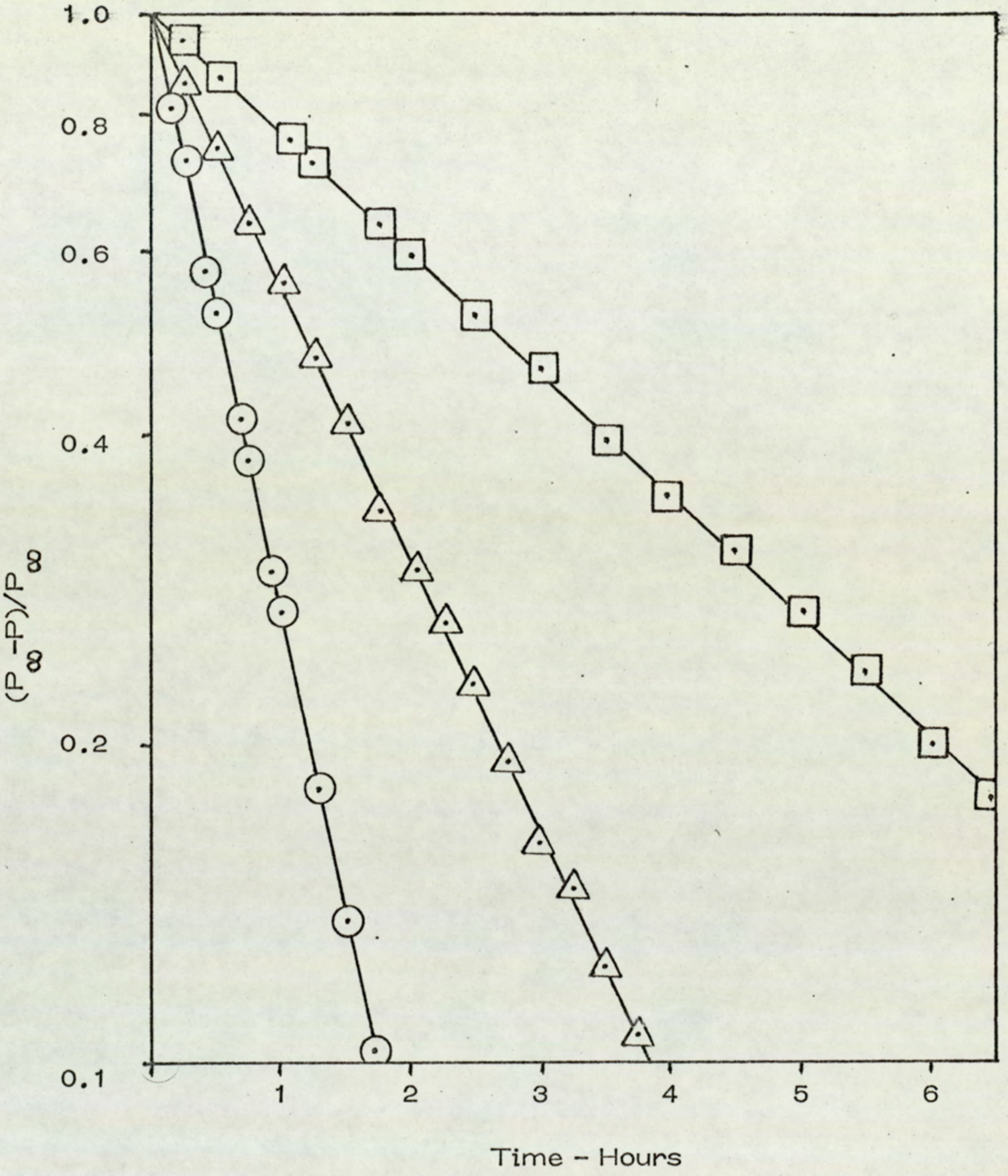


Fig. 8.1 First-order semi-logarithmic plots for the decomposition of PFAAC in nitrobenzene in the presence of equimolar amounts of pyridine at;

⊙ $60.3^{o}C$

△ $50.2^{o}C$

⊡ $40.0^{o}C$

$[PFAAC]_{o} = [Py] = 0.25\ mol.\ litre^{-1}$.

of activation ($\Delta S^{\ddagger}$) obtained were of comparable order to those experienced during the initiated decomposition of MAAC using pyridine. However, the energy of activation was some 15 KJ mol.$^{-1}$ higher than in the latter case. In view of the complexity of the mechanism suggested, the activation energy may not be taken as a direct reflection of the effect of temperature on the rate determining step, but as the effect of temperature on the product of the equilibrium constant (K) and rate constant governing the decomposition of the intermediate (k_d), equation 59.

The concentration of pyridine that is required for a rate of reaction equivalent to the decomposition of MAAC with a 10% molar concentration of pyridine, is about a 2 molar excess (with respect to monomer), and considering the activity of the C(4) carbonyl to nucleophilic attack, it was decided that further spectroscopic investigations to identify the charge-transfer complex intermediate that has been postulated may prove to be successful.

Infrared investigations were carried out under similar reaction conditions to those used for the decomposition of MAAC. The whole reaction was carried out in an infrared liquid cell of 0.025 cm. thickness, using tetrahydrofuran (T.H.F.) as solvent. A matched solvent cell blank was also used. The concentration of monomer used was 0.9 mol. litre^{-1} and that of pyridine 1.8 mol. litre.$^{-1}$ Spectra were recorded at intervals of time which enabled the disappearance of monomer to be measured concurrently with the rate of formation of polymer. Two infrared kinetic runs were carried out, the first covering the range 2000-1400 cm^{-1}, which is essentially in the carbonyl region for both the monomer and the polymer, and the second in the range 1400-700 cm^{-1}, which covers the C-N stretching frequency. In neither of the two runs was there any indication of a small concentration of intermediate. The experiment, however, served to enable a graph to be produced, similar to the one given in Fig. 7.5, in which the rate of formation of polymer was shown to be coincident with the rate of disappearance of monomer.

Further infrared investigations were carried out in an attempt to ascertain whether pyridine was able to complex with a polar carbonyl. The infrared spectrum of trichlorotrifluoroacetone was recorded in T.H.F. in the range 2000-1400 cm^{-1}, and a second spectrum recorded using the same concentration of trichlorotrifluoroacetone and an equivalent concentration of pyridine in the same solvent. No additional peaks were observed and no shift of carbonyl absorption or pyridine absorptions was found.

Infrared investigations were not wholly successful in that no evidence was found for any relatively stable intermediate or transient intermediate between pyridine and monomer or pyridine and the activated carbonyl in trichlorotrifluoroacetone.

N.M.R. spectroscopy has developed into an invaluable technique for studying the formation of transient charge-transfer complexes in solution. Many investigations have been concerned with the formation of complexes between an aromatic system and a solute molecule such as chloroform and 1,2-dichloroethane.(78) The formation of charge-transfer complexes in solution results in a shift in observed resonance frequency of the two components relative to their uncomplexed states as monitored by use of a non-interfering reference. In the case of pyridine, of which the n.m.r. spectrum is particularly complex, complex formation may justifiably be assumed, in certain instances, if the spectrum is diffuse and poorly resolved.

The n.m.r. spectrum of pyridine was recorded during the initiated decomposition of PFAAC, and the reaction conveniently carried out in the sample tube using T.H.F. as solvent. The concentration of monomer used was 1.08 mol.litre^{-1} and of pyridine, 2.15 mol.litre^{-1}. Cyclohexane was used as an internal reference, modulated with a 400 Hz. signal. The spectrum of pyridine recorded during the reaction was broad and diffuse, which superficially suggests that the pyridine molecule was involved in a form of complex formation. However, the position of the resonance did not sensibly change during the reaction as may be expected as the degree of complex formation decreased with time. At the end of the reaction the form of the spectrum was not unlike the spectrum obtained during the initial stages. However, the position of the pyridine resonance had shifted by 3-5 Hz. to lower field. This would tend to suggest that pyridine is capable of forming a charge-transfer complex with not only the monomer but also the polymer which is formed.

In order to verify this and to show that complex formation was not due to the solvent or reference, the spectrum of pyridine was recorded in a solution of identical composition to the previous reaction, but in the absence of monomer or polymer, and a reference modulation signal used to identify and measure any shift in position of the resonance. An amount of pre-formed polymer equivalent to that produced in the previous reaction was added and the spectrum re-recorded. By the addition of the polymer, the well resolved spectrum obtained previously became broad and diffuse and was moved to higher field by 9–10 Hz.

It would appear, therefore, that whilst the actual spectroscopic identification of the charge-transfer complex, which has been postulated, has not been made; the evidence obtained by use of n.m.r. techniques for the existence of complex formation during the initiated decomposition of PFAAC, must be considered demonstrative.

