FURTHER STUDIES ON THE CATIONIC POLYMERISATION OF CYCLIC OXYGEN COMPOUNDS

by

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Abstract

The work has been divided into three sections.

Section A. (Chapters 2 - 5)

This section is concerned with mechanism and kinetics of the polymerisation of 1,3-dioxolane with anhydrous perchloric acid as catalyst.

Chapter 2 shows that the triphenylmethyl carbonium ion reacts with 1,3-dioxolane to give the more stable dioxolenium ion, and that this ion is not involved in the polymerisation of 1,3-dioxolane.

Chapter 3 confirms that poly-1,3-dioxolane, made in the absence of water, is cyclic and it also shows that when water is added to the polymerisation mixture an equivalent quantity of hydroxyl-terminated polymer chains are formed. On this evidence a novel ring expansion mechanism involving secondary oxonium ions has been postulated for the polymerisation of 1,3-dioxolane.

In Chapter 4 values of k_p, the propagation rate constant, and k_d, the depropagation rate constant were determined for 1,3-dioxolane. The equilibrium constant of the polymerisation determined kinetically was in good agreement with the value determined thermodynamically, which shows that the values of k_p and k_d are genuine. From the variation of k_p with temperature the overall activation energy of the polymerisation reaction was calculated: $E_p = 5.5 \pm 0.3$ kcal mole^{-1}. This Chapter also contains a discussion on the value of the dissociation constant of the active centres of the polymerisation.

Chapter 5 deals with the electrical conductivity of perchloric acid and 1,3-dioxolane under polymerising and non-polymerising conditions.

Although part of the conductivity results appear to be due to the protonation of an unidentified impurity, these results do show that perchloric acid does not react extensively with 1,3-dioxolane whilst it reacts completely with poly-1,3-dioxolane.

<u>Section B</u> (Chapters 6 - 8)

This section is concerned with the polymerisation of 1,3-dioxepane (tetramethylene formal) with anhydrous perchloric acid as catalyst.

Chapter 6 describes the isolation of the crystalline cyclic dimer of 1,3-dioxepane and the polymer made in the absence of water is shown to be cyclic. The DP was found to be essentially independent of perchloric acid concentration but it increased linearly with increasing monomer concentration.

Chapter 7 describes the thermodynamics of the polymerisation of 1,3-dioxepane. The standard state ceiling temperature, $T_c^o = +27^o$, the standard state entropy of polymerisation, $\Delta S_{ss}^o = -11.7 \mp 1.5$ cal deg^{-1}mole^{-1}, the standard state heat of polymerisation, $\Delta H_{ss}^o = -3.5 \mp 0.3$ kcal mole^{-1} and the calorimetric heat of polymerisation $\Delta H_{ss} = -3.7 \mp 0.2$ kcal mole^{-1}.

In Chapter 8 values of k_p and k_d were determined for 1,3-dioxepane. The equilibrium constant of the polymerisation determined kinetically was considerably larger than the equilibrium constant determined thermodynamically. This discrepancy is almost certainly due to an error in the value of k_d. The electrical conductivity and kinetic results of this Chapter also show that perchloric acid reacts immediately with 1,3-dioxepane to produce an equimolar quantity of active centres. The overall activation energy of the polymerisation reaction was calculated: $E_p = 3.5 \pm 0.3$ kcal. mole^{-1}.

Section C (Chapter 9)

This section is concerned with basicity measurements. 1,3-Dioxolane ($pK_b = 7.4$) was found to be considerably less basic than poly-1,3-dioxolane ($pK_b = 6.5$), 1,3-dioxepane ($pK_b = 6.0$) and poly-1,3-dioxepane ($pK_b = 5.7$). This is in accord with the results of Sections A and B.

A theory, involving dipole moments, has been developed to explain these results.

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CHAPTER 1.

Experimental

Part I: Materials

1.1 **Methylene dichloride.** This solvent was purified, stored and dosed as described in my M.Sc. Thesis.

1.2 **Anhydrous Perchloric Acid.** The catalyst solution was prepared, stored and dosed as described[1].

1.3 **1,3-Dioxolane.** This monomer was purified, stored and dosed as described[2].

1.4 **Tetrahydrofuran.** This compound (L. Lights Ltd.) was purified as described by Sorenson and Campbell[3]. The tetrahydrofuran was refluxed over sodium and distilled; the middle fraction b.p. 66°/754 mm. (lit.[4] 64°/760 mm.) was collected. This fraction was then distilled under vacuum into a reservoir and dried on lithium aluminium hydride. The procedure for the drying and dosing of tetrahydrofuran was exactly as described for 1,3-dioxolane.

1.5 **1,4-Dioxane.** The commercial product (Hopkin and Williams) was refluxed with sodium for 24 hours to remove peroxides and water. The fraction b.p. 101-102° /747 mm. was collected (lit.[4] 101°/750 mm.).

1.6 **1,3-Dioxepane.** This monomer was prepared as described in my M.Sc. Thesis. The crude product was refluxed for 12 hours on sodium and carefully distilled; initially about 10% by volume of tetrahydrofuran distilled over, b.p. = 64-67°/757 mm. The fraction with b.p. 116-118°/757 mm. was collected, this was about 60% by volume of the total product. This fraction was then redistilled off sodium through a 3 ft. column at a reflux ratio of 5:1 and a product having b.p. 120°/753 mm. was collected (lit.[5] 117°/760 mm.).

The clean N.M.R. and I.R. spectra corresponded to the expected structure but analysis by vapour phase chromatography with a Perkin-Elmer F-11 instrument showed that tetrahydrofuran was present (1:10,000 vol/vol.); no other impurities could be detected.

This batch of 1,3-dioxepane was distilled under vacuum in a reservoir, dried with lithium aluminium hydride and used in exactly the same way as 1,3-dioxolane.

The second batch of 1,3-dioxepane was purified very carefully by distillation through a 3 ft. column at a reflux ratio of 50:1. Analysis by vapour phase chromatography showed that the quantity of tetrahydrofuran present in the 1,3-dioxepane was reduced to 1:50,000 vol/vol.

1.7 <u>2,2-Diphenyl-1,3-dioxolane</u>. This compound was synthesised following Ceder's procedure[6]. Equivalent quantities of ethylene glycol (30 g) and benzophenone (90 g) were dissolved in 400 ml. benzene and 0.25 g p-toluene sulphonic acid was added as catalyst. The reaction was carried out in a Soxhlet apparatus. Calcium chloride as dehydrating agent was placed in the thimble and this was replaced twice during the distillation. After the extraction was completed (31 hours) the benzene was distilled off and the residue was fractionated under reduced pressure b.p. 102-105°/0.2 mm. The product was then purified by repeated recrystallisation from light petroleum until the melting point was constant. m.p. 55-55.5° (lit.[6] 55-56°).

The infrared spectrum of 2,2-diphenyl-1,3-dioxolane in carbon tetrachloride was in agreement with the expected structure. However, u.v. spectra of solutions of 2,2-diphenyl-1,3-dioxolane in methylene chloride showed that about 1% by weight of benzophenone was always present. It was not possible to remove the last traces of benzophenone either by repeated recrystallisation from methanol or by chromatography on an alumina column.

1.8 Polymer Isolation. The isolation of poly-1,3-dioxolane and poly-1,3-dioxepane was carried out as described[2].

1.9 Water Phials. Glass phials were filled with small quantities of water with a micro-syringe as described in my M.Sc. Thesis.

1.10 Methanol-d_1. CH_3OD, isotopic purity better than 99 atom % D was supplied by CIBA (A.R.L.) Ltd., Duxford, Cambridge.

1.11 Triphenylmethyl Chloride. This compound (L. Lights Ltd.) was recrystallised from hexane until the melting point was constant. m.p. 112-113° (lit.[7] 112-113°).

1.12 Silver Perchlorate. The anhydrous product was used as supplied by B.D.H. without purification.

1.13 Silver Tetrafluoroborate. The anhydrous product was used as supplied by Alfa Inorganics without purification.

1.14 Antimony Pentachloride. This liquid (B.D.H. Technical) was purified by bulb to bulb distillation on the vacuum line and was finally distilled under vacuum into phials.

Part II: Apparatus and Procedures

The apparatus and experimental method was largely the same as already described in my M.Sc. Thesis. Only new apparatus and new techniques are described here.

1.15 Ultraviolet and visible spectroscopy. The spectra reported in this work were taken on a Beckman DB recording spectrophotometer. A special light-tight lid allowing a large amount of free space above the cell holder replaced the conventional lid when a spectroscopic device was used. The spectroscopic device is described in the enclosed reprint. This device was used for studying the reaction between 1,3-dioxolane and triphenylmethyl perchlorate. 1 mm. and 1 cm. silica cells were used in the "open" experiments.

1.16 Infrared spectroscopy. All infrared spectra were run on a Perkin Elmer 221 Grating Spectrophotometer. 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 solutio in methylene dichloride. Low molecular weight polymer samples which were viscous liquids at room temperature were pressed between sodium chloride plates. Liquids and crystalline compounds were scanned in carbon tetrachloride or methylene dichloride solution in 0.1 and 1.0 mm. cells.

1.17 Nuclear Magnetic Resonance Spectroscopy. All nuclear magnetic resonance spectra were run on a Perkin Elmer Model R.10 N.M.R. Spectrometer. This instrument has 'H resonance at 60 Mc $\sec^{-1}$ and is thermostatted at 35°. The position of the N.M.R. bands in carbon tetrachloride, deuterochloroform and methylene dichloride solution were determined by reference to T.M.S. at 10τ as an internal standard.

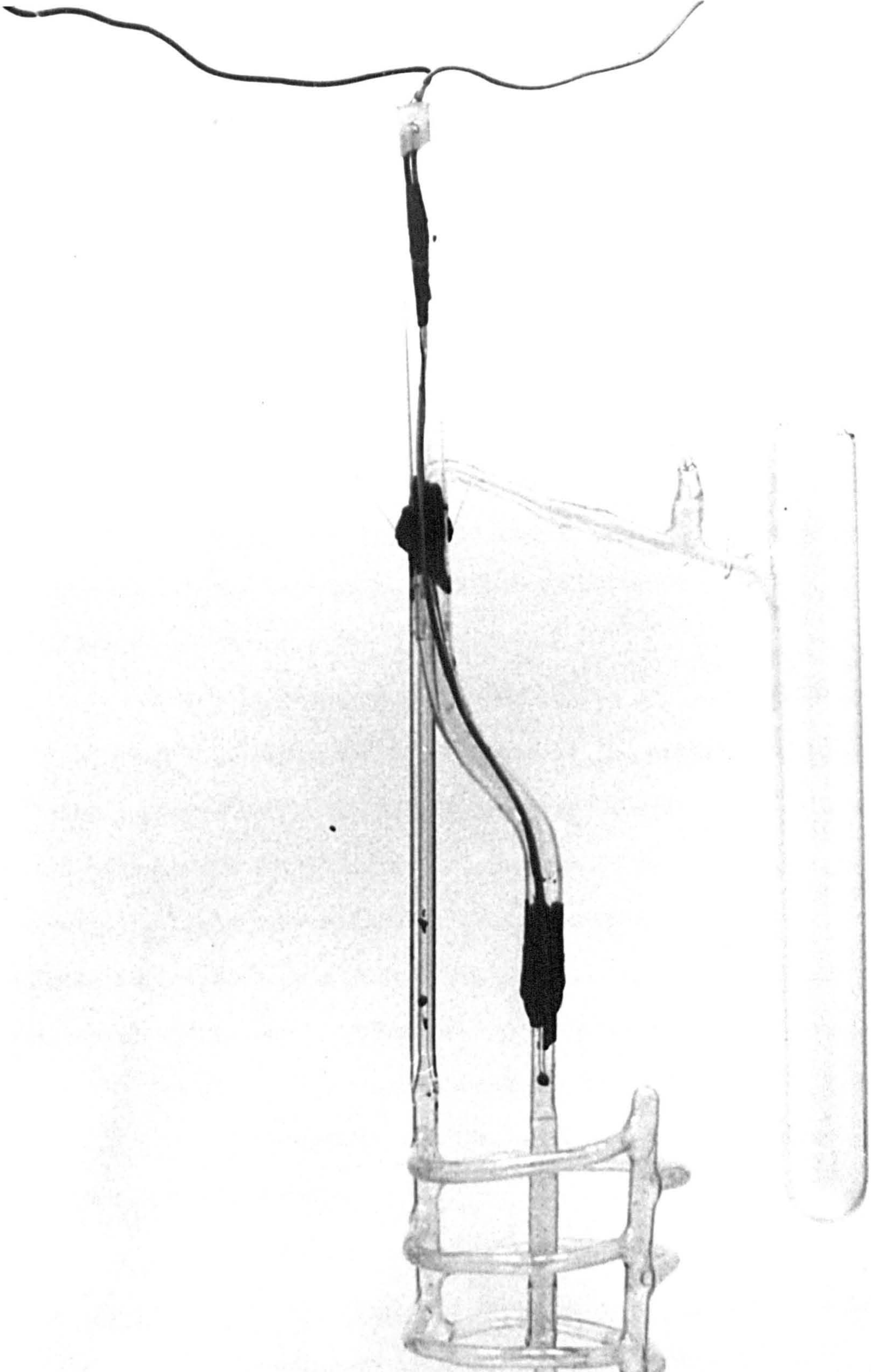
The experiments with 1,3-dioxolane and anhydrous perchloric acid were carried out under high vacuum. The soda glass sample tube was sealed onto the vacuum line by means of a soda glass-to-pyrex graded seal. The tube was filled, frozen down and sealed off; it was then thawed and warmed up to 35° so that the spectrum could be scanned.

1.18 Polymerisations. Fast polymerisations and depolymerisations of 1,3-dioxolane and 1,3-dioxepane, lasting from 20 seconds to 20 minutes, were carried out under vacuum in the adiabatic calorimeter as described in my M.Sc. Thesis. This apparatus allowed the addition of phials of further reagents such as water or more monomer at any stage of the reaction. Polymerisations were terminated by admitting ammonia gas direct from a reservoir of 0.880 ammonium hydroxide.

Slow polymerisations and depolymerisations of 1,3-dioxolane, lasting from 30 minutes to 48 hours, were followed in a dilatometer that was fitted

Fig. 1.1

Dilatometer fitted with electrodes.



with electrodes and that was similar to that described in the enclosed reprint. The dilatometer that was used for these experiments had electrodes as described but it had a large surface to volume ratio. This was achieved by constructing the bulb of the dilatometer in the form of a cage made of several thin glass tubes Fig. 1.1. This was done so that the liquid in the dilatometer would attain the temperature of the thermostat as soon as possible after immersion.

The 'first' polymerisation was carried out in the usual manner: The monomer solution was allowed to reach the correct temperature, the catalyst phial was then broken and the contents of the side tube were tipped into the dilatometer.

However subsequent depolymerisation and repolymerisation reactions were started by placing the dilatometer in thermostats at various temperatures (0° for depolymerisations and -20° for repolymerisations). For this reason rapid temperature equilibration of the contents of the dilatometer was essential. Tests were made with this dilatometer with the monomer solution before the catalyst phial was broken and it was found that the meniscus was stationary within four minutes of immersion in either thermostat.

The dilatometer was not calibrated as the position of equilibrium of the 1,3-dioxolane system could be predicted from the thermodynamic measurements already made.

1.19 <u>Electrodes in the Adiabatic Calorimeter</u>. This apparatus is fully described in the reprint enclosed at the end of this Chapter.

1.20 Cell Constants. The cell constant of the adiabatic calorimeter electrodes and of the dilatometer electrodes was obtained by Lind, Zwolenik and Fuoss's method[8]. It was assumed that the value of the cell constants, determined at 25°, could be applied in all measurements.

Cell constants: Calorimeter electrodes = 0.096 cm^{-1}.
Dilatometer electrodes = 0.619 cm^{-1}.

1.21 Conductivity Bridges and Recorders. Conductivities for calibration purposes were measured with a Wayne-Kerr B221 Universal Bridge. Routine conductivity measurements were made with a Chandos Linear Conductivity Meter. For fast polymerisations the output of this meter was connected to one pen of a Rikadenki Kogyo fast response two pen recorder. The time-temperature curve from the adiabatic calorimeter was recorded by the second pen.

1.22 Thermostats. Dilatometry experiments were carried out at 0°, -20° and -30°. A well stirred ice-in-distilled water bath in which the temperature was kept constant to ∓0.05° was used for the 0° thermostat. The lower temperatures were obtained by the use of a "Minus Seventy Thermostat Bath" (Townson and Mercer Ltd.). This is claimed to have a temperature variation of ∓0.05° but I found that it varied by ∓0.2° so that it was necessary to wait until the alcohol in glass thermometer showed a constant temperature before taking a meniscus reading of the dilatometer.

1.23 Vapour phase chromatography. All compounds were analysed on a Perkin Elmer F-11. This was fitted with a 3m. silicone-oil/chromosorb column or with a 3m. porapak column. Oven temperatures from 50° to 225° were used.

1.24 The Tipping Device. This device which was used for the preparation of phials of dilute perchloric acid solution, and also for the preparation of phials of triphenylmethyl salt solution, has been described by Gandini and Plesch[1].

1.25 Molecular Weight Determination. All molecular weights were determined with a Mechrolab Vapour Pressure Osmometer Model 301A, with a non-aqueous probe at 37°. The solvent used was 1,4-dioxane and the procedure is described in my M.Sc. Thesis.

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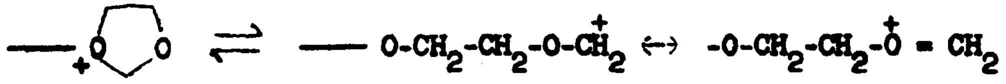
Introduction to Section A.

The work to be described in this section of the Thesis is concerned with the mechanism and kinetics of the polymerisation of 1,3-dioxolane. It forms an extension of my M.Sc. Thesis[1] which described the detailed chemistry and thermodynamics of the polymerisation of 1,3-dioxolane.

The essential results of this M.Sc. Thesis, which have been reported in a paper[2] submitted to the International Symposium on Macromolecular Chemistry, Prague 1965, are that the polymerisation of 1,3-dioxolane in methylene dichloride with anhydrous perchloric acid is a living equilibrium polymerisation that gives rise to cyclic polymer in the absence of water. The standard state ceiling temperature, entropy and heat of polymerisation were also determined.

Up to May 1965 there were very few papers[3-7] concerning the polymerisation of 1,3-dioxolane and as these have been dealt with in the introduction to my M.Sc. Thesis I will concentrate on the papers published after May 1965.

Okada[8] copolymerised 1,3-dioxolane with styrene in toluene solution at 25° with boron fluoride etherate as catalyst in order to determine the nature of the active centres in the polymerisation of 1,3-dioxolane. An equilibrium between oxonium ions and carboxonium ions was proposed,



$$\rightleftharpoons \text{—— O-CH}_2\text{-CH}_2\text{-O-}\overset{+}{\text{C}}\text{H}_2 \leftrightarrow \text{-O-CH}_2\text{-CH}_2\text{-}\overset{+}{\text{O}} = \text{CH}_2$$

because:

(1) The carboxonium ion derivable from 1,3-dioxolane is resonance stabilised, as was suggested by Kern[9] et al. for the ion derived from trioxane.

(2) 1,3-Dioxolane was found to copolymerise with styrene whilst tetrahydrofuran, which is generally supposed to polymerise by an oxonium ion mechanism, would not copolymerise with styrene.

However, no direct evidence, such as end group analysis or N.M.R. spectra of the ions in question, was presented to support the existence of this equilibrium and for the reasons given in Chapters 2 and 3 of this Thesis this proposal cannot be accepted.

The first kinetic study of the 1,3-dioxolane polymerisation was reported by Kucera[10] who polymerised bulk 1,3-dioxolane at 70° with octamethylcyclotetrasiloxane bisulphate as catalyst in open dilatometers with about 100 ppm of water present. Most of this work was concerned with kinetic measurements and their interpretation. Unfortunately Kucera based his kinetic scheme on the assumption that the active centres are carboxonium ions which were in equilibrium with unreactive tertiary oxonium ions, and although this scheme does fit the experimental results, this basic assumption is not justified by any supporting experiments.

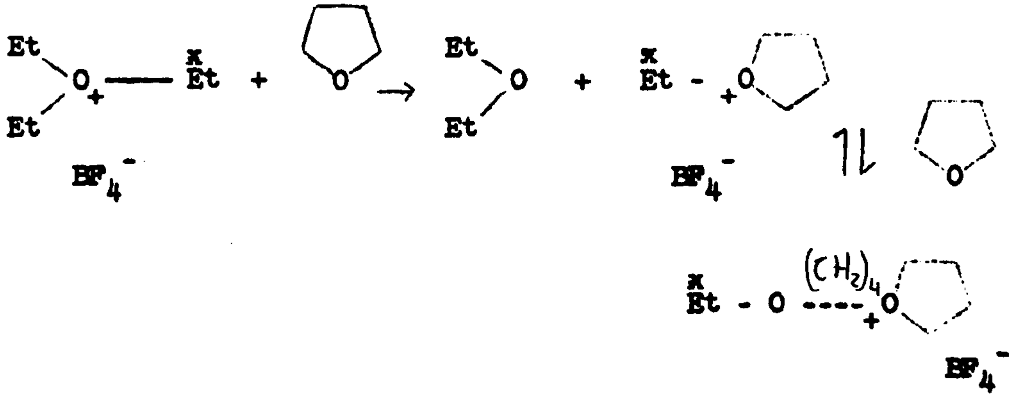
More recently, Gorin and Monnerie[11] studied the bulk polymerisation of 1,3-dioxolane at 25° with mercuric chloride or boron fluoride etherate as catalysts. The monomer and catalysts were carefully dried, but the polymerisations were carried out in test-tubes. This study was confined to kinetic measurements and the experimental results were used to test th validity of Kucera's kinetic scheme. The authors found that their results supported Kucera's scheme but no direct evidence for an equilibrium between carboxonium ions and oxonium ions was presented.

The only other information about the mechanism of the polymerisation of 1,3-dioxolane that has been published, are the reports[12,13] that 1,3-dioxolane will polymerise in the presence of maleic anhydride and benzoyl peroxide. By analogy with the mechanism of polymerisation of trioxane under similar conditions, this result implies that the dioxolenium ion is formed and that this ion causes the polymerisation of 1,3-dioxolane. This conclusion is in direct conflict with my results in Chapter 2. However a recent experiment in this laboratory[14] with 1,3-dioxolane, maleic anhydride and benzoyl peroxide failed to give any poly-1,3-dioxolane.

This literature survey shows that the mechanism of the polymerisation of 1,3-dioxolane has not yet been conclusively established and consequently the kinetic schemes that have been proposed are of limited value.

Chapters 2 and 3 of this Thesis are important as they show that the polymerisation of 1,3-dioxolane by anhydrous perchloric acid is a ring expansion mechanism which involves secondary oxonium ions; this is a new and unexpected result.

In contrast to 1,3-dioxolane, the polymerisation of tetrahydrofuran has been extensively studied; a recent review[15] on the subject contains 110 references. In particular, the mechanism of the polymerisation of tetrahydrofuran with C^{14} labelled triethyloxonium tetrafluoroborate has been studied by Tobolsky[16] who showed that one end of each polymer molecule is an ethyl group (only one third of the ethyl groups were labelled, denoted by x).



Tobolsky also showed that the initiation reaction was fast compared with the propagation reaction and that termination was very slow, so that the polymerisation curves could be interpreted in terms of the rate of reaction for an equilibrium polymerisation without termination. A similar study by Rozenberg[17] was in good agreement with these results.

In all the studies on the polymerisation of tetrahydrofuran the active centres have been taken to be tertiary oxonium ions because:

(1) The resulting carbonium ion cannot be resonance stabilised by an oxygen atom so that it is unlikely to exist in the presence of oxygen atoms.

(2) Rozenberg et al. have pointed out[17] that if carbonium ions were formed, the polymer chain should contain methyl branches as a result of isomerisation of the unstable primary carbonium ions to the more stable tertiary or secondary carbonium ions, but all studies indicate that polytetrahydrofuran is a linear polymer.

However, as far as I am aware, the possibility of an equilibrium between free ions and ion-pairs for these tertiary oxonium ions has never been seriously considered and no electrical conductivity measurements have been made to investigate the matter.

Thus Chapter 4 of this Thesis, which considers the possibility of an equilibrium between free ions and ion-pairs for the secondary oxonium ions of the 1,3-dioxolane polymerisation, and Chapter 5 which is an account of electrical conductivity measurements made during 1,3-dioxolane polymerisations should be useful contributions to the field of the cationic polymerisation of oxygen compounds.

Note

Although this account of the 1,3-dioxolane work is self contained a few items of information from the M.Sc. Thesis have been reproduced for clarity.

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Chapter 2

The Reaction of 1,3-Dioxolane with Triphenylmethyl Salts

The preparation of the triphenylmethyl salts is included in this Chapter because the reaction of 1,3-dioxolane with these salts was found to depend critically on the way that the salts were prepared.

2.1 Apparatus and Experimental Method.

Fig. 2.1. illustrates the apparatus that was used for the preparation of triphenylmethyl fluoroborate. The two reagents, silver tetrafluoroborate (0.2 g) and triphenylmethyl chloride (0.5 g), were placed in open phials and evacuated strongly for 8 hours with occasional heating. Methylene dichloride (20 ml.) and nitroethane (1 ml.) were distilled into the tube. The nitroethane was added to assist the solution of silver tetrafluoroborate. The phials were broken and the reaction was allowed to proceed for several hours; silver chloride was precipitated and the solution became darker yellow. The methylene dichloride and the nitroethane were then pumped off, leaving triphenylmethyl fluoroborate, silver chloride and some unreacted triphenylmethyl chloride. Several hours of pumping were allowed to make quite certain that all traces of nitroethane were removed from the system.

Dry hexane was then distilled in and the apparatus was sealed off at A. The hexane was allowed to thaw and was warmed slightly to dissolve the triphenylmethyl chloride. The hexane remained colourless and therefore did not dissolve any triphenylmethyl fluoroborate. Finally the hexane was tipped through the sintered disc and poured into B. The hexane was frozen in B and

Fig. 2.1

Apparatus for the preparation of triphenylmethyl fluoroborate.

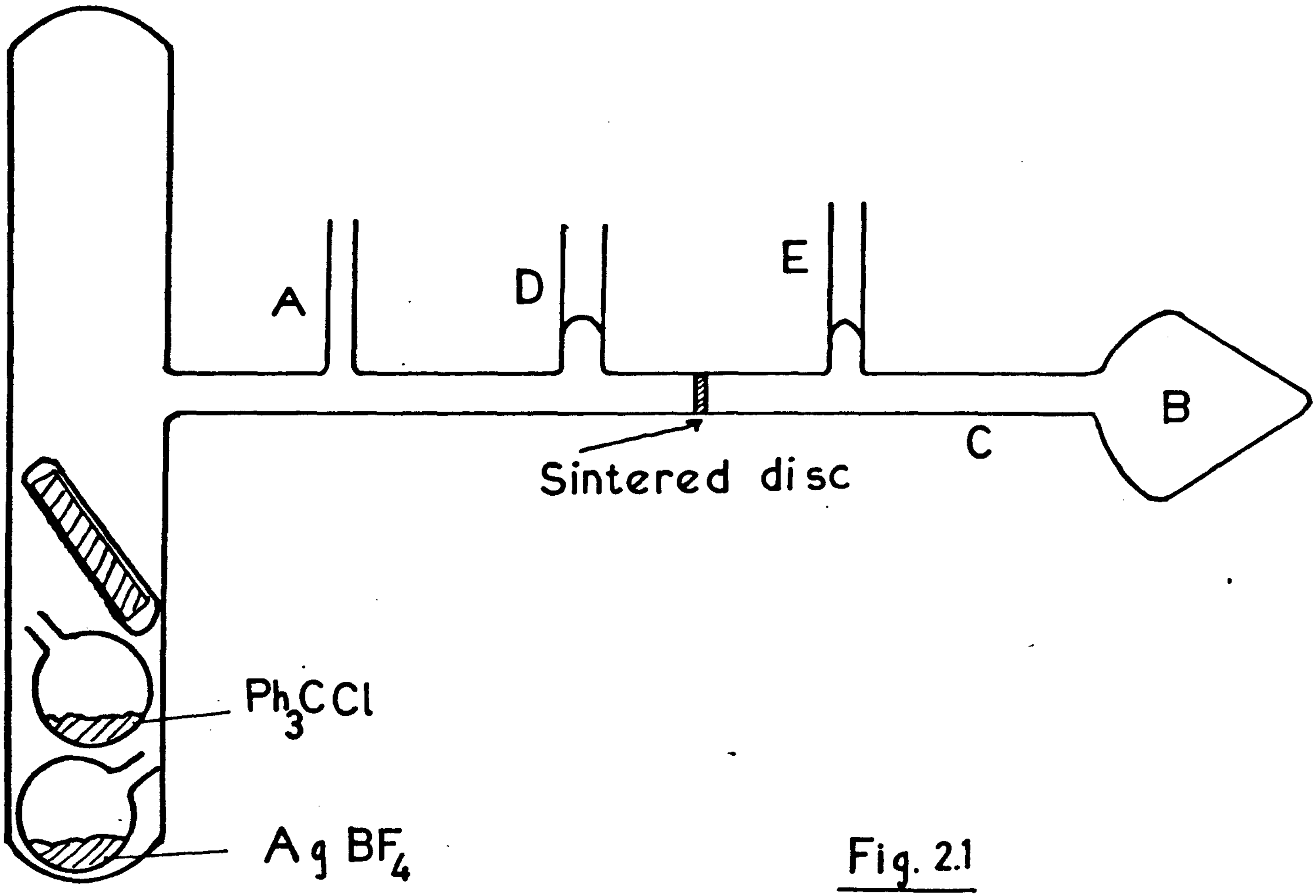


Fig. 2.1

the apparatus sealed off at C. The apparatus was then reattached to the vacuum line by means of break seal D; methylene dichloride (20 ml.) was distilled in and the apparatus sealed off at D. The methylene dichloride was thawed and warmed to dissolve the triphenylmethyl fluoroborate. The apparatus was then attached to a tipping device under vacuum by means of break seal E. The methylene dichloride solution was poured through the sintered disc into the tipping device. As much of the triphenylmethyl fluoroborate as possible was washed from the reaction vessel into the tipping device but some loss always occurred. Finally the tipping device was sealed off at E and the phials were filled and sealed off in the usual way. Some loss of triphenylmethyl fluoroborate occurred at this stage as well.

A phial of this solution was broken into a small flask and the solution was divided into two. To one part of the solution was added a few drops of silver nitrate in 95% ethanol. No precipitate of silver chloride formed, indicating that all the triphenylmethyl chloride had been removed by the hexane.

To the other part of the solution a few drops of dilute nitric acid and ethanol were added. The mixture was warmed and filtered. A few drops of aqueous sodium chloride were added to the filtrate. No precipitate of silver chloride was observed, indicating that no silver was present in this solution.

Triphenylmethyl perchlorate was prepared in three different ways.

Method A Triphenylmethyl chloride (2.5 g.) and silver perchlorate (2.5 g.) were evacuated in open phials in an apparatus similar to that shown in Fig. 2.1.

Methylene dichloride (20 ml) and nitroethane (1 ml) were distilled into the tube. The reaction was carried out and the solvent pumped off. As there was an excess of silver perchlorate the triphenyl methyl perchlorate was not washed with hexane. Methylene dichloride was distilled in and the solution was tipped and sealed into phials.

A phial of this solution was tested for chloride and silver as described above. No silver was present, but a large amount of unreacted triphenylmethyl chloride was present.

This first preparation of triphenylmethyl perchlorate was carried out with too large a quantity of triphenylmethyl chloride. There was an excess of silver perchlorate, but the excess was small and the silver perchlorate is so sparingly soluble in the mixture of nitroethane and methylene dichloride that reaction remained incomplete.

Method B The triphenylmethyl perchlorate was prepared as in Method A. The only difference was that a much smaller quantity of triphenylmethyl chloride was used: 0.3 g triphenylmethyl chloride and 1 g silver perchlorate.

A phial of this solution was tested for silver perchlorate by adding a few crystals of triphenylmethyl chloride to the solution. No precipitate of silver chloride was formed, which indicated that no silver perchlorate was present. Another phial was tested for unreacted triphenylmethyl chloride by treating the contents with a few drops of silver nitrate in ethanol. No precipitate was produced. It thus appeared that the triphenylmethyl perchlorate produced by this method was suitable for experiments with 1,3-dioxolane. After about ten polymerisation experiments it was noticed that one of the polymers turned black after having been left in the light for a few hours. This suggested the presence of silver in the triphenylmethyl perchlorate phials.

The test for silver perchlorate with triphenylmethyl chloride was repeated and was again negative, indicating that the silver was not present as the perchlorate. Another phial was broken into a small flask and treated with a few drops of dilute nitric acid and ethanol. The mixture was warmed and filtered. When a few drops of aqueous sodium chloride solution were added to this filtrate a white precipitate was immediately produced. This precipitate rapidly turned violet in the light and was soluble in concentrated ammonium hydroxide solution. This meant that silver was present in this solution, but not as the perchlorate.

It seemed possible that the silver was complexed with the nitroethane that was used at the start of the reaction, so a dummy run with just silver perchlorate was carried out. The silver perchlorate was dried, treated with methylene dichloride and nitroethane, the solvent pumped off and more methylene dichloride distilled in. Finally the methylene dichloride was tipped through the sintered disc and sealed into phials. The methylene dichloride did not contain any detectable quantity of silver.

It now appears that the silver present in the triphenylmethyl perchlorate prepared by Method B must have been complexed with the aromatic rings of the triphenylmethyl perchlorate.

<u>Method C</u> The triphenylmethyl perchlorate prepared by Method A contained no silver but some triphenylmethyl chloride. A few phials of this solution were broken under vacuum and the methylene dichloride pumped off. Dry hexane was distilled in and warmed to dissolve the unreacted chloride. The hexane was

tipped through the sintered disc, frozen and sealed off. Fresh methylene dichloride was distilled in, the triphenylmethyl perchlorate was dissolved and tipped into phials that were sealed off. A phial of this solution was tested and shown to contain no silver and no chloride.

Triphenylmethyl hexachloroantimonate was prepared from triphenylmethyl chloride (0.9 g) and antimony pentachloride (2 g). The apparatus used was similar to that in Fig. 2.1. except that the antimony pentachloride was contained in a sealed phial. Both reagents and the product are soluble in methylene dichloride so that nitroethane was not used. The phials were broken and the reaction allowed to proceed for a few hours. The methylene dichloride was pumped off and the pumping was continued for several hours to remove all traces of antimony pentachloride. Finally the salt was washed with hexane under vacuum to remove any triphenylmethyl chloride or antimony pentachloride. The hexane remained colourless and did not contain any chloride after this treatment.

The concentrations of all triphenylmethyl salt solutions were standardised spectrophotometrically, using a molar extinction coefficient of 36,000 at 410 mμ[1]. In all cases 30 to 40% less triphenylmethyl ions were found than were calculated. This discrepancy is in part due to the inevitable loss of some of the salt on the surface of the reaction vessel and the tipping device. It is also possible that some of the triphenylmethyl chloride had hydrolysed to the carbinol or that the silver perchlorate and tetrafluoroborate were not perfectly dry when weighed.

2.2 Polymerisation Experiments with 1,3-Dioxolane and Triphenylmethyl Salts.

Experiments 96 and 97 (Table 2.1) were carried out with triphenyl-methyl fluoroborate. No temperature rise was recorded and only a very small amount of low molecular weight polymer was isolated from experiment 96. No polymer at all was isolated from experiment 97. Equivalent quantities of perchloric acid as catalyst would have caused these polymerisations to reach equilibrium (36% yield) in about 5 minutes.

The initial conductivity, κ_0 was measured immediately the catalyst phial was broken. The relatively high conductivity is due to the triphenylmethyl fluoroborate. A simultaneous drop in conductivity and fading of the characteristic yellow colour was observed. In both experiments the conductivity became constant (κ_f), after about half an hour, by which time the yellow colour had completely faded and a fine white precipitate had formed. An attempt was made to isolate these crystals but they decomposed in a desiccator in a few hours.

Experiment 71 (Table 2.1) was carried out with triphenylmethyl perchlorate that had been prepared by Method A. This contains some triphenylmethyl chloride but no silver. After 10 hours only 4% of polymer was isolated; an equivalent quantity of perchloric acid would have caused the polymerisation to reach equilibrium (44% conversion) in about 4 minutes.

A slow drop in conductivity was observed; after half an hour the conductivity had fallen from 31.4 to 20.0 μmho cm^{-1}. After ten hours the conductivity was constant and the yellow colour had faded but no precipitate was observed in this experiment.

Table 2.1.

Data for Polymerisations of 1,3-Dioxolane with Triphenylmethyl Salts.

Run No.	96	97	71	94	110	95A	98A	113	104	106
[1,3-Dioxolane], M.	2.00	2.00	1.22	2.00	2.00	1.22	1.22	2.00	2.00	2.00
Catalyst	Ph_3CBF_4	Ph_3CBF_4	Ph_3CClO_4	Ph_3CClO_4	Ph_3CClO_4	Ph_3CClO_4	Ph_3CClO_4	Ph_3CClO_4	Ph_3CSbCl_6	Ph_3CSbCl
Method of Prep.			A	B	B	B	B	C		
[Catalyst], 10^3 M.	0.9	2.4	6.0	0.8	1.3	0.4	0.8	5.0	3.4	2.6
Initial Temp. deg.	+9	+9	-22	+9	+9	-20	-20	+9	+9	-22
Reaction Time, mins.	60	30	600	40	15	600	360	60	40	60
Yield %	1	0	4	36	34	-	-	1	33	11
κ_o μ mho cm^{-1}.	79.0	146	31.4	52.8	86.4	22.3	24.2	86.0	80.0	72.1
κ_f μ mho cm^{-1}.	0.94	0.96	3.00	2.78	4.80	1.08	1.12	0.66	9.58	46.0

Triphenylmethyl perchlorate that had been prepared by method B was used in experiments 94, 110, 95A and 98A (Table 2.1). This was later shown to contain some complexed silver.

Polymerisations 94 and 110 were followed on the adiabatic calorimeter. These polymerisations had a longer acceleration period than equivalent polymerisations with perchloric acid, but they did reach equilibrium in the times indicated.

Experiments 95A and 98A were carried out in dilatometers so that the depolymerisations could be studied as well. Fig. 2.2 compares the polymerisation curves of experiments 98A and 81A. Experiment 81A was carried out at the same monomer concentration and the same temperature as 98A, but 0.49×10^{-3} M perchloric acid was used instead of 0.8×10^{-3} M triphenylmethyl perchlorate. The polymerisations with this triphenylmethyl perchlorate solution were much slower than with an equivalent quantity of perchloric acid.

The polymers of experiments 98A and 81A were depolymerised in dilatometers at 0°. The first order rate constants were 0.11 min^{-1} and 0.14 min^{-1} for 98A and 81A respectively.

All these polymerisation reactions were accompanied by a simultaneous drop in conductivity and a fading of the yellow colour due to the triphenylmethyl ions. No precipitate was observed in these experiments.

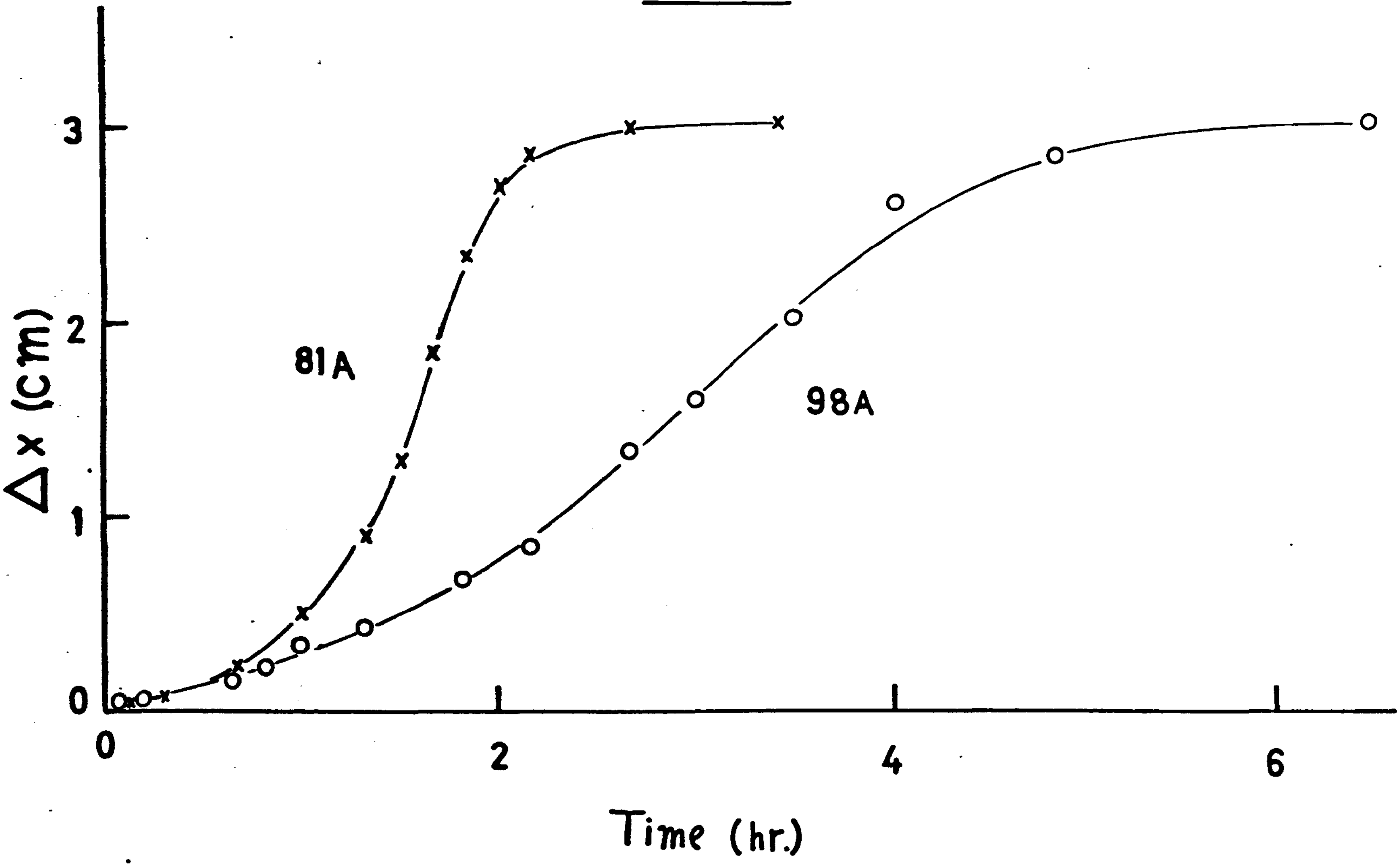
The infrared spectrum of polymer 94 was found to be identical to the spectra of polymers made with perchloric acid. There was no trace of any triphenylmethyl groups in the polymer.

Experiment 113 (Table 2.1) was carried out with triphenylmethyl perchlorate prepared by method C. This has no triphenylmethyl chloride and no silver present. No temperature rise was recorded and only a small amount of low

Fig. 2.2

Plots of dilatometer readings against time for experiments 81A (the polymerisation of 1.22 M 1,3-dioxolane with 0.49×10^{-3} M perchloric acid) and 98A (the polymerisation of 1.22 M 1,3-dioxolane with 0.8×10^{-3} M triphenylmethyl perchlorate) at -20° (Table 2.1).

Fig. 2.2



molecular weight polymer was isolated. An equivalent quantity of perchloric acid would have caused this polymerisation to reach equilibrium (36% conversion) in 2 minutes.

After 1 hour the solution was colourless and the conductivity was steady at 0.66 μ mhos cm^{-1}. This is a lower figure than for parallel experiments with triphenylmethyl perchlorate prepared by methods A and B. No precipitate was observed in this experiment.

The solution was neutralised with ammonia and ethanol after the experiment and all the solvent was evaporated on a steam bath. This left a white precipitate in the beaker and a very small quantity of low molecular weight polymer. Water was added and all the water soluble fraction, including the polymer, was removed. The water - insoluble precipitate was dissolved in 50 ml of 95% ethanol. The u.v. spectrum of this solution was found to be identical with the u.v. spectrum of pure triphenylmethane in 95% ethanol. From the extinction coefficient of triphenylmethane[2], λ_{max} (log ϵ) = 262.5 (2.92), it was possible to estimate that about 80% of the triphenylmethyl perchlorate was recovered as triphenylmethane.

