STUDIES ON THE CATIONIC POLYMERISATION
OF CYCLIC OXYGEN COMPOUNDS

by

Frank R. Jones, A.P.I.

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the requirements for the Degree of
Doctor of Philosophy.

I hereby certify that this Thesis
has been corrected to my satisfaction. May, 1970

P.H. Plesch.

Internal Examiner.

13.6.70.

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2 articles from 'Chem Comm' 1969 (between pages 107 & 108, and between pages 118 & 119)

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Abstract

The work has been divided into three sections.

Section A (Chapters 3 and 4)

This section is concerned with the polymerisability of some cyclic oxygen compounds.

Chapter 3 shows that 1,3-dioxan does not polymerise, but that at low temperatures a mixture of the cyclic dimer and trimer crystallises from the monomer in the presence of cationic polymerisation catalysts.

Chapter 4 discusses the problems concerned with the preparation and polymerisation of oxepan. Oxepan is difficult to polymerise.

Section B (Chapters 5 - 8)

This section is concerned with the polymerisation of 1,3-dioxolan by triethyloxonium tetrafluoroborate.

Chapter 5 shows that this catalyst is inefficient because of a competitive decomposition in which the catalyst is converted into non-conducting products (ethyl fluoride and boron trifluoride etherate).

Chapter 6 describes a study of the decomposition of three triethyloxonium salts. The rate of decomposition of triethyloxonium tetrafluoroborate is greater in the presence of ethers. A theory involving solvation of the oxonium ion has been proposed to explain the results.

Chapter 7 deals with the determination of the association constants of triethyloxonium tetrafluoroborate and hexafluorophosphate from conductivity measurements. Conductivity measurements in the

presence of diethyl ether prove that oxonium ions are solvated in the presence of ethers.

Chapter 8 is concerned with the scheme proposed to explain the results of the polymerisation of 1,3-dioxolan by triethyloxonium salts. The relative merits of the work of Yamashita and Lyudvig on the polymerisation of cyclic formals with triethyloxonium salts is discussed.

Section C (Chapters 9 and 10)

This section is concerned with the ring-expansion and back-biting mechanisms proposed for the formation of macrocyclic rings in the polymerisation of 1,3-dioxolan by anhydrous perchloric acid.

Chapter 9 describes further end-group analysis which was carried out in an attempt to distinguish between these mechanisms.

Chapter 10 discusses the mechanism of the polymerisation of the cyclic formals and shows that the 4-centred transition state of Plesch and Westermann may be applied to other organic reactions involving oxygen containing molecules.

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CHAPTER 4 - CYCLIC ETHERS

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CHAPTER 1

Introduction

The work to be described in this thesis is an extension of the work of Dr. P.H. Westermann who polymerised 1,3-dioxolan[1] and 1,3-dioxepan[2] with anhydrous perchloric acid. The original aim of this research was to see whether the novel ring-expansion mechanism of Plesch and Westermann[1,2] applied to other systems.
Section A deals with the polymerisability of some cyclic formals and ethers whereas Section B contains a discussion of the complex situation which arose when 1,3-dioxolan was polymerised by triethyloxonium tetrafluoroborate ($Et_3O^+BF_4^-$). Section C contains further evidence for the ring-expansion mechanism.

The present studies on cationic polymerisation are mainly concerned with an industrial monomer, 1,3-dioxolan and a catalyst, triethyloxonium tetrafluoroborate, which has been studied by industrial workers[3]. Therefore, it is hoped that this thesis will be of interest to polymer chemists, whether they be industrialists or academics, and come as a useful contribution to the growing field of cationic polymerisation.

In recent years the number of publications on the polymerisation of cyclic oxygen compounds has grown rapidly. Many papers and patents on the polymerisation of trioxan, related compounds and tetrahydrofuran have appeared,but these will only be discussed where they are relevant to the project in hand. Therefore, at this stage a general survey of the polymerisation of 1,3-dioxolan and 1,3-dioxepan will be given and the more relevant papers will be discussed in greater detail in the text.

Hill and Carothers[4] first investigated the cyclic formals. Tetramethylene, pentamethylene and hexamethylene formals were polymerised in the presence of catalytic quantities of sulphonic acid when heated to 100-150°. However, trimethylene formal (1,3-dioxan) did not polymerise and 1,3-dioxolan was not mentioned.

Gresham[5] polymerised 1,3-dioxolan with Lewis and mineral acids. He found that a 25% solution of dioxolan (4% sulphuric acid at 100°) yielded only a small amount of oil with a molecular weight of 250 whereas bulk polymerisation (0.02 boron trifluoride at 6°) gave a crystalline high polymer of molecular weight 196,000 (determined by viscometry). A polymer of molecular weight 1580 had negligible end-groups and he therefore concluded that it was cyclic.

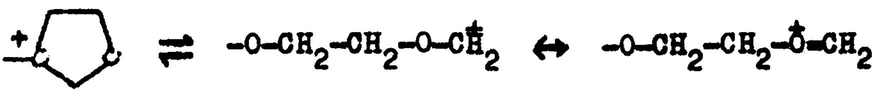
Another patent, by Muettertios[6], described the production of high molecular weight poly-1,3-dioxolan with phosphorus pentafluoride as the catalyst.

Since the work so far described was chiefly concerned with the commercial possibilities of these polymers, the detailed chemistry and mechanism of these polymerisations was not investigated.

The equilibrium polymerisation of cyclic formals was first observed by Strepikheev and Volokhina[7], but they were unable to explain their results by an equilibrium between monomer and polymer even though the work of Dainton and Ivin[8] was known at the time. However, Strepikheev and Volokhina did supply the heats of polymerisation of the di-, tri-, tetra- and pentamethylene formals, which appeared in a review by Dainton and Ivin[9].

Diethyl aluminium chloride - water, ethyl aluminium chloride - water, acetyl chloride - metal halide and acetic anhydride - perchloric acid were reported as catalysts by Okada, Yamashita and Ishii[10]. Although the conditions were essentially anhydrous, the monomer was dried with calcium hydride and distilled under nitrogen before use and polymerised in bulk, no details of the purification of the catalysts are given. No reaction curves were presented but the yields and intrinsic viscosity of the polymer at a fixed time, varying from 20 to 48 hours, were plotted against various molar ratios of the catalyst pairs, listed above. For example, the yield and intrinsic viscosity of the polymer were observed to pass through a maximum at an approximately equimolar ratio of water and diethyl aluminium chloride. In equilibrium polymerisations the yield is independent of the catalyst concentration. Therefore, these results must mean that either the rate of polymerisation is low or the catalyst is consumed during polymerisation. However, the shape of both curves indicates that the molecular weight is dependent on conversion. The yield and intrinsic viscosity also decreased with increasing temperature but the authors failed to recognise the system as one which is dominated by an equilibrium.

These authors proposed that an equilibrium between oxonium ions and carboxonium ions existed and that the active centre in the polymerisation was the carboxonium ion.



$$\rightleftharpoons -O-CH_2-CH_2-O-\overset{+}{C}H_2 \leftrightarrow -O-CH_2-CH_2-\overset{+}{O}=CH_2$$

This was based on the suggestion of Jaacks and Kern[11] that the active centre for the polymerisation of trioxan is a resonance stabilised carboxonium ion.

Okada et al[12] also report the cationic copolymerisation of 1,3-dioxolan with styrene, with boron trifluoride etherate as the catalyst. This they interpret as further evidence in favour of the carboxonium ion mechanism, because Kern et al[13] have been able to copolymerise trioxan with styrene, whilst tetrahydrofuran, which is generally supposed to polymerise by an oxonium ion mechanism, will not copolymerise with styrene.

This argument is exceedingly weak in view of the fact that Okada et al[14] have themselves reported the cationic copolymerisation of 1,3-dioxolan with tetrahydrofuran with boron trifluoride as the catalyst. The comparison of 1,3-dioxolan with trioxan is the only evidence presented in favour of the carboxonium ion mechanism, in particular no analysis for end-groups is reported.

Hayashi[15] reported that 1,3-dioxolan, 1,3-dioxepan and 1,3-dioxan polymerised in the presence of maleic anhydride and benzoyl peroxide. However, it will be shown in Section A that these results could not be repeated.

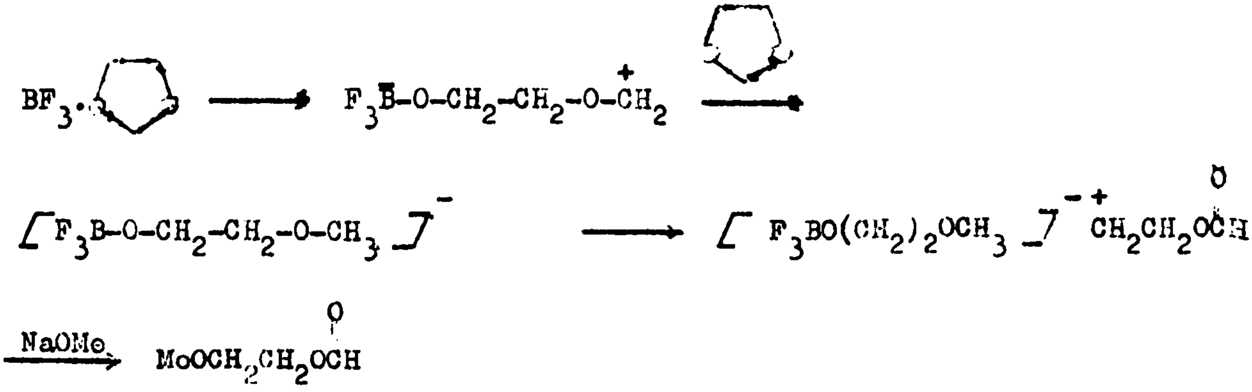
Kucera[16] and his coworkers have studied the polymerisation of 1,3-dioxolan by octamethylcyclotetrasiloxane bisulphate as the catalyst. The experiments were carried out in open dilatometers at temperatures between 40-70° and with the catalyst concentration between 10^{-1} to 10^{-3}M. Most of the work was concerned with kinetic measurements and their interpretation. Unfortunately, the kinetic scheme was based on the assumption that the active centres are carboxonium ions which were supposed to be in equilibrium with unreactive tertiary oxonium ions. Although the scheme does fit the experimental results the basic assumption is not justified by any supporting experiments.

However, some interesting phenomena were observed in the presence of water[17]. They observed a cocatalytic effect up to 50 ppm of H_2O, but on addition of further quantities of water the reaction became slower with a longer induction time. Equilibrium conversion was not achieved and the conversion depended on the water concentration. During the polymerisation the water concentration dropped to a constant value which was dependent on the initiator concentration. Therefore, water cocatalyses the polymerisation but free water causes termination.

Mercuric chloride and boron trifluoride etherate were used by Gorin and Monnerie[18] as catalysts for the polymerisation of 1,3-dioxolan. Although the monomer and catalysts were carefully dried, the polymerisations were carried out in test-tubes. Their kinetic measurements agreed with Kucera's scheme but no direct evidence for an equilibrium between carboxonium ions and oxonium ions was presented.

Yamashita et al.[19] showed that the complex of boron trifluoride and 1,3-dioxolan participated in the initiation because a linear relationship between log. R_p (the initial rate of polymerisation and log. K (the equilibrium constant for the exchange of ether molecules) existed. The complex formed from 1,3-dioxolan and boron trifluoride could also be isolated at low temperatures and this compound initiated polymerisation more rapidly than boron trifluoride etherate.

The following scheme was proposed because



2-methoxyethyl formate was isolated from a reaction mixture killed with sodium methoxide. It is not clear from this scheme how propagation occurs, the last initiation stage is obscure because 2-methoxyethyl formate can also be formed from a reaction of the 1,3-dioxolenium salt with sodium methoxide and also no quantitative data are presented to establish the extent of reaction and this is important because boron trifluoride etherate is an inefficient catalyst (see Chapter 5).

Miki[20], Higashimura and Okamura produced g.l.c. evidence for the formation of cyclic oxygen compounds in the polymerisation of 1,3-dioxolan with boron trifluoride etherate at 35°. The chemistry of this system has not been clarified, so that the formation of these compounds, in the presence of such high catalyst concentrations (about 10^{-1}M), at this temperature cannot be used as evidence for the back-biting mechanism of Jaacks[21] which will be discussed in Chapter 10. However, peaks other than those of monomer and solvent have been observed in g.l.c.'s of 1,3-dioxolan and its polymer solutions (see Chapter 5). These extra peaks in the g.l.c. are also present when the monomer is analysed, and they appear to be due to its decomposition in the machine. Although direct extrapolation of my observations to Miki's is not feasible, my results do suggest that the compounds which Miki isolated may have been formed in the chromatograph.

At the beginning of my research into the polymerisation of 1,3-dioxolan with triethyloxonium tetrafluoroborate Yamashita and his coworkers[22] published a paper on the same topic. Although essentially anhydrous conditions were obtained by distilling both monomer and solvent from calcium hydride, the handling procedure for the catalyst is not given and the reactions were carried out in test-tubes so that a sampling technique could be used to prepare the time-conversion curves.

However, they failed to recognise that only a small proportion of the initiator forms a propagating species. In fact they assumed the catalyst to be 100% efficient when calculating a second order rate constant which they erroneously interpreted as k_p.

In a later paper Yamashita[23] showed that part of the induction period was due to adventitious water, but high vacuum techniques did not reduce the induction period to zero.

More recently these workers extended the triethyloxonium tetrafluoroborate catalysis to 1,3-dioxepan[24] and 1,3,6,-trioxocan [25]. The procedures were the same as before, but they obviously were less certain of the mechanism and of the kinetics because k_p was not determined for either monomer.

Medvedev et al[26] have published several papers concerned with the polymerisation of 1,3-dioxolan by triethyloxonium hexachloroantimonate. They postulate the active centre to be a carboxonium ion because a solution of triethyloxonium hexachloroantimonate absorbs at 272 nm whereas in the presence of 1,3-dioxolan the solution absorbs at 228 nm. They consider the former absorption to be due to a tertiary oxonium ion and the latter to a linear carboxonium ion. However, there is no independent evidence for the absorption of oxonium ions in the u.v., so that the assignments are erroneous. It is most probable that the observed absorption at 272 nm is due to the $SbCl_6^-$ ion; the absorption at 228 nm is still obscure because Jaacks[27] observed the absorption of $CH_3CH_2O\overset{+}{C}H_2$ $SbCl_6^-$ (analagous to the carboxonium ion postulated) at 260 nm, and Penczek[28] showed that the absorption of a series of $SbCl_6^-$ salts only varied between 5-10 units away from 272 nm whereas $RO^+SbCl_4^-$ absorbs at about 240 nm.

Also, Medvedev et al[26] did not substantiate their mechanism by end-groups analysis and the reaction curves they presented did not appear to reach equilibrium.

Chil-Gevorgyan[29-31] and his coworkers have published several papers on the polymerisation of 1,3-dioxolan with $BF_3.Et_2O$ The reports were concerned with the kinetics of the polymerisation. Chil- Gevorgyan[31] observed the maximum rate of polymerisation and proceeded to treat the polymerisation mathematically as an auto-catalytic reaction to produce curves which fitted the experimental data. Much of this work is rather pointless since no evidence was presented for the actual chemistry behind the supposed process.

Plesch and Westermann[1,2] confirmed Gresham's findings[5] that the polymers are cyclic on the basis of end-group analysis and kinetic evidence and suggested a ring expansion mechanism. Anhydrous perchloric acid was the catalyst and the active centre was proposed to be a secondary oxonium ion.

However, there is much evidence to show that the active centres in the polymerisation of trioxan are tertiary oxonium ions and for this reason Jaacks[21] believes the propagation in the polymerisation of 1,3-dioxolan to be through tertiary oxonium ions. The results of his group pointed to the presence of tertiary oxonium ions, but are not conclusive since they did not always find the number of end groups to be equal to the initiator concentration. Jaacks explains this by incomplete protonation of the polymer, that is perchloric acil is an inefficient initiator under some experimental conditions. Jaacks has only identified one end of the polymer so that it remains to be seen whether, under his conditions, the concentration of end-groups for both ends of the polymer are the same. The whole question of the mechanism of the polymerisation of cyclic formals is discussed in Section C.

This literature survey on the polymerisation of the cyclic formals would not be complete without reference to the thermodynamics of their polymerisation. Since the work to be described in this thesis is not concerned with the determination of thermodynamic parameters a discussion of the various values for the enthalpy and entropy of polymerisation is not included. However, many schools have studied the equilibrium nature of the polymerisation of 1,3-dioxolan and 1,3-dioxepan and these references are included for completeness.

Yamashita[34] and his coworkers measured the thermodynamic parameters for the polymerisation of 1,3-dioxolan, 1,3-dioxepan and 1,3,6-trioxocan from the equilibrium monomer concentrations determined by g.l.c. and N.M.R. techniques at various temperatures.

Both Yamashita[34] and Enikolopyan[32,33] (1,3-dioxolan) polymerised the monomers with boron trifluoride etherate which is inefficient, so that they were obliged to use high temperatures and high monomer concentrations. At such high monomer concentrations the use of unit concentration instead of unit activity for the monomer may lead to serious errors. In fact, experiments have shown that the ceiling temperature is higher for higher monomer concentrations. Therefore it is not surprising that their values differ from those of Plesch and Westermann[1,2] who determined ΔH_{ss} and ΔS_{ss} by reaction calorimetry in vacuo, with monomer concentrations of about 1M or less.

More recently, Clegg and Melia reported values for the thermodynamic parameters of poly-1,3-dioxolan[35] and poly-1,3-dioxepan[36] and these agree well with those of Plesch and Westermann[1,2].

Enikolopyan[38] selected the reaction between dimethyl formal and 1,3-dioxolan catalysed by stannic chloride in carbon tetrachloride solution as a model system for determining the equilibrium monomer concentration for the polymerisation - depolymerisation equilibrium of 1,3-dioxolan.

If M represents the dimethyl formal molecule and D the 1,3-dioxolan molecule then

$$MD^+ + D \xrightleftharpoons{K_1} MDD^+$$

$$MDD^+ + D \rightleftharpoons MDDD^+$$

simulate the polymerisation - depolymerisation equilibrium. Since transfer to dimethyl formal occurs in this system

$$MDD^+ + M \rightleftharpoons MDD + M^+$$

they claim that the reaction allows the determination of K_1 within a wide range of concentrations and that it can also be employed in cases (e.g. heterogeneous systems) where this value cannot be determined by the classical approach.

By this method Enikolopyan obtained values for the floor concentration and the enthalpy of the polymerisation of 1,3-dioxolan which agreed with those of Plesch and Westermann[1].

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CHAPTER 2

Experimental

Part I - Materials

2.1. Solvents

2.1.1. Methylene dichloride. This solvent (I.C.I. Ltd.) was purified as described by Weissberger[1]. The final water washings had to be done carefully otherwise an impure product was obtained. The methylene dichloride was washed until the washings were neutral and by this time the organic phase had become crystal clear. It was then dried over freshly ground calcium chloride and finally distilled through a 160 cm column filled with nickel-gauze rings at a reflux ratio of 15:1. Head and tail fractions, each consisting of about 20% of the total volume, were rejected and the boiling point of the middle fraction was found not to vary by more that 0.1°, b.p. 39.0/745 torr (Literature[1] 40.1/760 torr). The fractionation was monitored by g.l.c. and the only impurity detectable in the middle fraction was chloroform (about 1:20,000 vol/vol).

The middle fraction was collected in dark bottles, mixed with fresh phosphorus pentoxide, decanted onto a further portion of phosphorus pentoxide, and finally the suspension was poured into a reservoir, attached to the vacuum line. The reservoir was then closed with a mercury seal and the solvent degassed and refluxed for several days.

Gandini[2] showed that the vacuum distilled methylene dichloride was free from acid, within the limits of detection (about 10^{-6}M).

Methylene dichloride stored in this way was used for the majority of experiments; however for the polymerisations with triethyloxonium tetrafluoroborate the solvent was dried over calcium hydride.

The dosing under vacuum of methylene dichloride has been described by Gandini[2] and by Longworth[25].

2.1.2. Hexane. The B.D.H. "Special for spectroscopy" product was distilled and stored over phosphorus pentoxide in a reservoir attached to the vacuum line.

For general laboratory procedures C_6 petroleum ether was distilled before use.

2.1.3. Diethyl ether. The B.D.H. product was purified according to the method of Vogel[3]. It was then fractionally distilled off sodium, discarding 10% head and tail fractions, b.p. 34°/750 torr (Lit.[1] 34.5°/760 torr). The ether was stored over lithium aluminium hydride under its own vapour pressure in a vessel attached to the vacuum line via a metal BiPl valve[7].

Phials containing very small quantities of diethyl ether were prepared by the vapour pressure technique described by Biddulph[4].

2.1.4. Carbon tetrachloride. This solvent (B.D.H. Ltd.) was distilled before use.

2.1.5. Maleic anhydride. (B.D.H. Ltd.) was recrystallised three times from chloroform and dried on the vacuum line, m.p. 54-55° (Lit.[5] 54°).

2.2. Monomers

2.2.1. 1,3-dioxolan. This monomer (Koch-Light Ltd.) was purified by refluxing over sodium hydroxide until no more sodium hydroxide was used up. It was then fractionally distilled, further refluxed for 24 hours over sodium metal, and finally fractionally distilled off sodium metal through a 3 ft. column at a reflux ratio of 5:1. A product having b.p. 75.1°/742 torr (Lit.[6] b.p. 75.0°/760 torr) was collected.

The monomer was then poured into a reservoir containing lithium aluminium hydride, which was attached to the vacuum line. With the 1,3-dioxolan frozen the vessel was degassed and the entry tube was sealed off. The monomer was completely degassed by repeated freeze-thawing. The monomer was isolated from the dosing line by a metal BiPl valve[7] and the dosing procedure has been described in more detail by Westermann[8].

Although 1,3-dioxolan is reported[9] to be stable to lithium aluminium hydride, the reservoir always needed degassing before each distillation, because there was a slight evolution of gas. However, the results obtained at the beginning and end of a particular batch were always in excellent agreement.

It is possible that the last quantity of water only reacts slowly with lithium aluminium hydride because gas chromatography has shown that our best 1,3-dioxolan still contained less than 5 p.p.m. (about 2 x 10^{-4}M)[10] of water but the sample under test was prepared on the vacuum line and then exposed to the atmosphere for sampling so that some water may have been introduced by this process. Regular degassing was also required for the other compounds stored over lithium aluminium hydride, namely diethyl ether, 1,3-dioxan and 1,3-dioxepan and with the last degassing was still required even after three years storage.

With methylene dichloride, which is considered to be more easily dried[10] than the cyclic ethers, the gassing phenomenon was also observed[11].

I have also observed that degassing takes longer when the volume in the reservoir is low, therefore I consider that the formation of the gas may be caused by partial decomposition of lithium aluminium hydride.

2.2.2. <u>1,3-Dioxan</u>. This monomer was prepared from 1,3-propanediol (B.D.H. Ltd.) and paraformaldehyde (B.D.H. Ltd.) by a procedure analogous[6,8] to that used for 1,3-dioxolan.

1 mole of 1,3-propanediol, 1.1 mole of paraformaldehyde and 5% of orthophosphoric acid were reacted in a flask fitted with a 60 cm fractionation column and condenser. A mixture of water and 1,3-dioxan distilled over with a boiling range of 88-104°. The aqueous and non-aqueous layers were separated by salting out with calcium chloride. The non-aqueous product was refluxed over sodium hydroxide until no more sodium hydroxide reacted with any acidic or hydroxyl containing impurities. The product was fractionated and then refluxed over sodium metal for 24 hours before the final fractionation. The fraction boiling at 106°/749 torr (Lit.[12] 105°/755 torr) was collected.

This monomer was stored over lithium aluminium hydride and dosed in the same way as 1,3-dioxolan.

2.2.3. <u>1,3-Dioxepan</u>. The preparation of this monomer was analogous to that of 1,3-dioxan, except that the glycol was 1,4-butanediol. The product was purified and dosed as described[8,13]. This batch

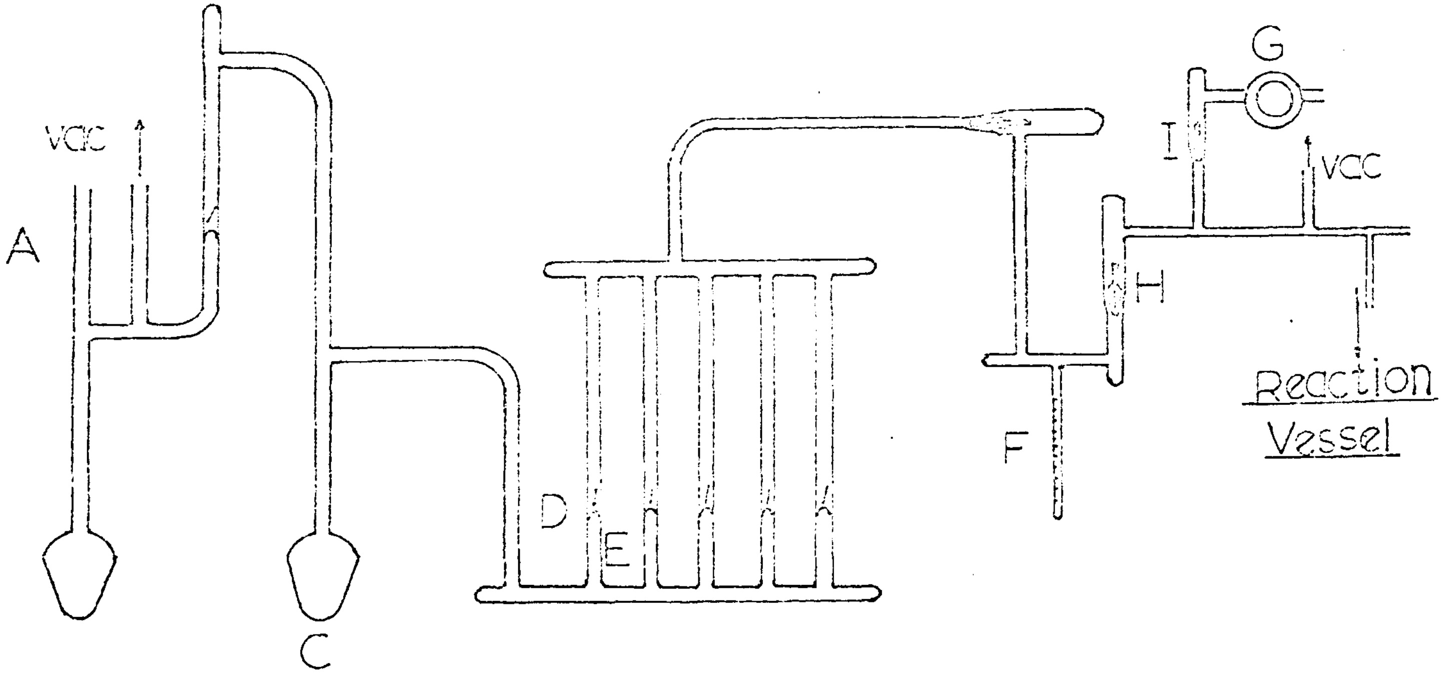


Fig. 2.1.

The Dosing Line for BF_3Et_2O

of monomer contained a small quantity of tetrahydrofuran (1:50,000 vol/vol) as shown by g.l.c. analysis.

2.2.4. 1,3-Dioxocan. This monomer is described in Section 3.4 of this thesis.

2.2.5. 1,3-Dioxonan. This is described in Section 3.5 of this thesis.

2.2.6. 1,4-Dioxan. This monomer (B.D.H. Ltd.) was purified by refluxing it over sodium for 2 days. It was refluxed over, and distilled off, lithium aluminium hydride immediately before use, b.p. 100.2°/744 torr (Lit.[1] 101.3°/760 torr).

2.2.7. Tetrahydropyran. This monomer (B.D.H. Ltd.) was purified by refluxing it over sodium for 2 days. Finally it was refluxed over, and distilled off, lithium aluminium hydride before use, b.p. 87°/749 torr (Lit.[5] 88°/760 torr).

2.2.8. Oxepan. See Section 4.3.1 of this thesis.

2.3. Catalysts.

2.3.1. Boron trifluoride etherate. This compound (B.D.H. Ltd.) was fractionally distilled in a nitrogen atmosphere. The fraction boiling at 124°/742 torr was collected. This was then redistilled under reduced pressure (54°/20 torr) with a nitrogen bleed (Lit.[14] 125.7°/760 torr).

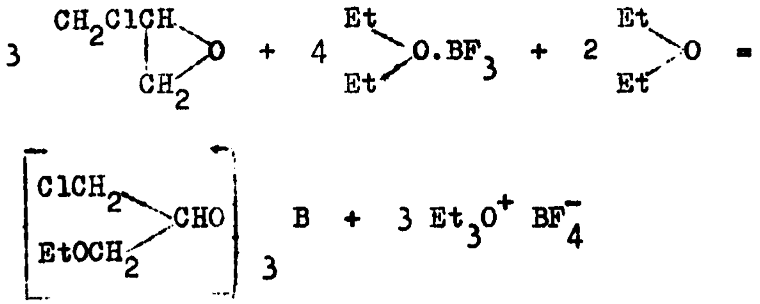
It was quickly transferred to a vessel attached to the vacuum line. The boron trifluoride etherate was frozen, degassed and the vessel sealed at A (Fig.2.1.). The compound was then distilled into flask C, leaving a generous tail fraction.

The boron trifluoride etherate reacted with the metal BiPl[7] valve, so that a series of breakseals had to be used for dosing

(Fig. 2.1.). Therefore, each time a sample was required, a break-seal (e.g. D) was broken and the boron trifluoride etherate distilled to the reaction vessel via the burette F, and then the reservoir was closed by sealing off at E. It was necessary to isolate the boron trifluoride etherate from the metal valve, G, by the dry valves H and I.

This method of dosing is rather tedious because the boron trifluoride etherate distils slowly and condenses at various points in the vacuum line. If the procedure allows, it is more convenient to dose the boron trifluoride etherate into phials which can be fused to the line nearer to the reservoir.

2.3.2. Triethyloxonium tetrafluoroborate ($Et_3O^+BF_4^-$). This was prepared on the vacuum line in the apparatus shown in Fig. 2.2. The method was based on that of Meerwein[15] in which boron trifluoride etherate, epichlorohydrin, and diethyl ether react together according to the equation.



The preparation assembly I was fused to the vacuum and reagent-supply line and pumped out for about 3 hours. The three reactants were then distilled into flask D (3 moles epichlorohydrin, 4 moles BF_3Et_2O and 16 moles Et_2O). With the contents of D frozen, the apparatus was sealed off from the line at B. The reactants were

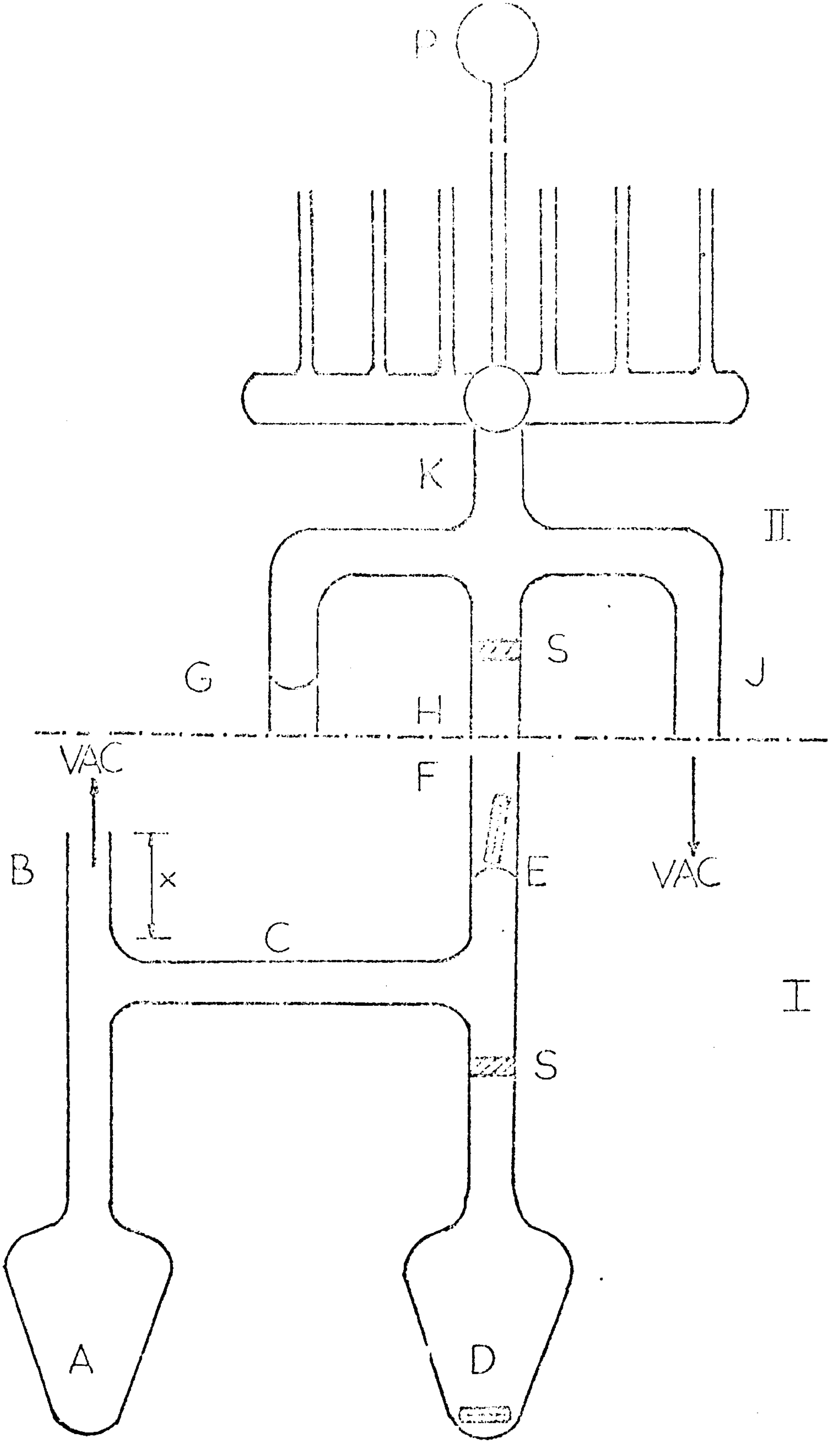


Fig. 2.2.

The Apparatus for the Preparation of $Et_3O^+BF_4^-$

then thawed and mixed by stirring them magnetically. A precipitate was formed which was a viscous oil at room temperature. Attempts to crystallise this oil were made by warming, cooling, and shaking but these failed. Stirring is very difficult because of the viscosity of the oily phase. However, the oil crystallises after standing at 0° for about 12 hours. This time could be shortened slightly by washing the oil. Washing was carried out by filtering the solution into flask A through the sintered filter S and redistilling the excess diethyl ether back into flask D by cooling it. Whereas the boric acid ester is soluble in diethyl ether, $Et_3O^+BF_4^-$ is insoluble.

After crystallisation the $Et_3O^+BF_4^-$ was washed about ten times in the manner described above. For this process it is important that X is long enough to hold all the filtrate. Filtration can be accomplished easily by slightly warming or cooling the appropiate flask. When washing was complete, the glass above S was washed by refluxing the ether in this part of the apparatus. This was best accomplished by stroking the glass with cotton wool soaked in liquid nitrogen. The contents of A were frozen to distil the remaining ether into it and then A was sealed off at C.

The tipping device II was sealed to the vacuum line at J and flask D containing $Et_3O^+BF_4^-$ (I) was sealed to II at H-F. The whole assembly down to the breakseal E was pumped out for about 3 hours and then E was broken. The pumping was continued for a further 2 hours. Then 10 ml of methylene dichloride were distilled into D and the whole assembly was sealed off at J.

The solution of $Et_3O^+BF_4^-$ in methylene dichloride was then distributed into the phials P by turning the apparatus upside down.

The apparatus was, once again, attached to the vacuum line via the breakseal G, and pumped for a further 3 hours. During this stage the phials were cooled to 0°. A plug of methylene dichloride was frozen at K, the breakseal G was broken, and the methylene dichloride distilled out of the phials, leaving the solid $Et_3O^+BF_4^-$ behind.

This distillation is tedious and it is advisable to distil the solvent to a receiver, attached to the vacuum line, rather than to distil it directly to the trap. This method allows more control of the rate of distillation. When most of the solvent has distilled a concentrated solution of $Et_3O^+BF_4^-$ remains in the phials. The bulk of the methylene dichloride was now distilled to the trap (or another flask isolated by a tap) so that the methylene dichloride remaining in the phials could be distilled out. In the latter process some solid remains on the necks of the phials and this was washed back into the phials with small quantities of solvent which were condensed in the necks of the phials by stroking them with cotton wool soaked in liquid nitrogen. The process was repeated until all the solid remained in the bulb in a dry state. The solid $Et_3O^+BF_4^-$ was then thoroughly evacuated by pumping for about one or two hours before the phials were sealed off.

The solid can be distributed into phials by this method, provided that there is no more than 0.1g to 0.2g in each phial. With larger quantities the distillation of solvent from the phials becomes too time-consuming and difficult. The quantity in each phial was determined by the mid-point method[16] (error involved ± 5mg). The yield was almost 90%. This salt is hygroscopic so that the melting point was determined by strapping a phial to a thermometer and warming them slowly in an oil bath, m.p. 91-92° (Lit.[15] m.p. 91°).

Phials containing smaller quantities of $Et_3O^+BF_4^-$ were prepared by diluting a phial in the tipping device which has already been described[17]. The solid salt was then obtained by a process similar to that described above.

The use of specific conductance as a calibration method for solutions of $Et_3O^+BF_4^-$ in methylene dichloride will be discussed in Chapter 5.

$Et_3O^+BF_4^-$ prepared in this way is stable for several months at 0°. After about 3-4 months a small quantity of oil can be noticed in the phials. However, oil formation only occurred in the phials containing a "large" amount of the salt. A possible explanation is the occlusion of some solvent which encourages decomposition.

2.3.3. Triethyloxonium hexafluoroantimonate. This catalyst was supplied by Dr. M.P. Dreyfuss. It was reprecipitated three times from methylene dichloride with carbontetrachloride immediately before use. m.p. 121-2°.

Initially, this compound had been prepared by me by the silver salt method of Meerwein[18], but it was impure, even when the preparation was done on the vacuum line. m.p. about 102° (Lit.[19] 111°).

2.3.4. Triethyloxonium hexafluorophosphate. This was supplied by Dr. M.P. Dreyfuss and purified by three precipitations from methylene dichloride solution with carbontetrachloride immediately before use.

The salt was filtered through a sintered glass filter and then dried in vacuo (20°/12 torr), before being introduced into the conductivity cell where it was thoroughly evacuated. m.p. 141-142°.

2.3.5. Triethyloxonium tetrachloroborate. An attempt was made to prepare this under vacuum by Meerwein's[15] method using borontrichloride. Unfortunately, this method was unsuccessful.

2.3.6. Anhydrous perchloric acid. This acid was prepared by dehydration of 72% perchloric acid (Hopkin and Williams) with 20% oleum. The method was derived from Eastham and Tauber's[20]; a full description is given by Gandini and Plesch[17]. The serious explosion hazard of this process has been eliminated by a new method developed in this laboratory by Mathias[11]; this involves a counter-current extraction of perchloric acid from a mixture of oleum and 72% aqueous perchloric acid with methylene dichloride. Some of the experiments described in Section C were done with perchloric acid prepared in this way. There was no apparent difference between the acid samples prepared by either method.

2.3.7. Phosphorus pentafluoride. This catalyst was prepared by thermal decomposition of benzene diazonium hexafluorophosphate (Ozark-Mahoning Co.) at 160°. The nitrogen and phosphorus pentafluoride generated were bubbled through the required monomer or monomer solution. The dosing was carried out in glass apparatus which was immediately immersed in 3N sodium hydroxide after use, to hydrolyse any remaining phosphorus pentafluoride.

2.3.8. Triphenylmethyl tetrafluoroborate. A phial containing a solution of this compound in methylene dichloride was available from

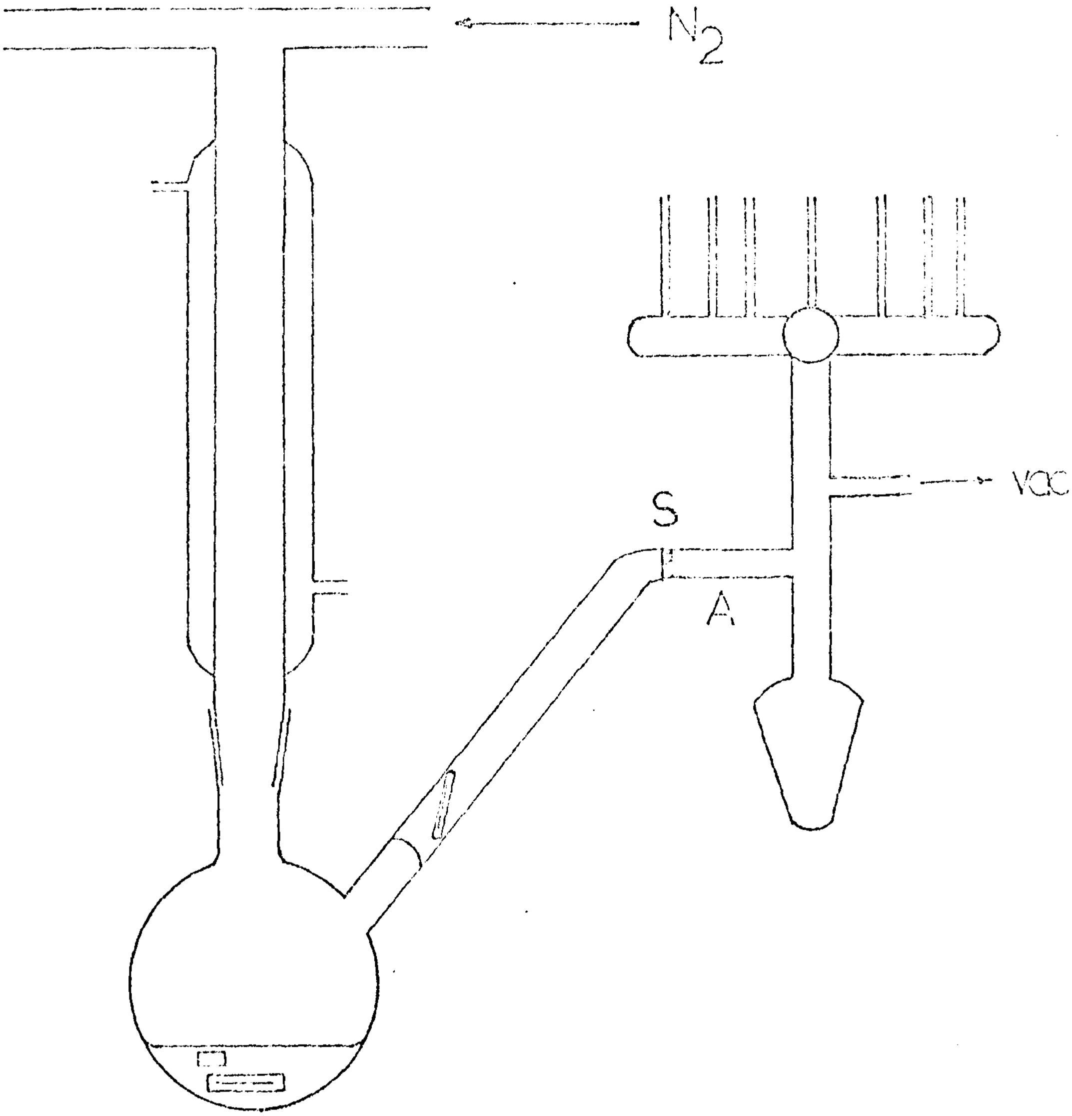


Fig. 2.3.

The Apparatus for the Preparation of NaOPh

Dr. P.H. Westermann. The method of preparation has been described[13].

2.4. Water Phials. A micro- syringe of 10 μl capacity, graduated in 0.2 μl, was used to fill small glass phials with the required quantity of distilled water. The quantities of water were quite large so that a vacuum filling device was not required. The phials were carefully dried, filled with the correct amount of water and then sealed off with a small flame so that the contents did not become warm. The additions were at 25° in the presence of large quantities of 1,3-dioxolan in which water is soluble.

2.5. Triethylamine. Phials of this compound were available from Dr. Beard. The preparation and purification of triethylamine have been described[21].

2.6. Sodium Phenoxide (NaOPh). 3 mmole of phenol dissolved in 12 ml of tetrahydrofuran (freshly distilled off potassium) was treated with an excess of clean sodium. The solution was stirred magnetically in a nitrogen atmosphere until no more hydrogen bubbles were produced. This usually took about 12 hours. The vessel was then closed with a carefully greased stopper, and connected to a vacuum tipping device[17] via a breakseal (Fig. 2.3.). After the tipping device had been pumped out for about 2 hours the solution was frozen, the breakseal broken and the solution degassed by freeze-thawing. The stirring was continued and the completion of the reaction was determined by testing the vacuum with a Tesla coil periodically, with the solution frozen. When no more hydrogen was produced, the apparatus was sealed off the line and the solution filtered through the sintered disc S into the tipping device. The reaction vessel was now sealed off at A and the solution distributed into the phials. The amount in the phials was determined by the mid-point method[16], and the concentration of the solution was determined by u.v. spectroscopy of the contents of a phial dissolved in N sodium hydroxide solution. The concentration estimated in this way agreed with the initial concentration of phenol.

Phials containing solid sodium phenoxide were prepared in a way analogous to that described in Section 2.3.2.

2.7. Epichlorohydrin. This compound (B.D.H. Ltd.) was fractionally distilled, discarding generous head and tail fractions. Any water present distil~~l~~s as an azeotrope and was thus readily removed. b.p. 115°/744 torr (Lit.[1] 116°/760 torr).

The pure epichlorohydrin was poured into a flask on the vacuum line. The flask was sealed and the compound degassed. It was distilled from bulb to bulb on the vacuum line. The middle fraction (about 60%) was stored behind a metal BiPl valve[7].

Part II - Apparatus and Procedures

2.8. Ultraviolet and Visible Spectroscopy. The spectra reported in this work were taken on a Beckmann DB recording spectrometer. A special light-tight lid allowing a large amount of free space above the cell holder replaced the conventional lid when a spectroscopic device[22] was used. In the "open" experiments 2mm and 1cm silica cells were used.

2.9. Infrared Spectroscopy. All infrared spectra were run on a Perkin-Elmer 257 Grating Infrared Spectrometer. The instrument was calibrated by means of a polystyrene film.

With high molecular weight polymers, transparent films were prepared directly on the rock salt plates by evaporating to dryness a concentrated solution in methylene dichloride. Low molecular weight polymers were scanned on sodium chloride plates or, as 1% solutions in carbontetrachloride. The crystalline dimers and trimers were scanned in carbon tetrachloride or carbon disulphide in order to cover the whole of the spectrum. 0.1 and 1mm cells were used.

2.10. *Nuclear Magnetic Resonance Spectroscopy (N.M.R.).* A Perkin-Elmer M-R10 N.M.R. Spectrometer, provided with an integrating circuit and a computer of average transients, was used throughout this work. This instrument has ^{1}H resonance at 60 Mcsec.$^{-1}$ and is thermostatted at 35°. The position of the N.M.R. bonds in carbon tetrachloride, and methylene dichloride solution were determined by reference to T.M.S. at 10τ as an internal standard. In a few experiments made under high vacuum, the soda glass tube was sealed onto the vacuum line by means of a soda glass-to-pyrex seal. The tube was filled, frozen down and sealed off; it was then thawed and warmed to 35° so that the spectrum could be scanned.

2.11. *Gas liquid Chromotography (g.l.c.).* All the analyses were run on a Perkin-Elmer F-11, fitted with dual column analyser, a flame ionisation detector, and two 3m. silicone oil SE-30/Chromosorb P 100-120 mesh columns. Occas~~s~~ionally a Poropak Q packing was used. The machine was adjusted so that at an attenuation of 1 the base line was straight.

For the experiments in which ethyl fluoride and ethane were detected, attempts were not made to separate these further because it usually took some time for the base line to become steady again and this governed the time between successive chromatograms.

2.12. Thermostats.

A temperature of -35° was obtained with a mush of ethylene dichloride, -80° from Drikold/Methylated spirits and the other temperatures below zero were obtained by use of a "Minus Seventy Thermostat Bath" (Townson and Mercer Ltd.).

A well stirred ice-in-distilled water bath in which the temperature was kept constant to $\pm 0.05^\circ$ was used for the 0° thermostat. $25^\circ \pm 0.02^\circ$ was obtained by a well stirred water bath regulated with a contact thermometer. For temperatures higher than this an "Ultra Thermostat" (Shandon Ltd.) was used.

2.13. Conductivity Bridges. For the measurement of association constants the Wayne-Kerr B221 Universal Bridge was used. This instrument which works on the transformer ratio-arm principle has a built-in source (1,592 cycles $sec.^{-1}$) and a magic-eye detector. The conductivity range is 10^{-1} to $10^{-10}\,\Omega^{-1}$ with an accuracy of $\pm 0.1\%$ down to 10^{-7}. The capacities and conductivities are both balanced at the null point.

Conductivity measurements during the polymerisation and decomposition runs were made with a Chandos Linear Conductivity Meter (range 10^{-2} to $10^{-7}\Omega^{-1} \pm 1\%$).

2.14. Cell constants. The cell constants of conductivity cells were determined by the method of Lind, Zwolenik and Fuoss[23]. Since

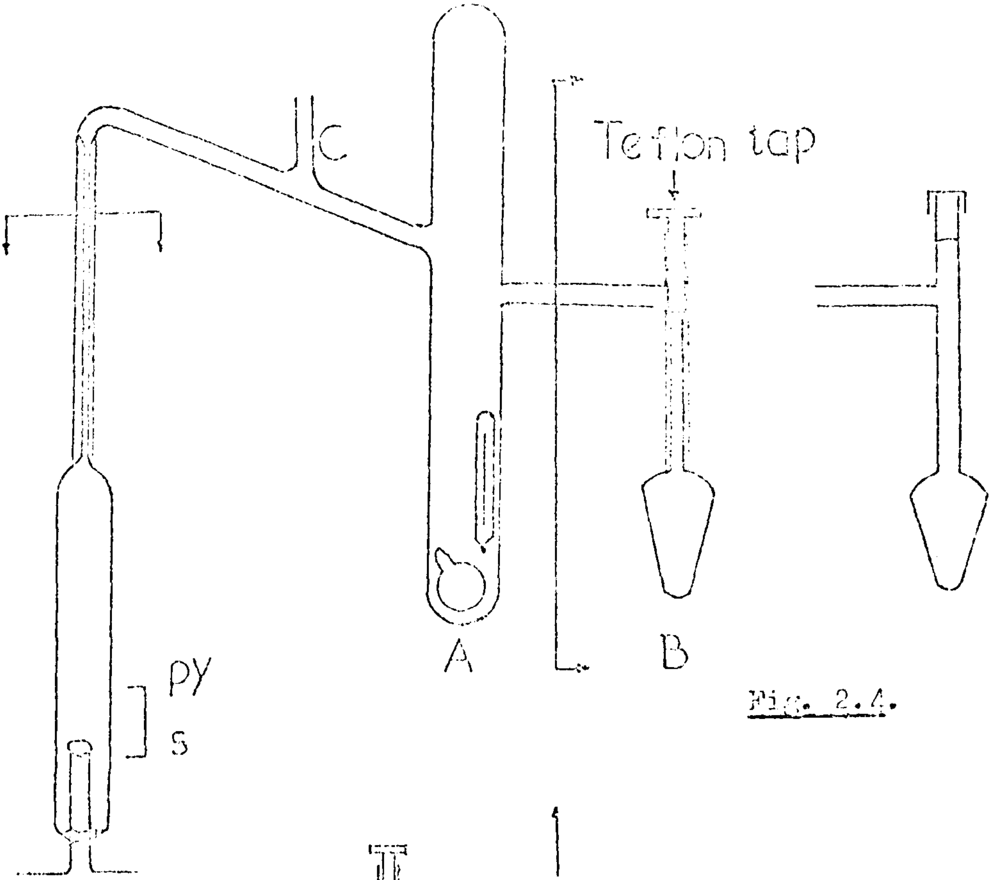


Fig. 2.4.

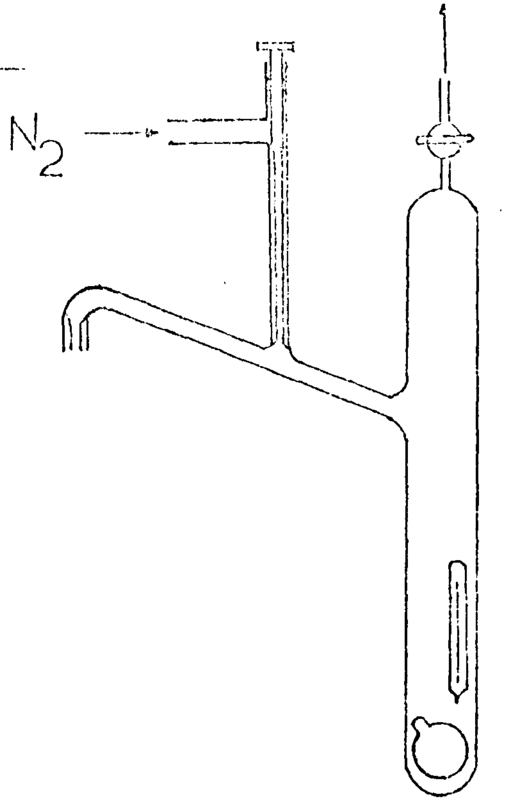


Fig. 2.5.

The Dilatometers

the range of temperature was small, the cell constant determined at 25° was applied to all measurements.

