ANTIOXIDANT BEHAVIOUR OF PHOSPHATE ESTERS
AND
DERIVED METAL COMPLEXES

by

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HBondara

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A series of aromatic and aliphatic cyclic phosphate esters have been prepared and the reactions of these with hydroperoxides investigated.

While acyclic aliphatic phosphates are inert towards hydroperoxides aliphatic cyclic phosphates were found to react with hydroperoxides in near stoichiometric proportions. The products from cumene hydroperoxide included phenol, acetone, α-methyl styrene and amyl alcohol indicating ionic and free-radical pathways for the reaction. Five-membered cyclic phosphate esters based on catechol were shown to be very powerful catalysts for the decomposition of hydroperoxides. With cumene hydroperoxide, the products were mainly acetone and phenol reflecting a non-radical mechanism. The effect of substituents, temperature and solvent on the reaction has been investigated in detail and thermodynamic parameters calculated. The mechanism has been shown to involve alternative ring opening and ring closure of the catechol phosphate. Restricted rotation of the C-C bond in the five-membered cyclic phosphate, the stability of the intermediate phenolate anion and the activity of the vicinal hydroxy group are important factors governing the reaction.

These esters were found to be very effective thermal stabilisers in decalin and they improved the u.v. stability of polypropylene by virtue of their reaction with hydroperoxide forming non-radical products.

A number of novel metal complexes derived from acyclic and cyclic phosphato-ligands were synthesised. The catechol phosphate metal complexes (ferric and copper) were very effective catalysts for the decomposition of hydroperoxides and they did so almost exclusively by an ionic mechanism. These complexes, particularly the copper complex , were very effective photostabilisers for polypropylene.

Attempts to prepare the nickel complex of catechol cyclic phosphate were not successful.

Cyclic phosphato-complexes
Hydroperoxides
Antioxidants
Stabilisers
Polypropylene

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CHAPTER 1.

1.1 INTRODUCTION

Polymers, both natural and synthetic, are susceptible to deterioration due to oxidative degradation. This results in the degeneration of useful properties and finally leads to the failure of the polymer. With the rapid increase in the use of polymeric materials in an array of diverse applications during the last few decades, research has been directed mainly in two directions to improve the useful properties and to lengthen the lifetime of polymers. One is the designing of monomers such that the resulting polymer will be least susceptible to oxidation. The second is the development of additives which when incorporated into the polymer will inhibit its destructive reactions. The development of polymers with inherent resistance to oxidative degradation has its own limitations and hence the need for the constant search for more effective additives to combat polymer degradation. The work described herein is a study of a class of compounds within this latter category known in general as antioxidants.

An understanding of the mechanisms by which polymers undergo deterioration is an essential prerequisite in developing antioxidants capable of bringing oxidative reactions of polymers under control.

The oxidation of a polymer begins even during its manufacture. A hydrocarbon will not remain inert to atmospheric oxygen under the influence of heat and/or radiations. High mechanical shear coupled with heat during processing can lead to chain scission resulting in the formation of macro-alkyl radicals, which have a notable affinity for molecular oxygen to form peroxy radicals.[1,2]

$$R\text{-}H \quad + \quad O_2 \xrightarrow{\text{heat/ u.v.radiation}} R^{\bullet} \quad + \quad {}^{\bullet}OOH$$

$$R\text{-}R \xrightarrow[\text{heat}]{\text{mech.shear}} R^{\bullet} \xrightarrow{O_2} ROO^{\bullet}$$

These reactions constitute the initiation of oxidative degradation and also mark the instant when the polymer begins to need the help of additives to bring about the subsequent reactions under control. The peroxy alkyl radicals so formed can abstract a hydrogen atom forming hydroperoxides.

$$ROO^{\bullet} \quad + \quad RH \longrightarrow ROOH \quad + \quad R^{\bullet}$$

These hydroperoxides can undergo homolytic bond fission under the influence of heat and/or u.v. radiation giving rise to more radical species.[3]

$$ROOH \xrightarrow{\text{low conc.}} RO^{\bullet} \quad + \quad {}^{\bullet}OH$$

$$ROOH \xrightarrow{\text{high conc.}} RO^{\bullet} \quad + \quad ROO^{\bullet} \quad + \quad H_2O$$

Transition metal residues such as those derived from Ziegler-Natta catalyst systems are also thought to be responsible for the free-radical decomposition of hydroperoxides by setting up redox systems.[4]

$$\mathrm{ROOH} + \mathrm{M}^{n+} \longrightarrow \mathrm{M}^{(n+1)+} + \mathrm{RO}^{\bullet} + \mathrm{OH}^{-}$$

$$\mathrm{ROOH} + \mathrm{M}^{(n+1)+} \longrightarrow \mathrm{M}^{n+} + \mathrm{ROO}^{\bullet} + \mathrm{H}^{+}$$

The accumulating radical species set up an autocatalytic kinetic chain and there is ample evidence to support its radical character.[1-3]

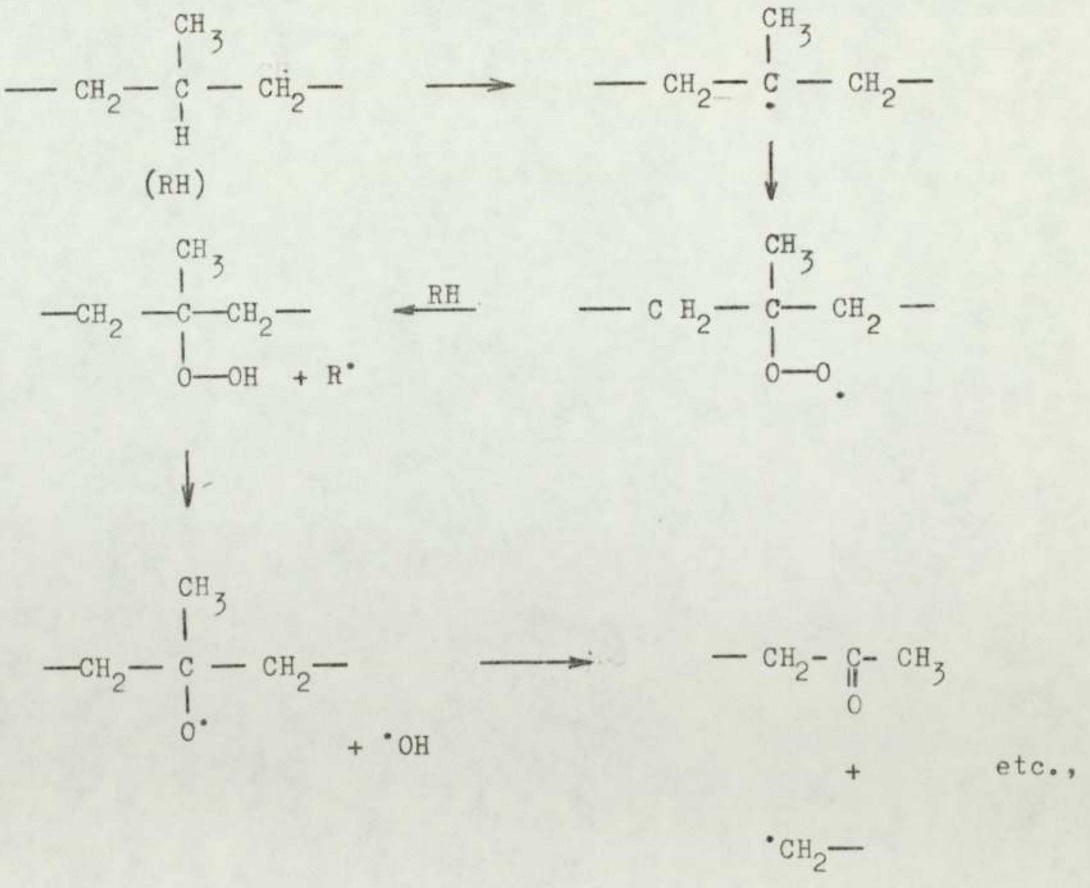
$$\mathrm{RO}^{\bullet} + \mathrm{RH} \longrightarrow \mathrm{ROH} + \mathrm{R}^{\bullet}$$

$$\mathrm{ROO}^{\bullet} + \mathrm{RH} \longrightarrow \mathrm{ROOH} + \mathrm{R}^{\bullet}$$

$$\mathrm{R}^{\bullet} + \mathrm{O}_2 \longrightarrow \mathrm{ROO}^{\bullet}$$

$$\mathrm{R}^{\bullet} + -\mathrm{C}{=}\mathrm{C}- \longrightarrow -\dot{\mathrm{C}}-\mathrm{C}^{\bullet}-\mathrm{R} \quad \text{etc.}$$

In polypropylene for example the following sequence of reactions can take place:



Termination of these chain reactions is possible by combination of these radicals to form molecular products.

$$RO_2^\bullet + {}^\bullet R' \longrightarrow ROOR'$$

$$2R^\bullet \longrightarrow R\text{-}R \qquad \text{etc.}$$

Under normal atmospheric conditions reaction of $R^\bullet$ with oxygen is very fast and the abstraction of $H^\bullet$ by $ROO^\bullet$ is rate determining and termination by recombination of alkyl radicals, $R^\bullet$, becomes less significant.[1,2,3]

1.2. PHOTOCHEMICAL INITIATION.

Although the ultra-violet radiation in sun light contains sufficient energy to break certain single bonds in most polymers direct absorption of u.v. light by pure polymers plays no significant role in the initiation due to very low quantum yield of such reactions. Electronically excited oxygen molecules can however be involved.[5]

Unsaturated sites can be excited by u.v. radiation and since oxygen molecules are known to be excellent triplet quenchers[6], production of peroxides can proceed through attack of oxygen (${}^1\Delta g$) produced by quenching of the excited chromophore.[7]

$$^1A \xrightarrow{u.v.} {}^3A$$

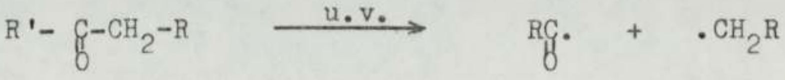
$$^3A + {}^3O_2 \longrightarrow {}^1A + {}^1O_2$$

$$^1O_2 + A \longrightarrow AO_2^\bullet$$

where A is an olefin with unsaturation.

Apart from the photolysis of hydroperoxides as mentioned earlier, secondary products derived from hydroperoxides can undergo photochemical reactions forming free-radicals. The photochemistry of aliphatic ketones suggests Norrish type I and II reactions for chain scission.[8]

Norrish type I.



$$R'-\underset{\underset{O}{\|}}{C}-CH_2-R \xrightarrow{u.v.} R\underset{\underset{O}{\|}}{C}\cdot + \cdot CH_2R$$

Norrish type II.

$$R'-\underset{\underset{O}{\|}}{C}-CH_2-CH_2-CH_2-R \longrightarrow R-\underset{\underset{O}{\|}}{C}-CH_3 + CH_2=CHR$$

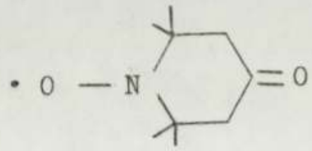
However there is accumulating evidence[9,10] to support the fact that 'hydroperoxide' is the primary product of oxidation of polyolefins and that it is the most important initiator under normal conditions of polymer degradation.

1.3. STABILISATION.

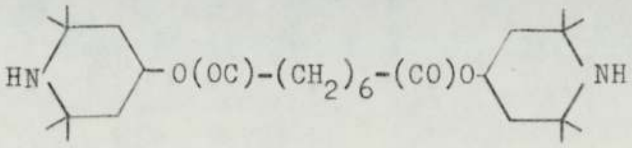
1.3.1. Radical Traps.

Since the autoxidation of polyolefins is manifested by the formation of free radicals it is clear that any substance that reacts with these radicals to form stable molecular products will act as an antioxidant.

Such stable radicals as 2,2,6,6-tetramethyl-4-piperidin-N-oxyl,



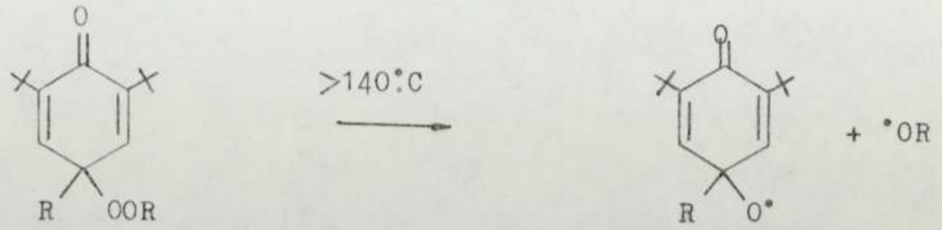
can react with $R^{\bullet}$ to give stable molecular products.[11] However, these will have to compete with molecular oxygen for $R^{\bullet}$ radicals. These are however of little practical importance as stabilisers against thermal oxidation. These has been confirmed[12] by the studies on



Particularly effective in trapping radicals are the hindered phenols and arylamines. The reactive hydrogen of these compounds compete with the polymer for the peroxy radicals and the chain propagation ceases due to hydrogen transfer.

This mechanism has been supported by the kinetic isotope effect observed when deuterium was substituted for labile hydrogen atom in these compounds.[13]

One drawback of these compounds is that the peroxy-dienone formed which is unstable at high temperatures breaks down to form radical products.



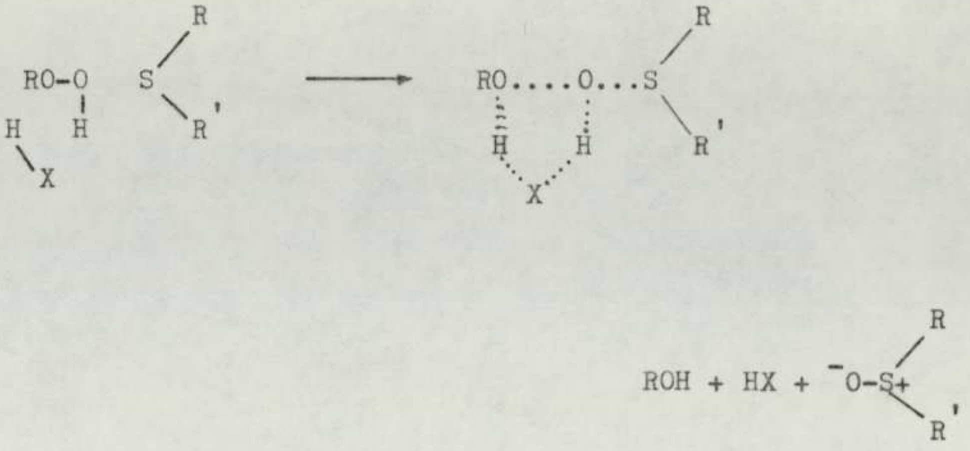
An indirect way of stabilising polymers by these phenols and amines is by complexing transition metal residues which may otherwise undergo electrontransfer oxidation reduction reactions generating free radicals.

1.3.2. Peroxide decomposers.

Peroxides play a prominent role in initiating the radical process of autoxidation[9,10]. Therefore materials that can decompose hydroperoxides effectively to form inactive molecular products have a great potentiality as antioxidants[14]. These include certain phenols, mercaptans, dialkyldithiocarbamates and dithiophosphates, some metal chelates, dialkyl mono- and disulphides alkyl and aryl phosphites and certain cyclic phosphates[16].

Studies by Holdsworth and Scott[17] showed that oxygenated sulphur compounds are responsible for non-radical decomposition and hence for the antioxidant action displayed by certain sulphur containing compounds.

The primary product of the reaction between saturated alkyl sulphides and hydroperoxides is the corresponding sulphoxide.[97] There is no evidence for the participation of free radical intermediates in this stoichiometric reaction. The following mechanism has been proposed by Bateman and Hargrave[97] for this reaction.



For unsaturated sulphides, however, the yield of the sulphoxide has been found to vary with the nature of the sulphide, the hydroperoxide and also the solvent.[98,99]

A detailed discussion on the reactions of phosphites and phosphates with hydroperoxides will follow later.

1.4 STABILISATION AGAINST PHOTODEGRADATION

Hydroperoxides, peroxides, carbonyl groups, titanium catalyst residues and polynuclear aromatic impurities are all potential photo-initiators. In the light of the knowledge of such initiation reactions a u.v. stabiliser may be able to act as a stabiliser in three different ways. viz:

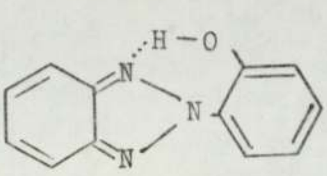
(a) By absorbing u.v. radiation and undergoing radiationless relaxation processes.

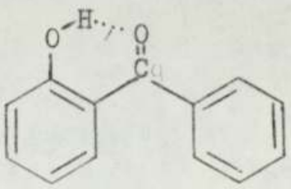
(b) By extracting energy from an excited chromophore in the polymer, and

(c) By acting as a hydroperoxide scavenger or by trapping free radicals.

1.4.1 U.V. absorbers.

Benzotriazoles and 2-hydroxybenzophenones are typical examples of u.v. absorbers.





They owe their effectiveness to their ability to absorb u.v. radiation up to 350-370nm and they will be effective whether incorporated into the polymer or used simply as a screen. Carlsson and Wiles [18] have pointed out that stabilisers which act solely due to their ability to absorb u.v. radiation are relatively ineffective . eg. Benzotriazoles, salicylates and acrylates.

Many 'u.v. absorbers are still widely used because they are able to photostabilise polymers by mechanisms other than u.v. absorption. Hydroxybenzophenones, oximes and certain nickel chelates have been shown to possess stabilising activity far in excess of that due to screening alone. Thus, Ranaweera and Scott[57] have shown that nickel dibutyldithiocarbamate acts as a u.v. screening agent as well as a hydroperoxide decomposer, and the same workers have demonstrated[100] that the nickel complex of 2-hydroxyacetophenone oxime did not act simply as a u.v. screen in the oxidation of cumene initiated by cumene hydroperoxide photolysis. This chelate was inactive towards hydroperoxides but still retarded themally initiated oxidation and a mechanism involving the trapping of $ROO^{\bullet}$, $RO^{\bullet}$ or $R^{\bullet}$ radicals has been proposed.[100]

1.4.2 Deactivation of excited chromophores.

The chromophores present in a polyolefin when excited by u.v. radiation may react, fragment or undergo relaxation and return to the ground state. The reactions of the excited chromophores can lead to the initiation of oxidative degradation. An excited state quencher Q, must be able to extract the energy from an excited state of a chromophore, C, and dissipate it as harmless long wave radiation.

$$C \xrightarrow{h\nu} C^{*} \xrightarrow{Q} C + Q^{*} \longrightarrow Q + h\nu'$$

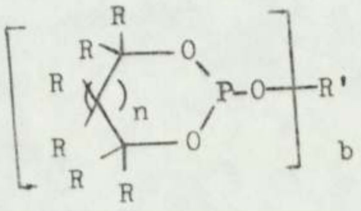
Excited carbonyl and singlet oxygen quenching are gaining ground as mechanisms of photostabilisation of polyolefins. Metal dithiocarbamates several nickel phenolates and oximes have been shown to be able to quench excited carbonyls.[101, 102.] Some of these are capable of quenching polynuclear aromatics also. Amines such as N-isopropyl-N' phenyl-p-phenylenediamine,[103] metal chelates such as nickel dialkyl dithiocarbamates and phenolates, and a host of other compounds (ferrocene, corotene, water and oxygen $^{3}O_2$) have been shown to quench singlet oxygen.[19]

It should however be noted that much of the existing evidence on quenching is conflicting,[104] certain compounds which are active quenchers, are ineffective in polymers and it appears that sensitisation of polyolefin oxidation by carbonyl chromophores is of little importance.

1.5 ORGANOPHOSPHORUS COMPOUNDS AS ANTIOXIDANTS

Organophosphorus compounds are used in a variety of industrial applications. They are used as fire retardants, plasticisers, heat and light stabilisers and as stabilisers against colour development in polymers.[20] A few examples may be quoted to justify the usefulness of organophosphorus compounds as stabilisers in polymers.

Irganox 1222 , diethyl-(3,5-di-t-butyl-4-hydroxyphenyl) phosphonate, and glycol phosphates have been shown to be effective heat stabilisers in PET. Warren[20] has claimed that phosphite estres of the type,

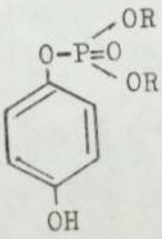


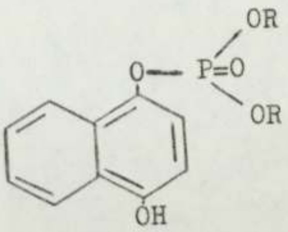
$R = H$ or C_{1-10}

$n = 0$ or 1

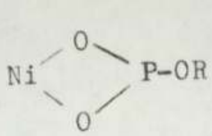
$b = 1$ or 2.

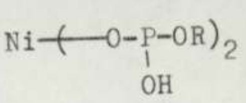
could stabilise polypropylene at 150°C in air giving induction periods of 300-400 hours. The following phosphates were shown to possess antioxidant activity by Sanon[21] et al.





A variety of organophosphites containing nickel have been patented[22] as effective stabilisers for polyolefins . These have the general formula,





$$\mathrm{Ni}\!\left(\!-\!\!-\mathrm{O}\text{-}\underset{\mathrm{OH}}{\overset{|}{\mathrm{P}}}\text{-}\mathrm{OR}\right)_2$$

where R has 1-20 carbon atoms and may contain phenolic hydroxyl groups.

Although considerable work has been done on the reactions of phosphites with peroxides and hydroperoxides, the mechanism of antioxidant action of these organophosphorus compounds is relatively little understood.

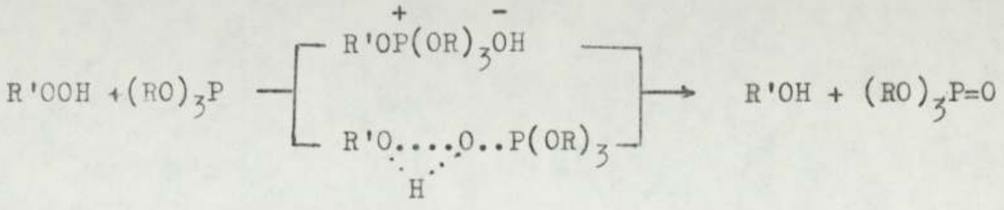
The antioxidant activity of phosphites is thought to be due to their ability to react with hydroperoxides in a stoichiometric reaction forming the phosphate.

$$(RO)_3\,P \quad + \quad ROOH \longrightarrow (RO)_3\,P{=}O \quad + \quad ROH$$

The concepts of the mechanism of the reactions of hydroperoxides with organophosphites are ambiguous. Walling[22a] has reported that these reactions were not inhibited by radical scavengers and has therefore proposed a polar mechanism involving an attack by phosphorus on the hydroperoxide, at the oxygen atom nearer to the alkyl group.

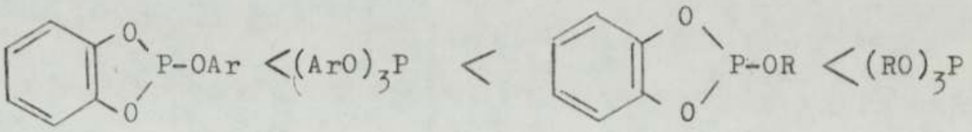
$$ROOH + (EtO)_3P \longrightarrow (EtO)_3\overset{+}{P}OR + {}^{-}OH \longrightarrow ROH + (EtO)_3PO$$

Later the isotopic studies by Denney et al[22b,c] indicated that either there was an attack by the phosphite on hydroxyl oxygen to form an intermediate ion pair, or that the reaction proceeded via a three-centre complex.



$$R'OOH + (RO)_3P \longrightarrow \left[\begin{matrix} R'O\overset{+}{P}(OR)_3\overset{-}{O}H \\ \\ R'O\cdots O\cdot\cdot P(OR)_3 \\ \;\;\cdot\,H\,\cdot \end{matrix}\right] \longrightarrow R'OH + (RO)_3P{=}O$$

Pobediminskii and Buchachenko[23] and a number of other workers, on the basis of kinetic studies have agreed that the order of reactivity of the following phosphites with hydroperoxides was,



These same workers then introduced a latent radical mechanism, in which they postulated the formation a radical pair(within a solvent cage) with a high probability of disproportionation to form molecular products.

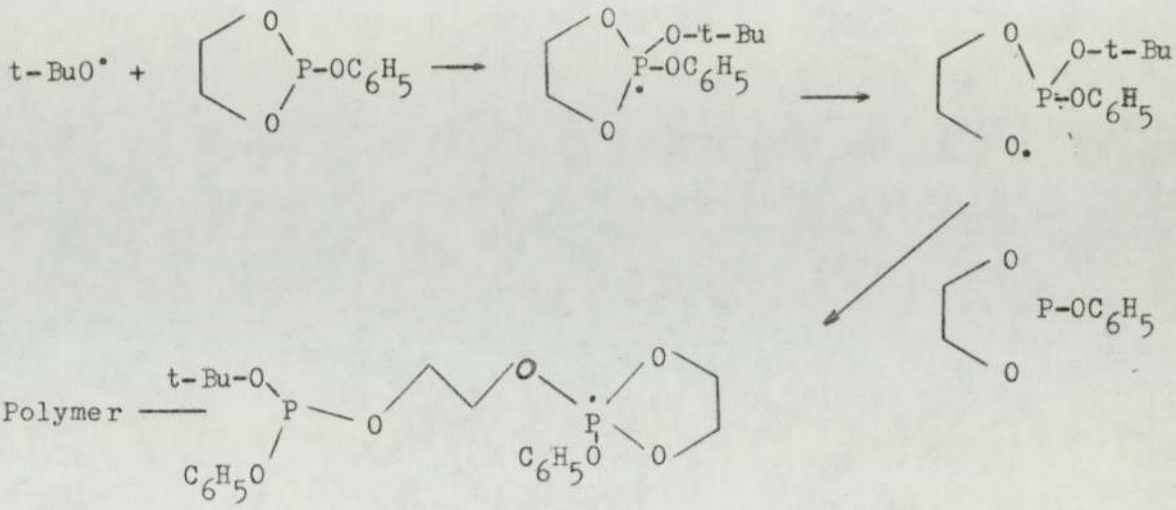
$$R'OOH + P(OR)_3 \longrightarrow \left[R'O^{\bullet}\ HO\dot{P}(OR)_3\right] \longrightarrow R'OH + (RO)_3PO$$

After an investigation of the chemical polarisation of the ^{31}P nuclei, they have recently presented evidence of competition of the radical and non-radical pathways disputing the latent radical mechanism.[23a]

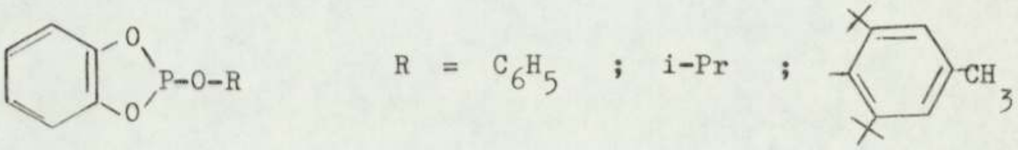
Alkoxy radical initiated autoxidation of a series of tertiary phosphites has been reported by Bentrude.[24] He proposed the following sequence for the reactions of alkoxy radicals with the phosphites.

$$R'O^{\bullet} + P(OR)_3 \longrightarrow R'O\dot{P}\text{-}(OR)_3 \longrightarrow \dot{R}' + (RO)_3PO$$

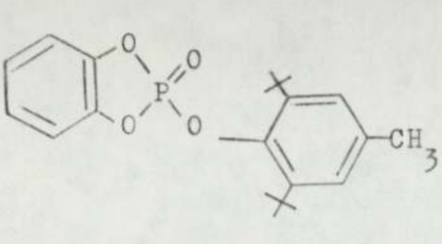
With cyclic phosphites polymeric products have been idntified and the following mechanism has been suggested.[24]

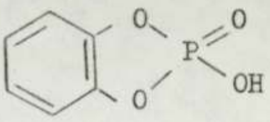


Detailed studies on the reactions of cyclic phosphites have been carried out recently by Humpris and Scott.[15] Cyclic phosphite esters based on catechol,

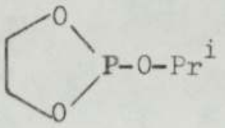


were found to be very effective catalytic decomposers of hydroperoxides. The reaction which at first is fast and second order changes later to a first order catalytic process. Though the reaction was not affected by radical scavengers, they have observed that these phosphite-hydroperoxide systems could initiate vinyl polymerisation.[15a] It is said that in the second stage of the reaction, a catalytic species is produced which could act like a Lewis acid decomposing the hydroperoxide by an ionic mechanism. The two phosphates,

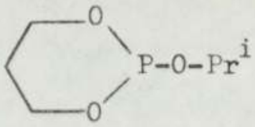




have been identified as reaction products and they too were shown to be powerful catalysts for the decomposition of cumene hydroperoxide. The aliphatic cyclic phosphites have also been studied.[15b] Cyclic ethylene phosphite,

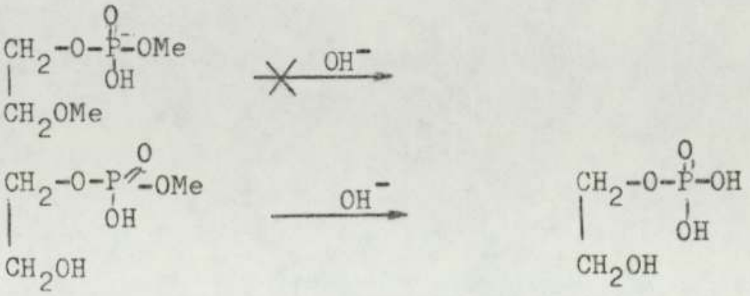


was found to react rapidly, while the phosphite with a six-membered ring,



also reacted though rather slowly. The acyclic phosphite, triphenyl phosphite was also able to react with hydroperoxides but failed to produce a catalytic species. Work carried out by Parsons[16], however, has shown that aliphatic cyclic phosphites were not cacalytic decomposers of hydroperoxides. The ring structure and the aromaticity or at least the unsaturation appear to be important factors responsible for the catalytic activity.

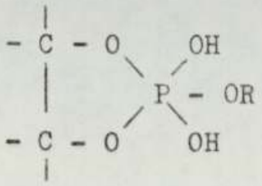
The hydrolytic cleavage of 1,2-diol phosphates may bear some relation to the reactions considered above. The reactivity of phosphates with a vicinal OH group is higher. Thus, while methyl-2-methoxyethyl phosphate is inert to base hydrolysis, it was found that methyl 2-hydroxyethyl phosphate is rapidly hydrolysed to 2-hydroxyethyl phosphate.[25]



$$\mathrm{MeOCH_2CH_2{-}O{-}P(O)(OH){-}OMe} \not\xrightarrow{OH^-}$$

$$\mathrm{HOCH_2CH_2{-}O{-}P(O)(OH){-}OMe} \xrightarrow{OH^-} \mathrm{HOCH_2CH_2{-}O{-}P(O)(OH){-}OH}$$

Brown and Todd[26] have pointed out that the process can be considered as an attack by the vicinal hydroxy group on P=O bond (catalysed by OH^- or H^+ ions) with simultaneous removal of ^-OR , possibly with the intervention of a cyclic intermediate like,



The catalytic decomposition of hydroperoxides by cyclic phosphates may, therefore be possibly due to alternative ring opening and ring closure of the phosphate.

1.6 SCOPE AND OBJECT OF THE WORK

The foregoing survey indicates that the cyclic phosphates derived from catechol are efficient hydroperoxide decomposers and that they do so by a non-radical mechanism. Therefore the possibility exists that these cyclic phosphates could act as effective hydroperoxide decomposing antioxidants in polymer systems.

Although considerable work has been done on the reactions of phosphites with hydroperoxides, relatively very little is known about the reactions between cyclic phosphates and hydroperoxides. It was therefore thought pertinent to carry out a systematic study in order to understand more fully the essential features of these reactions. It is intended to synthesise a series of cyclic phosphate esters with a view to study the effect of substituents on the reactivity. A major part of this work will be concerned with detailed kinetic studies in solution, in an attempt to establish a mechanism for the reaction.

Although transition metal ions are known to undergo redox reactions with hydroperoxides, this can be prevented by coordination and often metal chelates are capable of acting as quenchers. Therefore, an attempt will be made to synthesise metal complexes with cyclic phosphates as ligands. No such metal complexes have been so far reported in the literature. The reactions of these metal complexes can then be studied.

The antioxidant behaviour of cyclic phosphates and the derived metal complexes in a polyolefin will be studied in the latter part of this work.

CHAPTER 2

EXPERIMENTAL

2.1 SPECTROSCOPY

Infra red spectra were recorded on a Perkin-Elmer 457 grating spectrophotometer.

Ultra violet and visible spectra were recorded on a Perkin-Elmer 137 spectrophotometer.

Mass spectra were recorded on an A.E.I,M 59 double focussing spectrometer with a 70 eV accleration.

Nuclear magnetic resonanc spectra were obtained on a Perkin-Elmer 60 MHz and 100 MHz instruments. Tetramethylsilane was used as the internal standard.

2.2 QUANTITATIVE ELEMENTAL ANALYSIS.

Elemental analyses (C,H) have been carried out on a Perkin-Elmer analyser.

2.2.1 Determination of Phosphorus.

Phosphorus determination on phosphate esters was carried out gravimetrically as oxine-phosphomolybdate.

Procedure.

A sample of the compound (0.1g) was weighed accurately and transferred in to a flask, and distilled water (25ml) was added.

This solution was boiled for about 15 minutes with 10 ml of conc. HNO_3. Perchloric acid (2ml) was then added and the solution was boiled again for another 15 minutes. After cooling the solution was diluted to about 100ml and heated to about 70°C. Oxinemolybdate reagent (30ml) was then added and maintained the temperature at 70°C for a further 30 minutes. The mixture was allowed to stand for several hours and filtered through a sintered glass crucible (4). The precipitate was washed with ammonium nitrate solution (10ml,1.0%) and dried to a constant weight at 105°C.

$$P/(C_9H_7ON)_3 \cdot H_7\ P(Mo_2O_7)_6\ 2H_2O \quad = \quad 0.01327$$

Oxine-molybdate reagent.

This was prepared by mixing concentrated hydrochloric acid (42ml), ammonium molybdate solution (42ml; 10%) and 8-hydroxyquinoline solution (16ml; 5% in 5% hydrochloric acid)

2.2.2 Determination of Copper.[36]

Estimation of Cu^{2+} in the complexes was carried out by an iodometric method.

About 0.2g of the complex was accurately weighed and transferred into a conical flask containing distilled water (25ml) and acetic acid (2ml). To this was added KI (~2g) dissolved in distilled water (10ml) and the vessel was kept in the dark for about 10 minutes. The liberated iodine was titrated against a standard solution of sodium thiosulphate until the solution was faint yellow. A few drops of a starch solution was then added and continued the titration to the end point which is from blue to colourless.

2.2.3. Determination of Cobalt.[37]

Co^{2+} in the complexes was determined in the form of tetrapyridino-cobalt (II)-thiocyanate[37]:

About 0.2 g of the compound was weighed accurately and dissolved in distilled water (100 ml). Ammonium thiocyanate (~1 g) was added and the solution heated to boiling. Pyridine (4 ml) was added with rapid stirring. The solution was then allowed to cool and filtered through a sintered glass crucible (4). The blue precipitate was washed with (a) water (50 ml) containing pyridine (0.7%) and ammonium thiocyanate (0.5%) and (b) ether containing a few drops of pyridine. The crucible was then placed in a vacuum desiccator for about 20 minutes and weighed.

$$Co/\ Co\ Py_4.(SCN)_2 \quad = \quad 0.1199$$

2.2.4 Determination of Nickel.[37]

Ni^{2+} was estimated in a manner similar to that used for Co^{2+}. The same precipitation procedure was followed. The precipitate was washed (a) 4-5 times with alcohol (37%) containing ammonium thiocyanate (0.1 %) and pyridine (1.5 %)

(b) 2-3 times with alcohol (10ml) containing pyridine (1 %)

and finally (c) with ether containing a few drops of pyridine.

The sky blue precipitate of Ni $(C_5H_5N)_4\ (SCN)_2$ was dried for about 20 minutes in a vacuum desiccator and weighed.

$$\mathrm{Ni} / \mathrm{Ni}\ (C_5H_5N)_4 \cdot (SCN)_2 \quad = \quad 0.1195$$

2.2.5 Determination of Iron.

Fe^{3+} in the phosphate complexes was determined as Fe^{2+} after reduction with sulphurous acid.

Asample of the compound in water (25 ml) was boiled with sulphurous acid for about 15 minutes. Later sodium bicarbonate (1g) was added to the solution to expell excess sulphur dioxide. This solution was then titrated against standard potassium permanganate.

All the above analyses were performed in duplicate.

2.3. CHROMATOGRAPHY.

2.3.1. Thin Layer Chromatography. (T.L.C.)

T.L.C. was employed for the qualitative analysis of products obtained in the reactions between hydroperoxides and phosphate esters. Table 2.1 shows the compounds analysed, the solvent systems used and the developing agents along with the R_f values for the respective compounds.

Table 2.1

Compound	Developing Agent	R_f
Cumene hydroperoxide	NaI/Isopropanol	0.73
Phenol	$FeCl_3$ (aq)	0.64
o-Hydroxy phenyl phosphate		0.33
o-Hydroxy phenyl methyl phosphate	I_2vapour/$FeCl_3$(aq)	0.19
o-Benzoquinone		0.42

Solvent system.

Benzene : Acetic acid 2 : 1

Silica gel plates were used for all the experiments.

2.3.2. Gas-Liquid Chromatography. (G.L.C.)

A Pye 104 gas chromatograph with a flame ionisation detector was used for the analysis , both quantitative and qualitative , of hydroperoxide decomposition products.

Columns 5 feet long glass columns with 10 - 12 % Polyethyleneglycol adipate on celite. These columns were conditioned for about 30 hours before being used.

Gases. Gases were purified by passing through molecular sieves. (U.C. 13X)

Nitrogen gas was used as the mobile phase flowing at a rate of 40 ml /minute.

Temperature. Atemperature programming was found to give a good seperation of the reaction products.

Initial temperature - 100°C
Rate of increase - 12°C / minute
Final temperature - 180°C for 5 minutes

The detector temperature was 200°C

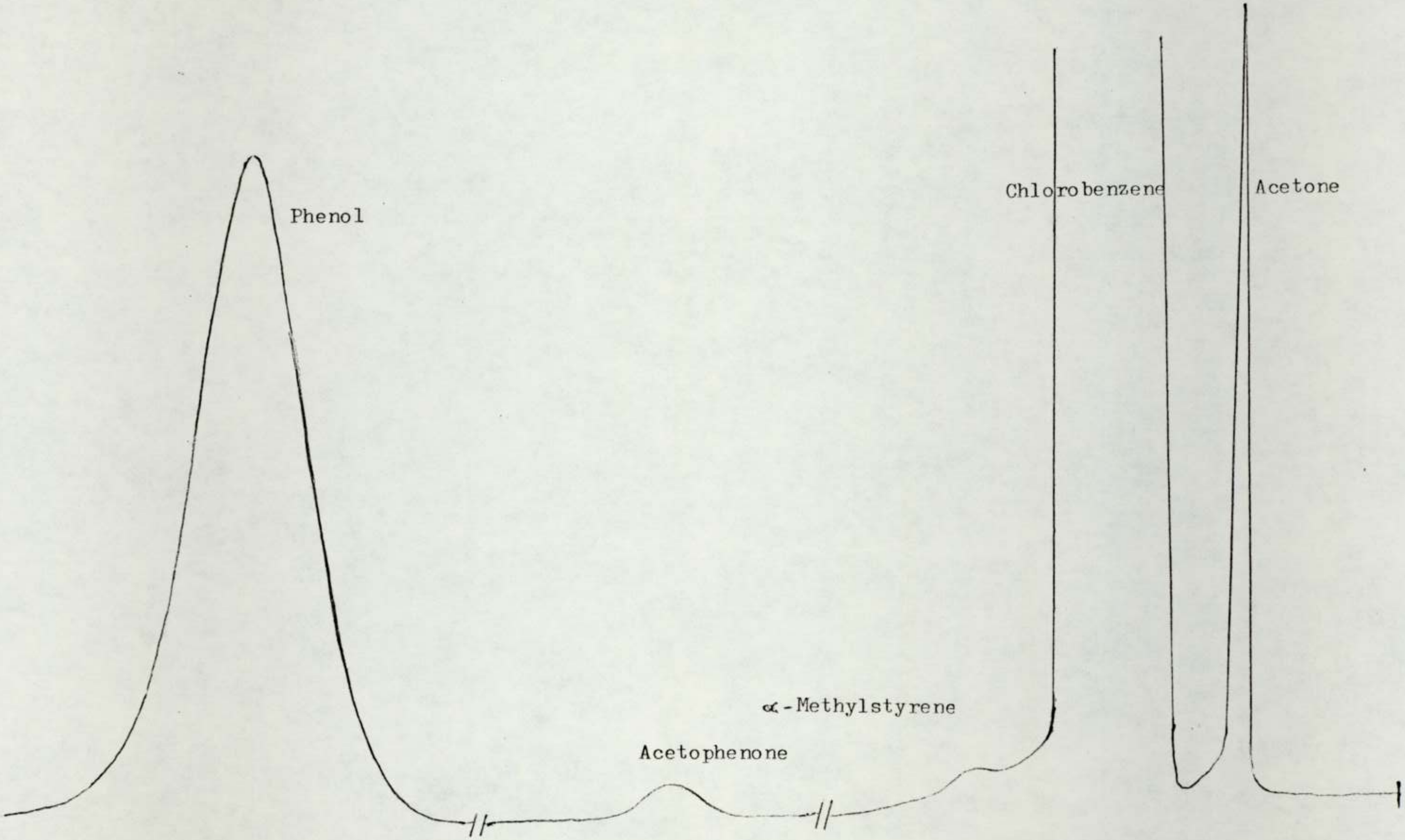
The retention distances for the compounds analysed by G.L.C. appear in the table 2.2.

Table 2.2.

Retention distance of compounds analysed by G.L.C.

Compound	Retention distance /cm (chart speed 40 mm / minute)
Acetone	2.2
Chlorobenzene	8.0
2-Chloroethane	11.7
α-Methyl styrene	13.1
Acetophenone	29.5
Cumyl alcohol	33.0
Phenol	39.6

A typical chromatogram is shown in figure 2.1.



<u>Figure 2.1</u> A typical chromatogram of the cumene hydroperoxide decomposition products.(Reaction between a cyclic catechol phosphate + CHP)

2.4. KINETIC EXPERIMENTS.

The rate of decomposition of hydroperoxides by various phosohorus compounds was followed iodometrically. Though various methods[33] including spectroscopic methods are avaliable for the determination of hydroperoxides, isopropanol-acetic acid method was chosen due to simplicity of the procedure and its reliability. A typical estimation is as follows.

25 ml of a solution containing 10 % (V/V) of glacial acetic acid in isopropanol was taken into a conical flask and 1.00 ml of reaction mixture was pipetted in. This was brought to boiling under reflux (this excludes air from the apparatus so that aerial oxidation of sodium iodide to iodine is prevented) and sodium iodide (10 %) in isopropanol (10 ml) was added. This was then refluxed for 5 minutes and the liberated iodine was titrated against standard sodium thiosulphate solution.

Sodium iodide is soluble in isopropanol and hence the determination of hydroperoxide by this method can be done in anhydrous non-aqueous solvents. The reaction between hydroperoxides and I^- is retarded by water.

The cyclic phosphates do not oxidise I^- to I_2 and hence do not interfere with the determination.

Due to the presence of excess I^- , liberated iodine is converted to I_3^-.All I_2 is therefore retained in isopropanol solution.

$$2H^{+} + 2I^{-} + ROOH \longrightarrow I_2 + ROH + H_2O$$

$$I_2 + I^{-} \longrightarrow I_3^{-}$$

$$I_3^{-} + 2S_2O_3^{--} \longrightarrow 3I^{-} + S_4O_6^{2-}$$

A three-necked 100 ml round bottom flask was used as the reaction vessel. This was fitted with a drying tube and the contents were stirred by a magnetic follower. The hydroperoxide of the required concentration in a particular solvent was allowed to reach the intended temperature in an oil (Risella oil) bath. The compound under investigation was then added and the concentration of the hydroperoxide in the reaction vessel was estimated at pre-determined time intervals.

2.5. PREPARATION OF FILMS

The compounds were incorperated into unstabilised polypropylene (H F 20 C / C V 170 I C I) in the RAPRA Torque Rheometer. Essentially this is a small internal mixer, with two mixing screws rotating in opposite directions. The mixing chamber could be kept closed to the atmosphere by means of a compressed air operated ram.

Polypropylene (35 g) along with the required quantity of the additive was placed in the chamber of the rheometer and mixed for a constant time (5 minutes) at 180°C. These mixing conditions were kept constant for all the samples. The samples so processed were removed from the Torque rheometer and chilled immediately in cold water. When cold they were dried, sealed in polyethylene bags and stored in refrigerator.

Films were prepared from these samples by compression moulding between stainless steel glazing plates. A temperature of 180°C was maintained for 2 minutes during pressing (under a pressure of 18 tons on a 6" diameter ram) and the plates were cooled to below 80°C before releasing the pressure to remove the films. Samples of constant thickness (0.007 inch) cut out from the middle of the film were used in the subsequent experiments.

2.6. MEASUREMENT OF ANTIOXIDANT ACTIVITY.

Accelerated ageing test are widely used in assessing the efficiency of antioxidants. However great care has to be taken when results of such experiments are used to evaluate the behaviour of these systems under actual conditions they are intended to be used.

Apart from measuring the rates of reactions of the antioxidants with the model hydroperoxides, the following techniques were used to measure the antioxidant effectiveness of compounds prepared.

(1) U.V. Irradiation experiments.

(2) Oxygen absorption in model compounds.

(3) Oxygen absorption in polypropylene.

2.6.1. U.V. Irradiation Experiments.

Polypropylene films 3 x 2 cm were mounted on cardboard frames and irradiated in a U.V. cabinet. The U.V. cabinet used in these experiments consisted of 15 Phillips TLV 20 /12 fluorescent sunlamps and 15 Atlas Black lamps mounted alternatively. The samples rotate inside this cabinet and this ensures isotropic exposure of all films.

Figure 2.2. compares the radiation from sunlamps and blacklamps with that from the sun.

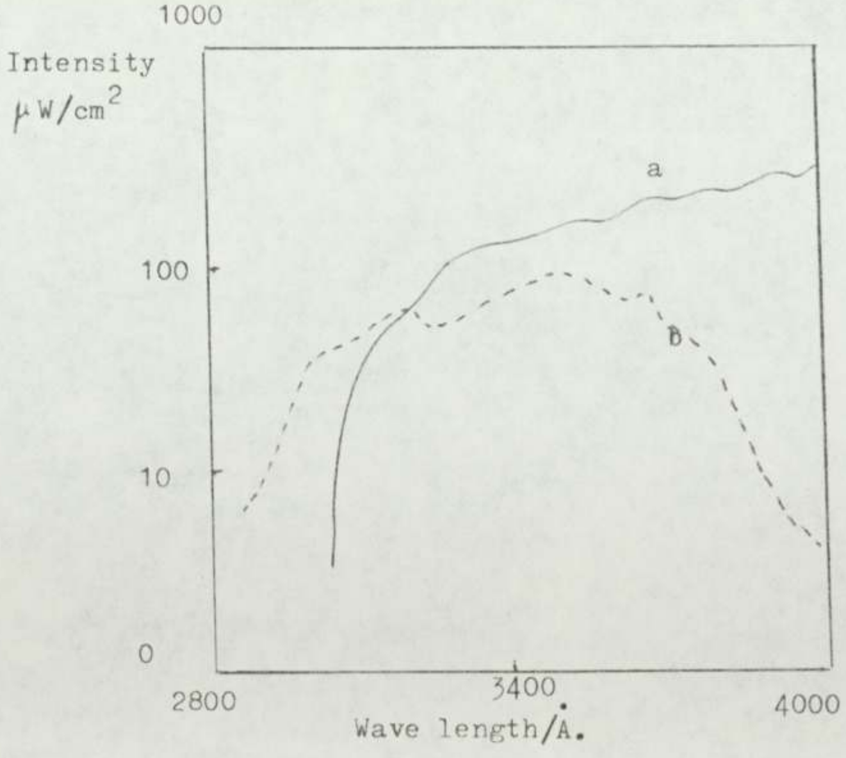


Figure 2.2. Combination of fluorescent sunlamp and blacklamp (b) compared with sunlight.(a)

The progress of oxidation of films was followed by monitoring the growth of the carbonyl absorption. The results are expressed in terms of carbonyl index.

$$\text{Carbonyl Index} \doteq \frac{\text{Absorbance due to } C=O}{\text{Absorbance of a reference peak}}$$

In polypropylene the carbonyl absorption is at 1710 cm^{-1} and the reference peak was chosen as that at 2720 cm^{-1}. This is due to a -C-H stretching vibration and its absorbance was time independent throughout the duration of the experiment. This technique therefore accounts for any slight variation in thickness of individual samples.

2.6.2. Oxygen Absorption.

Oxygen absorption has been widely used as an experimental tool in studying the rate of oxidation of polyolefins[28,29] and rubber vulcanisates[30].

Under normal conditions of oxidation it is the hydrogen abstraction by alkoxy and alkylperoxy radicals that is rate determining and the subsequent reaction with oxygen is relatively very fast. However at low pressures (below about 100 mm Hg) the reaction of alkyl radicals with oxygen becomes rate determining in olefin oxidation. Because of this limitation oxygen absorption studies were performed in a pure oxygen atmosphere at atmospheric pressure.

The rate of oxidation of a sample of polymer is primarily dependent on its absolute rate of oxidation and the rate of diffusion of oxygen can be important for thick samples at elevated temperatures when there is a greater demand for oxygen. The sample thickness therefore becomes a critical factor. There is much less information regarding sample thickness in oxygen absorption experiments of polyolefins in the literature. Hawkins has however reported that oxygen uptake of polyethylene at 150°C is not diffusion controlled at sample thickness upto 5mils. Humpris[62] and Evans[94] have used polypropylene films 0.008 inch thick in their experiments and have not observed any diffusion control. Samples of thickness 0.007 inch were therefore used in this work. When model compounds were used in solution, they were constantly stirred to prevent diffusion control oxidation.