Effect of varying the structure of the pyridine

The decomposition of PFAAC was carried out in the presence of various substituted pyridines. In the case of the decomposition of MAAC with the series; pyridine, α-picoline and 2,6-lutidine, relatively little change in the rate of reaction was observed due to the balance of steric effects associated with the attacking base. PFAAC contains a C(4) carbonyl which is more active to this form of attack and yet possesses a second substituent (methyl group) at C(5). It would, therefore, be expected that a somewhat different balance of steric and electronic effects would be experienced.

Fig. 8.2 shows rate curves for the decomposition of PFAAC in the presence of; 4-picoline, pyridine, 2-methoxy pyridine and 2,6-dimethoxy pyridine. A similar order of reactivity, as found

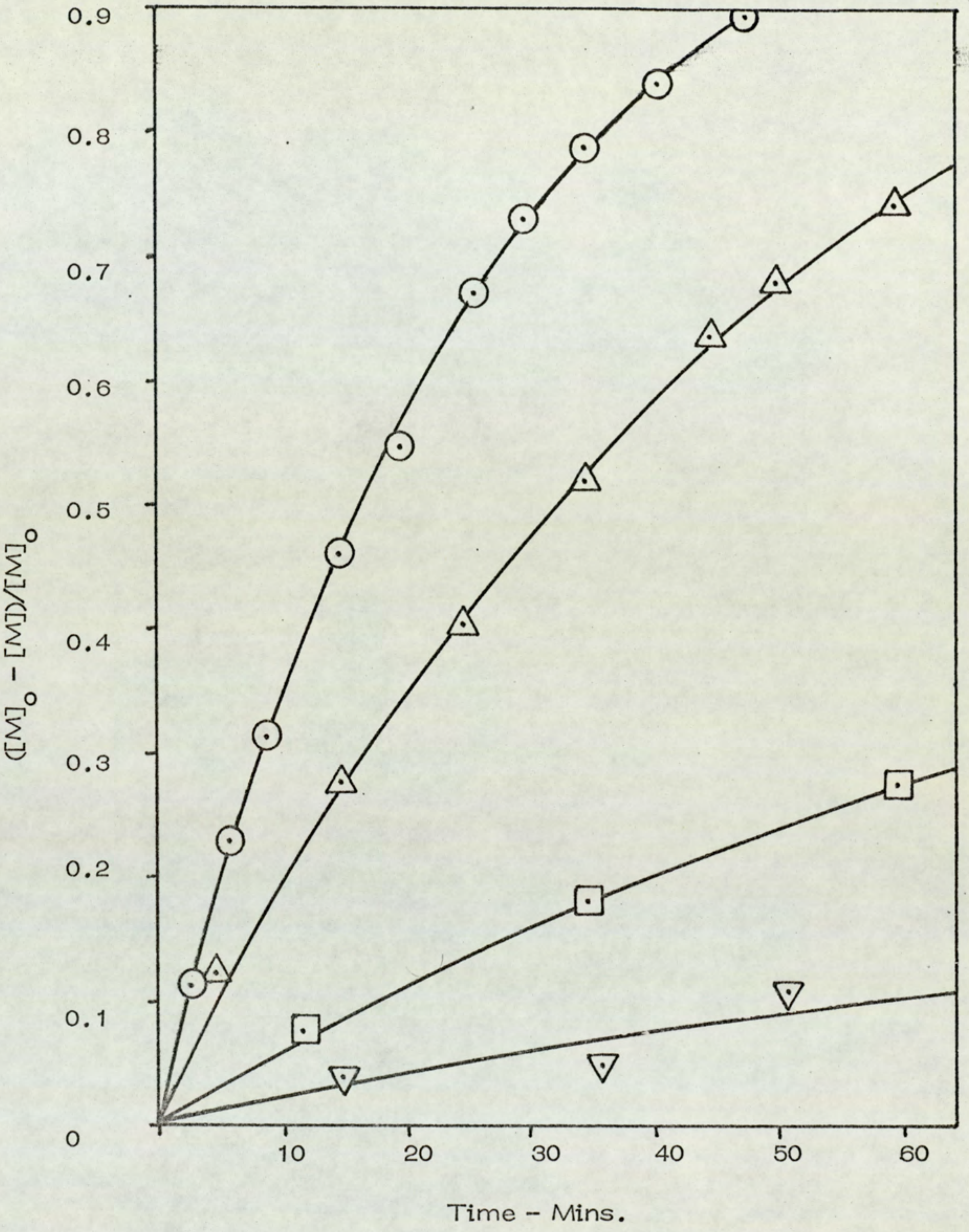


Fig. 8.2 Rate curves for the decomposition of PFAAC with;

⊙ Equimolar 4-picoline

△ Equimolar pyridine

⊡ 5 Molar excess 2-methoxy pyridine

▽ 5 Molar excess 2,6-dimethoxy pyridine

$[PFAAC]_o$ = 0.25 mol.litre^{-1} at 60.3°C.

with the analogous decomposition of MAAC, is shown, where the weaker bases, 2-methoxy and 2,6-dimethoxy pyridines are the least reactive. Table 8.2 tabulates the observed second-order rate constants obtained for the decomposition of PFAAC with a series of substituted pyridines. The increase in nucleophilicity of the pyridine nitrogen in moving from pyridine to 4-picoline is reflected in an enhanced rate of decomposition of PFAAC. However, when the electron donating methyl substituent is in the 2-position as in α-picoline the increase in rate is not as large as in the latter case due to the steric effect of the substituent in close proximity to the complexing site. The effect of an inductively electron withdrawing substituent as in the methoxy substituted pyridines, coupled with the steric effects associated with those substituents, drastically reduces the rate of decomposition.

Effect of varying the pyridine concentration

In the case of MAAC a simple first-order relationship between the observed rate of reaction and the concentration of pyridine was obtained. However, the decomposition of PFAAC with various concentrations of pyridine gave surprising results in that the derived second-order rate constants decreased with increase in pyridine concentration.

In view of the extent to which the solvent medium characteristics varied on varying the pyridine concentration (0.025 mol.litre^{-1} to 0.698 mol.litre^{-1} represents a 50% increase in solvent donicity - Table 8.3), values of the second-order rate constants were determined at the solvent donicity of nitrobenzene (i.e. 21).

Table 8.2

Second-order rate constants ($k_{obs.}$) for the decomposition of PFAAC with a series of substituted pyridines at 60.3°C.

$[PFAAC]_o = 0.25$ mol.litre.$^{-1}$ $[Py] = 0.25$ mol. litre.$^{-1}$

Substituted Pyridine	pKa(a)	$10^5 k_{obs.}$ l.mol.$^{-1}$ sec.$^{-1}$
pyridine	5.17	1.43
α-picoline	5.97	2.17
2,6-lutidine	6.75	1.91
4-picoline	6.02	2.95
4-tertiary-butyl pyridine	5.99	2.84
2-ethyl pyridine	5.97	1.38
2-n-propyl pyridine	5.97	1.42
2-methoxy pyridine*	3.3(b)	0.064
2,6-dimethoxy pyridine*	~1.5	0.017

* $[Py] = 1.25$ mol.litre.$^{-1}$

(a) obtained from reference (71)

(b) obtained from reference (72).

Table 8.3

Second-order rate constants ($k_{obs.}$) and the calculated corrected second-order rate constants ($k_{corr.}$) for the decomposition of PFAAC with various concentrations of pyridine. $[PFAAC]_o = 0.25$ mol.litre^{-1}.

Pyridine concentration (mol.litre^{-1})	$10^3 k_{obs.}$ l.mol.$^{-1}$ sec.$^{-1}$	$10^3 k_{corr.}$ l.mol.$^{-1}$ sec.$^{-1}$
0.025	10.1	9.91
0.061	7.06	6.69
0.120	4.29	3.82
0.240	2.53	2.09
0.472	1.55	0.98
0.698	1.64	0.84

The donicity range which was involved, 20-35 donicity units, occurs over the linear part of the rate constant versus solvent donicity curve constructed for the reaction of an anhydrocarboxylate with benzyl alcohol. As the formation of the intermediate involves nucleophilic attack comparable to that in the reaction with an alcohol, the linear part of the plot in Fig. 5.6 was used as a calibration graph for calculating the rate constants at a fixed solvent donicity.

Table 8.3 tabulates the observed second-order rate constants ($k_{obs.}$) with varying pyridine concentration and the corrected second-order rate constants ($k_{corr.}$) determined for the reaction at constant solvent donicity. Fig. 8.3 shows a plot of the corrected second-order rate constants versus pyridine concentration. As may be easily seen, this rate constant rapidly decreases as the concentration of the pyridine is increased.

The reaction throughout qualitatively resembles the decomposition of MAAC with pyridine and thus it is assumed that a similar sequence of reactions during the decomposition of PFAAC and the formation of the products occurs. Thus equation 59 may be considered to describe the decomposition process,

$$\frac{d\,[\mathrm{Prod}]}{dt} = k_d K\,[M]\,[Py] \qquad \ldots.\ (59)$$

where [Prod], [M] and [Py] refer to the concentrations of product, PFAAC and pyridine respectively and k_d and K are the rate constant governing the decomposition of intermediate and equilibrium constant governing its formation respectively, according to equation 55. However, it would appear from the form of the graph in Fig. 8.3, that the measured rate of reaction involves a further dependence upon concentration of pyridine, where the measured rate of reaction decreases with increase in pyridine concentration.