2.15. The polymerisations. The rate of polymerisation was measured in the dilatometer, fitted with electrodes for conductance measurements[25], shown in Fig. 2.4. Cell constant = 0.246cm^{-1}.

The vessel was attached to the vacuum line and pumped for about 3 hours. The monomer was distilled into B, the Teflon tap closed and the solvent was distilled into A. With the solvent frozen, the dilatometer was sealed off at C. The phial of catalyst was then broken into the methylene dichloride. After thermostatting, the solution was tipped into the bulb of the dilatometer to measure the conductivity of the solution. This was used to calibrate the catalyst concentration. The solution was returned to A and the monomer mixed with it by opening the Teflon tap. The solution was mixed and then tipped back into the dilatometer so that the reaction and conductivity changes could be followed. In some experiments the tap was replaced by a breakseal but this change had no effect on the reactions .

Depolymerisation was accomplished by warming the polymer solution to a temperature above the ceiling temperature, T_c. The solution was quickly mixed and tipped back into the dilatometer which was rethermostatted.

After polymerisation, the reaction mixture was returned to A for killing. Since high monomer concentrations were required (up to 4M) in the kinetic runs, the solution was so viscous that it was necessary to depolymerise the solution partly in this process.

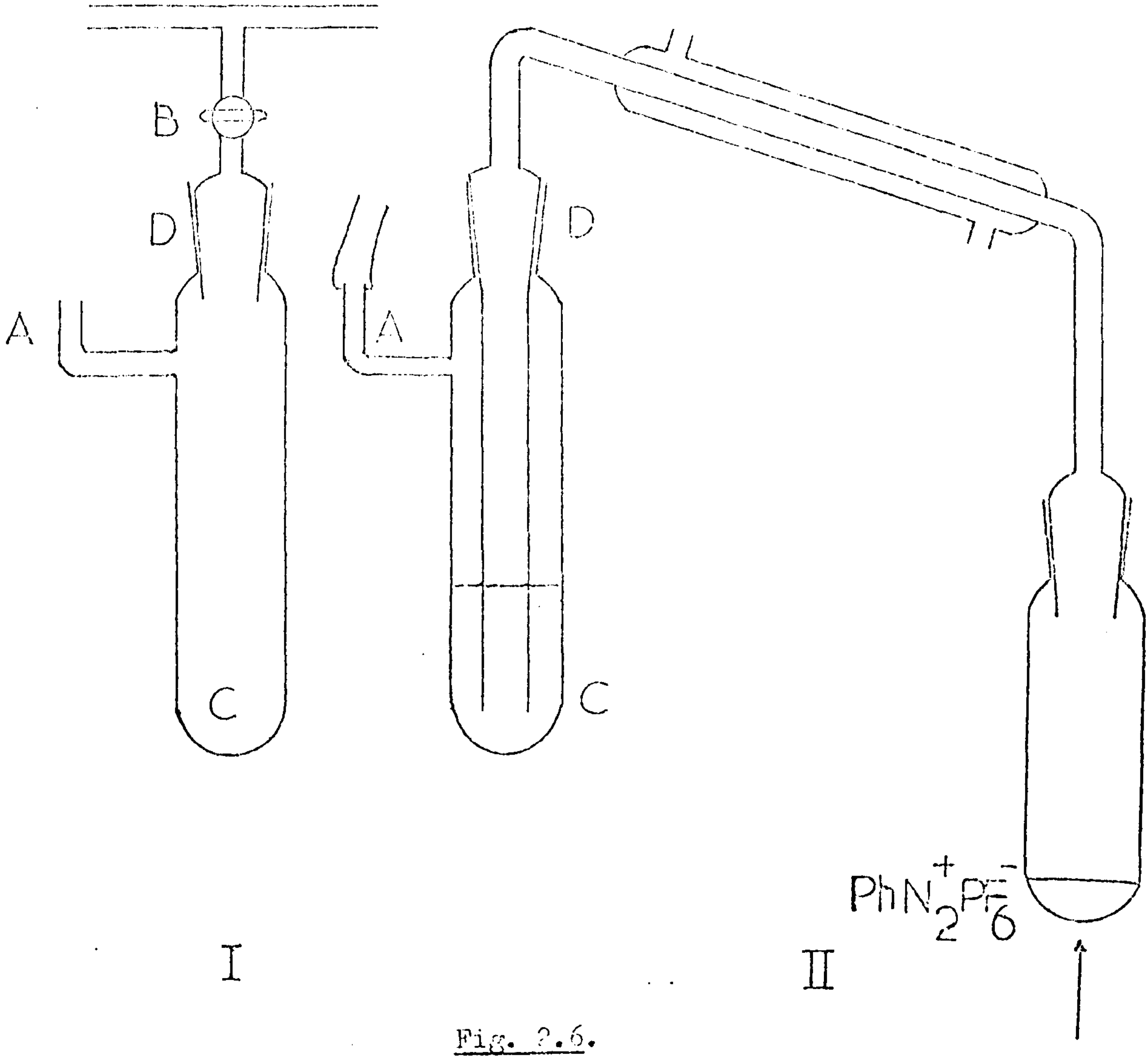


Fig. 2.6.

The Dosing of PF_5

The reaction mixture was rethermostatted for an hour before killing it.

For sampling experiments, two modifications of the dilatometer (Fig. 2.4.) were used. In the $Et_3O^+BF_4^-$ work B was replaced by a flask fitted with a rubber septum (and breakseal); a greased tap at C allowed reduction of the vacuum with nitrogen. With $HClO_4$, lower temperatures were necessary, therefore the dilatometer in Fig. 2.5. was used. The samples were taken with a syringe against a flow of dry nitrogen. The nitrogen was dried by cooling it with liquid nitrogen.

The other polymerisations were made in evacuated H-tubes (1 or 2 sealed together in series) which allowed the crushing of more than one phial of catalyst or killing agent and the division of the reaction solution into two.

For the reactions catalysed by phosphorus pentafluoride the following procedure was used. The reaction vessel I (Fig. 2.6.) was sealed to the vacuum line at A. After evacuating it for about 2 hours the monomer and/or solvent were distilled into C, the vessel was sealed off at A, and the vacuum let down with nitrogen by opening the greased tap B. The vessel was then opened at A and the open tube connected to a P.V.C. tube which vented the reaction vessel close to an extraction fan. The tap was removed from the vessel and the vessel was connected to the PF_5 dosing line (II). After bubbling the PF_5 through the solution, the generator was allowed to cool before the vessel was disconnected from the apparatus. A was closed with a rubber cap and D with a glass stopper and the vessel was thermostatted at the appropriate temperature. The reaction was killed with an ammonia/alcohol solution.

2.16. Polymer Isolation. All the kinetic runs were terminated by opening the dilatometer and quickly pouring in ethanol/ammonia. Other polymerisations were terminated with ammonia vapour (from 0.880 ammonium hydroxide) or by breaking phials of sodium phenoxide or triethylamine.

Low molecular weight polymers of cyclic formals are soluble[8] in many solvents, so that precipitation is an inefficient method of isolating the polymer. Therefore, the polymers were isolated by evaporation of the neutralised reaction mixture. The polymer was further dried by evacuating it (12 torr/35°) for a few hours. The polymer was then redissolved in methylene dichloride, carefully filtered, and isolated as before. During the distillation it was necessary to prevent depolymerisation and oxidation by keeping the solution alkaline with ammonium hydroxide. Finally, the polymer was pumped for 24 hours (12 torr/35°) to free it from remaining solvent, ammonia and water.

2.17. Molecular weight determination. Molecular weights were determined with a Mechrolab Vapour Pressure Osmometer Model 301A, with a non-aqueous probe at 37°. The solvent used for most measurements was 1,4-dioxan. Some molecular weights were determined in carbon tetra chloride solution, but the high molecular weight polymers were insoluble in this. The instrument was calibrated with triphenyl methane and triphenyl carbinol.

The number average molecular weight is determined by this

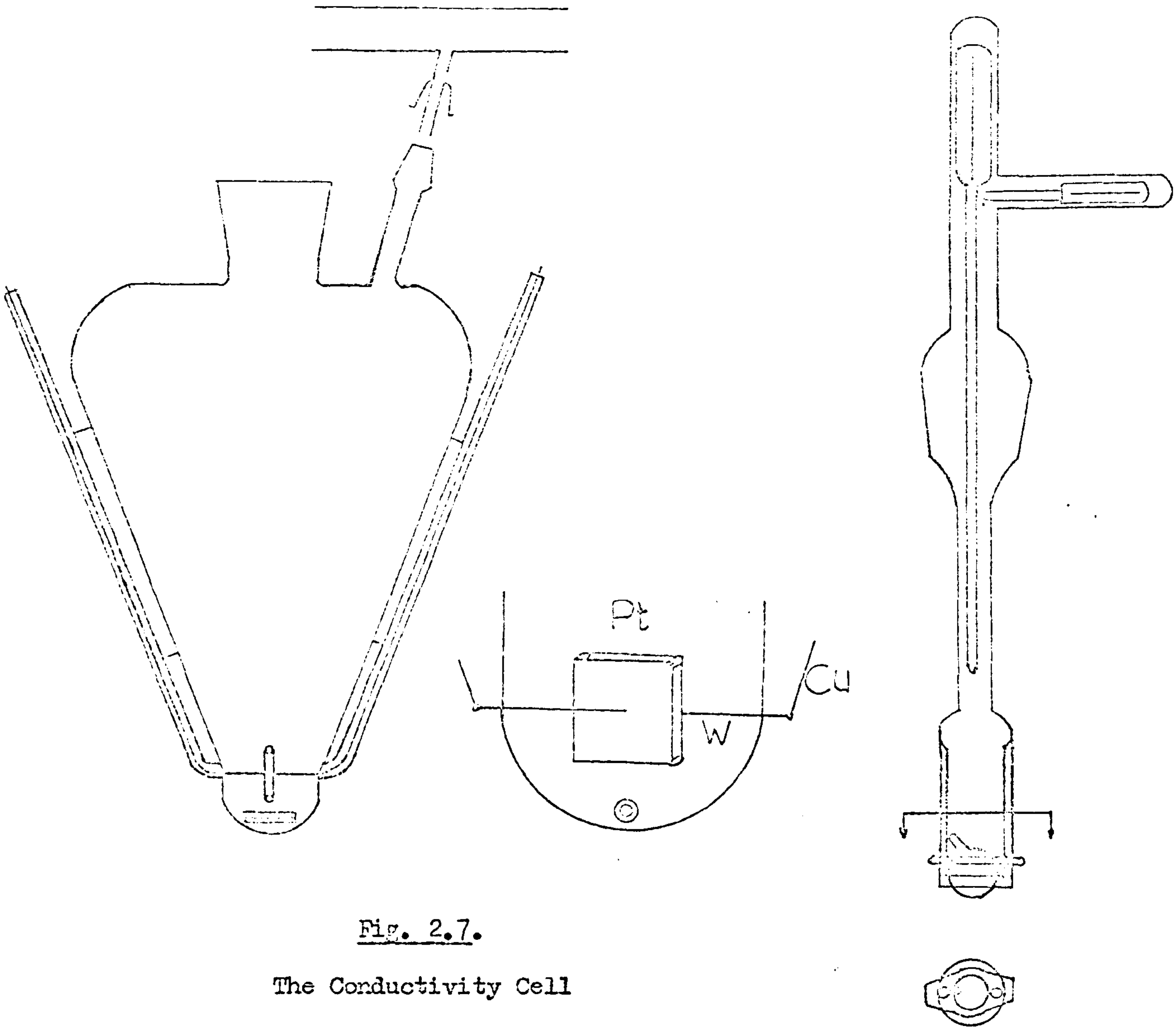


Fig. 2.7.

The Conductivity Cell

method, so that the degrees of polymerisation, D.P., quoted are also number average.

2.18. <u>The Decompositions</u>. In the experiments on the decomposition of triethyloxonium salts where the rate of evolution of ethyl fluoride was measured concurrently with the rate of loss of conductivity, the reaction vessel used was similar to that shown in Fig. 2.4. except that the flask B was replaced by a tipping device. The method and apparatus are described in Chapter 5 (see Fig. 5.16.).

The decomposition reactions involving only conductance measurements were undertaken in a simple dilatometer fitted with electrodes which has been described[24]. The procedure is described in Chapter 6. Cell constant = $0.305 cm^{-1}$.

In experiments in which the u.v. spectra were taken before and after decomposition a vacuum spectroscopic device, fitted with electrodes[22], was used. Cell constant = $0.195 cm^{-1}$.

2.19. <u>Conductance Measurements</u>. These were carried out in the cell shown in Fig. 2.7. It consisted of an inverted conical flask of 500 ml capacity with the electrodes fixed near the bottom. The two platinum electrodes (1cm x 1cm) were held about 2 mm apart with four soda glass beads. The platinum leads attached to the electrodes were spot-welded onto 1 mm diameter tungsten rods which were fused through the walls of the flask and were externally connected to two copper leads. The external wiring was enclosed in glass. The cell constant = $0.09656 cm^{-1}$.

The minimum volume of the cell was 25 ml and a Teflon coated magnetic stirrer was used.

For $Et_3O^+BF_4^-$, a phial of it was supported in a phial-crushing device fitted to the cell through a B29 joint. After pumping, the phial was broken into a small quantity of solvent. Diethyl ether was added in a similar way, except that the phial was always below the surface of the solution before crushing. $Et_3O^+PF_6^-$ and $Et_3O^+SbF_6^-$ were weighed on a Whites' Torsion balance, transferred directly into the conductivity cell and evacuated thoroughly.

Dilution was carried out by dosing the solvent into the cell, by the normal procedure[2,25]. Dilutions from 30 to 300 ml were possible.

The cell was thermostatted at 0° and the conductivity measured on the Wayne-Kerr B221 Bridge. The conductance reading was taken when the reading was steady and this was a good check on the temperature of the solution. About fifteen minutes were allowed for stabilisation between each addition of solvent and the complete experiment took about 2-4 hours.

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Introduction to Section A

In this part of the thesis the polymerisability of some cyclic oxygen compounds is discussed. In particular, 1,3-dioxan poses an interesting problem. The literature concerning the polymerisation of this cyclic formal was conflicting, so that it presented both a polymerisability problem and potentially a new monomer for generalising the ring-expansion mechanism[1].

Since 1,3-dioxan is a six membered ring with little strain, only sketchy attempts have been made to polymerise it.

The earliest report concerning the polymerisation of 1,3-dioxan was from Vaala and Carlin[2]. The polymers produced were from 1,3-dioxan and substituted 1,3-dioxans (e.g. 4-methyl-1,3-dioxan) by refluxing them with boron trifluoride and acetyl chloride in acetic acid. The structure of the polymer was not examined and it seems likely that the polymer was not poly-1,3-dioxan.

Sulphur trioxide[3] has also been claimed to polymerise 1,3-dioxan and some substituted 1,3-dioxans and 1,3-dioxolans.

Takakura, Hayashi and Okamura[4] claimed that 1,3-dioxan and 1,3-dioxolan and 1,3-dioxepan will polymerise in the presence of maleic anhydride and benzoyl peroxide. Although they later published[5] details for the polymerisation of trioxan and 3,3-bis-chloromethyl oxetan, no further experimental results were presented for the cyclic formals named above. By analogy with the mechanism proposed for trioxan polymerisation under the same conditions the polymerisation of 1,3-dioxolan would have to be initiated by a dioxolonium* ion. As this conflicts with other published mechanisms for the

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* The correct name for this ion is 1,3-dioxolan-2-ylium.

polymerisation of 1,3-dioxolan it was necessary to attempt the polymerisation of 1,3-dioxan and 1,3-dioxolan under these conditions.

Mercuric halides[6,7] polymerise 1,3-dioxolan but only form complexes[7] with 1,3-dioxan and 1,4-dioxan and this is another indication of the non-polymerisability of these monomers.

The monomer reactivityratios (r) for the copolymerisation of 3,3-bis-chloromethyl oxetan with several non-homopolymerisable monomers have been determined by Yamashita[8]. Since k_{22} (the rate constant for the homopolymerisation of theco-monomer) is zero, they assume the ideal case where $r_1r_2 = 1$ and compare th values for $1/r_1$. They found a linear relation between basicity, as measured by Gordy's method[9], and $1/r_1$ for the following co-monomers. 2-methyltetrahydrofuran, tetrahydropyran, 1,4-dioxan and 4-methyl-1,3-dioxolan. However, the reactivity of 4-phenyl-1,3-dioxan was much lower and did not lie on the straight line.

Yamashita[10] in his review on the copolymerisation of cyclic oxygen compounds, reports that the r_2 for 1,3- and 1,4-dioxan, 4-methyl and 4-phenyl-1,3-dioxan are zero with respect to 3,3-bis-chloromethyloxetan.

Geller[11] has shown that 1,4-dioxan did not copolymerise with 3-methyl-3-chloromethyl oxetan, whereas a small number of tetrahydropyran units could be incorporated into the polymer.

The heat of polymerisation for 1,3-dioxan is quoted as 0.0 kcals/mole[12] and the calculated value for cyclohexane is -0.7 kcals/mole[13]. If the actual value were slightly negative or the entropy change sufficiently positive, then polymerisation of 1,3-dioxan would be possible. The change of entropy (ΔS) for the hypothetical polymerisation of cyclohexane is -2.5 cals/deg./mole[13,14]; therefore, if ΔS is the same for the polymerisation of 1,3-dioxan, polymerisation would only be possible if the enthalpy were sufficiently negative.

From this brief review it is apparent that a systematic investigation of the polymerisability of 1,3-dioxan was necessary; therefore, Chapter 3 deals with such a study.

The reviews available on the thermodynamics of polymerisation[13,15] are lacking in thermodynamic data for the equilibrium polymerisation of cyclic ethers and cyclic formals, with more than 7 atoms.

We intended, at first, to extend the range of values available so that they could be compared with the calculated thermodynamic data available for cycloalkanes[12] and cyclic oxygen compounds. Unfortunately, for various reasons this was not possible. However, the results obtained are included in Chapters 3 and 4 so that the general problems which can arise with these monomers should be on record.

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SECTION A - CHAPTER 3

The Polymerisability of 1,3-Dioxan and a Note about the Preparation of 1,3-Dioxocan and 1,3-Dioxonan

This Chapter outlines the various attempts to polymerise 1,3-dioxan.

Polymer was not formed from 1,3-dioxan in open experiments in which the monomer was distilled off lithium aluminium hydride; boron trifluoride etherate and anhydrous perchloric acid were the catalysts. Therefore, the experiments described here were carried out in vacuo whereever possible. In experiments where it was not practical to dose the catalyst under vacuum (e.g. phosphorus pentafluoride) the monomer was distilled, under vacuum, into an evacuated vessel which was sealed off and opened so that dry nitrogen entered the vessel (see Fig. 2.6.).

3.1. Protonation of 1,3-Dioxan

These experiments were carried out, under vacuum, in the adiabatic calorimeter, which has been fully described by Panton[1]. The vessel was fitted with electrodes[2] for conductance measurements.

The results of these experiments are given in Table 3.1. When the acid phial was broken the conductivity immediately increased to a constant value but the temperature remained constant. The value of $\kappa_f / [HClO_4]$ of about $9 \mu\Omega^{-1}$ cm^{-1} $l.mole^{-1}$ can be compared with that obtained under similar conditions for 1,3-dioxepan[3] (about $7 \mu\Omega^{-1}$ cm^{-1} $l.mole^{-1}$). Since we know that 1,3-dioxepan is completely protonated, it follows that 1,3-dioxan is, also, completely protonated by perchloric acid. No polymer was produced and

Table 3.1.

The Protonation of 1,3-Dioxan in Methylene Dichloride, at -50°

Run No.	1	2
$[\text{1,3-dioxan}]$/M.	1.8	1.0
$[HClO_4]/10^3$M.	1.85	11.0
$\kappa_f/\mu\Omega^{-1}$ cm^{-1}.	17.3	91
$\kappa_o/\mu\Omega^{-1}$ cm^{-1}.	0.28	0.21

κ_f is the final specific conductivity

κ_o is the initial specific conductivity

Table 3.2.

The Attempted Polymerisation of Cyclic Formals in Maleic Anhydride Solution with Benzoyl Peroxide, Under Vacuum, at 50°

Run No.	4	5b	6b	26	5a	6a
$[\text{1,3-dioxan}]$ /M.	8.0	8.0	8.0	5.2	-	-
$[\text{1,3-dioxolan}]$ /M.	-	-	-	-	8.3	8.6
$[Bz_2O_2]$ /10^{2}M.	3.0	2.7	2.8	2.6	2.7	2.7
Reaction time / h.	4.5	5	24	52	5	24

g.l.c. showed that protonated 1,3-dioxan was not converted into other chemical species.

3.2. The Attempted Polymerisation of 1,3-Dioxan

3.2.1. Sulphuric Acid

0.2M sulphuric acid did not polymerise bulk 1,3-dioxan, under vacuum, after 20 hours at -35°. A small amount of insoluble grease was produced but there was insufficient for infrared spectroscopy.

3.2.2. Maleic Anhydride / Benzoyl Peroxide

Takakura, Hayashi and Okamura[4] have reported that 1,3-dioxan is polymerised by benzoyl peroxide in the presence of maleic anhydride. Therefore, this method was used in attempts to polymerise both 1,3-dioxan and 1,3-dioxolan.

In these experiments (Table 3.2.), large phials containing maleic anhydride and benzoyl peroxide, were sealed to the vacuum line and evacuated for several hours. The monomer was distilled into the phial which was then sealed off. The reaction vessel was then stored in a thermostatted bath at 50°. In all experiments a pink colour was formed which eventually turned purple after 30 mins. and this colour remained throughout the period of observation. After the desired time the phial was quickly opened and the contents poured into methanol. The colour could be discharged by adding a little ammonium hydroxide. No precipitate was formed at this stage; however, occasionally slight precipitation occurred overnight. The infrared spectra of these precipitates showed that they were not polymers of cyclic formals. The increased reaction time of 52 hours (Run 26) had little effect on the products.

Table 3.3.

The Oligomerisation of 1,3-Dioxan by Anhydrous Perchloric Acid in Methylene Dichloride Solution

Run No.	15	48A	44	40	43	39	38
[1,3-dioxan]/M.	11.7	11.0	10.6	10.5	10.6	10.3	10.5
$[HClO_4]$ /10^2M.	-	0.7	1.2	0.98	1.25	1.2	1.07
T_f / °C.	-37	-39	-39	-39	-39	-39	-39
Time/h.	48	20	0.4	0.55	1.25	1.0	2
Yield %	0	98	0.5	6.4	12.0	9.8	56

Run No.	30	14	17	18	20	31*	45
[1,3-dioxan]/M.	10.0	9.86	9.4	4.7	4.7	3.7	10.4
$[HClO_4]$ /10^2M.	1.45	16.7	22.0	7.8	7.8	1.6	1.45
T_f / °C.	-35	-37	-40	-40	-78	-35	+49
Time/h.	20	18	48	48	19	21	48
Yield %	37	30	32.5	0	0	1	0

T_f = Final temperature

Bulk 1,3-dioxan = 11.7M.

* This experiment was carried out with 1.65 base-M of dimer/trimer mixture (DP = 2.27)

Since poly-1,3-dioxolan is soluble in methanol I had to presume that poly-1,3-dioxan would behave similarly and therefore I looked for soluble oligomers in all the solutions. Thus, the alkaline methanol solutions were freed of methanol and free monomer by distillation on a water bath. The residue was further dried at 40° in a vacuum oven at 12 torr. Each sample was reduced to a yellow oil which had an odour similar to maleic anhydride. Hexane did not extract anything from the oil. These oils eventually went cloudy.

The infrared spectra of these oils showed that they were not polymers of 1,3-dioxolan or 1,3-dioxan because the typical absorption at 1100-1200cm^{-1} due to the formal group was absent.

Similar spectra were obtained from oils which were produced by direct extraction of the methanol solution with hexane.

From these spectra it was not possible to decide what the products were but they certainly were not polymers of 1,3-dioxan or 1,3-dioxolan.

3.2.3. The Oligomerisation of 1,3-Dioxan by Anhydrous Perchloric Acid

The experiments described here were carried out in vacuo, in sealed tubes. The solvent and monomer were distilled into the vessel and the acid dosed by crushing a phial, containing a solution in methylene dichloride, magnetically.

The results of these experiments are given in Table 3.3.

Crystalline oligomers of DP, 2.2-2.6, were formed when the monomer concentration was high; they precipitated from solution. When the monomer concentration was lower as in experiments 18 and 20 these oligomers were not formed. The temperature of experiment 18 was varied between -22° and -55° before it was killed at -40° and even the lower temperature of -78° (run 20) did not induce oligomerisation. In experiment 31, we attempted to polymerise these oligomers but they depolymerised under these conditions.

Therefore, crystalline oligomers of 1,3-dioxan are only formed when they can crystallise from solution. Thus when a non-solvent for the oligomers is used (e.g. hexane or diethylether) as a solvent for the monomer, oligomerisation does occur even at low monomer concentrations (see section 3.2.4.).

In one experiment (48A) quantitative formation of the cyclic oligomers occurred.

At +49° the reaction mixture (45) was a clear, light brown solution. A trace of oil was isolated, the infrared spectrum was similar to that of the monomer except for strong absorptions at 3,500cm^{-1} (hydroxyl group) and 1,730cm^{-1} (carbonyl group).

Although the kinetics of the oligomerisation were not measured, experiments 40-45 indicate that there is an induction period.

3.2.4. Phosphorus pentafluoride

The phosphorus pentafluoride was generated by heating benzene diazonium hexafluorophosphate (phosfluorogen) at 160°. The gas was bubbled through the monomer or monomer solution, which had been prepared on the vacuum line (see Chapter 2). In most cases a condenser was used to prevent the fluorobenzene passing over. However, in the initial attempts some fluorobenzene was carried over into the reaction vessel. In one experiment (12), in which

Table 3.4.

The Oligomerisation of 1,3-Dioxan with Phosphorus Pentafluoride

Run No.	$[M]$	T	time	Crystals		Grease		Carbonyl*
	M	°C	days	yield %	DP	yield %	DP	band
11B	11.7	0	17	0	–	trace	–	+
46	11.7	–36	0.1	35	2.3	0	–	o
11A	11.7	–36	2	1	–	0	–	
12	11.7	–36	3	4	2.96	0.4	8.2	+
13	11.7	–37	3	41	2.5	0	–	+
29	11.7	–35	4	28	2.3	0	–	o
28	11.7	–35	5	43	–	0	–	o
23	11.7	–36	5	34	–	0	–	o
3D	11.7	–78	4	0	–	0	–	
24	9.3[a]	–71	13	70	–	0	–	o
25	5.9[a]	–71	13	0	–	0.2	3.6	o
3E	5.0[a]	–78	3	0	–	trace	–	+
41	2.8[a]	–37	0.8	0	–	trace	–	
42	2.9[a]	–78	2	0	–	0	–	
35	3.9[b]	–35	1	0	–	trace	–	
56	5.9[c]	–39	1.9	31	–	0	–	
47	2.8[d]	–39	0.8	61	–	0	–	

$[PF_5]$ about 0.3M

[a] CH_2Cl_2 solvent; [b] 1.7 base-M rystalline oligomers; [c] Et_2O solvent

[d] C_6H_6 solvent

[*] + = present, o = absent in I.R. spectrum.

oil was formed, it was possible that some fluorobenzene was present in the reaction mixture. However, in subsequent experiments where fluorobenzene was allowed into the reaction mixture these oily oligomers could not be reproduced.

Table 3.4. shows the essential results of those experiments. The oligomers formed had an absorption due to a carbonyl group in their infrared spectra. A comparison of the spectra of 1,3-dioxan oligomers with and without the carbonyl absorption at 1730 cm^{-1}, showed that weak bands at 1450, 965 and 870 cm^{-1} were also associated with it. Therefore, the absorption at 1730 cm^{-1} appears to be due to an aliphatic aldehyde group. When $HClO_4$ was the catalyst, this group was only formed at high temperatures, whereas it was noticeable in some of the oligomers produced by PF_5 at -36°. However, as the dosing technique improved the aldehyde group was not noticed so often.

In experiment 3E, bulk 1,3-dioxan had not polymerised after 18 hours at 0°. By this time the solution had turned slightly brown; the solution was then diluted with methylene dichloride to 5M and left for 78 hours at -78° before killing it with ammonia in ethanol. After distillation a small quatity of yellow grease remained. There was only sufficient for a weak infrared spectrum and apart from absorptions at 1730 and 3500 cm^{-1} it appeared to be poly-1,3-dioxan. Since a small quantity of grease was produced in 3E, various reactions were carried out in order to produce a higher yield.

Some crystalline oligomers were precipitated from reaction mixture 12, but a 0.4% yield of yellow grease was also isolated.

This oligomer was soluble in carbon tetrachloride and had a D.P. of 8.2 but infrared spectroscopy showed that an aldehyde group was present. The crystalline product also absorbed at 1730 cm^{-1} but this was probably due to traces of higher molecular weight oligomer.

Experiment 13 was carried out so that less oxygen was present in the system. An H-tube fitted with a cold finger condensor and a greased tap was used. Benzene diazonium hexafluorophosphate was placed in the side arm which was fitted with a cold finger condenser and the whole was attached to the vacuum line and evacuated for several hours. The monomer was distilled in, the apparatus was sealed off from the line, and the vacuum let down with dry nitrogen. With the monomer at -37° the PF_5 was generated.

Although a larger yield of crystalline oligomers was formed, no grease could be isolated. The carbonyl absorption was still present in the infrared spectrum of these oligomers, therefore the carbonyl group was not formed from a reaction with atmospheric oxygen.

In run 25 a small yield of grease which had no carbonyl group was produced.

There seemed to be little correlation between experimental conditions and the formation of grease. Therefore, we considered the possibility that fluorobenzene affected the reaction and in experiment 29 some fluorobenzene was deliberately allowed into the reaction vessel. The crystalline oligomers were still formed but without a trace of grease and infrared spectroscopy showed the absence of a carbonyl group.

Table 3.5.

Experiments with $PhN_2^+ PF_6^-$

Run No.	3A[a]	3B	10[b]	22[b]	21
[1,3-dioxolan] /M.	14.5	-	-	-	-
[1,3-dioxan]/M.	-	11.7	11.7	11.7	4.7[c]
$[PhN_2^+ PF_6^-]$ /M.	0.02	0.02	0.02	0.2	0.1
T / °C	-	20-140	20	-36	-71
time/days	-	1	17	2	15
yield %	-	0	0	68	0

[a] 1,3-dioxolan polymerised immediately the temperature of the solution was above 0°.

[b] Initial period of 20 mins. at +50° (see reference 5)

[c] The solvent was methylene dichloride; in the other experiments bulk monomer was used.

Table 3.6.

The N.M.R. Spectra of 1,3-Dioxopan, 1,3-Dioxan, their Dimers, 1,3-Dioxocan and 1,3-Dioxonan

DP	Peak Position τ		
	1,3-dioxan		
1 (Monomer)	5.18^{a}	6.1^{b}	8.25^{c}
2.2 to 2.6	5.4^{a}	6.28^{b}	8.25^{c}
Peak-area ratio	1 :	2 :	1
Position of protons	2	4 and 6	5
	1,3-dioxopan		
1 (Monomer)	5.34^{a}	6.31^{b}	8.35^{c}
2	5.46^{a}	6.50^{b}	8.31^{c}
Peak-area ratio	1 :	2 :	2
Position of protons	2	4 and 7	5 and 6
	1,3-dioxocan		
1 (Monomer)	5.4^{a}	6.31^{d}	8.31^{d}
Position of protons	2	4 and 3	5,6 and 7
Peak-area ratio	1 :	2 :	3
	1,3-dioxonan		
1 (Monomer)	5.43^{a}	6.33^{d}	8.31^{d}
>1	5.4^{a}	6.5^{d}	8.53^{d}
Position of protons	2	4 and 9	5,6,7 and 8

[a] no fine structure

[b] Triplet

[c] Quintuplet

[d] unresolved

Different solvents, namely hexane and diethyl ether, which are non-solvents for the crystalline dimer at the reaction temperature, facilitated the formation of these crystals at lower monomer concentrations and higher molecular weight greases were not produced (runs 47 and 56).

The cyclic oligomers depolymerise in solution when treated with PF_5 (run 35).

3.2.5. Phosfluorogen

Phosfluorogen[5] (benzenediazonium hexafluorophosphate) polymerised tetrahydrofuran, therefore we tested it as a catalyst for the polymerisation of 1,3-dioxan. The experiments were carried out in an evacuated H-tube which contained a small quantity of the catalyst in one arm and the monomer and solvent in the other.

The results are shown in Table 3.5. The crystalline oligomers were still formed from bulk monomer at low temperatures (22) but they were brown and could not be purified by standard techniques. In the other experiments traces of brown greases were produced. Experiment 3A was done for comparison and it showed that 1,3-dioxolan polymerises rapidly with this catalyst.

3.2.6. The Structure of the Crystalline Oligomers

The crystalline products were shown to be a mixture of the cyclic dimer and trimer by molecular weight determination and N.M.R. spectroscopy. The DP of these products ranged from 2.2 to 2.6 whilst their N.M.R. spectra (in carbon tetrachloride) of them showed that there were no end-groups and that they must therefore be cyclic (Table 3.6.). Even when the spectra were re-run at higher sensitivities no other peaks were observed. A similar up-field shift was observed for protons in the 2-, 4- and 6-positions as was observed for the cyclic dimer of 1,3-dioxepan.

Infrared spectroscopy did not show any indication of end-groups, either.

Carbon and hydrogen analysis of the product from experiment 48A gave 54.7%C (54.6% in theory) and 9.06%H (9.1 in theory).

The crystalline oligomers of 1,3-dioxan melted at 83-87° and 101-104° with slight decomposition.

Although our molecular weight data show conclusively that a mixture is formed I decided to test this by differential scanning calorimetry. One sample of DP = 2.3 produced two melting peaks at 103.5°, 105° and then a vapourisation peak. A sample (DP = 2.05) had one peak with a shoulder(102.5°). A run at a lower scanning speed gave the shoulder at 99° and the peak at 101°. It appears that the dimer has the higher melting point which is about 102°.

Unlike poly-1,3-dioxolan and poly-1,3-dioxepan the cyclic oligomers of 1,3-dioxan are not susceptible to oxidative degradation, producing formaldehyde, at room temperature. However, Table 3.7. shows that after 2 years the molecular weights of some samples had dropped to values which were closer to that of the dimer. The possibility of calibration error was ruled out by measuring specimen 53B and this had the same molecular weight within experimental error. Therefore, the trimer of 1,3-dioxan appears to revert to the dimer over a period of time.

Table 3.7.

The Molecular Weights of 1,3-Dioxan Cyclic Oligomers

Product	13A	53B	38	29A
M.W. (1967)	213	180	214	202
M.W. (1969)	193	176	184	178

M.W. (Dimer) = 176

Table 3.8.

Separation Attempts

Run No.	Method	DP before	DP after
13	Extraction	2.5	CCl_4 2.6; Hexane 2.4
19	S, 0.01 torr/100°	2.3	2.6
49[*]	S, 0.01 torr/55°	2.3	A = 2.4; B = 2.1; C = 2.1
52	S, 49B,0.01 torr/50°	2.4	2.3
54	S, 49C+D,0.01 torr/50°	2.1	2.2
51[‡]	S, 14 torr/50°	2.3	A = 2.6; B = 2.3
53	R, H_2O	2.3	X = 2.3; Y = 2.05 (I)
53C	S, 53Y,12 torr/60°	2.05	2.2
59	R, Hexane	2.3	2.4
55	Chromatography	2.3	2.3

S = sublimation; R = recrystallisation; I = insoluble

[*] A fraction which had sublimed the furthest.

[‡] Slow sublimation, A after 12 hours, B after 1 day.

3.2.7. Separation attempts

The methods used to attempt the separation of the dimer and trimer of 1,3-dioxan included sublimation, chromotography and recrystallisation; however in none of these experiments did we succeed in separating the trimer from the dimer. The results given in Table 3.8. show that the products from 49C and D had DP's of 2.10 ± 0.05, but these were still mixtures. Interconversion between dimer and trimer is a possible reason for our unsuccessful attempts at isolating the dimer because one product from run 53 had a DP of 2.05 which on sublimation increased to 2.2. The other problem connected with these separations is the ease of formaldehyde formation when the crystalline oligomers were heated. When heated in water the crystalline oligomers gave a positive test for formaldehyde.

Westermann[3] could not fractionate poly-1,3-dioxolan by column chromotography. However I tried the same process with the oligomers of 1,3-dioxan and this was also unsuccessful. Only 12% of the product could be recovered from the column by elution with hexane, benzene and their mixtures and the DP of this fraction was 2.3. It appeared that depolymerisation occurred on the chromatographic column.

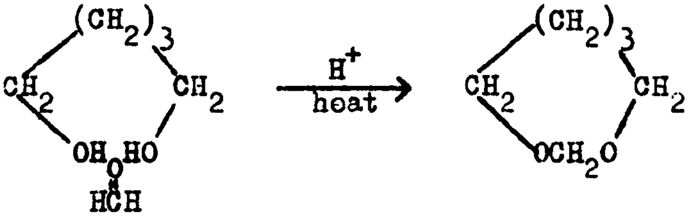
3.3. Discussion

We confirmed the non-polymerisability of 1,3-dioxan but we were able to produce oligomers whose DP ranged from 2.2–2.9. We showed them to be mixtures of the cyclic dimer and trimer, but we did not succeed in separating the mixture into its components.

Oligomers of 1,3-dioxan could only be formed at high monomer concentrations (almost bulk) and only when they could crystallise from the reaction mixture. This means that for 1,3-dioxan, ΔH_{ss}^{o} for oligomerisation must be insufficiently negative to set off the loss of entropy and that the dimer and trimer can only be formed when their latent heat of crystallisation, L_c, makes the total enthalpy change $\Delta H_{sc}^{o} = \Delta H_{ss}^{o} - /L_c/$ sufficiently negative.

3.4. 1,3-Dioxocan

This monomer cannot be prepared easily by the usual method[6], (see Chapter 2 for details), because the reaction



gives only a low yield. The cyclic ether tetrahydropyran is more stable and is produced by dehydration of the glycol in preference to its reaction with formaldehyde. Normally, a 10 mole% excess of formaldehyde is used in this synthesis, but the yield of tetrahydropyran thus obtained was 40% (b.p. 87–88°, 752 torr) and of 1,3-dioxocan was only 2% (b.p. 134°, 752 torr). These products were characterised by infrared and N.M.R. spectroscopy. Variation of the conditions did not increase the yield of 1,3-dioxocan appreciably except when a large excess of the glycol (2 mole : 1 mole HCHO) was used. In this experiment a yield of 9.5% 1,3-dioxocan was obtained.

With 60% aqueous perchloric acid as catalyst instead of phosphoric acid, the whole reaction mixture charred on heating.

This monomer polymerised readily with phosphorus pentafluoride as catalyst. The polymerisation was carried out on the microscale and the polymer was not examined.

3.5. 1,3-Dioxonan

Only a small yield of 1,3-dioxonan could be isolated from the reaction mixture of formaldehyde and 1,6-hexanediol (standard conditions - see Chapter 2) when it was vacuum distilled at a pressure of 12 torr. The product was redistilled off sodium hydroxide (b.p. 159-161°/746 torr). Although the infrared spectrum indicated that the product was 1,3-dioxonan there were two small extraneous absorptions at 1640 and 3640 cm^{-1}. These remained in the spectrum even after the product had been treated with sodium metal. Most of the reactants had formed a gel; extraction with carbon tetrachloride yielded an oil whose N.M.R. and infrared spectra showed it to be poly-1,3-dioxonan. It was not possible to obtain a molecular weight by vapour pressure osmometer.

No monomer could be isolated when the reaction was repeated at a pressure of 12 torr.

Water can be removed from a condensation reaction by azeotropic distillation. With hexane as the solvent the water was removed azeotropically but the product was still a gel.

With an excess of 1,6-hexanediol the reaction mixture also gelled.

With aqueous perchloric acid as the catalyst a violent reaction occurred which produced a charred mass. Although a sample of polymer could be isolated from the gel, it was not possible to determine its molecular weight by vapour pressure osmometry.

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SECTION A - CHAPTER 4

Cyclic Ethers

4.1. Introduction

As is outlined in the introduction to Section A the six-membered cyclic ethers have not been polymerised. With the experience gained in dimerising 1,3-dioxan it was decided to investigate the polymerisation of 1,4-dioxan and tetrahydropyran.

Oxepan, a seven membered cyclic ether, is an interesting monomer. It can be prepared in low yield by the method of Kirmann and Hamaide[1-4], but it contains two impurities which boil very close to oxepan. This monomer can be prepared by other methods also in low yield. High temperature dehydration over alumina[6] (300°; 29% yield) or calcium phosphate[7] (380°; 30% yield) has been used. The reaction of potassium hydroxide with 1,6-hexamethylenebromohydrin[8] has also been used. Hydrogenation of oxopin[9] is also mentioned in the literature as a method for preparing oxepan.

In this Chapter the methods used in an attempt to improve the yield of oxepan are enumerated for completeness. Oxepan polymerises very slowly with the catalysts chosen.

For the polymerisations the monomer was refluxed over and freshly distilled off lithium aluminium hydride before use. The monomer was distilled into the reaction vessel which was a tube fitted with a ground-glass joint or the reaction vessel described in Fig. 2.5. for the dosing of PF_5. The former vessel was closed with a ground-glass stopper sealed with a Teflon sleeve. The catalyst was dosed by breaking a phial magnetically.

Table 4.1.

1,4-Dioxan

Run No.	27	34	36	37	33
[1,4-dioxan] /M.	8.2	5.8	9.5	3.8	3.6
[catalyst] /M.	0.36[a]	0.2[b]	0.2[c]	0.07[c]	0.07[c]
time/days	3	0.9	1	1	1
T / °C	18	19	19	−36	−19

Table 4.2.

Tetrahydropyran

Run No.	58	62	57	61
[THP] /M.	8.5	9.9	9.9	5
[1,3-dioxan] /M.	−	−	−	5.7
[catalyst] /M	0.16[c]	0.2[b]	0.2[b]	0.2[b]
time/days	3.5	2	3.5	2
T / °C	−39	−78	−39	−39

[a] $HClO_4$ added as 3:1 Ac_2O / 70% Aqueous $HClO_4$

[b] PF_5

[c] anhydrous $HClO_4$

The solvent was methylene dichloride and bulk THP is 9.9M.

4.2. 1,4-Dioxan

Table 4.1. gives the details of the attempts to polymerise 1,4-dioxan.

Acetic anhydride/aqueous perchloric acid has been suggested[10] as a catalyst for the polymerisation of 1,4-dioxan, therefore, experiment 27 was attempted. The reaction mixture turned brown after a few hours, but no polymer was formed.

In the other experiments the solvent was methylene dichloride and this was used so that we could use temperatures lower than 12° (the f.p. of 1,4-dioxan). In none of the experiments was there any extensive polymerisation but smears of yellow greases could be isolated. Experiment 34 yielded sufficient for a weak infrared spectrum and this had the expected absorptions for poly-1,4-dioxan.

4.3. Tetrahydropyran (T.H.P.; Table 4.2.)

From our experience phosphorus pentafluoride seemed to be the best catalyst to use in an attempt to polymerise T.H.P. Since Westermann[11] showed that phosphorus pentafluoride and anhydrous perchloric acid polymerise tetrahydrofuran, both these catalysts were also used with T.H.P. In all the experiments traces of oils were produced, but there was only sufficient from experiment 57 for a weak infrared spectrum. This spectrum was not resolved but it did indicate that polytetrahydrofuran may have been formed.

Out of curiousity I tried to copolymerise T.H.P. with 1,3-dioxan (the conditions are given in Table 4.2. run 61) with phosphorus pentafluoride but no polymer resulted. The cyclic oligomers of 1,3-dioxan were not formed either.

Table 4.3.

Attempted Preparations of Oxepan

No.	Ref.	Method	Product
P26		Refluxing HD in "xylene" solution with molecular sieves.	0
		Refluxing HD in "xylene" solution with molecular sieves in the presence of 1% H_3PO_4.	0
P27		As P26 with fine mesh silica gel.	0
P28		As P26, "xylene" replaced by decalin.	0
P29		As P27, coarse mesh silica gel.	0
P30		As P26, Anhydrous EtOH solvent	0
P31		Molten HD dripped slowly into 98% H_2SO_4, 130°	Charring
P32		P31, room temperature at 12mm pressure	Charring
P41	15	2mole HD/1mole dimethyl sulphoxide, 24 hrs. 190°	1% oxepan + 4 other compounds
P53	8,13	Hexamethylene chlorohydrin + KOH	12% oxepan
P56	12	6-bromohexyl acetate + KOH	0
P54	14	1,5-pentamethylene dibromide + ZnO + H_2O, 150°	14%

HD = 1,6-hexanediol

4.4. Oxepan

4.4.1. The Preparation and the Impurities

Oxepan can be prepared by the method of Kirmann and Hamaide[1]: 1,6-Dibromohexane is converted into 1-methoxy,6-bromohexane by reaction with sodium methoxide. The product is cyclised by distilling it in the presence of ferric chloride. The yield of the final stage is quoted as 70% but the highest yield I obtained was 44% so that with a 40-50% conversion for the first stage the overall yield of oxepan from this process was low.

Moreover, there are two impurities in the final product at a level of about 5-10%. The boiling points of these impurities are very close to that of oxepan so that fractionation did not separate them. In the g.l.c. traces the impurities were shown as shoulders on the main peak and could only be separated under conditions which produced very long retention times. Therefore, we undertook a short study to attempt to improve the yield and the purity of the product. Table 4.3. enumerates these methods.

P53 was analogous to the preparation of oxetans by dehydrochlorination of the corresponding chlorohydrin[13].

Tetrahydropyran has been prepared in 90% yield by heating 1,5-pentanedibromide with zinc oxide and water in a sealed tube at 150° for several hours but this method only yielded 14% oxepan.

All these preparations except P53 yielded oxepan containing apparently the same impurities and even a sample of oxepan from B.A.S.F. had these impurities. Further work to prepare oxepan should be directed towards dehydrohalogenation of the halohydrin or the hydrogenation of oxepin.

In some preparations of oxepan by Kirmann and Hamaide's[1] method, a peak at 4.31τ in the N.M.R. spectrum was observed. This could be removed by treatment with bromine in carbon tetrachloride. Thus one impurity contains a double bond. However, this treatment did not affect the main impurities (g.l.c.).

N.M.R. spectroscopy shows that the impurities are characterised by a triplet at 8.8τ and a peak at 6.7τ. The other protons, due to the impurities are underneath the main oxepan peaks (the integration is not as close to the theoretical as normally expected). This indicates that one of the impurities has a CH_3-C-C-X or a CH_3-C-X group, where X is probably an oxygen atom.

In a later paper[2], Kirmann and Wartski reported that the attempted cyclisation of compounds containing tertiary halogens yielded only unsaturated compounds, e.g.

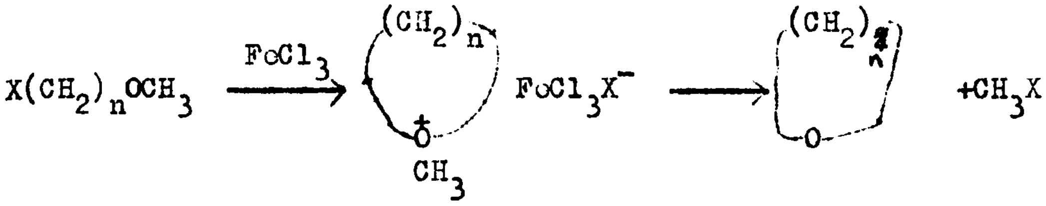
$$CH_3\text{-}CH(OCH_3)\text{-}(CH_2)_2\text{-}C(CH_3)_2Cl \xrightarrow{FeCl_3} CH_3\text{-}CH(OCH_3)\text{-}(CH_2)_2\text{-}C(CH_3)\text{=}CH_2$$

They concluded that primary halogenated compounds gave good yields of the oxacyclane whereas secondary halogen compounds yielded mixtures of the oxacyclane and the corresponding olefin.

Schuster and Lattermann[6a] also isolated some compounds containing two double bonds from the dehydration of 1,6-hexanediol.

The impurities, present in oxepan, are produced in the final cyclisation stage because they were still present in the oxepan produced, after careful purification of each of the intermediate products.

The following mechanism has been proposed for the cyclisation reaction:



where X is Cl or Br.

Kirmann and Hartski[3] proposed this mechanism since the corresponding oxonium salt could be isolated from the cyclisation of 1-Bromo,4-methoxybutane with antimonypentachloride. This tertiary oxonium salt produces tetrahydropyran on heating. This is analogous to the decomposition of triethyloxonium tetrafluoroborate by heat[16] and in solution[17].

Seven membered rings are difficult to form, so that it is not surprising that the more easily formed ring compounds with five and six members may be present in oxepan. This method of Kirmann and Hamaide[1] gave 100% of tetrahydrofuran and T.H.P. but only 70% of oxepan. Similarly, dimethoxyalcanes[4] can be cyclised to the corresponding oxacyclanes by treatment with a Lewis acid/hydrogen halide mixture (e.g. $SbCl_5$/HCl). Only 10% of oxepan was produced whereas the yields of T.H.P. and tetrahydrofuran were 90%.

It appears that the impurities may be ethyl substituted tetrahydrofurans and/or methyl substituted tetrahydropyrans, although these were not isolated. The 2-substituted compounds are the most likely because they could be isolated from the dehydration of 1,6-hexanediol vapour with alumina[6]. (2-methyltetrahydropyran b.p. 103°; 2-ethyltetrahydrofuran b.p. 106°). Franke[18] and his coworkers obtained a 70% yield of "oxidohexane" from the treatment

Table 4.4.

The Bulk Polymerisation of Oxepan

Run No.	60A	60B	75	63	60C	74	78	70
[oxepan] /M.	8.9	8.9	8.9	8.7*	5.3*	8.9	8.9	8.9
[catalyst] /10M.	4	4	2	0.5	0.4	2	1	2
catalyst	$PhN_2^+PF_6^-$	PF_5	PF_5	$HClO_4^-$	$HClO_4^-$	$Et_3O^+BF_4^-$		
T / °C	−35	−35	+20	+20	−78	+35	+35	+40
time / day	2	2	9	6	2	1.3	0.7	2
Polymer	t	t	0	0	t	+	+	+

t = trace

\+ = polymer

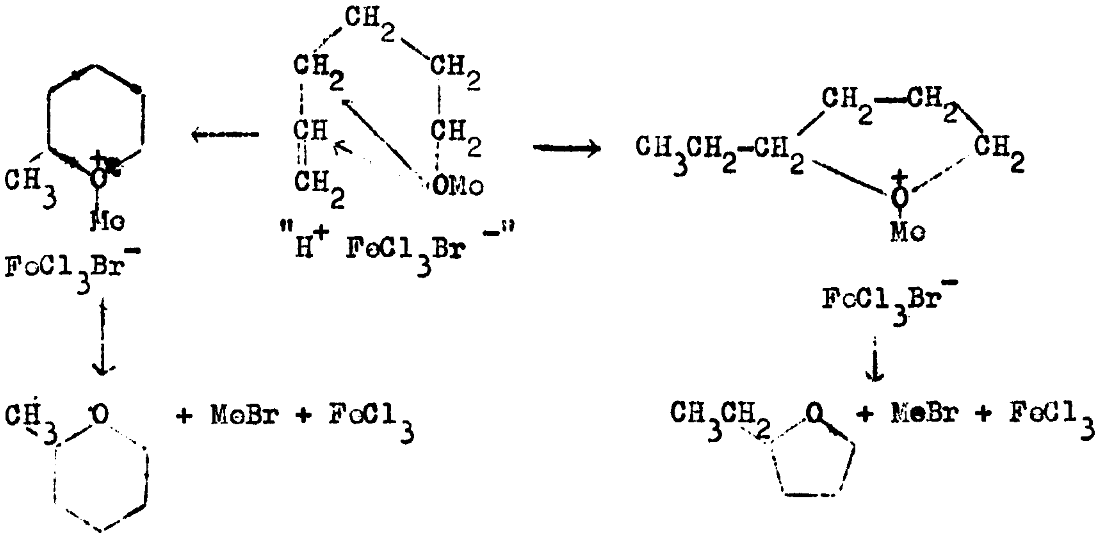
0 = no polymer

* Solvent is methylene dichloride

of 1,6-hexanediol with aqueous sulphuric acid. This was shown to be 10% 1,6 "oxidohexane" 25% 1,5 "oxidohexane" and 65% 1,4 "oxidohexane". Presumably the compounds were oxepan, 2-methyltetrahydropyran, and 2-ethyltetrahydrofuran.

By comparing the infrared spectra of oxepan containing 1% and 10% of impurity we see that the absorptions of 1380, 1280, 1050 and 940 cm^{-1} are due to the impurity. The absorption at 1380 cm^{-1} is most likely from an ethyl (or isopropyl group). Therefore, infrared and N.M.R. spectroscopy suggest that the impurities in oxepan are an olefin, methyl substituted T.H.P. and/or ethyl substituted tetrahydrofuran.

Since the olefin present in oxepan is probably $CH_2=CH-(CH_2)_4-OMe$, which can be formed by dehydrobromination of 1-bromo,6-methoxyhexane, the following mechanism is proposed for the formation of 2-ethyltetrahydrofuran and 2-methyltetrahydropyran.



4.4.2. The Polymerisation of Oxepan

It was not possible to obtain oxepan completely free from impurity. However, various attempts to polymerise small samples of oxepan were made. These were only qualitative experiments so that the catalyst concentrations are only approximate,(Table 4.4.).

I found it surprisingly difficult to polymerise oxepan, as polymer was only produced after a day at 35° in the presence of triethyloxonium tetrafluoroborate. Under the same conditions tetrahydrofuran polymerised rapidly.

