MECHANISTIC STUDIES OF
SOME PHOSPHITE
ANTIOXIDANTS

by

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SUMMARY

A number of esters of phosphorous acid were shown to be effective inhibitors for hydrocarbon oxidation catalysed by azobisisobutyronitrile and by hydroperoxides after an initial rapid, but short-lived, pro-oxidant stage. Cyclic compounds derived from catechol were particularly effective, exhibiting autoretardation even at low concentrations.

The reactions of some phosphites with cumene hydroperoxide were examined kinetically and by subsequent product studies, and their kinetic parameters determined. Common to all compounds studied was an initial second order reaction which showed features consistent with a redox process. This reaction led to stoichiometric reduction of hydroperoxide with concomitant formation of phosphate. This phosphite/hydroperoxide system showed features in common with the better known amine/peroxide systems, including the ability to initiate the polymerisation of vinyl monomers, and to absorb oxygen.

After this stage the linear phosphates formed were inert to hydroperoxide whilst the (5-membered) cyclic compounds underwent further reaction(s) with peroxide to yield an unidentified species which was an extremely powerful catalyst for destruction of hydroperoxide by a pseudo-first order process. Product studies and solvent effects suggested a Lewis acid for this unknown compound.

The effects of ring strain were not marked in these reactions nor in their rates of hydrolysis which were briefly examined. This contrasts strongly with the large rate enhancements often encountered in other cyclic systems.

The phosphites examined did not inhibit the polymerisation of styrene initiated by azobisisobutronitrile.

The catechol phosphates were shown to be as effective as the (patented) phosphites in stabilising polypropylene against thermo-oxidative degradation, and both types of compounds were shown by induction-period measurements to compare favourably with a commercial synergistic stabiliser composition.

The work described herein was carried out at the University of Aston in Birmingham between October 1968 and August 1971.

It has been done independently and submitted for no other degree.

October 1971

K. J. Humphries.

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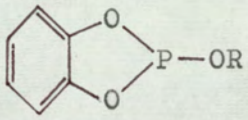
1. INTRODUCTION

The use of antioxidants and stabilisers to prevent the deterioration of plastics, rubbers, oils and foodstuffs is widespread. The incorporation of small amounts of additive (often less than one percent by weight) into many polymeric materials can enormously enhance their useful life. Polypropylene, a large tonnage polymer, requires efficient stabilisers to enable it to withstand the high temperatures inherent in modern fabrication processes, as well as needing protection against subsequent long-term ageing. The estimated world consumption of stabilisers at over 100,000 tons per annum[1] shows the importance of these materials.

Esters of phosphorous acid have been used as stabilisers for polymeric materials and lubricating oils for many years, and although a comprehensive patent literature exists[2] little is understood about the mechanisms by which they function. It has often been assumed that their activity is due to stoichiometric reaction with hydroperoxides.

Cyclic phosphites based on catechol



have been known for many years[3,4] but it was not until the extensive studies of Kirpichnikov and co-workers[5] on the improved syntheses of these compounds in the early 1960's that interest was re-awakened. Since then numerous technological papers have appeared from Russian workers on the antioxidant behaviour of catechol phosphites, the compounds with which the work herein is chiefly concerned.

Oxidation of hydrocarbons and hydrocarbon polymers can be simply expressed as a series of free-radical branched chain reactions involving initiation: $RH + O_2 \longrightarrow$ radicals (1)

$R. + O_2 \longrightarrow ROO.$ (2)

propagation: $ROO. + RH \longrightarrow ROOH + R.$ (3)

$$\text{ROOH} \longrightarrow \text{radicals} \qquad (4)$$

and termination : $$2\text{ROO}\cdot \longrightarrow \text{Products} \qquad (5)$$

The nature and ease of the termination step depends on the structural characteristics of the hydrocarbon, so that prevention of oxidation can be achieved either by terminating the alkylperoxy radicals produced in reaction (2), or by removing the hydroperoxide, the source of the degenerate branching mechanism, in a non-radical reaction. Both of these reactions may be possible with phosphites.

The reactions of phosphites with free-radicals and with hydroperoxides have been the subject of numerous publications[6,7]. In general phosphorus compounds tend to react heterolytically and trivalent phosphorus derivatives are often very nucleophilic owing to the relatively low ionisation potential of the 3s-electrons and the strong sp^3 bonds in the product. At the same time they are also electrophilic due to the relatively low electronic repulsion exerted towards a nucleophilic reagent, because of the greater radius and polarisability of phosphorus compared with say the first-row elements. Thus catenation can occur in which phosphorus acts both as nucleophile and electrophile, between a dialkyl phosphine and a dialkyl chlorophosphine

$$R_2PH + R'_2PCl \longrightarrow R_2P\text{-}PR'_2 + HCl$$

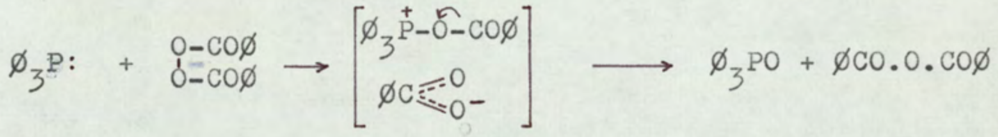
$$n\ RPH_2 + n\ R'PCl_2 \longrightarrow (RP\text{-}PR')_n + 2n\ HCl$$

Free-radical reactions are encountered with electronically symmetrical molecules such as oxygen and certain peroxides, and often proceed through an intermediate phosphoranyl radical in which the outer shell of phosphorus has expanded to accommodate nine electrons. Peroxides can also react by an ionic mechanism depending on the electronic asymmetry in the molecule. Thus diacyl peroxides react heterolytically whilst dialkyl peroxides react by a slow radical process. A change in nucleophile can also produce a change in mechanism, disulphides reacting ionically with trialkyl phosphines but via a radical intermediate with the less nucleophilic trialkyl phosphites.

Radical chain mechanisms have been proposed for the autoxidation of trialkyl phosphines[8,9], triphenyl phosphine[10] and alkyl and aryl phosphites[11]. Inhibition by hydroquinone was observed, and direct attack of molecular oxygen on the intermediate alkyl radical was postulated[8]

$$\begin{aligned} &\text{initiation} &&\longrightarrow && R. \\ &R. + O_2 &&\longrightarrow && ROO. \\ &ROO. + R'_3P &&\longrightarrow && RO. + R'_3PO \\ &RO. + R'_3P &&\longrightarrow && R. + R'_3PO \end{aligned}$$

In 1927 it was shown[12] that triphenyl phosphine reacted with dibenzoyl peroxide to give triphenyl phosphine oxide and benzoic anhydride. Horner and Jurgeleit[13] subsequently proposed an ionic mechanism for this reaction, which has since been substantiated by the tracer studies of Denney and co-workers[14,15]. Nucleophilic attack of phosphine on the peroxidic oxygen was suggested forming an ion-pair which subsequently decomposed by nucleophilic displacement.



$$\phi_3P: + \begin{matrix} O-CO\phi \\ O-CO\phi \end{matrix} \longrightarrow \left[\begin{matrix} \phi_3\overset{+}{P}-O-CO\phi \\ \phi C \overset{O}{\underset{O^-}{\lessgtr}} \end{matrix}\right] \longrightarrow \phi_3PO + \phi CO.O.CO\phi$$

Diacyl peroxides were thought to react with trialkyl phosphites in a similar manner in polar solvents[16],

$$(RO)_3P + \phi COOOCO\phi \longrightarrow (RO)_3PO + \phi CO.O.CO\phi$$

Whilst the uncontrolled reaction in the absence of solvent was thought to proceed at least in part via a homolytic route with the additional formation of phosphonate. In the case of unsymmetrical peroxides reaction occurred predominantly on the most electropositive oxygen atom[12,13]. With both phosphines and phosphites an exclusively radical reaction was discounted since no attack on solvent occurred and foreign anions were found to participate in the reaction. The known radical decomposition products of peroxide were also absent. A similar mechanism has been postulated for the oxidation of phosphines by peresters[17].

The reactions of trivalent phosphorus compounds with the less electrophilic dialkyl peroxides are rather different. Horner[11] assumed the same sort of nucleophilic displacement on peroxide as was found with the diacyl peroxides, this time with formation of an ether:

$$\phi_3P + ROOR \rightarrow \left[RO\text{-}\overset{+}{P}\phi_3 + RO^-\right] \longrightarrow \phi_3PO + R.O.R$$

Subsequent re-investigation of this reaction using a more sensitive gas-chromatographic technique[18] failed to identify ether among the reaction products, but identification of the hydrocarbon present was consistent with a homolytic reaction:

$$ROOR \longrightarrow 2RO.$$

$$RO. + (R'O)_3P \longrightarrow (R'O)_3\dot{P}OR \longrightarrow (R'O)_3PO + R.$$

$$2R. \longrightarrow R\text{-}R$$

The usual products of disproportionation of alkoxy radicals were not observed in the presence of phosphite indicating that addition of alkoxy radical to phosphite must be extremely rapid. Thus no acetophenone or α-cumyl alcohol, the usual products of cumyloxy radical breakdown[19], were observed in the induced decomposition of dicumyl peroxide[20]. Walling has shown that[21] the rate of formation of the phosphoranyl radical, reaction(1), is 500-1000 times as fast

$$tBuO. + (EtO)_3P \longrightarrow tBuO\dot{P}(OEt)_3 \qquad (1)$$

$$tBuO. + EtH \longrightarrow tBuOH + Et. \qquad (2)$$

as the hydrogen abstraction in reaction (2). Whilst breakdown of the phosphoranyl radical to products is generally accepted, an alternative direct reaction with oxygen has been postulated as one stage in the reduction of pyridine N-oxide by triethyl phosphite[22]:

$$(EtO)_3\dot{P}OR + O_2 \longrightarrow \left[(EtO)_3P{<}\begin{smallmatrix}OO\cdot\\ OR\end{smallmatrix}\right] \longrightarrow \text{products}$$

Further study is clearly required in this area.

No products corresponding to attack of alkyl radicals on phosphite have been observed and it has been suggested[20] that the addition of electrophilic radicals to trivalent phosphorus centres derives considerable driving force from the contribution of polar structures to the transition state

$$\mathrm{RO\text{-}\dot{P}(OR)_3} \rightleftharpoons \mathrm{R\bar{O}\ \dot{P}^{+}(OR)_3}$$

involving phosphorus acting as a Lewis base, whilst the subsequent breakdown to products owes its driving force to the strength of the phosphoryl bond formed. Recently, addition of the more electrophilic phenyl radical to trialkyl phosphites has been reported[23], which is consistent with the above proposal. The addition of alkyl radicals to alkyl diphenylphosphinites has also been reported[24]. Walling also showed that reaction of phosphite with dialkyl peroxide in oxygen led to the formation of much additional phosphate, suggesting[20] an autoxidation sequence similar to that for phosphines

$$\mathrm{R.} + \mathrm{O_2} \longrightarrow \mathrm{ROO.}$$

$$\mathrm{ROO.} + \mathrm{(R'O)_3P} \rightarrow \mathrm{(R'O)_3\dot{P}OOR} \longrightarrow \mathrm{RO.} + \mathrm{(R'O)_3PO}$$

The phosphoranyl radical decomposition has so far been written as a β-scission process, but α-scission can sometimes occur[25], for example when the radical generated is resonance-stabilised. Recent electron spin resonance studies[26] have confirmed such processes.

Although the early reports of a heterolytic reaction between triphenyl phosphine and di-tert.-butyl peroxide[13] were in error, this now appears to have been a consequence of steric hindrance. In less highly branched systems nucleophilic attack on oxygen can occur although the alkoxide ion displaced probably never becomes entirely free. At room temperature Denney has characterised a penta-coordinate pentaethoxyphosphorane from reaction of triethyl phosphite with diethyl peroxide[27]. Isotope studies showed that the five ethyl groups became equivalent during the course of the reaction. This penta-coordinate compound then broke down to give phosphate and ether, and similar species have since been reported from cyclic phosphites and tertiary phosphines[28,29]. In all cases it was thought that the first stage consisted of nucleophilic attack on oxygen to give an essentially covalent alkoxyphosphonium alkoxide.

$$\begin{tikzcd} (RO)_3P + EtOOEt \arrow[r] & (RO)_3\overset{+}{P}OEt\overset{-}{O}Et \arrow[r] \arrow[d] & (RO)_3P(OEt)_2 \\ & (RO)_3PO + EtOEt & \end{tikzcd}$$

More recent nuclear magnetic resonance studies, however, have shown that an alkoxide species is not involved, reaction proceeding through a covalent intermediate.[30]

The reaction of triphenyl phosphite with hydroperoxide was first reported as a simple de-oxygenation reaction[13]:

$$(\text{Ø}O)_3P + ROOH \longrightarrow (\text{Ø}O)_3PO + ROH$$

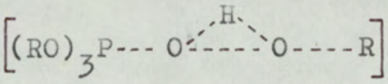
and phosphines were found to react in the same way[31]. Walling investigated the reaction of hydroperoxide with trialkyl phosphite[20] and found that the reaction was not inhibited by radical scavengers, and suggested a polar sequence involving attack by phosphorous at the oxygen atom adjacent to the alkyl group:

$$ROOH + P(OEt)_3 \longrightarrow \left[RO\overset{+}{P}(OEt)_3 + \overset{-}{O}H\right] \longrightarrow ROH + OP(OEt)_3$$

Davies and Feld, however , showed[32] that optically active α-phenylethyl hydroperoxide was reduced by triphenyl phosphine with retention of configuration indicating attack on the hydroxyl oxygen atom. The acceptability of the quasi-phosphonium intermediate was further reduced by Denney's isotope study of the reaction between trans-9-decalyl hydroperoxide and tri-n-butyl phosphite in ethanol/ H_2O^{18} mixture[33]. Configuration was retained in the product alcohol, no O^{18}-exchange was observed, and only a single alcohol was obtained. If the phosphonium intermediate was involved it would have to decompose to products faster than the hydroxyl ion can equilibrate with the labelled water. It was suggested that either attack by phosphite on hydroxyl oxygen occurred to give

$$\left[(RO)_3\overset{+}{P}\text{-OH} \;+\; \bar{O}R\right]$$

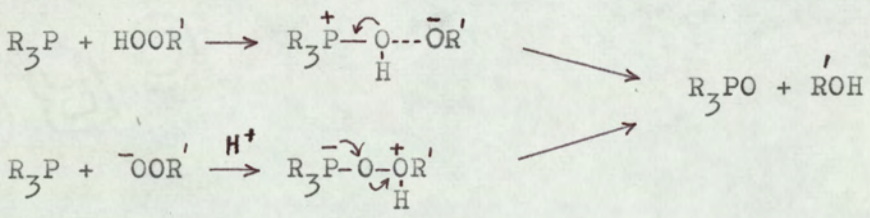
or that reaction proceeded via an initial displacement occurring with simultaneous proton transfer in a three-centered complex



$$\left[(RO)_3P\text{---}O\overset{H}{\cdots\cdots}O\text{----}R\right]$$

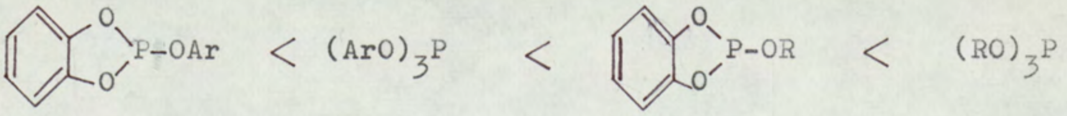
This is acceptable since the hydroxyl oxygen is the least sterically hindered and most electropositive. Subsequent work has confirmed the generality of these findings[34].

If these proposals are correct, and the first stage above is rate-determining, it is difficult to account for the marked difference in reactivity between peroxides and hydroperoxides. Hudson suggests[35] that the activity of the latter may involve catalysis by a proton:



A considerable amount of work has been published by Russian workers on the antioxidant activity of phosphites, especially in polymer systems, and particular interest has been paid to the cyclic catechol phosphites. However, adequate experimental detail is sometimes lacking and much of the work in polymer systems is empirical.

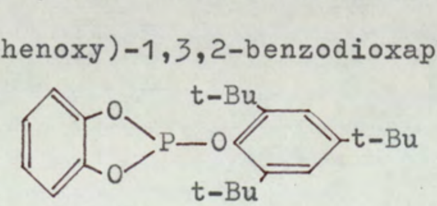
A number of workers examined the kinetics of the phosphite-hydroperoxide reaction, agreeing that it was first order in both components in the presence of excess phosphite[36-39]. The same authors correlated reactivity of phosphite with structure, agreeing that activity increased:



This series is consistent with phosphite acting as a nucleophile, and is in agreement with Kabachnik's observations on the relative nucleophilicity of phosphites[40], originally established for the Arbusov reaction. It was also found that both increasing the chain length of alkyl substituents, and the gradual replacement of alkyl groups by aryl in mixed phosphites, led to a decrease in reactivity towards hydroperoxide. A similar observation has since been made for decomposition of benzoyl peroxide by phosphites[41]. In addition, Rysavy and Slama postulated a radical mechanism for the phosphite-hydroperoxide reaction since they found that reaction rates were insensitive to changes in solvent dielectric[37].

Another common observation is that the antioxidant activity of phosphites in polypropylene[37,38,42], styrene-butadiene rubber[43], and free radical-initiated model alkene systems[38], showed the exact opposite of the above series. The aryl-substituted catechol phosphites were the most effective stabilisers found. In all cases a linear relationship between antioxidant concentration and length of induction period was found. These results prompted the suggestion that[37] different mechanisms might be operating at the greatly different temperatures used for the peroxide decomposition kinetics and the induction period measurements, but no other evidence was offered.

Another suggestion was that phosphites function chiefly as radical-deactivators[38,44], and in support of this Kirpichnikov showed[45] that the reactivity of a series of phosphites towards the stable radical diphenylpicrylhydrazyl paralleled the order of antioxidant activity; by far the most effective compound found was 2-(2,4,6-tri-t-butylphenoxy)-1,3,2-benzodioxaphosphole *



Later workers claim to have shown by means of a chemiluminescence

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* See appendix

technique that such phosphites were inactive towards alkylperoxy radicals[46].

It has been suggested that the activity of catechol phosphites as chain-breaking antioxidants is due to their hydrolysis products[46] and it was shown that the expected hydrolysis products do show synergistic behaviour in polyamides[47], in agreement with an earlier report on synergism between phenols and phosphonates in lubricating oils[48]. Other workers have discounted hydrolysis as a major contributor towards antioxidant activity[44].

It has recently been reported[49] that an optimum concentration range exists for catechol phosphites in polypropylene. Thus for catechol hindered-phenyl phosphite, a critical concentration of 5×10^{-3} moles/kg. exists below which no stabilisation is conferred, whilst at concentrations greater than 1.5×10^{-2} moles/kg., induction period is approximately independent of concentration.

Since this work began Pobedimskii and Buchachenko have reported evidence for the involvement of radical species in the reaction of phosphite with hydroperoxide[39]. They followed the decay in the electron spin resonance signal due to 2,2',6,6'-tetramethyl piperidine-1-oxyl(RNO.), in the presence of reacting phosphite-hydroperoxide mixtures, and showed that the same kinetics were followed as determined independently by hydroperoxide analysis. They postulated a reaction occuring in a solvent cage with a very low outflow of "free" radicals. The first stage consisted of an electron transfer from phosphite to hydroperoxide yielding an ion-radical complex, which was then converted monomolecularly into a radical pair:

$$\mathrm{ROOH} + \mathrm{P(OR')_3} \longrightarrow \left[\overset{\cdot}{\mathrm{R}}\overset{-}{\mathrm{O}}\mathrm{OH} \quad \overset{+\cdot}{\mathrm{P}}\mathrm{(OR')_3}\right] \longrightarrow \left[\mathrm{R}\dot{\mathrm{O}} \quad \dot{\mathrm{P}}\mathrm{(OH)} \quad \mathrm{(OR')_3}\right]$$

This radical pair can disappear either as a result of disproportionation within the solvent cage:

$$\left[R\dot{O}\ \ \dot{P}(OH)\ \ (OR)_3\right] \rightarrow ROH + OP(OR)_3$$

or by dissociation:

$$\left[R\dot{O}\ \ \dot{P}(OH)\ \ (OR)_3\right] \longrightarrow RO\cdot + \dot{P}(OH)(OR)_3$$

The same authors also claim to have detected a species which they suggest might be a cation-radical, by electron spin resonance, in the reaction of a catechol phosphite with peroxides and peresters. They also point out that one of Denney's arguments against a radical path, the absence of isotope exchange, is compatible with the theory presented since the ion-radical complex can be converted monomolecularly to the radical pair. In addition, a number of instances are now known[50,51] where configuration is retained in a reaction involving alkoxy radicals.

1.1 Scope and Object of the Present Work

The chemistry of phosphite antioxidant activity is at best imperfectly understood, much of the published work being the result of empirical studies in polymer systems. The object of the present study is broadly to try and establish chemically the nature of the reactions likely to lead to the inhibition of organic oxidation processes.

The reason for the high efficiency of the catechol phosphites as polymer stabilisers compared to their acyclic analogues has never been satisfactorily explained and contrasts with the reported low activity of the cyclic compounds towards hydroperoxides[36-39]. The bulk of this work is concerned with the detailed kinetics and mechanism of phosphite-hydroperoxide reactions in the liquid phase, in an attempt to relate structure and reactivity, and deduce the role (if any) of ring strain. Other relevant aspects examined in less detail are radical reactions and hydrolysis of phosphites.

In the case of sulphide antioxidants it is known that the sulphide itself is not the species chiefly responsible for the stability conferred, and product studies in the present work may indicate whether the phosphite or a derived product is the effective stabiliser. This is particularly important from the commercial aspect since phosphites are the subject of numerous patent disclosures[2].

It is hoped that the contents of this thesis will lead to a better understanding of the chemistry of phosphite antioxidant action, and that the application of this knowledge, taken together with other relevant factors such as volatility, may lead eventually to more efficient stabilising systems becoming available.

2. EXPERIMENTAL SECTION

2.1 Instrumental Techniques

1 Spectra

Infra-red spectra were generally recorded on a Perkin-Elmer 237, but where higher resolution was needed, or absorptions below 600cm.$^{-1}$ were of interest, a Perkin-Elmer 225 was used. Details of state of sample, path length etc., are recorded in the text where appropriate.

Ultra-violet spectra were recorded on a Perkin-Elmer 137 or Pye-Unicam SP700.

Nuclear magnetic resonance spectra were run on a Perkin-Elmer R10 (60 M/c./sec.) instrument. Tetramethylsilane was used as reference for proton spectra, whilst P^{31} spectra were recorded relative to 85% orthophosphoric acid.

Electron spin resonance studies were carried out using a Hilger and Watts Microspin spectrometer, with a cylindrical cavity and 100 K/c. modulation.

Mass spectra were recorded on an A.E.I. MS9 double-focussing spectrometer with 70eV. acceleration. Peak matching was done by reference to a convenient peak in the well-known fragmentation pattern of heptacosafluorotri-n-butylamine.

2 Gas Chromatography

All samples were run on a Pye Series 104 chromatograph using a flame-ionisation detector. Five foot all glass columns were packed with 10% polyethyleneglycoladipate on "Celite" support, and pre-heated for 48 hours at 190°C. All service gases were purified by passage through molecular sieves (Union Carbide type 13x), and nitrogen was used throughout as carrier gas. Output from the amplifier was fed to a millivolt recorder. In the quantitative work internal standards were used to eliminate the difficulties and inaccuracies inherent in measuring small volumes precisely. The determination of cumene hydroperoxide decomposition products was carried out at two temperatures, for convenience, and internal standards used as shown in Table 1. Standard solutions were made up containing a fixed concentration of standard and varying concentrations of product, and chromatogrammed. Two injections were made for each concentration, and the rubber septum on the injection port re-newed every 10 injections. Peak heights or areas were then measured, the latter by means of a fixed-arm planimeter, and calibration curves constructed in the desired concentration range, of concentration versus

$$\frac{(\text{peak area})_{\text{product}}}{(\text{peak area})_{\text{standard}}}$$

and excellent straight lines were obtained in all cases (Fig.2.1)

Product	Retention distance	Internal Standard	Retention distance	Temp. °C.
phenol	8.3 cm.	p-cresol	11.1cm.	140
acetophenone	6.6			
α-cumyl alcohol	3.6			
acetone	0.9	dioxane	2.3	65
α-methyl styrene	10.7			

Table 1

In all cases the mixture of internal standards was added to the reaction mixture after completion of the reaction after quenching, to ensure that no reaction occurred with the standards.

3 Quantitative Mass Spectrometry

This technique was used to estimate phosphate, using the integrated ion-current method due to Majer[52]. The spectrometer

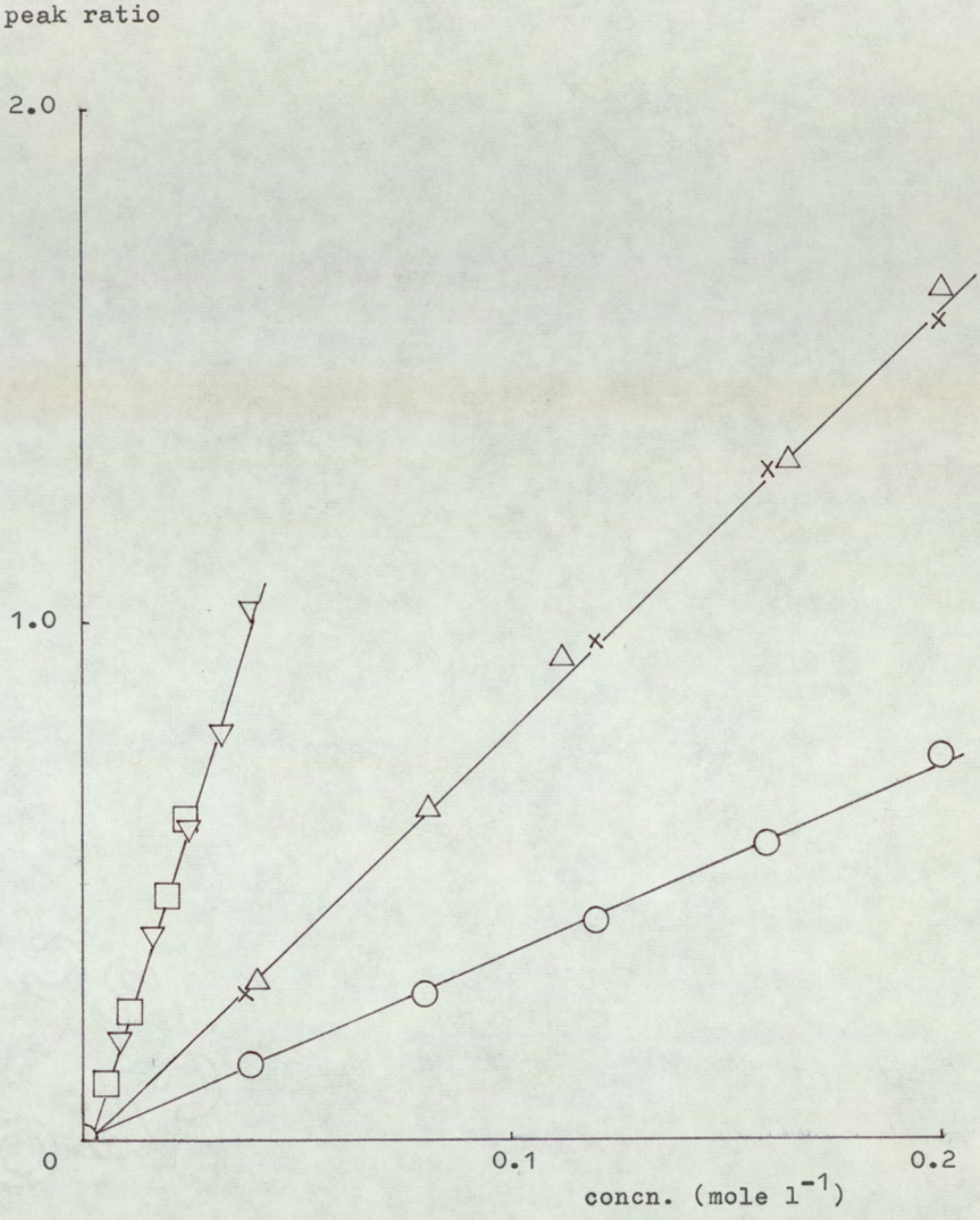

Figure 2.1: Gas chromatography calibration curves for

○ = phenol ; △ = acetone ; × = α-methyl styrene

□ = acetophenone ; ▽ = α-cumyl alcohol

was fitted with an insertion lock and direct evaporation probe, and samples were admitted in small Pyrex glass tubes which fitted into the end of the probe. A measured volume, usually 1μl., of the solution to be analysed was syringed into the sample tube which was then transferred to the vacuum system of the spectrometer through the insertion lock and held in the cool part of the system. The peak at m/e 374 (the parent ion) had previously been selected and displayed on the oscilloscope, and at the appropriate time the sample tube was lowered into the heated region of the source (about 300°C.), to allow evaporation of the sample. When evaporation began, the peak selected appeared on the oscilloscope and was recorded. Complete evaporation took up to 30 secs. and the peak ion then disappeared from the trace. The amount of compound evaporated is proportional to the integrated ion-current at m/e 374, and therefore to the area under the curve, which was measured by cutting out and weighing. A calibration curve is shown in Figure 2.2 , each point being the average of 2 injections.

2.2 Miscellaneous Techniques

1 Oxygen Absorption

Numerous types of apparatus for measuring gas absorption have appeared in the literature, the most common type consisting of a simple manometer[53], or sophisticated automatic versions of it[54,55]. Our simplified apparatus consisted of a round-bottom, 3-necked flask attached by a ground-glass joint to a capillary tube (internal diameter 0.067cm.) with a millimeter scale attached (Figure 2.3). A tap enabled the apparatus to be thoroughly flushed with oxygen prior to the start of the experiment, and the other neck of the flask contained a device for adding the antioxidant during the course of the experiment. The contents of the flask were

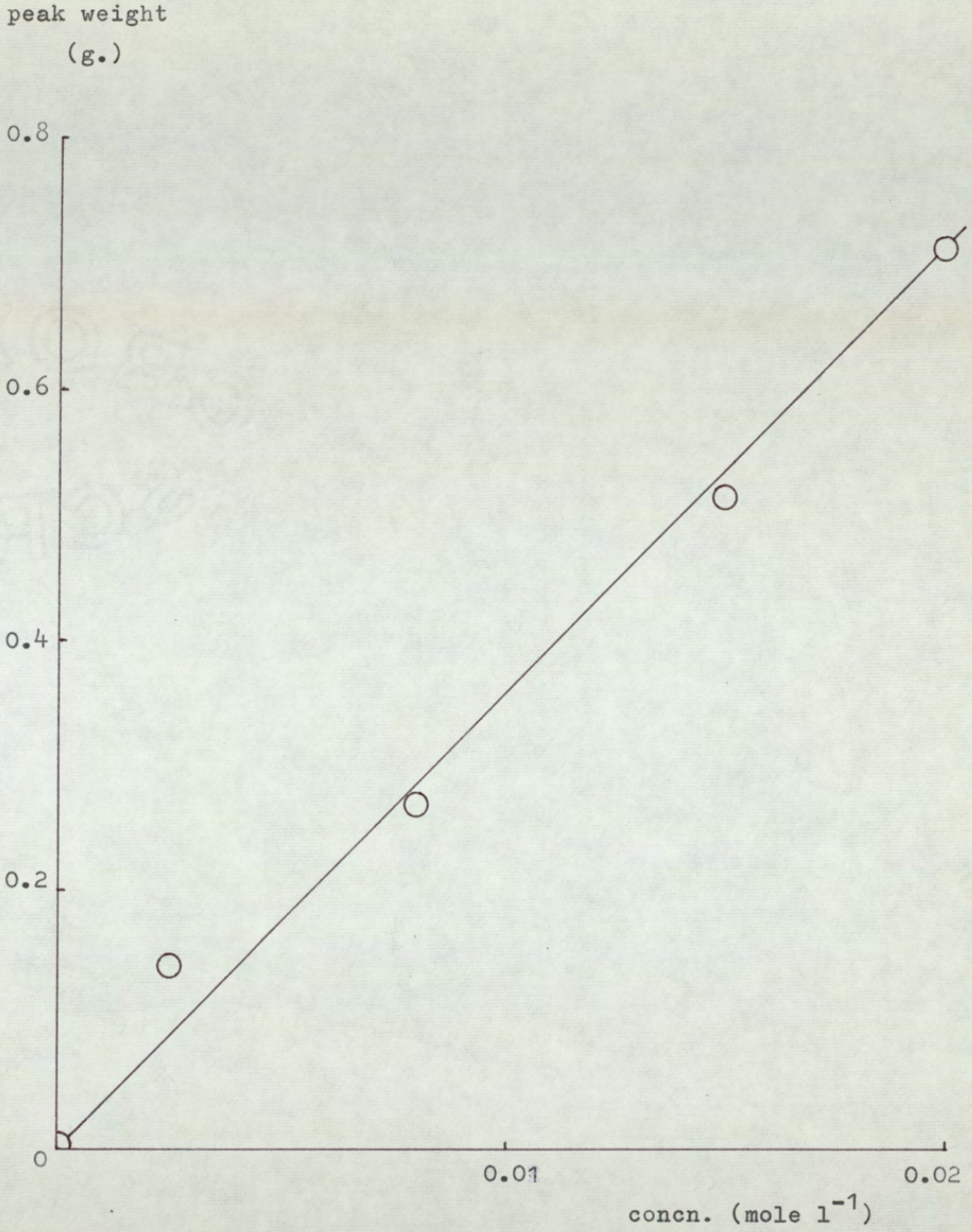

Figure 2.2: Calibration plot relating the concentration of catechol hindered-phenyl phosphate to the peak weight (proportional to the integrated ion current), for quantitative mass spectrometry.

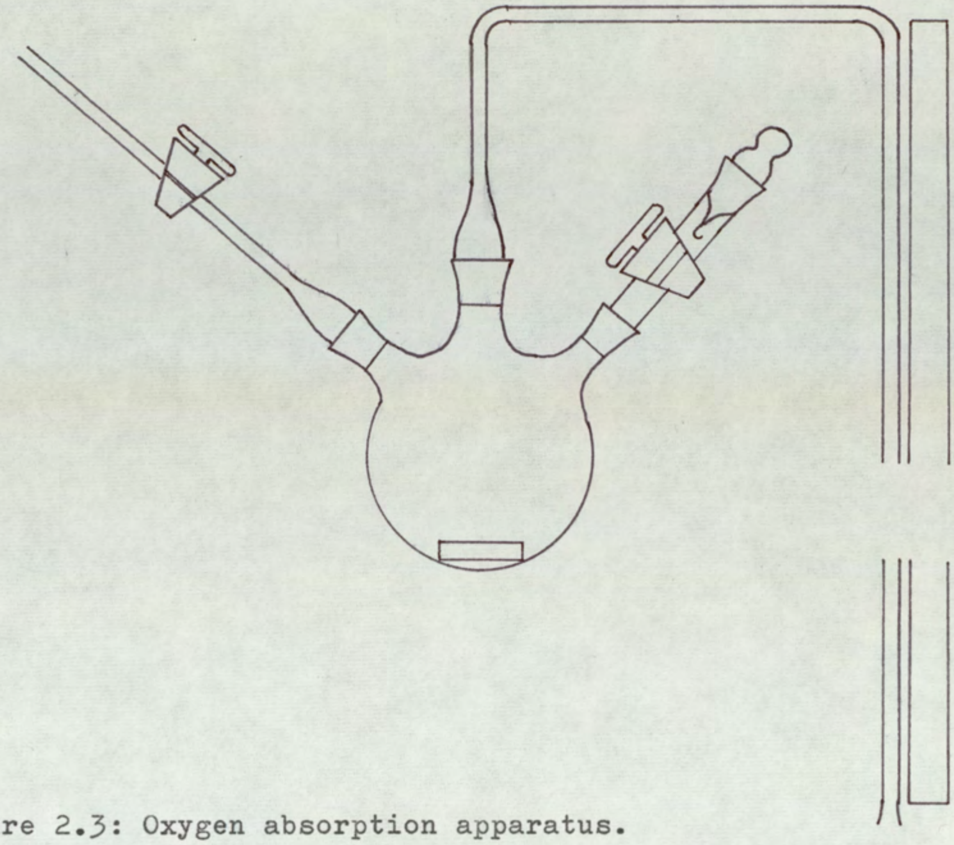

Figure 2.3: Oxygen absorption apparatus.

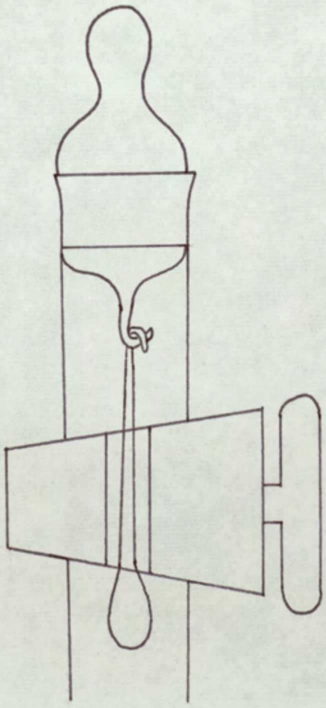

Figure 2.4 Device for adding antioxidant to reaction vessel.

agitated by a glass-covered magnetic follower activated by an external rotating magnet. The mode of operation was as follows. The apparatus was thoroughly cleaned with a stiff brush and scouring powder, rinsed with water , then with acetone , and dried. The capillary tube was additionally rinsed with carbon tetrachloride to remove traces of grease. The use of acid for cleaning was avoided. The hydrocarbon and initiator were weighed into the flask and the device in Figure 2.4 attached. The antioxidant was weighed into a fragile glass ampoule, sealed, and suspended inside the barrel of the wide-bore tap from a platinum hook attached to the stopper above the tap. All the joints were lightly smeared with silicone grease, and kept under tension by means of small springs. The flask was then flushed with oxygen, covered with aluminium foil to prevent photo-catalysed reactions, immersed in a thermostat bath, and agitated sufficiently quickly to ensure that the oxidation was not diffusion-controlled. After temperature equilibration, a short thread of liquid was introduced into the bottom of the capillary and the oxidation followed by observing the movement of the meniscus. The antioxidant was added by turning the tap, crushing the ampoule. The advantages of this system are : 1 cheapness of construction

2 sensitivity- 10mm. movement is equivalent to about 0.04 ml. absorption.

3 reversibility- gas evolution or absorption can be measured with equal facility.

4 since the antioxidant is added to an equilibrated autoxidising system, the instantaneous reaction is seen and no part of the reaction is missed.

It was found that when new flasks were used, or flasks which had been cleaned with strong acid, erroneous rates of steady-state oxidation were observed. Subsequent experiments showed a gradual falling off in rate until reproducible results were once more obtained, as shown in Figure 2.5 . This may be due to a surface catalytic effect which has been observed by other workers[56], and was avoided by "ageing" new flasks in an autoxidation reaction mixture for 48 hours.

For the measurement of induction periods to oxidation a novel apparatus was used whose principal of operation was devised in this laboratory[57] and which is shown in Figure 2.6a

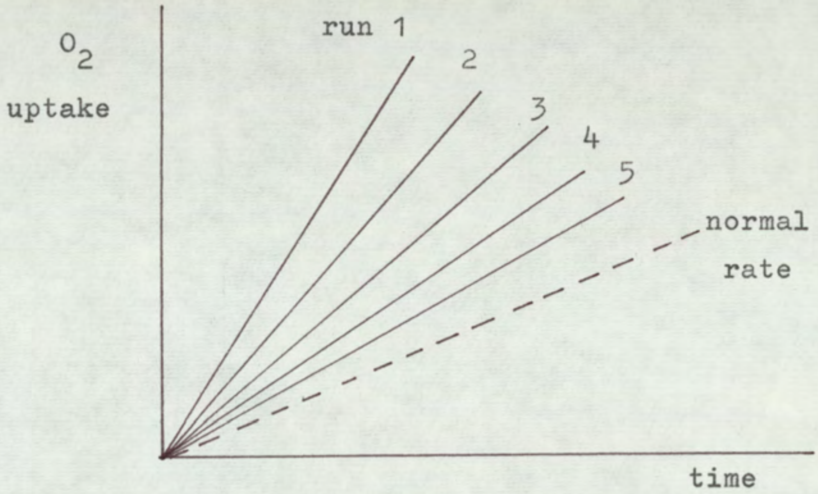

Figure 2.5

The lagged reservoir, attached by capillary tubing to the stirred reaction vessel, dipped into a beaker of an involatile fluid. As gas was absorbed in the reaction vessel an equal volume of fluid was drawn into the reservoir, and the decrease in weight of the beaker followed by means of strain gauges.* The reservoir consisted of a large glass bulb insulated by a covering of expanded polystyrene to minimise ambient temperature fluctuations. The volume of this reservoir was governed by the oxidation characteristics of the system being studied and the antioxidant used. The beaker of fluid (di-n-

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* For a comprehensive account of the theory and practise of strain gauges see M.Dean, R.D.Douglas-"Semiconductor and Conventional Strain Gauges", Academic Press, New York, 1962.

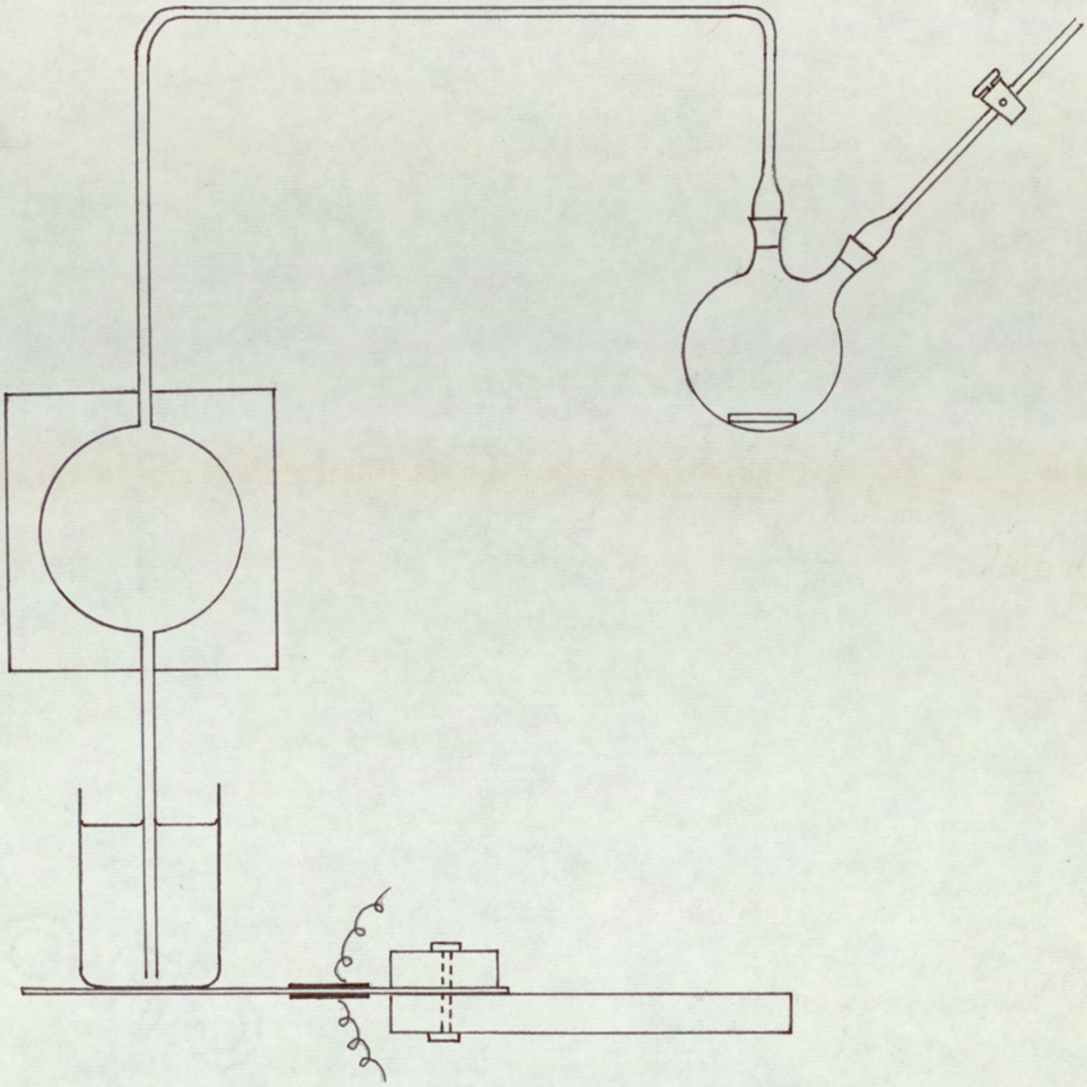


Figure 2.6a: Strain gauge apparatus for the measurement of induction periods to oxidation.

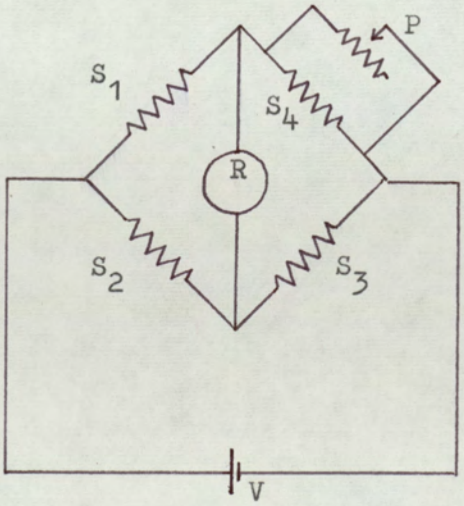


Figure 2.6b: Wheatstone Bridge circuit used for strain gauges.

butyl phthalate) was supported by a 6 x 2 x 1/16 inch flexible steel plate, securely clamped at one end to a rigid base, which deflected slightly under the weight of the full beaker. Two strain gauges (Phillips type PR 9810 F) were firmly bonded to each side of the clamped end of the plate with an epoxy adhesive (Araldite) and electrically connected so as to form the four arms of a Wheatstone Bridge circuit (Figure 2.6b). The pairs of strain gauges (S_1 and S_3) and (S_2 and S_4) were on the same side of the steel plate. A constant 3.0 volt D.C. supply was used and P was a variable resistance, which consisted of a 1 MΩ and a 1 kΩ potentiometer in series, on one arm of the bridge circuit to enable the recorder to be adjusted to zero. As the beaker decreased in weight due to oxygen absorption, the metal plate began to unbend, thus changing the resistance of the strain gauges, which led to an imbalance in the bridge circuit, which was recorded on a Leeds and Northrup "Speedomax" recorder. The apparatus was calibrated by pipetting known volumes of di-n-butyl phthalate into the beaker (Figure 2.7). Good straight lines were obtained confirming that the linear range of the strain gauges had not been exceeded, and that the auxiliary potentiometer circuit added to the basic Wheatstone Bridge had not introduced appreciable non-linearity of response. The procedure used was as already described, except that the antioxidants were dissolved in the hydrocarbon at the beginning of the experiment.

In the polymer studies the samples were prepared as follows. The weighed antioxidant was dissolved in 100ml. of methylene chloride and added to 50g. of polypropylene powder (ex Imperial Chemical Industries, batch no. HM40C) of initial melt flow index 1.56 (measured by B.S. test method 2782,part1,

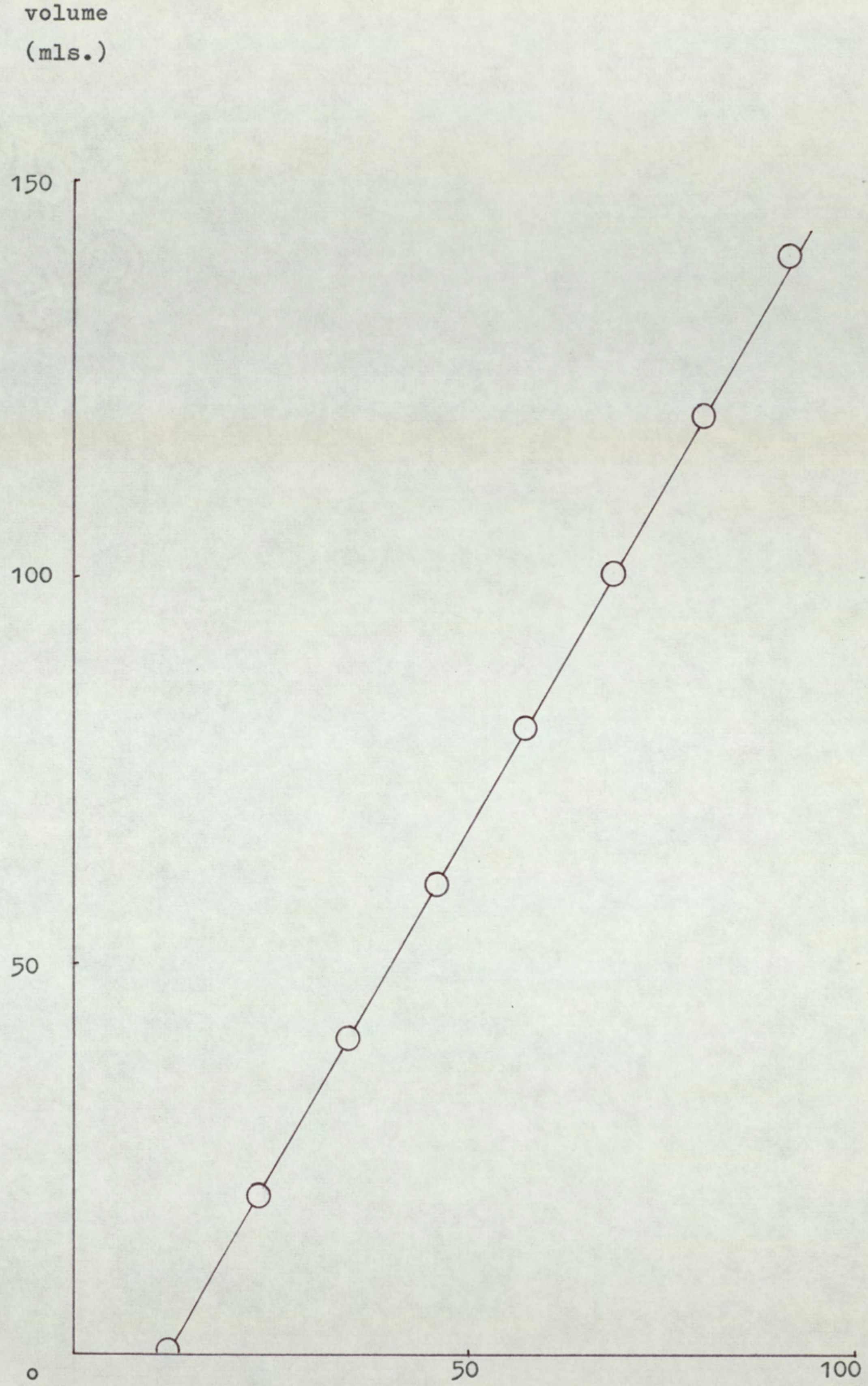


Figure 2.7: Strain gauge calibration curve relating volume of gas absorbed to scale reading.