An expression which describes the observed kinetic behaviour is given in equation 70,

$$\frac{d\,[P]}{dt} = k_d K\,[M]\,[Py] - K'\,[M]\,[Py]^n \qquad \ldots.\ (70)$$

in which $n \geqslant 2$ and K' may be composed of a rate constant and an equilibrium constant and has the dimensions $l^n.\ \mathrm{mol.}^{-n}\ \mathrm{sec.}^{-1}$

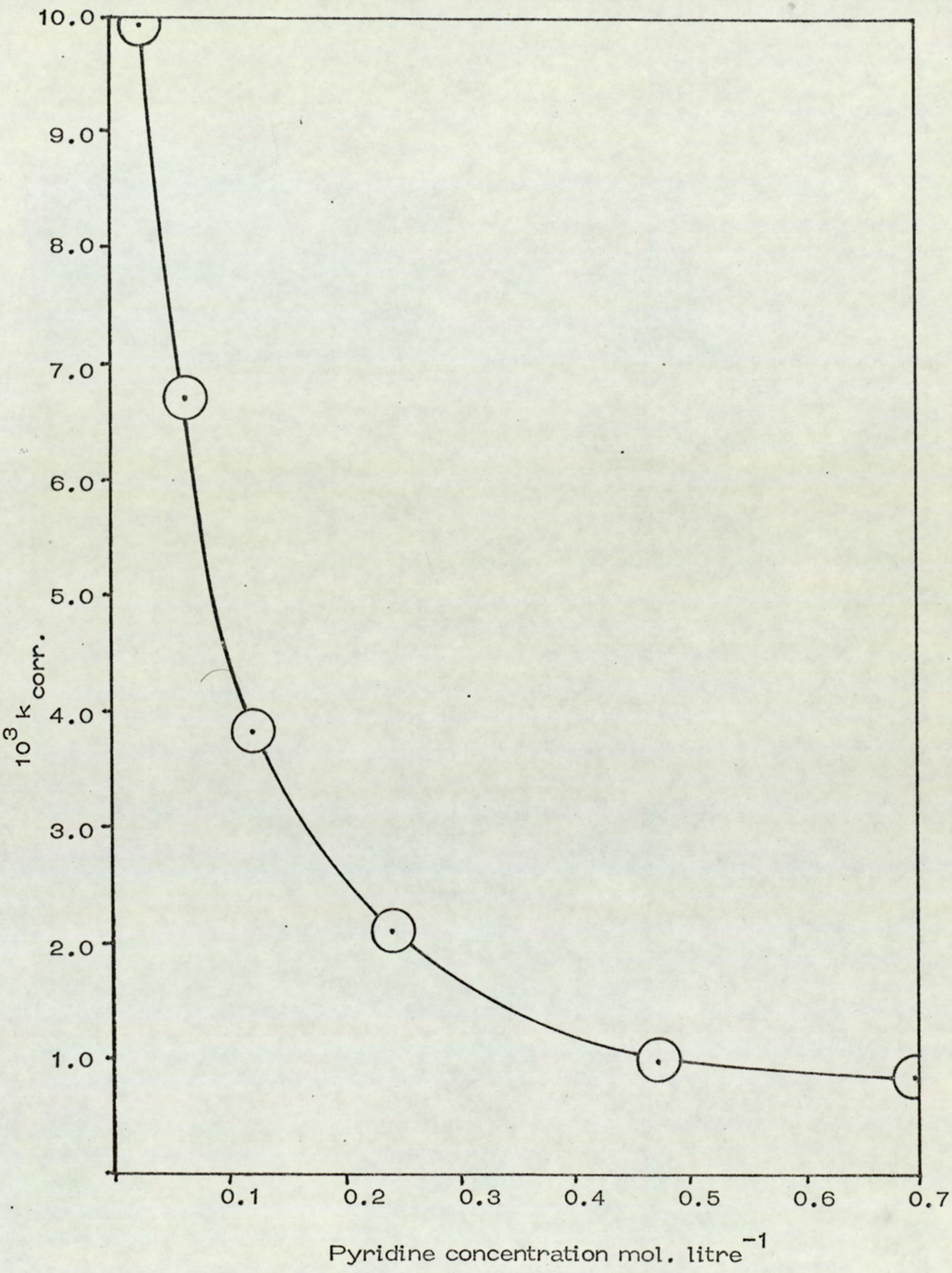


Fig. 8.3 A plot of the corrected second-order rate constant ($k_{corr.}$) versus pyridine concentration for the decomposition of PFAAC with pyridine, at 60.3°C.

At low pyridine concentrations the value of $K' [M] [Py]^n$ is small compared to the value of $k_d K [M] [Py]$, but at high pyridine concentrations the value of this term involving a high order of pyridine dependence becomes significant and may account for the decrease in observed rate constant which has been determined by measuring the rate of product formation.

As the pentafluorophenyl group is such a strongly electron withdrawing substituent the part of the monomer molecule from which carbon dioxide is lost may be stabilised by further pyridine molecules acting as a localised solvent and so inhibit the leaving group. This may also account for the diffuse n.m.r. resonance obtained for pyridine during decomposition of PFAAC, in which it may be suggested that the pyridine molecules not involved in the formation of a charge-transfer complex at the C(4) carbonyl, are held in a partly-restricted orientation. However, in some organic reactions, for example, certain aromatic nucleophilic substitutions which occur via charge-transfer complexes,(79) the apparent bimolecular rate constant is observed to diminish as the initial concentration of one of the reactants is increased. If this were so in the case of the monomer reactant a simple first-order dependence on monomer would not be observed. The quantitative treatment associated with this general phenomena may be applied with a degree of success for variation of pyridine concentration and is discussed in the latter part of the following section.

8.2 Discussion

A general qualitative comparison of the reactivity of PFAAC with MAAC and BAAC during the initiated decomposition with pyridine leads to the conclusion that PFAAC is less reactive than MAAC but more reactive than BAAC, in spite of the complexity of the reaction profile for BAAC. It would be tempting to suggest that the increased electron withdrawing power of the pentafluorophenyl substituent over a phenyl group would outweigh the increase in steric hindrance associated with the formation of the charge-transfer complex at the C(4) carbonyl. However, the observed rate of reaction not only depends upon the concentration of the complex but also on its rate of decomposition.

The relative rates of decomposition of PFAAC and the hydrocarbon analogue, AAAC, in the presence of a five molar excess of pyridine with respect to monomer, were assessed at 25°C. The second-order rate constants obtained were 4.5×10^{-4} l.mol.$^{-1}$sec.$^{-1}$ and 2.2×10^{-4} l.mol.$^{-1}$sec.$^{-1}$ respectively, and thus it would appear that the effect of a pentafluorophenyl group in increasing the reactivity of the anhydrocarboxylate to decomposition with pyridine is not as marked as reducing the size of the second substituent to a single hydrogen (MAAC). The somewhat high concentration of pyridine used in the previous case (5 molar excess on monomer), may reduce the observed rate of decomposition of PFAAC by the process introduced in the latter part of section 8.1. Alternatively, the stability of the charge-transfer complex in the case of PFAAC may be considerably greater than for one involving a phenyl substituted anhydrocarboxylate. This stability is reflected to a certain extent in the relative stability of the monomer ring during thermal decomposition.

The decomposition of PFAAC in the presence of pyridine was found to be first-order with respect to monomer. The products of decomposition were the corresponding poly-α-ester and carbon dioxide. Thus in spite of the decrease in observed second-order rate constants with increase in pyridine concentration, the same sequence of reactions leading to the formation of polymer during the decomposition, as was formulated for the decomposition of MAAC and BAAC, is suggested to occur.

The introduction of a strongly inductively electron withdrawing substituent such as a pentafluorophenyl group presents an interesting case in which two conflicting effects appear to be operative during the initiated decomposition. In the first instance enhanced electrophilicity of the C(4) carbonyl occurs which facilitates the formation of the charge-transfer complex. However, the presence of such a substituent leads to enhanced thermal stability of the monomer which will ultimately result in a more stable charge-transfer intermediate. Equation 64 is obtained by a treatment involving a steady state approximation with respect to the charge-transfer complex.

$$\frac{d\,[\mathrm{Prod}]}{dt} = \frac{k_d k_f\,[\mathrm{M}]\,[\mathrm{Py}]}{k_{-b} + k_d} \qquad \ldots.\ (64)$$

In the case of PFAAC, k_f and k_{-b} may well be of a similar order to the values experienced with MAAC and the magnitude of k_d determining the degree of observed reactivity. Conversely, due to the introduction of a methyl group as a second substituent, k_f may be of prime importance. The relative values of the rate constants associated with the equilibrium process for PFAAC and MAAC may not easily be made, but it may be suggested that k_d for the decomposition of PFAAC is of comparable order to k_d for MAAC, by comparison of thermal stabilities. Thus the approximation necessary for equation 64 to reduce to a simple first-order expression with respect to each reactant (i.e. $k_{-b} \gg k_d$), may be made with confidence.