It is not possible to say whether the impurities copolymerised but it is quite likely that the impurities may have reacted preferentially with the initiator. Certainly N.M.R. spectroscopy of the polymer indicated the presence of ethyl groups but these could have come from the initiation reaction. The polymer produced in reaction 78 was divided into two parts; one part was killed at 40° (DP = 14.3) and the other part killed at 20° (DP = 46).

From the plot of DP against temperature for experiment 78, $T_c = 41.5^{\circ}$. Therefore using $\Delta S_{ss}^{\circ} = -11.7$ cals/mole/deg. (ΔS_{ss}° for 1,3-dioxepan = -11.7 cals/mole/deg., -12.8 cals/mole/deg. for bulk polymerisation of T.H.F.) an approximate value of ΔH_{ss} can be calculated as -3.6 kcals/mole. This value is of the same order of magnitude as that for the polymerisation of 1,3-dioxepan ($\Delta H_{ss} = -3.7$ ± 0.2 kcals/mole).

4.5. Discussion

The thermodynamics of the polymerisation of oxepan has not been studied. However, an approximate value for ΔH_{ss} was calculated from the ceiling temperature of the bulk polymerisation ($T_c = 41^{\circ}$) using ΔS_{ss} for 1,3-dioxepan. Although ΔS_{ss} would most likely be different for the bulk polymerisation the value of -3.6 kcals/mole agrees with the value for 1,3-dioxepan ($\Delta H_{ss} = -3.5$ kcals/mole)[19].

The surprising fact is the apparent difficulty with which oxepan polymerises. Often the solubility of the catalyst was a problem. Triethyloxonium tetrafluoroborate was not readily soluble at room temperature but was sufficiently soluble to cause polymerisation at +35°. Soluble catalysts such as anhydrous perchloric acid and phosphorus pentafluoride did not polymerise oxepan, and only small quantities of greases were isolated. Both these catalysts polymerise tetrahydrofuran fairly rapidly[11].

The only report in the literature concerning the polymerisation of oxepan is by Gohm and Adam[20]. They, too, found the polymerisation to be slow. For example, 5% of phosphorus pentafluoride on bulk monomer only produced a 15% yield of polymer after 4 days at -15°. Similarly, aluminium trichloride only produced 18% of polymer after five days at room temperature. They also showed that epichlorohydrin accelerated the reaction.

Lal and Trick[21] prepared polyoxepan by heating 1,6-hexanediol with 0.9% of BF_3Et_2O and 0.5% of H_2SO_4. The yield was only 10%. Hobin[22] has also prepared polyoxepan by a similar method.

It is not known whether the slowness of the reaction is due to impurities or whether it is a property of the molecule.

The impurities are difficult to remove from oxepan, but I have tried to show that they are probably 2-ethyltetrahydrofuran an 2-methyltetrahydropyran.

The boiling point of oxepan quoted by Kirmann and Hamaide[1] is 116°/760 torr. I found that the fraction at this boiling point contained a large amount of impurity. Even at 120°/738 torr some impurity remained. At best the impurity could be reduced to 1% but this was after most of the oxepan had been distilled away. It seems that the figure of 121°/741 torr quoted by Schweizer and Parham[9b] is the more reliable.

Tetrahydropyran and 1,4-dioxan were confirmed to be non-polymerisable. The cyclic dimer of 1,3-dioxan was not formed in the presence of tetrahydropyran and this is probably due to the higher basicity of tetrahydropyran.

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SECTION B

The Polymerisation of Cyclic Formals by Triethyloxonium Salts

Introduction

This section of the Thesis is concerned with the polymerisation of 1,3-dioxolan catalysed by triethyloxonium tetrafluoroborate.

The original reason for trying this catalyst was that polymerisation was not expected to occur. It was thought that hydrogen abstraction from the 2-position of 1,3-dioxolan would be the preferred reaction, and that dioxolenium tetrafluoroborate would be formed together with ethane and diethyl ether. The dioxolenium ion was thought not to catalyse the polymerisation[1].

The catalyst was prepared under high vacuum so as to remove any moisture completely, because hydrolysis of triethyloxonium tetrafluoroborate produces fluoroboric acid which might well catalyse the reaction.

However, polymerisation does occur, but the initiation is not the simple unambiguous reaction which Yamashita[2] at one time believed it to be. He believed that complete transfer of the ethyl cation to 1,3-dioxolan occurred.

$$Et_3O^+\ BF_4^- + O\quad O \longrightarrow Et_2O + O\quad O^{+}\text{–}Et\ BF_4^-$$

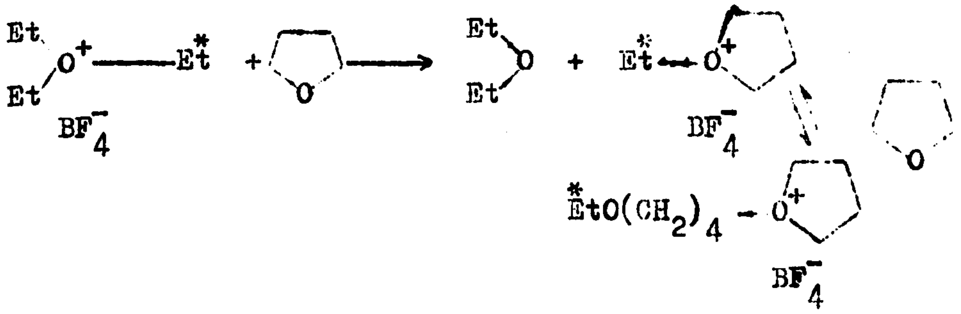
Chapter 5 is concerned with the polymerisation and it is shown there that the polymerisation is propagated by a much lower concentration of ions than is present initially. The main reaction is the decomposition of triethyloxonium tetrafluoroborate to non-conducting products. Chapter 6 presents the results of a study of this reaction.

In order to explain why the decomposition reaction continues as polymerisation takes place, and why there is not a continued increase of active centres, a study of the degree of ion association of triethyloxonium salts in methylene dichloride was made. The results are given in Chapter 7.

This study shows that triethyloxonium salts are associated in solution and that the tertiary oxonium ion can be solvated by other molecules.

The only studies on the polymerisation of 1,3-dioxolan by triethyloxonium salts are by Yamashita's[2,3] and Medvedev's[4] schools. These papers have been discussed in the general introduction to this Thesis (Chapter 1), and they show that the mechanism is far from clear.

In contrast to this, the polymerisation of tetrahydrofuran has been studied by many workers; the review by Dreyfuss and Dreyfuss[5] contains 110 references. In particular, the polymerisation by triethyloxonium tetrafluoroborate has been studied by Rozenberg[6] and by Tobolsky[7]. The latter paper is important because it was shown there by radioactive tracer techniques with C^{14}-labelled initiator that one end of each polymer molecule is an ethyl group (only one third of the ethyl groups were labelled, denoted by *).



Tobolsky also showed that the rate of initiation was fast compared to the rate of propagation and that termination was very slow. Thus the reaction curves could be analysed in terms of an equilibrium polymerisation without termination. The results were in agreement with Rosenberg's[6].

Whereas Tobolsky[7] used a reaction temperature of 0°, Dreyfuss[8] found that at 30°, termination by reaction with the anion was noticeable. The stability of the anions was in the order.

$$PF_6^- \simeq SbF_6^- > BF_4^- \geqq SbCl_6^-$$

With $Et_3O^+SbCl_6^-$, transfer to anion occurred, that is $SbCl_5$ was formed which initiated the polymerisation less efficiently than the salt. However, initiation by BF_3 (from $Et_3O^+BF_4^-$ reaction) is so slow that the reaction of the active centre with its gegenion was considered to be a termination.

It is now generally agreed that the active centre is a tertiary oxonium ion. If it were a carbonium ion it cannot be resonance stabilised and so is unlikely to exist in the presence of oxygen-containing molecules. Rosenberg[6] points out that the primary carbonium ion would isomerise to the more stable tertiary or secondary carbonium ion. In either case, methyl branches would be present in the polymer. In fact, the polymer has been shown to be linear.

This section of the Thesis shows that with 1,3-dioxolan tertiary oxonium ions are the active centres but a ring-opening polymerisation does not occur. The instability of the BF_4^- ion is still prevalent but only seems to occur when the attached groups are saturated. For instance triethyloxonium tetrafluoroborate is unstable, but 1-ethyl-1$\underline{H}^+$-1,3-dioxolanium tetrafluoroborate is stable.

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SECTION B - CHAPTER 5

Polymerisation Characteristics

5.1. End-Group Analysis

There are some difficulties associated with the search for end-groups formed when cyclic formals are polymerised by triethyloxonium salts. With the tetrafluoroborate the end-groups formed in polytetrahydrofuran are ethyl, fluoride (by termination) and an unknown end-group which depends on the killing agent. Both ethyl and fluoride end-groups are difficult to detect by infrared spectroscopy. The C-F bond absorbs at 1,110-1,000 cm^{-1} which is in the region at which the C-O bond absorbs.

Polymers were made with 1,3-dioxolan as the monomer and $Et_3O^+BF_4^-$ the catalyst, and analysed. As C-Cl bonds may be present due to transfer to solvent, these were also looked for. It was established by infrared spectroscopy of a low molecular weight (DP = 5.5) sample between sodium chloride discs that C-Cl bonds were absent. A Lassaigne sodium fusion test was made on three samples (84, 89C, 85). The acidified extract was treated with silver nitrate solution. A precipate was not formed, but the solution from 84 was very slightly cloudy. This could well have been due to occluded methylene dichloride.

Samples of the solution from the sodium fusion tests were treated with Alizarin-zirconium reagent[1]. Each test was negative, so that carbon-fluorine bonds are also absent from the polymer. (The sensitivity of this test is quoted as 100-200 γ of O-fluorobenzoic acid).

5.1.1. Infrared spectroscopy

These spectra were taken with 1% solutions in carbon tetrachloride.

The spectra of several samples of poly-1,3-dioxolan, made with $Et_3O^+BF_4^-$ catalyst, were compared. In particular the spectrum of a high molecular weight sample (DP = 34.6) and one of DP = 5.5 are the same. A low molecular weight polymer (DP = 7.8) prepared by anhydrous perchloric acid catalysis also had a similar spectrum. The only difference was an OH peak at 3,500 cm^{-1} and a very small absorption at 895 cm^{-1} in the latter spectrum. The peak at 895 cm^{-1} seemed to be associated with the OH group as its intensity varied with that of the OH band and disappeared when the OH band was absent. No other examples of the C-OH stretching appearing at about 900 cm^{-1} are known, but a spectrum of 2-methoxyethanol had an absorption at 890 cm^{-1}, which was absent from a spectrum of 1,2-dimethoxyethane. This shows that this band is due to the OH group.

As far as the triethyloxonium tetrafluoroborate polymerisation is concerned, the following end-groups could be shown to be absent.

OH	3500 cm^{-1}
Vinyl ether	3,105-3050 cm^{-1}
Carbonyl groups	1,740-1,720 cm^{-1}
Carbon-Chlorine	750-700 cm^{-1}
Primary or Secondary Amine	3,500-3,300 cm^{-1}
Quaternary Ammonium ion ($R-\overset{+}{N}H_3$)	3,130-3,030 cm^{-1}

(The values are taken from Cross[2])

End-groups which cannot be detected with certainty by infrared spectroscopy in the presence of the polymer spectrum include cyclic ends and methoxyl groups.

Similarly, the spectra of poly-1,3-dioxepans, prepared by a $Et_3O^+BF_4^-$ polymerisation, were compared and the absence of end-groups was also apparent.

By comparing the spectrum of poly-1,3-dioxolan with that of diethyl ether the possible absorption positions of an ethoxy end-group can be seen. The $C-CH_3$ should appear at 1380 cm^{-1} (1375 ± 5 cm^{-1})^2 as it is at this position in diethyl ether. A band appears at 1350 cm^{-1} which is most likely due to the symmetrical deformation vibration of the CH_3 group. The CH_3 stretching vibration appears at 2980 cm^{-1} (2975-2950 cm^{-1})^2. The two former absorptions could be seen in the presence of the polymer. However, these absorptions are not present in the spectrum of poly-1,3-dioxolan and therefore, it is reasonable to conclude that ethoxy end-groups are absent.

However, with poly-1,3-dioxepan it is not possible to observe these absorptions because of the absorption due to the polymer. The addition of diethyl ether to the polymer only produced a small shoulder on one of the absorptions due to poly-1,3-dioxepan.

The polymer of 1,3-dioxolan produced with triethyloxonium hexafluoroantimonate as a catalyst was not so clean. For instance, an OH band was noticed together with a carbonyl absorption at 1735 cm^{-1}, but the carbonyl group disappeared and the OH group was diminished when the polymerisation was killed with triethylamine instead of "0.880" ammonia.

In experiment 181, part of the reaction mixture was killed with ammonia (181A) whilst the other half was killed with anhydrous triethylamine (181B), 181A had 97.5 monomer units per OH group and 181B had 263 monomer units per OH group (see Section C for method). The DP of the polymer was 14.5.

This shows that OH groups are produced by the water in the killing agent. This suggests that either there are end-groups which react to produce an OH group or, more likely, that the polymer is cyclic and the water opens the ring. This has been shown to be the case for the perchloric acid polymerisation (Section C). The formation of the occasional carbonyl group cannot be explained at this time. A detailed study of the polymerisation of cyclic formals with triethyloxonium hexafluoroantimonate is required.

5.1.2. Nuclear Magnetic Spectra

The spectra of low molecular weight samples of poly-1,3-dioxolan and poly-1,3-dioxepan were taken with 10% solutions in carbon tetrachloride, with TMS as the internal standard. These spectra only showed the expected peaks, and the τ values are in complete agreement with the published values[3,4]; even at high sentivities no other peaks were present.

5.1.3. The Dimer of 1,3-Dioxepan

As it was not possible to locate ethyl end-groups with certainty by infrared and N.M.R. spectroscopy I decided to test the cyclic nature of the polymer from 1,3-dioxepan by attempting to isolate the cyclic dimer. Westermann[4] had shown that the crystalline dimer of 1,3-dioxepan was formed during the polymerisation with perchloric acid as a catalyst.

In experiment 93 1M 1,3-dioxepan was polymerised with $2X10^{-3}$M triethyloxonium tetrafluoroborate at 25°. After the reaction was complete, the reaction mixture was equilibrated at 10.7° and killed with ammonia vapour. The excess monomer and solvent were removed carefully at 20° at a pressure of 12 torr, pumping was continued for several hours at 12 torr/20°. The product contained white crystals. These crystals were isolated by vacuum sublimation (0.01 torr/60°); 4.7% of the product was the crystalline dimer. The melting point was 85-88° which on resublimation increased to 91-91.5° (Lit.[4] 90-92°). The N.M.R. spectrum agreed with that quoted by Westermann.

This is good evidence that the polymerisation of the cyclic formals by $Et_3O^+BF_4^-$ also produces cyclic polymer.

5.2. The Kinetics of the Polymerisation of 1,3-Dioxolan catalysed by Triethyloxonium Tetrafluoroborate

The most extensive kinetic study of 1,3-dioxolan and 1,3-dioxepan polymerisations was by Westermann[5]. He showed that the polymerisation of 1,3-dioxolan with anhydrous perchloric acid catalyst had an acceleration period followed by a first order phase, whereas the polymerisation of 1,3-dioxepan was wholly of first order with respect to monomer. He explained the acceleration observed for 1,3-dioxolan by the higher basicity of the polymer compared to the monomer. With 1,3-dioxepan the basicities of the polymer and monomer are almost the same. All the evidence pointed to the active species being secondary oxonium ions. In the

1,3-dioxolan polymerisations the perchloric acid was not ionised completely until 25% of the polymerisation had occurred. This was indicated by conductivity measurements taken during the polymerisation.

There was a linear relationship between perchloric acid concentration and the first order rate constant (k_1) over a ten-fold concentration range of the catalyst. Conductance measurements, under conditions such that no polymer was formed, showed that $\kappa / [HClO_4]$ was constant for a ten-fold dilution.

From these experiments he concluded that each perchloric acid molecule yielded an active centre. Therefore, the second order rate-constants were interpreted as the rate constants of propagation (k_p).

k_p (1,3-dioxolan) = $6.2 \pm 0.2 \times 10^2$ $l\,mole^{-1}\,min^{-1}$ at 0°
k_d (") = $3.4 \pm 0.5 \times 10^2$ min^{-1} at 0°
k_p (1,3-dioxepan) = $1.9 \pm 0.06 \times 10^5$ $l\,mole^{-1}\,min^{-1}$ at 0°
k_d (") = $1.8 \pm 0.3 \times 10^4$ min^{-1} at 0°

The polymerisation of cyclic formals is an equilibrium process so that the kinetic scheme of Tobolsky and of Rosenberg for the polymerisation of tetrahydrofuran by triethyloxonium tetrafluoroborate can also be applied to the polymerisation of 1,3-dioxepan and for the last half of the polymerisation of 1,3-dioxolan. Westermann[5] has shown this to be the case for the polymerisation of cyclic formals by anhydrous perchloric acid and his kinetic treatment is shown below.

$$P_n^+ + P_1 \underset{k_d}{\overset{k_p}{\rightleftharpoons}} P_{n+1}^+ \qquad \text{propagation}$$

where P_1 is monomer and P_n^+ is protonated polymer.

Above 25% conversion for 1,3-dioxolan (and wholly for 1,3-dioxepan)

$$[HClO_4] = [P^+] = a \qquad \text{where } [P^+] = \sum_{n=2} [P_n^+]$$

$$[P_1] = m$$

Then $$-dm/dt = k_p ma - k_d a$$

But $$k_d = k_p m_e$$

where m_e is the equilibrium concentration of monomer.

Substitution for k_d gives

$$-dm/dt = k_p\, a\, (m - m_e)\ ,$$

and substitution for k_p

$$+\, dm/dt = k_d\, (m_e - m)\ /m_e$$

Since for 1,3-dioxepan and the later part of the polymerisation of 1,3-dioxolan the reactions are of first order with respect to monomer,

$$-dm/dt = k_1\, (m - m_e)$$

where $k_1 = k_p a$

Similarly the first half of the depolymerisation of poly-1,3-dioxolan was also of first order, so that

$$+\, dm/dt = k_1'\, (m_e - m)$$

where $k_1' = k_d\, a\ /m_e$

Yamashita[6] and his coworkers used $Et_3O^+BF_4^-$ to polymerise 1,3-dioxolan. They calculated a second order rate constant from the maximum rate and identified it with k_p. As will be shown, this procedure is invalid for this system, because the catalyst[7] is not 100% efficient. My study of this system is discussed in this section of the Thesis.

In later studies on the polymerisation of 1,3-dioxepan[8] and 1,3,6-trioxocan[9] by the same catalyst Yamashita had become uncertain about the number of active centres. He did not calculate k_p or k_1 but only the maximum rate R_p. The kinetic curves obtained for these monomers are much the same. The rate of polymerisation of 1,3-dioxepan is greater than that of 1,3-dioxolan.

Most of the work of Kucera[10] and his coworkers was concerned with kinetic measurements and their interpretation of the polymerisation of 1,3-dioxolan by octamethylcyclotetrasiloxane bisulphate. The experiments were made under anhydrous conditions with known amounts of water present. Kucera[10a] based his kinetic scheme on the assumption that the active centres are carboxonium ions which were supposed to be in equilibrium with unreactive tertiary oxonium ions. Although this scheme does fit the experimental results, the basic assumption is not justified by any supporting evidence. The rate constant for the propagation was not calculated. Kucera did, however, determine two composite rate constants for each part of the conversion curve.

Gorin and Monnerie[11] studied the bulk polymerisation of 1,3-dioxolan at 25° with mercuric chloride and boronfluoride etherate as catalysts. These kinetic experiments were carried out in a semi-open system. The results were found to be in agreement with the scheme proposed by Kucera and Pichler[10a]. Sensibly, they refrained from calculating a rate constant from their data.

Chil-Gevorgyan[12] has polymerised 1,3-dioxolan in bulk and in methylene dichloride solution by boron trifluoride etherate. These experiments were not carried out under rigourously dry conditions since they only used "dry-box" techniques and the monomer was distilled off sodium metal before being stored under dry nitrogen. In a footnote[12a] it is noted that the results were not reproducible.

However, he does not calculate any rate constants from these results but in a later paper[12c] proceeds to explain the acceleration period mathematically as an auto-catalytic effect although no evidence is presented for this assumption.

Lyudvig[13] does, however, suggest a propagation rate constant for the polymerisation of 1,3-dioxolan catalysed by triethyloxonium hexachloroantimonate. The value of k_p given is 75 lmole^{-1} min^{-1} at 20° but from the data in the paper $k_1/c = 5$ lmole^{-1} min^{-1} at 20°. The rate constant has a much lower value than the one Westermann[5] obtained. It is probable that a similar effect occurs with this catalyst as with the tetrafluoroborate. That is, the catalyst is inefficient due to its decomposition. The relative merits of this paper will be discussed later as the mechanism proposed seems to be highly unlikely.

5.2. Experimental Results

Introduction

My polymerisations were carried out in vacuum dilatometers. In later experiments a dilatometer with electrodes for conductance measurements was used. The reaction is so slow that it was necessary to use high monomer concentrations, and a temperature of 25° was most convenient.

Table 5.1.

The Polymorisation of 4M 1,3-Dioxolan at T = +25°

Run No.	84	86	85	88	90
$[Et_3O^+BF_4^-]/10^3M.$	8.0	4.0	8.0	8.0	10.0
$[H_2O]/10^3M.$	4.0	-	-	-	-
k_1/min^{-1}	0.086	0.089	0.25	0.13	0.18
DP	45.3	40	48.6	-	-
% Conversion	64.8	65.5	65.8	63.8*	63.8*
X	45	48	45	34	32
Induction time, min	42	29	25	21	14

*Calculated from dilatometric contraction

X = % reaction which is of first order with respect to monomer.

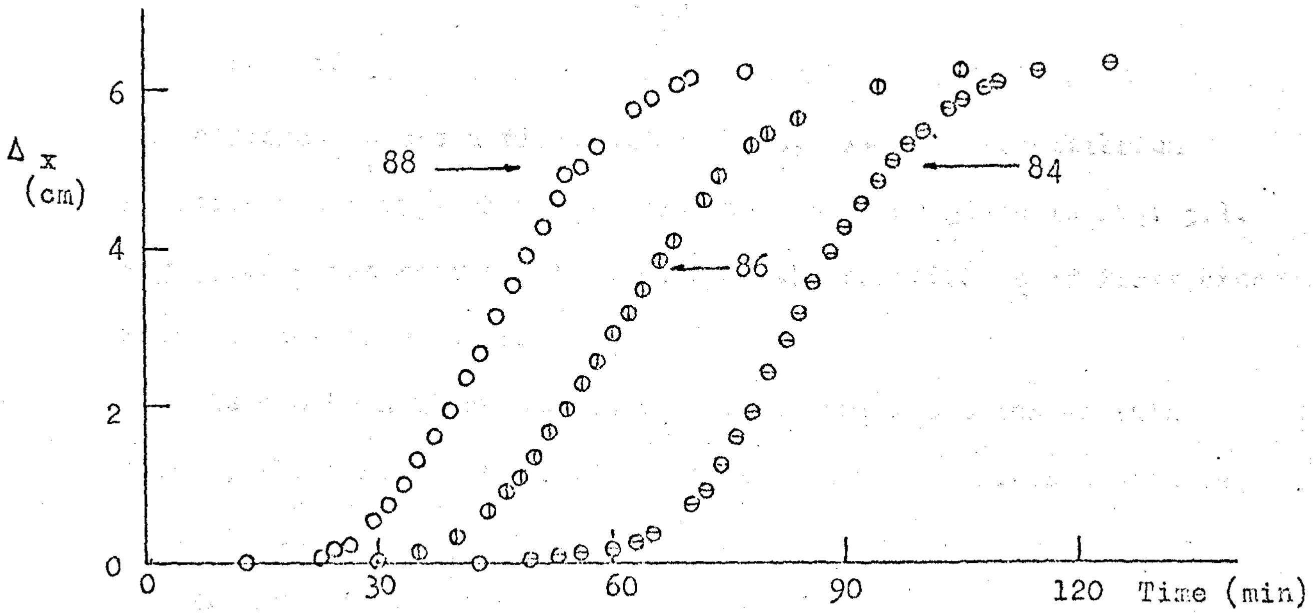
Fig. 5.1.

Conversion Curves for the Polymerisation of 1,3-Dioxolan at 25° showing the Effect of Water on the Rate of Polymerisation (Table 5.1.)

Fig. 5.2.

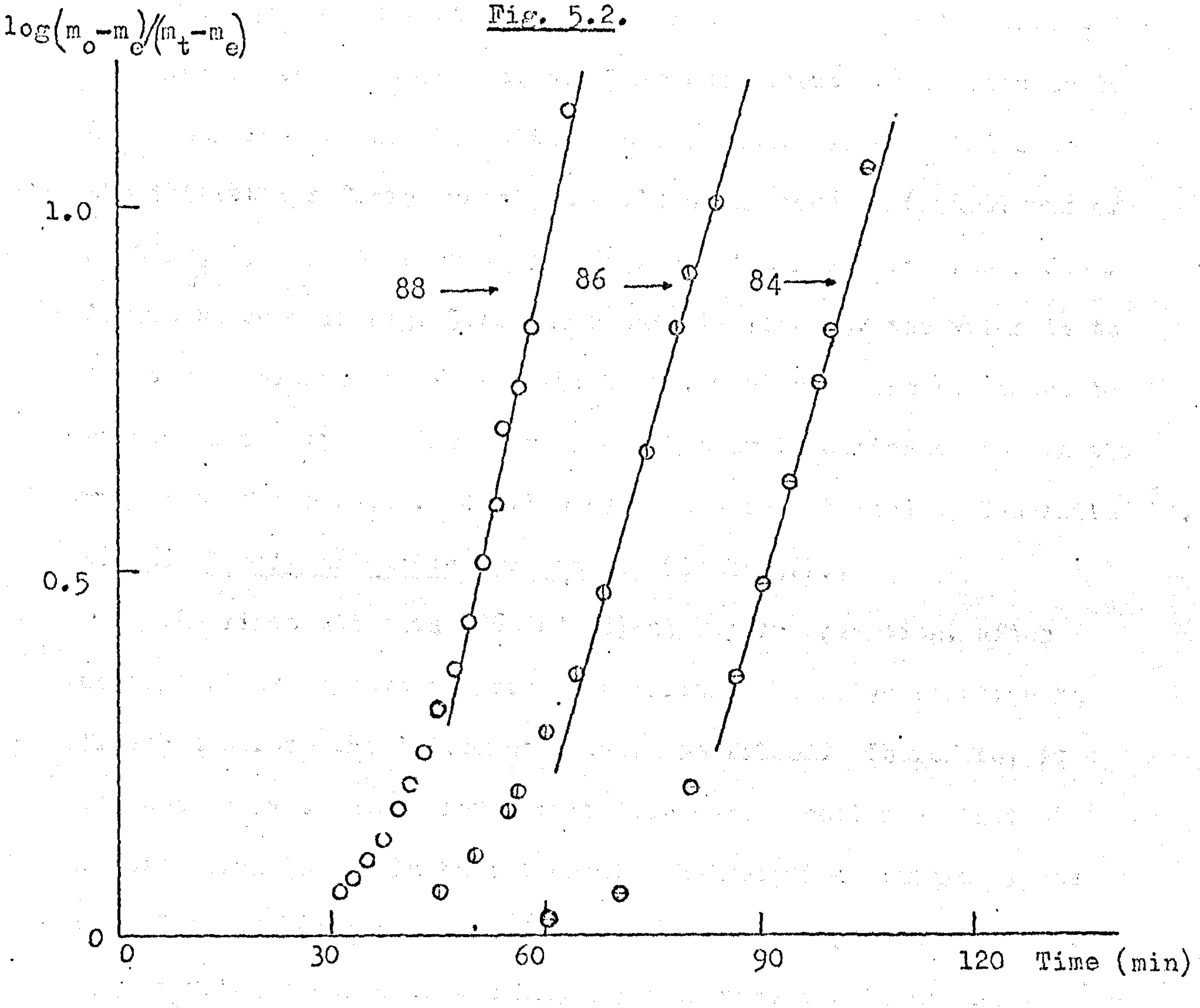
First Order Plots for Reactions 84, 86 and 88 (Table 5.1.)

Fig. 5.1.



Δ x (cm)
6
4
2
0
88
86
84
0
30
60
90
120
Time (min)

Fig. 5.2.



log(m_o - m_e)/(m_t - m_e)
1.0
0.5
0
88
86
84
0
30
60
90
120
Time (min)

The polymerisation is characterised by an induction period, an acceleration and a first-order phase. It is an equilibrium reaction and a typical time-conversion curve is given in Fig. 5.1. Fig. 5.2. shows that the last part of the reaction is of first order with respect to monomer.

As has been discussed in the experimental section of this Thesis, the concentration of triethyloxonium tetrafluoroborate is a little uncertain because of the method of dosing the catalyst.

5.2.2. Effect of Water

Only one experiment (84) was carried out to show the effect of water on the polymerisation. This experiment was undertaken to aid determination of the initiation reaction. If HBF_4 had been the initiator a faster reaction would have occurred (hydrolysis of $Et_3O^+BF_4^-$ is a fast process[14]). In fact, the reaction slowed down. As can be seen in Fig. 5.1. the apparent effect of the water is to react stoichiometrically with $Et_3O^+BF_4^-$, thus reducing the concentration of catalyst. There is also a longer induction period in the presence of the water. Similar results were obtained by Yamashita[6,15].

5.2.3. Repolymerisation Experiments (Table 5.2.)

The first attempts (86 and 88) at repolymerisation, after depolymerisation gave surprising results. The polymerisation had finished before the dilatometer could be filled. Therefore, it was necessary to use a lower initiator concentration so that the repolymerisation could be followed. The reaction mixture 89 was warmed to 60° (the calculated $T_c = 49°$, but I expected a slightly higher value because of the high monomer concentration) and

Table 5.2.

Repolymerisation of 1,3-Dioxolan at T = +25°

Run No.	89	89A	89B	105	105A
[Monomer]/M.	4.0	4.0	4.0	3.0	3.0
$[Et_3O^+BF_4^-]/10^3M$	2.0	2.0	2.0	1.0	1.0
k_1/min^{-1}	0.045	0.053	0.049	0.018	0.018
% Conversion	-	-	64	-	44[*]
% Conversion (calc.)	64.2	64.2	64.2	49	49
DP	-	-	41	-	19.1
X	17	70[I]	70[I]	16	58
Induction period/min	40	0	0	110	0

X = % of reaction which is of first order.

[I] This represents the observed part of the reaction but it appeared that whole reaction was first order.

[*] Estimated from the volume of polymer solution remaining after sampling, actual yield = 20%.

The Repolymerization of 1,3-Dioxolan (Experiment 89; Table 5.2.)

Fig. 5.3. Conversion Curves (by dilatometry)

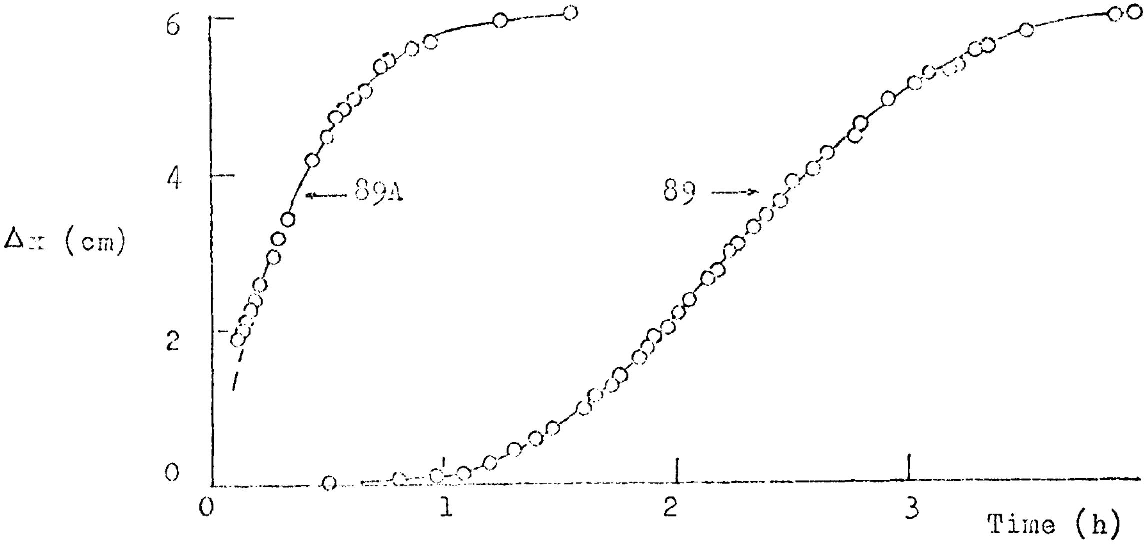
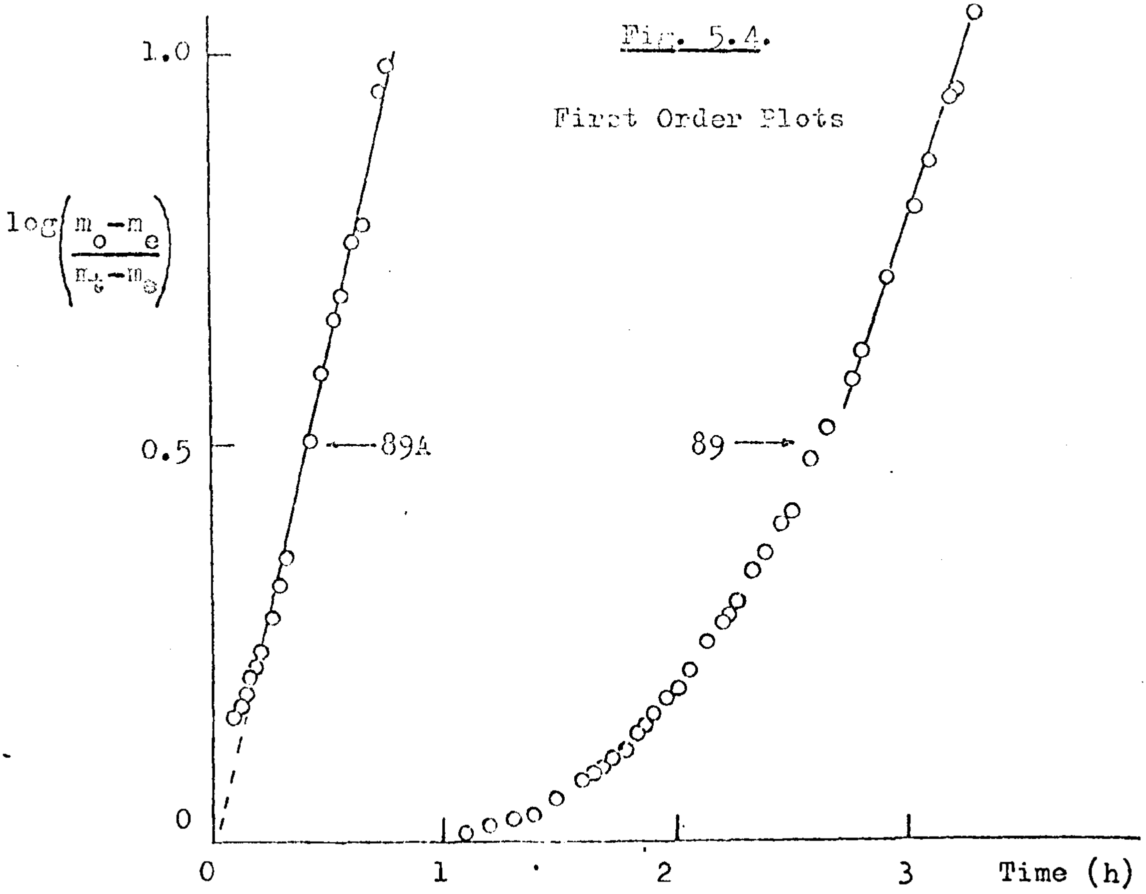


Fig. 5.4.

First Order Plots



depolymerisation occurred. The dilatometer was placed in a bath at 25° and the second polymerisation was followed. The procedure was then repeated. The initial cathetometer readings showed the contraction due to cooling as well as polymerisation.

When a dilatometer is used to follow equilibrium polymerisations at these monomer concentrations it is necessary to put the final mixture into the side arm for killing. This necessitates partial depolymerisation and rethermostatting with the solution in the side arm. As the yield of polymer obtained in this way did not vary outside experimental error it is safe to assume that the reaction does go to equilibrium after depolymerisation. The results of the repolymerisation experiments also agree with this assumption.

Therefore, I equated the final contraction that occurred on repolymerisation with that of the first polymerisation.

As is shown in Fig. 5.4., the ~~two~~ repolymerisation~~s~~ ~~are~~ is completely of first order with respect to monomer, and the rate constants (k_1) calculated from these plots are the same and equal within experimental error, to the k_1 calculated for the first polymerisation (Table 5.2.).

When conductivity measurements were made during the polymerisation it was found that the conductivity continued to drop for several hours after the polymerisation had reached equilibrium. Experiment 104 was left until the conductivity was apparently constant and repolymerisation was then attempted. Repolymerisation occurred rapidly, as before, thus showing that a loss of active centres was not responsible for the conductivity change. Experiment

Table 5.3.

The Polymerisation of 3M 1,3-Dioxolan at 25°

Run No.	105	105A	103	102	104	101	106	109	115
$[Et_3O^+BF_4^-]/10^3M$	1.0	1.0	6.0	6.0	6.0	6.0	8.0	12.0	12.0
k_1 /min^{-1}	0.018	0.018	0.05	0.052	0.077	0.085	0.127	0.077	0.092
% Conversion	-	44	48.8	48	51	48.5	49.6*	49*	51
X	16	58	34	50	33	35	38	50	55
DP	-	19.1	21.1	18.0	17.6	25.3	33.0	-	13.0
$\kappa_x/\ \Omega^{-1}cm^{-1}$	13.9	-	19.9	40.1	41.3	-	57.8	50.7	-
$\kappa_o/\ \Omega^{-1}cm^{-1}$	9.6	0.57	-	19.0	28.0	-	40.3	34.4	31.7
$\kappa_f/\ \Omega^{-1}cm^{-1}$	0.42	0.42	-	0.9	0.7	-	1.7	1.5	1.5
Induction period/ min	110	0	60	80	21	23	23	15	19

* Calculated from dilatometric contraction.

X = % of reaction which is of first order.

κ_x is the specific conductivity of the catalyst solution before addition of monomer.

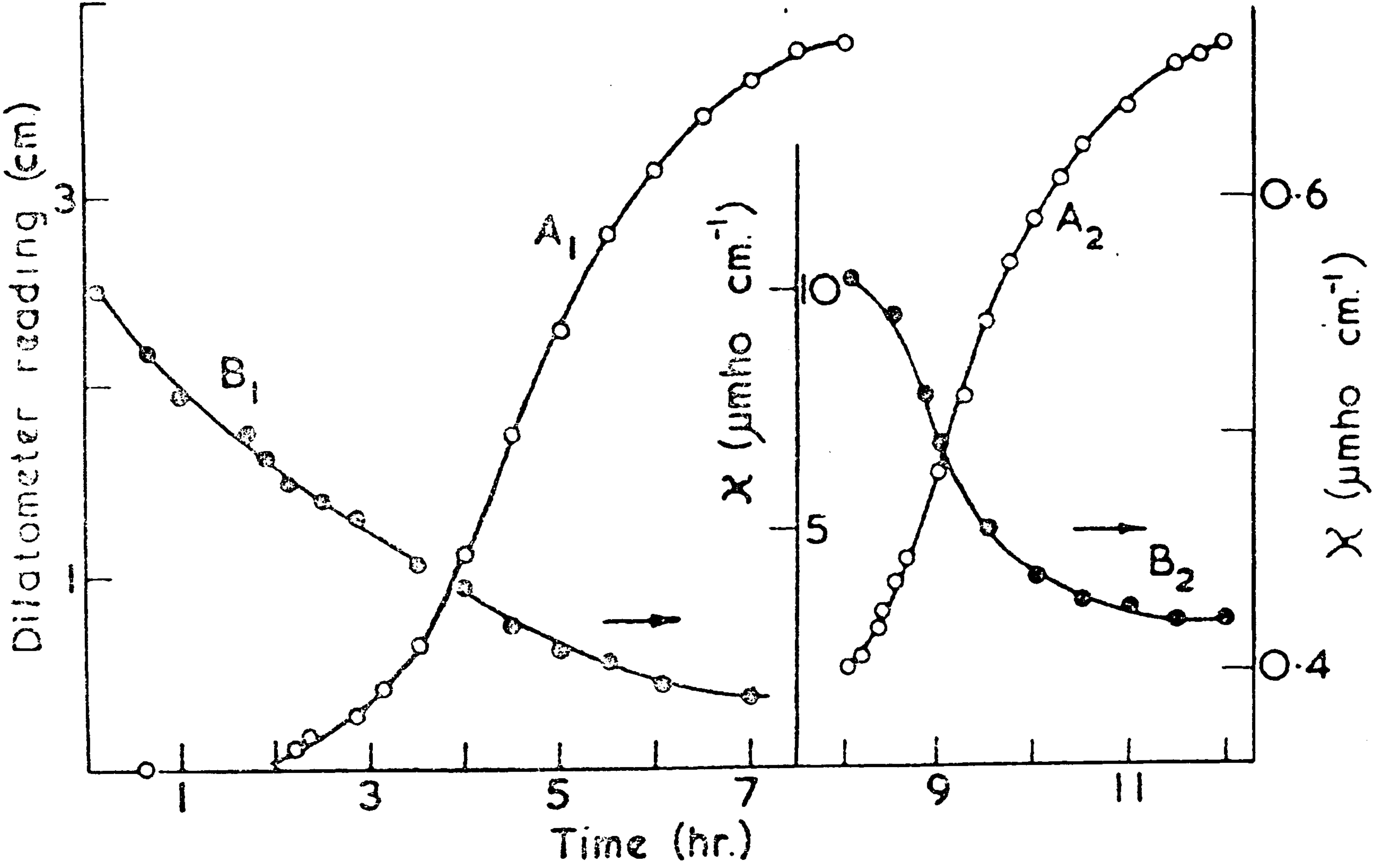
κ_o is the specific conductivity at the start of the experiment.

κ_f is the final specific conductivity, several hours after polymerisation had reached equilibrium.

Fig. 5.5.

The Polymerisation - Repolymerisation of 1,3-Dioxolan (Experiment 105 - Table 5.3.)

A_1, A_2 Dilatometer readings; B_1, B_2 Specific conductance (note different scales for B_1 and B_2)



105 was undertaken in the same way. A lower catalyst concentration was used so that the rate of repolymerisation could be measured. Once again the first order rate constants were the same. However, in this case the catalyst concentration was very low and a short acceleration period was noticed (Fig. 5.5.).

5.2.4. Conductivity Measurements during Polymerisation

The polymerisation of 1,3-dioxolan by $Et_3O^+BF_4^-$ is much slower than the corresponding reaction catalysed by anhydrous perchloric acid.

A dilatometer containing electrodes was constructed to see whether conductivity measurements would help to solve this problem. It was not expected to be of much help because $Et_3O^+BF_4^-$ itself is ionic. However, a slight change of conductivity could have been possible if the active centre had a different mobility to the triethyloxonium ion. As can be seen in Fig. 5.5. these runs are informative. The conductivity dropped steadily throughout the induction period until a slightly faster decrease of conductivity occurred due to the increased viscosity of the medium and the lesser mobility of the polymeric cation. After the polymerisation had reached equilibrium the conductivity still continued to drop. It did not reach a constant value until about 1-2 days after the polymerisation had finished. It was clear that some ionic species were being lost that were irrelevant to the polymerisation. In experiment 105 the system could be repolymerised even after the conductivity had reached its minimum ($0.42\mu\Omega^{-1}cm^{-1}$). Depolymerisation raised the specific conductivity (κ) to $0.57\mu\Omega^{-1}cm^{-1}$ (25^o). On polymerisation, the specific conductivity dropped back to $0.42\mu\Omega^{-1}\text{cm}^{-1}$, but this was largely ~~entirely~~ due to a viscosity change during polymerisation. The final conductivity of the reaction solution is much smaller than the initial conductivity due to triethyloxonium tetrafluoroborate. These values are listed in Table 5.3. The final conductivity will be seen (see section 5.3.) to be due to the active centre and also some dioxolonium tetrafluoroborate.

As shown in Fig. 5.6. the plot of the k_1 against $[Et_3O^+BF_4^-]$ is reasonably linear although the points are scattered either side of the line. Much of this scatter is due to some uncertainty in the catalyst concentration. Therefore, it was decided to use the conductivity of triethyloxonium tetrafluoroborate solution before addition of monomer (k'_x) as a calibration to determine the catalyst concentration more accurately. The plot of k_1 against the $[Et_3O^+BF_4^-]$ determined by this method is given in Fig. 5.7. The degree of scatter is reduced, but not completely. I have given less weight to experiment 102 because this reaction had an unusually long induction period and was also the first conductivity experiment. Also experiments 106 and 109 are some way out of the calibration range and may be erroneous. The value of k_1/c obtained from this plot is 9.5 $\text{lmole}^{-1}\ \text{min}^{-1}$. The scatter is not surprising because the number of active centres does depend on the $[Et_3O^+BF_4^-]$ but the dependence need not necessarily be linear.

The calibration was determined by diluting three phials containing 0.39, 0.68 and 0.45 mmoles of triethyloxonium tetrafluoroborate respectively, with methylene dichloride in a vacuum conductivity cell.

Table 5.5.

The Values of k_1 and actual $[Et_3O^+BF_4^-]_a$ at 25°

Run No.	105	103	104	102	109	106
$[1,3\text{-dioxolan}]$ /M.	3.0	3.0	3.0	3.0	3.0	3.0
$[Et_3O^+BF_4^-]_a$ $/10_3M$	1.6	3.5	8.0	8.7	11.0	12.7
k_1 $/min^{-1}$	0.018	0.05	0.077	0.052	0.08	0.127

Fig. 5.6.

The Plot of k_1 against $[Et_3O^+BF_4^-]$ (uncalibrated - Table 5.3.)

Fig. 5.7.

The Plot of k_1 against $[Et_3O^+BF_4^-]_a$ (calibrated - Table 5.5.)

Fig. 5.6.

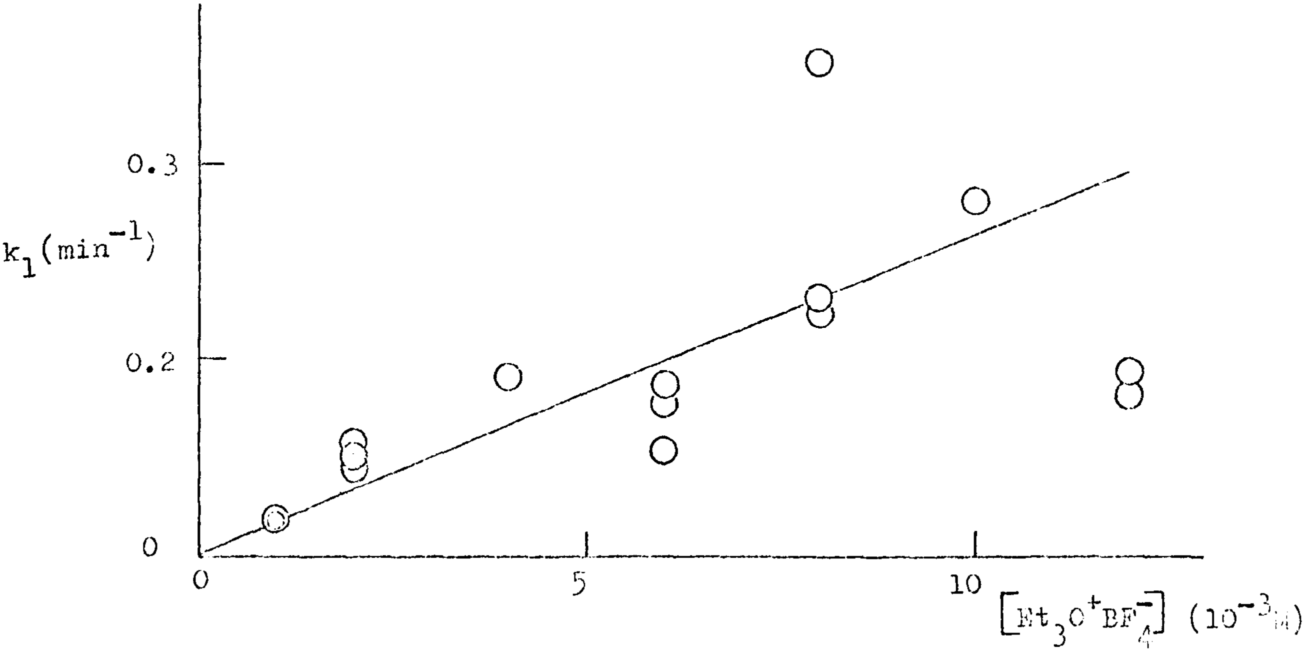

0.3
0.2
0
k_1(min^{-1})
0
5
10
[$Et_3O^+BF_4^-$] (10^{-3}M)

Fig. 5.7.

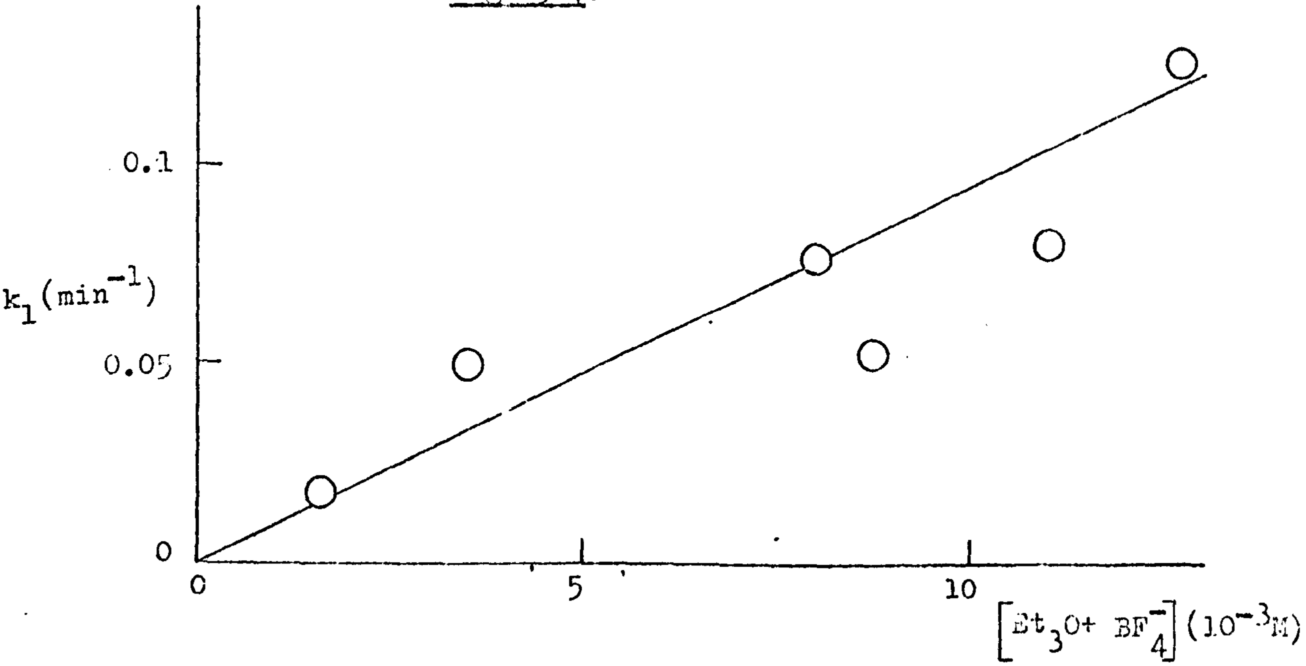

0.1
0.05
0
k_1(min^{-1})
0
5
10
[Et_3O+ BF_4^-] (10^{-3}M)

Table 5.4.

Conductivity data for solutions of $Et_3O^+BF_4^-$ in Methylene Dichloride at 25°

Run 126

0.129 ± 0.004 g
0.678 ± 0.021 mmoles

$[Et_3O^+BF_4^-]/10^3M$	9.69	6.78	4.52	3.39	2.51	1.83
$\kappa/\mu\Omega^{-1}\ cm^{-1}$	37.2	28.3	21.1	17.4	14.4	11.8

Run 127

0.086 ± 0.004 g
0.454 ± 0.021 mmoles

$[Et_3O^+BF_4^-]/10_3M$	6.49	4.54	3.03	2.27	1.82	1.45
$\kappa/\mu\Omega^{-1}\ cm^{-1}$	26.3	20.4	15.6	13.0	11.4	10.0

Run 131

0.073 ± 0.004 g
0.386 ± 0.021 mmoles

$[Et_3O^+BF_4^-]/10^3M$	12.9	7.72	3.86	2.57	1.54
$\kappa/\mu\Omega^{-1}\ cm^{-1}$	47.8	34.4	21.4	16.5	12.1

Fig. 5.8.

Plot of κ against $Et_3O^+BF_4^-$ at 25° (Calibration - Table 5.4.)

