A STUDY OF PHOSPHORUS-CONTAINING ANTIOXIDANTS IN POLYOLEFINS

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Doctor of Philosophy

THE UNIVERSITY OF ASTON IN BIRMINGHAM

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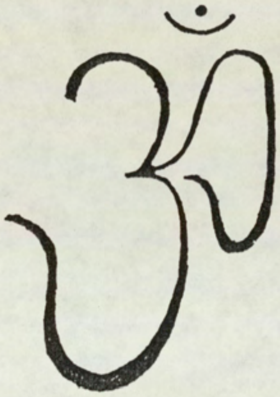

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BY PARMODE SHARMA

PhD THESIS,1988

SUMMARY

Metal dithiophosphonates (Ni, Zn, Fe, Co, Cu) and the corresponding sulphide, TPS, were examined as potential antioxidants in polypropylene. All the dithiophosphonates were very good melt stabilisers when compared to commercial controls. Their effectiveness as thermal antioxidants varied considerably from CuDiBuPn which was poor to NiDiBuPn which was excellent and appears to be better than Irganox 1076, a commercial antioxidant. The photostabilising activity of these compounds also varied considerably. The NiDiBuPn was found to be the most outstanding photostabiliser when compared to the other phosphonates both on a molar and weight basis and its activity was found to be highly dependent on concentration, alkyl substituent and processing severity. NiDiBuPn and CuDiBuPn were both found to synergise effectively with the U.V. absorber HOBP and their effectiveness was found to increase when an excess of the U.V. absorber was used.

The dithiophosphonates were shown to be effective radical traps (oxygen absorption) and peroxide decomposers (hydroperoxide decomposition). Mechanistic studies of NiDiBuPn also showed the complex to be highly stable to thermolysis and photolysis. The ^{31}P NMR studies of NiDiBuPn and TBH showed that the major transformation products are the corresponding sulphides, the acidic species, the phosphorus esters and some highly oxygenated inorganic species.

Key Words

Thiophosphonates, Antioxidants, U.V. Stabilisers, Sulphur-containing Antioxidants.

TO MY GRANDFATHER
Pt. LAHORI RAM SHARMA

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ABBREVIATIONS

PP	Polypropylene
HOBP	2-hydroxy-4-octyloxy benzophenone
Tinuvin 770	Bis-(2,2,6,6-tetramethyl-4-piperidinyl)-sebacate
Cyasorb 1084	2,2-thiobis(4-tert-octyl phenolato)butylamino nickel
Irganox 1076	Stearyl (3,5-di-tert-butyl-4-hydroxyphenyl) propionate
Irganox 1010	Pentaerythrityl tetrakis-(3,5-di-tert-butyl-4 -hydroxy phenyl) propionate
TPS	2,4-bis(4-hydroxy-3,5-ditertiarybutylphenyl) -2,4-dithio-1,3,2,4-dithiodi-phosphetane
NiDiBuP	Nickel diisobutyl dithiophosphate
NiDiBuC	Nickel diisobutyl dithiocarbamate
NiDiBuPn	Nickel diisobutyl dithiophosphonate
DRP	Dithiophosphate
DTC	Dithiocarbamate
DRPn	Dithiophosphonate
CHP	Cumene hydroperoxide
TBH	Tertiary butyl hydroperoxide
U.V.	Ultra violet/visible spectroscopy
I.R.	Infra-red
N.M.R.	Nuclear magnetic resonance
CM	Closed mixing
OM	Open mixing
ET	Embrittlement time
MB	Master batch
MFI	Melt flow index

CHAPTER 1

INTRODUCTION

1.0 PREFACE

The degradation of polymers is primarily due to oxygen but in addition various other environmental factors such as light, heat, ozone and metal ions also play a role(1,2). This results in the deterioration of physical, chemical and mechanical properties such as tensile strength, impact strength, optical clarity, embrittle time and resistance to fatigue. Degradation takes place during the processing and fabricating operations in which the polymer is subjected to high temperatures and mechanical stresses, and during the subsequent service life of the end-use articles. The nature of the degradation process varies in rate and extent, depending on the chemical and physical structure(3,4) of the polymer and the impurities present(5,6), which serve as sites of autoxidation. The inherent weakness of polymers coupled with challenging technological applications often in agressive environments, places a great demand on efficient stabilisers and antioxidants.

1.1 OXIDATION OF HYDROCARBONS

The reactions of oxygen with organic materials involves a free radical chain reaction described as autoxidation (7). The essential features of autoxidation as proposed by

Bolland and his co-workers(8-10) is shown in Scheme 1. The radical chain reaction is initiated by thermolysis, photolysis or catalytic residues left during polymerisation (Reaction 1). The nature of the initiation process has a dominating influence on the overall rate of oxidation. The autoxidation process involves two interrelated oxidation cycles, the first of which involves the formation of macroalkyl (R$^\cdot$) and alkyl peroxyl radicals (ROO$^\cdot$), whereas the second involves the formation of radical generators(11(a)). The propagation of oxidative radical chain reaction involves the reaction of alkyl radicals (Reaction 2) with oxygen at normal oxygen pressure, to give alkyl peroxyl radicals, followed by hydrogen abstraction from the polymer to form hydroperoxides (Reaction 3). These hydroperoxides generate new radicals such as RO$^\cdot$ and OH$^\cdot$ into the cycle (Reactions 4,5 and 6). Hence the formation of hydroperoxides is the most important source of initiating radicals. The termination of auto-oxidation involves the formation of inert and non-radical products (Reactions 7,8 and 9).

Initiation

$$RH \xrightarrow[\text{cat. residue}]{\Delta H, h\nu} R^{\cdot} \qquad (1)$$

Propagation

$$R^{\cdot} + O_2 \longrightarrow ROO^{\cdot} \qquad (2)$$

$$ROO^{\cdot} + RH \longrightarrow ROOH + R^{\cdot} \qquad (3)$$

$$ROOH \longrightarrow RO + ROO + H_2O \qquad (4)$$

$$ROOH \longrightarrow RO^{\cdot} + OH^{\cdot} \qquad (5)$$

$$ROOH \longrightarrow RO^{\cdot} + ROO^{\cdot} + H_2O \qquad (6)$$

Termination

$$2\,ROO^{\cdot} \longrightarrow \text{inert products} \qquad (7)$$

$$ROO^{\cdot} + R^{\cdot} \longrightarrow ROOR \qquad (8)$$

$$2R^{\cdot} \longrightarrow R - R \qquad (9)$$

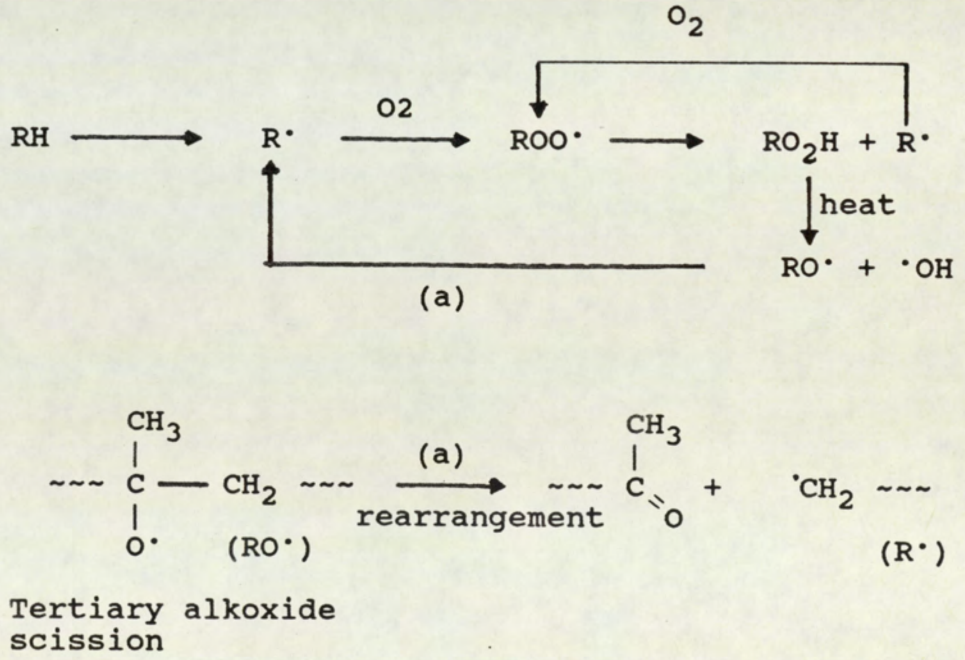
Scheme 1.0 The Auto-oxidation of Hydrocarbons

1.2 POLYMER DEGRADATION DURING PROCESSING AND IN SERVICE

1.2.1 Melt Degradation

Melt degradation occurs at high temperatures during the processing operations (e.g. extrusion), usually in machines where access of air to the hot polymer is restricted. During processing considerable shear is applied to the viscous polymer melt in the presence of oxygen which causes the polymer chains to undergo mechanochemical scission and formation of peroxides (11(b)). These peroxides generate further radicals leading to changes in the polymer melt viscosity, generally expressed in terms of melt flow index, MFI, which is inversely proportional to molecular weight.

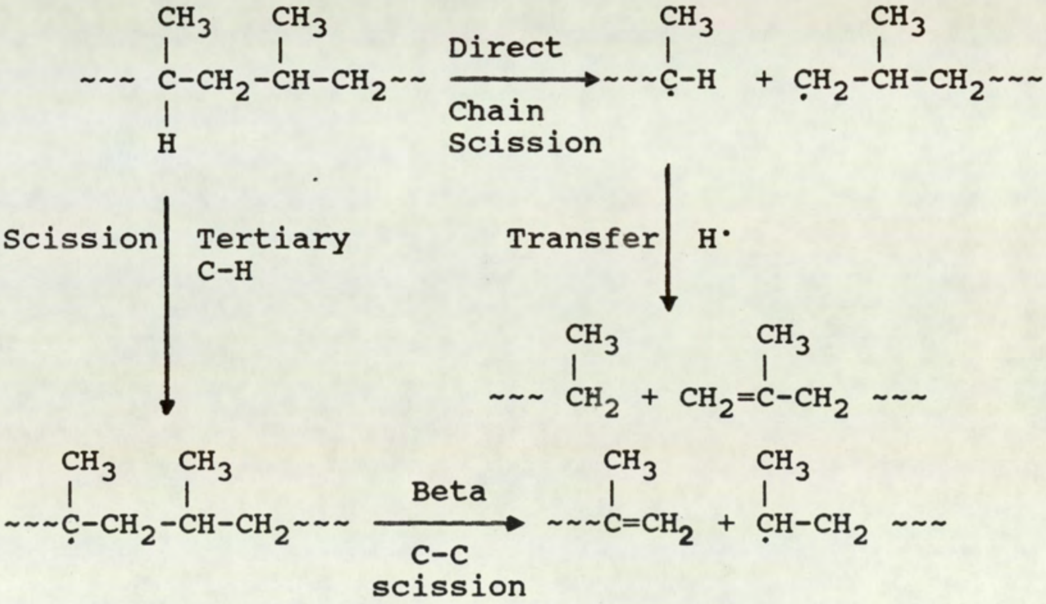
The nature and structure of the polymer matrix exert a profound effect on the melt degradation during processing. For example, the molecular weight of polypropylene decreases due to chain scission whereas polyethylene's molecular weight increases due to cross-linking (11(b),12,13). In the former case, the decrease in molecular weight is principally due to fragmentation of the tertiary alkoxyl radical (RO·) to a ketone, regenerating a primary alkyl radical which after rearrangement, can once again take part in the melt degradation cycle (Scheme 1.1).



Scheme 1.1 <u>Melt Degradation Cycle</u>

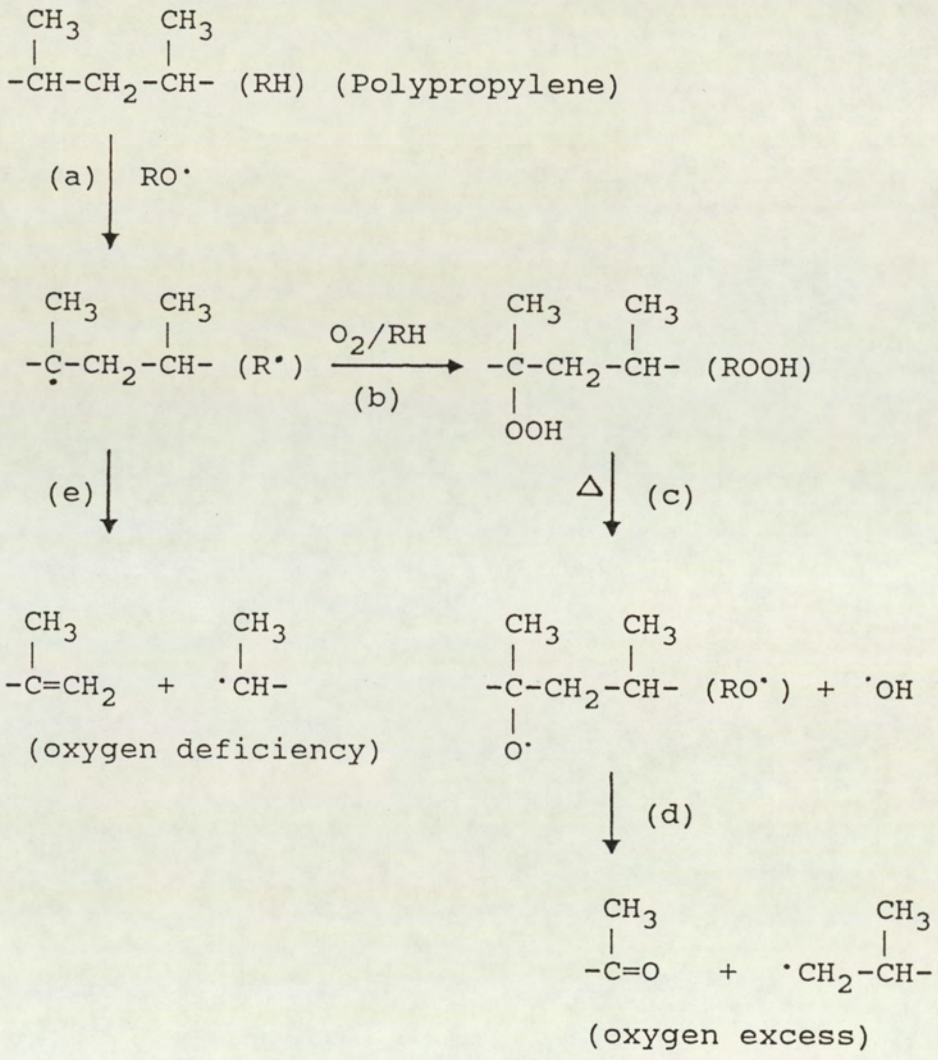
1.2.2. Thermal Degradation

The processing of polyolefines by extrusion, injection moulding, calending etc ... requires softening through thermal input, for facilitating the flow of the polymer. Temperatures that are required generally are such that the polymer is susceptible to some thermal breakdown which is accelerated by the presence of residual oxygen and / or oxygen from the atmosphere. Chain scission (Scheme 1.2) is one of the most important consequences of the autoxidation of polymers, thus the thermal oxidative treatment received during the processing stages will have a profound effect on its service performance.



Scheme 1.2 Thermal Scission of Polypropylene

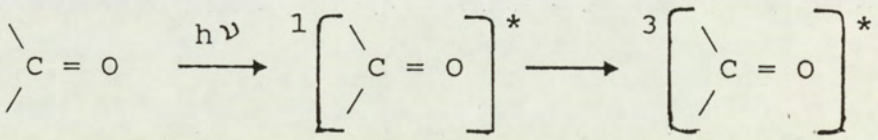
Hydrocarbon polymers at elevated temperatures during use (e.g. under the bonnet in the automotive industry) undergo degradation and produce peroxides which decompose to free radicals that initiate the chain reaction (Scheme 1.0)(14,15). The peroxide concentration increases with processing time in polypropylene but more rapidly in excess of oxygen (13) (Scheme 1.3).