The kinetic parameters obtained whilst not reflecting the effect of temperature on the bond scission process, do serve as an indication of how the rate of decomposition varies with temperature. The activation energy is considerably higher than values expected for nucleophilic attack and yet is not comparable to those involving a purely thermal scission of a covalent bond. The value is also higher than the activation energy obtained for the decomposition of MAAC with pyridine which would tend to suggest that in the case of PFAAC, k_d, the decomposition of the intermediate is more important than for MAAC. The pre-exponential factors and entropies of activation for both MAAC and PFAAC are very similar.

A necessary requirement for simple first-order kinetics with respect to monomer to be observed, is that the concentration of the charge-transfer complex prior to decomposition must be small compared to the overall concentration of initiator. Thus it is unlikely that such a complex would be observed using a technique such as infrared spectroscopy. Circumstantial evidence, in the form of a change in position of the pyridine resonance during the decomposition, in the n.m.r. spectrum has been presented for the existence of a complex involving pyridine.

The steric and electronic effects associated with PFAAC compared with MAAC and BAAC are somewhat more complicated and it would be anticipated that a different order of activity would be observed for the decomposition of PFAAC with a series of substituted pyridines. A decrease in reactivity is observed on changing the nucleophilic base from α-picoline to 2-ethyl pyridine and yet the two compounds have the same pKa value. This decrease in reactivity may be attributed to interference of the extended alkyl substituent with the C(5) substituents during the interaction leading to the formation of the charge-transfer complex. 2-Ethyl pyridine and 2-propyl pyridine have the same pKa value and show a remarkedly similar degree of reactivity with PFAAC in spite of the extension of the electron donating alkyl substituent by one methylene unit. When the electron donating substituent is situated para (the 4-position) to the complexing nitrogen centre and the pKa value of the bases are comparable as in the case of 4-methyl and 4-tert.-butyl pyridine, the second-order rate constants obtained are ostensibly similar in that the size of the substituent does not affect the observed rate of reaction.

In general it appears that in the case of PFAAC, the stronger the base (reflected in the magnitude of the pKa value) then the more rapid is the decomposition leading to polymer formation provided that the substituents on the base do not unduly sterically hinder the formation of the charge-transfer complex.

Variation of the concentration of pyridine produced results from which it is apparent that the observed rate of decomposition decreases with increase in pyridine concentration. An expression has been derived in which the rate of product formation is dependent upon not only the concentration of monomer and pyridine but also a term involving a negative dependence upon a high order pyridine concentration. However, in the reaction of 2,4-dinitrochlorobenzene with aniline in ethanol,(80) the second-order rate constant is observed to decrease with increase in amine concentration. This rate effect has been attributed to the formation of a molecular complex between the reactants. A similar treatment, with respect to pyridine, may be made for the reaction scheme which has been proposed. This scheme is given in equation 71.

$$M + Py \underset{}{\overset{k}{\rightleftharpoons}} [MPy^{*}] \xrightarrow{k_d} \text{Products} \quad \ldots.\ (71)$$

Thus;

$$K = \frac{[MPy^{*}]}{[M]\ [Py]} \quad \ldots.\ (72)$$

where $[MPy^{*}]$, $[M]$ and $[Py]$ are the concentrations of the complex, uncomplexed monomer and uncomplexed pyridine respectively. The total concentration of pyridine, $[Py]_T$, is given by;

$$[Py]_T = [Py] + [MPy^{*}] \quad \ldots.\ (73)$$

which may be written as;

$$[Py]_T = [Py]\,(1 + K[M]) \quad \ldots.\ (74)$$

and approximates to;

$$[Py]_T \simeq [Py] \qquad \ldots . (75)$$

A similar treatment may be carried out for the total concentration of monomer, $[M]_T$, and an equation similar to equation 74 results;

$$[M]_T = [M](1 + K[Py]) \qquad \ldots . (76)$$

which may be written in the form;

$$[M]_T = [M](1 + K[Py]_T) \qquad \ldots . (77)$$

The rate of formation of products is given by;

$$\frac{d[Prod]}{dt} = k_d[MPy^*] = k_d K[M][Py] \qquad \ldots . (78)$$

Since the concentration of intermediate is regarded as small, the total concentration of pyridine is essentially the same as the free pyridine concentration, and thus equations 75 and 77 may be substituted into equation 78.

$$\frac{d[Prod]}{dt} = \frac{k_d K[M]_T[Py]_T}{1 + K[Py]_T} \qquad \ldots . (79)$$

The corrected observed second-order rate constant for this reaction is given by equation 80,

$$\frac{d[Prod]}{dt} = k_{corr.}[M]_T[Py]_T \qquad \ldots . (80)$$

and from equations 79 and 80 it follows that the experimental rate constant $k_{corr.}$ is related to the pyridine concentration by the expression,

$$\frac{1}{k_{corr.}} = \frac{1}{k_d K} + \frac{[Py]_T}{k_d} \qquad \ldots . (81)$$

Thus from equation 81 a plot of $1/k_{corr.}$ versus pyridine concentration should give a straight line and the ratio of the slope to the intercept equals the equilibrium constant, K, for complex formation.

Fig. 8.4 shows a plot of $1/k_{corr.}$ versus pyridine concentration for the decomposition of PFAAC with various concentrations of pyridine. The graph is indeed a reasonably good linear plot and the value of K determined by this kinetic method is 29 $l.mol.^{-1}$ This value obtained may appear to be high for an equilibrium constant describing this form of interaction, however, the equilibrium constants obtained for n-donor complexes of pyridine-iodine in carbon tetrachloride and ammonia-iodine in n-heptane at 25°C are 97 and 67 $l.mol.^{-1}$ respectively.(81) It is worthy of note that the iodine complexes formed with trimethylamine and triethylamine in n-heptane at 25°C have equilibrium constants of 1.2×10^{4} and 6.3×10^{3} respectively.(81) Thus the use of the latter tertiary aprotic bases may give rise to a considerably increased rate of polymerisation.

In the case of MAAC the second-order rate constant was found to be insensitive to changes in pyridine concentration and a corresponding plot of this rate constant versus pyridine concentration would in effect result in a value of K approaching zero. Two explanations may be presented. In the first instance no correction has been made for the change in solvent property on increasing the pyridine concentration and thus the increase in rate due to increase in donicity of the solvent may balance the decrease in rate constant due to complex formation. Secondly, one