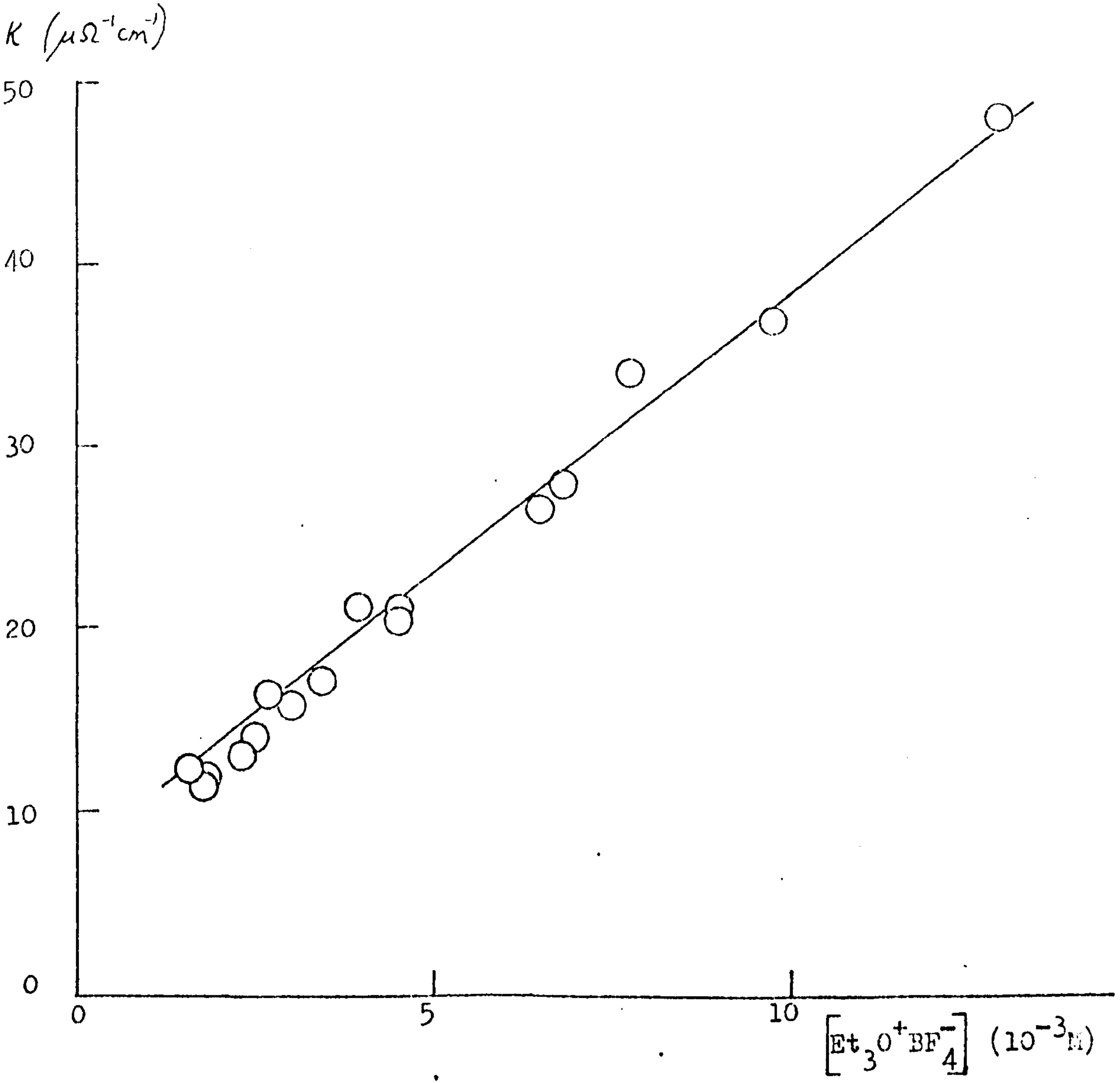


Table 5.6.

The Effect of Temperature on the Polymerisation of 3M 1,3-Dioxolan

Run No.	110	A	111
$[Et_3O^+BF_4^-]/10^3M$	8.0	-	8.0
$[Et_3O^+BF_4^-]_a\ /10^3M$	9.1	-	6.0*
$k_1\ /min^{-1}$	0.14	-	0.027
$k_1\ /c/lmole^{-1}\ min^{-1}$	15.5	9.5	4.5
$\log k_1\ /c$	1.19	0.98	0.65
% Conversion	34	-	72
% X	46	-	28
DP	14.3	-	27.4
$\kappa_x\ /\Omega^{-1}\ cm^{-1}$	42.1 (25°)	-	-
$\kappa_o\ /\Omega^{-1}\ cm^{-1}$	28.3 (35°)	-	23.4 (10.2°)
$\kappa_f\ /\Omega^{-1}\ cm^{-1}$	1.0 (35°)	-	-
Induction period/min	11	-	60
$T\ /^oC$	35	25	10.2
$10^3/T\ /\ ^oK^{-1}$	3.25	3.36	3.53

$[Et_3O^+BF_4^-]_a$ = actual concentration of $Et_3O^+BF_4^-$.

* Estimated from κ_o.

A Using $k_1\ /c$ as 9.5 $lmole^{-1}\ min^{-1}$ from graph (see Fig. 5.7.)

X = % of reaction which is of first order

Fig. 5.9.

Arrhenius Plot for the Polymerisation of 1,3-Dioxolan by $Et_3O^+BF_4^-$ (Table 5.6.)

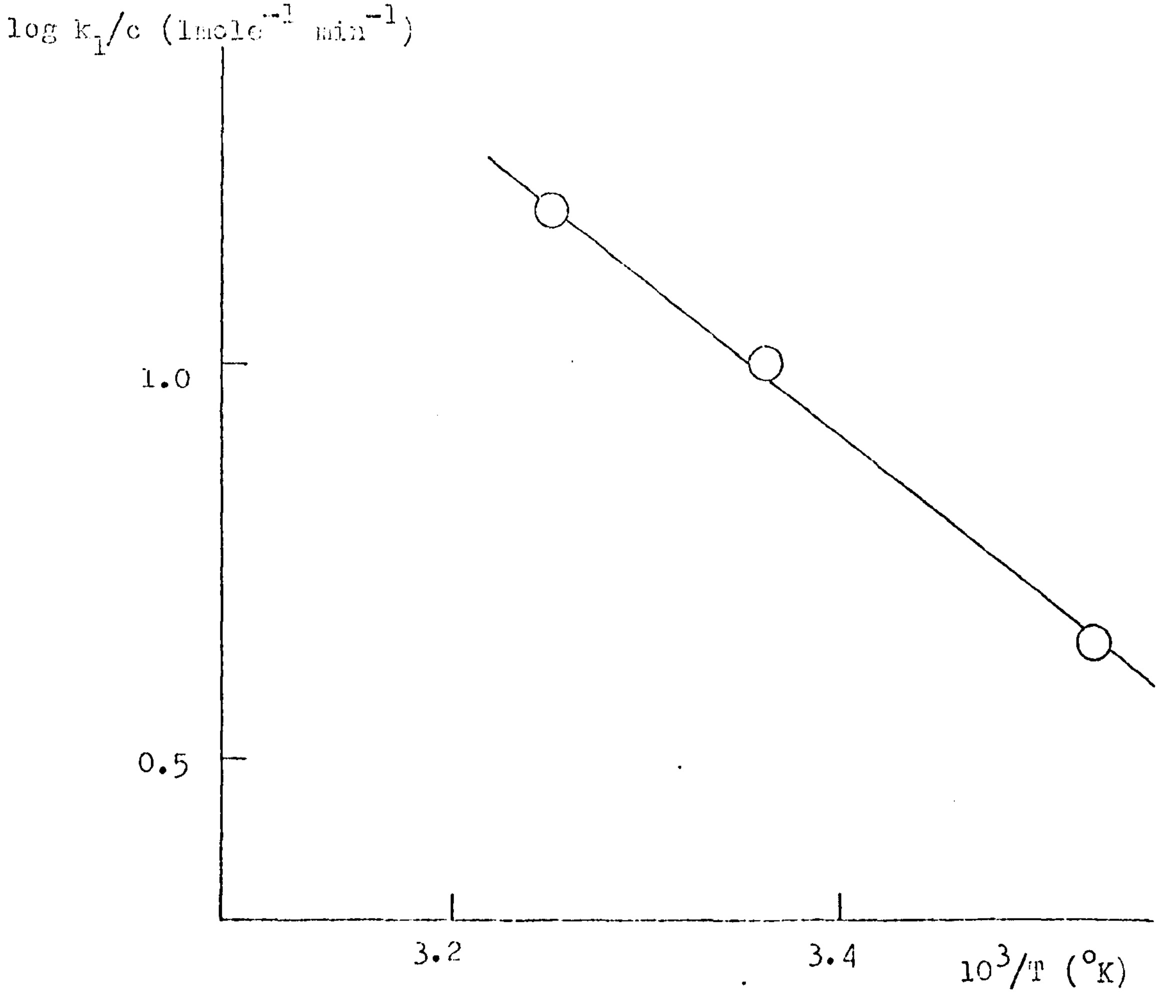


Table 5.7.

Polymerisation of 1,3-Dioxepan at 25°

Run No.	93	94
[Monomer]/M.	1.0	2.0
$[Et_3O^+BF_4^-]/10^3M.$	2.0	2.0
k_1 /min^{-1}	0.15	0.14
% Conversion	14*	64.5
DP	6.6‡	17.6
% Cyclic Dimer	4.7	-
X	58	43
Induction period/min	21	11

* Calculated assuming contraction for 1,3-dioxolan equals that of 1,3-dioxepan.

‡ Actual conversion 26% at 10.7°.

X = % of reaction which is of first order.

This calibration is also influenced by the error due to the mid-point method (see Chapter 2) but less than in the polymerisation experiments. The data are in Table 5.4. and the calibration graph is given in Fig. 5.8.

5.2.5. The Effect of Temperature

As the actual concentration of active centres is not known, Arrhenius values do not mean much. The activation energy for the polymerisation of 1,3-dioxolan by anhydrous perchloric acid was found to be 5.5 kcals/mole[5]. If the propagation is a ring opening rather than a ring-expansion the activation energy of the former maybe higher than the latter, therefore an approximate value of the activation energy is useful. Two runs (110 and 111) were made at temperatures other than 25°. Using the calculated catalyst concentration, an Arrhenius plot was constructed. The activation energy was found to be 8.9 kcals/mole. This is an approximate value but does give the order of magnitude.

5.2.6. Polymerisation of 1,3-Dioxepan by Triethyloxonium Tetrafluoroborate

The polymerisation of 1,3-dioxepan has the same characteristics as that of 1,3-dioxolan with $Et_3O^+BF_4^-$ except that 1,3-dioxepan polymerises a little faster. Experiment 93 (Table 5.7.) was killed at 10.7° so that a high yield[5] of the cyclic dimer could be obtained.

$$k_1/c = 75 \text{ lmole}^{-1} \text{ min}^{-1} \text{ at } 25^\circ$$

5.2.7. The Polymerisation of 1,3-Dioxolan with other catalysts

Since the conductivity change[7] observed is due to the decomposition[16] of $Et_3O^+BF_4^-$ to boron trifluoride etherate and ethyl

Table 5.8.

Polymerisation of 1,3-Dioxolan by other Catalysts at 25°

Run No.	108	148	182	130	132
$[\text{Monomer}]$/M.	4.0	8.4	3.0	3.0	3.0
$[BF_3Et_2O]/10^3$M.	8.0	-	-	-	-
$[EtF]/10^3$M.	-	5.1	-	-	-
$[Ph_3C^+BF_4^-]/10^2$M	-	-	1.0	-	-
$[Et_3O^+SbF_6^-]/10^3$M.	-	-	-	8.0	0.1
% Conversion	17.5*	-	48.7	46	44.5
DP	8.9*	-	17.7	19.9	23.2
Polymerisation time/h	24	-	-	-	-
Induction period/h	2.8	-	0.25	-	0.16
κ_o /$\mu\Omega^{-1}$ cm^{-1}	0.062	0.09	150	-	4.26
κ_b /$\mu\Omega^{-1}$ cm^{-1}	0.14	-	1.22	-	4.26
κ_m /$\mu\Omega^{-1}$ cm^{-1}	0.27	-	1.24	-	4.26
κ_f /$\mu\Omega^{-1}$ cm^{-1}	0.13	-	1.1	-	2.2
k_1 /mins^{-1}	-	-	0.09	-	0.34
X	-	-	26	-	92

κ_b = specific conductivity at the time polymerisation began.

κ_m = maximum specific conductivity.

* killed at +55° but did reach equilibrium at 25°.

fluoride, it was necessary to check that neither of those compounds polymerised 1,3-dioxolan at the same rate. Details of these experiments are in Table 5.8.

With boron trifluoride etherate, polymerisation began after an induction period of 2.8 hours and eventually reached equilibrium after 24 hours. An equivalent polymerisation with $Et_3O^+BF_4^-$ would have finished within an hour. The conductivity was measured during the polymerisation. These are the first conductivity measurements made on this system. The initial specific conductivity was 0.062 $\mu\Omega^{-1}$ cm^{-1} which rose steadily to 0.14 $\mu\Omega^{-1}$ cm^{-1} when polymerisation started. It reached a maximum at $\kappa = 0.27\ \mu\Omega^{-1}$ cm^{-1} and at the end had dropped to 0.13 $\mu\Omega^{-1}$ cm^{-1}.

The rate constant was not determined.

The reaction mixture was then depolymerised at 60°. The specific conductivity was 0.3 $\mu\Omega^{-1}$ cm^{-1} at 25°.

Then the solution was allowed to equilibrate at +55° before it was killed with ammonia. A low polymer (DP = 8.9) could be isolated. Examination by infrared spectroscopy showed the polymer to have the same spectrum as a polymer made by $Et_3O^+BF_4^-$ catalysis. Thus a polymer made with boron trifluoride etherate also, apparently, has no end-groups.

Ethyl fluoride does not polymerise 1,3-dioxolan.

One of the products from the reaction of $Et_3O^+BF_4^-$ with 1,3-dioxolan in methylene dichloride solution is dioxolonium tetrafluoroborate. Therefore, catalysis by this compound had to be considered. It can be formed "in situ" by the reaction of

1,3-dioxolan with triphenylmethyl tetrafluoroborate. Meerwein[17] had shown that this reaction is almost quantitative. The yield of

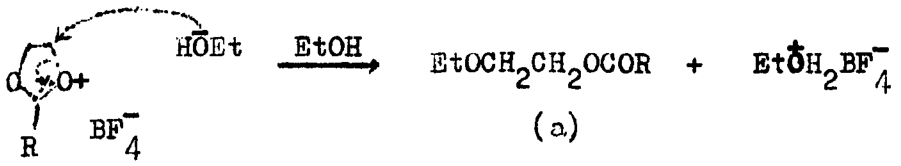
dioxolenium tetrafluoroborate was 88% and the salt precipitated from the reaction mixture. Also, Westermann[5] showed that triphenylmethane was produced in 80% yield when triphenylmethyl perchlorate was reacted with 1,3-dioxolan.

In a previous attempt[5] to polymerise 1,3-dioxolan with dioxolenium tetrafluoroborate low temperatures and low catalyst concentrations were used. Under these conditions perchloric acid polymerises 1,3-dioxolan rapidly but $Et_3O^+BF_4^-$ would not have polymerised 1,3-dioxolan.

Therefore in experiment 182, 3M 1,3-dioxolan was dosed with 10^{-2}M $Ph_3C^+BF_4^-$. κ_0 was about $150\mu\Omega^{-1}$ cm^{-1}, the value dropped quickly to $1.45\mu\Omega^{-1}$ cm^{-1} after 6 mins. The change in conductivity occurred simultaneously with a change from yellow to colourless and the formation of a white precipitate which is dioxolenium tetrafluoroborate.

After polymerisation the mixture was depolymerised by warming it to 50° for 30 mins. The white crystals dissolved and the solution turned slightly yellow. The repolymerisation was fast, as expected, but it was still possible to record the last 20% of the reaction. Although there was some contraction due to the temperature change the contraction observed was 3cm which is greater than the effect due to temperature, The reaction was complete in 10 mins. and the first order rate constant (k_1) was 0.75 min^{-1}. The value of k_1 for the first polymerisation was 0.09 min^{-1}. The rate was presumably greater because more active centres were formed when the dioxolonium tetrafluoroborate dissolved on heating, but [illegible] only increased from 1.1 to 1.4 [illegible]$^{-1}$ cm^{-1}.

Ethanol reacts with dioxolonium salts by the following reaction[18]:



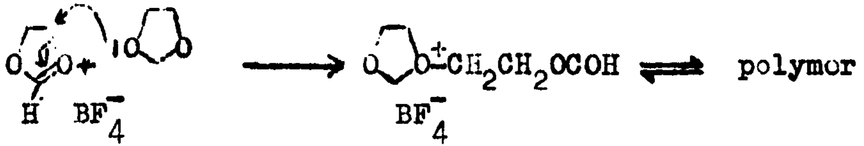
5.1.

Therefore, the polymerisation mixture was stabilised at 25° and killed with ethanol. A sample of this solution was analysed by g.l.c. for 2-ethoxyethyl formate (i.e. (a) when R = H) and this was found to be absent. A 4×10^{-3}M solution of 2-ethoxyethyl formate in the reaction mixture was analysed by g.l.c. and the peak due to 2-ethoxyethyl formate was observed. Therefore, the dioxolonium ion was absent in the final polymerisation mixture. This test is not completely conclusive for the absence of the dioxolonium ion since Meerwein[18] had demonstrated reaction 5.1. for R = Me or Et. However, since sodium iodide[18] does react in an analogous manner with dioxolonium salts when R = H, Me or Et, the extrapolation of reaction (1) to R = H seems reasonable.

The polymer was isolated in the usual way. Some white crystals were present in the product. The polymer would not dissolve in 95% ethanol, therefore, a quantitative measurement of the triphenylmethane by u.v. spectroscopy was not possible. The triphenylmethane was slowly sublimed from the polymer at 50°/12 torr. The product was dissolved in 95% ethyl alcohol. The u.v. spectrum of this solution was identical with the u.v. spectrum of pure triphenylmethane in 95% ethyl-alcohol. By means of the extinction coefficient^{19}, λ_{max} (log ε) = 262.5 (2.92) the yield of triphenylmethane was estimated to be 70%.

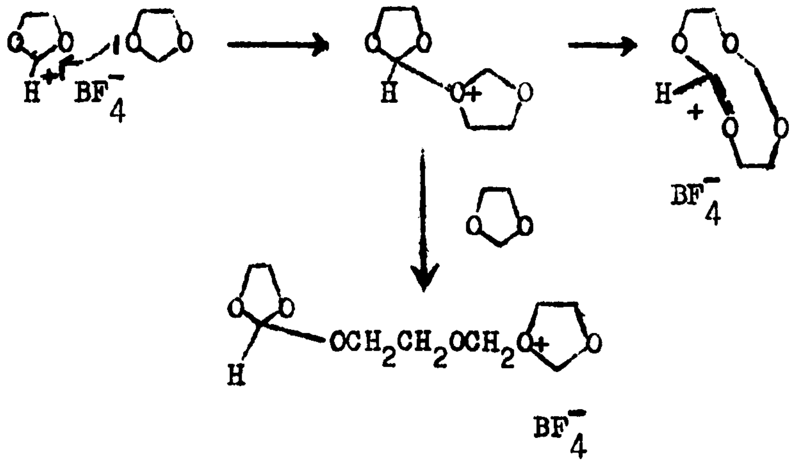
The infrared spectrum of the polymer was identical with the infrared spectrum of poly-1,3-dioxolan prepared by other catalysts. There was a small band at 3,500 cm^{-1} due to an OH group. There was no evidence in the N.M.R. or infrared spectra for triphenylmethyl groups.

Two mechanisms can be written for the polymerisation of 1,3-dioxolan by dioxolenium ions. These are possible but it must be remembered that initiation by some species other than this ion is not excluded. Since the rate of polymerisation was increased when the dioxolenium salt dissolved, initiation by this compound has to be considered.



(A)

5.2.



5.3.

5.4.

(B)

The Simultaneous Plots of Conversion and Conductivity against Time

Fig. 5.10. Catalyst: $Ph_3C^+BF_4^-$ (Table 5.8.)

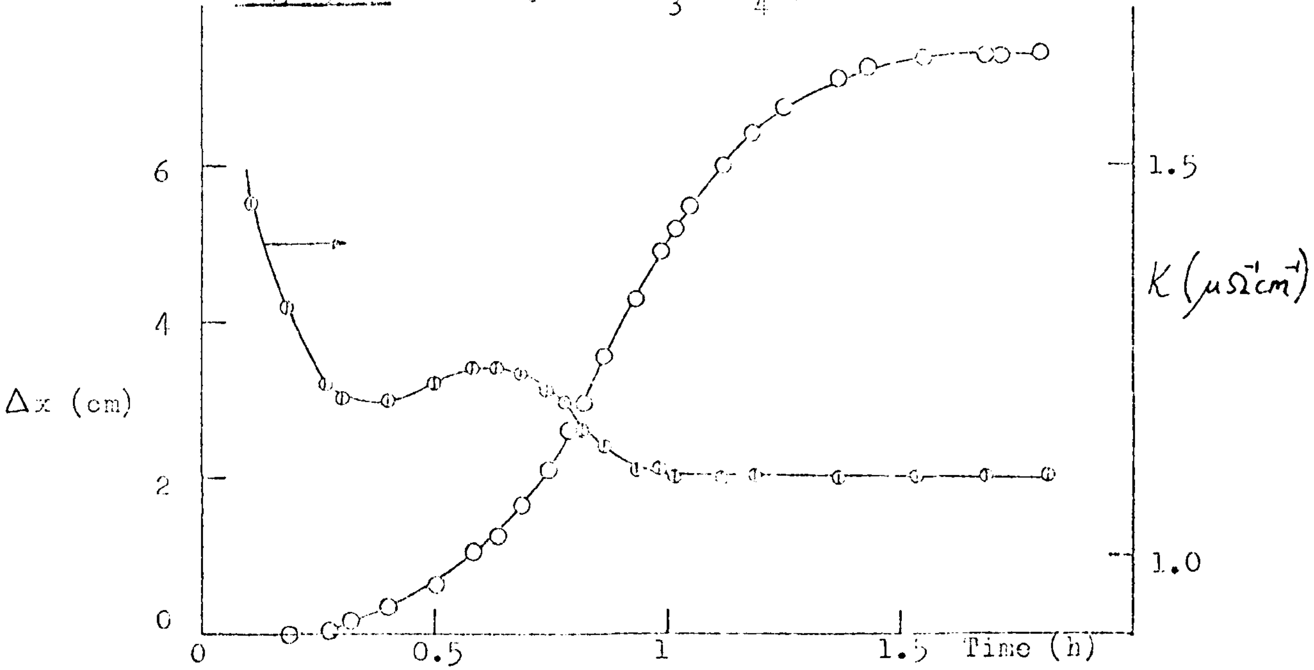
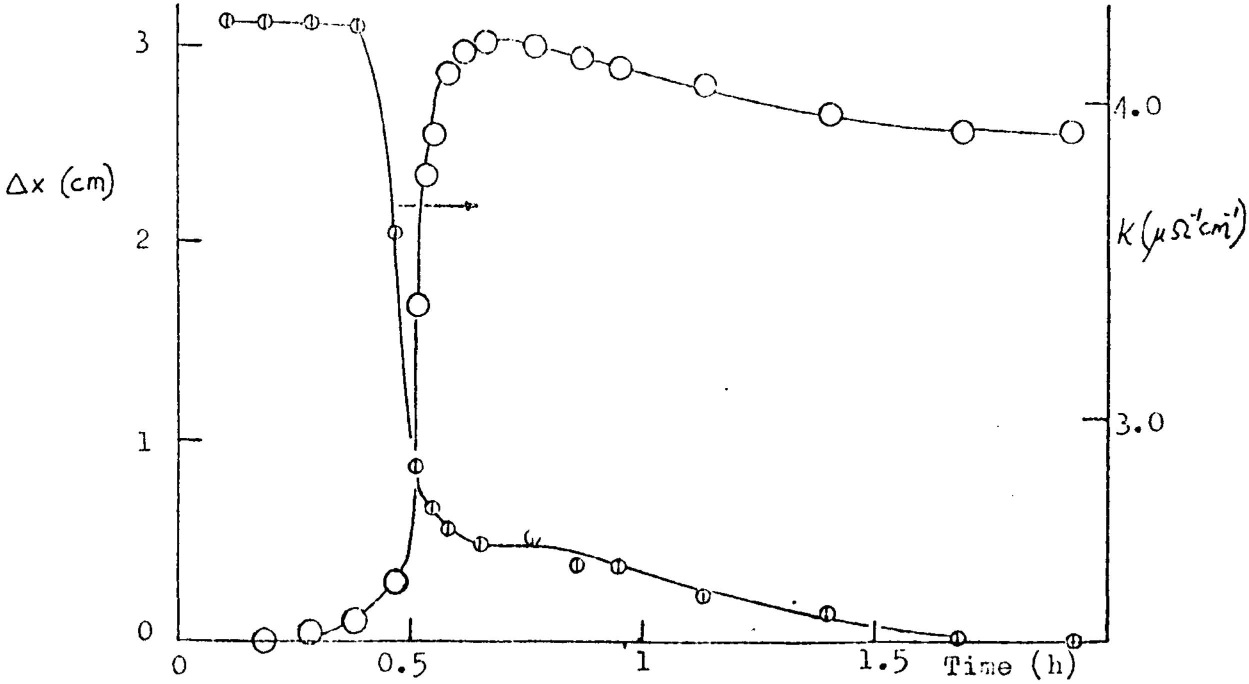


Fig. 5.11. Catalyst: $Et_3O^+SbF_6^-$ (Table 5.8.)



(A) and (B) could propagate to form polymer by the ring-expansion mechanism. As no carbonyl groups were visible in the infrared spectrum, route 5.2. is unlikely. The concentration of dioxolenium tetrafluoroborate was 10^{-2}M; therefore, if all the catalyst had formed a carbonyl group, it would have been observed in the I.R. spectrum.

Triethyloxonium hexafluoroantimonate polymerises 1,3-dioxolan much faster then $Et_3O^+BF_4^-$ and $k_1/c = 3.4 \times 10^3$ lmole^{-1} min^{-1}. The polymerisation did not go to equilibrium as shown by a low yield of polymer. The conversion curve (Fig. 5.11.) shows that the meniscus began to rise after the maximum contraction was reached. The reason for this is not known.

The conductivity was steady before and after polymerisation indicating the greater stability of this salt. Gas chromotagraphy showed that neither ethane nor ethyl fluoride were produced.

When 8 X 10^{-3}M $Et_3O^+SbF_6^-$ was used the solution turned yellow after 24 hours (the polymerisation was complete in a few minutes). The visible spectrum of this solution had a maximum at 746 nm. Colour formation[20] has been noticed before when the SbF_6^- salts were used to polymerise tetrahydrofuran.

However, with a reaction rate of this magnitude, the polymerisation of cyclic formals by $Et_3O^+SbF_6^-$ can be studied at lower temperatures. In this way side reactions, which prevent the equilibrium being set up and which produce coloured products, could probably be made negligible at these temperature. Therefore, a study of this system at low temperatures should lead to a clearer understanding of the polymerisation of cyclic formals.

5.2.8. The Rate Constants for the Polymorisation of Cyclic Formals

Various values of the propagation rate constant (k_p) for 1,3-dioxolan are recorded in the literature (Table 5.10.). In this section k_p for the polymerisation of 1,3-dioxolan by $Et_3O^+BF_4^-$ is estimated and compared with the other values cited.

An estimate of the concentration of active centres (c_a) in the polymerisation of 1,3-dioxolan by $Et_3O^+BF_4^-$ can be made from the final conductivity (κ_f) which is reached after decomposition is complete. Several assumptions have to be made to do this.

(1) That $Et_3O^+BF_4^-$ has decomposed to non-conducting products.

(2) That despite the presence of the dioxolenium ion, the concentration of active centres, c_a, can be calculated from κ_f.

(3) That the conductance parameter of $Et_3O^+BF_4^-$ in methylene dichloride can be extrapolated to the polymerisation solution. The effects of the size of the polymeric cation, of solvation and of the change of dielectric constant make this a tentative extrapolation. Since it was not possible to determine the conductivity of $Et_3O^+PF_6^-$ in 1M diethyl ether the parameters for $Et_3O^+BF_4^-$ in methylene dichloride are used as a first approximation.

(4) That the total concentration of ions is such that ion-pair formation can be neglected.

In Chapter 7 it will be seen that the equivalent conductivity at infinite dilution, Λ_{02}, for $Et_3O^+PF_6^-$ in methylene dichloride at 0° is $118.53\,\Omega^{-1}$ cm^2 mole^{-1}. From the crystallographic radii of the BF_4^- and the PF_6^- ions the value of Λ_{02} for $Et_3O^+BF_4^-$ can be

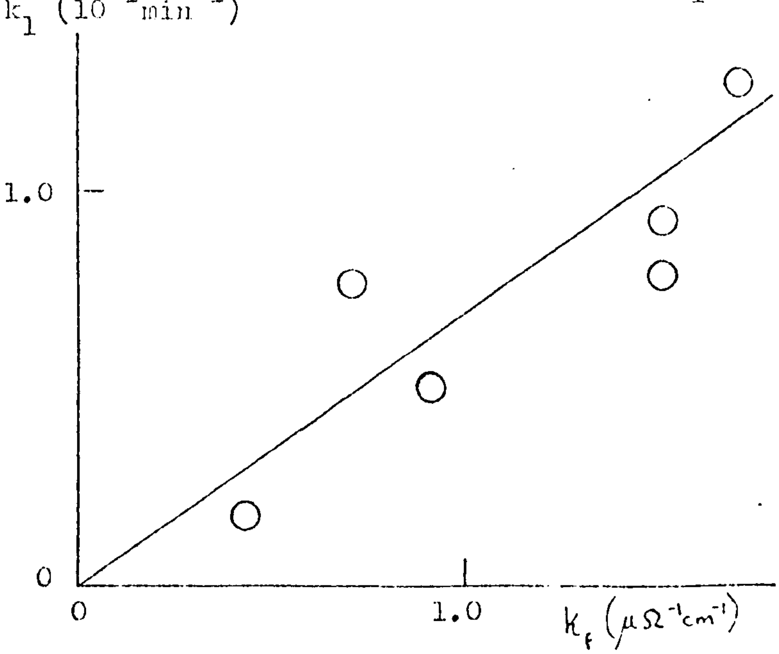
Table 5.9.

Values of k_1 and K_f for the Polymerisation of 1,3-Dioxolan by $Et_3O^+BF_4^-$

Run No.	105	105A	104	102	115	106
k_1 /min^{-1}	0.018	0.018	0.077	0.05	0.092	0.127
K_f/ Ω^{-1} cm^{-1}	0.42	0.42	0.7	0.9	1.5	1.7

Fig. 5.12.

The Plot of k_1 against K_f



computed from Stokes Law, and this gives $\Lambda_{02} = 136\Omega^{-1}$ cm^{2} mole^{-1}.

Fig. 5.12. shows the plot of k_1 against κ_f. From this $\kappa_f = 1.3\mu\Omega^{-1}$ cm^{-1} when $k_1 = 0.1$ min^{-1}. Therefore the concentration of active centres is

$$c_a = 10^3\kappa_f / \Lambda_{02} = 10^{-5}M. \qquad 5.5.$$

Furthermore, experiments 132 ($Et_3O^+SbF_6^-$) and 105A ($Et_3O^+BF_4^-$) show that the conductivity is approximately halved by the change of viscosity and the increased size of the cation which occurs during polymerisation. Therefore, the specific conductivity due to the monomeric active centres κ_a is about 2 x κ_f. Therefore, from equation 5.5. c_a is approximately 2 x 10^{-5}M.

But $k_p = k_1 / c_a$

From $k_1 = 0.1$ min^{-1} and $c_a = 2 \times 10^{-5}$M, $k_p = k_1 / c_a = 5 \times 10^3$ lmole^{-1} min^{-1}

Experiment 105A was a repolymerisation after the conductivity had dropped to a minimum; therefore, since κ_a is known experimentally no viscosity correction is required, and in this case

$k_1 = 1.8 \times 10^{-2}$ min^{-1} and $\kappa_o = \kappa_a = 0.57\mu\Omega^{-1}$ cm^{-1}.

Therefore, $c_a = 0.53 \times 10^{-5}$M and $k_p = k_1 / c_a = 3.4 \times 10^3$ lmole^{-1} min^{-1}.

The two calculated values of k_1 / c_a agree closely with the $k_p = 1.26 \times 10^3$ lmole^{-1} min^{-1} determined by Westermann[5] with perchloric acid at 25°. If the mechanism for the polymerisation of 1,3-dioxolan is that proposed by Plesch and Westermann[3] (ring-expansion by secondary oxonium ions with $HClO_4$) and not that proposed by Jaacks[29] (linear propagation by tertiary oxonium ions - see Chapter 10) then if we assume that k_p for our tertiary oxonium ions and that for the secondary oxonium ions in Westermann's[5] system should be very similar, this agreement shows that our assumptions are realistic. On the other hand, if we assume the validity of our assumptions, the results indicate that the k_p for secondary and tertiary oxonium ions are very similar. Further evidence for the last point is that $k_1/c_a = 3.4 \times 10^3$ lmole^{-1} min^{-1} for the polymerisation of 1,3-dioxolan by $Et_3O^+SbF_6^-$ (experiment 132) is also very close to the k_p determined by Westermann[5].

The above calculations are based on the assumption (2) that the dioxolenium ion makes only a small contribution to $\mathcal{K}_f$ and this will be discussed later.

On page 90 we saw that k_1/c_a determined from the plot of $\mathcal{K}_f$ against k_1 (Fig. 5.12.) where k_1 was determined from a polymerisation at high total ion concentration and k_1/c_a determined from experiment 105A (Tables 5.9. and 5.2.) which was a repolymerisation at low total ion concentration, are similar. Also the values of k_1 from 105 at high total ion concentration and k_1 from 105A at low total ion concentration are the same. Now in the experiments used for the plot of $\mathcal{K}_f$ against k_1 the catalyst concentration c was about 10^{-2}M and from the association constant K_2 we can calculate that the corresponding concentration of free ions, c_i, is 2×10^{-4}M (see Chapter 7 for the procedure), whereas c_a which is equal to the total ion concentration (assumptions 1 and 2), in experiment 105A was only 5×10^{-6}M and under these conditions $c_i = 3 \times 10^{-6}$M.

Therefore in most of the polymerisation most of the active centres were ion-pairs whereas in 105A most of the active centres were free ions. Since the plots of k_1 against c (Fig 5.7.) and of k_1 against κ_f (Fig. 5.12.) are linear, and since k_1 (105) is equal to k_1 (105A), and since the rate constants for successive repolymerisations (Table 5.2.), after further decomposition of $Et_3O^+BF_4^-$ had occurred, were the same, it follows that the propagation rate constant for ion-pairs must be approximately the same as that for free ions; in other words the solvated oxonium ion propagates at about the same rate regardless of whether it is paired or free.

Experiment 182 has shown that dioxolenium tetrafluoroborate can polymerise 1,3-dioxolan. Therefore, since κ_f of the polymerisations catalysed by $Et_3O^+BF_4^-$ depends on the contributions from both the dioxolenium and possibly the 1-ethyl-1$\underline{H}^+$-1,3-dioxolanium ions we need to decide which of these is the actual initiator in the polymerisations catalysed by $Et_3O^+BF_4^-$.

If we estimate the concentration of dioxolenium tetrafluoroborate c_d, it will help us decide whether the dioxolenium ion plays an important part in the initiation of the polymerisation.

In experiment 122 ($T > T_c$) where c was 10^{-2}M $Et_3O^+BF_4^-$, the concentration of ethane could be estimated from the height of the g.l.c. peak. From a calibration with gaseous ethane we could estimate that 2×10^{-3} mmoles were produced from 21.4 mls of the reaction mixture. That is, the concentration of dioxolenium tetrafluoroborate, c_d, was about 10^{-4}M at the start of the reaction. In experiment 115 ($c = 1.2 \times 10^{-2}$M) c_d was about 2×10^{-4}M. Therefore in experiment 115 where $k_1 = 0.08$ min^{-1}, $k_1/c_d = 4 \times 10^2$ lmole^{-1} min^{-1}. Since k_1/c_d is less than k_1/c_a it appears that in this experiment initiation cannot be solely due to the dioxolenium ion and that it may be due to both the dioxolenium and the 1-ethyl-1$\underline{H}^+$-1,3-dioxolanium ions. On the other hand, since c_d is greater than c_a the dioxolenium ion may have decayed to non-conducting products and therefore making assumption 2 (page 89) reasonable. The results of experiment 182 in which 10^{-2}M dioxolenium tetrafluoroborate was the catalyst, κ_f for the repolymerisation was only $1.3\mu\Omega^{-1}$ cm^{-1} and there was no unreacted catalyst present (section 5.2.7.). Moreover, $k_1/c_a = 4 \times 10^3$ lmole^{-1} min^{-1} calculated from κ_f and k_1 (where $c_a = 2 \times 10^{-5}$M) was of the same order of magnitude as k_p (page 90) so that according to conductivity measurements only a small proportion of the catalyst was converted into active centres which propagate at the expected rate.

As well as this the polymerisation of 1,3-dioxolan by $Et_3O^+SbF_6^-$ (132) gave a value of k_1/c of the same order of magnitude as that for the polymerisation of 1,3-dioxolan by perchloric acid. Therefore since $Et_3O^+SbF_6^-$ polymerises 1,3-dioxolan at a greater rate than $Et_3O^+BF_4^-$ without the formation of ethane, I believe the active centre in the polymerisation of cyclic formals by triethyloxonium salts to be the 1-ethyl-1$\underline{H}^+$-1,3-dioxolanium ion and not the dioxolenium ion.

In an analogous process, Tobolsky[28] has shown that the initiating species in the polymerisation of tetrahydrofuran by $Et_3O^+BF_4^-$ is the 1-ethyl-1$\underline{H}^+$-tetrahydrofuranium cation. Therefore the initiation of the polymerisation of 1,3-dioxolan by 1-ethyl-1$\underline{H}^+$-1,3-dioxolanium ion is quite reasonable.

Table 5.10.

The Rate Constants for the Polymerisation of Cyclic Formals

Monomer	Catalyst	k_1/c	k_1/c_a	T	Reference
		l mole^{-1}	min^{-1}	°C	
1,3-dioxolan	$HClO_4$	$1.26 \times 10^{3*}$	-	25	Westermann[5]
"	$Et_3O^+BF_4^-$	9.5	3×10^3	25	This work[7]
"	$Et_3O^+BF_4^-$	2.6	-	30	Yamashita[6]
"	$Et_3O^+SbCl_6^-$	75 (5.1)‡	-	20	Luydvig[13]
"	$Et_3O^+SbF_6^-$	3.4×10^3	-	25	This work
1,3-dioxepan	$HClO_4$	$1.9 \times 10^{5*}$	-	0	Westermann[5]
"	$Et_3O^+BF_4^-$	75	-	25	This work

c = total concentration of initiator

c_a = concentration of active centres

* These are very probably k_1/c_a values, as the initiating efficiency of $HClO_4$ appears to be very great.

‡ See section 5.1. for the explanation of the two values.

5.2.9. The Rate Constants reported by other Workers

The published rate constants for the polymerisation of the cyclic formals are shown in Table 5.10. Since the value of k_1/c_a ($Et_3O^+BF_4^-$) is approximately equal to the value of k_p ($HClO_4$) determined by Westermann[5] for the polymerisation of 1,3-dioxolan, the k_p's of Westermann for 1,3-dioxolan and 1,3-dioxopan are the most reliable in the literature.

For reasons which have already been discussed Yamashita's[6] value for k_p is invalid. Similarly, Lyudvig's[13] value of k_p (1,3-dioxolan) is subject to the same errors, because $Et_3O^+SbCl_6^-$ decomposes in a way similar to $Et_3O^+BF_4^-$:

$$Et_3O^+\ SbCl_6^- \longrightarrow EtCl + SbCl_5 + Et_2O$$

However, whereas $BF_3.Et_2O$ is an inefficient catalyst, Westermann[5] has shown that $SbCl_5$ polymerises 1,3-dioxolan rapidly without an acceleration period. The system did not go to equilibrium and a second addition of catalyst caused a further polymerisation which still did not reach equilibrium. The polymer contained chlorine. Moreover, Lyudvig observed a polymerisation without an acceleration and she explained it by assuming that her monomer was much drier than that used by others[21]. It appears that the true initiator of Lyudvig's polymerisation may have been $SbCl_5$ and that the rate determining step was the decomposition of the salt.

5.3. Analysis of Reaction Mixtures

As shown in this Chapter, the polymerisation of 1,3-dioxolan by $Et_3O^+BF_4^-$ is characterised by the decay of the catalyst to non-ionic species. This section deals with the results which led us to believe that the main reaction is the spontaneous but incomplete decomposition of $Et_3O^+BF_4^-$ to ethyl fluoride and boron trifluoride etherate.

5.3.1. Gas Liquid Chromotography of Poly-1,3-Dioxolan and Related Solutions (Tables 5.11. to 5.13.)

Samples of the reaction products of experiment 90 were sealed off under vacuum and then analysed by gas chromotography. 90B was not killed but opened at 20° and injected into the chromatograph. 90C was depolymerised, killed with diethylamine at 66° ($>T_c$) and then a sample injected into the chromatograph (Table 5.11.).

A comparison of the chromatograms of 90B, 90C and 1,3-dioxolan at column temperatures of 60° and 100°, respectively were made. There was no consistency between the size and the number of the peaks which followed the monomer. In 90B, at 100°, there is a peak with a retention time of about 9 mins. When the sample size was doubled this peak increased fourfold. In 90C, where no polymer was present the peak with a retention time of 9 mins was absent which suggests that it is formed by decomposition of the polymer. The retention time is too short for it to be the dimer, and the dimer of 1,3-dioxolan has never been isolated from a polymerisation mixture. The other peaks present in the chromatograms are very small and only occur as bumps in the base line. They also appear in the monomer but at slightly different retention times.

At 60°, for 90B, there was a peak with a retention time of 28 mins. This peak may be the same one which was observed at 100°, since it was also absent from the chromatogram of 90C. The

Table 5.11.

The Peaks observed in the Gas Chromatograms of Polymerisation Mixtures of 1,3-Dioxolan

Sample	CT °C	KA	Retention Times (mins)								
D	100	-	1.8 (4.6)	2.2 (2.6)	3.2 $(4\mathrm{x}10^{4})$	12 (6)	14 (1.3)	17 (0.1)			
CH_2Cl_2	100	-	-	2.2	-	-	-	-			
90B (1µl)	100	-	-*	2.2 $(1.3\mathrm{x}10^{4})$	3.2 $(3.5\mathrm{x}10^{3})$	9.4 (4)	11.4 (0.1)	13 (0.2)	22 (0.1)		
90B (2µl)	100	-	-*	2.2 $(2.1\mathrm{x}10^{4})$	3.2 $(5.5\mathrm{x}10^{3})$	9 (30)	11 (0.05)	13 (0.3)	15 (0.05)	19.4 (0.1)	23.4 (2.1)
90C	100	Et_2NH	1.9 (10.2)	2.4 $(2.2\mathrm{x}10^{4})$	3.5 $(1.1\mathrm{x}10^{4})$	11 (0.5)	12 (0.5)	13.2 (0.1)	18 (5.3)		
Et_2NH					3.4						
D	60	-	2.6‡ (0.3)	3.6 (1.7)	5.9 $(1.8\mathrm{x}10^{4})$	20 (0.05)	25 (0.1)	31 (110)			
90B	60	-	-*	3.8 $(1.6\mathrm{x}10^{4})$	7 $(4\mathrm{x}10^{3})$	14 (0.1)	28 (10.5)	36 (0.2)			
90C	60	Et_2NH	1.8 (4.5)	3.2 $(1.6\mathrm{x}10^{4})$	5.9 $(6.3\mathrm{x}10^{4})$	17 (0.1)	24 (0.1)	31 (0.5)	38 (0.1)		
Et_2NH	60	-			4.4						
EtH	60	-	1.6								
90C	25	Et_2NH	2.4 (3.9)	4.5 (0.2)	7.3 $(1.4\mathrm{x}10^{4})$	15.5 $(4.6\mathrm{x}10^{3})$					
EtH	30	-	2.2								

Table 5.11.

Notes

* The early peaks were not looked for.

‡ This peak is reduced on diluting with CH_2Cl_2

( ) The figure in parenthesis is the relative height of the peak whose retention is given above. The smallest peaks were measured at an attenuation of 5 x 1 whilst that of the large peaks was 50 x 10^2 or 10^4

CT = Column temperature, which is given because the samples were injected directly into the column and the injection port temperature varies with the column temperature. The injection temperature at 100° was about 190° and that at 60° was about 140°.

KA = Killing agent.

D = 1,3-dioxolan.

Table 5.12.

The Chromatograms of $Et_3O^+BF_4^-$ Solutions in Methylene Dichloride

Sample	Retention times (mins)							
	EtH	EtF (a)	*	CH_2Cl_2 or Et_2O	BF_3Et_2O			
120/11		2	3	3.6	7.4			
($Et_3O^+BF_4^-$ after 138 h at 25°)		(2.2×10^2)	(1)	(3.6×10^4)	(1.3)			
115	1.8	2.2	3.2	4		7.4	27	38
	(3.8)	(25)	(1.7)	(2.5×10^4)		(7.2×10^3)	(4)	(0.4)
118		2.0		3.7	7.0			
($Et_3O^+BF_4^-$ after 10 mins at 25°)		(1.4)		(3×10^4)	(0.1)			
114		2.3	3.4	4.2		7.8		
($Et_3O^+BF_4^-$/D after 10 mins at 25°)		(4)	(1.7)	(4.5×10^4)		(3×10^4)		
BF_3Et_2O /CH_2Cl_2				4.6	9.3			
BF_3Et_2O /Et_2O				4.0	8.0			
"				3.6	7.4			
EtF/CH_2Cl_2		2.7		4.5				
"		2.0		3.6				

( ) The figures in parenthesis are the relative peak heights.

* Possibly Et_2O

D = 1,3-dioxolan

Column temperature = 60°

chromatogram of 90B had 6 peaks following the monomer when tested with a column temperature of 100°, whereas with the same size sample at 60°, only three peaks were observed. No other samples came off the column after a further two hours (Table 5.11.).

The chromatograms of other samples of monomer also had some small impurity peaks following it, but they were rounded and their retention times were inconsistent.

From these experiments, I conclude that decomposition of the polymer occurs in the chromatograph together with a small amount of decomposition of 1,3-dioxolan. This disagrees with the results of Miki[22] who isolated several cyclic oxygen compounds from the g.l.c. separation of poly-1,3-dioxolan solutions produced by boron trifluoride etherate. His results cannot be discarded since he used different polymerisation and chromatographic conditions.

In the early part of these chromatograms a peak with a retention time of two mins. was observed. At first it was thought to be ethane but the retention time of ethane was slightly shorter. However, it was also present in methylene dichloride solution of $Et_3O^+BF_4^-$. The other possible volatile compound was ethyl fluoride. The retention time of an authentic sample was the same, so that the unknown compound was ethyl fluoride (Table 5.12.). There was also a peak in the chromatogram of a partly decomposed solution of $Et_3O^+BF_4^-$, which corresponded to boron trifluoride etherate. Typical chromatograms of these solutions are given in Fig. 5.13.

When the vacuum sampling device, described later, was used to sample a reaction mixture containing $Et_3O^+BF_4^-$ and 1,3-dioxolan (115),

Fig. 5.13.

g.l.c.'s: I- $Et_3O^+BF_4^-$ in CH_2Cl_2

II- $Et_3O^+BF_4^-$ in 1,3-dioxolan / CH_2Cl_2

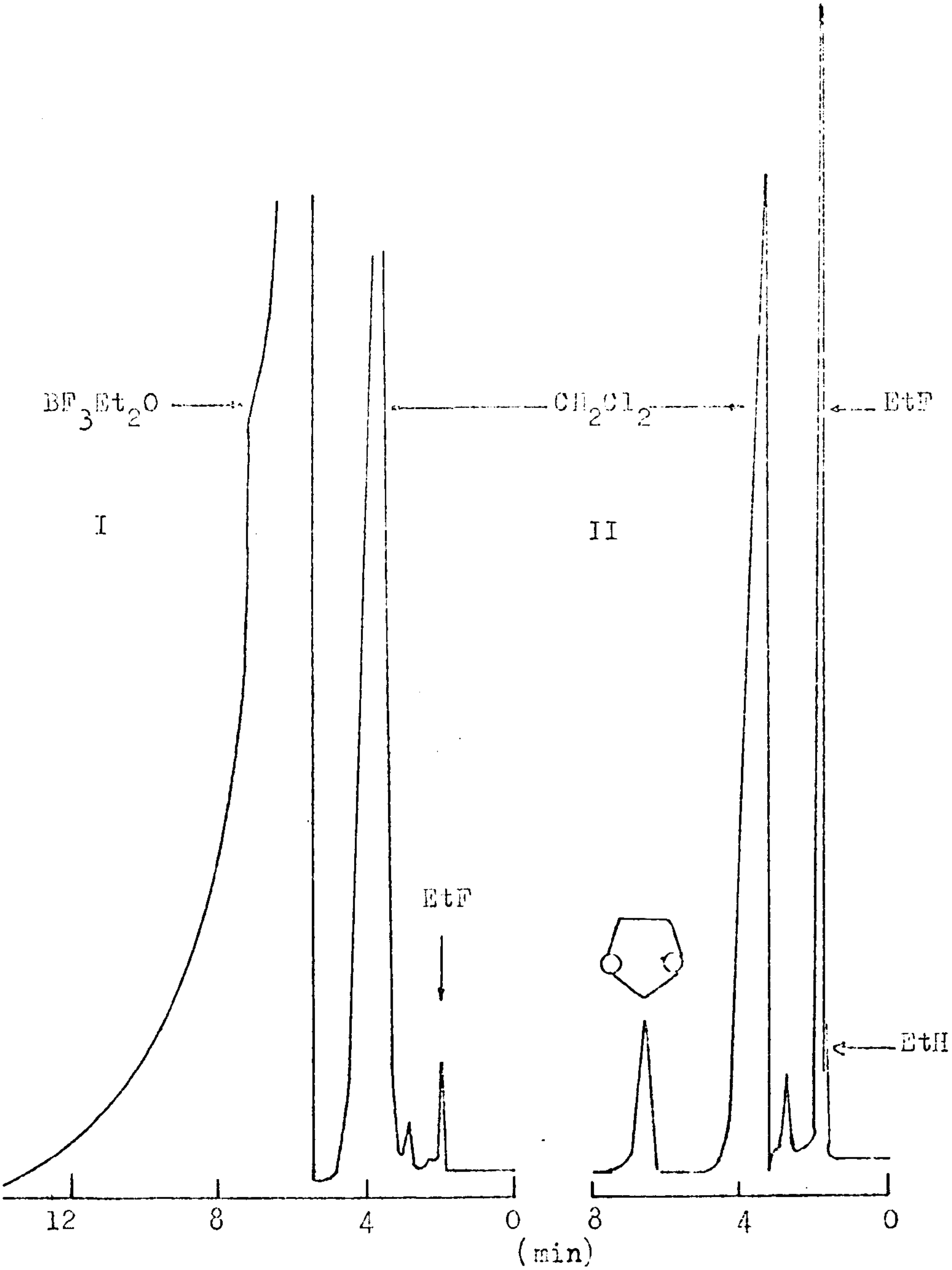


Table 5.13.

The g.l.c., at 60°, of 10^{-3}M $Et_3O^+BF_4^-$ in 1M 1,3-Dioxolan in Methylene Dichloride after standing for 3 Months at 20°

Retention time/mins	1.9[a]	2.2	2.8[b]	3.4[c]	6.4[d]
relative peak height	1.2×10^2	8.8	4×10	1.6×10^4	1.7×10^3

Retention time/mins	10	13	15	17	22.6	24.6	27	31	35
relative peak height	15	25	30	6.7	0.3	0.5	1.1	2.6	0.2

[a] is ethyl fluoride

[b] may be diethyl ether

[c] is methylene dichloride

[d] is 1,3-dioxolan

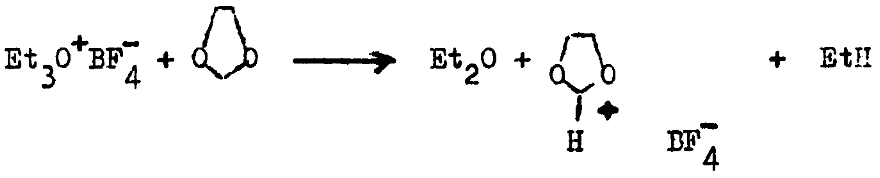
a peak at 1.8 mins was observed in the chromatogram. The retention time agreed with that of an authentic sample of ethane.

The other possibility for this peak was ethyl chloride which might have been formed by a halogen exchange reaction of ethyl fluoride with methylene dichloride. This was discounted because ethyl chloride was expected to have a longer retention than ethyl fluoride, also the exchange reaction is normally very slow and this peak was noticeable in the earliest sample analysed and its size did not increase with time. (See Table 5.16.)

Therefore, in solution $Et_3O^+BF_4^-$ decomposes

$$Et_3O^+BF_4^- \longrightarrow EtF + BF_3Et_2O$$

It also reacts with 1,3-dioxolan by hydrogen abstraction to produce dioxolonium tetrafluoroborate and ethane.



Other side reactions occur in this system as shown by the polymerisation mixtures eventually turning yellow on standing. Therefore, a 10^{-2}M solution $Et_3O^+BF_4^-$ in 1M 1,3-dioxolan in methylene dichloride was allowed to stand for three months at 20° ($> T_c$) before analysis by g.l.c. By this time it had turned brown. Table 5.13. shows that peaks at 10, 13, 15 and 17 minutes are due to other compounds which had been produced. Since this is a very complex mixture no attempt was made to isolate the compounds responsible for these peaks. However, Rozenberg[23] has isolated ethyl-

Table 5.14.