Triphenylmethyl hexachloroantimonate was used as the catalyst for polymerisation experiments 104 and 106 (Table 2.1). For 104 a very slow temperature rise was recorded on the calorimeter. The polymerisation had not quite reached equilibrium after 40 mins. An equivalent quantity of perchloric acid would have caused this polymerisation to reach equilibrium (36% conversion) in about 3 minutes. The conductivity fell rapidly and became steady at 9.58 μ mho cm^{-1} after 40 minutes. The solution was colourless after 30 minutes and no precipitate was formed.

The polymerisation at -22° (106) went much more slowly. After 1 hour the conversion was only 11% (equilibrium is at 44% conversion under these conditions). The conductivity also fell very slowly and after 1 hour it was 46 μ mho cm^{-1} and the solution was still bright yellow. An equivalent quantity of perchloric acid would have caused this polymerisation to reach equilibrium in about 8 minutes.

Both polymerisations were killed with ammonia and ethanol. The neutralised catalyst was precipitated and filtered off, and the polymers isolated by evaporation of the solvent. The infrared spectra of both polymers showed a large hydroxyl group peak at 3500 cm^{-1} and a carbonyl peak at 1720 cm^{-1}. There was also evidence of chlorine (732 cm^{-1}) in the polymer. Definite conclusions cannot be made because of the difficulty of removing all traces of catalyst from the polymer.

A few exploratory experiments were carried out with antimony pentachloride as catalyst for the polymerisation of 1,3-dioxolane. 2.1 x 10^{-3}M Antimony pentachloride caused immediate polymerisation of 1.22 M 1,3-dioxolane at -22°. Although the polymerisation was very rapid and without any acceleration period, the system did not reach equilibrium. A second addition of antimony pentachloride caused another burst of polymerisation but still the system did not reach equilibrium. The apparatus was opened to the air but no further polymerisation occurred. The polymer was isolated and found to contain chlorine, as there was a peak at 732 cm^{-1} in the infrared spectrum. Throughout this experiment the conductivity rose steadily from 1.1 to 2.5 μ mho cm^{-1}.

2.3 Spectroscopic Measurements on the System Triphenylmethyl Perchlorate - 1,3-Dioxolane.

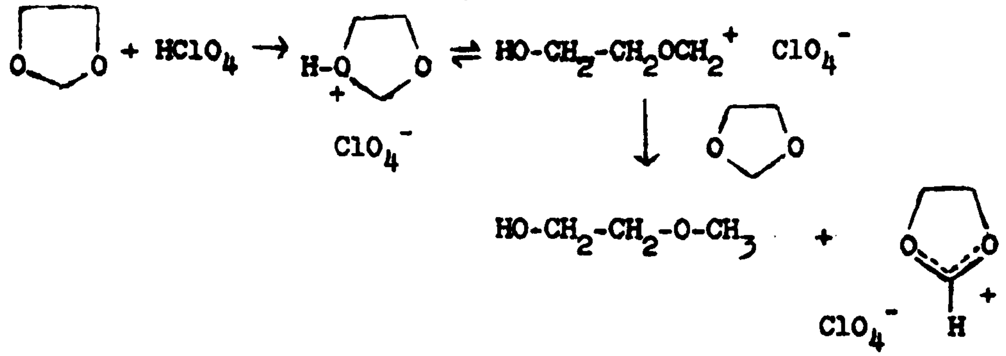
The reaction between 1,3-dioxolane and triphenylmethyl perchlorate (prepared by method B) was also studied spectrophotometrically. In experiment 75, 0.5 x 10^{-3} M triphenylmethyl perchlorate was allowed to react with 3.0 M 1,3-dioxolane at room temperature under vacuum. When the phial of triphenyl--methyl perchlorate was broken, the yellow colour due to the triphenylmethyl ion was too intense to be measured. However this colour rapidly faded and within four minutes the visible part of the spectrum was blank. In the u.v. the characteristic spectrum of triphenylmethane with peaks at 256, 262 and 270 mμ was present. No other peaks were present down to 230 mμ. From the extinction coefficient of triphenylmethane[2], λ_{max} (log ϵ) = 262.5 (2.92), it was estimated that the concentration of triphenylmethane was 0.48 x 10^{-3} M. This shows that all the triphenylmethyl perchlorate was converted to triphenylmethane.

The spectroscopic device was opened to the air and a few drops of ammonia and ethanol were added but the spectrum was unchanged by this.

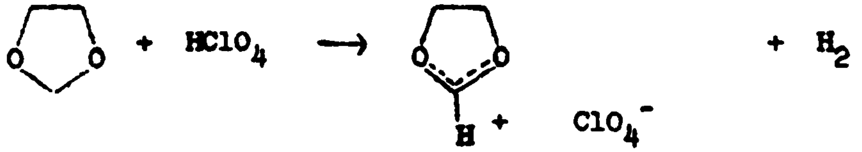
2.4 Experiments to Detect Dioxolenium Perchlorate in Polymerisations of 1,3-Dioxolane Catalysed by Perchloric Acid.

At one stage of this work it seemed possible that dioxolenium perchlorate was either the active species in the polymerisation of 1,3-dioxolane with perchloric acid or at least that it was involved in the reaction mechanism. There are only two ways in which dioxolenium perchlorate could be formed from 1,3-dioxolane and perchloric acid.

(i)



(ii)



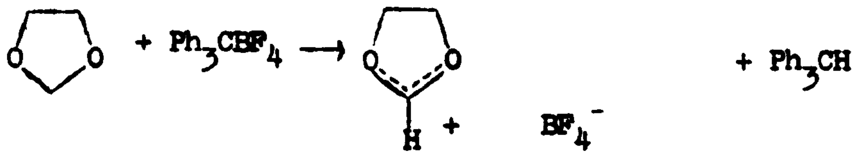
One involves formation of 2-methoxyethanol and the other the formation of hydrogen. As there was no simple conclusive test for small quantities of dioxolenium perchlorate, tests were carried out to detect 2-methoxyethanol and hydrogen.

<u>Results</u> In experiment 109, 2.5 M 1,3-dioxolane was polymerised with 0.1 M perchloric acid in a previously evacuated tube. After the polymerisation the contents of the tube were frozen with liquid nitrogen. The discharge from a Tesvac showed that the vacuum was as good as before the experiment (10^{-4} mm). Since 0.45 m mole of perchloric acid was used in this experiment, even if 1% of the perchloric acid had reacted to produce hydrogen this would have been noticed.

The contents of the tube were thawed and the polymerisation was killed at 0° with sodium carbonate. The solution now contained methylene dichloride, 1,3-dioxolane, polymer and possibly 2-methoxyethanol. 10 μ litre of this solution was injected into a gas phase chromatograph and the chromatogram recorded. A 0.1% (vol/vol) solution of 2-methoxyethanol in methylene dichloride containing 2.5 M 1,3-dioxolane was made up and 10 μ litre of this was injected into the chromatograph. The retention time and peak height of the 2-methoxyethanol was recorded. By a careful comparison of the two chromatograms it is estimated that there was less than 1 part in 40,000 (vol/vol) of 2-methoxyethanol in the solution tested (experiment 109). The concentration of perchloric acid in the solution tested was 1 part in 350 (vol/vol) so that not more than 1% of the perchloric acid could have reacted to produce 2-methoxy-ethanol.

2.5 Discussion.

1,3-Dioxolenium structures were first proposed by Winstein and Buckles[3] in 1942. In two papers by Meerwein[4,5] the preparation and reactions of several dioxolenium salts are reported. In particular the preparation of dioxolenium fluoroborate is described. This compound was made by the reaction of triphenylmethyl fluoroborate with 1,3-dioxolane in liquid sulphur dioxide as solvent.



Dioxolenium fluoroborate is reported to be insoluble in methylene dichloride. The yield is quoted as 88% of the theoretical and 58% of the triphenylmethyl fluoroborate was recovered as triphenylmethane. Although the reaction was carried out with 1.6 M 1,3-dioxolane under dry conditions in liquid sulphur dioxide, no polymer is reported to have been formed.

The salt was identified by the production of the 2-iodoethyl formate when it was treated with sodium iodide in acetonitrile.

A more recent paper by Winstein[6] deals with the nuclear magnetic resonance spectrum of 2-methyl-cis-4,5-tetra-methylene-1,3-dioxolenium tetrafluoroborate in acetonitrile solution. The absorption due to the methyl group is at 7.28 τ which indicates that the compound is ionic in acetonitrile.

Magnuson[7] has prepared 2,4,4,5,5-pentamethyl-1,3-dioxolenium perchlorate. This too is ionic in acetonitrile as the absorption due to the methyl group is at 7.3 τ.

Wtih this information the results of the polymerisation experiments with 1,3-dioxolane and triphenylmethyl salts can be explained. It is clear that in experiments 96 and 97 with triphenylmethyl fluoroborate and 1,3-dioxolane, dioxolenium fluoroborate was formed and precipitated out of solution. This explains why the conductivity dropped as the yellow colour due to the triphenylmethyl ion faded. It also explains why the final conductivity in these experiments was independent of the initial triphenylmethyl fluoroborate concentration.

Experiment 113, with triphenylmethyl perchlorate prepared by method C and 1,3-dioxolane, is most important. This experiment shows that pure triphenylmethyl perchlorate does not catalyse the polymerisation of 1,3-dioxolane at a rate comparable with that caused by perchloric acid. About 1% of polymer was isolated after an hour but this could have been due to traces of water hydrolysing dioxolenium perchlorate to perchloric acid. The fact that 80% of the triphenylmethyl perchlorate was recovered as triphenylmethane in this experiment and that 96% was recovered in the spectroscopic experiment (experiment 75) strongly suggests that the only reaction to occur under these conditions is the formation of dioxolenium perchlorate.

The positive charge in dioxolenium perchlorate is delocalised between the two oxygen atoms and dioxolenium perchlorate is more stable than triphenylmethyl perchlorate so that the value of the dissociation constant for the dioxolenium perchlorate ion pair should be slightly larger than for the triphenylmethyl perchlorate ion pair. In fact during experiment 113 the conductivity fell from 86.0 μ mho cm^{-1} to 0.66 μ mho cm^{-1}. The initial conductivity is due to triphenylmethyl perchlorate and the final conductivity must be due to dioxolenium perchlorate as no precipitate was observed.

This result suggest that, contrary to expectations, dioxolenium perchlorate exists almost entirely as ion pairs. An alternative possibility is that dioxolenium perchlorate is essentially covalent under the experimental conditions. The quoted nuclear magnetic resonance spectra of some substituted dioxolenium salts show that these compounds are ionic in acetonitrile. In principle nuclear magnetic resonance spectra of dioxolenium perchlorate under the experimental conditions, i.e. in methylene dichloride or deuterochloroform, would resolve this problem. This has not been attempted yet.

The experiments with triphenylmethyl hexachloroantimonate (104 and 106) are less satisfactory. A reasonably rapid polymerisation was observed in these experiments, but the presence of hydroxyl and carbonyl groups, and special the presence of chlorine in the polymer, suggest that there were extensive side reactions. These polymerisations could well have been due to traces of antimony pentachloride as antimony pentachloride alone polymerised 1,3-dioxolane to give polymers containing chlorine.

However the same general features were observed with the hexachloroantimonate as with the perchlorate and fluoroborate salts. The yellow colour faded slowly and the conductivity dropped. The final value of the conductivity in experiment 104 was 9.58 μ mho cm^{-1}. This is much larger than for the equivalent perchlorate experiment (experiment 113). A possible reason for this difference is that a covalent form of dioxolenium hexachloro-antimonate cannot be written.

Experiment 109 is important as it shows that dioxolenium perchlorate was not involved in the polymerisation of 1,3-dioxolane by perchloric acid. This result is discussed fully in Chapter 3. It is more difficult to draw any conclusions from experiments 94, 110, 95A and 98A in which the polymerisation of 1,3-dioxolane with triphenylmethyl perchlorate made by method B was studied. These polymerisations are not due to triphenylmethyl perchlorate itself but are almost certainly due to the presence of a silver perchlorate complex in the catalyst solution. As silver perchlorate benzene complexes have been isolated in the solid state[8], the silver is probably complexed with the aromatic rings of the triphenylmethyl perchlorate.

In a recent paper Smets and Hermans[9] reported on the study of the silver perchlorate initiated polymerisation of styrene in organic solution under rigorously dry conditions in the absence of perchloric acid. They found evidence to suggest that 1:1 and 2:1 complexes of silver perchlorate and styrene are formed and they propose a coordination polymerisation mechanism with the silver ion complexed to the olefinic double bond of styrene. It is possible that a similar silver complex with the lone pair electrons of oxygen in 1,3-dioxolane could be formed and that this could cause the polymerisation of 1,3-dioxolane.

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Chapter 3

The Mechanism of the Polymerisation of 1,3-Dioxolane

In Chapter 5 of the M.Sc. Thesis some possible mechanisms for the polymerisation of 1,3-dioxolane were set out, and in this Chapter further experiments that were undertaken to elucidate this polymerisation mechanism are described and discussed.

3.1 N.M.R. Spectra.

In Table 3.1 the experimental data and τ values for the N.M.R. spectr of the system 1,3-dioxolane and perchloric acid are given. These N.M.R. spectr were made in methylene dichloride solution, as anhydrous perchloric acid is only available in this solvent. Methylene dichloride itself gives a large peak at 4.55 τ but this did not interfere unduly with the rest of the spectrum.

Experiment 84A shows that the N.M.R. spectrum of 0.5 M 1,3-dioxolane in methylene dichloride has two simple peaks at 5.12 and 6.16 τ due to the hydrogens of the $-O-CH_2-O-$ and $-O-CH_2-CH_2-O-$ units, respectively.

The N.M.R. spectra of 0.5 M 1,3-dioxolane with 0.25 and 0.7 M perchloric acid were recorded in experiments 84B and 85. These spectra were stable for a period of 12 hours at 35° and consisted of two simple peaks that corresponded almost exactly with the N.M.R. spectrum of experiment 84A. The only difference was a slight shift down-field for the spectra of protonated 1,3-dioxolane. Protonated and non-protonated species cannot be resolved as the relaxation time for N.M.R. spectroscopy is 1-2 seconds, whilst the proton exchange between oxygen atoms is very much faster. If even 5% of an open chain structure involving a carbonium ion had been formed, the spectra obtained in

Table 3.1.

The N.M.R. Spectra for the system 1,3-Dioxolane - Perchloric Acid.

Run No.	84A	84B	85	85
[1,3-Dioxolane],M.	0.5	0.5	0.5	3.0
[$HClO_4$], M.	-	0.25	0.7	0.5
N.M.R., τ .	5.12 and 6.16 No other peaks	4.99 and 6.00 No other peaks	4.94 and 5.95 No other peaks	5.09 and 6.09 Small peaks at 5.6 and 6.4

All spectra were recorded at 35°.

experiments 84B and 85 would have shown this. In particular, the splitting of the peak for the hydrogens of the $-O-CH_2-CH_2-O-$ unit would have been observed at about 6.0 τ.

These experiments show that under the experimental conditions used the only detectable reaction is protonation of 1,3-dioxolane. In experiment 8 3.0 M 1,3-dioxolane was used and as this has a ceiling temperature of about +38° some polymerisation probably occurred. A white precipitate was formed as soon as the perchloric acid phial was broken into the solution of 1,3-dioxolane. By the time that the solution had been tipped into the N.M.R. tube, frozen down, sealed off, and allowed to reach 35°, the precipitate had just started to turn brown. After the spectrum had been recorded the white precipitate had nearly gone and the solution had turned a light brown colour. The spectrum became more complicated as the solution turned a darker brown. It is clear that under these conditions extensive decomposition occurs, so that no conclusions can be drawn from this experiment.

3.2 The Protonation of 2,2-diphenyl-1,3-dioxolane with Perchloric Acid.

The 2,2-diphenyl-1,3-dioxolane that was prepared from ethylene glycol and benzophenone could not be isolated pure. The U.V. spectrum of 1×10^{-3} M 2,2-diphenyl-1,3-dioxolane in methylene chloride was found to have a peak at 252 mμ with an optical density of 0.21. This was found to be identical with the spectrum of benzophenone in methylene dichloride (λ_{max} 252 mμ) lit[1]. (λ_{max} 252 mμ $\varepsilon = 20{,}000$).

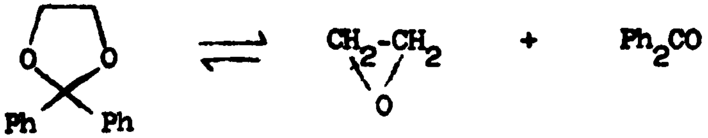
$$D = \varepsilon .C.l.$$

$$0.21 = 20{,}000.\ C, \quad C = 1 \times 10^{-5}\ M,$$

here C is the molar concentration of benzophenone in 1×10^{-3} M 2,2-diphenyl-1,3-dioxolane.

However Ceder[2], who studied the hydrolysis of cyclic acetals, reports that 2,2-diphenyl-1,3-dioxolane shows no maximum above 210 mμ in a mixture of 1,4-dioxane and water.

In experiment 86 a small crystal of 2,2-diphenyl-1,3-dioxolane was placed in the side tube of a spectroscopic device with a phial of perchloric acid When the device was evacuated the crystal of 2,2-diphenyl-1,3-dioxolane became partly liquid even though the Tesvac had not been used and the spectroscopic device had been carefully cleaned before use. After 5 minutes pumping 10 ml of methylene dichloride were distilled into the device to make a 1.3×10^{-4} M solution of 2,2-diphenyl-1,3-dioxolane. Before the perchloric acid phial was broken the U.V. spectrum of this solution was run, and a large peak from 270 to 240 mμ was found to have blotted out the U.V. spectrum. On opening the device and diluting the solution with methylene dichloride a spectrum identical with that of benzophenone was observed. It appears that an equilibrium between 2,2-diphenyl-1,3-dioxolane and benzophenone and ethylene oxide exists and that under vacuum the ethylene oxide is removed to leave benzophenone.



This equilibrium would explain why 2,2-diphenyl-1,3-dioxolane could not be isolated pure.

In experiment 86 1.3×10^{-4} M 2,2-diphenyl-1,3-dioxolane was protonated with 1×10^{-2} M perchloric acid. A small crystal was sealed under atmospheric pressure into a compartment that was connected to the spectroscopic device by a breakseal. The spectroscopic device which contained a phial of perchloric acid was evacuated, 10 ml of methylene chloride was distilled in, and finally it was sealed off from the vacuum line. The break seal was crushed and the crystal of 2,2-diphenyl-1,3-dioxolane was introduced into the solution.

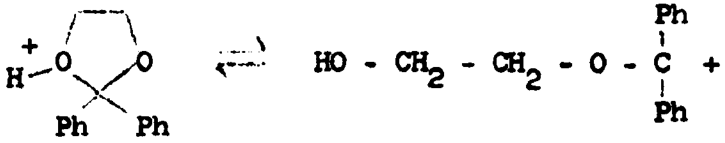
The U.V. spectrum of this solution showed a small peak at 252 mμ due to a trace of benzophenone, above this wavelength the spectrum was clear. The perchloric acid phial was then broken, the solution mixed, and the U.V. spectrum was run again. There were two prominent peaks at 291 and 337 mμ, but nothing in the visible spectrum. The spectrum remained unchanged for half an hour, so the device was opened and the mixture neutralised with a few drops of ammonia. The characteristic peak of benzophenone at 252 mμ occupied most of the U.V. spectrum but the rest of the U.V. and visible was clear. There is considerably more benzophenone present after the protonation of 2,2-diphenyl-1,3-dioxolane than before, so that some decomposition seems to occur on protonation.

The next step was to protonate 1 x 10^{-5} M benzophenone with 1 x 10^{-2} M perchloric acid. The spectrum consisted of two peaks at 292 and 340 mμ. This is in good agreement with Olah's report[3] that protonated benzophenone has peaks at 291 and 344 mμ in FSO_3H - SbF_5 solution. It thus appeared that the spectrum of protonated 2,2-diphenyl-1,3-dioxolane was due entirely to that of protonated benzophenone.

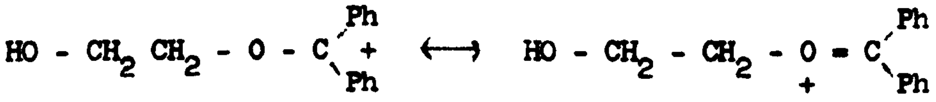
However protonated ketones absorb at lower wavelengths than the corresponding carbonium ion because in the carbonium ions the charge delocalisation is less than in the protonated ketones. In protonated benzophenone two resonance forms are important

$$\mathrm{Ph} - \overset{\mathrm{OH}}{\underset{+}{\mathrm{C}}} - \mathrm{Ph} \quad \longleftrightarrow \quad \mathrm{Ph} - \overset{+\mathrm{O}-\mathrm{H}}{\overset{\|}{\mathrm{C}}} - \mathrm{Ph}$$

It was intended to see whether the ring of 2,2-diphenyl-1,3-dioxolane opened when it is protonated by perchloric acid, as the carbonium ion that would be produced should be detectable spectroscopically.



However this carbonium ion is very similar to protonated benzophenone in that two resonance forms are important.



Because of the inevitable presence of protonated benzophenone in the spectrum of protonated 2,2-diphenyl-1,3-dioxolane it is impossible to decide whether any 2,2-diphenyl-1,3-dioxolane was opened by protonation.

3.3 Polymerisation of 2,2-Diphenyl-1,3-dioxolane.

An attempt was made to polymerise a 2 M solution of 2,2-diphenyl-1,3--dioxolane in methylene chloride with 5×10^{-2} M perchloric acid under anhydrous conditions. The solution was kept at -70° for 12 hours and then neutralised with ammonia, but no polymer was isolated.

This observation is in agreement with the prediction made by Dainton and Ivin[4] that substituted 1,3-dioxolanes would probably not polymerise.

3.4 Quantitative Measurements of Hydroxyl Groups.

Table 3.2 shows the experimental data for polymerisation experiments that were carried out at various perchloric acid concentrations, with and without added water. The polymerisations were started by breaking a phial of perchloric acid, water was added by breaking a water phial, and the reactions were stopped at +10° either by admitting ammonia gas direct from a reservoir

Table 3.2.

Quantitative Estimation of Hydroxyl Groups.

Run No.	15	119	120	121	123	116	118	122
$[HClO_4]$, 10^2 M.	0.36	3.20	3.10	3.20	3.00	2.00	3.20	5.00
Added $[H_2O]$, 10^2 M.	-	-	-	-	-	2.50	2.00	5.00
Final Temp., deg.	15	10	10	10	10	10	10	10
D, optical density of OH.	0.020	0.033	0.045	0.042	0.040	0.130	0.130	0.200
Measured Number of Monomer Units per OH group.	160	95	70	75	80	23	23	15
Calculated Number of Monomer Units per OH group.	infinity	infinity	infinity	infinity	infinity	20	25	10
D.P.	13.7	15.7	15.4	16.0	15.0	15.0	12.1	11.5
Yield %	35	41	42	39	40	40	41	38

All polymerisations were carried out with 2.0 M 1,3-dioxolane of 0.88 ammonium hydroxide or by breaking a phial of ethanol saturated with ammonia gas. In experiment 118 the water phial was broken before the perchloric acid phial.

Infrared measurements on the polymers were made at constant film thickness, 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 hydroxyl groups at 3500 cm^{-1}, was measured. The system was calibrated by adding small known quantities of butane-1,4-diol to a known quantity of a low molecular weight poly-dioxolane (No. 15) and measuring D, the optical density of the hydroxyl groups at 3500 cm^{-1}. D was found to be directly proportional to the hydroxyl group concentration and an optical density of 0.105 corresponds to one hydroxyl group per 30 units of monomer. From this figure, the optical densities were converted into the number of monomer units per hydroxyl group. The results are expressed in this way so that they can readily be compared with the DP of the polymers produced. In order to show that the hydroxyl groups measured did belong to the polymer molecules and not to ethylene glycol which might be formed by hydrolysis of the monomer, some ethylene glycol was added to a solution of polydioxolane (No. 119) and the polymer was then isolated in the usual manner. (8 hrs at 60° and 20 mm). It was found that all the ethylene glycol was removed from the polymer by this treatment. Furthermore, the optical density of hydroxyl groups for polymers 116, 118 and 122 was found to be unaltered even after the polymer had been several days in the vacuum oven.

In the M.Sc. thesis it was shown that typical polymerisations carried out under vacuum in the calorimeter, for example experiment 15, produced polymers that had no detectable end groups other than very small traces of hydroxyl groups. Table 3.2 shows that the polymer from experiment 15 had only 1 hydroxyl group for 160 units of monomer while the DP is only 13.7.

When the perchloric acid concentration was increased by a factor of 10 (experiments 119, 120, 121 and 123) the polymer produced had about 1 hydroxyl group for 80 units of monomer. The ratio of the number of moles of monomer polymerised to the number of moles of catalyst used is $2.0 \times 0.40/3.0 \times 10^{-2}$ approx. 26.

The polymers produced in these experiments were carefully examined by I.R. and N.M.R. spectroscopy, but no other end groups were detected. As the polymerisation mixtures were neutralised with ammonia, it was possible that amine end groups might be present. The Lassaigne sodium fusion test[5] failed to show nitrogen in the polymer and the sodium nitroprusside test[5] did not reveal a primary amine end group. Small quantities of ethylamine were added to the polymer that was tested and the quantity of ethylamine was reduced until the tests were just positive. In this way it is estimated that one amine group per thousand units of monomer would have given positive tests.

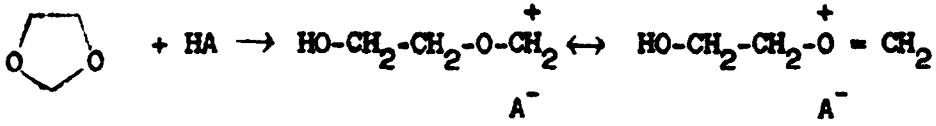
In experiments 116, 118 and 122 approximately equimolar quantities of water and perchloric acid were used to polymerise 1,3-dioxolane and polymers with between 23 and 15 monomer units per hydroxyl group were produced. The calculated number of monomer units per hydroxyl group (as listed in Table 3.2) was based on the assumption that the polymer is 100% cyclic and that each water molecule added reacts with the polymer to produce two hydroxyl groups. The agreement between the experimental and the calculated ratios for experiments 116, 118 and 122 is good and this shows that essentially all the water added produces hydroxyl groups in the polymer.

When no water was added to the polymerisations (experiments 15, 119, 120, 121, 123) the calculated number of monomer units per hydroxyl group is ∞ as the system was assumed to be perfectly dry. The experimental results show that some hydroxyl groups are produced even under 'dry' conditions.

3.5 Discussion.

This discussion is concerned with the mechanism of the polymerisation of 1,3-dioxolane and with the nature of the active centre involved. I will first set out the conclusions reached by other research workers in this field and then I will examine my own experimental results.

Okada et al.[6] proposed that the mechanism of the polymerisation of 1,3-dioxolane by acetyl chloride - metal halides, and acetic anhydride - perchloric acid initiators involved carboxonium ions and not oxonium ions. This was based on the suggestion made by Kern et al.[7] that the active centre for the cationic polymerisation of trioxane is a resonance stablised carboxonium ion. For dioxolane the formation of the analogous ion can be represented thus:



$$+ \mathrm{HA} \rightarrow \mathrm{HO{-}CH_2{-}CH_2{-}O{-}}\overset{+}{\underset{A^-}{\mathrm{CH_2}}} \leftrightarrow \mathrm{HO{-}CH_2{-}CH_2{-}}\overset{+}{\underset{A^-}{\mathrm{O}}} = \mathrm{CH_2}$$

More recently Okada et al.[8] have reported the cationic copolymerisation of 1,3-dioxolane with styrene, with boron fluoride etherate as catalyst. This they interpret as further evidence in favour of the carboxonium ion mechanism, because Kern et al.[9] have been able to copolymerise trioxane and 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. have themselves reported[10] the cationic copolymerisation of 1,3-dioxolane with tetrahydrofuran with boron fluoride etherate as catalyst.

The comparison of 1,3-dioxolane with trioxane is the only evidence presented in favour of the carboxonium ion mechanism; in particular no analysis for end groups is reported.

There are three separate pieces of evidence from my work that show that the polymerisation of 1,3-dioxolane is not propagated by carboxonium ions.

1. The N.M.R. experiments 84B and 85, with approximately equimolar quantities of perchloric acid and 1,3-dioxolane in methylene dichloride solution show only protonated 1,3-dioxolane to be present. There is no trace of any carboxonium ions or rearrangement products. These experiments indicate that oxonium ions formed from 1,3-dioxolane are more stable than the resonance stabilised carboxonium ions postulated by Okada.

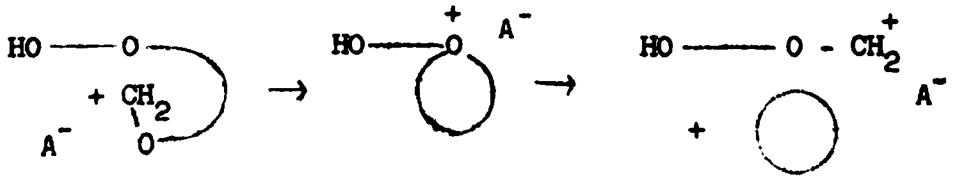
2. Chapter 2 shows that dioxolenium ions do not catalyse, and are not involved in, the polymerisation of 1,3-dioxolane; and that triphenylmethyl carbonium ions are converted wholly to the more stable dioxolenium ions. From this observation it follows that only carbonium ions or carboxonium ions that are more stable than dioxolenium ions can exist in the presence of 1,3-dioxolane. Thus it appears highly unlikely that the carboxonium ion postulated by Okada can exist in the presence of 1,3-dioxolane, as this ion is resonance stabilised by one oxygen atom whilst the dioxolenium ion is resonance stabilised by two oxygen atoms.

3. The quantitative measurements of hydroxyl groups show that poly-1,3-dioxolane is essentially cyclic, provided that the polymerisation is carried out under anhydrous conditions. If 1,3-dioxolane were to polymerise by the traditional carboxonium ion mechanism as suggested by Okada et al., then the end groups in the polymer would be essentially the same as in polyformaldehyde.

Jaacks and Kern[7], in their study of the polymerisation of trioxane in cyclohexane at 60° with perchloric acid, find that about 15% of the polymer is cyclic. The mechanism which they propose for ring formation is back-biting. The rest of the polymer is linear and has end groups approximately as follows:-

Dialkoxy 30%, hydroxyl 25%, methoxy 20% and formate 10%.

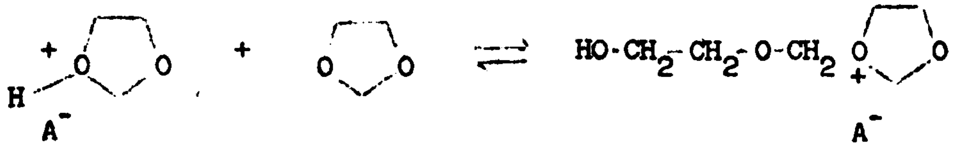
For a carboxonium ion mechanism to produce essentially cyclic polymer the back-biting reaction would have to be predominant and there is no reason why this should be so. Furthermore a number of hydroxyl groups equal to the number of active centres would still be produced.



Experiments 119, 120, 121 and 123 show that each molecule of perchloric acid does not produce a hydroxyl group, whilst Chapter 4 shows that under these conditions each perchloric acid molecule does produce an active centre. These experimental results are not compatible with a polymerisation involving carboxonium ions.

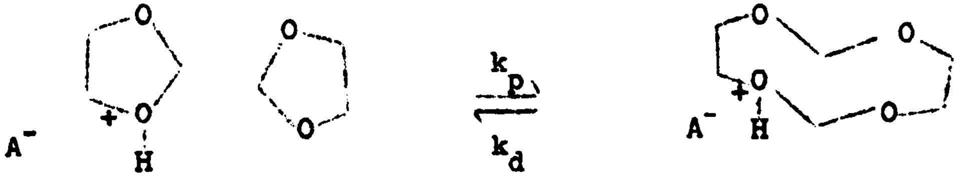
Another possible way for a carboxonium ion mechanism to produce cyclic polymer is for the growing end of the chain to attack the hydroxyl group at the other end of the same chain. However this is so improbable that the possibility of extensive end-to-end ring closure cannot be considered seriously.

I have eliminated the traditional carboxonium ion mechanism for the polymerisation of 1,3-dioxolane and I will now examine the traditional oxonium ion mechanism in the light of my experimental results.



This mechanism is compatible with the results of the N.M.R. experiments and also with the experiments with triphenylmethyl salts and 1,3-dioxolane, as oxonium ions cannot react with 1,3-dioxolane to give dioxolenium ions. Howeve this mechanism is open to exactly the same objections as the carboxonium ion mechanism when the end group analysis results are considered; there is no reason why the traditional oxonium ion mechanism should give more cyclic polymer than the carboxonium ion mechanism.

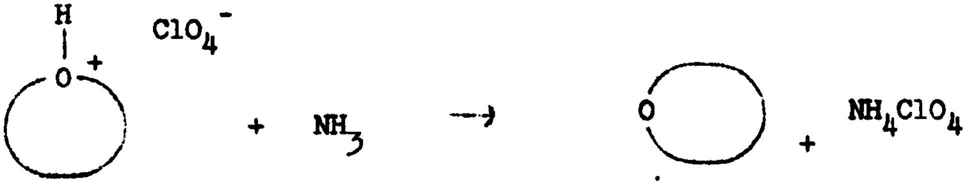
As I cannot accept either the traditional carboxonium mechanism or the traditional oxonium ion mechanism for the polymerisation of 1,3-dioxolane, I propose a new mechanism to explain my experimental results. This mechanism is a ring expansion for the propagation step, and a ring contraction for the depropagation step. At no stage does the ring open.



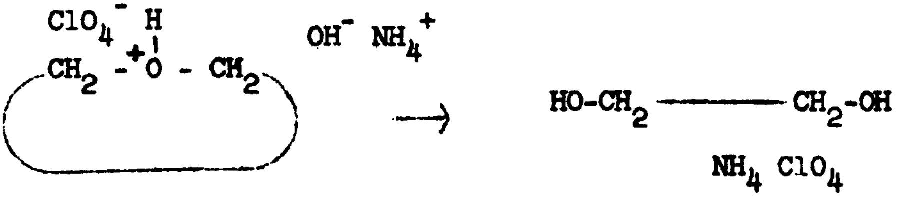
Both the ring expansion and the ring contraction steps probably involve a 4 membered cyclic transition state. The active centres in this mechanism are stable secondary oxonium ions (protonated monomer or protonated polymer) and the transfer reaction is simply the movement of a proton from polymer to polymer or monomer.

This mechanism, like the traditional oxonium ion mechanism, is compatible with the results of the N.M.R. experiments and also with the experiments with triphenylmethyl salts and 1,3-dioxolane, but it is the only mechanism that can offer an explanation for the absence of end groups.

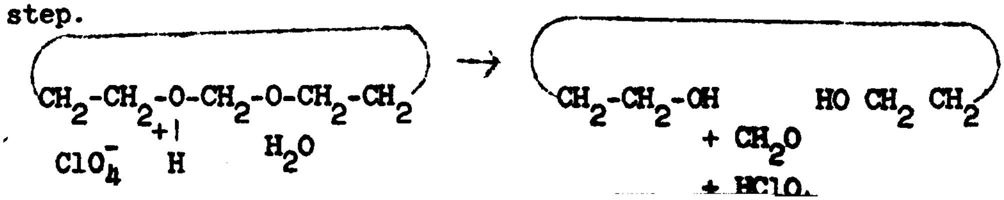
It explains why the polymer made under anhydrous conditions is cyclic, and why, as in experiments 119, 120, 121 and 123, there are less hydroxyl groups than perchloric acid molecules. A ring expansion mechanism implies that the protons are on the cyclic polymer and when this is treated with ammonia gas or ammoniacal ethanol the protons transfer to the more basic ammonia, leaving cyclic polymer molecules.



However the polymers 15, 119, 120, 121 and 123 contained some hydroxyl groups, and these are more than can be explained by the residual water content of the system. These background hydroxyl groups probably come from the neutralisation of the reaction mixtures with ammonia gas or ammoniacal ethanol that were not rigorously dry.



The polymerisations that were carried out with added water (experiments 116, 118 and 122) show that each molecule of water gives rise to two hydroxyl groups in the resulting polymer. The reaction is probably analogous to the acid catalysed hydrolysis of 1,3-dioxolane[2] so that formaldehyde may also be formed in this step.



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Chapter 4

The Kinetics of the Polymerisation of 1,3-Dioxolane.

A preliminary Chapter on the kinetics of the polymerisation of 1,3-dioxolane was presented in my M.Sc. Thesis, but no firm conclusions could be drawn from the experimental results, as at that time the nature of the active centres in the propagation reaction and the nature of the initiation and transfer reactions was uncertain. Furthermore, the depolymerisations that had been carried out in the adiabatic calorimeter were unreliable as it was not possible to purify polydioxolane satisfactorily.

I decided to investigate the kinetics further dilatometrically as the 1,3-dioxolane - perchloric acid system is a living equilibrium polymerisation with a convenient standard state ceiling temperature ($T_c^o = + 1.5^o$). This meant that it was possible to prepare polymer in the dilatometer at low temperatures and then to depolymerise it at higher temperatures. This allowed the study of polymerisations at much lower perchloric acid concentrations than in the calorimeter, and it allowed depolymerisations to be followed accurately. In addition I could study the effect of repeatedly polymerising and depolymerising 1,3-dioxolane.

In this Chapter I will present the new results from the dilatometry experiments and then I will re-examine some of the kinetic results that were obtained with the adiabatic calorimeter.

4.1 Dilatometry Experiments with 1,3-Dioxolane.

Fig. 4.1 and Table 4.1 illustrate experiment 79. The polymerisation curve 79A represents the first polymerisation and 79B represents the second polymerisation of the system. The first polymerisation was started, after the dilatometer had reached thermal equilibrium at -20°, by breaking the perchloric acid phial and then quickly tipping the solution of catalyst and monomer into the dilatometer. This curve has the same general shape as polymerisation curves that were obtained at higher concentrations of perchloric acid with the calorimeter, but it has a more extended acceleration period.

In Chapter 4 of the M.Sc. Thesis the equilibrium concentration of monomer was determined as a function of temperature. Thus at any temperature the equilibrium concentration of 1,3-dioxolane is known. The percentage conversion at equilibrium can thus be determined from the temperature of the system and the initial concentration of 1,3-dioxolane. For experiment 79 at -20° the conversion at equilibrium is calculated to be 75%.

An attempt was made to follow the depolymerisation of this solution at +34°, which is just above the ceiling temperature of 2 M 1,3-dioxolane. However, the solution of polymer was too viscous to allow the level in the dilatometer to be adjusted until the depolymerisation had almost finished. All the polymer was allowed to depolymerise at +34° and the second polymerisation 79B was started by placing the dilatometer in the -20° bath.

There is an apparent difference in conversion between the curves 79A and 79B but this is almost certainly due to slight variations in temperature from the start to the finish of these polymerisations, as the thermostat bath was not working well.

The important point is that the shape of the first polymerisation, 79A,

Table 4.1

Data for Dilatometry Experiments with 1,3-Dioxolane.

Run No.	79A	79B	79C	81A	81B	81C	81D	81E	81F	82A	82B	82C
[1,3-Dioxolane], M.	2.0	2.0	2.0	1.22	1.22	1.22	1.22	1.22	1.22	1.22	1.22	1.22
$[HClO_4]$, 10^3 M.	0.56	0.56	0.56	0.5	0.5	0.5	0.5	0.5	0.5	0.25	0.25	0.25
Reaction Temp., deg.	-20	-20	-20	-20	0	-30	0	-30	-20	-20	0	0
Calc. Conversion %.	75	75	75	59	18	73	18	73	59	59	18	18
κ_o μ mho cm^{-1}.	-	-	-	0.025	1.35	2.54	1.34	2.36	3.06	0.046	1.12	0.98
κ_m μ mho cm^{-1}.	-	-	-	3.21	-	-	-	-	-	3.08	-	-
κ_f μ mho cm^{-1}.	-	-	-	1.31	2.68	1.28	2.66	1.30	1.41	0.97	1.86	1.96
k_1 min^{-1}.	-	-	-	0.050	-	-	-	-	-	-	-	-
k_1' min^{-1}.	-	-	-	-	0.157	-	0.155	-	-	-	0.081	0.080
Acceleration Period, min.	48	50	200	90	-	20	-	20	150	1140	-	-

κ_o is the initial conductivity at the start of an experiment, κ_m is the maximum conductivity and κ_f is the final conductivity. k_1 is the first order rate constant for polymerisations and k_1' is the first order rate constant for depolymerisations.

Fig. 4.1

Plots of dilatometer readings against time for experiment 79A (the first polymerisation of 2.0 M 1,3-dioxolane with 0.56 x 10^{-3} M perchloric acid) and experiment 79B (the second polymerisation) at -20° (Table 4.1).

Fig. 4.2

Simultaneous plot of dilatometer readings and electrical conductivity for experiment 81A (the polymerisation of 1.22 M 1,3-dioxolane with 0.5 x 10^{-3} M perchloric acid at -20°) Table 4.1.