Scheme 1.3 <u>High Temperature Processing of Polypropylene</u>

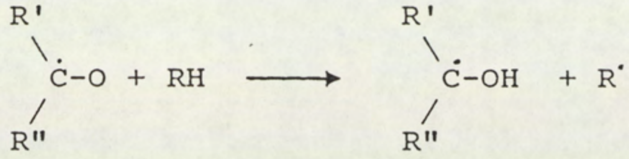
1.2.3. Photodegradation

The mechanism of photo-oxidation of polyolefins is basically similar to that involved in thermal oxidation, except the rate of the initiation step is much higher in the former case (due to the more rapid formation of hydroperoxides) which leads to higher radical concentrations and consequently shorter kinetic chains (11(a)). Chromophores produced during processing and fabrication of polyolefins contribute substantially more to the photoinitiation step than those generated during manufacture or environmental exposure (16). These chromophores such as carbonyl containing compounds are commonly associated with the absorption at longer wavelengths of the sun spectrum (>285 nm) (11(a)). Carbonyl compounds have strong absorbance and show characteristic luminence associated with excitation to the triplet state(17) (Reaction 10).



(10)

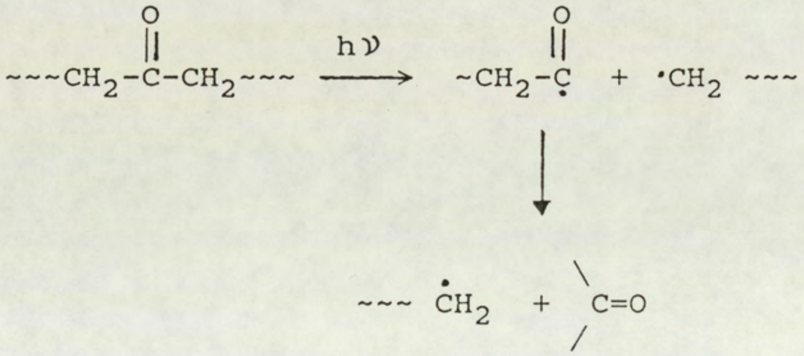
The triplet state of carbonyl compounds are highly chemically reactive than singlet, since the former has a longer life time and can undergo three different kinds of transformation in polymers. The most important transformation is their reduction by hydrogen abstraction from the polymer (13) (Reaction 11).



$$R'R''\dot{C}\text{-O} + RH \longrightarrow R'R''\dot{C}\text{-OH} + R^{\cdot} \qquad (11)$$

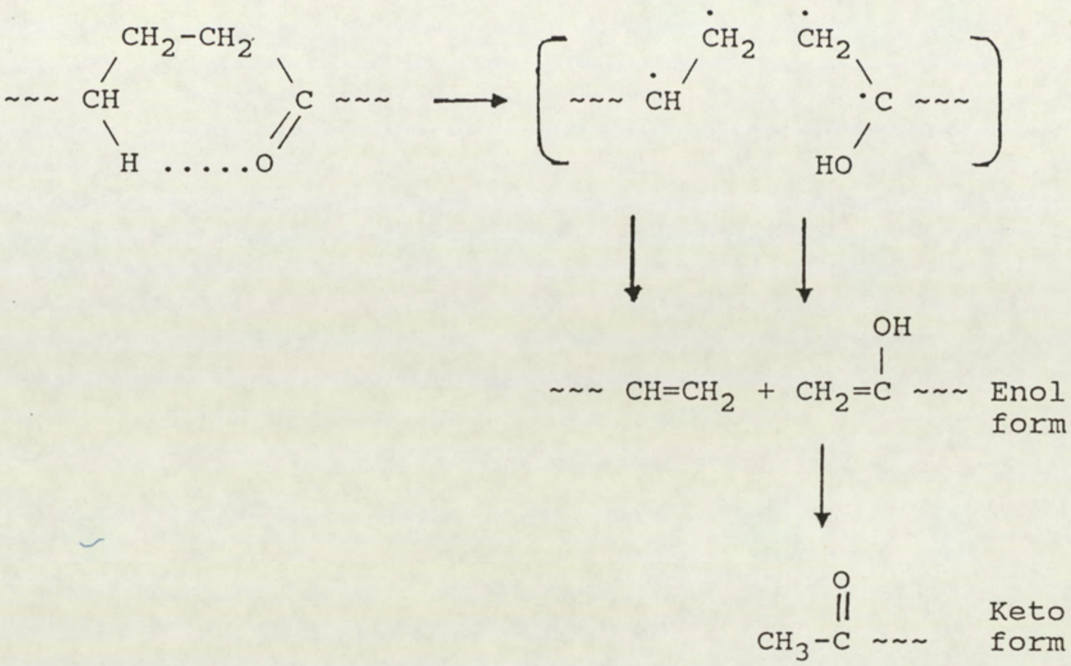
The other two transformation of triplet states are the Norrish I and Norrish II reactions $^{(18,19)}$.

In the Norrish type I reaction, the bond between the carbonyl group and an adjacent carbon is homolytically cleaved producing two radicals (Reaction 12).



$$\sim\sim\sim CH_2\text{-}\overset{O}{\overset{\|}{C}}\text{-}CH_2\sim\sim\sim \xrightarrow{h\nu} \sim CH_2\text{-}\overset{O}{\overset{\|}{\underset{\bullet}{C}}} + {\cdot}CH_2\sim\sim\sim \longrightarrow \sim\sim\sim \dot{C}H_2 + \rangle C{=}O \qquad (12)$$

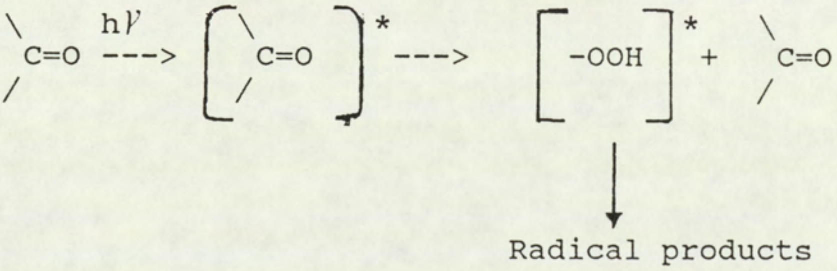
A non-radical intermediate process which occurs with the formation of a six membered cyclic intermediate is involved in the Norrish type II reactions (Scheme 1.4).



Scheme 1.4 Norrish Type II Reactions

Although both types I and II lead to scission only type I has radical products which is therefore the main photoinitiating path.

Carlsson and Wiles (20,21) have shown that hydroperoxide formed in polymers during processing are potentially significant initiators of photoxidation of polyolefins (22,23). They summarised that the excited carbonyl species can transfer their energy to hydroperoxide groups (Reaction 13) (24,25).



(13)

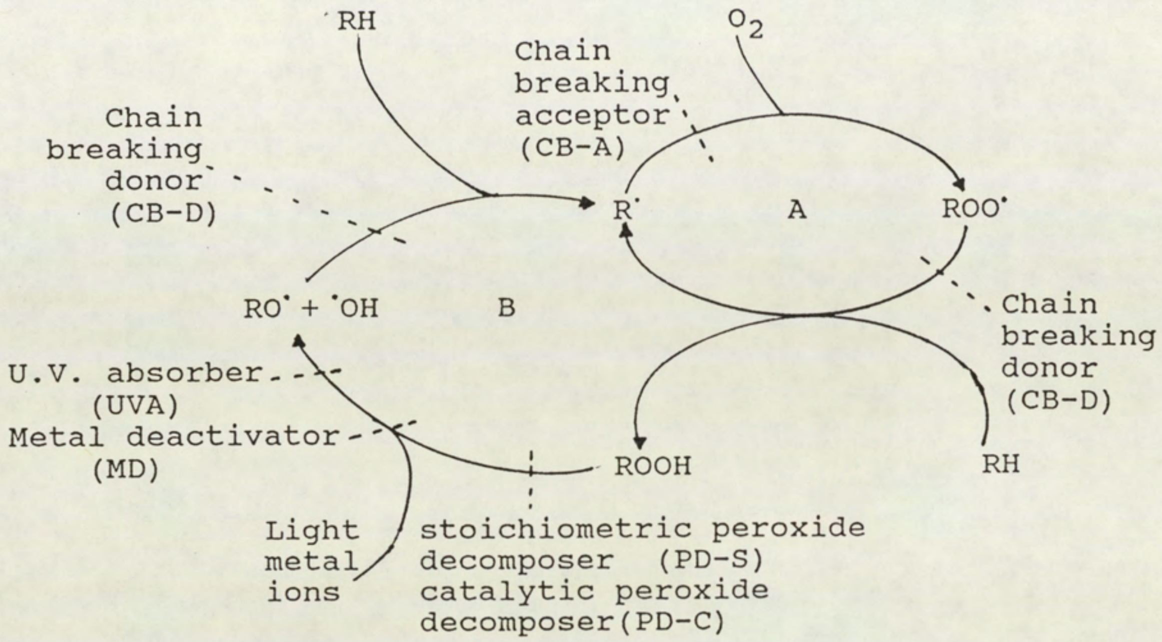
Scott and co-workers (26-29) have also shown that hydroperoxides formed during processing operations are the main photoinitiators in the early stages of photo - oxidation.

Hydroperoxides undoubtedly play a major part in the photo-oxidation of polypropylene either from the onset of irradiation or very soon after the start of oxidation regardless of the photoinitiating species at the early stages (23,30).

1.3 MECHANISMS OF ANTIOXIDANTS

Antioxidants are inhibitors for auto-oxidation. They include heat, melt and light (U.V.) stabilisers, antifatigue agents and antiozonants. These agents interfere with the free radical reactions that lead to the incorporation of oxygen into macromolecules.

The autoxidation chain mechanism (Scheme 1.0) involves two interacting cyclical processes (Scheme 1.5A and B). Antioxidants operate by "disturbing" these cycles at different stages (Scheme 1.5) (13(b)).

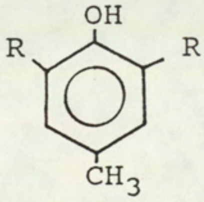


Scheme 1.5 <u>Mechanisms of antioxidant action</u>

1.3.1 CHAIN BREAKING ANTIOXIDANTS

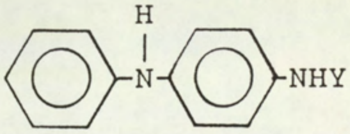
1.3.1.1 Chain Breaking Donor (CB-D)

The two well known sub-classes of this type of antioxidants are hindered phenols (I) and aromatic amines (II). Both are able to donate a H atom to an alkyl peroxyl radical (ROO˙).



(I)

R = tBu (BHT)

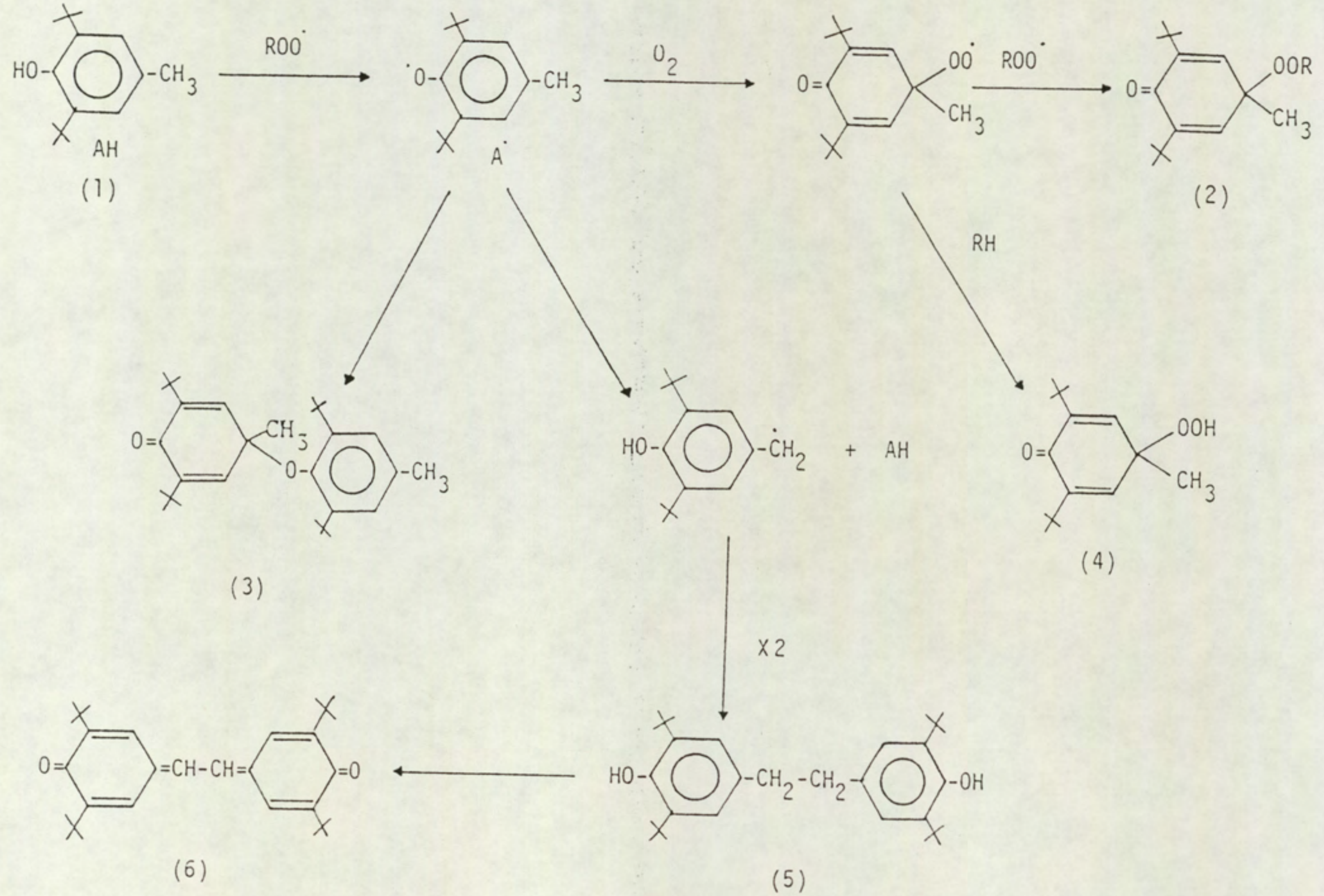


(II)

Y = iPr (IPPD)
Y = phenyl (DPPD)

The effectiveness of the amine antioxidants is believed to be due to regeneration of nitroxyl radicals which are the oxidation products of the parent amine (13(b),31,32).

The simplest most important member of the hindered phenols is 2,6-ditert-butyl phenol (BHT). These hindered phenols have the ability to donate a H-atom to an alkyl peroxyl radical (ROO•) by a chain breaking donor (CB-D) mechanism. The products formed by further reaction of the initially formed phenoxyl radical are complex and may have either antioxidant or pro-oxidant activity (7(b),33,34). Scheme 1.6 is a summary of a typical hindered phenol reactions and the products formed. The stilbene quinone (6) is also an effective antioxidant although it functions by a complementary CB-A mechanism. On the other hand, the peroxydienones (2) and (4) are potential pro-oxidants due to the presence of a labile peroxide bond. The stilbene quinonoid products are less volatile (increased molecular mass) than the parent phenols and are therefore superior antioxidants where volatility is important (35).