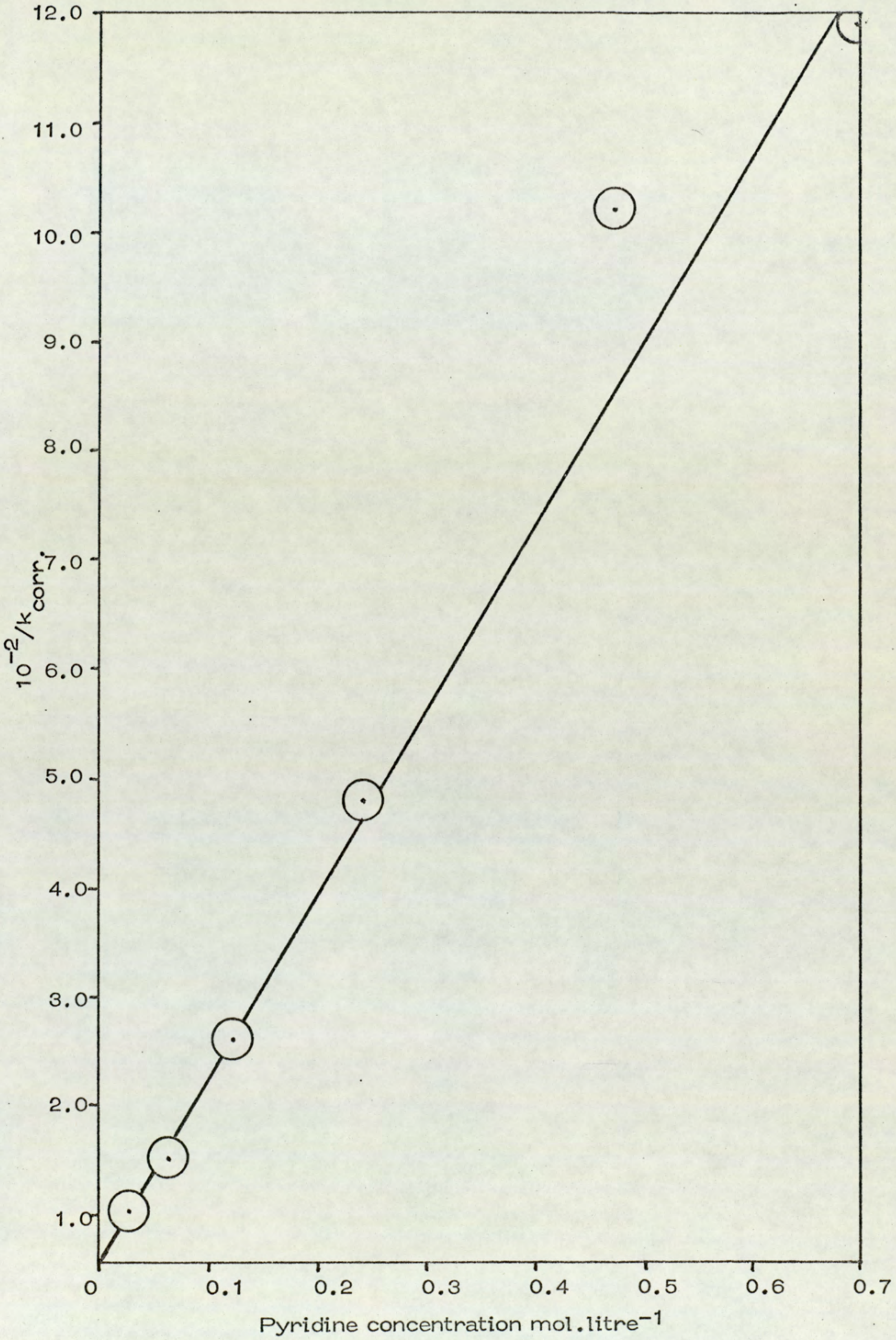


Fig. 8.4 A plot of $1/k_{corr.}$ versus pyridine concentration for the decomposition of PFAAC with various concentration of pyridine.

of the reactants (probably MAAC) may be sufficiently strongly solvated that there is no appreciable tendency for complex formation to the extent experienced in the case of PFAAC.

It would appear that the introduction of a pentafluorophenyl group onto the anhydrocarboxylate ring does offer a degree of reactivity which is not available in the hydrocarbon analogue. However, the decomposition of PFAAC in the presence of pyridine, whilst yielding the corresponding poly-α-ester, proceeds at a rate slower than would be anticipated. Use of stronger bases such as trimethylamine and triethylamine may present a degree of reactivity which could be exploited for the low temperature polymerisation of this monomer and others in the phenyl substituted anhydrocarboxylate series.

CHAPTER 9

Poly-α-Esters

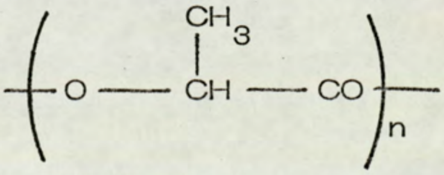
Several systems of nomenclature have been used to describe individual poly-α-esters; for simplicity and consistency in this thesis the prefix poly- will be used with the abbreviation for the parent anhydrocarboxylate (See Appendix).

9.1 Introduction

In general poly-α-esters have not been well studied mainly because of the limited number of synthetic routes to this type of polymer. Linear aliphatic polyesters are of particular interest in the history of synthetic fibres. From the work of Carothers, however, aliphatic polyesters have been shown to have low melting points and tend to be susceptible to organic solvents and to hydrolysis, which excludes them from use as textile materials. Two exceptions to this generalisation occur in the simple poly-α-ester series (XXXVI), (XXXVII). These polymers have quite high

$$-\!\!\left(O - CH_2 - CO\right)_n\!\!-$$

XXXVI

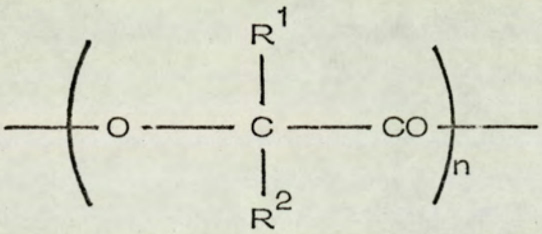


$$-\!\!\left(O - \underset{}{\overset{\displaystyle CH_3}{\overset{|}{CH}}} - CO\right)_n\!\!-$$

XXXVII

melting points of 228° and 185°C respectively, and may easily be made into fibres. The polymer XXXVII may exist in optically active forms and the melting point quoted is for the polymer derived from the L(+)-monomer. The racemic form of the polymer melts at a much lower temperature, over the range 130°-135°C. Fibres formed from polymer XXXVII have been recommended for use as surgical sutures.(46)

More recently a series of poly-α-esters containing alkyl and spirocycloalkyl groups pendant to the main chain has been prepared via the thermal decomposition of anhydrosulphites.(49) The simple dimethyl substituted polymer (VIII; $R^1 = R^2 = CH_3$) has been reported to have a melting point of 240°C.(34)



$$-\left(O - \overset{\displaystyle R^1}{\underset{\displaystyle R^2}{\overset{|}{\underset{|}{C}}}} - CO\right)_n-$$

VIII

In general, symmetrically substituted poly-α-esters (VIII; $R^1 = R^2$) are relatively crystalline whereas the unsymmetrical polymers are amorphous. The amorphous polymers tend to be soluble in solvents such as chloroform, the crystalline polymers of reasonably high molecular weight are insoluble in chloroform. Spirocycloalkyl substituted poly-α-esters are amorphous and soluble in organic solvents.

The thermal stability of the poly-α-ester series shows a trend in that the temperature at which degradation commences decreases with substituent size and yet the melting temperatures of the crystalline polymers tend to increase, and thus for higher derivatives the melt working temperature is narrow. The dimethyl polymer (VIII; $R^1 = R^2 = CH_3$) has markedly superior thermal stability over the higher analogues.

Whilst it appears that the widespread use of poly-α-esters as textile and general purpose synthetics is not feasible, polymers whose particular use requires peculiar combinations of thermal, chemical and oxidative stabilities, etc., is continually growing.

It has been recently stated(3) that, "although it is not anticipated that the production of any one fluoropolymer will approach the current commercial polymers (e.g. polystyrene, polyethylene, polyvinylchloride, etc.) in tonnage, it can be expected that in the future they will be the most important group because of the superior and unique properties of some of these compounds."

The work presented herein, has been primarily concerned with the elucidation of polymerisation mechanisms and structure/reactivity relationships in the monomer, however, some properties of poly-PFAAC and poly-MAAC were briefly examined on samples of relatively low molecular weight.

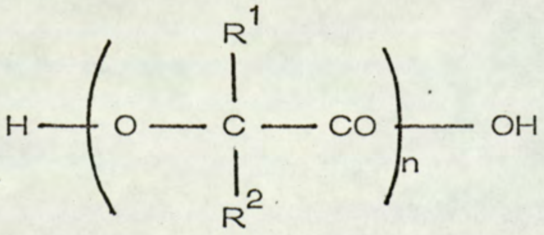
9.2 Preparation and Characterisation of Polymer Samples

Polymers from MAAC and PFAAC were prepared by the pyridine initiated decomposition of the monomer. To facilitate product isolation the reaction was carried out in the 'MAR' grade of diethyl ether. Concentrations of 0.5, 1.0 and 4.0 mol. litre^{-1} in diethyl ether were used and the reactants made up under dry-box conditions. The reaction vessel possessed three quickfit joints, one of which was vented to air through an anhydrous calcium chloride drying tube. After removal from the dry-box, the required quantity of pyridine was introduced by means of a hypodermic syringe through a "suba-seal" over one of the quickfit joints. A stopper in the third joint isolated the system from atmospheric moisture.

When the polymerisation was complete (usually 24 hours) the solvent, diethyl ether, was removed by evaporation and the resultant polymer redissolved in chloroform and precipitated by the addition of iso-octane. The polymer was separated by centrifuging and finally dried from solvents under vacuum at room temperature for several hours.

In the case of the polymerisation of MAAC by this method, a gum-like precipitate formed during the polymerisation; the nature of this precipitate and the soluble fraction will be discussed in a subsequent section.

Polymers prepared in this way, using a range of initiator concentrations, were examined by gel permeation chromatography and additionally characterised by infrared and n.m.r. techniques. Infrared spectra were recorded in the form of KBr discs for the solid polymer samples obtained from the pyridine initiated decomposition. Typical ester carbonyl absorptions were observed at 1755 cm^{-1} and 1760 cm^{-1} for poly-MAAC and poly-PFAAC respectively. The structure of the polymer was consistent with that of a poly-α-ester (XXXVIII), which in the case of low molecular weight material the hydroxyl and carboxylic acid end groups were easily identified.



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

XXXVIII

Comparison of the ratio of the strengths of the -OH and the C = O absorptions in the parent α-hydroxy acids and the polymer indicated that the degree of polymerisation in the case of poly-MAAC was of the order 25-30 and for poly-PFAAC, 10-15. The n.m.r. spectrum of poly-MAAC was obtained with a 10% w/v solution in deuterated chloroform and produced broad resonance peaks for both the phenyl group protons and the single main chain proton, these were centred at 2.71 τ and 3.92 τ respectively.. A weak resonance peak was observed at 6.24 τ , which was identified as the hydroxyl proton of the terminal group. Integration of the spectrum and comparison of the terminal group peak and the peak for the single hydrogen gave a degree of polymerisation of the same order as that by the infrared technique. The methyl resonance of poly-PFAAC was also observed as a broad peak centred at 7.87 τ and the hydroxyl proton occurred at 6.25 τ . The degree of polymerisation obtained by comparison of the integrated peaks was in the range of that by the infrared technique.