Decalin was used as a model compound in oxygen absorption experiments. This is a saturated hydrocarbon with tertiary hydrogen atoms and therefore simulates the structure of polypropylene.

After distillation under nitrogen, decalin was stored under nitrogen in a refregerator. The required amount of decalin was taken out with a syringe through a rubber septum. Hydroperoxides could not be detected when this decalin was tested with NaI / Acetic acid.

The amount of oxygen absorbed by samples was automatically and continuously measured by means of a pressure transducer of strain gauge type manufactured by Pye-Ether Ltd. (model U P 3 ± 5psi) The complete apparatus used for oxygen absorption has been adequately explained by previous workers.[30,31] A thermostated silicone oil bath at 140°C (± 0.1°C) was used to carry out thermal oxidation.

2.7. PURIFICATION OF REAGENTS.

A.R. grade Acetic acid and Isopropanol were used for kinetic experiments without further purification.

Decalin.

Decalin (General purpose reagent) (250 ml) was heated with triphenyl phosphine (~5g) and distilled under nitrogen. The distillate was washed with sulphuric acid solution (10 %) and then with dilute sodium carbonate (10 %) solution. It was then dried over anhydrous sodium sulphate and redistilled fractionally under nitrogen. The distillate was stored under nitrogen in the refrigerator. (B.P. 191°C)

Cumene hydroperoxide.

Cumene hydroperoxide (Koch-Light), was obtained as a solution stabilised with 6 % of a 15 % w/w slurry of aqueous sodium carbonate. Purification of this was carried out through its sodium salt by the method described by Kharasch[32]. The product was vacuum distilled and the fraction boiling at 52-54°C / 0.1 mm Hg was collected. Iodometric titration[33] showed a purity higher than 98.5 % (B.P. 60°C /0.2 mm Hg)[34].

G.L.C. Standards.

Acetone.

A.R. grade was used without further purification.

Acetophenone.

Redistilled fractionally and the fraction boiling between 201-202°C was collected. (202 / 760 mm Hg)[35]

Chlorobenzene.

General purpose reagent (B D H) was fractionally distilled over phosphorus pentoxide and the fraction distilling at 130°C being collected. (131.7°C / 760 mm Hg)[35]

2-Chloro ethanol (Ethylene chlorohydrin).

Redistilled and the fraction boiling at 129°C was used.

α-Cumyl alcohol (2-Phenyl propan 2-ol)

This was recrystallised from petroleum ether (60 / 80°C) M.P. 34°C (Lit.[32] 36°C)

α-Methyl styrene (2 Phenyl propene)

This was fractionally distilled under nitrogen. Fraction boiling at 165°C was collected.

Phenol.

Fractionally distilled. The fraction boiling at 182°C was collected. (M.P. 40°C)

CHAPTER 3

SYNTHESIS AND CHARACTERISATION OF COMPOUNDS.

3.1.1. Acyclic phosphate esters.

Trimethyl phosphate , triethyl phosphate and triphenyl phosphate (British Drug House) were fractionally distilled over calcium hydride before use.

3.1.2. Diisopropyl hydrogen phosphite.[39]

Isopropyl alcohol (90g 1.5 mol) was dissolved in an equal volume of carbon tetrachloride and phosphorus trichloride (69g; 0.5 mol) in carbon tetrachloride (20 ml) was added dropwise. The reaction mixture was kept cool in an ice bath. The solution was left standing for 1 hour and a stream of nitrogen was passed through the solution to remove hydrogen chloride. The solvent was then distilled off and the product distilled under reduced pressure. (80°C / 15 mm Hg) (Lit.[39] 82.5°C / 17 mm Hg)
Yield 72g (88 %)

I.R. (Neat)

3500 cm^{-1}	(broad)	O-H	(bonded)
2900-3000 cm^{-1}	(strong)	C-H	stretch
2410 cm^{-1}	(strong)	P-H	stretch[42]
1375, 1460 cm^{-1}		C-H	deformation

1260 cm^{-1}	(strong)	P=O	stretch[43]
950-1000 cm^{-1}	(strong, broad)	P-O-C	(alkyl)

N M R (CCl_4)

8.7 τ	(doublet)	12 H	CH_3 protons
5.4 τ	(multiplet)	2 H	tert-H
-2.0 τ	(singlet)	1 H	P-O-H

3.1.3. Diisopropyl chlorophosphate.

Diisopropyl hydrogen phosphite (70g; 0.35 mol) was cooled in a flask immersed in an ice bath and a slow stream of chlorine was passed into the solution until a permanent yellow colouration appeared. Chlorine was then replaced by a stream of air to remove hydrogen chloride, and the product distilled under reduced pressure. (46°C / 0.4 mm Hg ; Lit[39] 41°C 0.08 mm Hg)
Yield 54g (79 %)

Analytical.

Calculated for $C_6H_{14}O_3PCl$	Cl	17·50 %
Found	Cl	17.92 %

I.R. (Neat)

3000-2900 cm^{-1}	C-H stretch
1375-1500 cm^{-1}	C-H deformation

1280 cm^{-1}	(very strong)	P=O	stretch
1000 cm^{-1}	(strong , broad)	-P-O-C	alkyl

N M R

8.6 τ	doublet	(12 H)	$-CH_3$ protons
5.4 τ	multiplet	(2 H)	-tert.protons

3.1.4. Diisopropyl methyl phosphate.

Diisopropyl chlorophosphonate (65.3g , 0.33 mol) in dry benzene (250 ml) and pyridine (26.6g , 0.33 mol) was cooled to about 5°C and a solution of methanol (10.7g , 0.33 mol) in dry benzene (20 ml) was added dropwise with constant stirring. The solution was then left to attain room temperature and the precipitated pyridine hydrochloride filtered off. Benzene was then removed in a rotary evaporator and the product was then distilled under reduced pressure. (40°C , 0.4 mm Hg)

Analytical

Calculated for $C_7H_{17}O_4P$	C 42.85 %	H 8.67 %
Found	C 42.03 %	H 8.63 %

I.R.

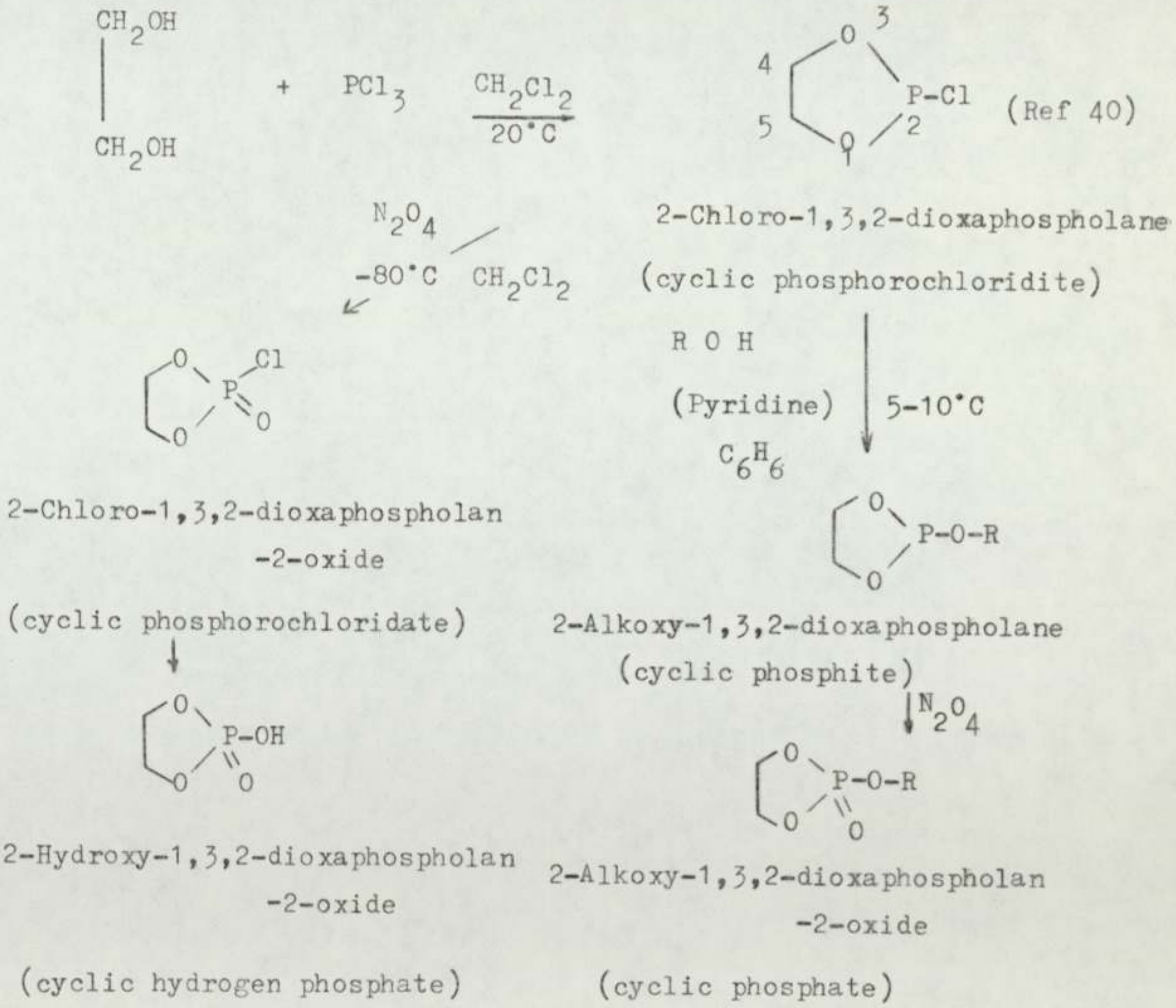
2920-2990 cm^{-1}		C-H	stretch
1380 cm^{-1}	(doublet , strong)	C-H	deformation
1280 cm^{-1}	(strong)	P=O	stretch
1180 cm^{-1}	(sharp , strong)	P-O-Me[46]	

N M R

8.7 τ	(12 H)	doublet	$J_{H-H} = 6$ Hz	$-CH_3$ (isopropyl)
6.4 τ	(3 H)	doublet	$J_{P-H} = 11$ Hz	$-CH_3$ (methyl)
5.5 τ	(2 H)	heptet	$J_{H-H} = 6$ Hz	-tert-H

3.2. CYCLIC ALIPHATIC ESTERS.

These esters derived basically from ethan 1,2 diol were prepared by the following sequence of reactions.



3.2.1. 2-Chloro-1,3,2-dioxaphospholane.[40]

In a three necked flask , fitted with a dropping funnel and a reflux water condenser carrying a calcium chloride tube , was placed anhydrous methylene chloride (500 ml) and redistilled phosphorus trichloride (275g , 2 mol). Redistilled ethane-1,2-diol (124g , 2 mol) was added to the above solution at such a rate the solution was under gentle reflux during the addition. The solvent was then removed by simple distillation and the product was obtained by distillation under reduced pressure. B.p. 45-47°C / 15 mm Hg (Lit.[40] 46.5°C / 15 mm Hg) Yield 160g

Analytical

Calculated for $C_2H_4ClO_2P$	Cl	28.06 %
Found	Cl	28.18 %

I.R. (Neat)

2910-3000 cm^{-1}		C-H stretch
1470 cm^{-1}		C-H deformation
1010 cm^{-1}	(strong)	P-O-C alkyl

N M R

5.6 τ	doublet	dioxaphospholane ring protons

3.2.2. 2-Chloro-1,3,2-dioxaphospholan-2-oxide.

2-Chloro-1,3,2-dioxaphospholane (68g , 0.5 mol) in anhydrous methylene chloride (300 ml) was oxidised using dinitrogen tetroxide at -80°C by the method described by Cox and Westheimer[41]. The required product was distilled (80-82°C / 0.1 mm Hg) (Lit[41] 89-91°C / 0.8 mm Hg) after removing the solvent.
Yield 24g 32 %.

Analytical.

Calculated for	$C_2H_4ClO_3P$	Cl	24.91 %
	Found	Cl	25.13 %

I.R. (Neat KBr disc)

2900-3000 cm^{-1}		C-H	stretch
1430; 1450; 1470 cm^{-1}		C-H	deformation
1300 cm^{-1}	(v.strong)	P=0	stretch
1025 cm^{-1}	(strong)	P-0-C	alkyl

3.2.3. 2-Hydroxy-1,3,2-dioxaphospholan-2-oxide.

2-Chloro-1,3,2-dioxaphospholane 2-oxide (29g , 0.2 mol) was dissolved in 1,4-Dioxane and water (3.6g , 0.2 mol) was added with stirring Stirring was continued for another 30 minutes and the dioxane was distilled off in the rotary evaporator. 2-Hydroxy-1,3,2-dioxaphospholan-2-oxide was then distilled under reduced pressure. The product solidifies to a colourless mass M.P. 130-132°C (Lit 133-135°C)

I.R. ($CHCl_3$)

3500 cm^{-1}	-O-H	
2900-3000 cm^{-1}	C-H	stretch
1260 cm^{-1}	P=O	stretch

N M R

5.5 τ	(doublet)	(4H)	J_{P-H} = 11Hz
-1.2 τ	(singlet)	(1H)	

3.2.4. 2-Methoxy-1,3,2-dioxaphospholane.

2-Chloro-1,3,2-dioxaphospholane (18.9g , 0.2 mol) and anhydrous benzene (100 ml) were placed in a two-necked flask fitted with a dropping funnel and a calcium chloride guard tube. The contents were cooled to 5-10°C and pyridine (15.8g , 0.2 mol) was added. Methanol (6.4g , 0.2 mol) was dissolved in dry benzene (20 ml) and this solution was added dropwise to the chlorophosphite with constant stirring. After the addition of methanol the reaction mixture was allowed to stand at room temperature for a few hours and filtered. Solvent was removed in a rotary evaporator and the residue was distilled under reduced pressure. (B.P. 54°C 25 mm Hg) (B.P. 42-44°C / 15 mm Hg)

I.R.

2960 , 2910 cm^{-1}	C-H	stretch
1460 cm^{-1}	C-H	deformation

1290 cm^{-1}	(strong)	P=O stretch
1190 cm^{-1}		P-O-C (methyl)[46]

N M R

6.0 τ	doublet		(4 H)	ring protons
6.5 τ	doublet	J_{P-H} = 11 Hz	(3 H)	CH_3 protons

3.2.5. 2-Isopropoxy-1,3,2-dioxaphospholane.

This was prepared from 2-Chlorodioxaphospholane and propan-2-ol by the same procedure as for the methoxy ester (3.2.4.) (B.P. 58-60°C / 15 mm Hg ; 64-66°C / 20 mm Hg)[40]

I.R.

2900-3000 cm^{-1}	C-H stretch
1025 cm^{-1}	P-O-C (alkyl)

N M R

6.0 τ	doublet		(4 H)	ring protons
5.8 τ	multiplet		(1 H)	tert protons
8.8 τ	doublet	J_{H-H} = 6 Hz	(6 H)	CH_3 protons

3.2.6. 2-Methoxy-1,3,2-dioxaphospholane-2-oxide.

and

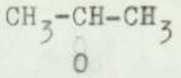
3.2.7. 2-Isopropoxy-1,3,2-dioxaphospholane-2-oxide.

These phosphates were prepared by the oxidation[41] of the corresponding phosphites (3.2.4. and 3.2.5.) using dinitrogen tetroxide at -80°C.

I.R. (Neat)

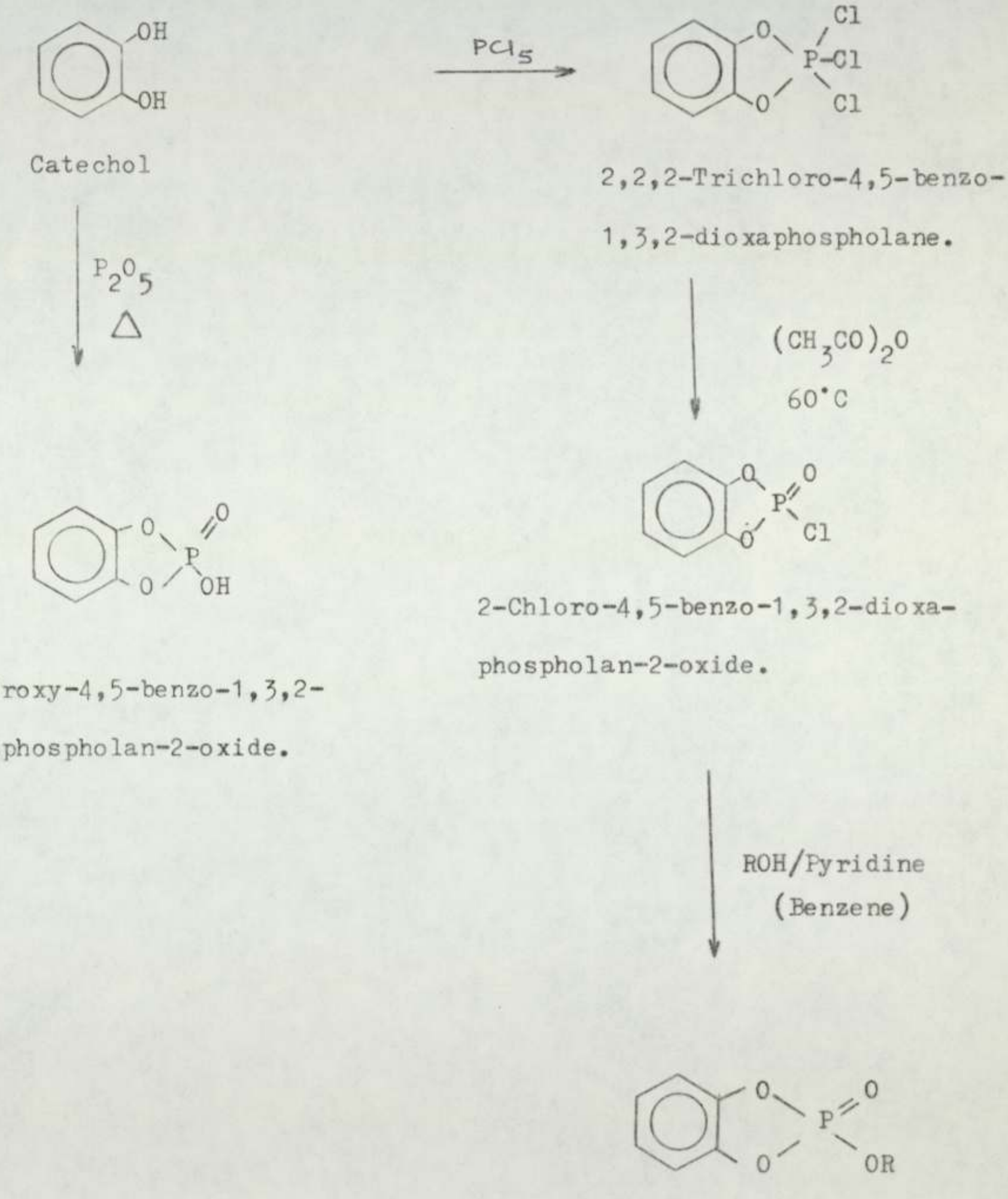
2920 , 2960 cm^{-1}	C-H stretch
1290 cm^{-1}	P=0 stretch
1030 cm^{-1}	P-0-C (aliphatic)

N M R.

5.5 τ	multiplet		(1 H)	 $CH_3-\underset{O}{CH}-CH_3$
5.7 τ	doublet	J_{P-H} = 11 Hz	(4 H)	ring protons
8.7 τ	doublet	J_{H-H} = 6 Hz	(6 H)	Me(of i-Pr group)

3.3. CYCLIC AROMATIC ESTERS.

These esters based on catechol were prepared by the following sequence of reactions.[45, 49]



Catechol

2,2,2-Trichloro-4,5-benzo-1,3,2-dioxaphospholane.

2-Hydroxy-4,5-benzo-1,3,2-dioxaphospholan-2-oxide.

2-Chloro-4,5-benzo-1,3,2-dioxaphospholan-2-oxide.

2-Alkoxy-4,5-benzo-1,3,2-dioxaphospholan-2-oxide.

3.3.1. 2,2,2-Trichloro-4,5-benzo-1,3,2-dioxaphospholane (v).[45]

Catechol (110g , 1 mol) was added in small quantities into a well-stirred suspension of phosphorus pentachloride (208g; 1 mol) in dry benzene (750 ml). The mixture was then refluxed on an oil bath for about 2 hours , benzene was removed in a rotary evaporator and the residue distilled under reduced pressure. Unreacted phosphorus pentachloride sublime over first and later the benzodioxaphospholane distilled out as a pale yellow liquid. (B.P. 96-8°C /1 mm Hg ; Lit.[45] 104°C at 1.3 mm Hg) (190g ; 76 %)

Analytical

Calculated for $C_6H_4Cl_3O_2P$		Cl ; 43.38 %
	found	Cl ; 43.02 %

I.R.(Neat)

2990-3100 cm^{-1}		C-H stretch
1605 cm^{-1}		C=C (aromatic)
1200 cm^{-1}	(strong)	P-O-C (aromatic)
580 cm^{-1}		P-Cl

N M R.

2.9 τ	(broad, singlet)	aromatic ring protons

3.3.2. 2-Chloro-4,5-benzo-1,3,2-dioxaphospholan-2-oxide.

2,2,2-Trichloro-1,3,2-benzodioxaphospholane (180g, 0.73 mol) was heated to 60-65°C and acetic anhydride (74g, 0.73 mol) was added dropwise while the reaction mixture was kept under reflux. The yellow colour of the compound disappeared and solution became colourless at the end of the reaction. Acetyl chloride was removed in a rotary evaporator and the product distilled under reduced pressure. It solidified as colourless crystals. (B.P. 84-6°C / 1-2 mm Hg ; Lit[45] 80-81°C / 1.2 mm Hg)

Analytical

Calculated for	$C_6H_4ClO_3P$	Cl	18.63 %
	Found	Cl	19.05 %

I.R. (Neat)

3010 cm^{-1}	C-H stretch
1600 cm^{-1}	C=C (aromatic)
1250 cm^{-1}	P=O stretch
1200 cm^{-1}	P-O-C (aromatic)

N M R

2.8τ singlet(broad) aromatic ring protons.

3.3.3. 2-Methoxy-4,5-benzo-1,3,2-dioxaphospholan-2-oxide.

2-Chloro-4,5-benzo-1,3,2-dioxaphospholan-2-oxide (47.6g,0.25mol) and pyridine (20g, 0.25mol) were dissolved in anhydrous benzene (250 ml) in a 500 ml round bottomed flask fitted with a calcium chloride guard tube and a dropping funnel. The contents were cooled to about 10°C and anhydrous methanol (8 ml ; 0.25 mol) was added dropwise with magnetic stirring. The precipitate of pyridine hydrochloride was filtered off after a few hours and the benzene evaporated. The residue was then distilled under reduced pressure to give a colourless product. (B.P. 106-8°C /1 mm Hg) Yield 32g ; 69 %.

Analytical.

Calculated for	$C_7H_7O_4P$	C	45.16 %	H	3.76 %
	Found	C	44.82 %	H	3.70 %

I.R.(Neat).

2960 ; 3100 cm^{-1}	C-H aliphatic and aromatic
1590 cm^{-1}	C=C aromatic
1290 cm^{-1}	P=O stretch
1230 cm^{-1}	P-O-C aromatic

N M R.

3.0 τ	singlet	(4 H)	aromatic protons
6.2 τ	doublet J_{P-H} = 12 Hz	(3 H)	$-CH_3$ protons

3.3.4. 2-Isopropoxy-4,5-benzo-1,3,2-dioxaphospholan-2-oxide.

This was prepared by exactly the same procedure as for 3.3.3. using 2-Chloro-1,3,2-benzodioxaphospholan-2-oxide and propan-2-ol. (B.P.115-118°C / 1 mm Hg)

I.R.(Neat).

3060 ; 2980 cm^{-1}	C-H stretch
1590 cm^{-1}	C=C aromatic
1470 cm^{-1}	$C-CH_3$
1300 cm^{-1}	P=0 stretch
1230 cm^{-1}	P-0-C aromatic[46]
740 cm^{-1}	1,2 disubstituted benzene ring

N M R.

3.0 τ	singlet	(4 H)	aromatic ring protons
5.2 τ	multiplet	(1 H)	$CH_3-\underset{\overset{|}{O}}{\underline{CH}}-CH_3$
8.5 τ	doublet J_{H-H} = 6 Hz	(6 H)	CH_3 protons

3.3.5. 2-Phenoxy-4,5-benzo-1,3,2-dioxaphospholan-2-oxide.

This was prepared by the same procedure using 2-Chloro-1,3,2-benzodioxaphospholane-2-oxide and phenol. This was distilled under reduced pressure and is a viscous liquid at room temperature.

Analytical.

Calculated for	$C_{12}H_9O_4P$	P	14.62 %
	Found	P	15.04 %

I.R. (Neat).

3075 cm^{-1}	C-H aromatic
1600 cm^{-1}	C=C aromatic
1310 cm^{-1}	P=O
1180 cm^{-1}	P-O-C aromatic

3.3.6. 2-(2-Chloroethoxy)-4,5-benzo-1,3,2-dioxaphospholan-2-oxide.

This was prepared using 2-chloro-4,5-benzo-1,3,2-dioxaphospholan-2-oxide and 2-chloroethanol in the presence of pyridine, as described in the procedure 3.3.3. (B.P. 152°C / 1 mm Hg.).

I.R. (Neat).

2960 ; 3080 cm^{-1}	C-H aliphatic ; aromatic
1600 cm^{-1}	C=C aromatic
1310 cm^{-1}	P=O stretch[46]
1180 cm^{-1}	P-O-C aromatic

N M R (CCl_4)

3.0 τ	singlet	(4 H)	aromatic ring protons
5.6 τ	multiplet	(2 H)	$\text{-O-}\underline{\text{CH}}_2\text{-CH}_2\text{Cl}$
6.2 τ	triplet	(2 H)	$\text{-O-CH}_2\text{-}\underline{\text{CH}_2}\text{Cl}$

3.3.7. 2-Methoxy-4,5-(p-methyl, benzo)-1,3,2-dioxaphospholane-2-oxide.

This was synthesised starting with 4-Methylcatechol and following the procedures 3.3.1. ,3.3.2. and 3.3.3. The product is a colourless viscous liquid at room temperature.
(B.P. 132°C / 1-2 mm Hg)

I.R.(Neat).

2980 ; 3020 cm^{-1}	C-H stretch
1600 cm^{-1}	C=C aromatic
1300 cm^{-1}	P=0 stretch
1250 ; 1050 cm^{-1}	P-0-C (aromatic)
1190 cm^{-1}	P-0-C (aliphatic)

N M R (CCl_4).

3.0 τ	doublet		(3 H)	aromatic ring protons
6.2 τ	doublet	J_{P-H} = 10 Hz	(3 H)	$-OCH_3$ protons
8.7 τ	singlet		(3 H)	$-CH_3$ protons on benzene ring

3.3.8. 2-Methoxy-4,5-(p-tert-butyl)benzo-1,3,2-dioxaphospholane-2-oxide.

4-Tert-butyl catechol was used as the starting material. This was converted to the trichloro compound by procedure 3.3.1. and then to the phosphorochloridate by the procedure 3.3.2. and finally to the required compound by procedure 3.3.3. The final product again is a colourless thick liquid. (B.P. 148°C / 1 mm Hg)

Analytical.

$C_{11}H_{15}O_4P$	requires	C 54.54 %	H 6.20 %
	found	C 53.51 %	H 6.83 %

I.R.(Neat).

2980-3100 cm^{-1}	C-H stretch
1610 cm^{-1}	C=C aromatic
1310 cm^{-1}	P=O stretch[47]
1180 ; 1230 ; 1050 cm^{-1}	P-O-C aromatic[48]

N M R (CCl_4).

2.9 τ	doublet	(3 H)	aromatic ring protons
6.2 τ	doublet J_{P-H} = 11 Hz	(3 H)	$-O-CH_3$ protons
8.7 τ	singlet	(9H)	$-CH_3$(tert-butyl)

3.3.9 o-Hydroxyphenyl phosphate[49]

2-Hydroxy-4,5-benzo-1,3,2-dioxaphospholan-2-oxide (15g) was dissolved in a small quantity of water by warming. This was then extracted with hot ethyl acetate and the ethyl acetate extract was poured into benzene. The required product precipitated from benzene. (M.P. 139°C ; Lit M.P. 139°C)

3.3.10 o-Hydroxyphenyldimethyl phosphate.

2-Methoxy-4,5-benzo-1,3,2-dioxaphospholane-2-oxide was allowed to stand with excess methanol for 10-12 hours and excess alcohol removed. This yielded a white solid on cooling.

Analytical.

Calculated for $C_8H_{11}O_5P$ C,44.03; H,5.04; P,14.22 %

Found C,44.24; H,4.90; P,15.05 %

I.R. (Neat).

3280 cm^{-1}	(broad)	-OH phenolic (bonded)
1600 cm^{-1}	(doublet)	C=C aromatic
1470 cm^{-1}		-C-H (deformation)
1050 cm^{-1}		P-O-C aromatic
1310 cm^{-1}		P=O
1180 cm^{-1}		P-O-C methyl[46]

N M R (CCl_4).

1.6 τ	singlet	(1 H)		phenolic proton
3.0 τ	singlet	(4 H)		aromatic ring protons
6.2 τ	doublet	(6 H)	J_{P-H} = 12 Hz	methyl protons

3.3.11. o-Methoxyphenyldimethyl phosphate.

o-Hydroxyphenyldimethyl phosphate (5g ; 0.02 mol) was dissolved in ether and methylated by passing diazomethane. At the end of the reaction ether was evaperated to obtain the required product.

Analytical.

Calculated for	$C_9H_{13}O_5P$	P,	13.36 %
	Found	P,	12.96 %

I.R. (Neat , NaCl).

2900-3100 cm^{-1}	C-H stretch
1470 cm^{-1}	C-H deformation
1300 cm^{-1}	P=O stretch[46]
1185 cm^{-1}	P-O-C (methyl)
1050 cm^{-1}	P-O-C (aromatic)

3.4. PREPARATION OF METAL COMPLEXES.

3.4.1. Bis-(dimethylphosphato)-cobalt(II).[50]

Anhydrous cobalt chloride (6.46g ; 0.05 mol) and trimethyl phosphate (28g ; 0.2 mol) were heated with constant stirring at about 140°C. Cobalt chloride slowly dissolved in trimethyl phosphate giving a deep blue solution and eventually a dark blue precipitate was formed. It was filtered, washed with dry ether

to remove excess trimethyl phosphate and dried in a vacuum desiccator. The product did not answer the test for chlorides when tested with aqueous silver nitrate.
(Yield 12.4g ; 79 %) M.P. 162-3°C.

Analytical.

Calculated for	$C_4H_{12}CoO_8P_2$	Cl,15.53	H,3.88	Co,19.03 %
	Found	Cl,15.87	H,4.06	Co,19.33 %

I.R.(KBr disc).

2960 cm^{-1}		C-H stretch (aliphatic)
1450 cm^{-1}		C-H deformation
1190 cm^{-1}	(strong)	P=O stretch[53]
1120 cm^{-1}		P-O-C aliphatic

3.4.2. Bis-(diethylphosphato)-cobalt (II).[51]

Anhydrous cobalt chloride (6.46g ; 0.05 mol) and triethyl phosphate (36.4g ; 0.2 mol) were heated at about 140°C for several hours. Cobalt chloride dissolved in triethyl phosphate forming a dark blue solution and later a blue precipitate was formed. The product was filtered, washed with dry ether and vacuum dried.
Yield 12.4g; 68 %. M.P. 179°C (Lit.[51] 181-2°C)

Analytical

Calculated for	$C_8H_{20}CoO_8P_2$	Co, 16.14;	C, 36.30;	H, 5.48 %
	Found	16.08;	26.34;	5.68 %

I.R. (KBr disc).

2980 cm^{-1}	C-H stretch
1450 cm^{-1}	C-H deformation
1190 cm^{-1}	P=O stretch[53]
1119 cm^{-1}	P-O-C aliphatic

3.4.3. Bis-(dimethylphosphato)nickel(II)[50].

A mixture of finely powdered anhydrous nickel chloride (6.48g ; 0.05 mol) and trimethyl phosphate (28g; 0.2 mol) was treated as in 3.4.1. The yellow product formed was washed with ether and vacuum dried. M.P. above 280°C.

Analytical.

Calculated for	$C_4H_{12}NiO_8P_2$	C , 15.54;	H ; 3.88;	Ni , 20.01 %
	Found	15.64	3.76	20.04 %

I.R (KBr disc)

2980 cm^{-1}	C-H stretch
1380, 1400 cm^{-1}	C-H deformation
1175 cm^{-1}	P=O stretch
1100 cm^{-1}	P-O-C aliphatic

3.4.4 Bis-(diethylphosphato)copper (II)

This compound, not previously reported in the literature, was prepared by heating anhydrous cupric chloride (5.4g, 0.04 mol) and triethyl phosphate (18.2g, 0.1 mol) at about 130°C for several hours. The gas evolved during reaction was trapped in a cold trap and n.m.r. and mass spectrometry showed it to be ethyl chloride. The product was washed with ether and vacuum dried. The light-blue complex gave negative results when tested for chloride. M.P. 164°C

Analytical

Calculated for	$C_8H_{20}CuO_8P_2$	C, 25.97;	H, 5.41;	Cu, 17.19 %
	Found	26.02;	5.50;	17.16 %

I.R (KBr disc)

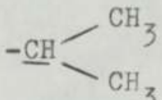
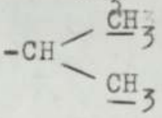
2900-3110 cm^{-1}	C-H stretch
1400, 1450 cm^{-1}	C-H deformation
1185 cm^{-1}	P=O stretch
1115 cm^{-1}	P-O-C aliphatic

3.4.5 Attempted preparation of Bis-(methylisopropyl phosphato) metal complexes.

Anhydrous cobalt chloride (3.23g ; 0.025 mol) and dimethyl-isopropyl phosphate (16.8g ; 0.1 mol) were heated at about 140°C for several hours. The blue solution yielded a blue precipitate with the evolution of a volatile product. The n.m.r. and mass spectral analysis showed this volatile product to be isopropyl chloride and not methyl chloride as expected. The precipitate was identified as 3.4.1., bis-(dimethyl phosphato)cobalt(II) , to be the exclusive product.

Volatile product analysis.

N M R (CCl_4).

5.8 τ	multiplet	(1 H)	 $-\underline{CH}(CH_3)_2$
8.4 τ	doublet	(1 H)	 $-CH(\underline{CH}_3)_2$

Mass spectrum.

m/e 78 (P^+) ; 63 (P^+-15) ; 43(P^+-35)

As it was observed in 3.4.5. that isopropylmoity is more easily lost as the chloride than the methyl group during complex formation, the isopropyl esters(rather than the methyl) were used in the subsequent preparations of metal complexes derived from cyclic catechol phosphates.

3.4.6. Bis-(catechol phosphato)cobalt(II).

Anhydrous cobalt chloride (5.2g ; 0.04 mol) and 2-isopropoxy-benzo-1,3,2-dioxaphospholan-2-oxide (21.4g ; 0.1 mol) were heated for several hours at about 140-150°C. The dark blue solution was allowed to cool and the product was filtered. This precipitate was washed several times with anhydrous benzene to remove excess catechol phosphate and then with anhydrous ether and vacuum dried. The product did not answer for chlorides when tested with aqueous silver nitrate solution. The compound did not melt and slowly blackened above 240°C.

Analytical.

Calculated for	$C_{12}H_8CoO_8P_2$	Co,14.69 %	P,15.46 %
	Found	Co,14.50 %	P,15.37 %

I.R. (Nujol mull).

2840-2980 cm^{-1}	(strong)	C-H stretch
1595 cm^{-1}	(sharp)	C=C aromatic
1455 cm^{-1}	(strong)	C-H deformation
1190 cm^{-1}		P=O stretch

3.4.7. Tris-(catechol phosphato)iron(III).

Anhydrous ferric chloride (3.25g ; 0.02 mol) was dissolved in a minimum quantity of anhydrous diethyl ether and excess of 2-isopropoxybenzo-1,3,2-dioxaphospholan-2-oxide (21.4g ; 0.1 mol) in chlorobenzene (20 ml) was added. The mixture was heated for several hours after distilling off the ether first. Isopropyl chloride was given out from the reaction mixture and a yellow product precipitated out. This was washed several times with anhydrous ether and vacuum dried. (Yield 8.4g ; 74 %)

Analytical.

Calculated for	$C_{18}H_{12}FeO_{12}P_3$	Fe, 9.81 %	P, 16.34 %
	Found	Fe, 9.76 %	P, 16.80 %

I.R. (KBr disc).

2900-2980 cm^{-1}	C-H stretch
1600 cm^{-1}	C=C aromatic
1460 cm^{-1}	C-H deformation
1190 cm^{-1}	P=0 stretch
1115 cm^{-1}	P-0-C

3.4.8. Bis-(catechol phosphato)copper(II).

This was prepared by the reaction between anhydrous cupric chloride (5.38g ; 0.04 mol) and 2-isopropoxybenzo-1,3,2-dioxaphospholan-2-oxide (21.4g ; 0.1 mol) following the procedure for 3.4.6. The product was washed several times with anhydrous ether and vacuum dried. The product did not give any turbidity with aqueous silver nitrate. It decomposed above 200°C.

Analytical.

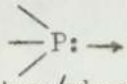
Calculated for $C_{12}H_8CuO_8P_2$	C,35.50	H,1.97	Cu,15.67 %
Found	C,34.92	H,1.95	Cu,15.63 %

I.R. (KBr disc).

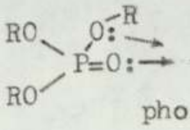
3010-3050 cm^{-1}		C-H aromatic
1610 cm^{-1}		C=C aromatic
1230 cm^{-1}	(strong)	P=0 stretch

5.5 DISCUSSION.

Transition metal complexes of phosphites[53] and substituted phosphines[53] P(III) are quite well known. This is due to the simple reason that these compounds have, on the phosphorus atom a lone pair of electrons which are easily donated. In contrast only a very limited number of complexes containing organophosphate ligands are known. In these organophosphate ligands the coordination has to be achieved through oxygen atoms.



phosphites/phosphines

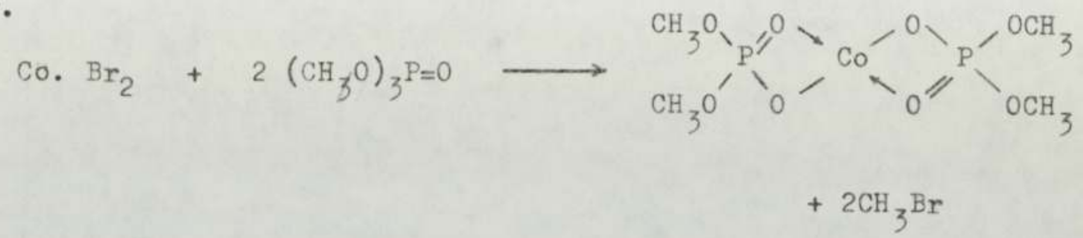


phosphates

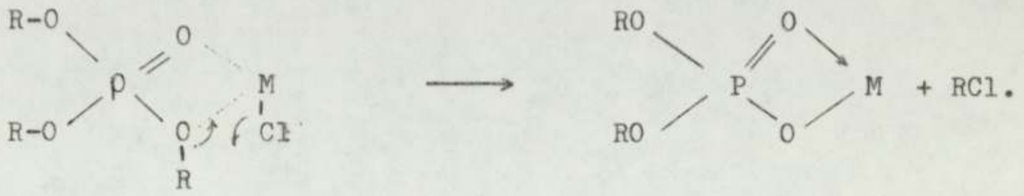
This interaction is reflected in the U.V. spectra of solutions of transition metal halides in trialkyl phosphates.[105] The lone pairs of electrons on oxygen in phosphates are back-donated to phosphorus forming $d_{\pi}-p_{\pi}$ bonds[53] and this makes these lone pairs less available for coordination than those, for example, in carbonyl compounds ($>C=O$) where no $d_{\pi}-p_{\pi}$ donds can be formed, due to absence of d orbitals on the carbon atom. In any case if a complex is to be formed, oxygen has no d orbitals to accept electrons from the filled d orbitals of the metal ion. These two factors make phosphates very undesirable ligands for complex formation.

However, under forcing conditions it has been recently possible to prepare organophosphato complexes of Co^{II} and Ni^{II} by a unique reaction between metal halides and the organophosphates[50].

eg.



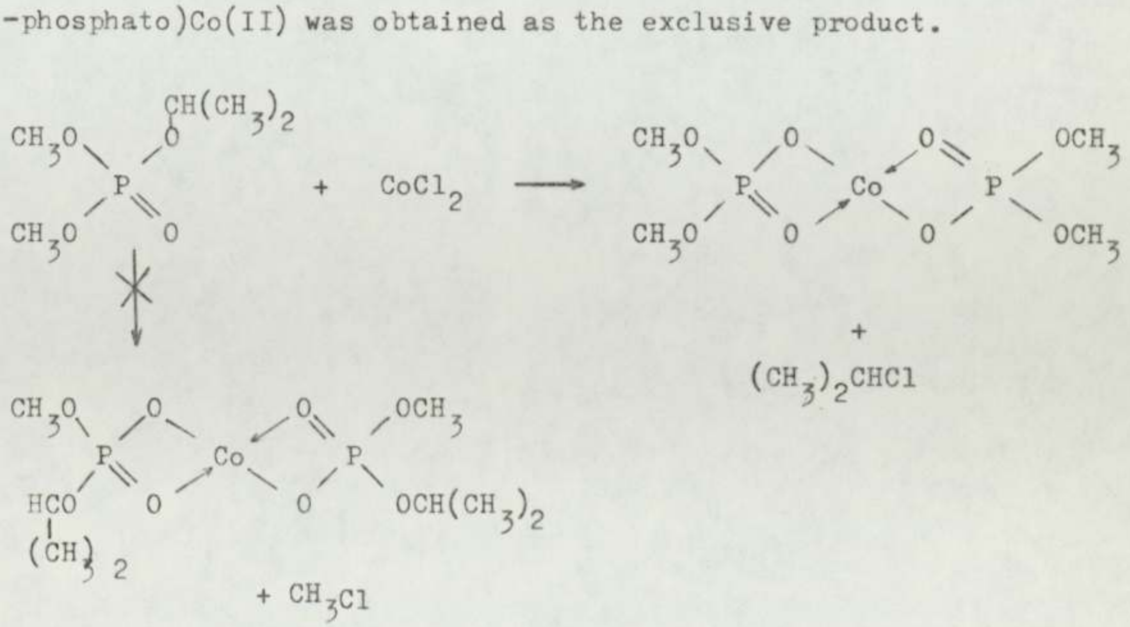
At the begining there can be coordination through oxygen of a alkoxy group leading to the loosening of O-R bond[53].



The dialkoxyphosphato group makes a $P_{d_\pi} - O_{p_\pi} - M_{d_\pi}$ delocalised chelate ring system making the complex stable.

The involvement of the lone pair of electrons on alkoxy oxygen $(-\ddot{O}-R)$ was demonstrated when dimethylisopropyl phosphate was reacted with cobalt chloride. (3.4.5.)

The isopropyl group was eliminated as isopropyl chloride in preference to the methyl group as methyl chloride and bis-(dimethyl-phosphato)Co(II) was obtained as the exclusive product.



The more electron repelling isopropyl group makes the lone pair on the isopropoxy oxygen atom more available for coordination, and hence the elimination of isopropyl chloride. The greater stability of the iso-propyl carbonium ion over the methyl carbonium ion can also be important.

Convincing evidence for complex formation comes from infra-red spectra of these compounds. In table 3.1. are listed the infra-red stretching frequencies (ν p = 0) of a number of metal complexes and those of the free phosphate esters from which they are derived. The $\nu_{P=O}$ in the phosphato complexes is lower than the $\nu_{P=O}$ in the parent phosphate ester. The lower frequency is associated with a lower force constant and hence a lower bond strength, indicative of back donation of electrons from filled d orbitals of the metal ion to the empty antibonding (π^*) orbitals of the P-0 bond.

Absorption in 400-600 cm^{-1} low frequency region have been assigned to M-0 bonds[54,55,56]. Identification of such bonds in these novel complexes provides further evidence for complex form formation. These M-0 absorptions are listed in table 3.2.

Table 3 . 1

The I.R stretching frequencies of the P=0 bond in phosphate esters and the derived transition metal complexes.

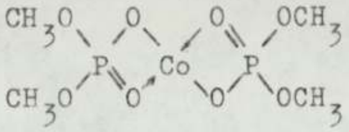
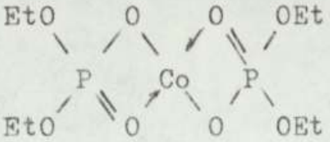
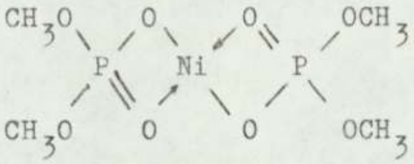
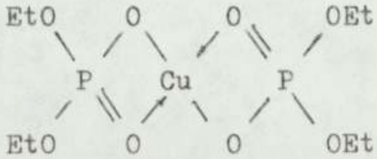
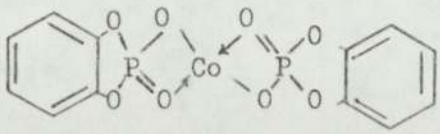
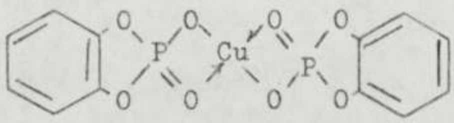
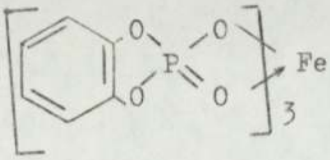
Complex.	$\nu_{P=0}/cm^{-1}$ (phosphate ester)	$\nu_{P=0}/cm^{-1}$ (complex)	$\Delta \nu_{P=0}$
	1280	1190	90
	1275	1190	85
	1280	1175	105
	1275	1185	90
	1300	1190	110
	1300	1230	70.
	1300	1190	110

Table 3.2

M-O bond stretching frequencies of the phosphato metal complexes.

Complex	ν_{M-O}/cm^{-1}	Bond	Reference
Bis-(dimethylphosphato) cobalt II.	480,525	Co-O	54,55
Bis-(diethylphosphato) cobalt II.	490,535,	Co-O	54,55
Bis-(dimethylphosphato) nickel II.	505,530.	Ni-O	55,56
Bis-(catechol phosphato) copper II.	410,480,540.	Cu-O	54,55.

CHAPTER 4

REACTIONS OF PHOSPHATE ESTERS WITH HYDROPEROXIDES.

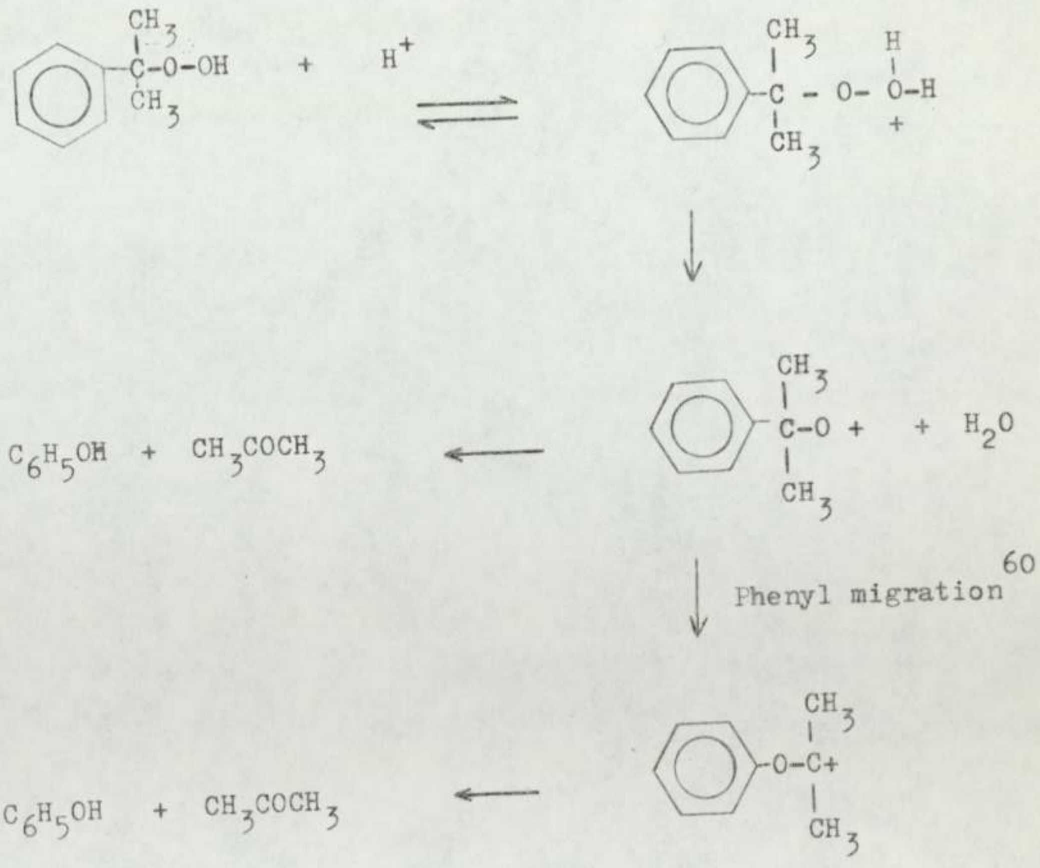
4.1. INTRODUCTION.

Hydroperoxides play a prominent role in the degradation of polymers. These are produced as a result of thermal oxidation during processing and either directly or indirectly by photoinitiation processes. As previously discussed in chapter one , hydroperoxide can be decomposed either by heat or ultraviolet radiation producing very reactive hydroxy ($^{\bullet}OH$) and alkoxy ($RO^{\bullet}$) radicals. In spite of the fact that hydroperoxides are instantly photolysed on u.v. irradiation in solution , in polypropylene the hydroperoxide groups have been calculated to have half-lives of 3 to 4 days during outdoor exposure[61]. Therefore there is a considerable amount of time for an efficient hydroperoxide decomposer to react with hydroperoxides before they are photolysed. On this basis hydroperoxide scavenging can be expected to play a significant role in u.v. and thermal stabilisation of polyolefins.