1965 at 230°C. using a 0.0465" diameter die) in a round-bottomed flask. The resulting slurry was agitated manually for a few minutes, and the solvent removed by rotary evaporation under reduced pressure. Occasionally the walls of the flask were washed down with an additional few mls. of solvent to incorporate final traces of antioxidant. Finally the distillate receiver of the evaporator was emptied and and rotary evaporation continued for a further 30 minutes to remove final traces of solvent. 15g. samples of the impregnated polymer were then pressed between polished stainless-steel plates in an induction press at a pressure of 28 tons per square foot for 2 minutes at 195°C. This resulted in a clear homogeneous film. 1 g. of 0.005" thick film was then cut into strips, placed in the reaction tube shown in Figure 2.8, purged with oxygen, and thermostatted. At the film thickness used rates of oxidation are independent of film thickness[58].

2 Polymerisation Studies

For polymerisations carried out in air a simple dilatometer was used, consisting of a bulb of 10 ml. volume attached to a precision bore capillary of internal diameter about 0.3cm., with two etched marks on the stem. The volume of the bulb and the precise bore of the stem between the etch marks, were determined by filling with mercury and weighing. For experiments in an inert atmosphere the apparatus in Figure 2.9 was constructed and calibrated in the same way. This was used as follows. First the initiator was weighed directly into tube C, and then a sufficient quantity of a solution of the antioxidant dissolved in monomer pipetted into B so that when the apparatus is inverted the bulb A is just filled. The solution was then de-gassed by successive

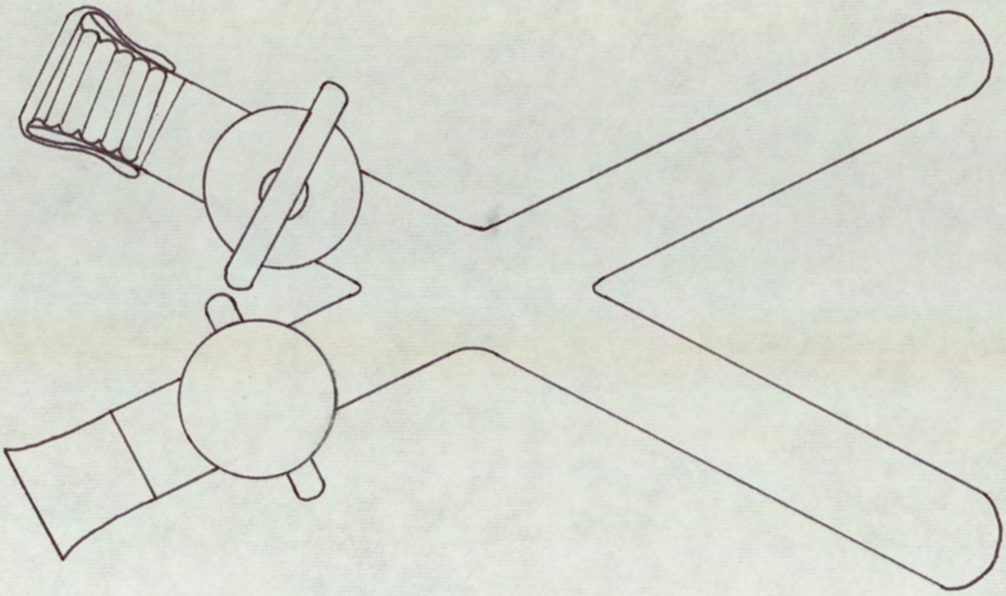


Figure 2.10: Reaction vessel used for kinetic studies

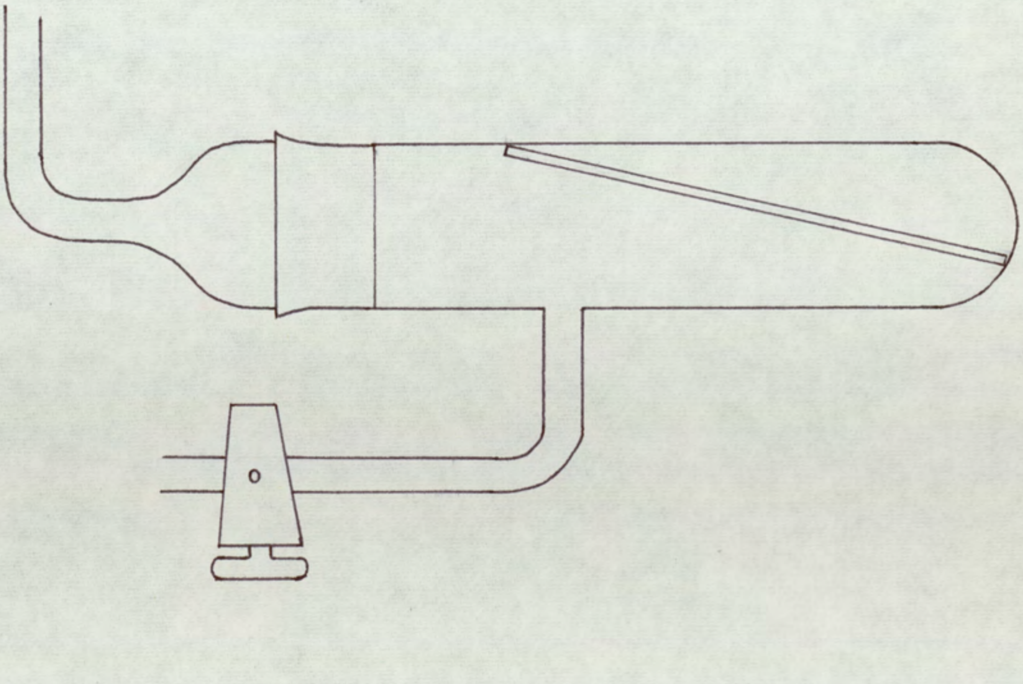


Figure 2.8: Polymer oxygen-absorption vessel

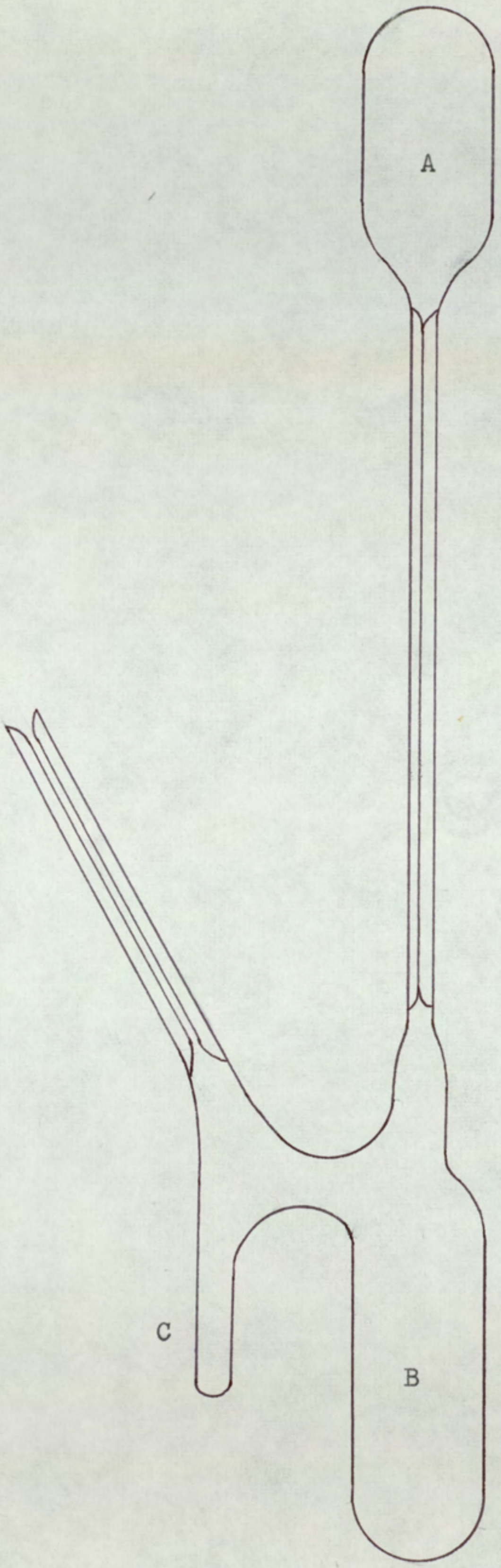


Figure 2.9: Vacuum dilatometer.

freeze-thaw cycles, a vacuum being applied at the side-tube T. The dilatometer was finally filled with nitrogen and sealed with a torch under a slight vacuum, tipped and shaken to dissolve initiator, and then inverted filling bulb A with solution. After allowing time for the walls of the capillary to drain, the level of the meniscus relative to the the bottom etch mark was measured so that by reference to the calibration figures the precise starting volume of monomer was calculated. Reaction was followed by measuring the meniscus level with a cathetometer to the nearest 0.002cm.

Literature values for the densities of styrene and polystyrene were used[59], and the rates of polymerisation calculated as follows.

If D_m = density of monomer

D_p = density of polymer

Then if 1g. of monomer polymerises, the volume change is given by

$$1/D_m - 1/D_p$$

$$\text{Thus \% contraction} = \frac{1/D_m - 1/D_p}{1/D_m} .100$$

$$= \left(1 - \frac{D_m}{D_p}\right) .100$$

If rate of meniscus contraction = $A\text{cm.min.}^{-1}$

bore of capillary = $B\text{ ml.cm.}^{-1}$

volume of bulb = C ml.

$$\text{Then \% contraction} = \frac{A.B}{C} .100\ \%\ \text{min.}^{-1}$$

$$\text{Thus \% conversion} = \frac{A.B}{C\left(1 - \frac{D_m}{D_p}\right)}\ \%\ \text{min.}^{-1}$$

In 1 litre of monomer 1% conversion per minute

$$= \frac{1000}{100} \cdot D_m \text{ g. l.}^{-1} \text{ min.}^{-1}$$

$$= \frac{10 \cdot D_m}{60 \cdot \text{Molecular weight}} \text{ mole l}^{-1} \text{ sec}^{-1}$$

Thus rate of polymerisation is given by

$$R_p = \frac{A.B}{C\left(1 - \frac{D_m}{D_p}\right) \cdot \text{Mol. Wt. Monomer}} \text{ mole l.}^{-1}\text{sec}^{-1}$$

Reactions were followed to low conversions (less than 10%) to ensure that the simple theoretical kinetics of polymerisation were obeyed[60].

3 Hydroperoxide Decomposition Kinetics

A multitude of techniques exist for the estimation of organic peroxide concentrations[61], of which the most widely used are the iodine-liberation methods[62] which rely on the reduction of the peroxide bond by iodide ion in acidic solution:

$$ROOH + 2I^- + H_2O \rightarrow I_2 + ROH + 2OH^-$$

The method used is a slight modification[63] of an earlier method utilising isopropanol-glacial acetic acid as solvent[64] which has the following advantages over other methods.

1 The use of sodium iodide in place of the potassium salt due to its greater solubility keeps the equilibrium

$$I_2 + I^- \rightleftharpoons I_3^-$$

far to the right with the result that:

(a) Loss of liberated iodine due to purging or boiling is prevented since triiodide ion is involatile.

(b) The triiodide ion will not add to olefinic double-bonds[65] so that errors due to unsaturation are eliminated.

2 The use of isopropanol as solvent and the absence of strong acids eliminates atmospheric oxidation of reagents, thus avoiding the need to work in an inert atmosphere.

3 The absence of water in the system avoids low results due to retardation of the iodide-peroxide reaction.

In addition the method is rapid, accurate, and needs only simple apparatus.

Reagents used: 10% v/v acetic acid: isopropranol (A.R. grade containing less than 0.1% water).

20% w/v sodium iodide: isopropanol.

Sodium thiosulphate solution was prepared with boiled distilled water, stabilised with chloroform, kept in a dark bottle, and standardised using potassium iodate(66). 25 ml. of acetic acid-isopropanol reagent and 10ml. of sodium iodide-isopropanol were mixed, and 100 μl. sample of the reaction mixture withdrawn with a syringe (S.G.E. Ltd. No. 100A-RN) and quenched in the mixture. The solution was refluxed for at least five minutes, 5-10 ml. of water added, and the liberated iodine titrated with 0.005N sodium thiosulphate solution. Starch indicator is ineffective in this medium, but the yellow-colorless end point was quite distinct. A blank, although very small, was performed with each batch of reagents. A simple reaction vessel was used (Figure 2.10) in which the reactants are placed in separate arms until equilibrated at the reaction temperature, and then mixed. Samples were withdrawn through the septum, and the two ground-glass sockets enabled the reaction mixture to be degassed when required.

The reaction of iodine with phosphites, especially

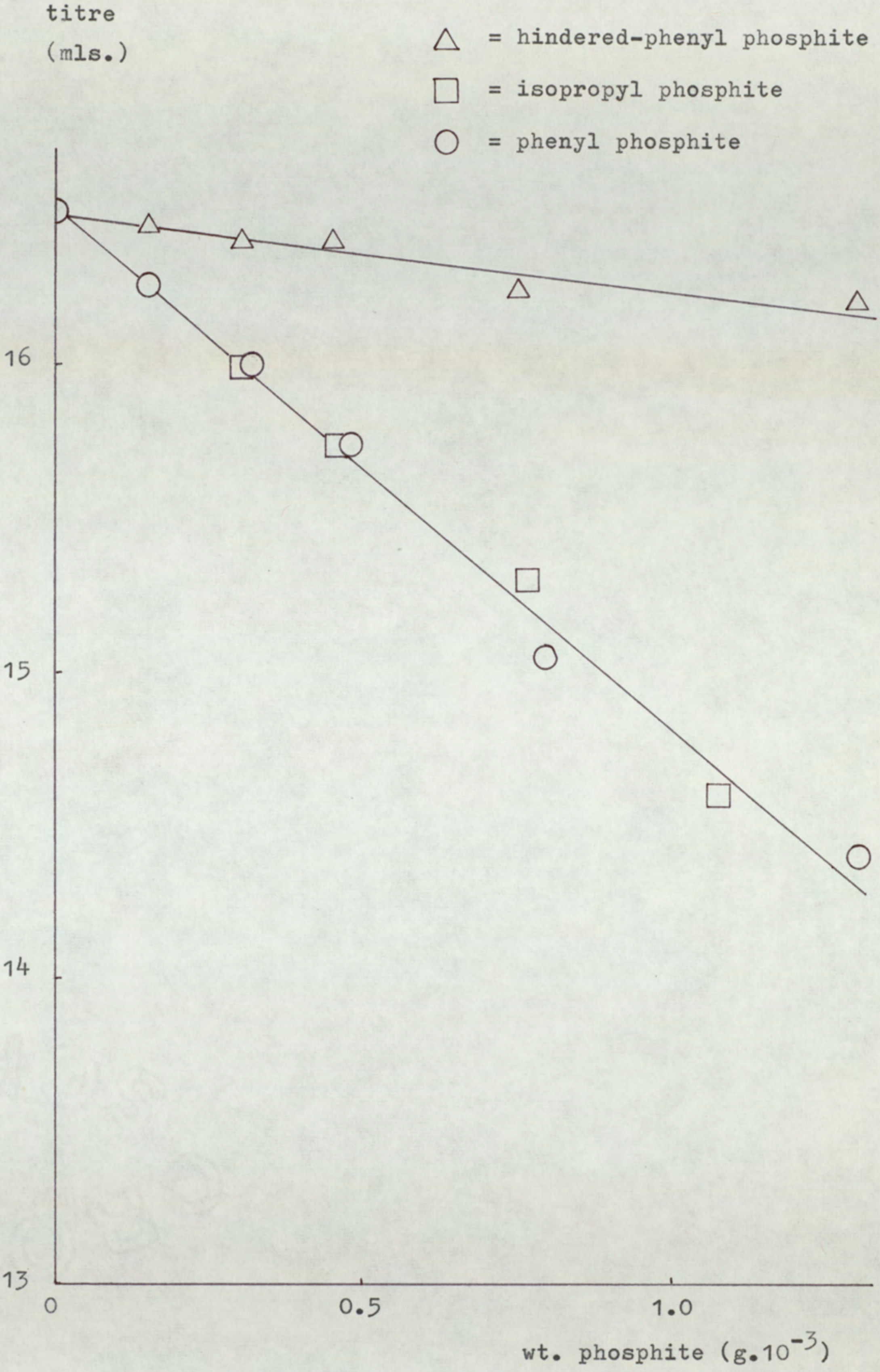


Figure 2.11: Effect of catechol phosphites on the titration of an aliquot of iodine solution with0.0065N sodium thosulphate solution.

catechol phosphites, has been reported[67], so that the effect of added phosphite on the titration was investigated. An iodine solution of known strength was prepared, and the effect of the three catechol phosphites examined on the titre obtained using the above procedure (Figure 2.11). It is clear that in the concentration range at which kinetic experiments have been performed, the error involved if all phosphite reacted with iodine is within experimental error, whilst for much less reactive catechol hindered-phenyl phosphite, considerably higher concentrations have little effect.

4 Kinetic Experiments

Kinetic experiments were performed in insulated baths fitted with a contact thermometer/heater/relay system. For experiments below 25°C., cooling was effected by passage of cold water through helical glass tubes immersed in the bath. For temperatures up to 50°C. water was used as heating medium and temperature control was ±0.02°C. Above 50°C. water was replaced by "Shell" Risella oil and at 75°C. temperature control was ±0.05°C. At 120°-150°C. silicone oil was used and control was ±0.5°C. For reactions over long periods or in an inert atmosphere, or where volatile products were expected, sealed Carius tubes were used; otherwise stoppered tubes were used. Temperatures are uncorrected.

5 Thin Layer Chromatography

Thin layer chromatography was performed on 20 x 20 cm. glass plates spread with Silica Gel G (Machery, Nagel and Co. Ltd.), developed in the normal way in a solvent tank, and components identified by spraying with a suitable reagent.

2.3 Purification of Reagents and Materials

Unless stated otherwise, physical constants are taken from one of several standard works[68].

Fractionation was usually carried out using a column packed with Fenski helices or Dixon gauze rings, but in a few cases the "Buchi" spinning band column was used, with a p.t.f.e. band and variable reflux ratio. The high efficiency of this column was shown[69] to be equivalent to 21 theoretical plates, although this was reduced under vacuum.

Vacuum sublimation was performed with a standard apparatus, the cold finger usually containing CO_2/Acetone.

1 Gas Chromatography Standards

Phenol- A.R. grade was distilled and a middle cut taken at 179°C./748mm.Hg, which cooled to colorless needles m.pt. 36°-40°C., and stored in a darkened dessicator. (182°C., 40.8°C.).

Acetone- A.R. grade was used without further purification.

Acetophenone was distilled at 199°-200°C./748mm.Hg, n_d^{22} = 1.5313 (202°C. n_d^{20} 1.5342).

2,6-di-tert-butyl-4-methyl phenol (ex. I.C.I. H.O.C.) was recrystallized three times from ethanol/water yielding off-white crystals m.pt. 71°C. (70°C.).

2-phenyl-propan-2-ol was distilled at 93°-94°C./13mm.Hg, cooled to a colorless solid, and re-crystallized three times from petroleum ether m.pt. 34°C. (93°C./13mm. 35°-37°C.).

2-phenyl-propene was distilled and a cut taken at 164°-166°C./755mm., n_d^{21} = 1.5362 (167°-170°C., n_d^{21} 1.5384).

p-Cresol- A.R. grade was used without further purification.

1,4-dioxan was washed several times with caustic soda solution, then with distilled water, dried with magnesium sulphate and finally fractionated from sodium through a twelve inch column packed with Dixon gauze rings. B.pt. 101°C./760 mm.Hg, n_d^{21} = 1.4212 (101°C., n_d^{20} 1.4224).

All compounds gave a single peak when chromatogrammed.

2 Reagents

Styrene (stabilised monomer ex Hopkins and Williams) was fractioned through a twelve inch column of Fenski helices and a middle cut taken at 34-35°C./10 mm.Hg, n_d^{21}= 1.5453 (33°C., n_d^{20} 1.5463). It was stored in the dark and re-distilled immediately before use. A more rigorous purification consisted of shaking with dilute caustic soda solution, then with distilled water, drying over anhydrous magnesium sulphate and fractionating from sodium, but the product was shown to give the same rates of polymerisation, and so the method was not used. The simple fractionation gave good reproducibility between different batches of monomer from the same supplier.

Tetralin (Hopkins and Williams Ltd.) was given a preliminary distillation at 206-209°C., then shaken successively with 10% of its volume of concentrated sulphuric acid, 10% sodium carbonate solution, and distilled water, and the sequence repeated five times. The resulting material was dried over anhydrous calcium sulphate and finally distilled from sodium under nitrogen (bubbled through alkaline pyrogallol, concentrated sulphuric acid, and granular caustic soda) at 207-208°C./751 mm.Hg, n_d^{23}= 1.5395 (207°C., n_d^{20}=1.5461). The material was stored in the dark below 0°C., and its hydroperoxide content was not detectable by iodometric titration.

Cumene was purified in the same way with the omission of the acid wash, and distilled at 151°C./746 mm.Hg, n_d^{20}= 1.4910 (151°C., n_d^{20}= 1.4911). Again peroxide content was below the limit of detection.

Cumene Hydroperoxide stabilised with 6% of a 15% w/w slurry of aqueous sodium carbonate (Koch-Light Ltd.) was purified by a modification of Kharasch's method[19]. 50g. (1.25 mole) of caustic soda in 100 ml. of water was added to 152g. (1.0 mole) of hydroperoxide in ligroin at 0°C., the sodium salt filtered, washed with 25%caustic soda solution, then with petroleum ether, and suspended in 500 ml. of water. A stream of carbon dioxide was bubbled through the suspension and when all the hydroperoxide had been re-liberated the solution became opaque and separated into two layers. The lower aqueous layer was extracted three times with petroleum ether, and the combined ethereal fraction washed with dilute sodium bicarbonate solution, and dried over anhydrous sodium carbonate. After removal of solvent the product was distilled at 52-55°C./0.01 mm.Hg as a colourless liquid, n_d^{22}= 1.5238 (53°C., n_d^{20}= 1.5242 [70]). Purity by iodometric titration was better than 98%.

Tertiary-Butyl Hydroperoxide was also purified via its sodium salt in a similar manner, b.pt. 40°C./19 mm.Hg, n_d^{22}= 1.4010 (35°C./17 mm., n_d^{20}= 1.4013 [70]).

Chlorobenzene (Hopkins and Williams Ltd.) was dried over phosphorus pentoxide and fractionated through a two foot column of Dixon gauzes at 131°C./760 mm. Hg, n_d^{21}= 1.5228 (132°C., n_d^{20}= 1.5246).

Nitrobenzene (Hopkins and Williams Ltd.) was purified in the same way, b. pt. 210°C./760 mm.Hg, n_d^{22}= 1.5515 (210°C., n_d^{20}= 1.5526).

Azobisisobutyronitrile (Koch-Light Ltd.) was recrystallised from ether, m.pt. 104°C. (106°C.).

Triphenyl Phosphite (Koch-Light Ltd.) was fractioned twice through a twelve inch column of Dixon gauzes, and collected at $170-172^{\circ}$C./1 mm.Hg, $n_d^{22} = 1.5905$ ($200-201^{\circ}$C./5 mm, $n_d^{20} = 1.5901$).

Triphenyl Phosphate (Koch-Light Ltd.) was recrystallised twice from ethanol/petroleum ether, m.pt. $50-51^{\circ}$C. (50°C.).

Tris(nonylphenyl)phosphite
(Monsanto Chemical's "polygard")
Dilauryl thiodiproprionate m.pt. $38-41^{\circ}$C.
(Robinson Bros. Ltd.)
"Irganox 1010" m.pt. $122-124^{\circ}$C.
(Geigy)

used without purification

2.4 Syntheses

Except where specified, materials were of general purpose reagent grade. P^{31} n.m.r. spectra for the phosphites used are quoted as chemical shifts in Table 2.

Tetralin Hydroperoxide was prepared by the method of Knight and Swern[71] by bubbling a slow stream of oxygen through tetralin at 70°C. After 48 hours about 25% conversion had occurred, which was not increased by further passage of oxygen. An improved purification step[72] was used which gave an improved yield and avoided the necessity to distil. The sodium salt was precipitated by addition of 60g. (1.5 mole) of sodium hydroxide in 500 ml. of water to 170g. of crude hydroperoxide, removed by filtration, washed with ether and air dried. This crude salt was dissolved in 1200 ml. of water and 66g. (0.67 mole) of concentrated sulphuric acid in 500 ml. of water added. Cooling in dry-ice/acetone reprecipitated the hydroperoxide which was filtered, vacuum dried, and recrystallised first from toluene, and then twice from 40/60 petroleum ether yielding 70g. (0.42 mole) of tetralin hydroperoxide as a white crystalline solid, m.pt. 55°C.(56°C.[70]).

The product was 100% pure by iodometric titration.

Catechol Chlorophosphite was prepared by the method of Crofts[73]. 141g. of phosphorus trichloride(1.03mole) was added all at once to 75g. (0.67 mole) of catechol moistened with 1ml. of water. If the reagents are dry the course of the reaction is altered[74]. After one hour a further 60g. (0.4 mole) of phosphorus trichloride was added and the mixture refluxed for two hours. The residue was distilled at 91-92°C./18 mm.Hg as a colourless liquid, n_d^{20} = 1.5710, which crystallised as long needles on storage at 0°C., and fumed in moist air. (91°C./18mm., n_d^{20} = 1.5724). Yield 60% based on catechol. The infra-red spectrum showed a doublet at 475 and 500 $cm.^{-1}$ assigned[75] to the P-Cl stretching mode.

Catechol Isopropyl Phosphite was also prepared by the method of Crofts[73]. 35g. (0.2 mole) of catechol chlorophosphite in 50 ml. ether was added over thirty minutes to a mixture of 12g. (0.2 mole) of isopropanol and 30g. (0.2 mole) of N,N'-diethylaniline in 150 ml. of ether at room temperature. After the addition the mixture was refluxed for thirty minutes, the amine hydrochloride filtered off, and the residue distilled at 91-92°C./10 mm.Hg. A second distillation through a short Vigreux column yielded 23g. of product (56% on chlorophosphite) b.pt. 76°C./3 mm.Hg, n_d^{18} = 1.5060 (73-74°C./3mm., n_d^{17} = 1.4724 [4]).

Found: C= 54.1 ; H=5.51 ; P= 15.09

$C_9H_{11}O_3P$ requires: C=54.5 ; H=5.5 ; P= 15.65.

Catechol Phenyl Phosphite was similarly prepared, b.pt. 155°C./12 mm.Hg, n_d^{20} = 1.5790 in 50% yield (150°C./12 mm.[3]).

Found: C = 61.9 ; H = 3.7 ; P = 12.7

$C_{12}H_9O_3P$ requires: C = 62.0 ; H = 3.8 ; P = 13.3.

Catechol Hindered-Phenyl Phosphite was prepared by a modification of Kirpichnikov's method[5] and choice of solvent was critical. 43g. (0.25 mole) of catechol chlorophosphite in 50 ml. of dry benzene was added dropwise, with stirring, to a mixture of 25g. (0.25 mole) of triethylamine and 55g. (0.25 mole) of 2,6-di-t-butyl-4-methyl phenol in 200 ml. benzene, cooled to 0°C. After the addition the mixture was refluxed for three hours, the precipitate of amine hydrochloride filtered off, and the product distilled at 203-204°C./5 mm.Hg, cooling to a white solid, in 75% yield based on catechol. Recrystallisation from absolute ethanol gave a solid m.pt. 104-105°C. (78-79°C.[5] and 86-89°C.[5]). By careful purification of the starting materials and closely controlled conditions it was possible to omit the difficult distillation step.

Found: C = 69.9 ; H = 7.7 ; P = 7.2

$C_{21}H_{27}O_3P$ requires: C = 70.2 ; H = 7.8 ; P = 8.6.

The proton n.m.r. of this compound was consistent with the proposed structure, and the mass spectrum gave a parent peak at m/e = 358 . By peak-matching

accurate mass = 358.169775

$C_{21}H_{27}O_3P$ = 358.170984 i.e. within 3.6p.p.m.

All three catechol phosphites showed a strong absorption at 1230-1240 $cm.^{-1}$ in the infra-red assigned to the P-O-C stretching mode[75].

Catechol Hindered-Phenyl Phosphate could not be prepared by reaction of catechol chlorophosphate, prepared by the method of Anschütz[76], with the hindered phenol. Intractable products containing the cyclic hydrolysis product catechol hydroxy phosphate were obtained. Attempts to oxidise the phosphite using active manganese dioxide[77], gaseous dinitrogen tetroxide[78] and ultra-violet irradiation in the presence of oxygen[79] were also unsuccessful and usually resulted in the partial decomposition of phosphite to unidentified fragments. Aqueous oxidations were considered unsuitable[80] due to the possibility of hydrolysis. Ozone oxidation[81] was finally found to give the desired product in low yield. 10g. of phosphite (0.028 mole) in 30 ml. of methylene chloride were cooled to -78°C. in dry-ice/acetone and 60 litres per hour of air, containing ozone equivalent to 0.7g. per hour, were bubbled through the solution for two hours. Removal of solvent followed by trituration with methanol gave a white solid, which was recrystallised from ethyl acetate, m.pt. 223-225°C. (yield 15%).

found: C = 67.21 ; H = 7.30 ; P = 8.35

$C_{21}H_{27}O_4P$ requires: C = 67.3 ; H = 7.25 ; P = 8.28.

The infra-red spectrum (Figure 2.12) was closely similar to that of the parent phosphite with an additional strong band at 1310 cm.$^{-1}$ assigned to the phosphoryl absorption[75], and the n.m.r. spectrum was consistent with the structure assumed throughout this work.

The mass spectrum showed a parent ion at m/e = 374. By peak-matching: accurate mass = 374.162995

$C_{21}H_{27}O_4P$ = 374.164134 i.e. within 3 p.p.m.

Subsequently it was found that phosphate could be obtained in better yield by reaction of phosphite with t-butyl hydroperoxide. 8g. of the catechol hindered-phenyl phosphite (0.025 mole) and 2g. (0.025 mole) of t-butyl hydroperoxide were thermostatted in 100ml. of chlorobenzene at 75°C. until no more hydroperoxide remained. Removal of solvent and volatiles by rotary evaporation yielded a brown solid from which the product was obtained in 80% yield by trituration with methanol, with the same physical constants as before.

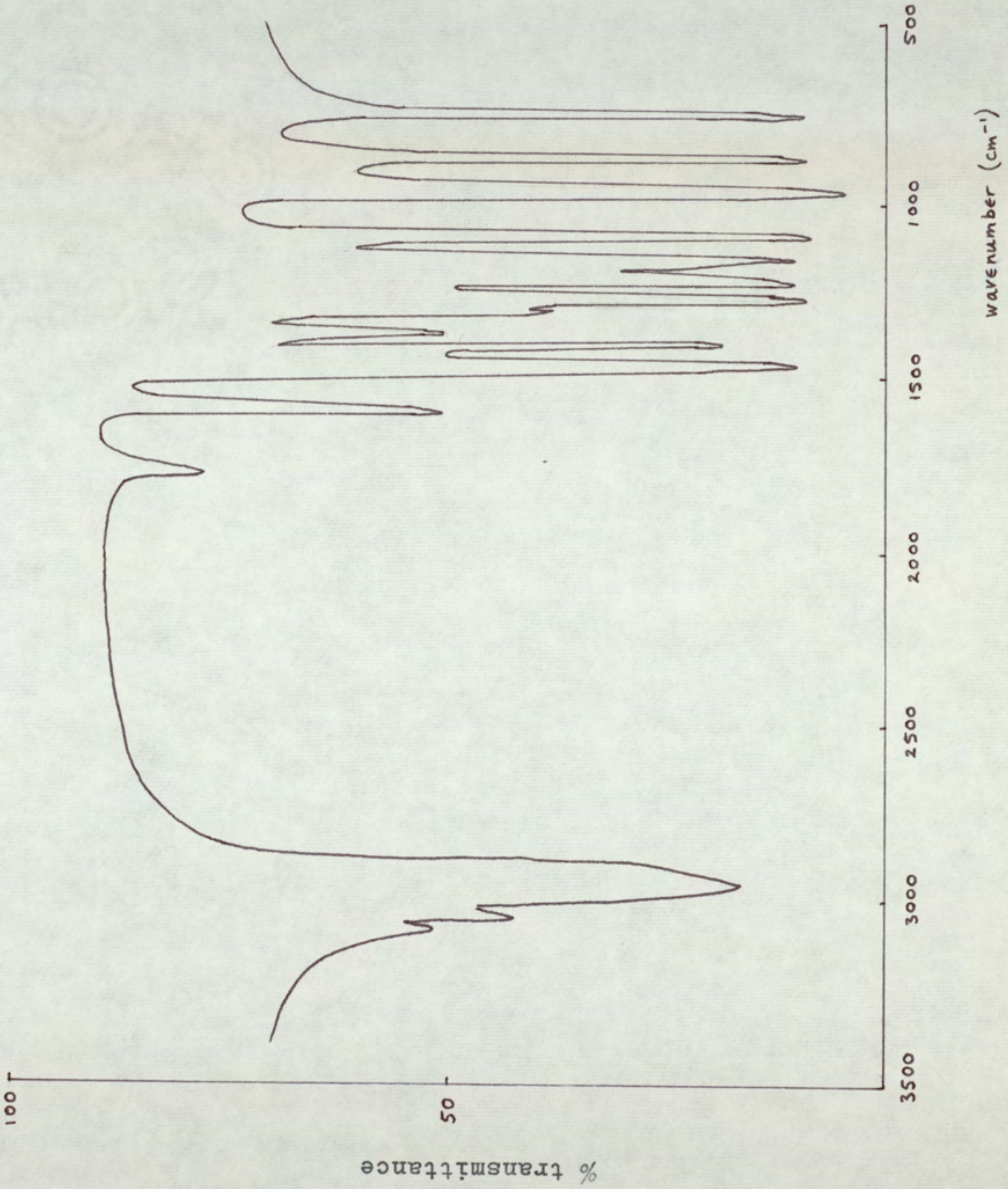


Figure 2.12: Infra-red spectrum of catechol hindered-phenyl phosphate (KBr disc; reference:air).

Catechol Hydroxy Phosphate was prepared by heating 71g. (0.5 mole) of phosphorus pentoxide with 137g. (1.25 mole) of catechol for thirty minutes at 100°C.[82]. Distillation at 135°C./3 mm.Hg yielded a viscous syrup which solidified to a glassy solid on standing. Attempts at purification by vacuum sublimation and by recrystallisation from a wide variety of solvents were unsuccessful, so that the product was finally fractionated through a Dufton all-glass column at 125-130°C./3 mm.Hg (125°C./3 mm.[82]). Exposure to the atmosphere resulted in rapid hydrolysis and an infra-red spectrum could not be obtained. The mass spectrum showed a parent-peak at 172, which by peak-matching ; accurate mass = 171.992257

$C_6H_5O_4P$ = 171.990853

i.e. within 2 p.p.m.

Mono(o-hydroxyphenyl)phosphoric Acid was prepared[82] by dissolving catechol hydroxy phosphate in a small amount of water, removing the excess by rotary evaporation to leave a syrup which solidified on cooling. Recrystallisation from benzene/ethyl acetate gave a white solid, m.pt. 139-141°C. (139°C.[82]). The infra-red spectrum contained a broad shallow band from 2,000-3,500 cm.$^{-1}$, with maximi at 2,700 and 3,300 cm.$^{-1}$ associated with considerable hydrogen-bonding[75].

Ethylene Chlorophosphite was prepared[83] by adding 139 ml. (2.5 mole) of anhydrous ethylene glycol, in portions, to 220 ml. (2.5 mole) of phosphorus trichloride in 500 ml. of methylene chloride at room temperature. When evolution of hydrogen chloride had ceased, the solvent was removed by rotary evaporation and the product distilled as a colourless liquid at 45-47°C./15 mm.Hg (46.5°C./15 mm.[83]).The phosphite, which fumed in moist air, was obtained in 66% yield.

Propylene Chlorophosphite was similarly prepared from propane-1,3-diol and distilled at 66°-67°C./15 mm.Hg. in 60% yield, n_d^{22} = 1.4885 (66°C./15 mm., n_d^{25} = 1.4884[83]).

Ethylene Isopropyl Phosphite- 24g. (0.4 mole) of isopropanol in 50 ml. of petroleum ether was added slowly, with stirring, below 5°C., to a mixture of 50g. (0.4 mole) of ethylene chlorophosphite and 48g. (0.6 mole) of pyridine in 250 ml. of petroleum ether. The amine hydrochloride was filtered off and the product distilled at 67°-69°C./25 mm.Hg. A second fractionation was performed using the "Buchi" spinning band fractionating column at 50°C./10 mm.Hg. n_d^{20} = 1.4365 (69°C./25 mm. n_d^{25} = 1.4347[83]).

Found: C = 39.7 ; H = 7.5 ; P = 19.1

$C_5H_{11}O_3P$ requires: C = 40.0 ; H = 7.3 ; P = 20.7

Propylene Isopropyl Phosphite was prepared in a similar manner and distilled first at 82°-83°C./25 mm.Hg. and then using the spinning band at 52°C./5 mm.Hg. n_d^{23} = 1.4415

Found: C = 43.2 ; H = 7.96 ; P = 17.35

$C_6H_{13}O_3P$ requires: C = 43.9 ; H = 7.94 ; P = 18.9

Galvinoxyl (2,6-di-t-butyl-α(3,5-di-t-butyl-4-oxo-2,5-cyclohexadiene-1-ylidene)-p-tolyloxy) was prepared exactly according to the method of Bartlett[84], m.pt. 157°-158°C. (153°C.). Purity by iodometric titration was better than 99%

Elemental analyses were performed in duplicate by Weiler and Srauss Ltd., of Oxford.

Table 2: P^{31} n.m.r. Spectra of Phosphites Studied.

Phosphite	Chemical Shift	Reported Value	Reference	Sample
Catechol isopropyl phosphite	-131	-		neat liquid
Catechol phenyl phosphite	-129	-		"
Catechol hindered-phenyl phosphite	-140	-		30% w/w in $CHCl_3$
Triphenyl phosphite	-129	-128 -127 -125	85,86 87 88	neat liquid
Ethylene isopropyl phosphite	-135	-134	89	"
Propylene isopropyl phosphite	-130	-		"

3. OXYGEN ABSORPTION -Results and Discussion.

As an attempted diagnostic test for determining the predominant mode of antioxidant action, the effect of a number of cyclic and linear phosphites on the oxidation of hydrocarbons has been evaluated. Oxidation was initiated by azobisisobutyronitrile (AZBN) and by the hydrocarbon hydroperoxide, and reaction followed using the technique described earlier. In this way earlier workers had shown that it is sometimes possible to distinguish chain breaking from peroxide decomposing antioxidants[90] by the type of reaction profile obtained. This approach will be described in detail in the discussion which follows. Two possible reaction intermediates and two phosphates were similarly evaluated.

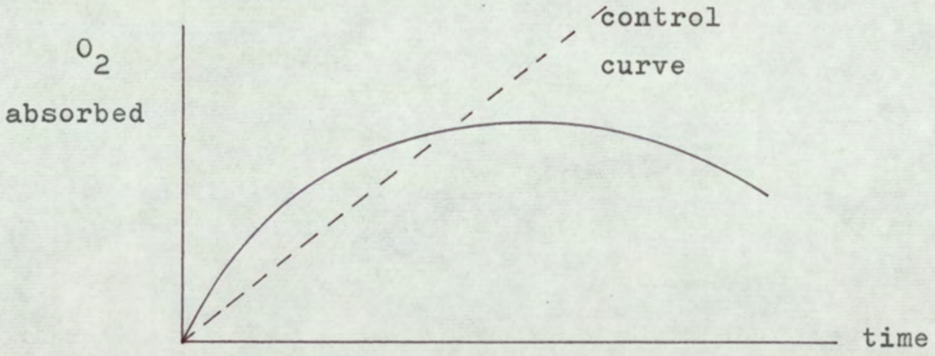
Tetralin was used initially, as it oxidises at a convenient rate at 50°C., has a crystalline hydroperoxide, and has been extensively studied[56,91-96]. Isopropyl benzene (cumene) was subsequently used, to facilitate product studies, at 75°C. In the main the latter results will be discussed, but the same results were obtained with both substrates.

In addition, induction periods to oxidation of cumene without added initiator were measured (at 120°C.) as a function of phosphite concentration.

3.1 Results

3.1.1 Hydroperoxide initiated experiments in every case were carried out with initial cumene hydroperoxide concentration = 0.20M and initial phosphite concentrations of 2×10^{-2} to 2×10^{-3}M. Prior to the addition of the antioxidant,at this hydroperoxide concentration, steady-state oxidation kinetics (i.e. linear oxygen absorption) were attained within the time required for thermal equilibration. The initial rate was $1.86 \pm 0.13 \times 10^{-5}$ moles O_2/ mole cumene/minute.

The three catechol phosphites were first evaluated. The isopropyl and hindered-phenyl compounds showed an initial pro-oxidant effect after addition i.e. the instantaneous rate of oxygen uptake was initially increased. Subsequently this rapid rate decreased, oxidation stopped, and was followed by gas evolution, as shown in Figure 3.1 and diagrammatically below



In all cases gas evolution eventually ceased.

The largest pro-oxidant effect occurred at the highest concentration of phosphite, and the effect occurred and stopped much more rapidly with the isopropyl compound. The catechol phenyl phosphite showed a rapid gas evolution immediately after addition to the oxidising system. In all cases the evolved gas was oxygen containing a small amount of methane. To overcome the masking effect of the gas absorption and evolution possibly occurring simultaneously

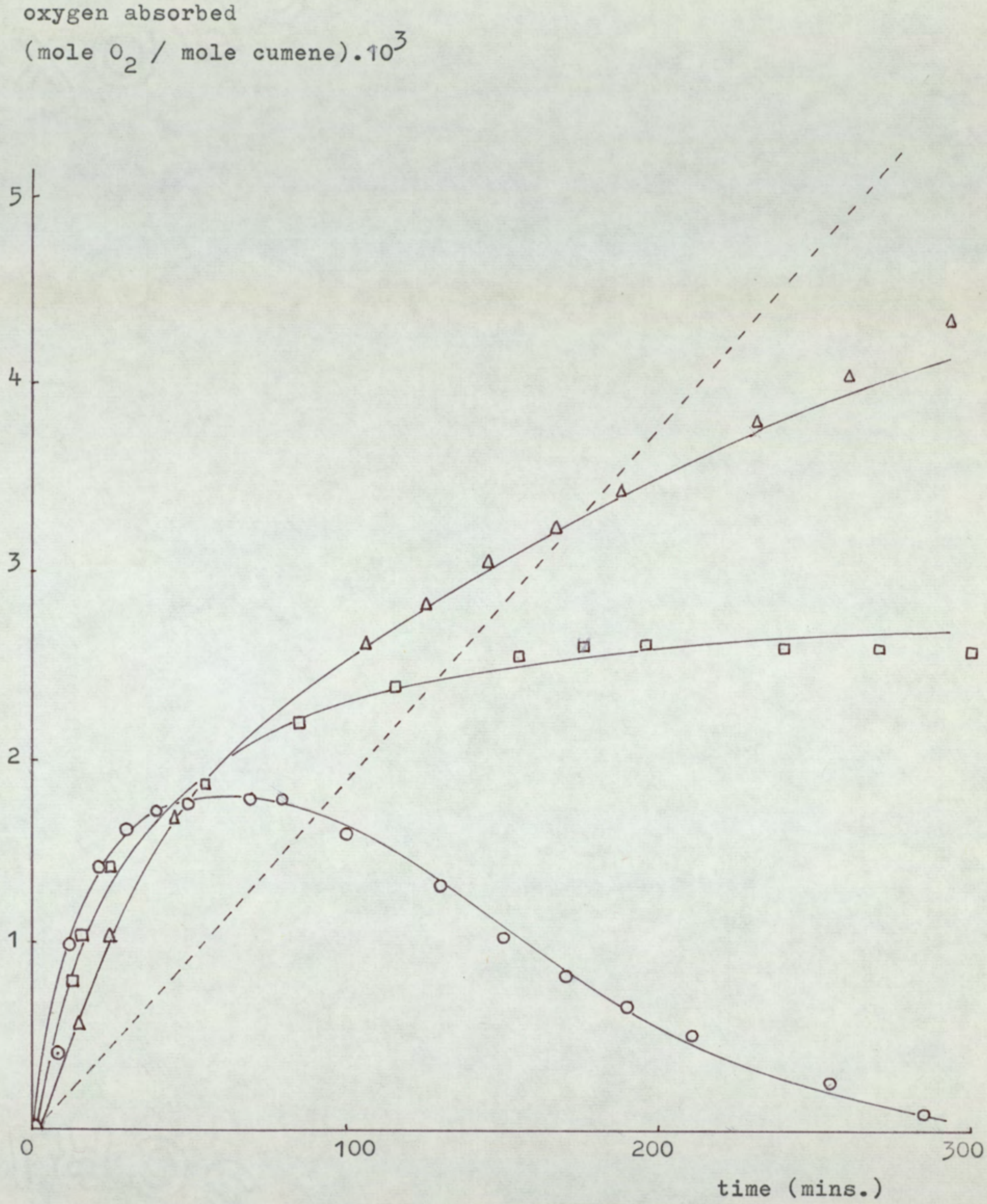


Figure 3.1: Inhibition of the cumene hydroperoxide-initiated oxidation of cumene in O_2 at 75°C. by catechol hindered-phenyl phosphite. $[CHP]_o = 0.2M$

△ = 2×10^{-3}M; □ = 1×10^{-2}M; ○ = 2×10^{-2}M.

the experiments were then repeated in a nitrogen atmosphere. Since no absorption could then occur, the true evolution was observed indicating that oxidation of the substrate did not cease at once, but, as in oxygen, evolution finally stopped. All the catechol phosphites eventually stop oxidation. At higher concentrations the curves obtained in nitrogen and oxygen were the same except for the initial portion (shown for the hindered-phenyl phosphite in Figure 3.2) indicating that oxidation was inhibited.

Triphenyl phosphite also showed a pro-oxidant effect, although much smaller than with the catechol compounds, after which the rate of oxidation was reduced to an approximately constant value, the greatest retardation occurring at the highest concentration (Figure 3.3). Analogous results were obtained using tris(nonylphenyl) phosphite in the tetralin system, and in both cases no gas evolution was observed.

The catechol hindered-phenyl phosphate was evaluated in the same way. This time no pro-oxidant stage was observed and there was no detectable gas evolution. The rate of oxygen uptake was again autoretarded. Somewhat surprisingly almost the same reaction profile was obtained over a 6-fold range of phosphate concentrations (0.005 to 0.03 mole l^{-1}), shown in Figure 3.4.

In contrast, triphenyl phosphate had no effect whatever on the rate of oxidation, over the same concentration range.

Catechol hydroxy phosphate, a phosphite-hydroperoxide reaction product was briefly examined. Duplicate experiments in oxygen and nitrogen showed that once again gas evolution occurred, and the reaction was autoretarded. (Figure 3.4 a)

Finally it was shown (Figure 3.5) that the reaction of phosphite and hydroperoxide in chlorobenzene in oxygen showed an initial small oxygen uptake followed by evolution. Since no oxidisable substrate is now present, the gas must have been absorbed by the reactants themselves.

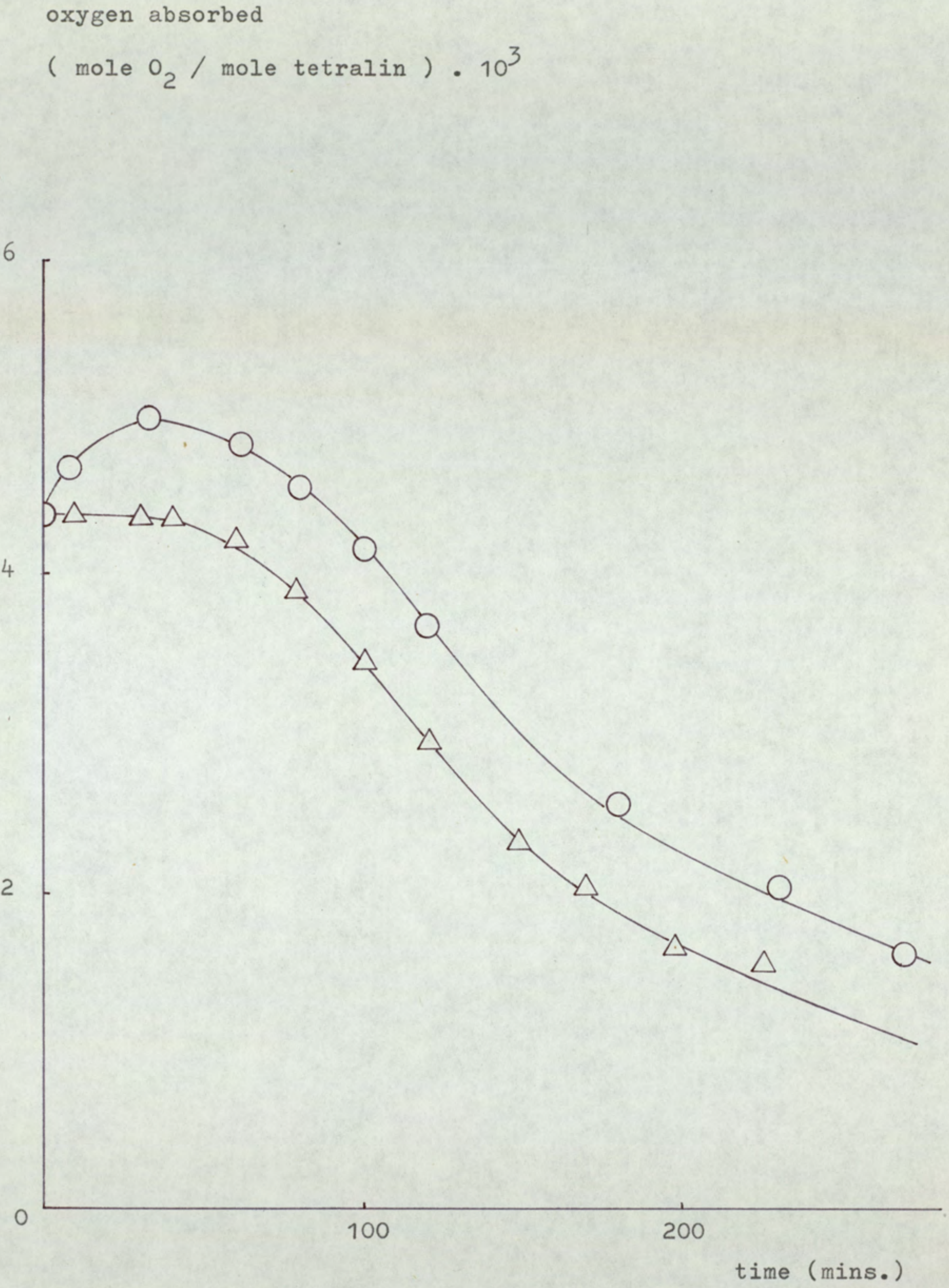


Figure 3.2: Gas evolution during the reaction of catechol hindered-phenyl phosphite (1.25×10^{-2}M) with tetralin hydroperoxide (0.25M) in tetralin at 50°C.