The structure of the polymers produced by tertiary base initiation appeared, therefore, to be in no way different from the general structure of those polymers obtained by thermal polymerisation of anhydrosulphites. Thus, the repeat unit and end groups are represented by the structure XXXVIII, where the value of n is independent of initial tertiary base concentration and is determined primarily by the concentration of moisture or residual parent acid in the system. Additional confirmation of the nature of the end groups was obtained by the use of combined vapour pressure osmometry/carboxyl micro-titration techniques previously used.(49)

The polymer samples obtained from the thermal decomposition of anhydrocarboxylates were difficult to isolate. The solvent, nitrobenzene, was partly removed by evaporation and the polymer precipitated and washed with iso-octane. Infrared spectra were run as thin films between KBr discs and were consistent with the poly-α-ester structure XXXVIII.

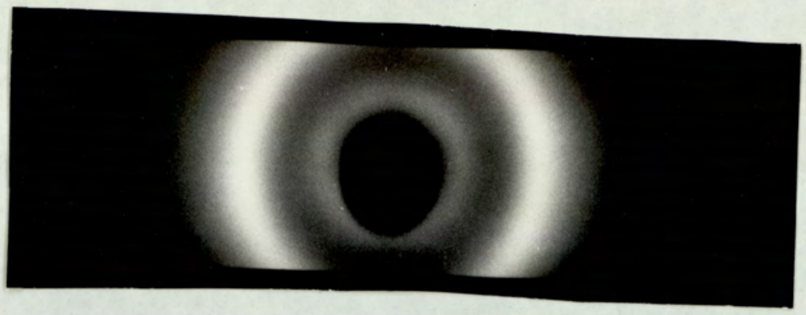
Some guide to the crystallinity of the polymers prepared was obtained by X-ray diffraction studies using the powder photograph technique. X-Ray powder photographs for the polymers; poly-PFAAC, poly-MAAC and the two optically active forms of poly-MAAC are given in Fig. 9.1. Very little crystallinity is shown by any of the polymers except perhaps in the case of the racemic form of poly-MAAC in which faint sharp lines are present.

It is interesting to compare the properties of the polymers whose preparation has been described herein with those previously obtained from anhydrosulphite polymerisation. The latter fall into three classes;

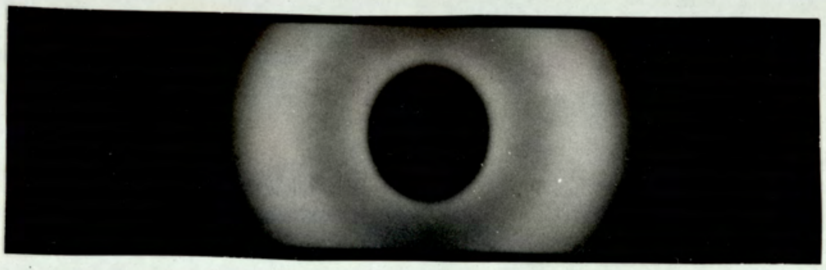
(a) the symmetrical dialkyl substituted polymers which are extremely crystalline as prepared, soluble in relatively few organic solvents and showing crystallisation behaviour typical of crystalline polyesters,

(b) the spirocycloalkyl polymers (XXXIX) which are readily isolated from solution as white amorphous solids but non the less show good solubility behaviour in a wide range of organic solvents.

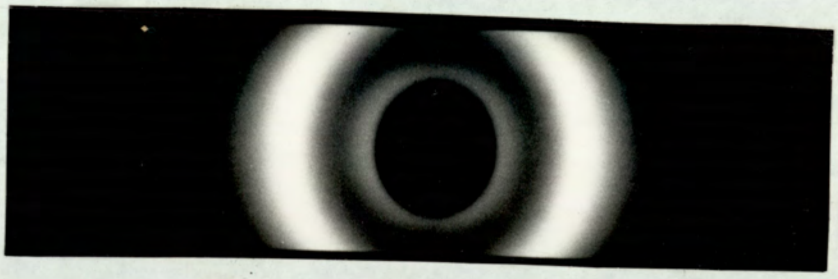
Fig. 9.1



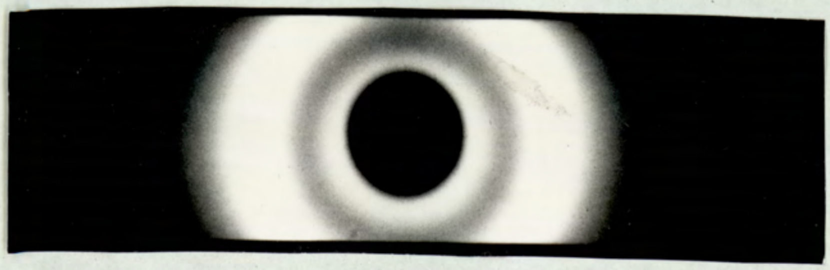
POLY-MAAC



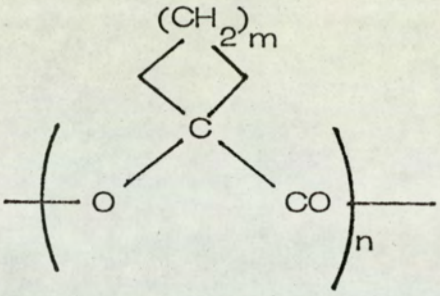
POLY-PFAAC



POLY-(D)-MAAC



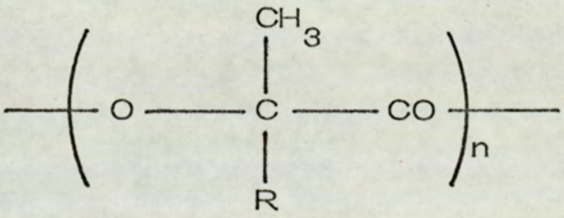
POLY-(L)-MAAC



XXXIX

They are not crystalline as prepared nor after prolonged annealing at temperatures above the glass transition temperature,

(c) the unsymmetrical methyl/n-alkyl substituted polymers (XL). These are similar in characteristics to those in category (b) but more soluble and difficult to isolate in powder form especially for values of R > C_2H_5.



$$-\left(O-\overset{CH_3}{\underset{R}{C}}-CO\right)_n-$$

XL

The phenyl and pentafluorophenyl substituted poly-α-esters, e.g. XL; R = C_6H_5 or C_6F_5, are much more readily isolated than the polymers in category (c) above, but share their ready solubility in organic solvents. They are non-crystalline as prepared but as yet no attempts have been made to study annealed samples. Considering the structure of the poly-α-ester backbone and the fact that propyl or butyl groups (i.e., VIII , $R^1 = R^2$ = propyl) can be symmetrically introduced without destroying crystallinity, it would seem possible that the phenyl and pentafluorophenyl substituted polymers could show crystallinity under certain conditions particularly if the groups were regularly disposed.

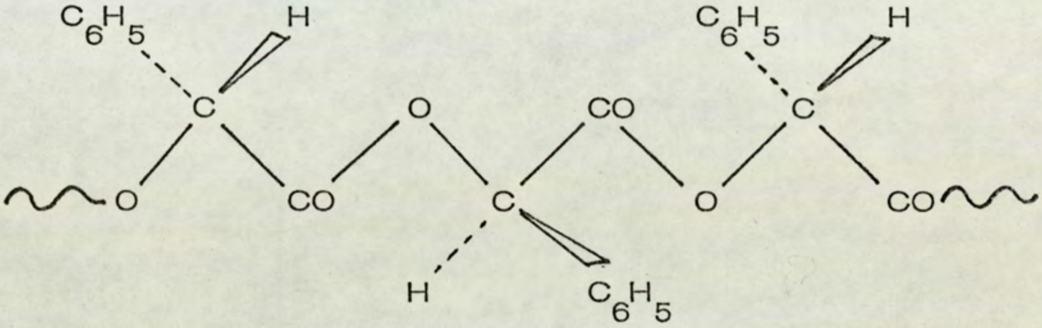
It would seem sensible to investigate this in two stages. Firstly, the effect of regular substituent disposition (i.e. induced stereoregularity) on polymers prepared and isolated in a similar way to that previously described. Secondly, the effect of annealing/ drawing on the crystallinity of powders or filaments. The first has been achieved by the use of optically active parent α-hydroxy acid precursors (Section 9.3). Lack of time has prevented investigation of the second.