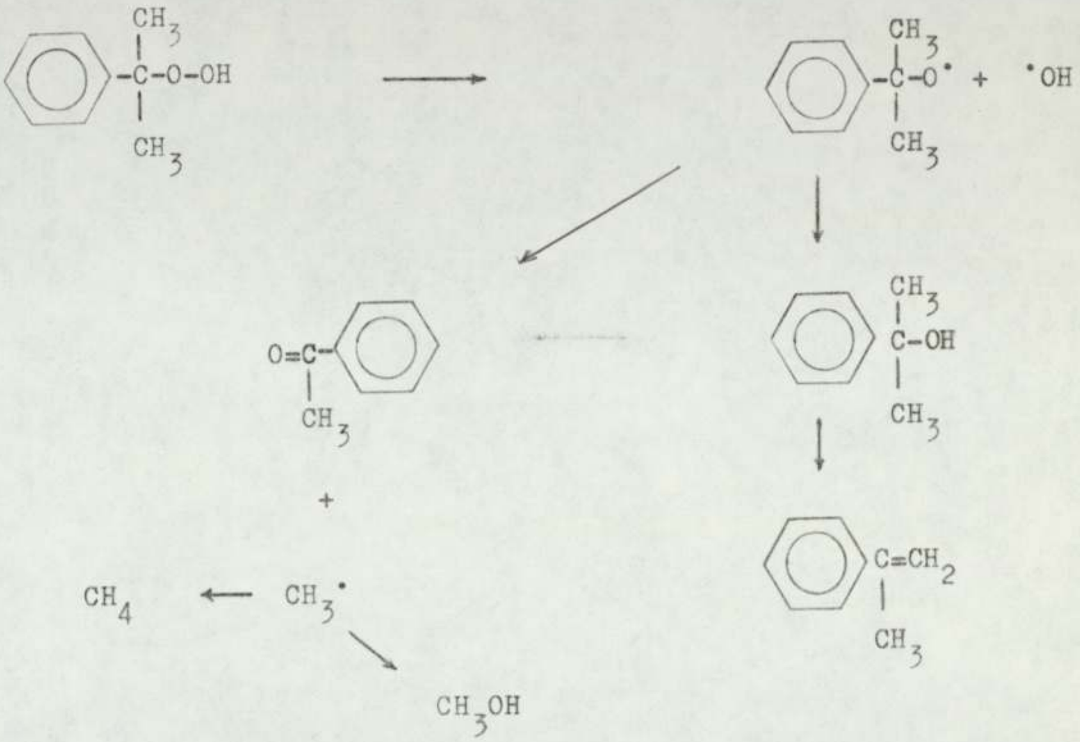
An effective stabiliser which owes its activity to its hydroperoxide decomposing ability must be able to do so forming stable molecular products without the intervention of radical species. Investigation of such reactions in a polymer which by itself is a complex chemical system is a laborious task and calls for the use of model compounds where simple chemical methods could be easily applied.

1-Methyl-1-phenylethyl hydroperoxide, (cumene hydroperoxide) was chosen for these studies on account of the following facts.

1. It is readily available and can be easily purified.
2. Reactions in solution (with the phosphate esters) can be carried out safely at elevated temperatures (up to about 100°C) without it being thermally decomposed.
3. The product formed during decomposition can be easily characterised by G.L.C..and T.L.C.
4. Completely different sets of products are obtained under different conditions so indicative of different reaction mechanisms involved[58,59].
   (a) Lewis acids react rapidly with cumene hydroperoxide forming acetone and phenol by an ionic mechanism[59].



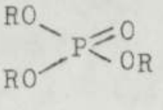
(b) Reactions involving one electron donors (and thermal decomposition) proceed through cumyloxy radicals and the products include cumyl alcohol , acetophenone ∝ - methylstyrene , dicumyl peroxide and in certain cases methane and methanol[59].



4.2. REACTIONS OF ACYCLIC AND CYCLIC ALIPHATIC PHOSPHATE ESTERS WITH HYDROPEROXIDES.

4.2.1. Acyclic and cyclic aliphatic esters.

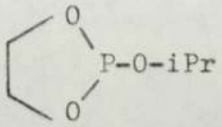
Acyclic phosphates of general formula

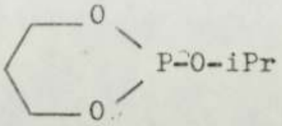


R = alkyl or aryl

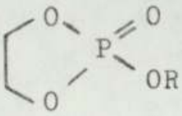
do not react with hydroperoxydes.

The studies [62] on the two aliphatic cyclic phosphites,



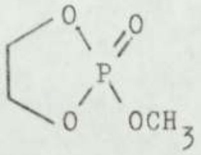


have indicated that these were catalysts for the decomposition of cumene hydroperoxide. This appears to be in conflict with the results of Parsons[63] who has observed near stoichiometric reactions for the corresponding phosphate esters of the type

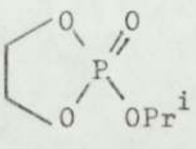


Hence it was desired to study the reaction of similar phosphates with hydroperoxides.

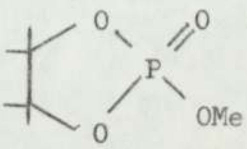
The following results were obtained for the reactions between cumene hydroperoxide and the cyclic phosphate esters I , II and III in chlorobenzene at 70°C.



I

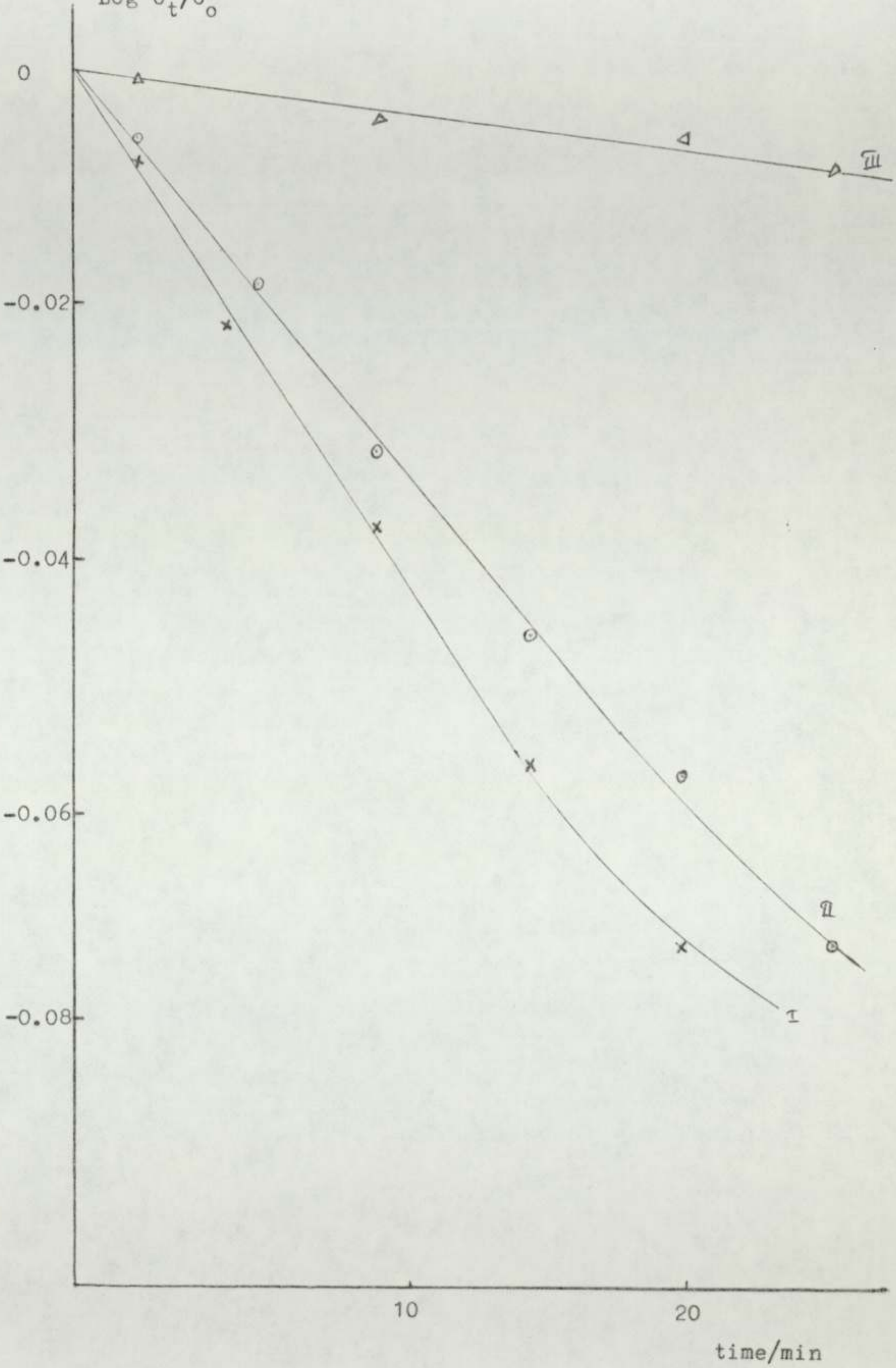


II



III

Figure 4.1. shows the pseudo-first-order plots for the reaction of these phosphates with cumene hydroperoxide and the table 4.1. gives the rate constants and the stoichiometry. The reactions were carried out at cumene hydroperoxide(CHP) : phosphate molar ratio of 5:1, (phosphate) being 0.02M.



<u>Figure 4.1</u> The rate of decomposition of CHP by the esters I, II and III in chlorobenzene at 70°C. (phosphate) = 0.02M

Table 4.1.

Rate constants and stoicheometry for reactions of aliphatic cyclic phosphates.

Compound	Rate constant / sec^{-1}	Stoichiometry
I	6.14×10^{-5}	1.8
II	5.0×10^{-5}	1.7
III	5.55×10^{-6}	0.9

The analysis of the products of the reactions showed the presence of phenol , acetone , and α -methyl styrene as major products with small amounts of cumyl alcohol and acetophenone. Exact product distribution in a typical experiment is depicted in table 4.2.

Table 4.2.

Product distribution (mole % ± 5 %) in the reactions of I, II and III with cumene hydroperoxide in chlorobenzene at 70°C

	Phenol	Acetone	α-Methyl styrene	cumyl alcohol	Acetophenone
I	52.1	58.2	40.6	1.6	0.8
II	48.7	40.2	42.2	1.4	1.2
III	36.5	38.8	57.4	1.8	-

4.2.2. Cyclic aromatic phosphate esters.

A typical reaction between a cyclic aromatic phosphate ester based on catechol and cumene hydroperoxide (CHP) will be mentioned to bring out the main features of such reactions.

(a) These reactions are much faster than the corresponding reactions of aliphatic cyclic esters. A pseudo-first-order plot for the decomposition of cumene hydroperoxide , (CHP) = 0.20 mol 1^{-1}, and 2-methoxy÷4,5-benzo-1,3,2-dioxaphospholan-2-oxide in chlorobenzene at 70°C is shown in figure 4.2.
First order rate constant = 3.07×10^{-3} sec^{-1}

(b) They are catalytic reactions and this feature is shown in figure 4.4. where more hydroperoxide has been added after the initially added hydroperoxide has been decomposed.

(c) The reaction products are mainly acetone and phenol with very small quantities of ∝-methyl styrene and acetophenone

The product distribution for the reaction described in (a) above is as follows. (table 4.2a).

Table 4.2a.

The product distribution for the reaction between cumene hydroperoxide and 2-methoxy-4,5-benzo-1,3,2-dioxaphospholane-2-oxide. (mole %)

CHP/phosphate	phenol	acetone	∝-me.styrene	acetophenone
1	88.5	70.8	8.1	trace

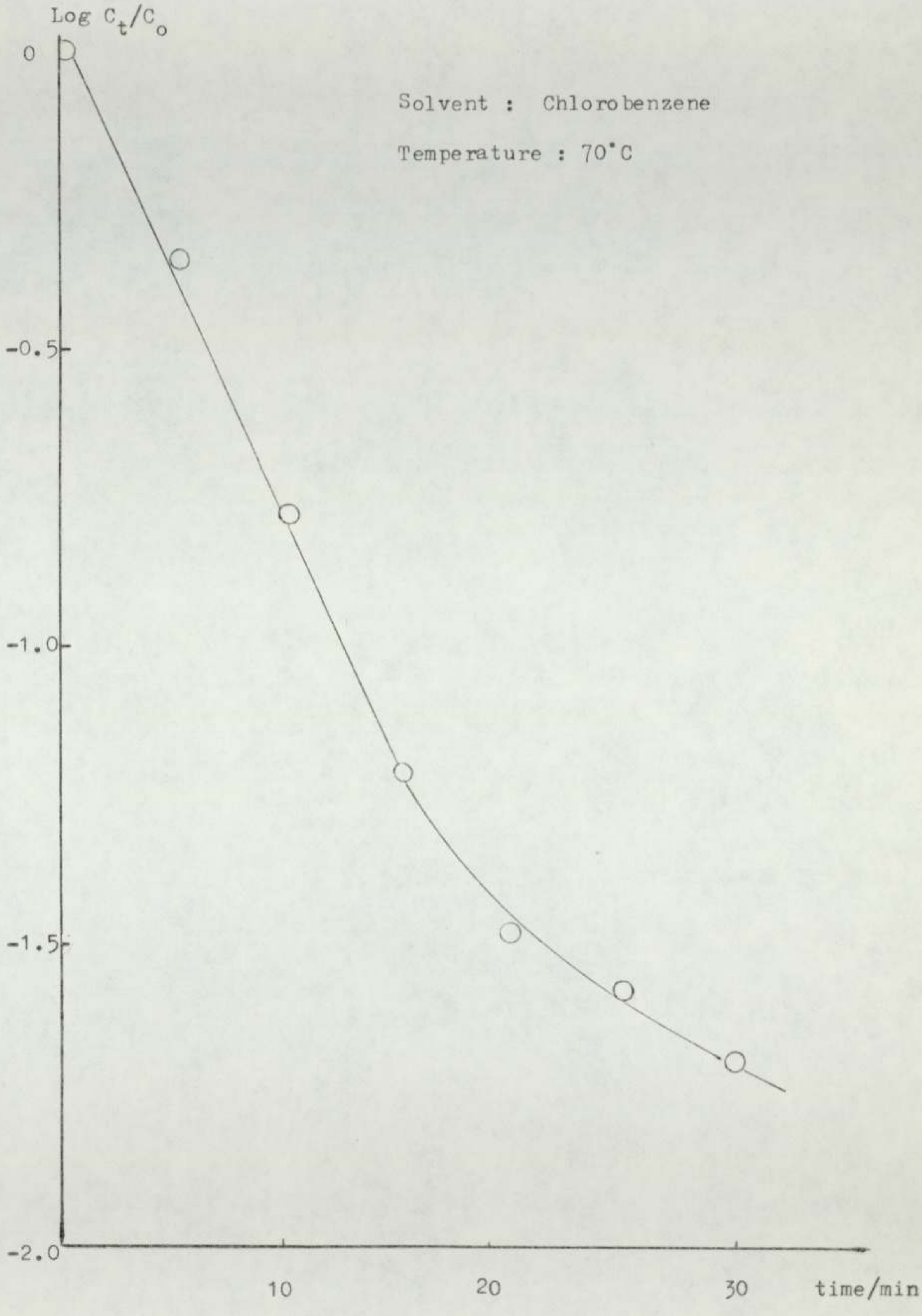


Figure 4.2 First order plot for the decomposition of cumene hydroperoxide by 2-methoxy-4,5-benzo-1,3,2-dioxaphospholan-2-oxide(0.02M).

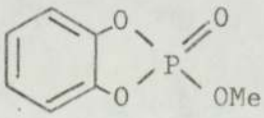
The purpose of this chapter is to describe the work carried out on various aromatic cyclic phosphates based on catechol and cumene hydroperoxide in order to understand more fully the mechanism of these reactions , since such an understanding will be fundamental in appreciating the antioxidant behaviour of these compounds.

4.3. PRODUCT ANALYSIS. (HYDROPEROXIDE DERIVED).

As the identification of decomposition products throws some light on the mechanistic aspect of the reaction[58,59] , product distribution of the reactions of a number of phosphate esters was studied under a variety of conditions. The cyclic phosphate was allowed to react with cumene hydroperoxide and the products were analysed by G.L.C. The reaction was always allowed to go to completion before G.L.C. analysis as undecomposed cumene hydroperoxide decomposes in the G.L.C. columns.

4.3.1. Effect of cumene hydroperoxide (CHP) / (phosphate) ratio.

It appears from table 4.3. that the major decomposition products are phenol and acetone for the reaction of methyl catechol phosphate with cumene hydroperoxide for a wide range of (CHP) / (phosphate).



2-Methoxy-4,5-benzo-1,3,2-dioxaphospholan-2-oxide.

(Methyl catechol phosphate)

Table 4.3.

Effect of (CHP) / (phosphate) ratio on product distribution at 70°C in chlorobenzene. (mol % 5%)

Phosphate = 2-Methoxy-4,5-benzo-1,3,2-dioxaphospholane-2-oxide

(phosphate) = 0.04 mol l^{-1}

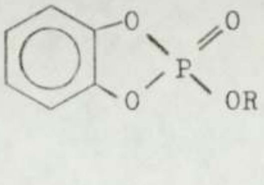
(CHP) / (phosphate)	phenol	acetone	α-methylstyrene	acetophenone
1	85.3	70.4	8.3	0.4
5	88.5	70.8	8.1	-
10	91.4	78.2	3.2	-
40	92.3	80.0	3.2	-

The polarity of the solvent was found to play a significant role in product distribution. In nitrobenzene at 70°C , 2-methoxy-4,5-benzo-1,3,2-dioxaphospholane-2-oxide gave at (CHP) / (phosphate) of 5 , phenol and acetone as the exclusive products.

4.3.2. Effect of substituents.

The variation of product distribution for a series of esters was studied to assess the inductive effects on the mechanism. These included the following.

a) variation of phosphoroyl substituents (R)



R = (a) CH_3, (b) $-CH(CH_3)_2$

(c) $-CH_2CH_2Cl$

(d) C_6H_5

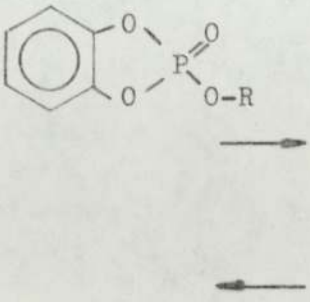
The product distribution for these esters is given in table 4.4. The reactions were carried out at 70°C in chlorobenzene at a fixed (CHP) / (phosphate) ratio of 10 : 1 with (phosphate) = 0.04 mol l^{-1}.

Table 4.4.

Effect of phosphoroyl substituent (R) on product distribution. (mol %)

substituent	phenol	acetone	α-methylstyrene	acetophenone
CH_3	91.4	78.2	3.2	0.8
i-Pr	87.8	72.4	6.4	1.2
CH_2CH_2Cl	94.2	82.4	1.5	-
C_6H_5	94.8	80.8	1.8	-

These results indicate that the percentage of phenol and acetone which are derived through an ionic mechanism increases as R becomes electron withdrawing and decreases as R becomes electron releasing.

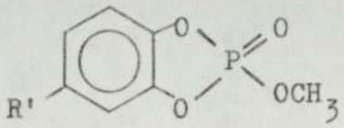


Electron withdrawing, more phenol and acetone formed.

Electron releasing, less phenol and acetone formed.

b) Variation of substituent on the benzene ring.

The following esters were examined under conditions similar to those described under (a) and the results are listed in table 4.5.



$R' = H$, CH_3 , t-Bu

Table 4.5.

Effect of benzene ring substituents on product distribution.
(mol % ±5 %)

substituent(R')	phenol	acetone	α-methylstyrene	acetophenone
H	91.4	78.2	3.2	0.8
CH_3	83.6	72.4	3.8	1.4
t-Bu	78.2	68.9	6.3	1.8

Small quantities of cumyl alcohol too were identified by G.L.C. for compounds with $R' = CH_3$ and t-Bu. Again it is seen that the electron releasing groups on benzene ring decrease the amount of phenol and acetone formed.

These results in relation to the proposed mechanism will be discussed in a subsequent section.

4.4. KINETIC STUDIES.

4.4.1. Preliminary experiments.

A reaction between 2-methoxy-4,5-benzo-1,3,2-dioxaphospholane-2-oxide and cumene hydroperoxide was carried out at 70°C in chlorobenzene at an initial molar ratio of 2:1 (CHP : phosphate) and the rate of disappearance of cumene hydroperoxide was determined iodometrically as described in section 2.4.

A plot of $\log_{10} C_t/C_o$ versus time , where

C_t = the concentration of cumene hydroperoxide at any time t

and C_o = the concentration of cumene hydroperoxide at t = 0

for this reaction is shown in figure 4.4.

$C_o = 0.04 \text{ mol } l^{-1}$

$(\text{phosphate}) = 0.02 \text{ mol } l^{-1}$

In figure 4.3. is shown a second order plot for the same reaction.

From these curves it appears that the initial reaction is pseudo-first order with respect to the hydroperoxide and this remains so for the major part of the reaction , in this particular case until the original concentration of CHP is reduced from 0.04 mol l^{-1} to 0.0022 mol l^{-1} as calculated from figure 4.2. At very low concentrations of CHP , the kinetics changes to higher orders of (CHP) (figure 4.3.) implying that the rate becomes more strongly dependent on its concentration.

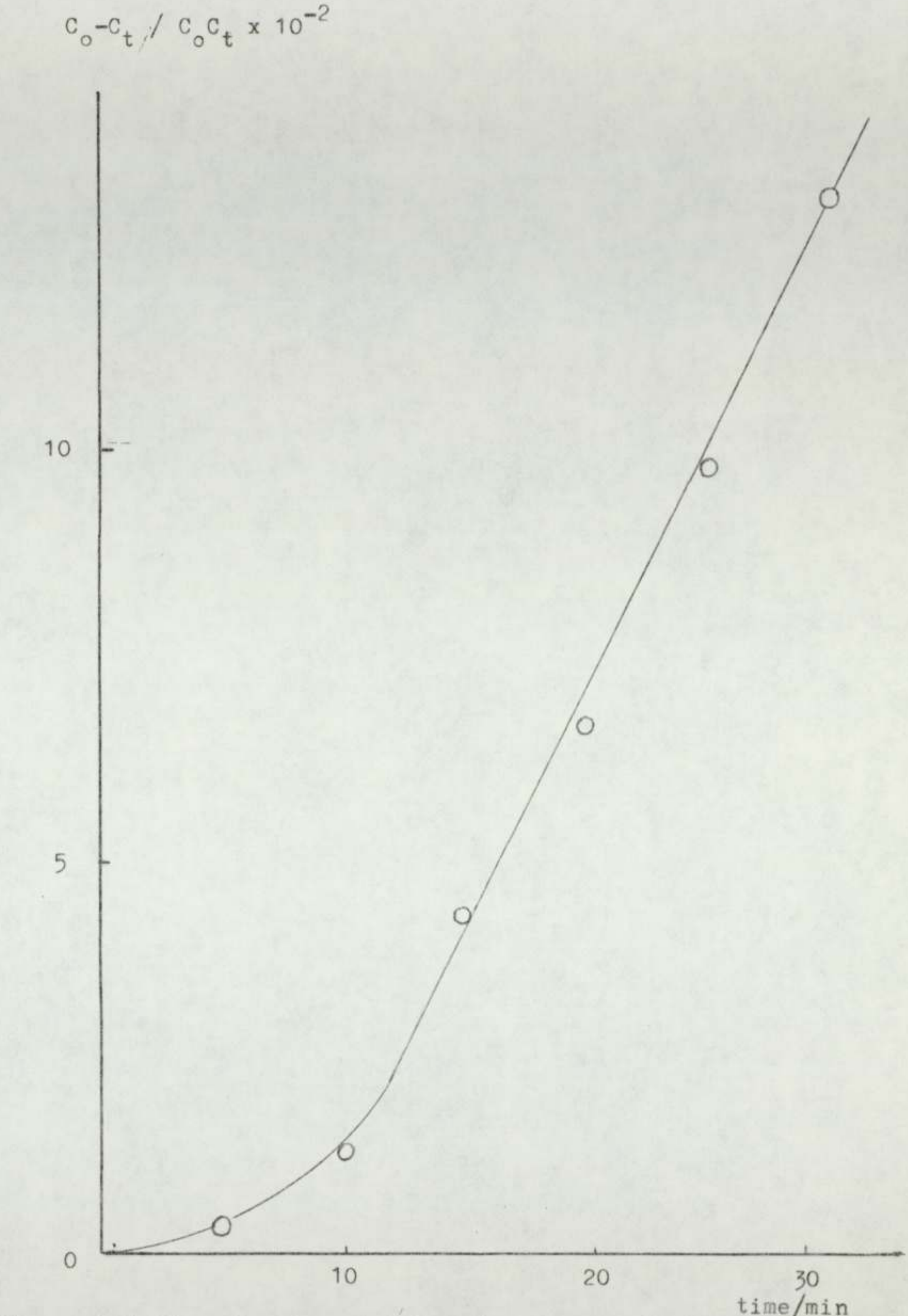


Figure 4.3 Second order plot for the decomposition of CHP by 2-methoxy-4,5-benzo-1.3,2-dioxaphospholan-2-oxide (0.02M).

(catechol methyl phosphate)

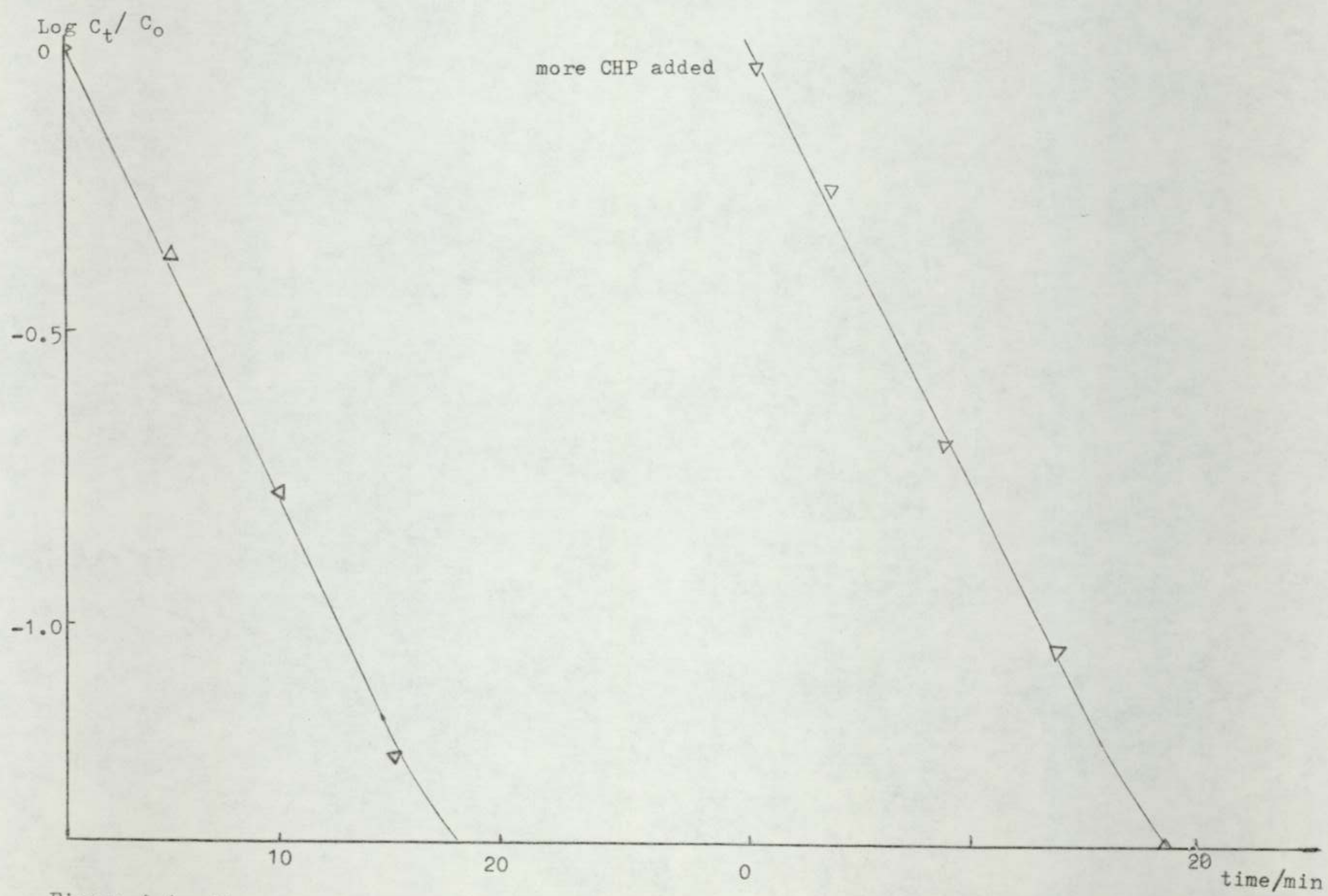


Figure 4.4 Decomposition of CHP by catechol methyl phosphate by catechol methyl phosphate in chlorobenzene at 70 C.

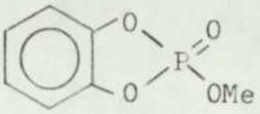
For the major part of the reaction therefore,

$$-(\mathrm{CHP})/dt \quad = \quad K_2\ (\mathrm{CHP})^1\ (\mathrm{phosphate})^x.$$

4.4.2 The effect of phosphate concentration on the rate of decomposition of cumene hydroperoxide (CHP).

(a) When (phosphate) $<$ (CHP)

The variation of the rate of decomposition of cumene hydroperoxide was investigated at a fixed concentration (0.08 mol l^{-1}) of hydroperoxide and varying concentrations of the phosphate 2-methoxy-4,5-benzo-1,3,2-dioxaphospholan-2-oxide (catechol methyl phosphate), IVa.



The results calculated from the curves in figure 4.5 are listed in table 4.6.

Table 4.6

The effect of phosphate concentration on the rate of decomposition of CHP in chlorobenzene at 72°C. (CHP) = 0.08 mol l^{-1}

(Phosphate) mol l^{-1} x 10^3	(CHP)/(phosphate)	-d(CHP)/dt initial (mol l^{-1} min^{-1} x 10^3)
8	10	2.05
16	5	4.50
24	3.3	7.14
32	2.5	9.18

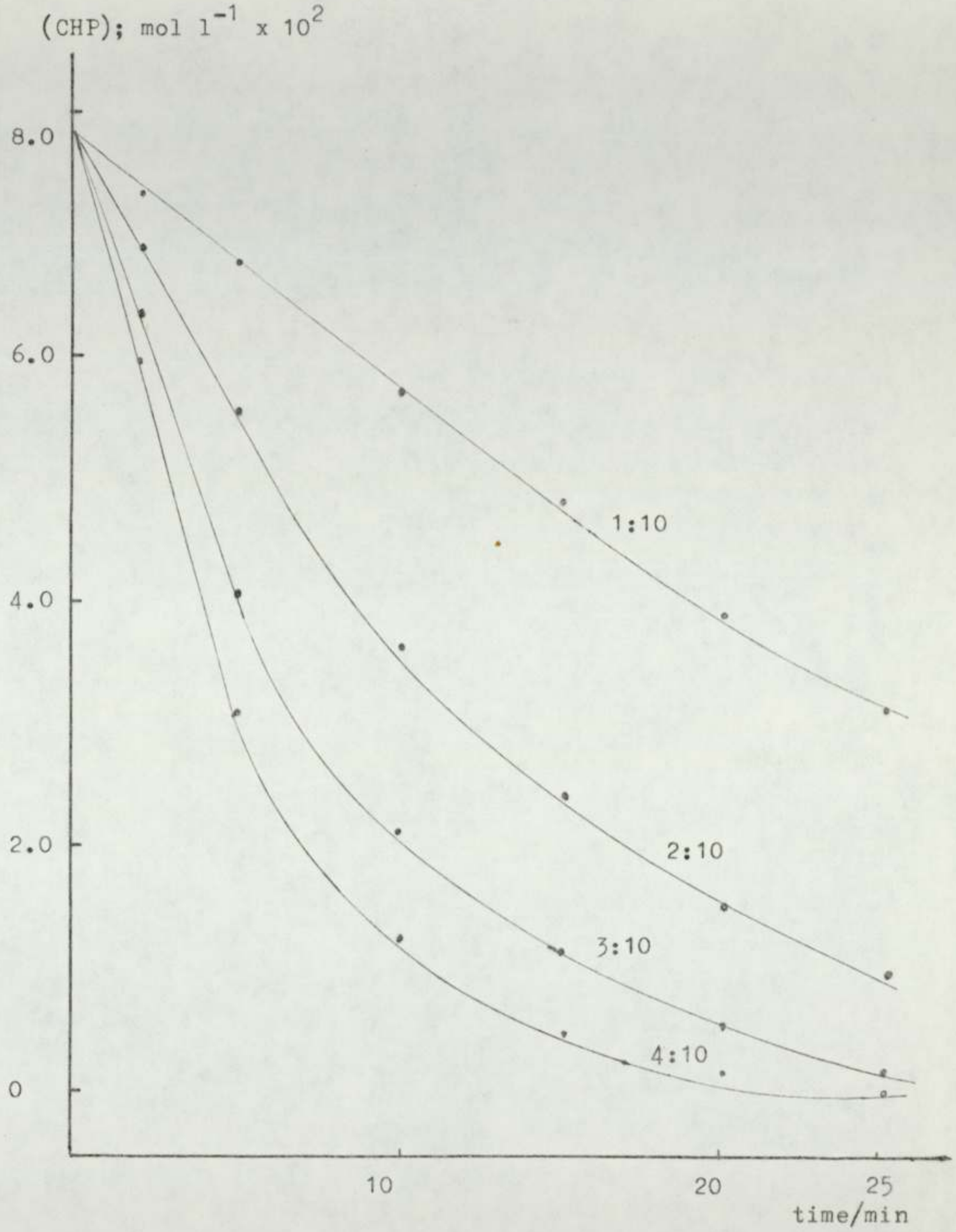


Figure 4.5 Concentration of CHP v time curves for the determination of initial rate for the reaction between CHP and Catechol methyl phosphate in chlorobenzene at 70°C

A double logarithmic plot of initial rate versus concentration of phosphate was constructed to determine the order of the reaction with respect to the phosphate. This is shown in figure 4.6. The The gradient of this was found to be 1.06.

Therefore the order of this reaction with respect to the cyclic phosphate is one.

i.e. $-d(\text{CHP})/dt = K_2 \ (\text{phosphate})^1 \ (\text{CHP})^y$.

(b) The effect of the phosphate concentration on the rate of decomposition of CHP when (phosphate) > (CHP)

The influence of the concentration of the phosphate on the rate was investigated at high concentrations of phosphate. It was found that in the concentration range investigated, (phosphate)/(CHP) from 1 :1 to 10:1, the rate was proportional to the concentration of the phosphate. The results are given in figure 4.7 and the initial rates calculated from that in table 4.7.

Table 4.7

The effect of phosphate concentration on the rate of decomposition of CHP at high (phosphate)/(CHP) ratios in chlorobenzene at 72°C

(Phosphate)/(CHP)	(phosphate) mol l^{-1}	-d(CHP)/dt initial. mol l^{-1} $\min^{-1}$ x 2
1.06	0.02	0.0027
5.33	0.10	0.0075
10.66	0.20	0.0150

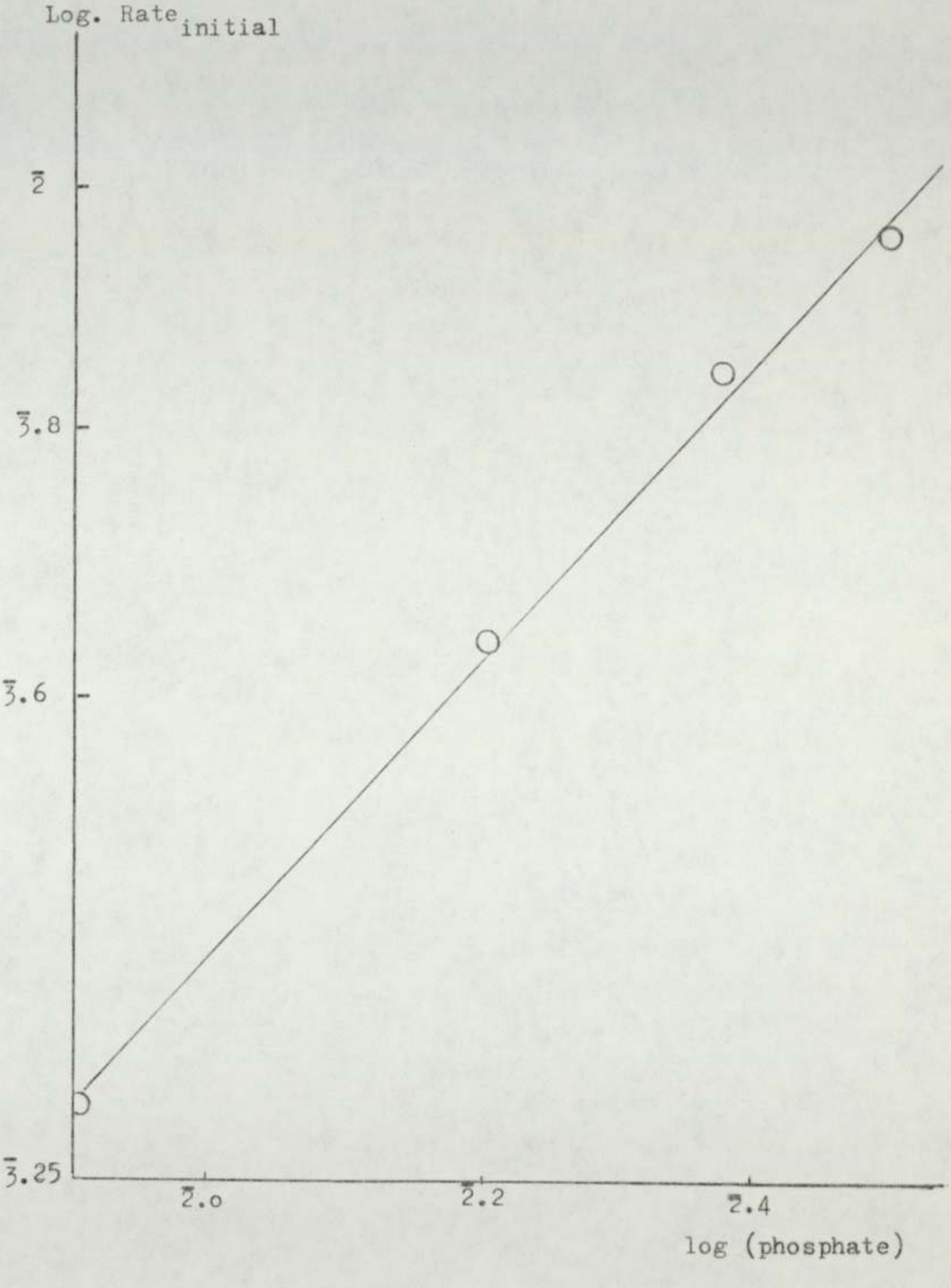


Figure 4.6 Plot of log.(initial rate) v log (phosphate) for the reaction between CHP and catechol methyl phosphate, in chlorobenzene at 72°C.

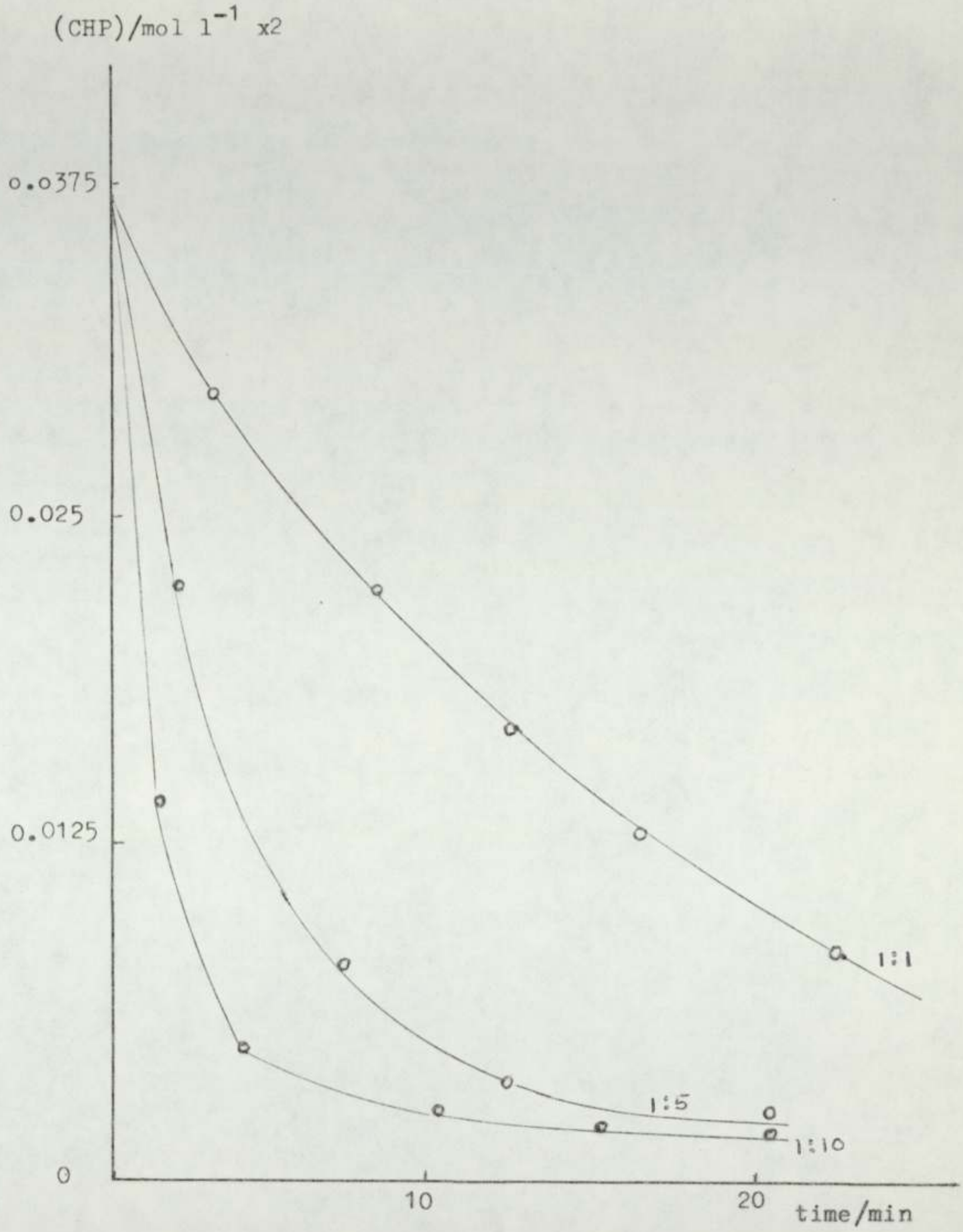


Figure 4.7 The decomposition of CHP by catechol methyl phosphate in chlorobenzene at 70°C. (CHP) < (phosphate)

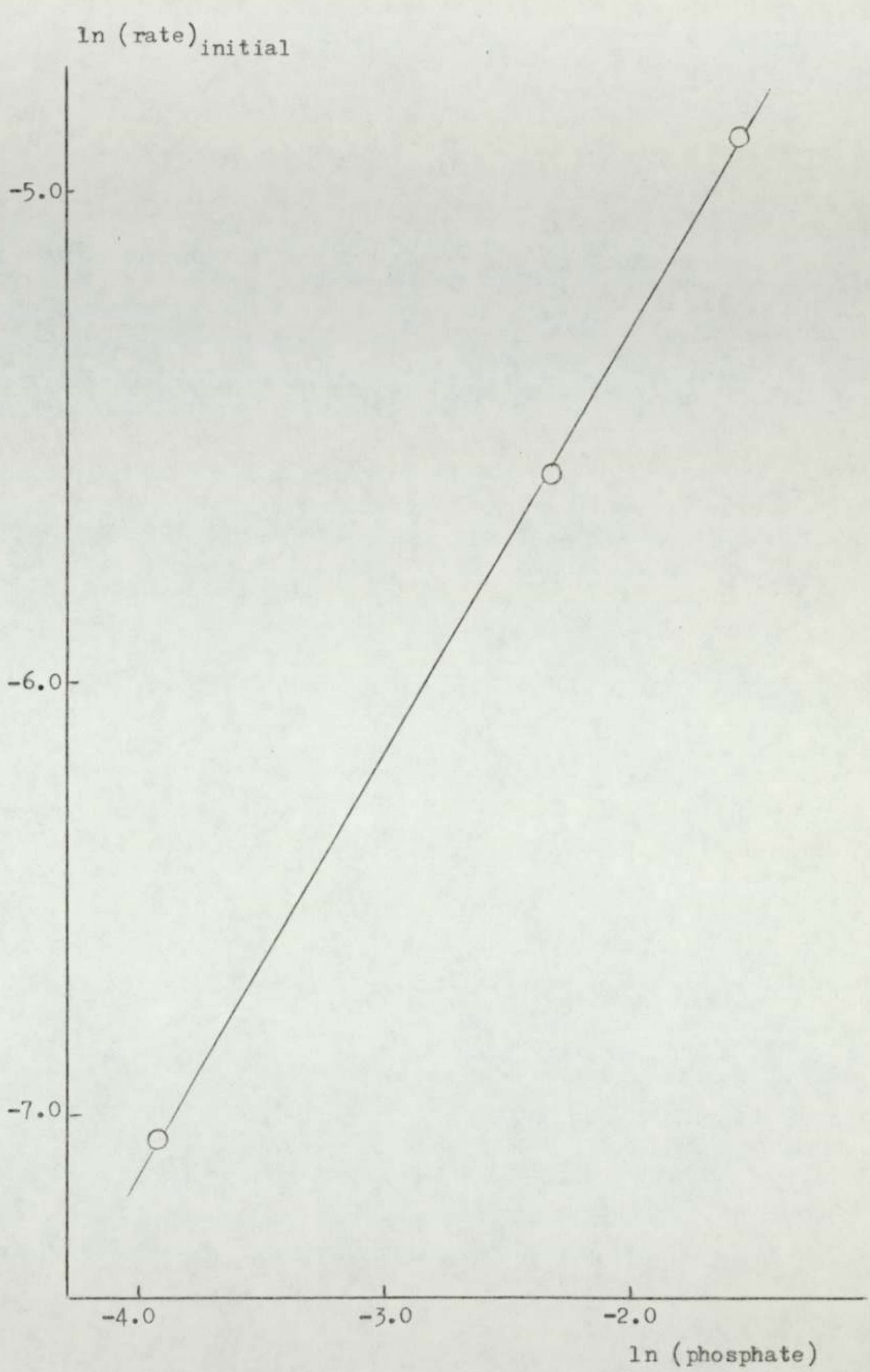


Figure 4.7a Double logarithmic plot of rate v phosphate concentration when (phosphate) $>$ (CHP).

The plot of log(initial rate) versus log (phosphate) shown in the figure 4.7a is linear with a gradient of 0.91 and therefore the reaction is still first order with respect to the phosphate. At ratios of (phosphate)/(CHP) greater than 10, the rate was extremely fast that the initial rate could not be measured with sufficient accuracy.

4.4.3 The effect of the concentration of CHP on its decomposition by 2-methoxy-4,5-benzo-1,3,2-dioxaphospholan-2-oxide

A series of experiments was carried out at a fixed concentration of the phosphate (0.02 mol l^{-1}) and varying concentrations of cumene hydroperoxide (from 0.0187 mol l^{-1} to 0.72 mol l^{-1}). The reduction in the concentration of cumene hydroperoxide with time for these reactions are shown in figures 4.9 - 4.13. The initial rates of hydroperoxide decomposition in these systems are listed in table 4.8.

Table 4.8

The effect of the concentration of CHP on its decomposition at a fixed concentration (0.02 mol l^{-1}) of the cyclic phosphate.