N.M.R. Data for the Decomposition Products of Triethyloxonium Tetrafluoroborate

Solvent	Compound	τ values (TMS = 10)	
		CH_3[†]	CH_2[*]
CH_2Cl_2	$Et_3O^+BF_4^-$ [a]	8.4	5.21
CH_2	$Et_3O^+BF_4^-$ [b]	8.30	5.1
CH_2Cl_2	BF_3Et_2O	8.6	5.75
CCl_4	Et_2O	8.8	6.6
CH_2Cl_2	EtF	8.76	5.64
CH_2Cl_2	Run 150	8.30; 8.5; 8.75	5.0; 5.65
CH_2Cl_2	Run 121	8.30; 8.6	5.0; 5.8;6.1

[a] Ref. 20

[b] This work

[†] triplets

[*] quartets

dichloromethane and diethyldichloromethane from a solution of $Et_3O^+BF_4^-$ in methylene dichloride which had turned brown. Although I have never observed a brown solution from the decomposition of $Et_3O^+BF_4^-$ in methylene dichloride under vacuum, brown solutions have been observed when $Et_3O^+BF_4^-$ solutions are stored in air. These homologues of methylene dichloride are presumably produced from alkylation reactions with borontrifluoride etherate and/or ethyl fluoride.

5.3.2. N.M.R. Spectra of $Et_3O^+BF_4^-$ and Related Solutions (Table 5.14.)

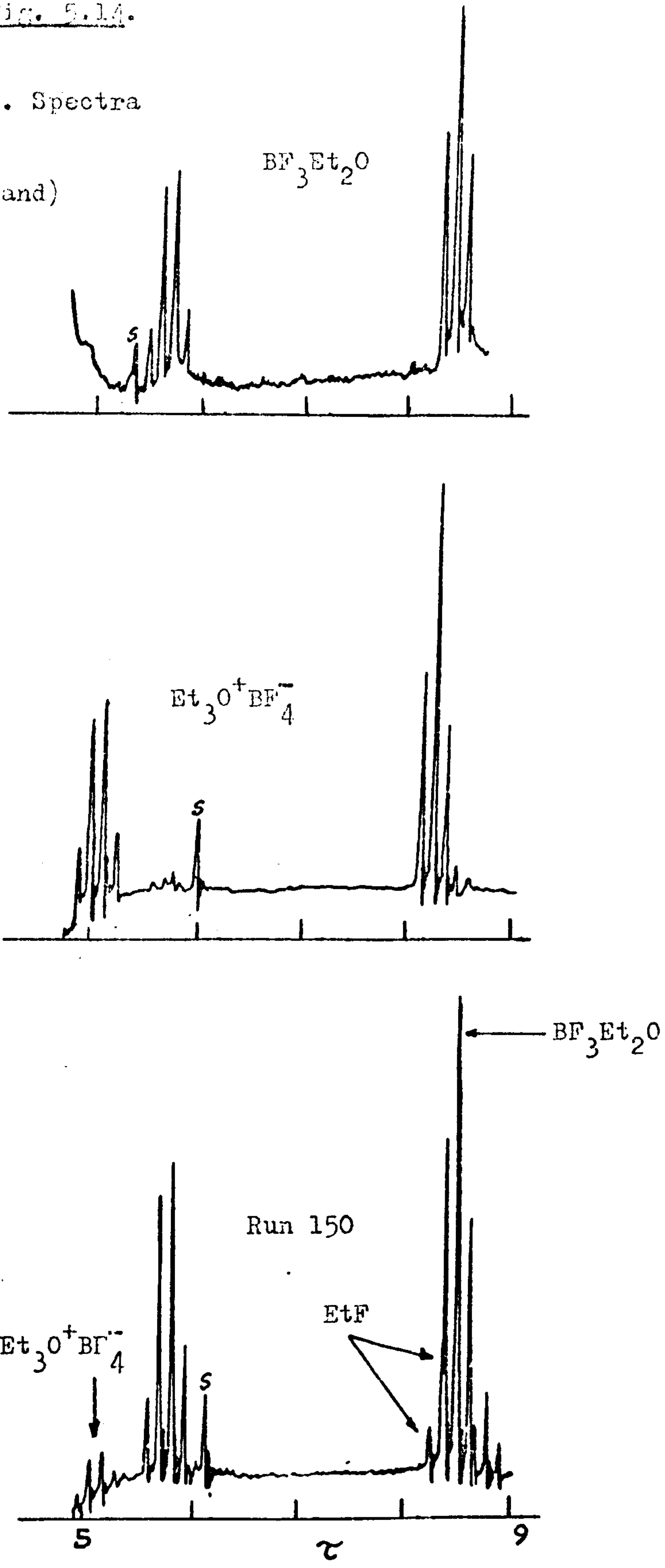
These spectra were made in N.M.R. tubes sealed to a vacuum tipping device via a pyrex-soda glass graded seal. The spectra were taken in methylene dichloride since $Et_3O^+BF_4^-$ is insoluble in carbon tetrachloride and no other solvent was available on the vacuum line. An external TMS sample was used as a standard and the methylene dichloride did not upset the spectrum of the salt unduly.

In Run 121, a 0.38M solution of $Et_3O^+BF_4^-$ in methylene dichloride was tipped, under vacuum, into a tube which was then sealed off. The spectrum was taken intermittently after storage at 35° for 4 hours. No noticeable change was observed but after one week at room temperature the spectrum had changed. The triplet at 8.3τ was much reduced in size and a new triplet appeared at 8.6τ. Similarly, the quartet at 5.0τ was reduced and a peak at 6.2τ had been formed. This showed that borontrifluoride etherate had been formed from the decomposition of $Et_3O^+BF_4^-$. Although there was a small triplet at 5.8τ there was no other evidence for ethyl fluoride. It was possible that most of the ethyl fluoride was in

Fig. 5.14.

N.M.R. Spectra

(S = spinning side band)



the vapour phase above the solution.

In Run 150 a 0.5M solution was decomposed at 70° for two hours and then tipped into the tube before sealing off. When the N.M.R. scale was expanded by two, three sets of triplets could be seen at 8.3, 8.5 and 8.75 τ, which were assigned to the methyl groups of the salt, ethyl fluoride and boron trifluoride etherate. The methylene protons of ethyl fluoride were presumably beneath the large peak due to boron trifluoride etherate and the integration also suggested this. (Fig. 5.14.)

This is further proof for the following reaction:

$$Et_3O^+BF_4^- \longrightarrow EtF + BF_3.Et_2O.$$

5.3.3. Experiments to Isolate the Products of the Reaction of 1,3-Dioxolan and Triethyloxonium Tetrafluoroborate

The rate of polymerisation of 1,3-dioxolan by $Et_3O^+BF_4^-$ was lower than expected and therefore some ionic species present in the solution were irrelevant to the polymerisation. If the chemical nature of these ionic species could be identified then the initiation could be partially solved. At this stage we thought that one of these might be the dioxolenium ion. Therefore, I decided to let $Et_3O^+BF_4^-$ react with a slight excess of 1,3-dioxolan in methylene dichloride solution under vacuum. By distilling off the solvent and monomer and adding a fresh portion of monomer solution it was hoped to increase the yield of the product which was formed. The formation of the volatile compound could be monitored by g.l.c. of the distillate. The resultant product could be analysed by N.M.R. spectroscopy or chemical means. In this way it was hoped to find out

Table 5.15.

The Attempts to Isolate Products from the Reaction of 1,3-Dioxolan and $Et_3O^+BF_4^-$ in CH_2Cl_2

Run No.	95	97	99	99A	100	100A
[1,3-dioxolan]/M.	110	1.0	1.0	1.0	4.0	2.0
[$Et_3O^+BF_4^-$]/M.	0.75[a]	0.75[a]	0.73[b]	0.36	0.11[b]	0.11
[Hexane]/M.	-	-	-	-	-	2.0
Time/h	2.5	0.5	1	1	0.5	-
Temperature/ °C	18	18	18	18	21	21

[a] $Et_3O^+BF_4^-$ was prepared at atmospheric pressure. The salt which was moist with diethyl ether was introduced into the reaction vessel and thoroughly evacuated.

[b] Vacuum prepared $Et_3O^+BF_4^-$.

whether dioxolenium tetrafluoroborate, 2-ethyl-1$\underline{H}^+$-1,3-dioxolenium tetrafluoroborate or both were formed.

However, in Run 95 (Table 5.15.) the solution turned brown when it was concentrated by distillation. The "early" peak (peak(a) Table 5.12.) was still present in the g.l.c. of the distillate.

In Run 97 (Table 5.15) the reaction time was shorter. The white crystals remaining after distillation were dissolved in methylene dichloride and tipped into a N.M.R. tube, under vacuum. The crystals had a N.M.R. spectrum identical to that of $Et_3O^+BF_4^-$. This signified that unreacted $Et_3O^+BF_4^-$ was present in the polymerisation mixture. Run 99 was a repeat of Run 95 using vacuum-prepared $Et_3O^+BF_4^-$ but the mixture still turned brown when the second addition of monomer and methylene dichloride was made.

An attempt (100) to precipitate these compounds from a polymerisation mixture with hexane failed. Hexane was added until the ceiling temperature of the solution was higher than the reaction temperature but the polymer was still precipitated.

Although these experiments were not satisfactory they did show that unreacted $Et_3O^+BF_4^-$ was present. This result is in agreement with the kinetic experiments and the analysis of the reaction solutions.

In experiments in which the monomer and solvents were removed from live polymerisations by bulb to bulb distillation, under vacuum, the polymerisation of the distillate has been observed. Very probably this can be explained as due to initiation by the volatile boron trifluoride etherate.

Table 5.16.

Sampling Experiments - $Et_3O^+BF_4^-$ in CH_2Cl_2 at 25°

Run No.	105	101	106	115*	122*	120*
[1,3-dioxolan]/M	3.0	3.0	3.0	3.0	1.0	-
$[Et_3O^+BF_4^-]/10^2M$	0.1	0.6	0.8	1.2	1.0	1.1
h_o.EtF/cm	0.6(0.3)	1.9(0.23)	1.0(0.3)	-	34(1.33)	5(0.67)
h_f.EtF/cm	2.5(23)	2.1(1.4)	3.4(50)	24.8(7)	163	223
$[EtF]_f/10^2M^a$	0.014	0.012	0.02	0.14	0.94	1.3
h_o.EtH/cm	-	-	-	1.5	1.3	-
h_f.EtH/cm	-	-	-	1.6	1.1	-
t^{I} /h	8.2	1.65	1.37	1.7	-	-

h_o is the height of the g.l.c. peak initially.

h_f is the height of the g.l.c. peak finally.

[a] calculated from h_fEtF.

[*] These experiments were carried out under vacuum (see Fig.5.15.), whilst 101, 105 and 106 were carried out in a nitrogen atmosphere (see Fig. 2.4.).

[I] Polymerisation time.

( ) Reaction time, in hours, for samples.

5.3.4. Sampling Experiments

The experiments described here were carried out to observe whether the peak (peak (a) Table 5.12.) found early in the g.l.c. varied in height throughout the polymerisation. At the time, the nature of the compound giving this peak was uncertain, but it is now known to be ethyl fluoride. In Run 101 the reactants were dosed under vacuum. After the dilatometer had been filled, the vacuum was let down to a nitrogen atmosphere so that samples could be taken through a rubber septum. During the dosing stage the rubber septum was protected by a breakseal which was broken in a stream of dry nitrogen. Runs 105 and 106 were carried out in much the same way, except that the dilatometer was isolated under vacuum, by a Teflon tap from the sampling compartment (Fig. 2.4.). Thus the polymerisation rate and the conductivity change could be observed under cleaner conditions. In these experiments the height of the ethyl fluoride peak increased slightly during the polymerisation. The final samples from 105 and 106 were taken some hours after polymerisation had ceased and when the conductivity had reached a constant minimum value.

It is obvious from the figures in Table 5.16. that the amount of ethyl fluoride measured was much less that the amount expected if the conductivity drop had been associated with the formation of ethyl fluoride.

It seemed that the probable reason for this was that most of the ethyl fluoride was in the vapour phase.

In order to prevent evaporation it was necessary to restrict

Fig. 5.15.

The Dilatometer used for Sampling under Vacuum

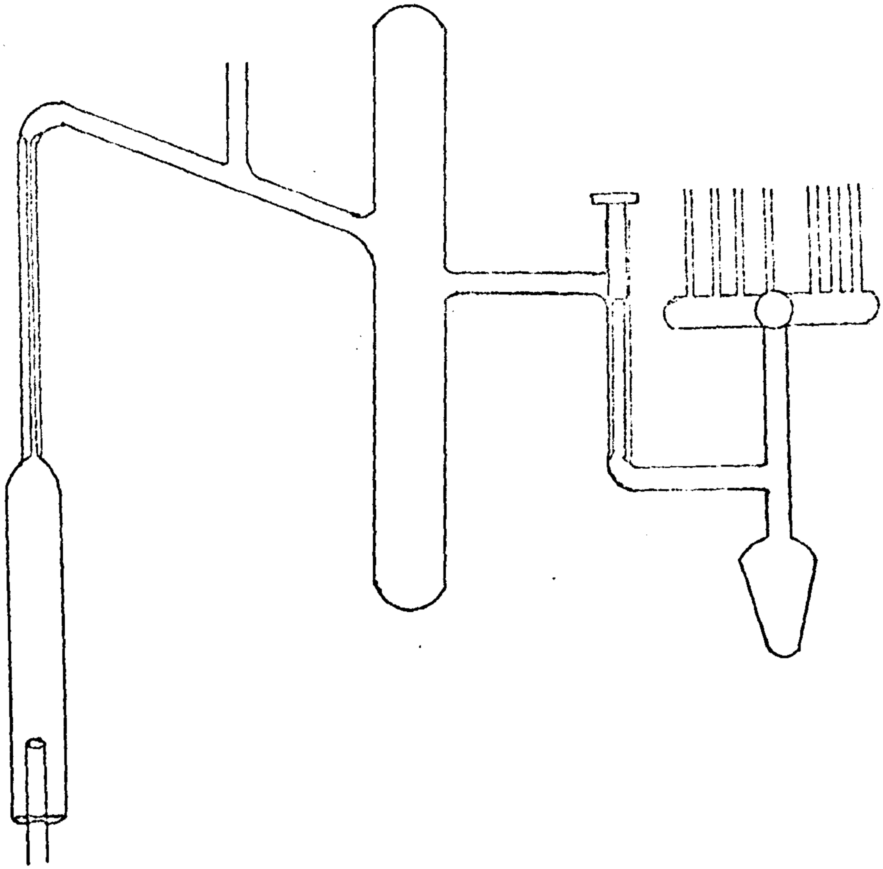
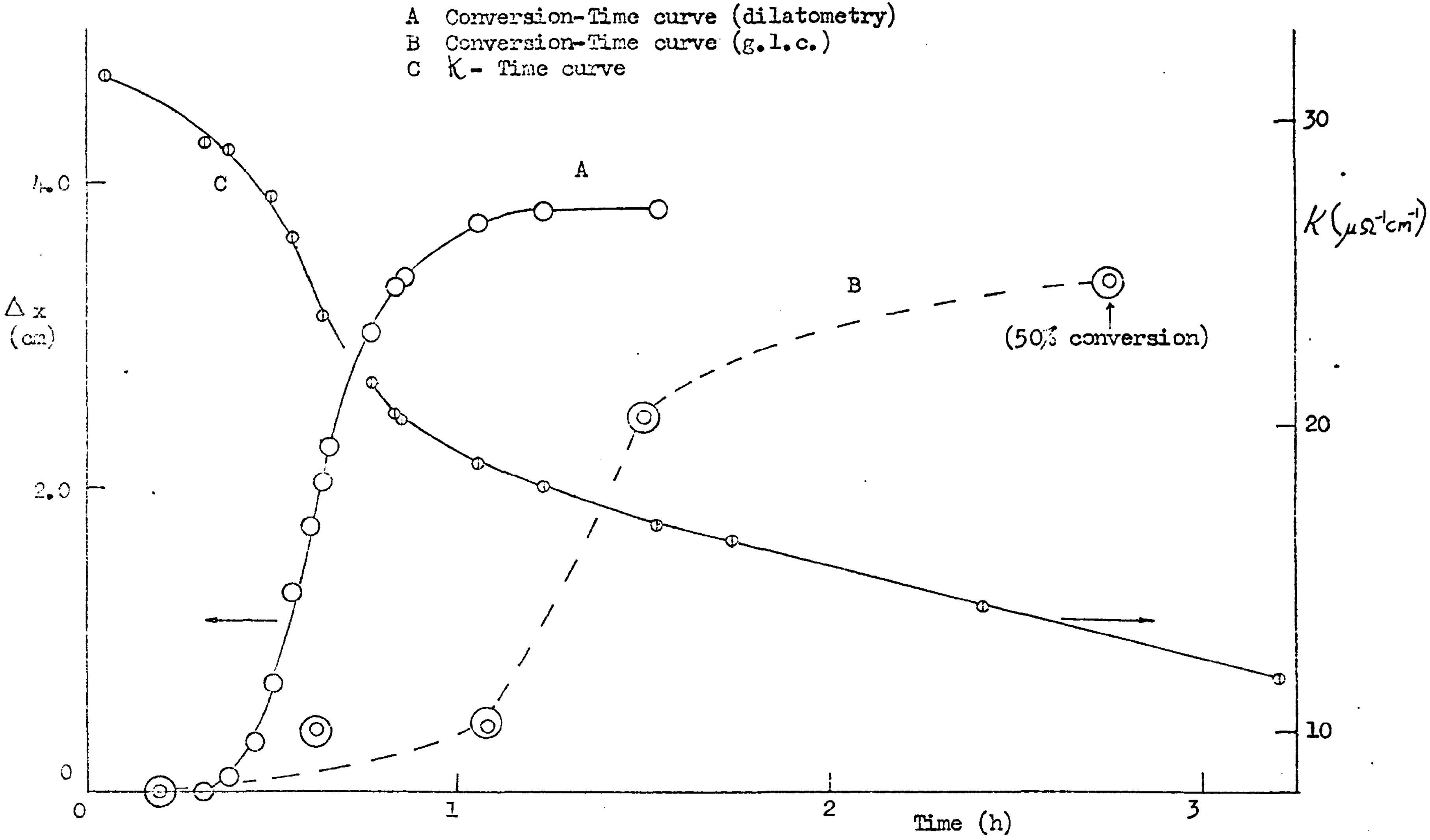


Fig. 5.16.

The Polymerisation of 1,3-Dioxolan (Experiment 115)



the vapour space above the sample. This was done by constructing a dilatometer which was attached to a tipping device via a Teflon tap (Fig. 5.15.).

The results for polymerisation 115 were obtained with this device. The procedure was as follows: the phial of $Et_3O^+BF_4^-$ was broken and the catalyst solution was mixed with the 1,3-dioxolan. Some of the solution was tipped into the tipping device. The tipping device was isolated by closing the Teflon tap. The tipping device was immersed in liquid nitrogen to freeze the solution and then sealed off. At this point the dilatometer was replaced in the bath at 25° and observations of conductance and contraction were started. The solution in the tipping device was distributed into phials which were immersed in liquid nitrogen and each phial was sealed off with a short neck. The phials were stored at 25° and opened at certain times for analysis. During the time the solution was cold it was assumed that the reaction was not continuing and this time interval was subtracted from the actual reaction time.

In this case two peaks appeared in the g.l.c. at a retention time of about two mins. (column temperature 60°). One was shown to be ethane and the other ethyl fluoride. Unfortunately, this method was not perfect as can be seen by the time lag in the polymerisation curve (Fig. 5.16.) measured by the g.l.c. technique. However, the ethyl fluoride peak was much larger than in previous sampling experiments but the final sample was taken before the conductivity had reached a steady value (Table 5.16.).

This partly explains why the concentration of ethyl fluoride

Fig. 5.17.

The Simultaneous Plots of the Height of EtF peak (g.l.c.), h_t, and the Conductivity against Time for the Decomposition of $Et_3O^+BF_4^-$ in 1M 1,3-Dioxolan in CH_2Cl_2 at 25° (run 122)

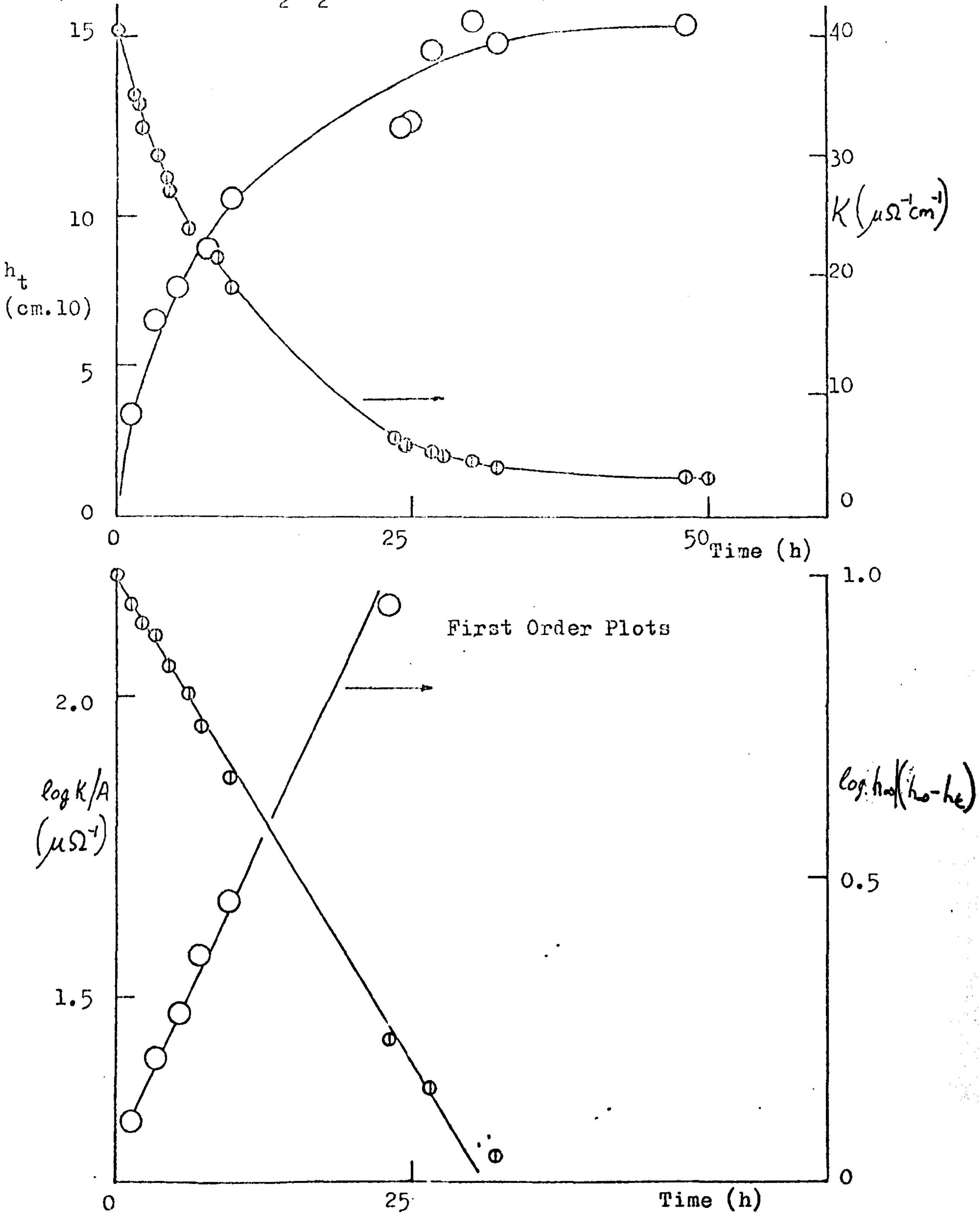
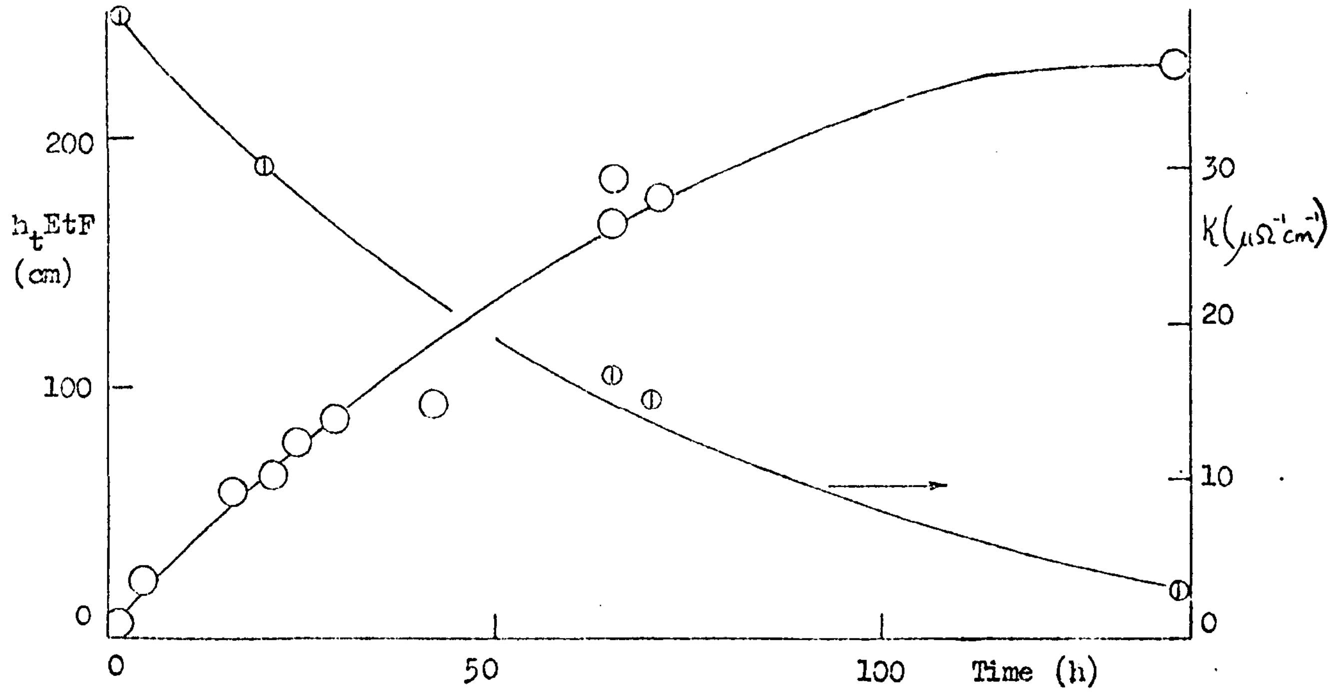
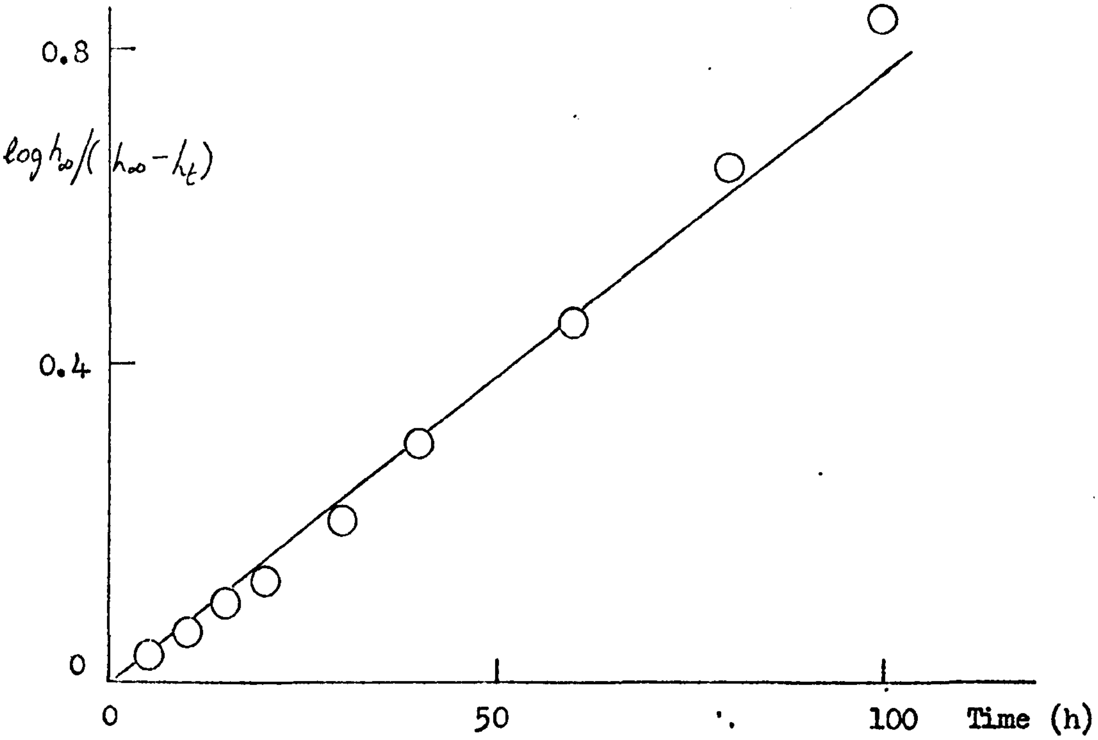


Fig. 5.18.

Decomposition of $Et_3O^+BF_4^-$ in CH_2Cl_2 at 25° (Experiment 120)



First Order Plot for the Evolution of EtF



appears to be relatively small. The other problem was that distillation from phial to phial had obviously occurred in the sampling process as shown by a variation in the size of the methylene dichloride peak. This may account for the time lag mentioned earlier because the monomer concentration would be different in each phial. Within these errors it could be seen that both the ethyl fluoride and the ethane concentrations were reasonably constant throughout the polymerisation. Also the conductivity change seemed to be associated with the formation of ethyl fluoride.

As many polymerisation results were available, the technique was made easier by using conditions in which no polymer was formed (i.e. at a $T > T_c$). The decomposition of $Et_3O^+BF_4^-$ was very slow at 25° so that the sampling could be done more accurately using the standard technique of phial preparation[24].

With this method experiments 120 and 122 were carried out. The results are shown as graphs in Figs. 5.18. and 5.17. Essentially the result of these experiments is that the rate of loss of conductivity is a measure of the rate of decomposition of $Et_3O^+BF_4^-$ to ethyl fluoride and boron trifluoride etherate which are non-conducting species.

5.4. Summary and some Conclusions

In Chapter 5, it is shown that the polymerisation of 1,3-dioxolan by triethyloxonium tetrafluoroborate in methylene dichloride solution is very complicated and is certainly not the unambiguous ethylation which Yamashita at one time believed it to be.

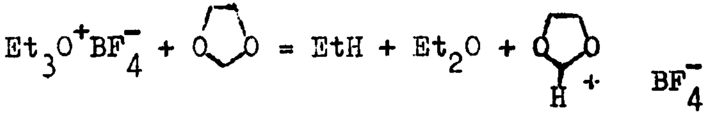
Several factors are apparent in the reaction scheme.

(1) $Et_3O^+BF_4^-$ decomposes in solution

$$Et_3O^+BF_4^- = BF_3Et_2O + EtF$$

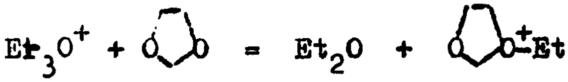
The same reaction takes place when $Et_3O^+BF_4^-$ is dry-distilled. $Et_3O^+BF_4^-$ can be formed from those two products if they are kept in an autoclave for a month[25]. Triethyloxonium salts[25] with simple anions are also unstable. This decomposition is also analogous to the termination observed by Dreyfuss[20] in the polymerisation of tetrahydrofuran by $Et_3O^+BF_4^-$.

(2) Ethane is produced The suggested reaction is as follows:



This reaction is analogous to the reaction of 2-phenyl-1,3-dioxolan[27] with $Et_3O^+BF_4^-$ and the reaction of methoxymethyl perchlorate[26] with 1,3-dioxolan.

(3) Ethylation of the monomer occurs as well, and this can be represented formally by the reaction



but the mechanism is much more complicated (see Chapter 8).

(4) Although the catalyst is unstable, the active centre for the polymerisation is stable, as shown by the same reaction rate being obtained after several polymerisation-depolymerisation cycles. These are carried out by cooling and heating respectively so that if the active centre was unstable it would certainly be decomposed at the depolymerisation temperature. Also, no fluorine could be found in the polymer which would be present if termination occurred by reaction with the anion.

(5) In the presence of 1,3-dioxolan the decomposition of $Et_3O^+BF_4^-$ in solution is faster than in its absence.

The addition of 1,3-dioxolan to methylene dichloride lowers the dielectric constant of the medium, which in turn increases the degree of ion association. This effect would increase the rate, but not therate constant, of decomposition if this reaction is a unimolecular one of the ion-pairs, as seems to be indicated by our evidence. Thus the fact that the rate constant is different in methylene dichloride and in 1M 1,3-dioxolan in methylene dichloride cannot be due to a dielectric effect.

(6) The polymerisation is characterised by an induction period, an acceleration and finally a first order part, up to 95% conversion.

Once the active centres have been produced the reaction is totally of first order. This is the conclusion from the repolymerisation experiment. If one uses the final conductivity of the polymer solution to estimate (see section 5.2.8.)the concentration of active centres, c_a, one obtains values of k_1/c_a which are of the sameorder of magnitude as the k_p determined by Westermann[5] for polymerisations catalysed by perchloric acid.

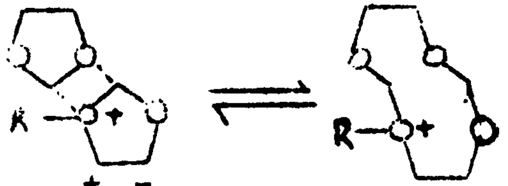
From these facts it can be concluded that the induction and acceleration periods are due to a slow production of active centres and not to the autocatalytic reaction suggested by Chil-Gevorgyan[12c]. Since the polymerisation of 1,3-dioxepan also shows the same acceleration pattern this shows that a difference between the basicity of the polymer and monomer is not solely responsible for the induction and acceleration.

(7) Although dioxolenium tetrafluoroborate does initiate the polymerisation of 1,3-dioxolan we have shown (section 5.2.8.) that it is far less efficient than the 1-ethyl-1$\underline{H}^{+}$-1,3-dioxolanium ion and therefore initiation due to the former can be neglected.

Boron trifluoride etherate polymerises 1,3-dioxolan at a lower rate (Table 5.8.) than $Et_3O^+BF_4^-$ and can therefore be ruled out as the catalyst.

In fact, it seems likely that BF_3Et_2O reacts slowly with 1,3-dioxolan to form the same active centre, 1-ethyl-1$\underline{H}^{+}$-1,3-dioxolanium, but most inefficiently.

(8) End-group analysis has proved negative. This suggests that the polymer is cyclic and therefore that it is formed by the ring-expansion mechanism. This is discussed further in Chapter 10.



where R = H or Et.

Thus, when $Et_3O^+BF_4^-$ is added to a solution of 1,3-dioxolan in methylene dichloride there are several observations that need explanation.

If the reaction producing active centres is slow, why does the concentration of active centres, c_a, not continue to increase with time when the catalyst is still present?

How is the dioxolenium tetrafluoroborate formed and why does its concentration not increase with time?

Why does $Et_3O^+BF_4^-$ decompose in solution?

It appeared that solvation of the oxonium ion may explain at least some of these phenomena. In fact, Chapter 6 and 7 give experimental evidence to prove this hypothesis. The whole mechanism of the polymerisation is not discussed here because Chapter 8 is devoted to the scheme which I propose to explain my results.

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SECTION B - CHAPTER 6

The Decomposition of Triethyloxonium Salts in Methylene Dichloride Solution

6.1. Introduction

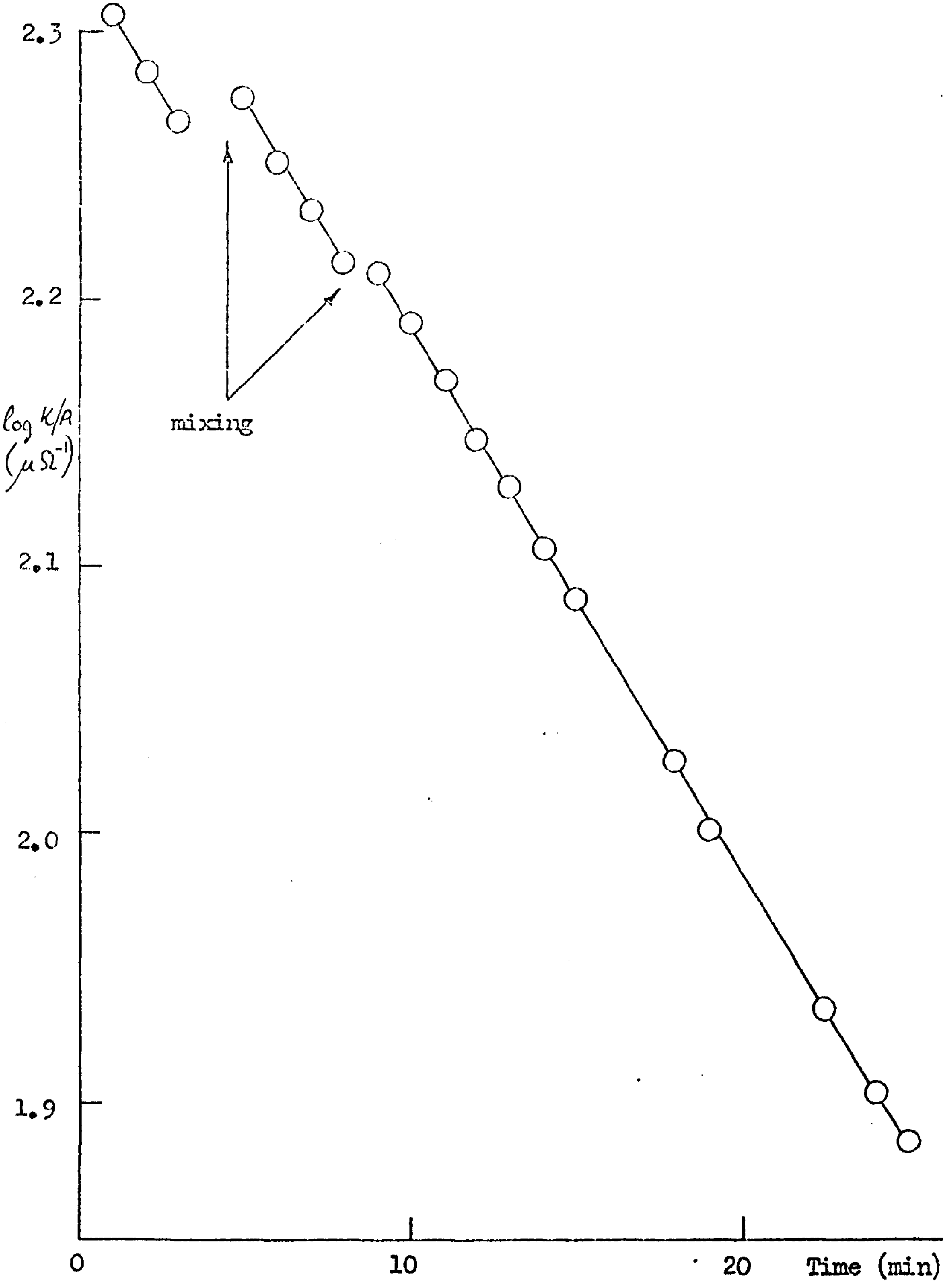
The chemistry of oxonium salts was explored by Meerwein[1]. He showed that triethyloxonium salts with simple anions (e.g. Cl^-) are unstable and that the tetrafluoroborate could be decomposed by dry-distillation. When the decomposition products, BF_3Et_2O and EtF, in Et_2O solution, were stored in a bomb for a month, $Et_3O^+BF_4^-$ was produced in 73% yield.

Dreyfuss[2] has shown that termination occurs in the polymerisation of tetrahydrofuran by $Et_3O^+BF_4^-$ by reaction of the growing cation with the anion and this is analogous to the spontanoous decomposition of $Et_3O^+BF_4^-$ in solution which was reported in Chapter 5.

The rate of the decomposition of $Et_3O^+BF_4^-$ is lower in pure methylene dichloride than in the presence of 1,3-dioxolan, and in Chapter 5 I suggested solvation of the tertiary oxonium ions as a possible explanation of this fact. Before the solvation hypothesis could be tested I decided to study the decomposition of some triethyloxonium salts to make sure that the different rates of decomposition were authentic. Since the rate of decomposition of $Et_3O^+BF_4^-$ was low I decided to use higher temperatures for this study. As other ionic species are formed by reaction of $Et_3O^+BF_4^-$ with the cyclic formals (see Chapter 5) it was decided to study the decomposition of $Et_3O^+BF_4^-$ in the presence of another ether. Diethyl ether was chosen because transfer of the ethyl group to the ether yields the

Fig. 6.1.

The First Order Plot for the Decomposition of 4.5×10^{-3}M $Et_3O^+BF_4^-$ in 1M Et_2O in CH_2Cl_2 at 60° (Experiment 145B)



same cation.

Since the rate constant of the decomposition obtained from conductance measurements was the same, within experimental error, as that obtained from the rate of evolution of ethyl fluoride, only the conductivity of the solution was used to monitor the decomposition in these studies. The results obtained are presented here.

6.2. Experimental Results

The decomposition of triethyloxonium salts in solution is slow, therefore I used evacuated conductivity cells which allowed the use of temperatures higher than the boiling point of the solvent. Because such temperatures were required to produce a measurable rate some notes of the procedure are given here.

For temperatures of 40° and less, the reaction, in most cases, was measured over about one quarter life. This meant that much of the salt remained in solution after the experiment. As the earlier experiments showed a linear dependence of log k on t, I made more than one rate measurement on each solution. At temperatures of 60° and 70° (and occasionally at 40°) distillation within the apparatus was a problem. In order to make sure that the conductivity change was not due to distillation the device was removed from the constant temperature bath, the contents mixed, and the conductivity measurements recontinued after the cell had been replaced in the bath. The cell was out of the bath for less than a minute but a break in the first order plot was observed. However, both first order plots had the same slope (see Fig. 6.1.). The concentration

Table 6.1.

The Decomposition of $Et_3O^+BF_4^-$ in Methylene Dichloride Solution

Run No.	120	141A	140	141B
$[Et_3O^+BF_4^-]/10^2M$	1.1	0.68	1.6	0.1
T / °C	25	40	60	70
$\kappa_o(25°)/\mu\Omega^{-1}\ cm^{-1}$	41.1	28.4	57	9.15
$\kappa_o\ /\mu\Omega^{-1}\ cm^{-1}$	41.1	28.6	48.2	10.6
$\kappa_f\ /\mu\Omega^{-1}\ cm^{-1}$	2.83	9.1	0.78	0.56
$k_1\ /h^{-1}$	0.02	-	-	-
$k_1'\ /h^{-1}$	0.018	0.115	1.2	2.17
Approx. No. of half lives	4	2	4	3

k_1 from g.l.c. measurements.

k_1' from conductivity measurements.

κ_o is the initial conductivity and κ_f is the final conductivity.

Table 6.2.

The Decomposition of $Et_3O^+BF_4^-$ in 1M 1,3-Dioxolan

Run No.	112	122	146C	146A	142A	146B	146D	142B
$[Et_3O^+BF_4^-]/10^2M$	1.33	1.0	1.0	4.2	2.3	2.0	0.8	0.54
T / °C	25	25	25	40	40	50	60	60
$\kappa_o(25^0)/\mu\Omega^{-1}$ cm^{-1}	50	40.4	38	168	78	-	-	23.8
κ_o /$\mu\Omega^{-1}$ cm^{-1}	50	40.4	38	246	74.1	112	29	24.04
κ_f /$\mu\Omega^{-1}$ cm^{-1}	24.6	3.7	30.2	124	25.6	39	11.6	5.5
k_1 /h^{-1}	-	0.1	-	-	-	-	-	-
k_1' /h^{-1}	0.1	0.08	0.1	0.62	0.69	2.7	4.7	3.0
Approx. No. of half-lives	1	3.5	0.5	1.5	1.5	1.5	1.5	2

of the salt was estimated by measuring the conductivity of the solution at 25° before each run. The necessary calibration curve for the conductivity of $Et_3O^+BF_4^-$ in methylene dichloride is given in Chapter 5.

6.3. $Et_3O^+BF_4^-$ in CH_2Cl_2

The rate constants from conductivity measurements (k_1') are given in Table 6.1. The evolution of EtF and the change of conductivity with time have been shown in Fig. 5.18. and $k_1' \simeq k_1$ (for the rate of evolution of EtF).

The Arrhenius plot for these results is shown in Fig. 6.3., whilst the activation parameters, determined from this plot, are given in Table 6.6.

In experiment 140 a u.v. spectroscopy cell with electrodes for conductivity measurements was used. There were no peaks in the u.v. and visible spectra down to 220 nm taken before and after decomposition.

6.4. $Et_3O^+BF_4^-$ with 1M 1,3-Dioxolan in CH_2Cl_2

The results of these experiments are given in Table 6.2. Fig. 6.3. shows the Arrhenius plot and the activation parameters calculated from this plot are given in Table 6.6. Since a yellow colour is often produced towards the end of the decomposition the u.v. and visible spectra of solutions 142 and 146 were taken before and after the reaction. Before the decomposition there was no absorption down to 220 nm, but after decomposition there was a very large peak with a maximum at about 280 nm. The solutions were too

Table 6.3.

The Decomposition of $Et_3O^+BF_4^-$ in the Presence of Diethyl Ether

Run No.	135	145C	145A	143A	143B	145B	144B	144A	144C
$[Et_3O^+BF_4^-]/10^2$M.	1.15	0.5	2.2	0.63	0.45	1.8	0.35	0.48	0.29
$[Et_2O]$/M.	1.0	1.0	1.0	1.0	1.0	1.0	3.0	3.0	3.0
T / °C	25	25	40	40	60	60	25	40	60
$\kappa_0(25^\circ)/\mu\Omega^{-1}$ cm^{-1}	47.9[‡]	21.8	73.9	26.1	20.9	-	9.6	12.4	9.3
κ_0 $/\mu\Omega^{-1}$ cm^{-1}	36.9	21.8	75	28.7	20.2	64.9	9.6	12.4	9.15
κ_f $/\mu\Omega^{-1}$ cm^{-1}	1.8	15.46	68	20.7	6.2	22.1	9.3	9.5	0.44
k_1 /h^{-1}	0.017	-	-	-	-	-	-	-	-
k_1' /h^{-1}	0.016	0.015	0.16	0.2	2.5	3.0	0.02	0.27	3.8
h_f(EtF)	15.2[*]	-	-	-	-	-	-	-	-
Approx. No. of half-lives	4	0.5	0.3	0.5	2	1.5	-	0.5	3
$[EtF]/10^2$M.	0.88[†]	-	-	-	-	-	-	-	-

[*] Attenuation = 50 x 1

[†] Estimated from h_f(EtF)

[‡] Conductivity of methylene dichloride solution before adding diethyl ether.

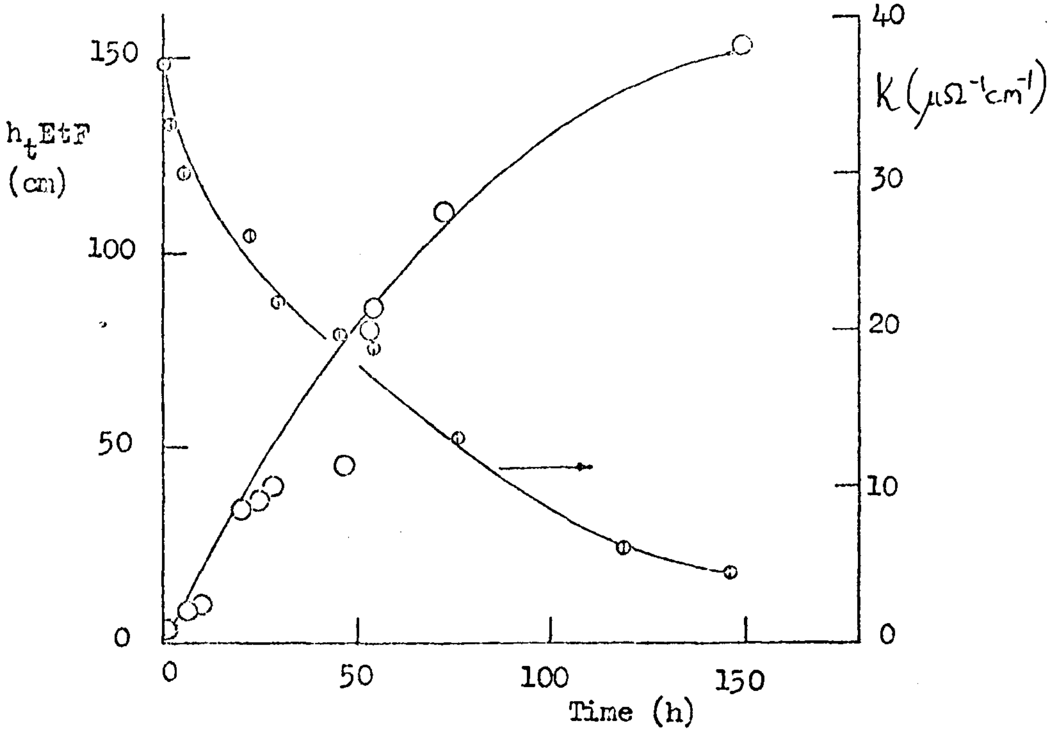
Table 6.4.

The Decomposition of $Et_3O^+PF_6^-$ in Methylene Dichloride

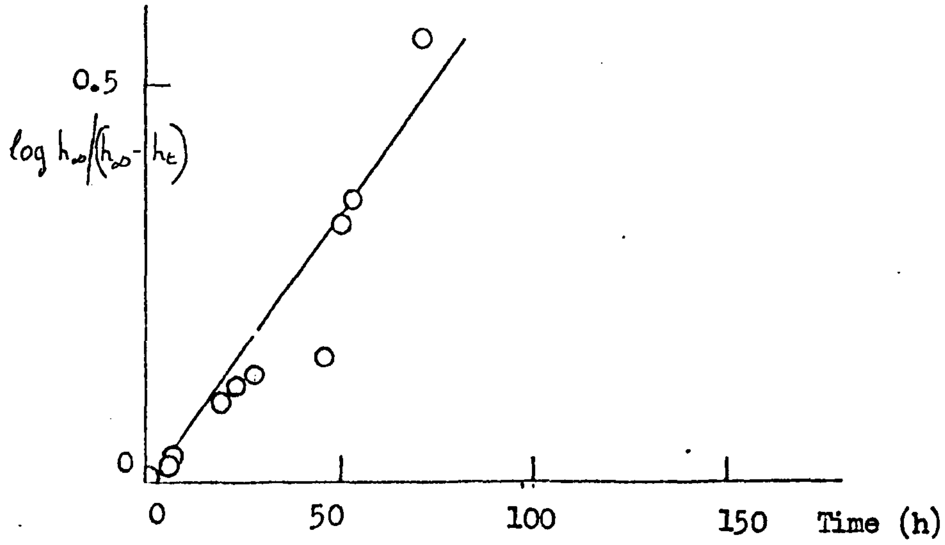
Run No.	154A	158A	154B	158C	158B
$[Et_3O^+PF_6^-]/10^2M$	0.54	1.5	0.34	0.44	1.0
T / °C	25	25	40	40	60
$\kappa_o(25^\circ)/\mu\Omega^{-1}$ cm^{-1}	40.3	115	28.7	-	100
κ_o $/\mu\Omega^{-1}$ cm^{-1}	40.3	115	28.6	40.9	101
κ_f $/\mu\Omega^{-1}$ cm^{-1}	28.7	100	21.4	1.8	41.9
k_1' $/h^{-1}$	0.0086	0.01	0.044	0.068	0.25
Approx. No. of Half lives	0.5	-	0.5	4	1

Fig. 6.2.

The Decomposition of $Et_3O^+BF_4^-$ in 1M Et_2O in CH_2Cl_2 at 25° (Experiment 135)



First Order Plot for the Evolution of EtF



concentrated for an accurate figure to be obtainable. There was also a peak at 418 nm. The colour was discharged on neutralisation.

6.5. $Et_3O^+BF_4^-$ with Diethyl Ether in Methylene Dichloride Solution

The rate of decomposition of $Et_3O^+BF_4^-$ in the presence of 1M and 3M diethyl ether was measured. Fig. 6.2. shows the evolution of ethyl fluoride and the loss of conductivity with time (run 135). The experimental values of k_1 and k_1' are given in Table 6.3., and Fig. 6.3. and Table 6.6. show the Arrhenius plot and the activation parameters for the reaction. The concentrations of $Et_3O^+BF_4^-$ shown in Table 6.3. are only estimated because the conductivity of the solution was not measured before addition of Et_2O and insufficient data on the conductivity of $Et_3O^+BF_4^-$ in the presence of ether were available.

Experiment 143 was carried out in the spectrometer cell which made it possible to determine the u.v. and visible spectra before and after decomposition. There was no absorption in both cases.

6.6. $Et_3O^+PF_6^-$ in CH_2Cl_2

The decomposition of $Et_3O^+PF_6^-$ in methylene dichloride was measured. The results are given in Table 6.4. The Arrhenius plot (Fig. 6.3.) gave the activation parameters in Table 6.5. Less weight has been given to k_1' obtained from 158C because distillation within the system was difficult to control.

In run 158 the u.v. and visible spectra were taken before and after decomposition. There were no peaks in the spectrum before decomposition but afterwards a noticeable shift of the base line was

Table 6.5.