Scheme 1.6 Mechanism of Antioxidant Activity of BHT

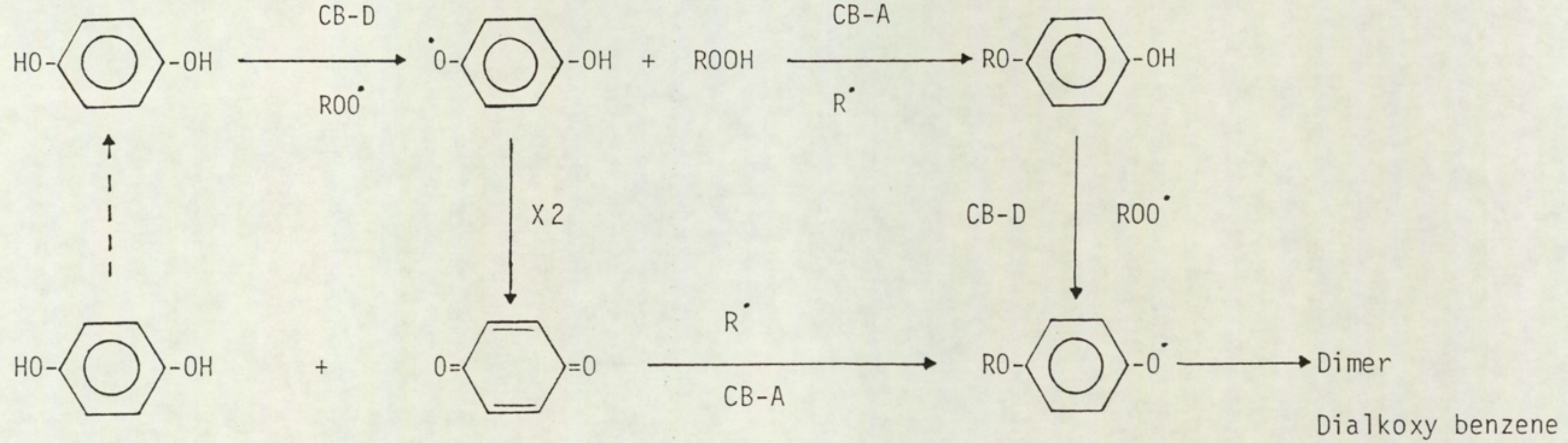
1.3.1.2 Chain Breaking Acceptor (CB-A)

Polymer alkyl radicals are not powerful oxidising agents but are themselves readily oxidised, so a variety of oxidising agents are capable of removing alkyl radicals from an autoxidising system (7(b)). They include quinones and aromatic nitro compounds, but the most important are the stable free radicals of which nitroxyls (36,37) and phenoxyls (38,39) are the most effective.

In the case of the production of stable phenoxyl radicals it is necessary that the reactive ortho- and para-positions be blocked by suitable groups which give increased resonance stabilisation or steric protection (38-42). Galvinoxyl is the most effective of the phenoxyl radicals and will be discussed later (Section 1.3.5.1).

1.3.1.3. Complementary mechanisms involving both CB-A / CB-D

Chain breaking Donor (CB-D) antioxidants function most effectively in the presence of excess oxygen while chain-breaking acceptor (CB-A) antioxidants operate best in oxygen deficiency. Antioxidants which operate by both mechanisms are expected to be far superior to those operating by a single mechanism, since in most oxidative processes the two radical species, alkyl and alkyl peroxyl are present to some extent. A well known example which involves both mechanisms is the hydroquinone. This is converted by the CB-D mechanism (Scheme 1.7) to benzoquinone which itself is an effective alkyl radical trap (33).



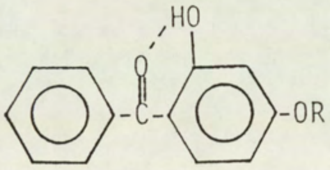
Scheme 1.7 <u>Complementary Mechanism of benzoquinone</u>

1.3.2. Preventive Antioxidants

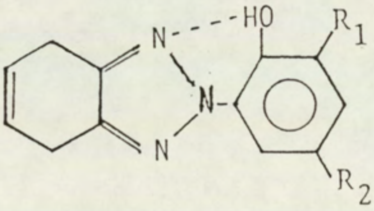
Preventive antioxidants either remove hydroperoxides in a process which does not involve free radical formation, or protect hydroperoxides from decomposition, effectively inhibiting oxidation. They include metal ion deactivators, peroxide decomposers, u.v. absorbers and quenchers.

1.3.2.1 U.V. Absorbers

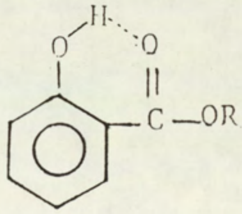
The most popular and successfully used u.v. absorber in rubber is carbon black. In spite of its success the use of carbon black is limited by its colour. Thus, non-coloured u.v. filters such as ortho-hydroxybenzotriazoles (II) and salicylates (III) (43,44) are used. All of them have a common structural feature, the intramolecular hydrogen bond, which permits energy transfer i.e. the u.v. radiation is absorbed but emitted harmlessly as thermal energy (13(b),45,46).



(I)



(II)



(III)

1.3.2.2. Metal Ion Deactivators

The function of a metal deactivator is to counteract the catalytic effect of the metal on hydroperoxide decomposition, this may be achieved by fully complexing the metal (e.g. copper, manganese) with an appropriate chelating agent (7(d),47-49).

1.3.2.3. Peroxide Decomposers

A variety of organic sulphur, nitrogen and phosphorus compounds accelerate the decomposition of hydroperoxides and in most cases without the production of free radicals and thus function as preventive antioxidants.

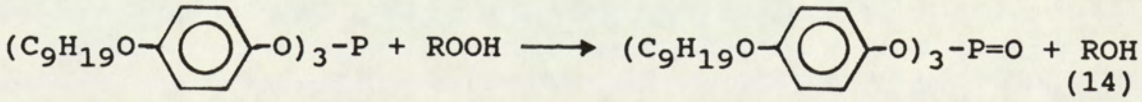
Peroxide decomposers fall into two main classes:

(a) Stoichiometric peroxide decomposer (PD-S)

(b) Catalytic peroxide decomposer (PD-C)

1.3.2.3(a) Stoichiometric Peroxide Decomposer (PD-S)

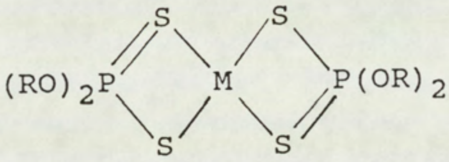
The main requirement of this class of compounds is that they should reduce hydroperoxides to alcohol without the formation of free radicals. Some of the compounds that fall into this category are nitrones (50), 2-hydroxy-acetophenone oximes and their metal complexes (51) and phosphite esters (52) of which tris nonyl phenyl phosphite (Reaction 14) is used commercially in the stabilisation of rubber.



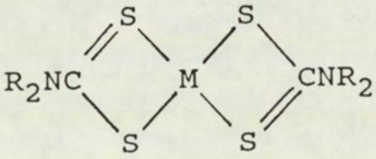
(14)

1.3.2.3(b) Catalytic Peroxide Decomposer (PD-C)

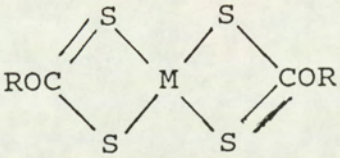
A range of phosphite esters (33) and a variety of sulphur compounds (33,53,50) fall into this class. These compounds have in common the ability to destroy hydroperoxides through the formation of acidic products in a radical generating reaction involving the hydroperoxide. In all cases the antioxidant function is preceeded by a pro-oxidant stage, and the importance of the pro-oxidant stage is a function of the structure of the sulphur compound (54). Thus, in the case of the dithiophosphates (I) (54-56), the dithiocarbamates (II) (33,56,57,58) and the xanthates (11(b),13(b),56,57,60), the pro-oxidant effect may be transient and of no great significance to the long term antioxidant function.



(I)



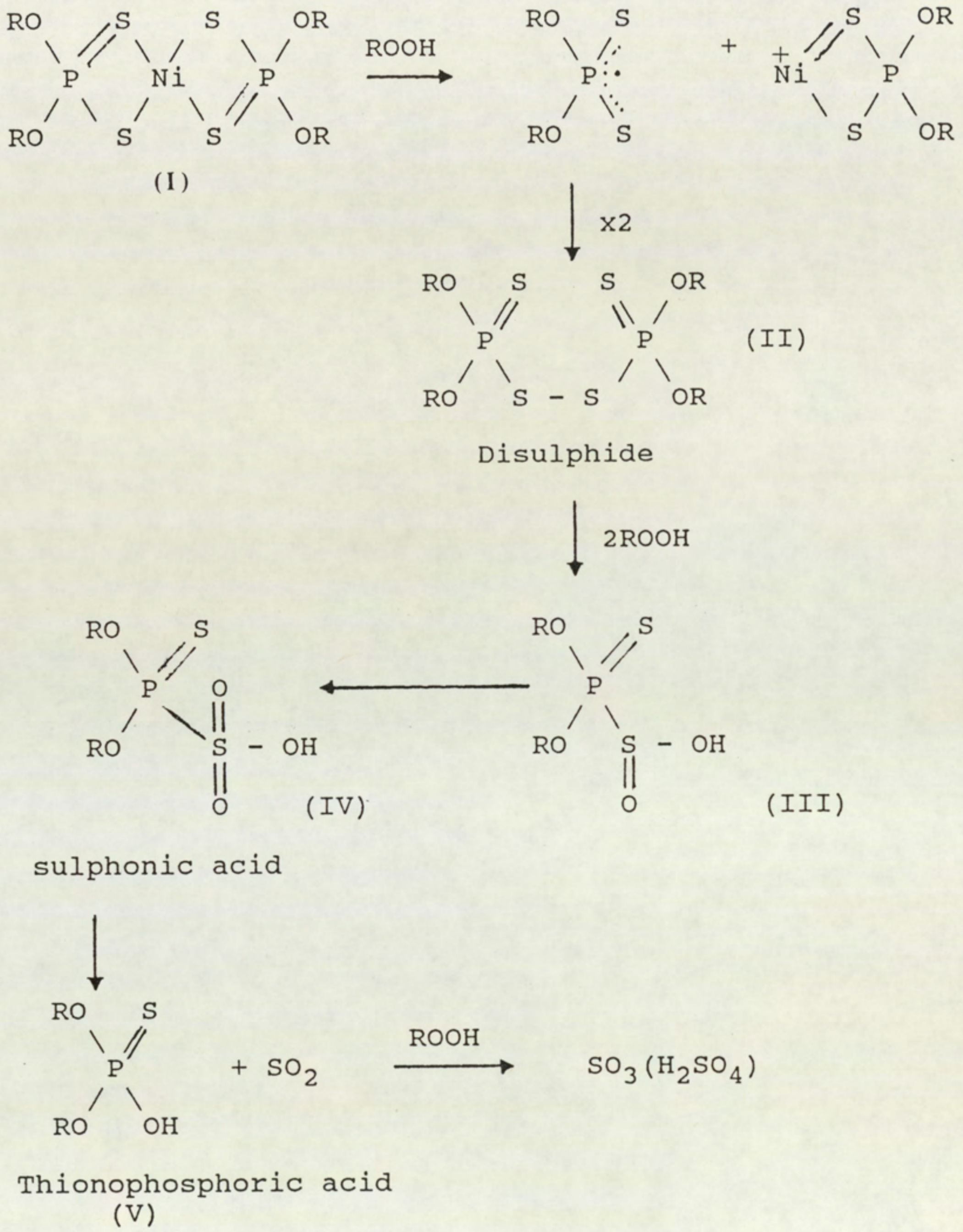
(II)



(III)

In the case of the dialkylsulphides R S(n) R' (n=1-8) or the diarylsulphides, R S(n) R' (R,R'=aryl, n>1) and the corresponding thiols (RSH), considerable initial pro-oxidant effects are normally observed (33).

The ability of dithiophosphates to decompose hydroperoxides was first demonstrated in 1956 by Kennerly and Patterson (61). Holdsworth and co-workers (41) later suggested that this hydroperoxide decomposition by the dithiophosphates was due to sulphur dioxide. Husbands and Scott (62) have since showed that sulphur dioxide only undergoes a stoichiometric reaction with hydroperoxides to form sulphur trioxide, which was found to be a powerful catalyst for the decomposition of cumene hydroperoxoide. Burn, Cecil and Young (63) studied the decomposition of hydroperoxides by zinc dithiophosphate and confirmed the three stage reaction reported by Shorpov and co-workers (64). Al-Malaika and Scott (56,65) also observed a similar three stage process during decomposition of cumene hydroperoxide by nickel dithiophosphate(I) (Scheme 1.8). Detailed product studies led these workers to conclude that the first rapid stage is associated with the formation of the disulphide (II) (56) which is then slowly converted to nickel free oxidation products (III) and (IV). The most important of these products is believed to be the sulphonic acid (IV) since it readily looses sulphur dioxide to give the relatively more stable thionophosphoric acid (V).



Scheme 1.8 <u>Peroxide Decomposition by Nickel Dithiophosphate</u>

Dithiophosphates have also been demonstrated to scavenge alkyl peroxyl radicals (ROO·). Colcough and Cunneens(66) first postulated an electron transfer mechanism with zinc dithiophosphate. Burn (67) later proposed an alternative mechanism where a stabilised peroxyl radical zinc complex intermediate is formed.

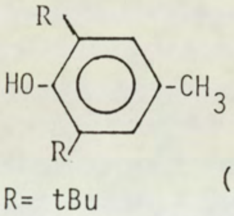
More recently Howard and co-workers (68,69) argued that both mechanisms were valid. They suggested that alkyl peroxyl radicals appear to react at the metal centre of dithiophosphates to displace a ligand radical, while the interaction with the latter takes place at the electron rich sulphur atom.

1.4 STABILISATION DURING PROCESSING AND SERVICE OF POLYMERS

Stabilisation of polymers during processing is not only important to the polymer converter, but it is basic to the subsequent service performance of the polymer.

1.4.1 Melt Stabilisation

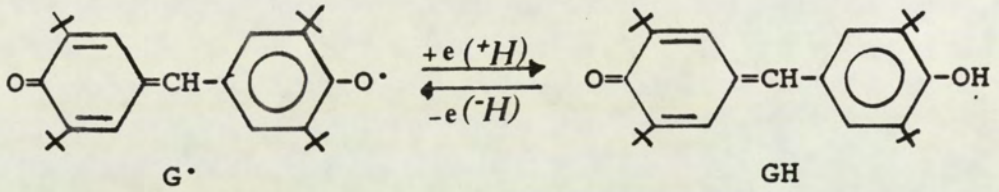
The primary objective is to maintain the viscosity of the polymer constant while it is being processed. An equally important function of a melt stabiliser is to inhibit the formation of hydroperoxides and other sensitising groups which would otherwise impair durability of the polymer in service (11(b),13(b)). It was shown in Section 1.2.1. that shearing of the polymer chain followed by the subsequent formation of peroxides are the primary cause of melt viscosity changes in the polymer melt. Both removal of macroradicals and destruction of hydroperoxides should therefore be effective melt stabilising processes. In practice, melt stabilisation of polyolefines is fairly readily achieved using a hindered phenol (CB-D) antioxidant BHT (I). BHT gives rise to oxidation transformation products which are more effective than the BHT itself (12,13(b),76).



(I)

BHT

Chain breaking donor (CB-D) antioxidants are generally less effective than chain breaking acceptor (CB-A) antioxidants as melt stabilisers. However they are still used for melt stabilisation because they are cheap and relatively non-discolouring additives. Antioxidants which can operate under conditions where both alkyl ($R^{\cdot}$) and alkyl peroxyl radicals are present by alternating between their oxidised and reduced states hence exhibiting a regenerative behaviour (Redox Chain Breaking Antioxidants), have a clear advantage over these operating by a single mechanism, an example is Galvinoxyl ($G^{\cdot}$). This stable free radical is particularly effective in polypropylene and was shown to involve a cyclical regenerative reaction involving alternating CB-A/CB-D antioxidant steps (see Scheme 1.9) (77). It has been shown that during processing when the shearing forces are at their highest a rapid formation of hydrogalvinoxyl (GH) resulted. However, as the shear decreased due to reduction in the polymer melt viscosity, GH is partially reoxidised to G• by alkyl peroxy radicals (Reaction 15).