△ in N_2 ; ○ in air.

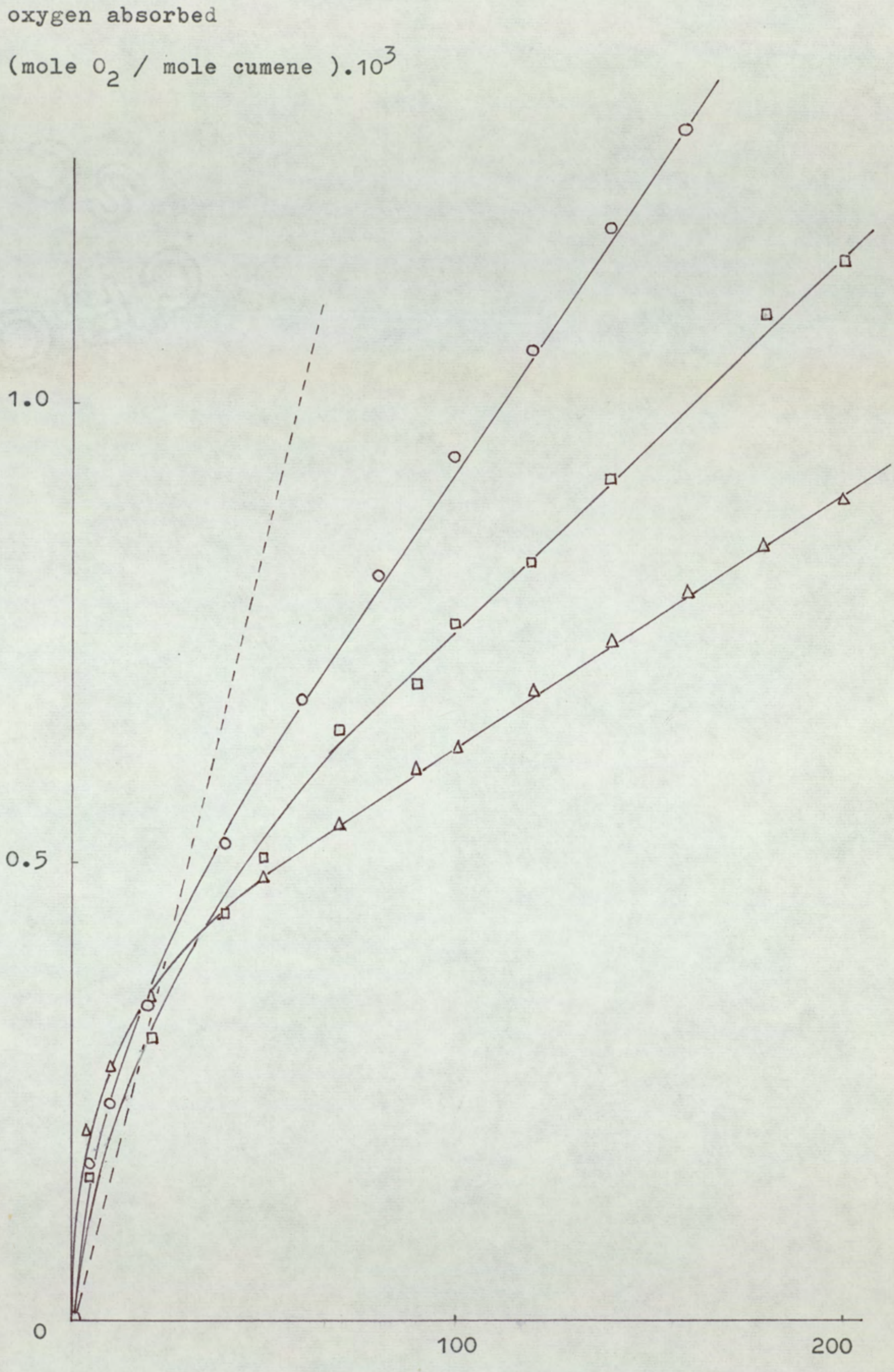


Figure 3.3: Triphenyl phosphite-inhibited oxidation of cumene initiated by 0.2M CHP in O_2 at 75°C.

○ = 0.01M ; □ = 0.02M ; △ = 0.03M phosphite.

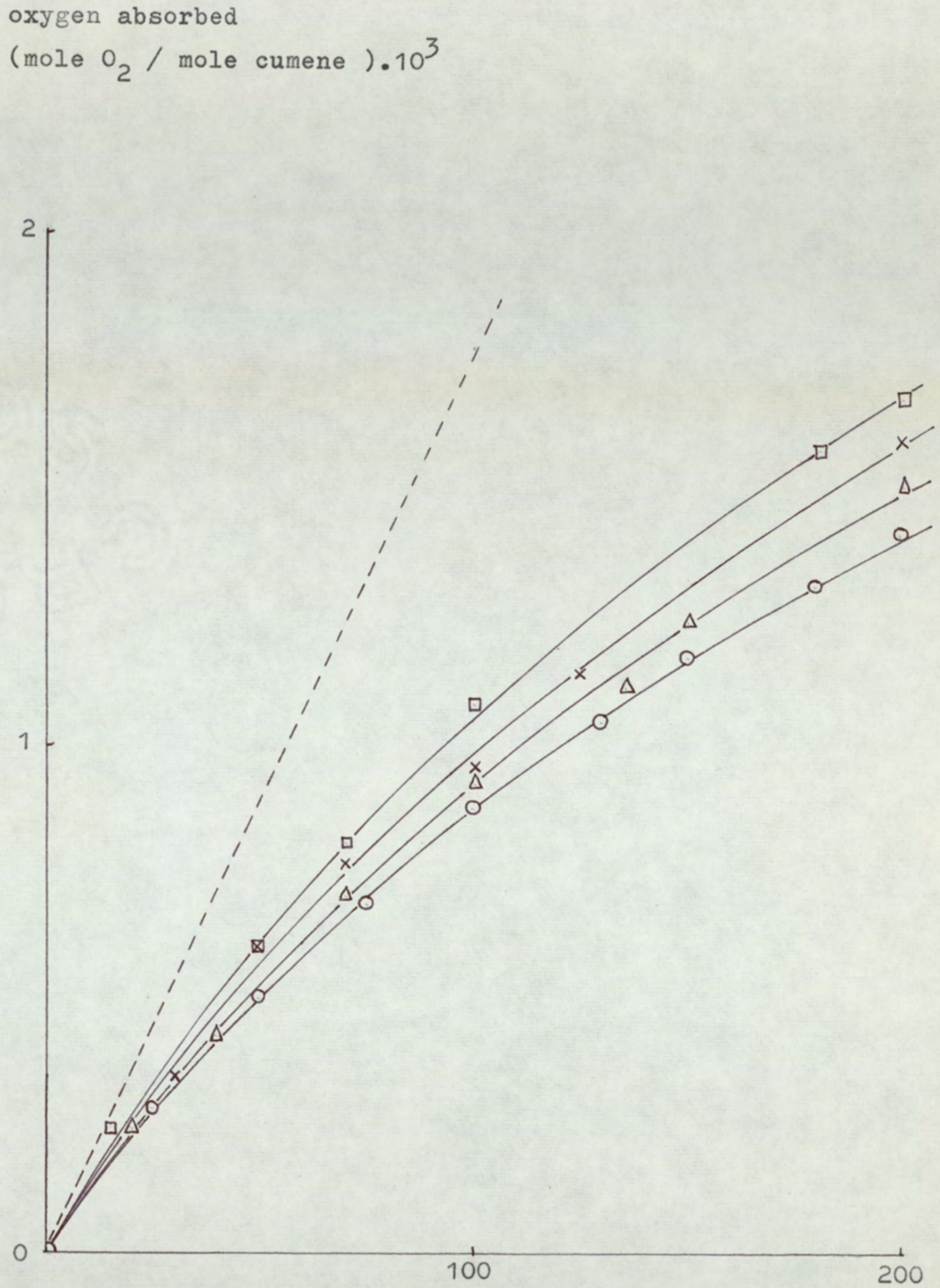


Figure 3.4: Inhibition of the cumene hydroperoxide-initiated oxidation of cumene in O_2 at 75°C., by catechol hindered-phenyl phosphate. $[CHP]_o$ = 0.2M.

○ = 0.005M ; Δ = 0.01M ; × = 0.02M ; □ = 0.03M.

(all curves are the average of 4 runs)

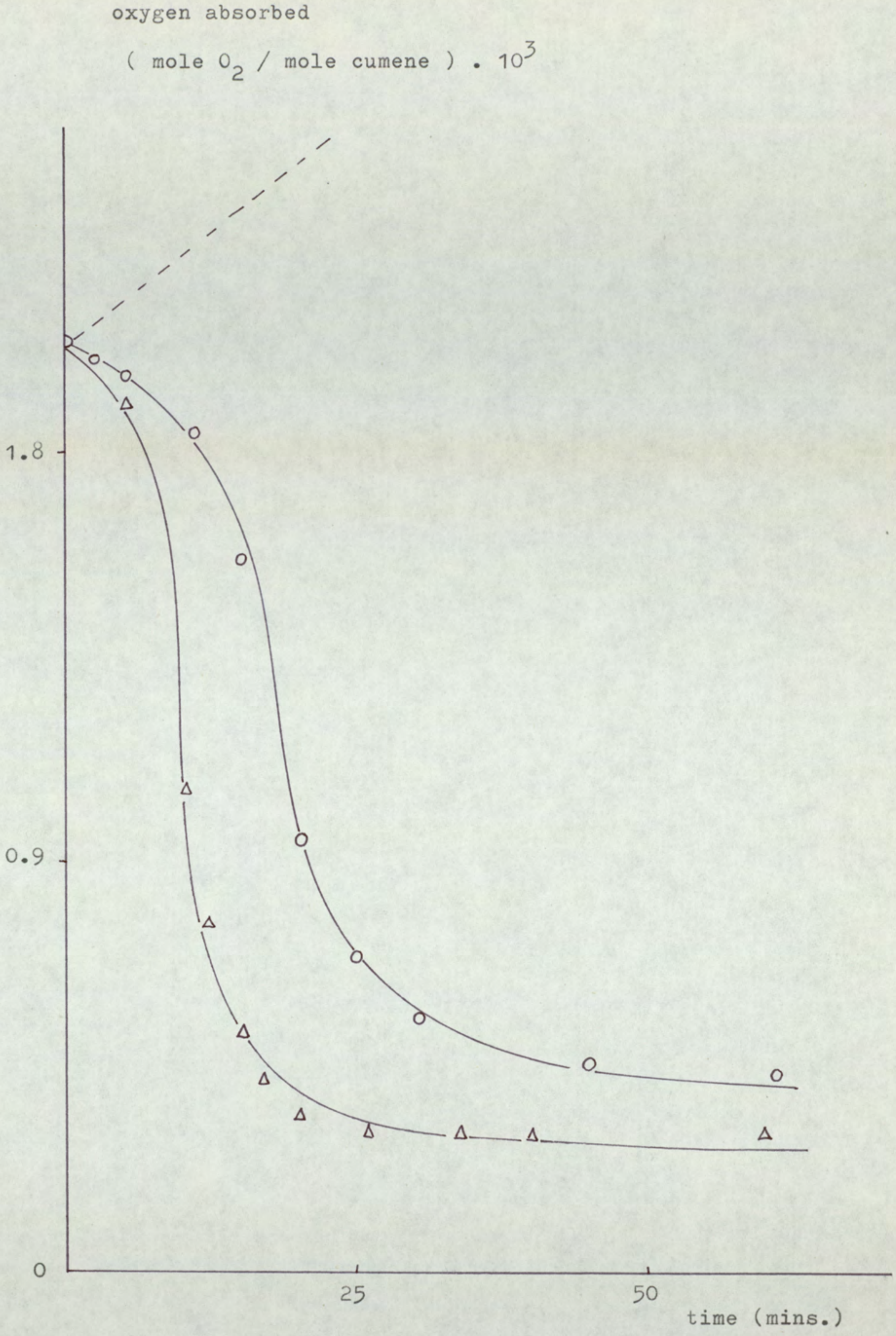


Figure 3.4a: Gas evolution during the reaction of 0.02M catechol hydroxy phosphate with 0.2M cumene hydroperoxide in cumene at 75°C.

○ in O_2; △ in N_2

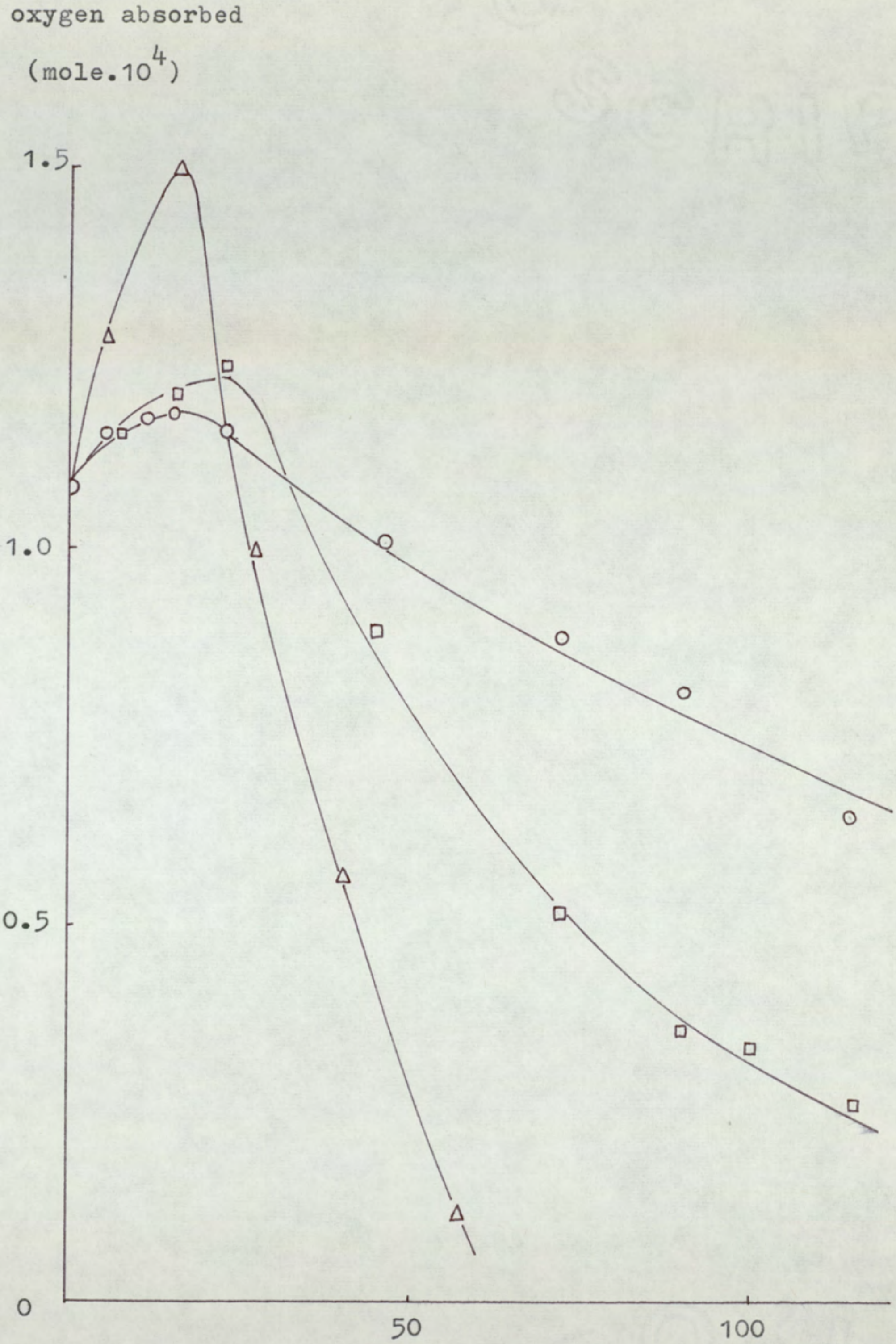


Figure 3.5: Gas evolution during the reaction of catechol hindered-phenyl phosphite with 0.2M cumene hydroperoxide in chlorobenzene at 75°C.

○ = 0.0095M ; □ = 0. 021M ; Δ = 0.04M.

3.1.2 AZBN initiated experiments were all performed with an initial AZBN concentration of 0.02 mole l^{-1}, which gave an initial steady-state rate of oxidation equal to $4.1 \pm 0.12 \times 10^{-5}$ moles O_2/ mole cumene/minute at 50°C., and $1.22 \pm 0.04 \times 10^{-4}$ moles O_2/mole cumene/minute at 75°C.

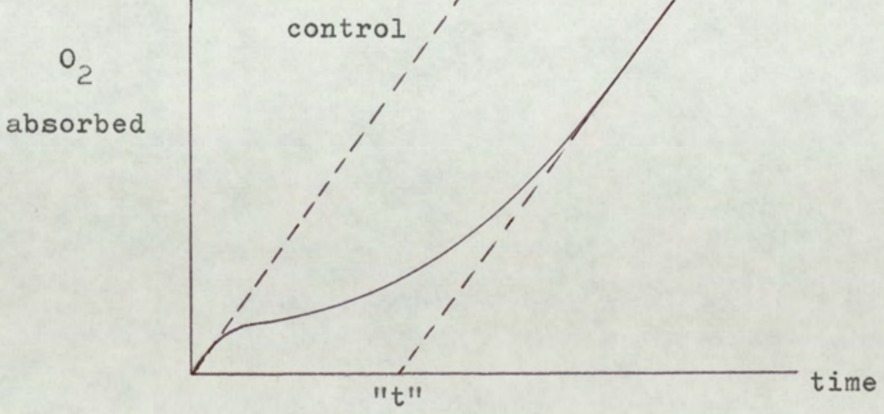
All three catechol phosphites were found to show autoretardation. Oxidation stopped more or less rapidly after addition, and the effectiveness decreased in the order:

R = phenyl $>$ isopropyl $>$ hindered-phenyl

The curves for the three phosphites are shown in Figure 3.6 and for the latter compound in detail in Figure 3.7.

The highest concentration of phosphite resulted in the least oxygen absorbed prior to complete inhibition, and the catechol hindered-phenyl phosphate showed the same type of behaviour.

Again a completely different type of behaviour was observed with the non-cyclic compounds. Triphenyl phosphite, after a short period of autoinhibition, showed a gradually increasing rate of oxygen absorption, until the rate of uptake regained the initial (uninhibited) rate (Figure 3.8). Again the highest concentration showed the greatest effect, and the time taken to regain the initial rate, "t" ,



obtained by extrapolation, was a function of the phosphite concentration, a plot of concentration versus "t" being a smooth curve.

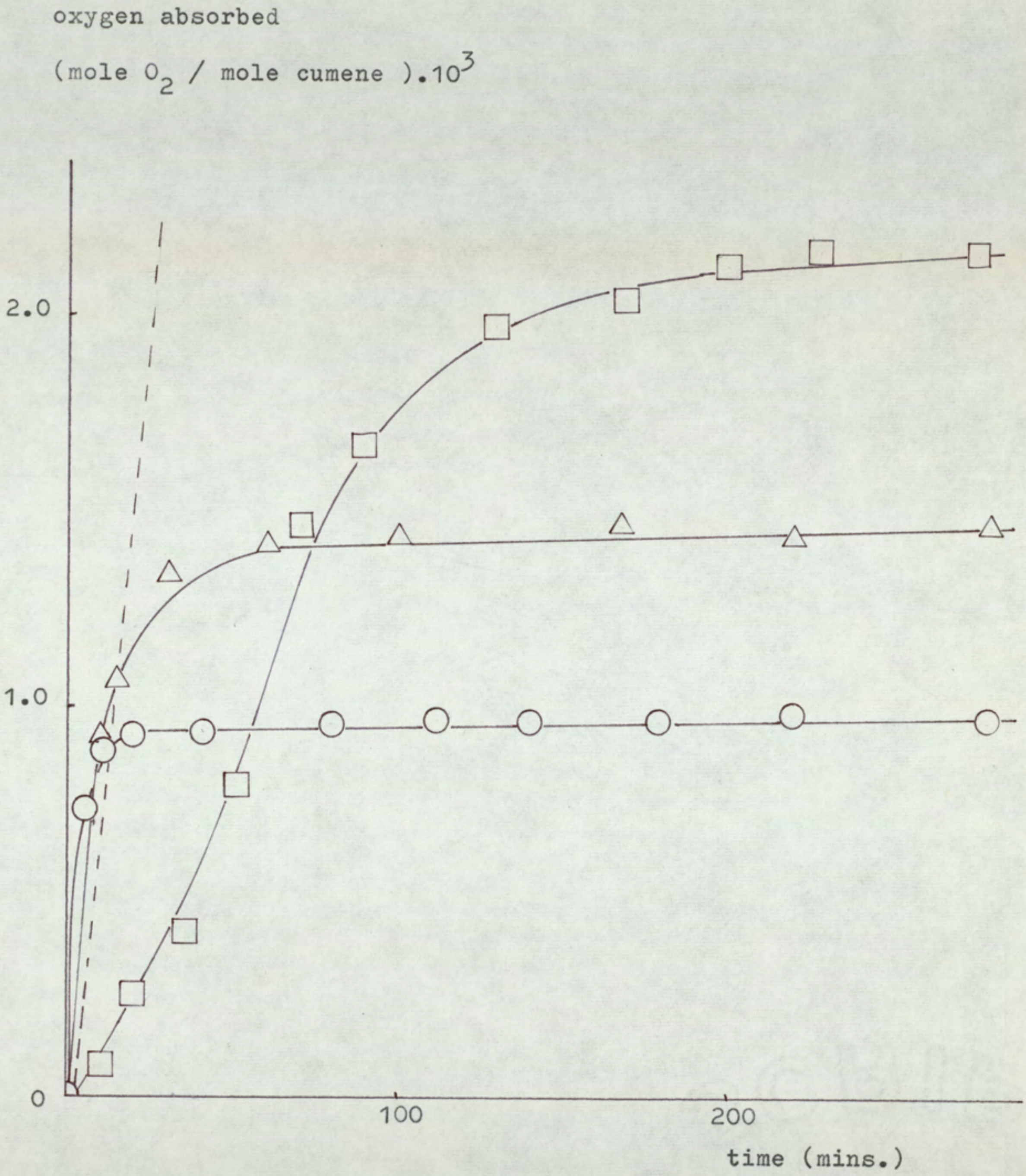


Figure 3.6: Inhibition of the AZBN-initiated oxidation of cumene in O_2 at 50°C. by 0.2M catechol phosphites

$[AZBN]_o = 0.02M$

□ = hindered-phenyl phosphite

△ = isopropyl phosphite

○ = phenyl phosphite

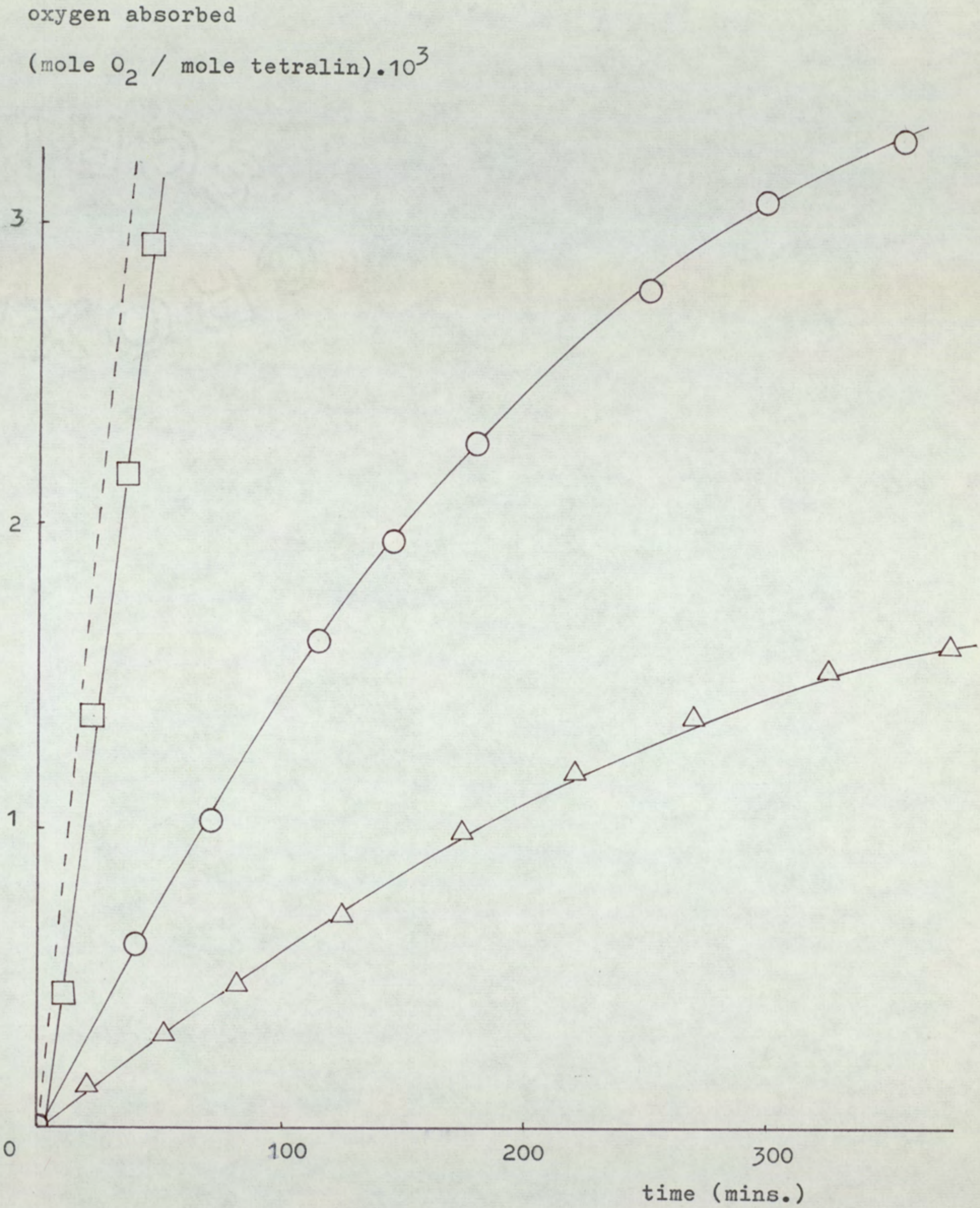


Figure 3.7: Inhibition of the AZBN-initiated oxidation of tetralin in O_2 at 50°C. by catechol hindered-phenyl phosphite. $[AZBN]_o = 0.025M$

□ = $2.5 \times 10^{-3}M$; ○ = $7.5 \times 10^{-3}M$; △ = $1.25 \times 10^{-2}M$

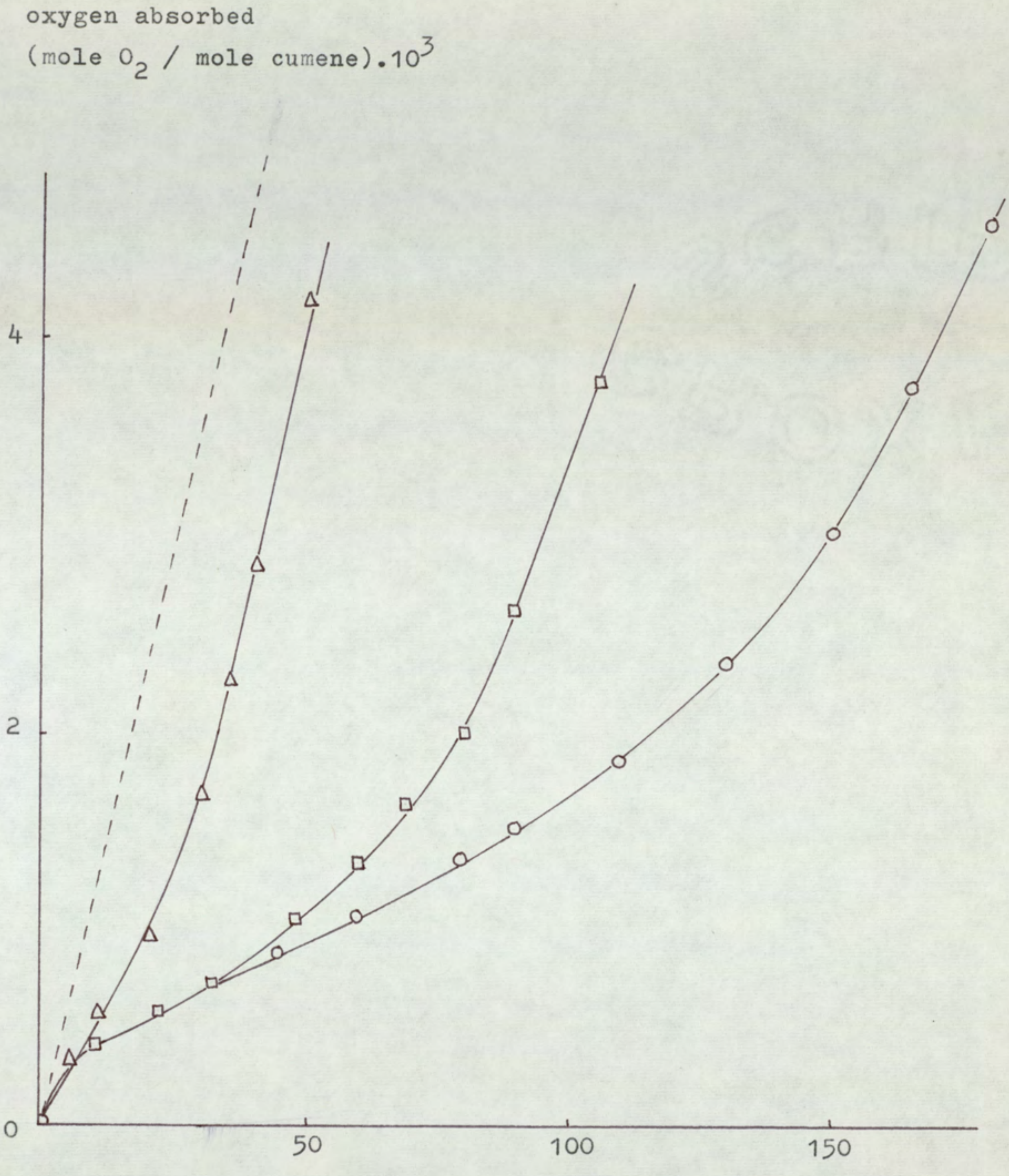


Figure 3.8: Inhibition of the AZBN-initiated oxidation of cumene in oxygen at 75°C. by triphenyl phosphite. $[AZBN]_o$ = 0.01M.

△ = 0.022M ; □ = 0.035M ; ○ = 0.051M.

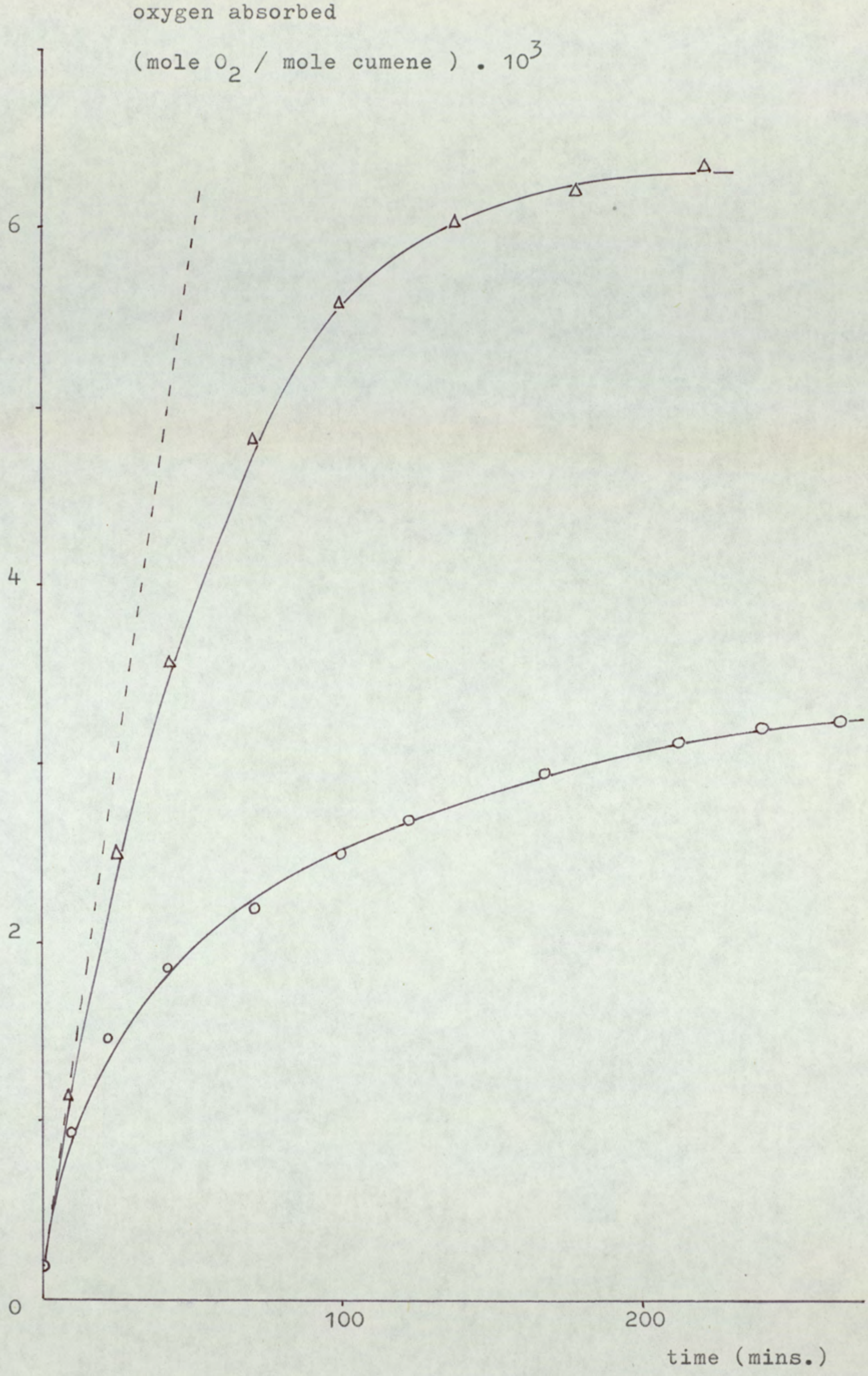


Figure 3.8a: Inhibition of the AZBN-initated oxidation of cumene in O_2 at 75°C. by catechol hindered-phenyl phosphate. $[AZBN]_o$ = 0.01M

Δ = 0.005M; o = 0.02M.

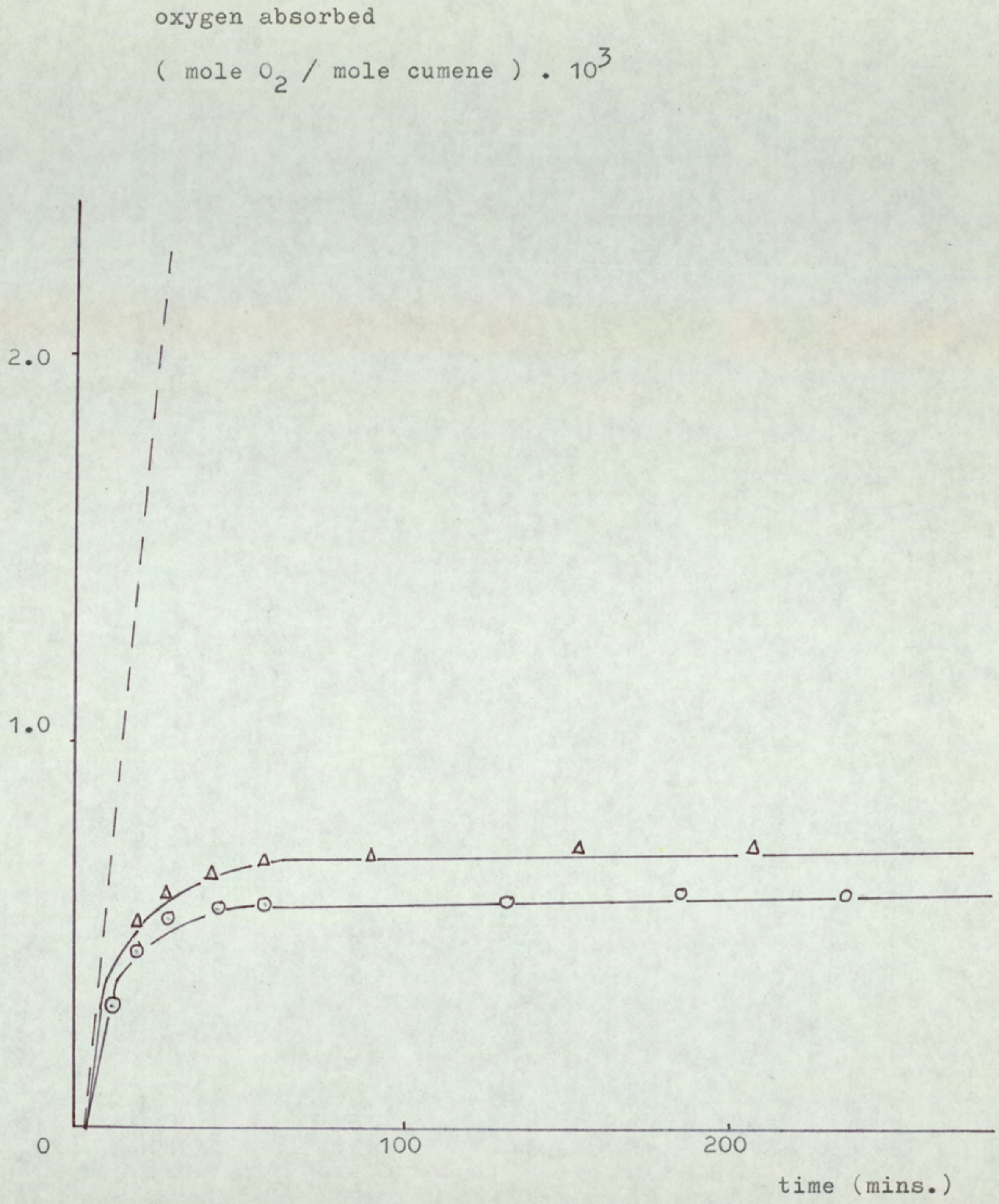


Figure 3.8b: Inhibition of the AZBN-initiated oxidation of cumene in O_2 at 75°C. by

○ = 0.02M catechol hydroxy phosphate

Δ = 0.02M mono(o-hydroxyphenyl)phosphoric acid

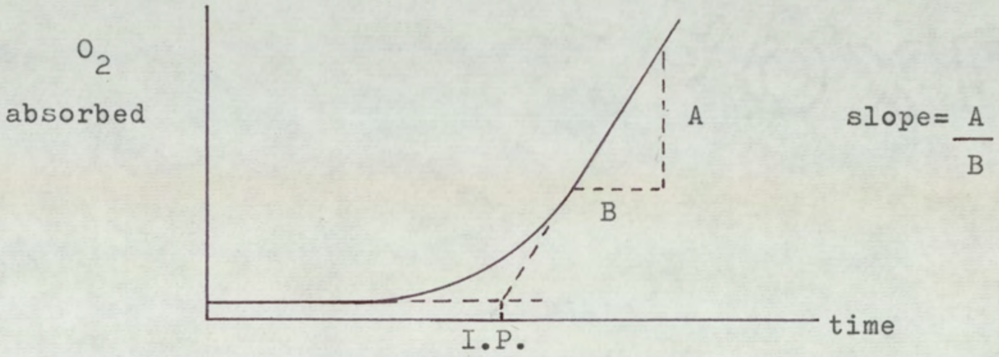
$[AZBN]_o$ = 0.02M

Again in contrast to the catechol compounds, triphenyl phosphate was inert in this oxidation, the former being shown in Figure 3.8a.

Catechol hydroxy phosphate and mono(o-hydroxyphenyl) phosphoric acid both showed autoretardation and eventually inhibited the reaction, the cyclic compound halting oxidation more rapidly than its hydrolysis product at the same concentration. (Figure 3.8b)

It was shown by carrying out duplicate experiments in which the antioxidant was added simultaneously with the initiator, rather than to the autoxidising system, that in the experiments described the amount of hydroperoxide formed before the addition of phosphite did not effect the reaction profile i.e. these inhibitions are not due to an initially formed phosphite-hydroperoxide reaction product.

3.1.3 Induction Period measurements were made using a range of concentrations of the hindered-phenyl phosphite in cumene, in oxygen, at 120°C. The induction periods were defined by extrapolation of the steady-state rate of oxygen uptake back to the base line:



The results, shown graphically in Figure 3.9 as a semi-logarithmic plot, show that up to a concentration of about 2.5 x 10^{-3} mole l^{-1} the induction period (as a logarithm) increased linearly with time. Above this "critical" concentration an enormous increase occurred, the induction period increasing to 500 hours at 2.8 x 10^{-3} mole l^{-1}.

At low phosphite concentrations(less than 2 x 10^{-3} molar) the end of the induction period was quite sharp, and the subsequent rate of oxygen uptake quite rapid. With increasing concentration, however, the ultimate slope A/B in the diagram decreased, and Figure 3.10 shows that this slope was directly proportional to phosphite concentration.

In all cases coloured products resulted, and a dark tarry residue, probably polymeric in nature, adhered to the bottom of the reaction vessel.

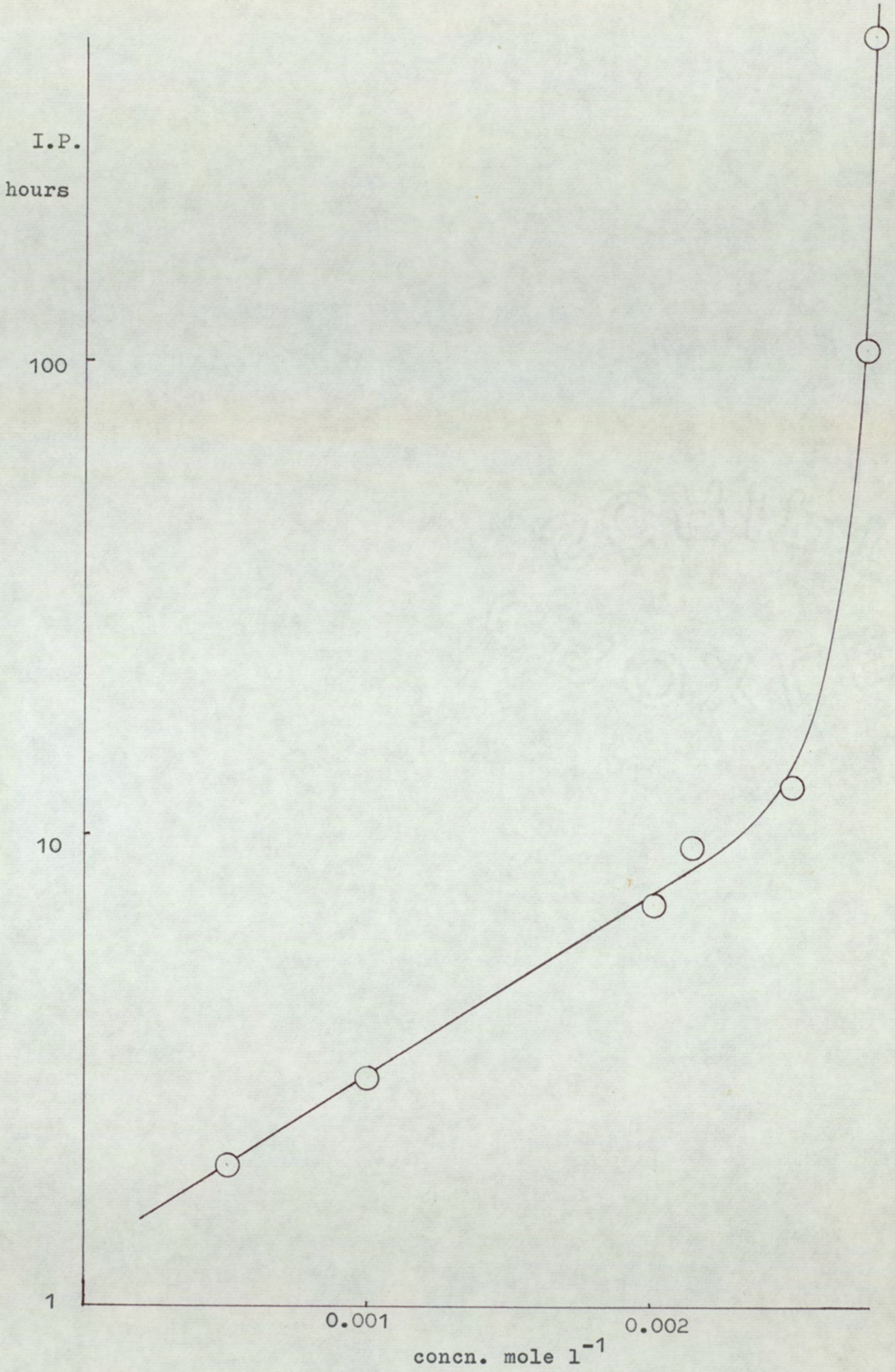


Figure 3.9: Semi-logarithmic plot of the induction period to oxidation of cumene stabilised by catechol hindered-phenyl phosphite in O_2 at 120°C.

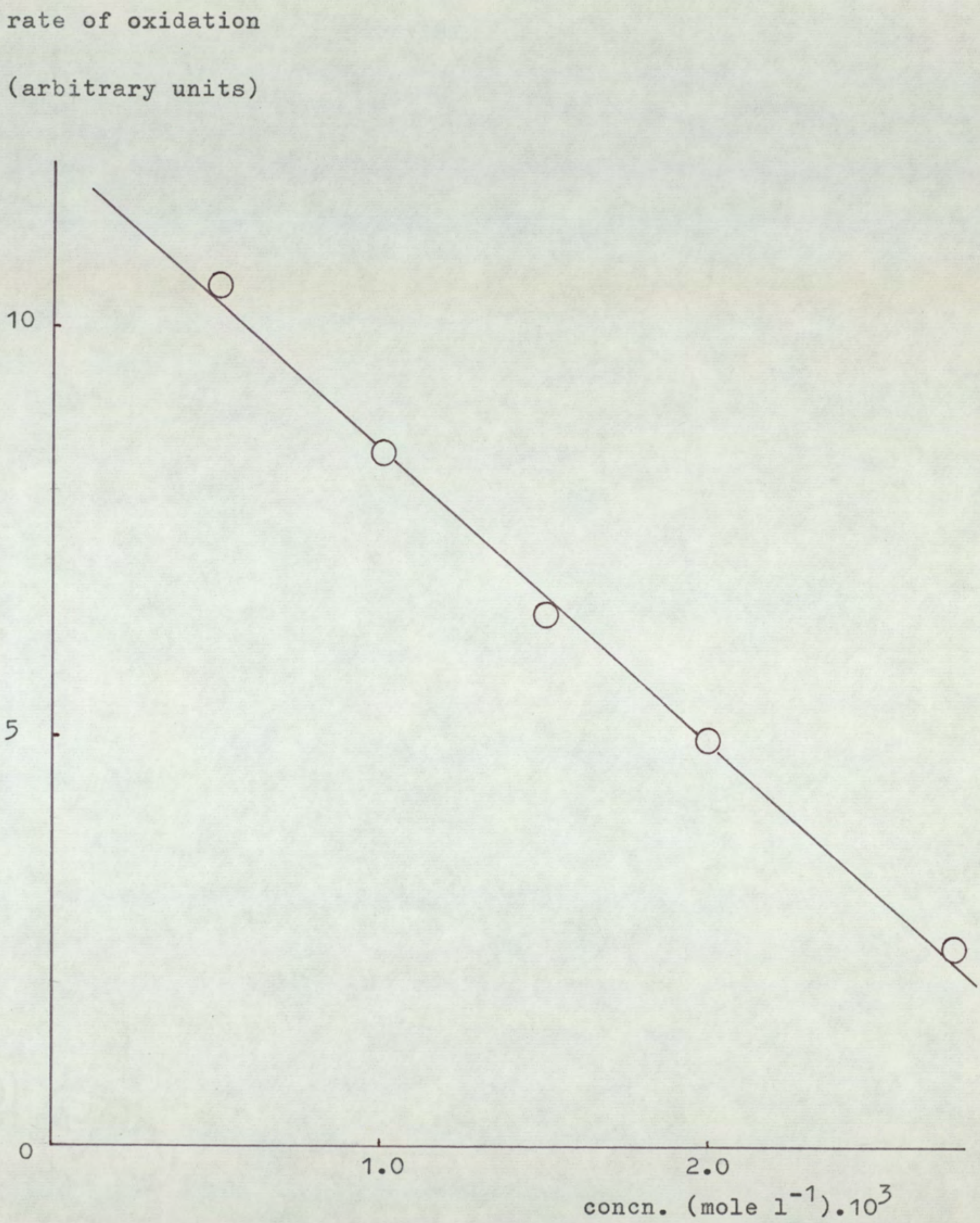


Figure 3.10: Variation in the rate of oxygen absorption after the end of the induction period, for the catechol hindered-phenyl phosphite-inhibited oxidation of cumene at 120°C.

3.2 Discussion

The autoxidations that have been performed involve a free radical chain process described by some of the following reactions[1,97]

initiation

$$RH + O_2 \longrightarrow \text{free radicals} \qquad (1)$$

propagation

$$R. + O_2 \longrightarrow ROO. \qquad (2)$$

$$ROO. + RH \longrightarrow ROOH + R. \qquad (3)$$

peroxide decomposition

$$ROOH \longrightarrow RO. + OH. \qquad (4)$$

$$2ROOH \longrightarrow RO. + ROO. + H_2O \qquad (5)$$

$$\left.\begin{array}{l} RO. \\ ROO. \end{array}\right\} + ROOH \rightarrow \text{Products} \qquad (6)$$

$$ROOH \longrightarrow \text{non-radical products} \qquad (7)$$

induced peroxide decomposition

$$X + ROOH \longrightarrow \text{free radicals} \qquad (8)$$

$$Y + ROOH \longrightarrow ROH + YO \qquad (9)$$

$$Z + ROOH \longrightarrow Z + \text{inactive products} \qquad (10)$$

$$M + ROOH \longrightarrow \text{free radicals} \qquad (11)$$

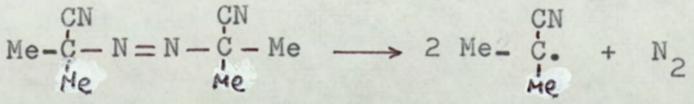
self-termination

$$2ROO. \longrightarrow \text{inactive products} \qquad (12)$$

chain termination

$$ROO. + IH \longrightarrow ROOH + I. \qquad (13)$$

In the absence of added initiators, initiation reaction (1) may be promoted by heat and light. In the experiments described, this step is brought about by thermal cleavage of the covalent bond in AZBN:



$$Me-\overset{CN}{\underset{Me}{C}}-N=N-\overset{CN}{\underset{Me}{C}}-Me \longrightarrow 2\ Me-\overset{CN}{\underset{Me}{C}}. + N_2$$

In the presence of even small amounts of hydroperoxide reaction (4) becomes the predominant mode of initiation (in the absence of added initiator), whilst at higher concentrations the contribution of reaction (5) becomes increasingly important. Reaction (4) clearly leads to chain-branching and is responsible for the observed autocatalysis.