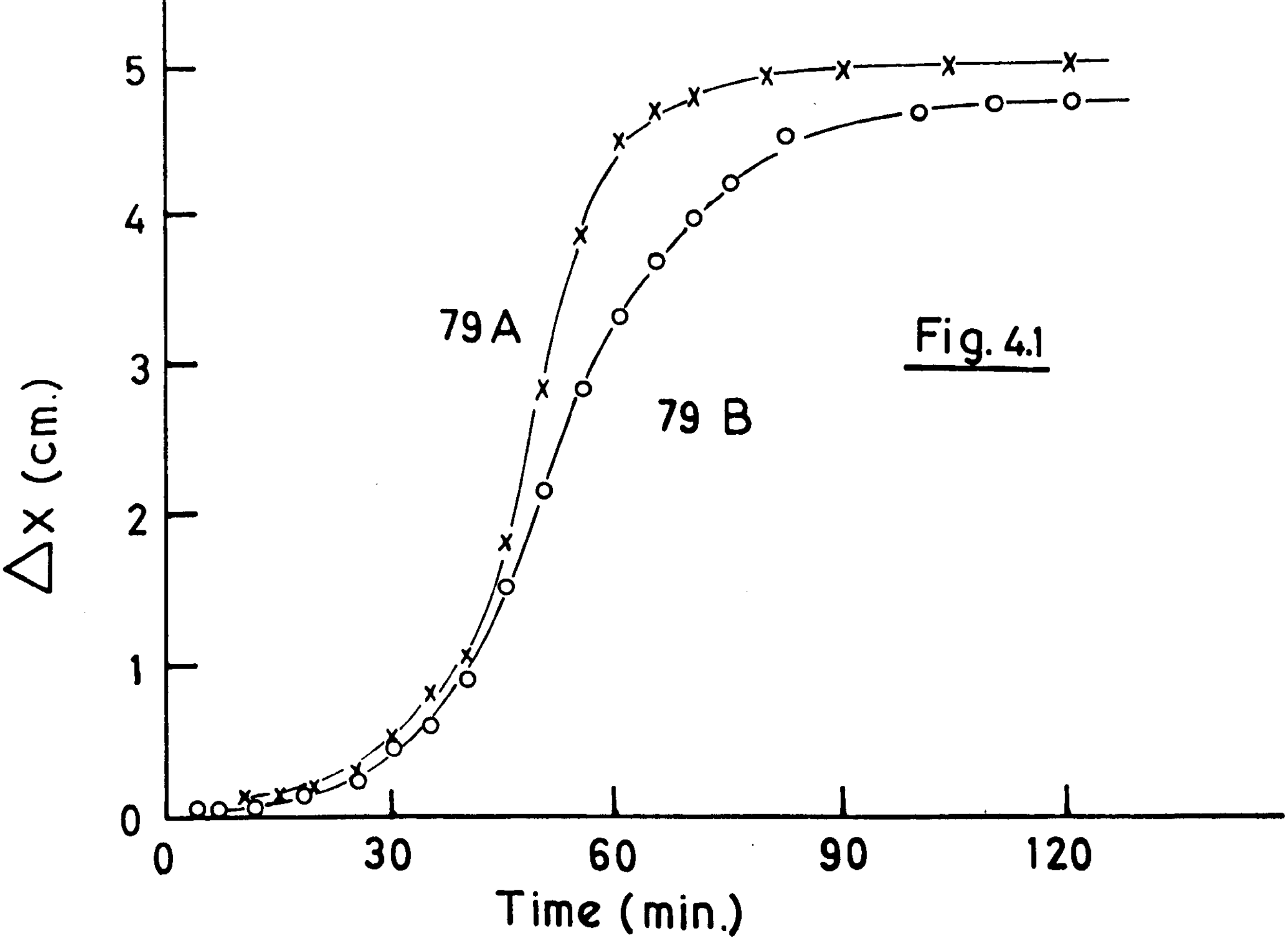


Fig. 4.1

79 A
79 B
Δx (cm.)
0
1
2
3
4
5
0
30
60
90
120
Time (min.)

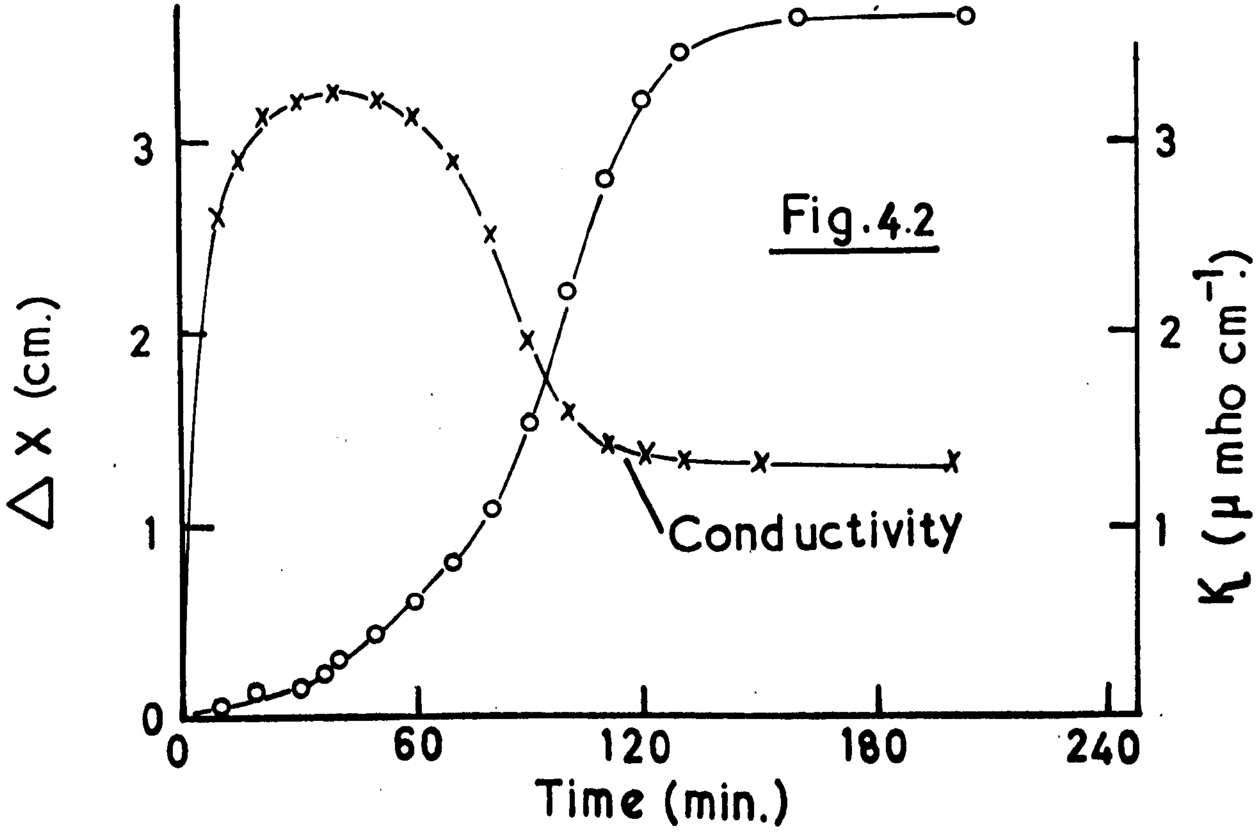


Fig. 4.2

Δ x (cm.)
0
1
2
3
κ (μ mho cm⁻¹.)
1
2
3
Conductivity
0
60
120
180
240
Time (min.)

is essentially the same as the shape of the second polymerisation, 79B; in particular both curves have acceleration periods of about 50 minutes. The acceleration period is the time that the polymerisation takes to reach its maximum rate.

After three depolymerisations reaction mixture 79 was polymerised a fourth time at -20° (79C), and the acceleration period was about 200 minutes. The polymer was isolated and the I.R. spectrum was found to be identical to that of polymers made in the calorimeter.

It is clear that there is a slow termination step, as the acceleration period for polymerisation increases with time, but it is difficult to draw any conclusions about the exact rate of the termination reaction as the temperature of the reaction mixture is continually being changed. Later experiments (81 and 82) show that the termination reaction is not detectable below 0°.

There are no conductivity readings for experiment 79 as the dilatometer used had no electrodes. However when it had been shown that dilatometry experiments were possible with this system, a new dilatometer with electrodes was constructed (Fig. 1.1).

Fig. 4.2 (Table 4.1) illustrates experiment 81A in which volume change and electrical conductivity were followed. The maximum in electrical conductivity appears when the polymerisation has reached about 8% of the equilibrium conversion. With higher concentrations of perchloric acid the maximum conductivity usually appeared just before the maximum polymerisation rate at about 45% of the equilibrium conversion. (Fig. 14 M.Sc. Thesis). However, the maximum and final conductivities agree well with previous experiments carried out in the calorimeter. (Fig. 5.3 Chapter 5).

The last half of this polymerisation gives a reasonable first order plot and the rate constant k_1 falls well on the plot of k_1 against perchloric acid concentration for polymerisations conducted in the calorimeter (Fig. 4.12). The calculated equilibrium conversion for 81A is 59% at -20°.

Fig. 4.3 illustrates experiment 81B (Table 4.1). Before this experiment the dilatometer was cooled to -30° and the system allowed to reach equilibrium (73% conversion). The dilatometer was then clamped in an ice thermostat at +0.4° and readings of the meniscus level and conductivity were taken to give the curves illustrated. After 50 minutes the conductivity was steady and the meniscus was rising at a low steady rate due to the distillation of solvent from the reservoir into the capillary. The value of the meniscus reading at t = 50 minutes was taken as the value for the attainment of equilibrium (18% conversion). No reading can be obtained for 73% conversion as the meniscus level changes rapidly when the dilatometer is first placed in the ice thermostat.

However a reasonable first order plot for the depolymerisation 81B was obtained (Fig. 4.4). It will be seen that after 12 minutes the reaction deviates from an accurate first order plot. This is for the last 10% of the reaction when the conversion is less than 23%. This is not due to the slow distillation of solvent into the capillary, as the readings were corrected for this effect. This depolymerisation was repeated (experiment 81D) and exactly the same value of k_1', calculated from the slope of the first order plot for the depolymerisations, was obtained for both experiments. The electrical conductivity was found to increase steadily during the depolymerisations.

Fig. 4.5 illustrates experiment 81C. In this experiment the dilatometer was allowed to equilibrate at 0° so that the conversion was 18%

Fig. 4.3

Simultaneous plot of dilatometer readings and electrical conductivity for experiment 81B (the depolymerisation of poly-1,3-dioxolane at 0°) Table 4.1.

Fig. 4.4

The first order plot for the depolymerisation 81B. From the graph $k_1' = 0.157\ \text{min}^{-1}$.

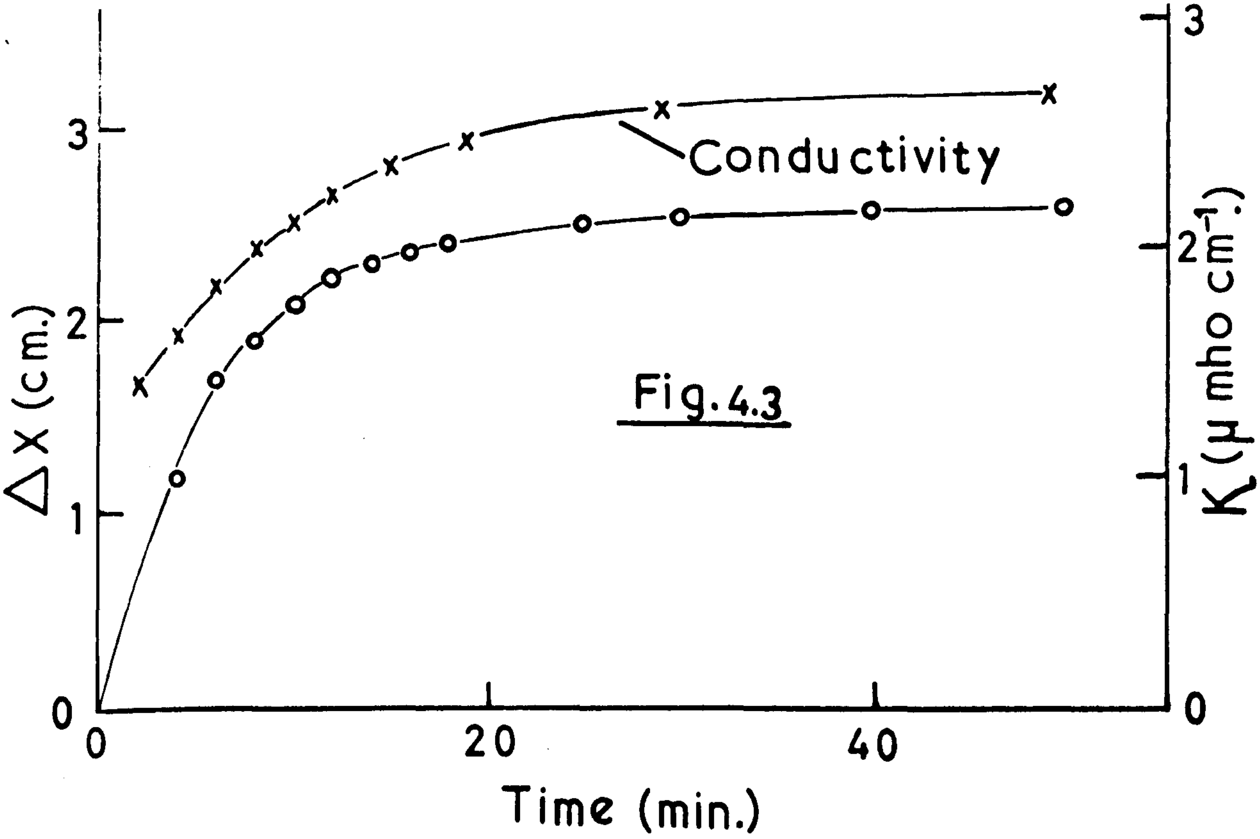

Conductivity
ΔX (cm.)
K (μ mho cm⁻¹)
Time (min.)
0
1
2
3
0
20
40
0
1
2
3

Fig. 4.3

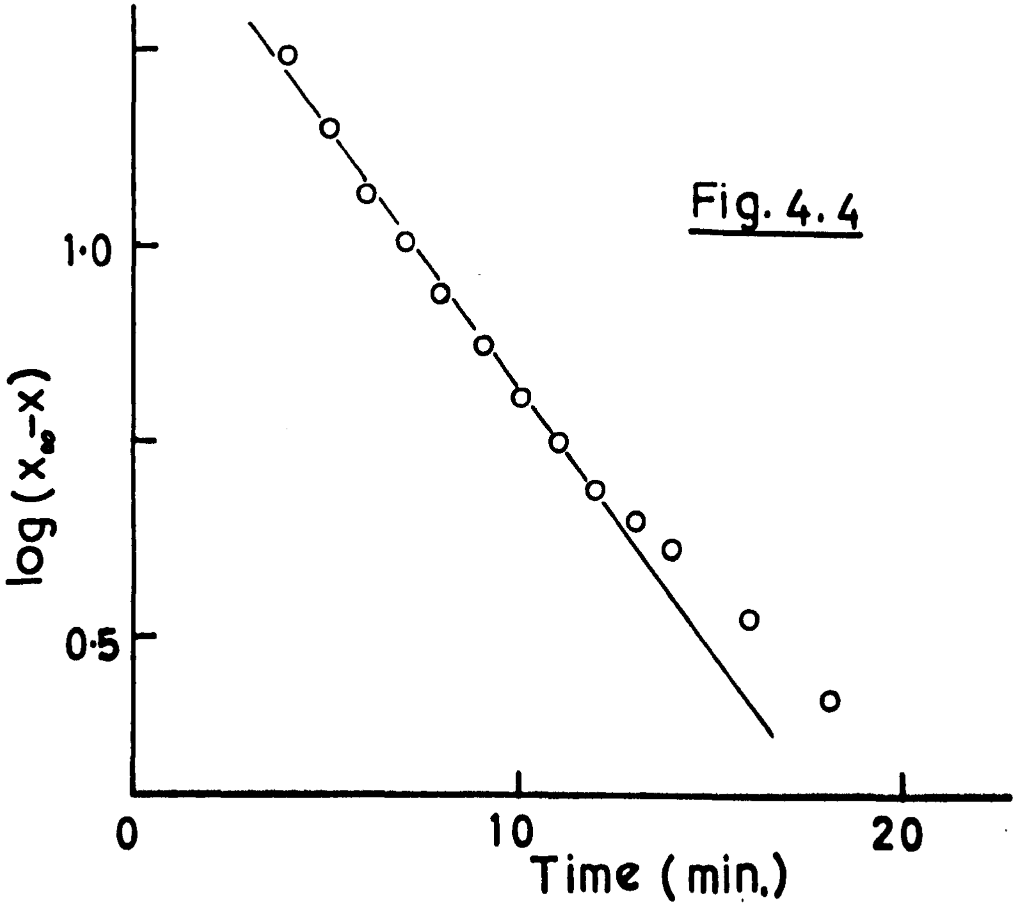

log (x∞–x)
1·0
0·5
Time (min.)
0
10
20

Fig. 4.4

of polymer. The dilatometer was then placed in a thermostat at -30° and readings of the meniscus level and conductivity were taken. It will be seen that there is only a very slight S-shape to this polymerisation curve, the acceleration period is only 20 minutes compared with an acceleration period of 90 minutes for the first polymerisation, 81A. Polymerisation 81C is in fact the same as the polymerisation 81A <u>after</u> the first 18% of conversion. An exact comparison is not possible as experiment 81A was carried out at -20°. Experiment 81C was repeated and identical results were obtained (81E).

After all these experiments the polymer in the dilatometer was depolymerised completely at +20°. Then the dilatometer was cooled to -20° and the system was polymerised again (experiment 81F). This polymerisation had an acceleration period of 150 minutes compared with 90 minutes for the first polymerisation 81A.

This illustrates that the termination reaction only occurred when the polymerisation mixture was warmed above 0°, as experiments 81B, 81C, 81D and 81E show no signs of any termination reaction.

Fig. 4.6 illustrates experiment 82A (Table 4.1). There is an exceedingly long acceleration period lasting 19 hours and then a relatively rapid polymerisation. The conductivity reaches a maximum in about 9 hours when very little polymer has been formed. The maximum conductivity for experiment 82A is almost the same as for experiment 81A.

Fig. 4.7 illustrates the depolymerisation experiment 82B (Table 4.1). This experiment is exactly the same as 81A, except that only half the perchloric acid concentration was used. The electrical conductivity increases only slightly during the depolymerisation. After 90 minutes the conductivity was steady and the meniscus was rising at a low steady rate due to the

Fig. 4.5

Simultaneous plot of dilatometer readings and electrical conductivity for experiment 81C (Table 4.1).

Fig. 4.6

Simultaneous plot of dilatometer readings and electrical conductivity for experiment 82A (the polymerisation of 1.22 M 1,3-dioxolane with 0.25×10^{-3} M perchloric acid at -20°). Table 4.1

Fig. 4.5

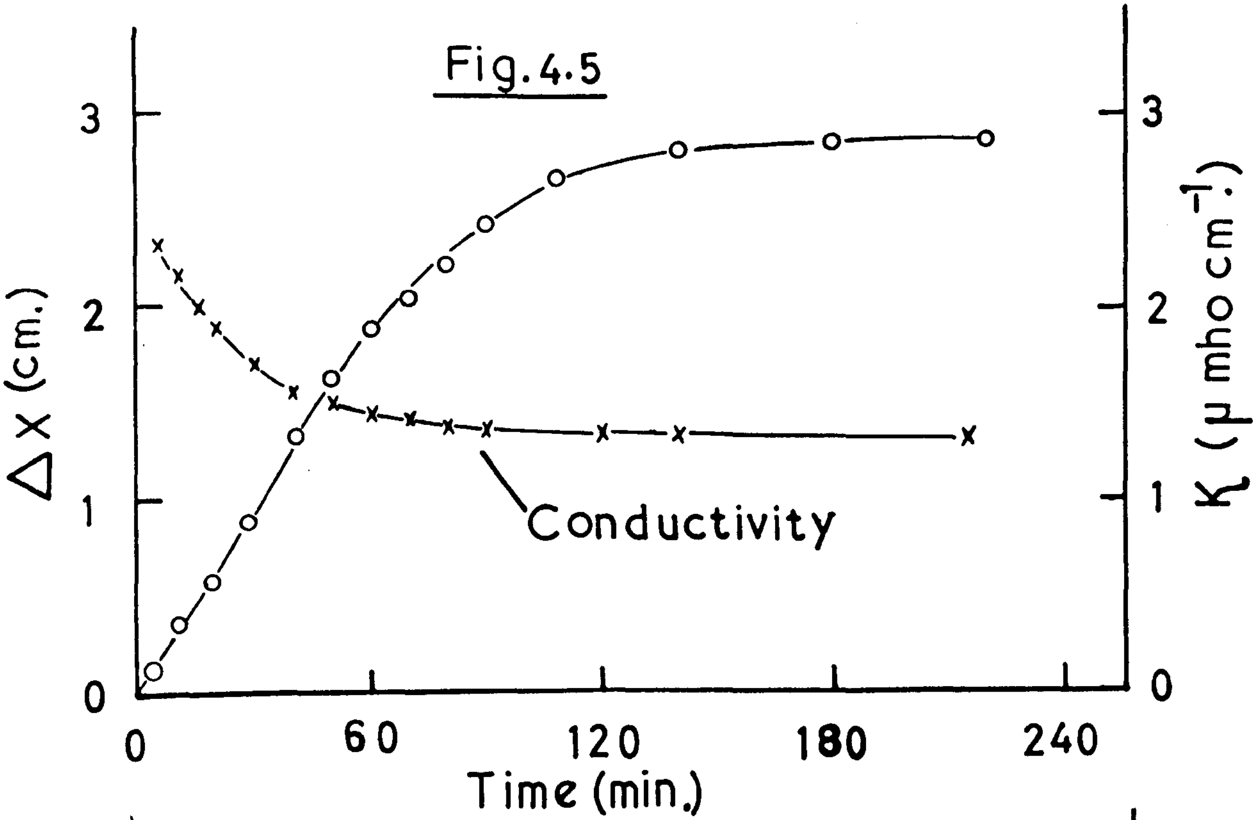

Conductivity
Δ X (cm.)
κ (μ mho cm⁻¹)
0
1
2
3
0
1
2
3
0
60
120
180
240
Time (min.)

Fig. 4.6

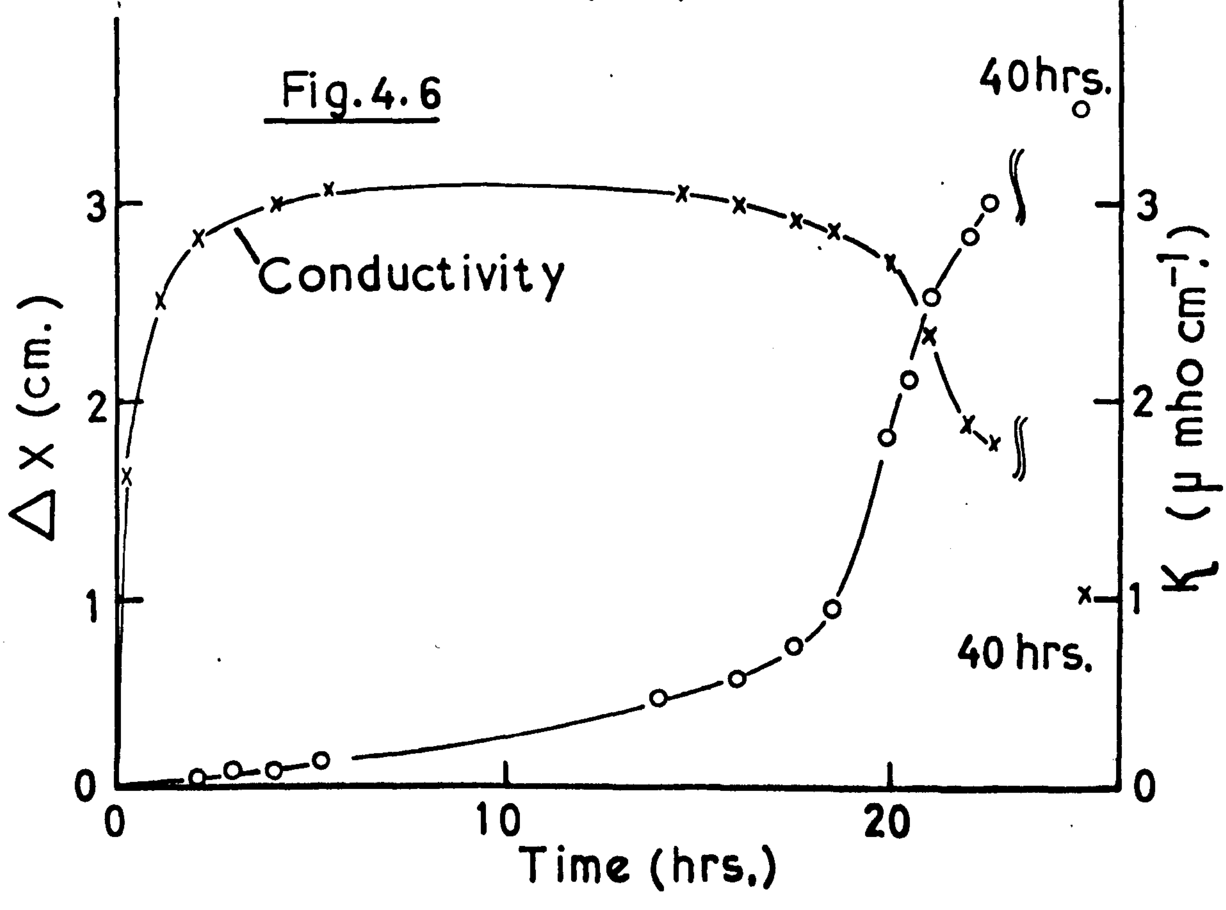

40hrs.
Conductivity
40 hrs.
Δ X (cm.)
κ (μ mho cm⁻¹)
0
1
2
3
0
1
2
3
0
10
20
Time (hrs.)

Fig. 4.7

Simultaneous plot of dilatometer readings and electrical conductivity for 82B (the depolymerisation of poly-1,3-dioxolane at 0°). Table 4.1

Fig. 4.8

The first order plot for the depolymerisation 82B. From the graph $k_1' = 0.081$ min^{-1}.

Fig. 4.7

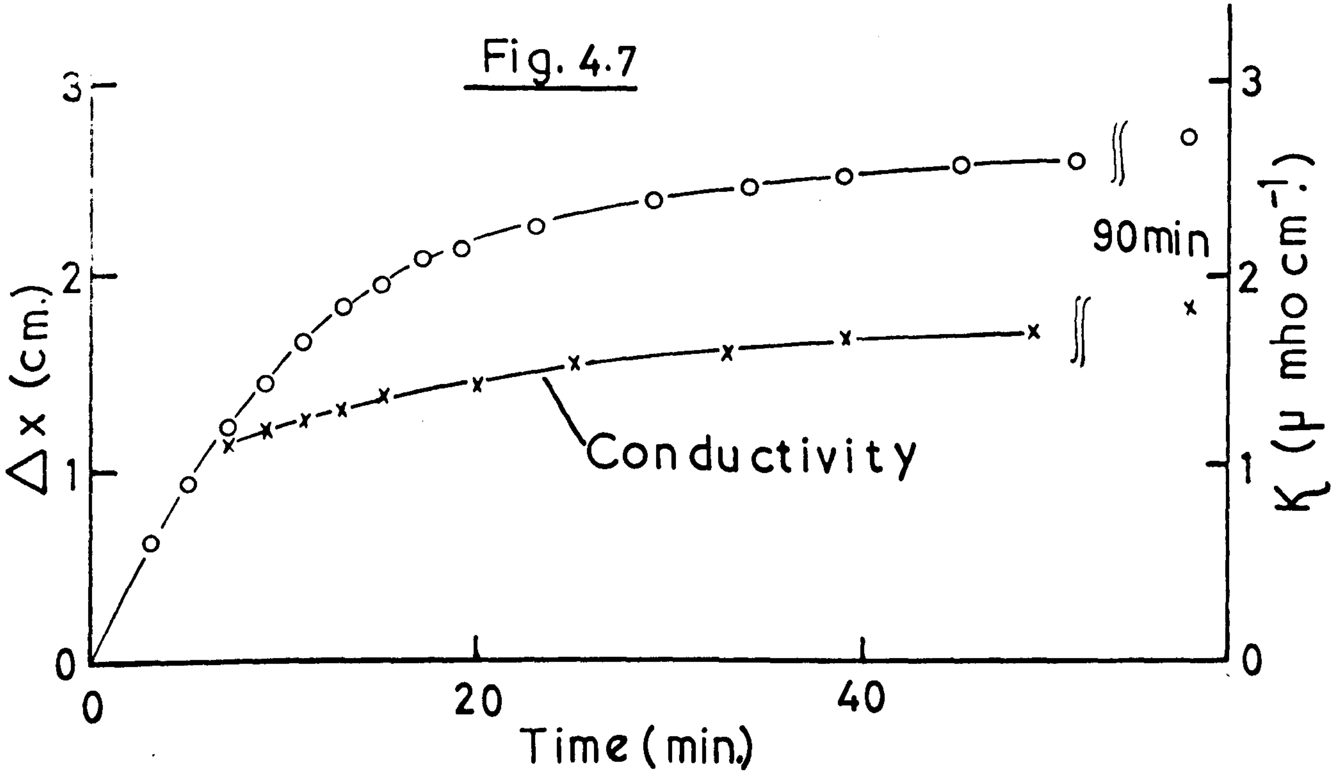
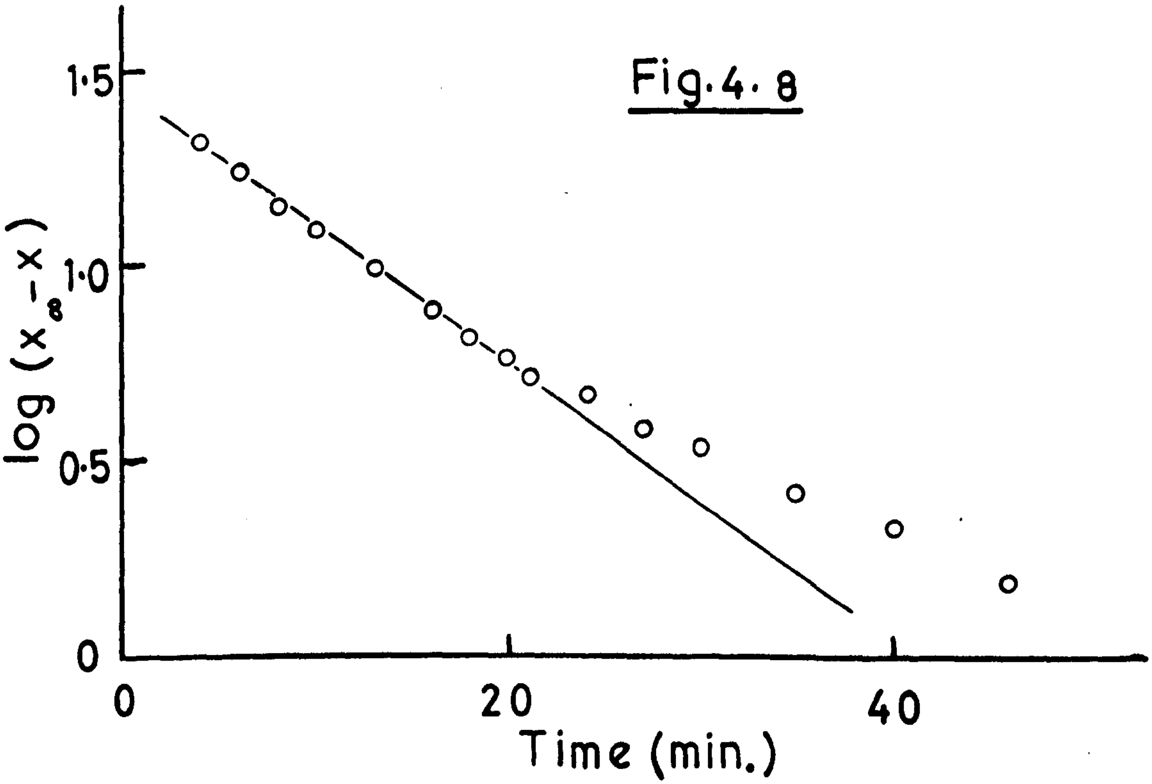

Δx (cm.)
0
1
2
3
0
20
40
Time (min.)
Conductivity
90min
κ (μ mho cm⁻¹)
0
1
2
3

Fig. 4. 8


log (x₈−x)
0
0·5
1·0
1·5
0
20
40
Time (min.)

distillation of solvent into the capillary. The meniscus reading at 90 minutes was taken as the value for the attainment of equilibrium. Fig. 4.8 is the first order plot for this depolymerisation.

After 21 minutes the reaction deviates from an accurate first order plot. The last 15% of the reaction when the conversion is less than 26% is slow. This depolymerisation was repeated (81C) and the same value of k_1' was observed for both experiments (Table 4.1). The two values of k_1' that were obtained from the depolymerisation experiments 81B, 81D, 82B and 82C are plotted against perchloric acid concentration in Fig. 4.9. The plot passes through the origin, so that k_1' depends linearly on the perchloric acid concentration. The value of k_d, the depropagation rate constant at 0°, was determined from the slope of this plot and the equilibrium concentration of 1,3-dioxolane at 0°.

$$\underline{k_d = (3.4 \mp 0.5) \times 10^{2}\ \text{min}^{-1}.\ \text{at}\ 0^{\circ}}.$$

The value of k_d at 0° could have been determined more accurately if the range of $[HClO_4]$ for the dilatometry depolymerisation experiments could have been extended. However, below 2.5×10^{-4} M $HClO_4$ the polymerisation becomes exceedingly slow. (A 2.0 M solution of 1,3-dioxolane and 2.0×10^{-4} M $HClO_4$ had not started to polymerise at all after 20 hours at -20°). If more than 5.0×10^{-4} M $HClO_4$ is used, the depolymerisation becomes too fast to follow.

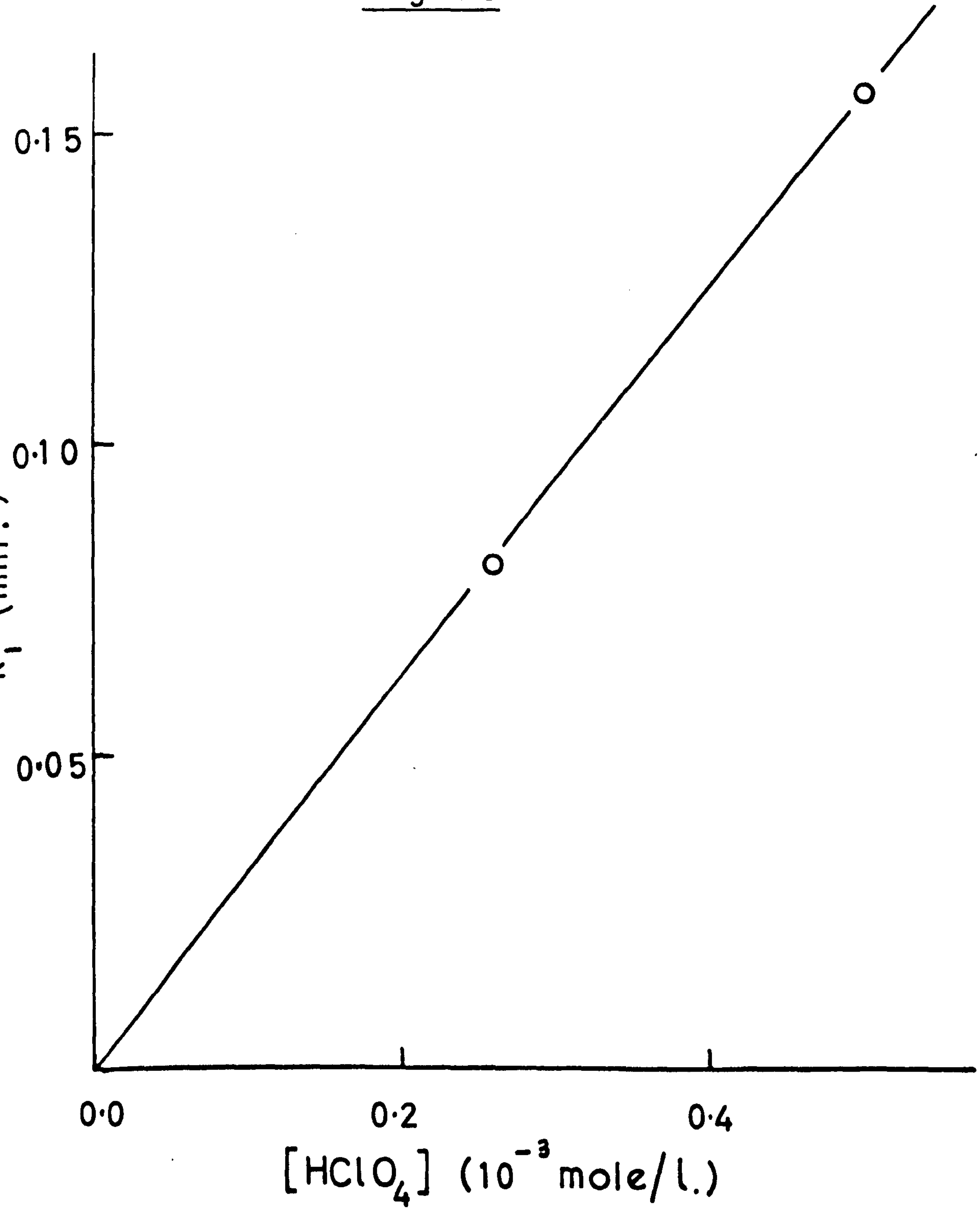
Only one determination of k_1, the first order rate constant for polymerisation reactions, was made from the dilatometric polymerisation curves. The reason for this was that the thermostat bath was not steady enough and in any case there are a lot of polymerisation results available from the adiabatic calorimeter.

Fig. 4.9

Plot of the first order rate constant, k_1', against perchloric acid concentration for depolymerisations 81B and 82B. From the graph

$$k_d = \frac{\text{slope}}{m_e} = (3.4 \mp 0.5) \times 10^2 \text{ min}^{-1} \text{ at } 0^\circ.$$

Fig. 4.9



4.2 Analysis of Polymerisation Curves of 1,3-Dioxolane.

When it became apparent that the depolymerisation reactions were first order down to about 25% conversion it seemed possible that polymerisation reactions might also be first order after 25% conversion. Fig. 4.10 and 4.11 are the first order plots for the last half of polymerisations 51 and 49 which were measured in the adiabatic calorimeter. These first order plots are reasonable straight lines from 50% of reaction (23% conversion) to 98% of reaction (45% conversion).

The data for polymerisations at -22° are shown in Table 4.2; k_1 is the slope of the first order plot for each reaction. The plot of k_1 against $[HClO_4]$ should pass through the origin and have a slope of k_p, the propagation rate constant. Fig. 4.12 is the experimental plot of k_1 against $[HClO_4]$ and this does not pass through the origin but has an intercept of approx. 3×10^{-4} on the perchloric acid concentration axis. This intercept represents an impurity that effectively neutralises some of the perchloric acid. As the experiments, except 81A, were carried out in the calorimeter, there is a temperature rise of about 6° during the polymerisations. The temperature of the polymerisations is thus about -18° at 70% of reaction. The value of k_p at -18°, calculated from the slope of the plot of k_1 against perchloric acid concentration is, $k_p = (3.1 \mp 0.1) \times 10^2$ litre mole^{-1} min^{-1}.

The data for polymerisations at +13.5° are shown in Table 4.3 and Fig. 4.13 is the plot of k_1 against perchloric acid concentration for these reactions. The value of k_p at +13.5°, calculated from the slope of this plot is, $k_p = (1.02 \mp 0.03) \times 10^3$ litre mole^{-1} min^{-1}.

Experiment 126 (Table 4.3) was carried out with five times the perchloric acid concentration of previous kinetic experiments. The reaction

Fig. 4.11

First order plot for experiment 49 (the polymerisation of 1.22 M 1,3-dioxolane with 4.95×10^{-3} M perchloric acid at -22°). See Table 4.2. From the graph $k_1 = 1.50\ \text{min}^{-1}$.

Fig. 4.10

First order plot for experiment 51 (the polymerisation of 1.22 M 1,3-dioxolane with 1.73×10^{-3} M perchloric acid at -22°). See Table 4.2. From the graph $k_1 = 0.52\ \text{min}^{-1}$.

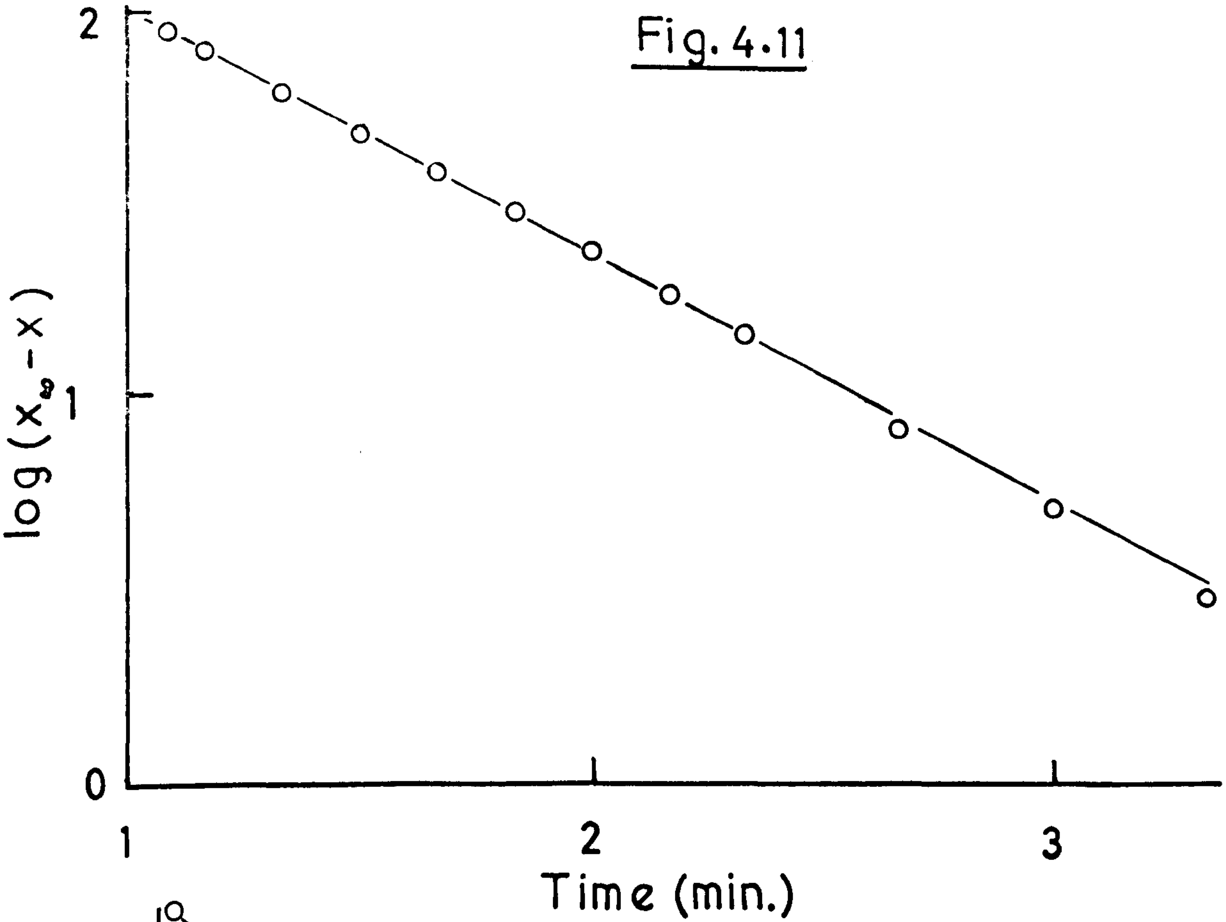


Fig. 4.11

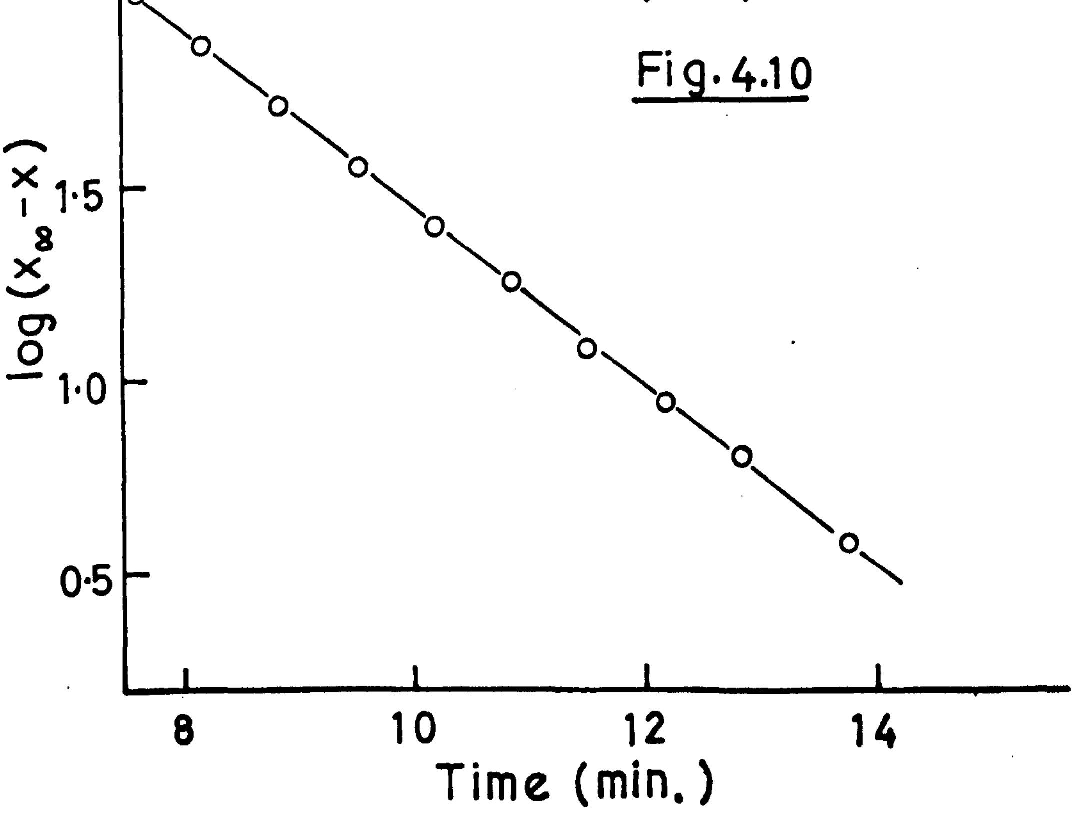


Fig. 4.10

Table 4.2

Data for Polymerisation Experiments with 1.22 M 1,3-Dioxolane

Initial Temp. = -22° Final Temp. = -16°

Run No.	81A[x]	51	45	47	49
$[HClO_4]$, 10^3M	0.5	1.73	2.80	4.15	4.95
k_1 min^{-1}.	0.05	0.52	0.74	1.28	1.50

[x] Experiment 81A was carried out in a dilatometer at -20°.