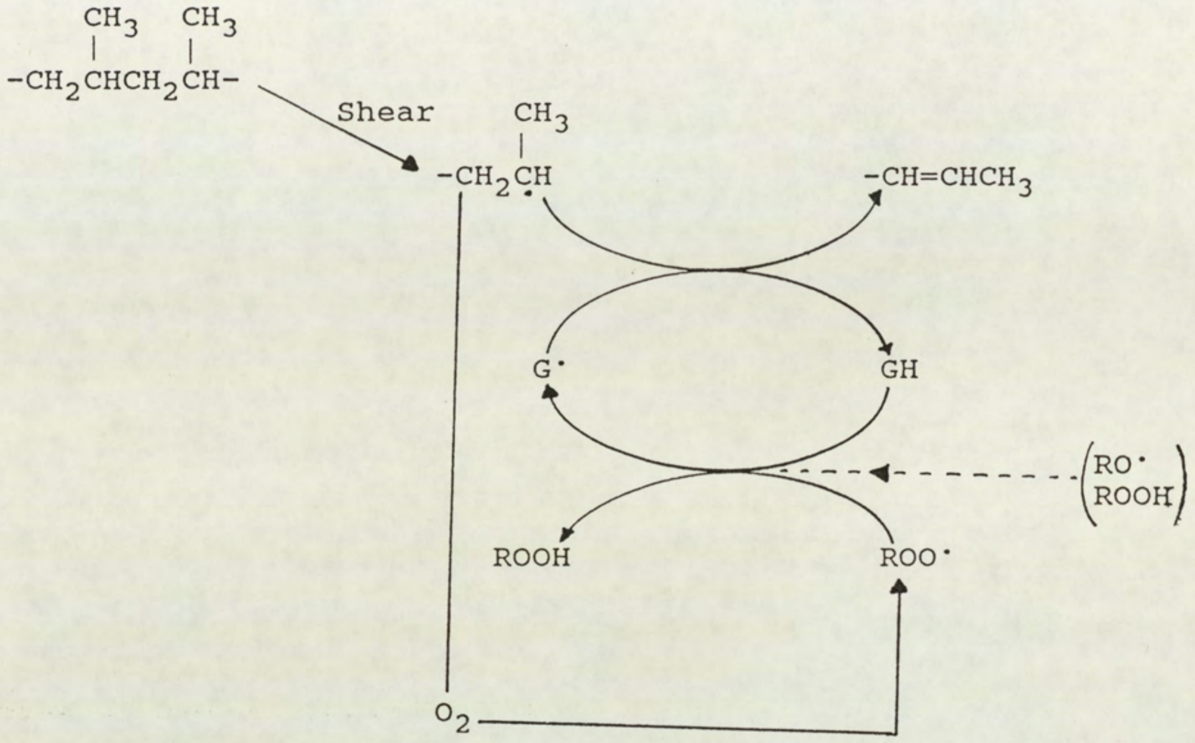


(15)

Galvinoxyl (G•) was found (77) to be relatively ineffective in an air atmosphere whereas GH is highly effective. This was attributed to the inability of G• to compete with oxygen for macroalkyl radicals under these conditions.

Peroxidolytic (PD) antioxidants are also effective melt stabilisers for polyolefines (Section 1.3.2.3). The two main classes of peroxidolytic antioxidants are the phosphite esters (33) and a large number of sulphur-containing compounds (33,60,78,79) (Section 1.3.2.3(b)).

Other peroxidolytic antioxidants are the thiolate metal complexes, for example zinc and nickel dinonyl dithiocarbamate, which are more effective than typical high molecular weight commercial hindered phenols (11(b),12,13(b),60).

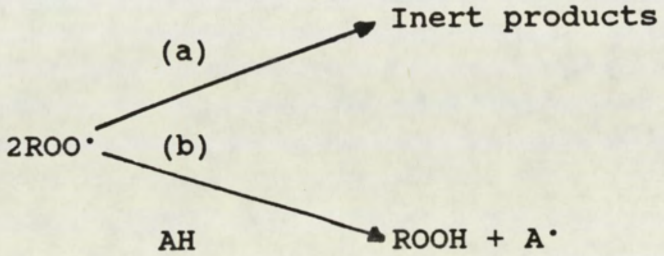


Scheme 1.9 Cyclical regeneration of Galvinoxyl(G·) during the melt stabilisation of polypropylene

1.4.2 Thermal Oxidative Stabilisation

An air oven test has been used as a criterion of polypropylene stability. Unstabilised polypropylene oxidises very rapidly at 140°C with an air flow rate over the surface of the sample of between 10-30 litres hr^{-1}. Under these conditions, the polymer becomes brittle in less than one hour (80). If thin samples are used ($< 3x10^{-3}$ cm) oxygen diffusion should not be rate determining, and the main termination reaction is the bimolecular reaction of alkyl-peroxyl radicals (Reaction 16(a)), and the most effective inhibitors are the chain-breaking donor (CB-D) antioxidants(81)

(Reaction 16(b)) such as hindered phenols and aromatic amines.



(16)

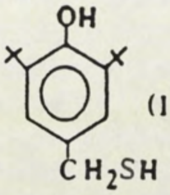
However, if thick sections (> 3×10^{-3} cm) are used, oxygen may be depleted in the centre of the sample, under these conditions alkyl radical trapping antioxidants (CB-A) are more effective.

Hindered phenols show remarkable variation in their ability to inhibit oxidative degradation in an air oven test in which air is continuously passed over the surface of the sample. Their relative effectiveness has been found to depend on physical factors such as temperature of the test, rate of air flow over the sample dimensions (82,83). Under thermo-oxidative conditions, the activity of antioxidants are governed by many factors such as diffusion, volatility and solubility.

Billingham and Calvert (84) have proposed two alternative mechanisms for the loss of additives from polymers. The first mechanism assumes diffusion to be rate limiting whilst the second assumes loss by surface evaporation. In thick samples, the rate of loss tends to be diffusion controlled, whereas in these samples, the volatilisation mechanism is rate controlling. Diffusion rate decreases with molecular size of the antioxidant but long flexible molecules appear to be able to diffuse more readily than rigid ones (84). The rate of diffusion also depends on the polarity of the additive which increases the cohesive energy of the polymer which in turn increases the activation energy of diffusion (84,85).

The volatility of stabilisers from polymers is affected by both the properties and structures of the stabilisers and polymer and the external physical conditions of the experiment. In addition the sample shape, structure and molecular weight has great influence on the volatility of the stabiliser (84,85). Only the high molecular weight hindered phenols (Irganox 1010 and 1076) show thermal oxidative stabilisation, lower molecular weight phenols such as BHT are very volatile (13(b)), which reflects the importance of non-volatility as a criterion for antioxidant effectiveness (83,86).

Another example which demonstrates the importance of increasing molecular weight and decrease in volatility is based on autosynergistic sulphur antioxidants (87). The high effectiveness of the volatile antioxidant (I) was shown to be due to conversion of this compound to higher molecular weight derivatives during processing.


(I)

The solubility of a series of antioxidants which contain the same functional groups in a hydrocarbon polymer, has been shown (85) to increase with the number, length and branching of the alkyl substituents, and the uniformity of the alkyl distribution in the molecule. In addition, transformation products of additives, the presence of polar groups or aromatic groups also affect solubility adversely (85). The equilibrium solubility of an additive in a polymer is the most important single physical property of the system since it determines how much additive can exist in the polymer as a homogeneous solution.

As was mentioned earlier high molecular weight hindered phenols are commercially used as thermal stabilizers. Sulphur-containing compounds are also efficient thermal antioxidants by virtue of their peroxidolytic activity, although they are not as effective as the hindered phenols. However, synergistic mixtures of the sulphur compounds with hindered phenols have been reported (11(b), 13(b),56,88) to result in improved performance under thermal oxidative conditions and this is attributed to to two mechanisms (PD-C/CB-D). Furthermore, it has been shown (88) that antioxidants which contain both PD-C and CB-D functions in the same molecule are twice as effective on a molar basis as compared to structurally related hindered phenols which do not contain the peroxidolytic sulphide function.

1.4.3 Photo-stabilisation

Photostabilisation of polyolefines can be achieved by four main phenomena (45).

(i) the prevention of u.v. excitation

(ii) deactivation of excited molecules

(iii) decomposition of important chromophores

(iv) scavenging of reactive radicals

U.V. absorbers such as hydroxybenzophenones and benzotriazoles stabilise the polymer by reducing the amount of energy absorbed by the chromophores. These u.v. absorbers have also been reported (13(b),89,90) to behave as weak CB-D antioxidants. Thus a secondary function in both cases is to scavenge alkyl peroxyl radicals by hydrogen transfer (CB-D), and this accounts for their ease of destruction under photo-oxidative conditions by thermally formed hydroperoxides (70,58(b),56,90).

Transition metal thiolates such as the dithiocarbamates, dithiophosphates and xanthates are generally excellent u.v. stabilisers, since they not only decompose hydroperoxides to non-radical products, but also absorb u.v. light strongly (12,11(a),13(b),60,88,56). In addition some u.v. stabilisers particularly the nickel chelates (e.g. nickel bisphenolate) act as 'quenchers' for excited states of polymer chromophores (23). Ranaweera and Scott (51,91,92) have demonstrated the importance of hydroperoxide decomposition by nickel chelate-based stabilisers both during processing of polyolefines in the molten state and in model liquid systems. Nickel dibutyl dithiocarbamate was clearly shown to act both as a radical scavenger and more effectively as a catalytic hydroperoxide decomposer in dark reactions (51).

Chakraborty and Scott have demonstrated that a synergistic inhibition of LDPE photo-oxidation is shown by mixtures of the hydroperoxide decomposing dialkyl-dithiocarbamates and 2-hydroxy-4-octyloxybenzophenone58(b)). This effect was not due to screening the hydroxybenzophenone, but was suggested to result either from deactivation of excited chelate molecules before dissociation or, a radical trapping mechanism (58(b)).

The hindered piperidines are unique among the effective u.v. stabilisers since they do not absorb u.v. light but their transformed products such as nitroxyl radicals are effective photo-antioxidants (11(a),12,13(b),45,89).

Most photoantioxidants (CB or PD) synergise effectively with u.v. absorbers and hence reinforce one another by complementary mechanisms (11(b),13(b),45,60,58,93). It has been suggested that the role of the u.v. absorber is primarily to protect the antioxidant from photo-oxidation under service conditions. The antioxidant on the other hand is responsible for the protection of the u.v. absorber from destruction by hydroperoxides during processing.

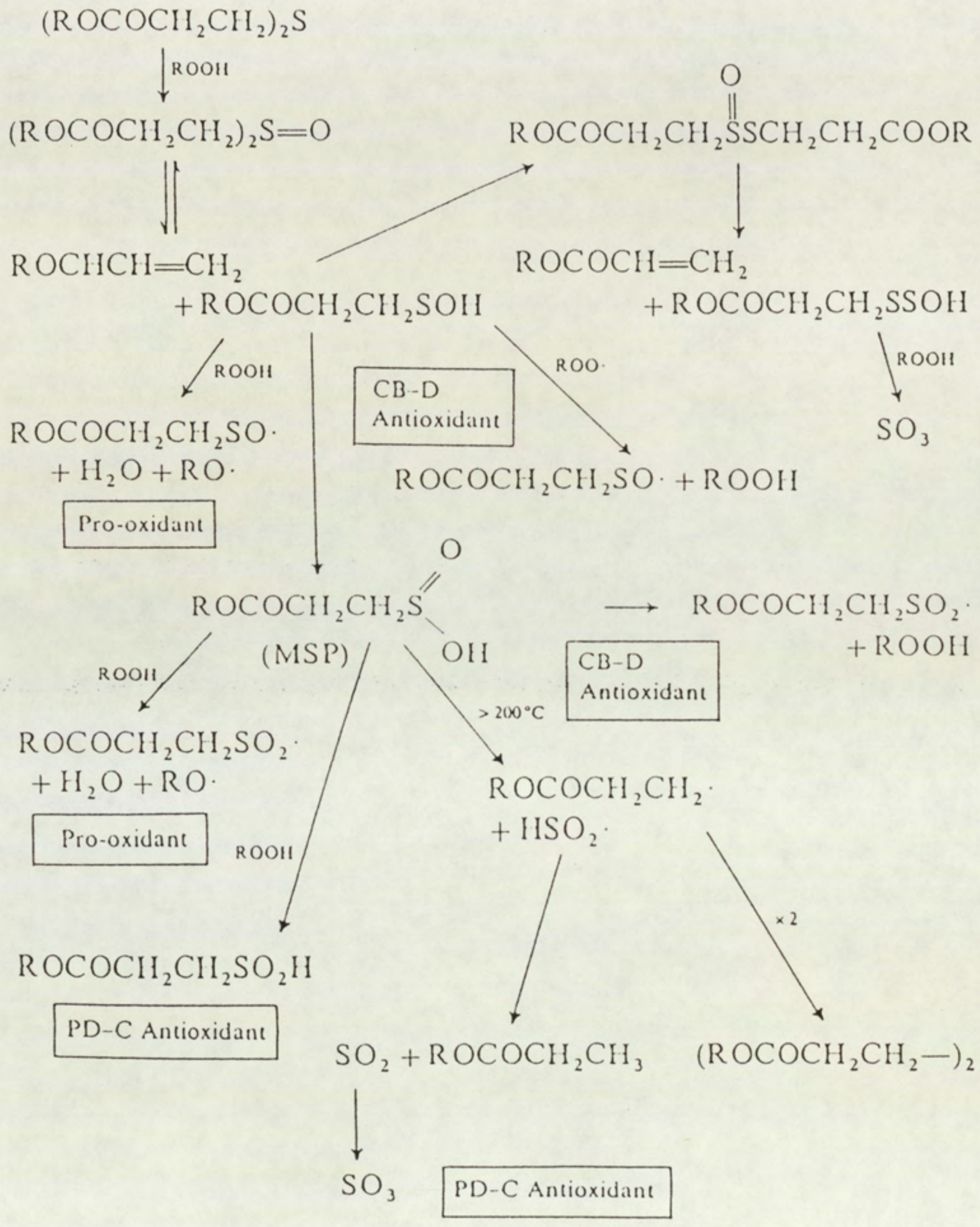
1.5 SYNERGISM AND ANTAGONISM

Most stabilisers for polymers contain a combination of antioxidants acting by different and normally complementary mechanisms. A hydroperoxide destroying antioxidant which reduces the concentration of radicals in the 'A' cycle (see Scheme 2), will as a consequence slow down the destruction of a chain-breaking antioxidant. By the same token, an effective chain-breaking antioxidant reduces the amount of hydroperoxide formed in an autoxidising system and hence protects a peroxide decomposer. This co-operative interaction which is commonly called synergism (11(b),13(b),49) leads to an overall antioxidant effect which is greater than the sum of the individual effects.