(Solvent: chlorobenzene, temperature: 70°C)

(CHP)mol l^{-1}x2	(CHP)/(phosphate)	-d(CHP)/dt mol l^{-1}min^{-1} x2x10^3
0.0375	0.93	2.70
0.1850	4.6	11.07
0.3750	9.4	22.50
0.7000	17.5	23.30
1.4400	36.0	24.60

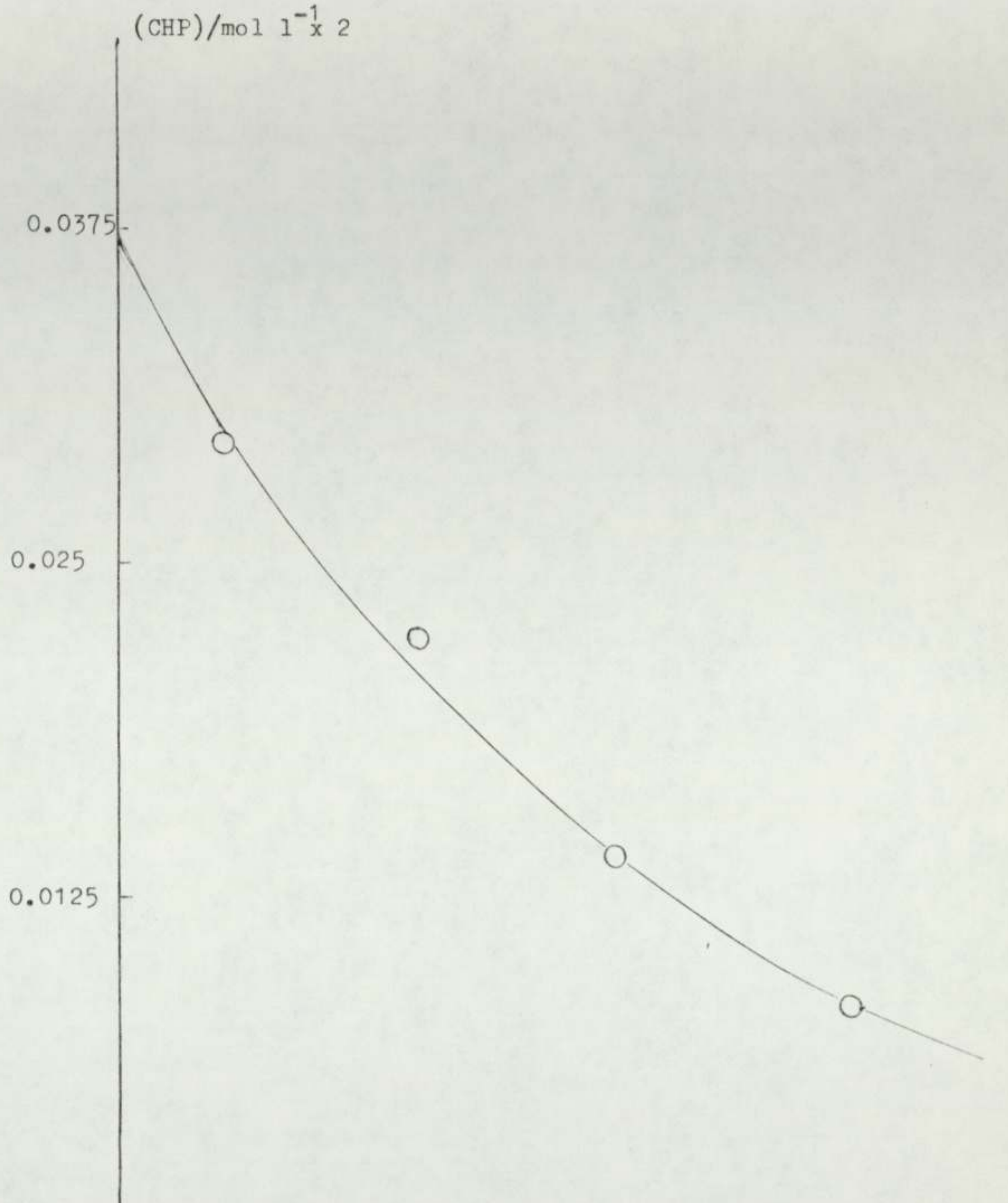


Figure 4.9 Decomposition of CHP by catechol methyl phosphate in chlorobenzene at 70°C. (CHP)/(phosphate)= 0.93

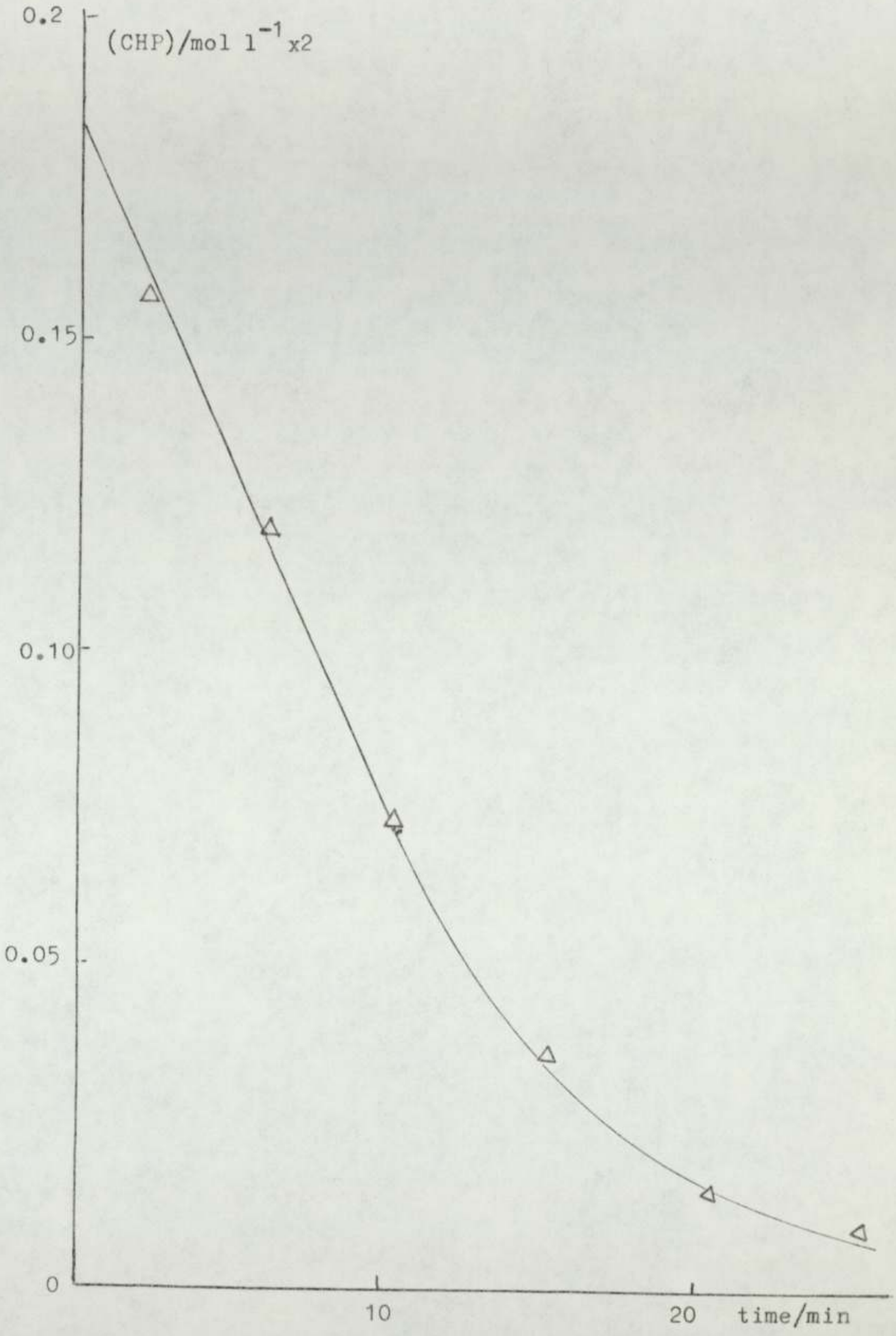


Figure 4.10 Decomposition of CHP by catechol methyl phosphate in chlorobenzene at 70°C. (CHP)/(phosphate)=4.6

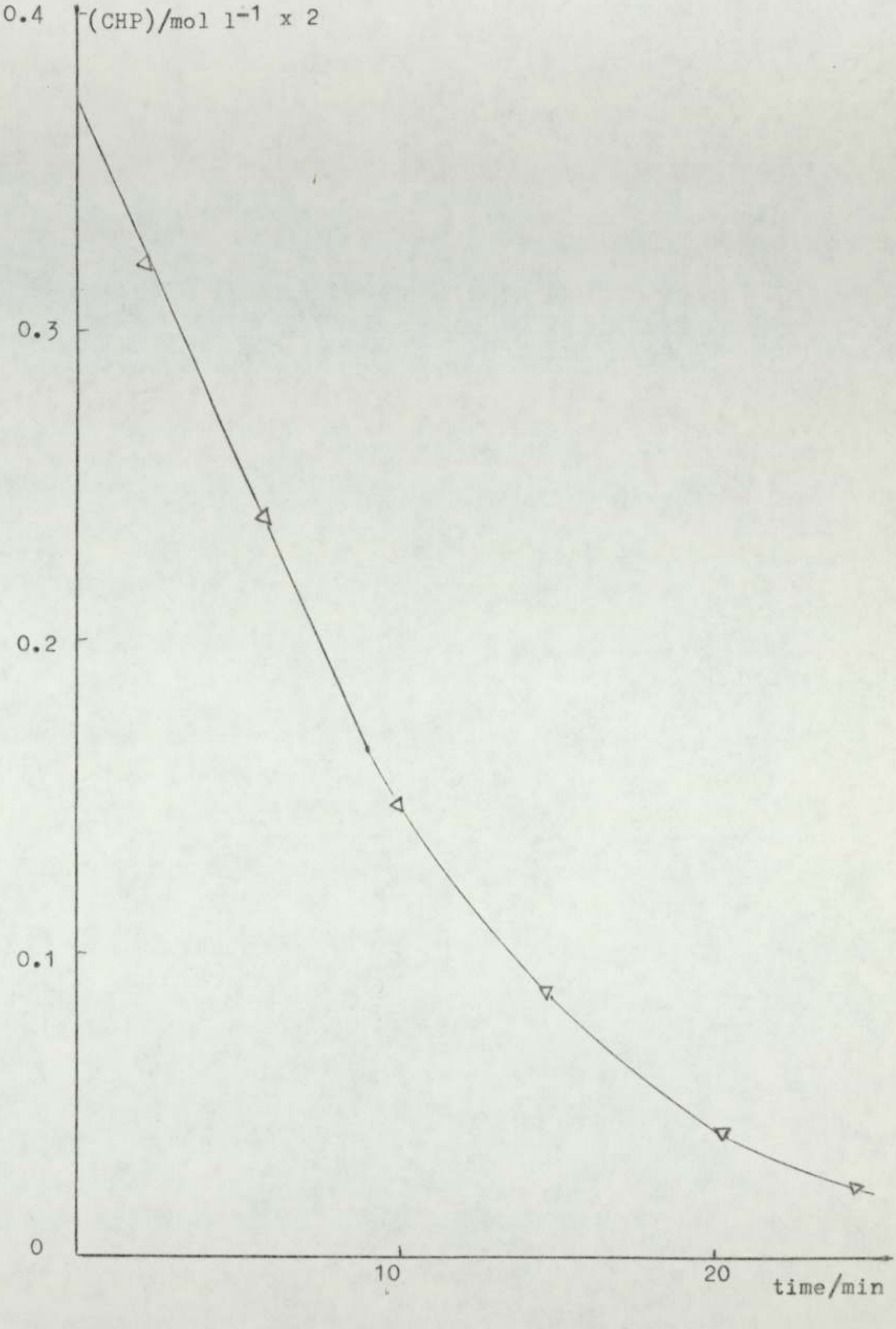


Figure 4.11 Decomposition of CHP by catechol methyl phosphate in chlorobenzene at 70°C. (CHP)/(phosphate)= 9.4

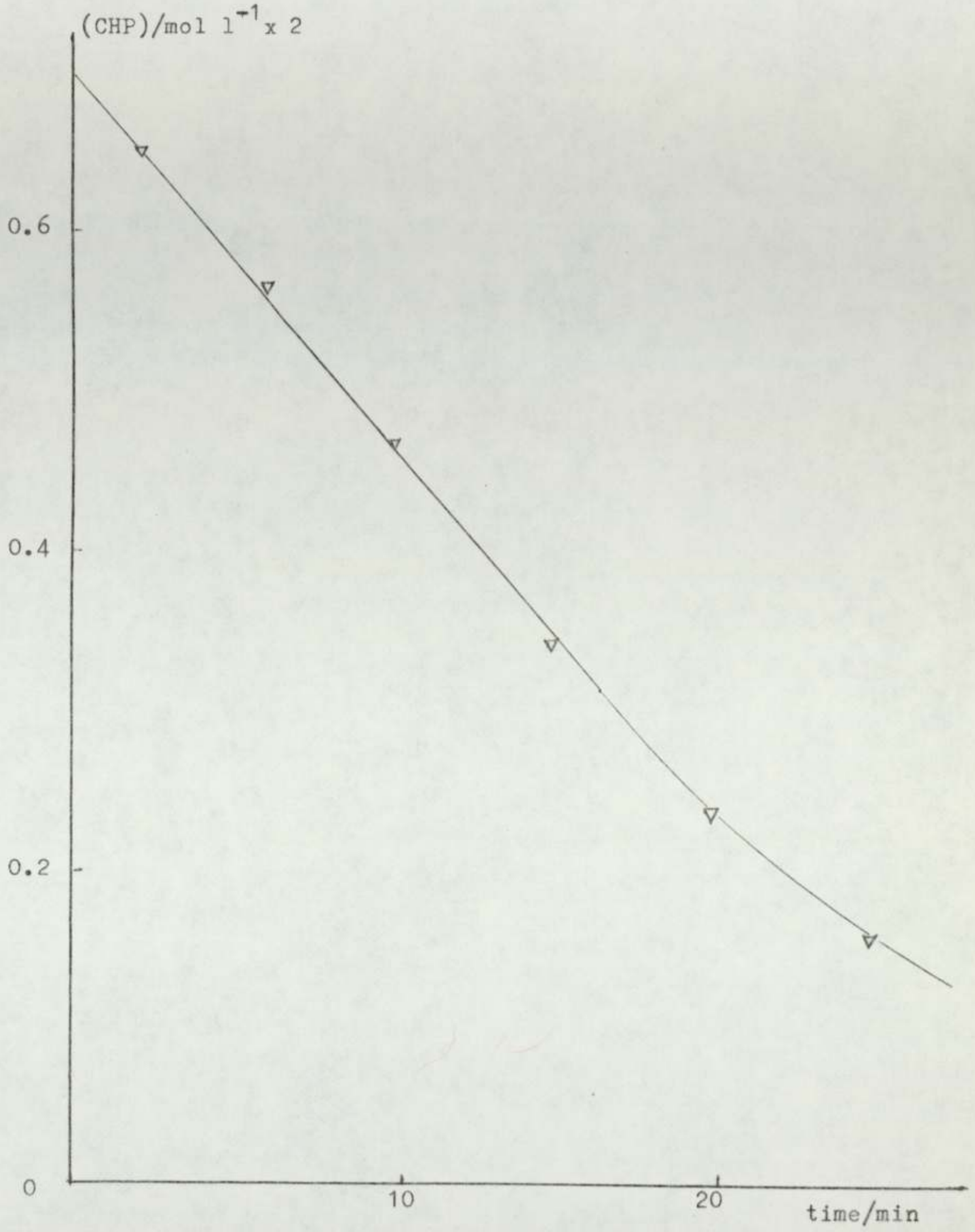


Figure 4.12 Decomposition of CHP by catechol cyclic phosphate in chlorobenzene at 70°C. (CHP)/(phosphate) = 17.5

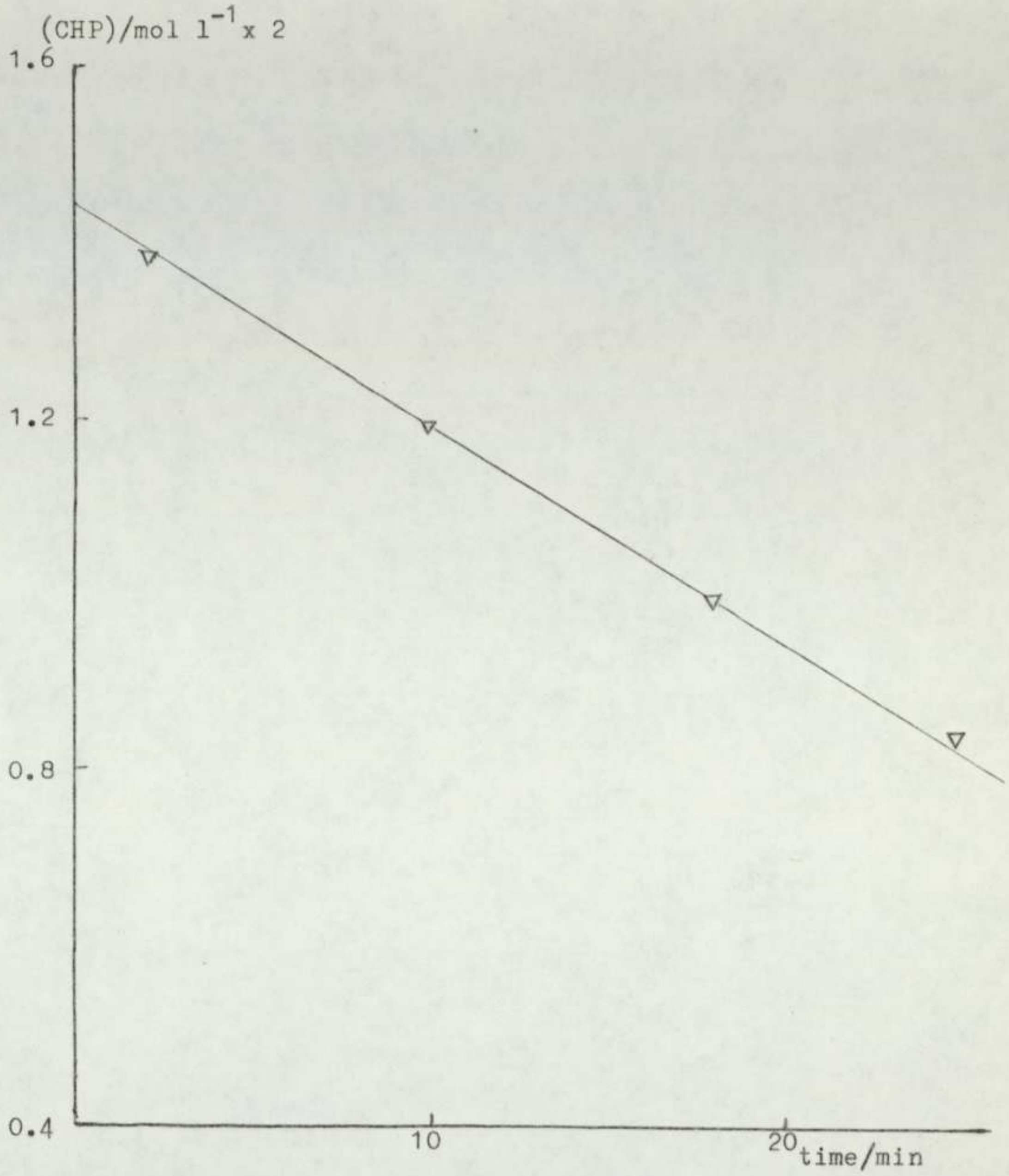


Figure 4.13 Decomposition of CHP by catechol methyl phosphate in chlorobenzene at 70°C. (CHP)/(phosphate) = 36

The above results are represented graphically in figure 4.14 where $\log_{10} -d(CHP)/dt$ is plotted against $\log_{10} (CHP)_o$. The gradient of the straight line part of this graph is 1.04.

This therefore indicates that at (CHP)/(phosphate) ratios of up to about 20:1, the reaction is first order with respect to cumene hydroperoxide. In this region, the rate of decomposition varies linearly with the concentration of the hydroperoxide for a given concentration of the phosphate.

This leads to a kinetic expression of the type,

$$-d(CHP)/dt \quad = \quad K_2 \ (CHP)^1 \ (\text{phosphate})^x$$

It was proved earliar that the order of the reaction with respect to the cyclic phosphate, was one. Therefore the rate expression becomes,

$$-d(CHP)/dt \quad = \quad K_2 \ (CHP)^1 \ (\text{phosphate})^1$$

and the over all order of the reaction, when the concentrations of the hydroperoxide and phosphate are comparable is two.

For pseudo-first order kinetics to hold true with respect to the hydroperoxide, either the phosphate concentration must be in large excess or it must not vary significantly during the reaction. As the experiments were performed under conditions contrary to the first requirement, the cyclic phosphate must be acting as a true catalyst in this reaction.

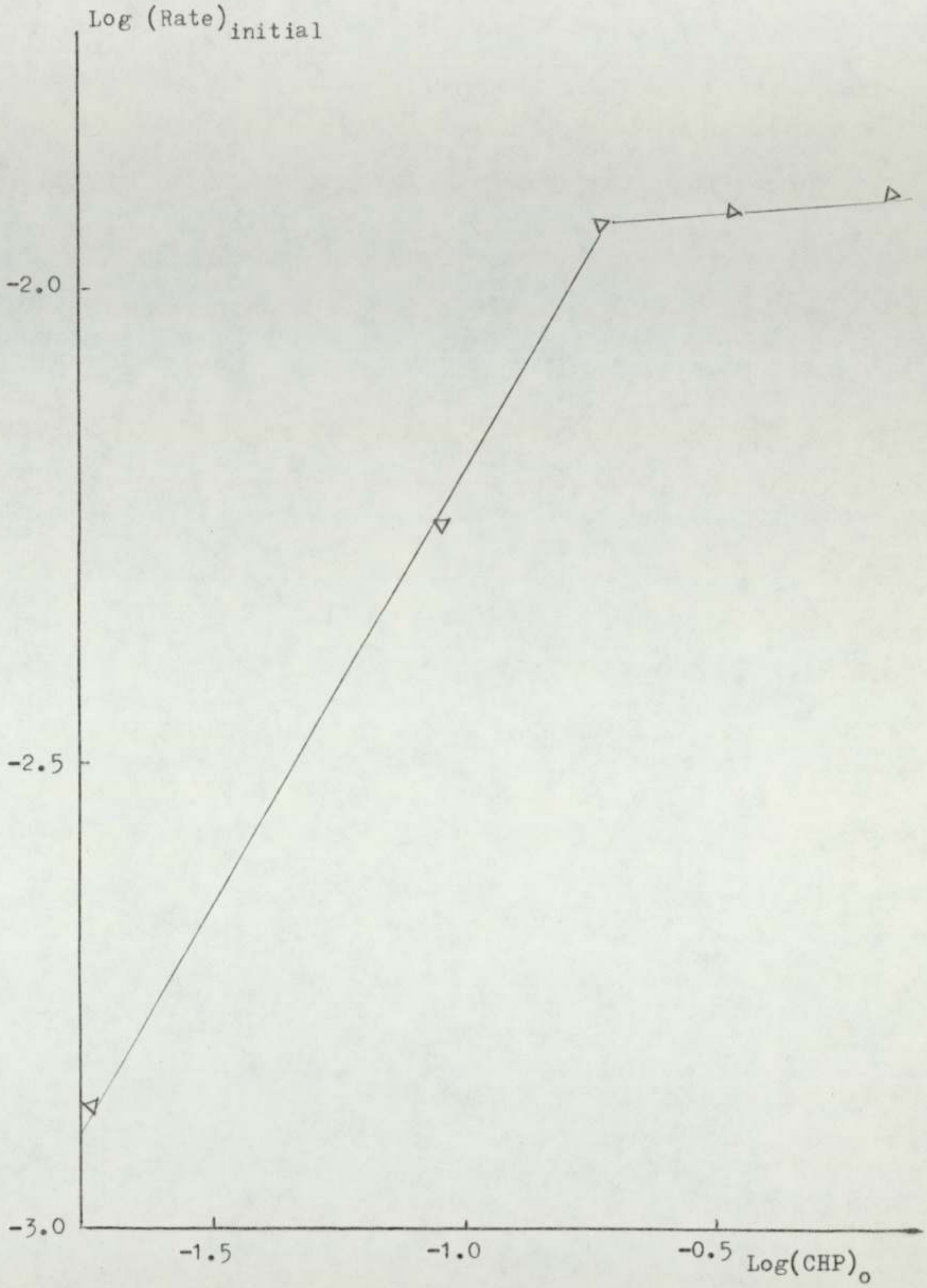


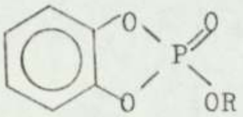
Figure 4.14 The effect of (CHP) on the rate of decomposition of CHP at a constant concentration of the phosphate.(0.02M)

When the concentration of the hydroperoxide was very high compared to that of the phosphate, the rate was independent of the hydroperoxide concentration and the order of the reaction with respect to the hydroperoxide is zero. This is indicated by the levelling off of the curve in figure 4.14.

4.5 The effect of the substituents on the rate of the reaction

(a) Phosphoroyl substituent (R)

The rate of the reaction of the following series of phosphate esters was measured in chlorobenzene at 70°C.



IV

R = H, Me, i-Pr, C_6H_5, CH_2CH_2Cl.

The pseudo-first order rate constants calculated from the first order plots for the reactions of these esters with cumene hydroperoxide (figure 4.15) are listed under table 4.9.

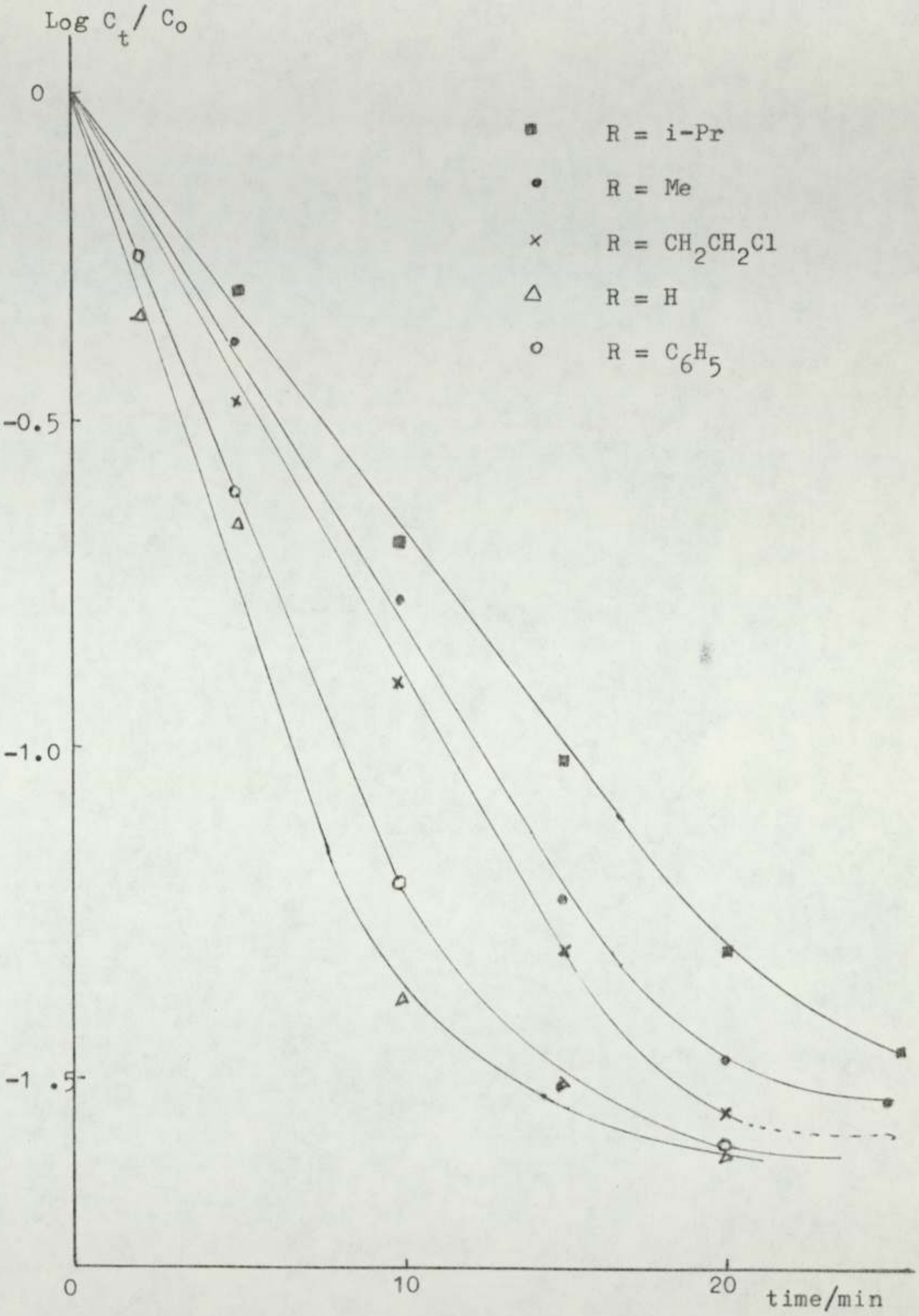
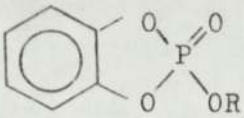


Figure 4.15 The effect of substituents on the rate of decomposition of CHP in chlorobenzene in 70°C

Table 4.9

Pseudo-first order rate constants for the reactions between cumene hydroperoxide and estrs IV in chlorobenzene at 70°C

(CHP)/(phosphate) = 2 : 1

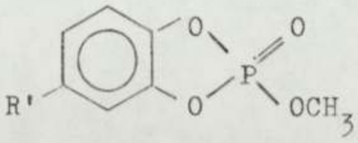


	Substituent(R)	Rate constant($sec^{-1}x10^{3}$)
	-H	5.75
←	-Me	3.07
←	-i-Pr	2.55
←+	$-C_6H_5$	4.61
←+	$-CH_2CH_2Cl$	3.22

(Arrows indicate the direction of the inductive effect of R relative to H)

The maximum error in these values is ± $0.08x10^{-3}sec^{-1}$. The rate is seen to be enhanced by the electron withdrawing groups while it is reduced by the electron releasing groups.

(b) Substituents on the benzene ring



V

R' = H, Me, t-Bu.

The reactions of these compounds with cumene hydroperoxide were carried out under conditions similar to those described under 4.5a.

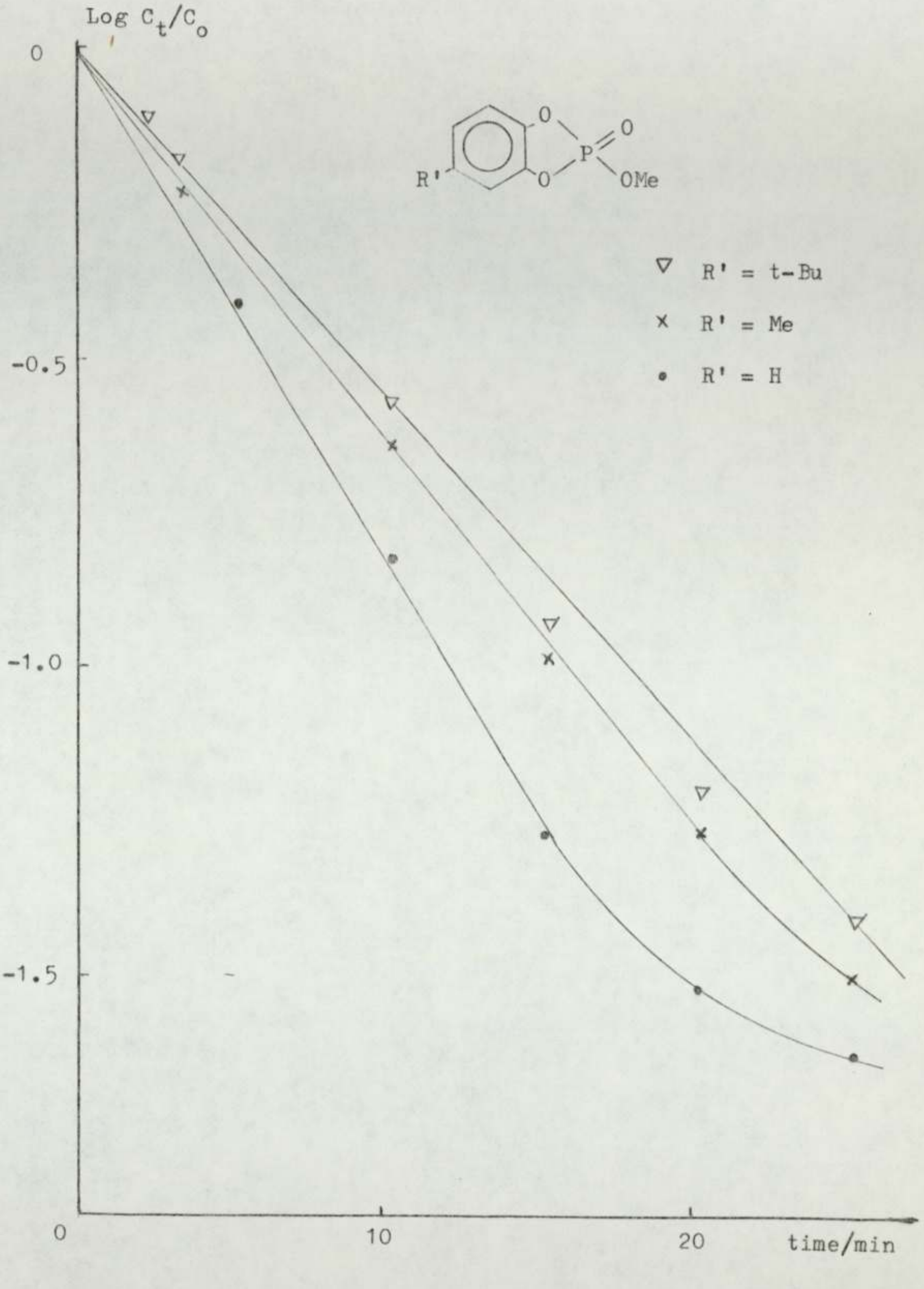


Figure 4.16 Rate of decomposition of CHP by esters V in chlorobenzene at 70°C.

The results are shown graphically as first order plots in figure 4.16 and the corresponding rate constants are given in table 4.10.

Table 4.10

Pseudo-first order rate constants for the reaction between cumene hydroperoxide and phosphate esters V, in chlorobenzene at 70°C

Substituent R'	Rate constant($sec^{-1} \times 10^{3}$)
H	3.07
CH_3	2.34
t-Bu	2.30

As seen from above results, the effect of the electron releasing substituents is to decrease the rate of the reaction.

The results so far indicate that,

1). There is no reaction between cumene hydroperoxide and acyclic phosphate esters.

2). Aliphatic five-membered cyclic phosphate esters do react with hydroperoxides but the reaction is not catalytic.

3). Cyclic phosphate esters based on catechol are powerful catalysts for hydroperoxide decomposition.

4). The product distribution indicates that the reaction proceeds through a polar or ionic intermediate, and

5). At comparable molar ratios, the reaction is first order with respect to the hydroperoxide and also first order with respect to the phosphate.

The determination activation parameters will be described in the following chapter and a mechanism will be proposed on the basis of these results. More evidence will be presented to consolidate the proposed mechanism.

CHAPTER 5

THE MECHANISM OF REACTION BETWEEN CYCLIC CATECHOL PHOSPHATE ESTERS AND HYDROPEROXIDES

The order of the reaction between cyclic phosphate esters, 2-alkoxy-4,5-benzo-1,3,2-dioxaphospholan-2-oxides, and cumene hydroperoxide was established in the previous chapter. It was shown that the reaction was first order with respect to each reactant. It was thought pertinent at this stage to study the effect of the products on the rate of the reaction, and the variation of the rate of the reaction with variation of temperature and and the polarity of the solvent, so that these information could be used to obtain further insight into the mechanistic aspects of the reaction.

5.1 THE ORDER OF THE REACTION WITH RESPECT TO TIME.

Comparison of the order of a reaction with respect to concentration, n_c, which is the true order, with the order with respect to time, n_t, reveals information regarding the effect of products formed in a reaction on its rate.[64,65] If the order with respect to time is greater than the order with respect to concentration, then as the reaction proceeds, the rate falls off more rapidly than it would do if the true order applied to the entire duration of the reaction. This indicates that certain products are acting as inhibitors of the reaction. On the other hand, if n_c is greater than n_t, the rate is falling off less rapidly than would be expected on the basis of the true order. The reaction is then activated by the products.[66] This is a feature of autocatalytic reactions.

In figure 5.1 is shown a hydroperoxide concentration versus time curve for the reaction between cumene hydroperoxide and the cyclic phosphate, 2-methoxy-4,5-benzo-1,3,2-dioxaphospholan-2-oxide. The rates of disappearance of hydroperoxide, -d(CHP)/dt, at various times calculated from the tangents to this curve are given in table 5.1.

Table 5.1

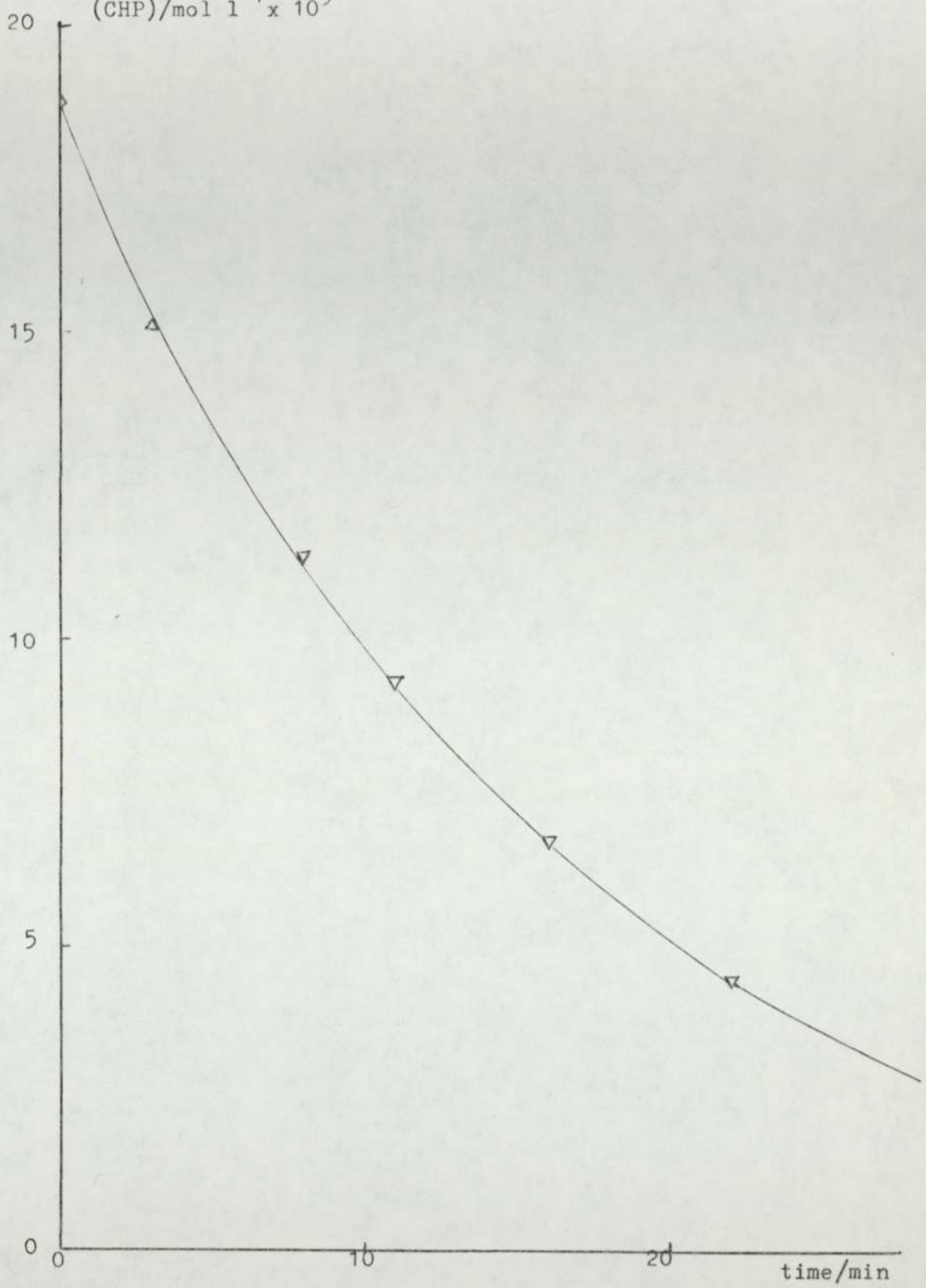
The rates of disappearance of CHP at various times for the reaction between CHP and 2-methoxy-4,5-benzo-1,3,2-dioxaphospholan-2-oxide

Solvent: Chlorobenzene; Temperature: 70°C; $(CHP)_o = 0.01875$ mol l^{-1}

$(phosphate)_o = 0.02$ mol l^{-1}.

Time(min)	$(CHP)_t$ mol $l^{-1}x10^3$	$-d(CHP)_t/dt$ mol $l^{-1}min^{-1}x10^4$
0	18.75	12.75
3	15.00	10.00
8	11.25	7.06
12	8.625	5.45
16	6.68	4.60
22	4.375	3.12

A double logarithmic plot of the rate of disappearance of cumene hydroperoxide, $-d(CHP)_t/dt$, at various times t, against the concentration of the hydroperoxide at that time, $(CHP)_t$, is represented



<u>Figure 5.1</u> (CHP) v time for the reaction between CHP and catechol methyl phosphate in chlorobenzene at 70°C (CHP) = 0.01875 mol l^{-1}, (phosphate) = 0.02mol l^{-1}.

in figure 5.2. The gradient of this graph, which is the order with respect to time, n_t, is 0.97. This is not significantly different from the true order n_c(1) and indicates that the products of the reaction have no pronounced effect on the rate of the reaction.

Phenol is a major product in the reaction and the validity of the above deduction was tested experimentally by running a reaction with initially added phenol. The results are compared with a run performed under similar conditions but where no phenol was added at the begining of the reaction. (figure 5.3.)

Two conclusions can be reached with these observations. As the order with respect to concentration , n_c , is within experimental error , equal to the order with respect to time , n_t , the products have no effect on the rate. If any radical species are formed in the rate determining stage the decomposition could have been autocatalytic and n_t should have been significantly less than n_t. However , as α-methyl styrene , cumyl alcohol and acetophenone have been observed to form in small quantities , these might arise through a radical pathway in a non-rate determining step.

The fact that added phenol has no effect on the rate indicates that phenol is not formed in a one-step reversible process from the reactants. Hence a reaction of the type.

$$\text{Cyclic phosphate} + \text{Hydroperoxide} \rightleftharpoons \text{Phenol} + \text{other products}$$

is ruled out.

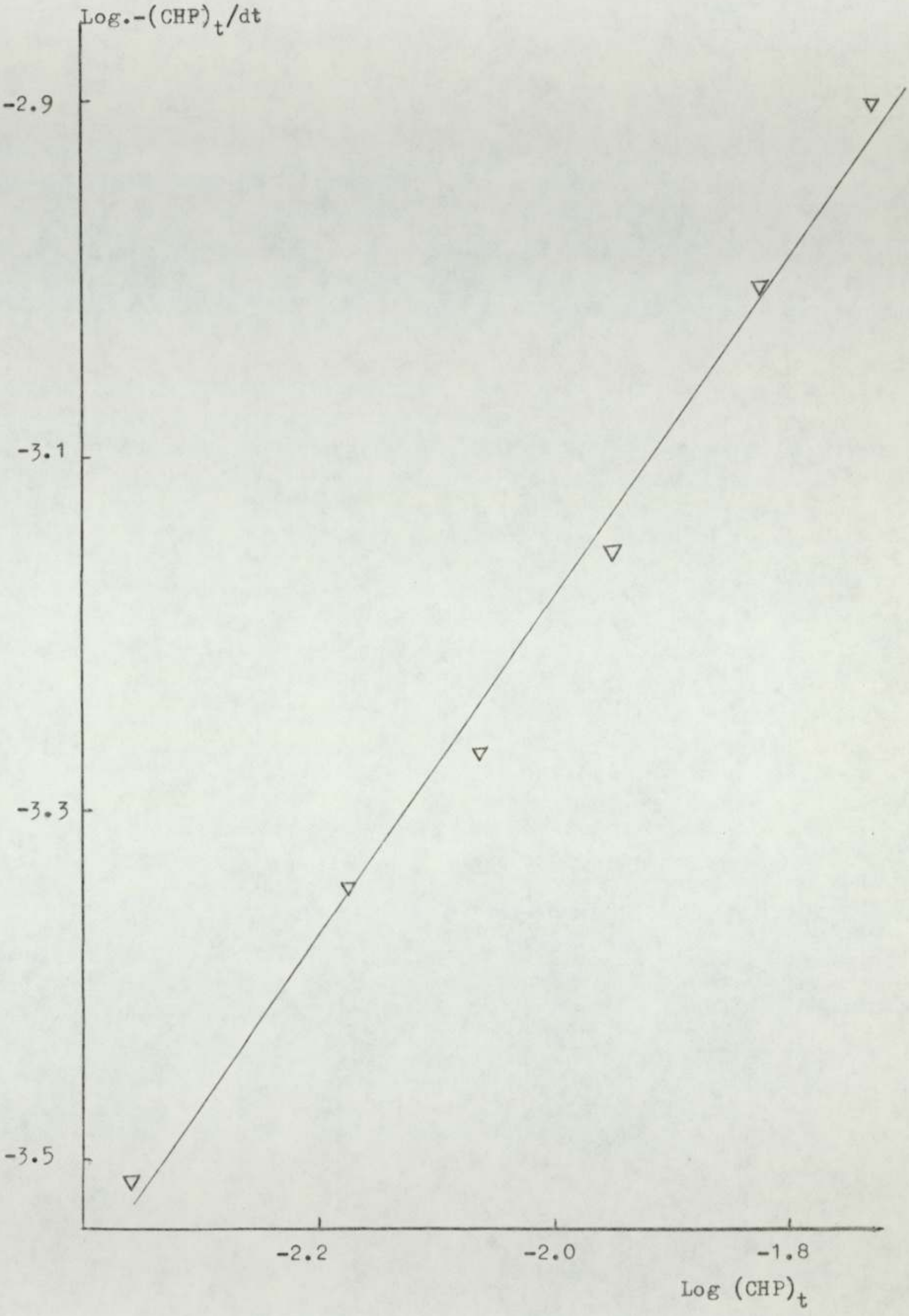


Figure 5.2 Double logarithmic plot of rate v (CHP) for the calculation of the order w.r.t. time.

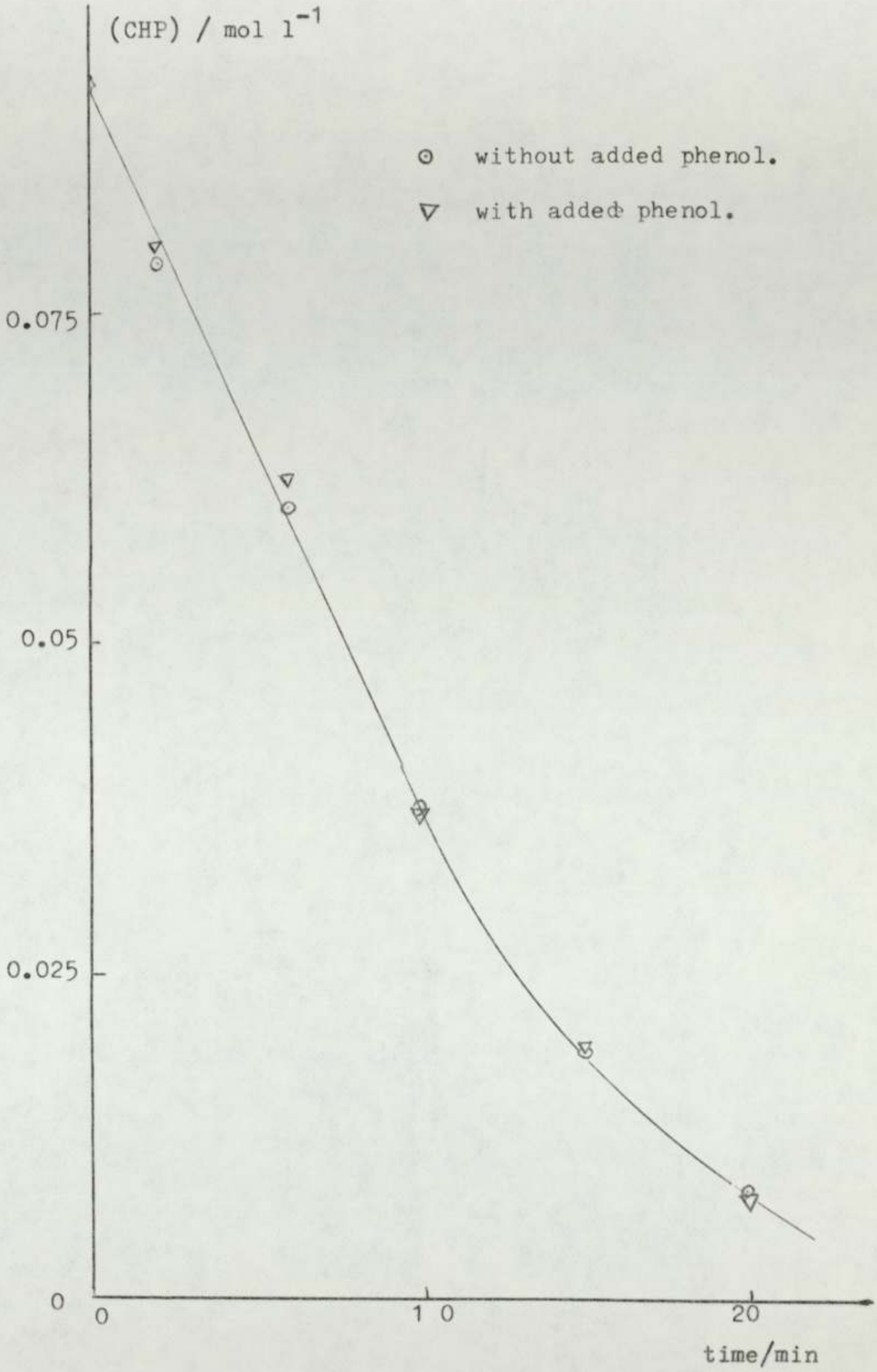


Figure 5.3 The effect of added phenol on the rate of reaction between CHP and catechol methyl phosphate in chlorobenzene at 70°C. $(CHP)_0 = 0.0925$ mol l^{-1}, (phosphate) = 0.02 mol l^{-1}, (phenol) = 4.25×10^{-2} mol l^{-1}.

This leads to the possibility of the involvement of an activated complex or an intermediate, but here again the two steps cannot both be reversible as products have no effect on rate.
Therefore

Cyclic phosphate + Hydroperoxide ⇌ (Intermediate) ⇌ Phenol +
other products

is not possible.

The formation of phenol and acetone and compounds like α-methyl styrene and acetophenone involves extensive structural reorganisations and hence such a step becoming reversible is highly unlikely.

Therefore a scheme of the type,

Cyclic phosphate + Hydroperoxide ⇌ (Intermediate) → products
(Irreversible)

is highly reasonable , and explains why the rate is not affected by added phenol which is a major product in the reaction.

The above scheme will be dealt with in detail in a subsequent section.

5.2 VARIATION OF RATE WITH TEMPERATURE AND THE DETERMINATION OF ACTIVATION PARAMETERS

A series of reactions, with a constant molar ratio (1:5) of phosphate : cumene hydroperoxide, was carried out at various temperatures from 55°C to 92°C in chlorobenzene. The first order plots for these reactions are shown in figure 5.4 and the rate constants calculated from these curves are given in table 5.2

Table 5.2

Rate constants at different temperatures for the reaction between CHP and catechol cyclic phosphate in chlorobenzene .

(phosphate) : (CHP) = 1 ; 5

Temperature(°C)	$1/T \times 10^3$(°K^{-1})	Rate constant$\times 10^3$(sec^{-1})
55	3.05	0.479
72	2.89	1.19
83	2.81	1.86
92	2.74	2.46

The rate constant of a reaction is related to the activation energy by the equation,

$$k = A\, e^{-E_a/RT} \qquad (1)$$

where E_a is the experimental energy of activation.

From (1), $\ln k = \ln A - E_a/RT$

A graph of log k against 1/T was constructed and this is shown in figure 5.5. The energy of activation calculated from this is 47.1 ± 3.4 kJ mol^{-1} (11.3 ± 0.8 kcal mol^{-1}).