Fig. 4.12 is a plot of k_1 against $[HClO_4]$ for 1.22 M 1,3-dioxolane at -22°

From Fig. 4.12

$$k_p = k_1 / [HClO_4] = (3.1 \pm 0.1) \times 10^2 \text{ litre mole}^{-1} \text{ min}^{-1}.$$

Table 4.3

Data for Polymerisation Experiments with 2.0 M 1,3-Dioxolane

Initial Temp. = +9° Final Temp. = +14.5°

Run No.	19	14	11	21	126
$[HClO_4]$, 10^3M	1.74	2.54	3.24	4.25	21.2
k_1 min^{-1}.	1.73	2.65	3.11	4.41	24.0

Fig. 4.13 is a plot of k_1 against $[HClO_4]$ for 2.0 M 1,3-dioxolane at +9°.

From Fig. 4.13

$$k_p = k_1 / [HClO_4] = (1.02 \pm 0.03) \times 10^3 \text{ litre mole}^{-1} \text{ min}^{-1}.$$

Fig. 4.12

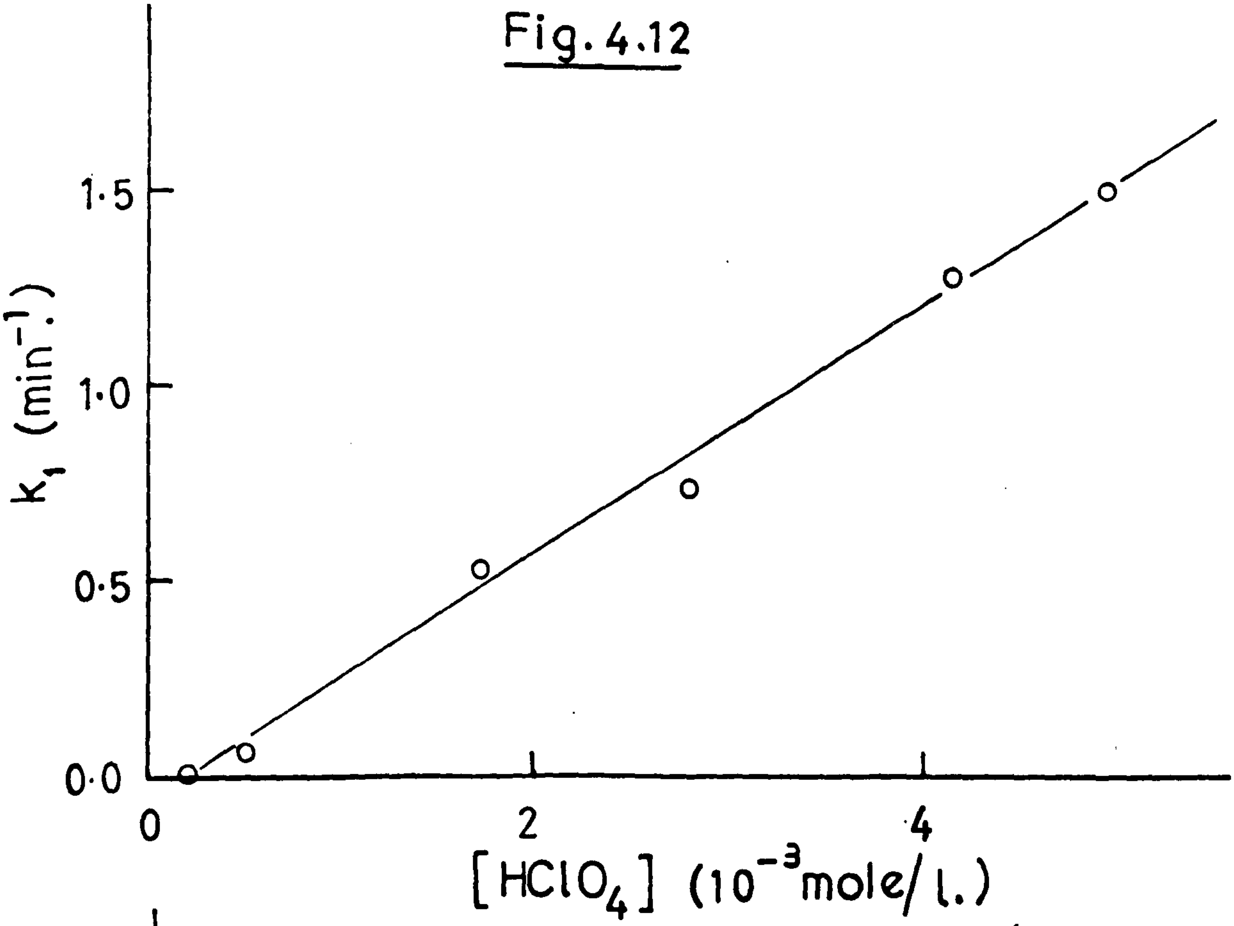
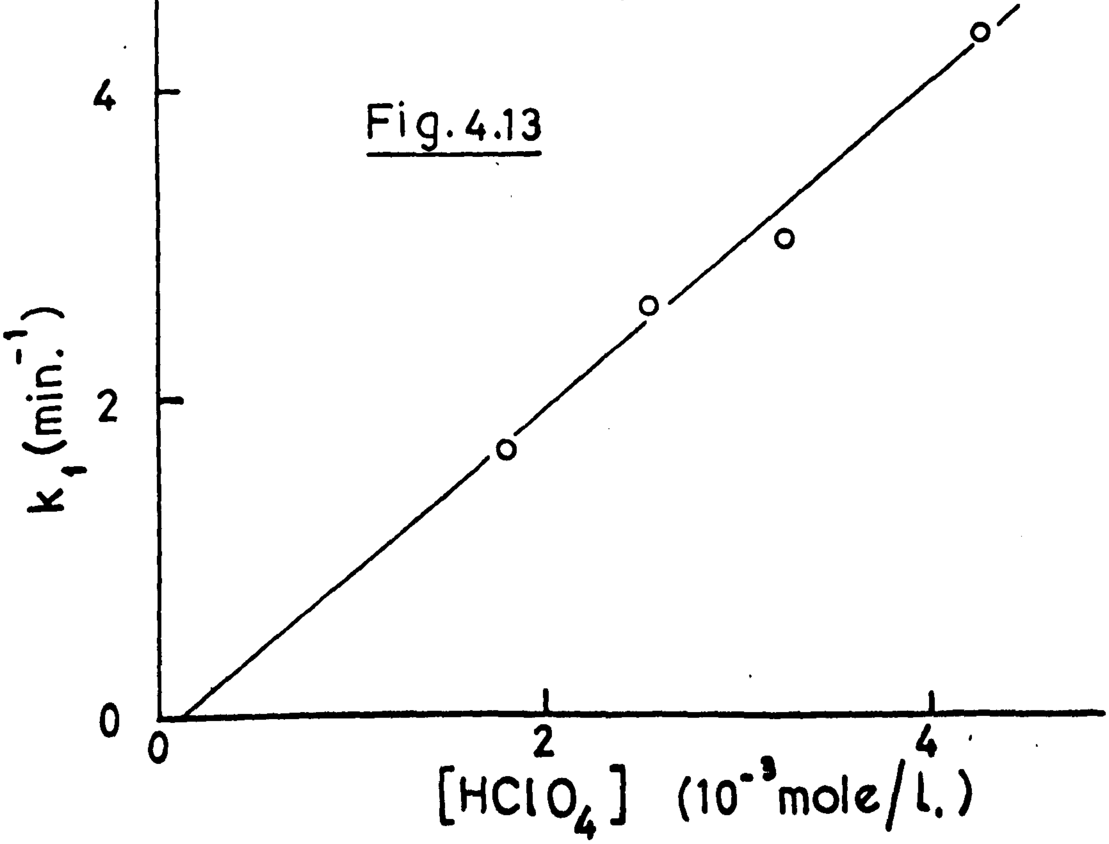


Fig. 4.13



To be completely rigorous, a comparison should be made of the value of k_p at 0° determined from polymerisation experiments with the value of k_p at 0° determined from depolymerisation experiments.

$k_p = (6.2 \mp 0.2) \times 10^2$ litre mole^{-1} min^{-1}. (Polymerisation)

$k_p = (3.1 \mp 0.5) \times 10^2$ litre mole^{-1} min^{-1}. (Depolymerisation) still gave an S-shaped curve and the first order rate constant for the last half of the reaction was determined. The value of k_p at +13.5° determined from this single point was $k_p = 1.1 \times 10^3$ litre $mole^{-1}$ min^{-1}. This compares very well with k_p determined from the graph of k_1 against perchloric acid concentration for experiments 19, 14, 11 and 21. The experiment shows that the rate of polymerisation of 1,3-dioxolane is still directly proportion~~ed~~al to the perchloric acid concentration up to 2.0×10^{-2} M perchloric acid.

The value of k_p at -45° was determined from experiment 20 in which 0.9 M 1,3-dioxolane was polymerised with 6.95×10^{-3} M perchloric acid at -50°. The last half of the polymerisation was accurately first order and the value of k_p at -45° was $k_p = (0.80 \mp 0.05) \times 10^2$ litre $mole^{-1}$ min^{-1}.

Fig. 4.14 is the Arrhenius plot for these three k_p values. The plot is a reasonable straight line from which the activation energy of the polymerisation of 1,3-dioxolane was calculated: $E_p = 5.5 \mp 0.3$ kcal $mole^{-1}$. It was also possible to estimate the value of k_p at 0° from this graph: $k_p = (6.2 \mp 0.2) \times 10^2$ litre $mole^{-1}$ min^{-1}.

The validity of the values of k_p and k_d at 0° can be tested by comparing the equilibrium constant determined thermodynamically with the equilibrium constant determined kinetically; ideally the two results should be identical.

The equilibrium constant at 0° for 1,3-dioxolane was determined graphically from the plot of log K against 1/T (Fig. 5 M.Sc. Thesis).

$K = 1.3 \mp 0.1$ litre $mole^{-1}$. (Thermodynamic determination).

Also

$$K = k_p/k_d = (6.2 \mp 0.2)/(3.4 \mp 0.5) = 1.8 \mp 0.7 \text{ litre mole}^{-1}.$$

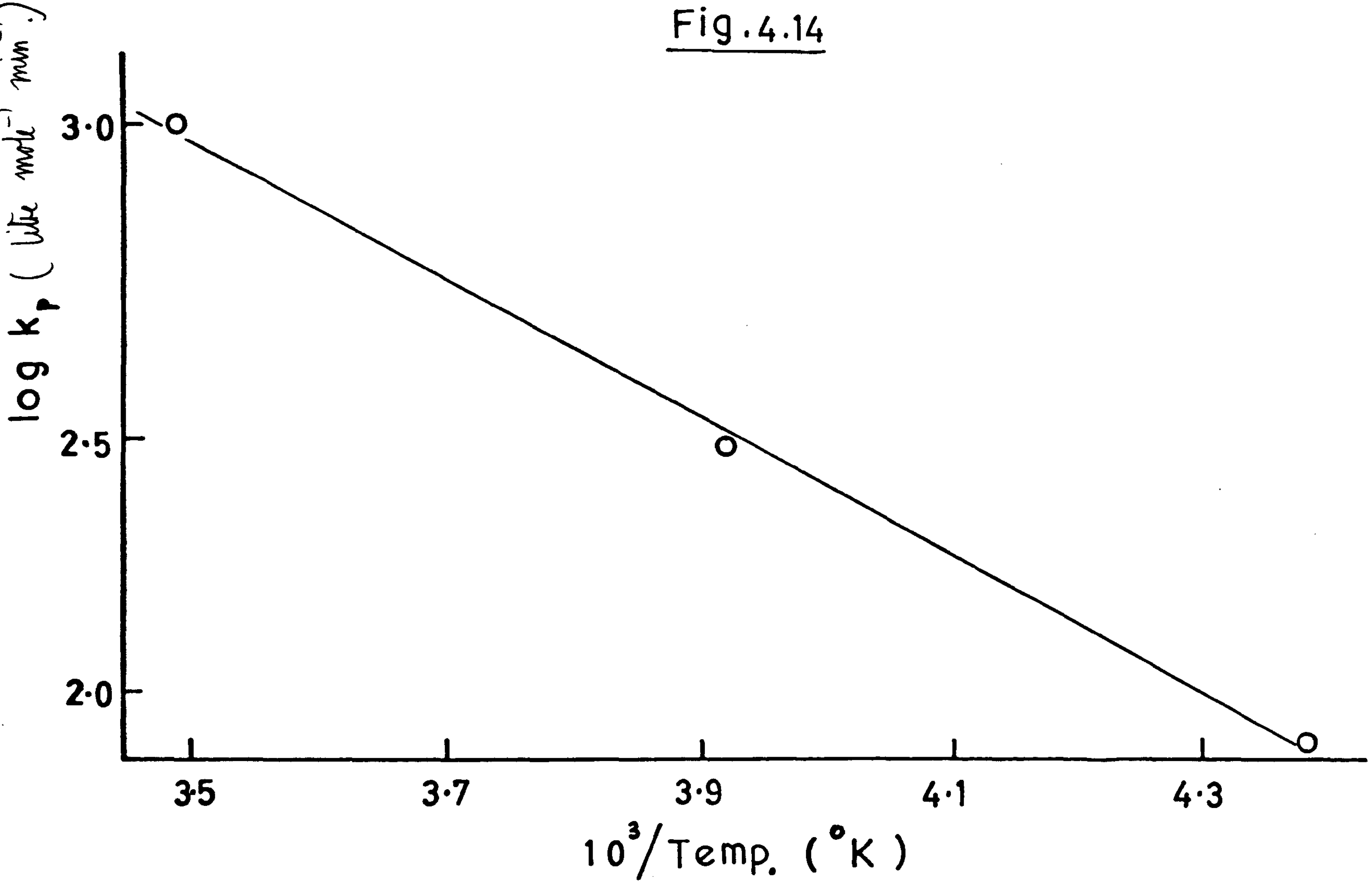
(Kinetic determination).

Fig. 4.14

The Arrhenius plot for polymerisations of 1,3-dioxolane.

From the graph $E_p = 5.5 \mp 0.3$ kcal $mole^{-1}$.

Fig.4.14



The agreement between these two values is within the estimated error of the measurements and this shows that k_p and k_d are true propagation and depropagation rate constants. The large error in the kinetic determination of K comes from the determination of k_d from only two experiments.

4.3 Discussion.

There are only two papers that deal with the kinetics of the polymerisation of 1,3-dioxolane and I will consider these first.

The kinetics of the bulk polymerisation of 1,3-dioxolane with octamethylcyclotetrasiloxane bisulphate as catalyst has been studied by Kucera and Pichler[1]. They polymerised 1,3-dioxolane at 70° in a semi-open system that contained approx. 100 ppm of water and obtained slightly S-shaped curves which they explained in terms of an equilibrium between carboxonium ions and oxonium ions.

More recently, Gorin and Monnerie[2] have studied the bulk polymerisation of 1,3-dioxolane at 25° with mercuric chloride or boron trifluoride etherate as catalysts. They polymerised 1,3-dioxolane in a semi-open system and obtained polymerisation curves that are almost of zero order. They used their results to test the validity of the reaction scheme proposed by Kucera and Pichler, and found that they are in perfect agreement with this scheme.

However Chapter 3 of this Thesis shows conclusively that under our conditions the polymerisation of 1,3-dioxolane involves oxonium ions only and that carboxonium ions cannot be present. Although the kinetic scheme proposed by Kucera and Pichler depends upon an equilibrium between carbonium and oxonium ions, the papers present no chemical evidence to support this view.

For these reasons the kinetic scheme proposed in the two papers is unacceptable for the kinetic results presented in this Thesis.

4.31 The Kinetic Scheme for Part of the Polymerisation and Depolymerisation Curves.

A complete kinetic treatment for the polymerisation and depolymerisation of 1,3-dioxolane could not be found. However the last half of the polymerisation reactions, when the conversion was greater than 25%, were found to be first order reactions. Also, the plots of k_1 against perchloric acid concentration (Figs. 4.12 and 4.13) were found to be linear, so that the last half of the polymerisation reactions are also of first order with respect to perchloric acid.

This observation is supported by the depolymerisation experiments (81B and D, 82B and C). In these experiments the depolymerisations were found to be accurately first order and also of first order with respect to perchloric acid, down to a conversion of about 25% polymer. When the conversion was less than 25% these reactions were found to be slower than for first order kinetics (Figs. 4.4 and 4.8). This corresponds exactly to the acceleration period at the start of polymerisation reactions when the conversion is low.

The following kinetic scheme is proposed for the latter half of polymerisations and for the first half of depolymerisation reactions.

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

where P_1 is monomer and P_n^+ protonated polymer.

$$P_n^+ + P_m \xrightarrow{k_{tr}} P_n + P_m^+ \qquad \text{Chain Transfer} \qquad (2)$$

At, and above, 25% conversion each perchloric acid molecule has produced an active centre, so that $\left[HClO_4\right] = \left[P^+\right]$, where $\left[P^+\right] = \sum_{n=2}^{\infty} \left[P_n^+\right]$

Let concentrations be denoted by lower case letters: a for $\left[HClO_4\right]$ and m for $\left[P_1\right]$.

The polymerisation rate is then

$$-dm/dt = k_p\, m\, a - k_d\, a \qquad (3)$$

But $k_d = k_p m_e$, where m_e is the equilibrium concentration of monomer.

Substitution for k_d in equation (3) gives

$$-dm/dt = k_p\, a\, (m - m_e) \qquad (4)$$

Substitution for k_p in equation (3) gives

$$+dm/dt = k_d\, a\, (m_e - m)/m_e \qquad (5)$$

The latter half of the polymerisation curves were first order reactions with first order rate constants k_1, so that equation (4) can be written as

$$-dm/dt = k_1\, (m - m_e) \qquad (6)$$

where $k_1 = k_p\, a$.

The graphs of k_1 against a were good straight lines so that the values of k_p at various temperatures could be calculated:

At $+13.5^\circ$ $k_p = (1.02 \pm 0.03) \times 10^3$ litre mole^{-1} min^{-1}.

-18° $k_p = (3.1 \pm 0.1) \times 10^2$ litre mole^{-1} min^{-1}.

-45° $k_p = (0.80 \pm 0.05) \times 10^2$ litre mole^{-1} min^{-1}.

The first half of the depolymerisation curves were also first order reactions with first order rate constants k_1', so that equation (5) can be written as

$$+dm/dt = k_1' (m_e - m) \qquad (7)$$

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

The graph of k_1' against a was a straight line from which a value of k_d was calculated:

$$\text{At } 0^\circ \; k_d = 3.4 \mp 0.5 \times 10^2 \text{ min}^{-1}.$$

The value of the equilibrium constant at 0° determined kinetically ($K = 1.8 \mp 0.3$ litre mole^{-1}) and the value determined thermodynamically ($K = 1.3 \mp 0.1$ litre mole^{-1}) are in good agreement with each other. This means that the above kinetic scheme is valid, within the limits specified for these results, and thus the values of k_p and k_d that were determined for 1,3-dioxolane are genuine.

A similar kinetic scheme has been reported by Tobolsky[3] and Rozenberg[4] for the polymerisation of tetrahydrofuran by triethyloxonium tetrafluoroborate. The values of k_p at 0° are reported to be 0.29 litre mole^{-1} min^{-1} and 0.23 litre mole^{-1} min^{-1} respectively, in good agreement with each other. No depolymerisations were carried out so that there is no direct value of k_d for these experiments.

The value of k_p at 0° for 1,3-dioxolane is $6.2 \mp 0.2 \times 10^2$ litre mole^{-1} min^{-1}, this is 2000 times greater than the k_p values for tetrahydrofuran. These are the first values of k_p that have been determined for 1,3-dioxolane polymerisations.

4.3.2 The Dissociation Constant of the Active Centres.

Chapter 3 has established that the active centres for the polymerisation of 1,3-dioxolane are secondary oxonium ions. It follows that there must be an equilibrium between free ions and ion-pairs for these active centres. The following points must be considered in deciding to what extent these ion-pairs are dissociated.

1. The dissociation constant, K_D, of an ion-pair at temperature T in a solvent of dielectric constant ϵ is given by the Bjerrum - Fuoss equation.

$$- \log K_D = A - B/x \epsilon T.$$

The terms A and B involve only fundamental constants, except that A also involves log x, where x is the interionic distance in the ion-pair.

The crystal structure of perchloric acid monohydrate has been determined[5] and the structure confirms that the solid is really hydronium perchlorate. From the atomic coordinates reported the distance between the chlorine atom and hydronium oxygen atom was calculated to be 3.73Å. This value has been taken as the smallest possible distance between protonated 1,3-dioxolane or poly-1,3-dioxolane and the perchlorate ion. With this value of x and $T = 273^\circ$ and the dielectric constant about 9.0, $K_D = 8.7 \times 10^{-8}$ mole litre^{-1}.

The concentration of free ions, C_f, is related to the total concentration of ions, C, and the dissociation constant K_D by the equation.

$$C_f = -K/2 + (K^2 + 4\, KC)^{\frac{1}{2}}/2.$$

For $K_D = 8.7 \times 10^{-8}$ and $C = 10^{-3}$ mole/litre, the concentration of free ions is 9.3×10^{-6}. The degree of dissociation $\alpha = 9.3 \times 10^{-3}$.

The Bjerrum - Fuoss equation has been applied to the dissociation of methyltriethylammonium iodide in methylene dichloride[6], but as far as I am aware it has not been applied to the dissociation of oxonium ions before. For this reason the results of the calculation can only be regarded as giving a rough indication of the magnitude of the dissociation constant of the system.

2. The electrical conductivity results that were obtained with the dilatometer show that some of the changes in conductivity are not directly related to the kinetics of the polymerisation and depolymerisation reactions (Chapter 5).

The maximum conductivity during polymerisations, κ_m, is about $3.2\ \mu$ mho cm^{-1} at -22° for 1.22 M 1,3-dioxolane and it is independent of the perchloric acid concentration over the range $2.5 \times 10^{-4} - 3.0 \times 10^{-3}$ M (Table 5.3 Chapter 5). This shows that κ_m cannot represent the concentration of free ion active centres.

However the final conductivity at the end of polymerisations, κ_f, is directly proportional to the perchloric acid concentration and it almost certainly represents the concentration of free ion active centres. By comparing the value of κ_f with the conductivity of other systems of known K_D under similar conditions it is possible to estimate the value of K_D for the active centres under consideration. It must be remembered however that κ_f is considerably reduced by the viscosity of the polymer that is present at the end of the reactions, so that this estimation of K_D can again only be a guide.

A typical value of κ_f is $2.3\ \mu$ mho cm^{-1} at $+10^\circ$ with 2 M 1,3-dioxolane and 2.5×10^{-3} M perchloric acid in methylene dichloride. Longworth and Mason[7] report that the conductivity of 2.7×10^{-3} M triphenylmethyl perchlorate at 0° in 1,2-dichloroethane is $63\ \mu$ mho cm^{-1} and K_D is 1.64×10^{-3} mole litre^{-1}. Clearly K_D for the active centres is much smaller than 1.64×10^{-3} mole litre^{-1}.

Szwarc[8] has measured the conductivity of living polystyrene at 25° in tetrahydrofuran. For a concentration of 2.2×10^{-3} M living ends with a Cs^+ counter ion the conductivity is reported to be 3.0 μ mho cm^{-1}. K_D for polystyrene Cs^+ ion-pairs is 2.8×10^{-9} mole $litre^{-1}$. These results suggest that K_D for the active centres of the polymerisation of 1,3-dioxolane is about the same as for the polystyrene Cs^+ ion-pair. This is in reasonable agreement with the value of K_D calculated by the Bjerrum - Fuoss equation.

3. Szwarc[8] has shown that the apparent rate constant, k_p, of homopropagation of living polystyrene in tetrahydrofuran is linear with $1/[\text{living polymer}]^{\frac{1}{2}}$. The apparent rate constant k_p is made up of the propagation rate constants of ion-pairs and free ions, the contribution of each depending on the degree of dissociation of the ion-pair. There is an increase of k_p with decreasing concentration of living ends and the free ion is estimated to be 400 times as reactive as the most reactive ion-pair. This increase is most marked for the Li^+ counter ion which has $K_D = 2 \times 10^{-7}$ mole $litre^{-1}$ and least marked for the Cs^+ counter ion which has K_D approx. 2×10^{-9} mole $litre^{-1}$.

Now K_D for the active centres for the polymerisation of 1,3-dioxolane has been estimated to be 8.7×10^{-8} mole/litre so that a variation of k_p with the concentration of active centres would be expected if for this system the ratio of the reactivity of free ions to that of ion-pairs were as great as that found by Szwarc for the anionic polymerisation of styrene.

The kinetics of the polymerisation of 1,3-dioxolane show no variation of k_p over the range 5×10^{-4} - 5×10^{-3} M perchloric acid. (Fig. 4.12). As it is unlikely that K_D for these active centres can be much smaller than the value calculated by the Bjerrum - Fuoss equation, this means that the ratio of the reactivity of free oxonium ions to that of ion-pairs for this polymerisation must be considerably smaller than the corresponding ratio for the anionic polymerisation of styrene.

A possible reason for this difference in behaviour is that in the styrene polymerisation the cation of the ion-pair must move at each propagation step, while in the case of the 1,3-dioxolane polymerisation the negative counter-ion need not move when the ring-expansion step takes place (Chapter 3).

Evidence from the results of other workers for the possibility of an equilibrium between free ions and ion-pairs in the polymerisation of cyclic ethers is scarce. Neither Tobolsky[3] nor Rozenberg[4] comment on this possibility and neither has made any conductivity measurements. Tobolsky polymerised 6.1 M tetrahydrofuran in 1,2-dichloroethane as solvent and there is a curvature to his graph of the rate of polymerisation against initiator concentration over the range 5×10^{-3} - 6×10^{-2} M triethyloxonium tetrafluoroborate.

Rozenberg polymerised bulk tetrahydrofuran and his graph of the rate of polymerisation against initiator concentration is a straight line over the same range of initiator concentration.

Thus Tobolsky, who worked in a medium of higher dielectric constant than Rozenberg, does have some evidence to suggest that there is an equilibrium between free ions and ion-pairs in his system.

4.3.3 A Qualitative Explanation of the Acceleration Period.

A detailed kinetic scheme for the whole polymerisation and depolymerisation curves has not been attempted, but a qualitative explanation of the results is as follows.

The conductivity measurements, discussed in Chapter 5, show that at the start of the acceleration period there can be virtually no conductivity due to protonated 1,3-dioxolane. As there is no reason to suppose that K_D of protonated monomer is different from K_D of protonated polymer, this means that only a small part of the perchloric acid protonates 1,3-dioxolane. The rest of the perchloric acid remains covalent.

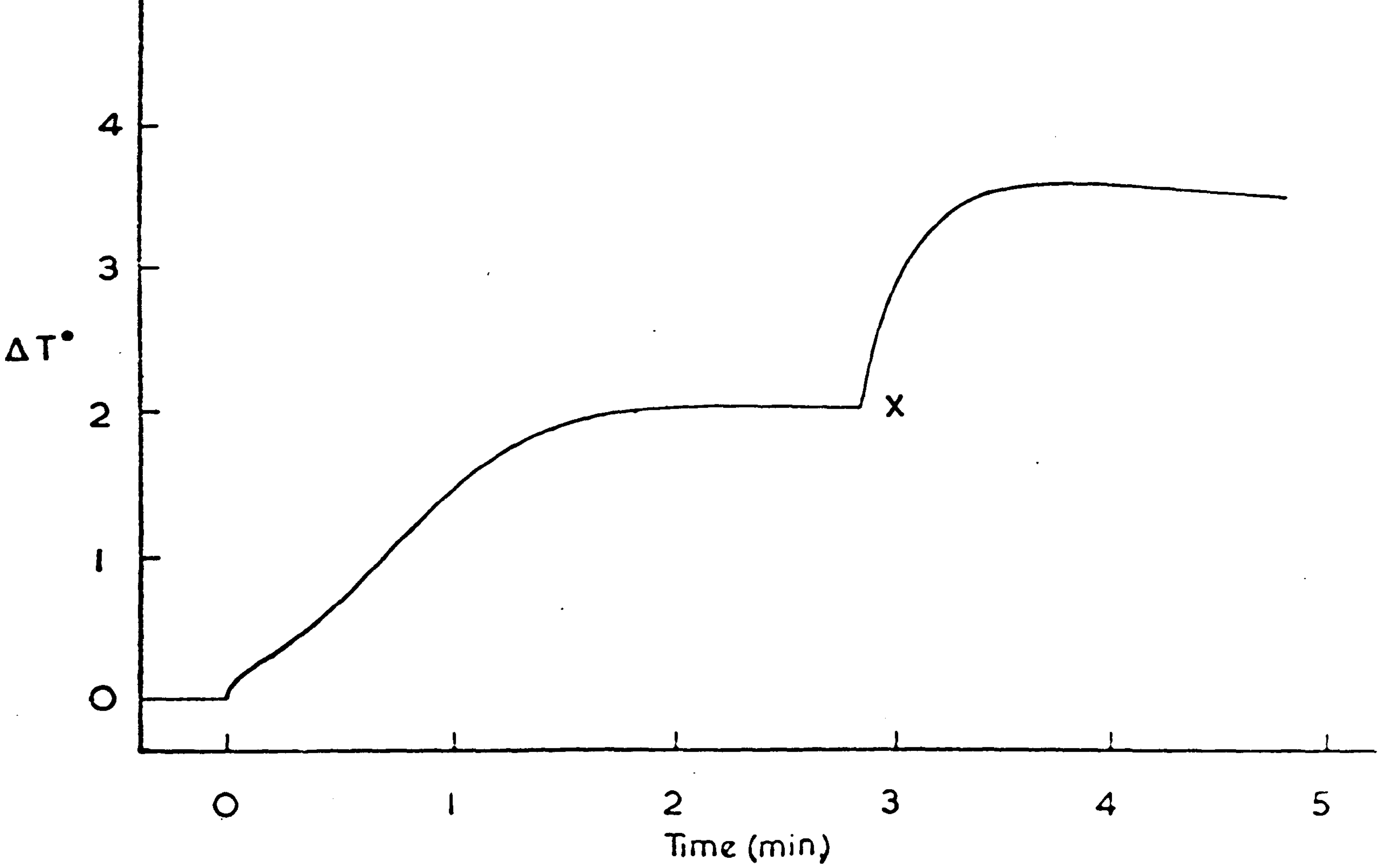
In the dilatometry experiments 79A and 79B the second polymerisation was found to have essentially the same reaction curve, complete with acceleration period, as the first polymerisation (Fig. 4.1). This shows conclusively that a slow protonation of 1,3-dioxolane by perchloric acid cannot be causing the acceleration period.

Polymerisation 81C, (Fig. 4.5), shows that when some preformed polymer is present at the start of a polymerisation the acceleration period is correspondingly reduced. This is in excellent agreement with experiments in which a second addition of monomer was made to a polymerisation mixture that had reached equilibrium. The polymerisation following this second addition of 1,3-dioxolane was found to have no acceleration period. (Fig. 13 M.Sc. Thesis). Furthermore, the kinetic scheme shows that above about 25% conversion each molecule of perchloric acid produces an active centre, and Chapter 5 shows that the final conductivity κ_f is partially due to free ion active centres. The only possible solution to these observations is that all the perchloric acid must protonate poly-1,3-dioxolane but that only a small part of the perchloric acid can protonate 1,3-dioxolane. In other words poly-1,3-dioxolane is more basic than 1,3-dioxolane. Basicity measurements were carried out, (Chapter 9), and this conclusion was verified. Poly-1,3-dioxolane has a $pK_b = 6.4$ and 1,3-dioxolane has a $pK_b = 7.4$.

Fig. 4.15 (Fig. 13 of M.Sc. Thesis)

Plot of ΔT against time for experiment 15 (the polymerisation of 1.6 M 1,3-dioxolane with 3.65 x 10^{3} M perchloric acid at +9°). At point x a phial of monomer was crushed and a further polymerisation occurred.

Fig. 4.15



The depolymerisation experiments that were carried out in the dilatometer (81B, 81D, 82B and 82C) support this kinetic scheme. These reactions were found to be of first order down to about 25% of polymer. Below this value the reactions were slower than first order because as the more basic poly-1,3-dioxolane was converted to the less basic monomer, covalent perchloric acid was again produced. This is the exact reverse of what happens during the acceleration period of polymerisations.

On these grounds we would expect the conductivity to fall during depolymerisations; in fact it rises. This is a very complicated problem that is resolved in Chapter 5.

References to Chapter 4

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Chapter 5

Electrical Conductivity Measurements.

5.1 The Electrical Conductivity of 1,3-Dioxolane and Perchloric Acid above the Ceiling Temperature

0.65 M 1,3-dioxolane in methylene dichloride was made to react with (0.5-3.5) x 10^{-3} M perchloric acid at +10° in the adiabatic calorimeter, and the electrical conductivity was measured. (Table 5.1). As the system is well above its ceiling temperature under these conditions, no polymerisation occurred.

The initial specific conductivity, κ_o, due to the conductivity of 1,3-dioxolane in methylene dichloride, is small and reasonably reproducible. Separate experiments showed that the specific conductivity of pure perchloric acid in methylene dichloride was about 0.04 μ mho cm^{-1} under our experimental conditions.

In these experiments the rise in conductivity from the initial value, κ_o, to the final value, κ_f, was found to be a first order reaction. However as the acid concentration was decreased the reactions progressively deviated from first order reactions. Experiment 59, with 0.5 x 10^{-3} M perchloric acid was almost a second order reaction as $t_{\frac{1}{2}}$ = 117 seconds and $t_{\frac{3}{4}}$ = 360 seconds. ($t_{\frac{3}{4}} = 3t_{\frac{1}{2}}$ for a second order reaction with equal concentrations of reactants). Fig. 5.1 is a plot of k_{κ} , the first order rate constant for the increase in conductivity, against perchloric acid concentration. This is a good straight line down to a perchloric acid concentration of about 1 x 10^{-3} M.

However Fig. 5.2, which is a plot of κ_f against perchloric acid

Table 5.1

The Effect of Perchloric Acid Concentration on the Conductivity of 0.65 M 1,3-Dioxolane at +10°.

Run No.	59	58	53	52	54	55[x]	194[I]
$[HClO_4]$, 10^3 M.	0.50	1.00	1.80	2.14	3.51	2.00	1.00
k_{κ} . min^{-1}.	-	2.7	11.9	15.8	28.8	16.2	-
κ_o, μ mho cm^{-1}.	0.043	0.024	0.042	0.036	0.047	0.041	0.035
κ_f, μ mho cm^{-1}.	2.58	2.49	2.92	2.58	2.78	2.00	5.15

[x] Experiment 55 was carried out with 0.32 M 1,3-dioxolane

[I] Experiment 194 was carried out with 1.0×10^{-3} M added water.

Fig. 5.1 The dependence of the first order rate constant, k_{κ}, on perchloric acid concentration for 0.65 M 1,3-dioxolane at +10°.

Fig. 5.2 The dependence of the final conductivity, κ_f, on the perchloric acid concentration for 0.65 M 1,3-dioxolane at +10°.

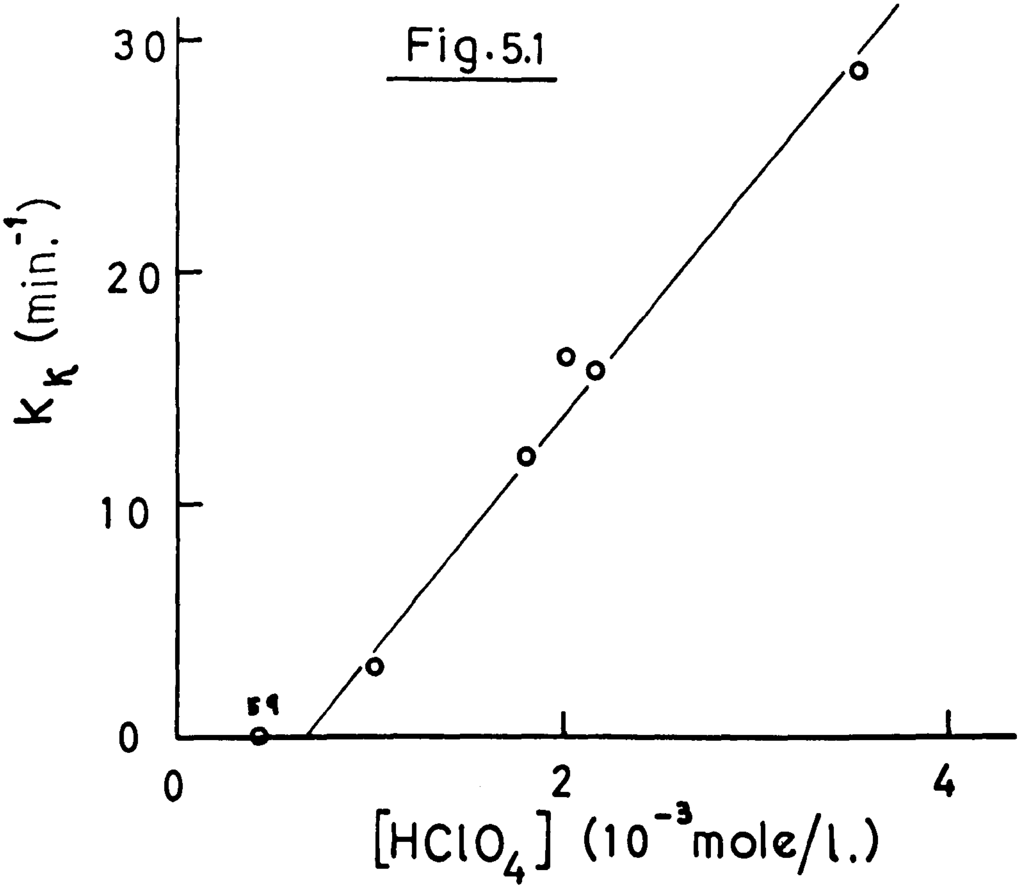

K_k (min.$^{-1}$)
30
20
10
0
0
2
4
59
[HClO$_4$] (10^{-3}mole/l.)

Fig. 5.1

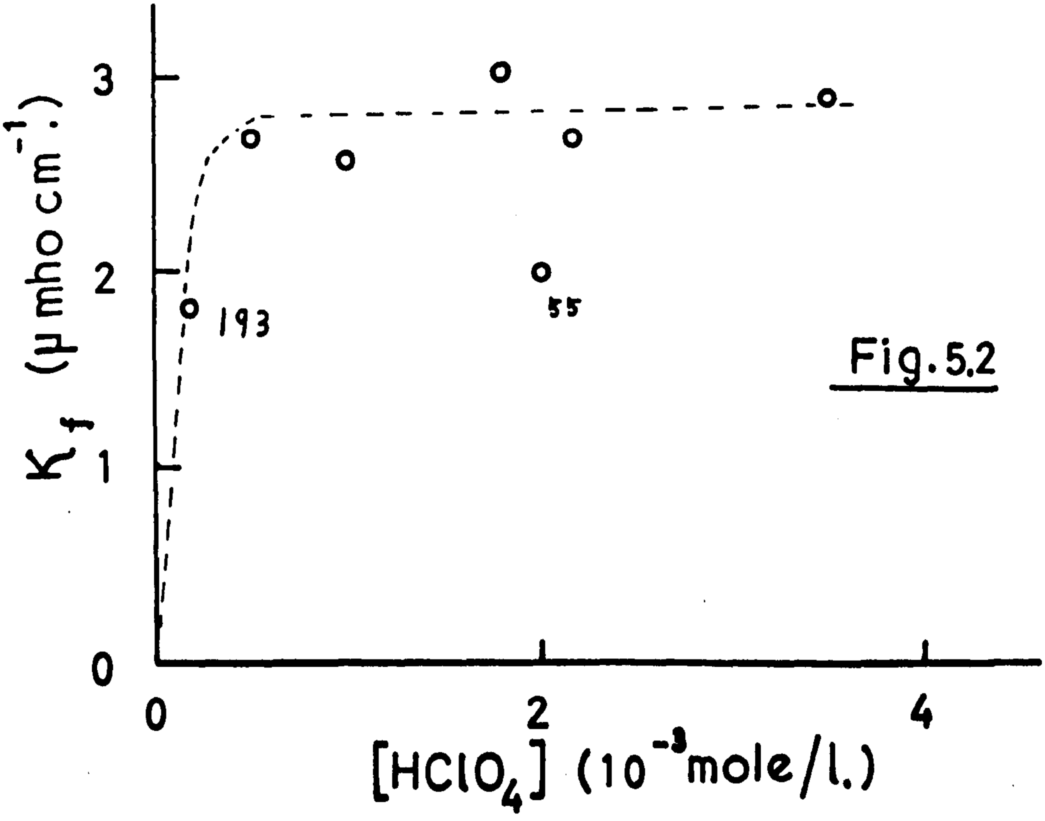

K_f (μmho cm^{-1}.)
3
2
1
0
0
2
4
193
55
[HClO$_4$] (10^{-3}mole/l.)

Fig. 5.2

Table 5.2

The Effect of Dilution on the Conductivity of 1,3-Dioxolane and Perchloric Acid at +10°.

Experiment 193

[1,3-Dioxolane] M	$[HClO_4]\ 10^4$ M	κ_f, μ mho cm^{-1}.	Λ mho cm^2.
0.65	1.9	1.82	9.57
0.32	0.95	1.00	10.5
0.16	0.47	0.44	9.36
0.09	0.27	0.22	8.15

κ_o, the initial specific conductivity was 0.02 μ mho cm^{-1}.

concentration for these reactions shows that κ_f is independent of the acid concentration. Experiment 55, which was carried out with 0.32 M 1,3-dioxolane gave a substantially lower value of κ_f, whilst experiment 194, which was carried out with 1.0×10^{-3} M added water gave an increased value of κ_f. The reaction mixture of experiment 194 was analysed by gas chromatography and it was found to contain 1×10^{-3} M ethylene glycol.

In experiment 193 (Table 5.2) the conductivity of 0.65 M 1,3-dioxolane in methylene dichloride and 1.9×10^{-4} M perchloric acid was measured in the calorimeter at +10°. The conductivity took 2 hours to rise from its initial value, $\kappa_o = 0.02$ μ mho cm^{-1}, to its final value $\kappa_f =$ 1.82 μ mho cm^{-1}. Then methylene dichloride was run into the calorimeter under vacuum and the solution was progressively diluted. On each addition of methylene dichloride the conductivity immediately reached a steady value which did not change for several hours. From the values of κ_f and the calculated concentration of perchloric acid, values of the equivalent conductivity, Λ , were calculated. Λ was found to be essentially constant for this system.

5.2 The Electrical Conductivity of 1,3-Dioxolane and Perchloric Acid During Polymerisations.

The electrical conductivity during 1,3-dioxolane polymerisations in methylene dichloride was measured in the calorimeter and in the dilatometer. The results of experiments at -20° are shown in Table 5.3. Conductivity results for polymerisations at -50° (Table 5.4) and +6° (Table 5.5) were also obtained, and these have been included so that there is a complete record of these measurements.

Fig. 5.3

Simultaneous plot of ΔT and electrical conductivity against time for experiment 50 (the polymerisation of 1.22 M 1,3-dioxolane with 3.9×10^{-3} M perchloric acid at -22°).