Assuming that initiation has taken place, and knowing that reaction (2) is extremely rapid, so that competition with oxygen for alkyl radicals is only a remote possibility, the oxidation sequence can be inhibited or retarded in two ways.

(1) By providing an alternative path for the peroxy radical which will lower its steady-state concentration, as in reaction (13) where I. is a relatively unreactive species incapable of starting further chains.

(2) By reducing the effective concentration of hydroperoxide by decomposition without the formation of free radicals. For example reaction (9) is characteristic of many compounds containing elements from groups 5 or 6 of the periodic table. An even more attractive mechanism is the catalytic decomposition of reaction (10), exemplified by Lewis acid-induced rearrangement.

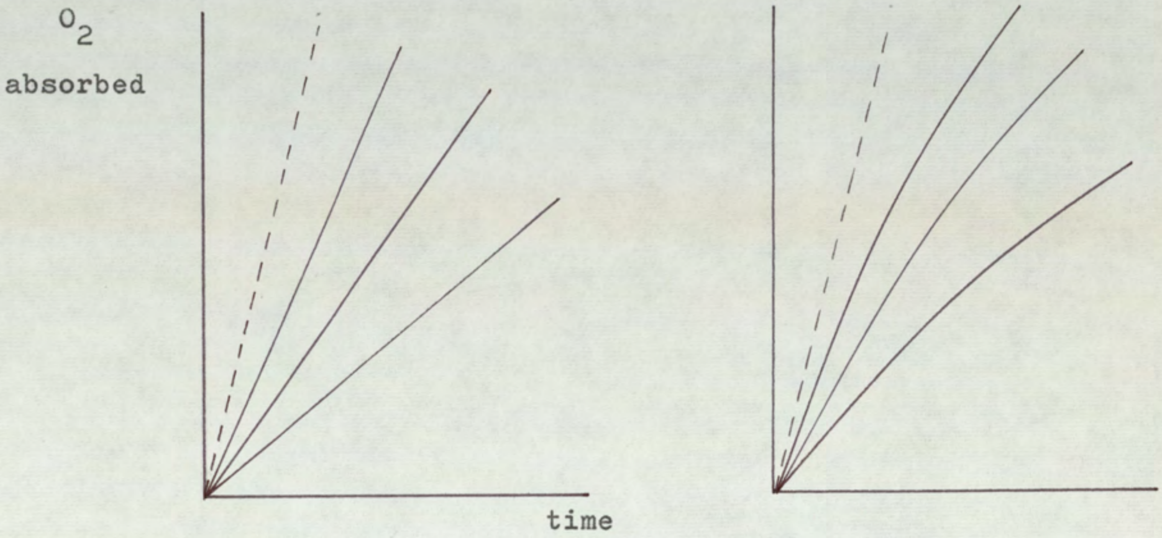
It has been suggested[90] that these two basic modes of antioxidant action can be distinguished by their effect on hydrocarbon oxidation initiated firstly by AZBN, which acts as shown above, and then using the hydrocarbon hydroperoxide as initiator, which at the temperature studied probably initiates principally by a solvent-induced decomposition[98]

$$\text{ROOH} + \text{RH} \longrightarrow \text{RO.} + \text{R.} + \text{H}_2\text{O}$$

The reaction profiles suggested as being diagnostic for these two types of behaviour are shown in Figure 3.11. A chain-breaking antioxidant with AZBN initiation should lead to an induction period to oxidation, whilst with hydroperoxide initiation, since the primary source of radicals is not removed, only retardation would be expected. With a peroxide decomposing antioxidant and hydroperoxide initiation, however, autoretardation is predicted (if the antioxidant is in excess or acts catalytically), since the source of radicals is gradually removed. Finally, peroxide decomposers are ineffective in inhibiting azo-initiated oxidation.

Figure 3.11: Oxidation profiles characteristic of antioxidants[90]

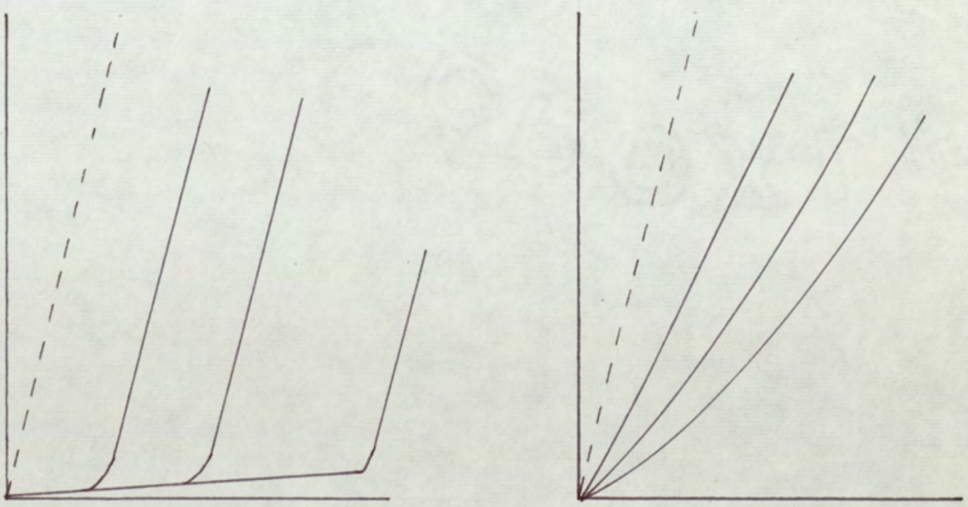
Hydroperoxide initiation:



chain-breaking antioxidant

peroxide-decomposing antioxidant

AZBN-initiation:



chain-breaking antioxidant

peroxide-decomposing antioxidant

From the results described, both types of activity are shown by the catechol phosphites, which show autoinhibition leading to an induction period with both azo- and peroxide-initiation. In the hydroperoxide system an initial pro-oxidant phase occurred with all the phosphites studied, the magnitude of the effect being greater in the case of the catechol compounds. This suggests a reaction involving a free radical intermediate which can either itself initiate oxidation, or generate a species capable of more rapid initiation (e.g. by a transfer catalysis process). This is interesting since phosphite-hydroperoxide reactions have long been considered ionic in nature[33]. The catechol phosphites were distinguishable by their autoretarding nature even at low concentrations (hydroperoxide:phosphite $>$ 10:1), suggesting the possibility of a non-stoichiometric reaction. The absorption of oxygen when the phosphite-hydroperoxide reaction was carried out in a non-oxidisable solvent suggests that some reaction intermediate itself can absorb oxygen, strongly suggesting radical involvement.

The AZBN results show that triphenyl phosphite too has both types of antioxidant activity, but differs from the catechol compounds in not being autoretarding. The latter feature may be interpreted as due to the gradual formation of the effective radical deactivator. If the reactions occuring in the AZBN system are those discussed in chapter 1 viz:

$$\mathrm{ROO.} + \mathrm{(RO)_3} \longrightarrow \mathrm{RO.} + \mathrm{(RO)_3PO} \qquad (14)$$

$$\mathrm{RO.} + \mathrm{(RO)_3} \longrightarrow \mathrm{R.} + \mathrm{(RO)_3PO} \qquad (15)$$

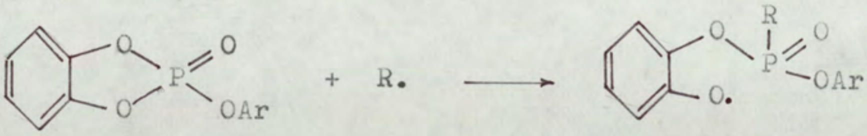
then for the greatest inhibition to occur, clearly the radicals formed must be of lower reactivity. This means that for the aryl-substituted phosphites, the intermediate phosphoranyl radical formed may undergo α-scission.

$$\mathrm{(ArO)_3\dot{P}OR} \longrightarrow \mathrm{(ArO)_2POR} + \mathrm{ArO\cdot}$$

The radical reactions of the isopropyl- and phenyl-substituted catechol phosphites would not be expected to lead to the formation of comparatively unreactive radicals, so that inhibition in those cases must be due to reaction (14) and (15). Oxidation of catechol phosphites to the corresponding phosphates with AZBN in oxygen certainly does occur, even with the hindered-phenyl compound, as described later (section 6.2).

In the case of the isopropyl- and phenyl-substituted catechol phosphites with AZBN initiation in cumene, a small but reproducible pro-oxidant effect was observed, which is too small to be shown graphically. A similar observation was made[99] in the case of the tertiary amine-inhibited oxidation of 9,10-dihydroanthracene initiated by 2,2',3,3'-tetraphenylbutane. This was attributed to the formation of radicals from the amine which could add oxygen, and a similar explanation may be true in the case of the phosphites. The smallness of the effect does not warrant further consideration.

Another difference between the cyclic and non-cyclic systems is the ability of the catechol phosphates to autoretard the AZBN initiated oxidations whilst triphenyl phosphate is inert. No information exists on the radical reactions of phosphoryl compounds which lack a labile hydrogen atom (which can be removed yielding a phosphinyl radical) other than reaction with alkali metals, so that we can only speculate as to the reactions occurring. One possibility is a ring-opening reaction



where R. = RO. or ROO.

Another difference between the catechol and non-cyclic phosphites this time in the hydroperoxide initiated oxidations is the small (mainly) oxygen evolution from the former. The rate of evolution did not appear to obey any simple kinetic law. Oxygen can be produced from hydroperoxides in a number of ways[100] including

(1) By reaction with a powerful oxidant capable of abstracting an electron e.g. certain metal salts

$$\mathrm{ROOH + oxid.} \longrightarrow \mathrm{ROO. + H^{+} + (oxid. + e)}$$

$$\mathrm{ROO. + oxid.} \longrightarrow \mathrm{R^{+} + O_2 + (oxid. + e)}$$

(2) Base catalysed decomposition involving attack of a carbanion on hydroperoxide

$$\mathrm{ROO^{-} + ROOH} \longrightarrow \mathrm{RO^{-} + ROH + O_2}$$

$$\mathrm{RO^{-} + ROOH} \longrightarrow \mathrm{ROO^{-} + ROH}$$

This reaction is strongly catalysed by compounds whose structures permit chelate formation.

(3) By particular chain termination reactions. The termination step in cumene oxidation is quite complex and oxygen is a product of at least two of the reactions involved[101]

$$\mathrm{2ROO.} \longrightarrow \mathrm{ROOOOR_{cage}} \longrightarrow \mathrm{ROOR + O_2} \qquad (1)$$

$$\searrow \mathrm{2RO. + O_2} \qquad (2)$$

$$\text{Ø}\mathrm{C(Me)_2O.} \longrightarrow \mathrm{CH_3.} + \text{Ø}\mathrm{COCH_3} \qquad (3)$$

$$\mathrm{CH_3^{\cdot} + O_2} \longrightarrow \mathrm{CH_3OO.} \qquad (4)$$

$$\mathrm{CH_3OO. + ROO.} \rightarrow \mathrm{HCHO + ROH + O_2} \qquad (5)$$

$$\mathrm{RO. + RH} \longrightarrow \mathrm{ROH + R.} \qquad (6)$$

$$\mathrm{RO. + ROOH} \longrightarrow \mathrm{ROH + ROO.} \qquad (7)$$

Clearly a sequence of reactions (1), (2), and (7) is a chain reaction leading to mainly alcohol and oxygen. The amount of each kind of termination reaction depends on competition between reactions (3), (6), and (7), but recent work[102] throws doubt on whether (5) results in termination.

The first way in which oxygen can arise is unlikely since it has never been observed in reaction of hydroperoxide with a reductant[100]. The base-catalysed mechanism is also unlikely since in the presence of a reducing solvent oxygen transfer can occur

$$\mathrm{ROO^{-} + R_3CH} \longrightarrow \mathrm{RO^{-} + R_3COH}$$

thus preventing or reducing gas evolution. Also it is difficult to rationalise the formation of the hydroperoxide anion.

If increased termination reactions are responsible for the gas evolution, the mechanism envisaged may involve co-ordination of two radicals in a cage about the phosphorus atom. With the evidence available we cannot choose between these, or any other, alternatives.

Another difference between the compounds studied is that catechol phosphate shows the same type of antioxidant behaviour in the hydroperoxide system as the parent phosphite, although no pro-oxidant effect is observed, whilst triphenyl phosphate is inert. This is consistent with the mechanism proposed later.

Although catechol hydroxy phosphate, and its open chain hydrolysis product both show the dual reactivity associated with the parent phosphite, they are probably not major products since they both give rise to a small gas evolution on reaction with hydroperoxide, whilst the phosphate, the known first step in the reaction sequence, does not give an evolution.

The induction period measurements show a critical concentration of about 2.5×10^{-3} mole l^{-1} for the hindered-phenyl phosphite. Below this concentration little stabilisation was conferred, whilst a spectacular increase occurred at higher concentrations.

For simple chain-breaking or peroxide-decomposing antioxidants it can be shown[103] that induction periods are proportional to the antioxidant concentration or $(\text{concentration})^2$ respectively. In view of the complex nature of the phosphite antioxidant action it is not surprising that no simple correlation exists. No literature data has appeared on catechol phosphites in liquid phase oxidation studies, but in polypropylene at 200°C. they are reported to give a linear concentration-induction period plot[42,104,105,106] with a critical concentration around 5×10^{-3} mole Kg.^{-1}, below which they are ineffective[42]. The kinetic exercises developed by Russian workers[107] to explain the existence of critical antioxidant concentrations cannot be usefully applied to obtain any relevant information about the system studied.

It is interesting to note that the ultimate rate of oxygen uptake depends on the initial concentration of inhibitor, since the end of the induction period is generally considered to correspond to complete destruction of inhibitor. It may be that although the effective peroxide decomposing species is exhausted, some compound capable of terminating free radicals remains (in concentration proportional to the starting concentration of phosphite) to retard the final oxidation.

4 REACTIONS OF PHOSPHITES WITH HYDROPEROXIDES - Results and Discussion

The reactions of a number of phosphites with (chiefly cumene) hydroperoxide were studied, using the iodine-liberation technique, to follow destruction of hydroperoxide.

The catechol phosphites are fundamentally different in their behaviour to trialkyl phosphites, being catalytic in action, and show similarities with certain sulphides.

Ring strain is probably not important in these reactions and the catalytic activity appears to be associated with the presence of phosphorus in a cyclic structure.

4.1 Results

The initial experiments were carried out with tetralin hydroperoxide in tetralin solvent under the same conditions as the earlier oxygen absorption studies, to enable an estimate to be made of concentration changes during inhibition at 50°C. The three catechol phosphites all caused catalytic decomposition and stoichiometries of greater than 100:1 were observed. This contrasted with tris(nonylphenyl) phosphite which was found to obey a strict 1:1 stoichiometry. The reaction profiles did not appear to obey any simple kinetic law, probably due to the presence of oxygen, and the fact that phosphite was added to an autoxidising system, but the order of reactivity, as shown in Figure 4.1 was clearly

R = phenyl $>$ isopropyl $>$ hindered-phenyl

for the catechol phosphites. The stoichiometric reaction of triphenyl phosphite was much faster than for the catechol compounds.

Some experiments were repeated using cumene hydroperoxide in cumene in nitrogen, and this time a general pattern emerged. Disappearance was initially rapid, decreasing quite rapidly to a good first order reaction, which continued for many half-lives (Figure 4.2).

The rate constants in Table 3 confirm the above order.

Table 3: Apparent first order rate constants for the decomposition of 0.2M cumene hydroperoxide in N_2 at 75°C. by 0.02M catechol phosphites.

Substituent R	k_1 sec^{-1}
phenyl	2.5×10^{-3}
isopropyl	8.0×10^{-4}
hindered-phenyl	6.7×10^{-5}

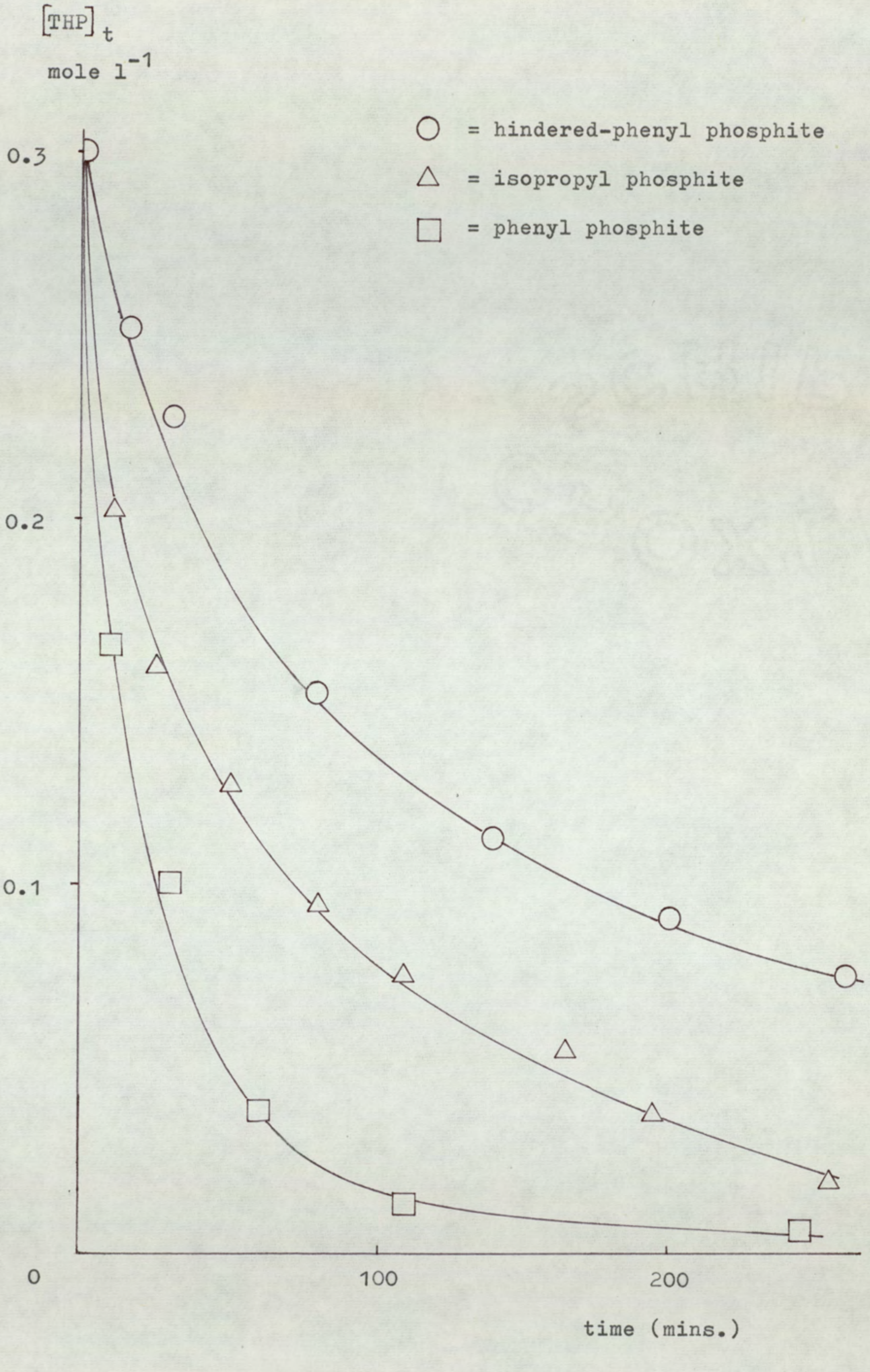


Figure 4.1: Decomposition of tetralin hydroperoxide in tetralin at 50°C. by 0.025M catechol phosphites

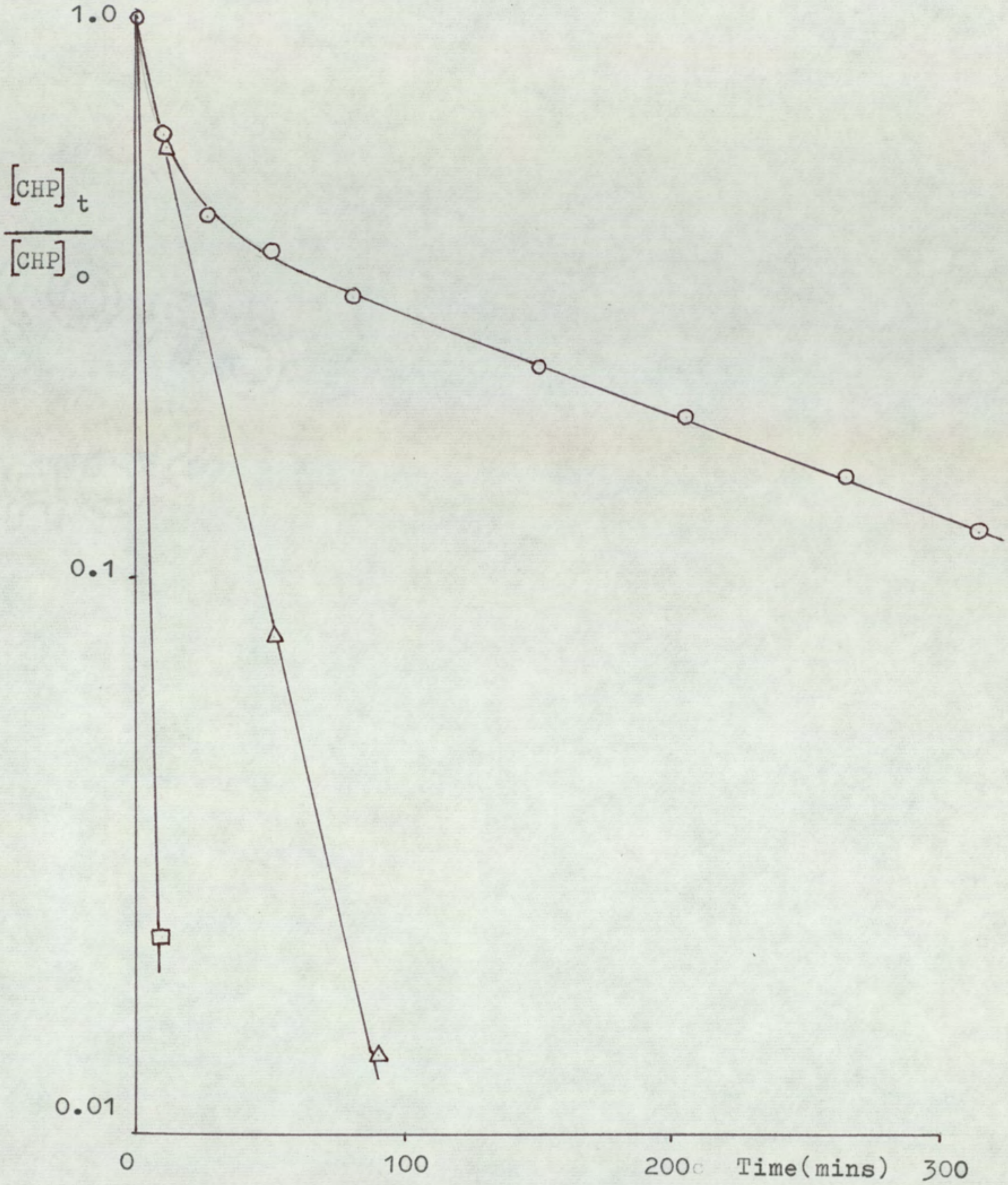


Figure 4.2: First order plot for the decomposition of 0.2M cumene hydroperoxide in cumene (in N_2) at 75°C. by 0.02M catechol phosphites.

○ = hindered-phenyl phosphite

△ = isopropyl phosphite

□ = phenyl phosphite

Subsequent work was carried out using the hindered-phenyl phosphite only, since it is hydrolytically stable as discussed in section 7, but the results will be generally applicable to all catechol phosphites.

The kinetics of the catechol phosphite-cumene hydroperoxide reaction were investigated in more detail, using chlorobenzene as an inert, high boiling solvent. It was shown (Figure 4.3) that the rate of reaction was not affected by the presence of oxygen so that for convenience all subsequent experiments were performed in air.

Although apparent first order kinetics had been observed, it was found that rate constant was dependent on initial phosphite concentration (Table 4) indicating a pseudo-first order reaction of the type:

$$-\frac{d\,[CHP]}{dt} = k_2\ [CHP]^1 . [P]^x$$

[CHP] = cumene hydroperoxide

[P] = concentration of some active peroxide decomposer

"P" must either be in large excess, or not be consumed in the reaction.

Table 4: Pseudo first order rate constants for decomposition of 0.2M CHP by hindered-phenyl phosphite in ØCl at 75°C.

[Phosphite] mole l^{-1}	k_1 (sec^{-1})
0.01	5.13×10^{-5}
0.02	1.08×10^{-4}
0.03	1.45×10^{-4}
0.04	2.02×10^{-4}
0.05	2.39×10^{-4}

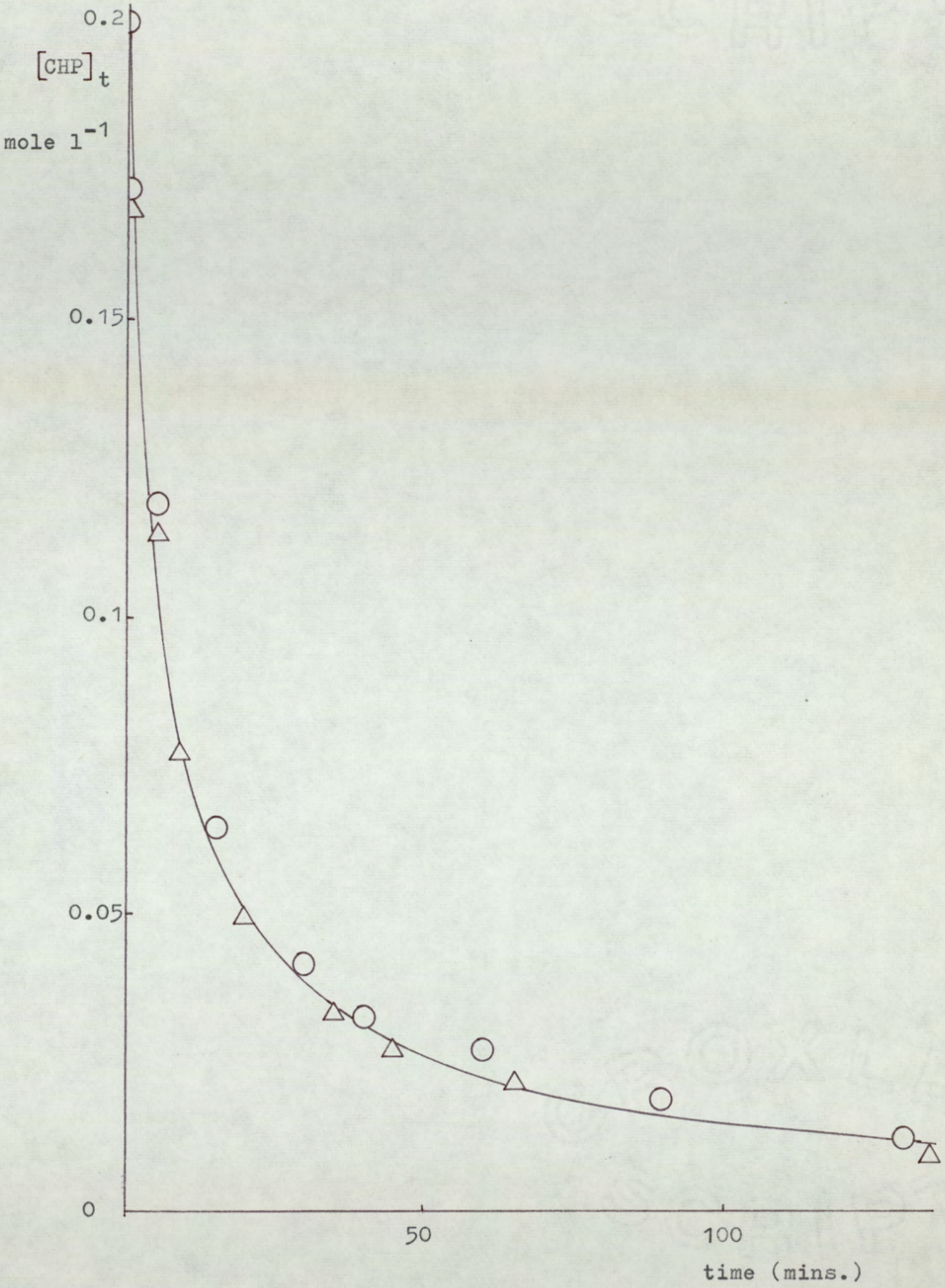


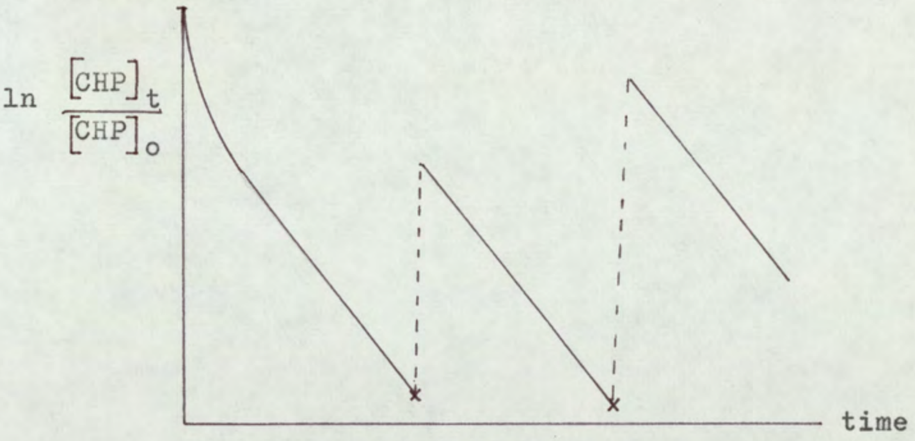
Figure 4.3: Decomposition of 0.2M cumene hydroperoxide by 0.02M catechol hindered-phenyl phosphite in ØCl at 75°C.

○ in air ; △ in N_2

The power "x" in this equation was found by constructing a logarithmic plot using the data in Table 4 , (Figure 4.4) which gave a good straight line of slope 1 i.e. the reaction is first order in the species "P". Therefore

$$-\frac{d\,[CHP]}{dt} = k_2\,[CHP]\,[P] \qquad \text{where } k_2 = k_1\,[P]$$

Since low concentrations of phosphite were used relative to hydroperoxide, it is unlikely that this active species is in excess so that for the above kinetic scheme to hold, this species must function as a true catalyst. This was shown to be the case by adding further hydroperoxide at the end of the experiment. The rate of hydroperoxide disappearance was the same (within experimental error) as the previous first-order rate, with the absence of the initial rapid reaction. This procedure was repeated many times over several hours and always the same rate was observed:



In this way several hundred fold excess of hydroperoxide was destroyed without any diminution in reaction rate. Further evidence for the proposed scheme was that for a fixed phosphite concentration, the pseudo-first order rate constant was independent of initial hydroperoxide concentration. Thus for 0.02 M phosphite, with $[CHP]_o$ = 0.1 mole l^{-1}, k_1 was 1.04×10^{-4} sec^{-1}, whilst for $[CHP]_o$ = 0.5 mole l^{-1}, k_1 equalled 1.11×10^{-4} sec^{-1}.

This behaviour of the catechol phosphites contrasts with the non-cyclic compounds. The reaction between cumene hydroperoxide and triphenyl phosphite in chlorobenzene was studied in the range 0-75°C.

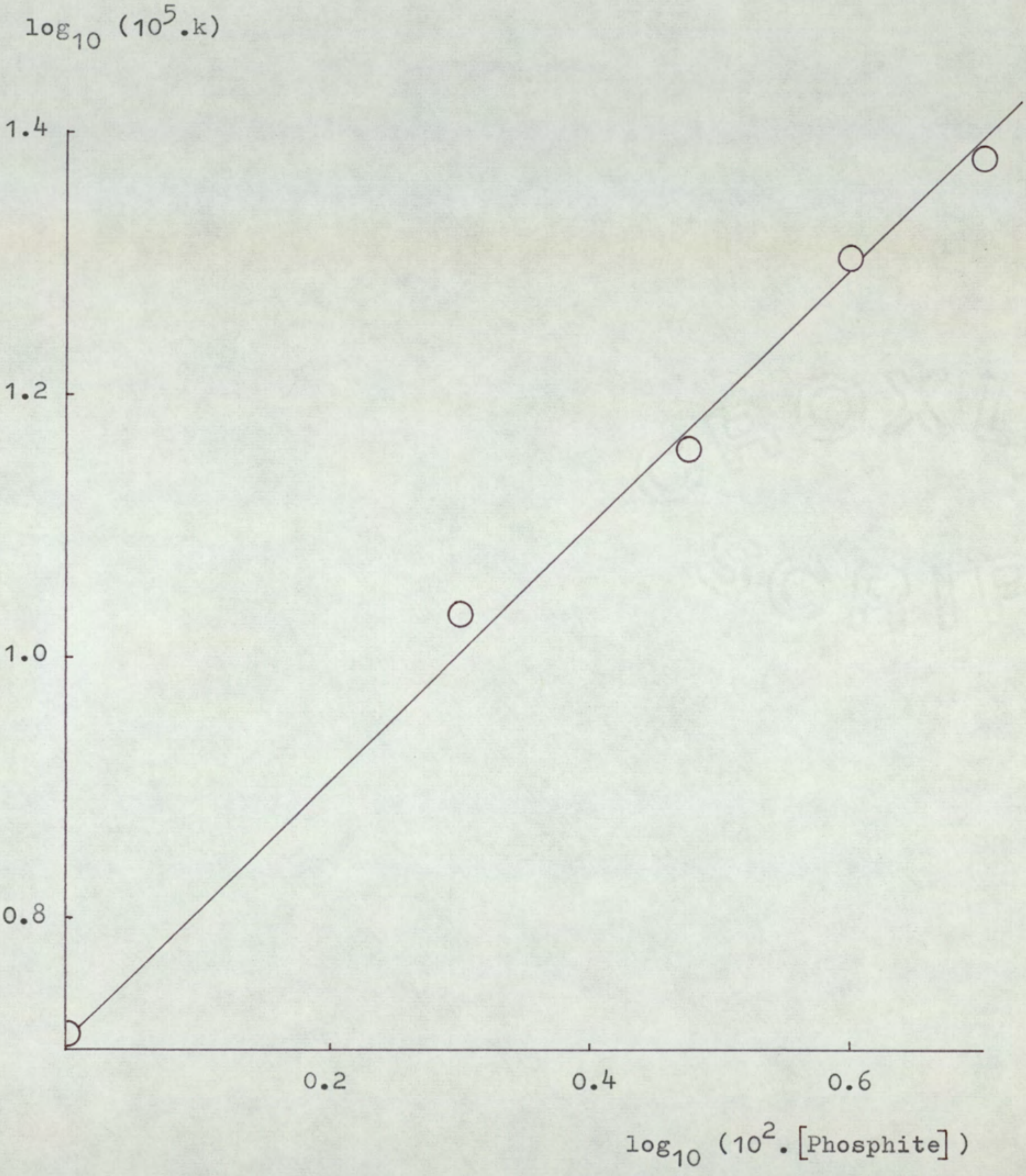


Figure 4.4: Logarithmic plot of the pseudo-first order rate constants for the catalytic decomposition of cumene hydroperoxide by catechol hindered-phosphite in ØCl at 75°C.

and in all cases a stict stoichiometry was observed (Table 5) In all cases reaction was extremely rapid being complete by the time the first sample was taken (usually after one minute) even at 0°C.

Table 5: Stoichiometry of the triphenyl phosphite-cumene hydroperoxide reaction.

[phosphite] mole l^{-1}	CHP destroyed, mole l^{-1}	phosphite:CHP stoichiometry
0.0235	0.025	1:1.06
0.0478	0.053	1:1.07
0.1003	0.104	1:1.03
0.2050	0.200	1:1.02

The pseudo-first order rate constants were measured for the catechol phosphite-hydroperoxide reaction over a range of temperatures as in Table 6.

Table 6: Temperature dependence of the pseudo-first order rate constant for the catalytic decomposition of cumene hydroperoxide by catechol hindered-phenyl phosphite in chlorobenzene.

$[P]_o = 0.02$ mole l^{-1}

T °C.	k_1 sec^{-1}
65	5.67×10^{-5}
70	8.18×10^{-5}
74.6	1.17×10^{-4}
80	1.57×10^{-4}
85	1.86×10^{-4}
90	2.36×10^{-4}

With this data an Arrhenius plot was constucted (Figure 4.5) which was a reasonable straight line, from the slope of which the activation energy = 14.4 ± 0.9 kcal.mole^{-1}

Unfortunately the entropy of activation, $\Delta S^{\ddagger}$, and the

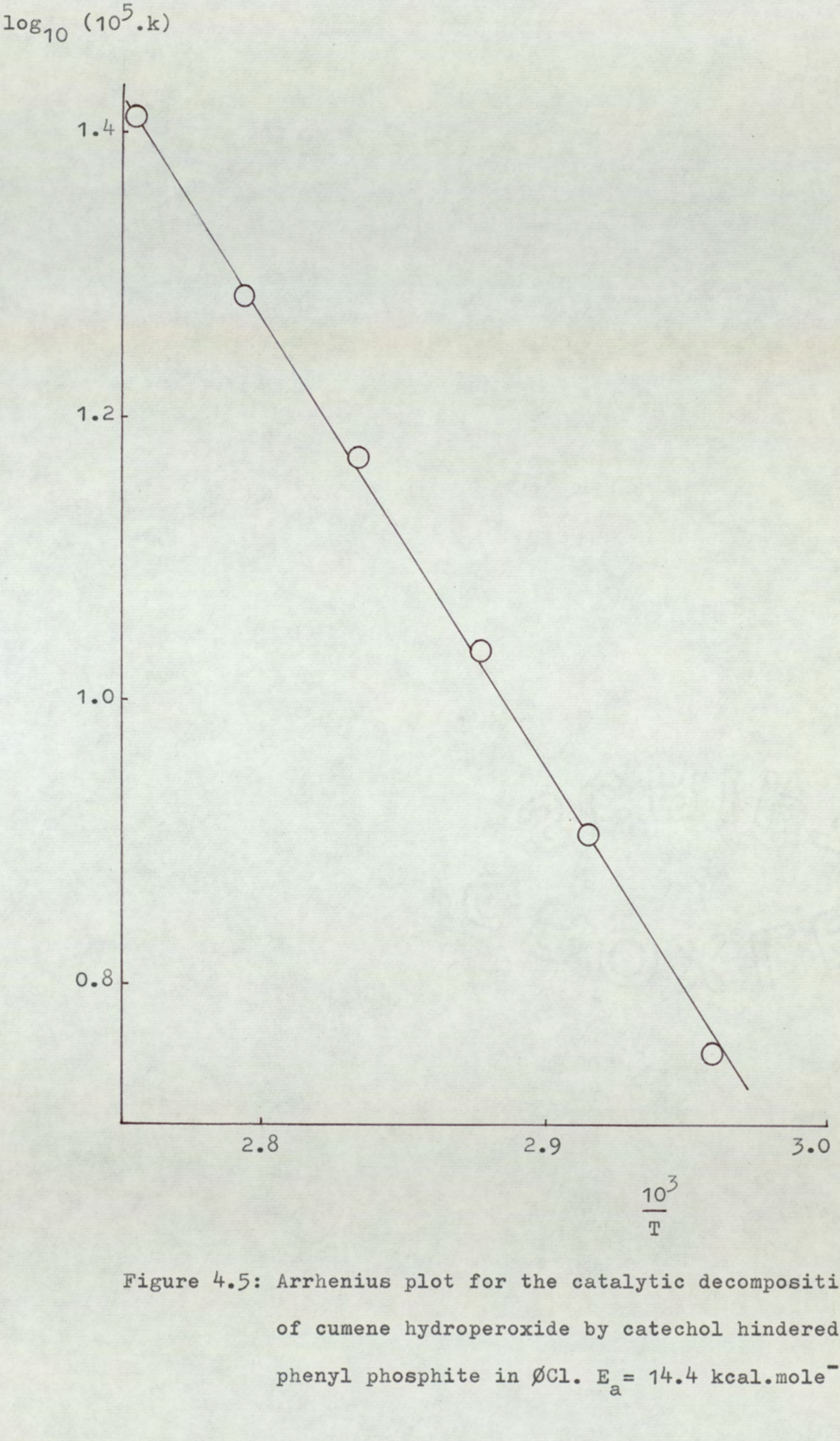


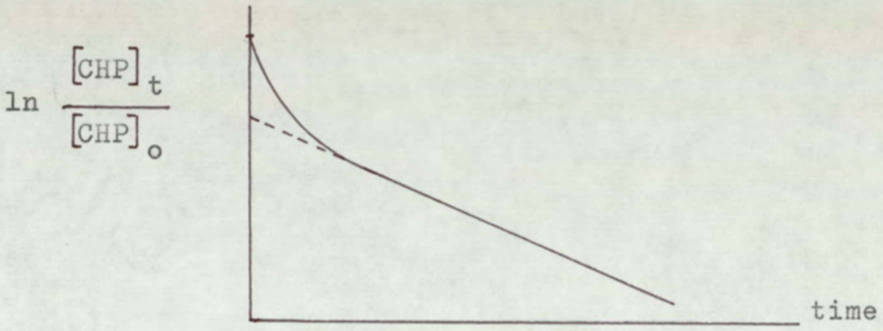
Figure 4.5: Arrhenius plot for the catalytic decomposition of cumene hydroperoxide by catechol hindered-phenyl phosphite in ØCl. $E_a = 14.4$ kcal.mole^{-1}

Arrhenius frequency factor cannot be computed since the second order rate constant

$$k_2 = k_1 [P]$$

requires knowledge of the concentration of the active species "P", derived from phosphite, and k_2 is needed for calculation.

Extrapolation of the straight line portion of the first order plot of hydroperoxide destruction to zero time, gave a fairly constant ratio (over a wide range of concentrations of



phosphite and hydroperoxide) of hydroperoxide:phosphite = 4.0±0.4:1. This may indicate the total stoichiometry of the reaction(s) leading to the formation of the active peroxide-decomposing species.

Since the primary reaction with hydroperoxide is probably:

$$(RO)_3P + R^1OOH \longrightarrow (RO)_3PO + R^1OH$$

the reactions of phosphates with cumene hydroperoxide were studied. Triphenyl phosphate was found to be inert, in chlorobenzene, over a range of concentrations, and temperatures from 0°- 75°C. The catechol hindered-phenyl phosphate, however, showed considerable activity. Over a wide concentration range the disappearance of cumene hydroperoxide was initially slow, and then increased, to become apparently first order over many half-lives. It was found that the pseudo-first order rate constants for catechol hindered-phenyl phosphite and phosphate were the same at equal concentrations. The rates were measured over a range of concentrations, and in all cases found to be the same (Table 7). This is shown graphically in Figure 4.6.

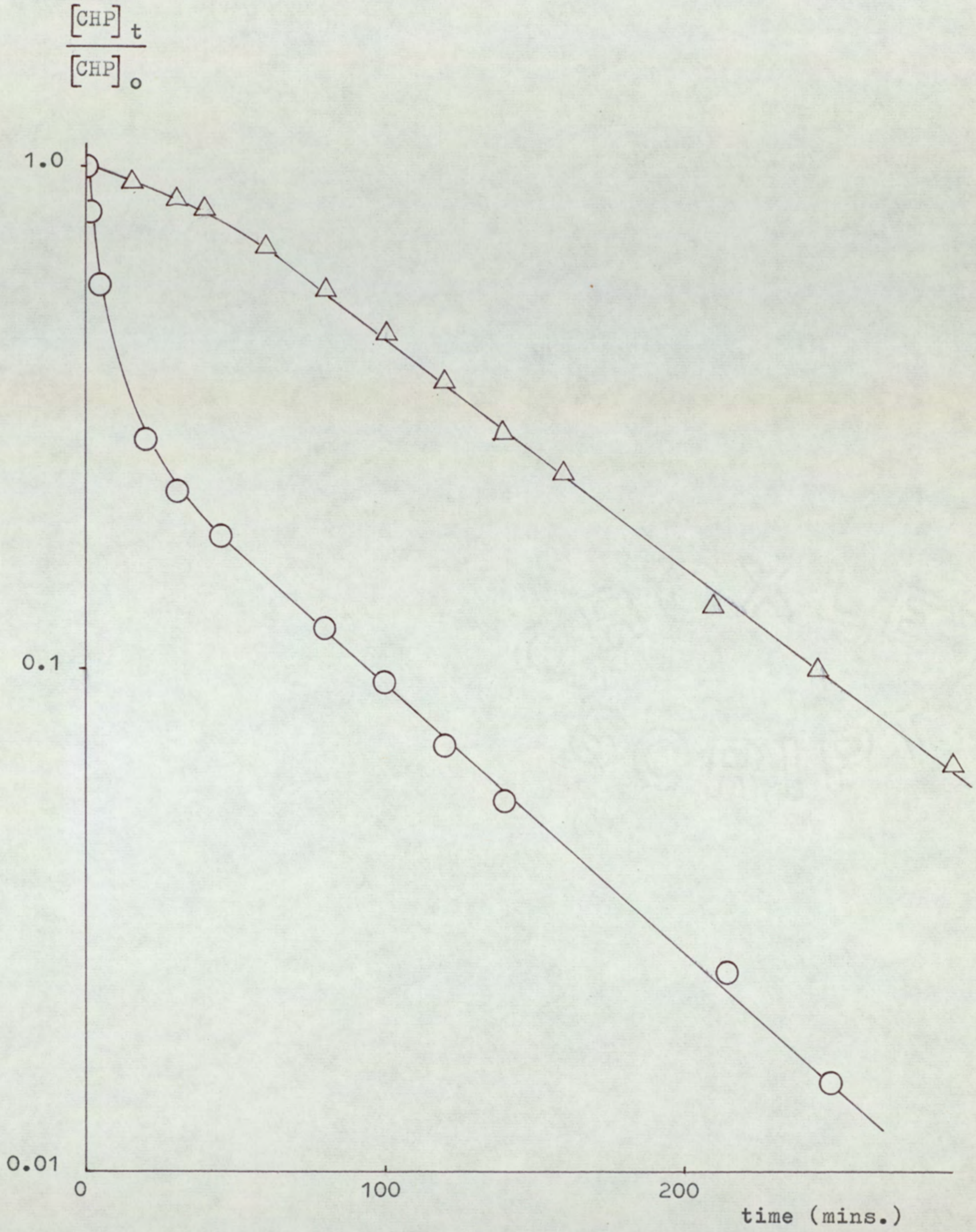


Figure 4.6: First order plot for the decomposition of 0.2M cumene hydroperoxide in ØCl at 75°C. by

○ = 0.04M catechol hindered-phenyl phosphite

△ = 0.04M catechol hindered-phenyl phosphate

Table 7: Pseudo-first rate constants for reaction with 0.2M CHP in ØCl at 75°C.

concentration mole l^{-1}	k in sec^{-1}	
	phosphite	phosphate
0.01	5.13×10^{-5}	5.36×10^{-5}
0.02	1.08×10^{-4}	1.15×10^{-4}
0.03	1.45×10^{-4}	1.44×10^{-4}
0.04	2.02×10^{-4}	1.86×10^{-4}

As found with phosphite, oxygen did not affect the rate of reaction of phosphate, and plotting the data of Table 7 logarithmically a slope of 1 was again obtained. Exactly parallel experiments were then performed as for the phosphite and once again it was shown that:

(1) The reaction was first order in hydroperoxide and in the active species.

(2) For a fixed phosphate concentration the rate constant was independent of the initial hydroperoxide concentration.

(3) Added hydroperoxide was removed at a constant rate.
The reaction rates were again measured over a range of temperatures (Table 8), and the Arrhenius plot shown in Figure 4.7 gave an activation energy of 14.5 ± 0.5 kcal. $mole^{-1}$.

It appears then, that kinetically the two reactions are identical.

Extrapolation of the linear part of the first order plot for the phosphate induced decomposition, to $[CHP]_t$ / $[CHP]_o$ = 1.0 gave an almost constant "induction period" equal to 32 ± 5 minutes. over a wide concentration range (see next page). This induction period decreased with increase in temperature, and an Arrhenius plot of reciprocal induction period versus 1/ T°C. also gave an energy of activation of 14.7 kcal. $mole^{-1}$.