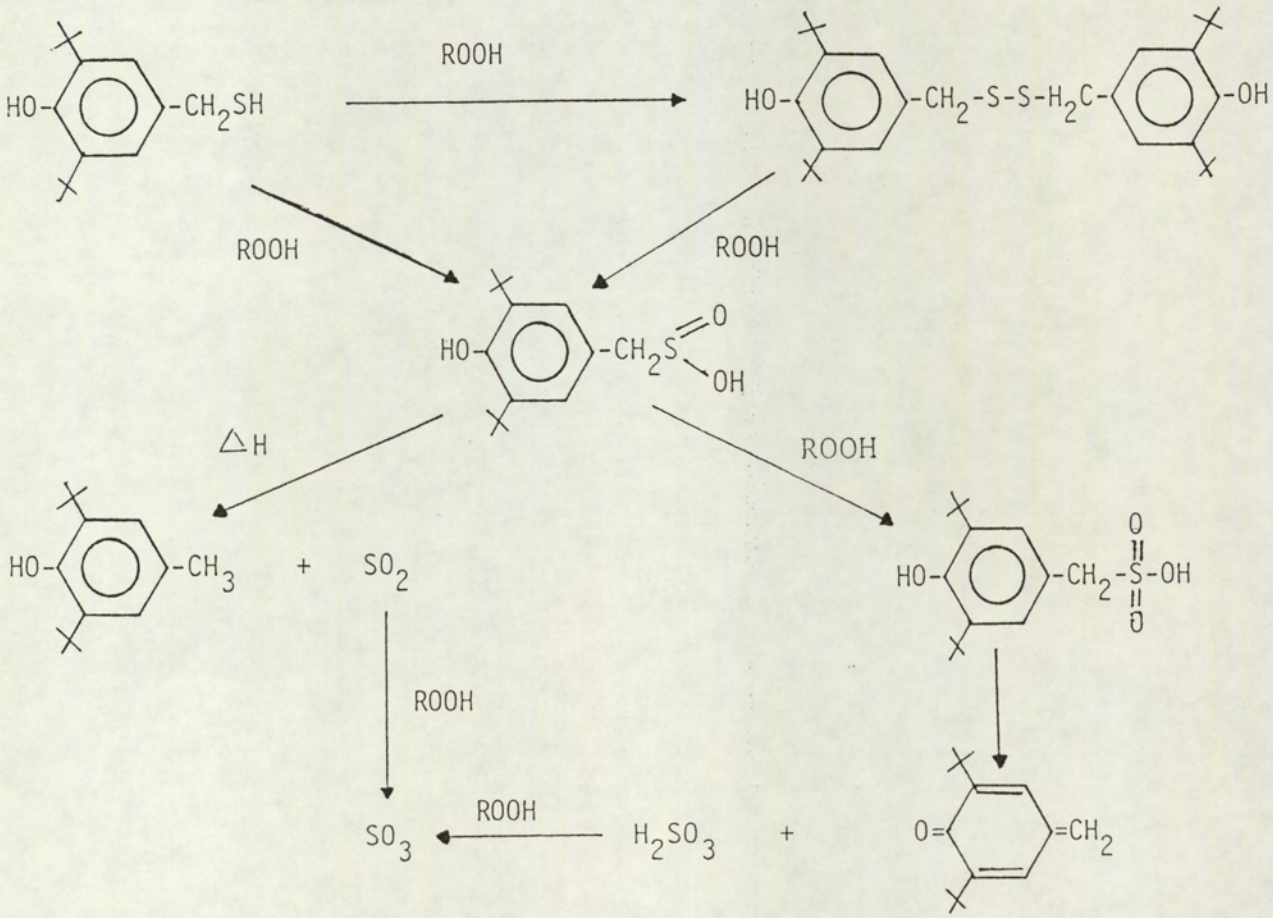
Occasionally the reverse phenomenon is observed, that is, two antioxidants interact to decrease the sum of their individual effects. This is described as antagonism (13(b)). For instance, observed antagonistic effects between certain hindered phenols and some peroxidolytic antioxidants have been reported to occur under photo-oxidative conditions, although they are synergists under thermal oxidative conditions (70,71).

1.5.1 Synergism between Peroxide Decomposers and Chain Breaking Antioxidants

The mechanism of the dithiopropionate esters has been extensively studied (72-74) and its chemistry is summarised in Scheme 1.10. These esters on oxidation produce products with both chain-breaking donor (CB-D) and peroxide decomposing (PD-C) activity. In addition to inhibition reactions the sulphur acid intermediates can also participate in radical forming redox reactions with hydroperoxides (74). The thiodipropionate esters have an initial pro-oxidant autoretarding behaviour and are therefore almost always used in synergistic combinations with a hindered phenol with the ability to scavenge the radicals produced in the redox process. Other sulphur compounds show synergistic effects with hindered phenols (56).



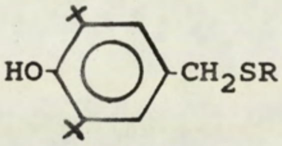
Scheme 1.10 Transformation Products and antioxidant mechanism of the thiodipropionate esters



Scheme 1.11 Transformation products of 3,5 di-tert-butyl-4-hydroxbenzyl mercaptan (BHBM)

1.5.2. Autosynergism

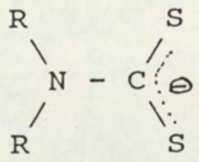
Sulphur containing phenols were recognised many years ago by Kennerly and Patterson (61) to be thermal antioxidants, which was in part due to their ability to catalytically destroy hydroperoxides. Recently related sulphur containing hindered phenols (e.g. I) have been studied in more detail (35).


(I)

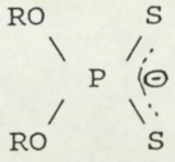
Phenols with this structure have a higher intrinsic molar antioxidant activity than the conventional hindered phenol BHT. This is due to their ability to act as a catalyst for peroxide decomposition in addition to their normal chain breaking function (35,75). The mechanism has been shown to involve the elimination of sulphur oxides from intermediate oxidised species and is summarised in Scheme 1.11.

1.6 PHOSPHONATES

Several classes of metal dithiolates are known to have powerful peroxide decomposing (PD) antioxidant properties; amongst the most important of these sulphur donor ligands are the dithiocarbamate (I), the dithiophosphate (II) (35,56-58,94,95) and the xanthates(III), all of which have found practical utility as antioxidants in a variety of polymers and hydrocarbon substrates (96).



(I)



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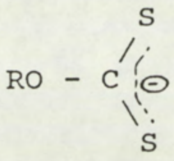
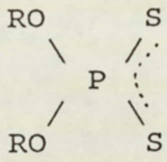


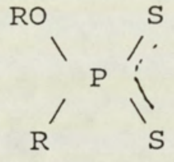
(III)

R=aryl,alkyl

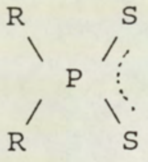
The dithiophosphorus compounds may be subdivided into dithiophosphate (IV), dithiophosphonate (V) and dithiophosphinate (VI).



(IV)



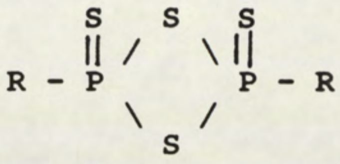
(V)



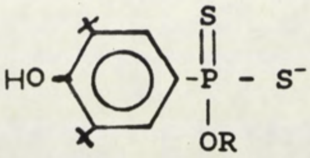
(VI)

Metal complexes of the dithiophosphinates and dithiophosphates (33,56-58,94,95,97) have been extensively studied but comparatively little work has been reported on the dithiophosphonate ligand except reports utilising phosphonates as pesticides (98) and thiophosphonates as detergents (99,100) and antioxidants (101) in oils. Different names were used in the literature for complexes containing the RO(R)PS$_2$(V) group viz dithiophosphonate , o-alkylalkyldithiophosphate and alkylalkylphosphinate.

Dithiophosphonic acids are usually prepared by the reaction of the alkylthiophosphine sulphide VII with alcohol (102).



VII



VIII

The acid can then be converted to the ammonium salt by neutralisation. Metal complexes of dithiophosphonic acid are usually prepared by the reaction of the ammonium salt of the acid with the required metal chloride.

There have been many studies on the thermal decomposition of dithiolate compounds and the thermal stability decreases (94) as follows:-

dithiocarbamate > dithiphosphate > xanthate

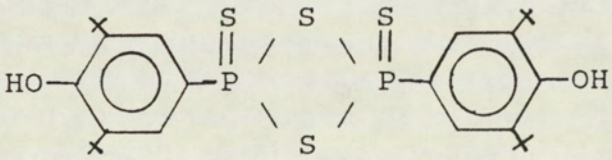
and also decreases for this series,

dithiophosphinate > dithiophosphonate > dithiophosphate

Little work has been published on the spectroscopic characterisation of metal dithiophosphonate complexes but the infra red (103-108), u.v., visible (109) e.s.r (110-114) and n.m.r. (115-117) data obtained from dithiophosphate complexes can be related to the corresponding dithiophosphonate.

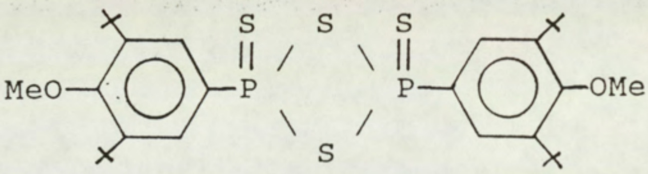
The phosphonate ligand(VIII) was first studied by Brois and Colclough (118). The preparation and characterisation of copper (I), copper (II), iron (III) and zinc (II) complexes of the phosphonate ligand has been reported by Hopkins (101). The preparation and analysis of the sulphide

2,4-bis(4-hydroxy-5-ditertiarybutyl phenyl)-2,4-dithioxo-1,3,2,4-dithiophosphetane, TPS (IX), has also been shown (101). The ^{31}P chemical shift for TPS was reported to be 19.8 ppm.



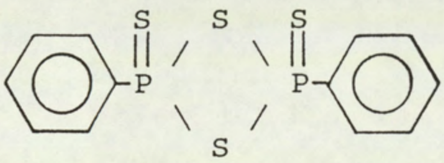
IX

This value can be compared with that of 2,4-bis(methoxyphenyl)-2,4-dithioxo-1,3,2,4-dithiophosphetane (X) called Lawesson's reagent (119-121) which has a ^{31}P chemical shift of 16.7 ppm.



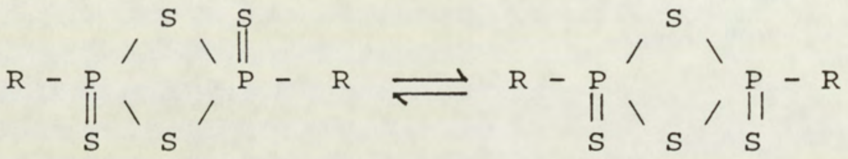
X

whereas phenylphosphonodithioic anhydride (XI) has a ^{31}P chemical shift of 15.4 ppm(122,123) and 72 ppm(124),



XI

no unanimous opinion has been expressed in the literature for the presence of these two very different chemical shifts both in this case and for many other phosphonodithioic anhydrides (125). However, it is thought, but has not been established, that such variation may be associated with the presence of dimers, trimers and polymers or may be due to an equilibrium (in solution) between cis and trans isomers. (Reaction 17) (125).

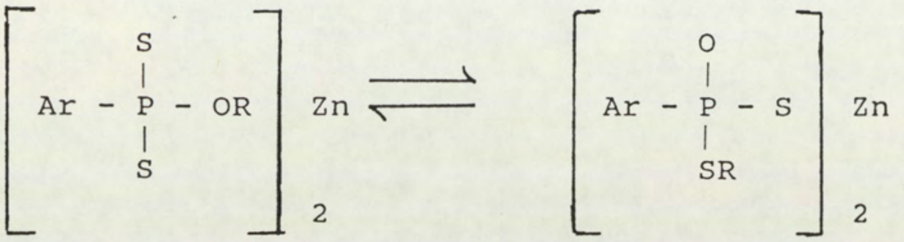


(17)

Colclough has studied the structure of TPS by mass spectroscopy and shown that it is most likely a polymeric material (33).

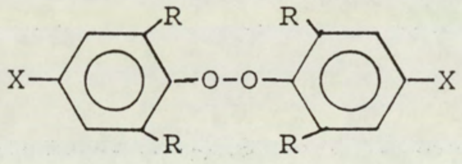
The x-ray structure of isobutyldithiophosphonic acid has been shown(101) to exhibit intermolecular hydrogen-bonding similar to that observed in the compound diphenyldithiophosphinate. The phosphonate ligand stabilises copper (II) unlike the dithiophosphates in which the copper (II) complex exists in equilibrium with copper (I) and the corresponding disulphide (127).

It has been suggested (126) that a contributing factor to the breakdown of zinc dithiophosphonate in oil is via a thiono-thiolo isomerization (Reaction 18)



$$\left[\mathrm{Ar}-\overset{S}{\underset{S}{P}}-\mathrm{OR}\right]_2\mathrm{Zn} \rightleftharpoons \left[\mathrm{Ar}-\overset{O}{\underset{SR}{P}}-\mathrm{S}\right]_2\mathrm{Zn} \qquad (18)$$

It is well known that phenols function via a CB-D mechanism (128). Phenoxyl radicals can undergo dimeristaion to form peroxides as in the case of the oxidation of phenol. The formation of the peroxide (XII) would depend on the size of the alkyl groups.



where $X=P(OR)S_2$

XII

Molecular mechanic calculations by Hopkins (101) showed that the tertiary butyl alkyl group is the critical size group to prevent dimerization of a phenoxyl radical.

It has been reported (101) that the iron dithiophosphonate is more effective than commercial additives in oils. The iron dithiophosphonate proved to be more effective than the corresponding zinc dithiophosphonate complex.

Copper and zinc dithiophosphonate have also been reported as stabilisers in lubricating oils (129). No literature was found reporting dithiophosphonates as antioxidants in polymers.

1.7 SCOPE AND OBJECT OF RESEARCH

Many antioxidants and u.v. stabilisers act by more than one mechanism due to more than one functional group within the same molecule. For example sulphur-containing phenols have high antioxidant ability due to being able to act as catalyst for peroxide decomposition (PD) (via the sulphur moiety) in addition to their chain breaking (CB) function (due to the phenolic group). This complementary mechanism is highly dependent on their oxidised products.

An initial object of this work was to examine the melt, thermal and photostabilising activity of various metal dithiophosphonates and their corresponding sulphide. Dithiophosphonates(DRPn'S) are sulphur-containing phenols and hence should show a complementary peroxide decomposing (PD) and chain breaking (CB) function. Dithiophosphates in general were found to be partially converted to oxidation products (which are more powerful than the parent molecule) at elevated processing temperatures and the activity of the DRP in particular was shown to depend on the processing conditions and the availability of oxygen. Attention was therefore focussed in this study on the effectiveness of the DRPn additives in the polymer under various processing conditions e.g. under both restricted and excess oxygen conditions. The photostabilising activity of complexes is partially dependent on their screening efficiency of u.v.

light. Therefore, the screening efficiency of copper and nickel dithiphosphonates were examined and compared to that of a commercial screener UV 531. Furthermore, the synergistic combinations of the dithiophosphonates with existing stabilisers were examined.

Attempts were made to investigate the mechanism of action of dithiophosphonates as stabilisers in polypropylene. Thus, on the basis of results obtained in the polymer analogous mechanistic studies were carried out, with the aim of identifying the major oxidation products which may be responsible for their antioxidant activity. This mechanistic investigation will be carried out by use of various analytical techniques such as O_2 absorption, hydroperoxide decomposition, IR, UV, ^{31}P NMR and GLC.

CHAPTER 2

EXPERIMENTAL

2.1 MATERIALS

2.1.1. Polymeric Materials

Unstabilised polypropylene (Propathene HF2) and Polyethylene (Alkathene BP D572) were supplied by Imperial Chemical Industries and B.P. Chemicals Ltd. respectively. They were stored in a freezer when not in use.