Fig. 5.3

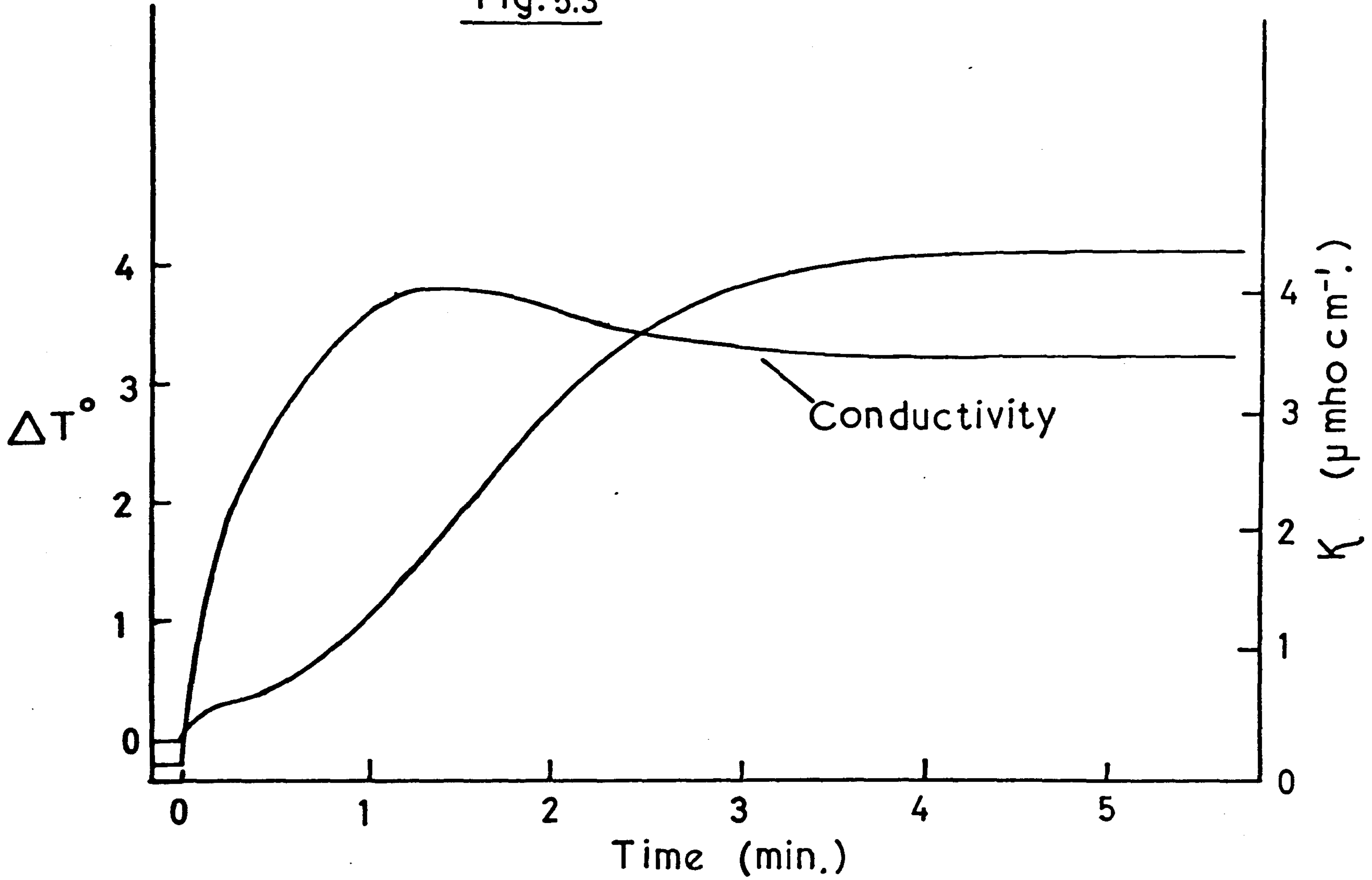


Table 5.3

The Effect of Perchloric Acid Concentration on the Conductivity of 1.22 M 1,3-Dioxolane Polymerisations at Initial Temp. = -22° and Final Temp. = -16°.

Run No.	82A	81A	46	45	44	50	47	49	63^x	62^x
$[HClO_4]$, 10^3 M.	0.25	0.50	1.21	2.81	2.83	3.91	4.15	4.95	4.87	2.6
κ_o, μ mho cm^{-1}.	0.046	0.025	0.024	0.027	0.048	0.014	0.035	0.065	0.046	0.070
κ_m, μ mho cm^{-1}.	3.08	3.21	3.18	3.32	3.17	3.94	4.15	4.75	12.9	14.4
κ_f, μ mho cm^{-1}.	0.97	1.33	1.74	2.68	2.65	3.34	3.46	4.05	7.50	-
Yield, %	-	-	54	-	-	-	-	54	57	-
DP	-	-	14.4	-	-	-	-	13.5	15.5	-

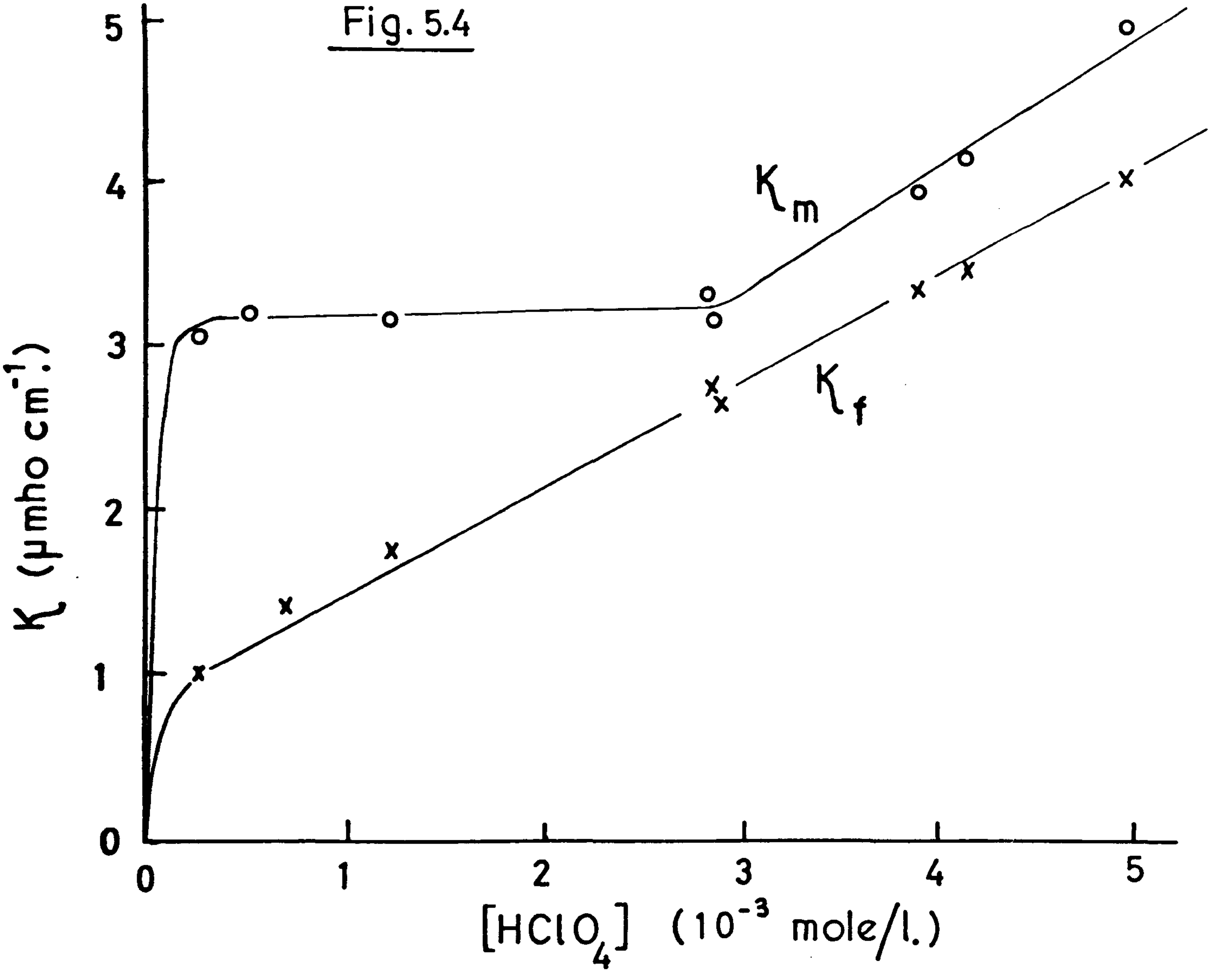
Experiments 82A and 81A were carried out in dilatometers at -20° and all the other experiments were carried out in the calorimeter.

No values of yield and DP are available for experiments 44, 45, 47 and 50 as the temperature was altered <u>after</u> these polymerisations had reached equilibrium and <u>before</u> the polymerisations were neutralised.

^{x} Experiments 63 and 62 were carried out with 2.4 x 10^{-3} M added water.

Fig. 5.4 The dependence of the maximum conductivity, κ_m, and the final conductivity, κ_f, on perchloric acid concentration for 1,3-dioxolane polymerisations at -22°.

Fig. 5.4



κ (μmho cm^{-1})
0
1
2
3
4
5
$[HClO_4]$ (10^{-3} mole/l.)
0
1
2
3
4
5
κ_m
κ_f

Table 5.4

Electrical Conductivity Data for the Polymerisation of 2.0 M 1,3-Dioxolane at Initial Temp. = -50° and Final Temp. = -32°

Run No.	60
$[HClO_4]$, 10^3 M.	3.47
κ_o μ mho cm^{-1}.	0.038
κ_m μ mho cm^{-1}.	2.90
κ_f μ mho cm^{-1}.	1.80
Yield, %	71
DP.	72

Table 5.5

Electrical Conductivity Data for Polymerisations of 2.0 M 1,3-Dioxolane at Initial Temp. = +6° and Final Temp. = +13°

Run No.	37	33
$[HClO_4]$, 10^3 M.	2.52	4.25
κ_o, μ mho cm^{-1}.	0.07	0.09
κ_m, μ mho cm^{-1}.	3.60	5.00
κ_f, μ mho cm^{-1}.	2.30	3.54
Yield, %	41	41
DP.	14.9	13.0

In every polymerisation experiment the conductivity rose slowly from its initial value, κ_o, to its maximum value, κ_m, and then fell as the polymerisation progressed to κ_f, the final value at equilibrium (Fig. 5.3). This rise in conductivity from κ_o to κ_m was found not to be a first order reaction.

In Fig. 5.4 the values of κ_m and κ_f (Table 5.3) are plotted as functions of the perchloric acid concentration. Below 3×10^{-3} M perchloric acid the value of κ_m is independent of the perchloric acid concentration, whilst κ_f is nearly proportional to it. Experiments 62 and 63, which were carried out with about 2.4×10^{-3} M added water, show that κ_m and κ_f are drastically increased by the presence of water. (There is no value of κ_f for experiment 62 as the polymerisation was killed before equilibrium was reached.) The position of the maximum conductivity, κ_m, relative to the polymerisation curve is not constant; it depends on the perchloric acid concentration. For low perchloric acid concentrations, such as in expt. 82A, κ_m was reached when the polymerisation had reached only about 6% of equilibrium conversion. At high perchloric acid concentrations (e.g. experiment 49) κ_m was reached when the polymerisation was at about 45% of equilibrium conversion.

The conductivity results that were obtained with the dilatometer for depolymerisations and second polymerisations are presented in Chapter 4 (Table 4.1). They will not be presented here again but they will be dealt with in the discussion.

5.3 Discussion

The electrical conductivity experiments with 1,3-dioxolane and perchloric acid that were carried out above the ceiling temperature of the system gave completely unexpected results.

At the higher perchloric acid concentrations (experiments 52, 53 and 54) the increase in conductivity was found to be an accurate first order process. As a first order increase in conductivity is almost impossible unless the conductivity is directly proportional to the concentration of ions, these experiments suggest that the equivalent conductivity of the system is constant over a large concentration range.

Experiment 193, the dilution experiment, was carried out to check this point. Although the exact concentration of ions is unknown, a value of the equivalent conductivity was obtained by dividing κ_f by the concentration of perchloric acid. Table 5.2 shows that this equivalent conductivity is essentially constant over the range considered.

In Chapter 4 the dissociation constant, K_D, for protonated 1,3-dioxolane and protonated poly-1,3-dioxolane was calculated to be 8.7×10^{-8} mole/litre. It was also pointed out in Chapter 4 that K_D cannot be much larger than the calculated value, as the values of κ_f, the final conductivities are so small. Thus if the conductivity were due to protonated 1,3-dioxolane the equivalent conductivity would have to increase with increasing dilution as is the case for the equivalent conductivity of living polystyrene with a Cs^+ cation which has $K_D = 2.8 \times 10^{-9}$ mole/litre[1]. It is very unlikely that the equivalent conductivity is constant due to triple ion formation as the concentrations used are too low.

Thus these experiments show that at any rate the greater part of the conductivity cannot be due to protonated 1,3-dioxolane. Further proof of this comes from the fact that the final conductivity, κ_f, is independent of the perchloric acid concentration (Fig. 5.2) whilst the first order rate constant, k_κ , is proportional to the perchloric acid concentration (Fig. 5.1).

In experiment 55 the concentration of 1,3-dioxolane was one half of that used for the other experiments, and κ_f was reduced from an average value of 2.8 μ mho cm^{-1} to 2.0 μ mho cm^{-1}. This result immediately suggests that some impurity in the monomer is being protonated and that this causes the conductivity.

If this is so then it follows that the protonated impurity must exist entirely as free ions as the equivalent conductivity of the system has been shown to be essentially constant. This is in fact a reasonable assumption as the concentration of the impurity is only about 5×10^{-4} M. However there should still be a small increase of equivalent conductivity with increasing dilution as the ionic activity coefficients increase. The magnitude of this increase is probably quite small as Beard and Plesch report[2] that the mean ionic activity coefficient of methyltriethylammonium iodide in methylene dichloride at 0° increases from 0.776 to 0.887 as the concentration is decreased from 4.55×10^{-4} M to 0.407×10^{-4} M.

If we accept that the conductivity is approximately proportional to the concentration of protonated impurity then the experimental results are easily explained.

When the concentration of perchloric acid is much greater than that of the impurity (experiments 52, 53 and 54) then κ_f is independent of acid concentration and proportional to the impurity concentration which is constant from experiment to experiment. The average value of κ_f is 2.8 μ mho cm^{-1}. The conductivity increase is a first order process as there is a large excess of perchloric acid over impurity and k_κ is proportional to the acid concentration. However as the concentration of acid is reduced it becomes comparable with the impurity concentration and the conductivity increase tends to a second order process, while κ_f remains unchanged. Experiment 59 is virtually a second order reaction with equimolar quantities of reactants from which the concentration of impurity is estimated to be about 5 x 10^{-4} M. When the perchloric acid concentration is less than the impurity concentration, experiment 193, then κ_f is less than 2.8 μ mho cm^{-1} as all the impurity is not protonated.

The next problem is to decide what the impurity is that is causing the results described.

The residual water content of the calorimeter and solvent under the experimental conditions used is reported[3] to be about 10^{-5} mole/litre. The concentration of impurity is estimated to be about 5 x 10^{-4} mole/litre and experiment 55 shows that most of the impurity must be present in the monomer. This means that the molar ratio of impurity to monomer must be about 1 to 1000. The gas chromatogram of 1,3-dioxolane showed no impurities to be present above a ratio of about 1:100,000 vol/vol, so that water is the most plausible impurity as this is not registered by a flame ionisation detector.

However κ_f was found to be constant from start to finish of any one batch of monomer, and constant from one batch of monomer to another. In particular, κ_f did not alter when activated barium oxide was used in place of lithium aluminium hydride to dry the 1,3-dioxolane. Because of these observations it is highly unlikely that the impurity could be water.

Another reason for thinking that the impurity is probably not water is the fact that for the 1,3-dioxepane polymerisations, that were carried out under identical conditions, the residual concentration of water in the system was estimated to be 1 x 10^{-4} M. (Chapter 8).

However experiment 194, which was carried out with 1 x 10^{-3} mole/litre of added water does show that K_f was increased by the addition of water. This experiment suggests that water may in fact be the impurity. The reaction mixture of experiment 194 was analysed and found to contain 1 x 10^{-3} mole/litre of ethylene glycol indicating that water and 1,3-dioxolane, in the presence of acid, reacted in the conventional way to give ethylene glycol and formaldehyde[4].

The possibility that 1,3-dioxolane is in equilibrium with small quantities of formaldehyde and ethylene oxide was considered, but this idea had to be rejected as lithium aluminium hydride would have reduced formaldehyde to methanol and thus in time it would have converted all the 1,3-dioxolane to methanol and ethylene glycol. This was not observed. Furthermore, if an equilibrium of this type did exist and the formaldehyde were protonated, the conductivity would be expected to increase with time until all the perchloric acid had reacted with formaldehyde. This also was not observed.

The conclusion is that although the conductivity results can only be explained in terms of an impurity being present and being protonated to give rise to the conducting species, there is not enough evidence available to decide conclusively what this impurity is. Clearly more experiments are needed to track down the impurity and to solve the problem conclusively.

However, if we accept the impurity theory then it follows that very little of the conductivity can be due to protonated 1,3-dioxolane and therefore that most of the perchloric acid remains covalent under the experimental conditions described.

The final problem is to explain the conductivity results that were obtained during polymerisations.

From Fig. 5.4 it will be seen that below 3×10^{-3} M perchloric acid the value of κ_m, the maximum conductivity, is independent of perchloric acid concentration. This shows that κ_m, like κ_f of the conductivity experiments under non-polymerising conditions, is due mainly to protonated impurity. Proof that κ_m is not directly related to the kinetics of the polymerisation of 1,3-dioxolane comes from the observation that the position of κ_m relative to the polymerisation curve is not constant but dependent on the perchloric acid concentration. Experiments 62 and 63, which were carried out with 2.4×10^{-3} M added water show that κ_m is increased by the addition of water.

The conductivity is observed to drop as the polymerisations proceed; this is (at least partly) due to the increasing viscosity of the solutions. We will assume that for a series of polymerisations at constant 1,3-dioxolane concentration there is a constant increase in viscosity as the number average molecular weight of polymers has been shown to depend on the concentration of 1,3-dioxolane but to be independent of acid concentration[5]. However as the weight average molecular weight of the polymers may not be independent of perchloric concentration, the viscosity of polymer solutions may vary with acid concentration and this assumption may not be valid.

The value of κ_f, the final conductivity after polymerisation, is proportional to the acid concentration, which suggests that κ_f is made up of two parts. One part is constant and due to the protonated impurity, whilst the other part is proportional to the acid concentration and thus probably represents the concentration of active centres.

From Fig. 5.4 it will be seen that above about 3×10^{-3} M perchloric acid the value of K_m is proportional to the concentration of acid. This is probably due to the fact that at high acid concentrations the rate of polymerisation, and thus the rate of production of active centres, is greater than the rate of protonation of the impurity.

It was pointed out in Chapter 4 that the conductivity rises during depolymerisations whilst the concentration of active centres is postulated to decrease. The reason for this is that the viscosity of the solution decreases as the reaction proceeds and at the end of the reaction the conductivity is due to protonated impurity. This could mask the fact that there is a decrease in the concentration of active centres.

It is impossible to arrive at any firm conclusions from the results that were obtained during polymerisation and depolymerisation experiments because of the uncertainty concerning the viscosity of the polymer solutions. Thus the explanations that have been postulated can only be regarded as tentative. In principle however it should be possible to solve the problem by making simultaneous measurements of conductivity and viscosity.

References to Chapter 5

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Introduction to Section B

This section of the Thesis is concerned with the polymerisation of 1,3-dioxepane with anhydrous perchloric acid in methylene dichloride solution. It follows closely the work on the polymerisation of 1,3-dioxolane that has already been described. I will only deal with papers that are directly concerned with the polymerisation of 1,3-dioxepane, since a general introduction to the polymerisation of cyclic oxygen compounds has been included at the start of Section A.

The polymerisation of 1,3-dioxepane was first investigated by Hill and Carothers[1], who showed that whilst 1,3-dioxane would not polymerise, the seven membered ring, 1,3-dioxepane, would polymerise when heated to 100° with a trace of sulphonic acid. Poly-1,3-dioxepane was found to depolymerise to a range of products that included the cyclic dimer and the original monomer.

Skuratov et al[2] report that the heats of polymerisation of the cyclic formals calculated from the difference in the experimental heats of combustion in the gaseous state and the heats of combustion calculated additively from the increments of the groups involved, were -6.2, 0.0 and -4.7 kcal/mole for 1,3-dioxolane, 1,3-dioxane and 1,3-dioxepane respectively.

An industrial report on the polymerisation of 1,3-dioxepane states that high molecular weight polymer can be prepared with either molecular sieve or aluminium alkyls as catalysts. The bulk polymerisation of 1,3-dioxepane with trialkylaluminium was carried out at 50° to give a low yield of poly-1,3-dioxepane which had an intrinsic viscosity in benzene at 30° of 8.2.

With borontrifluoride etherate, benzenediazonium fluoroborate and alkyl aluminium halides as catalysts the polymerisation of bulk 1,3-dioxepane at 50° gave polymers with intrinsic viscosities of between 0.36 and 1.36. The intrinsic viscosity was found to increase as the concentration of catalyst was decreased.

The report also states that substituted 1,3-dioxepanes, such as 2-phenyl-1,3-dioxepane and 2-propyl-1,3-dioxepane, polymerise very rapidly with strong acids to give low molecular weight oils in good yield.

Like 1,3-dioxolane, 1,3-dioxepane has been reported[3,4] to polymerise in the presence of maleic anhydride and benzoyl peroxide, but in view of the unsuccessful experiment with 1,3-dioxolane that was carried out in this laboratory, no conclusions can be drawn from these reports.

There is a large a number of patents that deal with the polymerisation of cyclic formals, and 1,3-dioxepane is reported to polymerise with a variety of catalysts, such as anhydrous magnesium iodide and acid activated bleaching earth, but I have not followed up these reports.

This literature survey shows that the polymerisation of 1,3-dioxepane has never been studied in detail. In particular the following aspects of the polymerisation of 1,3-dioxepane have been neglected:

(1) The nature of the end-groups and the factors that control the DP of the polymer.

(2) The thermodynamics of the polymerisation.

(3) The mechanism and kinetics of the polymerisation.

This section of the Thesis, which concentrates on these aspects of the polymerisation of 1,3-dioxepane, shows that 1,3 dioxepane is similar to 1,3-dioxolane in all respects except in the kinetics of the polymerisation.

References to Introduction to Section B

[1] J.W. Hill and W.H. Carothers, J. Amer. Chem. Soc., 1935, 57, 925.

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Chapter 6

The Structure and DP of Poly-1,3-Dioxepane

All polymerisations of 1,3-dioxepane were carried out on the adiabatic calorimeter under exactly the same conditions that were used for 1,3-dioxolane polymerisations. The residual water content of the 1,3-dioxepane system is estimated to have been about 1 x 10^{-4} M (Chapter 8).

6.1 Fractionation of the Polymer

After the polymerisations had reached equilibrium the polymerisation mixtures were immediately neutralised with ammonia gas. The polymers were isolated by evaporation of the solvent and monomer in a vacuum oven at 50° and 20 mm. It was noticed that small white crystals collected on the cool glass viewing plate of the vacuum oven under these conditions. These crystals were collected and found to have a m.p. = 90 - 92°. Not enough material was collected to allow infrared and NMR spectra to be run.

In experiment 134, a 1 M solution of 1,3-dioxepane containing 15g of monomer was polymerised at -40° with 1.2 x 10^{-4} M $HClO_4$ and the polymer was fractionated in the following way:

The solution of polymer in methylene dichloride was slowly poured into a litre of hexane with stirring. Most of the polymer was insoluble and separated out as a white rubbery solid (134 A), which was dried in the vacuum oven and weighed (6.1g). The number average degree of polymerisation was 70 and the intrinsic viscosity in benzene at 25° was 5.1 dl. g^{-1}.

The hexane, which was kept slightly alkaline with ammonia, was evaporated off on a steam bath. The last traces of hexane and monomer were removed in the vacuum oven to give product 134B. This weighed 2.7g and had a DP of 4.3. 134B was clearly a mixture of colourless crystals and a slightly viscous oil. This mixture was filtered to yield 134C, the oil, and white crystals 134D which were washed with very cold pentane. 134C had a DP of 6. 134D had a DP of 2.6 and a m.p. 85 - 92°. 134D was thus not a pure compound.

Then 0.5g of 134D was placed in a vacuum sublimation apparatus and heated to 65° under a vacuum of 20 mm. After a few hours 0.1g of small white crystals had collected on the cold finger. This material 134E had a m.p. 90 - 92° and a DP = 2.15 ∓ 1.0. 134E is thus a dimer, and identical with the original crystals collected from the vacuum oven.

6.2 Infrared Spectra

The infrared spectra of 1,3-dioxepane, and of polymers 134E, 134D, 134C, and 134A were all run in 1 mm cells with carbontetrachloride as solvent. In no case was any peak observed in the region of the hydroxyl group[1] (3543 cm^{-1}).

A careful examination of these infrared spectra was made and the following groups were found to be absent:

Vinyl ether	3,105 - 3,050 cm^{-1}.
Carbonyl groups	1,740 - 1,720 cm^{-1}.
Carbon-Chlorine bond	750 - 700 cm^{-1}.
Primary or Secondary Amine	3,500 - 3,300 cm^{-1}.

The values quoted 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.

6.3 Nuclear Magnetic Resonance Spectra

1. A 10% solution of 1,3-dioxepane in carbontetrachloride gave three peaks at 5.34, 6.31 and 8.35 τ in a ratio of 1:2:2. These peaks are ascribed to the 2 protons in the 2 position, the 4 protons in the 4 and 7 positions and the 4 protons in the 5 and 6 positions respectively. The peak at 5.34 τ was without fine structure, the peak at 6.31 τ was a triplet and the peak at 8.35 τ a quint~~r~~uplet. This is in accord with the structure of 1,3-dioxepane.

2. A 5% solution of 134E (DP = 2.15 ∓ 1) in CCl_4 gave three peaks at 5.46, 6.50 and 8.31 τ in a ratio of 1:2:2. These peaks had a similar fine structure to those of 1,3-dioxepane and no other peaks were observed.

3. A 5% solution of 134D (DP = 2.6) in CCl_4 gave three peaks at 5.46, 6.50 and 8.30 τ in a ratio of 1:2:2. These peaks had a slightly less well resolved fine structure than those of 134E, but no other peaks were observed.

4. A 10% solution of 134C (DP = 6.0) in CCl_4 gave three peaks at 5.44, 6.51 and 8.37 τ in a ratio of 1:2:2. These peaks were rather broad and the fine structure was not resolved. This spectrum was run several times at high sensitivity but no other peaks were observed.

5. A 5% solution of 134A (DP = 70) in CCl_4 gave a spectrum identical to that of 134C.

6.4 The DP of Poly-1,3-Dioxepane

All molecular weights were determined by Vapour Pressure osmometry so that the DPs quoted are number average DPs. The dimer present in the polymers causes the number average DP to be artificially low while the weight average DP is much higher, as indicated by the high intrinsic viscosity. It seemed as if the 1,3-dioxepane polymerisation might be similar to that of oxacyclobutane for which Rose[3] reported the simultaneous production of a crystalline polyether of high molecular weight and a cyclic tetramer. Thus it seemed that the DP results would be simplified if the cyclic dimer could be removed by vacuum sublimation. However, after the cyclic dimer had been removed at 65° and 20 mm it was found that the remaining polymer smelt strongly of formaldehyde, indicating that it had partly degraded. This was clearly no use for DP determinations.

When the vacuum sublimation was carried out at 30° and 0.1 mm it was found that an oil collected on the cold finger indicating that the cyclic dimer and some higher homologues were being removed from the polymer. The cyclic dimer was vacuum sublimed from several polymer samples to give the percentage of cyclic dimer in the polymer, but all the DP results that are quoted in this Thesis are for the whole polymer, i.e. including the cyclic dimer present.

In order to show the variation of DP with perchloric acid concentration for these polymerisations we must first consider the results of the kinetics Chapter (Chapter 8). The graphs of k_1, the first order rate constant for 1,3-dioxepane polymerisations, against perchloric acid concentration have various intercepts on the perchloric acid axis. This shows that varying quantities of impurities such as tetrahydrofuran and water were effectively neutralising some of the perchloric acid. Because of this the concentration of perchloric acid that was available for polymerisation, $\left[HClO_4\right]_A$, was correlated with the DP, where

$$\left[HClO_4\right]_A = \left[HClO_4\right] - \text{Intercept}$$

Fig. 6.1 shows the plot of DP against the concentration of available perchloric acid for polymerisations of 0.6 M 1,3-dioxepane at -65°. The date for this graph are given in Table 6.1. All polymerisations were allowed to reach equilibrium and then killed with ammonia gas. There is however a large scatter of points and a slight decrease of DP with increasing concentration of available perchloric acid.

Fig. 6.2 (Table 6.2) shows the plot of DP against the concentration of available perchloric acid for polymerisations of 0.6 M 1,3-dioxepane at -40°. Fig. 6.2 shows the same features as Fig. 6.1.

Fig. 6.3 (Table 6.3) shows the plot of DP against 1,3-dioxepane concentration for polymerisations at -20°. The point DP = 1 was calculated from the equilibrium concentration of 1,3-dioxepane at -17°, the temperature at which the polymerisations were neutralised. The concentration of available perchloric acid for each experiment is also included in Table 6.3. It will be seen that the DP is not very sensitive to changes in available acid concentration but that it increases sharply and linearly with increasing 1,3-dioxepane concentration.

Polymerisations 180 and 182 were neutralised before equilibrium conversion was reached. The exact point at which the polymerisations were neutralised is given by the value of $\Delta\left[\text{1,3-dioxepane}\right]$ which is the change in molar concentration of the monomer. The important point is that when the reactions are killed before equilibrium is reached a much higher DP is obtained than otherwise. Polymers 180 and 182 were almost clear and contained very little crystalline dimer.

Table 6.1

DP Data for Polymerisations of 0.6 M 1,3-Dioxepane at T = -65°

Run No.	148	153	152	149	158	157	156	155	150
$[HClO_4]_A$, 10^4 M.	0.5	1.0	1.8	2.1	2.2	2.9	3.2	3.6	3.7
DP	21.6	11.2	10.8	10.7	14.3	11.0	11.0	12.6	8.3

Fig. 6.1 Plot of DP against the concentration of available perchloric acid for 0.6 M 1,3-dioxepane polymerisations at -65°.

Table 6.2

DP Data for Polymerisations of 0.6 M 1,3-Dioxepane at T = -40°

Run No.	138	137	154	151	144
$[HClO_4]_A$, 10^4 M.	0.3	0.7	0.7	1.8	4.0
DP	10.8	11.0	7.8	7.6	7.6
% Cyclic Dimer	-	-	-	-	5.2

Fig. 6.2 Plot of DP against the concentration of available perchloric acid for 0.6 M 1,3-dioxepane polymerisations at -40°.

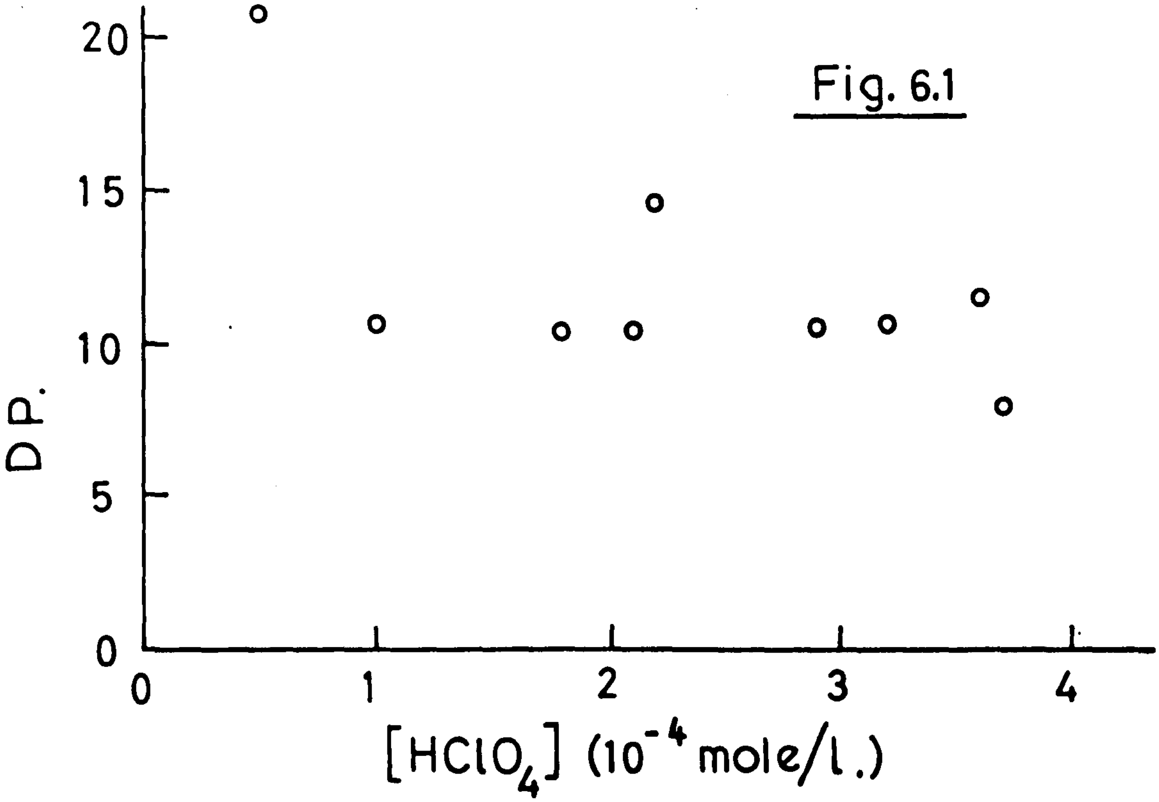

Fig. 6.1

20
15
10
5
0
DP.
0
1
2
3
4
[HClO$_4$] (10^{-4} mole/l.)

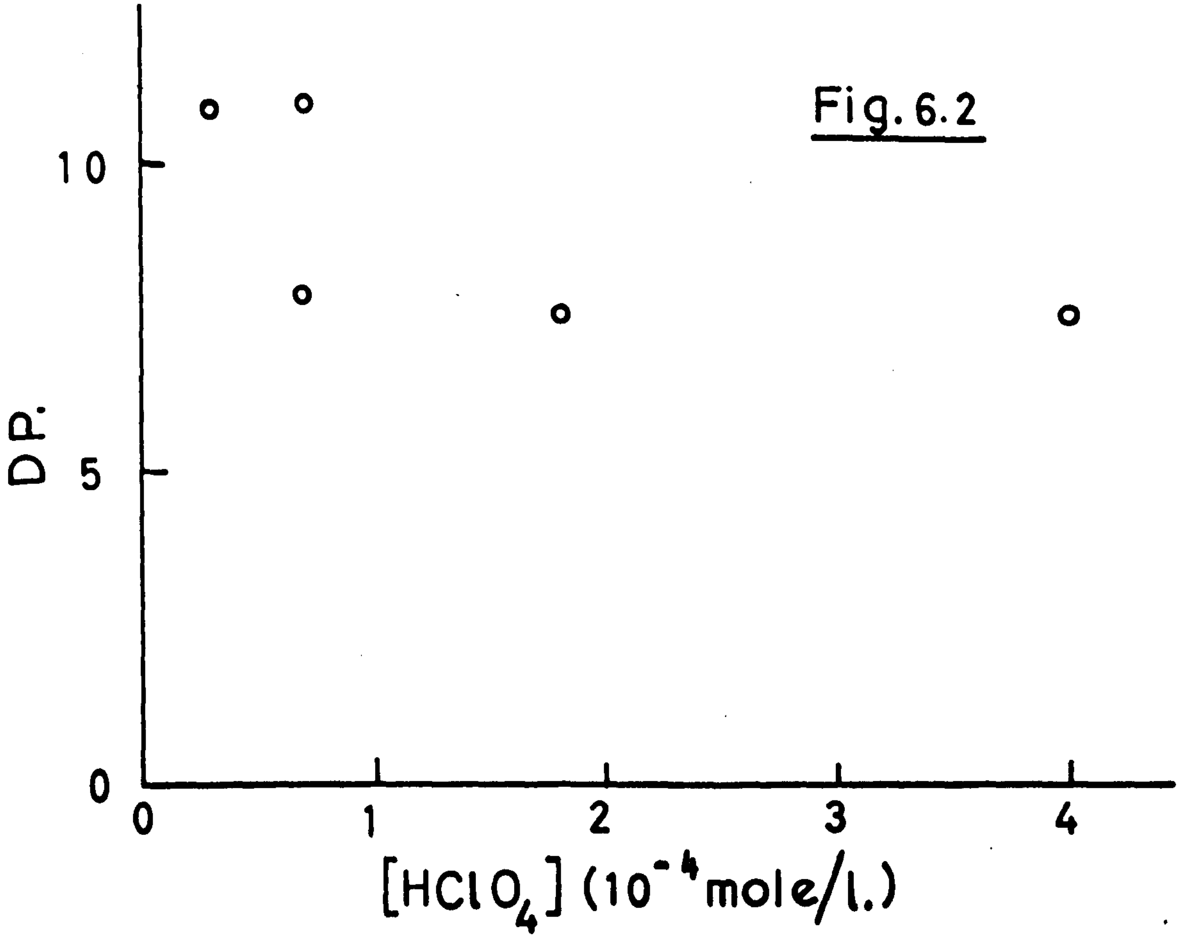

Fig. 6.2

10
5
0
DP.
0
1
2
3
4
[HClO$_4$] (10^{-4} mole/l.)

Table 6.3

DP Data for Polymerisations of 1,3-Dioxepane at T = -20°

Run No.	162	182^{x}	181	177	160	159	161	190^{x}	169	180^{x}	185
$[HClO_4]_A$, 10^4 M	0.8	0.25	0.29	0.31	0.60	1.3	1.8	2.6	1.9	0.2	3.8
[1,3-Dioxepane] M	1.00	0.80	0.80	0.80	0.80	0.80	0.80	0.80	0.60	0.60	0.35
Δ[1,3-Dioxepane] M	0.67	0.18	0.47	0.48	0.49	0.48	0.48	0.48	0.29	0.15	0.07
DP	12.7	16.7	10.8	9.1	9.4	8.7	9.2	7.8	6.1	14.2	3.3
% Cyclic Dimer	-	-	-	-	-	5.3	-	-	-	>1	-

Where Δ[1,3-Dioxepane] is the change in molar concentration of the monomer.

^{x} Experiments 182 and 180 were killed before equilibrium was reached.

^{x} Experiment 190 was killed 2 hours after equilibrium was reached.

Fig. 6.3 Plot of DP against 1,3-dioxepane concentration for polymerisations at -20°.

Table 6.4

DP Data for Polymerisations of 0.8 M 1,3-Dioxepane at T = 0°

Run No.	173	172	171
$[HClO_4]_A$, 10^4 M	0.9	1.5	2.4
DP	5.4	5.2	6.3
% Cyclic Dimer	-	11.0	-

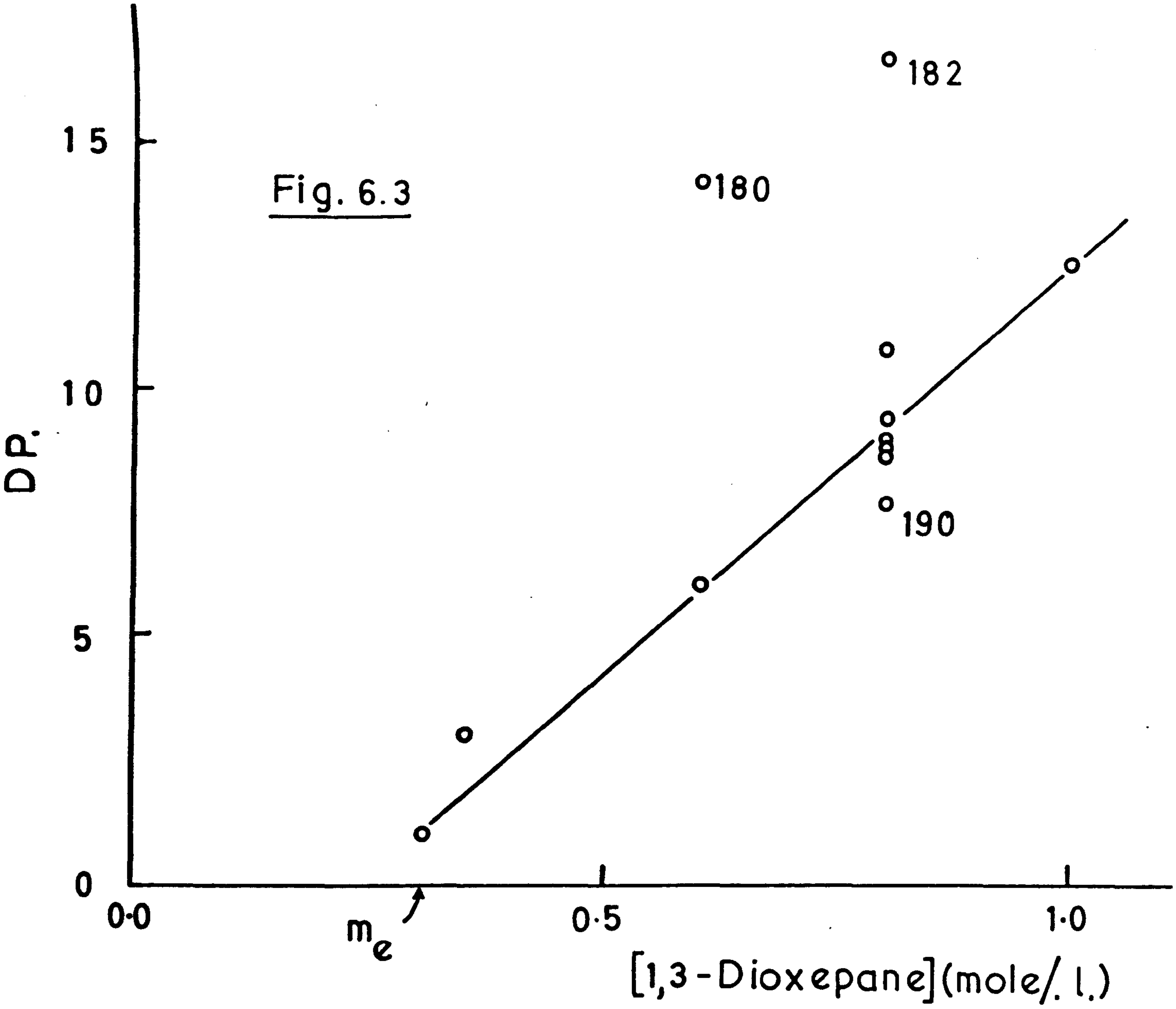

Fig. 6.3

In experiment 190 (Table 6.3) the polymerisation was allowed to remain at equilibrium at a constant temperature for two hours before neutralisation with ammonia. The number average DP of the polymer from experiment 190 was not significantly different from the number average DPs of similar polymerisations that were neutralised within a few minutes of the attainment of equilibrium conversion (experiments 159, 160, 161, 177 and 181). Furthermore, the electrical conductivity in experiment 190 was steady while the system was left at equilibrium which indicates that the viscosity of the solution did not change in this time.

Only three experiments are available for the polymerisation of 0.8 M 1,3-dioxepane at 0° (Table 6.4), and no significant variation of DP with the available concentration of perchloric acid is discernible.

6.5 Discussion

These results are interesting from several points of view. The infrared and N.M.R. spectra taken together show that product 134E (DP = 2.15 $\mp$ 1) m.p. = 90 - 92° is the cyclic dimer of 1,3-dioxepane and that polymers 134D (DP = 2.6) and 134C (DP = 6.0) are also cyclic. In no case was evidence found for the presence of any end groups. The N.M.R. spectra show that the polymers consist of regular units of the type;

$$- O - (CH_2)_4 - O - CH_2 - O - (CH_2)_4 - O - CH_2 -$$

These findings are in complete agreement with earlier findings[4,5] on the cyclic nature of poly-1,3-dioxolane prepared under anhydrous conditions. Recent experiments[6] in this Laboratory show that 1,3-dioxane can also be oligomerised by anhydrous perchloric acid to give the cyclic dimer of 1,3-dioxane and some cyclic oligomers as well.

The high polymer of 1,3-dioxepane is probably not all cyclic, as there will be enough residual water to break some of the rings. Previous experiments with 1,3-dioxolane showed that the residual water concentration was such that there was about one hydroxyl group per 100 molecules of polymerised monomer.