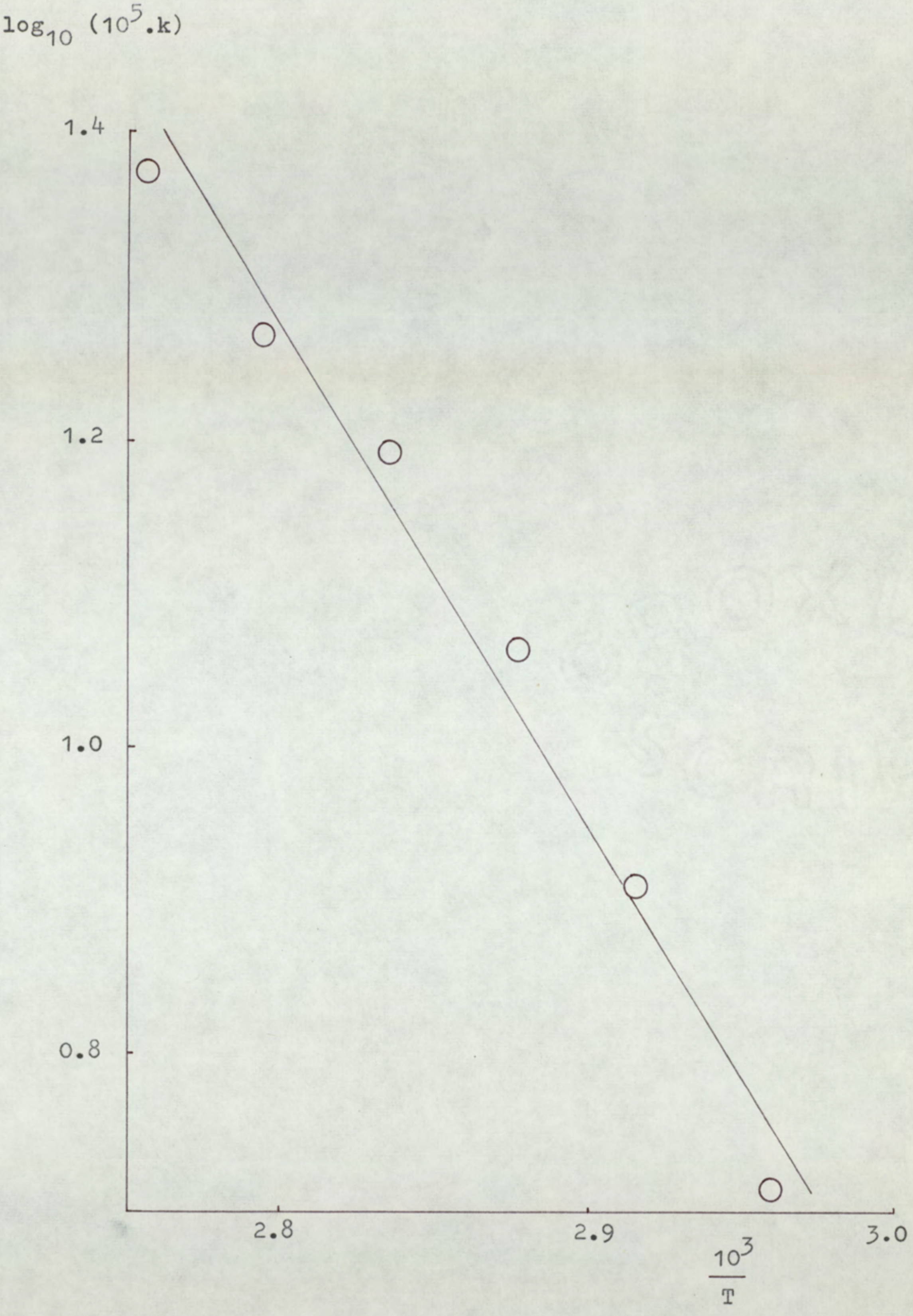


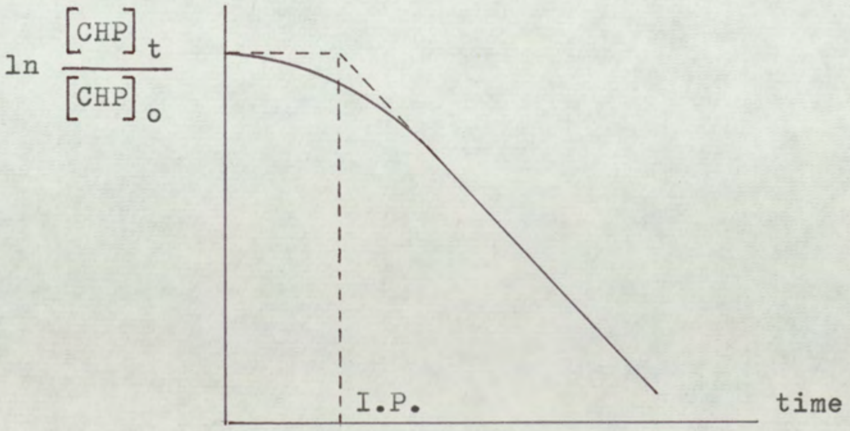
Figure 4.7: Arrhenius plot for the catalytic decomposition of cumene hydroperoxide by catechol hindered-phenyl phosphate in ØCl. $E_a = 14.5$ kcal.mole^{-1}

The results quoted so far are consistent with the initial rapid part of the phosphite-hydroperoxide reaction consisting of oxidation of phosphite to phosphate, which then reacts with more hydroperoxide to eventually form the active catalyst for further destruction of hydroperoxide.

Table 8: Temperature dependence of the pseudo-first order rate constant for the catalytic decomposition of cumene hydroperoxide by catechol hindered-phenyl phosphate in chlorobenzene. $[P]_o = 0.02$ mole l^{-1}.

T^o C.	k_1 sec^{-1}
65	5.67×10^{-5}
70	8.03×10^{-5}
74.6	1.09×10^{-4}
80	1.48×10^{-4}
85	1.93×10^{-4}
90	2.57×10^{-4}

To obtain information about this initial oxidation step, the disappearance of hydroperoxide was measured for reaction of equimolar phosphite and hydroperoxide, this time at lower temperatures to facilitate experimental procedure for the rapid reaction.



The reaction was not affected by the presence of oxygen, nor the efficient free radical trapping species 2,6-di-t-butyl-4-methyl phenol (Figure 4.8). Good second order kinetics were observed (Figure 4.9)

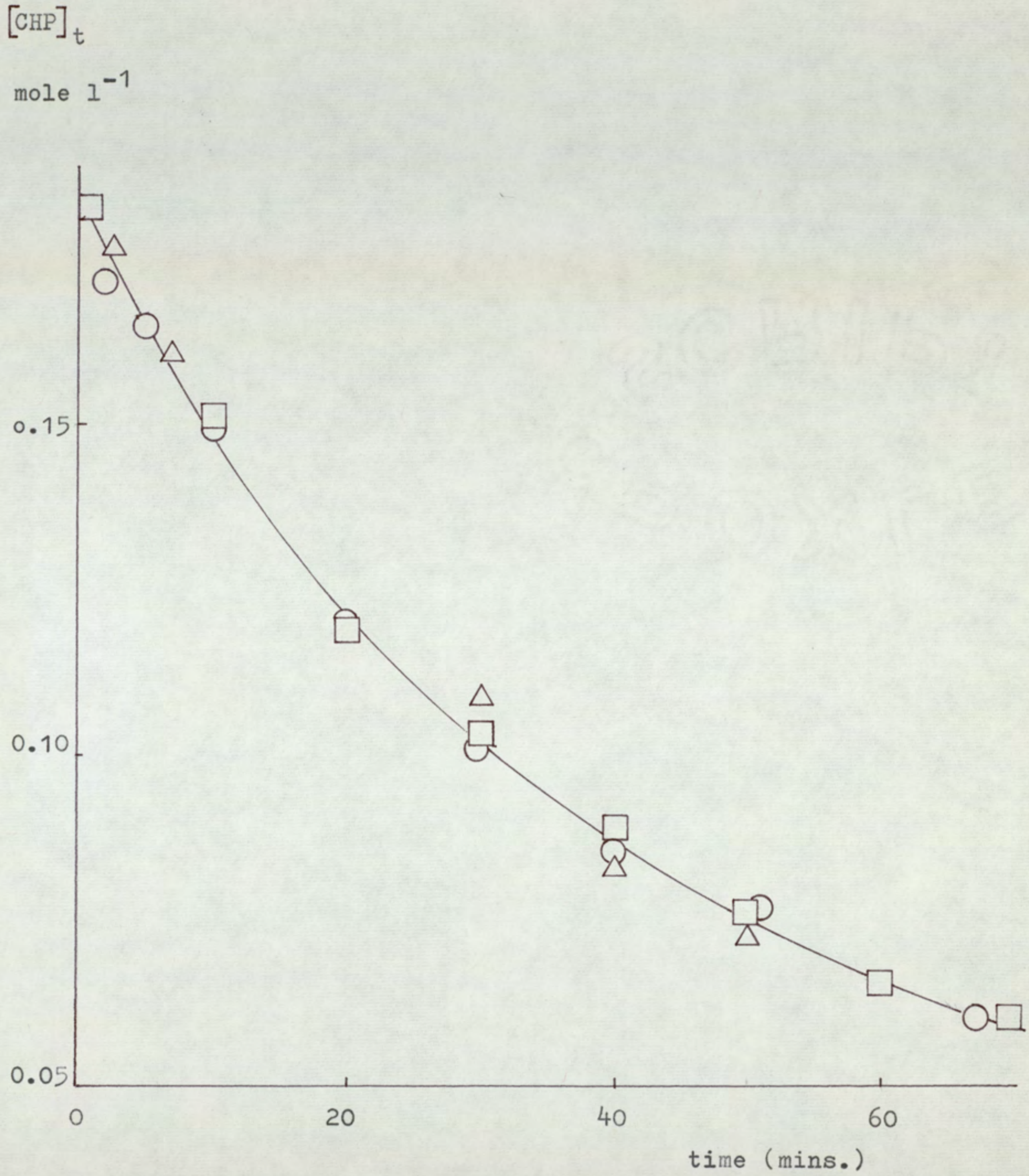


Figure 4.8: Decomposition of cumene hydroperoxide by catechol hindered-phenyl phosphite in ØCl at 25°C.

△ in N_2

□ in air

○ with added 0.05M 2,6-di-t-butyl-4-methyl phenol

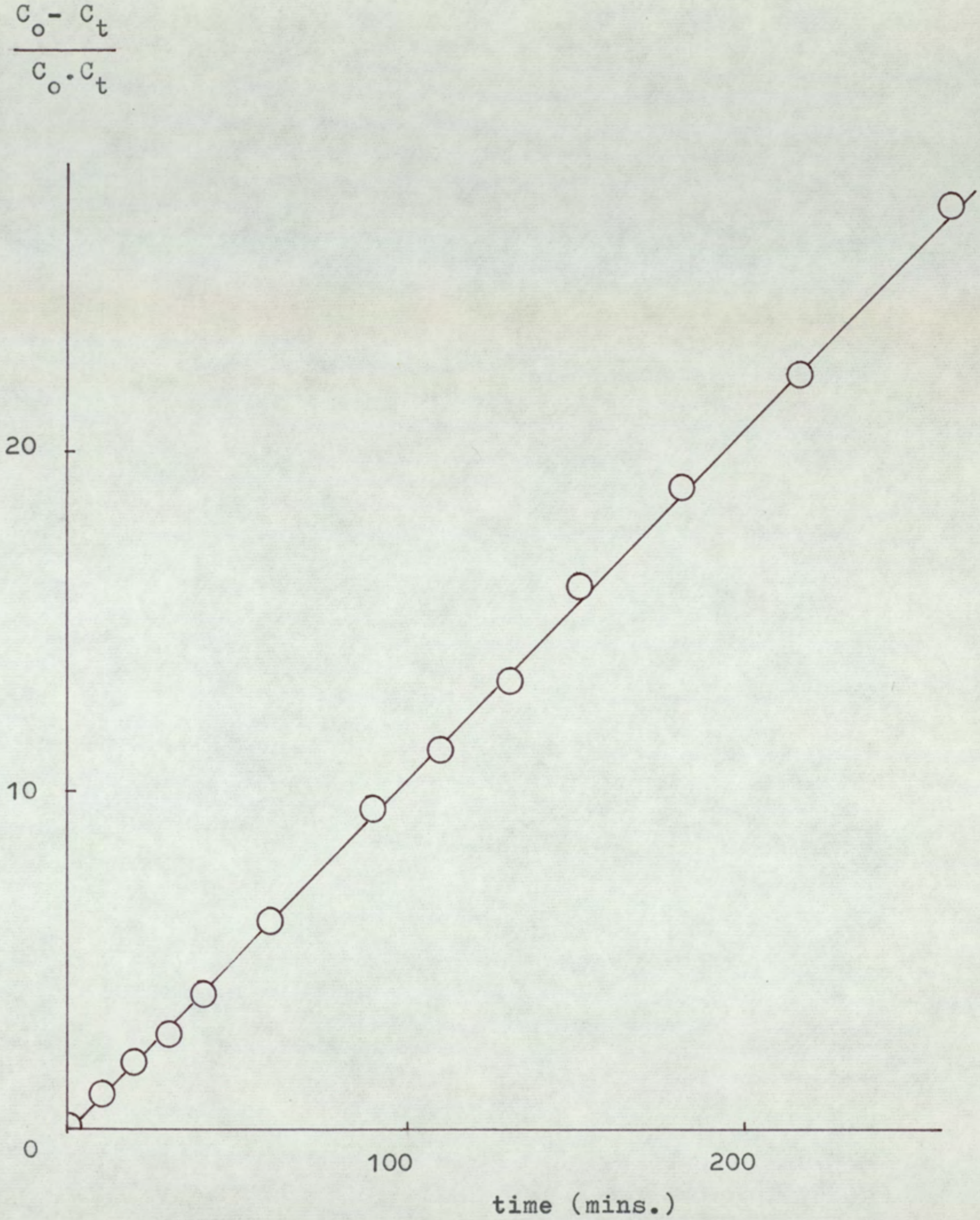


Figure 4.9: Second order plot for the oxidation of catechol hindered-phenyl phosphite by cumene hydroperoxide (both 0.2M) in ØCl at 20°C.

over a range of concentrations.

From the earlier experiments at 75°C., initial reaction rates were measured graphically as a function of concentration of phosphite (Table 9) and a logarithmic plot of initial rate versus initial phosphite concentration gave a good straight line of slope = 1.04 (Figure 4.10), i.e. reaction was first order in phosphite.

Table 9: Initial rates for reaction of catechol hindered-phenyl phosphite with 0.2M cumene hydroperoxide in chlorobenzene at 75°C.

$[\text{phosphite}]_o$ mole l^{-1}	initial rate mole l^{-1} sec^{-1}
0.01	6.68×10^{-7}
0.02	5.46×10^{-6}
0.03	1.35×10^{-5}
0.04	2.78×10^{-5}
0.20	1.67×10^{-3}

An exactly analogous procedure was then followed using the results of earlier experiments, this time with a constant 0.02 M phosphite concentration and varying amounts of hydroperoxide. Again an initial rate plot gave a straight line, of slope 1.02, so that the reaction was also first order in cumene hydroperoxide. Thus the overall reaction can be expressed by

$$-\frac{d\,[\text{CHP}]}{dt} = k_2\ [\text{CHP}].[\text{phosphite}]$$

Values of the second order rate constant, k_2, were measured over a range of temperatures, and are shown in Table 10. An Arrhenius plot of this data (figure 4.11), gave a good straight line from which the activation energy is 14.1 kcal. mole^{-1}.

Using the expression

$$k_2 = \frac{RT}{Nh} \cdot e^{\Delta S^{\ddagger}/R} \cdot e^{-E/RT}$$

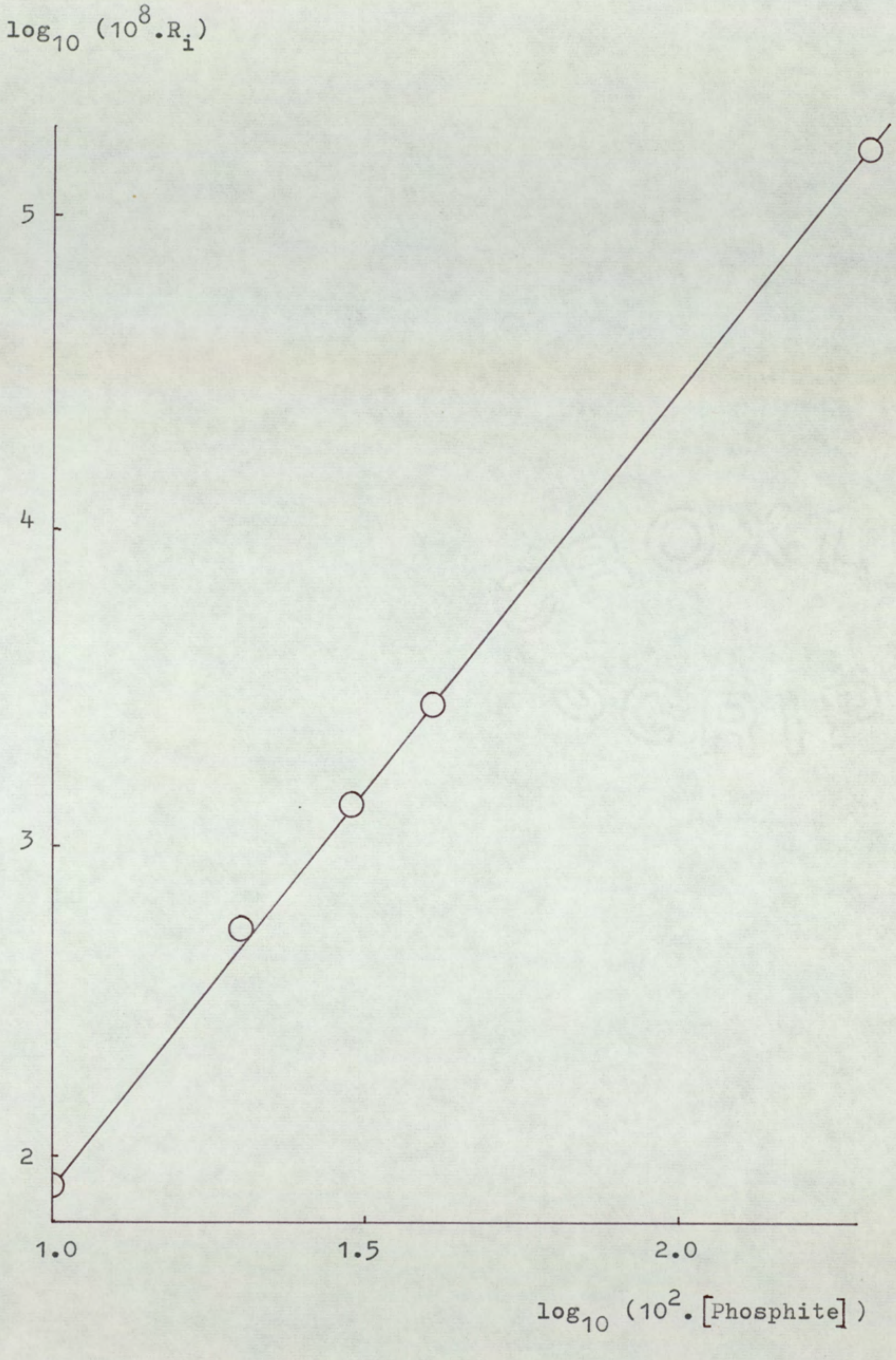


Figure 4.10: Initial rate plot for the reaction of 0.2M cumene hydroperoxide with catechol hindered-phenyl phosphite in ØCl at 75°C.

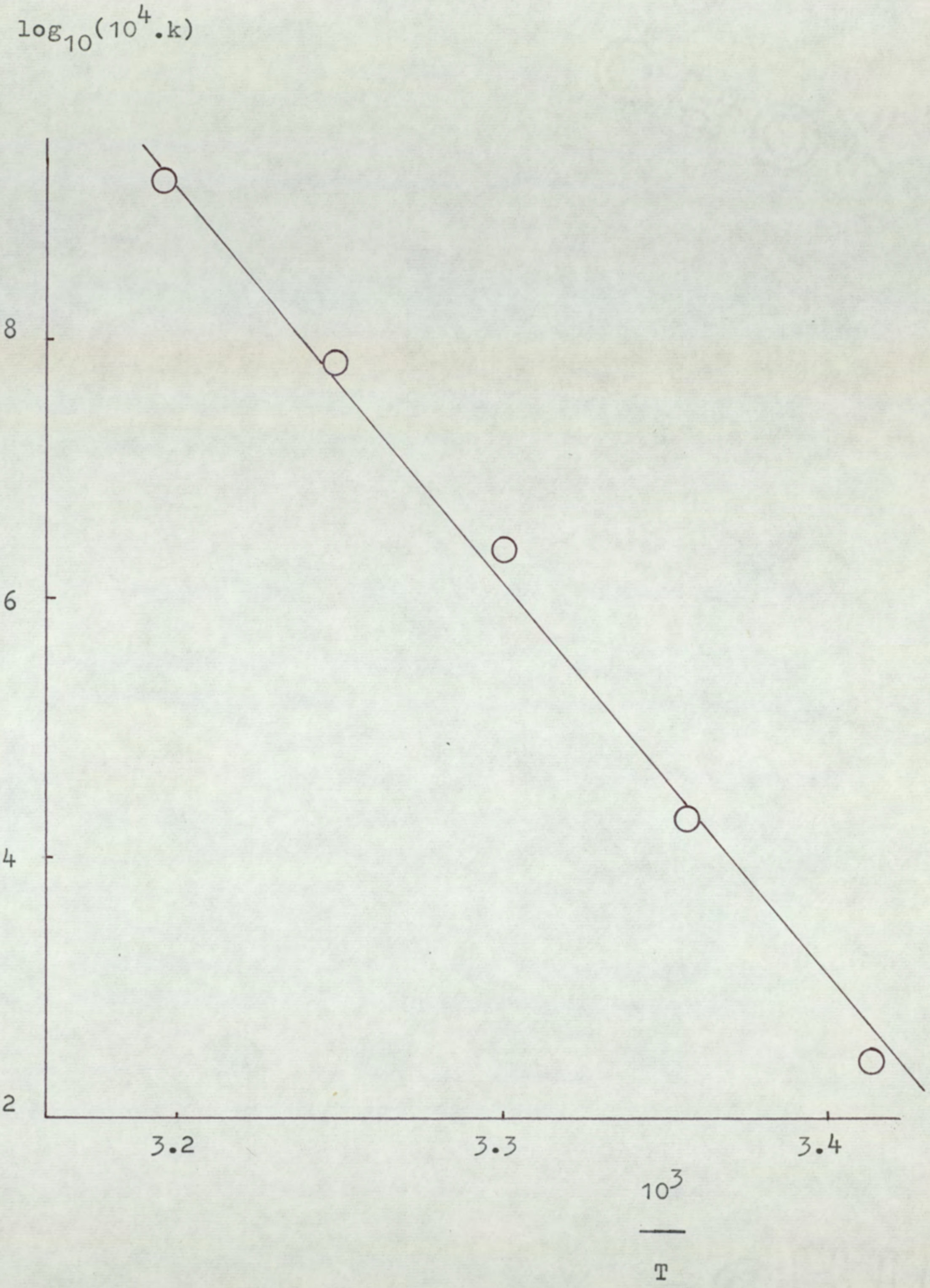


Figure 4.11: Arrhenius plot for the oxidation of catechol hindered-phenyl phosphite by cumene hydroperoxide in ØCl. E_a = 14.1 kcal.mole^{-1}

where: N = Avogadro's number

h = Planck's constant

R = gas constant

T = absolute temperature

we can calculate the entropy of activation, $\Delta S^{\ddagger}$, = -22.7 cal.mole^{-1} deg.$^{-1}$ (entropy units). Using the standard expression, the Arrhenius frequency factor, A, was computed to be 6×10^{7} l.mole^{-1} sec.$^{-1}$.

Table 10: Temperature dependence of the oxidation of catechol hindered-phenyl phosphite by cumene hydroperoxide in chlorobenzene.

T° C.	k_2 l.mole^{-1} sec.$^{-1}$
20	1.75×10^{-3}
25	2.71×10^{-3}
30	4.36×10^{-3}
35	6.06×10^{-3}
40	8.34×10^{-3}

The effect of solvent dielectric on the catalytic decomposition of hydroperoxide by phosphite was found to be considerable, (Table 11), but attempts to fit this data to any of the usual dielectric-rate constant relationships were unsuccessful. This is not unusual, since such relationships are often only obeyed over a limited concentration range.

Table 11: Effect of solvent on the catalytic pseudo-first order decomposition of cumene hydroperoxide by 0.02 M catechol hindered-phenyl phosphite at 75°C.

solvent	dielectric constant	k_1 sec^{-1}
cumene	1.9	6.7×10^{-5}
ØCl	4.9	1.08×10^{-4}
$ØNO_2$	26.9	1.9×10^{-3}

Two of the other cyclic phosphites were briefly examined for their peroxide-decomposing ability. The five-membered isopropyl ethylene phosphite was evaluated in chlorobenzene at 75°C., and like the catechol compounds showed an initial rapid reaction, probably oxidation to phosphate, followed by pseudo-first order kinetics. The reaction was again strongly catalytic, and for $[CHP]_o$ = 0.2M and initial phosphite concentration = 0.02M, k_1 was equal to 5.4×10^{-5} sec.$^{-1}$.

The analogous six-membered compound, isopropyl propylene phosphite, gave similar results, with a rather slower rate of decomposition.

Two of the products identified in the mass spectrum of the catechol phosphite- and phosphate-hydroperoxide reaction products were also briefly examined for their effect on hydroperoxide. Catechol hydroxy phosphate was insoluble in chlorobenzene, so that the observed reactions may be heterogeneous, but in spite of this great reactivity was observed. Catalytic, apparently first order kinetics were observed, and for $[CHP]_o$ = 0.2M and initial phosphate concentration = 0.02 M, k_1 was 8.4×10^{-3} sec.$^{-1}$ at 75°C.

The hydrolysis product of the above, mono(o-hydroxyphenyl) phosphoric acid,which is also insoluble in the reaction medium, showed a similar type of behaviour, the rate constant this time being 2.53×10^{-4} sec.$^{-1}$ at 75°C. for the same concentrations of reactants.

4.2 Discussion

From the results described it appears that cyclic and non-cyclic phosphites show quite different behaviour towards hydroperoxides. Triphenyl phosphite, in agreement with the literature, probably undergoes a rapid stoichiometric reaction.

$$P(RO)_3 + R^1OOH \longrightarrow \overset{\overset{\displaystyle O}{\|}}{P}(RO)_3 + R^1OH$$

and the resulting phosphate shows no further reactivity towards hydroperoxide. The cyclic phosphites appear to undergo this rapid initial oxidation, and the phosphate then undergoes a number of subsequent reactions, with a total stoichiometry of 4:1 hydroperoxide:phosphite, leading ultimately to an unidentified species which is a powerful catalyst for hydroperoxide destruction. From the experiments performed in cumene, for the catechol compounds, the rate of the catalytic reaction with cumene hydroperoxide increased in the order

hindered-phenyl $<$ iso-propyl $<$ phenyl

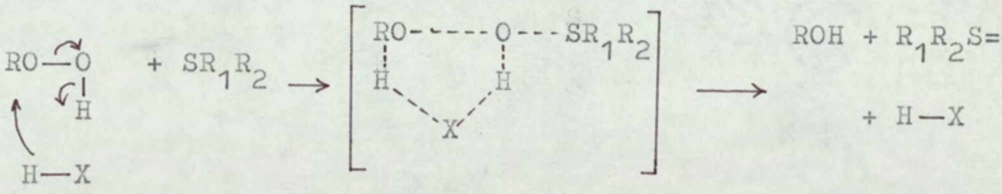
which is clearly not consistent with the order of nucleophilicity. The initial oxidation stage, which would be expected to be governed by inductive effects, was not examined as a function of structure.

For the catechol phosphite this initial oxidation step is first order in both reactants, with a low activation energy, small frequency factor, and a large negative entropy of activation. In addition the reaction rate is not effected by oxygen or free radical scavengers. These data are consistent with a (possibly bimolecular) polar reaction, proceeding via a fairly ordered transition state, and may correspond to Laidler's slow classification[108] characteristic of reactions involving either ions of the same sign, or the formation of opposite charges. Rysavy and Slama[37] have reported the activation energy for the oxidation of triphenyl phosphite by t-butyl hydroperoxide as 8.1 kcal.mole^{-1}, and the reaction is first order in both reactants. From their data we can compute $\Delta S^{\ddagger} = -40$e.u., and at 45°C. $k_2 = 3.1 \times 10^{-2}$ l.mole^{-1}sec^{-1}. These data are qualitatively the same as found for the catechol phosphite (the latter reaction being slower) and it would seem possible that the same reaction is occurring.

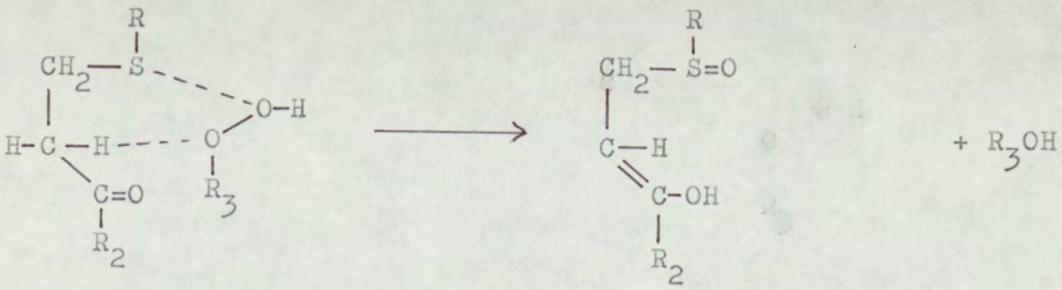
There are analogies between the phosphites discussed and certain sulphide antioxidants. The facile first stage of the reaction of the latter with hydroperoxide is the formation of sulphoxide, which parallels the phosphite reaction:-

$$R_2S + R^1OOH \longrightarrow R_2S = O + R^1OH$$

thus Marshall[109] found that the second order reaction of a variety of sulphides with tetralin hydroperoxide had a small activation energy, low frequency factor, and large negative entropy of activation. Bateman and Hargrave[110], in a thorough study, reported the same kinetic parameters for numerous sulphides, and found that oxygen and free radical scavengers did not affect the reactions. Both workers postulated a theory of complex formation, involving solvent molecules in the latter case:

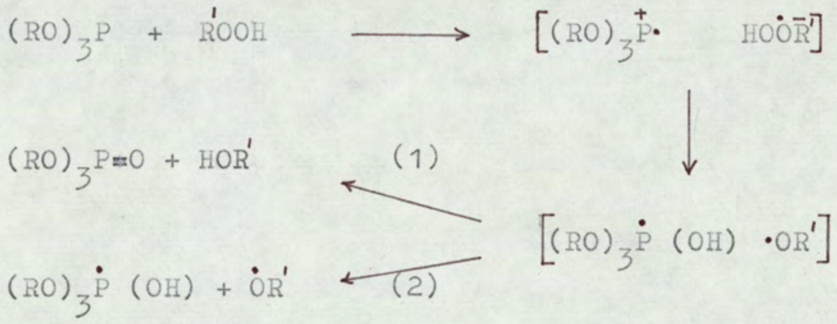


Bateman showed that in the absence of a hydroxylic solvent a second molecule of hydroperoxide assumes the function of X-H, the reaction becoming second order in hydroperoxide. Marshall's mechanism did not involve solvent molecules but was similar to that postulated earlier for β-keto sulphides[111]:-



Despite the superficial resemblance, the phosphite-hydroperoxide kinetics, and the absence of suitable protons in phosphite or solvent, rule out a similar mechanism to the sulphides.

The data pointing towards an ionic type of reaction between phosphite and hydroperoxide is difficult to reconcile with the pro-oxidant effect observed in the hydroperoxide-initiated oxidation studies of the previous chapter, and with the polymerisation results quoted in the following chapter, both of which strongly suggest involvement of a free radical species. The mechanism of Pobedimskii[39] referred to earlier is attractive. The first stage postulated is an electron-transfer from phosphite to hydroperoxide with formation of an ion-radical complex, which is then converted monomolecularly into a radical pair within a solvent "cage":-



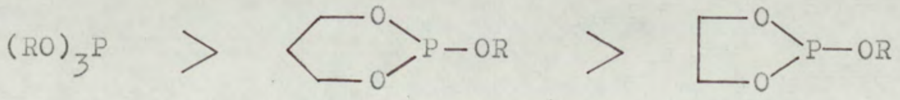
This radical pair disappears either due to disproportionation (1) within the solvent cage, or by dissociation (2).

If the first stage was rate controlling then the sort of kinetic parameters observed would be expected. The low outflow of radicals to the bulk suggested would account for the comparatively small amount of radical involvement, but it is difficult to reconcile the absence of any effect due to oxygen or free radical scavengers (unless the reaction occurs entirely within a solvent cage). In the next chapter a redox reaction very similar to the above is postulated, analogous to the well-known amine/peroxide systems, which is more satisfactory.

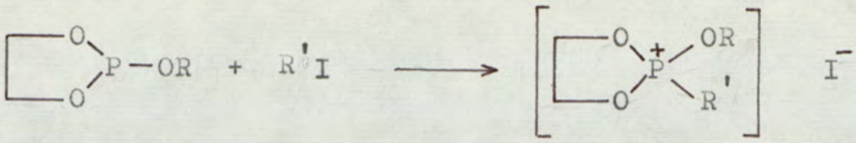
The rates of oxidation of cyclic phosphites are of interest in view of the high reactivity often associated with cyclic compounds. Ring strain, the principal cause of this rate-enhancement, is a thermodynamic property caused either by forcing the bonds between ring atoms into an angular distortion, or by steric interaction of substituents on the ring atoms. The rate of nucleophilic substitution on phosphorus in quadruply linked phosphorus compounds is enhanced when phosphorus is in a ring system, the effect being greatest in 1,3,2-dioxaphospholan systems. Thus for example 5-membered phosphates hydrolyse much more rapidly than their acyclic analogues[112] in acid[113] and alkaline[114] solution, the rate increase being as large as 10^7. Large increases in rate are not restricted to ring cleavage reactions, phosphoryl-oxygen exchange[115] and exocyclic cleavage[116] also being greatly enhanced in cyclic systems. The ring strain theory also finds support in the increased heats of hydrolysis (5-9kcal.mole^{-1}) found in the cyclic compounds[117,118]. The non-ring scission reactions are satisfactorily explained by the principle of pseudo-rotation[119] between trigonal-bipyramidal intermediates.

The influence of ring size in cyclic phosphites upon electrophilic substitution at phosphorus is less well known. It has been reported[118] that rates of hydrolysis of cyclic phosphites are little different from their open chain analogues, a situation existing in the parallel sulphur compounds. Ethylene sulphite is less easily hydrolysed in acid solution than dimethyl sulphite[120], in contrast to the rate enhancement found in the corresponding cyclic sulphate[118].

Similarly the reactivity of a series of phosphites with alkyl halides (Arbusov reaction) was found to be,



the difference between the most and least reactive being less than 1 power of 10[121]. The rate controlling first step was thought to be the formation of the phosphonium intermediate:-



Similarly cyclic phosphites are the least reactive towards condensation with biacetyl[122], and the most strained cyclic phosphites are reported to react least readily with benzoyl peroxide[41].

Thus our observation that reaction of hydroperoxide with the hindered-phenyl catechol phosphite, (and probably the isopropyl and phenyl compounds too) is slower than reaction with triphenyl phosphite, is consistent with the general pattern of reactivity, and the parallel experiments of the Russian workers[36-39]. The mechanism proposed for the phosphite-hydroperoxide reaction is discussed in detail, with the relevant evidence, in the next chapter.

One hypothesis suggests[115] that partial double bonding between the ester oxygen atoms and the hetero-atom in a five-membered ring is essential for kinetic acceleration. This requires that with phosphites and sulphites, the presence of an unshared pair of electrons on phosphorus (or sulphur) partially represses the formation of a double bond between the hetero-atom and the ester oxygen atoms. Such partial double bonding is generally accepted for phosphates[123]. The independent determination of shortened P-O bond lengths in some phosphates by X-ray crystallography[124] support this. Also P^{31} n.m.r. data show a much larger shift for phosphites than phosphates[125,126], indicating that the oxygen atom in phosphates contributes to shielding of the nucleus by partial bonding with the phosphorus d-orbitals.

It is possible that the reactivity of the catechol phosphate esters towards hydroperoxide, in contrast to triphenyl phosphate, may be a result of the type of ring strain discussed above.

The nature of the reaction profile for the phosphate-hydroperoxide reaction is similar to that observed in reaction of the latter with organic sulphoxides, an induction period preceeding first order kinetics[109,127]. In the case of sulphoxide the first reaction may be oxidation to sulphone

$$R_2S{=}O + R'OOH \longrightarrow R_2S\overset{\nearrow O}{\underset{\searrow O}{}} + R'OH$$

Bateman suggests[128] another reaction involving complex formation presumably analogous to the case of the sulphide. Clearly a sulphone-type of reaction is not possible with phosphates, and recent work from this laboratory[127] has shown that little complex formation occurs between dimethylsulphinyl diproprionate and cumene hydroperoxide.

The catalytic species derived from the catechol hindered-phenyl phosphate has an activation energy of 14.4 kcal.mole^{-1} for its reaction with cumene hydroperoxide in chlorobenzene, and the overall stoichiometry of 4:1 hydroperoxide: phosphite suggests at least two subsequent steps, due to the small probability of a reaction being termolecular (in hydroperoxide).

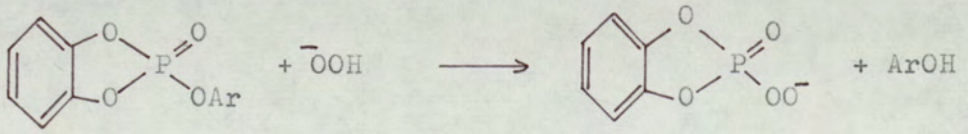
$$(RO)_3P + ROOH \longrightarrow (RO)_3P{=}O$$

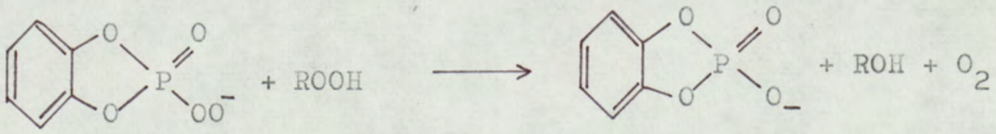
$$(RO)_3P{=}O + ROOH \longrightarrow [X]$$

$$[X] + ROOH \longrightarrow [P] \quad \text{active species}$$

The nature of the hydroperoxide decomposition products (reported in chapter 6) suggest that "P" is a Lewis acid species.

A number of plausible reaction schemes can be written for the reaction of catechol phosphate with hydroperoxide. For example, attack of perhydroxyl ion on phosphate has been observed in some systems [129].


(1)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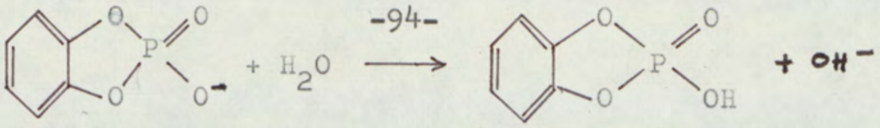
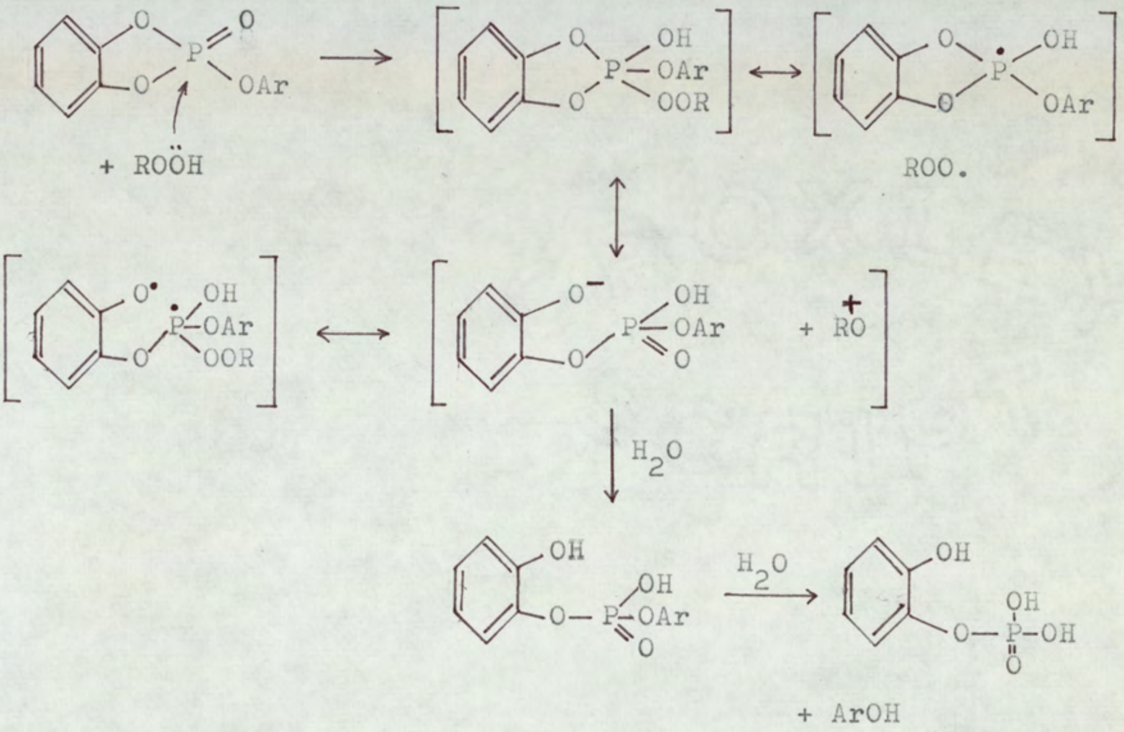


(3)

Step (2) of this reaction sequence is typical of base-catalysed decompositions of hydroperoxide[130], but is less likely in the present system since no gas evolution occurs with phosphate.

A scheme involving attack of hydroxyl oxygen on phosphorus can also be written, leading to formation of a penta-covalent intermediate. Radical species can also be invoked here.



It is difficult to see why any of these reactions should be specific to cyclic phosphates, since the steric effect of the ring structure is unlikely to control the reaction. Ring strain as discussed above may be responsible.

Once the ring is opened, catalysis by the neighbouring hydroxyl group may play a part (see chapter 7).

As discussed earlier, $\Delta S^{\ddagger}$ for the catalytic hydroperoxide decomposition cannot be determined (the apparent $\Delta S^{\ddagger}$ = -36 e.u.), but it is likely to be fairly large and negative since the steric requirements for approach to a tetrahedral molecule are more exacting than for a planar one, and in addition three partially charged oxygen atoms require solvation in the transition state, since $p\pi$- $d\pi$ bonding to phosphoryl oxygen is interrupted in penta-covalent structures.

5 FREE-RADICAL STUDIES - Results and Discussion

One aim of this section was to determine whether the phosphites and phosphates under investigation were able to react with alkyl or alkylperoxy radicals (derived from AZBN) in order to assess their degree of chain stopping activity. This was done by observing the effects of the different compounds on the polymerisation of styrene (and methyl methacrylate) first in nitrogen, and then in an atmosphere of oxygen.

The other aim was to observe the effect of various phosphites on the polymerisation of vinyl monomers initiated by cumene hydroperoxide, since the pro-oxidant effect described in section 3 suggested the involvement of a free radical species during reaction with hydroperoxide. The presence of such a species should be observable by its influence on the rate of polymerisation.

In addition some preliminary electron spin resonance studies were carried out in an attempt to positively identify any radical species formed.

5.1 Results

5.1.1 AZBN initiation

Using the vacuum dilatometer and the technique previously described the rates of polymerisation of styrene in nitrogen at 75°C. were measured for a range of initiator concentrations. The same experiments were then repeated in the presence of 0.01M catechol hindered-phenyl phosphite. The expected linear dependence of the rate of polymerisation on the square root of the initiator concentration was observed (Figure 5.1), and from the data in Table 12 it can be seen that the phosphite did not affect the polymerisation rate.

Table 12: Effect of phosphite on the rate of the AZBN-initiated polymerisation of styrene in nitrogen at 75°C.

AZBN		AZBN + 0.01 M phosphite	
[AZBN] mole $l.^{-1}$	R_p mole $l.^{-1}sec.^{-1}$	[AZBN] mole $l.^{-1}$	R_p mole $l.^{-1}sec.^{-1}$
0.00464	1.92×10^{-4}	0.00602	2.22×10^{-4}
0.0145	3.30×10^{-4}	0.0094	2.77×10^{-4}
0.00934	2.83×10^{-4}	0.0112	3.0×10^{-4}
0.00788	2.50×10^{-4}	0.0125	3.17×10^{-4}
0.0173	3.51×10^{-4}	0.0154	3.34×10^{-4}
0.0203	3.79×10^{-4}	0.0179	3.67×10^{-4}

Experiments over several months, using several different batches on monomer, with $[AZBN]_o = 0.01M$ gave a rate of polymerisation $= 2.70 \pm 0.15$ mole $l.^{-1}sec.^{-1}$. Results within one set of runs were often much better than this.

Next the same experiments were repeated in an oxygen atmosphere and Figure 5.2 shows that again phosphite shows no retardation of rate. Rates were consistently faster in the presence of oxygen.

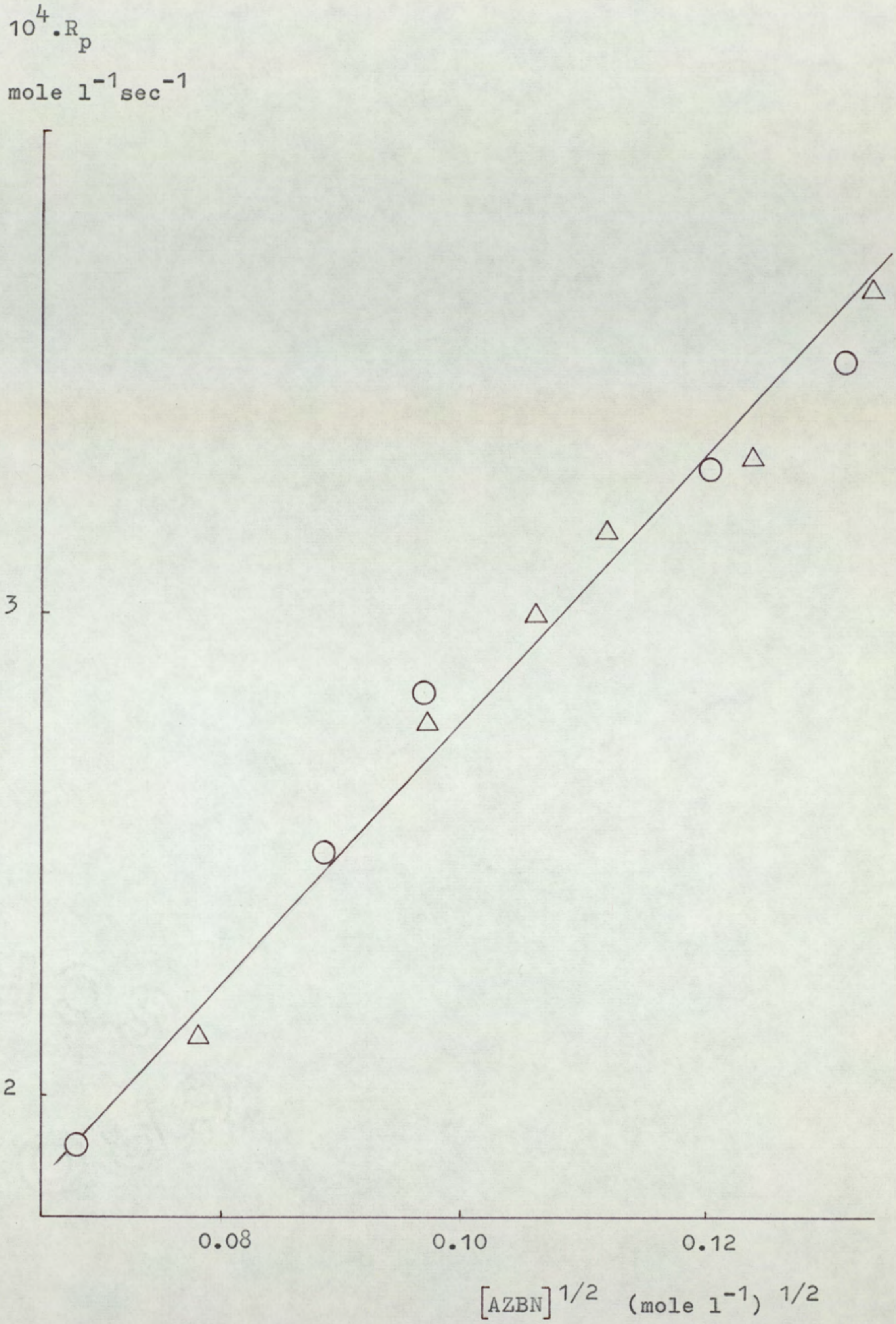


Figure 5.1: Dependence of the rate of polymerisation of styrene in N_2 on the concentration of AZBN in the presence (△) and absence (○) of 0.01M catechol hindered-phenyl phosphite.

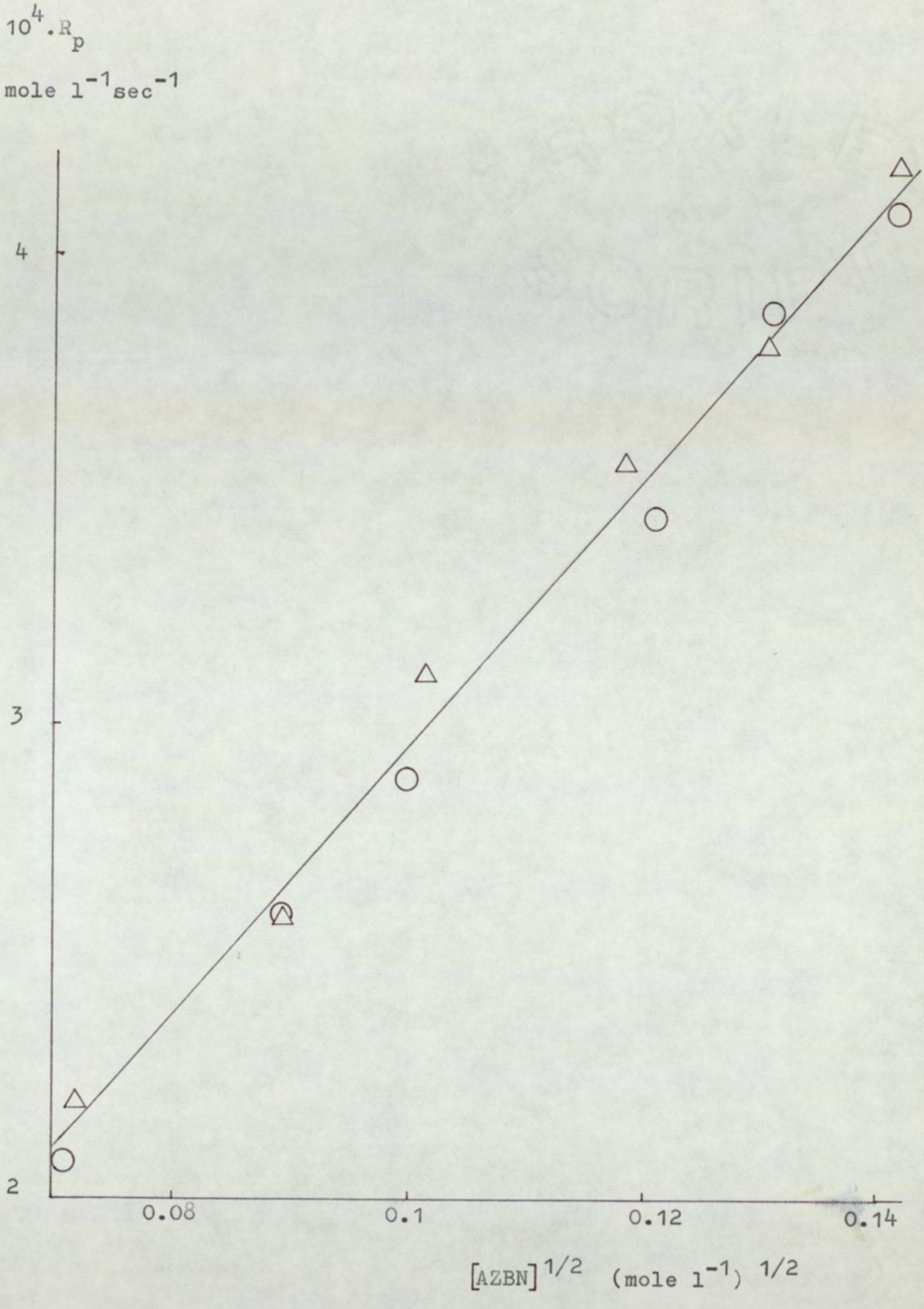


Figure 5.2: Dependence of the rate of polymerisation of styrene in O_2 on the concentration of AZBN, in the presence (△) and absence (○) of 0.01M catechol hindered-phenyl phosphite.