9.3 The Synthesis of Optically Active Poly (Mandelic Acid)

The two optically active forms of mandelic acid were used for the preparation of the anhydrocarboxylates, and finally the polymer by decomposition in the presence of a 10% molar concentration (on monomer) of pyridine initiator. Optical activity was checked at each stage of the polymer synthesis by O.R.D. analysis which showed that the particular configuration was retained during each step of the synthesis.

The relative thermal stability of the two optically active forms and racemic polymer as assessed by T.G.A. appeared to be the same, but it may be anticipated that the melting points of the two optically active polymers would be higher by at least $20C^{o}$, as the optically active anhydrocarboxylates have melting points in the range 72.3^{o} - 73.3^{o}C (cf. melting point of racemic MAAC, 53.7^{o} - 55.1^{o}C).

X-ray powder photographs showed that in spite of the ordered addition of units to the growing polymer chain during polymerisation, very little crystallinity was shown by these optically active polymers (Fig. 9.1) in the form in which they were prepared. If the poly-α-ester chain is represented in a planar zig-zag form (XLI), a syndiotactic polymer is formed and it is perhaps surprising that no crystallinity is shown by these polymers.



XLI

It will be necessary to examine both the effect of annealing under various conditions and the crystallinity of drawn filaments before reaching final conclusions however.

9.4 Thermal Stability

The general thermal stability of the polymers derived from MAAC, PFAAC and the anhydrocarboxylate of 2-hydroxy 2-pentafluorophenyl acetic acid,(82) was assessed by the use of T.G.A. Fig. 9.2 shows the corresponding T.G.A. traces for the polymers mentioned above. Caution must be taken in interpreting the results as all the polymer samples were of relatively low molecular weight. Traces (a) and (b) are for the ether soluble fraction of the polymer from MAAC (Section 9.2) and the MAAC polymer prepared at a concentration of 4.0 mol. litre^{-1} of monomer with 0.4 mol. litre^{-1} of pyridine (see Table 9.1) respectively. It would appear

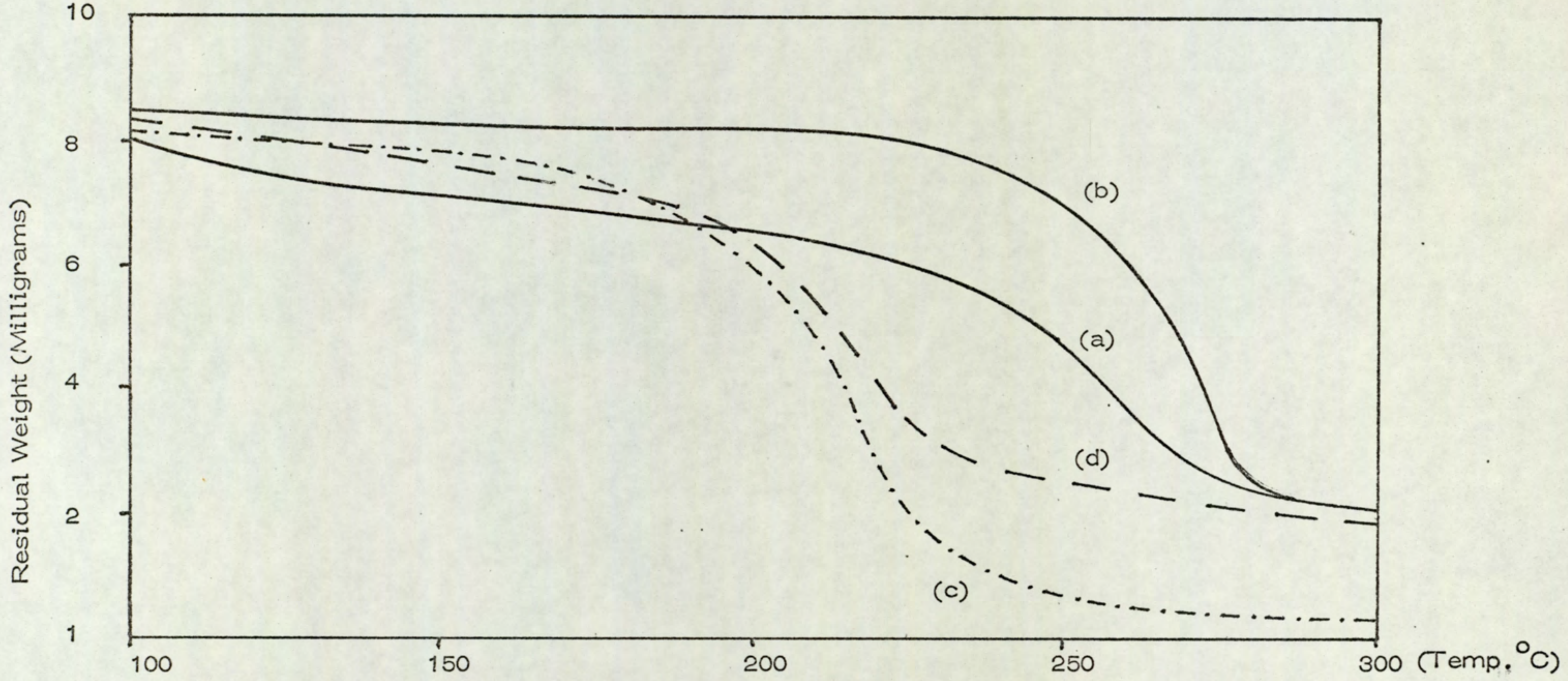
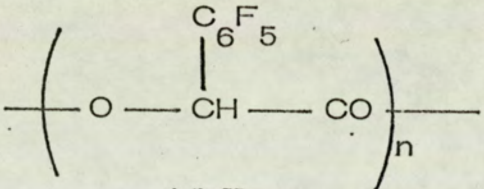


Fig. 9.2 T.G.A. traces for poly-MAAC (a and b), poly(2-hydroxy 2-pentafluorophenyl acetic acid) (c) and poly-PFAAC (d). Heating rate 10° min.^{-1} Atmosphere of nitrogen.

from the form of trace (a) that the ether soluble polymer fraction is simply of lower molecular weight than the insoluble fraction and presents a possible method of removing the lower molecular weight portion of this polymer.

Trace (c) is for poly(2-hydroxy 2-pentafluorophenyl acetic acid) of structure XLII. Whilst it would appear that the thermal stability of the fluorinated polymer was less than for the hydrocarbon it must be pointed out that the latter polymer sample (poly-MAAC) was of much higher molecular weight (see Table 9.1) and the general form of the trace for the polymer XLII is typical of low molecular weight samples.



$$\left(-O-\underset{}{\overset{C_6F_5}{\overset{|}{CH}}}-CO- \right)_n$$

XLII

The temperature at which decomposition starts to occur in the case of poly-MAAC (trace (c)) is approximately 205°C; this may be considered quite good when the fact that the molecular weight was only in the region of 4000 is taken into account. Poly-PFAAC, trace (d), showed apparently less thermal stability than poly-MAAC even though the molecular weight was over 2000, however, the average degree of polymerisation for this polymer is only 8-10, whereas in the case of poly-MAAC, it is in the range 30-32.

With reference to Table 9.1, it may be clearly seen that the molecular weights of the resultant polymers are independent of initial pyridine concentration and the polymerisation results in a

Table 9.1

Results of G.P.C. Analysis of Various Polymer Samples

Monomer	Pyridine concentration mol. litre^{-1}	$\bar{M}_n$	$\bar{M}_w$	$\bar{M}_w/\bar{M}_n$
$[PFAAC]_o$ =0.5mol.litre^{-1}	0.05	1060	1200	1.12
	0.15	1240	1380	1.11
	0.5	1390	1520	1.09
$[PFAAC]_o$ = 1.0mol.litre^{-1}	0.1	1810	2080	1.15
	0.3	2340	2650	1.13
	1.0	2220	2540	1.14
$[PMAAC]_o$ = 0.5mol.litre^{-1}	0.0005	430	510	1.21
	0.0015	440	530	1.21
	0.005	470	570	1.21
	0.015	480	620	1.29
	0.05	620	740	1.20
$[MAAC]_o$ = 4.0mol.litre^{-1}	0.04	3540	4860	1.38
	0.4	3940	4980	1.27
	4.0	1440	1910	1.33
$[PFMAAC]_o^*$ = 0.5mol.litre^{-1}	0.05	1230	1450	1.18

* [PFMAAC] = 2-hydroxy 2-pentafluorophenyl acetic acid anhydrocarboxylate.

fairly narrow molecular weight distribution. The molecular weight distribution does appear to broaden at higher molecular weights. It is also quite apparent that the limit of the molecular weight is determined by the amount of residual moisture in the solvent used.

The effect of molecular weight on polymer stability can only be commented on in a very speculative fashion and in the light of the extensive studies on the kinetics and mechanisms of poly-α-ester degradations already carried out.(83-87) It would appear from this work that molecular weight is only important in determining initial polymer stability at values of $\bar{M}n$ below 10,000-15,000 and above this value thermal stability is independent of molecular weight. At values of $\bar{M}n$ below 5,000 however, the effect is a dramatic one and the stability of such polymers is drastically reduced when compared with high molecular weight material.