2.1.2 Commercial Antioxidants

Commercial antioxidants were used as supplied, their chemical and trade names given in Table 2.1

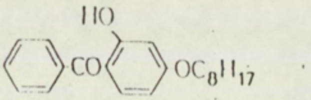
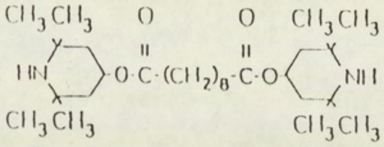
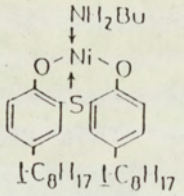
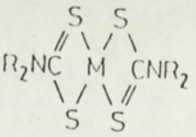
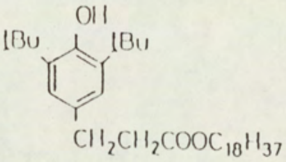
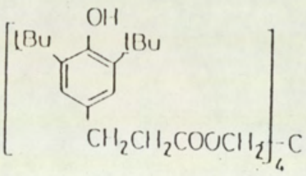
2.1.3 Synthesised Antioxidants

2.1.3.1 General Preparation of Dithiophosphonates

The general method of preparing dithiophosphonic acid and the corresponding metal complexes are as outlined in Scheme 2.0.

Isobutyl substituted copper (Figure 2.1(a) and (b)), zinc (Figure 2.2(a) and (b)) and iron (Figure 2.3(a) and (b)) dithiophosphonates and 2,4-bis (4-hydroxy-3,5-ditertiarybutyl phenyl) -2,4-dithioxo-1,3,2,4 - dithio -diphosphatane (TPS, see Section 2.1.4.4) were used as supplied by Exxon Chemicals. Similarly nickel and cobalt 2-ethyl hexyl DRPn were supplied by Exxon and used after purification (see Sections 2.1.3.4(b) and 2.1.3.5(b)

Table 2.1 Trade name, structure and supplier of commercial Antioxidents

Trade name*	Structure	Supplier
HOBP/UV 531		American Cyanamide
TINUVIN 770		Ceiba Geigy
CYASORB 1084		American Cyanamide
NiDnBuC R=nBu		Robinson Brothers
Irganox 1076		Ceiba Geigy
Irganox 1010		Ceiba Geigy

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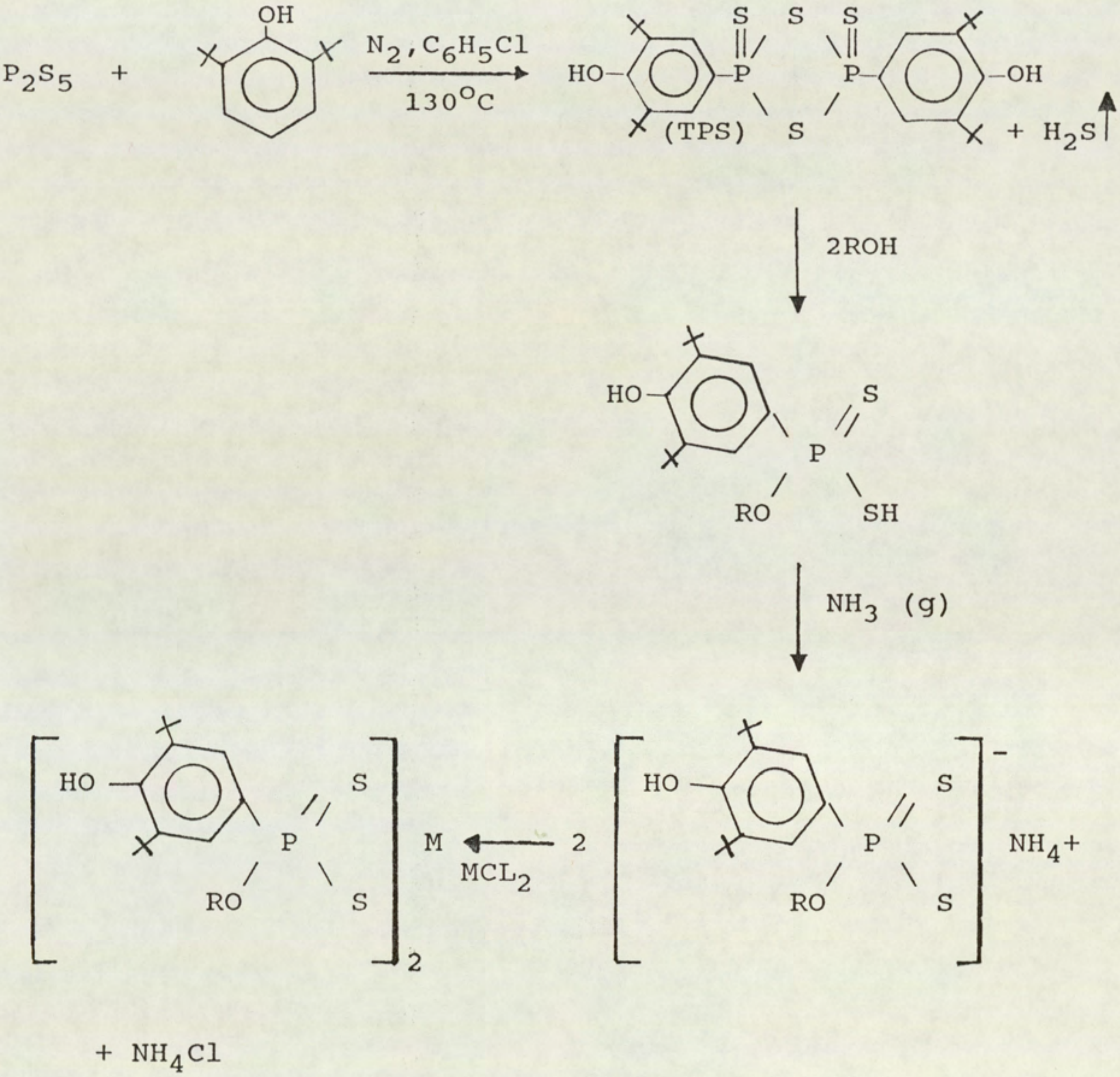
*For chemical name see list of abbreviations respectively).



Scheme 2.0 General Preparation of Dithiophosphonates

2.1.3.2 Preparation of Dithiophosphonic acid (DRPn acid)

14.8g (0.2 moles) isobutanol was added to 60 g (0.1 moles) TPS in chlorobenzene at 70°C under an atmosphere of nitrogen. The reactants were heated for two hours and then chlorobenzene was removed under vacuum leaving a white solid.

Analysis

^{31}P NMR = 88 δ

U.V. (solvent dichloromethane) λ_{max}= 233 nm, 242 nm

F.T.I.R.	Functional Group	Wave number (cm^{-1})
	-OH	3610
	-SH	2575
	-POC	1005
	P=S	660
	P-S	590

Elemental Analysis

Calculated	C = 57.8%	H = 8.3%
Observed	C = 58.1%	H = 8.5%

2.1.3.3 Preparation of Ammonium salt of Dithiophosphonic Acid (NH_4Pn)

60g (0.2 moles) of dithiophosphonic acid was dissolved in chlorobenzene and ammonia gas passed through for one and a half hours whilst stirring. During the reaction , a white solid precipitated out and stirring became difficult, more chlorobenzene was therefore added when required. The solid was filtered and dried (see Scheme 2.0).

Analysis

^{31}P NMR = 106 δ

F.T.I.R.	Functional group	Wave number(cm^{-1})
	-OH	3600
	-NH	3215
	-POC	1025
	-P=S	600

Elemental Analysis

Calculated	C = 55.7%	H = 7.9%	N = 3.6%
Observed	C = 54.8%	H = 8.1%	N = 3.4%

2.1.3.4(a) Preparation of Nickel isobutyl Dithiophosphonate

2.4g (0.01 moles) of aqueous nickel (II) chloride was added dropwise to 7.8g (0.2 moles) aqueous ammonium salt in 30 minutes whilst stirring vigorously. After addition, the stirring was continued for a further 30 minutes to ensure complete reaction. A purple solid remained after the solvent had been evaporated. The solid was recrystallised from a mixture of chloroform and methanol. (Mpt > 225°C)

Analysis

^{31}P NMR = 102 δ

U.V. λ_{max} = 243 nm, 326 nm, 396 nm, 698 nm*

* Only visible at very high concentration

F.T.I.R. Functional Group	Wave number(cm^{-1})
-OH	3592
-P-Ar	1585, 1430
-P-O-C	1006
-P-S-Ni	575
Ni-S	359
P=S	643

See Figures 2.4(a) - (c) respectively

2.1.3.4(b) Purification of Nickel 2-ethylhexyl Dithiophosphonate

NiDEhPn (supplied by Exxon Chemicals) was recrystallised (from a brown solid which had ^{31}P NMR signals at 102 δ ,82 δ and 21 δ) three times with methanol finally resulting in a purple solid.

Analysis

^{31}P NMR = 101.95 δ

U.V. λ_{max} = 396 nm, 327 nm

F.T.I.R. Functional group	Wave number (cm^{-1})
-OH	3600
-P-Ar	1580
-P-O-C	1000
-P-S-Ni	530
Ni-S	355

2.1.3.5(a) Preparation of Cobalt isobutyl Dithiophosphonate

2.38g (0.01 moles) of aqueous cobalt chloride was added dropwise over a period of 30 minutes to 7.82g (0.02 moles) of aqueous ammonium salt with vigorous stirring. After addition, stirring was continued for a further 30 minutes to ensure completion of reaction. The product was filtered and recrystallised with chloroform to yield an orange/brown solid (Mpt ~ 185^{o}C)

Analysis

^{31}P NMR = 97, 98 δ (forked peak)

U.V. λ_{max} = 347 nm, 424 nm

F.T.I.R	Functional group	Wave number(cm^{-1})
	-OH	3636
	-P-Ar	430
	-P-O-C	1006
	-P-S-Co	593
	-P=S	627
	Co-S	443

See Figures 2.5(a)-(c) respectively

2.1.3.5(b) Purification of Cobalt 2-ethylhexyl Dithiophosphonate

CoDEhPn (supplied by Exxon Chemicals) was also recrystallised from methanol to give an orange/brown powder.

Analysis

^{31}P NMR = 96.2, 97.7 δ (V. broad doublet)

U.V. λ_{max} = 345 nm, 425 nm

F.T.I.R	Functional group	Wave number(cm^{-1})
	-OH	3620
	-P-Ar	1435
	-P-O-C	1010
	-P=S	625
	-Co-S-P	593
	-Co-S	442

2.1.3.6 Preparation of Monosulphide of Dithiophosphonic Acid

10g (0.027 moles) of isobutyl dithiophosphonic acid was dissolved in 60 mls of dry ether, and 5.8g (0.027 moles) of dicyclohexyl carbodimide was added. The mixture was stirred vigorously for six hours at room temperature. The ether was evaporated under vacuum leaving a yellow viscous liquid.

Analysis (Figure 2.6)

^{31}P NMR = 84 δ

2.1.3.7 Attempted preparation of Disulphide Dithiophosphonic Acid

To 20g (0.055 moles) of aqueous dithiophosphonate ammonium salt was added dropwise to an approximate 1.0 M solution of iodine in 1M aqueous potassium iodide. The solution was stirred and addition of the iodine solution was continued until the colour of the iodine persisted , i.e. a change from colourless to yellow. The solution was extracted with chloroform and the organic layer washed several times with sodium thiosulphate solution to remove excess iodine. The organic layer was separated, dried with magnesium sulphate and the solvent evaporated to leave a yellow liquid.

Analysis (Figure 2.6)

^{31}P NMR = 93.4, 89.1 δ

2.1.3.8 Attempted preparation of Trisulphide Dithiophosphonic Acid

To 15.64g (0.04 moles) of aqueous dithiophosphonate ammonium salt was added 5 mls of ammonium solution (S.G.0.880). The mixture was stirred in an ice bath and 2.06g (0.02 moles) of sulphur dichloride added over a period of one hour. After addition of all the sulphur dichloride the solution became grey. This was filtered and an NMR spectrum was recorded of both the residue (in chloroform) and filtrate. An attempt was made to recrystallise the residue in heptane, a creamy solid and green liquid were obtained and an NMR spectra recorded of each. The results show two major peaks at 90.5 and 95.6 one of which may be trisulphide.

Analysis (Figure 2.6)

^{31}P NMR = 90.5, 95.6 δ

2.1.3.9 Attempted preparation of Tetrasulphide of Dithiophosphonic Acid

5 mls of ammonia solution (0.880.S.G) was added to 15.64g (0.04 moles) of aqueous isobutyl ammonium dithiophosphonate. To this 2.7g (0.02 moles) of sulphur monochloride was added dropwise over one hour at 0°C. A grey solution resulted, which was filtered to leave a grey solid. An NMR spectra was recorded of both the filtrate and residue. Several peaks were found 82 (ester) ,88.5 (acid), 90.3 δ and 91.5 δ . The 90.3 peak was also found in the attempted preparation of the trisulphide, therefore 91.5 may be the tetrasulphide (see Figure 2.6).

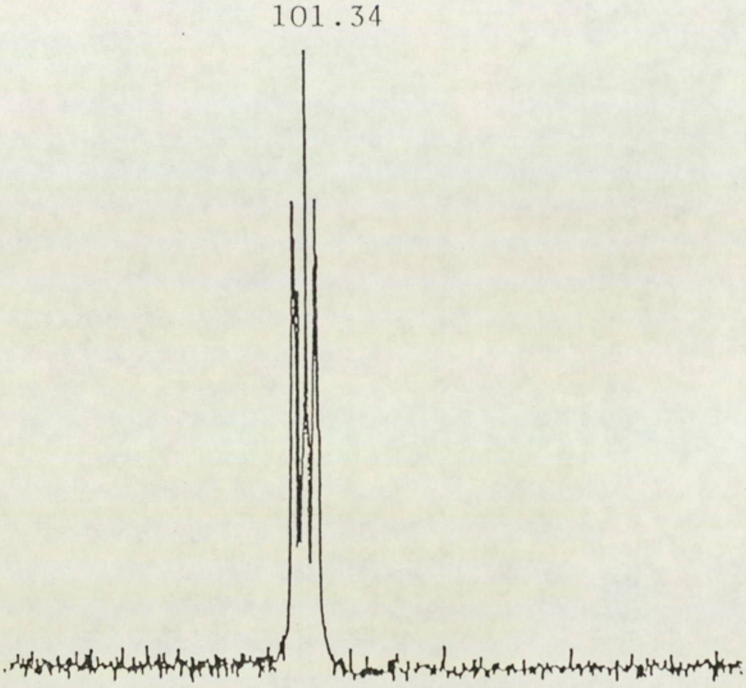


Fig. 2.1(a) ^{31}P NMR spectra of copper dithiophosphonate (iBu) in chlorobenzene.