Other phosphites were similarly evaluated in styrene, (Table 13) and in all cases no retardation was observed.

Table 13: Effect of phosphites on the rate of polymerisation of styrene $[AZBN]_o = 0.01M$ at 75°C.

phosphite	[phosphite] mole $l.^{-1}$	R_p mole $l.^{-1}sec.^{-1}$
catechol	0.0096	2.63×10^{-4}
isopropyl	0.0209	2.62×10^{-4}
phosphite	0.0324	2.62×10^{-4}
catechol	0.0113	2.54×10^{-4}
phenyl	0.0172	2.60×10^{-4}
phosphite	0.101	2.59×10^{-4}
triphenyl	0.012	2.75×10^{-4}
phosphite	0.102	2.76×10^{-4}
ethylene	0.05	2.66×10^{-4}
isopropyl	0.102	2.73×10^{-4}
phosphite	0.153	2.67×10^{-4}
"	0.198	2.64×10^{-4}

To ensure that no effect was missed individual experiments were carried out with hindered-phenyl catechol phosphite concentrations up to 0.2M, i.e. 20 x fold excess of inhibitor, without any observable effect. In addition some runs were repeated using methyl methacrylate monomer, which confirmed the generality of the results.

The catechol hindered-phenyl phosphate was evaluated in the same polymerisations in air and in nitrogen, and similarly failed to show any retarding effect.

5.1.2 Hydroperoxide initiation

Polymerisations were carried out in air, and in the first series of experiments initial rates of polymerisation were determined dilatometrically as a function of cumene hydroperoxide concentration in the presence and absence of a fixed concentration of the hindered-phenyl catechol phosphite.

Table 14: Effect of catechol hindered-phenyl phosphite on the rate of cumene hydroperoxide-initiated styrene polymerisation at 75°C.

cumene hydroperoxide		cumene hydroperoxide + 0.01M phosphite	
[CHP] mole l.$^{-1}$	R_p mole l.$^{-1}$sec.$^{-1}$	[CHP] mole l.$^{-1}$	R_p mole l.$^{-1}$sec.$^{-1}$
0.00982	0.655×10^{-4}	0.00982	1.17×10^{-4}
0.0244	0.892×10^{-4}	0.0166	1.81×10^{-4}
0.05	1.22×10^{-4}	0.0253	2.82×10^{-4}
0.088	1.63×10^{-4}	0.0289	3.24×10^{-4}
0.125	1.82×10^{-4}	0.0456	4.17×10^{-4}
0.170	2.07×10^{-4}	0.0671	4.65×10^{-4}
0.2025	2.21×10^{-4}	0.102	5.55×10^{-4}
0.254	2.43×10^{-4}	0.128	5.80×10^{-4}
		0.147	5.84×10^{-4}
		0.163	5.50×10^{-4}
		0.1845	4.89×10^{-4}
		0.222	4.17×10^{-4}
		0.262	4.02×10^{-4}

The uninhibited polymerisation showed the expected dependence once again of the rate of polymerisation on (concentration of initiator)$^{1/2}$, whilst in the presence of phosphite a considerable rate increase was observed, the rate often being more than doubled (Table 14). This rate increase followed a smooth curve passing through a maximum at a ratio of hydroperoxide:phosphite = 13:1, falling after that, but never regaining the "uninhibited" curve. Similar experiments were performed with the catechol isopropyl phosphite. A slightly smaller rate increase was found this time but again the rate-concentration curve passed through a maximum at hydroperoxide:phosphite = 13.7:1. (Figure 5.3).

The next series of experiments measured the rates of polymerisation of styrene containing various concentrations of catechol phosphite, initiated by a fixed concentration of cumene hydroperoxide (Table 15).

Table 15: Rate of polymerisation of styrene in the presence of catechol hindered-phenyl phosphite at 75°C.

$[\mathrm{CHP}]_o = 0.1\mathrm{M}$

[phosphite] mole $l.^{-1}$	R_p mole $l.^{-1}$ $sec.^{-1}$
0	1.7×10^{-4}
0.00495	3.15×10^{-4}
0.010	4.74×10^{-4}
0.0147	5.79×10^{-4}
0.020	7.03×10^{-4}
0.0253	7.85×10^{-4}
0.0303	9.45×10^{-4}

Figure 5.4 shows that this time a good linear relationship exists between polymerisation rate and concentration, for which

$$R_p = 0.025.[\mathrm{phosphite}] + 1.9 \times 10^{-4} \text{ mole } l.^{-1} sec.^{-1}$$

For comparative purposes rates of reaction in the presence of triphenyl phosphite were measured for a fixed concentration of hydroperoxide. Table 16 shows that this time the rates of

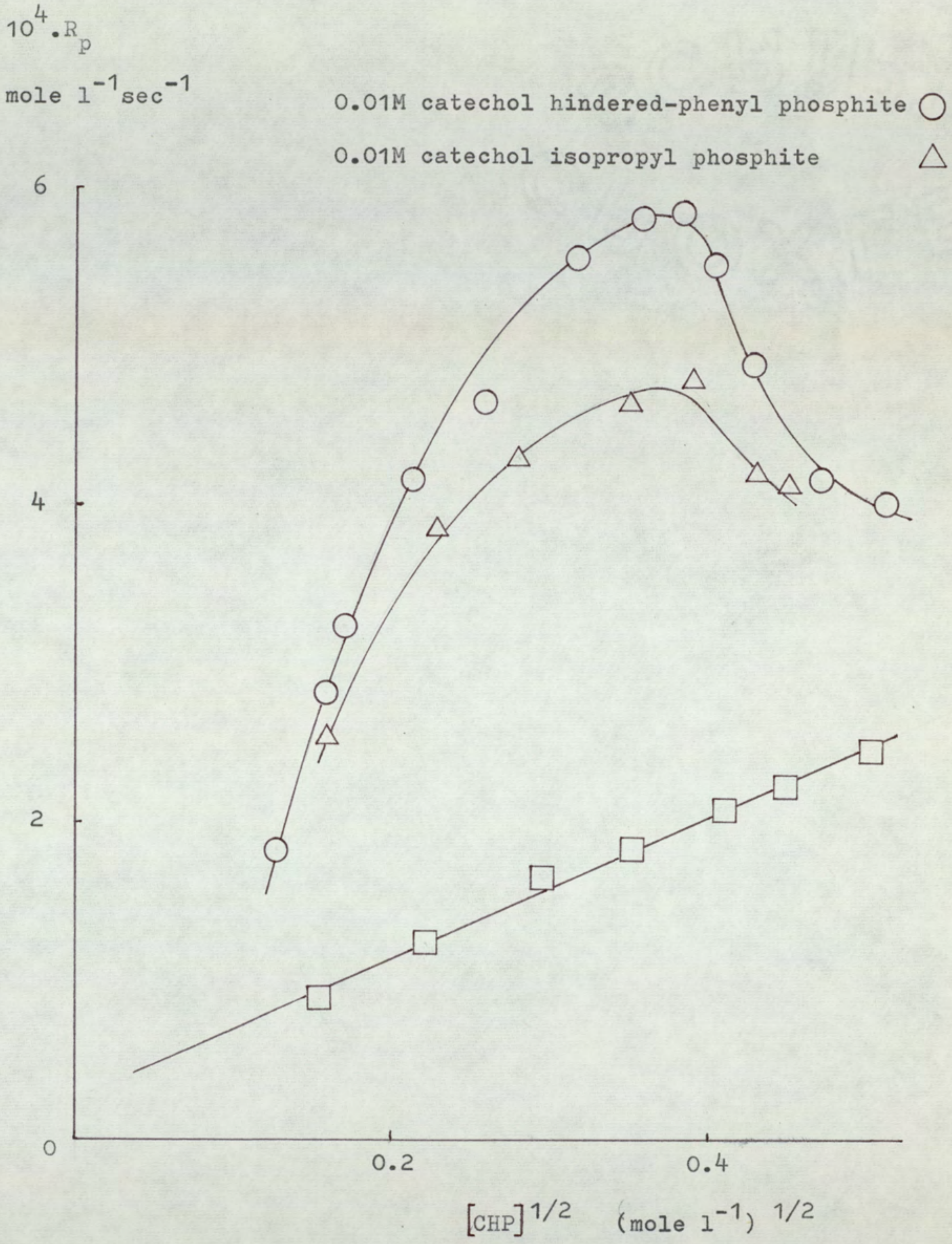


Figure 5.3: Dependence of the rate of polymerisation of styrene in O_2 on hydroperoxide concentration in the presence and absence (□) of catechol phosphites.

polymerisation are progressively decreased.

Table 16: Rate of polymerisation of styrene in the presence of triphenyl phosphite at 75°C.

$[\mathrm{CHP}]_o = 0.2\mathrm{M}$

[phosphite] mole $l.^{-1}$	R_p mole $l.^{-1}sec.^{-1}$
0	2.2×10^{-4}
0.049	1.88×10^{-4}
0.13	1.20×10^{-4}
0.158	1.04×10^{-4}
0.202	0.48×10^{-4}

Assuming from the previous work that a stoichiometric reaction occurs with hydroperoxide, then addition of x mole $l.^{-1}$ of triphenyl phosphite should leave (0.2-x) mole $l.^{-1}$ of hydroperoxide for initiation, assuming that the reaction products do not take part in the polymerisation. The rates of polymerisation corresponding to these values of initiator concentration were determined from a previous graph, and plotted with the data from Table 16 in Figure 5.5. The two sets of data are co-linear. This provides in a single experiment additional evidence that reaction of triphenyl phosphite with cumene hydroperoxide is rapid and quantitative and that triphenyl phosphate does not have any further reaction with hydroperoxide, or any radical deactivating activity.

Since the alicyclic phosphites and triphenyl phosphite react so rapidly with hydroperoxide, a slightly different technique had to be adopted to assess their radical-generating potential. A solution of initiator in styrene was thermostatted in a dilatometer in the usual way and allowed to react until a steady state rate of polymerisation was attained. The phosphite was then added by means of a pipette, and mixing achieved by gently blowing a stream of air through the styrene mixture. In this way the

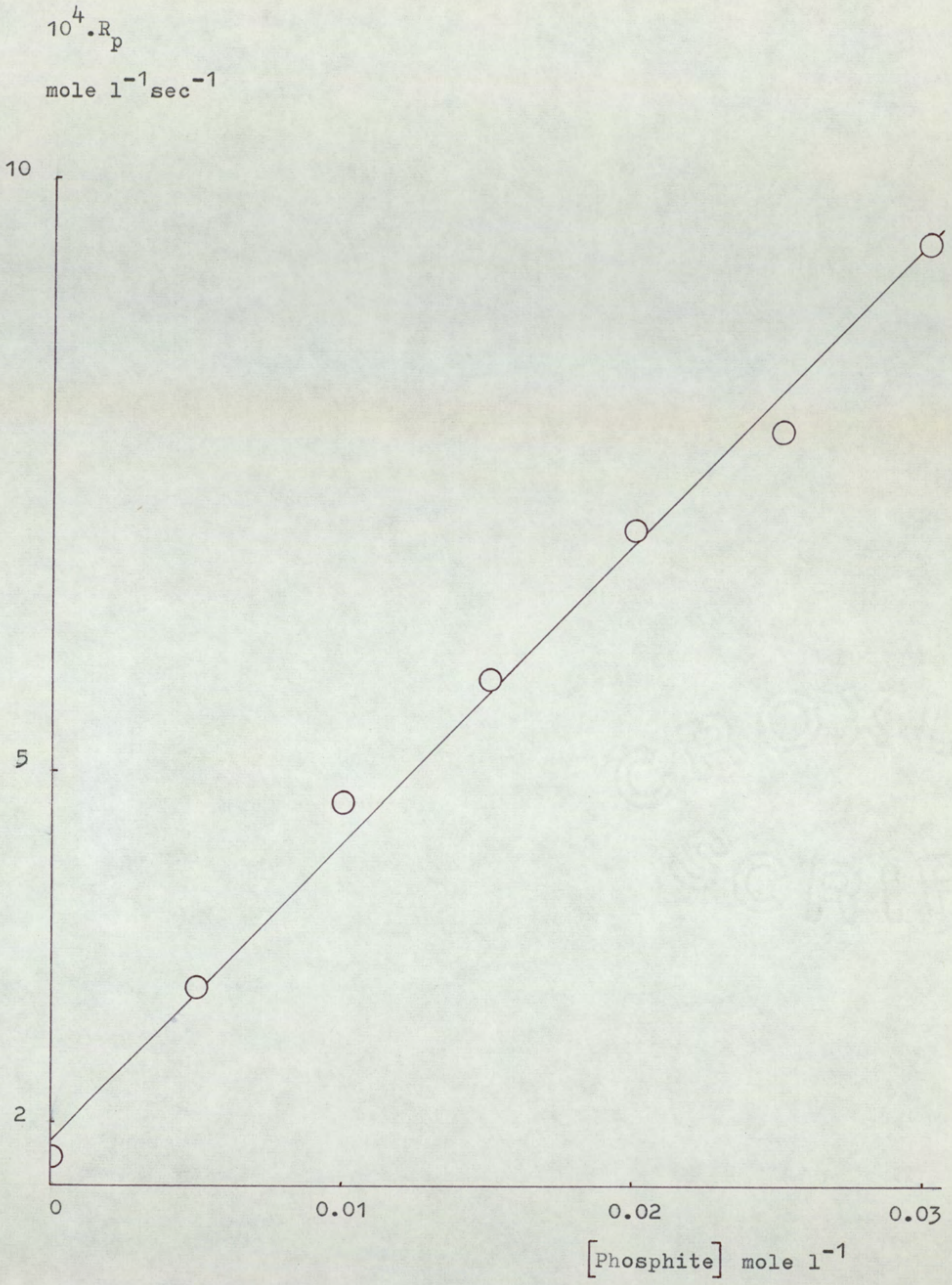


Figure 5.4: Dependence of the rate of polymerisation of styrene on concentration of catechol hindered-phenyl phosphite in the presence of 0.1M cumene hydroperoxide.

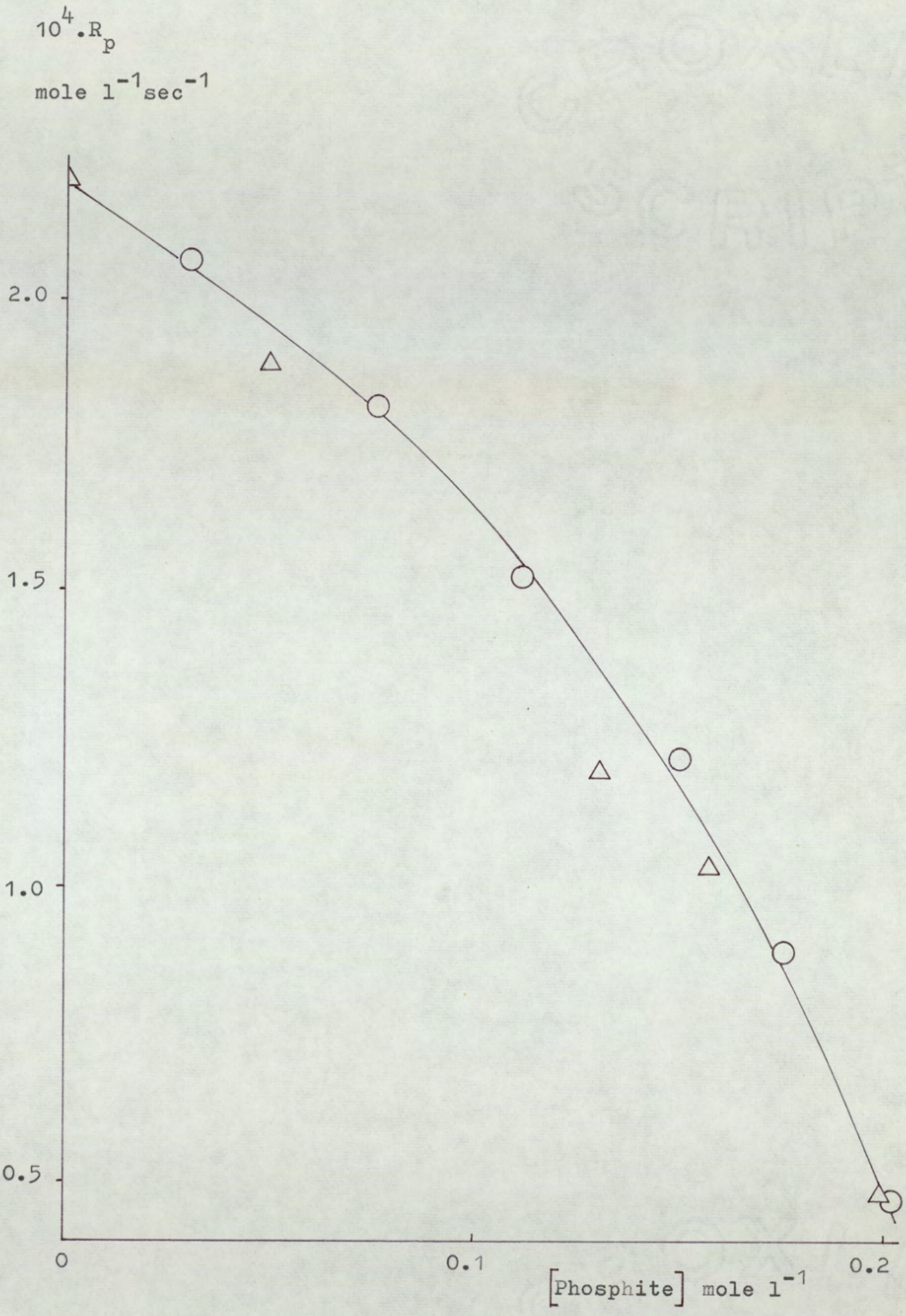


Figure 5.5: Polymerisation of styrene initiated by 0.2M CHP

△ in the presence of triphenyl phosphite

○ points calculated for stoichiometric phosphite-CHP reaction instantaneous effect was observed, and for triphenyl, and ethylene isopropyl phosphites, a large increase in polymerisation rate occurred (Figure 5.6). This rate fell off within a few minutes, and the final steady-state rate was lower than the initial rate due to the hydroperoxide destroyed. The cyclic compound is a catalytic peroxide decomposer, so that in time the rate of polymerisation in the presence of this compound would reduce to zero. The nature of the experiment did not allow the reaction to be continued to the higher conversions needed to show this.

Finally triphenyl phosphate, and catechol hindered-phenyl phosphate were shown to have no effect on the hydroperoxide-initiated polymerisation. The former compound was shown in section 4 to be inert towards hydroperoxide. The cyclic compound does destroy hydroperoxide after an induction period, but the low extents of polymerisation to which conversion was followed in these experiments meant that within the time scale employed, little decomposition of hydroperoxide would occur, and hence the rates of polymerisation were not significantly effected.

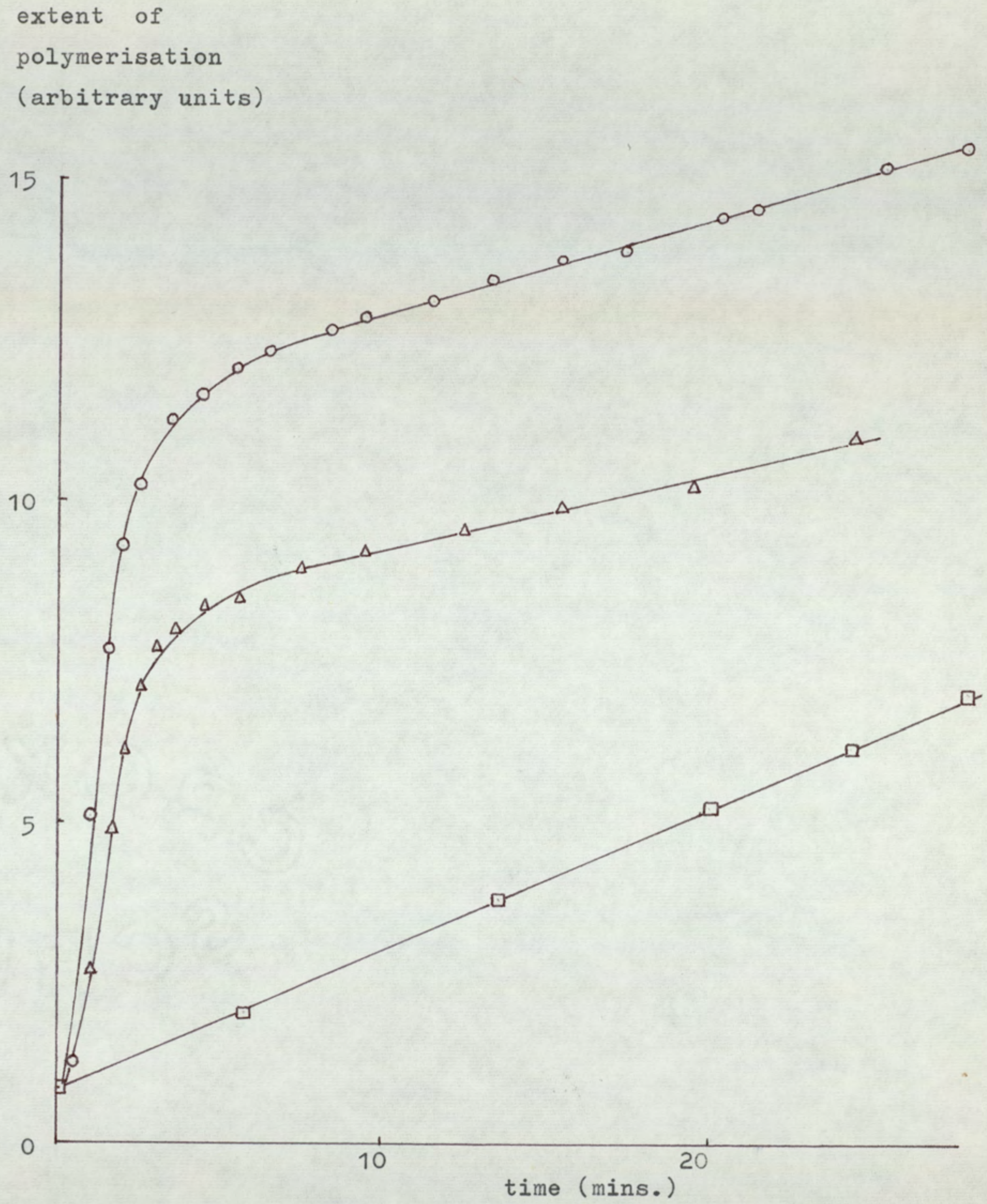


Figure 5.6: Polymerisation of styrene using 0.2M CHP and

△ 0.12M triphenyl phosphite

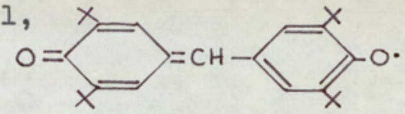
○ 0.155M ethylene isopropyl phosphite

□ 0.2M CHP only

5.1.3 Electron spin resonance studies.

A few experiments were carried out to see whether any radical intermediates from the phosphite-hydroperoxide reaction were present in sufficient concentration to enable a spectrum to be obtained. Even at equi(0.2)molar phosphite and hydroperoxide no signal was observed.

Another approach investigated was to react phosphite and hydroperoxide in the presence of Galvinoxyl,



a stable free radical. It was found that the intense colour of this compound disappeared rapidly when only hydroperoxide was present, leaving a yellow solution, presumably due to hydrogen abstraction. Thus the measurement of rates of radical formation by coupling with galvinoxyl was not possible. The less stable N-oxide radicals used by Russian workers[39] will probably react similarly. Surprisingly these authors claim to have identified a cation-radical species from the reaction of a catechol phosphite with t-butyl hydroperoxide in trifluoroacetic acid solution. As expected, hydroperoxide reacted violently with trifluoroacetic acid, and in our hands the system described did not produce a signal in the microwave region.

5.2 Discussion

In all the polymerisation rates quoted, the purely thermal polymerisation of styrene, reported as equivalent to 0.3% per hour at 75°C.[131], has been neglected. Our experiments fall in the range 5-25% per hour, and runs were taken to about 10% conversion.

Our result for initiation by 0.01M AZBN in nitrogen at 75°C. of 2.8×10^{-4} mole $l.^{-1}$ $sec.^{-1}$, is in reasonable agreement with Haward and Simpson's value[132] (by extrapolation) of 3.4×10^{-4} mole $l.^{-1}$ $sec.^{-1}$.

In the absence of oxygen, and assuming no transfer reactions, vinyl polymerisation occurs as follows[133].

$$\text{Initiator} \longrightarrow \text{R.} \tag{1}$$

$$\text{R.} + \mathrm{CH_2{=}CH\text{Ø}} \longrightarrow \mathrm{R{-}CH_2{-}\dot{C}H\text{Ø}} \tag{2}$$

$$\mathrm{R{-}CH_2{-}\dot{C}H\text{Ø}} + \mathrm{CH_2{=}CH\text{Ø}} \longrightarrow \mathrm{R{-}CH_2{-}CH\text{Ø}{-}CH_2{-}\dot{C}H\text{Ø}} \tag{3}$$

$$\mathrm{2R(CH_2{-}CH\text{Ø})_n{-}CH_2{-}\dot{C}H\text{Ø}} \longrightarrow \mathrm{R{-}(CH_2{-}CH\text{Ø})_{2n+2}{-}R} \tag{4}$$

For styrene, addition of monomer to the growing chain occurs almost exclusively head-to-tail, and termination is almost entirely by the combination reaction (4). None of the phosphites or phosphates examined had any effect on the rate of this AZBN initiated polymerisation, even with a 20xfold excess of inhibitor, in support of Walling's observations for triethyl phosphite[20].Reaction has been reported with the more electrophilic phenyl radical[23], so that presumably the electron-withdrawing power of the cyano group in the radical from AZBN does not impart sufficient electrophilic character to enable polar factors to stabilise the transition state for attack on phosphorus. Alkoxy radicals, on the other hand, are reported to react readily[25].

In the presence of oxygen, the polymerisation of styrene leads to the formation of "styrene peroxide", a 1:1 styrene:oxygen copolymer[134], the initiated reaction being envisaged as

$$R\text{-}R \longrightarrow 2R\cdot$$

$$R\cdot + O_2 \longrightarrow RO_2\cdot \qquad (5)$$

$$RO_2\cdot + CH_2 = CH\phi \longrightarrow RO_2\text{-}CH_2\text{-}\dot{C}H\phi \qquad (6)$$

$$RO_2\text{-}CH_2\text{-}\dot{C}H\phi + O_2 \longrightarrow RO_2\text{-}CH_2\text{-}CH\phi O_2\cdot \qquad (7)$$

$$RO\text{-}CH_2\text{-}CH\phi O_2\cdot + CH_2 = CH\phi \longrightarrow ROCH_2CH\phi O_2CH_2\dot{C}H\phi \qquad (8)$$

leading to formation of $\left[CH_2\text{-}CH(\phi)OO\right]_n$. Initiation by the peroxide is negligible in the presence of AZBN, and the usual half-order dependence of rate on initiator concentration was obeyed. The addition reaction (2) is greatly favoured over the possible hydrogen-abstraction reaction:

$$RO_2\cdot + CH_2 = CH\phi \longrightarrow ROOH + CH_2 = \dot{C}\phi$$

when the double bond is conjugated, as in styrene, with the aromatic group[135].

Again none of the phosphites or phosphates inhibited these reactions even in large excess, despite the reports from a number of authors[20,25] of the reaction

$$RO_2\cdot + (RO)_3P \longrightarrow RO\cdot + (RO)_3PO$$

unless the reaction is very slow. This result is a little surprising in view of the ability of all the phosphites studied to inhibit the AZBN-initiated oxidation of hydrocarbons. The explanation may be in the comparative rates of the reactions occurring.

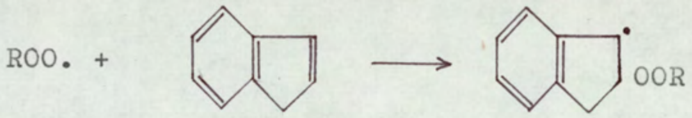
Reaction (5) of the above scheme is rapid[135], addition of oxygen being 10^6 faster than addition of monomer as in reaction (2). In addition, somewhat surprisingly, tertiary polyperoxy radicals are generally more reactive than the corresponding monomeric peroxy radicals[136], so that (8) > (6). Thus the oxidation and polymerisation results may be understood if the phosphite, or a species derived from it, is able to compete with the hydrocarbon for alkylperoxy radicals in the slow rate-determining step of the oxidation

$$ROO_2. + RH \longrightarrow ROOH + R.$$

whilst being ineffective in competing with monomer for alkylperoxy radicals in oxidative polymerisation.

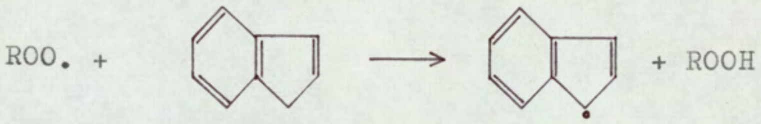
$$RO_2. + CH_2 = CH\emptyset \longrightarrow ROOCH_2\text{-}\dot{C}H\emptyset$$

This conclusion finds support in the work of Russell[137] who examined the oxidation of indene. He found that the addition of alkylperoxy radicals to the double bond of indene, reaction (1), was greatly favoured



(1)

over the hydrogen-abstraction reaction (2), to the extent that



(2)

only 5% of the absorbed oxygen was found as monomeric indenyl hydroperoxide. This indicates the comparative slowness of the hydrogen-abstraction reaction referred to, making competition with such a reaction easy compared to competition with the rapid addition reaction.

The mode of initiation in the hydroperoxide-initiated polymerisation of styrene is open to discussion. An early theory[138] proposed dissociation of hydroperoxide within a cage, some of

$$(ROOH)_{cage} \longrightarrow RO. + .OH \qquad (1)$$

the radicals formed adding to monomer before cage-recombination.

Other theories suggest styrene-induced decomposition such as[139]:

$$ROOH + CH_2 = CH\emptyset \longrightarrow ROO. + CH_3\text{-}\dot{C}H\emptyset \qquad (2)$$

and the same authors describe evidence for chain transfer reactions of the type

$$\sim\!\sim CH_2\text{-}\dot{C}H\phi + ROOH \longrightarrow \sim\!\sim CH_2\text{-}CH_2\phi + ROO.$$

which is supported by the later work of Hiatt[140].

Benson[141] on the other hand rules out reaction (1) and (2) in favour of a reaction which is bimolecular in monomer

$$2CH_2 = CH\phi + ROOH \longrightarrow \phi\text{-}\dot{C}HCH_2CH_2CH_2\phi + ROO.$$

Whatever the true nature of the initiation step, it is likely that alkylperoxy radicals are involved, so that from the results of the previous experiments (section 5.1.1) trapping of these radicals may not occur (although the concentration will be less in this case).

As shown, the rate of polymerisation in the presence of a fixed phosphite concentration passes through a maximum with increasing peroxide concentration, whilst for a fixed concentration of hydroperoxide the rate is a linear function of phosphite concentratio i.e.

$$R_p = k_3 \left[P \right]_o + k_4$$

By an empirical approach of "best fit" it was found that, at constant phosphite concentration the curves for both catechol phosphites studied were described adequately by an expression of the type

$$R_p = \frac{\left[CHP\right]_o}{k_1 + k_2 \left[CHP\right]_o^2}$$

This is shown in Figure 5.7 where by rearrangement of the above expression $\left[CHP\right]_o^2$ is plotted against $\left[CHP\right]_o/R_p$, to give straight lines from which k_1 = intercept, sec.$^{-1}$

k_2 = slope, mole^{-2}l.^{2}sec.$^{-1}$

Thus the overall rate of polymerisation in the presence of phosphite can be expressed as

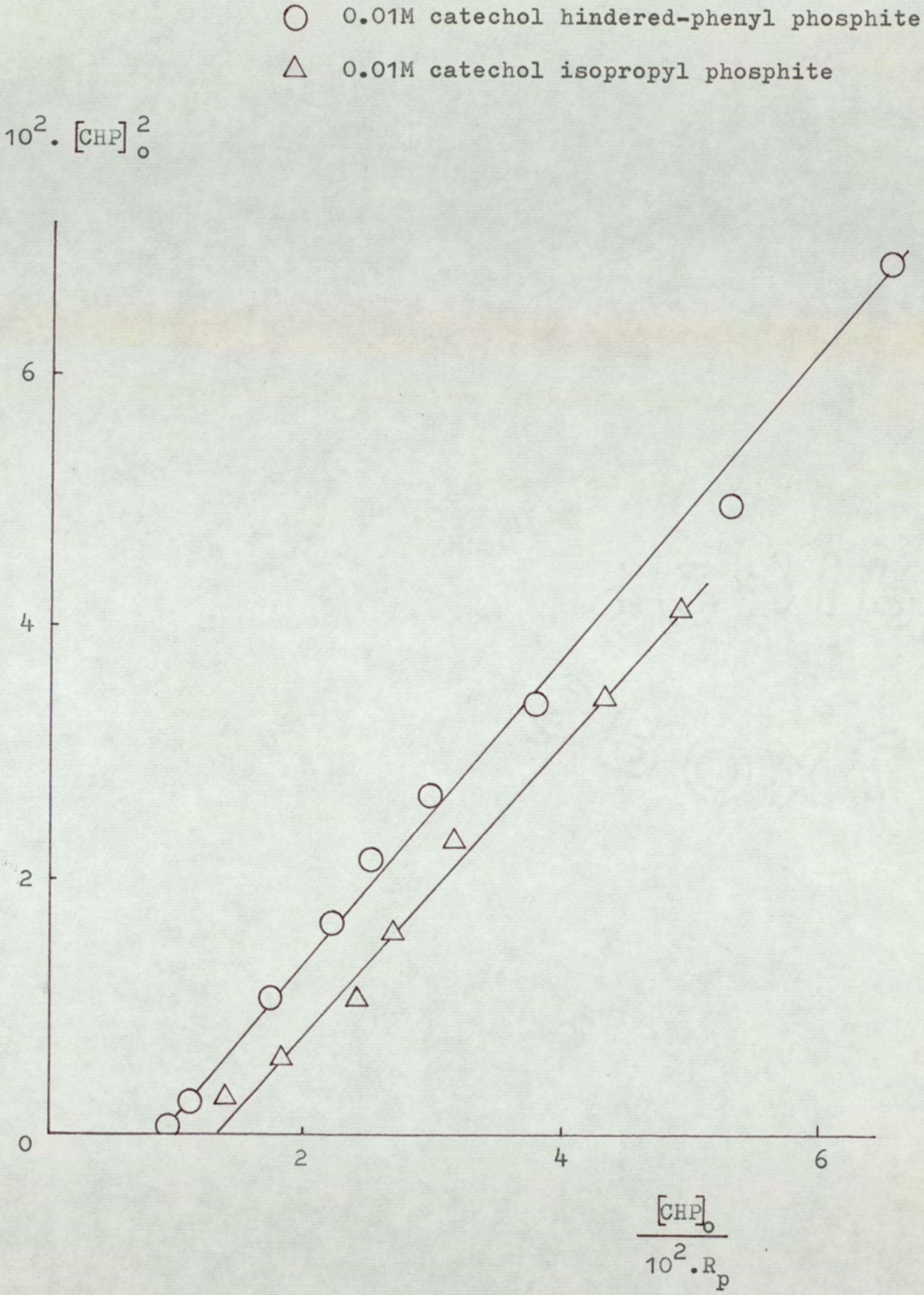


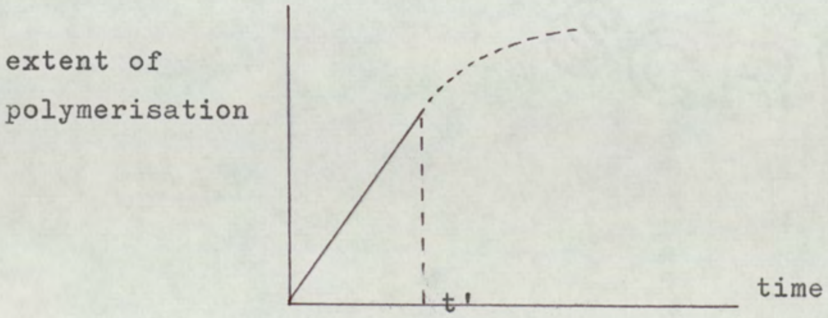
Figure 5.7: Empirical relationship between the rate of polymerisation of styrene & cumene hydroperoxide concentration, in the presence of catechol phosphites.

$$R_p = \left[\frac{k_3 \, [CHP]_o \, [P]_o}{k_1 + k_2 \, [CHP]_o} \right]^{1/2}$$

where $[P]_o$ = initial phosphite concentration.

If this is a genuine relationship, then the term in the denominator is of interest, since it appears to be independent of phosphite concentration. It seems likely that k_2 contains a concentration term related to phosphite or a derived product, and the expression may be due to the catalytic peroxide destruction already described, which leads to predominantly non-radical products, and hence appears in the expression for R_p because of removal of hydroperoxide rather than because of free radical involvement. Clearly more work needs to be done on this aspect of the phosphite-hydroperoxide reaction, but it was not felt that the details of such a scheme fell within the scope of the project.

However, all the phosphites examined lead to an increase in the rate of polymerisation. In the case of the alicyclic compounds, reaction with hydroperoxide was so rapid that rate acceleration was only observed for a few minutes at 75°C. (in accord with the rapid rate reported in the previous section). For the catechol compounds, the initial rapid rates of polymerisation gradually decreased:-



The length of time, t', after which the rate fell off was found to increase (for catechol phosphites):-

hindered-phenyl > isopropyl > phenyl

which is the reverse order of the peroxide-decomposing ability of the compounds.

An explanation consistent with the results described, and the inactivity of the phosphates, is that reaction of phosphite with hydroperoxide involves a free radical species capable of initiating polymerisation. The other alternatives which could lead to a rate increase seem less viable. For example it is unlikely that phosphite is acting as an efficient chain transfer agent in view of the AZBN-initiated polymerisation results. It is difficult also to imagine how the termination step could be altered to account for the observed results, but clearly molecular wieght measurements on the resulting polymer would uncover this type of reaction. Polymerisation initiated by ionic intermediates is also less likely in view of the comparatively modest rate enhancements found at a high temperature, and the lack of a suitably ionizing medium.

Walling and Indictor[142] report an ingenious method to determine initiator efficiency, in polymerisation systems, based on an earlier method for oxidation studies[143], by following the changing rate of polymerisation in a single experiment.

The standard rate of polymerisation is given by[133]

$$R_p = k_p [M] \left(\frac{R_i}{2k_t} \right)^{1/2} \qquad (1)$$

k_p = propagation rate constant

M = monomer concentration

R_t = termination (bycombination) rate constant

R_i = rate of initiation

From the kinetics of the phosphite-hydroperoxide reaction we found that:

$$-\frac{d[CHP]}{dt} = k_2 [CHP]_o [P]_o$$

$$\therefore R_i = 2ek_2 [CHP]_o [P]_o$$ where e = efficiency of initiation

Substituting in (1)

$$R_p = k_p[M] \cdot \left(\frac{ek_2[CHP]_o[P]_o}{k_t}\right)^{1/2} \qquad (2)$$

It can be shown[142] that the variation in polymerisation rate with time is given by

$$\log_{10} R_p = \log_{10} R_{po} - \left(\frac{k_2 t[\text{initiator}]_o}{2(2.303)}\right) \qquad (3)$$

Values of R_p at time intervals were measured by drawing tangents to the polymerisation-time curve, and substituted into equation (3) to obtain k_2, and an average value taken.

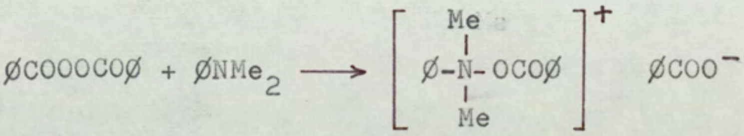
From (2) we can rearrange to:-

$$e = R_{po}^2 \cdot \frac{kt}{kp^2} \cdot \frac{1}{[M]^2 k_2 [CHP]_o [P]_o} \qquad (4)$$

So that with the calculated value of k_2, and using the literature values for k_t and kp[144], e can be calculated.

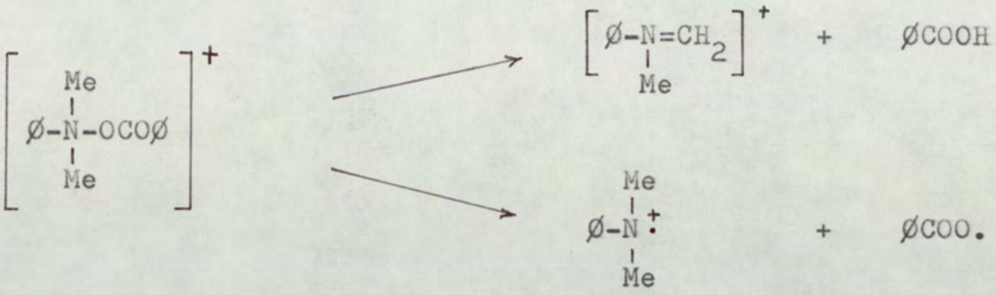
For the bulk polymerisation of styrene initiated by 0.2M cumene hydroperoxide + 0.2M hindered-phenyl catechol phosphite we obtain an efficiency of between 5 and 10%.

These polymerisation results show similarities with the amine/benzoyl peroxide redox system, which was the subject of an early review[145]. The mechanism of reaction of dimethylaniline with benzoyl peroxide has been envisaged as[142,146]



$$\text{Ø}COOOCO\text{Ø} + \text{Ø}NMe_2 \longrightarrow \left[\text{Ø}-\overset{Me}{\underset{Me}{N}}-OCO\text{Ø}\right]^+ \quad \text{Ø}COO^-$$

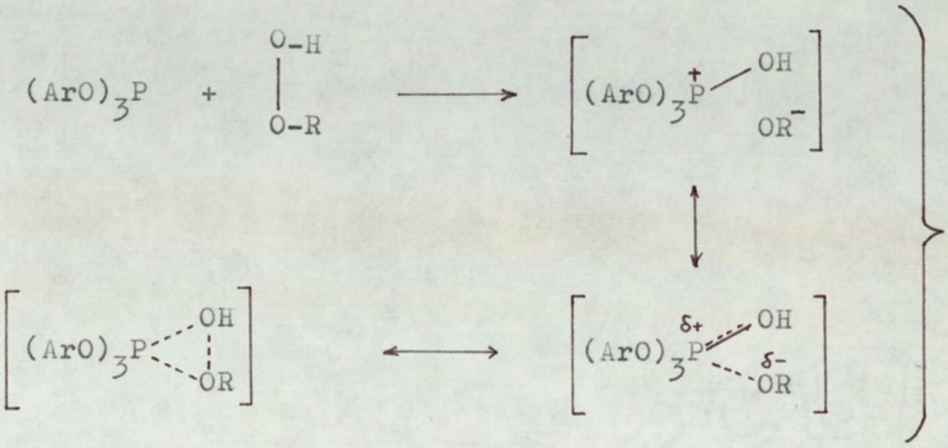
This quaternary hydroxylamine derivative has only transitory existence and decomposes by at least two possible routes, one of which involves radical species:-



Russian workers claim to have identified a radical-cation species from a similar reaction, by e.s.r.[147]. Evidence for radical production comes from the observation that the system absorbs oxygen and nitric oxide[148], and initiates vinyl polymerisation with kinetics consistent with a bimolecular radical-forming process[149,150]. Another characteristic of the reaction is the rapid initial rate of polymerisation, which falls off rapidly with time, not due to inhibitor formation but because of exhaustion of peroxide[151]. All of these features are common to the phosphite-hydroperoxide system. In addition, low values for efficiency of initiation have been reported[145,150] indicating that the major reaction occurs by an ionic path.

Less is known about the amine-induced decomposition of hydroperoxides, but in principle exactly analogous schemes can be written to the diacyl peroxide reaction. Hydroperoxides are rapidly destroyed to the corresponding alcohol in good yield[152,153] but oxidation to amine oxide is not stoichiometric, except in the presence of certain metal salts[154]. There is evidence[155] that the reaction of certain amines with hydroperoxides involves free radicals, and ethylene diamine/hydroperoxide is a known powerful redox initiator for vinyl polymerisation[156]. Direct spectroscopic evidence has been reported for free radicals from such systems[157], and Ingold has recently reported a blue Wurster cation-radical[158] from reaction of N,N,N',N'-tetramethyl-p-phenylene diamine and tertiary butyl hydroperoxide.

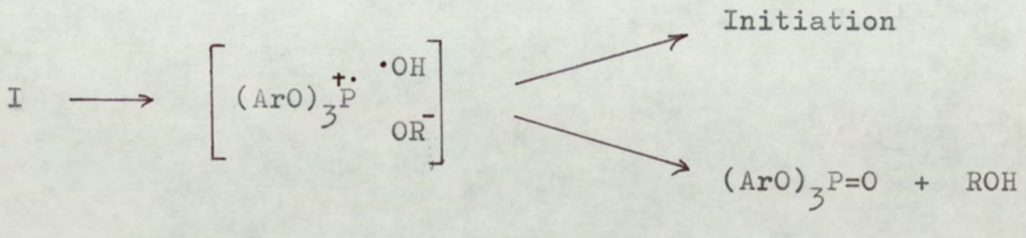
Thus a redox reaction between phosphite and hydroperoxide is suggested. The first stage will probably involve nucleophilic attack on hydroxyl oxygen, which is the most electropositive, and least sterically hindered, as suggested earlier[33]. It is doubtful whether an alkoxyphosphonium cation is formed, the truth probably lying somewhere between the species drawn:



I

If this first step is rate-determining it would be expected to have a negative entropy of activation, as found experimentally for the catechol phosphite/hydroperoxide and the amine/diacyl peroxide[142] systems. The activation energy is also small, in keeping with a redox process[159]. Also in agreement is the effect of substituents, electron-withdrawing groups on phosphite decreasing the rate of reaction with hydroperoxide[37].

The species I will only have a transient existence, decomposing to products at least partially via a free radical species:



Clearly there are many similarities with the mechanism of Pobedimskii referred to earlier[39]. Since no radicals are involved in the initial slow step, our observation that oxygen and free-radical scavengers did not affect the rate of peroxide disappearance is to be expected.

Further evidence of radical participation lies in the ability of the phosphite/hydroperoxide system to absorb oxygen (section 3). The low rates of vinyl initiation indicate that the majority of the reaction occurs via a non-radical path, as evidenced also by the small amount of radical-induced decomposition products.

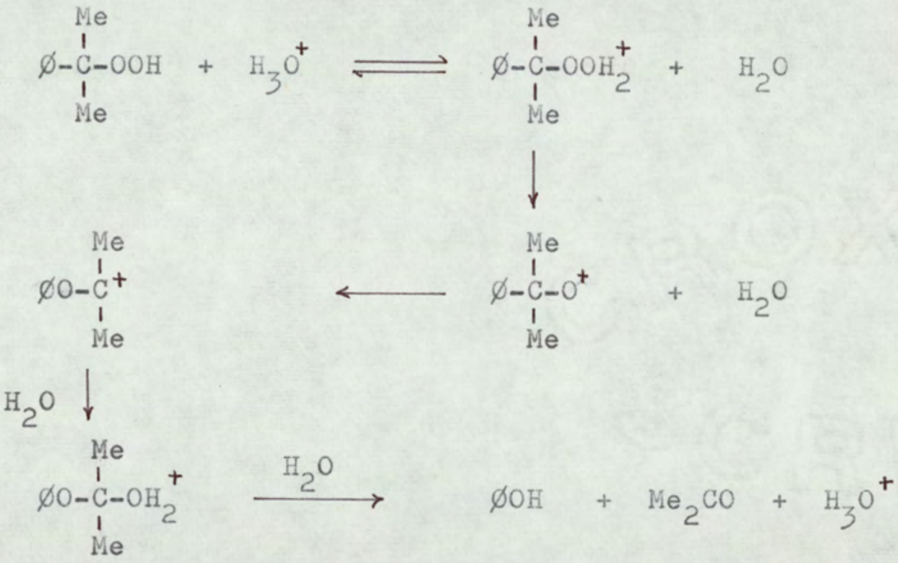
Useful evidence for the reaction proposed would be to perform the phosphite-enhanced polymerisation using isotopically labelled cumene hydroperoxide, $\emptyset\text{-CMe}_2\text{OOT}$, or $\emptyset\text{-CMe}_2\text{OO}^{18}\text{H}$, and after precipitation of polymer, to determine the radioactivity not removeable by washing. Determination of the molecular weight distribution of the polymer would then enable direct verification of the proposed scheme.

6 PRODUCT ANALYSES

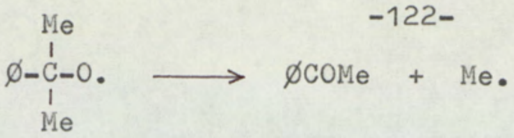
6.1 Hydroperoxide Decomposition Products

The reactions of phosphites with hydroperoxides are clearly of fundamental importance to the understanding of phosphite antioxidant action, and the reaction products give some insight into the mechanisms of the reactions occurring.

Cumene hydroperoxide can decompose to a large number of products under a variety of conditions[19]. Thus strong Lewis acids react rapidly and exothermically to yield exclusively phenol and acetone by an ionic mechanism[160-162]:



Reactions involving one electron reducing agents often go via α-cumyloxy radicals (including thermal decomposition), leading to products which include acetophenone, α-cumyl alcohol, dicumyl peroxide, and methane, and more rarely methanol, α-methyl styrene, dicumene, and α-methyl styrene dimer (2,4-diphenyl-4-methylpent-2-ene), may be obtained. Sensible reaction schemes can be written to account for most of these products[19,163]; for example, acetophenone arises because of the preference of alkyl groups over aryl groups to migrate in free radicals:



$$\varnothing\text{-}\overset{\text{Me}}{\underset{\text{Me}}{\text{C}}}\text{-O.} \longrightarrow \varnothing\text{COMe} + \text{Me.}$$

in contrast to the behaviour of the corresponding carbonium ion in the previous example.

In addition it appears that α-cumyl alcohol can arise by acid-induced decomposition of hydroperoxide, probably by hydrolytic attack of hydronium ion on hydroperoxide, with concomitant formation of hydrogen peroxide[161].