Whereas it would appear, therefore, that the thermal stability of these polymers will improve markedly as higher molecular weights are achieved it must be emphasised that no systematic studies have yet been carried out on the precise degradation mechanisms operating in these cases.

CHAPTER 10

Conclusions and Suggestions for Further Work

10.1 Conclusions

Reported syntheses of anhydrocarboxylates have not been altogether satisfactory. The synthetic route described in Chapter 3 is regarded as the best method of synthesis of these cyclic compounds. Initial investigations have shown that it may be used for the preparation of the analogous cyclic compounds derived from α-thiohydroxy carboxylic acids, and by the use of thiophosgene cyclic compounds possessing a C(2), C=S function may easily be prepared. The versatility of this method should enable a series of rings containing carbon, oxygen and sulphur (and possibly other elements in Group VI) to be prepared.

The kinetic behaviour during thermal decomposition has been investigated in order that the stability of the phenyl substituted anhydrocarboxylates in the absence of other reacting species may be assessed. The thermal decomposition of AAAC and BAAC in non-hydroxylic solvents proceeds predominantly by a first-order extrusion reaction with the loss of carbon dioxide and the formation of a polymerisable species, the α-lactone, which takes part in a rapid propagation reaction with a terminal hydroxyl group. BAAC, however, is susceptible to a secondary fragmentation process yielding benzophenone and carbon monoxide. Whilst the incorporation of a phenyl substituent unlike many polymerisations, increases the polymerisability of the anhydrocarboxylate ring, thermal decomposition is not a convenient method for polymerisation.

In the case of MAAC and PFAAC, the steric and electronic effects associated with the monomer gives rise to a mode of polymerisation which involves direct attack of the terminal hydroxyl group at the C(4) carbonyl as the propagation step. This bimolecular route is a more rapid process than purely thermal fragmentation of the ring, and in this context the effect a pentafluorophenyl group may be considered to increase the polymerisability of the ring.

It appears, therefore, that the introduction of large and electron withdrawing substituents to the ring confers a degree of reactivity which is compatible with polymer formation.

Extensive work regarding the activity of the C(4) carbonyl to weak nucleophilic attack has been carried out. The reactivity of this site may be explained in terms of the steric and electronic effects associated with both the anhydrocarboxylate ring and the attacking nucleophile, and in conclusion it may be inferred that this carbonyl is a potential site to be exploited for an initiated mode of polymerisation.

Increased electron withdrawing substituents as exemplified by a pentafluorophenyl group, enables considerable activation of the C(4) carbonyl to be achieved without undue loss of reactivity by increased steric hindrance. Trifluoromethyl substituents would probably represent a limit on the reactivity of this site to such attack.

Thermal polymerisation of anhydrocarboxylates is undesirable for many reasons but initiated decomposition of MAAC and PFAAC (and probably AAAC), using aprotic bases of the pyridine type, enables the polymers to be prepared with ease at room temperature. Polymerisation proceeds smoothly obeying a first-order rate law with respect to monomer. No detectable by-products are formed in the case of MAAC and PFAAC, but BAAC due to the high temperatures required for convenient reaction times, is susceptible to the formation of the same secondary ring fragmentation product as was experienced during thermal polymerisation. The use of more basic initiators such as trialkylamines would be expected to compensate for this bulky second phenyl substituent.

The pyridine initiated polymerisation is quite novel in that the role of pyridine is not as a conventional initiator but merely to initiate the decomposition of the anhydrocarboxylate to form a polymerisable intermediate, formally depicted as an α-lactone.

Provided that certain requirements are met regarding the reactivity of the C(4) carbonyl and the steric effects associated with the C(5) substituents, this tertiary base initiated decomposition may be considered as an excellent method of polymerisation of anhydrocarboxylates.

In the sequence of reactions leading to the formation of polymer, no bonds associated with the α-carbon (of the parent α-hydroxy carboxylic acid) are broken and thus by using an optically active acid, the corresponding optically active polymer may be prepared.

The polymers prepared via the pyridine initiated route were of relatively low molecular weight. The reason for this was principally the purity of the solvent medium with regard to moisture content. Improved molecular weights may be obtained by carrying out melt polymerisations of these compounds using tertiary base initiators.

Ring-opening polymerisation in which some elements of the ring are lost during polymerisation has many advantages over conventional condensation polymerisation modes. It is hoped that the contents of this thesis will help to provide a better understanding of the factors determining the polymerisability of anhydrocarboxylates, and afford a more general route to poly-α-esters whose substituents have been in the past the prohibiting feature of otherwise intriguing polymer structures.

10.2 Suggestions for Further Work

The general requirements, as regards the nature of the substituents on the anhydrocarboxylate ring, have been summarised in the previous section. It is quite apparent that changing the structure of the ring from an anhydrosulphite to an anhydrocarboxylate results in very different properties with regard to reactivity and polymerisability of the cyclic compound. Thus, it is suggested that an extension of the various rings available must be a obvious continuation of the work described herein. Increasing the number of available anhydrocarboxylates to include two pentafluorophenyl substituents and fluoroalkyl substituents must be carried out and the synthesis of the polymers necessarily follows. However, airing a somewhat pessimistic note of caution, such substituents may represent limitations to the synthetic routes to polymer achieved. But fortuitism is often the essence of progress and such rings analogous to the anhydrosulphites and anhydrocarboxylates may present a degree of reactivity with certain substituents that is compatible with the formation of polymers.

A rather less speculative extension would involve the polymerisation of anhydrocarboxylates containing CH_2Cl, CCl_3 and CH_3COCH_2 substituents, whose polar substituent constants are 1.05, 2.65 and 0.60 respectively. Bearing in mind that the polar substituent constant for a phenyl group is 0.60 units, such substituents are likely to provide the desired degree of reactivity of the anhydrocarboxylate ring for polymerisation using a strong aprotic base.

This thesis has been concerned with an assessment of the effect of various substituents on the reactivity and polymerisability of phenyl and pentafluorophenyl substituted anhydrocarboxylates, and whilst polymers have been prepared, no attempt has been made to produce relatively high molecular weight samples. The problem undoubtedly lies in the extent to which the solvent medium may be dried. However, bulk melt polymerisation of these relatively low melting point solids should provide quite an easy route to high molecular polymer. A detailed investigation of structure/property relationships would necessarily follow.

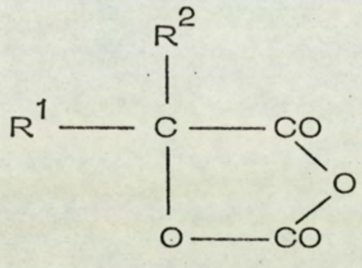
The relative ease by which MAAC and PFAAC polymerise by a bimolecular process and AAAC and BAAC by a thermal ring fragmentation route, would enable block copolymers to be prepared with other polymers possessing terminal hydroxyl groups. Choice of the copolymer system with respect to the anhydrocarboxylate gives a degree of flexibility in the properties of the resultant copolymer system. Polymers having nucleophilic groups pendant to the main chain offer suitable sites to which an anhydrocarboxylate may be grafted. Such groups include hydroxyl functions in polyvinyl alcohol, secondary amine groups in polyamino acids and the amide function in polyamides.

It is hoped that the work presented herein will provide a system which is capable of many extensions in the various fields of polymer science.

APPENDIX

Nomenclature

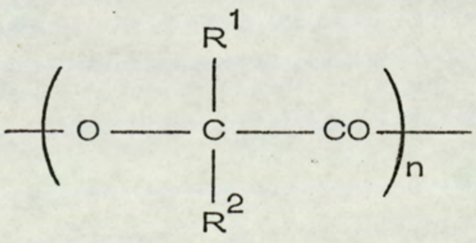
The work has been concerned with the synthesis and polymerisability of cyclic compounds of the type II.



II

I.U.P.A.C. nomenclature$^{(88)}$ requires that the ring be called 1,3-dioxolan 2,4-dione. However, it is more commonly known as an α-hydroxy carboxylic acid anhydrocarboxylate, for example benzilic acid anhydrocarboxylate, and convenient abbreviations such as BAAC for the latter case have been used throughout the text.

Simple poly-α-esters (VIII), in which for example $R^1 = R^2 = H$, have in the past been named according to the parent α-hydroxy carboxylic acid and thus the latter case would be known as poly (glycollic acid). Higher members of the alkyl substituted poly-α-ester series do not have trivially named parent acids and thus the



VIII

I.U.P.A.C. nomenclature is more explicit, for example $R^1 = R^2 = CH_3$ (VIII) is systemmatically known as poly(isopropylidene carboxylate).

As the majority of the parent acids which have been used have trivial names and abbreviated names have been used for the derived anhydrocarboxylates, for the sake of brevity throughout the text the polymers have been identified by the prefix poly- and the anhydrocarboxylate abbreviation. Thus in the case of mandelic acid the derived polymer is named poly-MAAC.

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