The N.M.R. of Et_3O^+ X^- in Methylene Dichloride Solution

X^-	Solvent	Concentration	τ values (TMS = 10τ)					
		M		Et_3O^+			Et_2O	
			$CH_3^{\ddagger}$	CH_2^{*}	$\Delta\tau(CH_2)$	$CH_3^{\ddagger}$	CH_2^{*}	$\Delta\tau(CH_2)$
-	Et_2O	-	-	-	-	8.85	6.62	-
BF_4^-	-	-	8.30	5.10	-	-	-	-
BF_4^-	0.96MEt_2O	0.58	8.40	5.20	+0.1	89	6.5	-0.12
PF_6^-	-	0.5	8.30	5.10	-	-	-	-
PF_6^-	1MEt_2O	0.5	8.35	5.15	+0.05	8.85	6.45	-0.17
SbF_6^-	-	0.5	8.30	5.10	-	-	-	-
SbF_6^-	1MEt_2O	0.5	8.30	5.10	0	8.8	6.5	-0.12

‡ triplets

* quadruplets

+ represents a shift to a higher value.

observed, without the formation of a peak. A small amount of a white precipitate was formed in 158C and this presumably accounts for the spectral change. This precipitate is probably phosphorus pentafluoride etherate since other complexes of PF_5 are solids[3] (e.g. $PF_5 \cdot O$ ).

6.7. $Et_3O^+SbF_6^-$ in CH_2Cl_2

A 2.4×10^{-2}M solution of triethyloxonium hexafluoroantimonate in methylene dichloride was decomposed at 60°. The initial conductivity dropped from $146\mu\Omega^{-1}$ cm^{-1} to $103.7\mu\Omega^{-1}$ cm^{-1} in 70 hours. The rate constant was $4.5 \times 10^{-3}h^{-1}$. The solution had turned very slightly yellow after 46 hours. The u.v. and visible spectra of the solution were taken after the cell had been opened to the atmosphere. There were two peaks, one at 382 nm and the other at 302 nm.

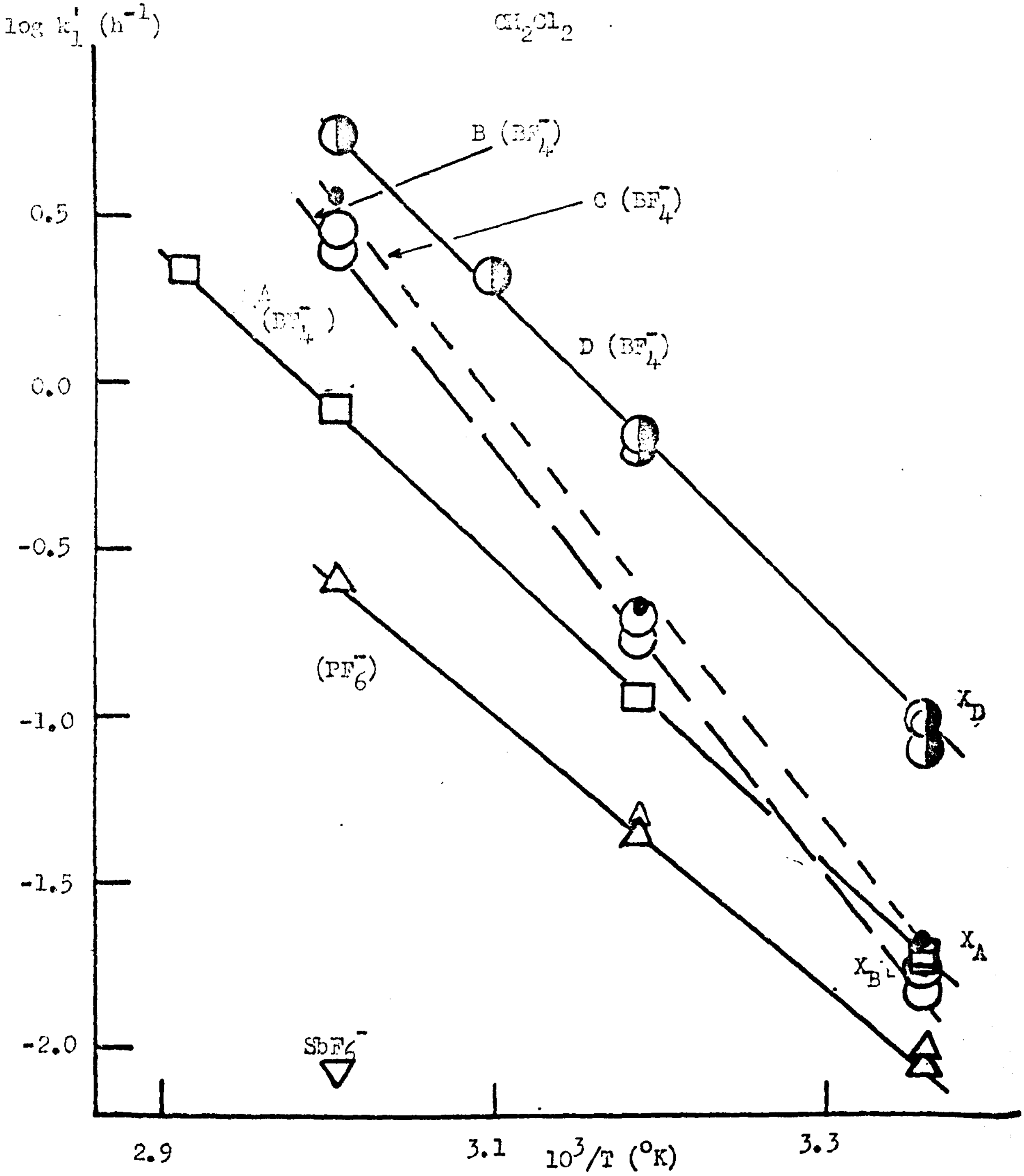
Gas Chromatography showed that ethyl fluoride was present in the solution. There was also a peak between those of methylene dichloride and ethyl fluoride which is believed to be diethyl ether. Another small peak with a retention time of 11 mins. was not identified.

6.8. The N.M.R. Spectra of Triethyloxonium Salts in the Presence of Diethyl Ether

The Arrhenius plots for the decomposition of some triethyloxonium salts are shown in Fig. 6.3. The slope of the line was greater in the presence of diethyl ether. Solvation of the oxonium ion by ethers was thought to be responsible for this phenomenon. Therefore, the N.M.R. spectra of three tertiary oxonium salts were made in Et_2O solution to see whether the close proximity of the

Fig. 6.3.

The Arrhenius Plot for the Decomposition of Triethyloxonium Salts in CH_2Cl_2



A, no ether; B, 1M diethyl ether; C, 3M diethyl ether; D, 1M 1,3-dioxolan

Points marked X are g.l.c. measurements

Et_2O molecule caused a shift in the spectrum. If the positive charge on the oxonium ion is reduced an upfield shift would be expected.

The results are shown in Table 6.5.; the τ values were the same in two spectra of the same solution. There is a slight upfield shift of up to 0.1τ for the CH_2-protons of the triethyloxonium ion. This may be significant since it varies from salt to salt, but it was necessary to discover whether this was purely due to a change of the solvent characteristics. Therefore, the N.M.R. spectra of 0.5M 1,4-dioxan in methylene dichloride and in 1M diethyl ether solution were made. The τ values for the protons of 1,4-dioxan (6.4) were not affected by the addition of ether. Thus, it can be concluded that the proton shift which is observed when diethyl ether is added to a solution of a triethyloxonium salt is due to an interaction with diethyl ether and not to a solvent effect.

6.9. Discussion

Chapter 7 shows that the association constants for ion-pair formation of $Et_3O^+BF_4^-$ and $Et_3O^+PF_6^-$ are about 10^5 l mole^{-1} at 0°. Calculation shows that at concentrations of less than 10^{-2}M the concentration of triple ions is much less than the concentration of ion-pairs. Therefore it is proposed that the ion-pair is the chemical entity which decomposes. This can be illustrated by the following equation:

$$A + B \xrightleftharpoons{K_2} AB \xrightarrow{k_1} X$$

where A represents Et_3O^+, B represents BF_4^-, PF_6^- or SbF_6^- and X represents the products, namely BF_3, PF_5 or SbF_5, Et_2O and EtF. AB is

Table 6.6.

The Paramaters derived from the Arrhenius Plot

$Et_3O^+BF_4^-$ in Methylene Dichloride

Ether added	Ea kcals mol^{-1}	$\log_{10}A$ A in h^{-1}	$\Delta S^{\ddagger}$ cals^{-1} mole^{-1}deg^{-1} T = 25°C
-	21.5 ± 0.5	14.4 ± 0.4	-4.5 ± 1.9
1M 	23.1 ± 0.5	16.0 ± 0.5	-2 ± 2
1M Et_2O	28.7 ± 0.4	19.3 ± 0.3	+13.3 ± 1.4
3M Et_2O	28.7 ± 0.4	20.3 ± 0.3	+17.9 ± 1.4

$Et_3O^+PF_6^-$ in Methylene Dichloride

-	18.9 ± 0.4	11.8 ± 0.5	-20.8 ± 2

an ion-pair.

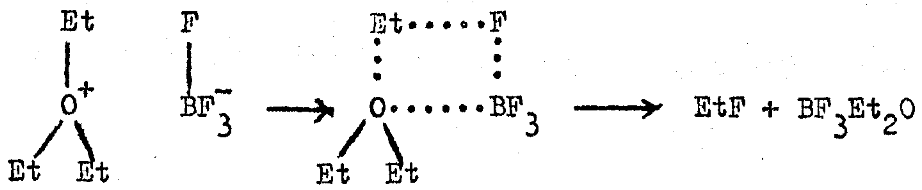
The rate of evolution of ethyl fluoride can be derived very simply thus: if $[A] = [B] = a$, $[AB] = y$, $[X] = x$ and $c_o = y+x$, because under the conditions of the relevant experiments $a \ll y$, then since $dx/dt = k_1 y = k_1(c_o - x)$ we have the first-order law for the formation of EtF. The integrated equation is $x = c_o(1-e^{-k_1 t})$

The derivation of the rate-law for the change of conductivity has proved more difficult and this is still under investigation.

However, at 0°, the plot of K' against c (the concentration of the triethyloxonium salt) is linear between 10^{-2}-10^{-3}M (Fig. 7.1. and 7.5.), therefore we consider that k_1' determined from conductance measurements is related simply to k_1 from the rate of evolution of ethyl fluoride. Therefore the parameters derived from the Arrhenius plot (Fig. 6.3.) will be discussed below.

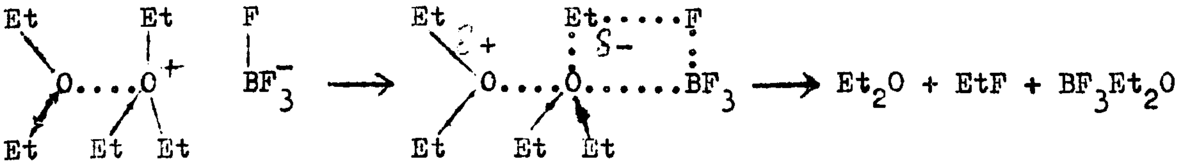
I propose the following scheme to explain my results. The solvation of tertiary oxonium ions by ether molecules is postulated and this is further substantiated in Chapter 7.

IN METHYLENE DICHLORIDE ion-pairing occurs, therefore, the decomposition can be represented in the following way:



the activation energy (E_a) for this process is 21.5 kcals/mole and the activation entropy $\Delta S^{\ddagger}$ is -4.5 cals deg^{-1} $mole^{-1}$.

IN THE PRESENCE OF DIETHYL ETHER the following scheme is postulated:



The formation of the solvated oxonium ion reduces the effective positive charge on the oxonium ion. In the transition state the ether is less strongly bound than in the initial state, which is the solvated ion-pair. This explains the positive $\Delta S^{\ddagger}$, because in the transition state there will be more degrees of freedom of rotation than in the initial state because the charge density on the oxonium ion is less than in the initial state. The activation energy for the decomposition is higher than in the absence of ether, which shows that more energy is required to form the transition state from the solvated ion-pair than from the unsolvated one. This is in agreement with the proposed scheme because the reduced positive charge on the oxonium ion reduces the attraction between the cation and anion.

The effect of 1,3-dioxolan on the rate of decomposition is an intermediate case, since 1,3-dioxolan donates its lone pair of electrons less efficiently than diethyl ether. This is shown by the basicity of 1,3-dioxolan, $pK_b = 6.81$, and that of diethyl ether, $pK_b = 5.65$. These values were determined by Okada[4] using Gordy's method.

Thus the results of these studies on the decomposition of triethyloxonium salts can be explained using the hypothesis of solvation.

References to Chapter 6

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SECTION B - CHAPTER 7

The Dissociation Constant of Triethyloxonium Salts

7.1. Introduction

Ionic polymerisation is propagated by macromolecules endowed with reactive ionic   groups. It is therefore essential to know the detailed structure of these groups. This is difficult because these species may exist in a variety of forms; free ions, ion-pairs, triple ions or higher aggregates. As well as this the ions may be coordinated with solvent and/or monomer molecules.

Electrolytic conductance is the most direct evidence for the existence of ions in solution and its variation with concentration the most obvious way of studying ionic equilibria. It is for these reasons that this study of the ion association of triethyloxonium salts in methylene dichloride was made. Moreover, it was important to decide whether triple ions were present in solutions with concentrations of about 10^{-2}M and, therefore, were contributing to the rate of decomposition.

Beard[1] has determined the association constants (K_2) for ion-pairs of **triethylmethylammonium** iodide in methylene dichloride solution at various temperatures. The results were analysed by Shedlovsky's method and at 0°, $K_2 = 1.11 \times 10^5$ l mole^{-1} and the equivalent conductivity at infinite dilution (Λ_{02}) was 111.8 Ω^{-1} cm^2 mole^{-1}, and K_3 (the association constant for ion-pairs to triple ions) was 86.9 lmole^{-1}.

Apart from the famous curves of Fuoss[2] and Kraus for the conductance of tetraisoamylammonium nitrate in 1,4-dioxan/water solutions very few data are available on the conductance of ionic solutions in media of low dielectric constant.

Recently Justice and Treiner[3] have reported a study of the ion association of tetra-n-butylammonium perchlorates and bromides in various mixtures of tetrahydrofuran and water at 25°. At a dielectric constant of 10 (CH_2Cl_2 at 0°, D = 10.02) $K_2 = 2.4 \times 10^4$ $lmole^{-1}$ (ClO_4^-).

More recently, Ledwith[4] gives the dissociation constants for hexachloroantimonate salts of stable organic cations in methylene dichloride.

Klages[5] gives some date for the conductance of tertiary oxonium salts in sulphur dioxide solutions but no attempt was made to analyse the results. Therefore, the results reported here are useful to both the electrochemistry and the polymer chemistry of oxonium ions.

7.2. Experimental details

The conductivity of solutions of triethyloxonium salts was measured in the vacuum cell described in Chapter 2. Methylene dichloride was dosed, as described, (Chapter 2) with an accuracy of ±0.05 ml at room temperature. The volume at 0° was calculated from the coefficient of volumetric[6] expansion ($\alpha = 0.00178$ cm^3 $°C^{-1}$). Small corrections to the volume due to the use of a vacuum system were considered but were not made because Beard[1c] had shown (for a similar cell) that this correction was only required, at temperatures above 0°, when the total volume of liquid was less than 30 ml. The minimum volume of this cell was 25 ml. The solution

Fig. 7.1.

Λ - c curve for $Et_3O^+BF_4^-$ in CH_2Cl_2 at 0°

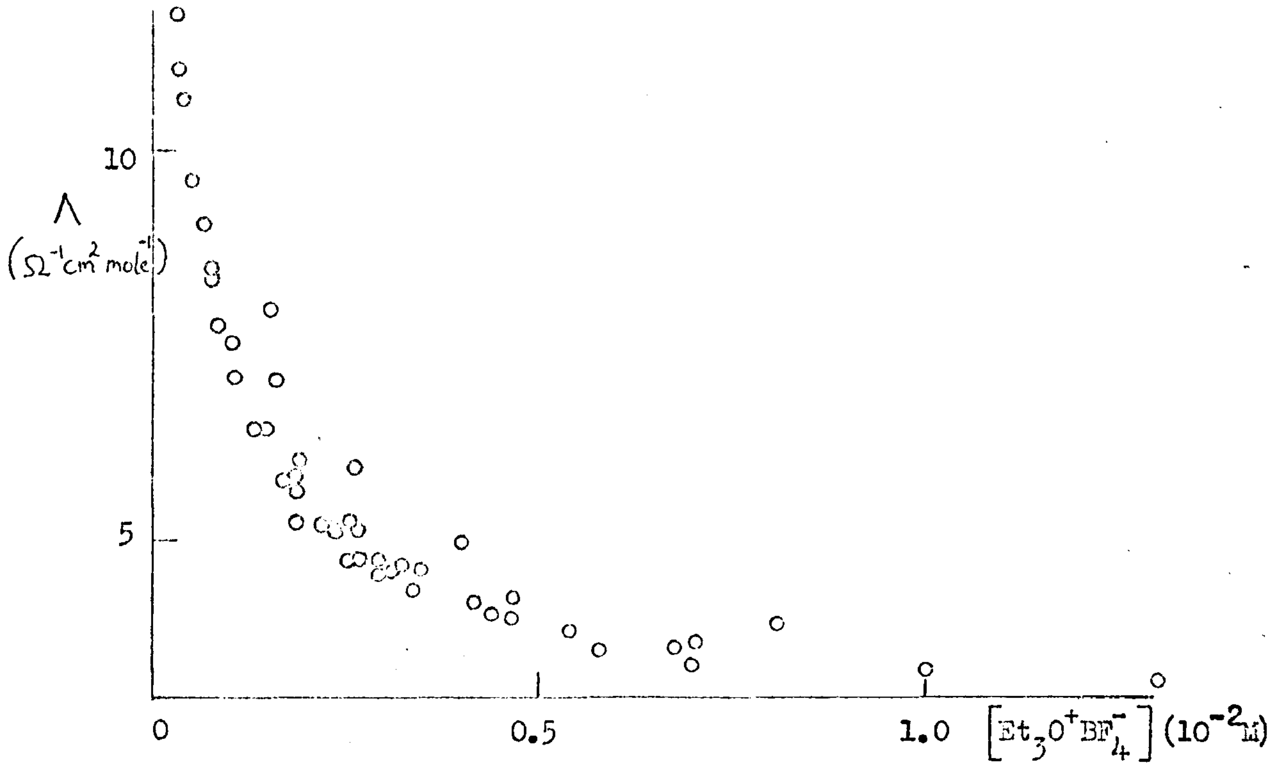
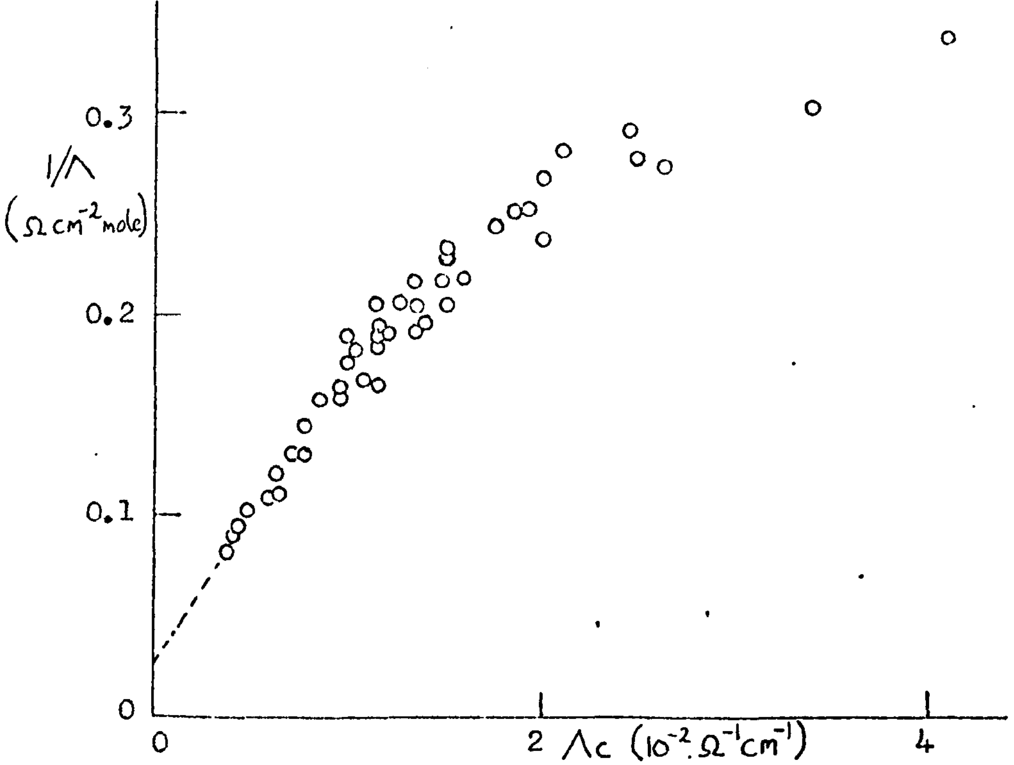


Fig. 7.2.

Kraus - Bray Plot for $Et_3O^+BF_4^-$ in CH_2Cl_2 at 0°



concentrations were calculated in mole l^{-1} by assuming the densities of the solutions to be the same as that of the pure solvent. Board had confirmed this for solutions of methyltriethylammonium iodide in methylene dichloride.

The specific conductivity (κ) of the methylene dichloride was 1.309 $n\Omega^{-1}$ cm^{-1} at 0°. The values of κ in the literature are 3 $n\Omega^{-1}$ cm^{-1} (Board[1c]) and 0.043 $n\Omega^{-1}$ cm^{-1} at 25°[7].

$Et_3O^+BF_4^-$ was dosed by breaking a phial into methylene dichloride whereas $Et_3O^+PF_6^-$ was purified and weighed on a Whites Torsion balance to ±5μg before being transferred to the conductivity cell where it was thoroughly evacuated.

7.3. $Et_3O^+BF_4^-$

Due to an uncertainty in the concentration of this salt the results obtained could only be analysed by the limiting law of Ostwald. For analysis by the Fuoss-Kraus and Shedlovsky equations an internal scatter of less than 0.1% is required.

The results obtained are given in Table 7.1., and Fig. 7.1. shows the plot of Λ against c.

The Ostwald dilution function is generally believed to be a close approximation to the behaviour of strong electrolytes in solvents of low dielectric constant and gives the association constant, K_d, in terms of the equivalent conductivity Λ, the equivalent conductivity at infinite dilution, Λ_{02}, and the concentration c.

$$K_d = \Lambda^2 . c/\Lambda_{02}(\Lambda_{02} - \Lambda) \qquad (1)$$

Kraus and Bray[8] rearranged this equation.

$$1/\Lambda = 1/\Lambda_{02} + \Lambda c/K_d(\Lambda_{02})^2 \qquad (2)$$

Table 7.1.

The Conductivity of $Et_3O^+BF_4^-$ in Methylene Dichloride at 0°C

Parameters of CH_2Cl_2 at 0°C viscosity, η, = 5.357 mP

Dielectric Constant, D, = 10.02

Run 123

$c/10^2$M.	1.406	0.703	0.540	0.440	0.340	0.293	0.260	0.220	0.190
$\Lambda/\Omega^{-1}cm^2mole^{-1}$	2.94	3.46	3.72	4.00	4.37	4.59	4.78	5.14	5.23

Run 126

$c/10^2$M.	1.01	0.706	0.470	0.353	0.262	0.191
Λ	3.36	3.71	4.26	4.62	5.19	6.02

Run 127

$c/10^2$M.	0.675	0.473	0.315	0.236	0.189	0.151
Λ	3.61	4.00	4.63	5.17	5.61	6.28

Run 131

$c/10^2$M.	1.34	0.805	0.403	0.268	0.161
Λ	3.25	3.93	4.96	5.94	7.08

Run 124

$c/10^2$M.	0.580	0.417	0.324	0.292	0.263	0.223
Λ	3.60	4.22	4.66	4.55	4.75	5.16

Run 124 cont'd

$c/10^2$M.	0.172	0.133	0.108	0.088	0.077
Λ	5.78	6.44	7.08	7.78	8.34

Run 125

$c/10^2$M.	0.265	0.189	0.147	0.101	0.078	0.066	0.051	0.041	0.036	0.032
Λ	5.15	5.80	6.39	7.59	8.40	9.06	9.63	10.56	11.06	11.70

Thus, a plot of $1/\Lambda$ against $c\Lambda$ should be a straight line of slope $1/K_d\Lambda_{02}^2$ and intercept $1/\Lambda_{02}$.

The Kraus-Bray plot is shown in Fig. 7.2. and is quite scattered. Extrapolation leads to an improbably low value of Λ_{02} (approx. $25\,\Omega^{-1}\ \mathrm{cm}^2\ \mathrm{mole}^{-1}$. The upwards convex nature of the curve suggests ternary or perhaps higher association.

Two types of ternary association are possible:

$$AB + A^+ \rightleftharpoons A_2B^+ \qquad (3)$$

$$AB + B^- \rightleftharpoons AB_2^- \qquad (4)$$

where AB is the ion-pair of A^+ and B^-.

If both processes occur - bilateral ternary association, the plot due to Fuoss and Kraus[2,9] is used (equation 5).

For $$A^+ + B^- \rightleftharpoons AB$$

$$K_2 = [AB] / [A^+][B^-]$$

Then from 3 and 4 $$K_3 = [AB_2^-] / [AB][B^-] = [A_2B^+] / [AB][A^+] \qquad (5)$$

The final equation is

$$\Lambda c^{\frac{1}{2}}.g(c) = \Lambda_{02} / K_2^{\frac{1}{2}} + \Lambda_{03}.K_3.c(1-\Lambda/\Lambda_{02})/K_2^{\frac{1}{2}} \qquad (6)$$

where the g(c) term is given by the following equation in which S_Λ is the theoretical limiting slope of the plot of Λ against $c^{\frac{1}{2}}$, S_f is the theoretical limiting slope of the plot of the rational activity coefficient $f_\pm$ against $c^{\frac{1}{2}}$.

$$g(c) = \frac{\exp\left[-2.303\ S_f\ (c\Lambda/c\Lambda_{02})^{\frac{1}{2}}\right]}{\left[1-S_\Lambda(c\Lambda/\Lambda_{02})^{\frac{1}{2}}/\Lambda_{02}\right](1-\Lambda/\Lambda_{02})^{\frac{1}{2}}}$$

$$\log g(c) \doteq (0.4343\ S_\Lambda - S_f\Lambda_{02})(c^{\frac{1}{2}}\Lambda^{\frac{1}{2}}/\Lambda_{02}^{\frac{3}{2}}) + 0.2171\Lambda/\Lambda_{02}$$

For further details see reference 9.

At low concentrations the equation reduces to

$$\Lambda c^{\frac{1}{2}} = \Lambda_{02}/K_2^{\frac{1}{2}} + \Lambda_{03}K_3\,c/K_2^{\frac{1}{2}} \qquad (7)$$

Therefore, a plot of $\Lambda c^{\frac{1}{2}}$ against c should be a straight line of slope, $\Lambda_{03}K_3K_2^{-\frac{1}{2}}$ with an intercept of $\Lambda_{02}K_2^{-\frac{1}{2}}$. If only one process occurs, i.e. either the formation of AB_2^- or A_2B^+ - unilateral ternary association - then the equation due to Wooster[10] is used.

$$(\Lambda f_{\pm}/m)^2\, c/(1-\Lambda/\Lambda_{02}) = \Lambda_{02}^2/K_2 + (2\Lambda_{02}\Lambda_{03} - \Lambda_{02}^2)K_3c(1-\Lambda/\Lambda_{02})/K_2 \qquad (8)$$

where $m = 1 - (S_{\Lambda}/\Lambda_{02}^{\frac{3}{2}})(c\Lambda)^{\frac{1}{2}}$

and $f_{\pm}$ is defined by $-\log f_{\pm} = \beta(c\Lambda/\Lambda_{02})^{\frac{1}{2}}$

In instances of unilateral triple ion formation at low total ion concentration (e.g. dilute solution in a solvent of low dielectric constant) the following simplified equation can be used.

$$c\Lambda^2 = \Lambda_{02}^2/K_2 + c(2\Lambda_{02}\lambda_0 - \Lambda_{02}^2)K_3/K_2 \qquad (9)$$

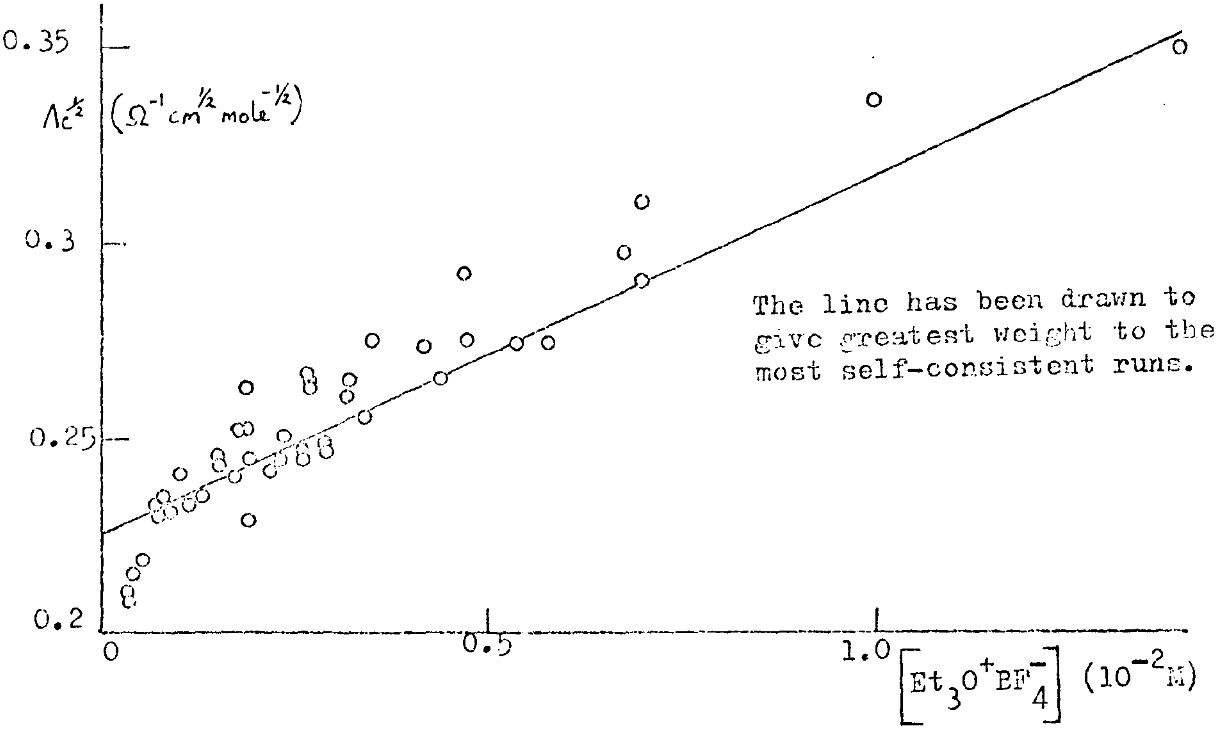
where λ_0 is the sum of the limiting conductances of the triple ions and of the simple cations.

Although unilateral ternary association cannot usually be distinguished from bilateral ternary association both these plots were made in an attempt to estimate the association constants K_2 and K_3. The overall curvature is reduced in both cases, but the separate plots are still curved. This may mean that the curvature is due to experimental uncertainty.

In order to apply these equations a value of Λ_{02} is required. Therefore, taking Et_4N^+ as a reasonable analogue of Et_3O^+, Λ_{02} for $Et_3O^+BF_4^-$ can be estimated[11]. In ethylene dichloride at 25°

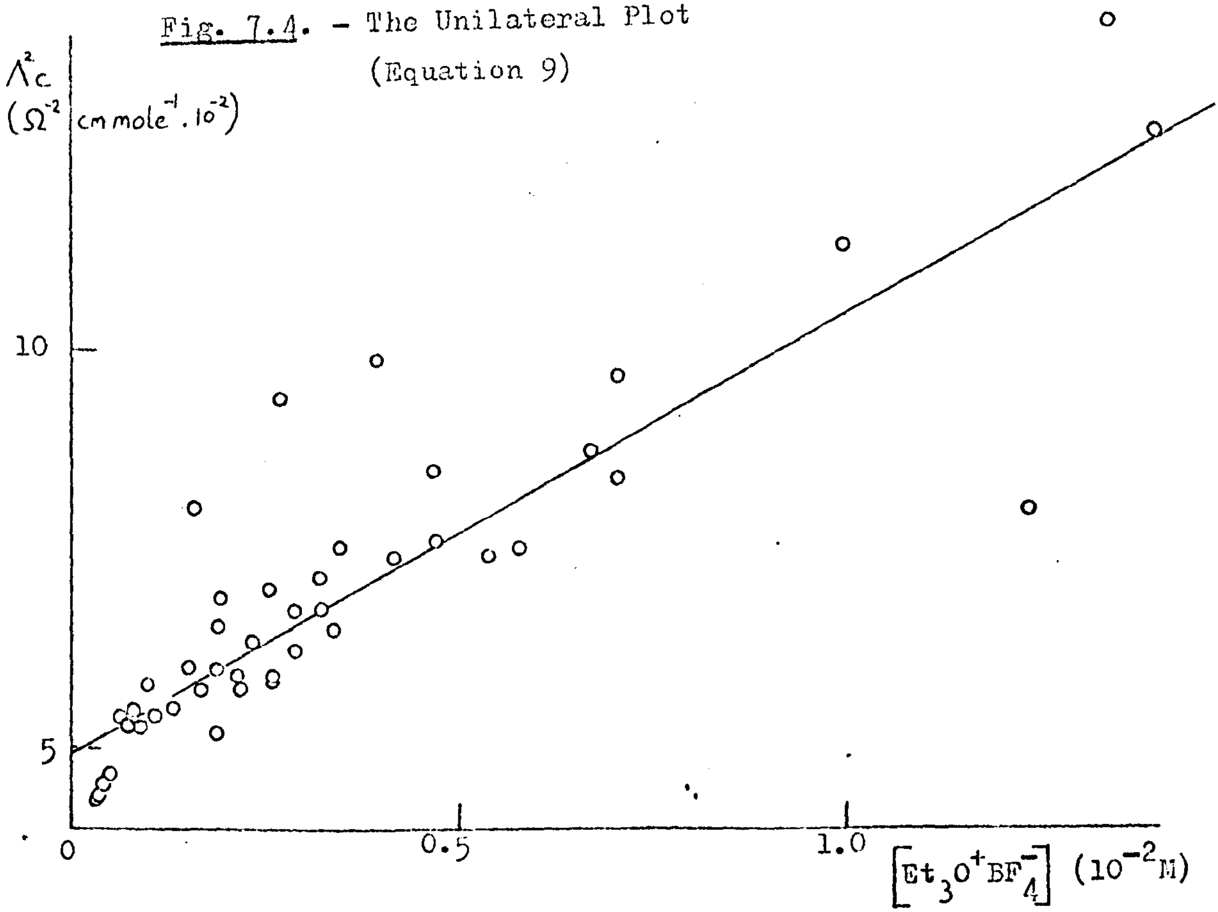
Ternary Plots for $Et_3O^+BF_4^-$ in CH_2Cl_2 at 0°

Fig. 7.3. - The Bilateral Plot (Equation 7)



The line has been drawn to give greatest weight to the most self-consistent runs.

Fig. 7.4. - The Unilateral Plot (Equation 9)



the viscosity is 7.85 mP and Λ_{02} for $Et_4N^+BF_4^-$ is 81.0 Ω^{-1} cm^2 mole^{-1}. The viscosity of methylene dichloride at 0° is 5.357 mP, then by Walden's rule[12], Λ_{02} ($Et_3O^+BF_4^-$) should be about 106 Ω^{-1} cm^2 mole^{-1}.

7.3.1. The Bilateral Ternary Plot ($\Lambda c^{\frac{1}{2}}$ against c – equation 7)

This plot is shown in Fig. 7.3. From the best straight line slope (S) of 9.059 and an intercept (I_t) 0.226 are obtained. Assuming $\Lambda_{02} = 106$ and that $\Lambda_{03} = \Lambda_{02}/3$, the following values of K_2 and K_3 are obtained.

$$S = 9.059 = \Lambda_{03}K_3 / K_2^{\frac{1}{2}}$$

$$I_t = 0.226 = \Lambda_{02} / K_2^{\frac{1}{2}}$$

The binary association constant, $K_2 = 2.2 \times 10^5$ lmole^{-1}

The bilateral ternary constant, $K_3 = 120$ lmole^{-1}

7.3.2. The Unilateral Ternary Plot ($\Lambda^2 c$ against c – equation 9)

Fig. 7.4. shows this plot; the slope (S) = 5.5 and the intercept (I_t) = 5 x 10^{-2} for the best straight line.

From equation (7), $I_t = \Lambda_{02}^2 / K_2$; $S = (2\Lambda_{02}\lambda_0 - \Lambda_{02}^2)K_3/K_2$

But $\Lambda_{02} = 106$

If we assume that $\lambda_A = \lambda_B = 106/2$

Then $\lambda_0 = \Lambda_{03} + \lambda_A$

Since $\Lambda_{03} = \Lambda_{02} / 3$

Therefore $\lambda_0 = 88$ Ω^{-1} cm^2

So $K_2 = 2.2 \times 10^5$ lmole^{-1}

The unilateral ternary constant, $K_3 = 190$ lmole^{-1}

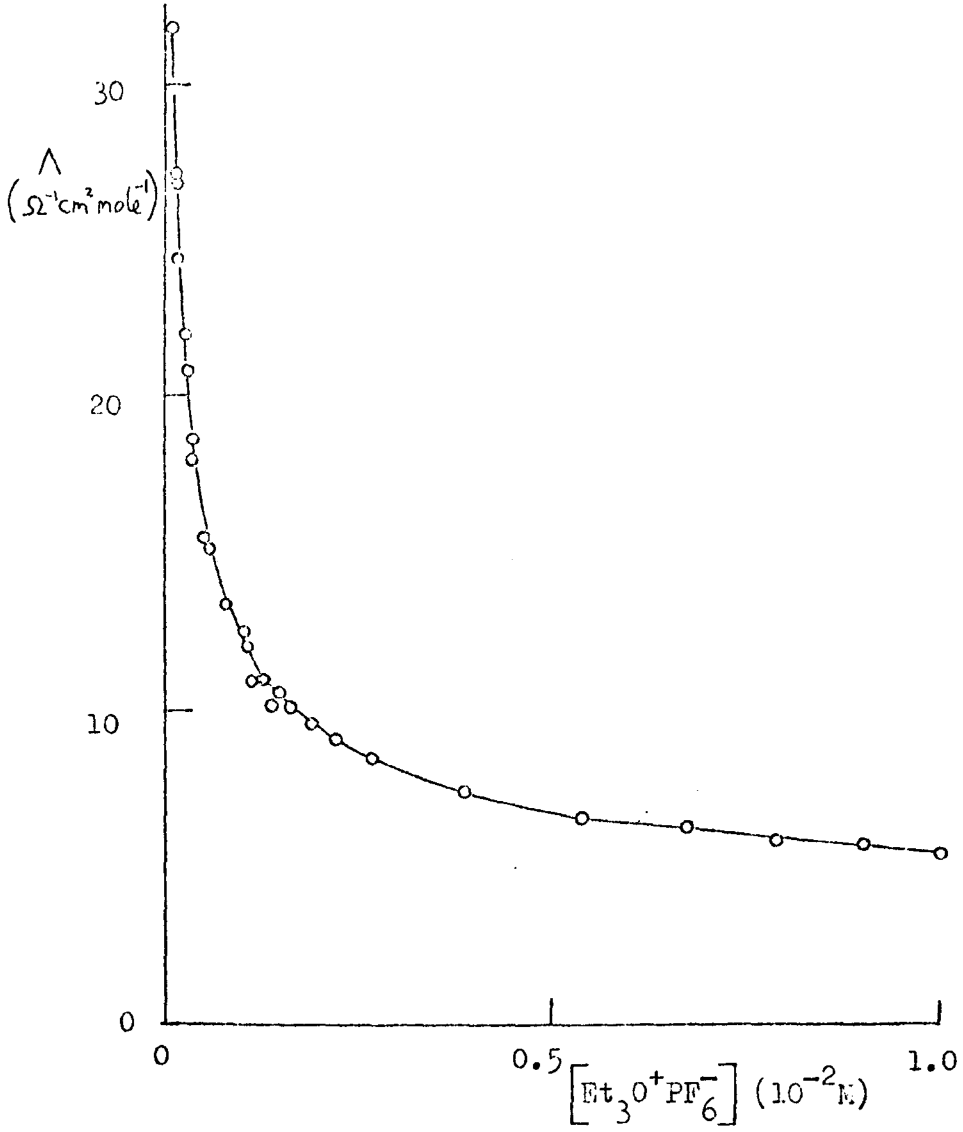
7.3.3. The Concentration of Free Ions and Ion-Pairs

If c_i is concentration of free ions,

then $c_i = -K_d/2 + (K_d^2 + 4K_dc)^{\frac{1}{2}}/2$

Fig. 7.5.

Λ - c curve for $Et_3O^+PF_6^-$ in CH_2Cl_2 at 0°



For $c = 10^{-2}$M and $K_d = 1/K_2 = 0.45 \times 10^{-5}$ mole l^{-1}

then $c_i = 2 \times 10^{-4}$M and

therefore concentration of ion-pairs = 0.98×10^{-2}M.

But from equation (5) $K_3 = [A_2B^+]/[AB][A^+]$

Assuming $K_3 = 120$, $[A_2B] = 2.4 \times 10^{-4}$ M

This shows that at 10^{-2}M the most abundant species are ion-pairs.

7.4. $Et_3O^+PF_6^-$

Since the method of dosing $Et_3O^+BF_4^-$ led to uncertainties in the concentration of solutions a similar salt was required for accurate conductance studies. $Et_3O^+PF_6^-$ is less readily hydrolysed and can be dosed directly to the cell. Over the time period of the experiment the amount of decomposition at 0°, is negligible. Therefore, it is a suitable tertiary oxonium salt for this study.

The results of my dilution experiments with $Et_3O^+PF_6^-$ are given in Table 7.2. and the plot of Λ against c is shown in Fig. 7.5. In run 166 the solution was diluted and reconcentrated and the results obtained from both processes were consistent.

These data on the conductivity of $Et_3O^+PF_6^-$ in methylene dichloride at 0° for $c < 1.3 \times 10^{-3}$M were analysed in three ways.

7.4.1. The Fuoss-Kraus[13] (FK) Binary Plot (for $c < 1.3 \times 10^{-3}$M)

The equation used is:

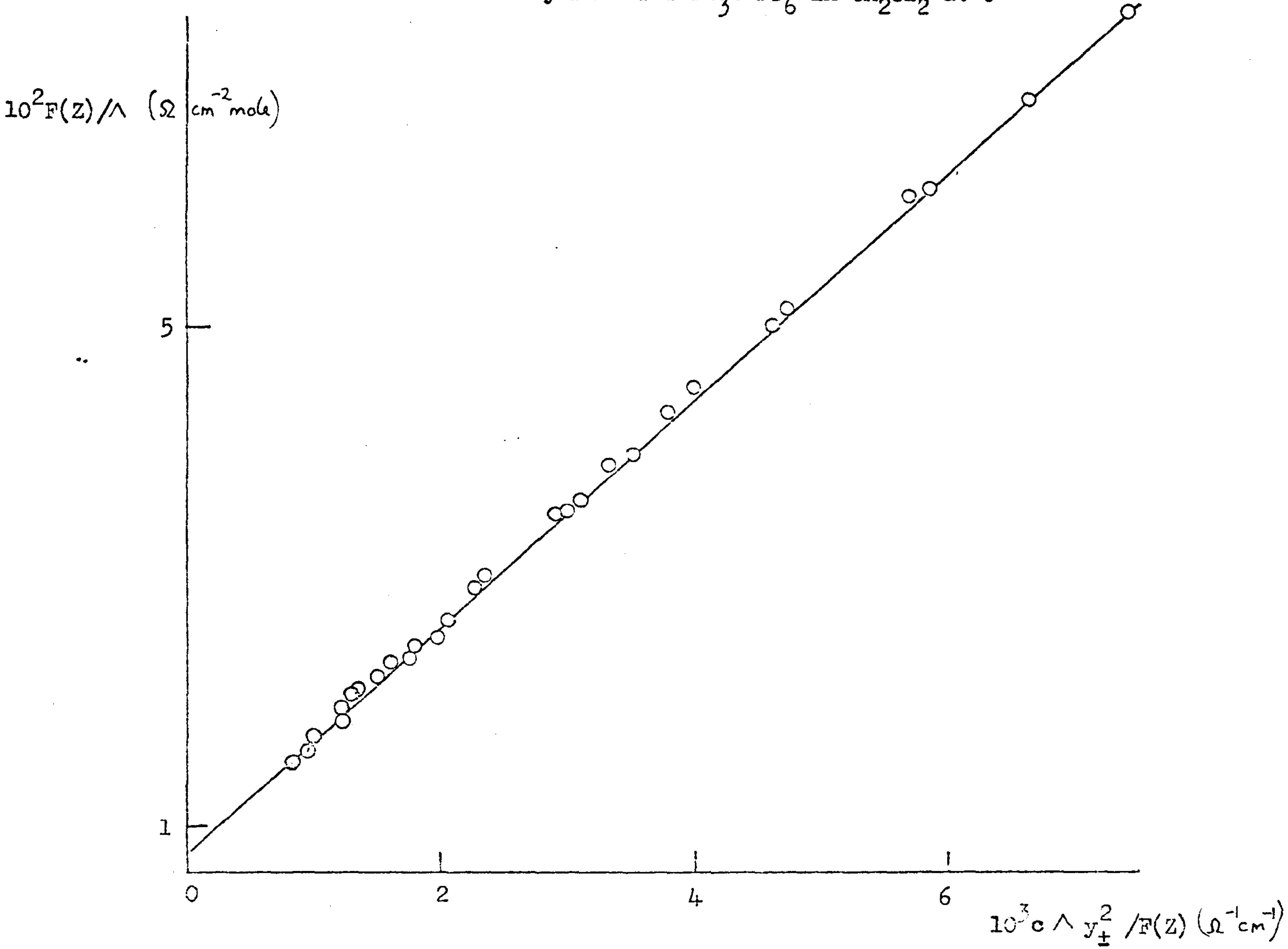
$$F(Z)/Z = 1/\Lambda_{02} + \left[c\Lambda y_{\pm}^2 / F(Z)\right] K_2/\Lambda_{02}^2 \qquad (10)$$

The derivation of this equation is given in detail by Harned and Owen[14], so it is not described here.

The parameters in the equation are as follows:

Fig. 7.6.

The Fuoss-Kraus Binary Plot for $Et_3O^+PF_6^-$ in CH_2Cl_2 at 0°



$$F(Z) = 1 - Z\left\{1 - Z\left[1 - Z \ldots\ldots^{-\frac{1}{2}}\right]^{-\frac{1}{2}}\right\}^{-\frac{1}{2}}$$

Values of $F(Z)$ have been calculated and tabulated, by Fuoss[13b], from the equation $F(Z) = 4/3 \cos^2 1/3 \cos^{-1}(-3(3Z)^{\frac{1}{2}}/2)$ where $Z = S_{\Lambda} (\Lambda c)^{\frac{1}{2}} (\Lambda_{02})^{-3/2}$. $y_{\pm}$, the mean molar activity coefficient of free ions, is given by

$\log y_{\pm} = -S_f (\alpha c)^{\frac{1}{2}}$ where α is the degree of dissociation.

From equation (10) a plot of $F(Z)/\Lambda$ against $\alpha \Lambda y_{\pm}^2/F(Z)$ gives a straight line of $I_t = 1/\Lambda_{02}$ and $S = K_2/\Lambda_{02}^2$. Such a plot for $Et_3O^+PF_6^-$ is shown in Fig. 7.6. The value of Λ_{02} is then used to calculate a more accurate value of $F(Z)$ and $y_{\pm}$. The reiterative procedure is repeated until Λ_{02} is constant. K_2 is then obtained from the best values of $F(Z)$, $y_{\pm}$ and Λ_{02}. Table 7.2. gives the values obtained from this procedure. a_F is the distance between the point charges calculated from the Fuoss[15] equation, which is a modification of the Bjerrum[22] equation. That is $a_F = r_+ + r_-$ where r_+ and r_- are the radii of the cation and anion respectively.

$$1/K_2 = (3000/4\pi a^3 N) \exp. (-e^2/aDkT) \qquad (11)$$

where N is Avogadros Number

k is Boltzmann's constant

D is Dielectric constant

e is electronic charge

The shortcomings of this equation have been discussed by Szwarc[16] and by Prue[17].

7.4.2. The Fuoss-Onsager Limiting Law and the Fuoss-Hsia equation (for $c < 1.6 \times 10^{-4}$M)

If Λ_i is the hypothetical molar conductance of an electrolyte if it were completely dissociated into ions at a concentration αc and d is the ion size parameter identified as the closest distance of approach of free ions (association distance) then:

$$\Lambda / \Lambda_i = \alpha$$

$$\Lambda_i = F(\Lambda_{02}, z, \alpha c, d)$$

At each concentration, if Λ_{02} and d are fixed α can be iteratively calculated (z is the charge number of the ions).

For each point K_2 is calculated from the equation

$$K_2 = (1 - \alpha)/\alpha^2 cy^2$$

y is the mean activity coefficient of free ions (the activity of ion-pairs is assumed to be unity). For the Limiting Law (L.L.) computation y is given by the Debye- Hückel[19] limiting law.

$$\log y = - Az^2 I^{\frac{1}{2}}$$

where $A = (2\pi N/1000)^{\frac{1}{2}} e^3/2.303k^{3/2}(DT)^{3/2}$

I = Ionic strength $= \frac{1}{2}\Sigma c_i z_i^2$

For the <u>Fuoss-Hsia equation [20](FH)</u> the Debye- Hückel equation is used, where A and B depend on the solvent.

$$- \log y = Az^3 c^{\frac{1}{2}}/(1 + Bzdc^{\frac{1}{2}})$$

where $B = (8\pi Ne^2/1000k)^{\frac{1}{2}}(DT)^{-\frac{1}{2}}$

The average value of K_2 is then used with the same values of Λ_{02} and d (F.H. only) to calculate Λ_{calc} for each point (equation 12). The standard deviation, $(\Lambda_{obs} - \Lambda_{calc})/n$, is obtained. The value of d is then increased and the cycle repeated. Now another value of Λ_{02} is fed to the computer and the program repeated. The best fit is that when the standard deviation is minimised.

$$\Lambda = \Lambda_{02} - S c^{\frac{1}{2}} + Ec \ln c + J_1 c - J_2 c^{3/2} \qquad (12)$$

Table 7.2.

The Equivalent Conductivity of $Et_3O^+PF_6^-$ in Methylene Dichloride at 0°C

Parameters from Fuoss-Kraus computation:- $\Lambda_{02} = 118.53\ \Omega^{-1}cm^2mole^{-1}$

$K_2 = 1.260 \times 10^5\ lmole^{-1}$

$a_F = 4.6557$ Å

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‡ These points were analysed by Fuoss-Hsia (F.H.) and Limiting Law (L.L.) equations.

* These points were rejected after initial computation by F.H. and L.L.

Run 162

$c/10^3M$	0.5838	0.3887	0.2775	0.1882	0.1423‡	0.09611‡
Λ	15.360	18.134	20.831	24.416	27.297	31.809
$10^3b\Lambda y_\pm^2/F(Z)$	5.6986	4.7231	4.0268	3.3320	2.8922	2.3548
$10^2F(Z)/\Lambda$	6.0271	5.1532	4.5167	3.8805	3.4868	3.0097_5

Run 160

$c/10^3M$	0.3658	0.1829	0.09237	0.06579
Λ	19.214	25.450	33.448	38.074
$10^3b\Lambda y_\pm^2/F(Z)$	-	-	-	1.9786
$10^2F(Z)/\Lambda$	-	-	-	2.5253

continued ...

Table 7.2. cont'd

Run 159

$c/10^3M$	0.2063	0.1031	0.05157	0.02803^{I*}	0.01862^{I*}
Λ	23.865	32.701	42.538	52.765	60.344
$10^3 c\Lambda y_\pm^2/F(Z)$	3.5290	-	-	1.2347	0.96027
$10^2 F(Z)/\Lambda$	3.9621_5	-	-	1.8394	1.6147

Run 166 (by dilution)

$c/10^3M$	0.1604^I	0.08908^I	0.05727^I	0.04220^I	0.02970^I
Λ	26.200	33.047	39.111	43.742	49.276
$10^3 c\Lambda y_\pm^2/F(Z)$	3.0914	2.2788	1.7925	1.5083	1.2229
$10^2 F(Z)/\Lambda$	3.6253	2.8995	2.4638	2.2108	1.9699

Run 166 (by concentration)

$c/10^3M$	0.03463^I	0.03320^I	0.04795^I	0.07197^I	0.1838
Λ	46.500	47.223	41.718	36.140	25.794
$10^3 c\Lambda y_\pm^2/F(Z)$	1.3337	1.3018	1.6208_5	2.0452	-
$10^2 F(Z)/\Lambda$	2.0844	2.0534	2.3147	2.6584	-

Run 164

$c/10^3M$	1.051	0.8180	0.6118	0.3678	0.2455	0.1498^I
Λ	12.145	13.479	15.155	18.687	22.068	26.935
$10^3 c\Lambda y_\pm^2/F(Z)$	7.4044	6.6567	5.8458	4.6293	3.8189	2.9869
$10^3 F(Z)/\Lambda$	7.4985	6.8054	6.1000	5.0053	4.2723	3.5302

continued ...