Results and Discussion

The products of reaction of phosphites with hydroperoxide were determined by gas chromatography using two internal standards as described in the experimental section. At the higher of the two temperatures used, unreacted hydroperoxide decomposed on the column of the chromatograph; at the lower temperature decomposition again occurred. In the latter case this was probably due to involatile residues trapped on the column since the support material itself was shown to be inert. This meant that only the final products were determined, after the reaction had gone to completion.

It was found that all three catechol phosphites decomposed cumene hydroperoxide to give mainly phenol, acetone, and α-methyl styrene, with small amounts of acetophenone and α-cumyl alcohol. For a fixed concentration of hydroperoxide (0.2M), it was found that the product distribution varied considerably with phosphite concentration. The results for the catechol hindered-phenyl compound are shown in Table 17.

Table 17: Variation in the distribution of cumene hydroperoxide decomposition products by reaction with catechol hindered-phenyl phosphite, in chlorobenzene at 75°C. $[\mathrm{CHP}]_0 = 0.2\mathrm{M}$.

$\frac{[\mathrm{CHP}]}{[\mathrm{phosphite}]}$	mole % product				
	phenol	acetone	aceto-phenone	α-methyl styrene	α-cumyl alcohol
0.5	0.1	1.0	0.25	100	trace
1.0	12.0	11.5	0.55	85	"
2.0	35.5	26.2	1.4	63.5	0.4
5.0	49	48	2.0	32.8	0.6
10.0	59	50	2.45	31.0	0.75

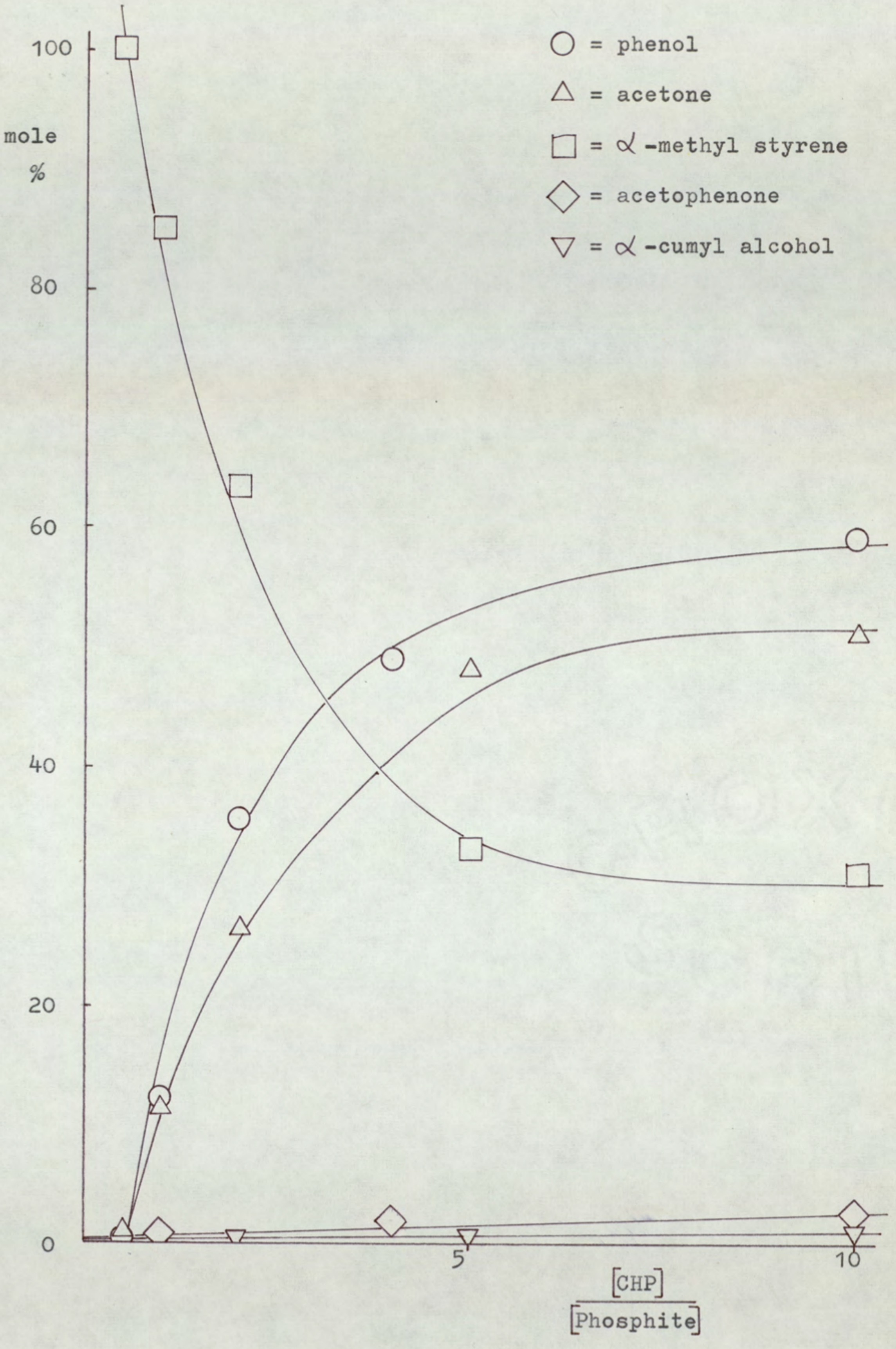


Figure 6.1: Product distribution from the reaction of cumene hydroperoxide with catechol hindered-phenyl phosphite in ØCl at 75°C.

These results are shown graphically in Figure 6.1 from which it appears that the product distribution probably becomes constant at lower phosphite concentrations.

It was found that the same results were obtained whether the experiments were performed in air, vacuum, or nitrogen, with a reproducibility of better than ±5%.

The experiment was then repeated first in cumene in a nitrogen atmosphere and then in nitrobenzene. Table 18 shows that change in solvent dielectric considerably alters the product distribution, shown diagrammatically in Figure 6.2 for nitrobenzene solvent. In nitrobenzene, a large unidentified peak appeared with the same retention time as α-cumyl alcohol, which therefore could not be determined.

Table 18: The effect of solvent on the products of the catechol phosphite-induced decomposition of cumene hydroperoxide at 75°C.

$\frac{[CHP]}{[P]}$	mole % product									
	phenol		acetone		α-methyl styrene		aceto-phenone		α-cumyl alcohol	
	RH	ØNO$_2$	RH	ØNO$_2$	RH	ØNO$_2$	RH	ØNO$_2$	RH	ØNO$_2$
0.25	5.0	15.5	9.2	46.0	83.5	-	*	*	1.8	-
0.5	8.0	22.0	12.0	52.5	82.5	26.5	*	*	2.2	-
1.0	15.0	31.5	18.5	45.0	70.7	26.0	0.3	*	-	-
2.5	34.0	44.5	24.5	59.0	58.0	7.0	0.5	*	1.8	-
5.0	51.2	60.0	27.8	69.5	44.0	4.0	0.7	*	2.0	-
10.0	56.5	81.5	28.0	74.7	38.5	3.5	0.5	*	2.0	-

* = trace

RH = cumene

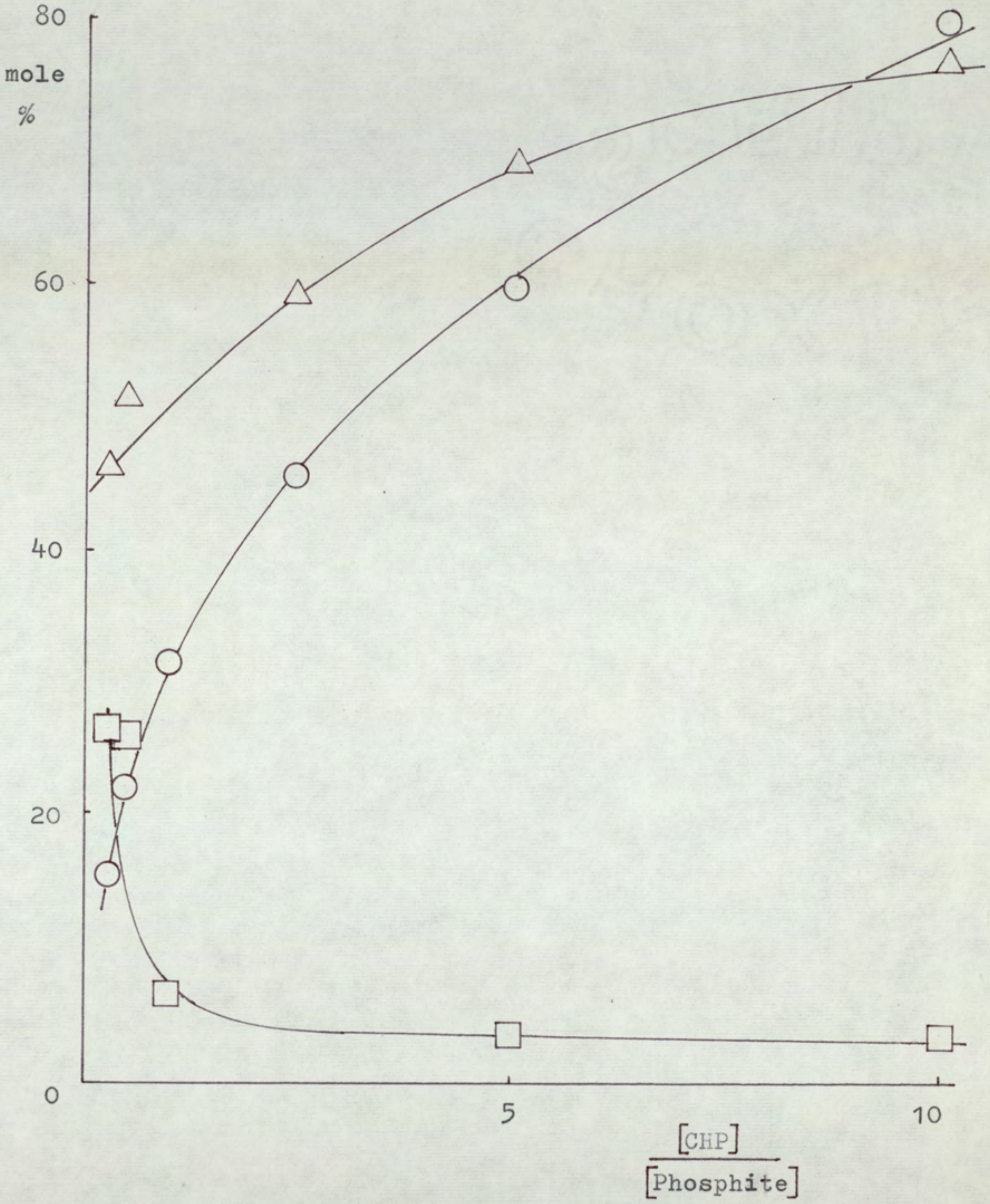


Figure 6.2: Product distribution from the reaction of cumene hydroperoxide with catechol hindered-phenyl phosphite in $\varnothing NO_2$ at 75°C.

○ = phenol

△ = acetone

□ = α-methyl styrene

Qualitative experiments with the two alicyclic phosphites, ethylene, and propylene isopropyl phosphites, showed that these too gave phenol, acetone, and α-methyl styrene as major products with small traces of acetophenone and α-cumyl alcohol.

The products of reaction of triphenyl phosphite with cumene hydroperoxide over a range of concentrations, on the other hand, gave almost quantitative yields (mean = 97.5 mole %) of α-cumyl alcohol, and no other products.

It should be pointed out that the values obtained for concentrations of α-methyl styrene are liable to variations. It was found that if the reaction mixture was thermostatted for a longer time than was necessary for destruction of hydroperoxide the values obtained progressively diminished. This must be due to subsequent reactions, possibly polymerisation.

Next 0.2M CHP + 0.05M phosphite were reacted in chlorobenzene until all hydroperoxide was consumed, and the products analysed. Another portion of hydroperoxide was then added to the reaction mixture to bring the concentrations again to about 0.2M, and the products analysed on completion of degradation. The results are shown in Table 19.

Table 19: Principal hydroperoxide and phosphite decomposition products.

solution	mole % product		
	phenol	acetone	α-methyl styrene
original reaction mixture	49	42	37
final reaction mixture	58	46	27
∴ products distribution from added hydroperoxide	67	50	17

Clearly the decomposition of the subsequently added hydroperoxide gave rise to a greater concentration of phenol and acetone, and less α-methyl styrene

The catechol phosphate-cumene hydroperoxide products were examined next after reaction in chlorobenzene at 75°C. The same products were found as for the phosphite, and as shown in Table 20, again a variation in product distribution was observed with change in phosphate concentration. This time however the range of distribution was much smaller, particularly for α-methyl styrene.

Table 20: Variation in the distribution of cumene hydroperoxide decomposition products by reaction with catechol hindered-phenyl phosphate, in chlorobenzene at 75°C. $[CHP]_o = 0.2M$

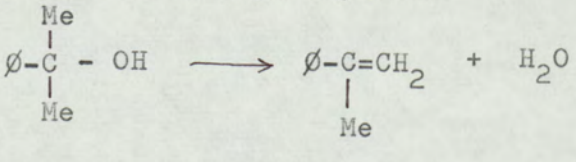
$\frac{[CHP]}{[phosphate]}$	mole % product				
	phenol	acetone	aceto-phenone	α-methyl styrene	α-cumyl alcohol
0.5	43.1	22.3	3.3	33.1	3.3
1.0	45.5	27.9	3.0	32.1	3.0
2.0	48.3	30.8	3.3	31.6	3.5
4.0	54.7	37.2	2.8	29.7	3.2
10.0	55.5	42.5	2.2	27.7	2.3

These results are shown graphically in Figure 6.3.

In contrast to the cyclic compounds, triphenyl phosphate did not react with cumene hydroperoxide in chlorobenzene at 75°C.

The two identified intermediates, catechol hydroxy phosphate and mono(o-hydroxyphenyl) phosphoric acid, also reacted with cumene hydroperoxide in chlorobenzene at 75°C. to yield phenol, acetone, and α-methyl styrene as the principal products.

It was found that all the cyclic phosphites (and phosphate) had the facility to react with α-cumyl alcohol in a non-stoichiometric (catalytic) reaction to form α-methyl styrene:



$$\text{Ø}-\overset{\text{Me}}{\underset{\text{Me}}{C}}-OH \longrightarrow \text{Ø}-\underset{\text{Me}}{C}=CH_2 + H_2O$$

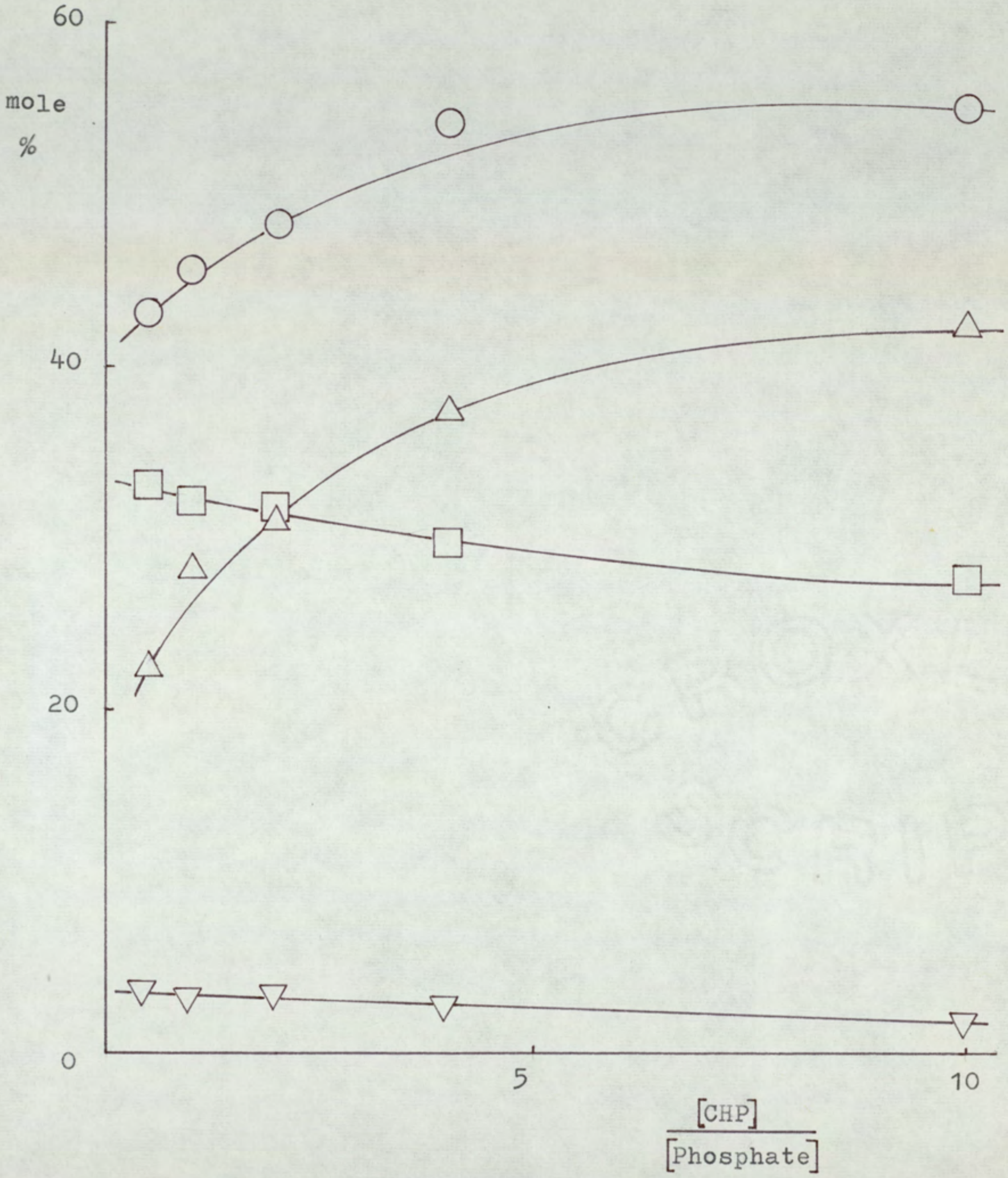


Figure 6.3: Product distribution from the reaction of cumene hydroperoxide with catechol hindered-phenyl phosphate in ØCl at 75°C.

○ = phenol

△ = acetone

□ = α -methyl styrene

▽ = acetophenone

The reaction between catechol hindered-phenyl phosphite and α-cumyl alcohol was studied kinetically (using equimolar initial concentrations for convenience), by monitoring the production of α-methyl styrene by gas chromatography. Second order kinetics were observed throughout the reaction (Figure 6.4), and in chlorobenzene at 75°C. the rate constant was equal to 2.1×10^{-3} l.mole sec.$^{-1}$. The reaction was not catalysed by hydroperoxide. Subsequently it was found that the catechol phosphate also induced this de-hydration, and although only a qualitative investigation was made, the reaction was much more rapid than with phosphite.

Again a different type of behaviour was found with triphenyl phosphite and triphenyl phosphate, neither of which reacted with α-cumyl alcohol after many hours at 75°C.

Finally gas analysis of the catechol phosphite-hydroperoxide reaction products was attempted using gas chromatography. With a four foot long "Porapak Q" column at 28°C., a single peak was observed and identified by peak enrichment as methane.

It was shown by means of thin layer chromatography on silica gel plates, using the development technique and spray reagent of Baronowski and co-workers[164], that dicumyl peroxide was not a product of any of the reactions studied.

Not surprisingly an exact material balance between cumene hydroperoxide and its decomposition products was not observed. This is probably due to:
(1) gaseous products
(2) polymeric residues
(3) dimerisation of α-methyl styrene to an involatile product

all of which were neglected in the material balance.

More surprising is the apparent non equivalence of phenol and acetone, which should arise as a result of a Lewis acid induced reaction. In the cases where the acetone concentration is less than

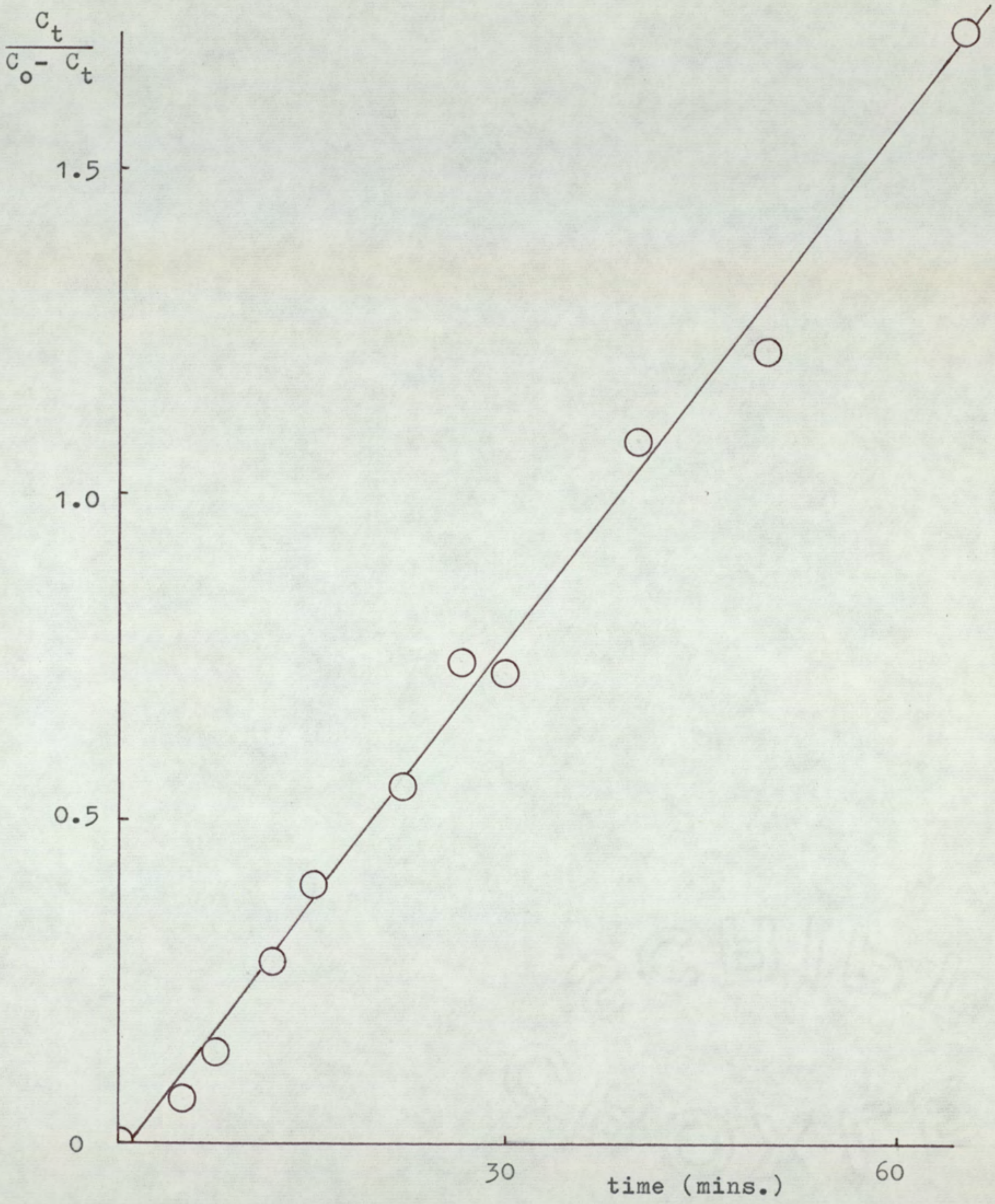


Figure 6.4: Second order plot for the dehydration of α-cumyl alcohol (0.2M) by catechol hindered-phenyl phosphite (0.2M) in ØCl at 75°C.

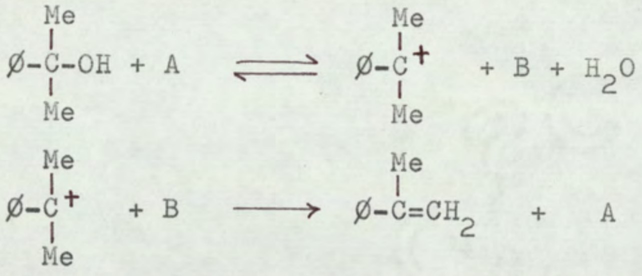
expected, loss by evaporation cannot be ruled out, or in general non equivalence may be due to subsequent reactions. Previous workers have reported similar results in acid-catalysed reactions[162, 165].

The origin of α-methyl styrene as a product is obscure. Kharasch[19] noted its formation under a variety of conditions, and suggested that its formation from cumene hydroperoxide was connected with the oxygen evolution thought to be due to reaction of hydroperoxide with its anion:

$$\text{Ø}CMe_2OOH + \text{Ø}CMe_2O\bar{O} \rightarrow \text{Ø}CMe_2OH + \text{Ø}CMe_2O^- + O_2$$

Earlier suggestions of α-methyl styrene arising from bimolecular termination of cumyloxy radicals[166] have since been disproved[167,101, 102].

A de-hydration reaction involving α-cumyl alcohol seems the most likely source of the α-methyl styrene, and the most common reaction type for such reactions is an acid-catalysed elimination[168],



$$\text{Ø}\!-\!C(Me)_2\!-\!OH + A \rightleftharpoons \text{Ø}\!-\!C^+(Me)_2 + B + H_2O$$

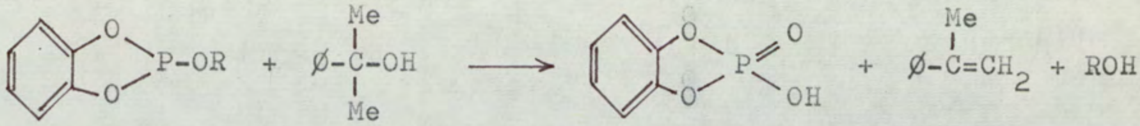
$$\text{Ø}\!-\!C^+(Me)_2 + B \longrightarrow \text{Ø}\!-\!C(Me)\!=\!CH_2 + A$$

where B is the conjugate base of A.

However, it is difficult to see how this reaction, or the less common base-induced reaction, could occur with either the phosphite or phosphate.

A different reaction path is that proceeding through an intermediate ester, which then decomposes either thermally, or by an elimination reaction, to yield the olefin product. Such reaction schemes have been suggested for the de-hydration of tertiary alcohols by perchloric[169] and phosphoric[170] acids.

Trans-esterification reactions are possible with both phosphites and phosphates, but it is not obvious how the olefin elimination could occur from the ester formed. One possible reaction with phosphite:



does not occur since the de-hydration was shown to occur without the liberation of any free phenol derived from the phosphite.

The very small amount of acetophenone observed as a product probably corresponds in quantity to the methane found by gas analysis, and both may arise by an induced decomposition of hydroperoxide caused by the radical species formed in the phosphite-hydroperoxide reaction.

The formation of oxygen was discussed in the oxygen absorption section, but one possible source is the attack of alkoxy radical on hydroperoxide

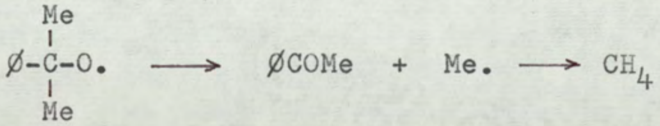
$$RO. + ROOH \longrightarrow ROH + ROO. \qquad (1)$$

$$2ROO. \longrightarrow 2RO. + O_2 \qquad (2)$$

$$RO. + ROOH \longrightarrow etc.$$

which constitutes a possible cyclic chain reaction, yielding alcohol and oxygen.

The small amounts of acetophenone and methane found may arise by the alternative breakdown of the cumyloxy radicals produced in (2)



$$\text{Ø}-\overset{\text{Me}}{\underset{\text{Me}}{\text{C}}}-O. \longrightarrow \text{ØCOMe} + Me. \longrightarrow CH_4$$

The quantity of oxygen produced was small (a few mole percent).

The reaction between catechol phosphite and cumene hydroperoxide was shown to produce more phenol and acetone and less α-methyl styrene as the ratio of hydroperoxide:phosphite increased. On the basis of the proposed reaction scheme this is to be expected. The first stage of the reaction is the rapid oxidation to phosphate:

$$(RO)_3P + R^1OOH \longrightarrow (RO)_3P{=}O + R^1OH \qquad (1)$$

The alcohol formed is then dehydrated to olefin by the phosphate or a derived product. Further reaction of the phosphate with hydroperoxide eventually leads to the formation of an active species which decomposes hydroperoxide predominantly to phenol and acetone (possibly with some α-methyl styrene). In Figure 6.5 are plotted the amounts of α-methyl styrene resulting from decomposition by phosphite and phosphate together with the amount expected on the basis of the oxidation reaction (1) followed by dehydration, for different phosphite concentrations. At equimolar phosphite and hydroperoxide concentrations the theoretical and observed amounts are closely similar, whilst as the concentration of phosphite is decreased, less α-methyl styrene is formed, the amount tailing off to an almost constant amount similar to that resulting from reaction with phosphate (31 and 28 mole % respectively). On the basis of the proposed scheme it would be expected that at $[CHP]_o = 0.2M$ and $[Phosphite]_o = 0.02M$, that 10 % more α-methyl styrene should appear for the phosphite reaction than for the phosphate, and this was found from Figure 6.5 to be the case ($\frac{31}{28} = 1.1$). Clearly the larger the excess of hydroperoxide, the less effect the phosphite oxidation reaction will have on the overall products. For the same reason at high phosphate concentrations, there is still appreciable phenol and acetone formed since in this case all the hydroperoxide has not been used up in the stoichiometric oxidation reaction.

The overall scheme is further supported by the experiment in which additional hydroperoxide was added to the exhausted reaction mixture of phosphite and hydroperoxide. The "active species" destroyed hydroperoxide to yield more phenol and acetone and less α-methyl styrene than previously.

It is likely that this active species is acidic in nature, and thus will probably destroy hydroperoxide to yield ionic products only.

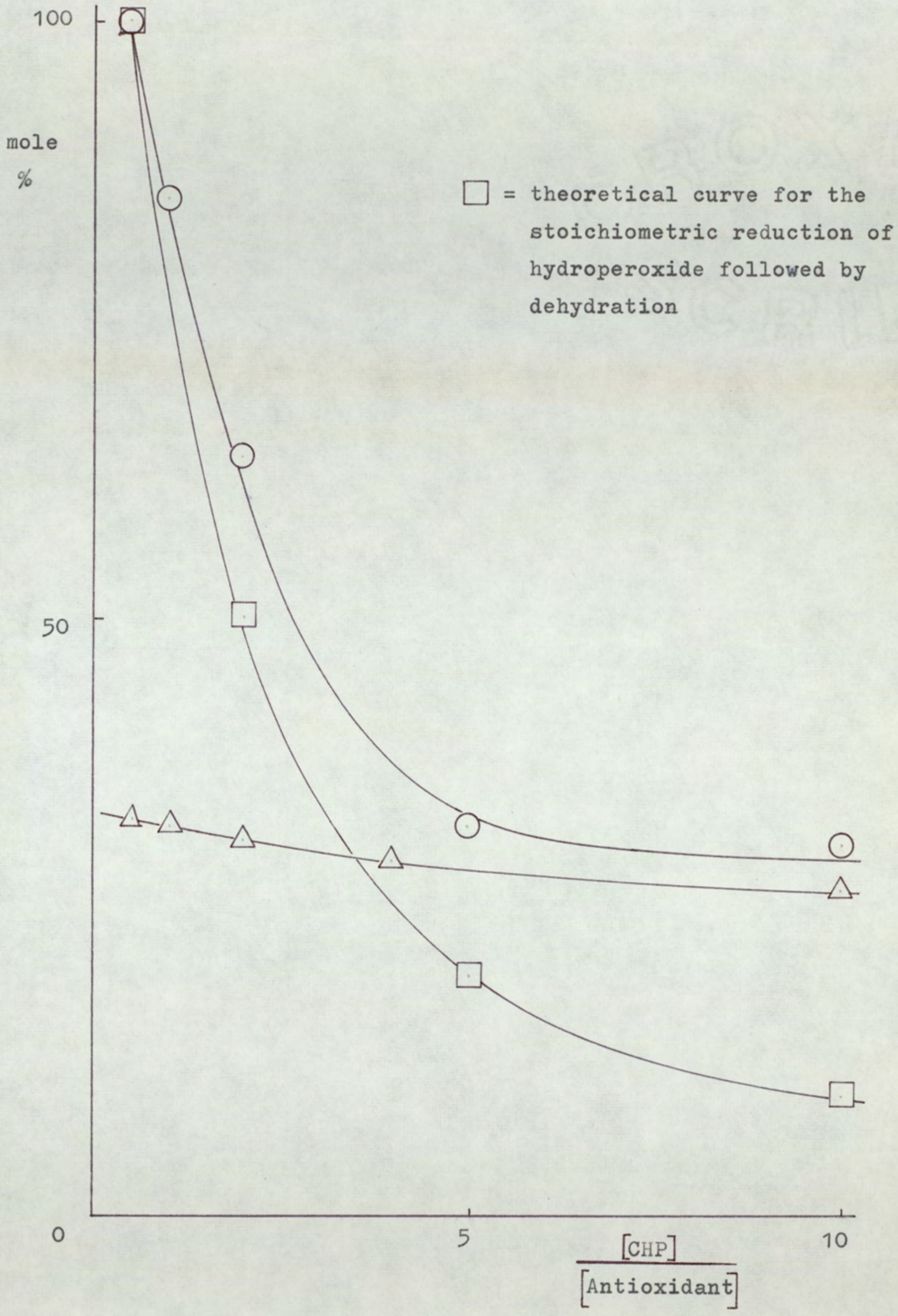


Figure 6.5: Yield of α-methyl styrene from the decomposition of cumene hydroperoxide by

○ = catechol hindered-phenyl phosphite

△ = catechol hindered-phenyl phosphate

The proportion of phenol and acetone increased with respect to α-methyl styrene, for the phosphite-induced decomposition, as the solvent dielectric was increased. If α-methyl styrene is not a free radical product, then perhaps the rate of dehydration of α-cumyl alcohol decreases with increased dielectric (as would be the case if, for example, reaction was occurring between an ion and a neutral molecule) or else the rate of decomposition by the active species is greatly enhanced over the dehydration reaction, in a solvent of high dielectric. Alternatively, the reaction cycle mentioned above as a possible source of oxygen, in the presence of a reducing solvent such as cumene, may lead to a greater yield of α-cumyl alcohol:

$$RO. + RH \longrightarrow ROH + R.$$

which in turn will become dehydrated. This is perhaps a more viable explanation of the greater proportion of α-methyl styrene observed in cumene. Also in agreement with this suggestion is the slightly greater (although small anyway) amount of α-cumyl alcohol observed from the reaction performed in cumene.

6.2 Phosphorus Products - Results and Discussion

Hindered-phenyl catechol phosphate was first identified in the mass spectrum of the phosphite-hydroperoxide decomposition products, by peak-matching of the parent ion (at m/e = 374). subsequently the compound was synthesised by reaction of the catechol phosphite with t-butyl hydroperoxide in chlorobenzene at 75°C. Physical data (i.r.,n.m.r.,mass spectrum, elemental analysis) indicated the assigned structure.

Integrated-ion-current mass spectrometry was used to estimate the disappearance of phosphite during reaction with hydroperoxide, since other techniques proved unsuccessful. The infra-red absorption of P=O is of no use in view of the numerous reactions probably occurring which involve phosphoryl groups. For $[CHP]_o$=0.2M and $[phosphite]_o$= 0.02M, in chlorobenzene , the first sample, taken after ten minutes at 75°C., showed that only a trace ($<$1%) of phosphite remained. When the kinetic parameters of the reaction were later determined (section 4),calculation showed that reaction would be complete in less than ten minutes.

The same mass spectrometry method , using the technique already described, was used in an attempt to monitor the disappearance of catechol phosphate during reaction with hydroperoxide (0.02M and 0.2M respectively) in chlorobenzene. The results show considerable scatter (Figure 6.6), but an initial rapid reaction was apparent, after which the rate fell off. The accuracy of the results was insufficient for any kinetic information to be derived. Reaction was followed to about two half-lives. An interesting point is that by comparison of Figure 6.6 with the data on peroxide decomposition in the same system, the pseudo-first order disappearance of hydroperoxide begins before complete reaction of phosphate has occurred. This is consistent with the formation of a catalytic species.

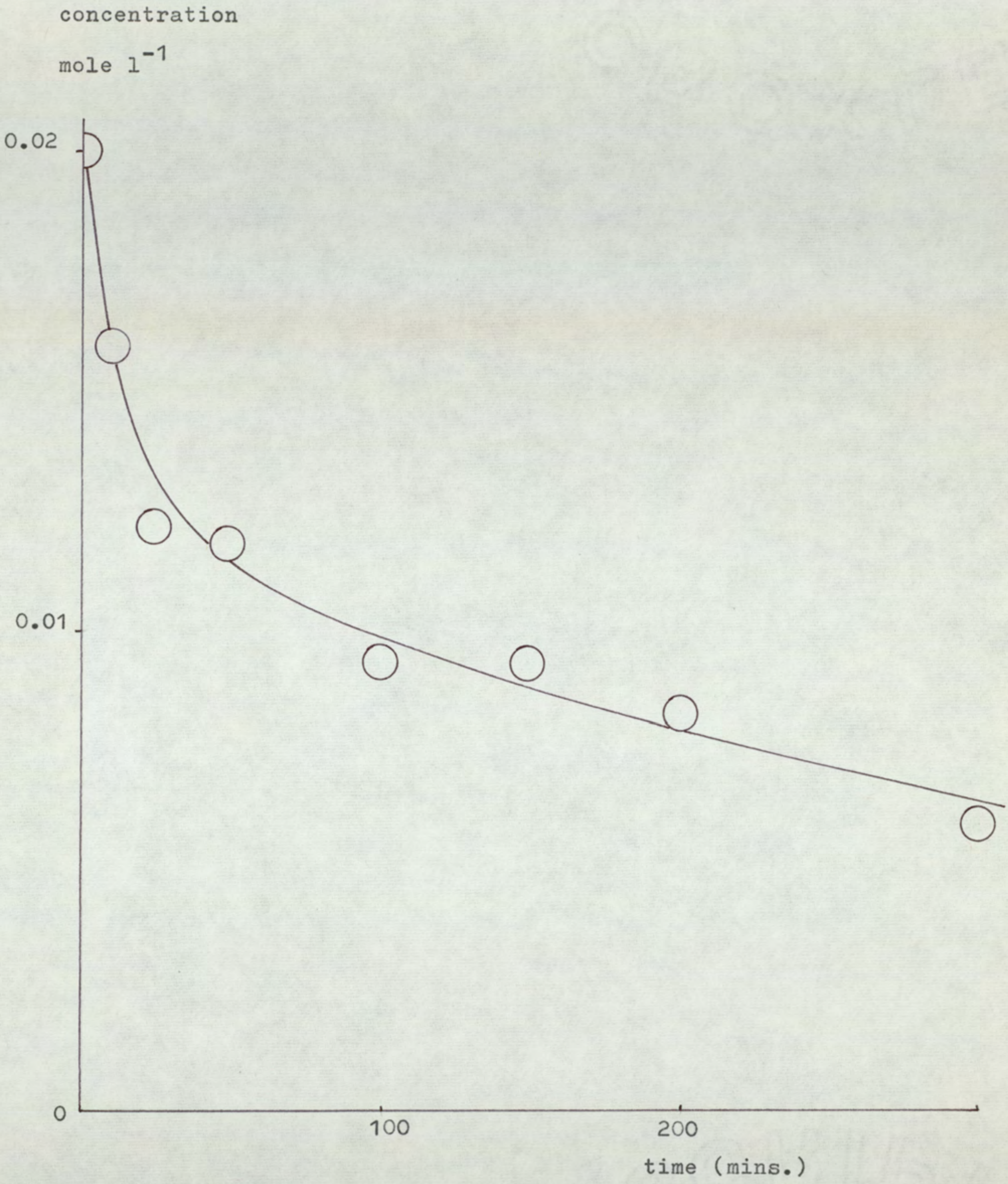
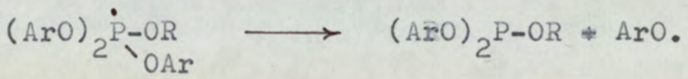


Figure 6.6: Decomposition of catechol hindered-phenyl phosphite during reaction with 0.2M cumene hydroperoxide in ØCl at 75°C.
(by integrated ion-current mass-spectrometry)

AZBN was shown to oxidise catechol phosphites to phosphates. A 0.1M solution of catechol hindered-phenyl phosphite in chlorobenzene containing 0.01M AZBN, was thermostatted in oxygen at 75°C. until all the initiator had decomposed (about 20 hours). The concentration of phosphate was then determined by mass spectrometry, and found to be 0.0065M i.e. 6.5% oxidation had occurred. This is almost certainly due to α-scission of the intermediate phosphoranyl radical[25].



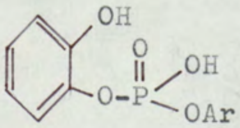
$$(ArO)_2\dot{P}(OR)(OAr) \longrightarrow (ArO)_2P\text{-}OR + ArO.$$

The alkyl -substituted phosphites would be expected to yield a much larger conversion to phosphate.

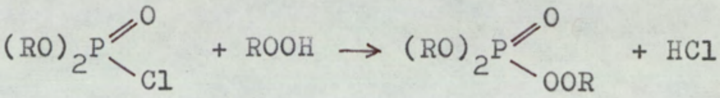
Little success was achieved in identifying the other phosphorus-containing products. They were insufficiently volatile to be analysed by gas chromatography, even using a short non-polar column at 200°C., so that thin-layer chromatography was investigated. Considerable effort was expended in trying a wide range of solvents, solvent mixtures, and developing reagents, both on silica gel and cellulose coated plates, but without success. The known hydroperoxide decomposition products overlapped with the apparently complex mixture of other products in all cases. Many spots were obtained, many of which tailed badly in most of the solvent systems tested.

Both the phosphite- and phosphate-hydroperoxide reaction products were shown to contain catechol hydroxy phosphate by mass spectrometry (accurate mass = 171.992544). Due to ease of hydrolysis of this compound, mono(o-hydroxyphenyl)phosphoric acid will also probably be present, but this compound failed to give a molecular ion. These products may account for the small quantities of free 2,6-di-t-butyl-4-methyl phenol (derived from phosphite) which were observed at high hydroperoxide to phosphite ratios.

No evidence was found for the other possible ring-opened product:



The possibility of an intermediate phosphorus peroxide was considered unlikely. The thermal instability of these compounds as a class[171] will probably preclude their formation under the conditions employed, except possibly as transient intermediates. In addition, the only known syntheses of these compounds is via the corresponding chlorophosphate:



$$(RO)_2P(=O)Cl + ROOH \rightarrow (RO)_2P(=O)OOR + HCl$$

where the strength of the hydrogen-chlorine bond formed is probably a major driving force for the reaction.

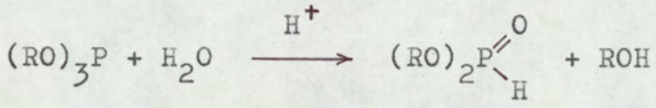
Clearly it is desirable to be able to perform a detailed product analysis of the catechol-phosphate-hydroperoxide reaction products, but the complex (and perhaps high molecular weight) products formed make this a difficult task.

7 HYDROLYSIS - Results and Discussion

In view of the reactivity of trivalent phosphorus compounds towards nucleophiles, it was necessary to know to what extent the observed reactions were due to hydrolysis, particularly since a number of workers have ascribed the antioxidant activity of phosphites to their hydrolysis products[46,47].

In addition water is a known product of hydroperoxide decomposition, and will inevitably be present to some extent in the systems studied.

Simple trialkyl phosphites are reported[172] to be fairly stable in water with the exception of the first member of the series. Phosphites hydrolyse in the presence of acids[172] generally as follows:



$$(RO)_3P + H_2O \xrightarrow{H^+} (RO)_2P(=O)H + ROH$$

More recently it has been shown[173] that this reaction occurs readily in the presence of dialkyl phosphite, whilst basic conditions retard the rate of hydrolysis. Imajev[174] found that the rate of hydrolysis of a series of phosphites decreased in the order

$$R = Me > Et > \phi > i\text{-}Pr > t\text{-}Bu$$

and dialkyl phosphite was found to have an autocatalytic effect on the reaction. This autocatalysis is not observed in certain solvents[175].

The only information available for cyclic phosphites is the report[176] that 2-methyl-1,3,2-dioxaphospholane hydrolyses 3000 times faster in basic solution than trimethyl phosphite (its acyclic analogue), whilst other results show that no such kinetic acceleration occurs in an acid medium[118]. This data is in line with the work discussed earlier showing that little kinetic acceleration occurs with cyclic five-membered trivalent compounds, in contrast to the large rate increases observed for the tetrahedral phosphates over their acyclic analogues.

7.1 Results

First the effect on the rate of decomposition of cumene hydroperoxide by catechol phenyl phosphite, of adding small amounts of water, was examined using cumene as a solvent. It was found (Figure 7.1) that increasing amounts of water led to decreasing reaction rates, and as little as 0.5% (v/v) water had a marked effect.

Since the primary hydrolysis of phosphites leads to the release of the corresponding alcohol or phenol (vide infra), the rates of hydrolysis of the three catechol phosphites were measured in neutral solution in 95% (v/v) aqueous ethanol, by following the formation of alcohol by gas chromatography. Using a five foot long column of "Celite" coated with polyethylene glycol adipate, the following internal standards were found to be satisfactory:

alcohol	R_t of alcohol	standard	R_t of standard	$T^\circ C$.
iso-propanol	3.7cm.	iso-butanol	11.0cm.	55°
phenol	25.3cm.	lauryl alcohol	21.7cm.	150°
hindered phenol	18.3cm.	"	"	"

The results, in Figure 7.2, show that sinusoidal curves were obtained with the first two compounds, whilst the hindered-phenyl compound was very resistant to hydrolysis, requiring 285 hours for 90% reaction.

The rate of hydrolysis of catechol hindered-phenyl phosphate was examined under the same reaction conditions, with $[\text{phosphate}]_o$

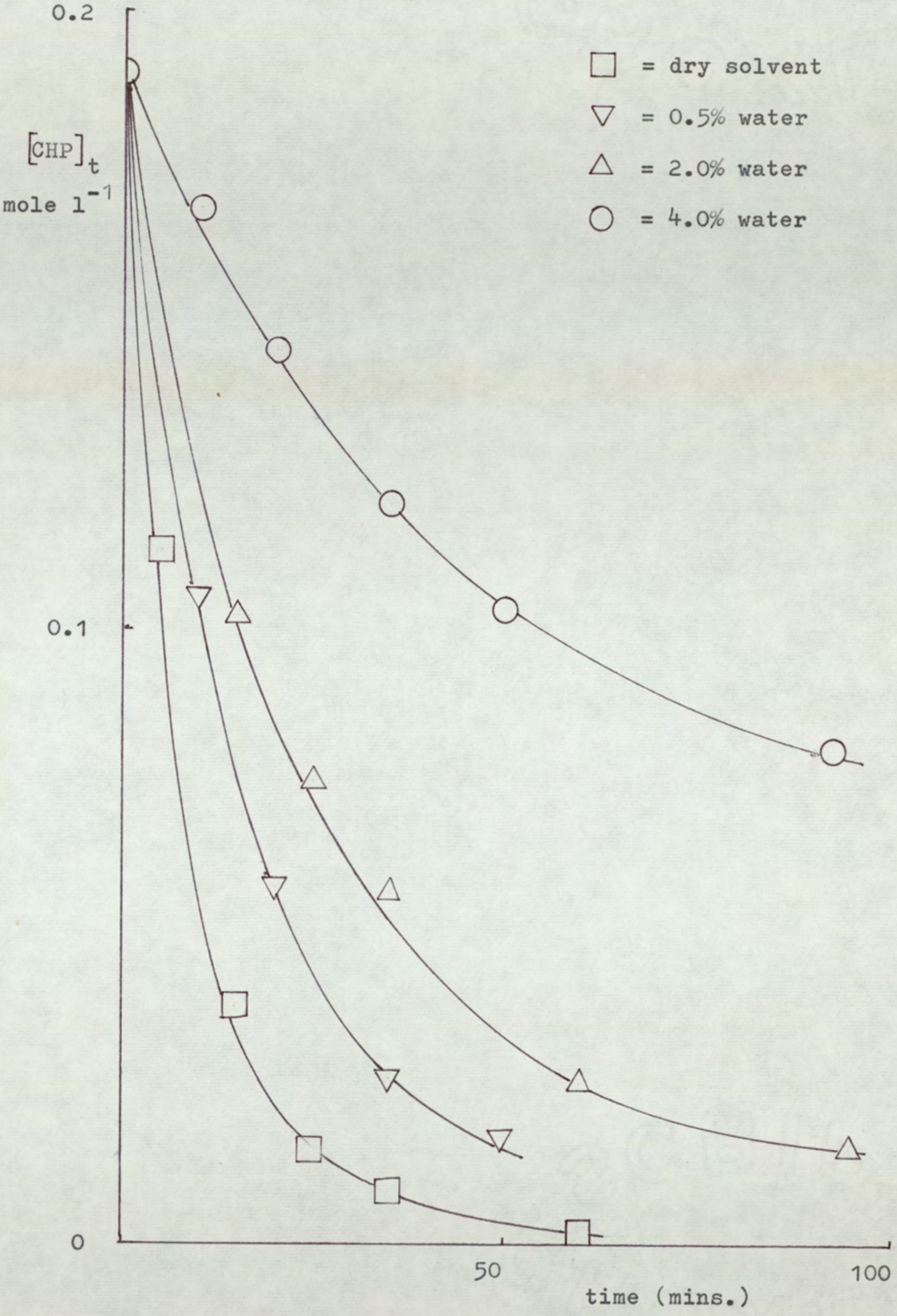


Figure 7.1: Effect of water on the decomposition of cumene hydroperoxide by catechol phenyl phosphite (0.002M) in cumene at 75°C.