The production of a relatively large percentage of cyclic dimer is unusual, and was not observed with 1,3-dioxolane. The fractionation results for poly-1,3-dioxepane show that the whole range of molecular weights from dimer to very high polymer are produced. This is clearly a different situation from that described by Rose[3] for the polymerisation of oxacyclobutane by boron trifluoride, where linear high polymer and cyclic tetramer are produced simultaneously but the tetramer has no higher homologues.

The results concerning the dependence of the DP at equilibrium on the concentration of 1,3-dioxepane and the available concentration of perchloric acid are more difficult to understand. The first point that must be considered is the result from the Kinetics Chapter, (Chapter 8), that polymerisations of 1,3-dioxepane are without a termination step under the conditions used.

The simplest possible dependence of DP on monomer and catalyst concentrations, for a system with no termination step, has been reported by Szwarc[7] for the anionic polymerisation of styrene. The number average DP, at time t, is given by the expression

$$DP = (m_o - m_t)/c = \Delta m/c$$

where m_o is the initial concentration of monomer, m_t the concentration of monomer at time t and c is the concentration of active centres.

Polymerisations that are immediately killed have a narrow molecular weight distribution. However if the polymerisations are left, they establish the equilibrium molecular weight distribution which Brown and Szwarc[8] have shown to be of the Flory type if all the equilibrium constants K are identical. This redistribution of molecular weight in a living polymer system does not change the number average molecular weight. However the weight average molecular weight, and all other higher averages, increase as the system changes from the narrow molecular weight distribution to the Flory distribution.

The simplest possible case for the 1,3-dioxepane system is thus

$DP = \Delta m/a_A$ where a_A = the concentration of available perchloric acid. This should be valid at whatever stage the polymerisation is killed. In fact the DPs of poly-1,3-dioxepanes are found to be a hundred to a thousand times lower than this ideal DP. This suggests that the DP is being controlled by a transfer reaction, and as there is no evidence for transfer to solvent, the case of a living polymerisation with transfer to monomer will be considered.

Pepper[9] has derived theoretical equations for the effect of monomer-transfer on the DP in living polymerisations. His scheme is essentially as follows:

$P_1 + HA \longrightarrow P_1^+$ Fast initiation

$P_n^+ + P_1 \xrightarrow{k_p} P_{n+1}^+$ Propagation

$P_n^+ + P_1 \xrightarrow{k_{tr}} P_n + P_1^+$ Transfer where P_1 is monomer, P_n^+ protonated polymer, HA catalyst, and k_p and k_{tr} are the rate constants for the propagation and transfer reactions. If the initiation is complete we can write HA = c, the concentration of active centres.

The number average DP at any conversion, $(m_o - m_t)$ after time t, is given by the ratio of the number of moles of monomer consumed (N) to the total number of chains formed both by initiation (N_i) and by transfer (N_{tr}).

$$DP = N/(N_i + N_{tr})$$

$$= \int_o^t (k_p + k_{tr}) c\, m\, dt / (c + \int_o^t k_{tr}\, c\, m\, dt)$$

$$= (k_p + k_{tr}) \int_o^t m\, dt / (1 + k_{tr} \int_o^t m\, dt)$$

$$\text{Since } m_t = m_o \exp \left\{ - (k_p + k_{tr})\, c.t \right\}$$

$$\therefore \int_o^t m\, dt = (m_o - m_t)/(k_p + k_{tr})\, c$$

Substitute $\Delta m = m_o - m_t$

$$\text{then } DP = \frac{\Delta m}{c + \Delta m\, k_{tr}/(k_p + k_{tr})}$$

$$\therefore \quad 1/DP = c/\Delta m + k_{tr}/(k_p + k_{tr})$$

The reciprocal of the observed DP is thus equal to the reciprocal of the ideal DP (no transfer) plus a constant. This equation was tested by putting the available concentration of perchloric acid in place of c and Δ [1,3-dioxepane] for Δm for polymerisations at -20°. Experimentally the DP of poly-1,3-dioxepanes was found to vary much more with a change of 1,3-dioxepane concentration than with a change of the available concentration of perchloric acid. As Pepper's equation is only concerned with the ratio of catalyst concentration to the concentration of monomer polymerised it does not fit the experimental results. But Pepper's equation is valid for the change of DP with conversion in a system that is well below its ceiling temperature. What is required for the 1,3-dioxepane results is a scheme that will give the DP of the polymer at equilibrium. The following scheme was written as an attempt to adapt Pepper's scheme to the case of an equilibrium polymerisation.

$$P_1 + HA \longrightarrow P_1^+ \qquad \text{Fast initiation}$$

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

$$P_n^+ + P_1 \xrightarrow{k_{tr}} P_n + P_1^+ \qquad \text{Transfer}$$

$$DP = N/(N_i + N_{tr})$$

$$= \int_o^t k_p\, c(m - m_e)dt/(c + \int_o^t k_{tr}\, c\, m\, dt)$$

The rate of polymerisation is proportional to $(m - m_e)$, where m_e is the equilibrium concentration of monomer, whilst the rate of transfer depends on m.

At equilibrium

$$\int_0^t (m - m_e)dt = (m_o - m_e)/k_p c$$

and $$\int_0^t m\,dt = (m_o - m_e)/k_p c + m_e t$$

Let $m_o - m_e = \Delta m$

Thus $$DP = \frac{\Delta m}{c + k_{tr} c (\Delta m/k_p c + m_e t)}$$

This equation is clearly wrong as it implies that the DP will decrease with time as the transfer reaction continues after equilibrium has been reached. Experiment 190 shows that the DP did not change in 2 hours after equilibrium had been established and also that the viscosity of the solution did not alter. This indicates that the system had reached the equilibrium molecular weight distribution within a few minutes of the end of the polymerisation reaction.

For experiments 180 and 182 the polymerisations were neutralised well before equilibrium was reached and the DP of the resulting polymers was found to be considerably higher than for equivalent experiments that were allowed to reach equilibrium. It is clear that as equilibrium is approached, a relatively large amount of very low molecular weight poly-1,3-dioxepane is produced, in particular the cyclic dimer.

An alternative approach to the problem is to integrate the instanteous DP, $\overline{DP}$, from m_o to m_e to give the DP at equilibrium.

$$\overline{DP} = k_p\, c\, (m - m_e)/k_{tr}\, c\, m$$

The DP at equilibrium $= \int_{m_o}^{m_e} dm \Big/ \int_{m_o}^{m_e} \frac{1}{\overline{DP}}\, d\, m$

However $\int_{m_o}^{m_e} \frac{m}{m - m_e}\, d\, m$ tends to minus infinity so that the expression cannot be evaluated.

Probably the simplest approach would be to neutralise the polymerisation at very low conversions so that $m = m_o$ and the DP would be identical to the instantaneous DP.

The essential features of the DP results for the 1,3-dioxepane polymerisations are:

1. The DP at equilibrium is independent of the perchloric acid concentration. (The polymerisations with very low acid concentration were probably neutralised too soon i.e. before the system had reached the equilibrium molecular weight distribution, so that the DP is too high in these cases).

2. The DP at equilibrium depends on the initial monomer concentration and the final temperature only.

The general equation of the line in Fig. 6.3 is

$$DP = k'' \left(m_o - m_e \right) = k'' \Delta m$$

A similar relationship was found by Sims for the DP of polytetrahydrofuran at low conversions, catalysed by phosphorus pentafluoride and epichlorohydrin.

Sims states that this relationship is in accordance with a reversible living system showing no termination or transfer up to this point. However as this equation does not contain the catalyst concentration it is impossible to state that transfer has not occurred.

Conclusion

As far as I am aware no satisfactory treatment of the DP at equilibrium for equilibrium polymerisations with transfer to monomer has been published. The attempts that have been made in this thesis to describe the DP of the system at equilibrium have all failed.

References to Chapter 6

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Chapter 7

Thermodynamics of the Polymerisation of 1,3-Dioxepane.

Introduction Chapter 4 of my M.Sc. Thesis contains a section on the theory of equilibrium polymerisation and it describes the thermodynamics of the polymerisation of 1,3-dioxolane. This study of the thermodynamics of the polymerisation of 1,3-dioxepane has been carried out along the same lines. The equilibrium constant, K, for these polymerisations was calculated from the expression[1]

$$K = (DP-1)/DP\ m_e,$$

where m_e is the equilibrium concentration of monomer and DP is the number average degree of polymerisation of the polymer formed. This expression is valid provided that the equilibrium constant, K, does not vary with DP. When the DP is very large (DP-1)/DP tends to unity and $K = 1/m_e$.

7.1 Measurement of the Equilibrium Constant at Constant Temperature.

Results A series of polymerisation experiments was carried out with various initial concentrations of monomer (Table 7.1) and the reaction mixtures were neutralised when equilibrium was reached. The final temperature for each reaction was approximately constant at -17°. The equilibrium concentration of monomer was measured by weighing the polymer isolated and subtracting this weight from the mass of monomer used. The DP of each polymer was also determined so that the equilibrium constant could be determined in each case.

Discussion For polymerisations with initial concentration of 1,3-dioxepane between 0.5 and 1.0 M the value of K is essentially constant at constant

Table 7.1

The Measurement of the Equilibrium Constant for 1,3-Dioxepane Polymerisations at Constant Temperature.

Run No.	185	165	163	160	161	162
[Dioxepane], M.	0.35	0.5	0.60	0.80	0.8	1.00
m_e, M.	0.28	0.32	0.31	0.30	0.32	0.33
DP.	3.3	5.5	6.1	9.4	9.2	12.7
K, M^{-1}.	2.43	2.60	2.70	2.94	2.76	2.80
Final Temp. deg.	-17	-19	-18	-17	-17	-16

temperature.

The equilibrium monomer concentration for poly-1,3-dioxepane of infinite DP at -17° was calculated by taking the average value of $K = 2.85\ M^{-1}$ for experiments 160 and 161 and substituting into the expression $K = 1/m_e$. From this $m_e = 0.35$ M at -17°.

Experiment 185 was carried out at this concentration of 1,3-dioxepane so that formation of high polymer was impossible. In fact about 18% of oligomers (DP approx. 3) was formed above the ceiling temperature for high polymer.

This can happen when (a) ΔH becomes more negative as the DP decreases; (b) ΔS becomes less negative as the DP decreases.

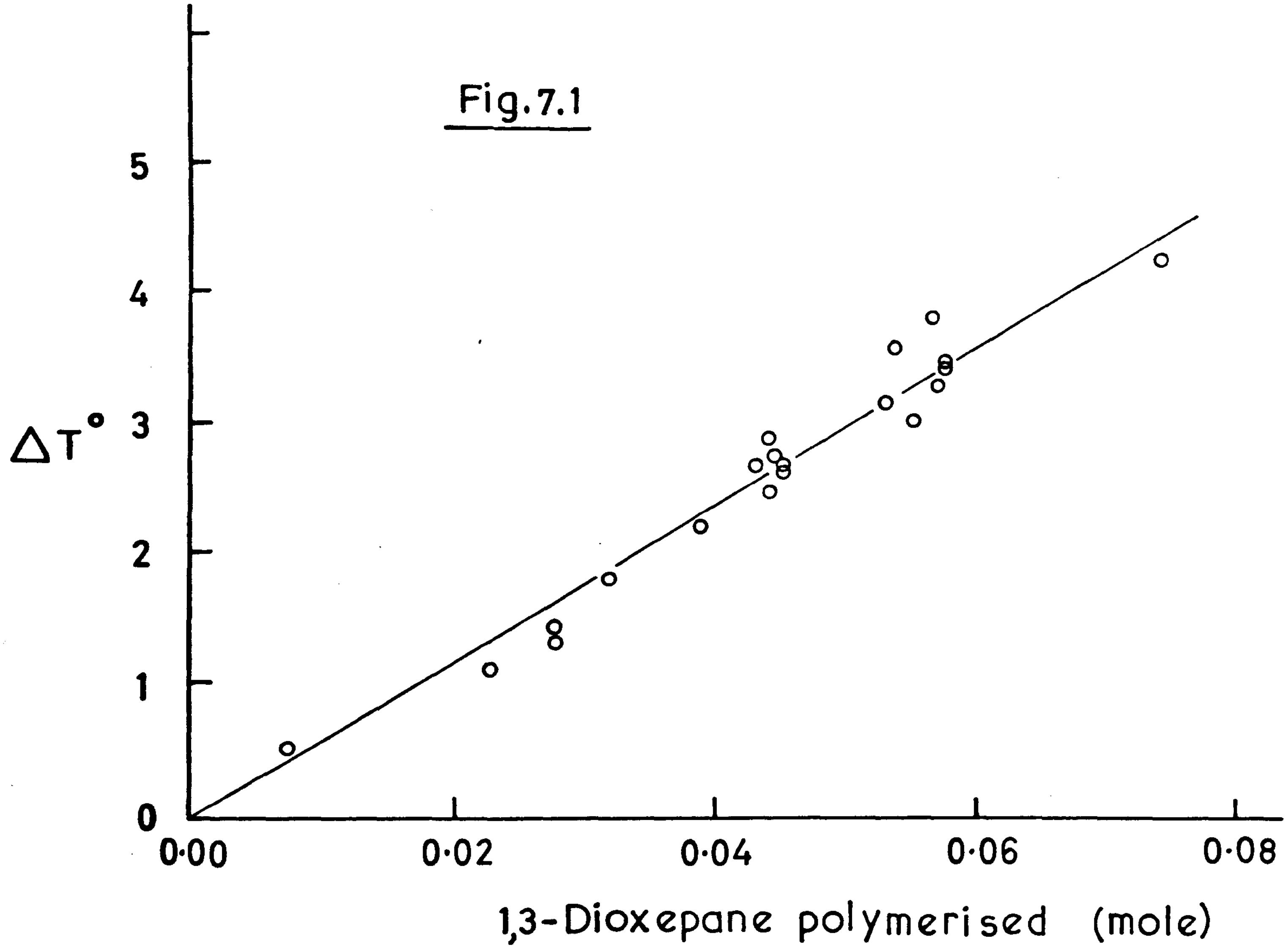
The heat of oligomerisation calculated from the temperature rise for experiment 185 is $\Delta H_{ss} = -4.2$ kcal.mole^{-1}. This compares with a heat of polymerisation of $\Delta H_{ss} = -3.7$ kcal.mole^{-1}. calculated from the graph of ΔT against the number of moles polymerised (Fig. 7.1), which is valid for polymers having a DP of approx. 10. The value of ΔH calculated from one experiment only is subject to quite large errors, so that this comparison of the heats of oligomerisation and polymerisation can only suggest that there may be a slight increase of ΔH as the DP decreases. It is difficult to say whether the heat of polymerisation for the formation of cyclic dimer and trimer should be greater or smaller than for high polymer.

The reason why ΔS should become less negative as the DP decreases is as follows. The standard entropy of the monomer in the gaseous state $S_g{}^{o}$ is given by the sum of the translational entropy S_t, external rotational entropy S_r, vibrational entropy S_v and internal rotational entropy S_{ir}. For

Fig. 7.1

Plot of ΔT against the number of moles of 1,3-dioxepane polymerised (Table 7.2).

Fig.7.1



high polymer $S_v + S_{ir}$ is much greater than $S_t + S_r$ so that S_t and S_r may be neglected. However, for dimer and trimer S_t and S_r will still be significant, so that the entropy of these species will be considerably higher than for high polymer. This means that ΔS will be less negative for the production of oligomers than for high polymer.

7.2 Variation of Equilibrium Constant with Temperature.

Results

Table 7.2 contains the data for polymerisations carried out at various temperatures. It consists essentially of a series of values of m_e as a function of temperature. m_e is independent of the initial monomer concentration and of the catalyst concentration, but the calculation of K from m_e does involve the DP of the polymer produced.

A graph of log K against 1/T has a slope

$$d(\log K)/d(1/T) = -\Delta H^o/2.3\ R\,.$$

This graph is shown in Fig. 7.2 and the value calculated from the slope of the graph is

$$\underline{\Delta H^o_{ss} = -3.5 \mp 0.3\ \text{kcal.mole}^{-1}.}$$

The standard free energy change was calculated from the relation

$$\Delta G^o_{ss} = -RT\ \ln K$$

These values of ΔG^o_{ss} are included in Table 7.2. Fig. 7.3 shows a graph of ΔG^o_{ss} against temperature. ΔG^o_{ss} becomes zero at the ceiling temperature for the system in the standard state, $T_c^{\,o}$. From the graph

$$\underline{T_c^{\,o} = 300^oK = +27^oC.}$$

Table 7.2

The Variation of the Equilibrium Constant with Temperature for 1,3-Dioxepane Polymerisations.

Run No.	148	149	150	153	155	156	136	137	138	139	144	146	154	x143	165	163	160	161	162	135	171	172	[illegible]
[Dioxepane], M.	0.60	0.60	0.60	0.60	0.60	0.60	0.60	0.60	0.60	0.60	0.60	0.60	0.60	0.60	0.50	0.60	0.80	0.80	1.00	0.35	0.80	0.80	[illegible]
m_e, M.	0.07	0.08	0.05	0.07	0.08	0.08	0.21	0.19	0.20	0.21	0.20	0.21	0.19	0.28	0.32	0.31	0.30	0.32	0.33	0.29	0.48	0.47	0.47
DP	21.6	10.7	8.3	11.2	12.6	11.0	6.5	11.0	10.8	14.8	7.6	7.1	7.8	4.1	5.5	6.1	9.4	9.2	12.7	3.3	6.3	5.2	5.4
K, M^{-1}.	14.24	11.70	16.50	12.22	11.50	11.72	4.00	4.80	4.54	4.40	4.30	4.11	4.54	2.70	2.60	2.70	2.94	2.76	2.80	2.43	1.70	1.64	1.70
ΔG^o_{ss}, cal. $mole^{-1}$.	-1114	-1036	-1175	-1050	-1023	-1032	-642	-732	-710	-692	-681	-662	-710	-484	-477	-500	-550	-518	-525	-453	-304	-274	-304
Final Temp. deg.	-62	-61	-62	-62	-62	-62	-37	-37	-37	-37	-37	-37	-37	-25	-19	-18	-17	-17	-16	-17	+ 2	+ 2	+ 2
ΔT. deg.	3.3	3.8	3.6	3.5	3.7	3.5	-	2.7	2.5	-	2.9	2.7	2.6	2.7	1.1	1.8	3.0	2.9	4.2	0.5	1.0	[illegible]	-
Monomer Polymerised, Moles	0.057	0.056	0.053	0.058	0.057	0.057	0.043	0.045	0.044	0.042	0.044	0.043	0.045	-	0.023	0.032	0.055	0.053	0.074	0.007	0.035	0.034	0.035
[$HClO_4$], 10^4 M	4.1	5.7	7.3	3.0	5.6	5.2	11.5	1.6	1.2	1.0	5.0	4.0	1.6	10.4	2.06	2.1	1.4	2.6	2.1	[illegible]	2.4	1.5	0.9

x Reaction 143 was carried out at -40° but was killed at -25°.

Fig. 7.2

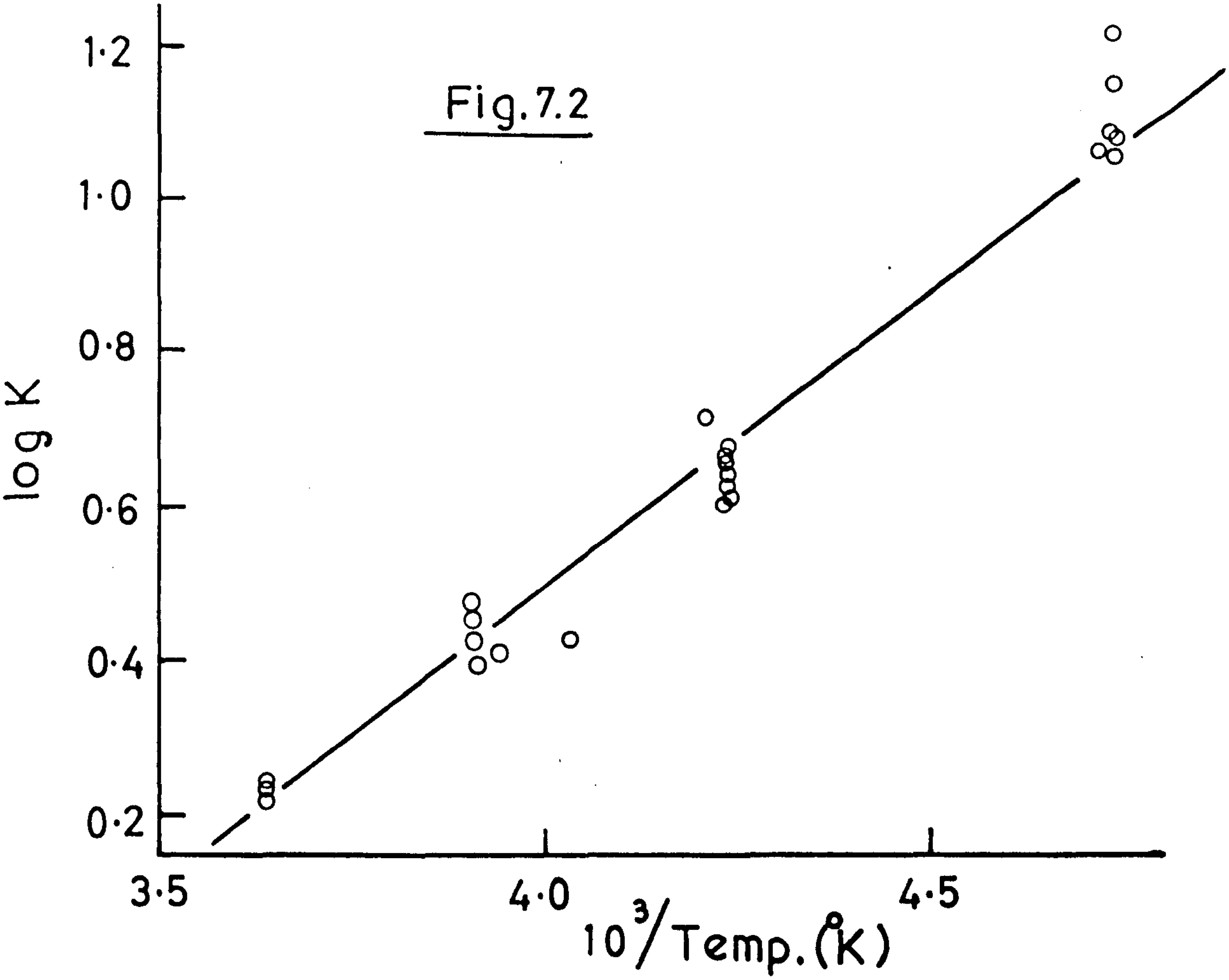
Plot of log K against 1/T for 1,3-dioxepane polymerisations (Table 7.2).

Fig. 7.3

Plot of ΔG^{o}_{ss} against temperature for 1,3-dioxepane polymerisations (Table 7.2).

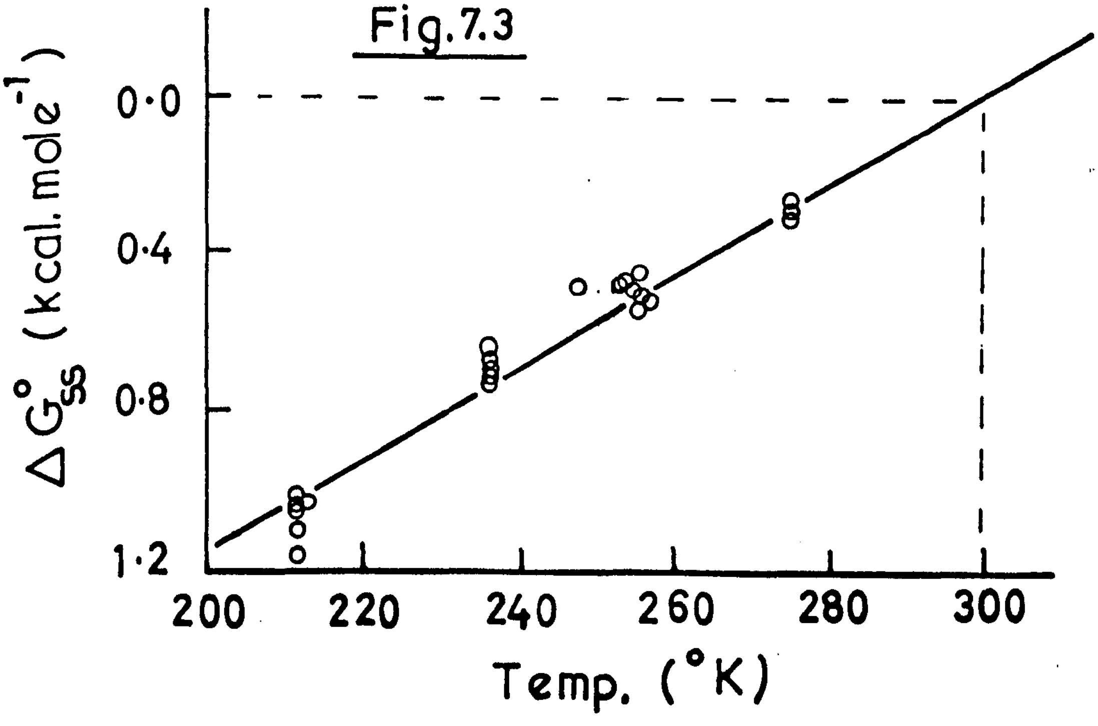
$\Delta G^{o}_{ss} = 0$ at 300°K

Fig. 7.2



1·2
1·0
0·8
0·6
0·4
0·2
log K
3·5
4·0
4·5
10³/Temp. (°K)

Fig. 7.3



0·0
0·4
0·8
1·2
ΔG°ss (kcal. mole⁻¹)
200
220
240
260
280
300
Temp. (°K)

The slope of the graph gave the standard entropy change for the polymerisation reaction

$$\underline{\Delta S^{o}_{ss} = -11.7 \mp 1.5 \text{ cal.deg}^{-1}.\text{mole}^{-1}.}$$

Another determination of $T_c^{\ o}$ was made from the same data. Substitution of $\Delta H^{o}_{ss} = -3.5$ kcal. mole^{-1} and $\Delta S^{o}_{ss} = -11.7$ cal.deg^{-1}.mole^{-1} gives

$$\underline{T_c^{\ o} = \Delta H^{o}_{ss}/\Delta S^{o}_{ss} = 299^{o}\text{K} = +\ 26^{o}\text{C}.}$$

Discussion

The graph of log K against 1/T (Fig. 7.2) is essentially linear, which shows that the heat of polymerisation does not vary much with temperature over the range considered. Thus ΔH_{ss} can be considered equivalent to ΔH^{o}_{ss}.

The value of $\Delta H^{o}_{ss} = -3.5 \mp 0.3$ kcal.mole^{-1} is in good agreement with the value of $\Delta H_{ss} = -3.7 \mp 0.2$ kcal.mole^{-1} determined calorimetrically. This is to be compared with a value of $\Delta H_{gg} = -4.7$ kcal.mole^{-1} that has been estimated[2] for the heat of polymerisation of 1,3-dioxepane.

The standard heats and entropies of polymerisation and the standard ceiling temperatures for 1,3-dioxolane[3] and 1,3-dioxepane are listed below.

Table 7.3

	1,3-Dioxolane	1,3-Dioxepane
ΔH^{o}_{ss} kcal.mole^{-1}.	-5.1	-3.5
ΔS^{o}_{ss} cal.deg^{-1}.mole^{-1}.	-18.6	-11.7
$T_c^{\ o}$ deg.	+1.5	+27

If the polymers produced are assumed to be essentially free from strain, the heat of polymerisation provides a direct measure of the strain energy in the ring compound itself. The 5-membered ring 1,3-dioxolane is strained because of bond angle deformation. The 7-membered ring 1,3-dioxepane is strained because of the crowding of hydrogen atoms within the ring and the 6-membered ring -1,3-dioxane was estimated[2] to have ΔH_{gg} = 0.0 kcal.mole^{-1}.

There are no values available in the literature for the entropies of polymerisation of 1,3-dioxolane and 1,3-dioxepane, but the entropies of polymerisation for the cycloalkanes have been estimated[4]. These entropies of polymerisation are for liquid monomer to condensed (liquid or amorphous solid) polymer. For the 5-membered ring ΔS_{1c} = -10.2 cal.deg^{-1}.mole^{-1} and for the 7-membered ring ΔS_{1c} = -0.7 cal.deg^{-1}.mole^{-1}. A direct comparison between these results and the experimental results for 1,3-dioxolane and 1,3-dioxepane is not good because of the different states of the monomer and polymer and because of the presence of oxygen atoms in the monomers studied. However the entropy of polymerisation of the 7-membered ring is 9.5 cal.deg^{-1}.mole^{-1} less negative than that of the 5-membered ring. Experimentally the entropy of polymerisation of 1,3-dioxepane is 7 cal.deg^{-1}.mole^{-1} less negative than that of 1,3-dioxolane. The experimental difference in the entropy of polymerisation between the 7 and the 5 membered ring monomers is in good agreement with the estimated difference in the entropy of polymerisation for the corresponding cycloalkanes.

7.3 Calorimetric Determination of the Heat of Polymerisation of 1,3-Dioxepane.

Results

Table 7.2, also contains the temperature rise ΔT that was recorded for each polymerisation. The polymer was isolated and weighed so that the number of moles of 1,3-dioxepane polymerised could be calculated, and a graph of ΔT against moles polymerised could be drawn Fig. 7.1.

Although various quantities of monomer and solvent were used at different temperatures, the total volume of reagents in the calorimeter at the temperature of the experiment was kept constant at 110 ml. Before some of the polymerisations, the heat capacity of the calorimeter plus contents was measured. The heat capacity = 62 ∓ 2 cal.deg^{-1}. From the graph 1 mole of 1,3-dioxepane produces a temperature rise of 59° on polymerisation.

$$\underline{\Delta H_{ss} = -3.7 \mp 0.2 \text{ kcal.mole}^{-1}.}$$

Two depolymerisations were carried out (168 and 170); full details of these experiments will be found in Table 8.6. The two values of ΔH from these experiments are,

$\Delta H_{ss} = + 2.9$ kcal.mole^{-1}. for Expt. 168

$\Delta H_{ss} = + 3.2$ kcal.mole^{-1}. for Expt. 170

Average value $\underline{\Delta H_{ss} = + 3.0 \mp 0.4 \text{ kcal.mole}^{-1}.}$

Discussion

The graph of ΔT against the number of moles of 1,3-dioxepane polymerised is linear and it passes through the origin. This is valid for polymers having DPs from 3 to 20 and shows that ΔH_{ss} is essentially independent of DP over this range.

The values of ΔH_{ss} obtained from the depolymerisation experiments are in reasonable agreement with ΔH_{ss} obtained from polymerisations.

References to Chapter 7

1 A.V. Tobolsky, 'Properties and Structure of Polymers'. John Wiley and Sons, Inc., New York, 1960.

2 S.M. Skuratov, A.A. Strepikheev, S.M. Shtekher and A.V. Volokhina, Doklady Akad. Nauk, S.S.S.R., 1957, 117, 263.

3 P.H. Plesch and P.H. Westermann, International Symposium on Macromolecular Chemistry, Prague, 1965, P.506.

4 F.S. Dainton, T.R.E. Devlin and P.A. Small, Trans. Faraday Soc., 1955, 51, 1710.

Chapter 8

The Kinetics of the Polymerisation of 1,3-Dioxepane.

8.1 Description of the Polymerisations. All polymerisations of 1,3-dioxepane were carried out in the adiabatic calorimeter. Fig. 8.1 illustrates a typical polymerisation (experiment 137) the experimental details of which are given in Table 8.2. The polymerisation was accurately first order (Fig. 8.2) and the electrical conductivity of the solution was found to rise to a maximum immediately the perchloric acid phial was broken. The conductivity then fell steadily as the polymerisation proceeded.

8.2 Polymerisation Kinetics. The data for polymerisations at -65° are shown in Table 8.1. k_1 was calculated from the slope of the first order plot for each polymerisation reaction. The plot of k_1 against perchloric acid concentration should go through the origin and have a slope of k_p, the propagation rate constant. Fig. 8.3 is the experimental plot of k_1 against perchloric acid concentration. Experiments 148, 149 and 150, were all carried out with a pumping time of 1 hour. The plot of k_1 against perchloric acid concentration for these points is a reasonable straight line and the value of k_p was calculated from its slope. However there is a large intercept of approx. 3.6×10^{-4} M on the perchloric acid concentration axis.

When the pumping time was increased to 4 hours (experiments 152 and 153) the intercept was cut to about 2.0×10^{-4} M. Polymerisations carried out with a pumping time of 3 hours (experiments 156 and 155) gave a similar intercept. All other polymerisations in this work were carried out with a pumping time of 3 hours. However previous experience with this apparatus

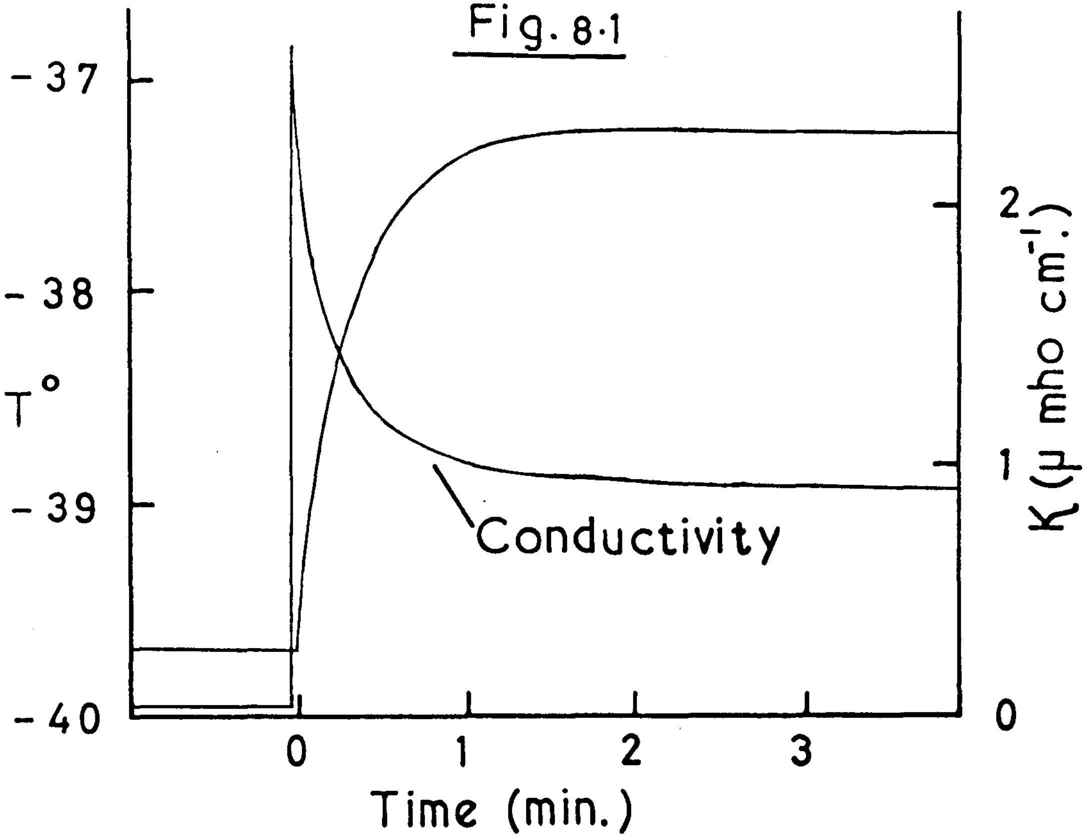
Fig. 8.1

Simultaneous plot of temperature and electrical conductivity against time for experiment 137 (the polymerisation of 0.6 M 1,3-dioxepane with 1.6×10^{-4} M perchloric acid at -40°) Table 8.2.

Fig. 8.2

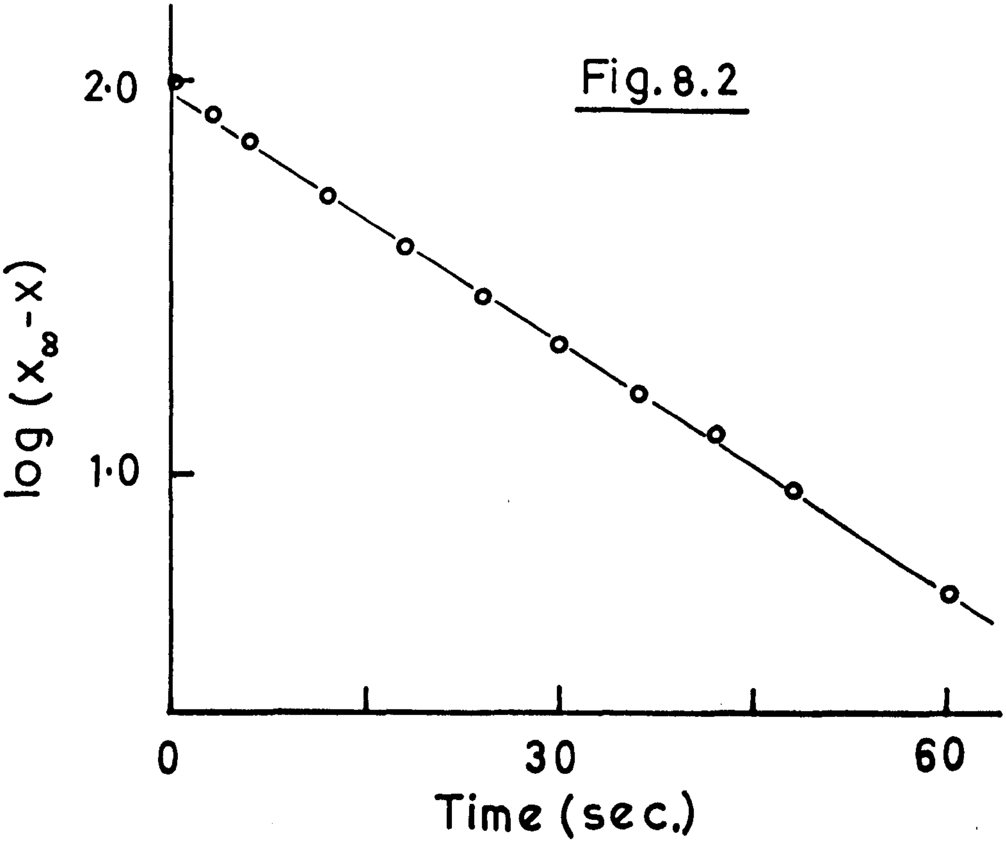
First order plot for experiment 137. From the graph $k_1 = 0.049 \text{ sec}^{-1}$.

Fig. 8.1



- 37
- 38
T°
- 39
- 40
0
1
2
3
Time (min.)
Conductivity
K (μ mho cm^{-1})
2
1
0

Fig. 8.2



2·0
1·0
log $(x_\infty - x)$
0
30
60
Time (sec.)

Table 8.1

Data for Polymerisations of 0.6 M 1,3-Dioxepane at T = -65°.

Run No.	148	149	150	153	152	156	155	158^x	157^x
$[HClO_4]$, 10^4M.	4.1	5.7	7.3	3.0	3.8	5.2	5.6	4.2	6.5
k_1, sec^{-1}.	0.027	0.089	0.17	0.042	0.078	0.12	0.14	0.052	0.13
DP	21.6	10.7	8.3	11.2	10.8	11.0	12.6	14.3	11.0
Conversion %	86	85	90	87	-	87	87	86	88
Pumping time, hrs.	1	1	1	4	4	3	3	3	3

[x] Experiments 158 and 157 were carried out with 2.0 x 10^4 M added water.

Fig.8.3 Plot of k_1 against perchloric acid concentration for 0.6 M 1,3-Dioxepane at -65°.

From Fig.8.3 $k_p = k_1/[HClO_4] = (2.6 \mp 0.1) \times 10^4$ litre mole^{-1}min^{-1}.

Table 8.2

Data for Polymerisations of 0.6 M 1,3-Dioxepane at T = -40°.

(Pumping Time 3 hours).

Run No.	138	137	154	151	164
$[HClO_4]$, 10^4M.	1.2	1.6	1.8	2.7	4.0
k_1, sec^{-1}.	0.036	0.049	0.070	0.190	0.29
DP	10.8	11.0	7.8	7.6	-
Conversion %	67	68	68	67	-

Fig.8.4 Plot of k_1 against perchloric acid concentration for 0.6 M 1,3-Dioxepane at -40°.

From Fig.8.4 $k_p = k_1/[HClO_4] = (5.5 \mp 0.2) \times 10^4$ litre mole^{-1} min^{-1}.

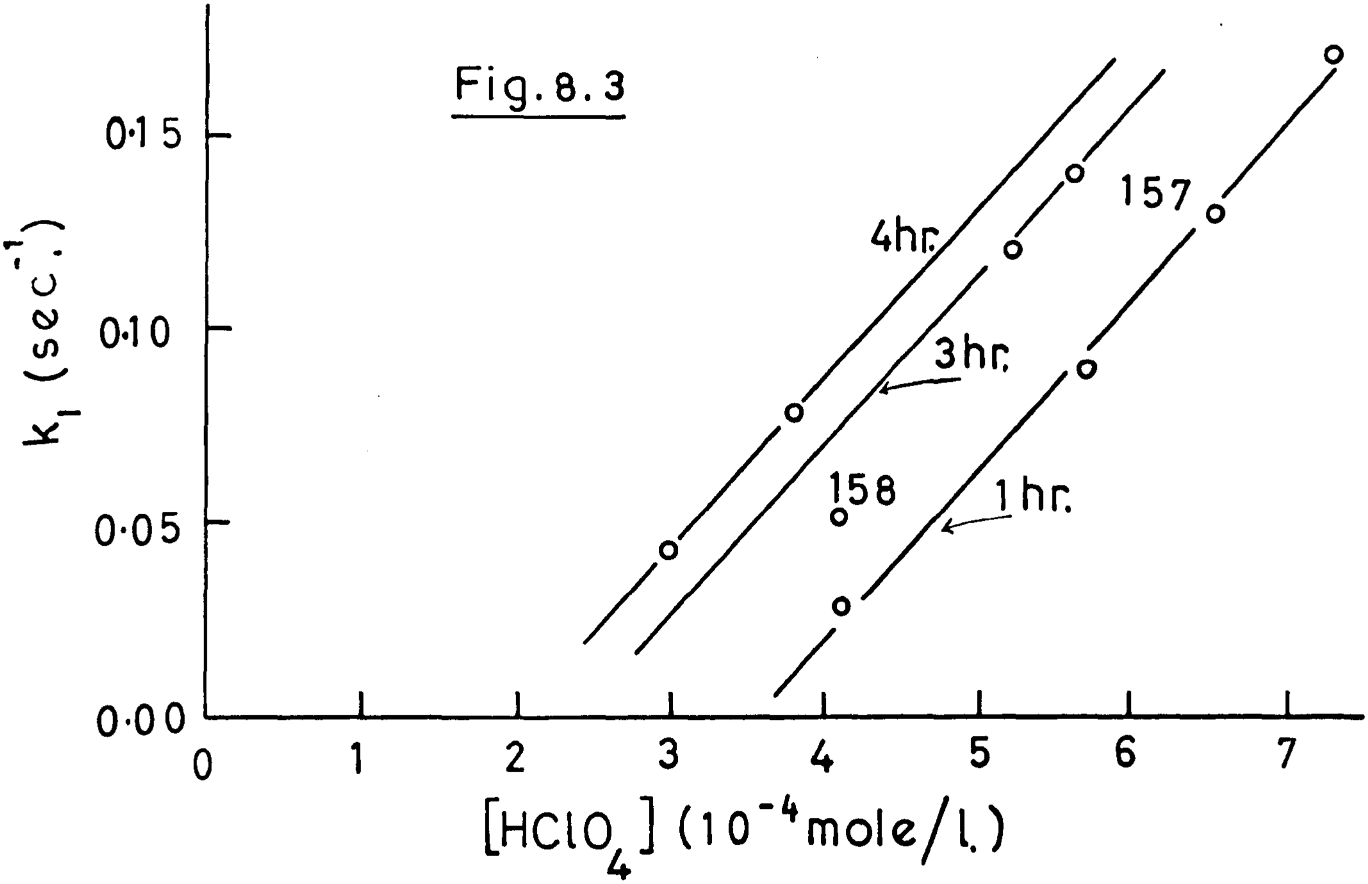


Fig. 8.3

k_1 (sec.$^{-1}$)
0·15
0·10
0·05
0·00
4hr.
3hr.
1hr.
157
158
0
1
2
3
4
5
6
7
[$HClO_4$] (10^{-4}mole/l.)