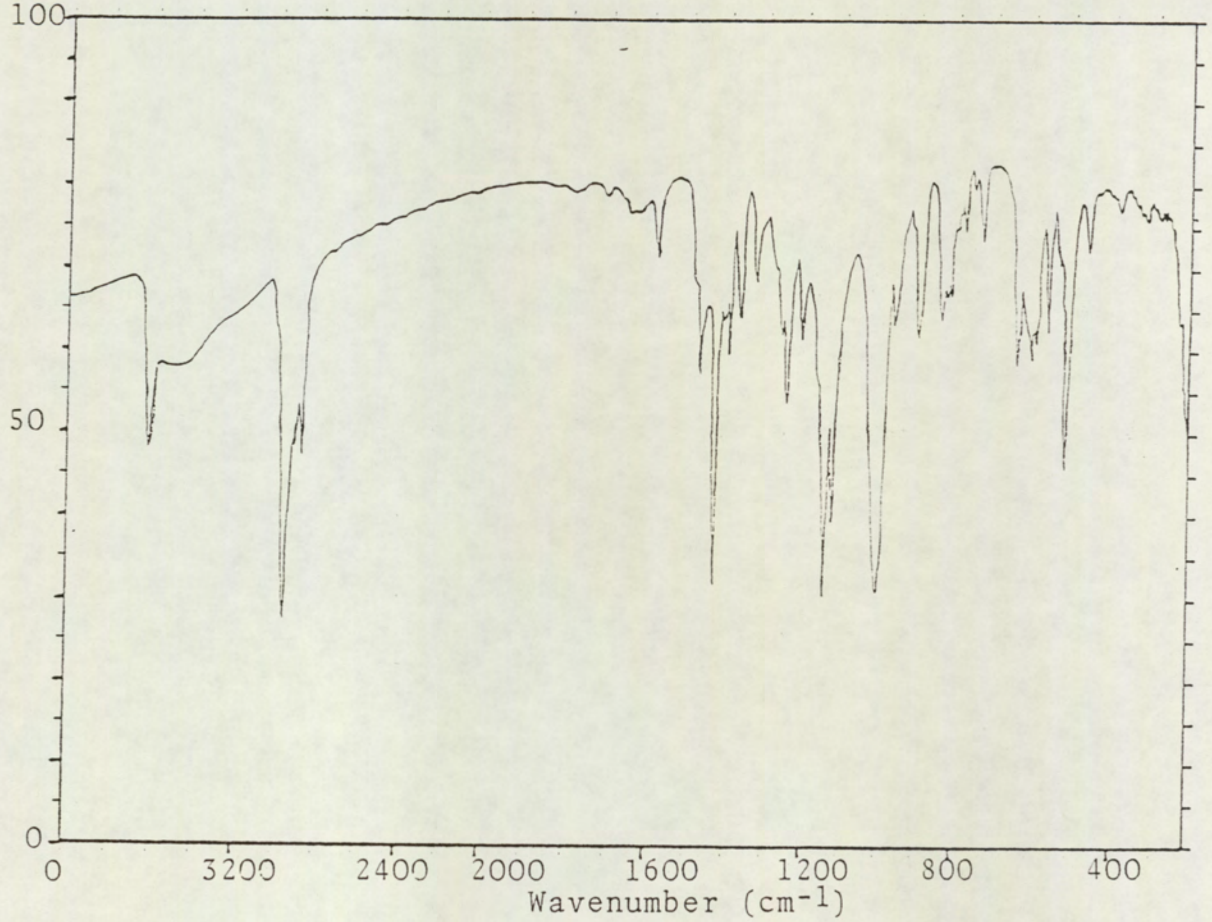


Figure 2.1(b) IR spectrum of CuDiBuPn (KBr disc).

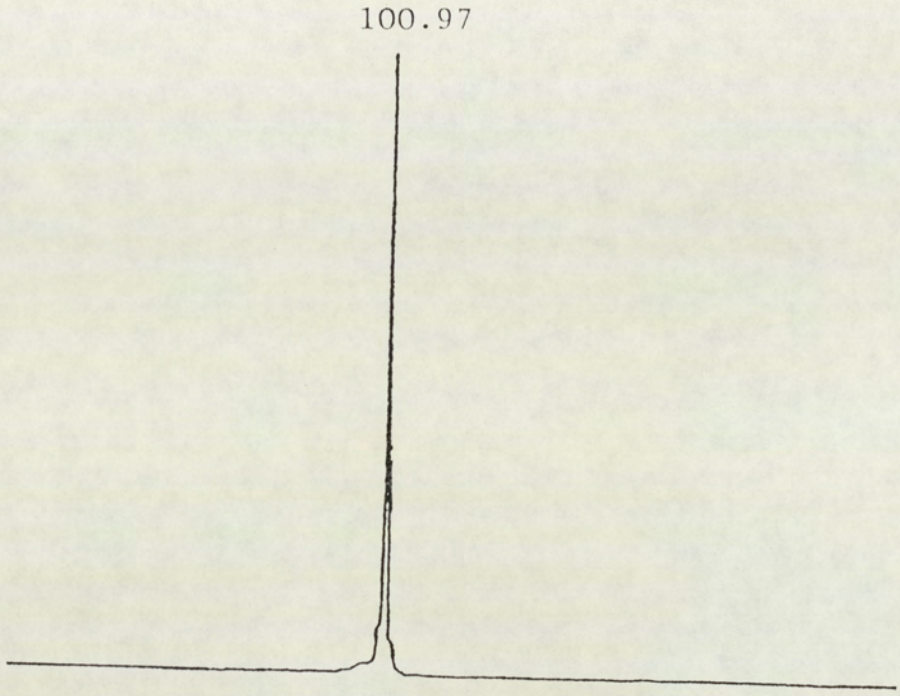


Figure 2.2(a) ^{31}P NMR of zinc dithiophosphonate (iBu) in chlorobenzene.

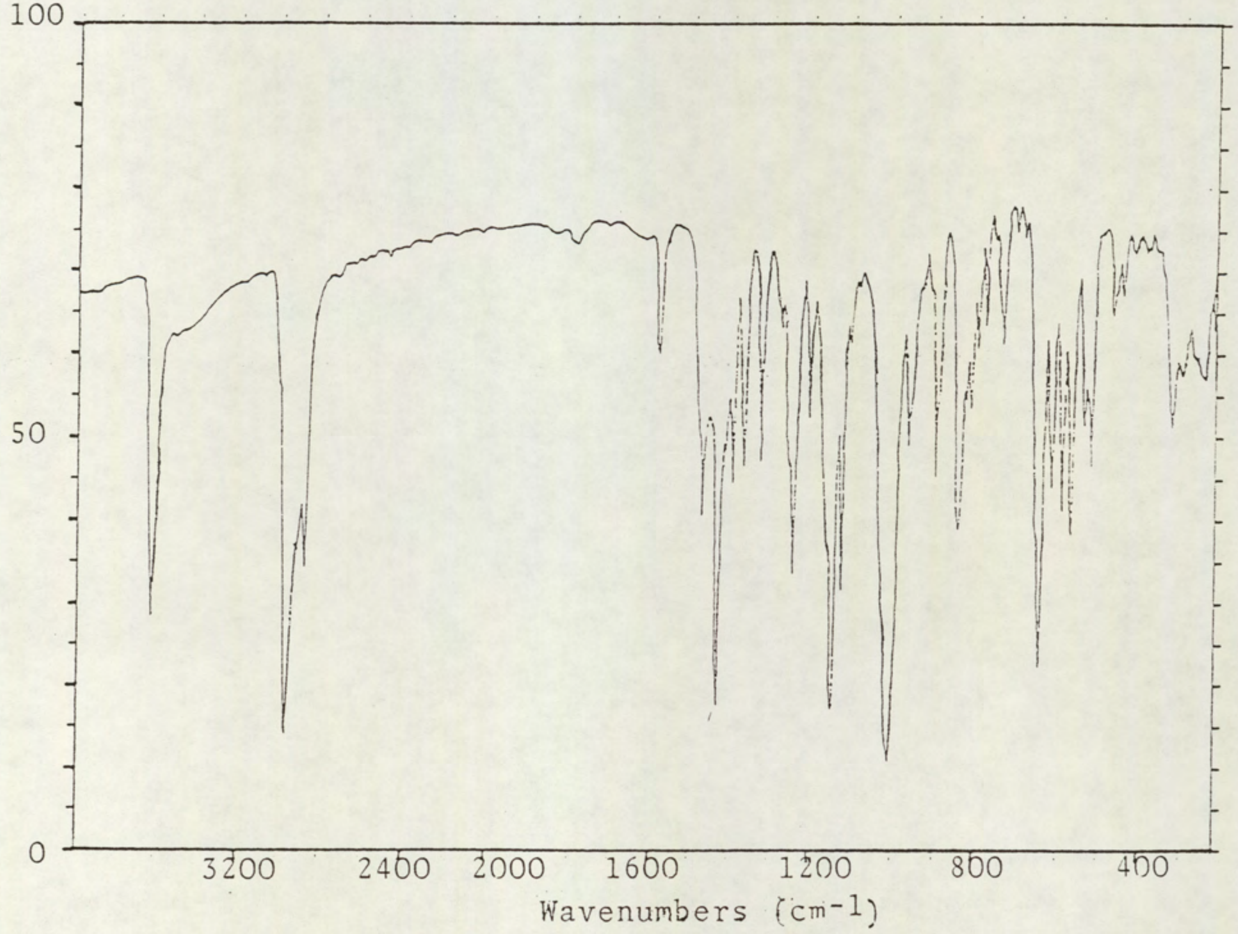


Figure 2.2(b) IR spectrum of ZnDiBuPn (KBr Disc).

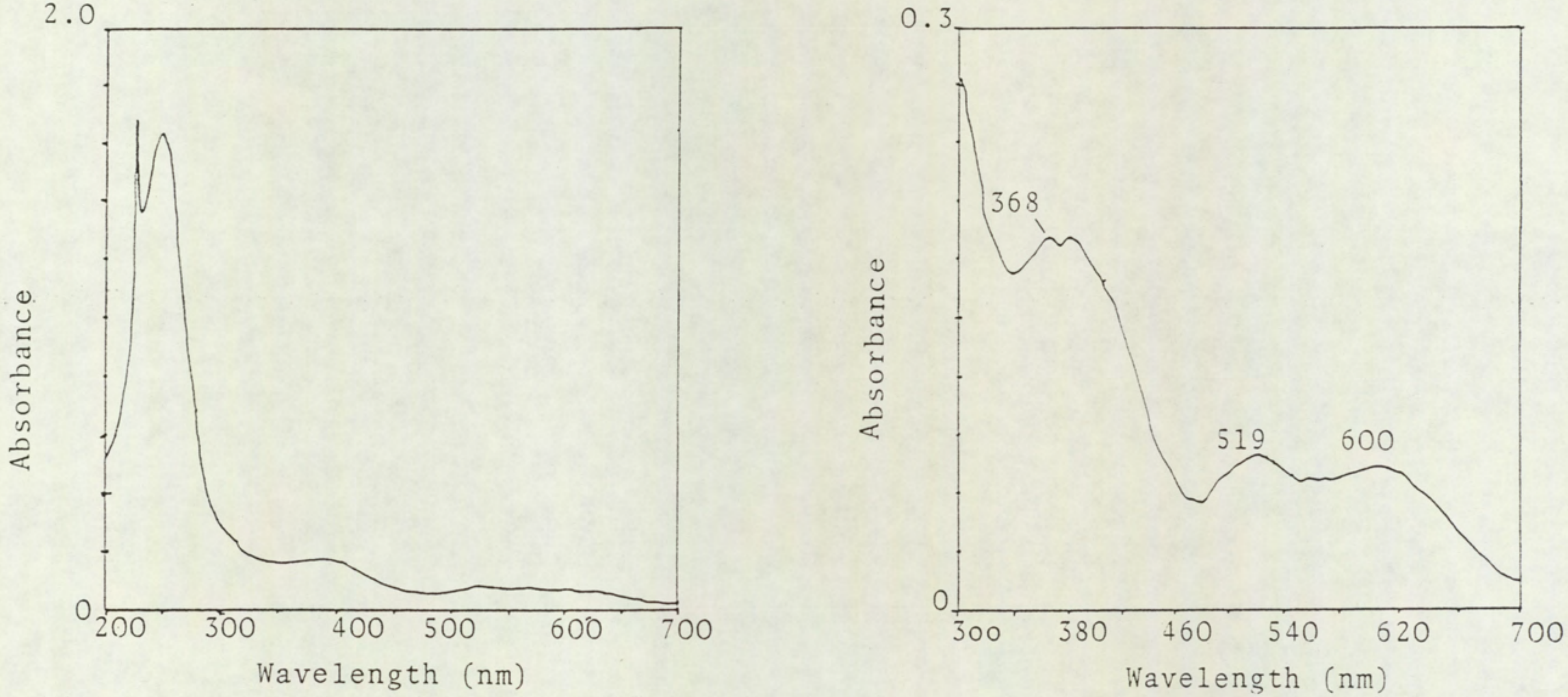


Figure 2.3(a) UV spectra of iron dithiophosphonate in cyclohexane

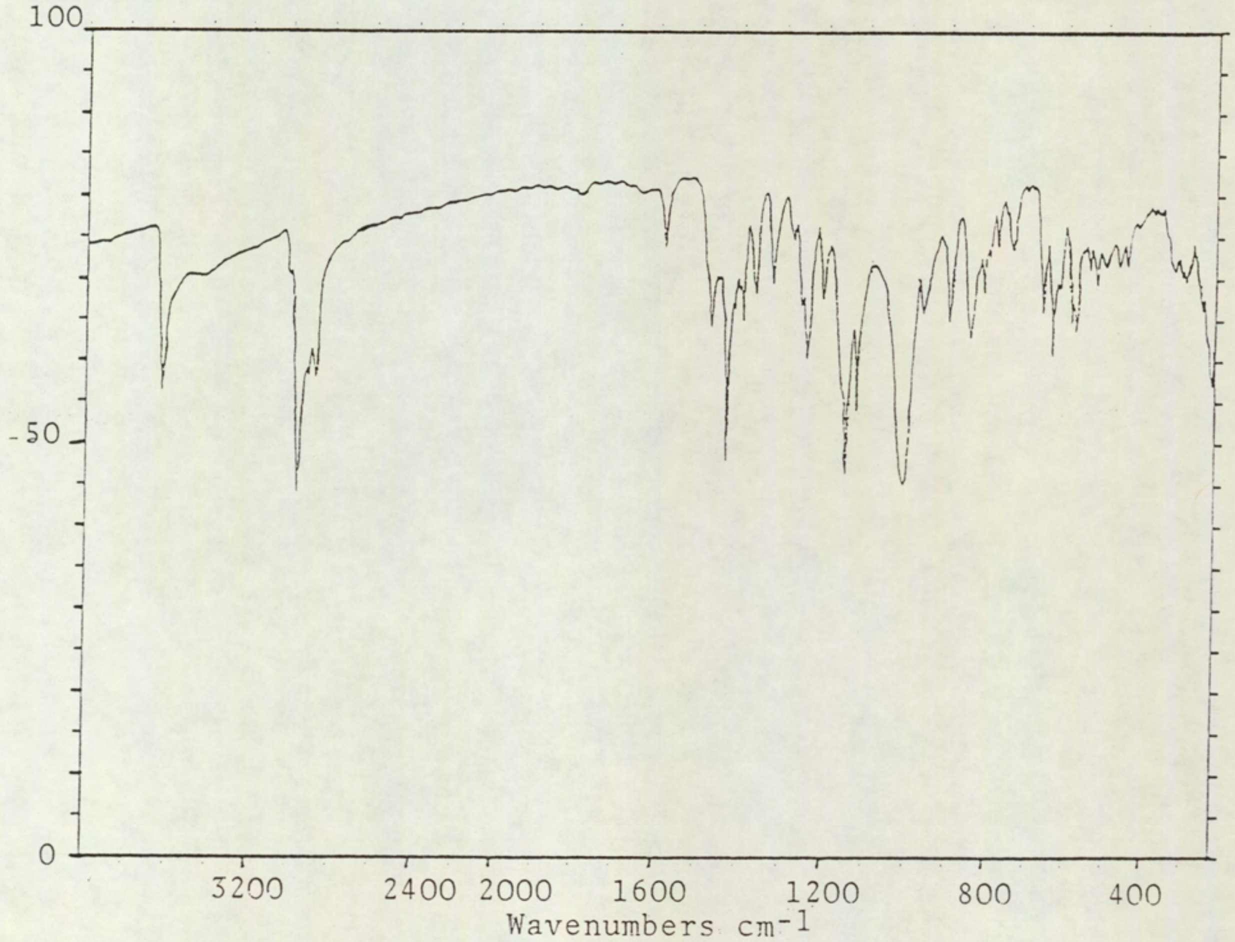


Figure 2.3(b) IR spectrum of FeDiBuPn (KBr disc).