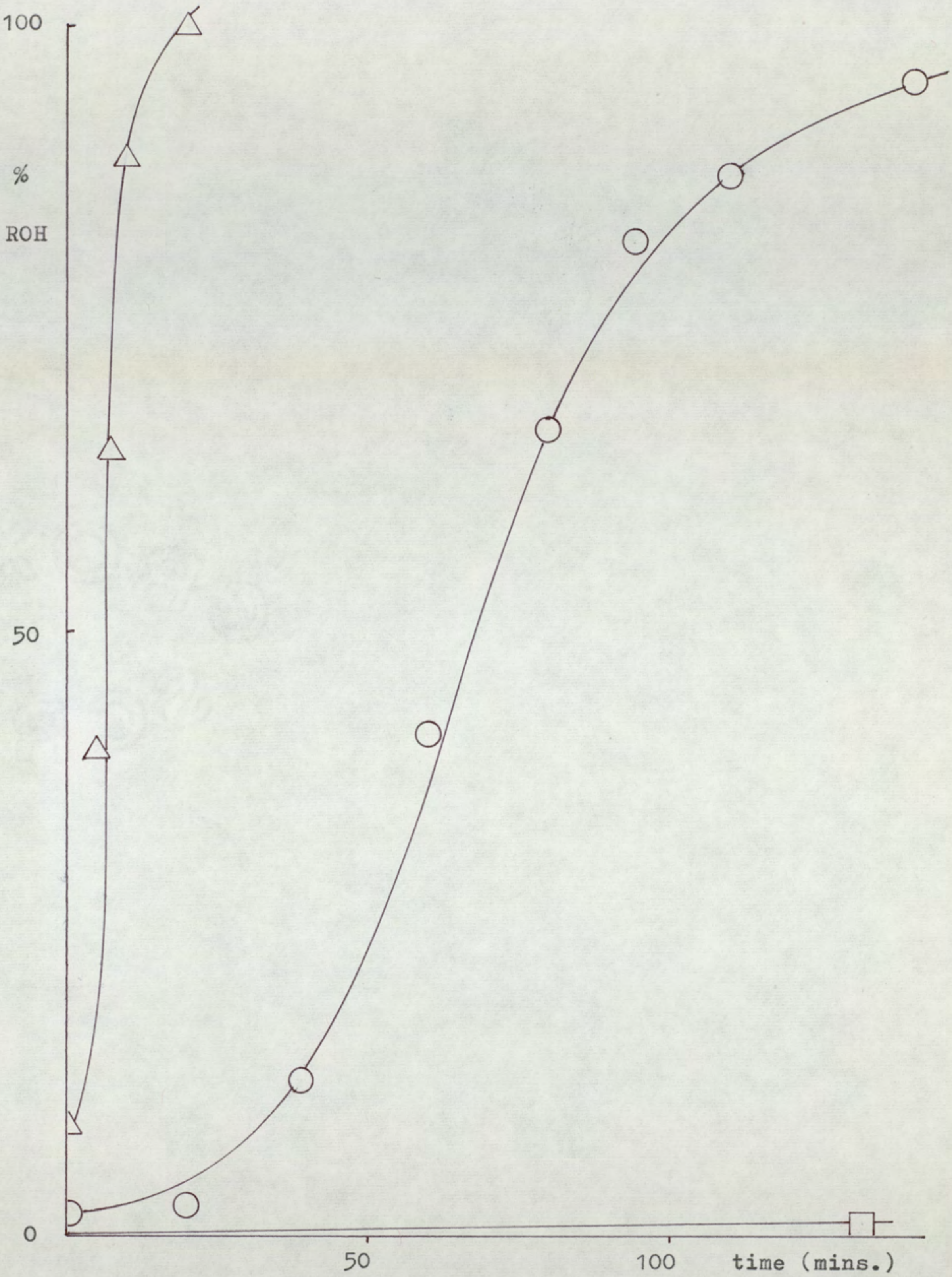


Figure 7.2: Hydrolysis of catechol phosphites (0.02M) in 95% (v/v) aqueous ethanol at 75°C.

□ = catechol hindered-phenyl phosphite

△ = catechol phenyl phosphite

○ = catechol isopropyl phosphite

=0.02M, in two ways. First the formation of 2,6-di-t-butyl-4-methyl phenol was followed by gas chromatography. Reaction was slow, and only about 5 mole % of the available phenol was detected after 211 hours. In addition the disappearance of phosphate was measured directly by means of quantitative integrated ion-current mass spectrometry. This time hydrolysis was more rapid, about 40 % reaction occurring in 80 hours, being a little faster than the rate for the corresponding phosphite (Figure 7.3).

All three catechol phosphites gave a white solid as one of the products of prolonged exposure to moist air. For example, a small quantity of catechol isopropyl phosphite was exposed on a watch glass inside a dessicator containing an open dish of distilled water, for two weeks. After this time the characteristic smell had disappeared, and a small amount of solid separated. This was removed by filtration, washed with carbon tetrachloride, and finally re-crytallised from benzene, m.pt. 97-98°C. Infra-red, mass spectrum, and elemental analysis showed the product to be catechol.

Finally, analysis of all three catechol phosphite hydrolysis residues by high resolution mass spectrometry, showed a molecular ion at m/e = 172 which was identified by peak matching as catechol hydroxy phosphate.

Ethylene and propylene isopropyl phosphites were qualitatively examined by gas chromatography for their hydrolytic stability. The addition of a few drops of water to a benzene solution of ethylene isopropyl phosphite almost completely removed the peak due to phosphite (analysed on P.E.G.A. at 95°C.), whilst the peak due to the six-membered compound was only slightly reduced in size after the same treatment.

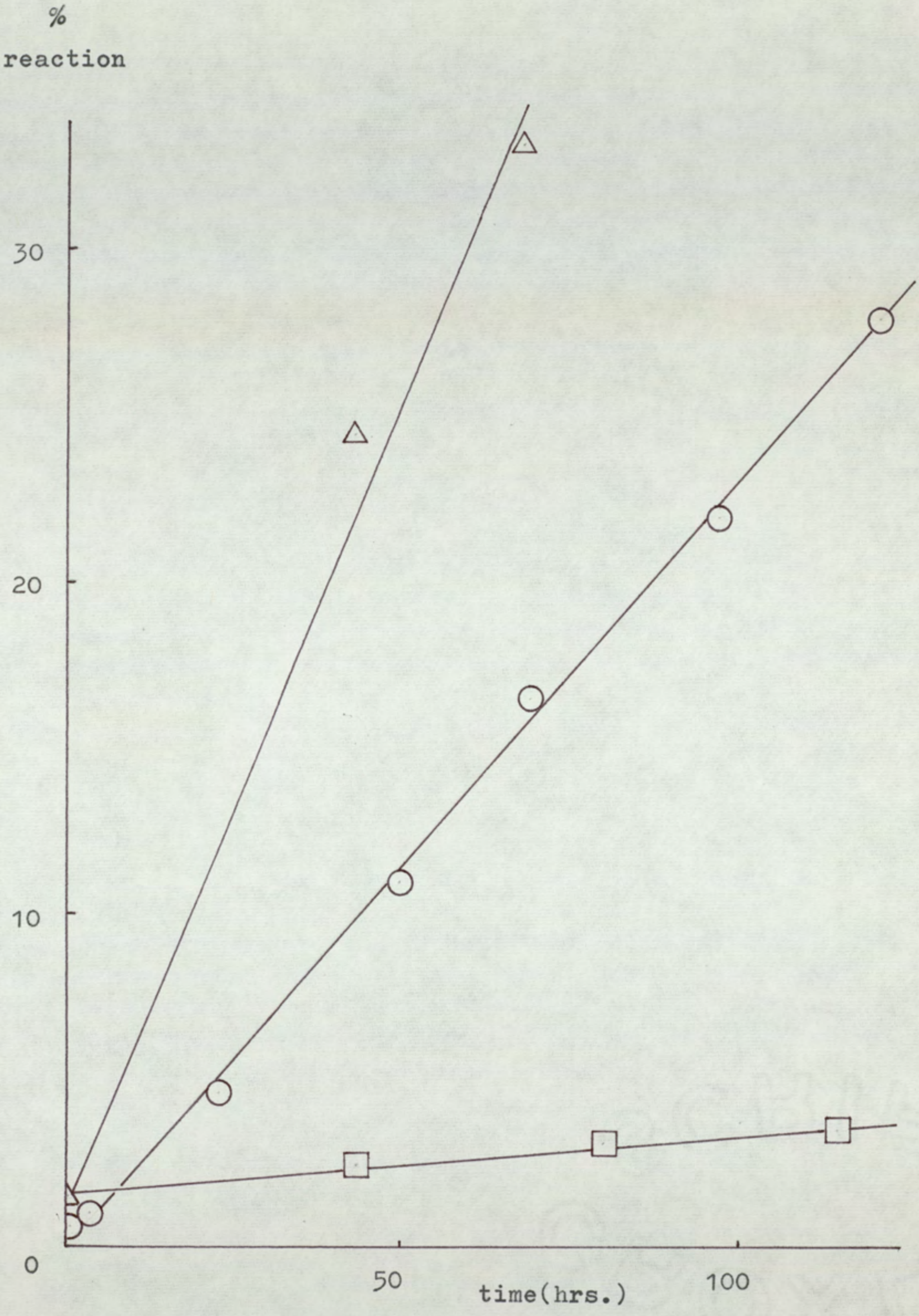


Figure 7.3: Hydrolysis of catechol compounds in 95% ethanol at 75°C.

□ = hindered-phenyl phosphate (by phenol formation)

△ = " " " (by decomposition)

○ = hindered-phenyl phosphite

7.2 Discussion

Since the rates of decomposition of hydroperoxide by phosphites were progressively diminished by increasing amounts of water, then the dialkyl phosphonate product must be comparatively inert towards hydroperoxide, since the increase in solvent dielectric on addition of water would be expected to lead to a rate increase. Hence to be an effective peroxide decomposer, phosphite needs to be hydrolytically stable. From the results quoted, high hydrolytic stability parallels low reactivity towards hydroperoxide. For the catechol phosphites:

peroxide decomposition: R= phenyl > isopropyl > hindered-phenyl
hydrolytic stability : R= phenyl < isopropyl < hindered-phenyl

This order of reactivity is in agreement with the results of Imajev[174]. Thus in designing a commercial antioxidant a compromise may have to be reached. However, the primary hydrolysis product, the phosphonate, will have some degree of radical-trapping ability, and if an aromatic phosphite is used, the phenol produced will probably synergise with the phosphonate[48,177]. The great stability of the catechol hindered-phenyl phosphite is probably due to the steric hindrance of the bulky tertiary-butyl groups.

The hydrolyses of the catechol phosphites are autocatalytic, shown best by the isopropyl compound, which is consistent with catalysis by phosphonate as reported previously.

For a second-order autocatalytic reaction,

$$A \longrightarrow B + \cdots\cdots$$

where B accelerates the disappearance of A, the rate of reaction is given by:

$$-\frac{d[A]}{dt} = k_2 [A][B]$$

If $[A]_o$ = initial concentration of phosphite

$[B]_o$ = initial concentration of phosphonate

$[A], [B]$ = concentrations at time t

Then $$[A]_o - [A] = [B] - [B]_o$$

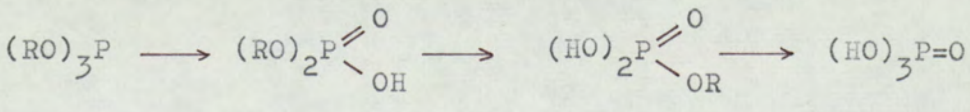
i.e. $$[B] = [A]_o - [A] + [B]_o$$

Integration by partial fractions yields the following expression[178]:

$$\frac{1}{[A]_o + [B]_o} \log_e \left(\frac{[A]_o [B]}{[B]_o [A]} \right) = k't \qquad (1)$$

For catechol isopropyl phosphite, assuming that 1 mole of phosphite gives 1 mole of alcohol and 1 mole of phosphonate, a plot of the left hand side of equation (1) versus time was made (Figure 7.4). This was a reasonable straight line of slope = k' = 0.065 mole l. min.$^{-1}$. Theoretically, if no phosphonate were present to begin with the reaction would not take place, since equation (1) would always equal zero. Assuming 1 % impurity of phosphonate i.e. $[B]_o$ = 0.0002 mole l.$^{-1}$, and using k' as found graphically, values of phosphite concentration as a function of time were calculated using equation (1). Figure 7.5 shows that this theoretical curve is in good agreement with the experimental reaction profile, so that the hydrolysis is adequately described by second-order autocatalytic kinetics. The fact that the hindered-phenyl phosphite hydrolysis does not appear to be autocatalytic may be due also to steric repulsion preventing the close approach of phosphite and phosphonate.

Considering phosphate hydrolysis now, in general the rate of hydroysis of triesters is about the same as that of the corresponding di- and mono-esters[179] so that in principle complete hydrolysis could occur:



$$(RO)_3P \longrightarrow (RO)_2P(=O)OH \longrightarrow (HO)_2P(=O)OR \longrightarrow (HO)_3P{=}O$$

In the case of catechol compounds the latter two reactions will

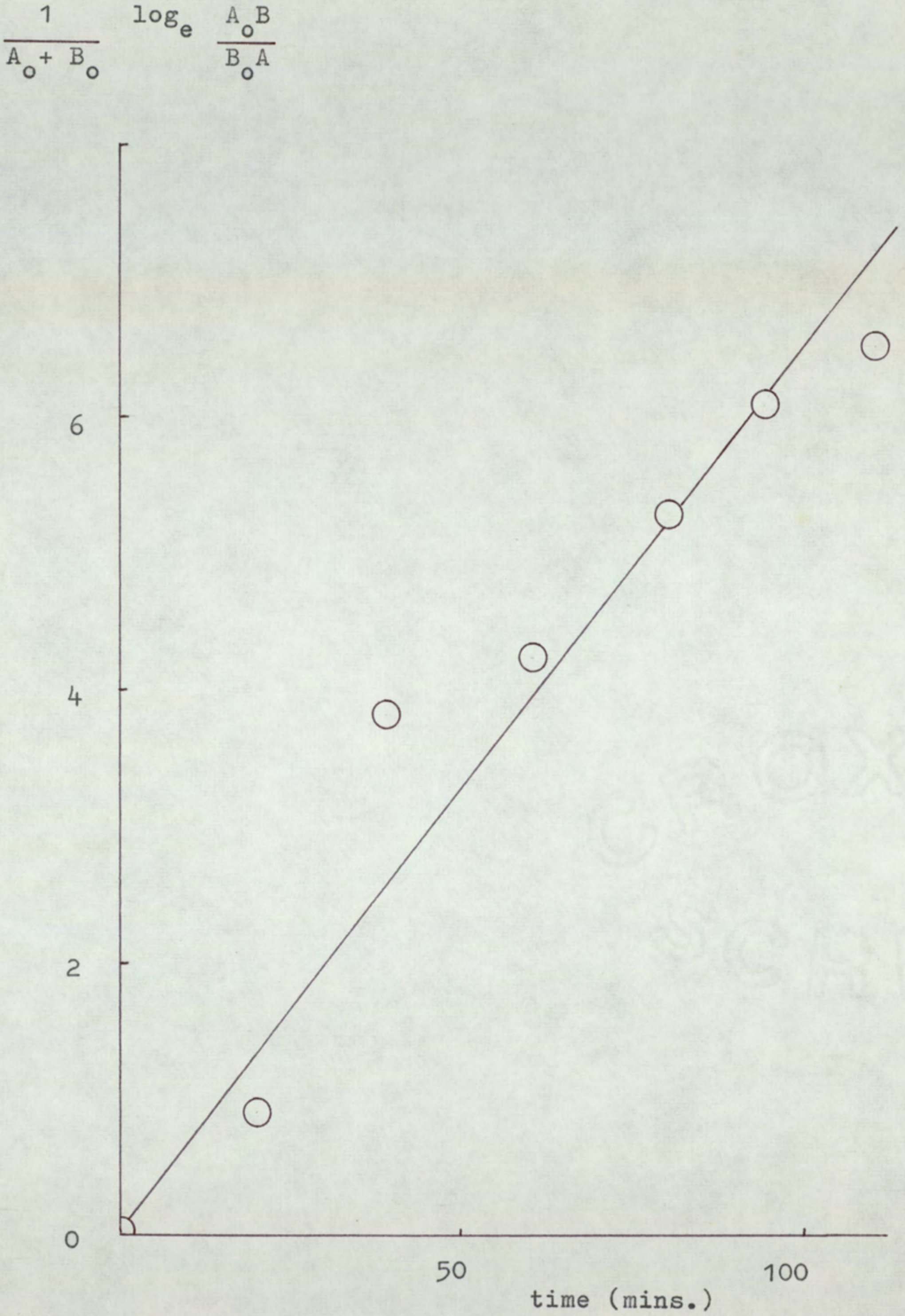


Figure 7.4: The hydrolysis of catechol isopropyl phosphite in 95% (v/v) aqueous ethanol at 75°C. plotted as a second- order catalytic reaction.

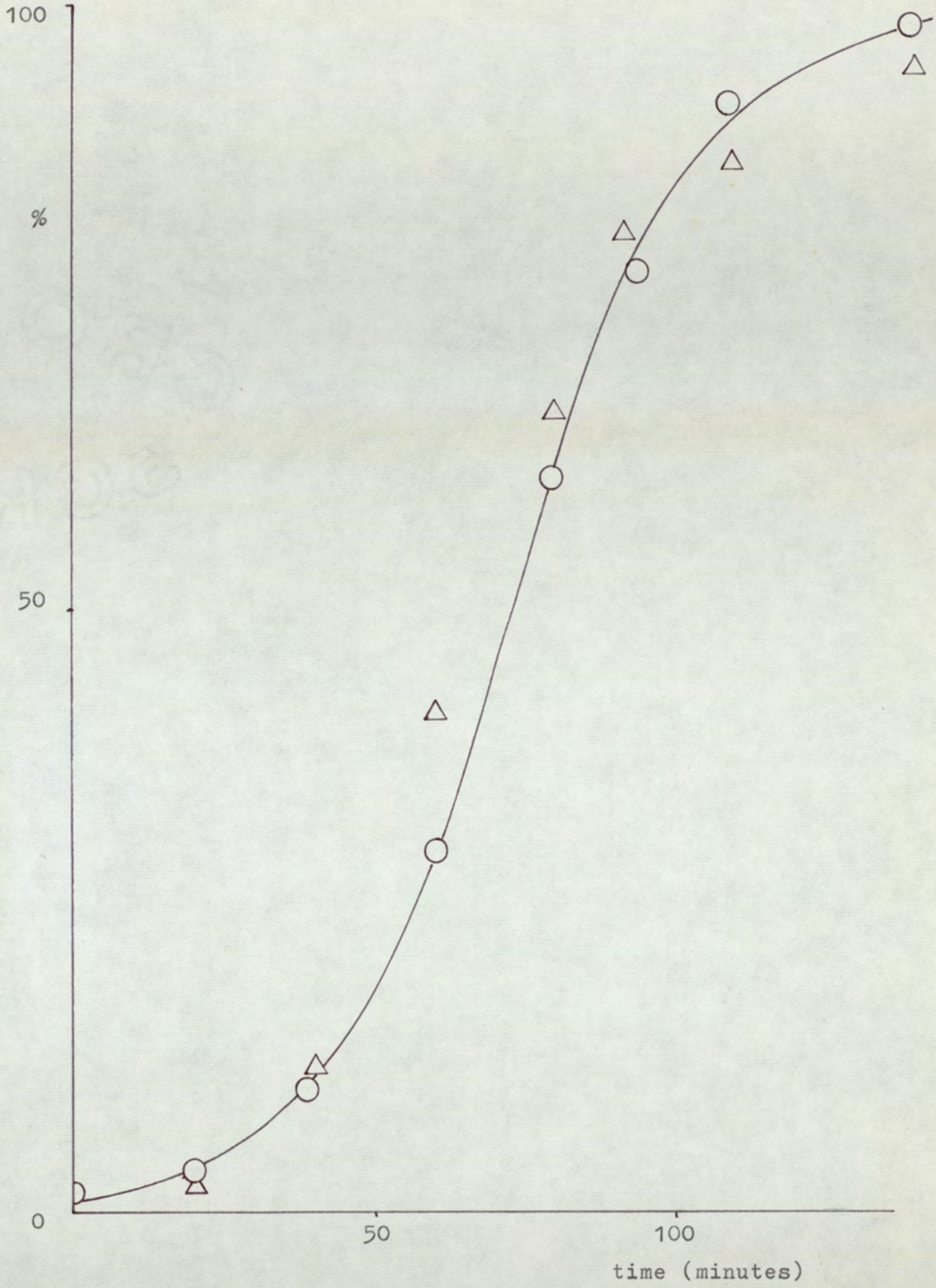
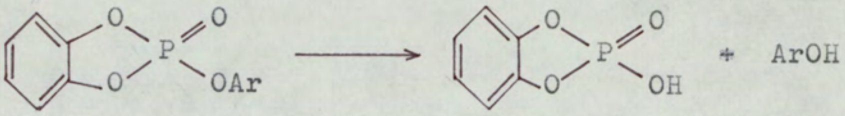


Figure 7.5: Plot of extent of reaction versus time for the hydrolysis of catechol isopropyl phosphite in 95% (v/v) aqueous ethanol at 75°C.

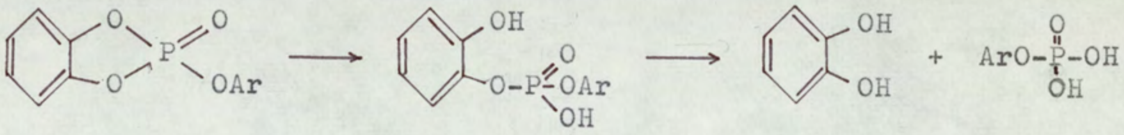
△ experimental data

○ theoretical curve for second order reaction involve ring-opening, and the final products will be alcohol and phosphoric acid.

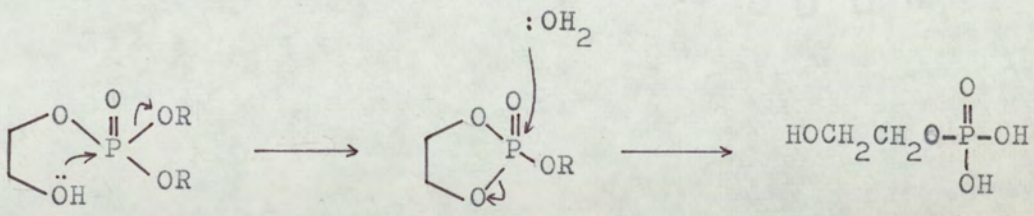
Since the rate of liberation of hindered-phenol from the catechol phosphate was very slow compared to the disappearance of phosphate, the reaction



cannot be very important. From product studies the hydrolysis reaction appears to be complex. It was suggested[180,181] that reaction proceeded entirely with ring-opening:

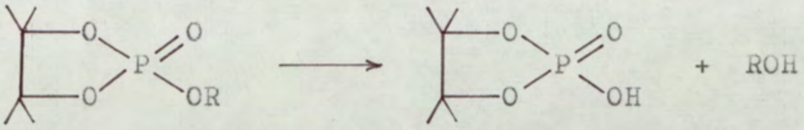


yielding monoalkyl phosphate and catechol, whilst other workers [182,183] considered that the second stage did not occur. The analogous cyclohexane compounds appear to undergo this second stage, and a cyclic intermediate was considered possible[184]. Further evidence for this comes from the fact that linear esters containing a neighbouring hydroxyl group lose one esterifying group very easily, a reaction ascribed to ring-closure followed by rapid ring-opening[185,186]:



The alkaline hydrolysis of RNA probably follows a similar type of reaction path[187-189]. Reactions in which a five-membered ring may be formed usually follow this sort of route in preference to an intermolecular reaction[190].

Ramirez has shown [191] that suitably substituted five-membered cyclic phosphates can undergo hydrolysis with exclusive exocyclic cleavage:

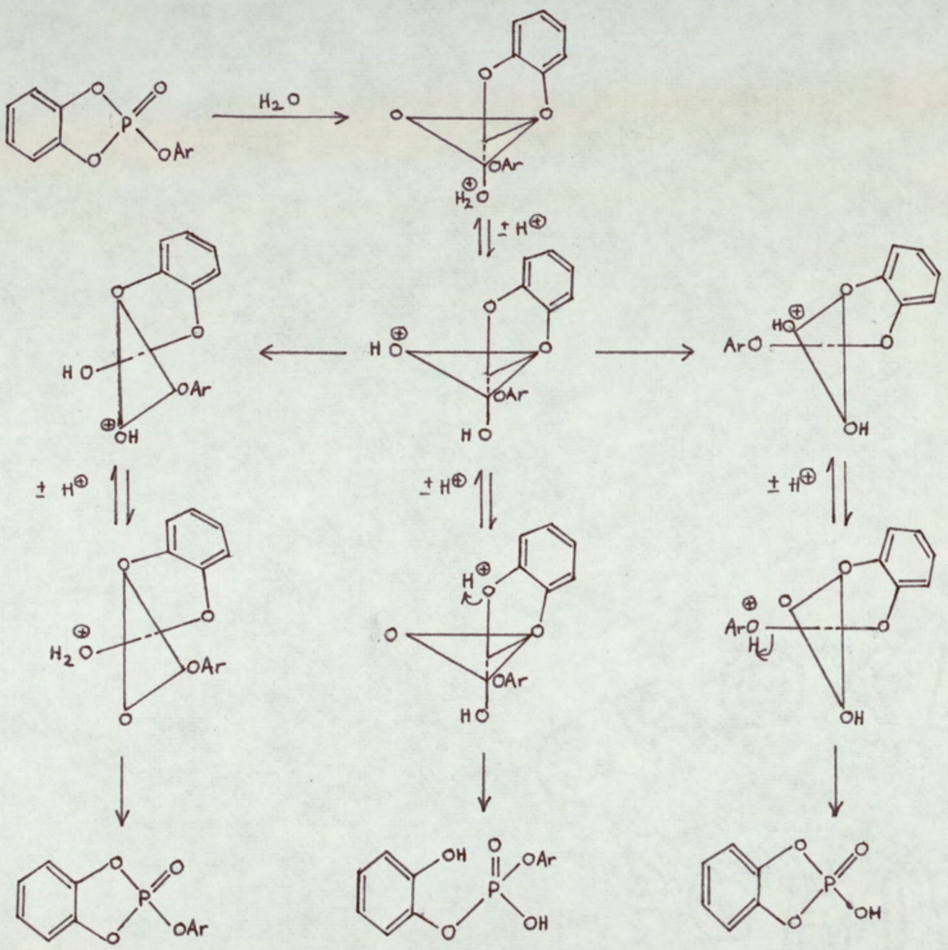


However, in general such hydrolyses are accompanied by ring-opening reactions[115,192]. As discussed in an earlier section, ring strain may account for the enhanced rates of hydrolysis of cyclic phosphates, whilst the high rates of the exocyclic reactions[116] are explained by the phenomenon of pseudo-rotation[119]. This is defined as the intramolecular process in which a trigonal bipyramidal molecule is transformed by deforming its bond angles in such a way that it appears to have been rotated by 90° about one of the interatomic bonds. The five-membered ring occupies one apical and one equatorial position in the trigonal bipyramidal intermediate. Pseudo-rotation takes place about the phosphorus-oxygen bond as pivot. In the case of the catechol phosphate both exocyclic and ring-opening hydroyses will occur since pseudo-rotation is possible, and in addition oxygen exchanges can occur (Figure 7.6)

The extensive experimental evidence for pseudo-rotation[119] has recently been supported by theoretical molecular orbital studies[193].

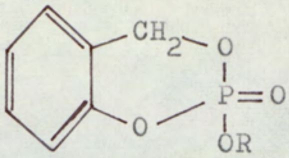
From the available literature[194,195] 6- and 7-membered cyclic phosphates appear to be considerably more stable to hydrolysis than the 5-membered compounds, and hence appear attractive as potential antioxidants, since in any practical application, particularly in a polymer system, moisture will be present. It is a matter for conjecture whether the larger ring phosphates are sufficiently reactive towards hydroperoxide.

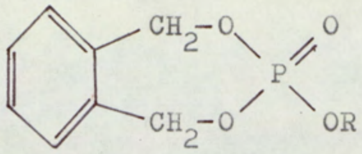
Preliminary attempts to synthesise the corresponding 6- and 7-membered phosphates analogous to the one used i.e.



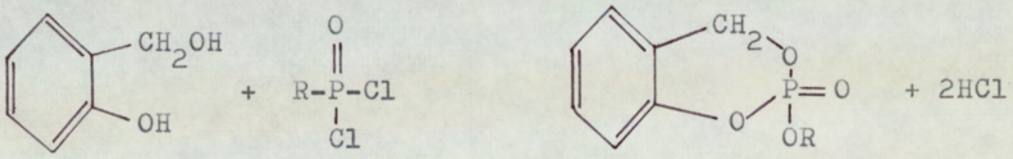
(1) (2) (3)

Figure 7.6: Possible intermediates for oxygen-exchange (1), ring-opening (2), and exocyclic cleavage (3) reactions during the hydrolysis of catechol hindered-phenyl phosphate.





by reaction of phosphorus oxychloride with salicyl and phthalyl alcohols respectively, were unsuccessful. A general method for the synthesis of the salicyl derivatives has been reported[196], by reaction of the desired phosphoryl dichloride with salicyl alcohol:



We were unable to synthesise the required dichloride, (where R = hindered-phenyl) which was needed for direct comparison with the catechol hindered-phenyl phosphate.

8. ANTIOXIDANT ACTIVITY IN POLYPROPYLENE - Results and Discussion

The antioxidant activity of the catechol hindered-phenyl phosphite, and its corresponding phosphate were estimated by measuring the induction period to oxidation of 1g. of 0.005 inch thick polypropylene film in oxygen at 150°C. using the technique and apparatus described in the experimental section. The results for phosphite and phosphate are shown in Table 21.

Table 21: Induction periods to oxidation of polypropylene stabilised by catechol hindered-phenyl phosphite and phosphate, at 150°C.

[phosphite] mole $kg.^{-1}$	I.P. hours	[phosphate] mole $kg.^{-1}$	I.P. hours
2.79×10^{-3}	0.6	2.67×10^{-3}	0.9
4.17×10^{-3}	62.7	4.35×10^{-3}	75.6
5.58×10^{-3}	198.0	5.35×10^{-3}	176.3
6.55×10^{-3}	291.0	6.48×10^{-3}	295.0
6.98×10^{-3}	302.0	8.73×10^{-3}	381.0
8.53×10^{-3}	393.0	9.12×10^{-3}	420.0
9.49×10^{-3}	413.0		

The induction period for unstabilised polymer was 0.6 hours.

It is clear that there is little difference between the phosphite, and its primary oxidation product the phosphate, and that both compounds are effective stabilisers for polypropylene above a critical concentration, which is around 2.7×10^{-3} mole $kg.^{-1}$ for both compounds. As discussed earlier, since this work was begun a critical concentration for catechol phosphites has been reported at around 5×10^{-3} mole kg.$^{-1}$ at 200°C. but there is doubt regarding the purity of the materials used in this case, and there is evidence to suggest that such critical concentrations increase with increase in temperature[197]. It was also observed that the polypropylene samples remained clear and colorless until the onset of oxidation at the end of the induction period, i.e. both compounds appear to be non-staining, a desirable characteristic for any potentially useful antioxidant for commercial exploitation.

The experiment was then repeated under the same conditions using di-lauryl-β,β'-thiodipropionate (DLTP), a widely used peroxide decomposing antioxidant. It was found that concentrations up to 1.4×10^{-2} moles DLTP per kg. polymer (0.75 weight%) had no appreciable effect, the induction periods all falling in the range 1-2 hours.

It is known that DLTP forms powerful synergistic mixtures with phenolic stabilisers, so that finally the two phosphorus compounds were compared in polypropylene with a 3:1 mixture of DLTP:Irganox 1010, the latter being a high molecular weight phenol. The performance of this mixture is reported[198] as being particularly good in thin films.

In Figure 8.1 the induction periods are plotted as a function of total antioxidant concentration, and it can be seen that the phosphite and phosphate are considerably better than the synergistic mixture. The results are summarised in Table 22.

Thus phosphite and phosphate, which are both completely compatible with polymer, relatively involatile, and fairly hydrolytically stable, appear to have potential commercial use both as process and service stabilisers.

The involvement of radicals during the oxidation of phosphite to phosphate in the polymer does not appear to be detrimental in the test performed, since the induction period does not decrease

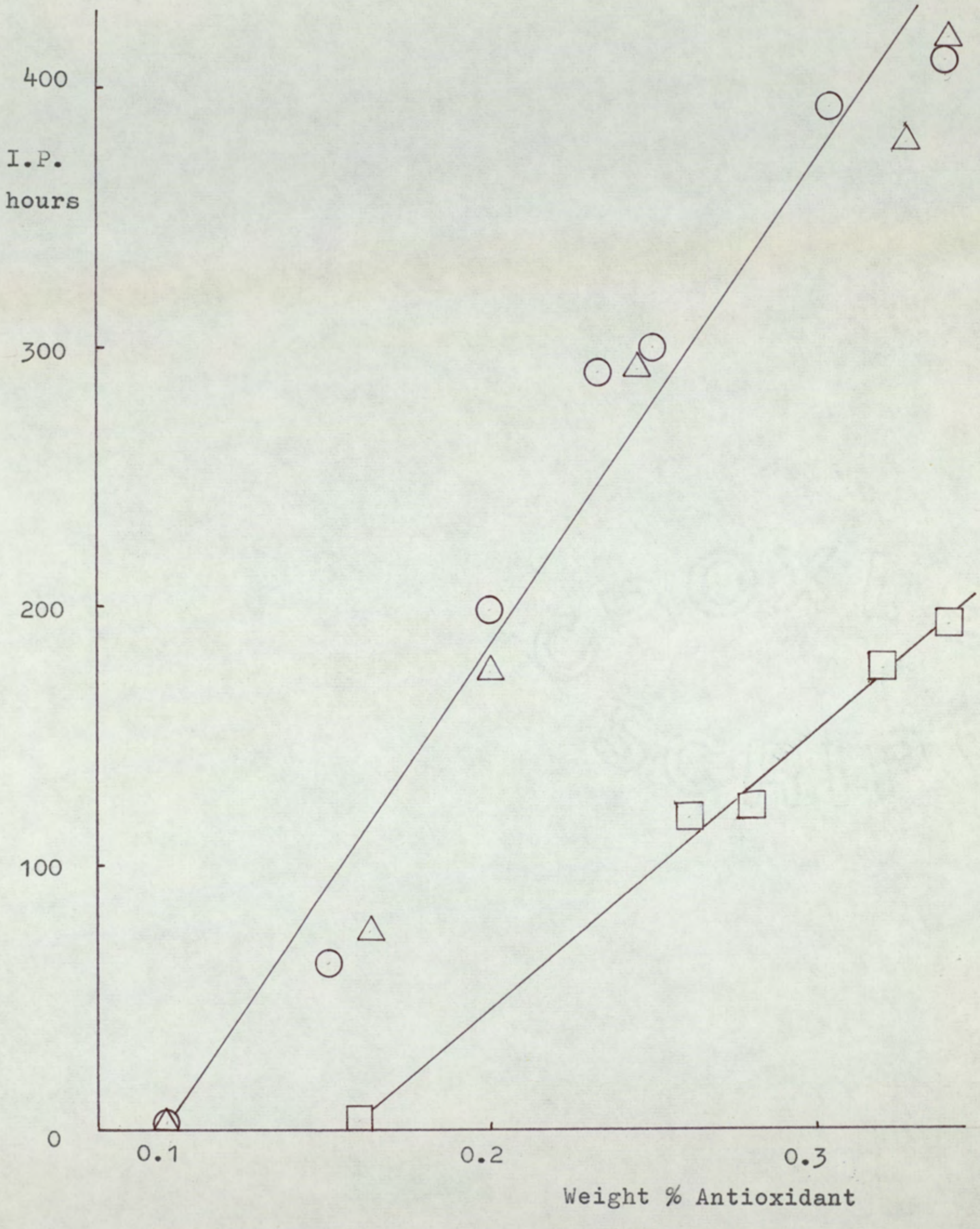


Figure 8.1: Induction periods to oxidation of polypropylene at 150°C. stabilised by

○ = catechol hindered-phenyl phosphite

△ = catechol hindered-phenyl phosphate

□ = 3:1 of DLTP:Irganox "1010".

significantly, but phosphates have the clear advantage of being completely free from patent cover. In a processing situation the free radical reactions of the phosphite may be a distinct disadvantage, since the melt flow index of the phosphite-stabilised system may decrease more rapidly due to radical induced chain scission, leading to manufacturing difficulties.

Table 22: Induction periods to oxidation of polypropylene stabilised by 3:1 DLTP:Irganox, at 150°C.

total concentration weight %	induction period hours
0.10	1.3
0.16	2.5
0.26	119.0
0.28	123.0
0.32	177.0
0.34	194.0

Catechol phosphite esters have been evaluated by Russian workers in a variety of polymer systems including polypropylene [105,199], polypropylene fibres[200], polyolefin copolymers[201], polyamides[202], polyvinyl chloride[203], natural rubber[204], and butyl rubber[205]. The synergistic action of catechol phosphites with phenols[104,106] and sulphides[105] is also known.

The use of catechol phosphites as polymer stabilisers is the subject of a number of patents[206]. The catechol phosphates appear to be free of any patents or reported antioxidant activity in the open literature.

Also as a class phosphites exhibit considerable toxicity, acting on the nerve centres and abdominal glands[207], in contrast to the generally less harmful phosphates, which is another attractive feature of the latter as potential stabilisers.

Note added in proof:

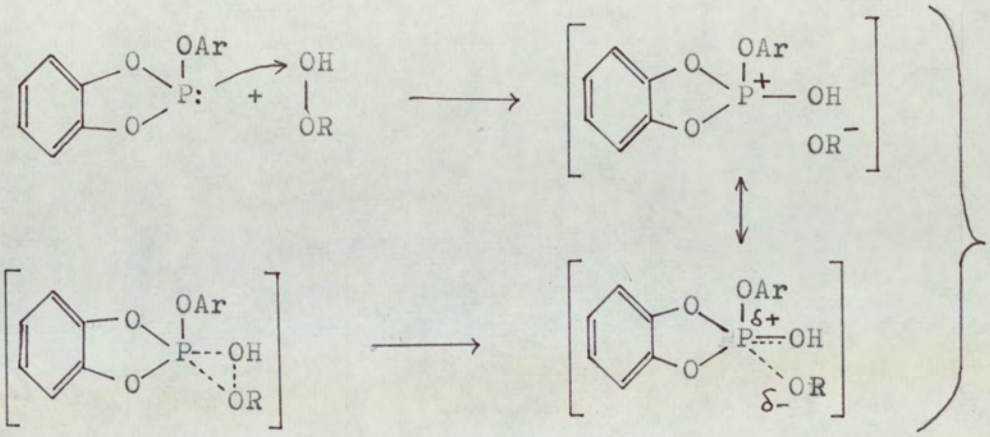
Very recent work in this laboratory, forming part of a program to extend the present studies, has shown that catechol hindered-phenyl phosphite and phosphate are effective melt stabilisers for polypropylene[208]. In the former case, an initial small increase in melt flow index occured, which may be associated with the pro-oxidant effect found in this work. In addition both compounds appear to be excellent ultra-violet stabilisers, being more effective than the widely used hydroxybenzophenone compounds.

CONCLUSIONS

The work that has been described shows that some reactions of phosphite esters in which the phosphorus atom forms part of a five-membered ring system differ from those of their acyclic analogues. The greater antioxidant activity associated with the cyclic compounds is due at least in part to these differences.

The catechol phosphites effectively inhibit hydrocarbon oxidation initiated by azobisisobutyronitrile, and by hydroperoxides, showing autoretardation in both cases. Linear phosphites show only a lowering of oxidation rate at the same concentration. All phosphites appear to have radical-deactivating ability, being oxidised by AZBN, but the catechol phosphate thus formed still retains this activity in contrast to the inert triphenyl phosphate. In the presence of hydroperoxide initiator, all the phosphites studied initially increased the rate of oxidation, before the inhibition stage was attained.

The characteristics of the catechol hindered-phenyl phosphite-cumene hydroperoxide reaction were a second order reaction with a small activation energy (14.1 kcal. mole^{-1}), low frequency factor (10^7 l.mole^{-1}sec.$^{-1}$), and large negative entropy of activation (-23 cal.mole^{-1}deg.$^{-1}$), all of which are paralleled with non-cyclic phosphites. In addition the reaction rate was not altered by the presence of oxygen or free radical scavengers. The catechol phosphite-hydroperoxide system was found to absorb oxygen, however, and could also initiate the polymerisation of styrene, albeit with a low efficiency, as could triphenyl phosphite-hydroperoxide mixtures. These observations are consistent with reaction, common to all phosphites, occurring by a redox mechanism, in contrast to the usually accepted ionic route. The first (rate controlling) stage probably involves nucleophilic attack of phosphorus on the hydroxyl oxygen atom of the hydroperoxide, this being the most electropositive and least sterically hindered oxygen atom:



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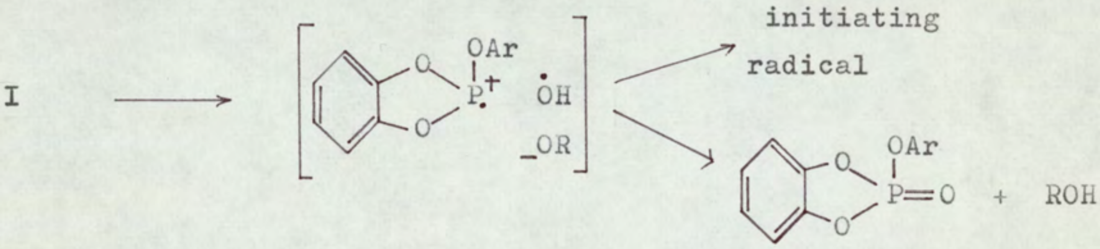
These species will have only transient existence, decomposing to products largely ionically, but in part via a homolytic species:



The free radical contribution to the whole is small, and in one case the efficiency of initiation of styrene polymerisation by the phosphite-hydroperoxide system was shown to be between 5 and 10 %.

This mechanism is analogous to the better-known amine-diacyl peroxide reaction, and similar to that suggested by Pobedimskii for the phosphites while this work was in progress.

The rate control exercised by the first step explains the insensitivity of the reaction to added free radicals. The free radical involvement is of course responsible for the pro-oxidant stage observed in the oxidation studies. The experimental kinetic parameters are wholly in accord with the proposed scheme.

Perhaps surprisingly, the rates of reaction of the catechol phosphites with hydroperoxide were not greater than their acyclic analogues, in contrast with the large rate enhancements observed in cyclic compounds containing quadruply connected phosphorus. However, the reaction scheme postulated occurs through a phosphonium type intermediate in which phosphorus is probably sp^3-hybridised, whereas, for example, the hydrolysis of phosphates proceeds through an sp^3d-hybridised state. Clearly the steric requirements, as well as the energy differences in these two cases may vary considerably, so that triply- and quadruply-linked phosphorus compounds need in no way be comparable.

In the case of the non-cyclic phosphites, reaction with hydroperoxide ceased when the oxidation to phosphate was complete. The 5-membered cyclic compounds were able to undergo at least two further reactions to eventually yield an unidentified species which was an extremely powerful catalyst for further hydroperoxide destruction. The overall stoichiometry of the formation of this catalyst is probably 4:1 hydroperoxide:phosphite. This catalytic reaction, which obeys pseudo-first order kinetics, can lead to the removal of at least several hundred fold excess of hydroperoxide (based on phosphite), without any diminution on rate, which suggests a Lewis acid species. For the same concentrations, the catalytic rates due to the catechol phosphites increased in the order:

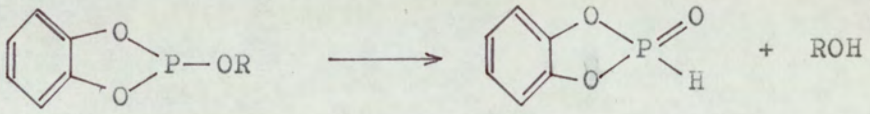
$$\text{hindered-phenyl} < \text{isopropyl} < \text{phenyl}$$

which does not parallel nucleophilic reactivity (or its converse).

Further support for the above scheme came from product studies. Triphenyl phosphite reacted with cumene hydroperoxide to give a quantitative yield of α-cumyl alcohol. The catechol phosphites reacted with excess hydroperoxide to yield less than the stoichiometric amount of alcohol, together with phenol and acetone, the products expected from a Lewis acid induced decomposition. The α-cumyl alcohol was dehydrated by the phosphate simultaneously formed, or by a derived product, to yield α-methyl styrene in a second order reaction. In addition small amounts of the free radical products acetophenone and methane were found, probably due to a minor amount of radical-induced breakdown during the pro-oxidant stage.

Another minor product specific to the reaction of cyclic phosphites was oxygen. Its origin was not established, but it may be a consequence of alkoxy (or hydroxy) radical attack on hydroperoxide.

Ring strain in the catechol phosphites did not greatly effect their rates of hydrolysis, which exhibited classical second order catalysis, presumably due to the phosphonate product:



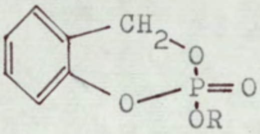
Electron-withdrawing substituents on phosphorus enhanced the ease of hydrolysis, which in turn reduced the peroxide-decomposing ability.It was found that steric hindrance could greatly reduce this sensitivity to moisture, and the half-life for the hydrolysis of catechol phenyl phosphite was increased by about a factor of 10^3 by the introduction of two ortho tertiary butyl groups into the benzene ring. The catechol hindered-phenyl phosphate was slightly more susceptible to hydrolysis than the corresponding phosphite, and this probably occurred mainly by ring-opening, with some exocyclic cleavage, in accordance with the literature. Brief studies of two alicyclic phosphites indicated that 6-membered rings were more hydrolytically stable than 5-membered ones.

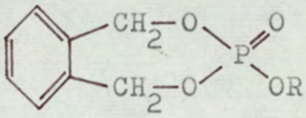
The antioxidant activities of the catechol hindered-phenyl phosphite and phosphate were equivalent in polypropylene, as measured by induction periods. In addition both were compatible with the polymer, and non-staining, an important consideration for use in light-coloured articles.

The use of catechol phosphates as polymer stabilisers is thus attractive. As well as being equally effective they are less toxic, and lack the pro-oxidant activity of the phosphites, which may be detrimental during polymer processing. Any radical species may lead to polymer chain scission, leading to a fall in molecular weight, with the concomitant reduction in physical and mechanical properties. Resistance to hydrolysis may be imparted by the use of suitable steric substituents, without loss of activity, and finally no patent literature exists.

Suggestions for further work

The catechol phosphates are effective stabilisers, and the basis for their enhanced activity lies in their cyclic structure. It is of interest to see whether, for example, the catalytic peroxide decomposition reactions occur with other cyclic phosphates of different ring size. In the first instance the analogous 6- and 7-membered rings should be examined, based on salicyl and phthalyl alcohols respectively:



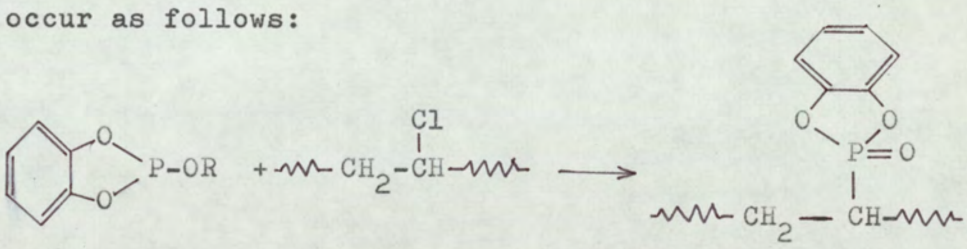


In addition the work could profitably be extended to rings based on other aromatic species, and to alicyclic systems. The effects of structural variations as well as ring strain on peroxide decomposition may give some idea of the active species. Clearly a thorough product analysis of such systems, as well as for the catechol compounds, would be advantageous.

Parallel with such studies, the hydrolytic stability of the compounds would be of interest. It has been seen how suitably placed bulky groups can greatly enhance the stability of phosphites. The catechol phosphates may be precluded from commercial exploitation by the high cost of the raw materials, but if, for example, the phosphates produced from ethylene glycol (a cheap, readily available material) could be stabilised against hydrolysis, then a viable product could result. If it was easier to first prepare the cyclic phosphite than the phosphate, a cheap oxidation process would have to be developed for the conversion of the latter. Air oxidation would be the obvious first method for examination.

As indicated earlier, phosphites are capable of powerful synergism with, for example, phenols and sulphides. In view of the great effectiveness of catechol phosphites alone, and the equivalence of phosphite and phosphate in polypropylene, the cyclic phosphates may also show synergism. Studies in model hydrocarbons would be a useful first stage, together with the commonly used phenols and sulphides, on an empirical basis.

Since volatility of antioxidants is often of considerable importance, it would be of interest to study the feasibility of synthesising high molecular weight, or even polymeric cyclic phosphates and phosphites. These would be involatile, and unlikely to be leached out of the polymer in use, and the ultimate in this direction would be to actually graft phosphate onto the polymer backbone, to give a bound antioxidant. Such techniques would be much more readily applied to condensation polymers, for example by using a phosphorylated diol in the preparation of a polyester. A novel way of doing this for halogenated polymers would be to utilize the Michaelis-Arbusov reaction. Thus for a catechol phosphite and polyvinyl chloride, grafting could occur as follows:



The use of phosphites as antiozonants is a field in which no work appears to have been done. Since ozone has been shown to oxidise phosphites to phosphates they may have some potential use as sacrificial stabilisers, reacting with ozone to form another antioxidant in the case of the catechol compounds.

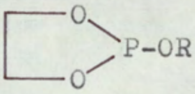
The very recent work showing the powerful ultra-violet stabilisation conferred by the catechol compounds[208] clearly opens up a whole new area of exploration, in which much profitable work remains to be done.

APPENDIX

Nomenclature

Whilst trialkyl phosphite and trialkyl phosphate are agreed names for simple esters of phosphorous and phosphoric acid respectively[209], numerous ways have been used for naming the cyclic compounds.

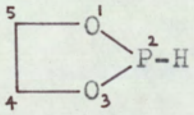
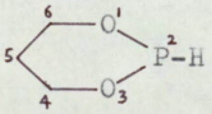
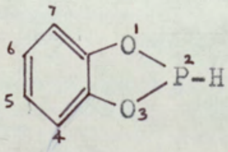
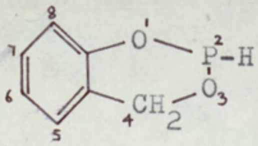
Early workers used the name of the diol which had been esterified e.g.



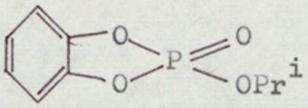
became alkoxy ethylene phosphite.

and the compounds with which this thesis is chiefly concerned have often been called o-phenylene phosphites.

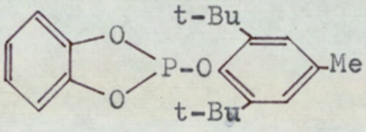
Standard terminology does exist for these cyclic compounds[210] as follows:

structure	name	ring index number
	1,3,2-dioxaphospholane	104
	1,3,2-dioxaphosphorinane	218
	1,3,2-benzodioxaphosphole	1100
	4H-1,3,2-benzodioxaphosphorin	1528

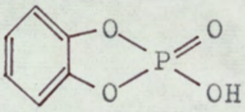
Thus



is named 2-oxo-2-isopropoxy-1,3,2-benzodioxaphosphole. However, for convenience, in the text phosphites and phosphates will be named from their parent diol. Thus the above compound will be called catechol isopropyl phosphate. The most commonly used compound in this study



will be abbreviated to catechol hindered-phenyl phosphite for brevity, and



will be called catechol hydroxy phosphate.

With these exceptions I.U.P.A.C. nomenclature will be used.

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