The frequency factor was calculated to be 1.8×10^4 sec^{-1}.

The entropy of activation, ΔS^* for the reaction was calculated using the relation,

$$k' = ekT/h.\ e^{\Delta S^*/R} - e^{-E_a/RT}$$

where k' is the rate constant.

$$\Delta S^* = -172.2 \text{ J } K^{-1} mol^{-1} \ (-41.2 \text{ cal } K^{-1} mol^{-1})$$

As $k' = kT/h\ e^{-\ G^*/RT}$,

at. 72°C, ΔG^* was found to be 103.6 $kJmol^{-1}$ (24.8 k cal mol^{-1})

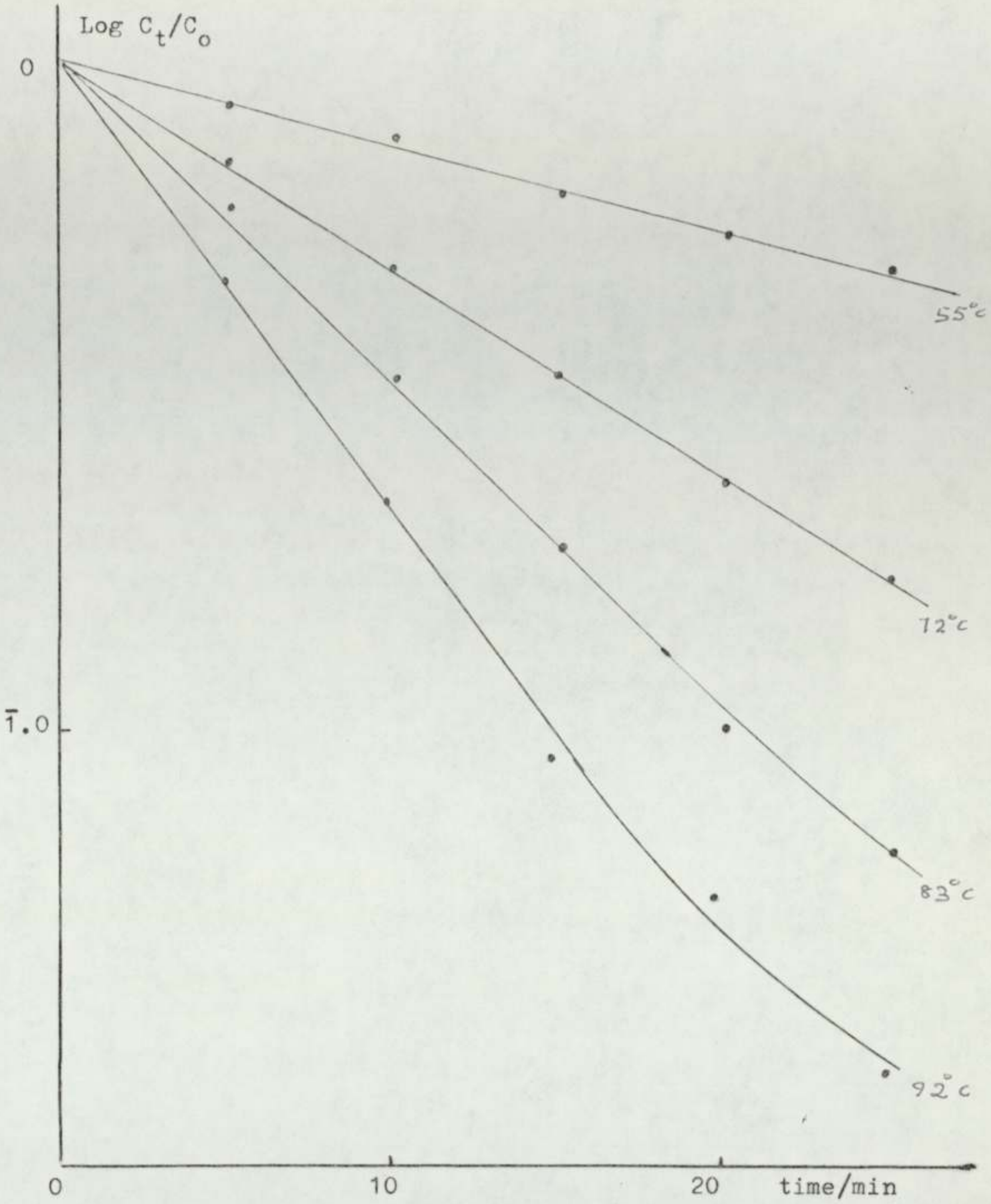
and since $\Delta G^* = \Delta H^* - T\Delta S^*$,

ΔH^*, the enthalpy of activation could be calculated.

$$\Delta H^* = 44.3 \text{ kJ } mol^{-1} \ (10.6 \text{ k cal } mol^{-1})$$

5.3 THE EFFECT OF SOLVENT ON THE RATE

The degree of solvation of the reactants and the activated complex has a marked effect on the rate of a reaction. If the reactants are comparatively less solvated than the activated complex



<u>Figure 5.4</u> First order plots for the reaction between CHP and catechol methyl phosphate at various temperatures.

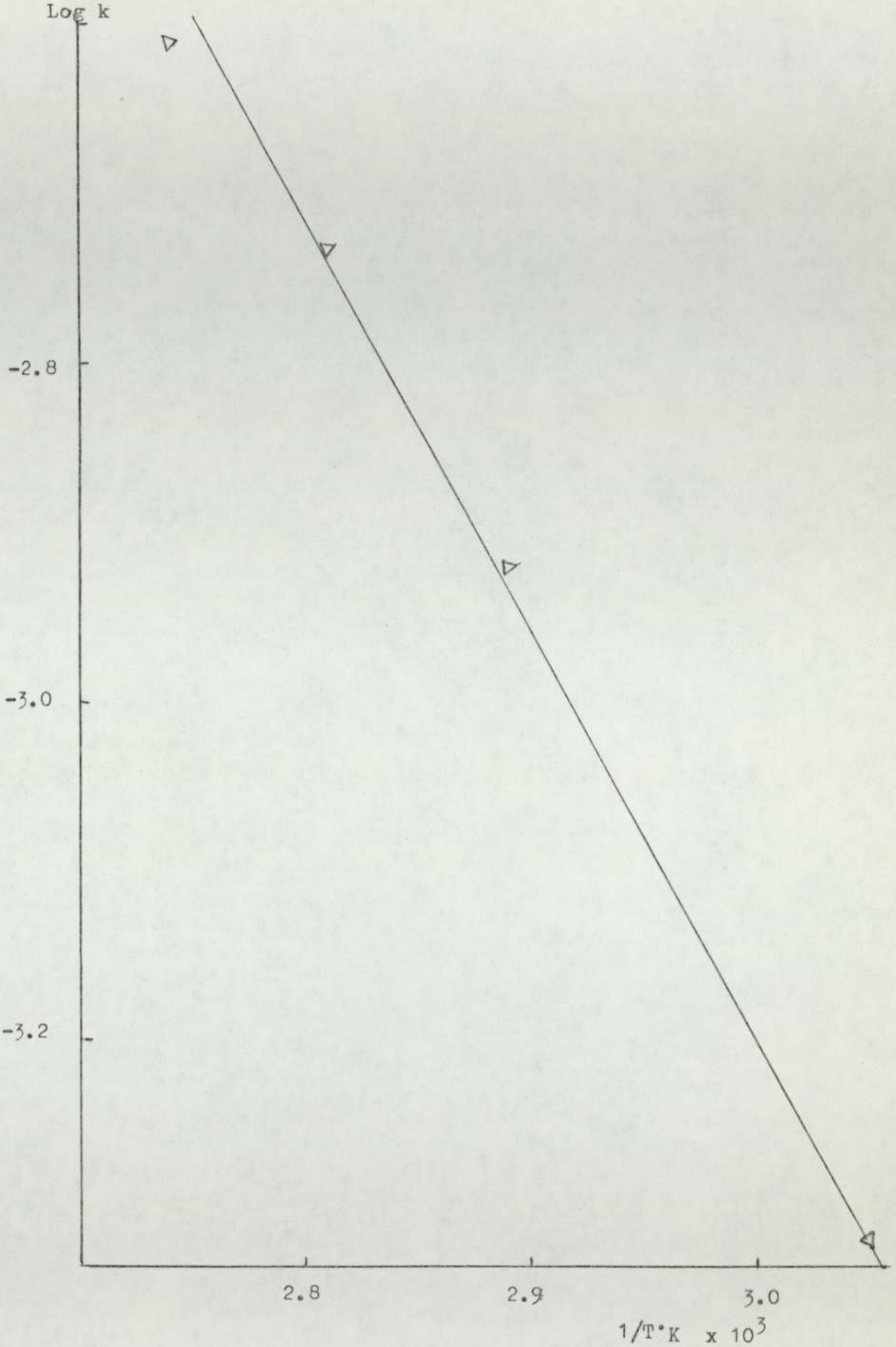


Figure 5.5 The variation of the rate constant with temperature for the reaction between CHP and catechol methyl phosphate.

is, then the rate of the reaction is greater in polar solvents.

The variation of the rate of the reaction between cumene hydroperoxide and catechol cyclic phosphate was investigated in solvents having different dielectric constants. First order rate constants for these reactions calculated from the first order plots (figure 5.6) are given in table 5.3.

Table 5.3

The effect of solvent polarity on the rate of reaction between CHP and catechol cyclic phosphate at 70°C. (CHP):(phosphate) = 5 : 1

Solvent	Rate constant(sec^{-1})
1,1,1-Trichloroethane	0.87×10^{-3}
Chlorobenzene	1.50×10^{-3}
Nitrobenzene	6.01×10^{-3}

The maximum error in these figures being $0.3 \times 10^{-3} sec^{-1}$, these results clearly show that the rate is significantly affected by the polarity of the solvent, the rate being enhanced in solvents having higher dielectric constants. This observation therefore suggests an ionic or a highly polar intermediate for the activated complex. This is in accord with the possibility of an ionic pathway proposed earlier on the basis of product distribution.(chapter 4).

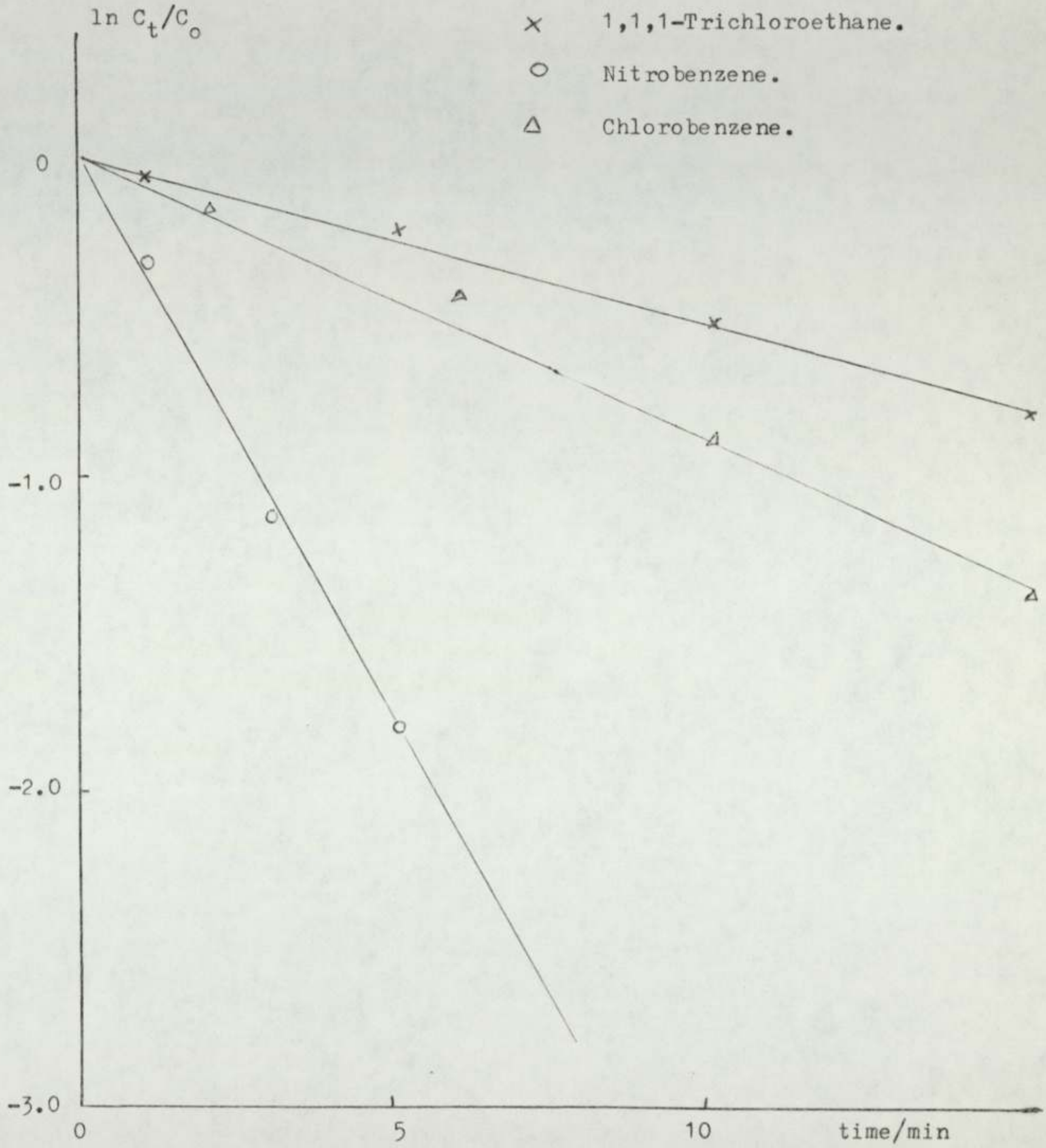
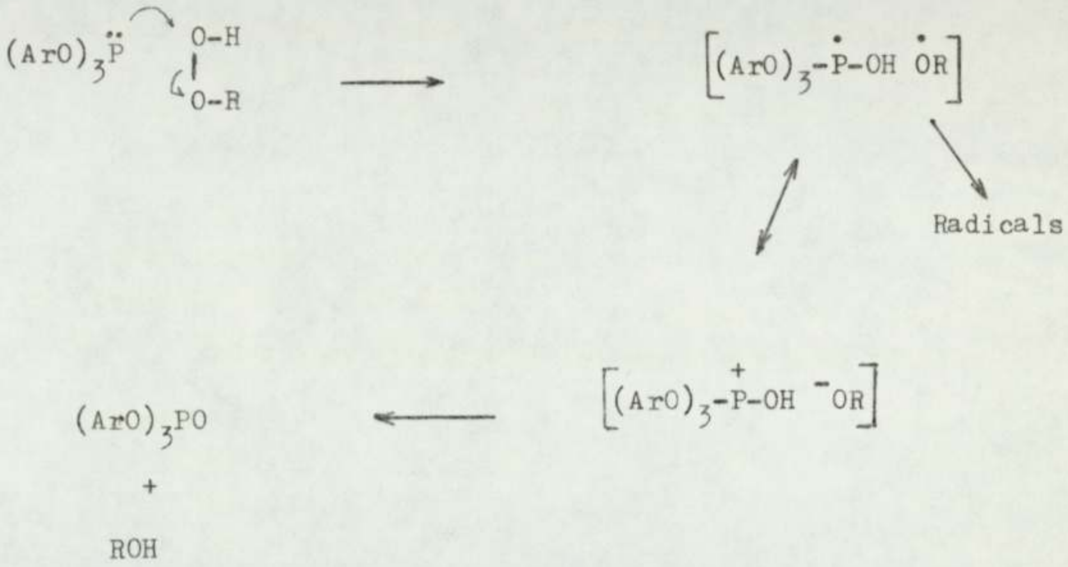


Figure 5.6 First order plots for the decomposition of CHP by catechol methyl phosphate in various solvents at 70°C. (CHP):(phosphate) = 10 : 1.

5.4 THE MECHANISM

5.4.1 The reaction of phosphites with hydroperoxides.

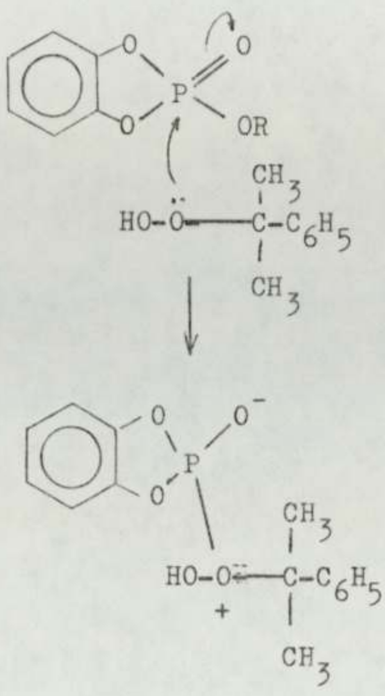
A mechanism involving a nucleophilic attack by the lone pair of electrons (on the phosphorus atom) on the hydroxy oxygen atom of the hydroperoxide has been proposed for the reaction between phosphites and cumene hydroperoxide by Humpris and Scott.[79] This is essentially similar to that proposed by Pobedimskii and Buchachenko.[80]



5.4.2 The reaction of phosphates with hydroperoxides.

A nucleophilic attack by the hydroperoxide on the phosphorus atom appears to be the only plausible mechanism for a reaction between catechol cyclic phosphates and hydroperoxides.

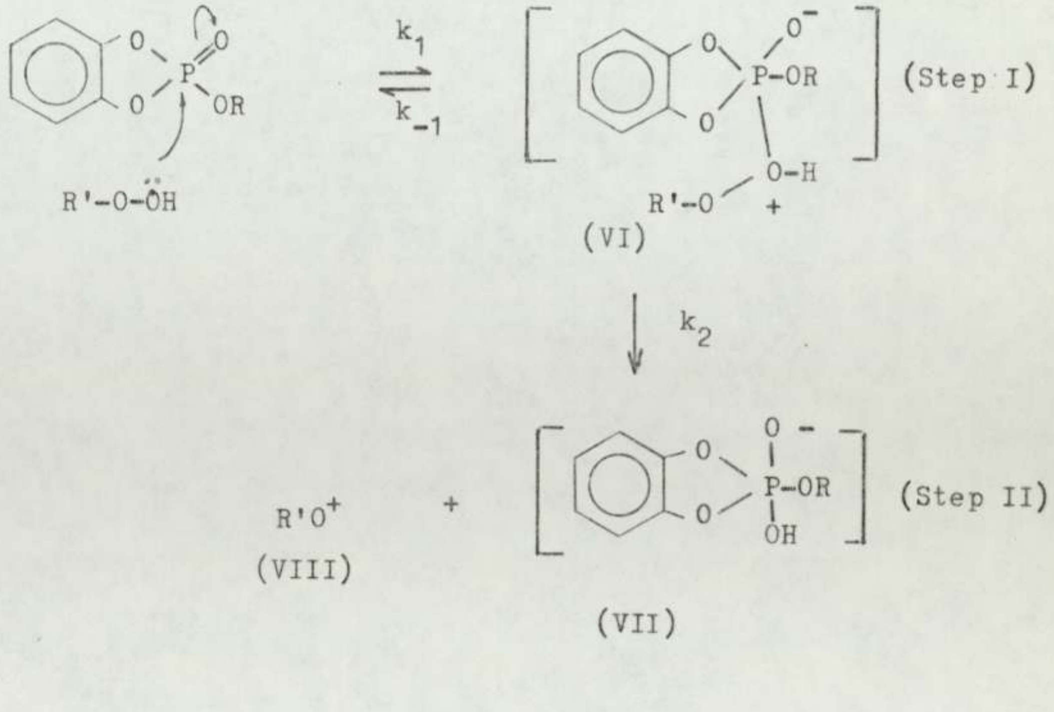
An attack by the alkyl-oxy oxygen atom on the phosphorus atom of the phosphate will not explain the formation of observed products. Further, such a reaction is discouraged by steric factors.

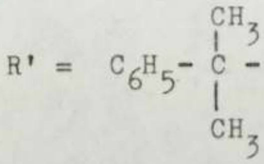


Scheme I

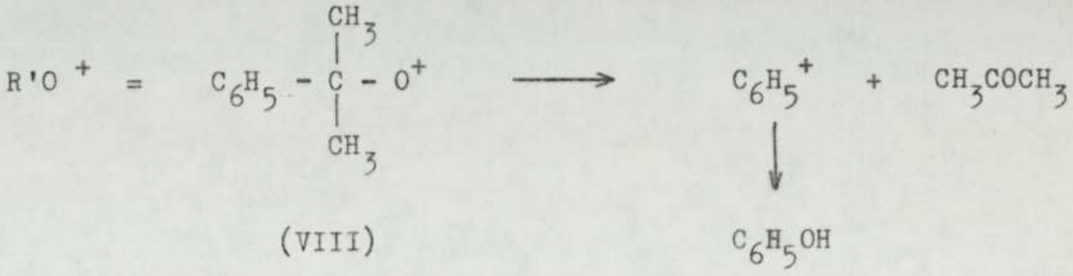
Attack by the alkyl-oxy oxygen on phosphorus

On the other hand the attack by the hydroxy-oxygen atom on phosphorus atom as shown in scheme II is more likely.





$R' = C_6H_5-C(CH_3)_2-$ when R'OOH is cumene hydroperoxide.



$R'O^+ = C_6H_5-C(CH_3)_2-O^+ \longrightarrow C_6H_5^+ + CH_3COCH_3$; $C_6H_5^+ \rightarrow C_6H_5OH$

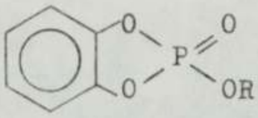
(VIII)

Scheme II

This scheme envisages, in step I, the formation of an activated complex which involves charge separation. Such reactions are associated with abnormally low frequency factors.[68,69.] The Arrhenius frequency factor, A, for this reaction was calculated to be 1.8×10^4 sec^{-1} and accordingly suggests the formation of a polar intermediate.

This is further confirmed by the value of the entropy of activation, ΔS^*, which is -172.2 J $K^{-1} mol^{-1}$ (41.2 cal $K^{-1} mol^{-1}$). The large negative value for the entropy of activation implies reduction in the degree of freedom of the system as the activated complex is formed. This is consistent with a transition state more polar than the reactants.

It was shown that the order of reactivity for the reaction between cumene hydroperoxide and the cyclic phosphate esters IV



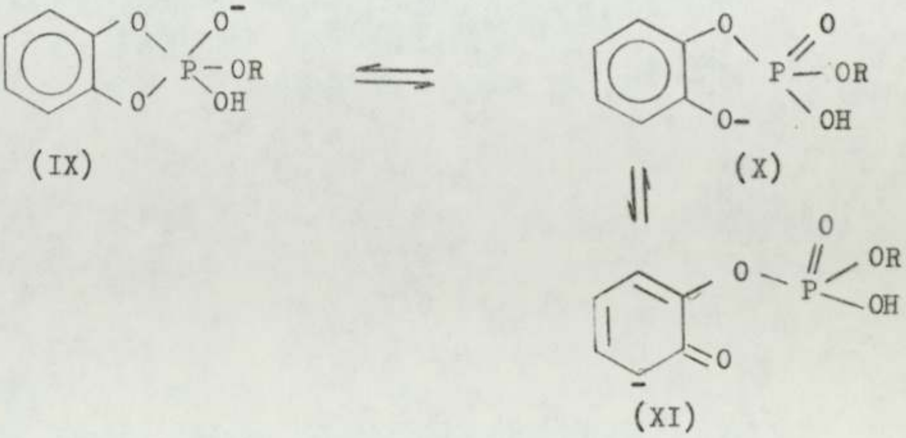
(IV)

was,

$$R = H > C_6H_5 > CH_2CH_2Cl > CH_3 > i\text{-Pr.}$$

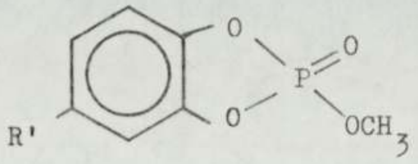
This is in keeping with the nucleophilic attack by the hydroxy oxygen atom of the hydroperoxide on the phosphorus atom of the cyclic phosphate. Electron releasing substituents (R) will decrease the electrophilicity of phosphorus and hence reduce the polarity of the P=0 bond making the reaction slower and vice versa. A similar explanation holds true in the case of substituents on the benzene ring.

The anion VII formed in step II of the scheme II is stabilised as follows.



Scheme III

Electron withdrawing substituents on the benzene ring can therefore add to the stability of these structures, while the electron releasing substituents will have the opposite effect. This is reflected by the reactivities of the following series.

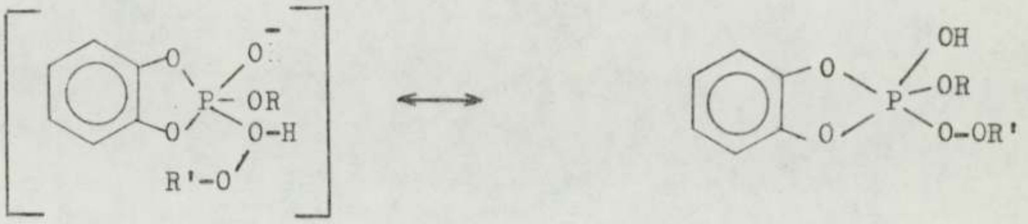


Reactivity: $R' = H > CH_3 >$ t-Bu

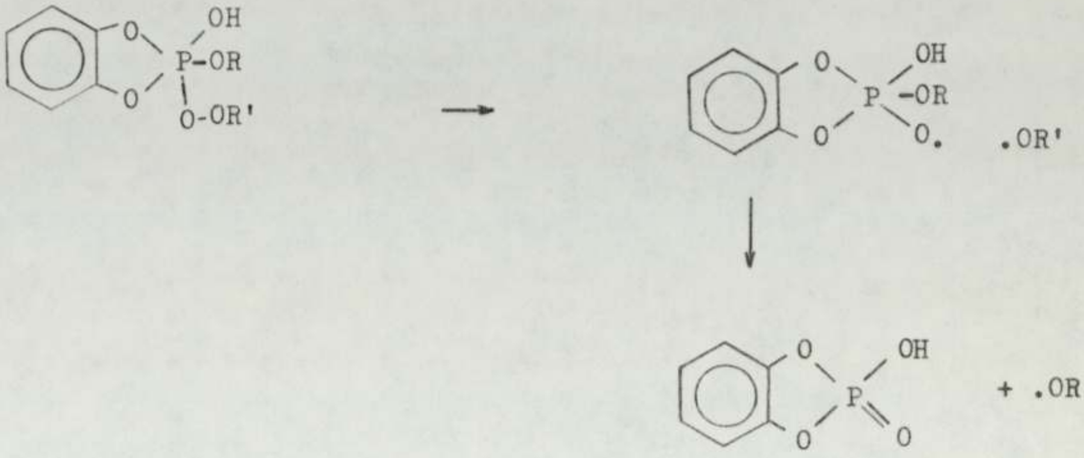
5.4.3 Formation of cumyl alcohol, methylstyrene and acetophenone

As mentioned previously, the formation of cumyl alcohol, methylstyrene and acetophenone, which are the characteristic products of a radical reaction can be explained as follows:

The activated complex VI in scheme II can generate a peroxy-intermediate XXIII.



This can then undergo homolytic cleavage to form radical species.



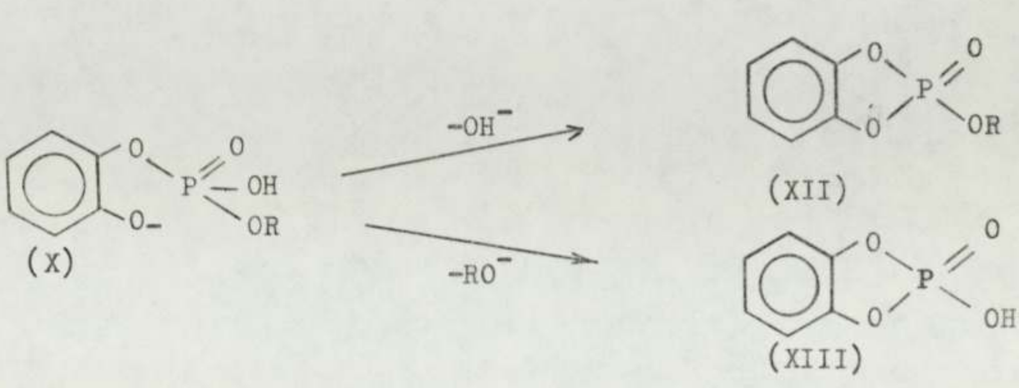
.OR' ⟶ Cumyl alcohol ⟶ α-Methylsryrene.

.OR' ⟶ Acetophenone.

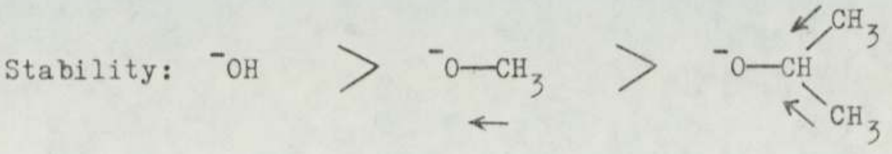
This is analogous to the reaction between phosphites and hydroperoxides described by Pobedeminskii[80] and also to the reaction between cyclic phosphites and hydroperoxides described by Humpris and Scott.[79]

5.4.4 The fate of the substituent R

The ring closure of X can lead to the formation of the cyclic phosphate with the elimination of ^-OR or ^-OH anions.



Methanol or isopropanol could not be detected in the early stages of the reaction mixture when the esters with R = CH_3 or i-Pr were used. This indicates that ^-OH is eliminated in preference to the alkoxy anions. This can be attributed to the lower stability of the alkoxy anions in comparison with hydroxy anion due to the inductive effect as indicated.

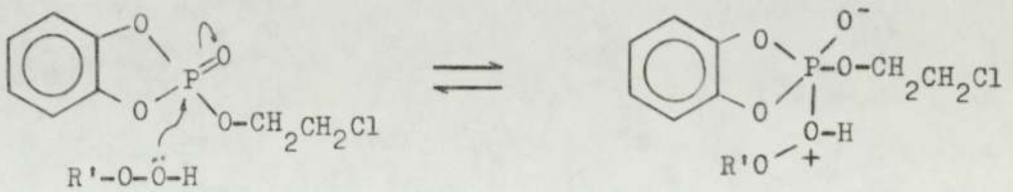


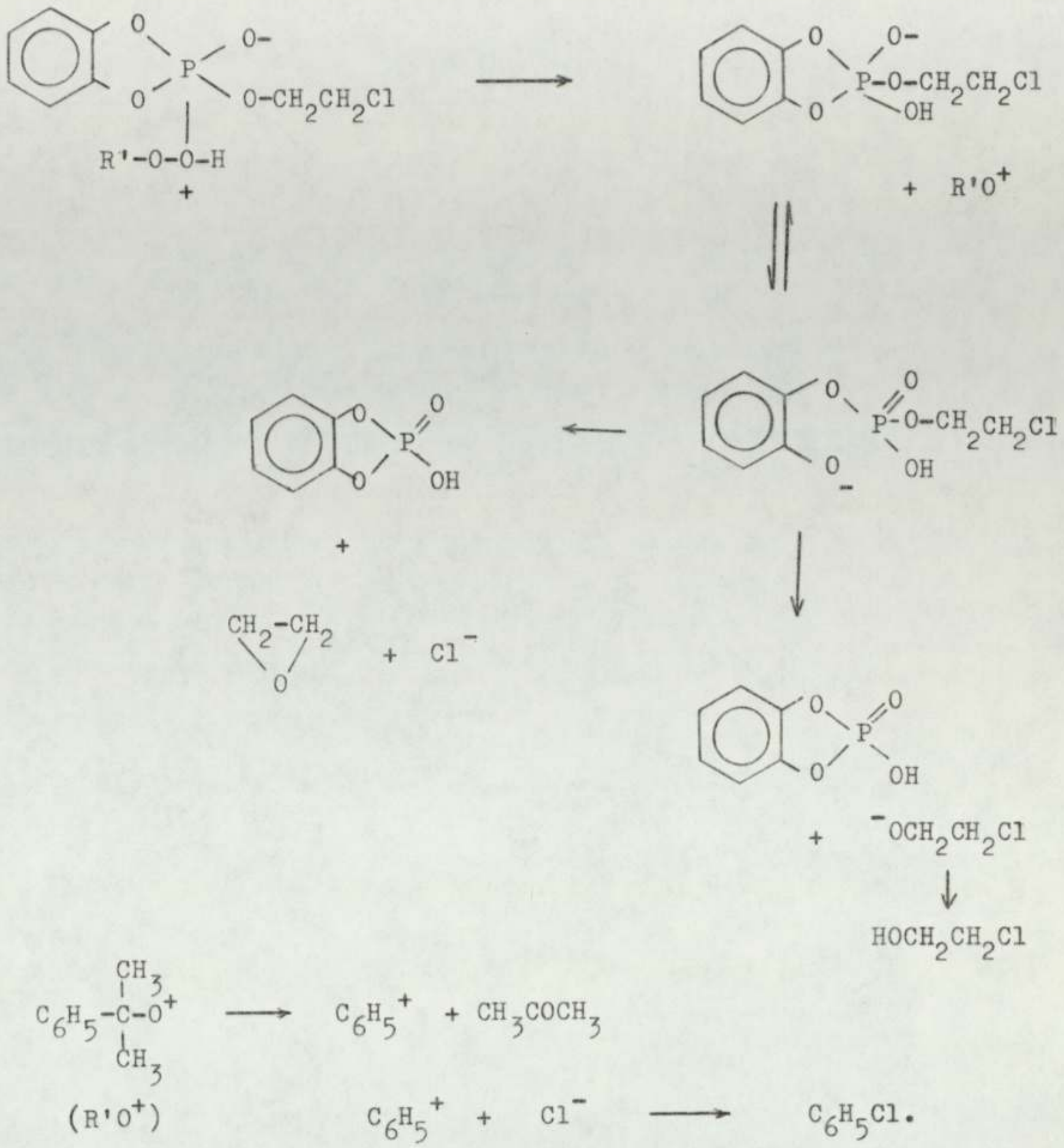
$$\text{Stability: } {}^-OH > {}^-O{-}CH_3 > {}^-O{-}CH(CH_3)_2$$

However, when R = C_6H_5 or $-CH_2CH_2Cl$, it was possible to detect by g.l.c, the presence of phenol (when t-butyl hydroperoxide was used) and 2-chloroethanol in the very early stages of the reaction. With these esters therefore $^-OC_6H_5$ and $^-OCH_2CH_2Cl$ ions are eleminated in preference to ^-OH.

Stability: $^-OH < {}^-OCH_2CH_2Cl$; $^-OH < {}^-OC_6H_5$.

Further, with the cyclic phosphate ester where R = $-CH_2CH_2Cl$, chlorobenzene could be detected when the reaction was carried out with cumene hydroperoxide in benzene.





(Scheme IV)

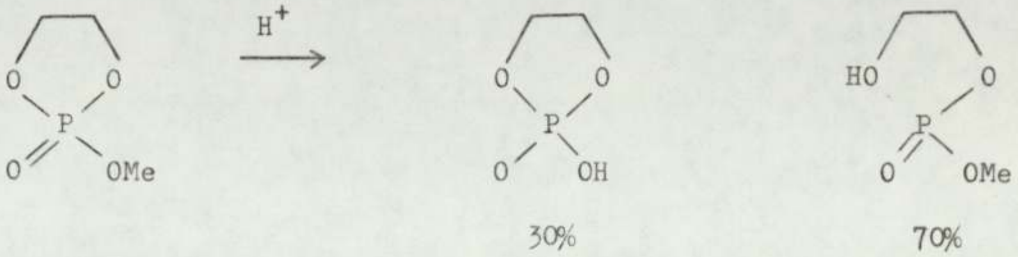
This provides conclusive evidence for the elemination of $^{-}OCH_2CH_2Cl$ anion.

It can therefore be concluded that the fate of group R in these esters depends on its structure. Electron releasing groups (R) are retained and ^{-}OH is eliminated while electron withdrawing groups are eliminated with the retention of ^{-}OH. In the former case the original ester is regenerated and in the latter, the cyclic hydroxy phosphate is formed. In either case this offers an explanation for the regeneration of the catalyst.

5.4.5 Pseudorotation

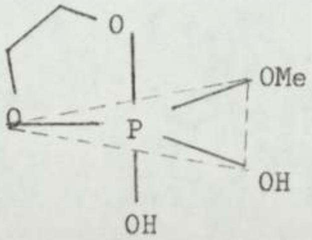
The concept of pseudorotation introduced by Berry[70] to explain the ^{19}F n.m.r spectrum of phosphorus pentafluoride PF_5, has been used successfully by Westheimer [71] in an attempt to clarify the features of five-membered cyclic phosphate ester hydrolysis.

The ester XIV undergoes acid hydrolysis as shown below.



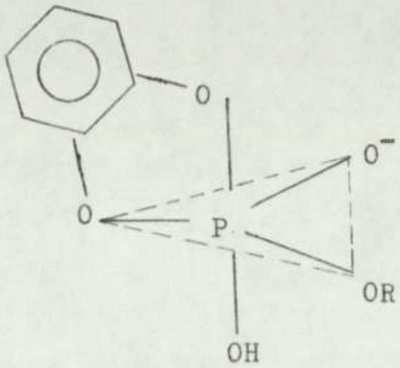
(XIV) (XV) (XVI)

A large percentage of the ester remains with the ring intact. An intermediate, XVII, with the phosphoroyl oxygen protonated and the in-coming hydroxyl group apically placed was postulated, to account for these observations.[71, 74, 89]



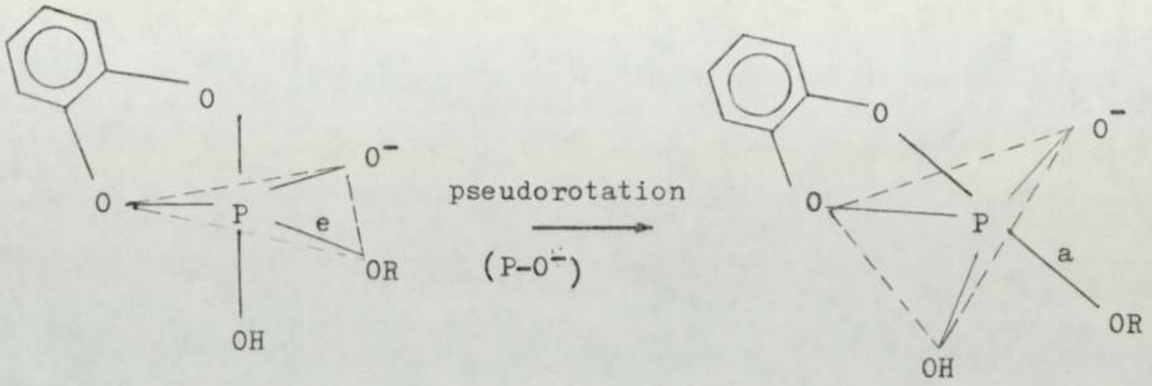
A leaving group departs from an apical position and in XVII, this will lead to the formation of ring-opened product XVI. The intermediate XVII was thought sufficiently long lived to permit pseudorotation. Pseudorotation of this with equatorial -OH as the pivot will bring the methoxy group to an apical position from which it can depart leaving a product in which the ring is preserved.

The pentacoordinate intermediate VII in scheme II proposed for the mechanism of reaction of cyclic catechol phosphate with cumene hydroperoxide, is exacty similar to the intermediate XVII postulated by Westheimer.[71] The pentacoordinate VII is produced by the nucleophilic attack on phosphorus by hydroxy-oxygen of the hydroperoxide and subsequent cleavage of the peroxy bond. Accordingly this intermediate must have the structure,



(VII)

Cleavage of apical P—O bond of the ring will lead to the formation of the ring-opened phosphate ester X. Pseudorotation of VII, with ring O—P bond as pivot will make the ring diequitorial and this is not energetically favoured.[72] Pseudorotation with -OR as the pivot will exchange the positions of ring P-O bonds, while that with $P-O^-$ as pivot will bring O-R to an axial orientation. (Scheme III). This makes the departure of ^-OR possible. More electro-negative substituents prefer to occupy axial positions[73] and $P-O^-$ prefers to be equitorial.[73] Substituents like $-OCH_2CH_2Cl$ are more electronegative than $-OCH_3$ or -O-i-Pr and hence tend to favour apical positions. Therefore pseudorotation of the type shown in scheme III is favoured

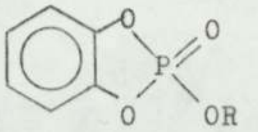


SCHEME III

in such cases. This offers an alternative explanation for the prompt cleavage of more electro negative groups, R, during these reactions.

5.4.6 Hydrolysis of cyclic phosphate esters.

At this stage it was of interest to study the fate of the alkyl group R in the ester,



R = Me

during hydrolysis as the mechanism of hydrolysis is essentially similar to that involved in the reaction with hydroperoxides.

The n.m.r spectrum (figure 5.7) of pure 2-methoxy-4,5-benzo-1,3,2-dioxaphospholan-2-oxide consists of the following signals:

2.7 τ	multiplet	4H	aromatic protons
5.9 τ	doublet	3H	methyl protons. (J_{P-H}=11Hz)

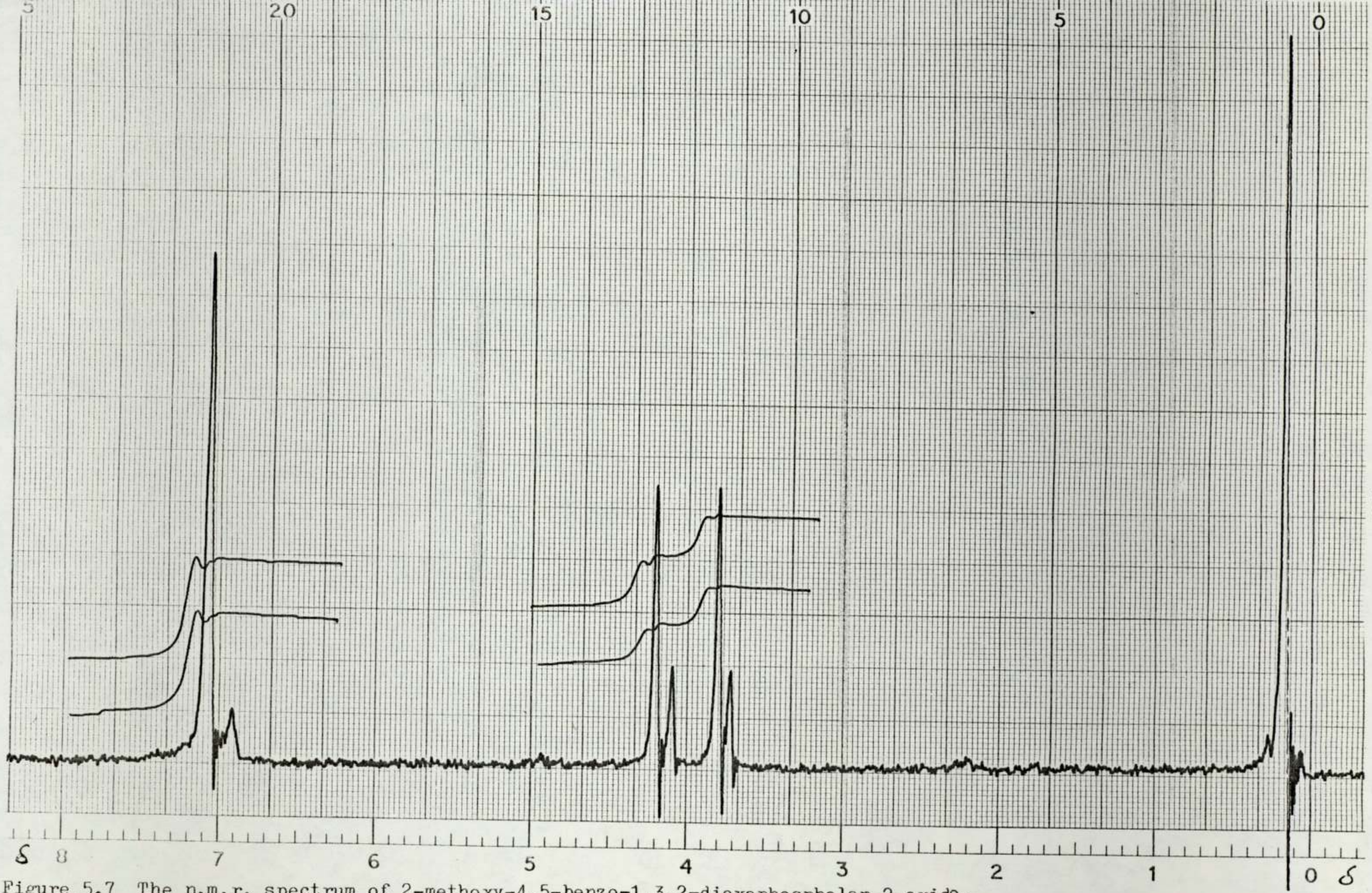
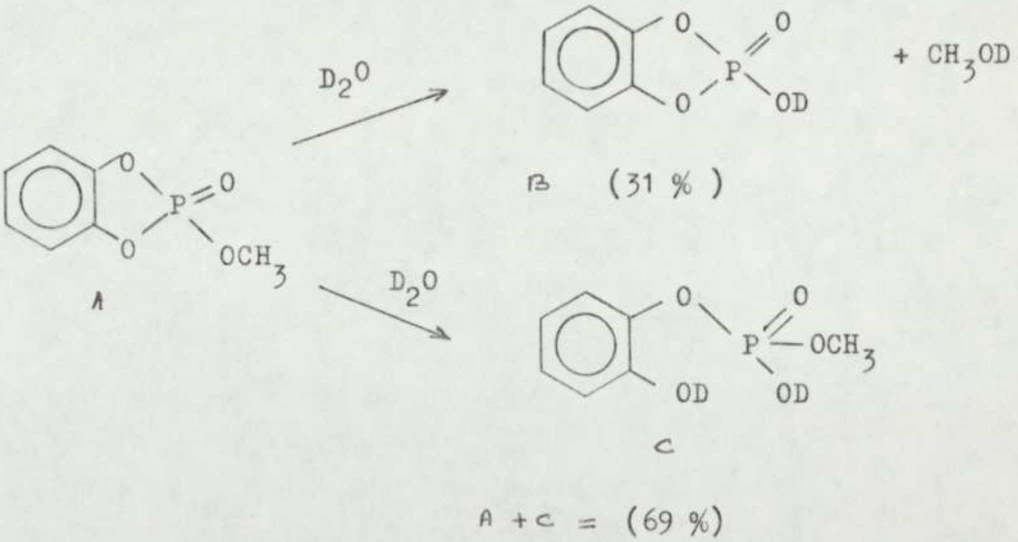


Figure 5.7 The n.m.r. spectrum of 2-methoxy-4,5-benzo-1,3,2-dioxaphospholan-2-oxide.

The n.m.r spectrum of the ester in deuterium oxide taken immediately after making the solution shows the appearence of a new signal at 6.3 (singlet) due to the formation of CH_3OD. Deuterium oxide, D_2O, was used to avoid complications due to the appearence of signals due to O<u>H</u> after hydrolysis.

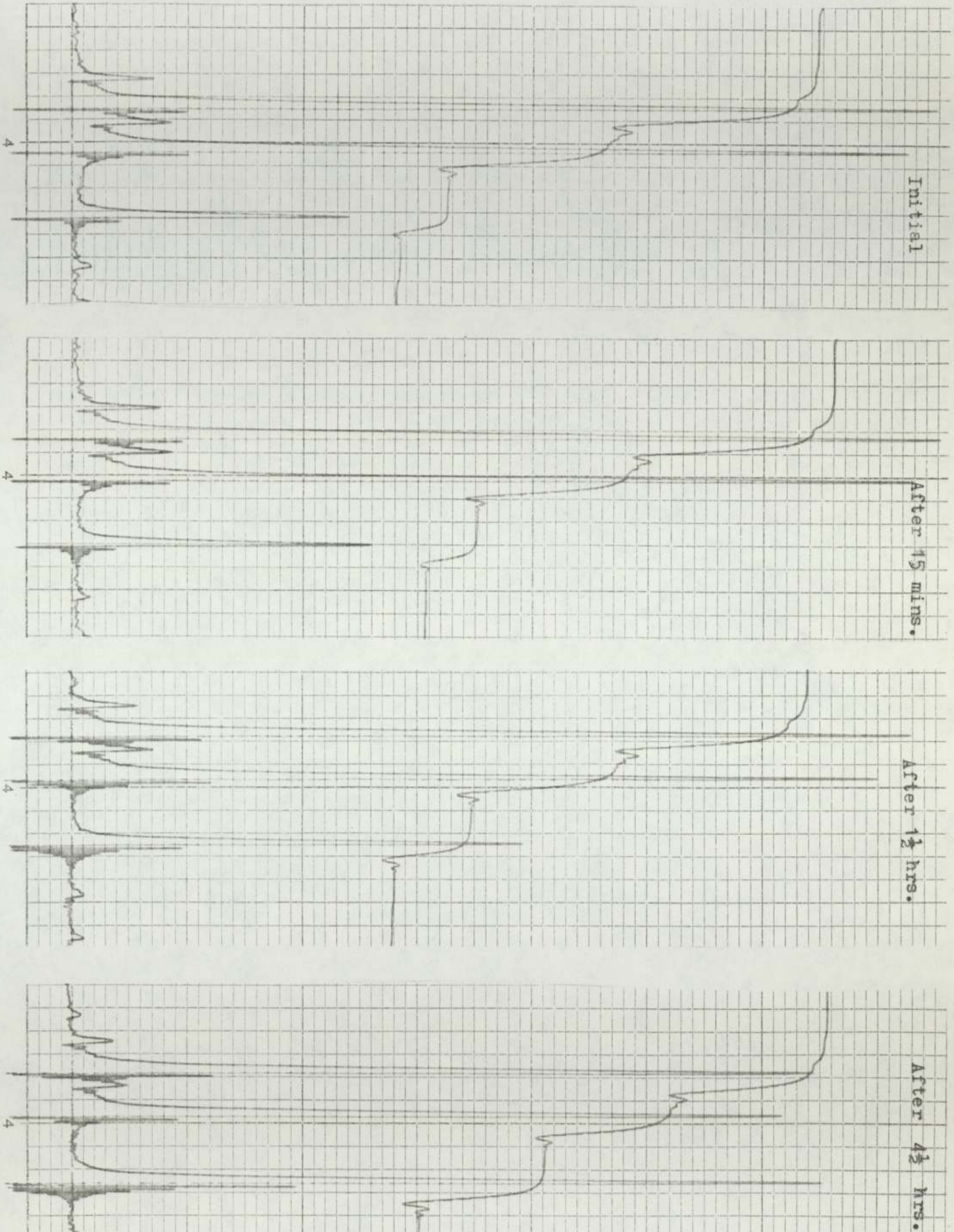
With time the doublet due to the methyl group in the ester decreased in intensity with simultaneous increase in the signal due to CH_3 protons in CH_3OD formed.(figure 5.8). After several hours the doublet due to the methyl group in the ester was still present and the calculations show that 69 % of the ester (cyclic + acyclic) still has the methyl group intact.(A + C)



5.5 THE CATALYTIC FEATURE OF THE REACTION.

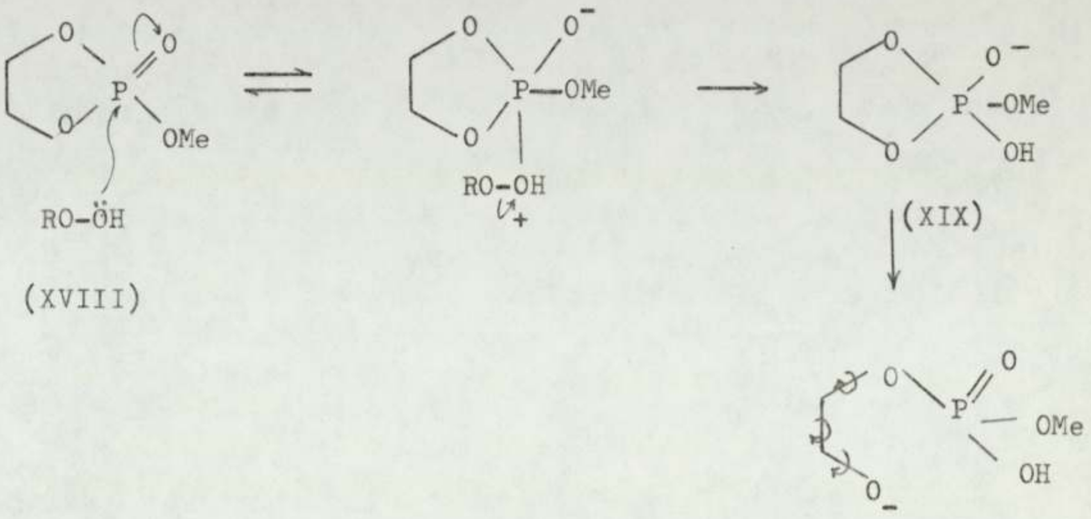
Five membered cyclic phosphate esters react with hydroperoxides but there is an important difference between between aliphatic cyclic phosphates and aromatic cyclic phosphates. Aromatic cyclic phosphates are powerful catalysts for the decomposition of hydroperoxides

Figure: 5.8. Variation of the n.m.r. spectrum of 2-methoxy-4,5-benzo-1,3,2-dioxaphospholane-2-oxide in deuterium oxide.(34°C)



whereas aliphatic ones are not.