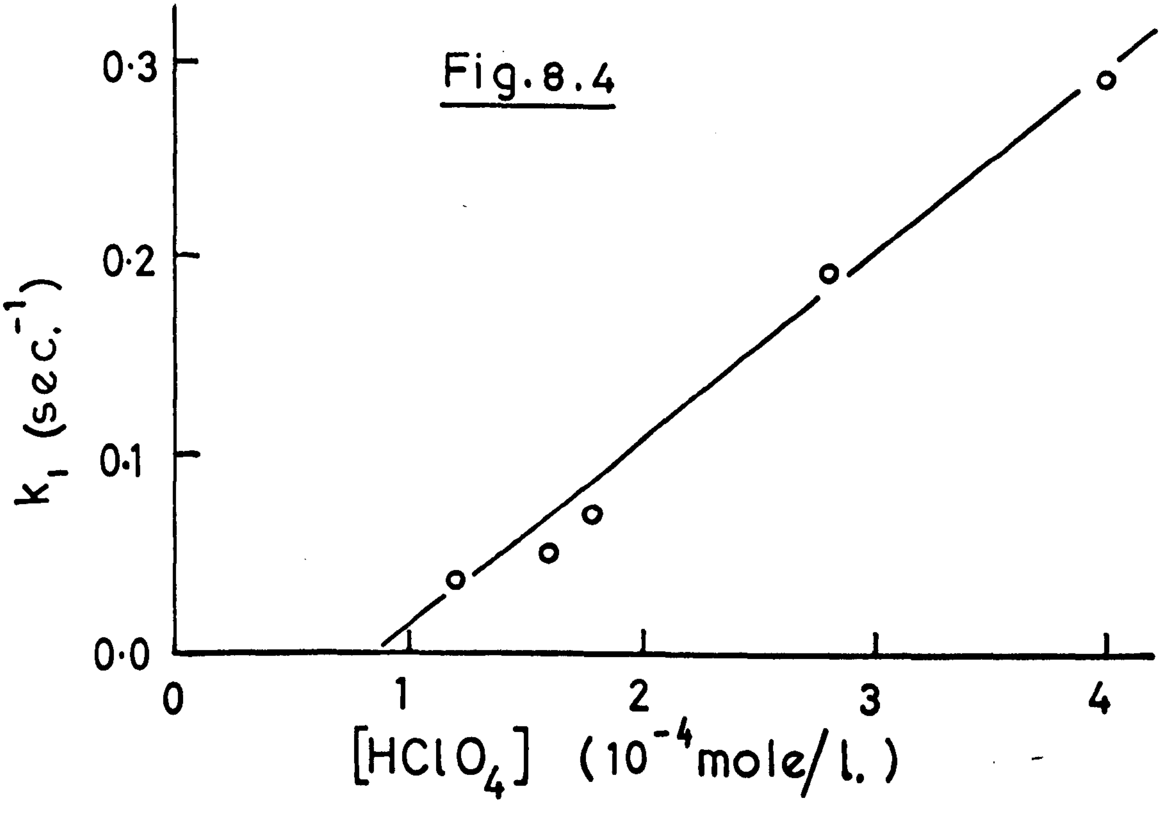


Fig. 8.4

k_1 (sec.$^{-1}$)
0·3
0·2
0·1
0·0
0
1
2
3
4
[$HClO_4$] (10^{-4}mole/l.)

and with the techniques used indicated that a residual water concentration of about 10^{-5} M should have been obtained. The intercept is thus not wholly due to the residual water.

Additions of water (experiments 158 and 157) were made in the following way. After the vessel had been evacuated for 3 hours and isolated from the vacuum line, a phial of water was broken. The vessel was then cooled and 1,3-dioxepane and solvent were distilled in. The polymerisation was carried out in the usual way. This method is not ideal as some of the water is adsorbed on the walls of the vessel, but the effect of the added water is clearly shown by the reduction in k_1. These polymerisations were all first order reactions.

Table 8.2 shows the data for polymerisations at -40°. Fig. 8.4 is the plot of k_1 against perchloric acid concentration. The pumping time was 3 hours and no additions of water were made. The intercept is about 1×10^{-4} M on the perchloric acid concentration axis.

Table 8.3 shows the data for polymerisations at -20° and Fig. 8.5 is the plot of k_1 against perchloric acid concentration. Experiments 160, 159 and 161 were carried out with 0.8 M 1,3-dioxepane. The plot of k_1 against perchloric acid concentration is a good straight line and the value of k_p was calculated from its slope. Experiment 162 was carried out with 1.0 M 1,3-dioxepane and 163 with 0.6 M 1,3-dioxepane. It will be seen from Fig. 8.5 that the intercept increases as the concentration of monomer increases. Fig. 8.6 is a plot of k_1 against 1,3-dioxepane concentration for constant perchloric acid concentration = 2.1×10^{-4} M at -20°. This graph shows that there is some impurity in the 1,3-dioxepane that is neutralising the perchloric acid.

Table 8.3

Data for 1,3-Dioxepane Polymerisations at T = -20°. (Pumping Time 3 hours).

Run No.	162	160	159	161	163	181^x	177^x	176^x
[1,3-Dioxepane],M.	1.00	0.80	0.80	0.80	0.80	0.80	0.80	0.80
$[HClO_4]$, x 10^4 M.	2.1	1.4	2.1	2.6	2.1	0.29	0.31	1.73
k_1, sec^{-1}.	0.133	0.104	0.236	0.322	0.353	0.07	0.084	0.35
DP	12.7	9.4	8.7	9.2	6.1	10.8	9.1	-
Conversion %	67	62	60	60	48	58	61	-

^{x} Experiments 181, 177, 176 were carried out with a new batch of 1,3-dioxepane.

Fig. 8.5 Plot of k_1 against perchloric acid coneentration for 1,3-Dioxepane Polymerisations at -20°.

From Fig. 8.5 $k_p = k_1/[HClO_4] = (1.1 \mp 0.06) \times 10^5$ litre mole^{-1} min^{-1}.

Table 8.4

Data for Polymerisations of 0.8 M 1,3-Dioxepane at T = 0°.

(Pumping Time 3 hours).

Run No	173	172	171
$[HClO_4]$ 10^4,M	0.9	1.5	2.4
k_1, sec^{-1}.	0.285	0.457	0.629
DP	5.4	5.2	6.3
Conversion %	39	39	41

Fig. 8.7 Plot of k_1 against perchloric acid concentration for 0.8 M 1,3-Dioxepane at 0°.

From Fig. 8.7 $k_p = k_1/[HClO_4] = (1.9 \mp 0.06) \times 10^5$ litre mole^{-1} min^{-1}.

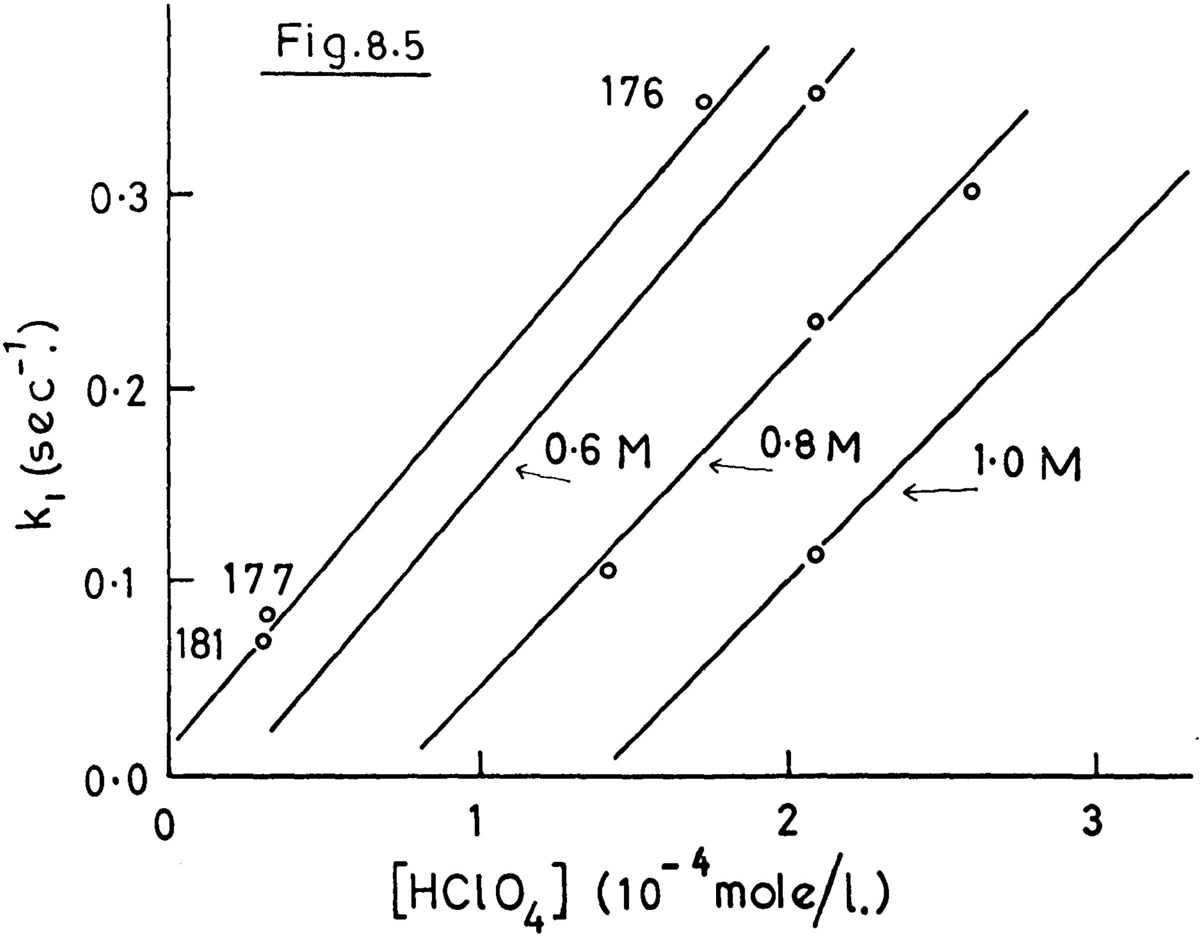


Fig. 8.5

176
177
181
0.6 M
0.8 M
1.0 M
0.0
0.1
0.2
0.3
0
1
2
3
k_1 (sec^{-1}.)
[HClO$_4$] (10^{-4} mole/l.)

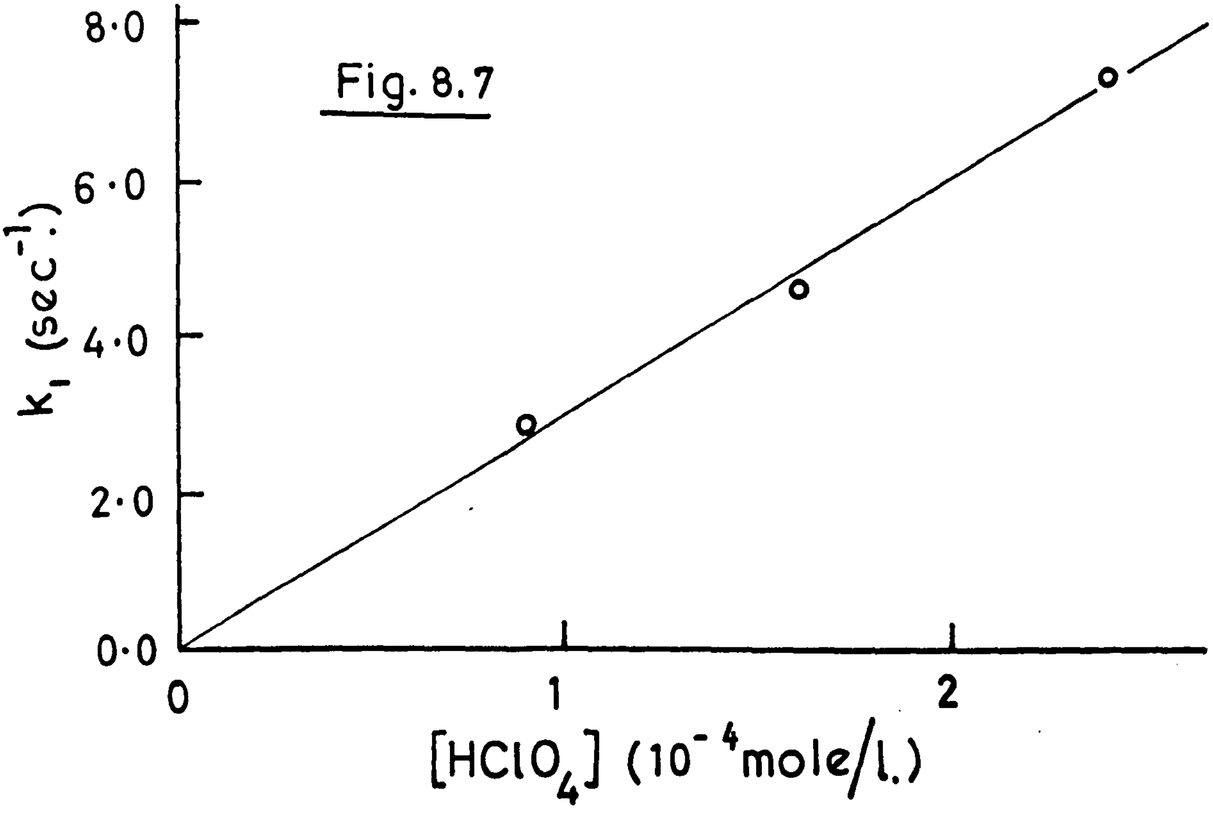


Fig. 8.7

0.0
2.0
4.0
6.0
8.0
0
1
2
k_1 (sec^{-1}.)
[HClO$_4$] (10^{-4} mole/l.)

Fig. 8.6

Plot of k_1 against 1,3-dioxepane concentration for polymerisations of 1,3-dioxepane at constant perchloric acid concentration = 2.1×10^{-4} M at -20° (Table 8.3).

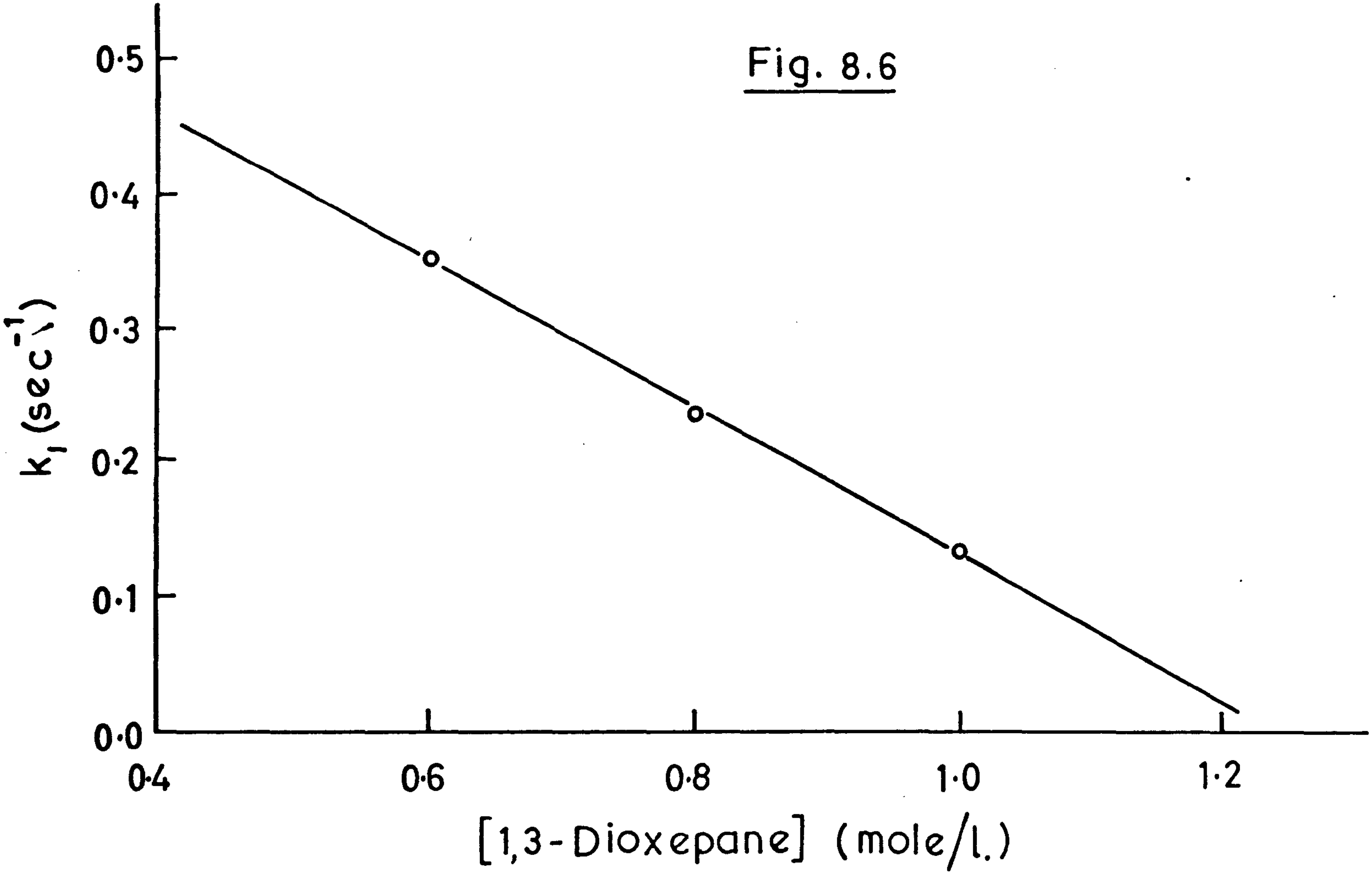


Fig. 8.6

The 1,3-dioxepane in the reservoir was analysed and found to contain 100 ppm of tetrahydrofuran. For 1 M 1,3-dioxepane this would give an intercept of approx. 1×10^{-4} M if all the tetrahydrofuran neutralised an equivalent of perchloric acid. Another batch of 1,3-dioxepane was prepared and carefully distilled until it contained less than 20 ppm of tetrahydrofuran. Experiments 181, 177 and 176 were carried out with this monomer and the plot of k_1 against perchloric acid concentration passes through the origin (Fig. 8.5).

Table 8.4 shows the data for polymerisations at 0°. Fig. 8.7 is the plot of k_1 against perchloric acid concentration; this is a reasonable straight line, but it is observed to pass through the origin. These experiments were carried out with the old batch of monomer which contained 100 ppm of tetrahydrofuran, so that some intercept should have been observed. However these polymerisation curves were found to be very slightly S-shaped (Fig. 8.8). Only the last half of these polymerisations is of first order (Fig. 8.9).

In all these experiments the conversion was found to be independent of the perchloric acid concentration and dependent on the initial concentration of 1,3-dioxepane and on the temperature. Not only was the DP dependent on the initial concentration of 1,3-dioxepane and the temperature, but is also decreased slightly as the perchloric acid concentration increased (Figs. 6.1 and 6.2).

Fig. 8.10 is the Arrhenius plot for polymerisations at -65°, -40°, -20° and 0°. The plot is a reasonable straight line from which the activation energy of the polymerisation of 1,3-dioxepane was calculated as

$E_p = 3.5 \pm 0.3$ kcal.mole^{-1}.

Fig. 8.8

Simultaneous plot of temperature and electrical conductivity against time for experiment 172 (the polymerisation of 0.8 M 1,3-dioxepane with 1.5×10^{-4} M perchloric acid at 0°) Table 8.4.

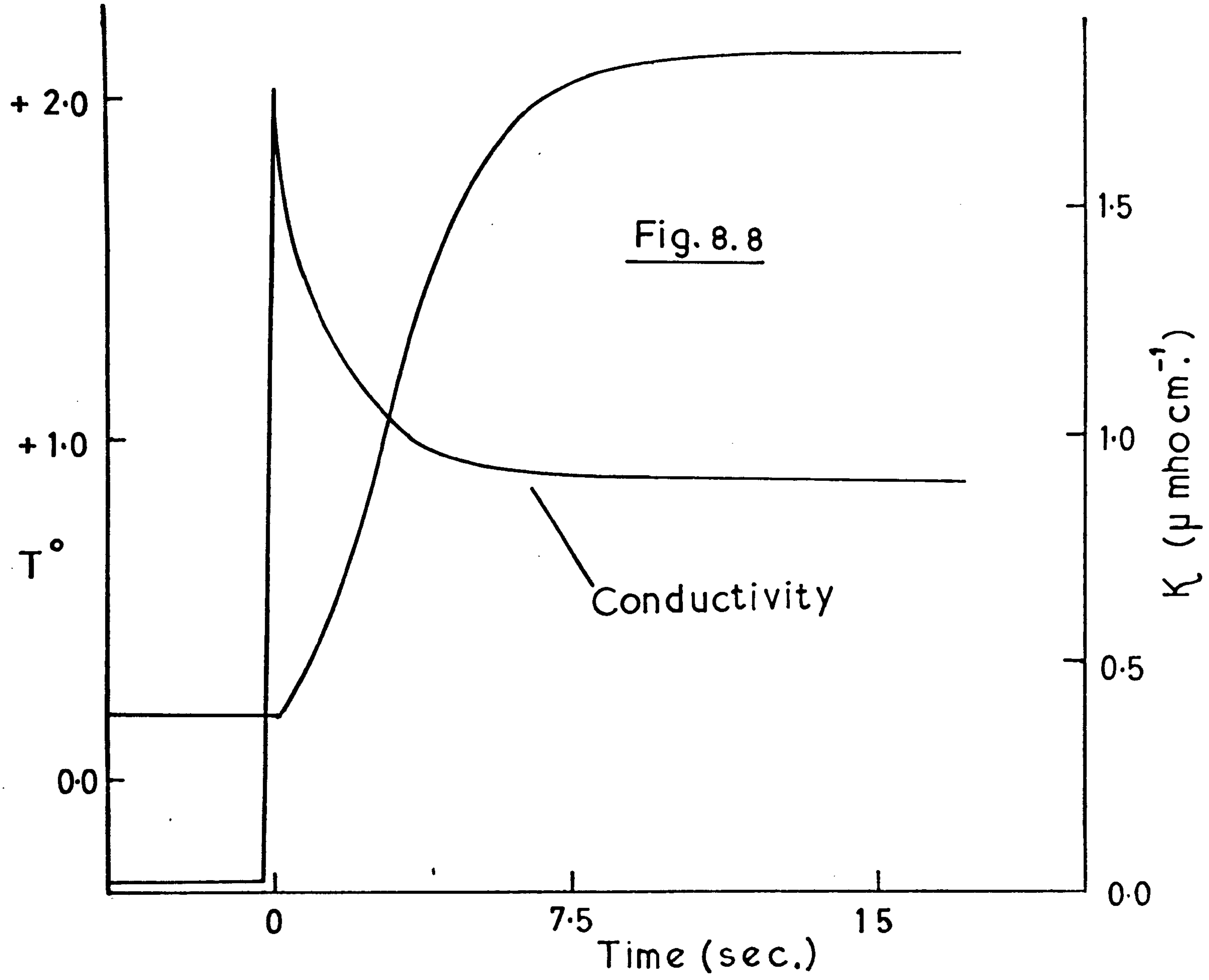


Fig. 8.8

Fig. 8.9

First order plot for experiment 172. From the graph $k_1 = 0.457 \text{ sec}^{-1}$.

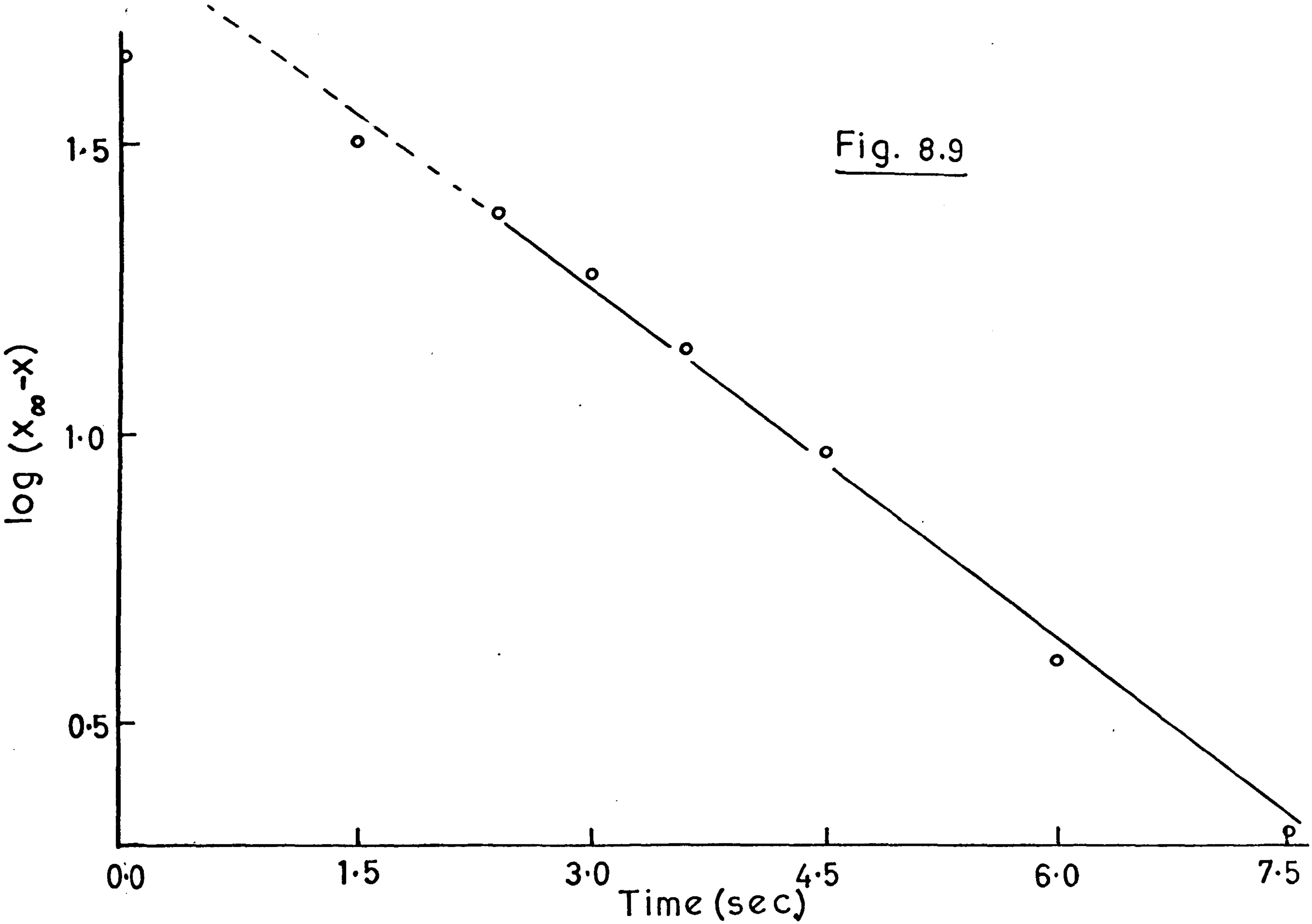


Fig. 8.9

8.3 Electrical Conductivity of Polymerisation Reaction Mixtures. The electrical conductivity was automatically recorded for each polymerisation that was carried out in the adiabatic calorimeter. κ_o, the initial specific conductivity of the 1,3-dioxepane in methylene dichloride, was usually between 0.006 and 0.016 μ mhos cm^{-1}. The specific conductivity of pure perchloric acid in methylene dichloride was found to be in the region of 0.04 μ mhos cm^{-1} under our experimental conditions. In every polymerisation experiment the conductivity instantaneously rose to a maximum, κ_m, when the perchloric acid phial was crushed and it then fell slowly during the polymerisation to κ_f, the final value at equilibrium. The value of the conductivity at equilibrium was found to be constant for several hours, provided that the temperature was kept constant. Table 8.5 contains the electrical conductivity data for polymerisations carried out at -20°.

The important features of these results are as follows:

(1) Although the 1,3-dioxepane contained a small quantity of tetrahydrofuran, the electrical conductivity of the protonated tetrahydrofuran is not significant. This fact is illustrated by experiment 190 which was carried out with the highly purified batch of 1,3-dioxepane that contained only 20 ppm tetrahydrofuran. The conductivity readings are in excellent agreement with experiment 161 which was carried out under identical conditions, but with 1,3-dioxepane that contained 100 ppm tetrahydrofuran.

It must also be remembered that a 0.8 M solution of 1,3-dioxepane that contained 100 ppm of tetrahydrofuran contains less than 1×10^{-4} M tetrahydrofuran.

Experiment shows that 1×10^{-4} M tetrahydrofuran in 3×10^{-3} M

Table 8.5

Electrical Conductivity Data for Polymerisation Experiments at T = -20°.

Run No.	162	178^x	160	159	161	190^x	163
[1,3-Dioxepane],M.	1.00	0.80	0.80	0.80	0.80	0.80	0.60
$[HClO_4]$, 10^4 M.	2.1	0.23	1.4	2.1	2.6	2.6	2.1
κ_o, μ mho cm^{-1}.	0.009	0.016	0.030	0.006	0.008	0.012	0.007
κ_m, μ mho cm^{-1}.	1.00	0.75	1.50	1.20	1.78	1.60	2.40
κ_f, μ mho cm^{-1}.	0.62	0.21	0.55	0.93	1.01	1.L5	1.28
DP	12.7	10.0	9.4	8.7	9.2	7.8	6.1

[x] Experiments 178 and 190 were carried out with a new batch of 1,3-dioxepane.

Fig.8.11 Plot of κ_m and κ_f against perchloric acid concentration for polymerisations of 0.8 M 1,3-dioxepane at -20°.

Fig.8.10

The Arrhenius plot for the calorimetric experiments (Tables 8.1, 8.2, 8.3, 8.4. Figs. 8.3, 8.4, 8.5 and 8.7).

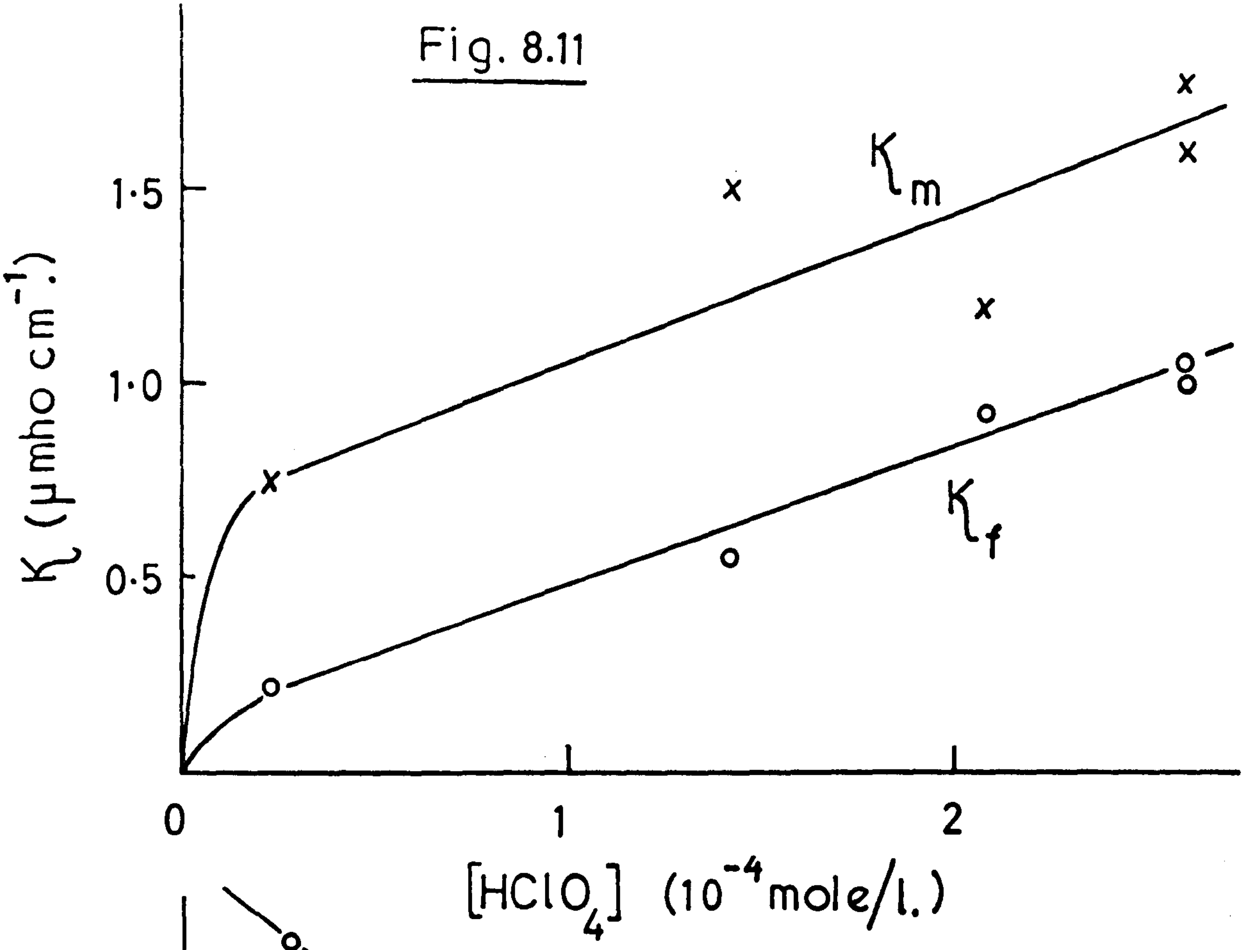


Fig. 8.11

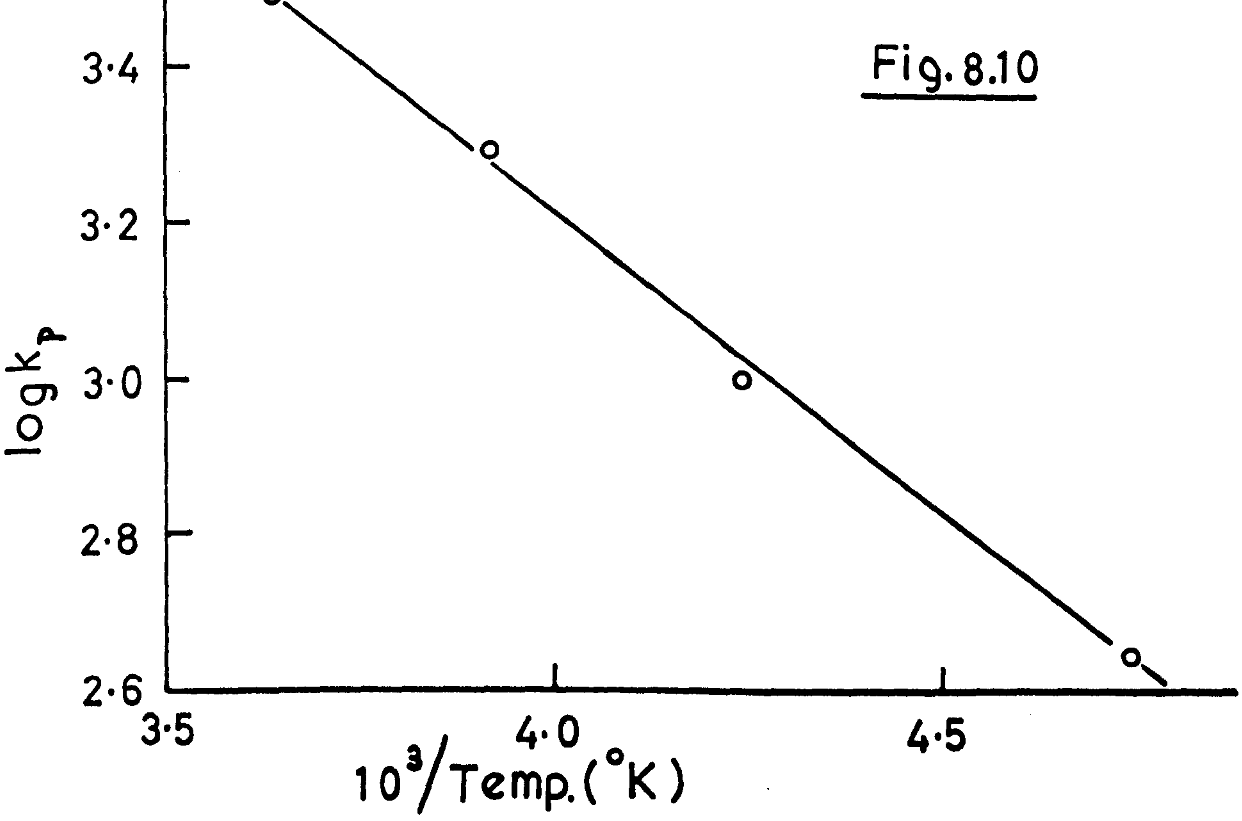


Fig. 8.10

perchloric acid has a conductivity of about 0.2 μ mhos. It follows that the conductivity that was measured during the polymerisations is nearly all due to the protonation of 1,3-dioxepane.

(2) The sharp rise in conductivity shows that 1,3-dioxepane is protonated immediately by perchloric acid. The fall in conductivity during the polymerisation is probably mainly due to the increasing viscosity of the medium as polymer is formed. Another factor is that as the polymerisation proceeds the contribution to the conductivity by the growing oxonium ions diminishes progressively.

(3) The maximum and final conductivity values depend on the original concentration of 1,3-dioxepane (see experiments 162, 159 and 163). The final conductivity value could well decrease with increasing 1,3-dioxepane concentration as the viscosity of the polymer solutions at equilibrium also increases. However, there seems to be no good reason why the maximum conductivity should also decrease as the concentration of 1,3-dioxepane increases, as hardly any polymer has been formed by the time protonation is completed.

(4) Both the maximum and final conductivity values increase with increasing perchloric acid concentration Fig. 8.5. The absolute values of the final conductivity are in reasonable agreement with the final conductivities for 1,3-dioxolane polymerisations under similar conditions (Fig. 5.3 Chapter 5).

8.4 **Description of the Depolymerisations.** Depolymerisations of poly-1,3-dioxepane were carried out in the calorimeter. The polymer was evacuated in the calorimeter for 3 hours, then allowed to dissolve in methylene dichloride and the reaction was started by breaking a phial of perchloric acid. Fig. 8.12 illustrates a depolymerisation (experiment 170). The depolymerisation is a first order reaction (Fig. 8.13), and the conductivity rises steadily during the depolymerisation.

8.5 **Depolymerisation Kinetics.** The data for the depolymerisation experiments at 0° are shown in Table 8.6. All depolymerisations were carried out with the same batch of polymer. The equilibrium monomer concentration at 0° is 0.48 M and although the final monomer concentration at 0° was only about 0.28 M for these experiments, about 10% of the original polymer did not depolymerise. It remained as very low molecular weight oligomers (DP approx. 3). This observation is in perfect agreement with experiment 185 (Chapter 7).

k_1' is the slope of the first order plot for each depolymerisation reaction. The plot of k_1' against perchloric acid concentration is a straight line with an intercept of about 1.5×10^{-4} M on the perchloric acid concentration axis (Fig. 8.14). The value of k_d, the depolymerisation rate constant at 0°, was determined from the slope of this plot and the equilibrium concentration of 1,3-dioxepane at 0°.

8.6 **Electrical Conductivity of Depolymerisation Reaction Mixtures.** In the depolymerisation experiments κ_o, the initial specific conductivity of poly-1,3-dioxepane in methylene dichloride, was between 0.17 and 0.12 μ mho cm^{-1}.

Fig. 8.12

Simultaneous plot of temperature and electrical conductivity against time for experiment 170 (the depolymerisation of poly-1,3-dioxepane at 0°) Table 8.6.

Fig. 8.13

First order plot for experiment 170. From the graph $k_1' = 0.45\ \text{sec}^{-1}$.

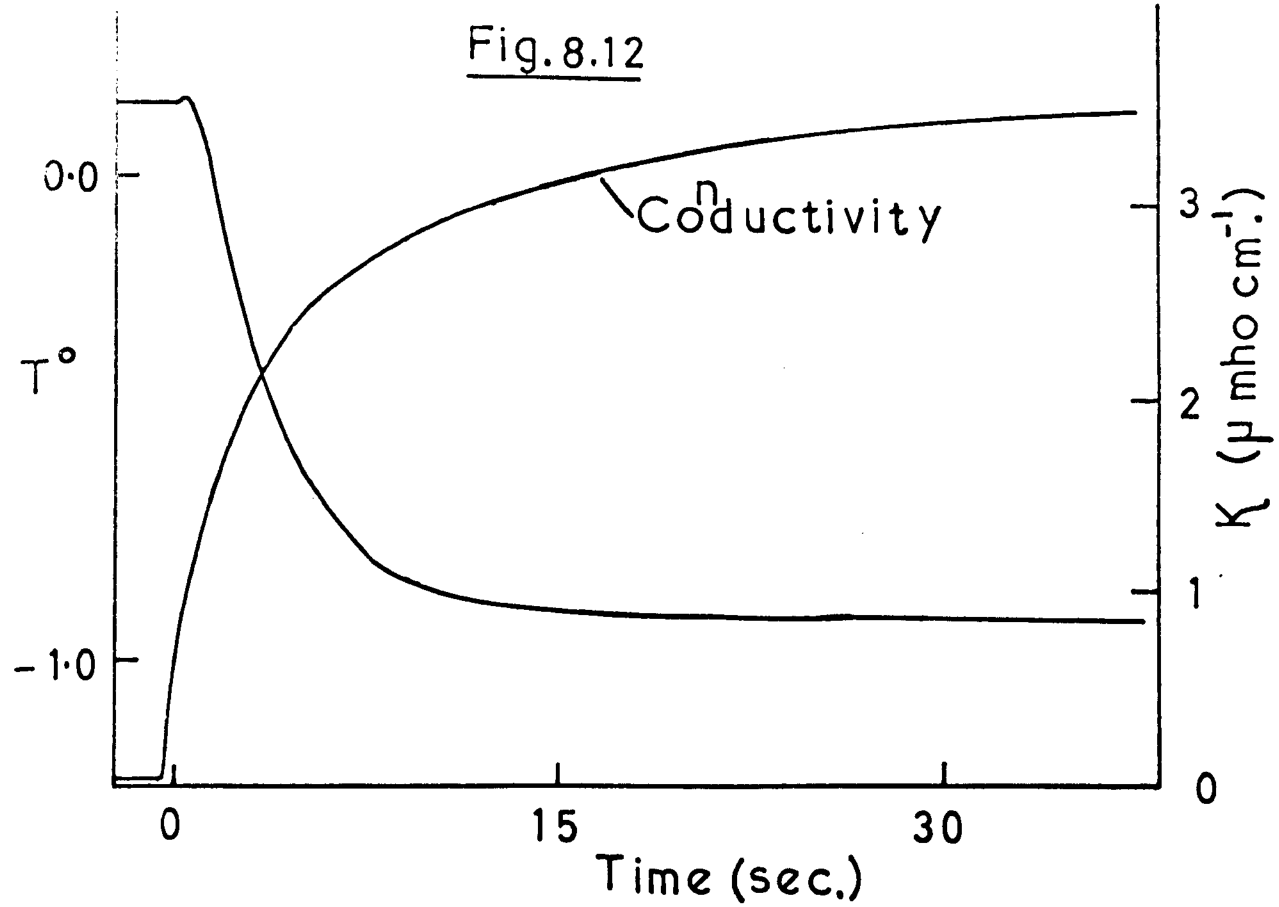


Fig. 8.12

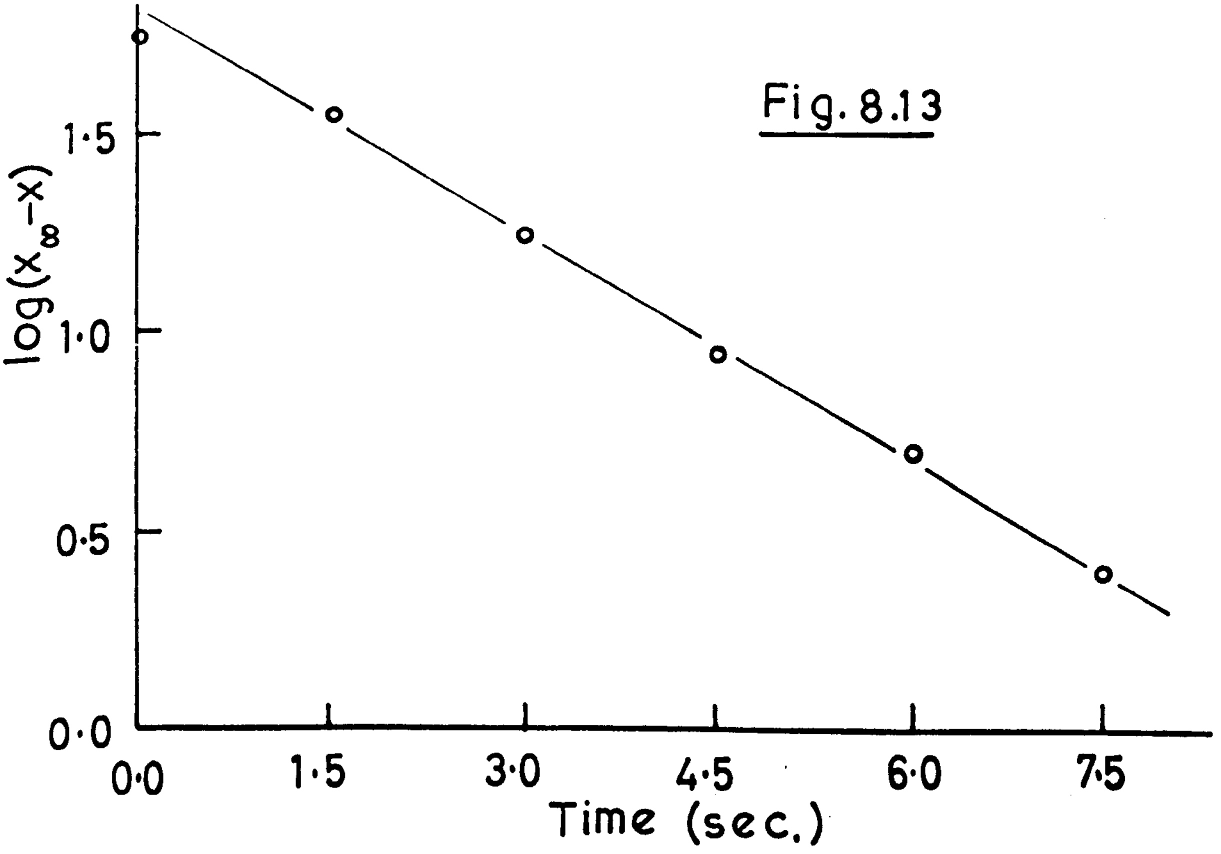


Fig. 8.13

Table 8.6

Data for Depolymerisations at 0° with Poly-1,3-Dioxepane of Molecular Weight = 6000.