Table 7.2. cont'd

Run 163

$c/10^3M$	0.05344^{I}	0.02137^{I}	0.01374^{I}	0.008365^{I}
Λ	40.923	56.107	64.170	73.186
$10^3 c \Lambda y_{\pm}^2 / F(Z)$	1.7548	1.0193	0.7673	-
$10^3 F(Z)/\Lambda$	2.3558	1.7351	1.5230_5	-

Run 165

$c/10^3M$	10.874	9.060	7.909	6.795	5.436	3.883	2.718
Λ	5.379	5.822	5.955	6.309	6.748	7.532	8.529

Run 165 cont'd

$c/10^3M$	2.250	1.931	1.	1.504	1.3550	1.0761
Λ	9.136	8.640	10.250	10.695	11.094_5	12.166
$10^3 c \Lambda y_{\pm}^2 / F(Z)$	-	-	-	-	8.3068	-
$10^2 F(Z)/\Lambda$	-	-	-	-	8.1360	-

Run 161

$c/10^3M$	7.926_5
Λ	6.068

Run 167

$c/10^3M$	19.854	9.906
Λ	4.776	5.748_5

Run 168

$c/10^3M$	38.956	14.478
Λ	4.5987	5.2621

Table 7.3.

Quantities Derived from the Conductance Equations

	Equation	Λ_{02} $\Omega^{-1}cm^2mole^{-1}$	$10^{-5}K_2$ $lmole^{-1}$	$(\Lambda_{obs}-\Lambda_{calc})/$ $\Omega^{-1}cm^2mole^{-1}$	No. of points computed
1	F.K.	118.53	1.260	-	29
2	L.L.	118.53	1.251	0.761	19
3		118.53	1.269	0.355*	16
4		117.00	1.227	0.371*	16
5	F.H.	118.53	1.220	0.741	19
6		118.53	1.237	0.379*	16
7		117.00	1.195	0.362*	16
8		116.00	1.168	0.363*	16

* The points marked by * in Table 7.2. were omitted in the other cycles of the programme.

Where L.L. is equation (12) with only the S term and c replaced by αc, F.H. is equation (12) with c replaced by αc, S is the slope of the Limiting law, E depends on z, Λ_{02} and the solvent and J_1 and J_2 are functions of d. For a detailed account of the pro~~d~~cedure the reader is referred to the papers by Fernandez-Prini[21], Fuoss and Hsia[20] and by Prue [18].

The values of Λ_{02} and K_2 obtained by these processes are given in Table 7.3. The L.L. gives $\Lambda_{02} = 118.53\ \Omega^{-1}\ \text{cm}^2\ \text{mole}^{-1}$ and $K_2 = 1.269 \times 10^5\ \text{lmole}^{-1}$ whilst the F.H. equation gives the better fit to the data with $\Lambda_{02} = 117.00\ \Omega^{-1}\ \text{cm}^2\ \text{mole}^{-1}$ and $K_2 = 1.195 \times 10^5\ \text{lmole}^{-1}$ and this corresponds to an association distance, d, of 26.7Å

The Limiting Law (L.L.) calculation is no different in principle from the F.K. calculation since both are based on $\Lambda = \alpha\left[\Lambda_{02} - S_\Lambda (\alpha c)^{\frac{1}{2}}\right]$ Lines 1, 2, and 3 (Table 7.3.) show that the results from both equations agree. The slight differences are due to the computation of less points in the case of L.L. Up to 10^{-3}M there is no evidence of ternary association. Certainly, ternary association becomes more likely at 10^{-2}M, but the Λ,c plot shows that the Λ is still decreasing with increasing concentration of $Et_3O^+PF_6^-$. So it is likely that ternary association is negligible at these concentrations. A bilateral ternary plot was made but it was a curve.

7.5. The Effect of Diethyl ether on the Conductivity of $Et_3O^+PF_6^-$ in Methylene Dichloride solutions

The solvation of oxonium ions by ether molecules is a hypothesis

Table 7.4.

The Conductivity of $Et_3O^+PF_6^-/CH_2Cl_2$ in the Presence of Diethyl Ether at 0°

Run 169 2.315×10^{-5} moles $Et_3O^+PF_6^-$, mole ratio $Et_2O:Et_3O^+PF_6^- = 2.02:1$

$10^4c/M$	0.8638	1.241	1.675	2.395
$\Lambda/\Omega^{-1}cm^2mole^{-1}$	33.194	29.194	26.048	22.639
$10^3\Lambda y_\pm^2/F(Z)/\Omega^{-1}cm^{-1}$	2.2011_5	2.6680_5	3.1163	3.7217
$10^2F(Z)/\Lambda/\Omega cm^{-2}mole$	2.8469	3.2438	3.6151	4.1288

Run 169 cont'd

Λ_b			14.942	12.397
$10^4c/M$	3.522	5.323	6.843	9.581
$\Lambda/\Omega^{-1}cm^2mole^{-1}$	18.432	16.446	14.920	
$10^3\Lambda y_\pm^2/F(Z)/\Omega^{-1}cm^{-1}$	4.4774	5.4057	6.0516	
$10^2F(Z)/\Lambda/\Omega cm^{-2}mole$	4.7670	5.5711	6.0936_5	

Run 171 3.357×10^{-5} moles $Et_3O^+PF_6^-$, $Et_2O : PF_6^- = 1.56 : 1$

Λ_b					12.658
10^4c	2.627	3.938	5.323	7.667	9.832
Λ	21.538	18.238	16.166	13.943	12.602
$10^3\Lambda y_\pm^2/F(Z)$	3.9076	4.7259	5.4347	6.3914	7.1092
$10^2F(Z)/\Lambda$	4.3542	5.0972	5.7075	6.5508	7.1924

Run 172 1.638×10^{-5} moles $Et_3O^+PF_6^-$, $Et_2O : Et_3O^+PF_6^- = 1.01 : 1$

Λ_b						16.813
10^4c	0.4735	0.6552	1.060	1.542	2.423	4.847
Λ	41.605	37.073	30.915	26.686	22.278	16.804

continued ...

Table 7.4. cont'd

Run 172 cont'd

$10^3c\Lambda y_\pm^2/F(Z)$	1.5875	1.9105	2.4774	3.0053	3.7616	5.2116
$10^2F(Z)/\Lambda$	2.3166	2.5888	3.0829	3.5497	4.2165	5.5041

Run 173 0.717 x 10^{-5} moles $Et_3O^+PF_6^-$, Et_2O : $Et_3O^+PF_6^-$ = 2.2 : 1

Λ_b							23.486
10^4c	0.2251	0.3215	0.4098	0.5649	0.8779	1.357	2.132
Λ	51.533	46.345	43.680	38.998	33.079	28.047	23.443
$10^3c\Lambda y_\pm^2/F(Z)$	0.9752	1.2235	1.2235	1.7324	2.2021	2.7699	3.4679_5
$10^2F(Z)/\Lambda$	1.8816	7.0834	2.2028	2.4564	2.8766	3.3669	3.9922

Run 174 1.194 x 10^{-5} moles $Et_3O^+PF_6^-$, Et_2O : $Et_3O^+PF_6^-$ = 4.4 : 1

Λ_b					19.039
10^4c	0.4297	0.6174	0.9193	1.462	3.551
Λ	41.122	36.492	31.872	26.580	18.958
$10^3c\Lambda y_\pm^2/F(Z)$	1.4146	1.7516	2.1971	2.7862	4.3281
$10^2F(Z)/\Lambda$	2.3341	2.6156	2.9742	3.5356	4.8522

Run 175 0.173 x 10^{-5} moles $Et_3O^+PF_6^-$, Et_2O : $Et_3O^+PF_6^-$ = 9.25 : 1

Λ_b						39.275
10^5c	0.476	0.5584	0.8016	1.336	2.122	5.153
Λ	71.649	69.251	64.583	57.927	51.838	39.200
$10^4c\Lambda y_\pm^2/F(Z)$	2.9158	3.4829	4.5862	6.6713	9.2119	15.864
$10^2F(Z)/\Lambda$	1.3714	1.4164	1.5141	1.6794	1.8664	2.4380

Λ_b = Equivalent conductivity before addition of Et_2O

Table 7.5.

Parameters from the Fuoss-Kraus Analysis of the Conductivity of $Et_3O^+PF_6^-$ in the Presence of Diethyl Ether

Run No.	Ratio of Et_2O : $Et_3O^+PF_6^-$	Λ_{02} $\Omega^{-1}cm^2mole^{-1}$	$10^{-5}K_2$ $l mole^{-1}$	a_F Å
-	0	118.531	1.260	4.656
172	1.01 : 1	110.208	1.070	4.732
171	1.56 : 1	110.125	1.072	4.731
169	2.02 : 1	101.423	0.869	4.834
173	2.2 : 1	98.666	0.8292	4.858
174	4.4 : 1	91.349	0.7248	4.927
175	9.25 : 1	88.422	0.6404	4.993

that needs confirming. In Chapter 6 the N.M.R. study indicated that solvation of oxonium ions occurs, whilst the results of the polymerisation studies (Chapters 5 and 8) and the decomposition studies (Chapter 6) can be explained by this hypothesis. Therefore, I decided to test the theory by a conductimetric technique.

First of all we attempted to titrate $Et_3O^+PF_6^-$ by introducing diethyl ether into a solution of it in methylene dichloride and measuring the changes in conductivity. Unfortunately the results that we obtained were inconsistent because the technique was unsatisfactory. Therefore we decided to add small quantities of ether, in phials, and then to dilute the solution, as before, and measure κ. In these experiments, the conductivity of the $Et_3O^+PF_6^-$ solution was measured, the phial of ether broken, and the dilution continued (the ether phial was covered with the solution when it was broken so that the diethyl ether did not remain in the vapour phase). The Fuoss-Kraus equation (10) was used to compute Λ_{02} and K_2 from the data. In the calculations, it was assumed that the quantity of ether ($1.4 - 0.05 \times 10^{-3}$M) did not affect the viscosity, the dielectric constant or the density of the solution. If the ether had affected these parameters the Fuoss-Kraus plots would have been curved (the concentration of ether varies through out each dilution) and they were not. The concentration of $Et_3O^+PF_6^-$ was of the same order of magnitude as that of the diethyl ether, so that corrections would have been required for the viscosity of solutions even in the dilution experiments without diethyl ether.

The values obtained from the Fuoss-Kraus computation are in

Fig. 7.7.

The Effect of Et_2O on Λ_{02}, K_2 and a_F for $Et_3O^+PF_6^-$ in CH_2Cl_2 at 0°

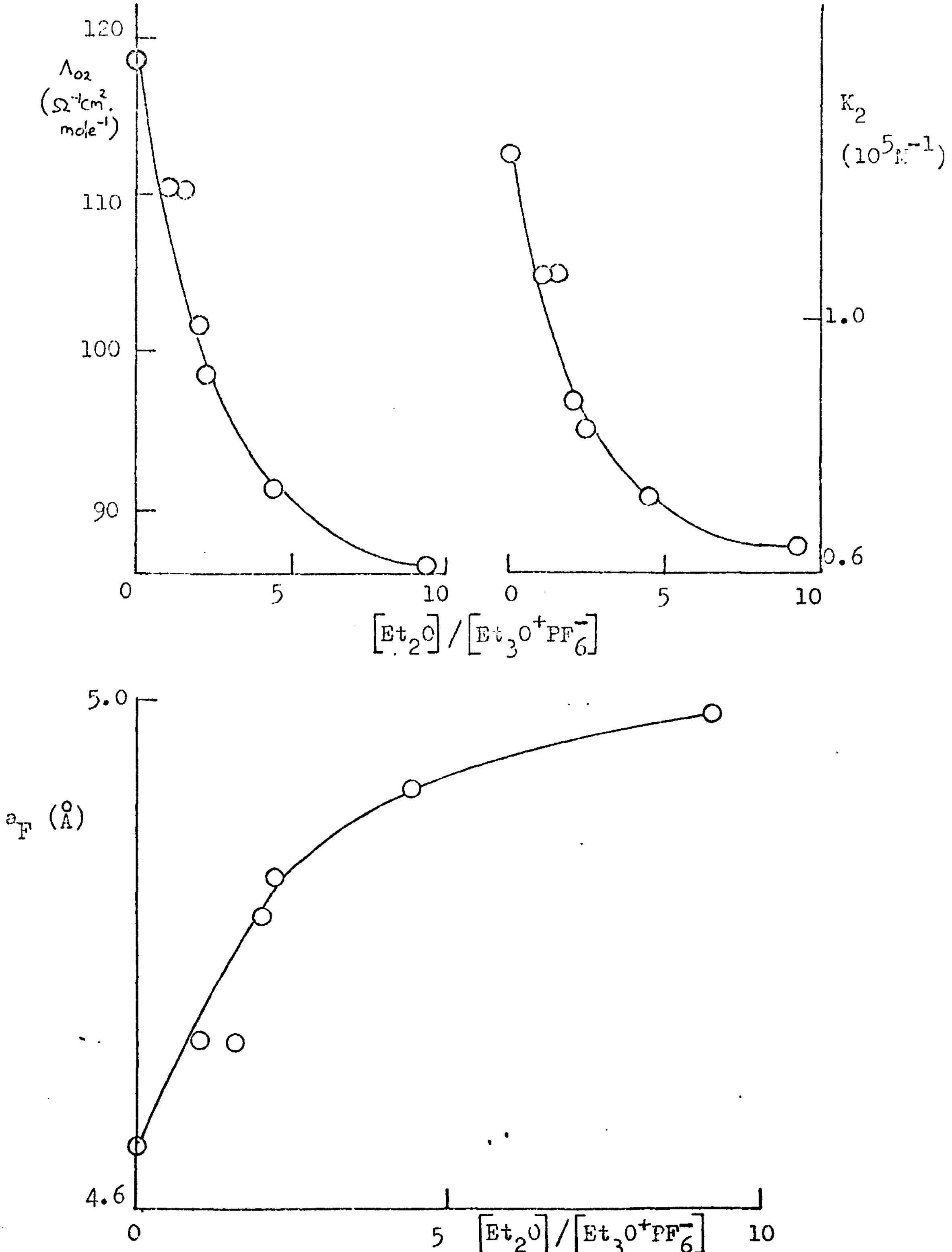

Table 7.5. In Fig. 7.7. Λ_{02} and K_2 are plotted with respect to the ratio of diethyl ether to salt. This shows that Λ_{02} appears to go to an asymptote at about 88 Ω^{-1} cm^2 mole^{-1} whereas K_2 reaches 6×10^4 lmole^{-1}.

These results are considered to be good evidence for the solvation of oxonium ions. The a_F value is only increased by 0.34Å in the presence of diethyl ether so that it suggests that ether-separated ion-pairs are not formed. This is in agreement with the decomposition hypothesis (Chapter 6). On the other hand the ethyl group may be exchanging rapidly with the Et_2O molecule so that these measurements cannot distinguish between the solvent separated ion-pair and a solvated oxonium ion-pair. Therefore these experiments should be repeated using a less basic ether.

In order to extend the measurements to higher concentrations of Et_2O, an attempt was made to measure the conductivity of $Et_3O^+PF_6^-$ in 1M Et_2O but this was unsuccessful because of unstable resistance readings.

7.6. $Et_3O^+SbF_6^-$

It was hoped to extend this study to $Et_3O^+SbF_6^-$ because it is more stable and appears to be a better alkylating agent than $Et_3O^+BF_4^-$. However, the dilutions which have been made gave inconsistent values for Λ_{02} and K_2. The reason for this is not known but these inconsistencies may be due to adsorption of the salt on to the glass or to a reaction with impurities. It is hoped to clarify this in the near future.

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SECTION B - CHAPTER 8

The Mechanism of the Polymerisation of Cyclic Formals by Triethyloxonium Salts

8.1. The Polymerisation of 1,3-Dioxolan by $Et_3O^+BF_4^-$ (This work)

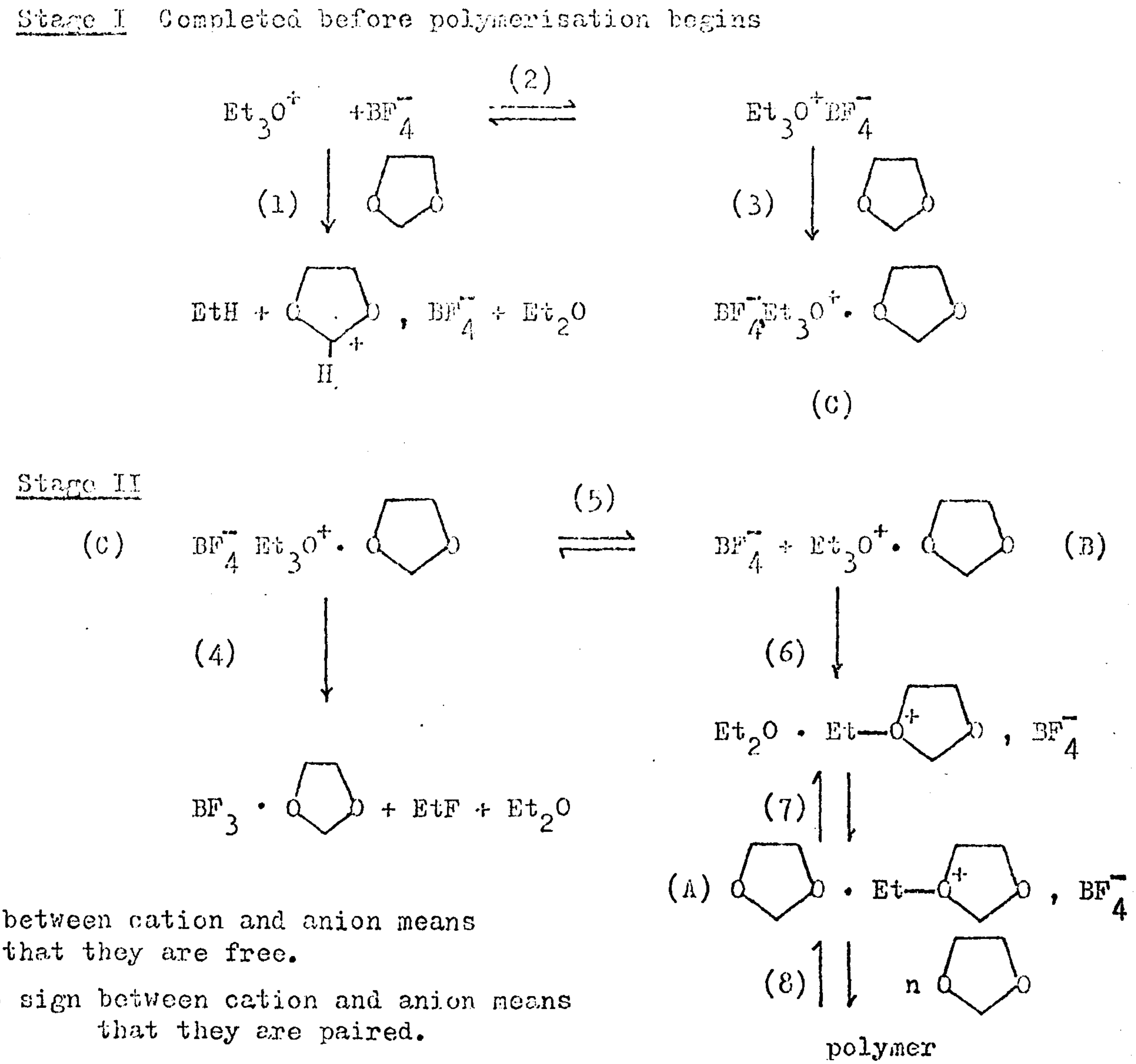
In Chapter 5 we have seen that the polymerisation of 1,3-dioxolan by $Et_3O^+BF_4^-$ is characterised by a slow production of active centres (A) whose concentration c_a is very much less than the initial concentration of $Et_3O^+BF_4^-$. The concentration of stable active centres builds up to a steady value as shown by the last part of the polymerisation and the repolymerisations being of first order with respect to monomer. Any explanation of these observations must also take into account the results on the decomposition of $Et_3O^+BF_4^-$ (Chapters 5 and 6). In particular, we recall that superimposed upon the polymerisation is the formation of ethane which only occurs at the start of the reaction and then stops and the production of ethyl fluoride which continues throughout the polymerisation and is accompanied by a reduction in the specific conductivity. The reaction scheme proposed to account for our results is shown in Fig. 8.1.

(1) Fast attack of free cations on monomer.

In the sampling experiments in which ethane was observed (Chapter 5), the monomer was added to a solution of $Et_3O^+BF_4^-$ in methylene dichloride. The methylene dichloride solution had a free ion concentration of about 2 x 10^{-4}M and the concentration of dioxolenium tetrafluoroborate (calculated from the amount of ethane formed) was of the same order of magnitude and did not increase

Fig. 8.1.

The Proposed Scheme for the Polymerisation of 1,3-Dioxolan by $Et_3O^+BF_4^-$



+ between cation and anion means that they are free.

no sign between cation and anion means that they are paired.

, between cation and anion signifies that both free and paired ions are meant.

with time. Therefore, it is proposed that the dioxolenium ion is produced very rapidly by reaction of 1,3-dioxolan with the free triethyloxonium ions present initially (reaction 1).

(3) Fast solvation of ion-pairs by monomer

Our explanation of why reaction (1) does not continue is that the remaining ion-pairs become solvated by 1,3-dioxolan (reaction 3) forming a relatively stable species and since solvation of anions by ethers has not been observed[1], an equilibrium (5) is set up between the solvated ion-pairs, the solvated triethyloxonium ions, and the unsolvated anions.

(4) Slow decomposition of (C) competing with route (5), (6), (7) and (8).

(6) Slow ethylation of monomer which determines the rate of formation of active species (A).

Chapter 7 shows that at the relevant salt concentrations the concentration of ion-pairs is much greater than the concentration of free ions; therefore the solvated ion-pair (C) cannot rearrange directly to A, otherwise c_a would continue to increase throughout the polymerisation and after the polymerisation had reached equilibrium. Therefore c_a would not reach a steady value and the polymerisation would not become of first order with respect of monomer. On the other hand, the free ion (B) can rearrange to form (A) which is also involved in an ion-pair, free ion equilibrium. The ether-exchange (7) may or may not be slow relative to (6) but is more likely to be fast. Therefore, if equilibrium (5) is maintained efficiently the yield of A depends on the relative rates of (4) and (6). The rate of step (6), R_6, must be low, because polymerisation starts only when a large enough concentration of A has been produced. This is our interpretation of the induction period.

Since the rate constant for the polymerisation of 1,3-dioxolan at low total ion concentration is the same as that at high total ion concentration and since the association constant for tertiary oxonium ions is about 10^5 $lmole^{-1}$ (Chapter 7), the propagation rate constant for ion-pairs must be approximately the same as that for free ions; in other words, the solvated oxonium ion propagates at about the same rate regardless of whether it is paired or free.

The scheme proposed (Fig. 8.1.) is not satisfactory in one respect because it does not explain why the polymerisation becomes of first order and why the successive repolymerisations are totally of first order with the same rate constant. If equilibrium (5) is maintained efficiently one would expect a slow build up of A during the period after polymerisation had ceased and before depolymerisation because (C) is still present in the solution. Therefore since we observed the same first order rate constant for a repolymerisation (105A) which was made some 20 hours after the first polymerisation had reached equilibrium we conclude that the active centres (A) are stable and that some process prevents the equilibrium (5) being maintained. A possible explanation of the latter is that when polymer (which is more basic[2] than the monomer) progressively replaces 1,3-dioxolan in species (B) and (C) the equilibrium constant of (5) progressively changes in favour of ion-pairs as the DP and/or the concentration of the polymer increases. Coupled with this is the fact that when (C) is solvated by polymer the rate of step (4) may be greater.

When $Et_3O^+SbF_6^-$ is used as the catalyst, step (4) does not occur, so that the concentration of (B) is much greater in this case. Therefore, R_6 will be correspondingly increased. Since this polymerisation also becomes of first order with respect to monomer it means that all the $Et_3O^+SbF_6^-$ produces active centres (A). In fact, the k_1/c value for polymerisation by $Et_3O^+SbF_6^-$ is of the same order of magnitude as that for the polymerisation of 1,3-dioxolan by $HClO_4$, where c is the initial concentration of catalyst.

Since $Et_3O^+SbF_6^-$ polymerises 1,3-dioxolan at a greater rate than $Et_3O^+BF_4^-$ and without the formation of ethane, I believe the active centre in the polymerisation of cyclic formals by triethyloxonium salts to be the 1-ethyl-1$\underline{H}^+$-1,3-dioxolanium ion. Dioxolenium tetrafluoroborate does catalyse the polymerisation of 1,3-dioxolan, but for the reasons discussed in Chapter 5 we decided that the production of polymer from this process is negligible in this system.

Once the active centre A is produced, pro$\overset{p}{g}$agation is by the ring-expansion mechanism which is discussed in detail in Chapters 5 and 10. It should be noted here too that the low DP's signify extensive transfer reactions and that in our view these are at least partly due to the mobility of the Et^+ over all the oxygen atoms in the system

8.2. <u>The work of Medvedev's school</u>

These authors[3] observed that a solution of $Et_3O^+SbCl_6^-$ in ethyl chloride absorbs at 272 nm, that a reaction mixture containing

1,3-dioxolan and $Et_3O^+SbCl_6^-$ absorbs at 228 nm, and that a solution of n-butylvinyl ether and $Et_3O^+SbCl_6^-$ absorbs at 231 nm. Since they assumed that the absorptions of the polymerising n-butylvinyl ether is due to the $-CH_2-CH=\overset{+}{O}-C_4H_9$ ion and that the absorption of $Et_3O^+SbCl_6^-$ at 272 nm is due to the Et_3O^+ ion, they concluded that the absorption at 228 nm which they found for the polymerisation of 1,3-dioxolan by $Et_3O^+SbCl_6^-$ is due to the carboxonium ion $RO(CH_2)_2\overset{+}{O}=CH_2$ which is closely related to the carboxonium ion derived from the alkylvinyl ether. However, there is no independent evidence that trialkyloxonium ions absorb near 270 nm or that carboxonium ions absorb near 230 nm; in fact I have shown that $Et_3O^+BF_4^-$, $Et_3O^+PF_6^-$ and $Et_3O^+SbF_6^-$ do not absorb above 220 nm. On the other hand, Penczek[4] has shown that $SbCl_5$ and $SbCl_6^-$ absorb at 270-272 nm in methylene dichloride and $Et\overset{+}{O}SbCl_4$ absorbs at somewhat lower wavelengths. Therefore, the mechanism of Lyudvig et al. is extremely unconvincing.

In any case, the active centre cannot be the carboxonium ion which Okada[5] and Weichert[6] suggested, independently, for the polymerisation of 1,3-dioxolan, by analogy with Kern and Jaack's[7] mechanism for the polymerisation of trioxan, because it does not explain the formation of macrocyclic rings. Polymers free from end-groups can only be produced by this mechanism if an effecient end-to-end ring closure occurs. This is highly unlikely and only possible when initiation is by protonic acids where the polymer has a hydroxyl group at one end. For initiation by trialkyloxonium ions the terminal group would be an alkoxy group so that macrocyclic rings could only be formed by a back-biting mechanism[7,8]. A process like this implies that there should be a number of linear fragments corresponding to the number of catalyst molecules. Careful examination of the reaction mixtures has shown that if such fragments are present, their concentration is much lower than that of the initiator (see Chapter 5).

As well as this, Jaacks[9] has shown that methoxymethyl perchlorate reacts with 1,3-dioxolan to give dimethyl ether and dioxolenium perchlorate.

Since the organic part of methoxymethyl perchlorate is a very close analogue to the carboxonium ion formed from 1,3-dioxolan, propagation by this ion is effectively ruled out, because the dioxolenium ion is an inefficient initiator.

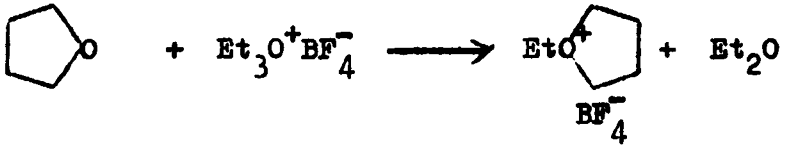
Westermann[2] showed that antimonypentachloride polymerises 1,3-dioxolan rapidly without an acceleration period and the reaction did not reach equilibrium. Dreyfuss[10] has shown that the polymerisation of tetrahydrofuran by $Et_3O^+SbCl_6^-$ is characterised by a transfer to anion which is analogous to the decomposition of $Et_3O^+BF_4^-$. $SbCl_5$ is formed which can initiate the polymerisation of tetrahydrofuran but less efficiently than the oxonium ion. Therefore, in solution $Et_3O^+SbCl_6^-$ most probably decomposes in a manner similar to $Et_3O^+BF_4^-$:

$$Et_3O^+SbCl_6^- \longrightarrow EtCl + SbCl_5 + Et_2O$$

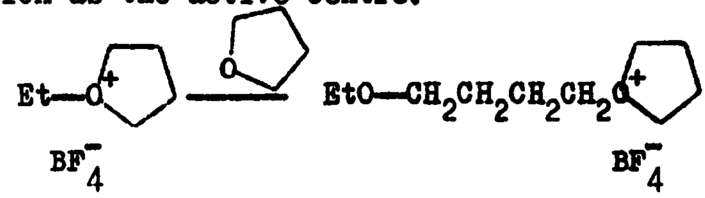
Since $SbCl_5$ can polymerise 1,3-dioxolan without induction period or acceleration[2], the true initiator in Medvedev's system is most likely $SbCl_5$, and the reported absence of an acceleration is not due to the absence of water, as they have suggested. This theory could be tested by end-group analysis because Westermann[2] found absorptions due to chlorine, carbonyl and hydroxyl groups in the infrared spectra of polymers made from $SbCl_5$, but unfortunately Lyudvig has not carried out such studies on her polymers.

8.3. The work of Yamashita's school

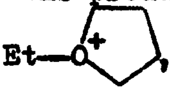
Yamashita[11] at one time believed that $Et_3O^+BF_4^-$ initiated the polymerisation of 1,3-dioxolan by a simple transfer of the Et group to 1,3-dioxolan, a process analogous to the initiation of tetrahydrofuran polymerisation.



He considered the propagation to be similar to the polymerisation of THF, which is a ring-opening polymerisation with a tertiary oxonium ion as the active centre.



The only evidence presented for this assumption was that $EtOCH_2CH_2OCH_2OCH_3$ was formed when a reaction mixture of $Et_3O^+BF_4^-$ and 1,3-dioxolan was killed with sodium methoxide. Actually, this product could be formed from both the ions —Et and $EtOCH_2CH_2OCH_2$, and therefore this does not differentiate between the ring-expansion mechanism and a ring-opening polymerisation.

Yamashita[12] also reacted 1,3-dioxepan with $Et_3O^+BF_4^-$ under conditions such that no polymer was formed and killed the resulting mixture with sodium methoxide. He identified (by g.l.c.) tetrahydrofuran, $C_2H_5O(CH_2)_4OCH_3$, and $C_2H_5O(CH_2)_4OC_2H_5$ but the expected product $C_2H_5O(CH_2)_4OCH_2OCH_3$ was not present. Therefore he concluded that these compounds were produced by degradation of small amounts of polymer. However, Westermann[2] showed that tetrahydrofuran is a very persistent impurity in 1,3-dioxepan, so that the products that Yamashita identified probably come from the ion, , and the $C_2H_5O(CH_2)_4OCH_2OCH_3$ is not formed because initiation probably occurs through the 1-ethyltetrahydrofuranium ion.

Yamashita[13] has polymerised 1,3,6-trioxocan by $Et_3O^+BF_4^-$ and showed that the reaction is similar to the polymerisation of other cyclic formals, but some chain breaking reaction also seems to occur.

8.4. Conclusion

In conclusion, the polymerisation of cyclic formals by triethyloxonium salts has been studied by other workers, who failed to recognise that the catalysts were inefficient. They are inefficient because of a competitive decomposition reaction which occurs through the ion-pair and the rate of this reaction is enhanced in the presence of an ether (Chapter 6). I have proposed the scheme given in Fig. 8.1., in which the solvated oxonium ion plays an essential part, to explain the results of the polymerisation and decomposition experiments.

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Fig. C.1.

The Mechanism of the Polymerisation of Cyclic Formals of Jaacks[3]

(Anions omitted for clarity)

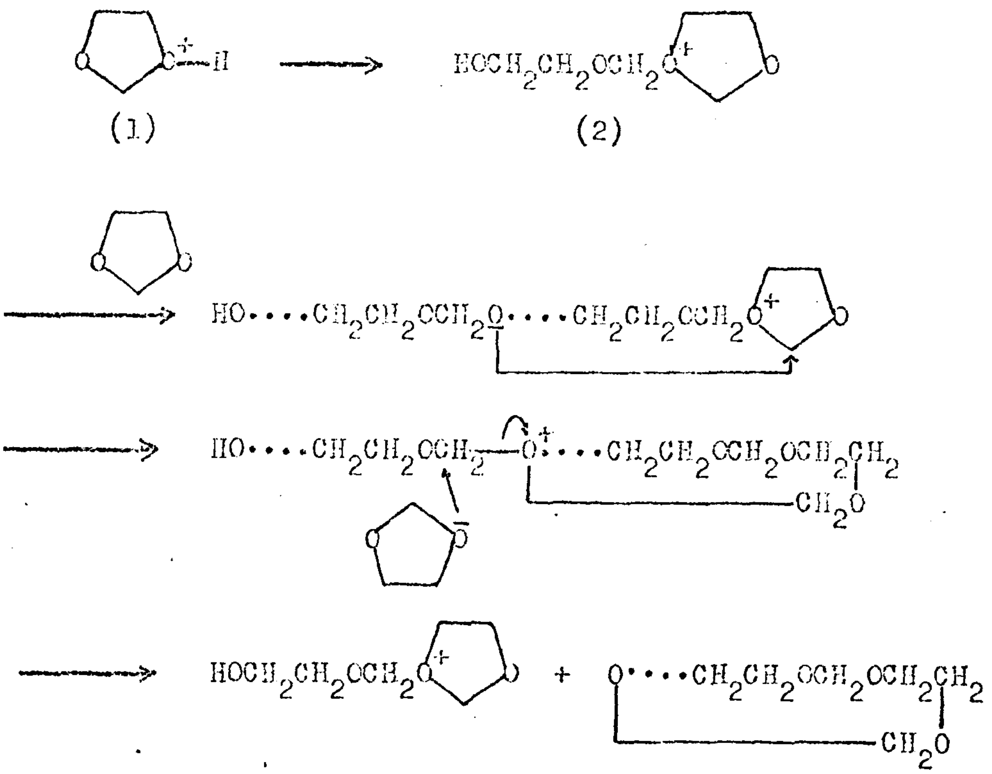
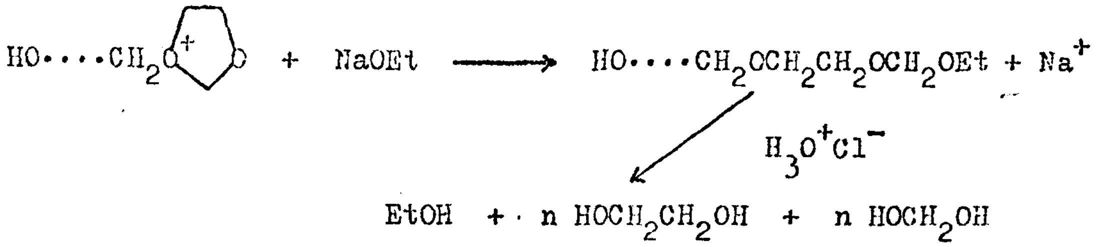


Fig. C.2.

Jaacks' Method of Estimating End-Groups

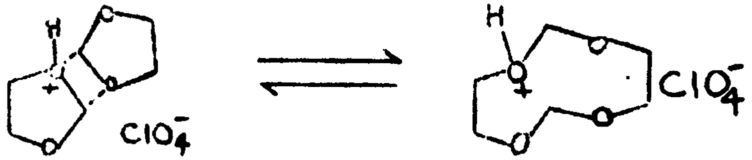


SECTION C

The Mechanism of the Polymerisation of Cyclic Formals by Anhydrous Perchloric Acid

Introduction

Westermann and Plesch proposed that the equilibrium polymerisation of 1,3-dioxolan[1] and 1,3-dioxepan[2] by anhydrous perchloric acid occurred through a 4-centred transition state to produce cyclic polymer.



The mechanism proposed was a ring-expansion in which the ring never opened. This mechanism accounts simply for the cleaness of the monomer-polymer equilibrium and for the high yields of cyclic dimer[2] which are obtainable from 1,3-dioxan and 1,3-dioxepan.

Although Jaacks[3] agrees that the polymers are cyclic, he has questioned the ring-expansion mechanism and proposed his own mechnism for the production of macrocyclic rings. He considers the polymerisation to be a ring opening with back-biting, which is illustrated in Fig. C.1.

If this mechanism is correct, each $HClO_4$ molecule must produce a linear fragment with a terminal OH group. Jaacks' explanation is based on his mechanism for the production of cyclic polymers from trioxan[4] and on experiments[3] in which the polymerisation was killed with sodium ethoxide (see Fig. C.2.).

By this method Jaacks claims to be able to differentiate between the tertiary oxonium ion (2, Fig. C.1.) and the secondary oxonium ion (1, Fig. C.1.) because on reaction with sodium ethoxide

(1) produces ethanol by proton abstraction and (2) produces a polymer with a terminal -OEt group. The ethanol from the former reaction was removed from the polymer by repeated distillation of an azeotrope of water and ethanol from a solution of the polymer. The polymer was then hydrolysed in aqueous hydrochloric acid which converted the -OEt group into ethanol which was determined by g.l.c.

His results indicated that tertiary oxonium ions equivalent to up to 95% of the $HClO_4$ could be found, but conversions of less than 95% were explained by the supposition that production of tertiary oxonium ions from protonated 1,3-dioxolan and protonated poly-1,3-dioxolan is a slow process. In fact, evidence was published[3b] showing the slow formation of tertiary oxonium ions at the expense of secondary oxonium ions throughout the polymerisation.

I decided to differentiate between these two mechanisms by determining the number of hydroxy groups produced in the polymerisation of 1,3-dioxolan by $HClO_4$ and since neutralisation by NaOR appears to differentiate between the two mechanisms I carried out experiments similar to those of Jaacks and coworkers. As I disliked decomposing the polymer, I used sodium phenoxide as a terminating agent because this would enable me to determine the PhO end-groups by u.v. spectroscopy. Fortunately much of the back-ground work for this technique had been done by Saegusa[5] who terminated tetrahydrofuran polymerisations by sodium phenoxide. This Section describes the results of the experiments in which the polymerisation of 1,3-dioxolan by $HClO_4$ was terminated by sodium phenoxide (Chapter 9). Chapter 9 also included further results on the analysis of polymers for OH end-groups. Chapter 10 discusses the merits of the ring-expansion mechanism[1] and the back-biting mechanism[3] for the polymerisation of 1,3-dioxolan.

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5b. T. Saegusa and S. Matsumoto, Macromolecules, 1968, **1**, 442.

Table 9.1.

Quantitative Measurements of Hydroxyl Groups in Polymers of 1,3-Dioxolan

Run No.	PHW15	PHW123	FJ128	FJ178A	FJ178B	FJ179A	FJ179B	FJ180A	FJ180B	FJ181A	FJ181B
Temperature	15	10	17	12	12	11	11	10	10	10	10
Optical density of OH	0.02	0.04	0.04	0.04	0.122	0.086	0.817	0.023	0.023	0.036	0.012
Monomer units/OH	160	80	80	80	26	37	185	137	137	97	263
DP	13.7	15.0	13.5	13.9	11.6	7.8	11.9	11.6	11.4	15.4	14.5
Yield %	35	40	41	33	33	20	20	35	35	37	37
$[Et_3O^+SbF_6^-]/10^2M$	-	-	-	-	-	-	-	-	-	10.0	10.0
$[HClO_4]/10^2M$ (C)	0.36	3.00	4.00	6.00	6.00	10.00	10.00	10.00	10.00	-	-
$[OH]/10^2M$ (H)	0.45	1.00	1.00	0.77	2.4	0.9	0.19	0.53	0.53	0.69	0.26
$Y/10^2M$	-	-	-	0.14	0.14	0.13	0.13	0.14	0.14	0.14	0.14
Killing agent	$.88NH_3$ Vapour	$.88NH_3$ Vapour	$NH_3(g)$	$.88NH_3$ Vapour	H_2O	$.88NH_3$ Vapour	Et_3N $(+H_2O)$	Et_3N	Et_3N $(+H_2O)$	NH_3 Vapour	Et_3N $(+H_2O)$

M = 2M Except 179 M = 1.8M

Y = Concentration of end-groups determined from NaOPh experiments.

SECTION C - CHAPTER 9

Polymerisations and Related Experiments

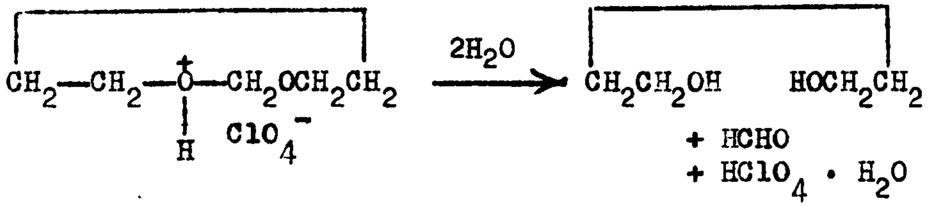
9.1. Hydroxyl Group Determination

Infrared measurements on polymers of 1,3-dioxolan were made on 1% solutions in carbon tetrachloride in 0.1cm cells. The peak due to the C-H stretching frequency at 2926 cm^{-1} of the CH_2 groups in the polymer chain was used as an internal standard and D, the optical density of the hydroxyl groups at 3500 cm^{-1} was measured. Westermann[1] had calibrated this system by adding small known quantities of 1,4-butanediol to a known quantity of a low molecular weight polymer (DP = 13.7) and measuring D for the absorption at 3500 cm^{-1}. D was found to be directly proportional to the hydroxyl group concentration and an optical density of 0.105 correspnded to one OH group per 30 units of monomer. He also showed that D remained unaltered even after the polymer had been in the vacuum oven for several days and that any ethylene glycol which might have been formed by hydrolysis was removed from the polymer in the isolation procedure.

The results are shown in Table 9.1. The two results of Westermann (PHW15 and PHW123) show that my experimental results are consistent with his. When the concentration of OH groups (H) is compared with the concentration of $HClO_4$ one sees that there may be some substance in Jaacks' theory. On the other hand, the determination of OH groups by infrared spectroscopy is rather inaccurate when the number of monomer units per OH group is as large as 160.

Run FJ128 was killed with ammonia gas from a cylinder instead of ammonia gas from a resevoir of 0.880 ammonium hydroxide, but H remained the same although the concentration of $HClO_4$, c, was slightly higher.

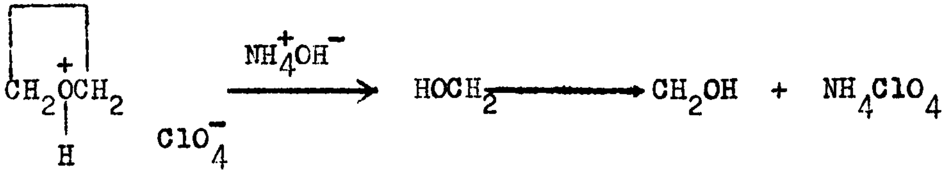
If, however, the reaction is killed with water (FJ178B) H is increased considerably, so that we conclude that a larger portion of linear polymer must have been formed. It is believed that the following reaction is responsible for this effect.



$$\mathrm{CH_2{-}CH_2{-}\underset{\displaystyle H}{\overset{+}{O}}{-}CH_2OCH_2CH_2}\quad \mathrm{ClO_4^-} \xrightarrow{2H_2O} \mathrm{CH_2CH_2OH}\quad \mathrm{HOCH_2CH_2} + \mathrm{HCHO} + \mathrm{HClO_4 \cdot H_2O}$$

Since H is less than c it appears that some of the active centres are also deprotonated by the water molecule.

In run FJ179 the reaction mixture was divided into two. Half of it was killed with the vapour from 0.880 ammonium hydroxide, whilst the other half was killed under vacuum by breaking a phial of anhydrous triethylamine. Killing the reaction with triethylamine (FJ179B) reduces H by a factor of five. If the polymer from the solution containing triethylamine is isolated in the usual manner, the polymer turns brown. It is, therefore, necessary to treat the polymer solution with water before the isolation procedure can be carried out (FJ179B and FJ180B). There was no evidence of any amine groups in the polymers killed with triethylamine (infrared spectroscopy) so that deprotonation must occur without ring opening. Therefore the OH groups produced in FJ179A must have originated from a reaction of the active centre with the small quantities of water which are present in the ammonia vapour. The following reaction accounts for this phenomenon.



$$CH_2\underset{H}{\overset{+}{O}}CH_2 \quad ClO_4^- \xrightarrow{NH_4^+OH^-} HOCH_2 \longrightarrow CH_2OH + NH_4ClO_4$$

A similar observation was made when $Et_3O^+SbF_6^-$ was the polymerisation catalyst, that is H was greater when the reaction was killed with 0.880 ammonia vapour than when triethylamine was the killing agent.

In section 9.2. it will be shown that a small number of phenoxy end-groups are present in the polymer when the reaction is killed with sodium phenoxide. There is a linear relationship between the monomer concentration and the concentration of phenoxy end-groups. Therefore from the monomer concentration we can estimate the concentration of end-groups expected when 1,3-dioxolan is polymerised by $HClO_4$. This has been denoted by Y and included in Table 9.1. to provide a means of comparison between the results of both methods of end-group analysis.

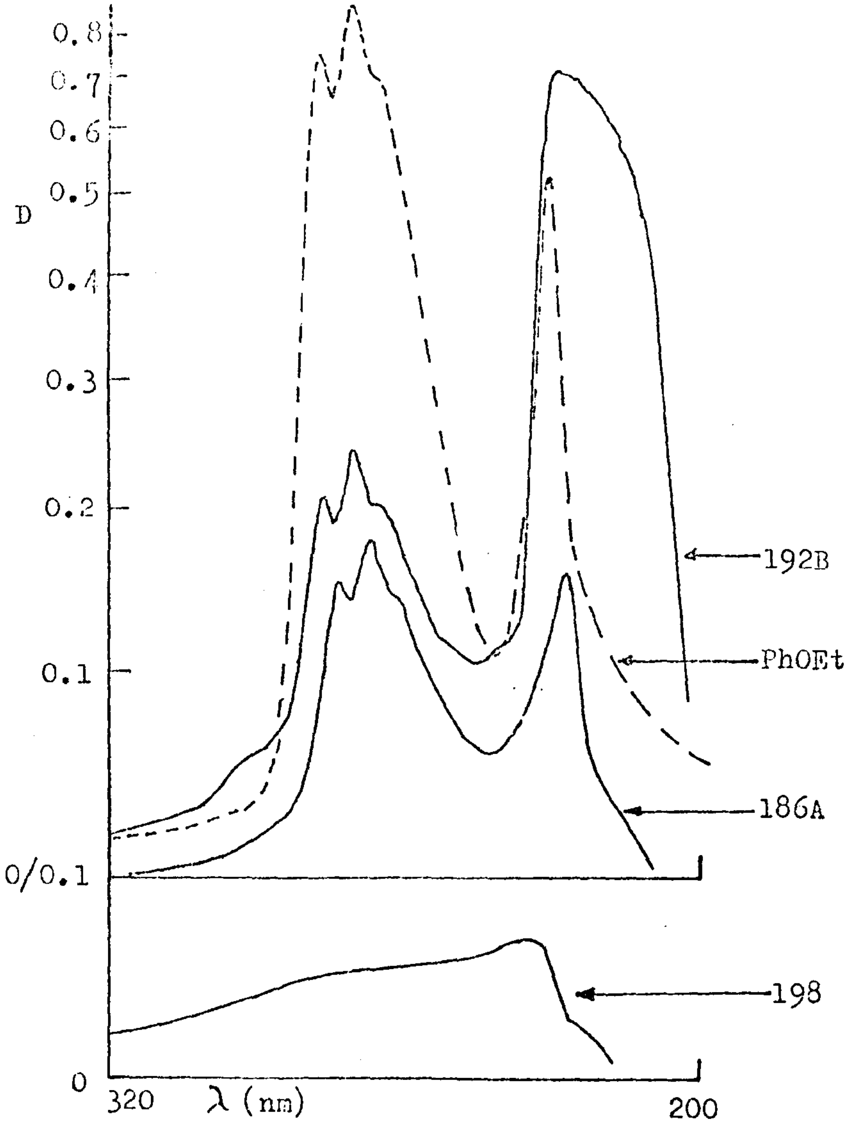
When the reactions are killed with triethylamine, H, the concentration of hydroxyl groups, is very close to the concentration predicted by the sodium phenoxide experiments. The difference between these figures (Y and H) is probably due to experimental error because the OH band in the infrared spectra is rather small and this leads to a relatively large error in the measurements.

9.2. Experiments with Sodium Phenoxide

Saegusa[2] has shown that the tertiary oxonium ions which polymerised tetrahydrofuran can be estimated quantitatively by reaction

Fig. 9.1.

The u.v. Spectra of Poly-1,3-Dioxolan with Phenoxy End-Groups



with sodium phenoxide. This reaction introduces a phenoxy end-group which can be determined by u.v. spectroscopy. Therefore this method was applied to the 1,3-dioxolan-$HClO_4$ polymerisation system.

9.2.1. Method

The polymerisations were killed with phials of sodium phenoxide which had been prepared on the vacuum line. The sodium phenoxide was introduced either as a solid (S) or as a solution in tetrahydrofuran (L) (Table 9.2.).

These reaction mixtures were then extracted with N aqueous sodium hydroxide to remove the excess of sodium phenoxide and any phenol which was produced. The aqueous solution was made up to 250 ml with N sodium hydroxide and the methylene dichloride solution was dried with anhydrous magnesium sulphate and made up to 100 ml with dry methylene dichloride. A separate reference solution was extracted in the same manner and this blank test showed that the polymer was transferred almost quantitatively (96%) into the methylene dichloride.

Each of the solutions was subjected to u.v. spectroscopy. The concentration of phenyl ether (ROPh) in the methylene dichloride solution and the concentration of PhO^- in the aqueous sodium hydroxide were determined by use of the appropriate molar extinction coefficient. Examples of the u.v. spectra obtained are shown in Fig. 9.1.

Saegusa[2a] has shown that phenetole and 4-methoxybutyl phenyl ether absorb at 272 nm (secondary band), that the molar extinction coefficient, E, is 1.93×10^3 $l mole^{-1} cm^{-1}$, and that Beer's Law

Table 9.2.

The Quantitative Estomation of Phenoxy End-Groups

Run No.	198	183	201	184	185A	185B*	186A	186B	186C
$[M]/M$	2.0	2.0	1.0	0.5	1.0	0.8	1.0	0.88	0.77
$[HClO_4]/10^2M$	0.65	0.5	0.106	1.78	1.95	1.55	1.07	1.23	1.4
D_{270}	0.05	0.35	0.27	0.09	0.14	0.045	0.18	-	0.08
$[ROPh]/10^3M$	-	1.45	0.27	0.33	0.5	0.13	0.594	-	0.32
Yield %	-	77	-	-	-	-	-	4	2
DP	-	29	-	-	-	-	-	-	-
$[NaOPh]_o/10^3M$	-	13.5	-	26.2	28.5	21.5	17.7	20.1	24.4
$[HaOPh]_f/10^3M$	-	11.6	-	25.5	28.1	24.0	22.6	8.8	4.7
T /°C	0	-43	-22	+25	+25	-43	+25	-35	-85
NaOPh, phase	-	L	L	L	L	L	S	S	S
$[OH]/10^3M$	-	-	-	-	-	-	1.2	-	-

Run No.	188A	188B	189A	189B‡	191A I	191B	192B	195	196
$[M]/M$	3.0	1.76	2.0	1.07	1.7	1.49	1.7	2.0	1.0
$[HClO_4]/10^2M$	0.8	0.4	1.2	0.38	1.27	0.43	0.75	0.64	0.58
D_{270}	-	0.6	-	1.0	1.0	0.17	0.245	0.4	0.2
$[ROPh]/10^3M$	-	1.5	-	3.9	1.3	0.85	1.1	1.4	0.7
Yield %	44.4	73	47	37	10	53	47	67	65
DP	-	-	-	9.7	4.9	15.6	17.4	17.8	10.8
$[NaOPh]_o/10^3M$	-	9.0	-	33	-	16.2	14.7	12.9	12.3
$[NaOPh]_f/10^3M$	-	6.4	-	16	-	14.8	13.7	11.4	10.3
T / °C	+25	-43	0	-33	0	-16	-16	+25	-64
NaOPh, phase	-	L	-	S	S	L	L	L	L
$[OH]/10^3M$	-	-	-	-	2.0	6.6	-	5.0	3.9

* In the presence of tetrahydrofuran

‡ The prepolymerised solution was mixed at 30°

I The prepolymerised solution was mixed at 25°

The monomer for all except 195 and 196 is 1,3-dioxolan.
195 and 196 - 1,3-dioxepan.

applies. The spectra of both these phenyl ethers were the same as a spectrum of polytetrahydrofuran with a phenoxy end-group, so that this spectrum could be assigned to the end-group of the polymer.

In a similar way I have shown that the 1,3-dioxolan polymer having a phenoxy end-group has a spectrum identical to that of phenetole (Fig. 9.1.). The maximum absorption of the secondary band was at 270 nm and E = 1.90×10^3 lmole^{-1} cm^{-1}. Since the spectrum due to polymer was very weak and because some reactions were killed above the ceiling temperature the results were not corrected for the absorption due to the polymer.

An aqueous sodium hydroxide solution of sodium phenoxide absorbs[3] at 285 nm (secondary band), E = 2.6×10^3 lmole^{-1} cm^{-1}.

9.2.2. Results

The reaction time for the protonations and polymerisations described here were usually in excess of 20 mins. so that according to Jaacks[4] theory the conversion of the secondary ions to tertiary oxonium ions would have been complete.

The first two experiments (183 and 184) were carried out according to the conditions given in Table 9.2. In 183, polymer was produced whilst 184 was killed above the ceiling temperature of the system. Since the concentrations of ROPh in the polymers produced in experiments 183 and 184 were in the same ratio as the monomer concentrations, we considered at first that the tertiary oxonium ions (see page 145) were formed in a reaction of $HClO_4$ with an impurity.