According to the mechanism discussed earlier, ring opening of the ester is possible during the reaction. With an aliphatic cyclic ester such as 2-methoxy-1,3,2-dioxaphospholan-2-oxide, XVIII, this leads to the formation of the anion XX.



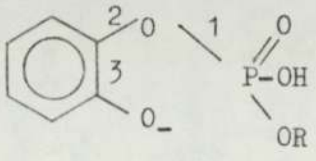
(XVIII)

(XIX)

(XX)

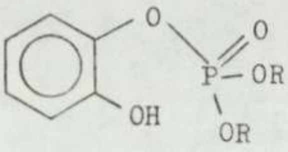
Free rotation of bonds in XX is possible as shown. (There is some restriction to the rotation about the P-O-alkyl bond due to $p_{\pi} - d_{\pi}$ bonding). This free rotation makes the regeneration of the cyclic phosphate less likely.

With aromatic cyclic phosphate esters, the anion formed is

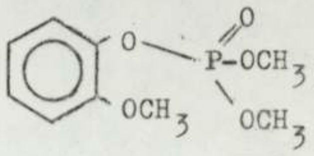


and there is restricted rotation about P-O bond (1), O-C bond (2) and the C-C bond (3). This restricted rotation therefore leaves the oxy-anion moiety close to the electrophilic phosphorus atom and the ring closure leading to the formation of the cyclic ester is possible.

If this theory of catalytic activity, ie. one involving alternative ring opening and ring closure of the phosphate, is true, then an ester such as, (XXI),

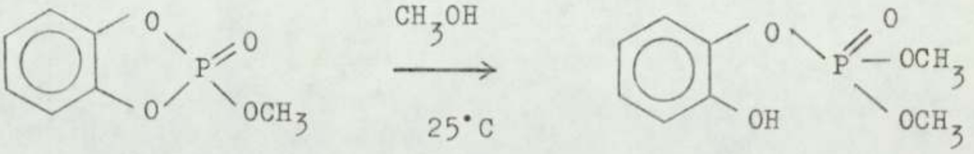


(XXI)



(XXII)

must also be a catalytic decomposer of hydroperoxides. This ester where R = CH_3 was synthesised by the following route.



(IV)

(XXI)

and it was found that it was almost as efficient a hydroperoxide decomposer as its cyclic analogue. Furthermore, the reaction was catalytic. In figure 5.9 is compared the rates of the reactions of the cyclic ester IV and the acyclic ester XXI with cumene hydroperoxide. The corresponding rate constants are given in table 5.4.

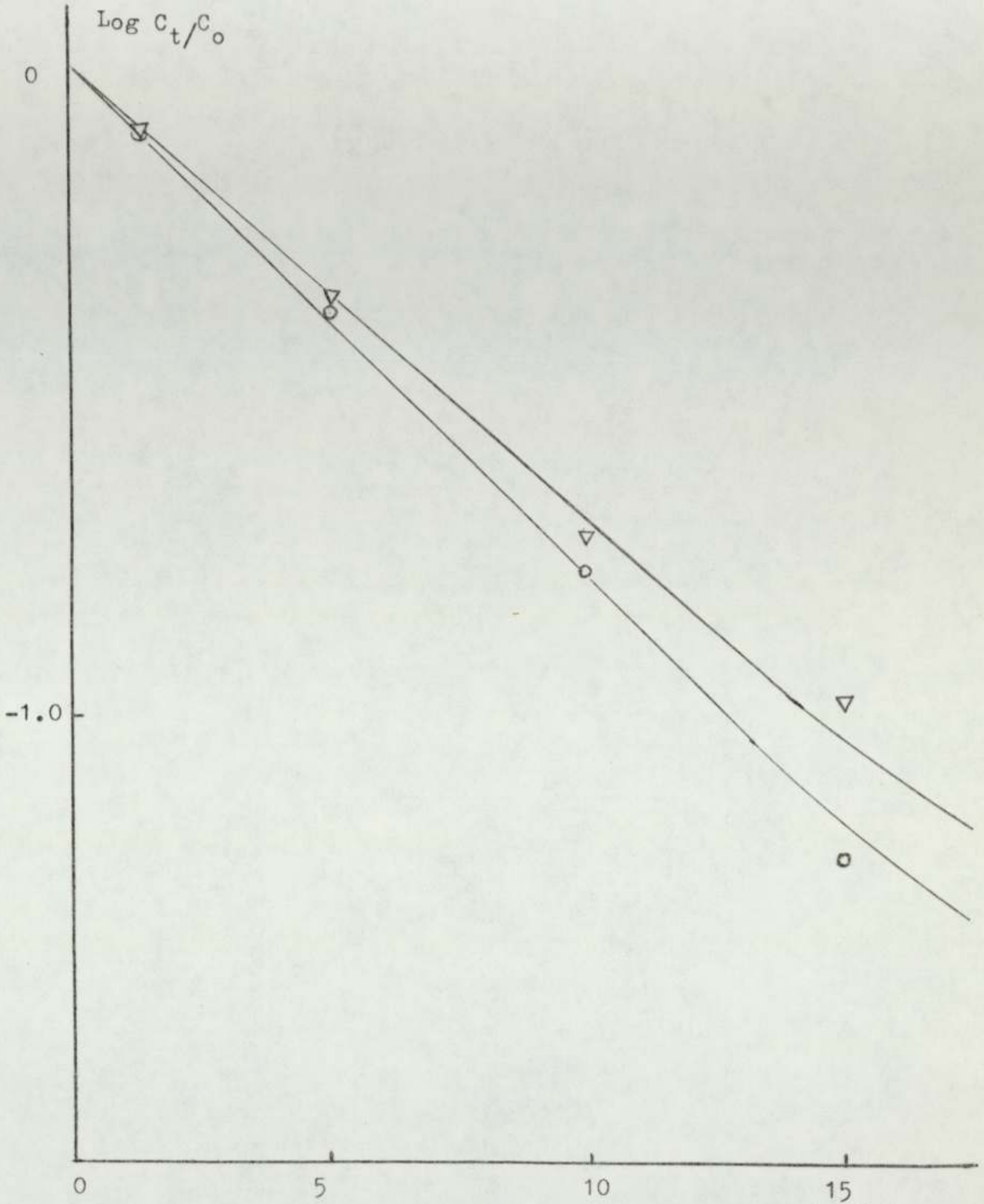


Figure 5.9 The rate of decomposition of CHP by the esters IV and XXI in chlorobenzene at 70°C. (CHP)= 0.04mol l^{-1} (phosphate) = 0.02 mol l^{-1}.

Table 5.4

Rate constants for the reaction of esters IV and XXI with cumene hydroperoxide in chlorobenzene at 70°C. (CHP) : (phosphate) = 2:1

(CHP) = 0.04 mol l^{-1}

Ester	Rate constant/sec^{-1}
IV	3.0×10^{-3}
XXI	2.7×10^{-3}

In contrast to the ester XXI, o-methoxyphenyl dimethyl phosphate XXII was found to be completely inert towards hydroperoxides, just as triphenyl phosphate is. This provides confirmatory evidence for the proposed mechanism.

5.6 KINETIC TREATMENT OF HOMOGENEOUS CATALYSIS IN SOLUTION.

The rate of the reaction between catechol cyclic phosphates and cumene hydroperoxide is proportional to the first power of the phosphate concentration (chapter 4). The dependence of the rate on substrate (hydroperoxide) concentration is as shown in figure 5.10. The rate varies linearly with hydroperoxide concentration at low concentrations (first order kinetics) and becomes independent of it at high concentrations (zero order kinetics) at a given concentration of the phosphate.

This is very similar to the behaviour of enzyme catalysed reactions.[75,76] (figure 5.11).

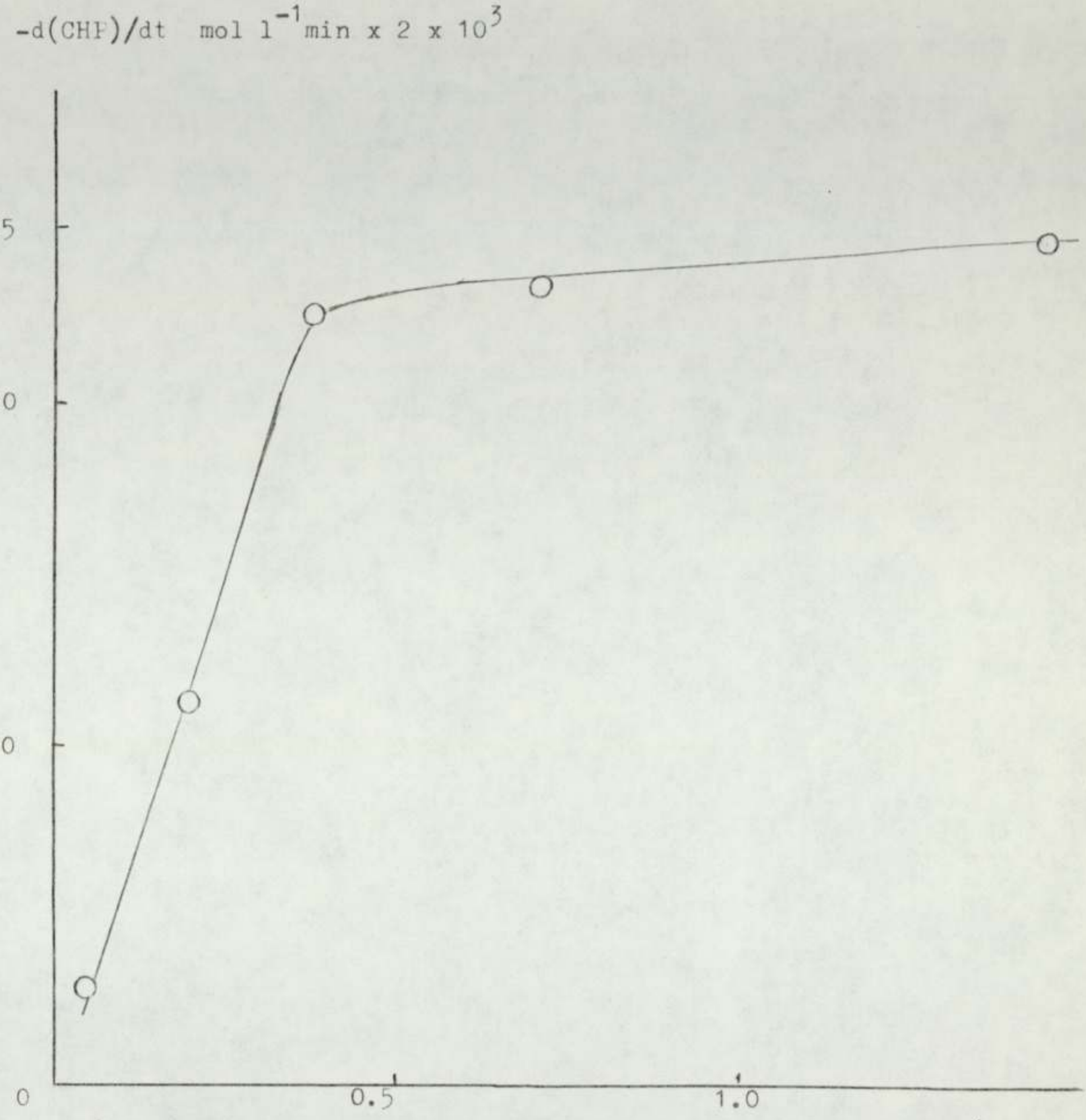


Figure 5.10 The dependence of the rate of decomposition of CHP on its concentration.

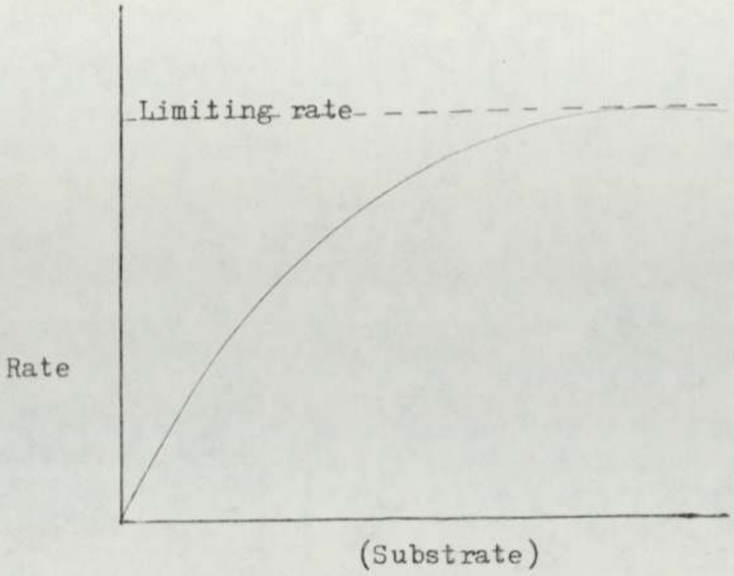


Figure 5.11 The variation of the of an enzyme catalysed reaction with substrate concentration.[75]

The reaction between a hydroperoxide and a cyclic catechol phosphate may be represented as,

$$HP + P \underset{k_{-1}}{\overset{k_1}{\rightleftharpoons}} HPP \qquad (1)$$

$$HPP \xrightarrow{k_2} P + \text{Products.} \qquad (2)$$

where, HP = Hydroperoxide,
P = Phosphate ester and
HPP = Reaction intermediate.

This is the scheme presented in section 5.4.2. and the steady state equation for this will be,

$$k_1\,(HP)(P) - k_{-1}(HPP) - k_2(HPP) = 0 \qquad (3)$$

The total concentration of the phosphate ester $(P)_o$ will be the sum of the concentration of the free phosphate (P) and the concentration of the complex (HPP) at any time.

$$(P)_o = (P) + (HPP) \qquad (4)$$

Therefore, $(P) = (P)_o - (HPP) \qquad (5)$

Substituting for (P) in equation (3),

$$k_1(HP)\left[(P)_o - (HPP)\right] - (HPP)(k_{-1} + k_2) = 0 \qquad (6)$$

$$\therefore \quad (HPP) = \frac{k_1(HP)(P)_o}{k_{-1} + k_2 + k_1(HP)} \qquad (7)$$

The rate of the reaction, $v = -\,d(HP)/dt = k_2\,(HPP)$

Therefore, $v = k_1k_2\,(HP)(P)_o / k_{-1} + k_2 + k_1(HP) \qquad (8)$

$$v = \frac{k_2\,(HP)(P)_o}{K + (HP)} \qquad (9)$$

where, $K = (k_{-1} + k_2)/k_1$ and is equivalent to the Michaelis constant K_m in enzyme reactions.[77]

If, (HP) is very small compared to K, equation (9) becomes,

$v = \frac{k_2}{K}\,(HP)(P)_o$ and the rate is first order with respect to the hydroperoxide.

On the other hand when the hydroperoxide concentration, (HP) is very large, i.e. $(HP) \gg K$, the equation (9) becomes,

$$v = k_2 (P)_0$$

and the rate is zero order with respect to the hydroperoxide.

Equation (9) may be written in the form,[78]

$$\frac{1}{v} = \frac{K_m}{k_2(HP)(P)_o} + \frac{1}{k_2(P)_o}$$

and the applicability of the equation to experimental data can be tested by plotting $1/v$ versus $1/(HP)$; a straight line graph should be obtained and from this it is possible to calculate[81,82] the specific rate constant k_2 and a value for the constant K.

A graph of this type for the results given in table 5.5 is shown in figure 5.12.

Table 5.5

Rates of decomposition of CHP by 2-methoxy-4,5-benzo-1,3,2-dioxaphospholan-2-oxide (0.02 mol l^{-1}) at various concentrations of CHP at 70°C

(CHP)/mol l^{-1}	-d(CHP)/dt mol l^{-1} min^{-1}	1/(CHP) (l mol^{-1})	1/(rate) (l min mol^{-1})
0.0187	0.00135	53.3	740.7
0.050	0.0035	20.0	285.7
0.0925	0.0055	10.8	180.6
0.1875	0.0112	5.33	88.8
0.350	0.0116	2.85	85.5
0.720	0.0123	1.38	81.3

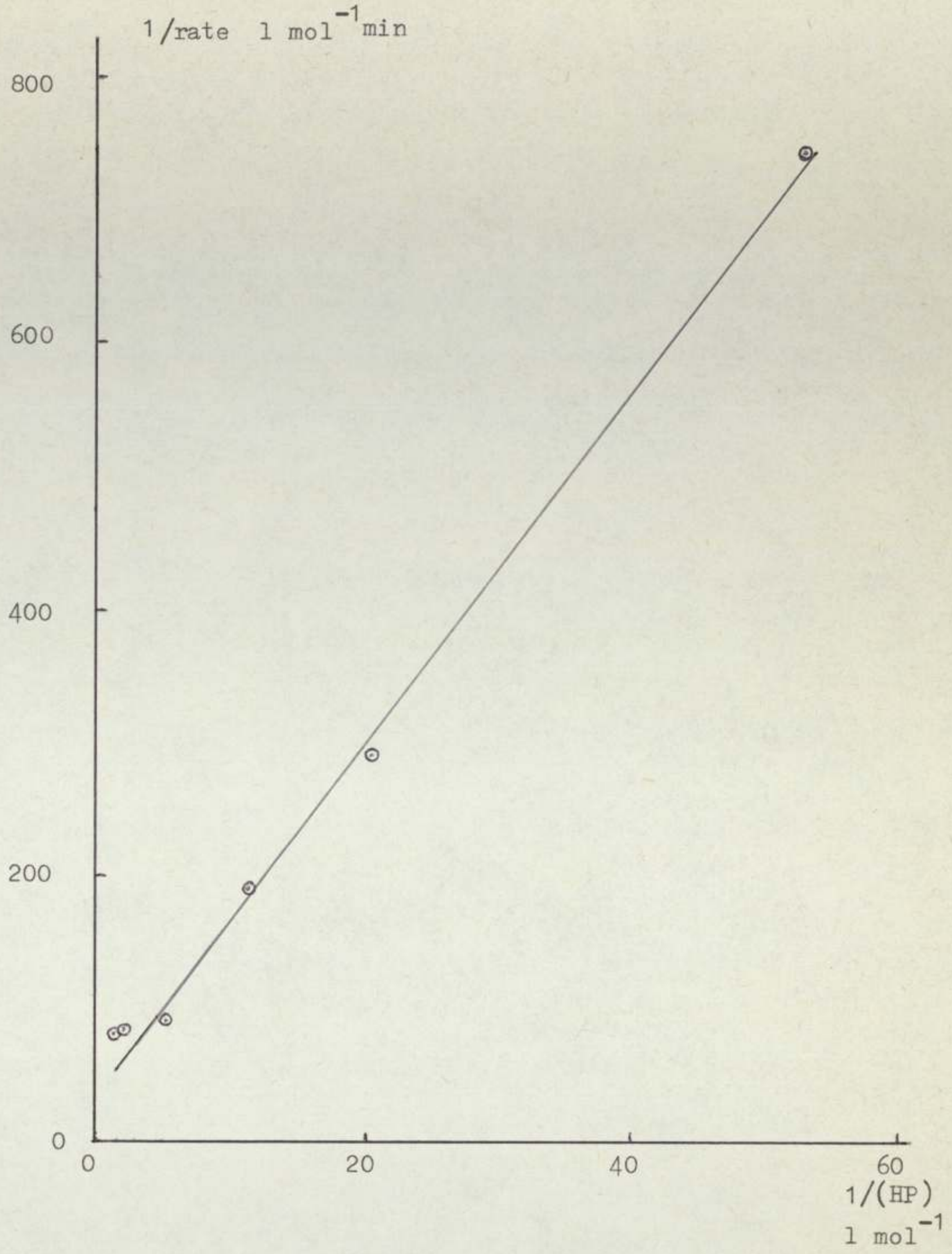


Figure 5.12 A plot of 1/rate v 1/(HP) for the reaction between CHP and catechol methyl phosphate at various molar proportions as given in table 5.5

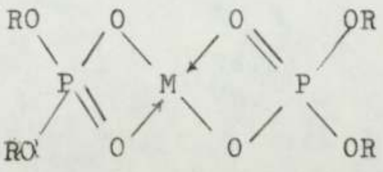
CHAPTER 6

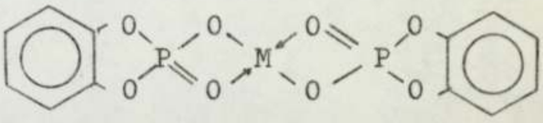
REACTIONS OF ORGANOPHOSPHATE METAL COMPLEXES WITH HYDROPEROXIDES.

6.1 INTRODUCTION

Cyclic phosphate esters based on catechol are excellent catalysts for the decomposition of alkyl hydroperoxides and as they perform this function by a non-radical mechanism, they act as good u.v. and thermal stabilisers in saturated hydrocarbons (chapter 7).

Instability of these esters in air (deliquescence) is one of their main disadvantages. They have a u.v. absorption maximum near 270 nm (figure 6.1) and do not absorb at all above 300 nm, the high frequency limit of solar radiation reaching the atmosphere. Therefore there is no possibility for these compounds to act as effective u.v. screening agents . It was therefore decided to make an attempt to prepare the transition metal complexes of the type,





(and the corresponding complexes of trivalent metal ions) with the hope that these will have increased stability and improved u.v. screening characteristics.

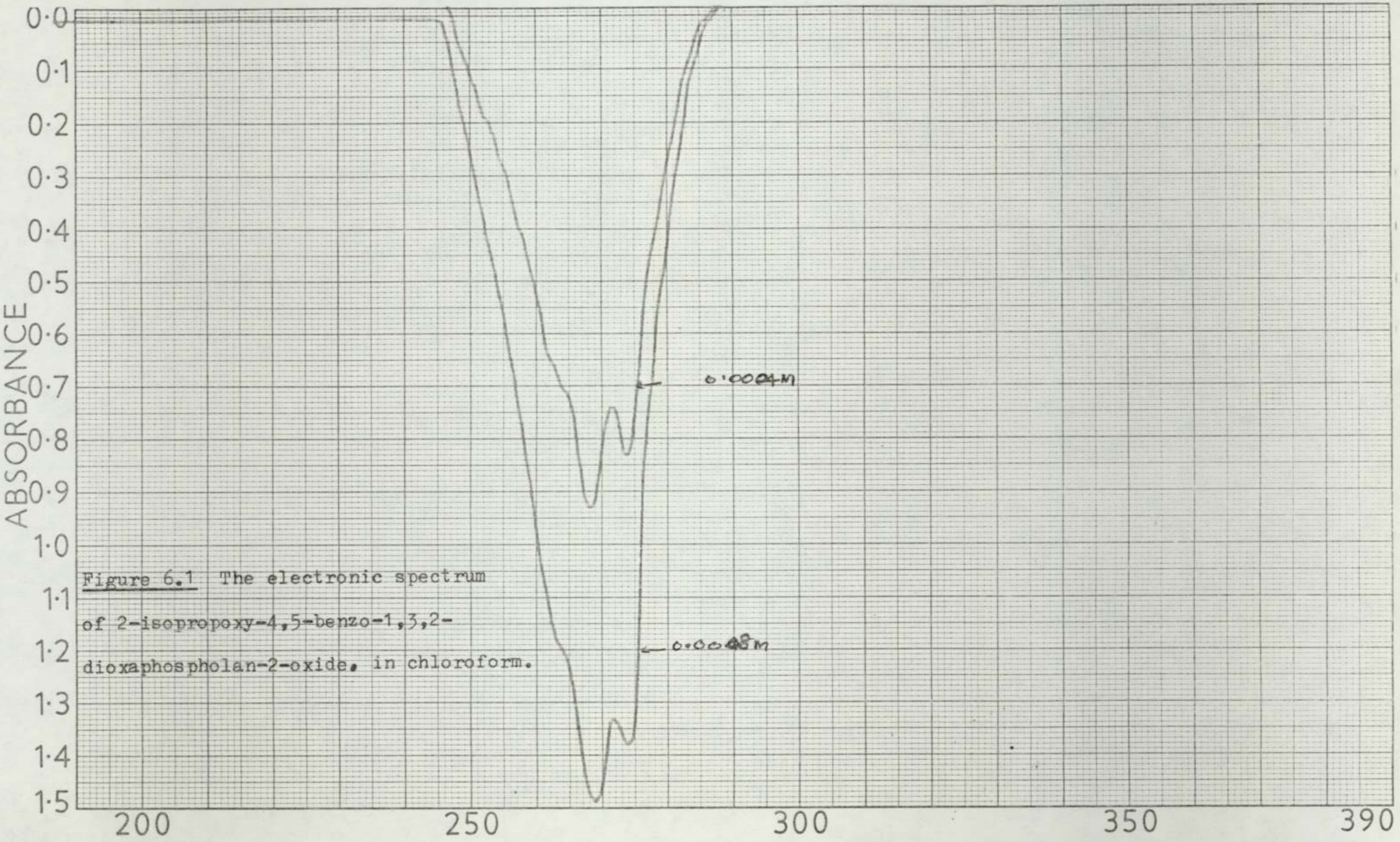


Figure 6.1 The electronic spectrum of 2-isopropoxy-4,5-benzo-1,3,2-dioxaphospholan-2-oxide, in chloroform.

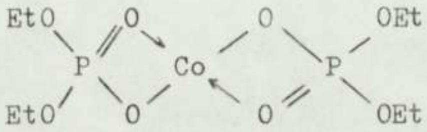
Though the transition metal ions are well known to decompose hydroperoxides through one-electron transfer reactions giving rise to free radicals,[4] it was thought that this could be suppressed if a true coordinate complex is formed. Infact polydentate ligands such as EDTA and polyhydric phenolic compounds can deactivate transition metal residues in polymers by complex formation. The donation of electrons from the phosphato-ligands to the empty d orbitals of metal ions can theoretically reduce the possibility of redox reactions with hydroperoxides.

6.2 Results and discussion

The reactions of bis-(dimethylphosphato)cobalt II and bis-(diethylphosphato)cobalt II with t-butyl hydroperoxide indicated that they could decompose hydroperoxides and they do so catalytically. Figure 6.2 shows a first order plot for the disappearance of t-butyl hydroperoxide at 50°C in benzene when the initial hydroperoxide concentration is 7.86×10^{-2} mol l^{-1} and the complex, bis-(diethyl phosphato)cobalt II, concentration is 1.09×10^{-2} mol l^{-1}. The decomposition follows pseudo-first order kinetics with a specific rate constant of $8.88 \pm 0.55 \times 10^{-4}$ sec^{-1}.

6.2.1 Reaction site.

Although cyclic phosphates react with hydroperoxides, acyclic aliphatic phosphates such as triethyl phosphate are inert towards them, and it is unlikely that the acyclic phosphate moiety in this complex would react.



Recently, Pobediminskii et al[80] have reported a process of catalytic decomposition of t-butyl hydroperoxide by triethyl and triphenyl phosphites in the presence of catalytic quantities of acetylacetonato complexes of dioxomolybdenum (Mo VI) and vanadyl (V IV). The

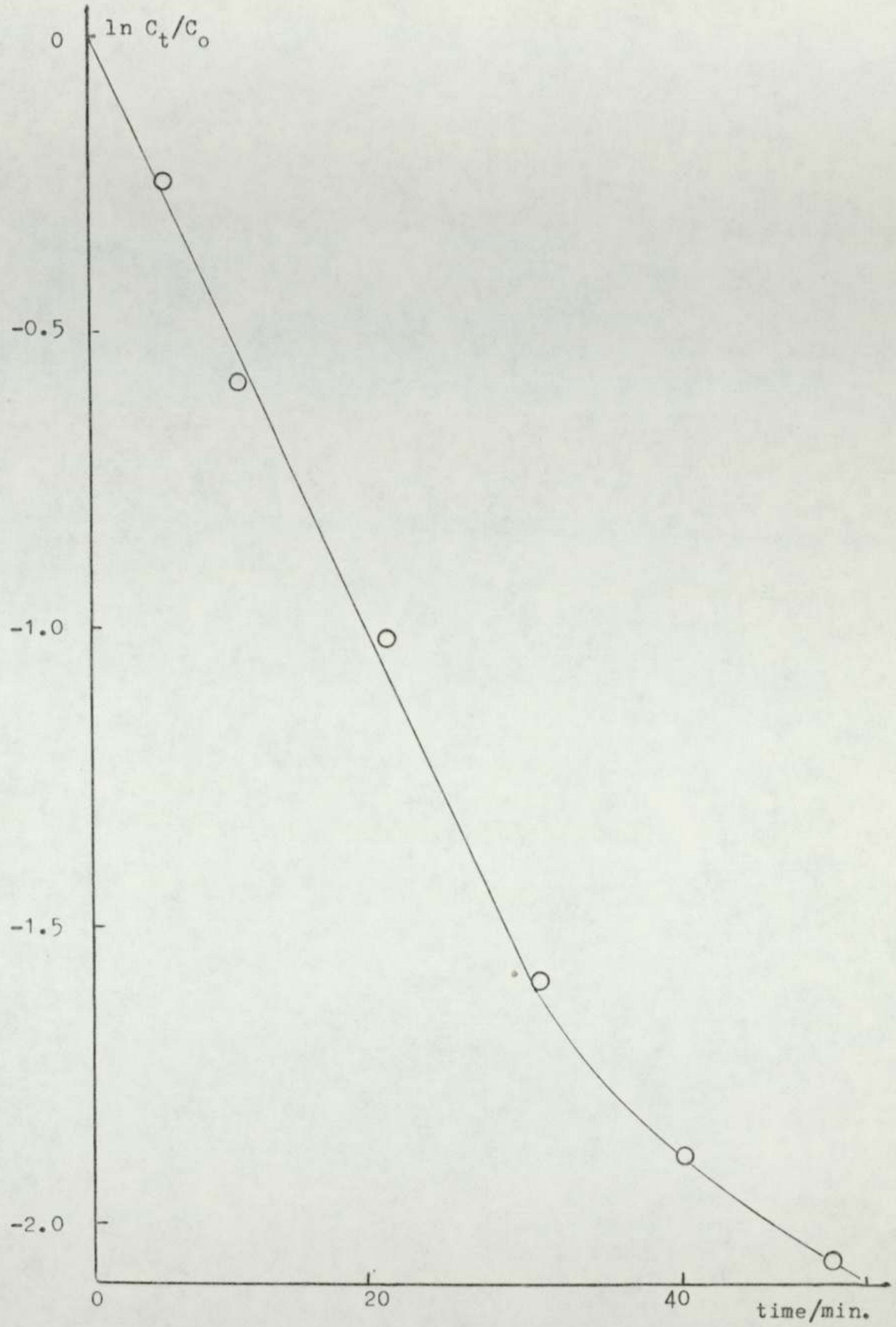


Figure 6.2 Decomposition of t-butyl hydroperoxide by bis-(dietyl-phosphato) cobalt II. First order plot.

products of the reaction are t-butyl alcohol and the corresponding phosphate. The reaction was not affected by the addition of nitroxyl radicals.[23] The chemical polarisation of the ^{31}P nuclei in the molecules of the products observed earlier[23a] in the absence of transition metal ions during this reaction has not been observed in the presence of Mo (VI) and V (IV) ions. On the basis of this evidence they have postulated that the mechanism could be non-radical. Further, they maintain that it is necessary to postulate the formation of ROOH ..... Metal complexes during this reaction.

This situation bears many similarities to the reaction under consideration, since the immediate product of the reaction between triethyl phosphite and a hydroperoxide is triethyl phosphate. However, they have pointed out that ions with a low nuclear charge such as Co(II) were ineffective in this particular reaction.

The most likely reaction centre in bis-(diethylphosphato)cobalt II complex is the metal ion. The electronic absorption spectrum (figure 6.3) of this complex has a maximum at 636 nm and shoulders on the high frequency side at 610 nm, 590 nm and 560 nm. This is identical to the characteristic tetrahedral 'blue' spectrum of Co(II).[83] (figure 6.4) In the presence of added cumene- or t-butyl hydroperoxide the spectrum shifts to the high frequency region (figure 6.3 a) and is then similar to the octahedral (red) cobalt (II) absorption(fig 6.4)

This provides evidence for the hydroperoxide entering into the coordination sphere of cobalt ion. Similar spectral changes have been observed[84,85] for other cobalt complexes. The addition of

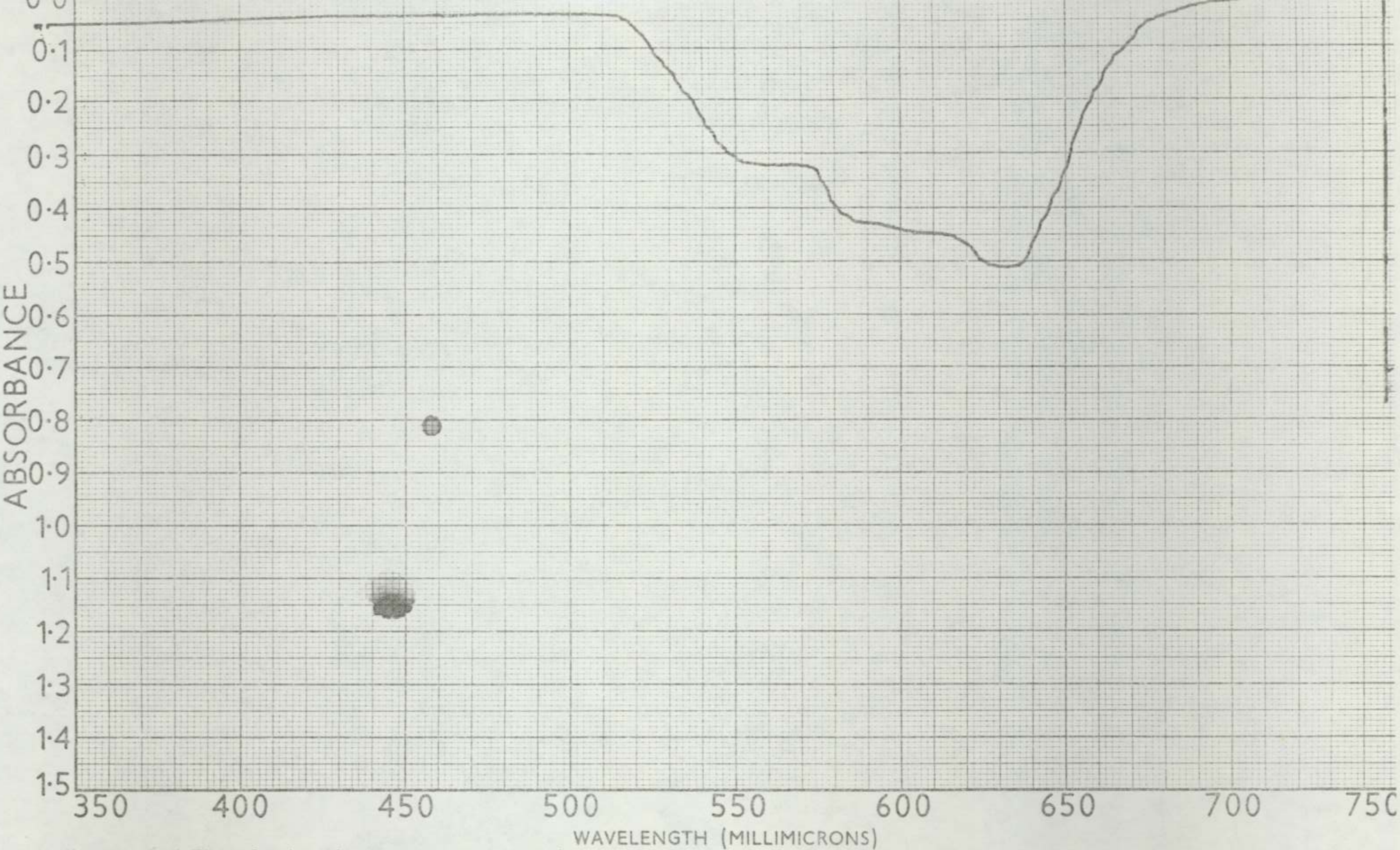


Figure 6.5 The electronic spectrum of bis-(diethylphosphato)cobaltII in chloroform. (2.0g/1).

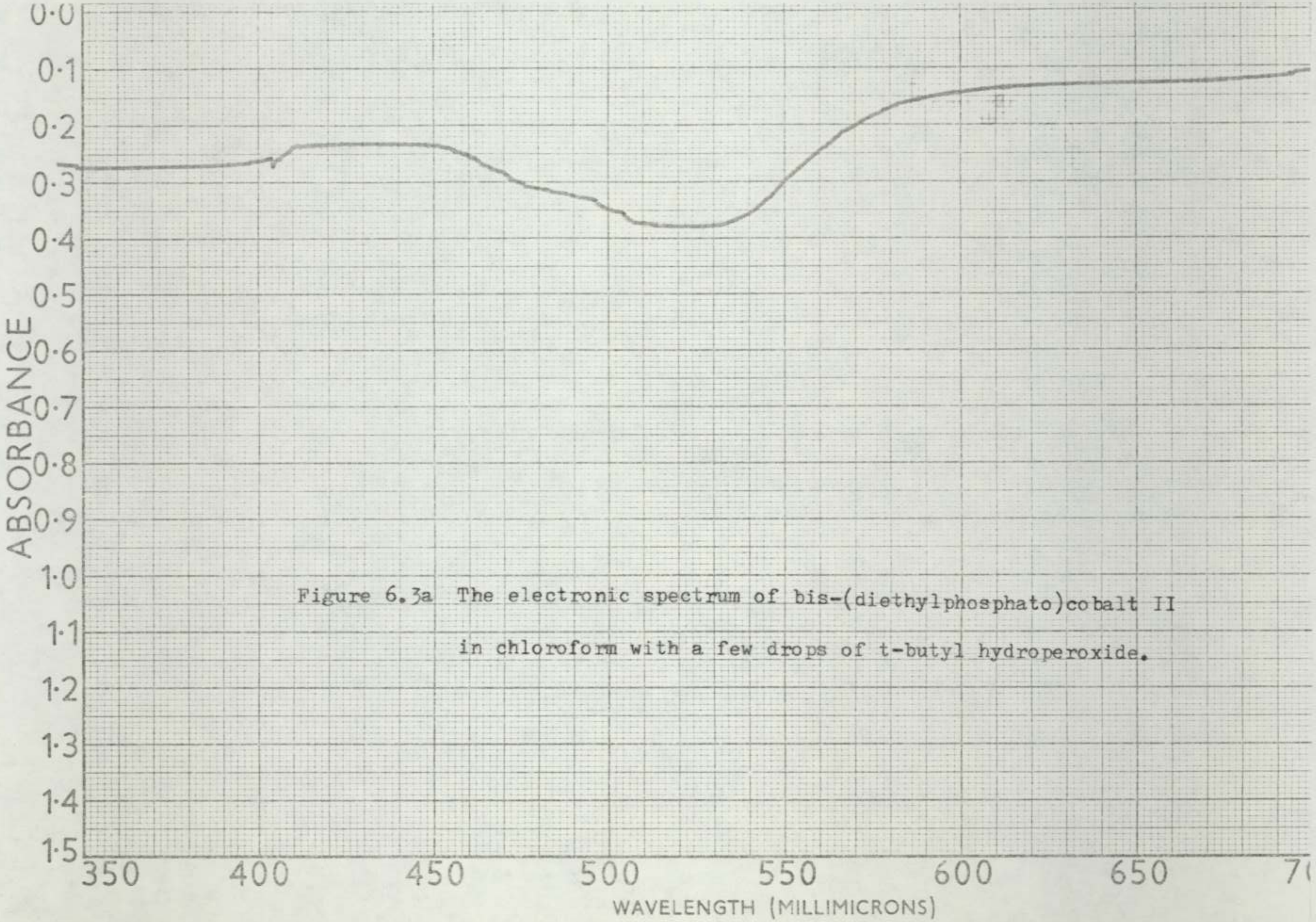


Figure 6.3a The electronic spectrum of bis-(diethylphosphato)cobalt II in chloroform with a few drops of t-butyl hydroperoxide.

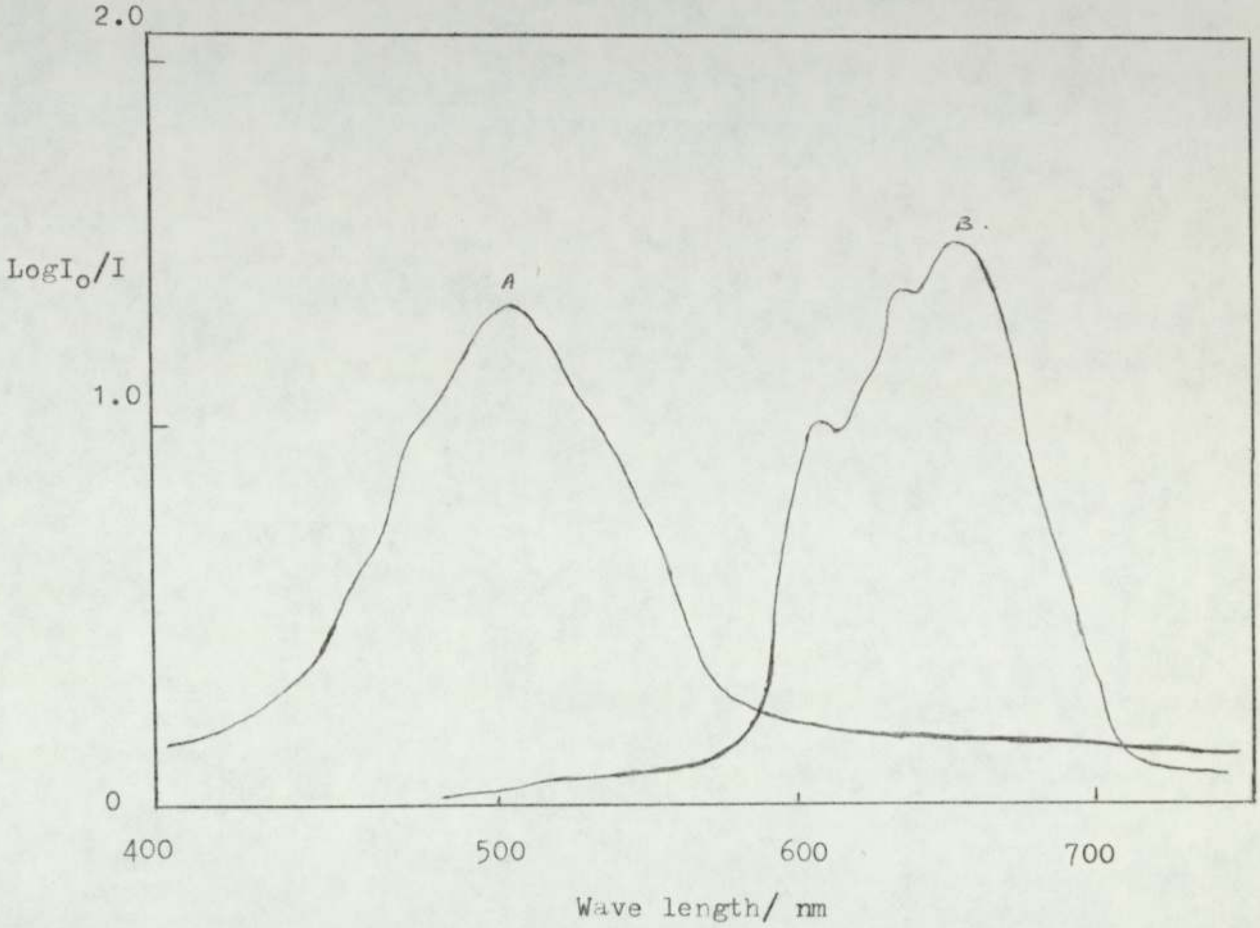


Figure 6.4 Absorption spectra of cobalt solutions.

A. 'Red' cobalt absorption.

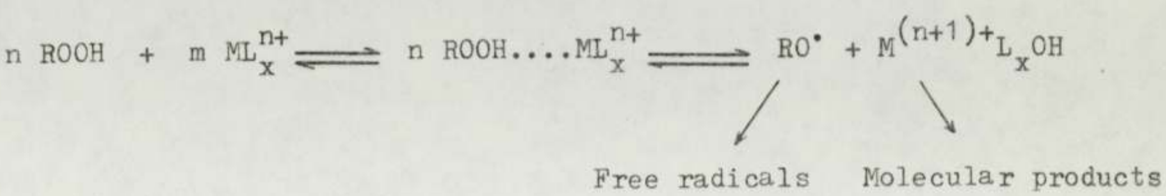
B. 'Blue' (tetrahedral) absorption.(Ref 83) cumene hydroperoxide to a solution of bis-(o-vanillalaniline) Co(II)[84] leads to a decrease in the intensity of the u.v absorption maximum of the catalyst and to shift of the maximum towards high frequency region. Broadening and shifting of n.m.r signals of cumene hydroperoxide have also been observed[85] during complex formation with cobalt II ions.

6.2.2 Cumenehydroperoxide decomposition products.

Analysis of the decomposition products was carried out by g.l.c and t.l.c. A typical g.l.c trace of the products appears in figure 6.5. The major products are cumyl alcohol and acetophenone with a very small amount of α-methylstyrene. These are the typical homolytic decomposition products of cumene hydroperoxide. No acetone and phenol could be detected.