Run No.	167	168	170
$[HClO_4]$, 10^4 M.	3.2	5.8	9.4
k_1' sec^{-1}.	0.087	0.29	0.45
K_o, μ mho cm^{-1}.	0.17	0.15	0.12
K_f, μ mho cm^{-1}.	2.8	4.0	5.5
Mass of polymer used, g.	3.2	3.2	3.2
ΔT, deg.	-0.95	-1.3	-1.4
Moles of polymer depolymerised	-	0.0274	0.0270
Mass of polymer unpolymerised, g	-	0.28	0.30
DP of residual polymer	-	3.0	2.9

Fig. 8.14 is a plot of k_1' against perchloric acid concentration for depolymerisations at 0°.

From Fig. 8.14 $k_d = k_1' \, m_e / [HClO_4] = (1.8 \mp 0.3) \times 10^4 \text{ min}^{-1}$.

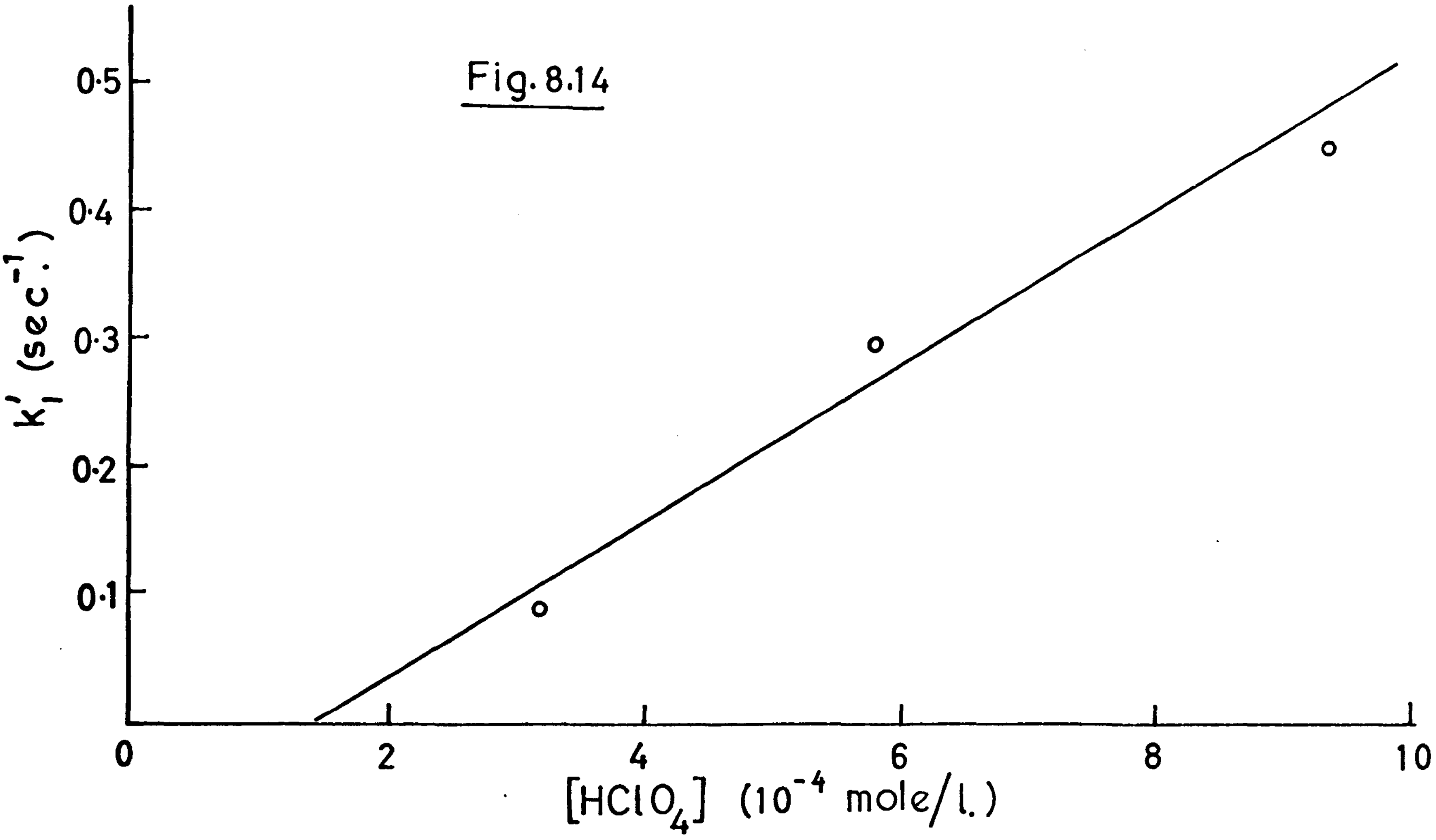


Fig. 8.14

This is considerably larger than the conductivity of monomer in methylene dichloride. When the perchloric acid phial was crushed, the conductivity rose slowly to a steady value, κ_f. The electrical conductivity data for the depolymerisation experiments are shown in Table 8.6.

The fact that the conductivity rises steadily throughout the depolymerisation does not mean that protonation of the polymer is slow; it merely reflects the decreasing viscosity of the solution.

The final value of the conductivity for depolymerisations is about the same as the maximum value for polymerisations. (Compare experiments 167 and 163) and the final value of the conductivity increases as perchloric acid concentration increases.

8.7 Second Addition of Monomer.

The experimental details of a second addition of monomer to the reaction mixture when the first polymerisation had ceased, are shown in the Table below.

Table 8.7

Run No.	186
$[HClO_4]10^4$, M.	3.7
Initial [1,3-dioxepane], M.	0.61
2nd Addition [1,3-dioxepane], M.	0.19
Total [1,3-dioxepane], M.	0.80
ΔT_1, deg.	1.8
ΔT_2, deg.	1.5
$\Delta T_1 + \Delta T_2$ deg.	3.3
DP.	9.1
Conversion %	61
Final temp. deg.	-17

The conversion, total temperature rise and DP of the final product are all in good agreement with reactions completed in one step.

The temperature trace obtained for the second polymerisation was not of first order. This is probably due to insufficiently rapid mixing and the resulting very fast local polymerisation of 1,3-dioxepane when the phial of monomer was broken. However both polymerisations occurred at similar rates.

8.8 Discussion

8.8.1 Introduction.

Chapter 3 of this Thesis shows that the polymerisation of 1,3-dioxolane involves only oxonium ions as chain carriers and that carboxonium and carbonium ions cannot be produced. As the same arguments apply equally to 1,3-dioxepane, this polymerisation mechanism must also only involve oxonium ions as chain carriers.

The results of Chapter 6 show that poly-1,3-dioxepane, like the polymer of 1,3-dioxolane, is cyclic. This means that the polymerisation mechanism for these two monomers is identical, i.e. a ring expansion involving secondary oxonium ions.

Because of this the dissociation constant of the active centres in the polymerisation of 1,3-dioxepane should be the same as that calculated for the 1,3-dioxolane active centres in Chapter 4. The similarity between the values of K_f, the final conductivity, for the two systems under similar conditions supports this view.

8.8.2 General Features of the Polymerisations.

In most respects the

1,3-dioxepane polymerisations were similar to polymerisations of 1,3-dioxolane.

The second addition of monomer, experiment 186, shows that termination is unimportant for 1,3-dioxepane polymerisations. Further proof that these reactions are living polymerisations comes from experiment 143 (Table 7.2) in which the DP of the polymer and the position of equilibrium were altered when the final temperature of the polymerisation mixture was altered.

However, 1,3-dioxepane polymerisations were at least ten times faster than equivalent 1,3-dioxolane polymerisations. Because of this the concentration of perchloric acid used with 1,3-dioxepane was ten times less than for 1,3-dioxolane. The result is that 1,3-dioxepane polymerisations are more sensitive to traces of impurities.

Fig. 8.3 shows that the rate of polymerisation of 1,3-dioxepane is affected by traces of water, whilst the DP is not noticeably altered (Table 8.1).

Fig. 8.6 (Table 8.3) indicates the presence of some impurity in the 1,3-dioxepane, and an analysis showed tetrahydrofuran to be present in about the required concentration. The second batch of 1,3-dioxepane which contained five times less tetrahydrofuran gave a plot of k_1 against perchloric acid concentration that passed through the origin. The slopes of the plots of k_1 against perchloric acid concentration are the same for both batches of 1,3-dioxepane (Fig. 8.5). This indicates that tetrahydrofuran can effectively neutralise perchloric acid in the presence of 1,3-dioxepane. The reason for this is that the basicity of tetrahydrofuran is greater than that of

1,3-dioxepane (Chapter 9).

One feature of these results that is difficult to explain is the fact that although polymerisations at -65°, -40° and -20° were all accurate first order reactions, the polymerisations at 0° gave S-shaped curves (Fig. 8.8). However, the last part of these polymerisation curves were of first order and the value of k_p that was obtained fitted well on the Arrhenius plot (Fig. 8.10).

The electrical conductivity results for the 1,3-dioxepane polymerisations show that in every case (including polymerisations at 0°) there was an immediate increase in conductivity as soon as the perchloric acid phial was crushed. This can only be interpreted as a rapid protonation of 1,3-dioxepane by perchloric acid. The simple kinetics that were observed for polymerisations at -65°, -45° and -20° indicate that under these conditions every molecule of perchloric acid must protonate 1,3-dioxepane. This behaviour is in marked contrast to that of 1,3-dioxolane for which protonation is incomplete until a large quantity of polymer is present (Chapter 5). The reason for this difference lies in the difference in basicity of the two monomers. Chapter 9 shows that 1,3-dioxepane with a $pK_b = 6.0$ is more basic tha~~t~~n 1,3-dioxolane with a $pK_b = 7.4$. Experiments 160 and 172 are polymerisations of 0.8 M 1,3-dioxepane with 1.5×10^{-4} M perchloric acid that were carried out at -20° and 0° respectively. The value of κ_m, the maximum conductivity, is 1.5 μ mho cm^{-1} at -20° and 1.4 μ mho cm^{-1} for the polymerisation at 0°. This suggests that the S-shaped curves of polymerisations at 0° are not due to incomplete protonation of 1,3-dioxepane.

8.8.3 The Kinetic Scheme.

The kinetic scheme reported separately by Rozenberg[1] and Tobolsky[2] for the polymerisation of tetrahydrofuran by triethyloxonium salts requires rapid and complete initiation and no termination (stationary state of the Second Kind). Although 1,3-dioxolane polymerisations have no termination step, protonation was not complete until about 50% of reaction, so that only the last half of these polymerisation curves fitted this scheme.

However, 1,3-dioxepane polymerisations, which also have no termination, have a rapid and complete protonation, as shown by the conductivity results, so that all the polymerisation and depolymerisation reaction curves fitted this scheme. The only exceptions were the polymerisations of 1,3-dioxepane at 0^{o}. These reaction curves were similar to the 1,3-dioxolane polymerisations in that only the last half of the curves were first order reactions.

The kinetic scheme for the 1,3-dioxepane polymerisation and depolymerisation reactions is identical to the scheme presented in Chapter 4 for 1,3-dioxolane, so it will not be repeated here. The k_p values were calculated for the polymerisations of 1,3-dioxepane at various temperatures.

To be completely rigorous, a comparison should be made of the value of k_p at 0° determined from polymerisation experiments with the value of k_p at 0° determined from depolymerisation experiments.

$k_p = (1.9 \mp 0.06) \times 10^5$ litre mole^{-1} min^{-1}. (Polymerisation)

$k_p = (3.6 \mp 0.5) \times 10^4$ litre mole^{-1} min^{-1}. (Depolymerisation)

Table 8.8

Values of k_p and k_d for 1,3-Dioxepane.

Temp., deg.	k_p litre $\text{mole}^{-1}\text{min}^{-1}$	k_d min^{-1}
-65	$(2.6 \mp 0.1) \times 10^4$	
-40	$(5.5 \mp 0.2) \times 10^4$	
-20	$(1.1 \mp 0.06) \times 10^5$	
0	$(1.9 \mp 0.06) \times 10^5$	$(1.8 \mp 0.3) \times 10^4$

The validity of the values of k_p and k_d at 0° can be tested by comparing the equilibrium constant determined thermodynamically with the equilibrium constant determined kinetically; ideally the two results should be identical.

The equilibrium constant at 0° for 1,3-dioxepane was determined graphically from the plot of log K against 1/T (Fig. 7.2 Chapter 7).

$$K = 1.7 \mp 0.1 \qquad \text{(Thermodynamic determination)}$$

$$\text{Also } K = k_p/k_d = (1.9 \mp 0.06) \times 10^5/(1.8 \mp 0.3) \times 10^4$$

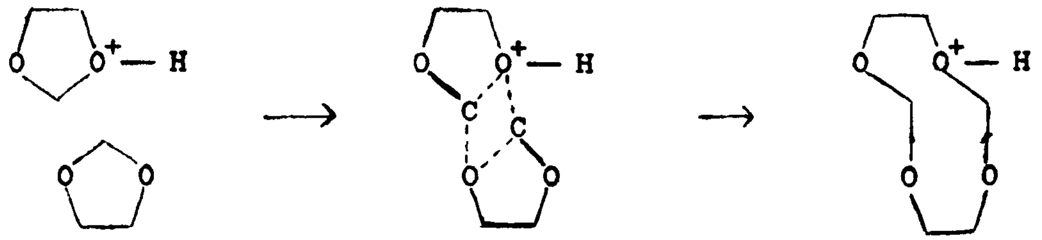
$$= 10.5 \mp 0.9 \qquad \text{(Kinetic determination)}$$

The agreement between these two values is not within the estimated error of the measurements. The disagreement is almost certainly due to an error in the value of k_d, as the value of k_p at 0° fits well on the Arrhenius plot (Fig. 8.10).

The value of k_d for 1,3-dioxolane was determined by depolymerising poly-1,3-dioxolane that had been formed in situ in the dilatometer, whilst the value of k_d for 1,3-dioxepane was determined calorimetrically by depolymerising polymer that had been made in a previous experiment. Because of the difficulty of isolating pure poly-1,3-dioxepane free from impurities such as ammonium perchlorate and water, the k_d value for 1,3-dioxepane is less reliable than the value of k_d for 1,3-dioxolane.

However, the values of k_p for 1,3-dioxepane are probably reliable because of the simple kinetics of the system. The value of k_p for 1,3-dioxepane at 0° is: $k_p = 1.9 \times 10^{5}$ litre mole^{-1} min^{-1}. The value of k_p for 1,3-dioxolane at 0° is much smaller: $k_p = 6.2 \times 10^{2}$ litre mole^{-1} min^{-1}. The Arrhenius frequency factor, A_p, was calculated for the 1,3-dioxolane and 1,3-dioxepane polymerisations as $A_p = 1.5 \times 10^{7}$ litre mole^{-1} min^{-1}. and $A_p = 1 \times 10^{8}$ litre mole^{-1} min^{-1}. respectively. This shows that the difference in polymerisation rates must be mainly due to the difference in activation energy for the two reactions. The activation energy, E_p, for the 1,3-dioxolane and 1,3-dioxepane polymerisations was calculated as $E_p = 5.5 \mp 0.3$ kcal.mole^{-1} and $E_p = 3.5 \mp 0.3$ kcal.mole^{-1} respectively. The most obvious difference between these two monomers is that 1,3-dioxolane, $pK_b = 7.4$, is less basic than 1,3-dioxepane, $pK_b = 6.0$. (Chapter 9). A possible explanation for the decrease of E_p with increasing basicity is as follows.

The polymerisations of 1,3-dioxolane and 1,3-dioxepane are both postulated to involve a 4-centred cyclic transition state. The case for 1,3-dioxolane is illustrated.



The more basic the monomer, the greater will be the electron density at the oxygen atoms and thus the less energy will be required to delocalise lone pair electrons (partly) over the four centres of the transition complex. Thus the transition complex for 1,3-dioxepane will be more stable than that for 1,3-dioxolane, so that the activation energy for the polymerisation of 1,3-dioxepane will be less than for the polymerisation of 1,3-dioxolane.

The standard entropy of activiation, ΔS_p^o, was calculated for 1,3-dioxolane as $\Delta S_p^o = -33.5$ cal. deg.$^{-1}$ mole^{-1} and for 1,3-dioxepane as $\Delta S_p^o = -29.5$ cal. deg.$^{-1}$ mole^{-1}. These values are considerably more negative than the respective standard entropies of polymerisation and thus reflect the large decrease in entropy that occurs in the formation of the 4-centred transition state. The fact that the two values are so similar for both monomers is another indication that both polymerisations occur by the same mechanism.

References to Chapter 8

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Introduction to Section C

The kinetic results of Chapter 4 and the electrical conductivity results of Chapter 5 indicate that only a small part of the perchloric acid can protonate 1,3-dioxolane, whilst under the same conditions all the perchloric acid protonates poly-1,3-dioxolane. This means that poly-1,3-dioxolane is more basic that its monomer.

Furthermore, the kinetics of the 1,3-dioxepane polymerisation (Chapter 8) indicate that all the perchloric acid immediately protonates 1,3-dioxepane. This conclusion is supported by the conductivity measurements that were made during these polymerisations. These results show that 1,3-dioxepane is more basic than 1,3-dioxolane.

For these reasons it was decided to measure the basicity of both monomers and their polymers to see whether these conclusions were true.

As the results of Chapters 4, 5 and 8 are concerned with the basicity of the two monomers and their polymers under polymerising conditions, ideally the value of the equilibrium constant, K_b' for the reaction of each base with anhydrous perchloric acid in methylene dichloride should be measured.

$$HClO_4 + B \rightleftharpoons HB^+ + ClO_4^-$$

$$K_b' = [HB^+][ClO_4^-]/[HClO_4][B]$$

This would allow a comparison of the various standard state free energy changes accompanying each reaction to be made. Experimentally, a direct measurement of K_b' is difficult for this reaction, so that another method of determining basicity had to be found.

Okada et al.[1-3] measured the basicity of a large number of cyclic ethers, formals and esters and successfully correlated basicity with copolymerisation parameters. They used the method that was first reported by Gordy and Stanford[4] and that has since been extensively used for basicity measurements with cyclic ethers.[5,6] In this method 1.0 M methanol-d_1 (and not 0.1 M methanol-d_1 as reported by Okada et al.) is dissolved in the weak base to be studied and the position of the O-D band in the infrared is compared with the position of the O-D band of 0.1 M methanol-d_1 in benzene. $\Delta\mu$ is the difference between these two bands expressed in millimicrons. In Gordy's original papers the values of $\Delta\mu$ for several aromatic amines were plotted against their corresponding basicity constants. The basicity constant pK_b is defined as K_1/K_w. Where K_1 is the ionisation constant of the base in water and K_w is the ionic product of water. The following empirical equation was found:

$$\Delta\mu = 0.0147 \log K_b + 0.194$$

The graph was then extrapolated so that values of $\Delta\mu$ for compounds of unknown basicity could be converted into pK_b values. The pK_b values that this relationship gives are in terms of the ionisation constant of the base in water. Thus these values of pK_b cannot be applied directly to the systems under consideration.

Arnett[7], in a review on weak organic bases, comments on the amazingly good correlation that has been found to exist between $\Delta\mu$ and pK_b values as the relationship found by Gordy is linear over a K_b range of twenty-two powers of ten. We used Gordy's method to measure basicities, as it is the most convenient method available, but the intrinsic limitations of these measurements must be borne in mind.

References to Introduction to Section C

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2 Y. Ishii, S. Iwatsuki, M. Okada, N. Takikawa and Y. Yamashita, Makromol. Chem., 1965, 82, 16.

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Chapter 9

Basicity Measurements.

9.1 Method and Results.

In order to measure the basicities of the various species under consideration 1.0 M methanol-d_1 was dissolved in 1,3-dioxolane, 1,3-dioxepane and their polymers, and the positions of the O-D bands were compared with that of 0.1 M methanol-d_1 in benzene. A 1mm cell was used for the 0.1 M methanol-d_1 solution and a 0.1 mm cell for the 1.0 M solutions. The results of these experiments are shown in Table 9.1. The I.R. spectrometer was calibrated by means of 0.07 mm polystyrene foil. It is estimated that all ν_{OD} values have an error of ∓ 1 cm^{-1} (approx. 0.04%). This gives an error of 0.04% which is approximately 0.0016 mμ in μ. The error in Δμ is thus 2 x 1.6% = approximately 3%. This leads to an error of 3% in pK_b i.e. 0.2 in 7 or 0.15 in 5. 1,3-dioxolane was distilled under vacuum into phials direct from the reservoir and these phials were opened immediately before the basicity measurements were made. The basicity of pure 1,3-dioxolane and the basicity of a 50% solution of 1,3-dioxolane in benzene were found to be identical. The experimental value of $pK_b = 7.4$ is in good agreement with the literature[1] ($pK_b = 7.55$).

A low molecular weight poly-1,3-dioxolane (DP approx. 7) was prepared in the vacuum calorimeter and the reaction mixture was neutralised with ammonia gas. The polymer was isolated and dried in the vacuum oven at 45°. The polymer was a slightly viscous clear oil that was introduced directly into 0.1 mm cells. Methanol-d_1 was added to the polymer in the cell with a micro-syringe and the solution was mixed well. The basicity was

Table 9.1

The Basicity of 1,3-Dioxolane, 1,3-Dioxepane and their Polymers.

	ν_{OD}, cm^{-1}	μ_{OD}, mμ	Δμ, mμ	pK_b
Benzene	2670	3.745		
1,3-Dioxolane	2611	3.830	0.085	7.4
50% 1,3-Dioxolane	2611	3.830	0.085	7.4
Poly-1,3-Dioxolane	2601	3.845	0.100	6.4
50% Poly-1,3-Dioxolane	2603	3.842	0.097	6.6
1,3-Dioxepane	2597	3.851	0.106	6.0
50% 1,3-Dioxepane	2595	3.854	0.109	5.8
20% 1,3-Dioxepane	2593	3.857	0.112	5.6
50% Poly-1,3-Dioxepane	2594	3.855	0.110	5.7
20% 1,3-Dioxepane Dimer	2593	3.857	0.112	5.6

0.1 M CH_3OD in benzene was used for obtaining the reference peak and 1.0 M CH_3OD was used for all other measurements.

The basicities were calculated by means of the Gordy equation:

$$\Delta\mu = 0.0147 \log K_b + 0.194$$

measured several times and was found to be reproducible. In order to be certain of this result, a second batch of poly-1,3-dioxolane (DP approx. 10) was prepared and the basicity was measured in 50% benzene solution. These two results are in good agreement and show that poly-1,3-dioxolane is more basic by about 1 pK_b unit than 1,3-dioxolane itself.

The basicities of pure 1,3-dioxepane, 50% 1,3-dioxepane in benzene and 20% 1,3-dioxepane in benzene were measured and a slight shift of basicity with dilution was found. However, the experimental value for pure 1,3-dioxepane, $pK_b = 6.0$, is in excellent agreement with the literature[1] ($pK_b = 6.12$).

A low molecular weight sample of poly-1,3-dioxepane (DP approx. 6) was prepared and isolated as described above; this material contained so much crystalline dimer that it could not be used directly. The basicity measurements were made in 50% solutions in benzene. The dimer of 1,3-dioxepane was isolated by vacuum sublimation and as it is only moderately soluble in benzene the basicity measurements were carried out on a 20% dimer solution in benzene.

These results show that 1,3-dioxepane, the dimer and poly-1,3-dioxepane all have essentially the same basicity.

9.2 Discussion.

For the reasons already outlined in the introduction to this Chapter the values of the basicity constants that were measured are not directly applicable to the kinetic or conductivity results. We can only observe that the relative order of basicity is as expected.

However, we can attempt to answer the question as to why there is a large difference in basicity between 1,3-dioxolane and poly-1,3-dioxolane, whilst the basicities of 1,3-dioxepane and poly-1,3-dioxepane are almost identical and greater than that of dioxolane.

Although the basicity of cyclic ethers has been reviewed by Arnett[2], no satisfactory correlation between basicity and structure appears to exist. In principle, dipole moments can be used to give a measure of the electron density on the basic site, but in practice there is often no correlation between basicity and dipole moment. For example, Gordy compared the dipole moments of several typical solvents (1,3-dioxane, diethylether, acetone, nitrobenzene, aniline etc.), with the shift of the O-D band that they produced. He found that the tendency of a solvent to acquire protons from a hydroxyl group bears little relation to the dipole moment of the solvent. As he was comparing molecules with different kinds of basic site this result is not entirely surprising.

However, if the basicities of a series of similar molecules are compared with the dipole moments that act at the basic site, then some correlation of basicity with dipole moment should be apparent. It is the dipole moment that is acting at the basic site that will influence the electron density and hence the basicity of the molecule. In many cases the direction of the measured dipole is through the basic site (tetrahydrofuran), but if the net resultant dipole does not go through the basic site, then the dipole moment must be resolved, so that the component vector acting through the basic site can be estimated.

In Table 9.2, the measured dipole moments,[3,4] and basicities[1] of some cyclic ethers are listed. In the case of the cyclic ethers containing one oxygen atom the observed dipole acts along the bisector of the angle at

Table 9.2

The Correlation between Dipole Moment and Basicity for some Cyclic Ethers

	Dipole Moment, D.	Ref	pK_b	Ref
Trimethylene Oxide	1.92	3	3.13	1
Tetrahydrofuran	1.75	3	5.00	1
Tetrahydropyran	1.55	3	5.42	1
1,3-Dioxane	0.4	4	5.71	1
1,3-Dioxolane	1.47	3	7.55	1

the oxygen atom and there is a direct correlation between dipole moment and basicity. For compounds containing two oxygen atoms (1,4-dioxane and 1,3-dioxolane) this is not so.

We will consider the case of 1,4-dioxane first. Gibbs[5] measured the molar polarisation of 1,4-dioxane over a range of temperatures in the vapour phase in order to obtain some information concerning the population of molecules in the various possible configurations. Although he was not able to estimate the actual populations he concludes that trans-1,4-dioxane is the prevalent form, as the molar polarisation is small and due to small quantities of symmetrical and unsymmetrical cis-1,4-dioxane.

Fig. 9.1 is a photograph of a Courtauld atomic model of trans-1,4-dioxane. The two component dipoles at each oxygen atom (represented by matchsticks) are parallel but opposite. Thus trans-1,4-dioxane has zero dipole moment and consequently a low basicity.

Fig. 9.2 is a photograph of a model of symmetrical cis-1,4-dioxane. In this case the two component dipoles are at approximately 90° to each other, so that there is a large resultant dipole moment. Since neither component affects the other, there is a large dipole acting through each of the oxygen atoms which must therefore be more basic than in the trans form.

The basicity measurements that were made with solutions of 1,3-dioxepane in benzene (Table 9.1) show that the method is sensitive to low concentrations of base. In fact a 20% solution of 1,3-dioxepane in benzene gave rise to a slightly larger $\Delta\mu$ value than pure 1,3-dioxepane. Thus the basicity of 1,4-dioxane, as measured by this method, will be mainly due to the small concentration of the more basic cis form.

In 1,3-dioxolane the resultant dipole moment[3] of 1.47 D, composed

Fig. 9.1

A Courtauld atomic model of trans-1,4-dioxane.

Fig. 9.2

A Courtauld atomic model of symmetrical cis-1,4-dioxane.

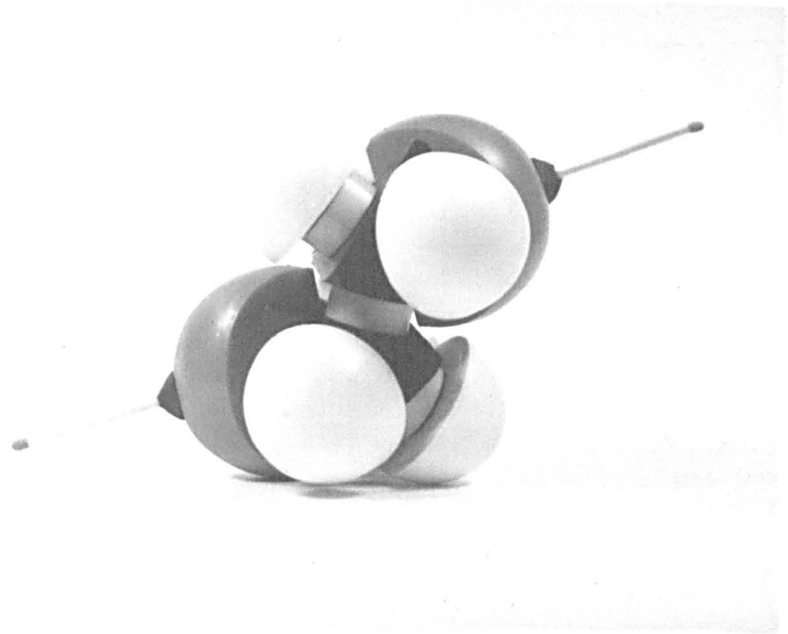

Fig. 9.1

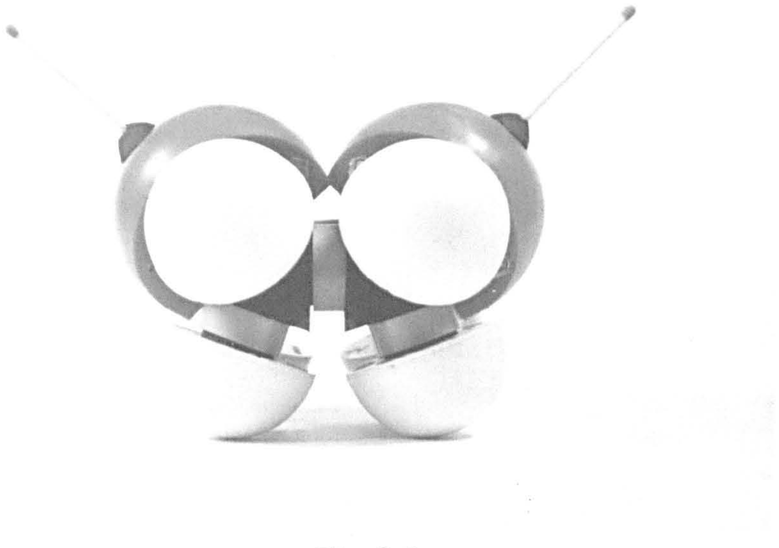

Fig. 9.2

of those through the two oxygen atoms, goes through the carbon atom between them. The exact configuration of 1,3-dioxolane[6] is C - C = 1.54 Å, C - O = 1.42 Å, ∠CCO = 108° and ∠COC = 108°. An accurate drawing of the molecule and models show that the preferred form is a slightly puckered ring.

In Fig. 9.3 the molecule of 1,3-dioxolane has been drawn as planar, which involves distorting the COC angles by only about 1°, so that the error introduced is small. The experimental dipole moment AB = 1.47 D has been drawn so that it acts through the central carbon atom. The effect of this dipole in the direction of either oxygen atom is 1.47 cos 72° = 0.45 D. This small dipole moment at the basic site is the cause of the relatively low basicity of 1,3-dioxolane. ($pK_b = 7.4$).

Fig. 9.4, which is a photograph of a Courtauld atomic model of 1,3-dioxolane, illustrates the direction of the two opposing component dipoles by means of matchsticks attached to the oxygen atoms.

Poly-1,3-dioxolane cannot assume the nearly planar configuration of the monomer. Fig. 9.5 is a photograph of a model of the cyclic dimer of 1,3-dioxolane which shows the two component dipoles at about 90° to each other. If a C - O bond moment of 1.7 D is assumed, which is a typical value for cyclic ethers and formals[3], and the COC angle is 112° then the resultant dipole acting at each oxygen will be 1.9 D, provided that these dipoles are at 90° to each other. Because so many configurations of the 1,3-dioxolane dimer are possible the effective dipoles that act at the oxygen atoms of the molecule cannot be estimated. However, every configuration of poly-1,3-dioxolane involves larger effective dipoles at the oxygen atoms than for the monomer. The higher basicity of poly-1,3-dioxolane over 1,3-dioxolane is due to this fact.

Fig. 9.3

An accurate drawing of 1,3-dioxolane.

The experimental dipole moment AB is 1.47 D.

The effect of this dipole in the direction AO is AG.

$$AG = 1.47 \cos 72^{\circ} = 0.45D.$$

Fig. 9.3

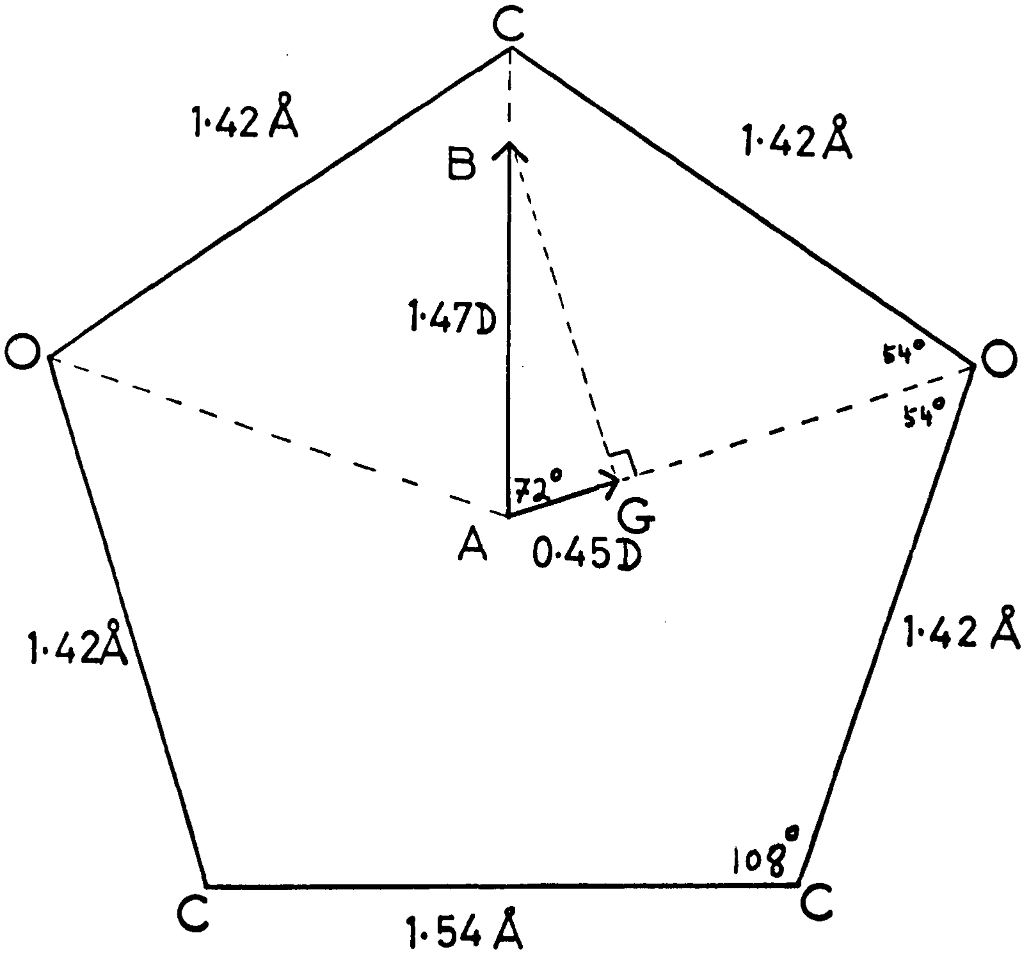

Fig. 9.4

A Courtauld atomic model of 1,3-dioxolane.

Fig. 9.5

A Courtauld atomic model of the cyclic dimer of 1,3-dioxolane.

Fig. 9.6

A Courtauld atomic model of 1,3-dioxepane.

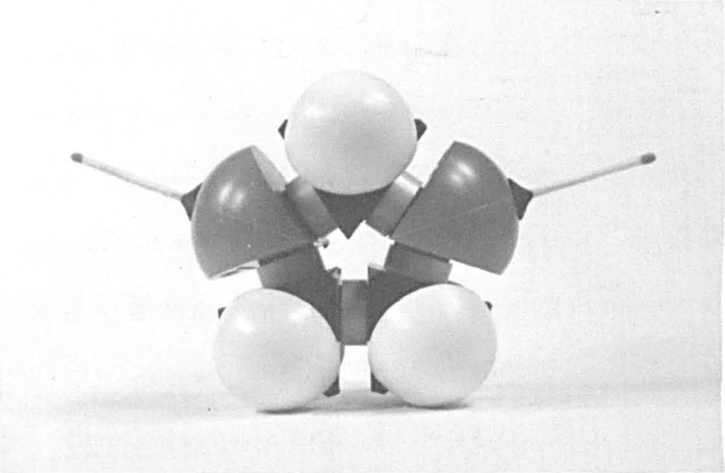

Fig. 9.4

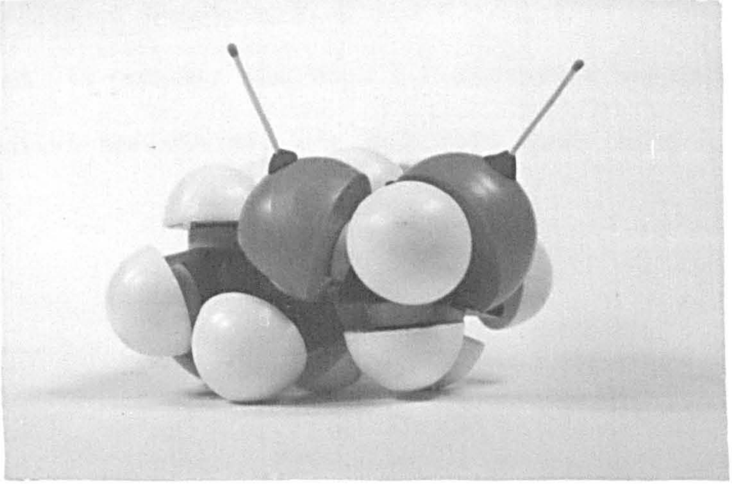

Fig. 9.5

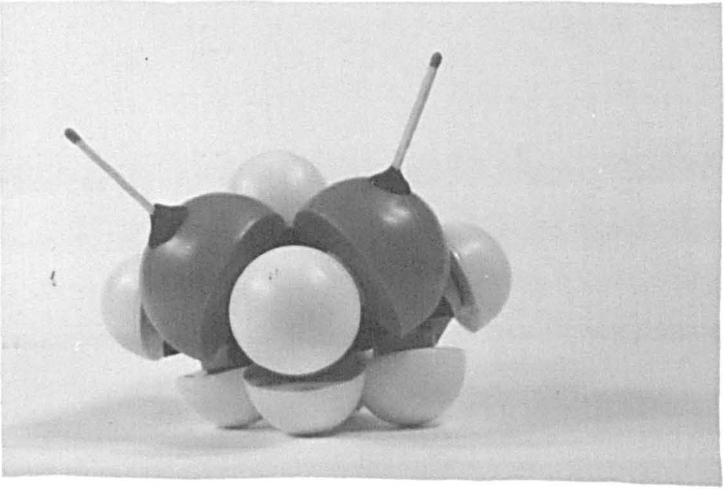

Fig. 9.6

Fig. 9.6 is a photograph of a model of 1,3-dioxepane which shows that the molecule is not planar and that the component dipoles at the oxygen atoms are at about 90° to each other. Models of poly-1,3-dioxolane are similar to the monomer in this respect so that the dipoles acting at the oxygen atoms of 1,3-dioxepane and poly-1,3-dioxepane will be similar. Table 9.1 shows that the basicities of the two species are almost identical.

9.3 Conclusion.

The basicity measurements confirm the kinetic and conductivity results of Chapters 4, 5 and 8 i.e. that poly-1,3-dioxolane is more basic than its monomer and that 1,3-dioxepane and poly-1,3-dioxepane, which have similar basicities, are both more basic than 1,3-dioxolane.

References to Chapter 9.

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Chapter 10

Problems Outstanding and Suggestions for Further Work

Although the active centres for the polymerisation of 1,3-dioxolane and 1,3-dioxepane have been shown to be secondary oxonium ions (the protonated cyclic polymers), the magnitude of the dissociation constant of these active centres is still uncertain.

It has been shown that all the perchloric acid must react with both polymers to give active centres as the values of k_p are always constant over large ranges of perchloric acid concentration. On the other hand the values of electrical conductivity show that only a small fraction of these active centres exist as free ions. This apparent contradiction has been taken as an indication that the k_p of free ions is very similar to the k_p of ion-pairs under these circumstances. However it should still be demonstrated that the active centres do not exist entirely as free ions or entirely as ion-pairs.

If there is an extensive equilibrium between free ions and ion-pairs, then the protonation of 1,3-dioxepane with perchloric acid under non-polymerising conditions and the subsequent dilution of the system should result in a large increase of the equivalent conductivity. The analogous experiment with 1,3-dioxolane failed because of the presence of an unidentified impurity and because 1,3-dioxolane is scarsely protonated by perchloric acid.

It should also be possible to demonstrate that the k_p of free ions is very similar to the k_p of ion-pairs by polymerising 1,3-dioxepane in a medium of lower dielectric constant than methylene dichloride, for example chloroform or carbon tetrachloride. Under these circumstances the electrical conductivity should be much less, as there are less free ions, but the value of k_p should be essentially unaltered.

Perhaps the most urgent need is to extend electrical conductivity measurements to the polymerisation of other cyclic oxygen compounds (tetrahydrofuran, trioxane etc.). This should give independent measurements on the rate of the initiation reactions, and it should provide a measure of the dissociation constants of the active centres involved.