Therefore, to test this we recycled the monomer. In experiment

185, the reaction was killed above T_c and the volatiles were distilled into a reaction vessel isolated by a Teflon tap where another $HClO_4$ phial was broken. However, very little polymer was produced in the second polymerisation (at -43°) therefore the reaction was killed with sodium phenoxide and subjected to analysis. The residue from the first protonation (185A) contained the expected concentration of ROPh, even though polymerisation did not occur. Polymerisation probably was prevented by the presence of tetrahydrofuran which was preferentially protonated. Therefore, this whole experiment was repeated (186) with solid sodium phenoxide in place of the solution in tetrahydrofuran.

The apparatus consisted of two H-tubes with a Teflon tap connecting the horizontal arms of each H-tube. In one arm of each H-tube there was a phial of $HClO_4$ and in the other a phial of NaOPh. The first protonation was made by breaking an acid phial into the 1,3-dioxolan solution. After 8 mins. at 25°, the reaction was killed with solid sodium phenoxide. The reaction mixture turned red and eventually colourless with the production of a pink precipitate. If the time the solution remains coloured is a measure of the time required to kill all the active centres then solid sodium phenoxide is inefficient for this purpose. However, the volatiles were distilled to the second reaction vessel by cooling it with iced water. The residue (186A) in the first reaction was isolated by the Teflon tap, removed and analysed.

When the acid phial was broken into the distillate from the first reaction in the second H-tube the solution turned red and polymerisation did not occur. Therefore the reaction was killed and the vessel was reconnected to the vacuum line, via the Teflon tap so that the volatiles could be distilled onto sodium hydride to remove the phenol which had obviously come over in the distillation. The volatiles were then distilled into another reactor containing a $HClO_4$ phial and a sodium phenoxide phial and the procedure was repeated. The residue (186B) from the second recycling was analysed together with the product (186C) from the final protonation. Polymerisation did not occur to a great extent in 186C, but there was still a phenyl ether group present in the product. The methylene dichloride solution from experiment 186B had a rather large absorption at 270 nm, but as the peak was not resolved it could not be assigned to ROPh with certainty and therefore this result is not included in Table 9.2.

The previous experiments showed that phenoxy end-groups were still present in the polymers produced from the recycled monomer but we were still not convinced that the end-groups were formed by a reaction of 1,3-dioxolan and $HClO_4$. Therefore in order to keep the system as clean as possible, the monomer and solvent were distilled off two live polymer solutions(188 and 189)and repolymerised. The repolymerisations were killed with sodium phenoxide. In 188B, ROPh was formed in the same concentration as one would have expected from the first polymerisation, whereas in 189B a much larger amount was formed. The only difference between the two experiments was that in experiment 189A the $HClO_4$ phial was broken at 20° and the solution mixed at 35°, whereas experiment 188A was mixed at 20°.

The results suggest that ROPh is more readily formed at temperatures higher than 20° and that it may be volatile.

Although these experiments seemed to indicate that an impurity was not responsible for the ROPh produced, the evidence was not convincing, and thus experiments 191 and 192 were carried out. In these experiments the procedure for 186 was used except that the distillate from the first reaction was collected in a flask so that it could be analysed by g.l.c. In experiment 191 the first polymerisation was killed with sodium phenoxide and the volatiles were distilled onto sodium hydride so that any phenol carried over would be removed. Then, after degassing (by freeze-thawing), the volatiles were distilled into a flask fitted with a Teflon tap. The flask was then sealed off the line and re-fused to the line for gravity dosing. The same procedure was used in run 192 except that the reaction was killed with the non-volatile amine N,N'-di-(2-naphthyl)-p-phenylenediamine.

The u.v. spectrum of the distillate from run 191 did not have an absorption at 270 nm which proved that the phenyl ether produced is not volatile. Analysis by g.l.c. of the distillates from 191 and 192 showed that the small impurity peaks present in 1,3-dioxolan were not removed by pre-protonation above the ceiling temperature. The solutions distilled from experiments 191 and 192 were polymerised with $HClO_4$ (see Table 9.2.) and then killed with sodium phenoxide. Both the polymers obtained from these experiments contained the ROPh group.

Since 1,3-dioxepan (in contrast to 1,3-dioxolan) is known to be completely protonated[1] by $HClO_4$, two experiments (195 and 196) with this monomer were killed with sodium phenoxide and it was found that ROPh was present in the products in the same concentration as found for 1,3-dioxolan. This shows that the degree of protonation does not affect the concentration of ROPh.

As has been mentioned, solid sodium phenoxide (S) is an inefficient killing agent because of its low solubility in the reaction solution. The red colour produced in the solutions during the time it took to kill the reaction may have been due to protonated phenol or oxidation products formed from phenol and $HClO_4$, because there was some material which was insoluble in the aqueous sodium hydroxide used, and the methylene dichloride, for extraction. This is shown by a discrepancy between the initial concentration of sodium phenoxide $[NaOPh]_o$ and the final concentration $[NaOPh]_f$. On the other hand a red solution was not formed when sodium phenoxide was added as a solution (L) and the recovered amount of sodium phenoxide agreed well with the initial quantity.

9.2.3. The Concentration of Tertiary Oxonium Ions Throughout the Polymerisation

As the concentration of $HClO_4$ in the experiments described previously in this chapter was about 10^{-2}M, one possible explanation for the inequality of $[HClO_4]$, $[ROPh]$ and $[OH]$ was that the polymer had not been protonated completely. Therefore, experiment 201 was carried out with a lower acid concentration (10^{-3}M) in a dilatometer which allowed concurrent sampling and conductance measurements. The device (Fig. 2.5.) was designed so that the vacuum in the dilatometer

Table 9.3.

The Polymerisation of 1M 1,3-Dioxolan with 1.06×10^{-3}M $HClO_4$ at -22.2°

Sample No.	Time min.	$[ROPh]$ 10^{-3}M	$[PhOH]$ 10^{-3}M
1	13	0.35	-
2	13	-	0.77
3	34	0.35	-
4	34	-	1.30
5	44	0.28	-
6	44	-	1.0
7	60	-	1.8
8	92	0.27	-
9	92	-	2.4

could be let down to a dry nitrogen atmosphere to facilitate sampling through the greased tap against a flow of dry nitrogen.

Samples of the reaction mixture were taken at specific time intervals (see Table 9.3. and Fig. 9.2.) and killed with a known volume of sodium phenoxide solution. The weight of the sample was determined by difference. Alternate samples were then treated with an excess of $Et_3O^+PF_6^-$ to kill off the remaining sodium phenoxide. The solutions were analysed as before so that the latter solutions gave a measure of the quantity of phenol produced when the reaction was killed.

Thus conductivity, the rate of polymerisation by dilatometry, and the concentration of "tertiary oxonium" ions could be measured simultaneously. We also hoped to determine the amount of phenol produced by proton abstraction from secondary oxonium ions, but the results shown in Table 9.3. indicate clearly that the method was not satisfactory.

The initial value for the concentration of phenol produced, which is a measure of the concentration of secondary oxonium ions is reasonable, but the subsequent figures are larger than the concentration of $HClO_4$. A possible explanation is that phenol was produced in the sodium phenoxide solution by reaction with atmospheric moisture. Although this could have been checked by a more refined technique this has not been done.

Fig. 9.2. shows the polymerisation curve, the conductivity curve and the concentration of tertiary oxonium ions at certain times. These ions appear to be formed before polymerisation starts and

their concentration remains reasonably constant throughout the polymerisation, and it certainly does not increase as Jaacks' experiments suggested.

9.2.4. Attempted Isolation of ROPh

Since the ROPh was formed in a reaction mixture which was killed with sodium phenoxide above the ceiling termperature of the solution I decided to attempt to isolate it for analysis. Therefore the residue from reaction 184 was dissolved in carbon tetrachloride and an N.M.R. spectrum was taken. There were peaks at 5.4 τ (polymer), 6.3 τ (doublet; polymer), 8.7 τ and 2.8 τ (phenyl). The last was small compared to the others, and therefore the residue was eluted with 50:50 chloroform/methylene dichloride on a thin layer chromatographic plate of silica gel. The greater part of the sample remained behind, but the phenyl compound was eluted. The phenyl compound was removed from the silica gel by extraction with methylene dichloride and subsequently the solvent was removed by distillation. The N.M.R. spectrum of the residue in carbon tetrachloride showed a peak at 8.7 τ which was about 12 times larger than the other peaks in the spectrum. The accumulated spectrum had peaks at 2.9 τ and 8.1 τ in the ratio of 2:1 apart from the peak at 8.7 τ. The peak at 8.1 τ may be extraneous because accumulated spectra often show this peak. It is believed to be due to a residue from the silica gel.

Therefore no conclusions about the structure of ROPh could be drawn from these experiments. The residue from 191A was also treated in this way; there was no peak at 8.7 τ and no conclusions could

Fig. 9.2.

he Simultaneous Plots of Conductivity and Dilatometer Readings and 10^3M [ROPh] against Time for Experiment 210 (Table 9.2.)

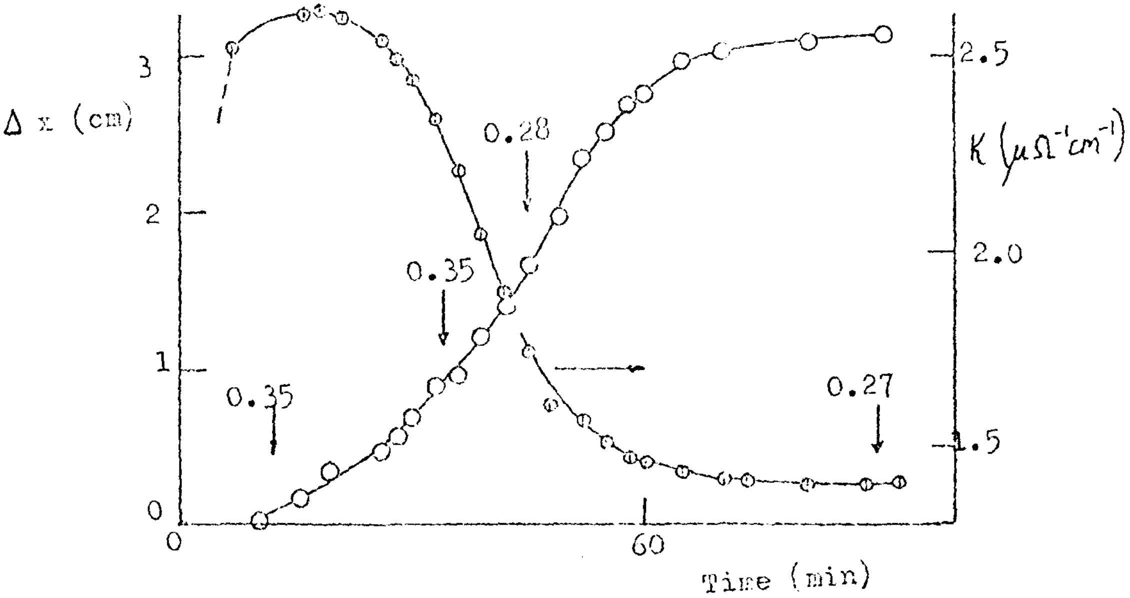


Fig. 9.3. - Plot of [ROPh] against [Monomer]

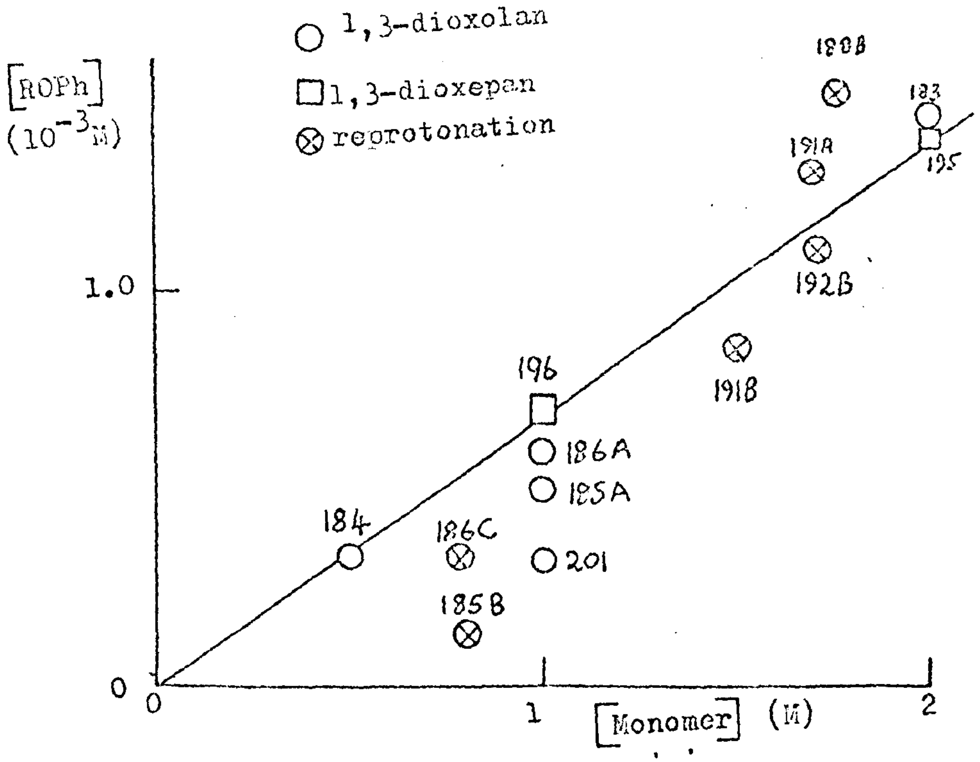


Fig. 9.4.

The Plot of $[ROPh]/[Monomer]$ against $[HClO_4]$

T ≠ constant

Note - See Fig. 9.3. for explanation of signs.

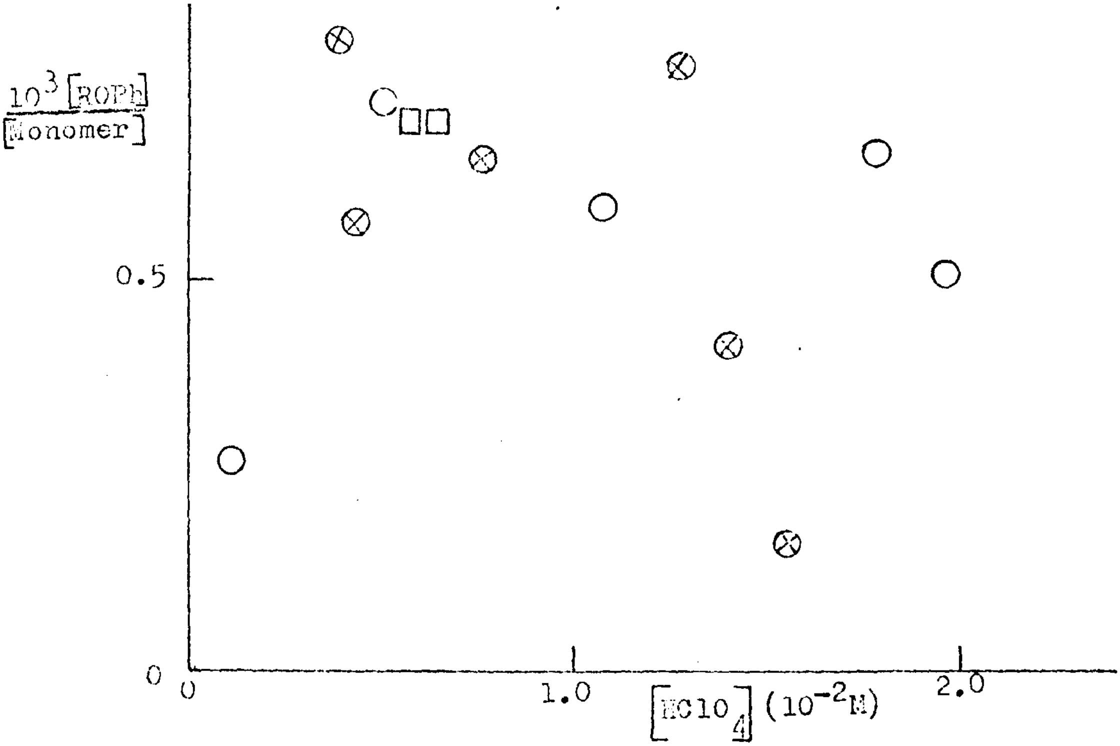
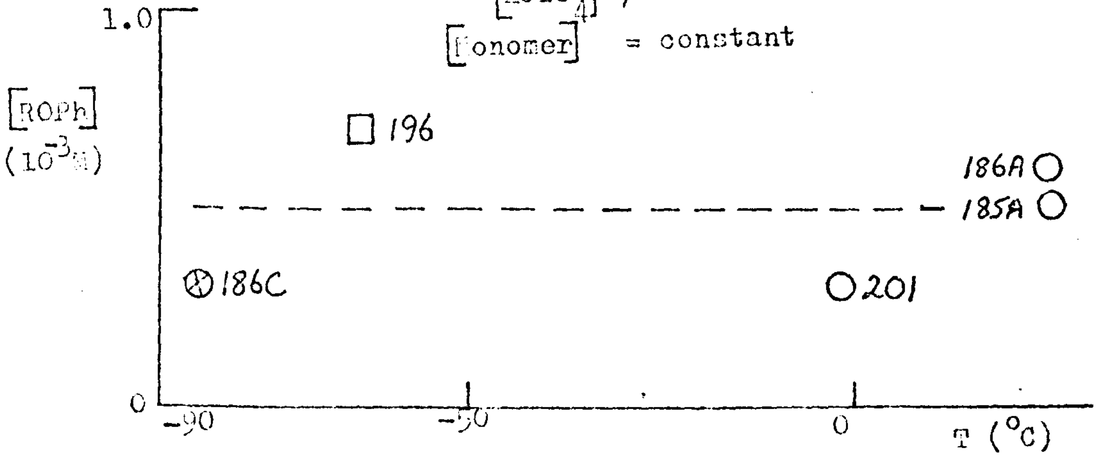


Fig. 9.5.

The Plot of $[ROPh]$ against Temperature

$[HClO_4]$ ≠ constant

$[Monomer]$ = constant



be drawn.

9.3. Discussion

Fig. 9.3. shows that there is a reasonably linear dependence of $[\mathrm{ROPh}]$ on $[\mathrm{M}]$ which is the same for both 1,3-dioxolan and 1,3-dioxepan. A plot of $[\mathrm{HClO_4}]$ against $[\mathrm{ROPh}]/[\mathrm{M}]$ (Fig. 9.4.) shows that there is no dependence of one on the other. Fig. 9.5. shows that there is no apparent relation between temperature (when it is less than 25°) and $[\mathrm{ROPh}]$ (the $[\mathrm{HClO_4}]$ was not constant in the experiments of this Fig.).

Westermann[1] found that when $[\mathrm{HClO_4}]$ was greater than 5×10^{-4}M the specific conductivity of 0.65M 1,3-dioxolan in methylene dichloride at 10° was independent of the $[\mathrm{HClO_4}]$ whereas below 5×10^{-4}M the specific conductivity of the solution was dependent on the acid concentration. Therefore he invoked the protonation of an imputity in the monomer to explain these results. Fig. 9.3. shows that at 0.65M 1,3-dioxolan the $[\mathrm{ROPh}]$ is the same as the concentration of "impurity" (Westermann). Both Westermann's and my results suggest an impurity in the monomer at a concentration of 10^{-2}M. However the experiments (185, 186, 188, 189, 191 and 192) in which the monomer was recycled have failed to prove this theory and, besides, an impurity at the level of 10^{-2}M in monomer was not found by g.l.c. of the monomer.

We had hoped that the concentration of hydroxyl groups H determined from the infrared spectra of poly-1,3-dioxolan and poly-1,3-dioxepan would agree with the concentration of phenoxy end-groups in the same polymers killed with sodium phenoxide. Unfortunately, those two methods of end-group analysis do not agree in that H is greater than the [ROPh] (Table 9.2.). An explanation of the discrepancy might be that phenol reacts with the polymers during or after killing to produce hydroxyl groups, because [ROPh] and H determined in separate experiments do agree (Table 9.1.).

At this point I will briefly discuss the possible reactions by which end-groups are formed in the polymerisation of 1,3-dioxolan by $HClO_4$.

It might be that the "impurity" originates from the walls of the glass vessel, but this can be excluded because the residual water concentration (10^{-4}M) of the system is less than the concentration of end-groups and the concentration of "impurity" depends on the monomer concentration. The concentration of residual water in 1,3-dioxolan was found[5] to be about 2×10^{-4}M whereas the concentration of the "impurity" in the monomer is 10^{-2}M, so that residual water cannot explain our results.

Whereas under our conditions the protonation of 1,3-dioxolan by $HClO_4$ is incomplete, that of 1,3-dioxepan[1] is complete. Therefore the formation of phenoxy end-groups in 1,3-dioxepan is all the more puzzling. Although 1,3-dioxepan is known[1] to contain a very small concentration of tetrahydrofuran this cannot be the cause of the end-groups in this polymer, because in experiment 185B, where tetrahydrofuran was present in the polymerising solution, the concentration of ROPh was not unusually great.

The results of the experiments with 1,3-dioxepan might be explained on the supposition that the reaction of the protonated cyclic formal with sodium phenoxide does not go completely by deprotonation, but that it produces some ROPh by a minor side-reaction. Against this is the fact that Jaacks[5] was able to deprotonate protonated diethylformal completely with sodium ethoxide. However it only needs a very small percentage of ring-fission to occur to account for our results. Furthermore this hypothesis does explain the formation of OH groups in the polymerisations killed with sodium phenoxide, but it does not of course explain the formation of OH groups in the absence of sodium phenoxide. Since the concentration of OH groups was of the same order of magnitude as the concentration of ROPh from separate experiments (Table 9.1.) we can probably rule out the possibility that sodium phenoxide does not completely deprotonate a protonated cyclic formal.

ROPh is formed even when a 1,3-dioxolan reaction mixture is killed with sodium phenoxide above T_c. Experiment 201 shows that the concentration of phenoxy end-groups does not alter significantly throughout the polymerisation and that it was less than the concentration of $HClO_4$.

The end-group analysis presented here shows that the concentration of end-groups depends on the dryness of the killing agent (Table 9.1.) and that the concentration of end-groups is always less than the acid concentration, provided that the monomer concentration is not too high, because the number of end-groups depends on the monomer concentration. The end-group concentration is in agreement with the concentration of an "impurity" invoked by Westermann[1] to explain his conductivity results.

Therefore if we accept that the phenoxy end-groups come from tertiary oxonium ions, then some tertiary oxonium ions are formed in the polymerisation of 1,3-dioxolan with $HClO_4$ but not from the protonation of an "impurity" because this could not be proved. The whole question of the mechanism of the polymerisation of 1,3-dioxolan by $HClO_4$ is discussed in Chapter 10.

References to Chapter 9

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SECTION C - CHAPTER 10

The Mechanism of the Polymerisation of Cyclic Formals By Perchloric Acid

10.1. Introduction

In Chapter 9 we have seen that a small concentration of end-groups is formed in the polymerisation of 1,3-dioxolan and 1,3-dioxepan which is less that the concentration of $HClO_4$. We have shown that an impurity is not responsible for those end-groups which are believed to be caused by tertiary oxonium ions. Since these tertiary oxonium ions are formed at the beginning of the reaction (Fig. 9.2.) and their number does not increase during the polymerisation, we believed that they are concerned in some way with the initiation. Therefore, in this Chapter some suggestions are put forward as to how those tertiary ions are formed and then the polymerisation mechanism is discussed.

10.2. Initiation

10.2.1. Ring-opening

One possibility is that ring-opening occurs in the initial stage of the polymerisation.

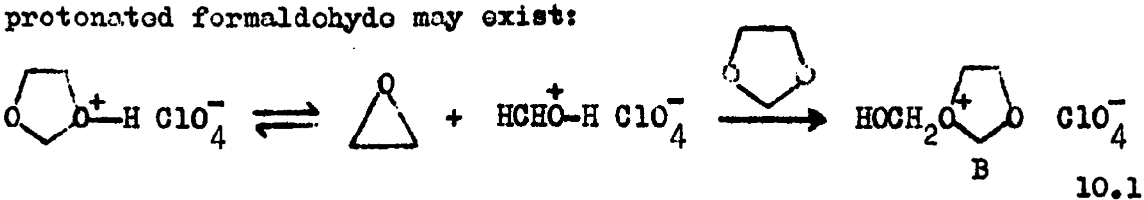
A

Further tertiary oxonium ions are not formed because A can polymerise by a ring-expansion mechanism in a way analogous to the polymerisation of 1,3-dioxolan by triethyloxonium salts (Chapters 5 and 8) and once the dimer is formed it is protonated (because it is more basic than the monomer[1]) and propagation can then occur through both secondary and tertiary oxonium ions.

10.2.2. Equilibrium between Formaldehyde and Ethylene Oxide and 1,3-Dioxolan

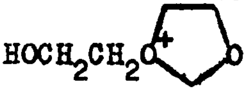
We considered that these might be in equilibrium but rejected this idea because lithium aluminium hydride would have reduced formaldehyde to methanol and thus in time it would have converted all the 1,3-dioxolan to methanol and ethylene glycol. This was not observed. Furthermore, if an equilibrium of this type did exist and the formaldehyde were protonated, Westermann would not have observed that the conductivity of 0.65M 1,3-dioxolan, $HClO_4$ in methylene dichloride above T_c was independent of $[HClO_4]$ above $5 \times 10^{-4}M$. Moreover tests^2 for formaldehyde on the reaction mixtures before and after polymerisation gave negative results. The absence of formaldehyde after reaction could be explained by its protonation and subsequent reaction to the product B in the reaction scheme 10.1.

Whereas the equilibrium in pure monomer is ruled out none the less an equilibrium between $1\underline{H}^+$-1,3-dioxolan,ethylene oxide and protonated formaldehyde may exist:



10.1.

If on the other hand, ethylene oxide were protonated,

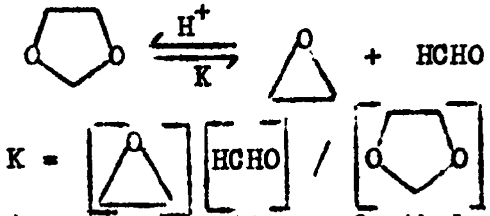


could be formed by reaction with 1,3-dioxolan.

As in scheme 10.1., both these alkylated-$1\underline{H}^+$-1,3-dioxolans could polymorise 1,3-dioxolan by the ring-expansion mechanism.

However an equilibrium of the type 10.1. does not fully explain the facts, because there was no dependence of the concentration of tertiary oxonium ions on the concentration of perchloric acid. Therefore the following alternative explanation is proposed for the formation of small quantities of tertiary oxonium ions in the polymerisation of 1,3-dioxolan, whose concentration depends on the monomer concentration.

We suppose that the establishment of the equilibrium between 1,3-dioxolan, ethylene oxide and formaldehyde is catalysed by acid:



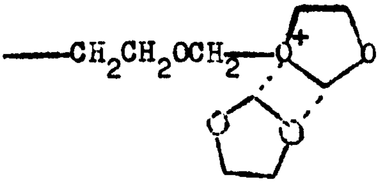
If the equilibrium concentrations of ethylene oxide and formaldehyde are small, and if we assume that both these species can produce tertiary oxonium ions, and if the equilibrium becomes "frozen" once all the acid has been consumed by protonations, then according to my results (Chapter 9) and the results of Westermann[1], K is about 10^{-6} moles l^{-1}. It is relevant that Westermann[1] observed the analogous equilibrium for 2,2-diphenyl-1,3-dioxolan which did not require an acid catalyst.

Both formaldehyde and ethylene oxide could be protonated and then initiate polymerisation as described previously. If the rate of polymerisation is greater than the rate of establishment of this equilibrium then the independence of the concentration of end-groups of acid concentration can be explained.

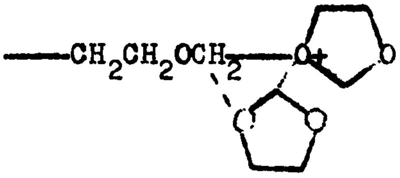
10.3. Propagation

The carboxonium ion mechanism for the polymerisation of 1,3-dioxolan has been discussed and rejected[1,3,4]. Therefore, we are left with the two alternative mechanisms for the polymerisation of 1,3-dioxolan which have been proposed. One is the ring-expansion of Plesch and Westermann[1,5] and the other is the mechanism of Jaacks[4,6] in which propagation is by tertiary oxonium ions and macrocyclic rings are formed by back-biting.

Both mechanisms are illustrated in the introduction to Section C and therefore they will not be given again. If one looks closely at the mechanisms, one sees that both can be considered as insertion mechanisms; whereas the ring-expansion is an insertion across the ring (C), Jaacks' mechanism can be considered as an insertion across the linear branch of the molecule (D).



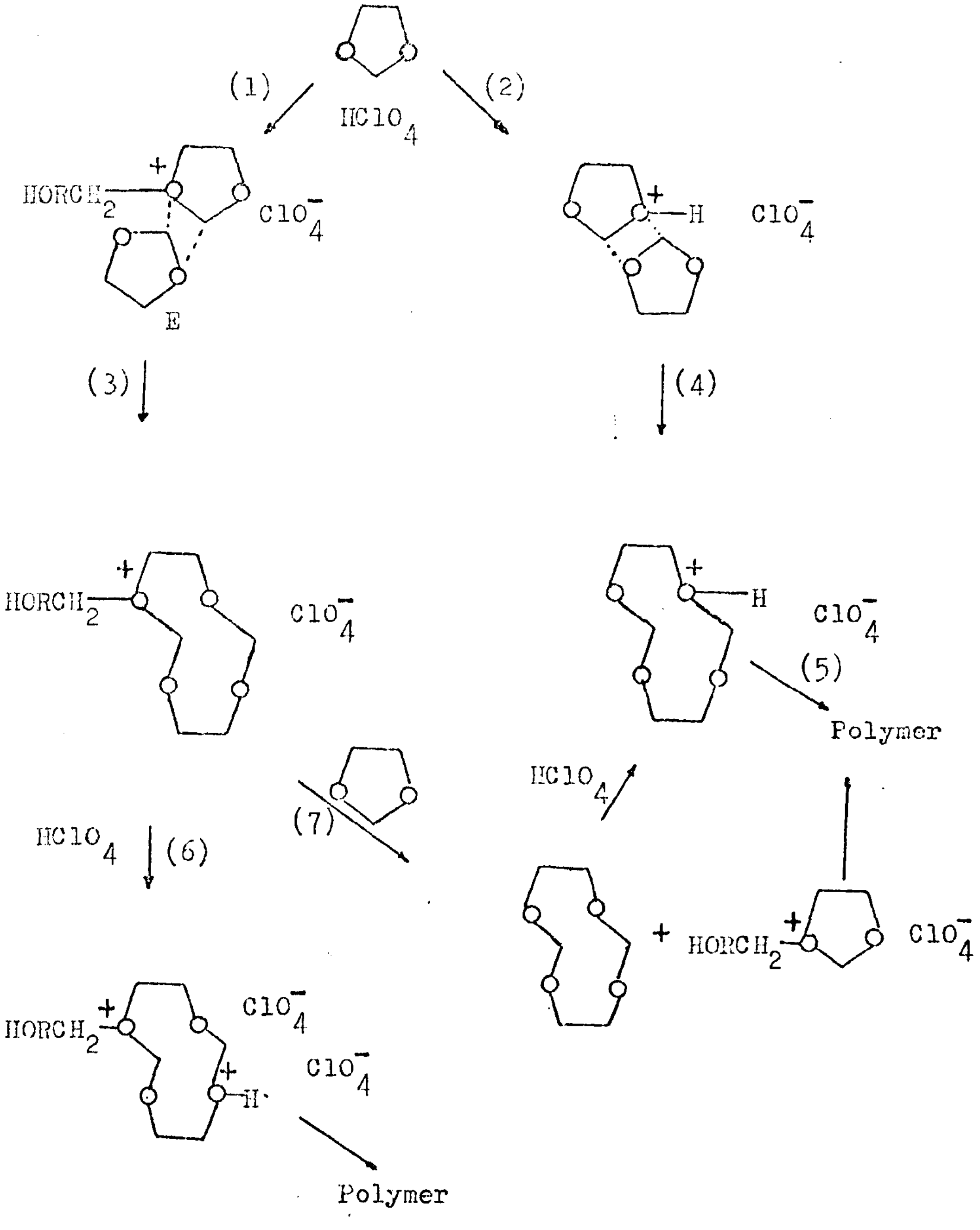
C



D

We consider that an insertion mechanism across the ring (D) is more likely for the following reasons. If the macrocyclic rings were formed by back-biting[4,6], then we would expect to find that the concentration of end-groups was the same as the concentration of $HClO_4$ and this has not been observed. Jaacks[4] considers that protonated 1,3-dioxolan is slowly transformed into tertiary oxonium ions which are the propagating species, but this is not in agreement with the results of Westermann[1] who found that over a ten-fold variation of catalyst concentration there was a linear relation between the first order rate constant and the perchloric acid concentration and that the final conductivity of the polymer

FIG.10.1.



$R = -, CH_2$ or CH_2CH_2O

The Scheme Proposed for the Polymerisation of 1,3-Dioxolan solution was dependent on the initial acid concentration. Furthermore Westermann[1] observed that on depolymerisation the conductivity fell back to a low value which could only be explained by the formation of covalent perchloric acid. The repolymerisation followed the same course as the first polymerisation and the conductivity reached the same value as before. Moreover in the polymerisation of 1,3-dioxepan which is completely protonated by perchloric acid the initial and final values of specific conductivity depended on the concentration of perchloric acid. Also, the low DP's observed for these polymers were considered to be due to excessive transfer in which th H^+ was mobile over all the oxygen atoms in the system.

These experiments show that all the perchloric acid produces active centres. Therefore, since Chapter 9 shows that some tertiary oxonium ions are formed, both tertiary and secondary oxonium ions must be involved in the propagation. Therefore the scheme in Fig. 10.1. is proposed for the polymerisation of 1,3-dioxolan by anhydrous perchloric acid.

(1) This stage has been discussed above (section 10.2.).

(2) and (4) These represent protonation and the ring-expansion mechanism of Plesch and Westermann[5].

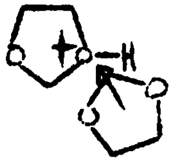
With 1,3-dioxolan the evidence suggests that under the polymerisation conditions (2) and (4) do not occur. However both Westermann[1] and Jaacks[7] have observed protonation of 1,3-dioxolan at higher acid concentrations than are required for polymerisation, therefore (4) is still a possible propagation step. Stage (2) is included here because undoubtedly 1,3-dioxepan must propagate by stage (4) in this way

because the monomer is completely protonated by perchloric acid.
(6) This step is included for completeness. Although it is less likely to occur than step (7) beause of the proximity of the two positive charges, it certainly would occur if the ring were large.
(7) This step is due to the mass-action effect because at the start of polymerisation the concentration of 1,3-dioxolan is much greater than the concentration of the dimer and higher oligomers, and the greater abundance of the monomer compensates for its lower basicity.

Therefore, we believe that the ring-expansion mechanism is more likely than the mechanism of Jaacks[4,6] for the production of macrocyclic rings, but we have not ruled out completely that E may also propagate by a linear insertion mechanism.

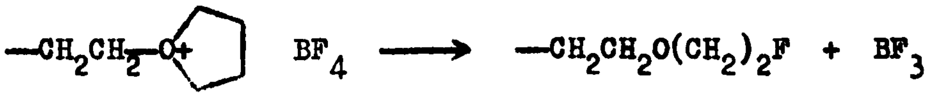
Jaacks[4] bases his mechanism on the slow production of tertiary oxonium ions at the expense of secondary oxonium ions but when we compare his experimental conditions with ours we find that both sets of experiments can be reconciled. In his experiments Jaacks used a monomer concentration of 3-4M and the perchloric acid concentration was about 10^{-3}M. From Fig. 9.3. we see that under those conditions the concentration of tertiary oxonium ions will be fortuitously equal to the acid concentration. Since the reaction times of Jaacks[4] were only about 2 mins., it appears that he may be observing the rate of attainment of the equilibrium between ethylene oxide, formaldehyde and 1,3-dioxolan (see section 10.2.).

We have shown in Section B that tertiary oxonium ions are solvated by ether molecules. Kinetic measurements will not differentiate between the polymerisation of the solvating molecule or of an in-coming monomer molecule because if the solvating molecule were polymerised it would be immediately replaced by another monomer or polymer molecule. However, if one considers that the solvating molecule is oriented according to the direction of its dipole moment, the ring-expansion mechanism becomes the more plausible because the solvating

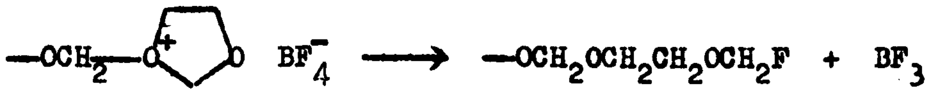


molecule is in the correct position to form the four-centred transition state proposed. The orientation of solvating molecules in the direction of their dipoles has been discussed by Szwarc[8]. This is a further ~~piece of evidence~~ argument in favour of the ring-expansion mechanism.

Furthermore, Dreyfuss[9] has shown that in the polymerisation of tetrahydrofuran by $Et_3O^+BF_4^-$ there is a termination which is a reaction analogous to the decomposition of triethyloxonium salts:



Therefore if the polymerisation of 1,3-dioxolan were a ring-opening process, as Jaacks[4,6] has suggested, then by analogy a similar termination would be expected:



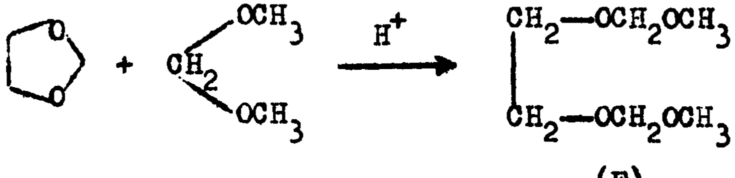
This was not observed (Chapter 5) and my explanation is that the mechanism of polymerisation is not analogous to that of tetrahydrofuran and is not that proposed by Jaacks[4,6]. Therefore non-termination is consistent with the ring-expansion mechanism. On the other hand, Jaacks'[7] objects to this argument because he considers that the $—CH_2OCH_2F$ group is unstable and that therefore it would not be formed.

10.4. Other Chemistry which Supports the Ring-Expansion Mechanism

Ring-expansion seems to be a good mechanism for the polymerisation of cyclic formals but it would be better if evidence for this could be found elsewhere. Fortunately some reaction mechanisms have been proposed which are similar to the ring-expansion.

10.4.1. Acetal Exchange

The exchange of acetal groups is well known[10] and the reaction of 1,3-dioxolan and dimethyl formal is a typical example. Gresham[11] showed that this reaction is catalysed by sulphuric acid and he obtained a low yield of the product (F).

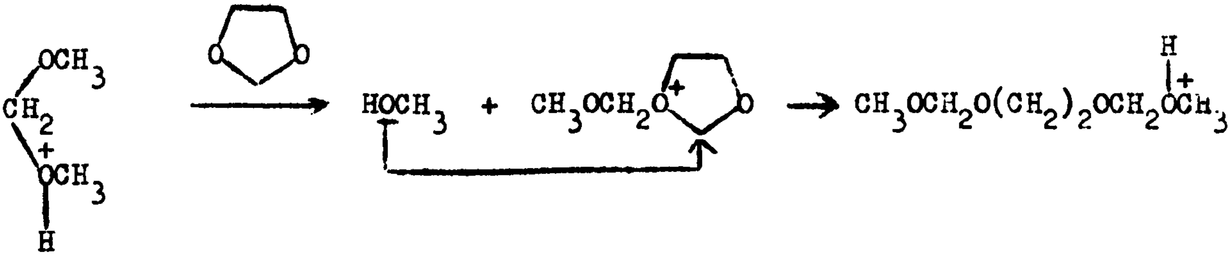


(F)

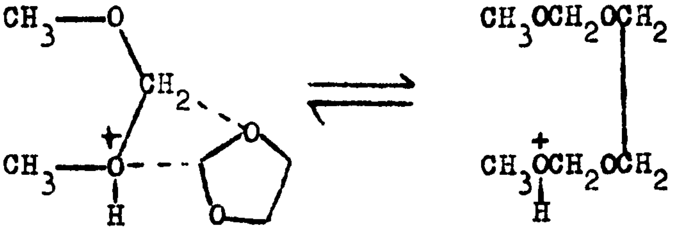
The equilibria involved in these reactions have been studied in carbon tetrachloride solution at 20° by Ivanov et al.[12]. These workers formed oligomers by further reaction of (F) with 1,3-dioxolan and found that the thermodynamic parameters of this equilibrium agreed will with those for the polymerisation of 1,3-dioxolan determined by Plesch and Westermann[5]. Therefore, the low yield of (F), observed by Gresham is explained by the equilibrium nature of the reaction because calculation shows that his conditions were close to the ceiling temperature and floor concentration of this system.

If Jaacks' mechanism were correct, the product observed could only be formed by two concerted reactions: (In the following mechanisms the anions are omitted for clarity)

Jaacks mechanism:



Ring-expansion mechanism

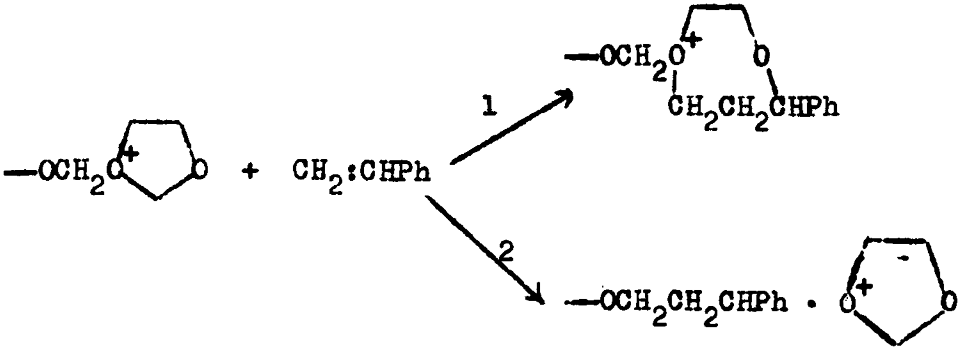


If Jaacks' mechanism were correct, it would be difficult to imagine the establishment of a clean equilibrium between the products and the reactants, whereas the ring-expansion mechanism yields the correct product and the simple equilibrium nature of the reaction is readily explained.

10.4.2. Copolymerisation with Styrene

A quite different phenomenon, which helps to elucidate the propagating mechanism, is the copolymerisation of 1,3-dioxolan with styrene[13]. Since the triphenylmethyl cation reacts with 1,3-dioxolan by hydride abstraction giving triphenylmethane and the 1,3-dioxolenium ion, it follows that the more reactive styryl ion would react in a similar way, so that copolymerisation would not occur. Moreover, styrene cannot be polymerised cationically in the presence of ethers or other oxygen compounds, since these are much more basic than the olefin. Therefore, for copolymerisation of styrene and 1,3-dioxolan the propagation step must take place without the formation of a carbonium ion. An obvious alternative mechanism involves the insertion of the double bond into one branch of the oxonium ion.

Jaacks mechanism

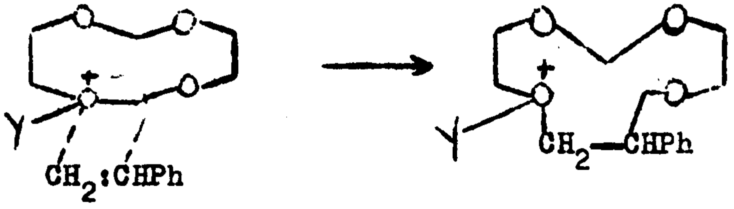


(G)

(H)

A further unit of styrene can be incorporated into (G) by a reaction analogous to path 2 whereas a further unit of styrene can be incorporated into (H) by path 1.

Ring-expansion mechanism



(J)

Since the copolymerisation experiments[13] were done with boron trifluoride etherate as the catalyst, whose mode of action is still quite obscure, the activating group derived from the catalyst is denoted by Y(which may be Et) above.

In the ring-expansion example further units of styrene can be incorporated by this reaction if Y is mobile over all the oxygen atoms. Certainly, this is the case with perchloric acid where Y = H, and we see no reason why an ethyl group should not transfer by a similar process. This would produce an alternating polymer with not more than 50% of styrene.

However, experiment has shown that if an excess of styrene is used, sequences of up to four styrene units can be formed, although the formation of styrene sequences is under all conditions less probable than the formation of 1,3-dioxolan sequences. Therefore, both reaction mechanisms require a reaction (K) by which sequences of styrene units can be formed:

$$—O(CH_2)_3CHPh—\overset{+}{O}\Big[\quad + \quad CH_2{:}CHPh \longrightarrow —O(CH_2)_3CHPhCH_2CHPh—\overset{+}{O}\Big[\qquad (K)$$

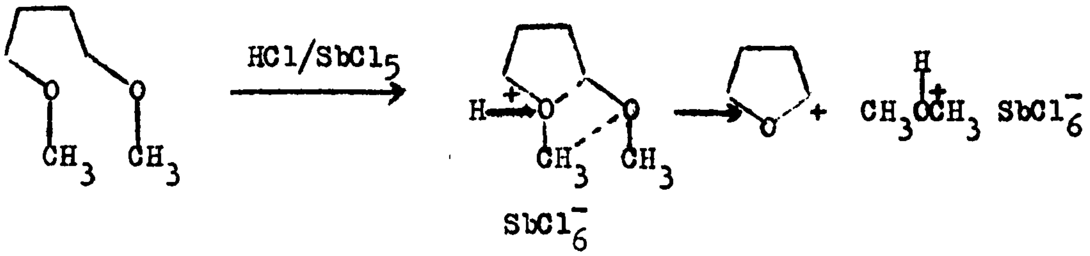
The remarkably high molecular weights of copolymers of 1,3-dioxolan and styrene, which were achieved by Yamashita[13], are easily intelligible in terms of the insertion mechanisms shown above (G, H, and J). Cationic polymerisation of styrene yields low molecular weight polystyrenes because of proton transfer to monomer, from the carbon atom next to the growing end. Therefore if the growing species are oxonium ions the principal chain breaking reaction is frustrated.

Since the insertion mechanisms proposed above (G, H, and J) are examples of the ring-expansion (except that [illegible] is formed by insertion across the linear branch of the oxonium ion) we consider these results of Yamashita to be further evidence for the ring-expansion mechanism for the polymerisation of 1,3-dioxolan. However, it remains to be seen whether these copolymers are cyclic and, if so, whether they are wholly so, or whether they also contain linear fragments; thus we could distinguish between the theories of Plesch and Westermann and of Jaacks.

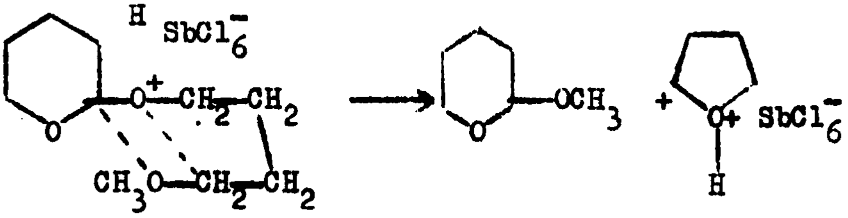
10.4.3. <u>The Preparation of Cyclic Ethers</u>

There are some reaction mechanisms in the literature which involved 4-centred transition states of the type involved in the ring-expansion mechanism.

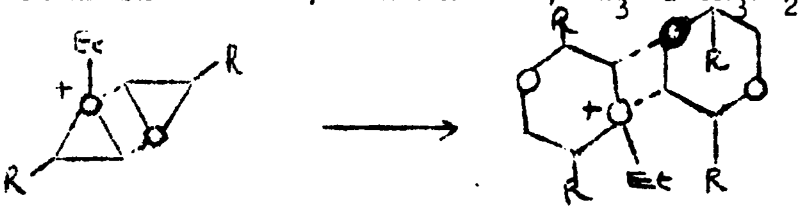
For example, Wartski and Wakselman[14] prepared oxacyclanes by distilling α,ω-dimethoxyalkanes in the presence of $HCl/SbCl_5$ with the liberation of dimethyl ether. These reactions, e.g. the preparation of tetrahydrofuran, can be represented by a mechanism which is closely related to the depolymerisation of polyformals, as interpreted by the ring-expansion mechanism.



Another example from these authors[14] is the following reaction which involves a formal group:



Similarly, the formation of cyclic tetramers and dimers from ethylene oxide[15] can be readily explained by a similar mechanism. The catalysts were $Et_3O^+BF_4^-$ and BF_3 ; the mechanism can be represented as shown below, where R = Cl, CH_3 or CH_3CH_2.



Since the reactions above involve ethers rather than formals it appears that the 4-centred transition state proposed for the polymerisation of 1,3-dioxolan may be important in the reactions of oxygen compounds other than formals.

However, these examples pose a problem, in that the polymerisation of tetrahydrofuran is considered to yield linear polymers by a linear propagation. However, much of the work on the polymerisation of tetrahydrofuran has been done with initiators which are expected to produce end-groups. For example triethyloxonium salts[9] have been used as catalysts and with these termination occurs so that it is not surprising that linear polymers are produced. It remains to be seen whether the polytetrahydrofuran prepared under carefully controlled conditions is linear or cyclic.

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CHAPTER 11

Suggestions for Further Work

Whereas triethyloxonium tetrafluoroborate is an inefficient catalyst for the polymerisation of 1,3-dioxolan, triethyloxonium hexafluoroantimonate appears to react with 1,3-dioxolan and its polymer to give a 100% yield of active centres. Therefore, a study of the polymerisation of 1,3-dioxolan and 1,3-dioxepan by triethyloxonium hexafluoroantimonate should give authentic values of k_p. Coupled with this study, the association constants for triethyloxonium hexafluoroantimonate in methylene dichloride and in solutions of methylene dichloride and 1,3-dioxolan need to be determined. By varying the concentration of the catalyst it should be possible to demonstrate that the k_p of free ions is similar to the k_p of ion-pairs.

Since the ring-expansion mechanism has been criticised by Jaacks[1] further end-group analysis may be necessary to establish the mechanism of the polymerisation. This analysis could be carried out on the lines used by Jaacks[1,2]. The polymerisation of 1,3-dioxolan and 1,3-dioxepan by $HClO_4$ should be terminated by sodium ethoxide, the polymer hydrolysed and the concentration of ethanol determined by g.l.c. The same method could also be applied to the reaction catalysed by $Et_3O^+SbF_6^-$, except that termination should be by a basic molecule to which the ethyl group can transfer.

The copolymerisation of cyclic formals and styrene is also a possible method[2] by which we could distinguish between the theories of Jaacks[1] and Plesch and Westermann[3].

The reactions of the cyclic formals with $HClO_4$ and with $Et_3O^+SbF_6^-$ above the ceiling temperature should be studied in more detail. In the latter case it may be possible to isolate the 1-ethyl-1$\underline{H}^+$-1,3-dioxolanium hexafluoroantimonate. By means of the reaction of 1,3-dioxolan with dimethyl formal it should be possible to show that no hydroxylic products are formed.

A further suggestion is the use of triphenyloxonium hexafluoroantimonate as the catalyst, in which case k_p should not be significantly different if Jaacks' mechanism applies whereas in the ring-expansion mechanism k_p would be expected to be smaller due to the delocalisation of the positive charge on to the benzene ring.

Therefore, by these experiments we may be able to determine the true mechanism of the polymerisation of cyclic formals and also determine even better values of k_p than those available from this work.

Furthermore the polymerisation of tetrahydrofuran should be studied under conditions in which hydride abstraction and termination are absent. By use of a suitable catalyst which might be anhydrous perchloric acid we can ascertain whether the polymer is linear or cyclic.

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Appendix

A Report on My Visit to the University of Mainz
15th to 25th March, 1970

In Section C of this Thesis the relative merits of the two mechanisms proposed for the polymerisation of 1,3-dioxolan by perchloric acid are discussed. Jaacks maintains that the polymerisation proceeds by a linear propagation in which the active centres are tertiary oxonium ions, whereas we consider that the active centres are secondary oxonium ions and that propagation proceeds by a ring-expansion mechanism.

It appeared, after lengthy discussion with Dr. Jaacks, that it would be useful for me to visit his group. The University of Keele provided funds to pay for the journey, and the University of Mainz paid my living expenses whilst I was there.

I visited the research group of Dr. V. Jaacks mainly to compare his experimental methods with ours. Whereas we use high vacuum techniques, their experiments are carried out in a N_2 atmosphere in vessels which were pumped for a short time under an oil-pump vacuum (and flamed periodically during the pumping). The dosing is done by syringe-through-rubber septum techniques. However we showed that both the Keele monomer and the Mainz monomer contained about the same concentration of water.

Our discussions showed that the views of Dr. Jaacks are mainly based on an organic-chemical point of view whereas our views are based more on an analysis of kinetic experiments and end-group analysis. Moreover we narrowed the differences down to only a few points and now think that these can be reconciled. When we compared the conditions of Jaacks' experiments with ours, we found that with his monomer and acid concentrations we would also find that the concentration of end-groups would be fortuitously equal to the acid concentration.

My visit to Mainz led directly to a visit by three of Dr. Jaacks' coworkers to Keele (14th to 16th April) in order to see our experimental techniques. Therefore we are beginning to clarify the situation and we hope that the mechanism of the polymerisation of 1,3-dioxolan will soon be settled by our joint efforts.

Whilst in Germany I was able to visit the Institut für Makromolekulare Chemie in Darmstadt. There I talked with Professor R.C. Schulz and his coworkers about their work on the electrochemical polymerisation of 1,3-dioxolan.

To conclude I wish to thank all the people who made this very useful and interesting trip possible.