Reversible formation of hydroperoxide-catalyst complexes, as a rule decreases the stability of the hydroperoxide which decomposes readily with the formation of free radicals.[85] It seems likely that such complexes are of universal occurence in the reactions between metal ions and hydroperoxides.[86]

Bulgakova et al[85] have proposed the following mechanism for the reaction between bis-(o-vanillal-o-anisidine)cobalt II and cumene hydroperoxide.



$$n\,ROOH + m\,ML_x^{n+} \rightleftharpoons n\,ROOH....ML_x^{n+} \rightleftharpoons RO^{\bullet} + M^{(n+1)+}L_xOH$$

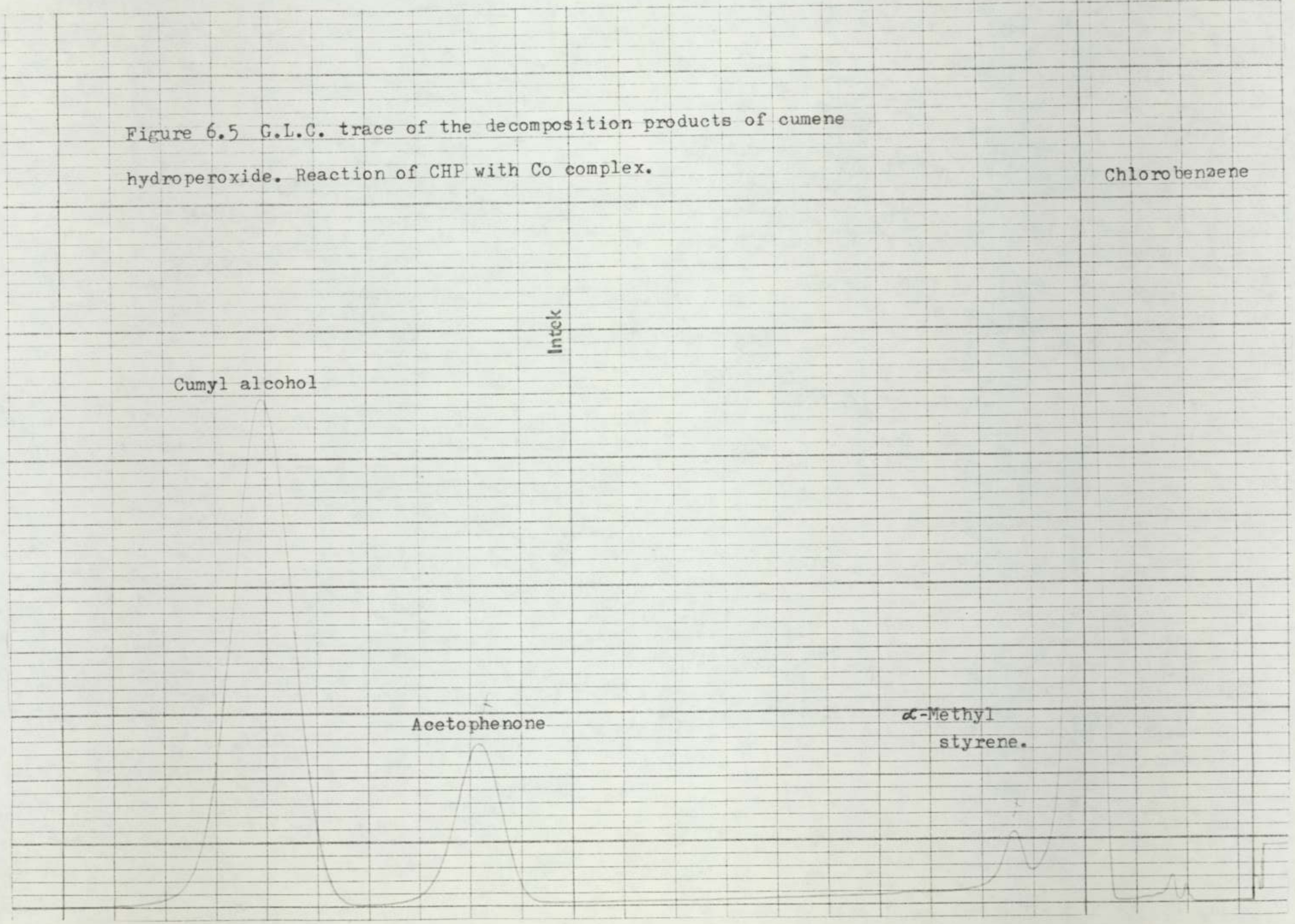


Figure 6.5 G.L.C. trace of the decomposition products of cumene hydroperoxide. Reaction of CHP with Co complex.

It has been further demonstrated[85] that compounds of metal ions of variable valence may not only initiate but also terminate the oxidation chain , reacting with free radicals ROO$^\bullet$. An identical reaction is quite possible with the phosphato complexes of cobalt. Evolution of oxygen was observed to occur and this is probably by the disproportionation of alkyl peroxy radicals.[87]

$$2\ ROO^\bullet \longrightarrow 2\ RO^\bullet + O_2$$

6.2.3 The effect of solvent on the reaction.

The concentration against time curves for the reaction between t-butyl hydroperoxide and the phosphato cobalt complex in benzene, chlorobenzene and chloroform at 50°C are shown in figure 6.6. First order plots for these appear in figure 6.7, and the relevant rate constants are given in table 6.1.

Table 6.1

Rate constants for the reaction of t-butyl hydroperoxide with bis-(diethylphosphato)cobalt II in various solvents at 50°C

(Hydroperoxide)= 7.8×10^{-2} mol l^{-1}; (Complex)= 1.1×10^{-2} mol l^{-1}

Solvent	Rate constant/sec^{-1}
Benzene	1.01×10^{-3}
Chlorobenzene	1.21×10^{-3}
Chloroform	6.41×10^{-4}

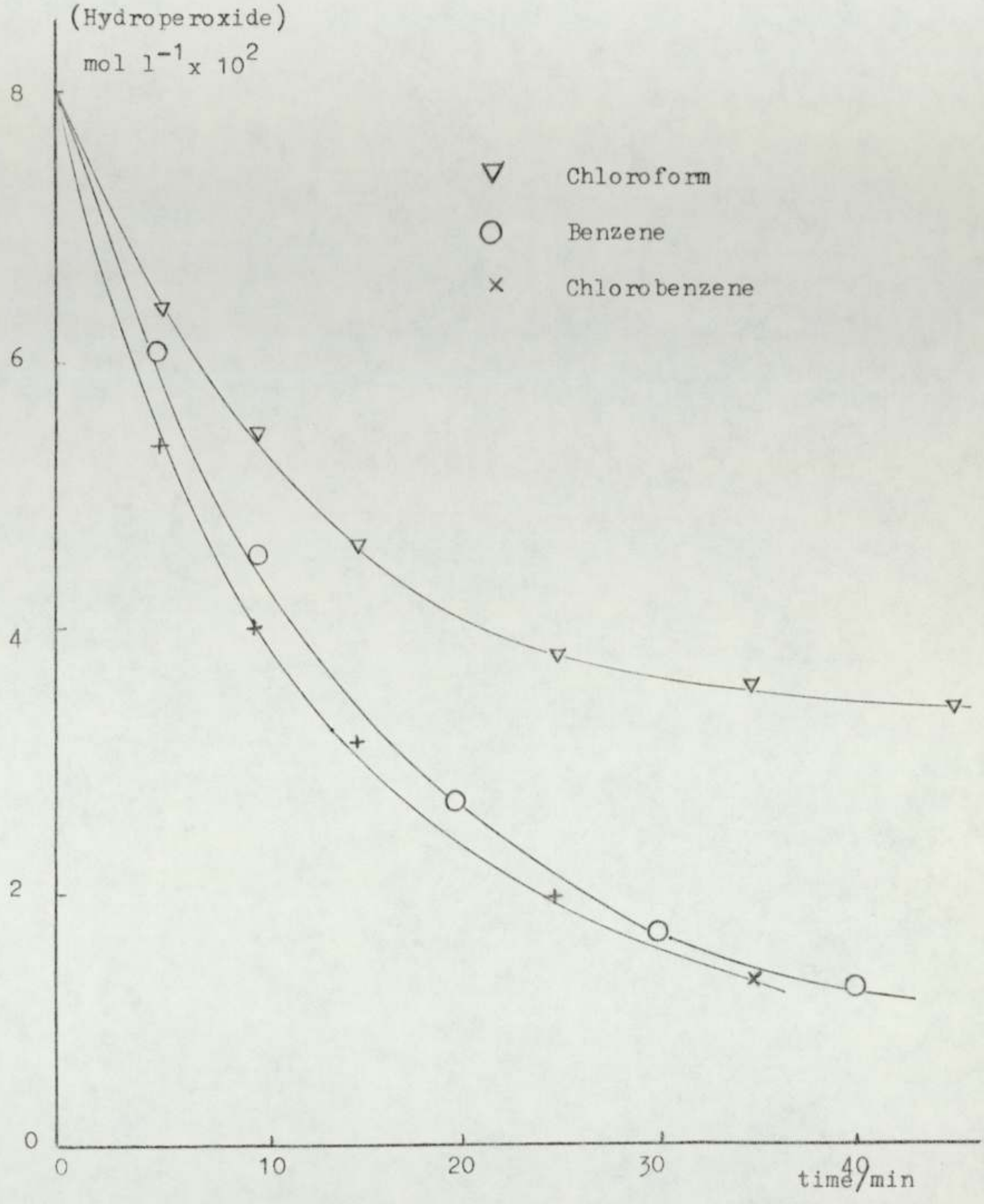


Figure 6.6 Decomposition of t-butyl hydroperoxide by bis-(diethyl-phosphato)cobalt II in various solvents at 50°C

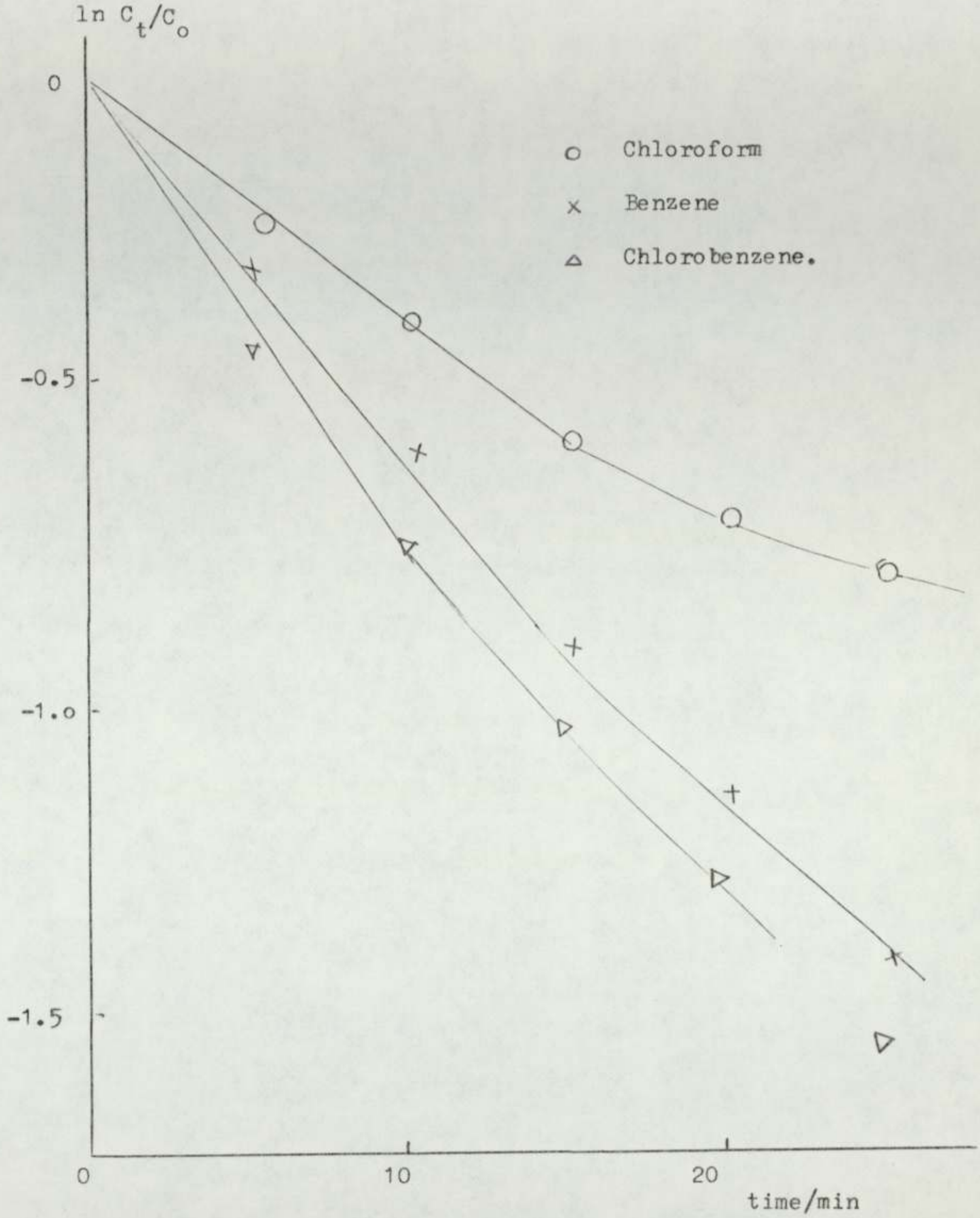


Figure 6.7 First order plots for the decomposition of t-butyl hydroperoxide by the cobalt complex in various solvents.

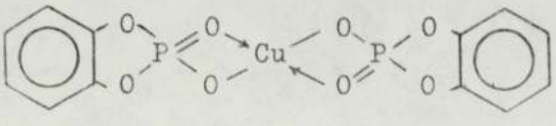
The rate of decomposition of the hydroperoxide is significantly slower in chloroform than that in benzene or chlorobenzene. There is not much difference in rates in benzene and chlorobenzene. This rules out ionic mechanisms for the reaction. The reduced rate and also the lower extent of the reaction in chloroform could be due to the competition between the solvent and the hydroperoxide for coordination with the metal ion, and also due to hydrogen transfer to radicals.

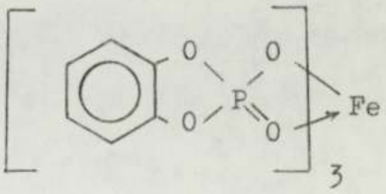
$$\begin{matrix}RO^{\bullet}\\ ROO^{\bullet}\end{matrix} \quad + \quad CHCl_3 \longrightarrow \begin{matrix}ROH\\ ROOH\end{matrix} \quad + \quad {}^{\bullet}CCl_3$$

This suppresses radical induced decomposition of the hydroperoxide. Infra red spectrum of the solution showed the development of a sharp carbonyl peak indicative of the formation of carbonyl chloride by the oxidation of chloroform.

6.3 Reactions of hydroperoxides with catechol phosphate metal complexes.

Preliminary experiments with Cu^{+2} and Fe^{+3} complexes of catechol cyclic phosphate,





showed them to be powerful catalysts for the decomposition of cumene hydroperoxide. Figure 6.8. shows that there is an 'induction period' before the catalytic reaction commences, in the case of the ferric complex. The same was found to be true for the Cu^{+2} complex.

The disappearance of cumene hydroperoxide with time for the reaction of the Fe^{+3} complex and the Cu^{+2} complex with hydroperoxide in chlorobenzene is shown in figure 6.8. After the initial induction period the kinetics appear to follow a first order relation. The rate constants for the two complexes are given in table 6.2. These have been calculated from curves in figure 6.8.

Table 6.2.

Rate constants for the reaction of metal complexes with cumene hydroperoxide in chlorobenzene at 59°C.

[CHP] = 0·038M
[Cpx] = 0·004M·

	Rate constant / sec^{-1}
Ferric complexes	4.1×10^{-4} $(\pm 0.4 \times 10^{-4})$
Copper complexes	5.8×10^{-4} $(\pm 0.3 \times 10^{-4})$

6.3.1. Decomposition products.

G.l.c. analysis of the products after completion of the reactions for a wide range of concentrations indicated the formation of acetone and phenol as the only products in these reactions. Even traces of cumyl alcohol or α-methyl styrene could not be detected. This points to the fact that the ligand, cyclic catechol

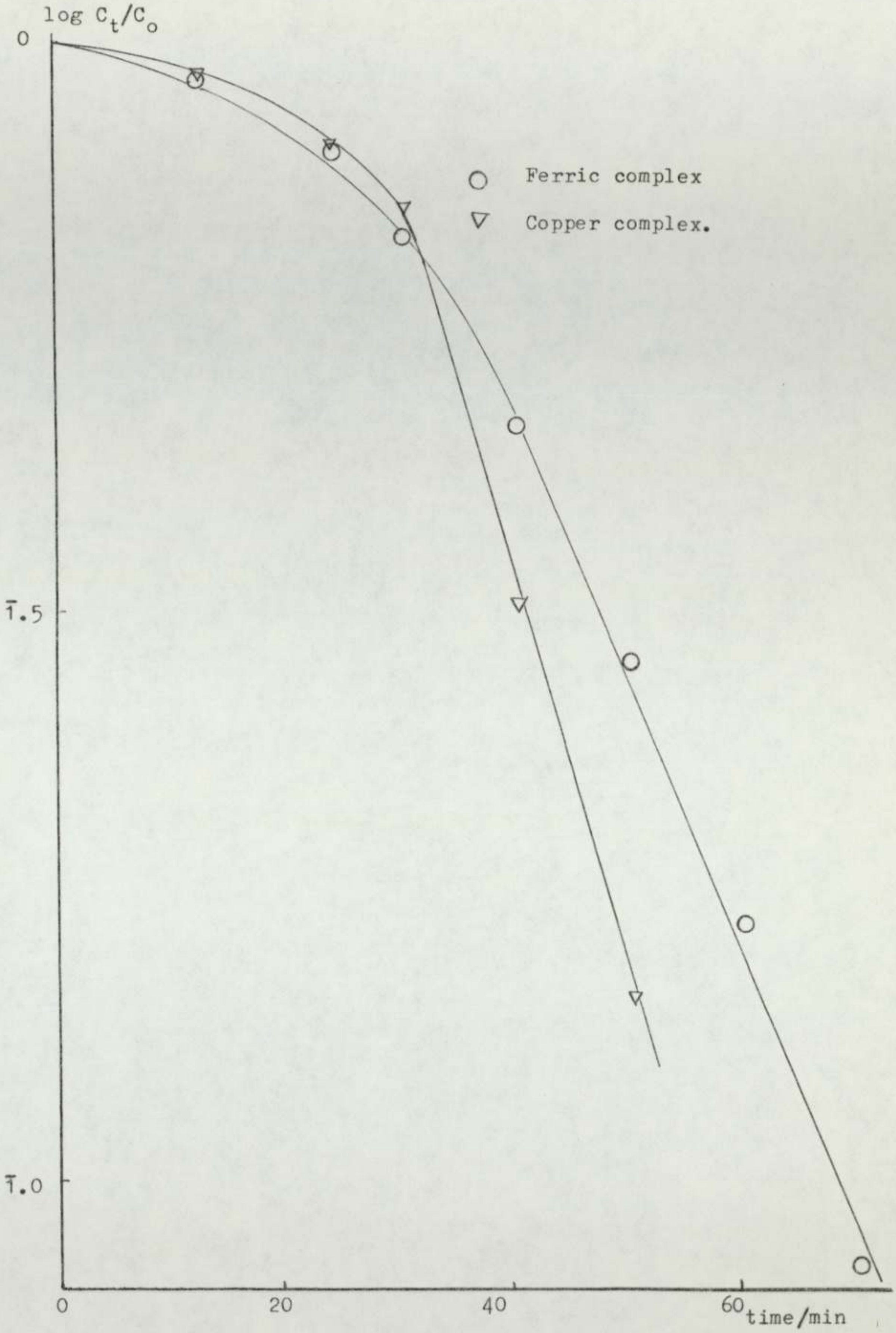


Figure 6.8 First order plots for the decomposition of CHP by metal complexes in chlorobenzene at 59°C.

phosphate is the exclusive reaction site , and that metal catalysed redox reactions are completely supressed most probably due to the formation of phenol and acetone both of which are good co-ordinating solvents for metal ions , and the high reactivity of the cyclic phosphate ligand. On this basis they can be expected to be effective u.v. and thermal stabilisers.

6.3.2. The effect of solvent.

Product analysis proves that the reactions follows an ionic route , the products being acetone and phenol. On this basis rate enhancement is to be expected in polar solvents , and this infact was found to be true when the reaction was conducted in nitrobenzene. (figure 6.9.) The appropriate rate constants appear in table 6.3.

Table 6.3.

Rate constants for the reaction of ferric complex with CHP.

[CHP] = 0.038 M.

[Cpx] = 0.004 M

Solvent	Rate constant /sec^{-1}
Chlorobenzene	4.1×10^{-4}
Nitrobenzene	7.5×10^{-4}

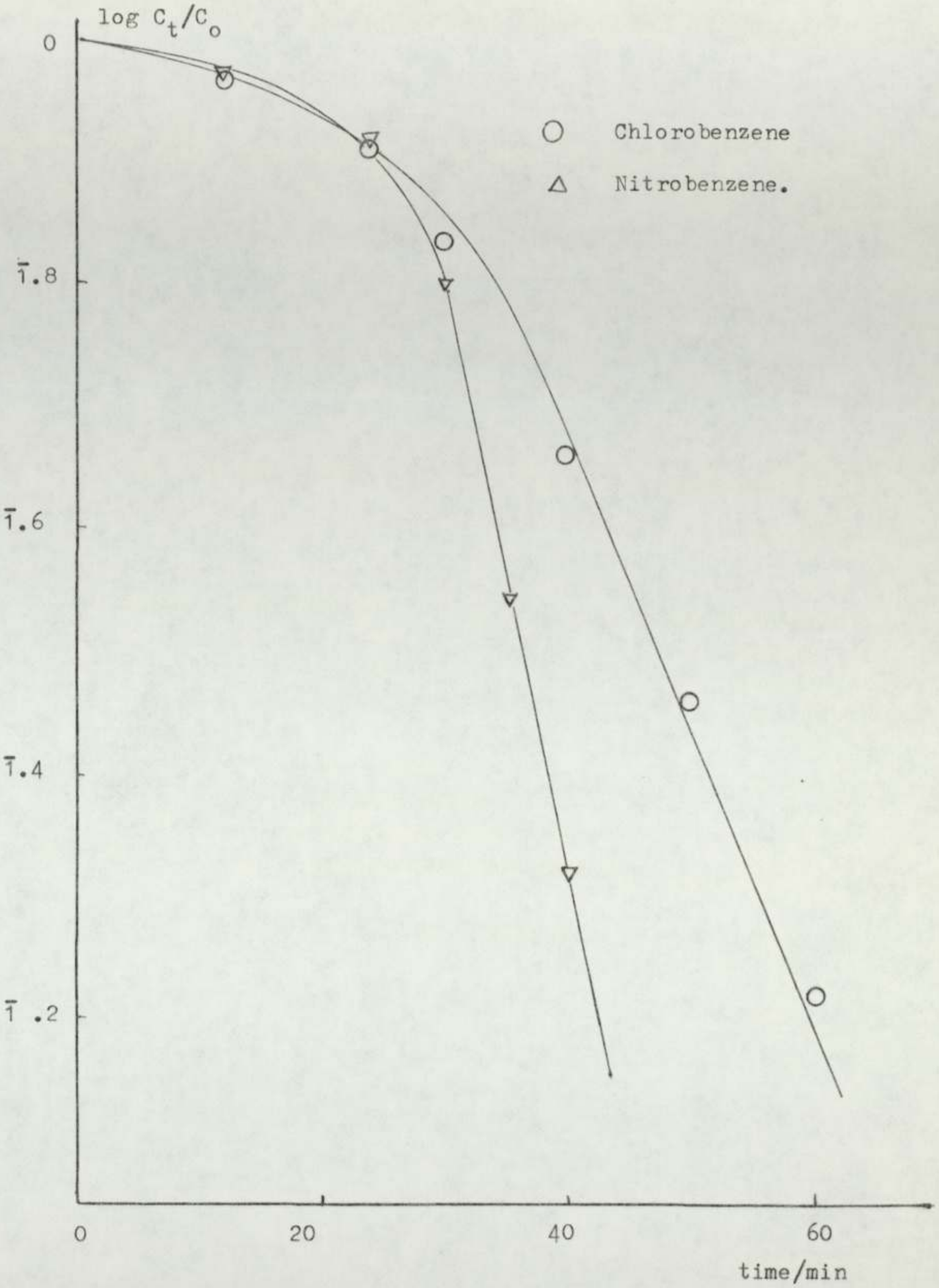


Figure 6.9 The effect of the solvent on the rate of decomposition of CHP by the ferric complex at 59°C

6.3.3. The mechanism.

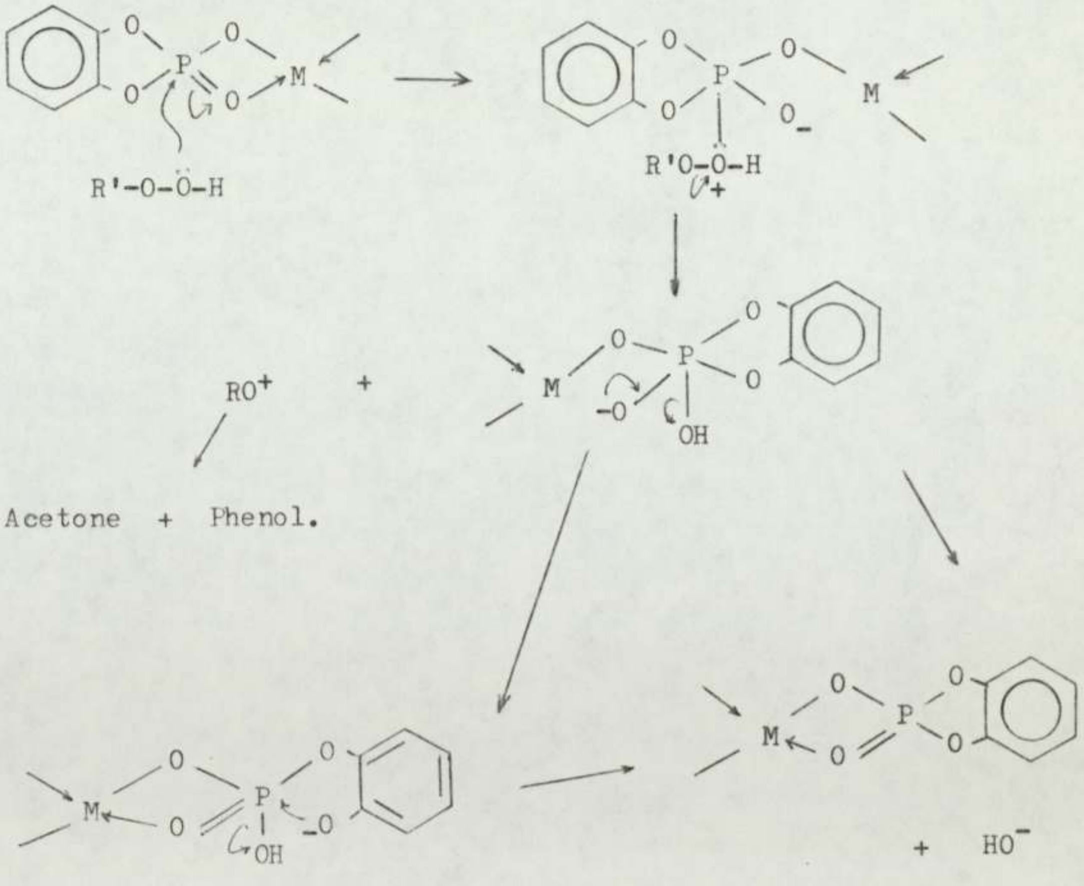
The above evidence show that the reaction between the phosphato complexes and cumene hydroperoxide

(a) is catalytic

(b) follows an ionic or heterolytic path

and (c) that the reaction takes place with the cyclic phosphate ligand.

The mechanism is therefore essentially similar to that postulated and substantiated for the reaction between simple cyclic catechol phosphate esters and hydroperoxides (chapter 5)



CHAPTER 7

PHOSPHATE ESTERS AND DERIVED METAL COMPLEXES AS STABILISERS IN SATURATED POLYOLEFINS.

7.1. INTRODUCTION.

The effectiveness of the phosphate esters and the metal complexes was assessed by studying their effect on the oxidation of decalin and polypropylene. Oxidation of decalin was followed by oxygen absorption as described in the experimental section , whereas oxidation of polypropylene during u.v. irradiation was followed by carbonyl index measurements. These accelerated ageing tests however , cannot be considered as ideal but rather a compromise between time and the amount of information they provide , regarding the long term effects of an antioxidant on a polymer.

7.2. HYDROCARBON OXIDATION STUDIES.

7.2.1. Decalin oxidation: Oxygen absorption studies.

Liquid hydrocarbons (tetralin , decalin , squalene , cumene etc) have been used by earlier workers[88,90,91,92] for determining the effectiveness of antioxidants at elevated temperatures. Under such conditions the rate of oxidation is fast and there is strong possibility that the oxidation might become diffusion controlled , if the solution is not adequately stirred. There seem to be no reports in the literature where dependance of the rate of oxidation

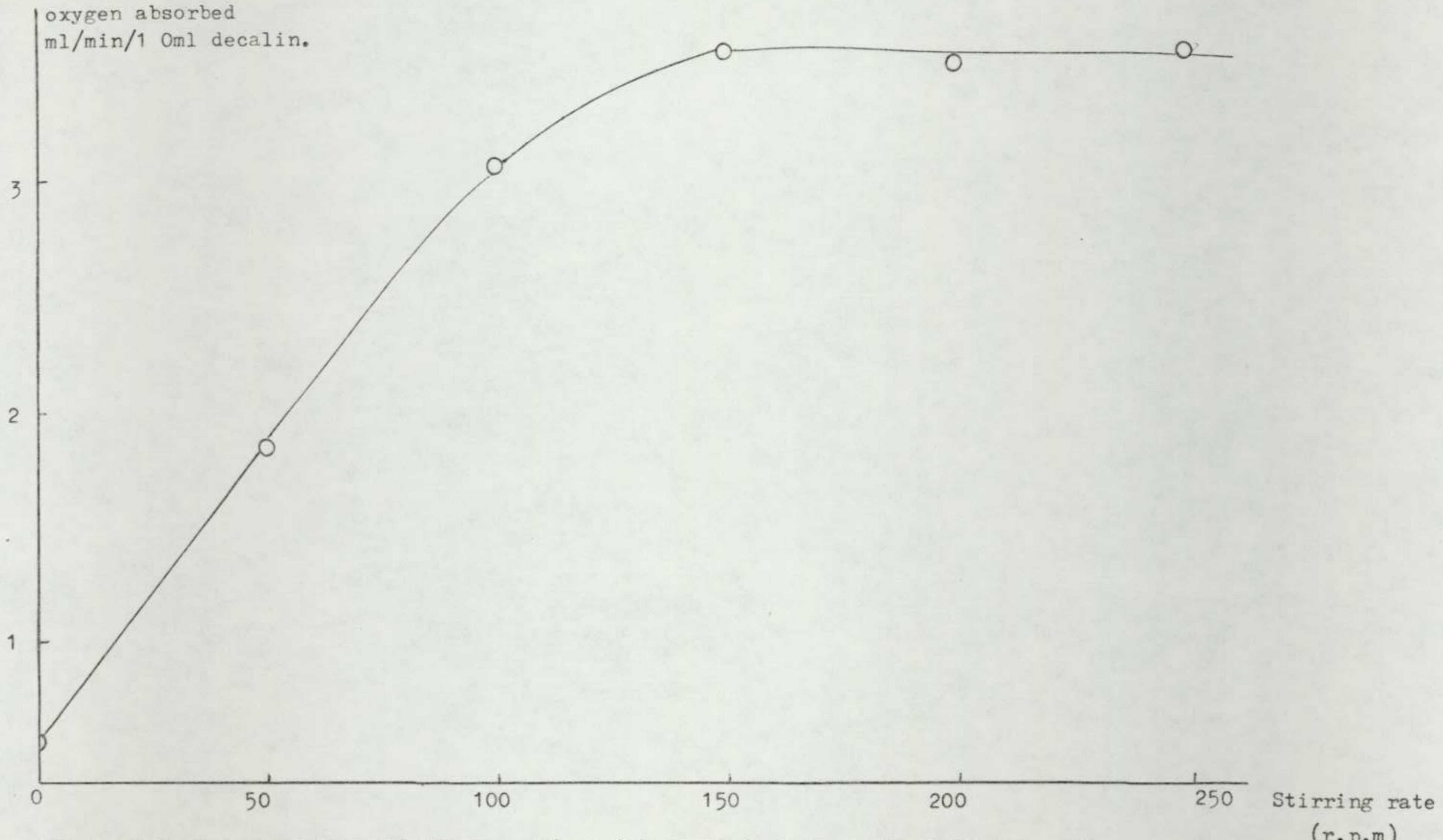


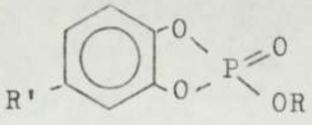
Figure 7.1 The dependence of the rate of oxidation of decalin on the stirring rate

on the stirring rate has been investigated. It was therefore thought pertinent to study the effect of stirring rate on the oxidation of decalin at 140°C. The rate of oxidation was followed by oxygen absorption. In figure 7.1. is given the relation between the linear rate of oxidation of decalin (at 140°C) and the stirring rate in r.p.m. It is evident that up to about 150 r.p.m. the solution is not saturated with oxygen and the rate is diffusion controlled.

The oxidation studies described herein were therefore carried out at a stirring rate well above the limiting value stated above. At 140°C , decalin oxidises without exhibiting any induction period , the rate of consumption of oxygen being about 0.1 ml / min / ml decalin. (figure 7.2.)

All the phosphate esters based on catechol have induction periods (measured as the time required to attain linear rate of oxidation) of several hours as seen by table 7.1. and figures 7.3. and 7.4.

The trend observed in the rates of decomposition of hydroperoxides is again reflected in these figures. Electron releasing substituents on the benzene ring considerably reduce the induction period while the same is true for the phosphoroyl substituents.



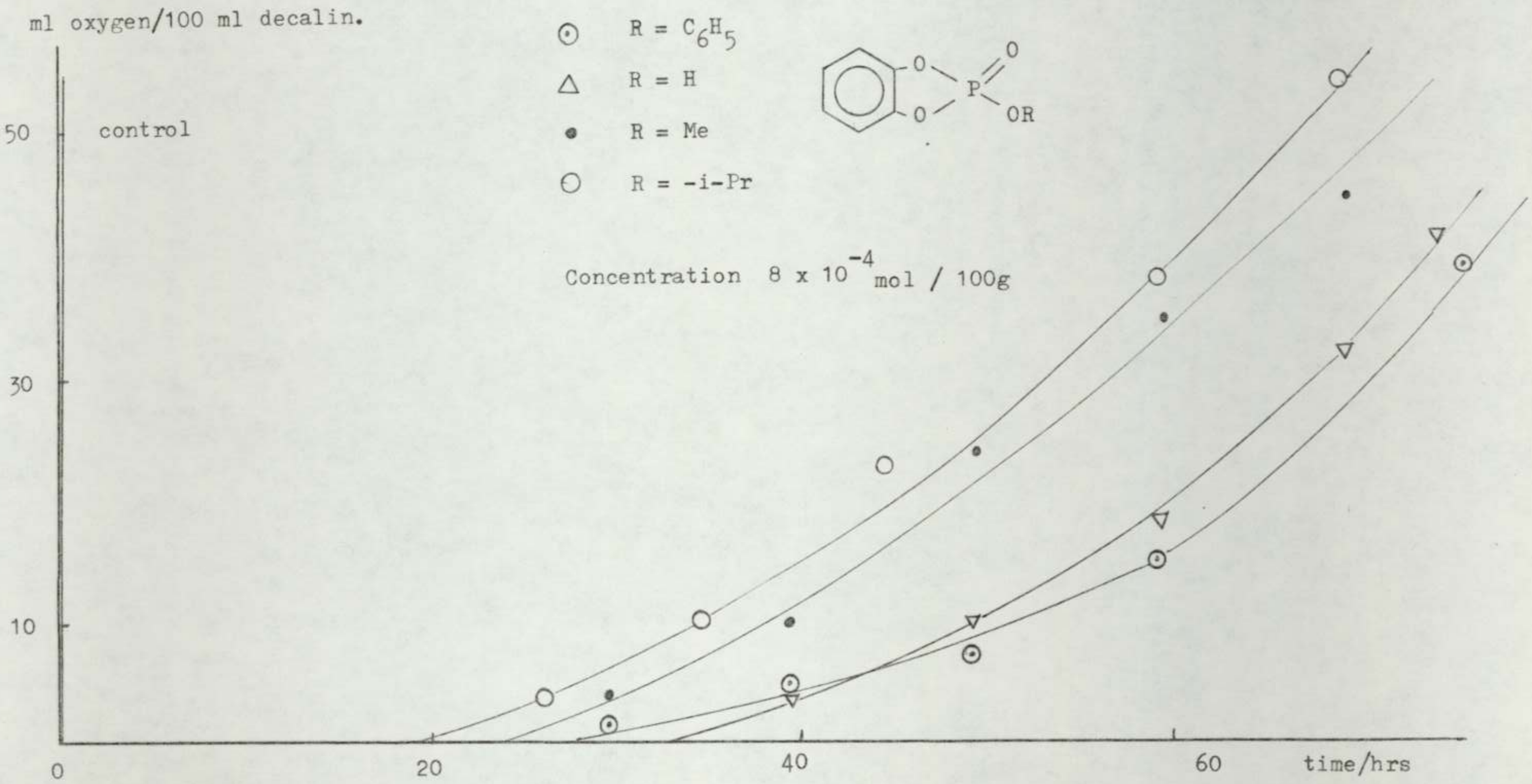


Figure 7.2 Effect of phosphate esters on the thermal oxidation of decalin.

140°C

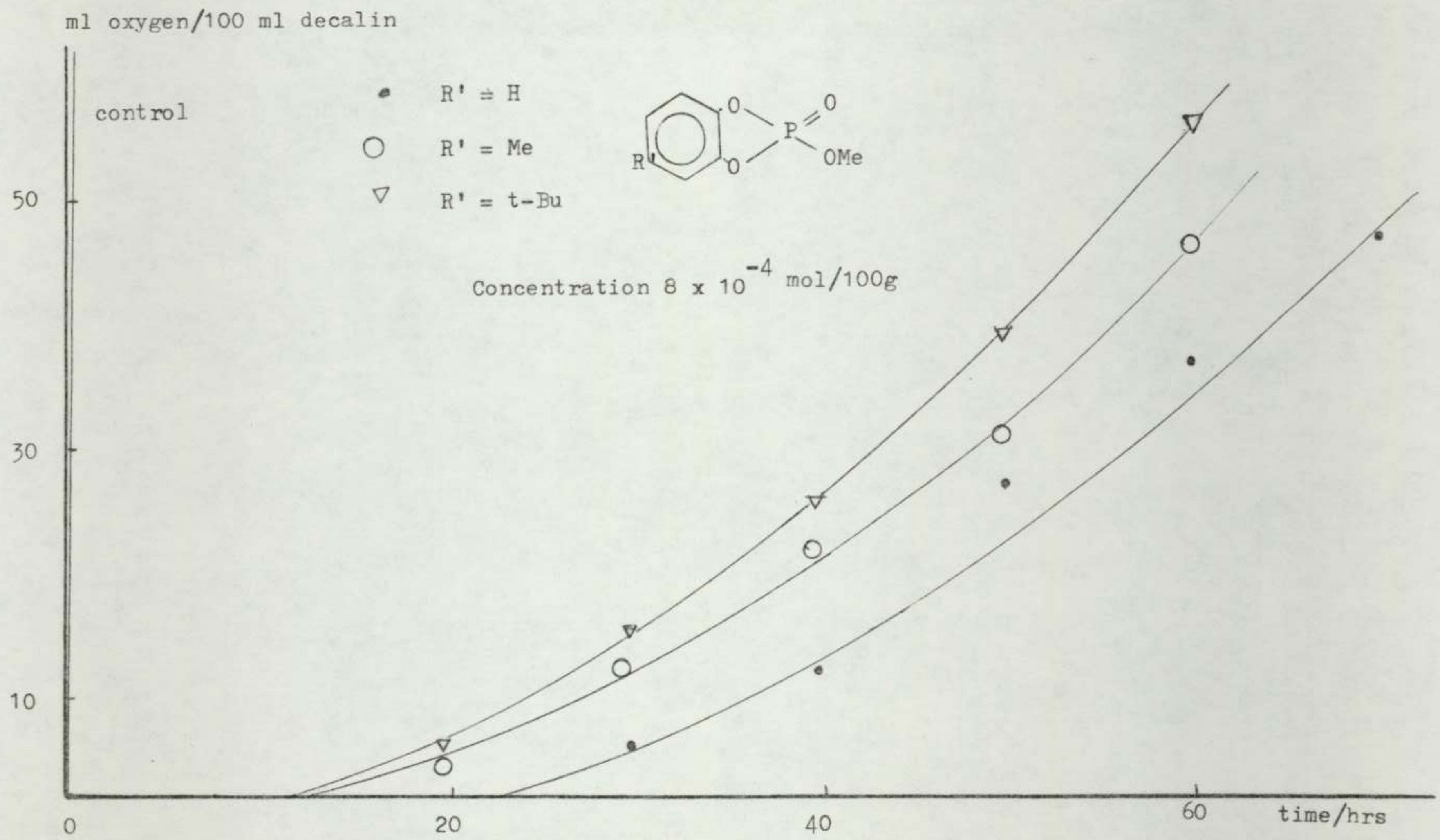


Figure 7.3 The effect of catechol phosphate esters on the thermal oxidation of decalin at 140°C

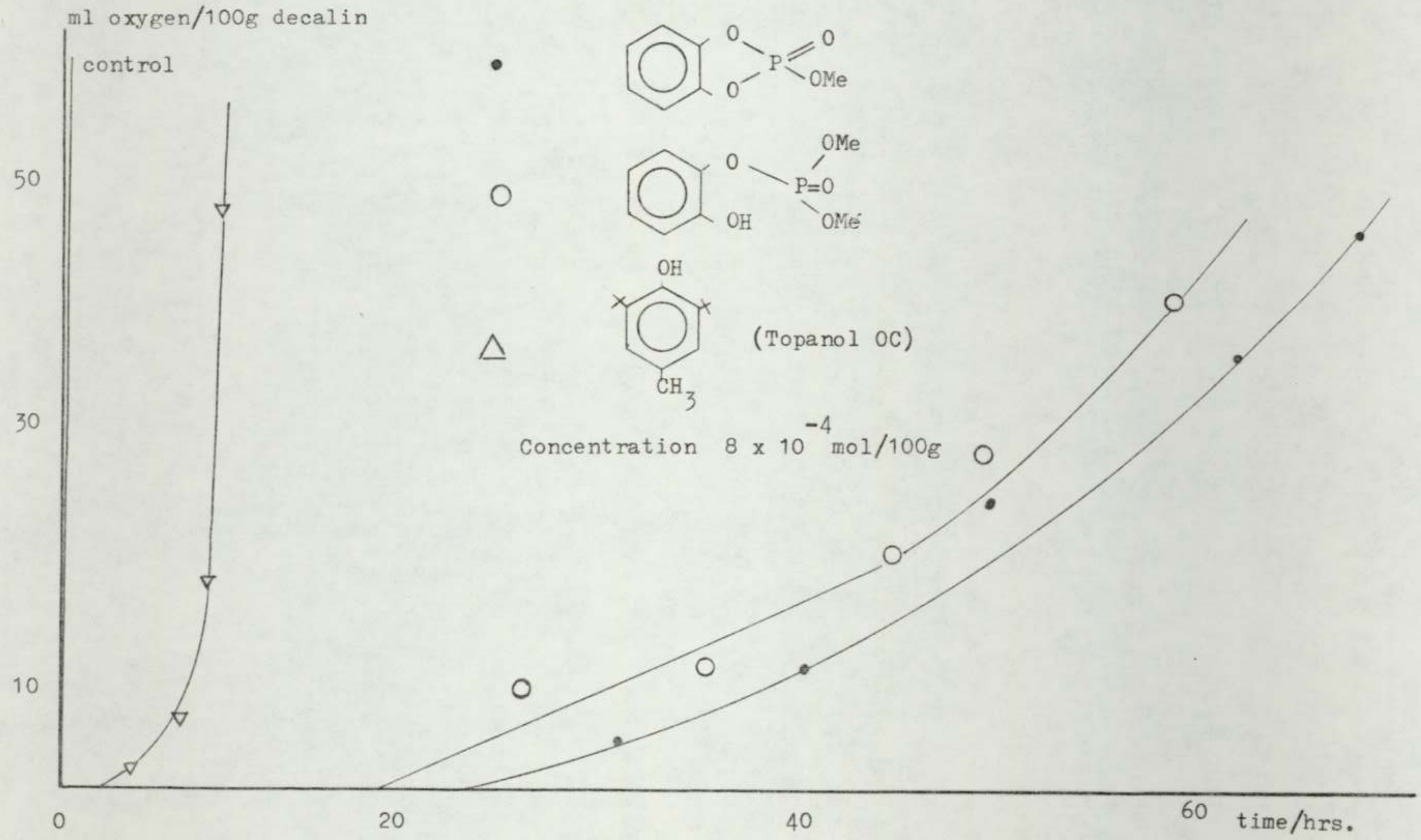


Figure 7.4 Effect of phosphate esters and topanol OC on the thermal oxidation of decalin at 140°C

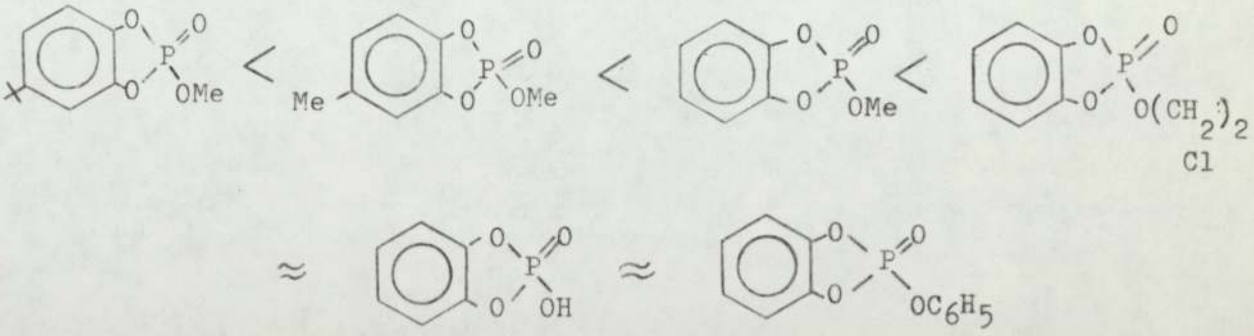
Table 7.1.

The induction period for oxidation of decalin at 140°C in the presence of phosphate esters.

(phosphate) = 4×10^{-4} mol / 100 ml decalin

Ester	Induction period / hrs.
None	0
$R' = H$; $R = H$	52
$R' = H$; $R = CH_3$	35
$R' = H$; $R = i\text{-}Pr$	30
$R' = H$; $R = C_6H_5$	53
$R' = H$; $R = CH_2CH_2Cl$	50
$R' = Me$: $R = Me$	30
$R' = t\text{-}Bu$; $R = Me$	24

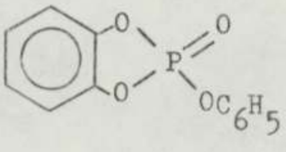
The variation of the induction period, is in the following order:



All these esters are very effective hydroperoxide decomposers and the oxidation of decalin is suppressed by virtue of their ability to decompose hydroperoxides by an ionic mechanism. It is interesting to note that o-hydroxyphenyl dimethyl phosphate, which was shown earlier to be almost as effective as the correponding cyclic phosphate in decomposing hydroperoxides is also a good thermal stabiliser of similar standing.(figure 7.4)

After the induction period the rate of oxygen absorption increases gradually in all cases, but this is quite small compared to that of pure decalin. It was observed in chapters 4 and 5, that one mole of catechol phosphate ester can decompose several hundred moles of hydroperoxide and for a given concentration of the ester, the rate of decomposition increases with the hydroperoxide concentration until a limiting value beyond which the concentration of phosphate becomes rate determining. This is quite consistent with the curves in figures 7.3-7.5. As the oxidation sets in the small amount of hydroperoxide formed is decomposed and the oxidation is supressed but gradually as the hydroperoxide concentration increases above the limiting value, the oxidation becomes autocatalytic but still at a reduced rate.

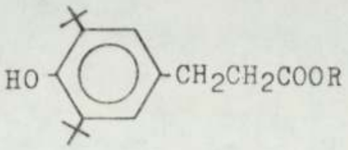
Comparison of these results with those obtained by Scott[93] are very encouraging . The induction periods for the oxidation of decalin at 140°C in the presence of a variety of hindered phenols are given in table 7.2. The data presented in tables 7.1 and 7.2 show that for catechol esters like,



the induction period is nearly twice that for the hindered phenols, even though the catechol phosphates have been used at a concentration five times lower than that of the hindered phenols.

Table 7.2

The induction periods for the oxidation of decalin at 140°C containing hindered phenols. Concentration: 2×10^{-3} mol / 100ml decalin.



R	Induction period/hrs
Methyl	27
Hexyl	24
Lauryl	22
Stearyl	18

However, these hindered phenols give considerably long induction periods in the oxidation of decalin at the lower temperature of 120°C. This is evident from the data in table 7.3.

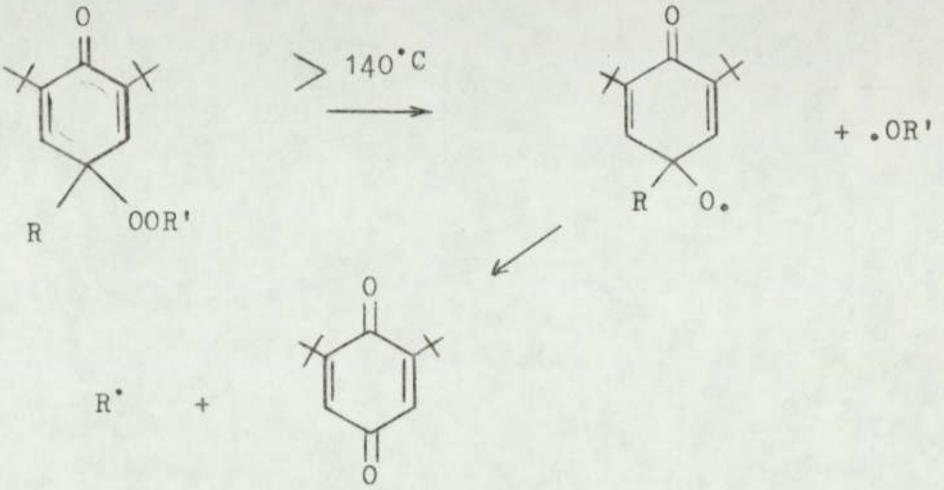
Table 7.3

Induction periods for the oxidation of decalin at 120°C, containing hindered phenols.

Compound	Conc. mol/100ml decalin	Temperature/°C	Ind.period/hrs
Topanol OC	2×10^{-4}	120	345[a]
	4×10^{-4}	140	8
Irganox 1076	2×10^{-4}	120	133[a]
	2×10^{-3}	140	18[b]

(a : ref 94 ; b : ref 93)

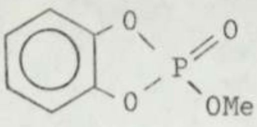
Although the relevent induction periods at 120°C for decalin containing catechol phosphate esters are not available, these can be expected to compare favourably with those for hindered phenols. An essential feature of the mechanism of chain breaking by radical trapping in the case of hindered phenols lies in the stability of the peroxydienone formed at the end of the reaction. 140°C is just about the temperature at which these peroxydienones are thermally decomposed forming radicals. This makes the hindered phenols less effective at high temperatures.



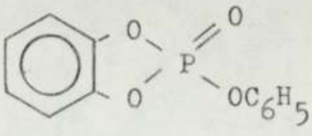
7.3 Thermal stability of polypropylene containing cyclic catechol phosphate antioxidants.

Since it was found that the cyclic phosphate esters act as thermal stabilisers in decalin, it was desired to study these esters as thermal stabilisers in polypropylene films. The oxidation was followed through oxygen absorption at 140°C. The amount of oxygen absorbed with time by the two esters,

(IVa).



(VIb).



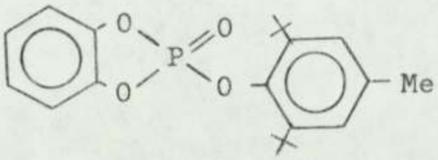
at a concentration of 8×10^{-4} mol / 100 g of polypropylene (0.2 %) is shown in figure 7.5. The induction periods to oxidation are given in table 7.4.

Table 7.4

Induction periods to oxidation of polypropylene films containing catechol phosphate esters at 140°C. Concentration: 8×10^{-4} mol/100g

Antioxidant	Induction period/hrs
IV a	180
IV b	188
None	0

Humpris[62] has reported an induction period of 381 hours for the oxidation of polypropylene films (at 150°C) containing the ester,



at a concentration of 8.7×10^{-4} mol/100g. This considerably higher value for the induction period could be due to the contribution from the hindered phenol moiety which could act as a chain breaking antioxidant on its own.

7.4 U.V LIGHT STABILITY OF POLYPROPYLENE CONTAINING PHOSPHATE ESTERS AS ANTIOXIDANTS

Aliphatic cyclic phosphate esters have been found to act as

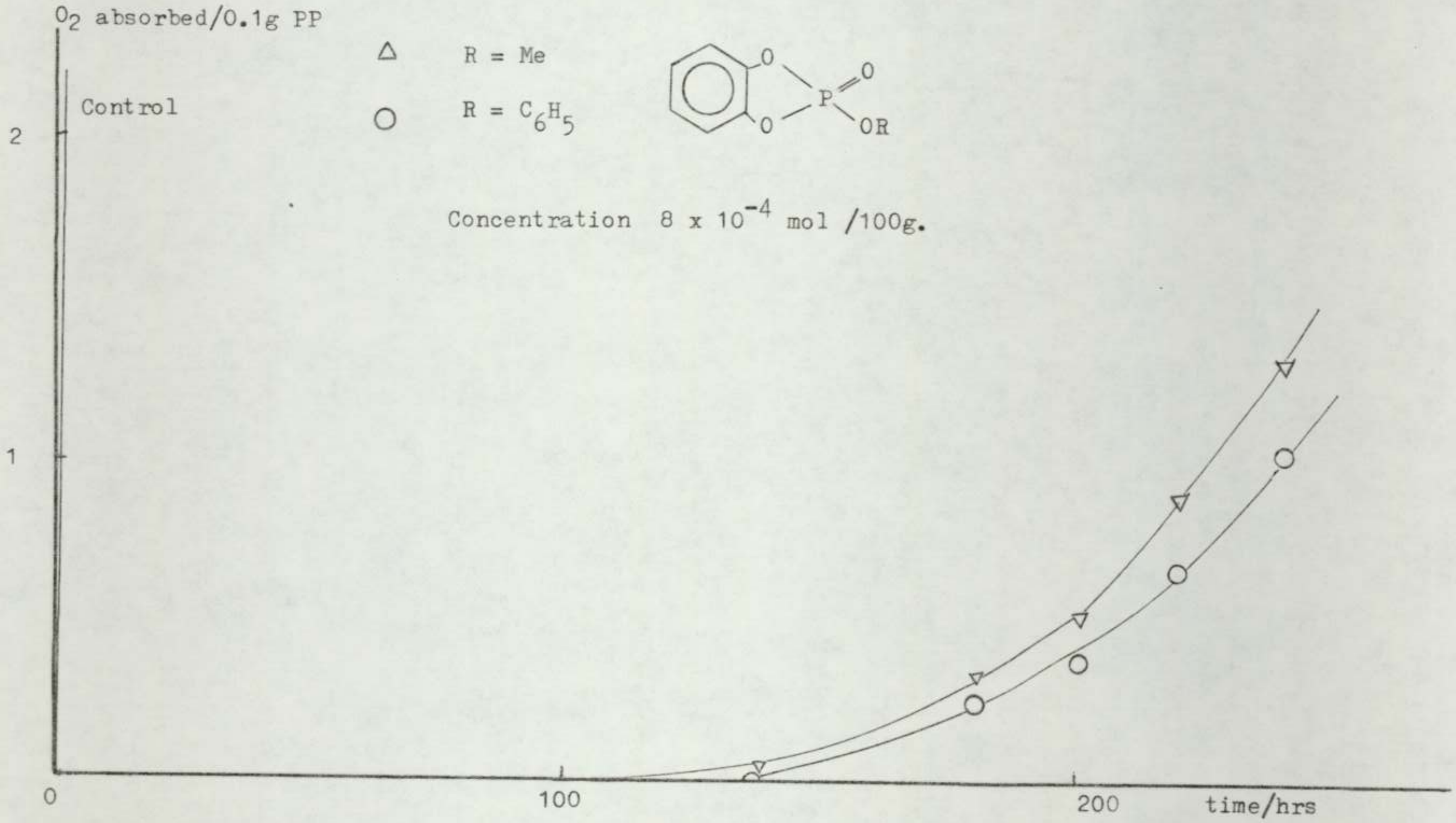
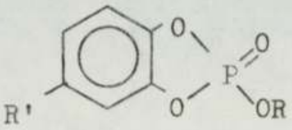


Figure 7.5 The effect of catechol phosphate esters on the thermal stability of PP at 140°C

pro-oxidants in polypropylene during u.v irradiation. This is consistent with the formation of a large proportion of radical-derived products in their reactions with hydroperoxides (chapter 4).

In contrast to this, catechol cyclic phosphates shown below,

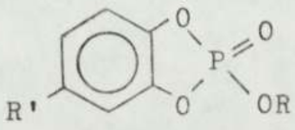


$R' = H$, $R = CH_3$
$R' = H$, $R = C_6H_5$
$R' = CH_3$, $R = CH_3$

were found to impart a considerable amount of u.v stability on polypropylene. This is evident from the curves for the development of the carbonyl peak at 1710 cm^{-1} shown in figure 7.6, and the embrittlement times given in table 7.5.

Table 7.5

Embrittlement times of polypropylene films containing cyclic phosphate esters during u.v. irradiation. Concentration: 8 x 10^{-4} mol/100g. T=29°C



Substituents	Embrittlement time/hrs
$R'=H$, $R=CH_3$	120
$R'=H$, $R=C_6H_5$	135
$R'=CH_3$, $R=CH_3$	80
Control	70

There is a considerable reduction in the embrittlement time for the ester in which the benzene ring is substituted with a methyl group. This is in keeping with the observation that esters with electron

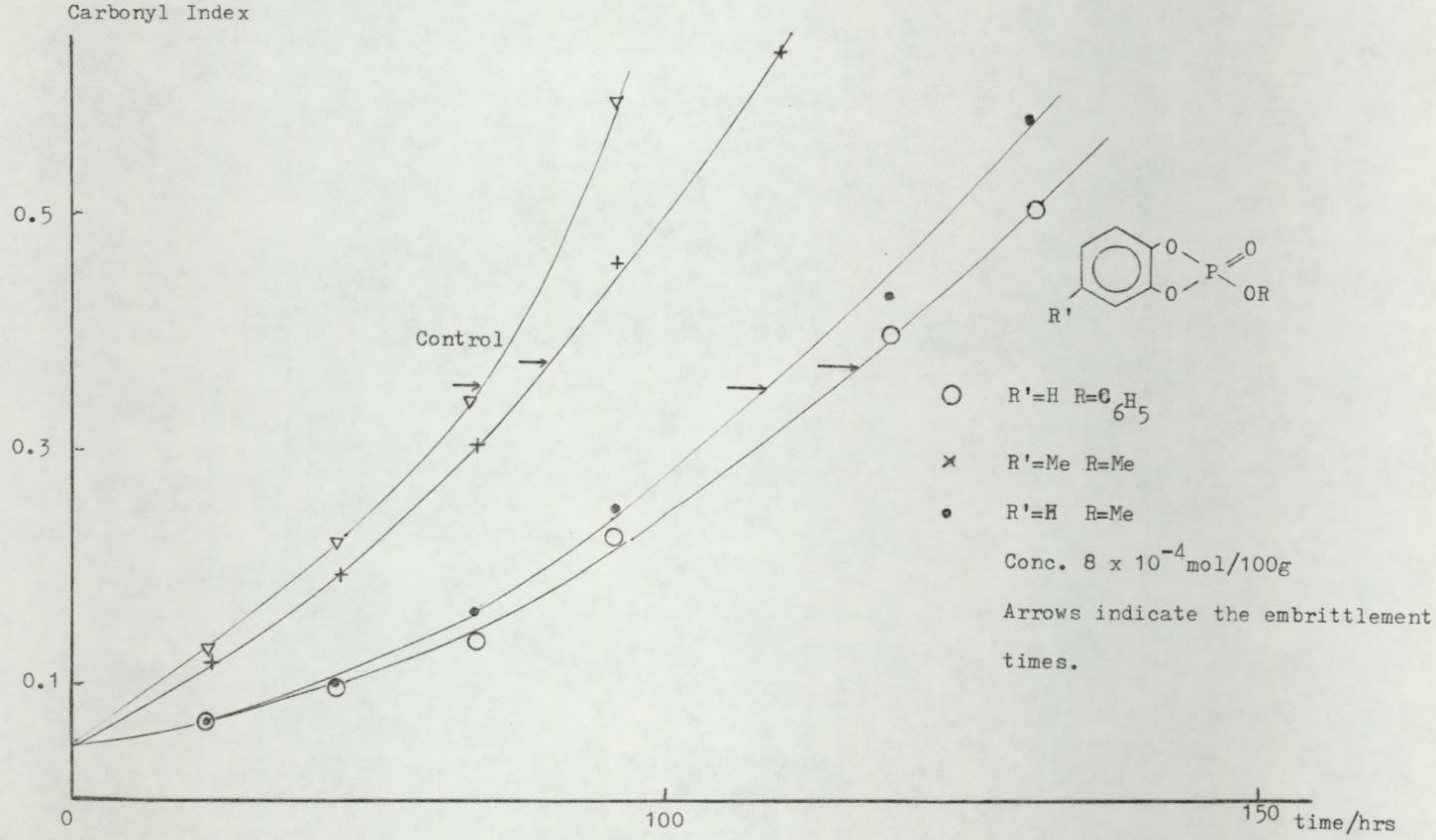
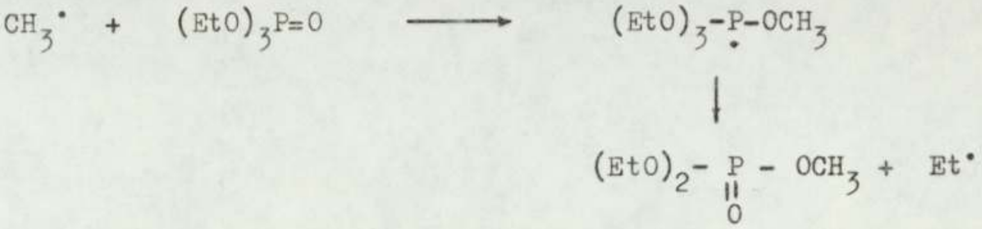


Figure 7.6 Effect of catechol phosphate esters on the photostability of polypropylene(PP)

releasing substituents on the benzene ring give a larger proportion of radical-derived products in reaction with hydroperoxides.

7.5 Radical trapping by phosphates.

Preliminary studies have indicated that phosphate esters based on catechol cannot trap alkyl radicals as evident from their inability to suppress AZBN (azo-bis-isobutyronitryle) induced polymerisation of styrene.[95] It has been shown by Levin[96] et al that triethyl phosphate reacts with methyl radicals forming phosphoranyl radicals.



$$CH_3^{\bullet} + (EtO)_3P{=}O \longrightarrow (EtO)_3\text{-}\underset{\bullet}{P}\text{-}OCH_3$$

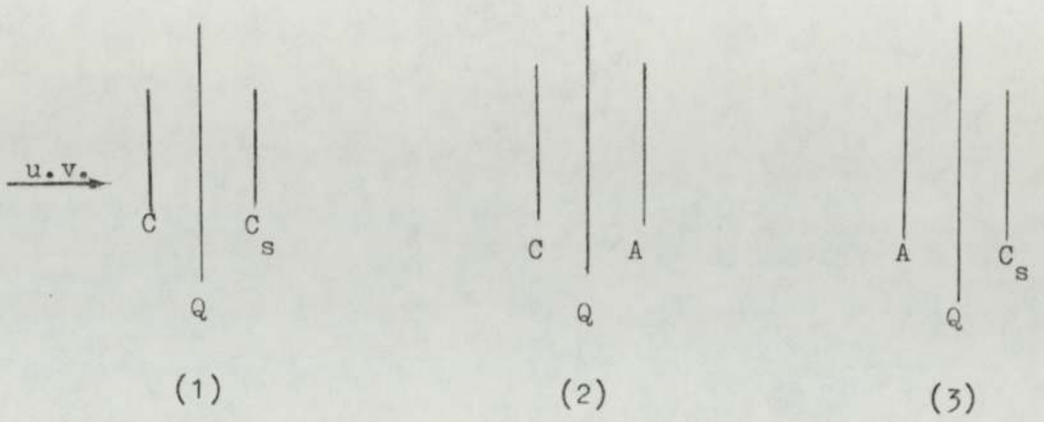
$$\downarrow$$

$$(EtO)_2\text{-}\underset{\underset{O}{\|}}{P}\text{-}OCH_3 + Et^{\bullet}$$

A reaction of this type may or may not occur with cyclic phosphates derived from catechol, but if it does occur, it might not lead to chain termination due to the resultant radicals being too reactive.

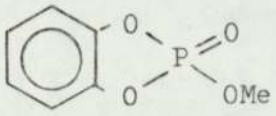
7.6 Screening experiments.

As was mentioned previously, these esters do not absorb above 280 nm and therefore cannot act as u.v screens. This was further demonstrated by following the changes in carbonyl index during u.v. irradiation of films screened by films containing the additive, as shown in the diagram.



Q= Quartz plates; C = Films with no additive; A = Films with additive

Difference between 1C_s and 2A indicates the effectiveness of the compound as an additive and the difference between 1C_s and 3C_s will indicate the screening ability of the compound. The results are shown graphically in figure 7.7 for the ester,



The ineffectiveness of these as u.v. screens is clearly reflected by these curves. It is effective only when it is present as an additive in the film.

The above observations suggest that hydroperoxide decomposition is the most important and most probably the sole mechanism of antioxidant action of catechol based phosphate esters.

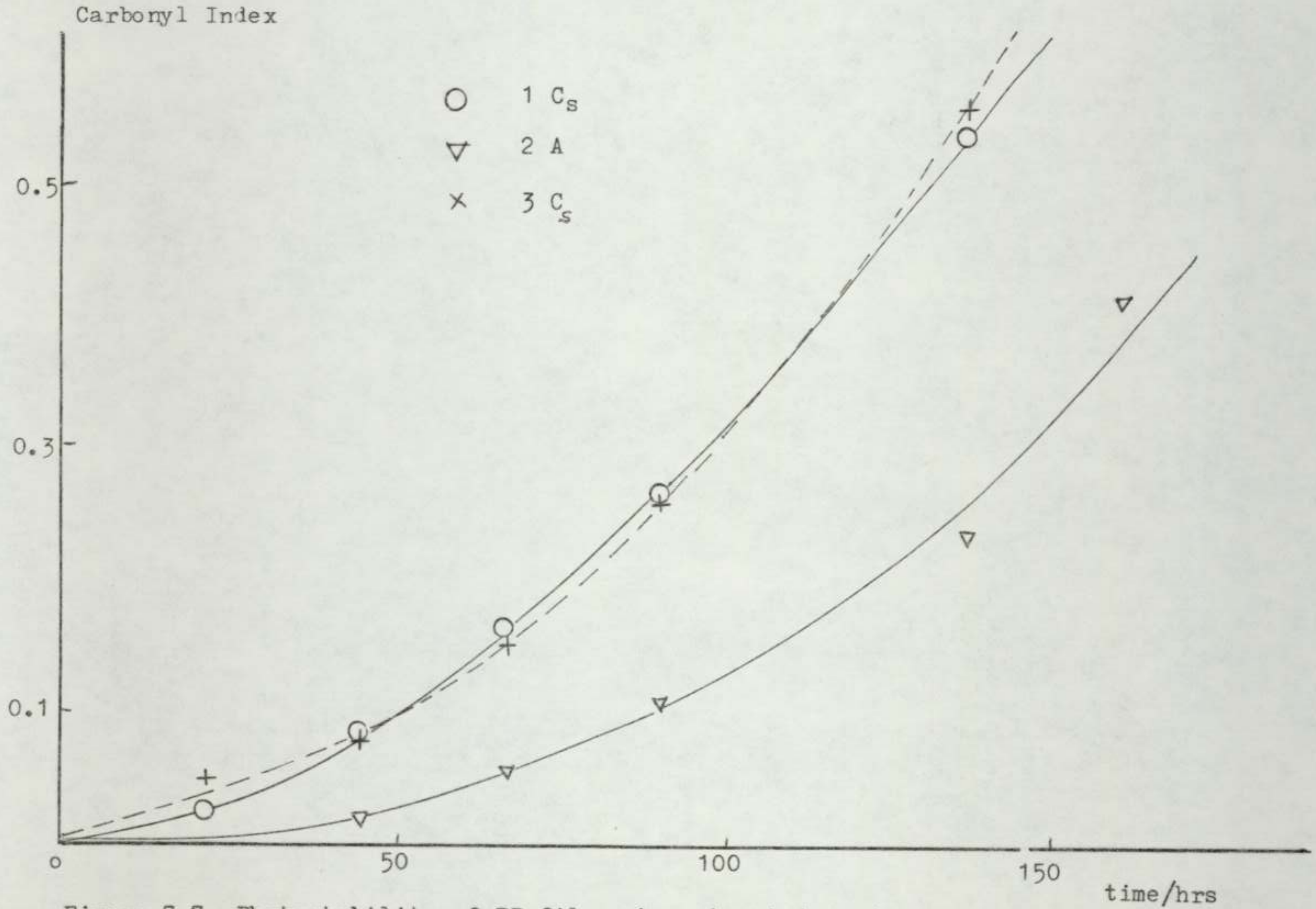
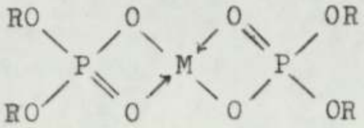


Figure 7.7 Photostability of PP films when phosphate esters are present as an additive and as a screen.

7.7 U.V. STABILITY OF POLYPROPYLENE CONTAINING PHOSPHATO METAL COMPLEXES

7.7.1 Complexes derived from aliphatic phosphates

The effect of the following alkyl phosphato metal complexes on the u.v. stability of polypropylene was studied.



1). $R = CH_3$ $M = Co^{2+}$
2) $R = C_2H_5$ $M = Co^{2+}$
3) $R = C_2H_5$ $M = Ni^{2+}$
4) $R = C_2H_5$ $M = Cu^{2+}$

The Co^{2+} and Cu^{2+} complexes do not impart any improvement of polypropylene stability compared to the control. This is consistent with their inability to decompose hydroperoxides by a non-radical mechanism. Due to the fact that the metal ions are co-ordinatively bonded to the metal ion, redox reactions are however suppressed and hence do not show any enhanced pro-oxidant activity either. These inferences are drawn from the curves in figures 7.8 and 7.9.

The behaviour of the Ni^{2+} complex was however different. As seen in figure 7.10, there is a small reduction in the growth of carbonyl and an improvement in the embrittlement time. Unlike the cobalt and the copper complex, the nickel complex was inert towards hydroperoxide and this may at least be partly responsible for the difference.

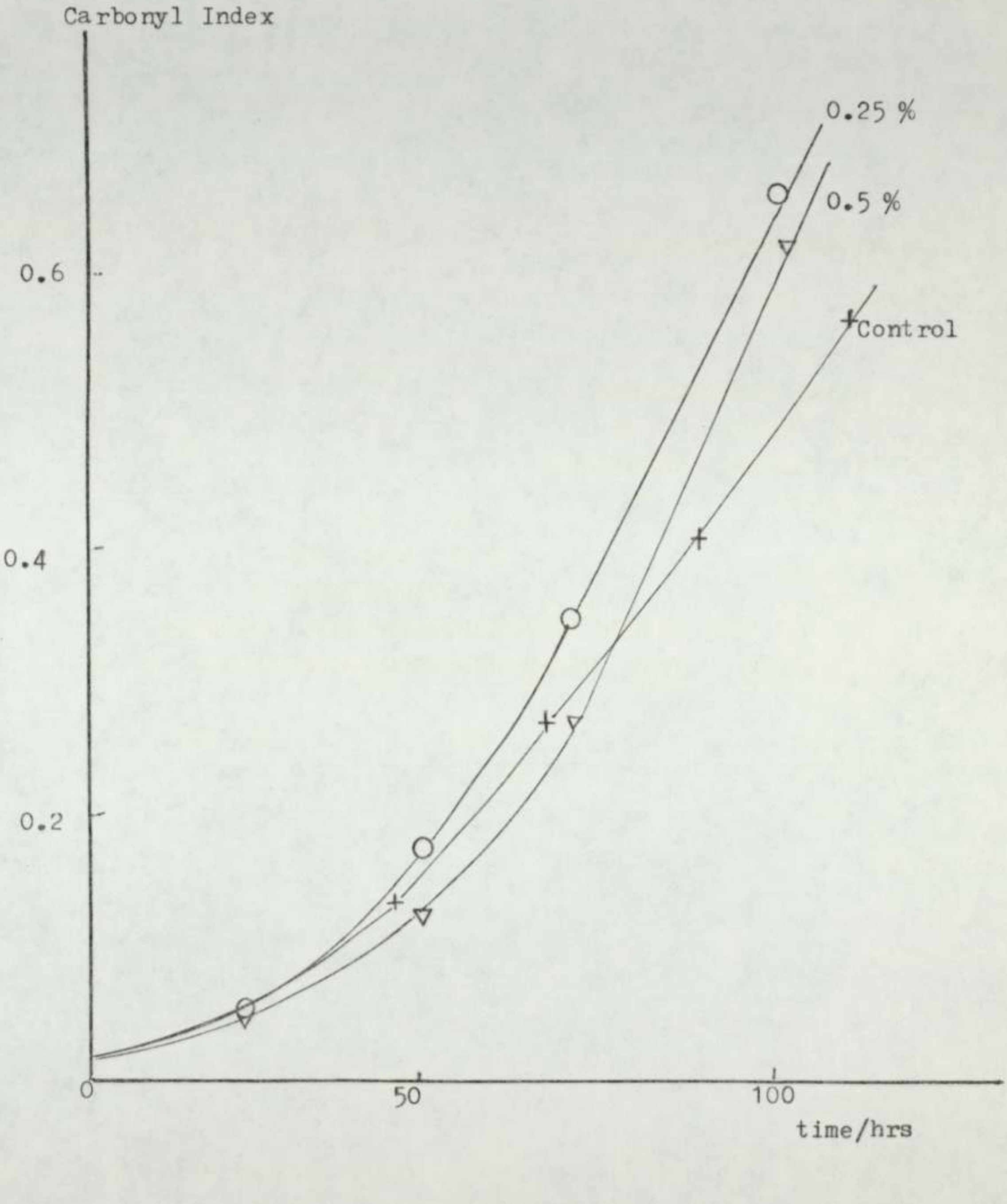


Figure 7.8 The photostability of PP films containing the copper complex 4.

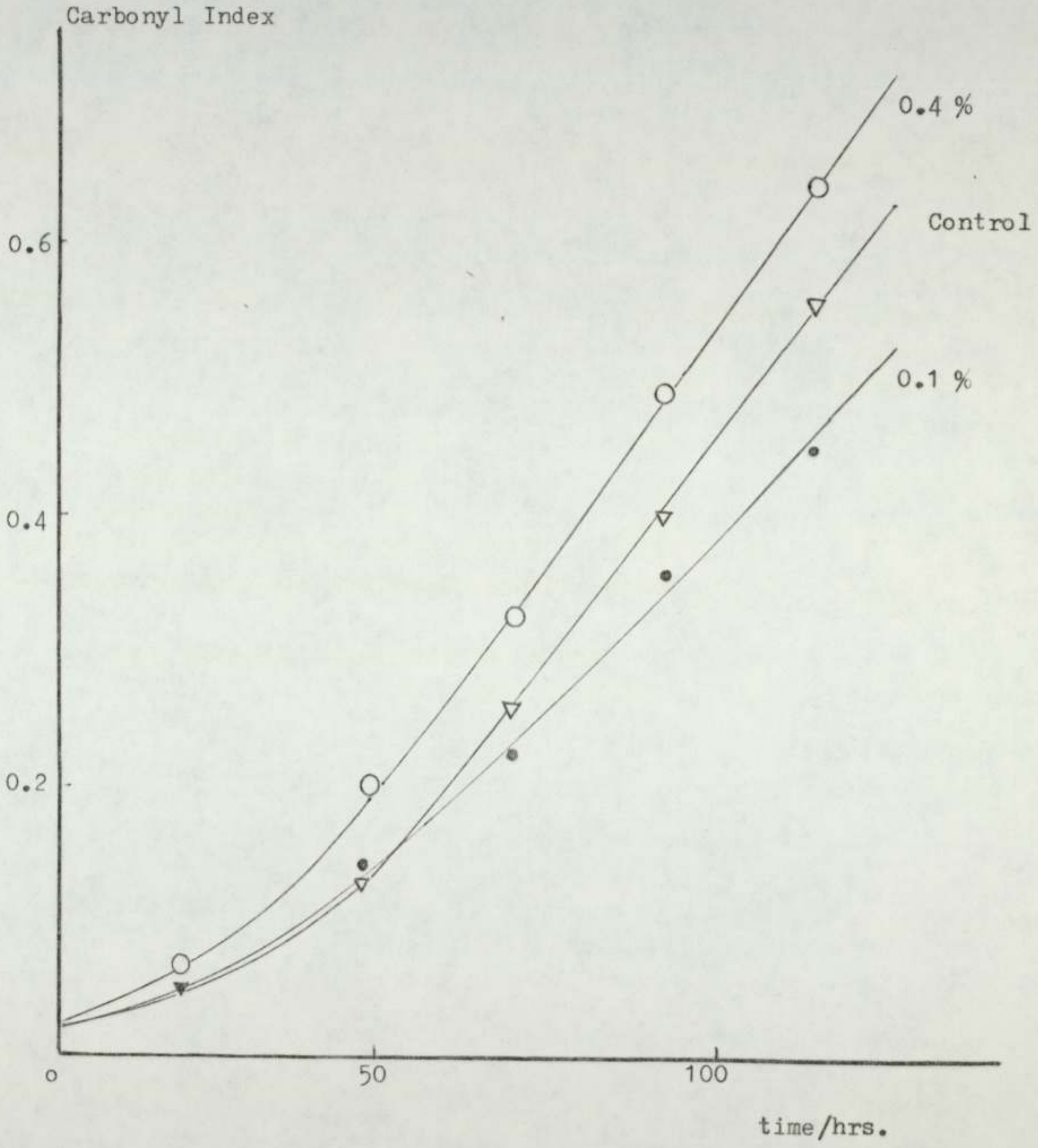


Figure 7.9 The photostability of PP films containing the cobalt complex 1.

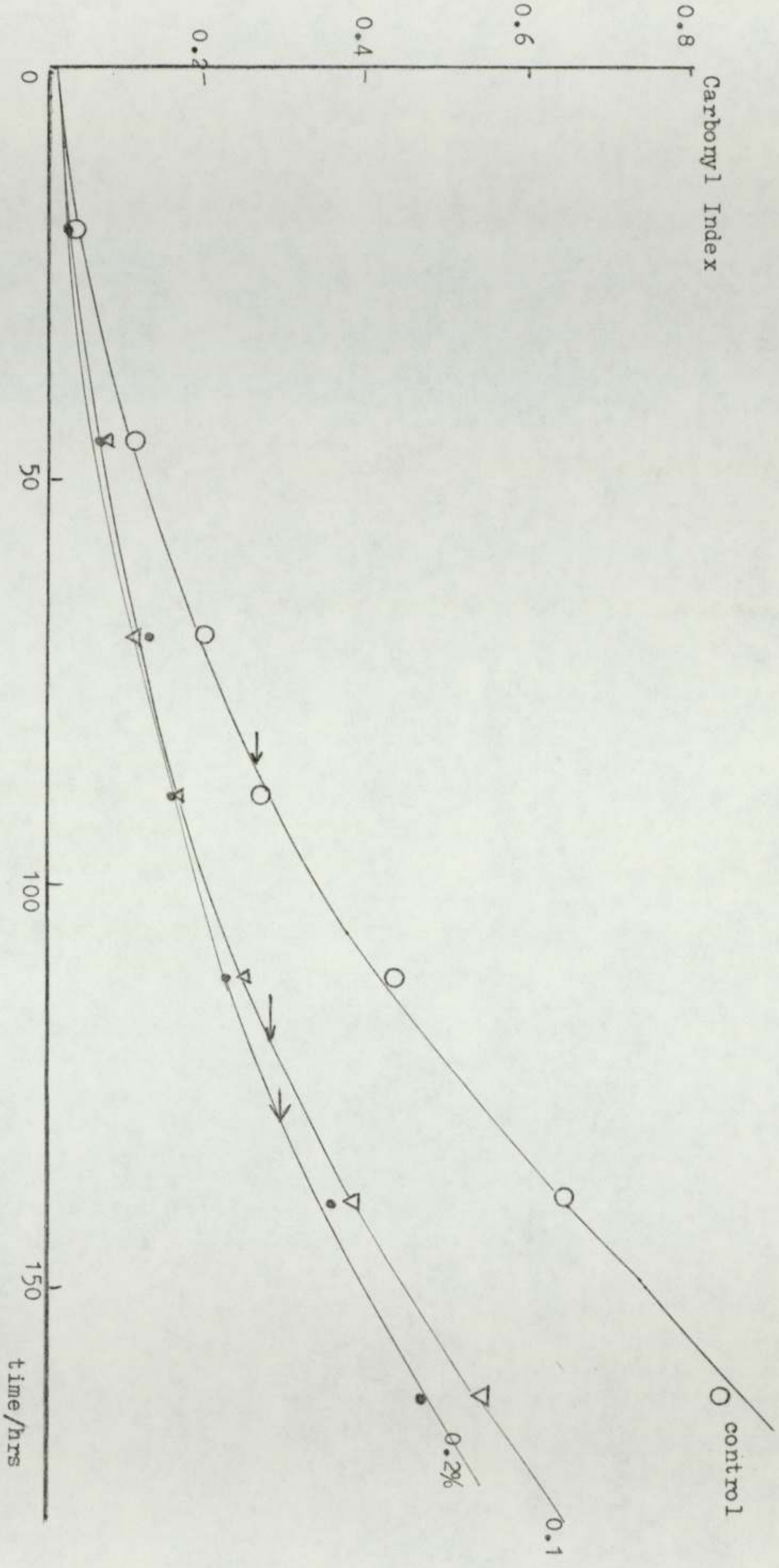


Figure 7.10 The photostability of PP cotaining the nickel complex.

7.7.2 Complexes derived from cyclic catechol phosphates.

The photostability of polypropylene films was measured as carbonyl index variation with time during u.v. irradiation. The results for the ferric and the copper complexes are shown in figure 7.11 and 7.12. It is seen that both these compounds impart considerable u.v. stability to the polymer and that the effect increases with concentration. The embrittlement time of polypropylene films containing these two metal complexes is given in table 7.6.

Table 7.6

Embrittlement time of polypropylene films containing catechol phosphate metal complexes.

Concentration (%)	Embrittlement time/hrs	
	Ferric complex	Copper complex
None	75	75
0.05	85	102
0.1	-	110
0.25	130	225
0.5	260	525

Because of the impressive results given by the copper complex of catechol cyclic phosphate, further work was concentrated on this compound.

Darkening of polypropylene was observed during processing with the copper complex in the torque rheometer. As such discoloration

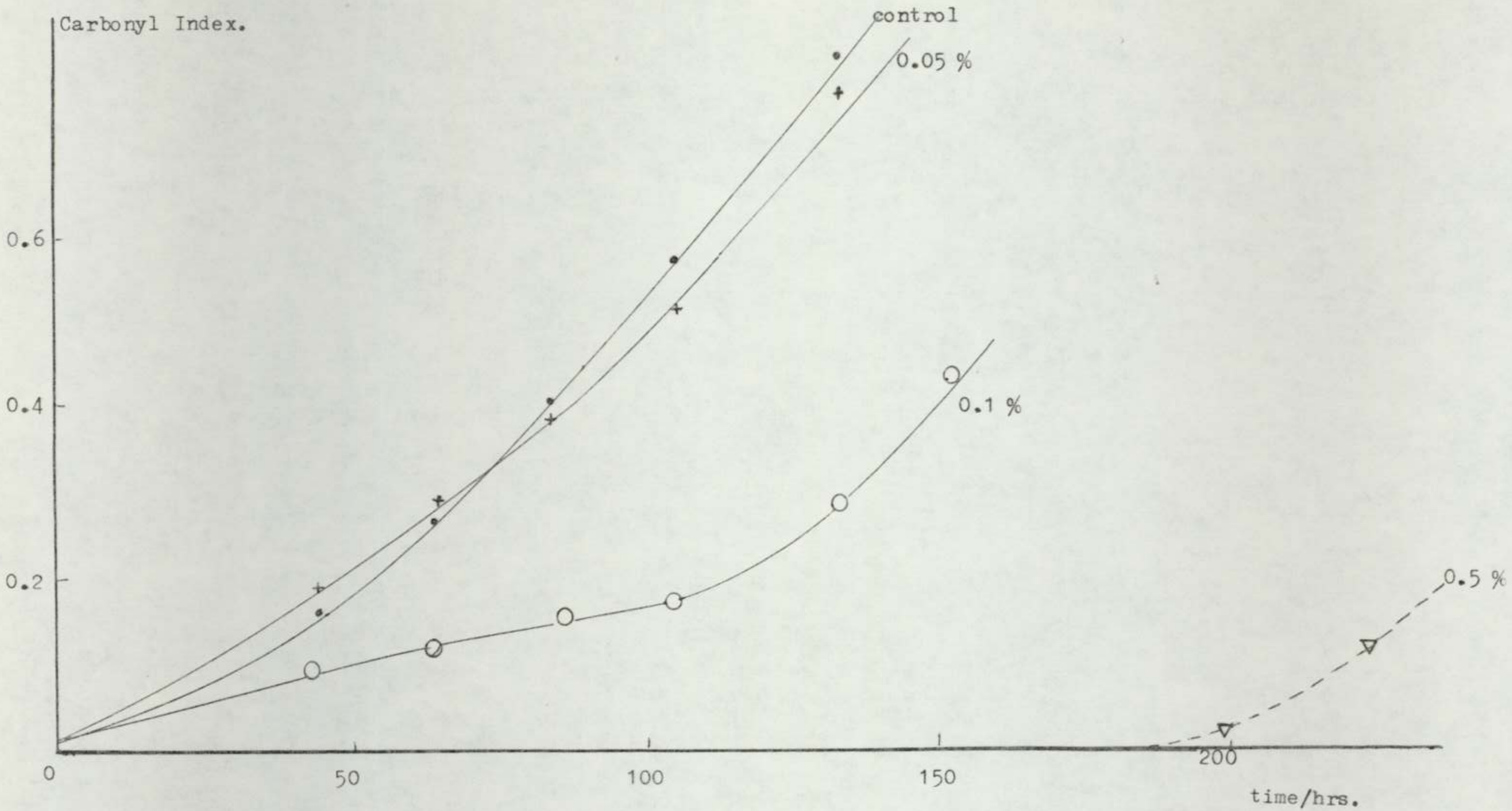


Figure 7.11 The photostability of PP containing ferric complex of catechol phosphate.

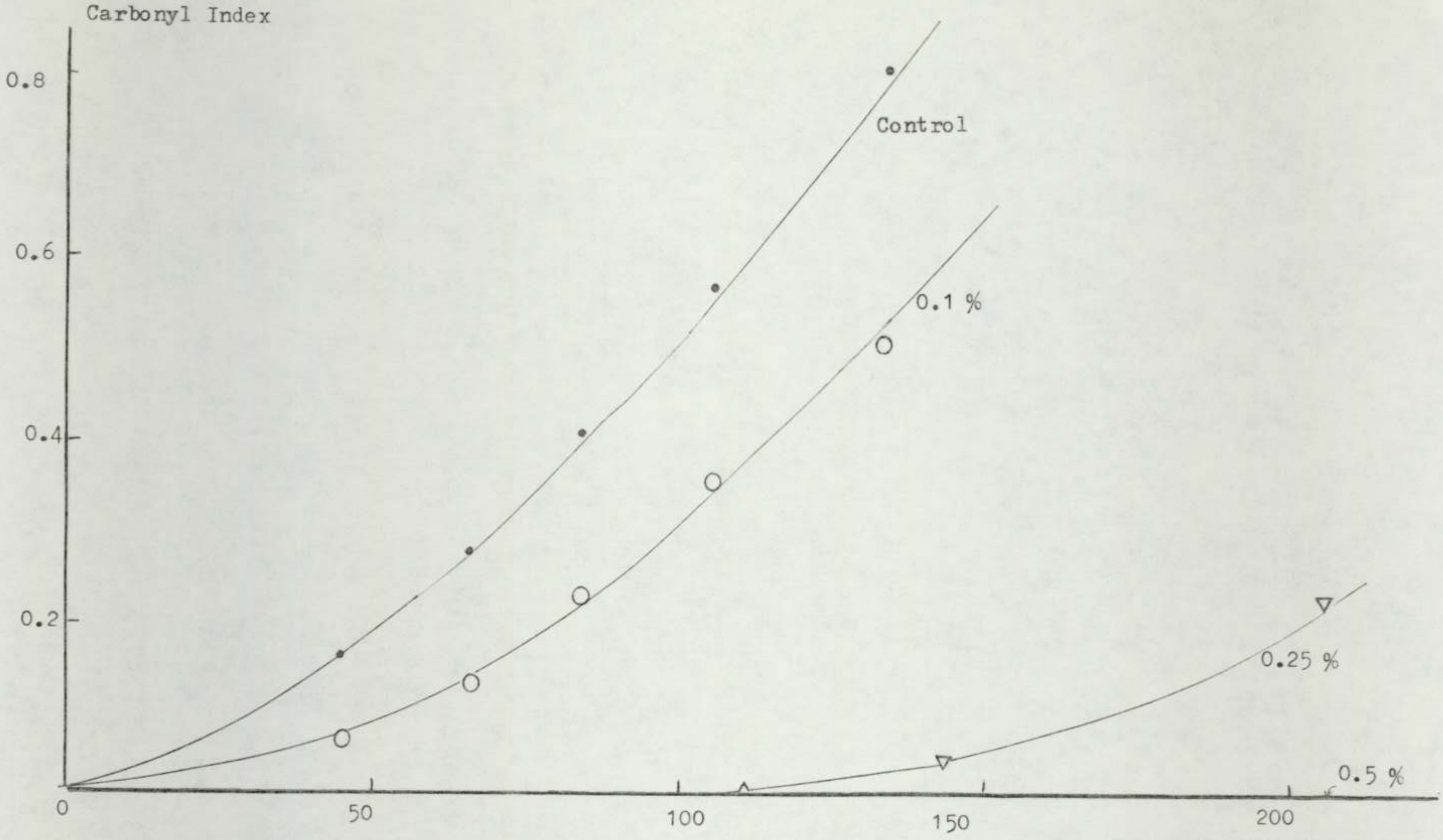


Figure 7.12 U.v. stability of PP films containing the copper complex of cyclic catechol phosphate.

was not observed with the simple cyclic catechol phosphate or with the ferric complex, it appears that this is a specific combined effect of copper and the catechol phosphate ligand.

When the copper complex was heated in hydroperoxide-free dodecane under nitrogen, at temperatures comparable to those involved in processing no colour change could be observed. In the presence of oxygen, there was a gradual darkening of the complex in several hours. In the presence of hydroperoxides, this colour change was quite rapid. It therefore seemed likely that the discoloration was due to some product derived from the complex during the reaction with hydroperoxides.

Thin layer chromatography was used to identify the products of the reaction of the copper complex with t-butyl hydroperoxide in dodecane. The presence of o-benzequinone in the reaction mixture was established. o-Hydroxyphenyl phosphate was the only other aromatic product that could be identified. (Experimental details and the R_f values are given in the experimental section).

7.7.3 U.v. screening by copper complex.

In view of its ability to absorb in the u.v. region, the effectiveness of the copper complex as a u.v. filter was examined in the same way as for the ligand, the simple cyclic phosphate ester, described earlier. The variation of the intensity of the carbonyl function with time for the samples used in this experiment is shown in figure 7.12a It is seen that the film screened by the film with the additive has a longer life and this indicates the

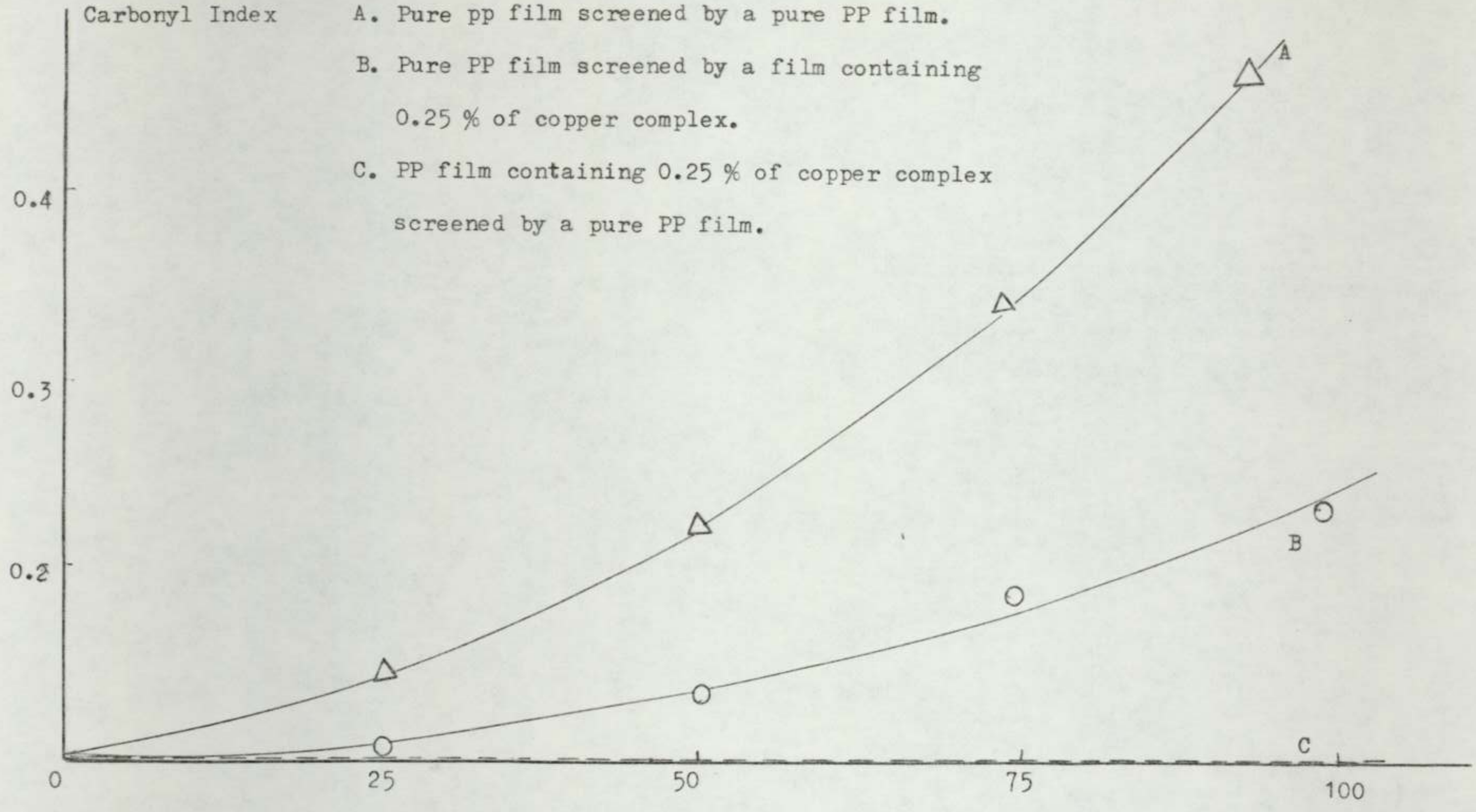


Figure 7.12a Effectiveness of the copper complex of cyclic catechol phosphate as an additive and as a u.v. screen.

effectiveness of the complex as a u.v. screen.

Table 7.7

U.V. Embrittlement times of polypropylene films used in screening experiments

	Embrittlement time/hrs
1) Polypropylene(PP) film screened by pure PP film	98
2) PP film screened by PP film with 0.25 % copper complex	152
3) PP film containing 0.25 % copper complex screened by pure PP film	260

It should, however, be noted that the screening ability of the complex as reflected by the difference between 1) and 2) in the table 7.7 will not be effective at the same scale when present in the polymer. In 2) above, the u.v radiation has to pass through the whole thickness of the film containing the complex used as the screen and every molecule of the complex threfore can absorb light, before it falls on the film being screened. When present in the film as an additive this situation is not realised. The relative ineffectiveness of stabilisers acting solely by u.v. screening has been stressed by Carlsson and Wiles.[18]

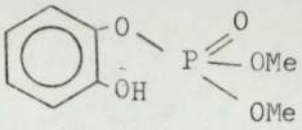
CONCLUSIONS

Though it seems unlikely at first sight , cyclic phosphate esters do react with hydroperoxides. With five-membered ring phosphates derived from aliphatic 1,2-diols the reaction is near stoichiometric. With cumene hydroperoxide , a mixture of acetone phenol , cumyl alcohol , acetophenone and methyl styrene is formed indicating two mechanisms for the reaction , one involving radical intermediates and the other involving ionic intermediates.

Studies of a series of cyclic phosphates derived from catechol indicates that they were powerful catalysts for the decomposition of hydroperoxides.

With cumene hydroperoxide , acetone and phenol were the main reaction products. The rate was enhanced by polar solvents. With these and other evidence, an ionic mechanism has been postulated for the reaction. The reaction is characterised by a small value for the energy of activation (47.1 kJ mol^{-1}) a low frequency factor (1.8×10^4 sec^{-1}) and a negative entropy of activation (-172.2 J $K^{-1}\text{mol}^{-1}$), all consistent with a reaction involving polar intermediates.

The proposed mechanism envisages alternative ring opening and ring closure of the cyclic phosphate and this has been substantiated by demonstrating the ability of the ester,



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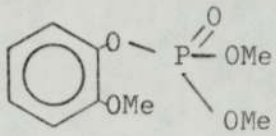
to decompose hydroperoxide catalytically. The importance of the vicinal hydroxyl group is shown by the inactivity of the o-methoxyphenyl dimethyl phosphate towards cumene hydroperoxide.



The following appear to be the most important factors contributing towards a catalytic, ionic reaction between hydroperoxides and cyclic phosphates.

1). Presence of phosphorus atom as part of a five membered ring (or potentially capable of becoming so as in ester XXI.

2). The presence of C_4-C_5 double bond leading to the restricted rotation and also increasing the stability of the intermediate phenolate anion. These requirements are most favourably achieved by 4,5-benzo compounds ie. catechol based esters.

Electron withdrawing phosphoroyl substituents enhanced the rate of the reaction while the electron releasing ones had the opposite effect. Electron withdrawing substituents on the benzene ring also had a positive effect on the rate.

When the molar ratios of the reactants was comparable, the reactionwas first order with respect to each of the reactants. At high concentrations of the hydroperoxides, the reacion is pseudo-first order with respect to the hydroperoxide. The kinetic behaviour was found to be more or less similar to that of enzyme catalysed reactions.

All the esters based on catechol strongly inhibited the autoxidation of decalin at 140°C. Esters with electron withdrawing groups had the highest effect. The ability to suppress oxidation is attributed to their ability to decompose hydroperoxides by a non-radical mechanism. These esters were far more effective than the hindered phenols at this temperature. They were also shown to be effective inhibitors of the oxidation of polypropylene at elevated temperatures (140°C) and also during u. v. irradiation.

Metal complexes were prepared with alkyl phosphato and catechol phosphato ligands, a number of these being novel compounds not previously reported. The alkyl phosphato-metal complexes gave mainly cumyl alcohol in their reactions with cumene hydroperoxide and were ineffective as u.v. stabilisers in polypropylene.

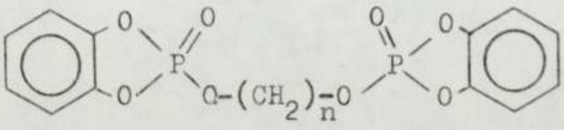
Ferric and copper complexes of cyclic catechol phosphate were found to react catalytically with hydroperoxides, and with cumene hydroperoxide, gave acetone and phenol as the reaction products. The essential features of the reaction are similar to those of the simple catechol phosphate esters. Both these complexes, particularly the copper complex, were found to be good photostabilisers in polypropylene. The attempts to synthesise the corresponding nickel complex were not successful.

SUGGESTIONS FOR FURTHER WORK

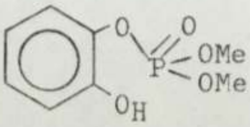
Although it was intended to synthesise cyclic catechol phosphate esters with electron withdrawing substituents on the benzene ring, this could not be achieved during this work due to lack of time. From the results of the reactions of other substituted cyclic catechol phosphates , it can be expected that those esters with electron withdrawing substituents on the benzene ring ought to react faster with hydroperoxides and hence would act as better stabilisers in polyolefins.

As previously mentioned , it was not possible to synthesise the nickel complex of catechol cyclic phosphate employing the general method used for the other complexes. In view of the highly documented ability of nickel chelates to act as stabilisers by virtue of their ability to quench excited states of chromophores it would certainly be rewarding to develop a method to synthesise this complex.

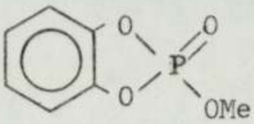
Since the volatility of antioxidants is often an important factor , it would be of interest to study the feasibility of preparing high molecular weight aromatic cyclic phosphates for eg.



One important aspect emerged from this work was that phosphate esters such as o-hydroxyphenyl dimethyl phosphate,



are also almost as effective as the corresponding cyclic esters such as,



This, therefore possibly eliminates the necessity to prepare cyclic esters which involves difficult synthetic procedures. A detailed study of O-hydroxyphenyl phosphate esters as antioxidants would be profitable.

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