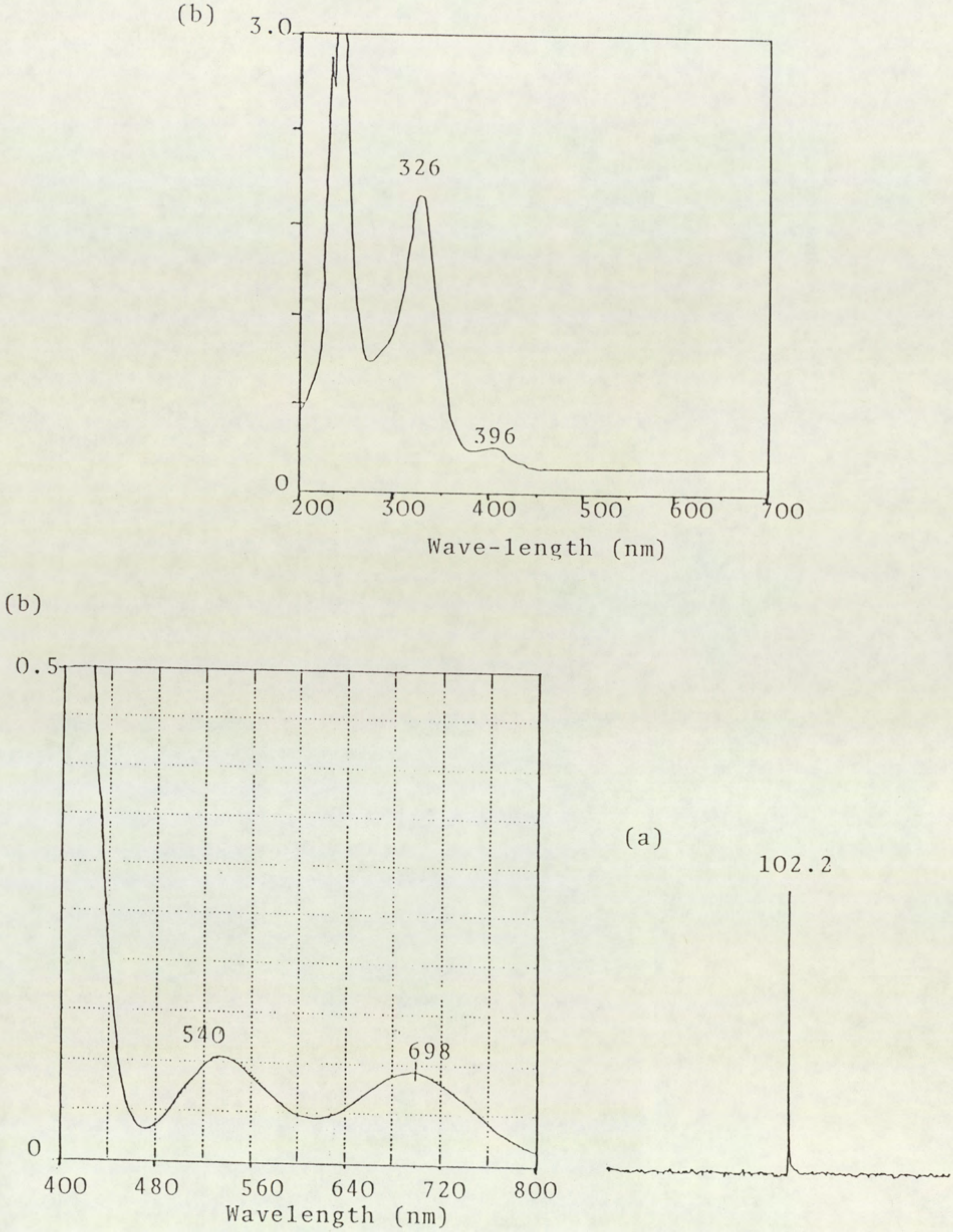


Figure 2.4 (a) ^{31}P NMR spectra of NiDiBuPn in chlorobenzene

(b) UV spectra of NiDiBuPn in cyclohexane

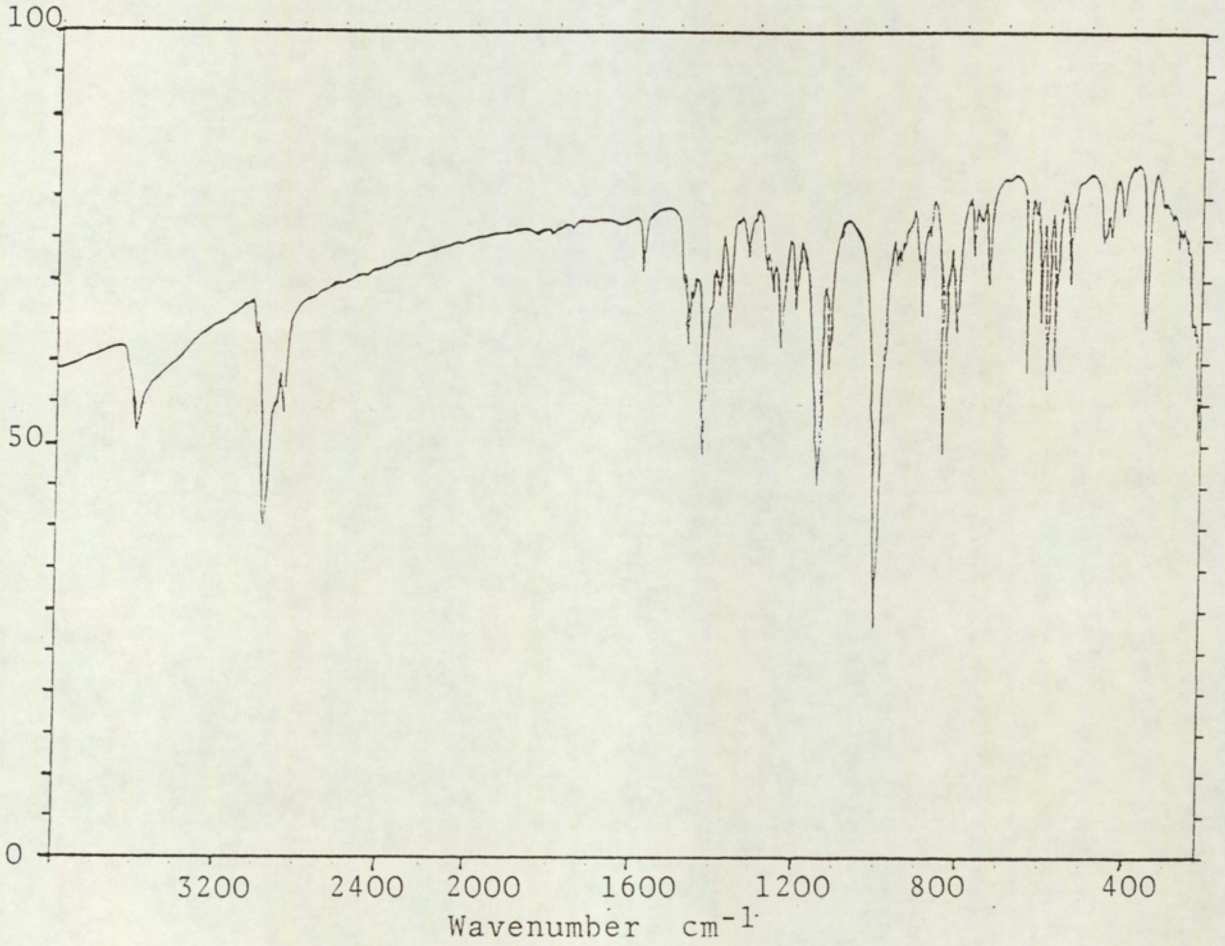
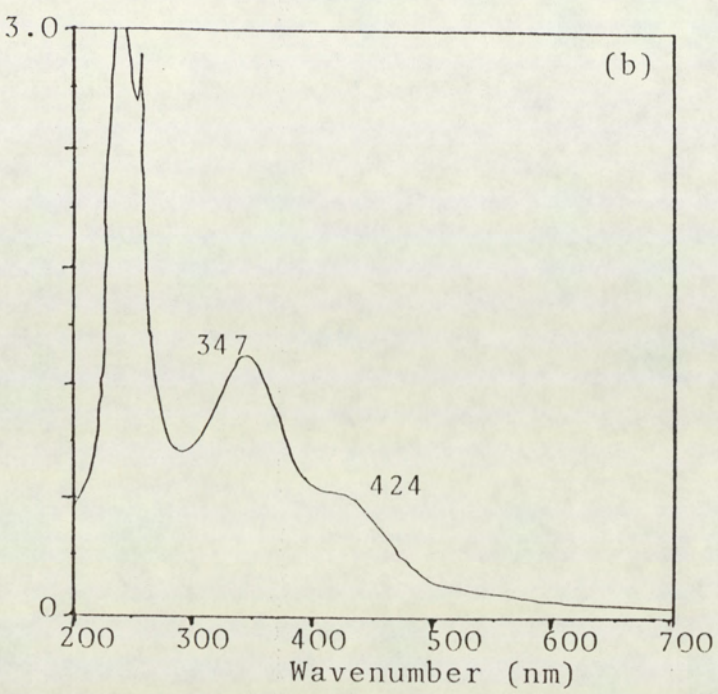


Figure 2.4(c) IR spectrum of NiDiBuPn (KBr disc).



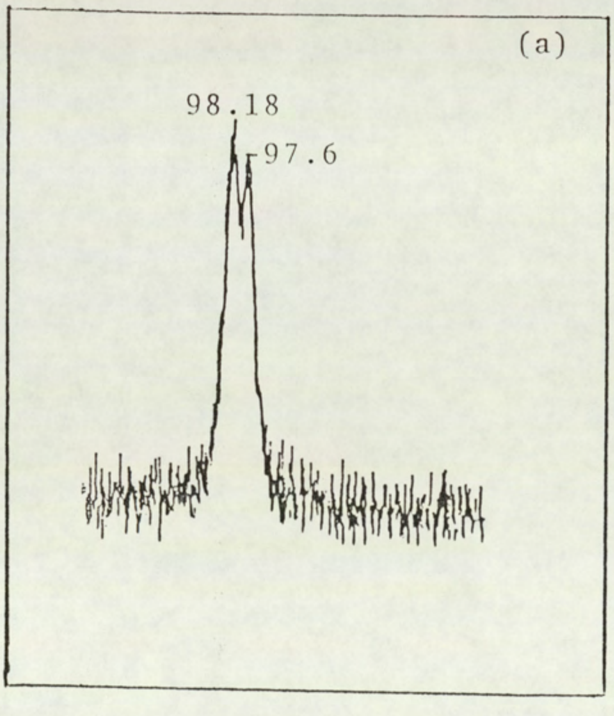


Figure 2.5 (a) ^{31}P NMR of cobalt dithiophosphonate in chlorobenzene.

(b) UV spectra of CoDiBuPn in cyclohexane

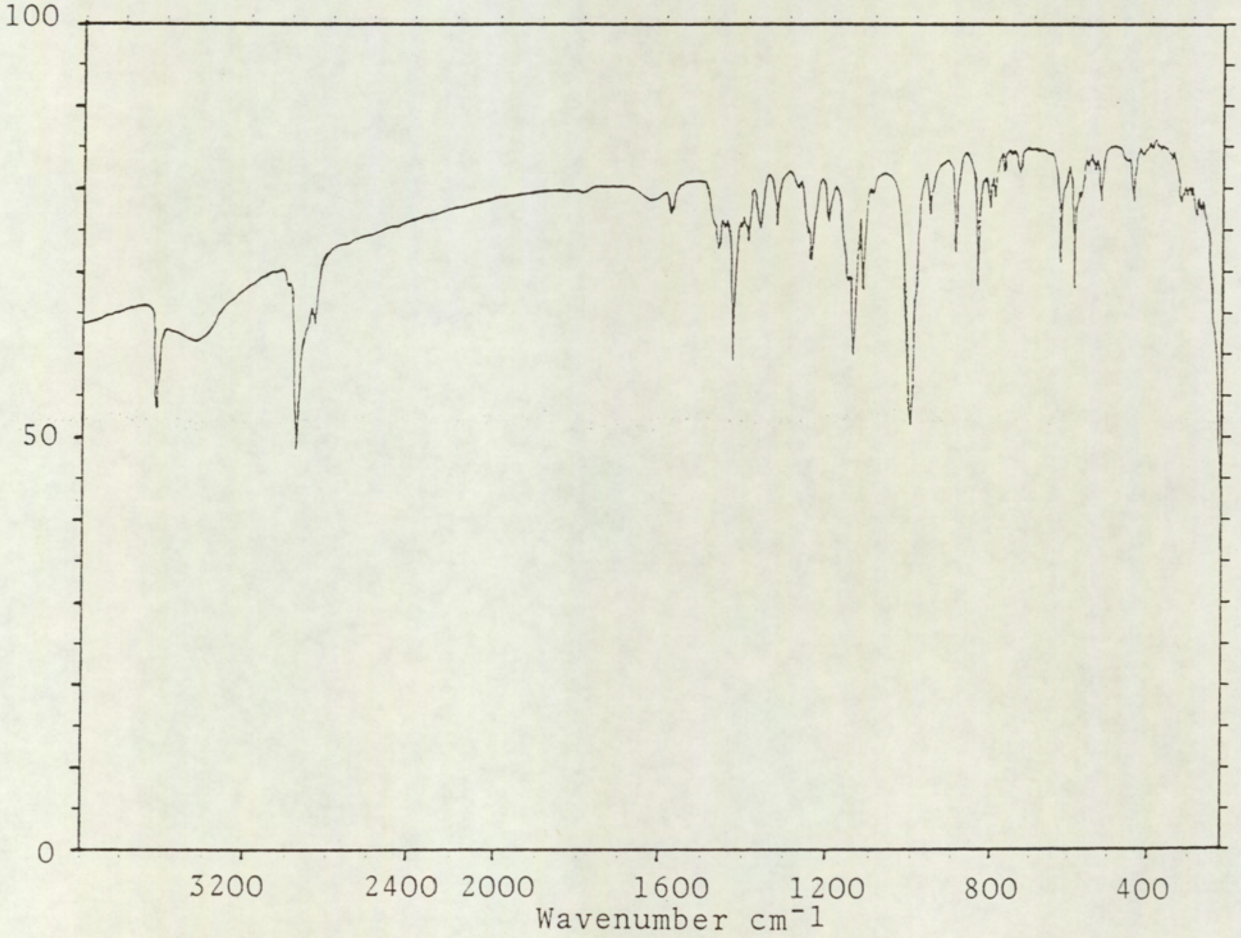
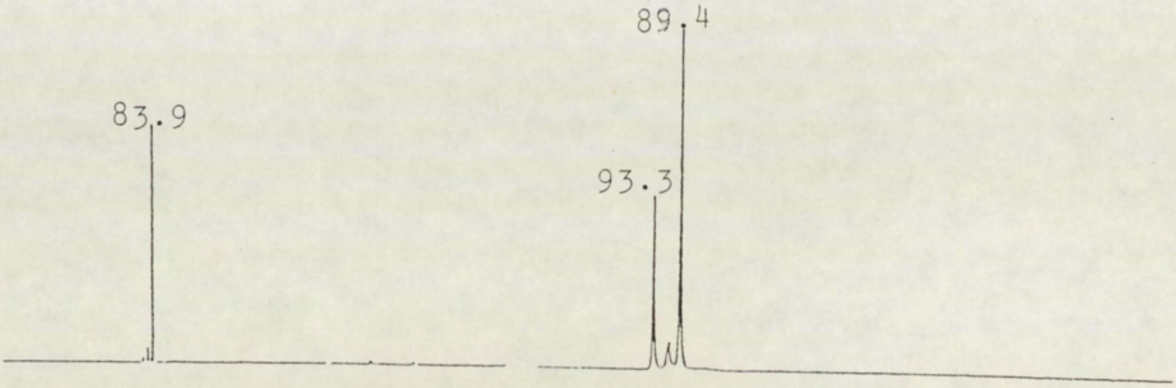


Figure 2.5(c) IR spectrum of CoDiBuPn (KBr disc).

Monosulphide Dissulphide



Attemted Trisulphide Attempted Tetrasulphide

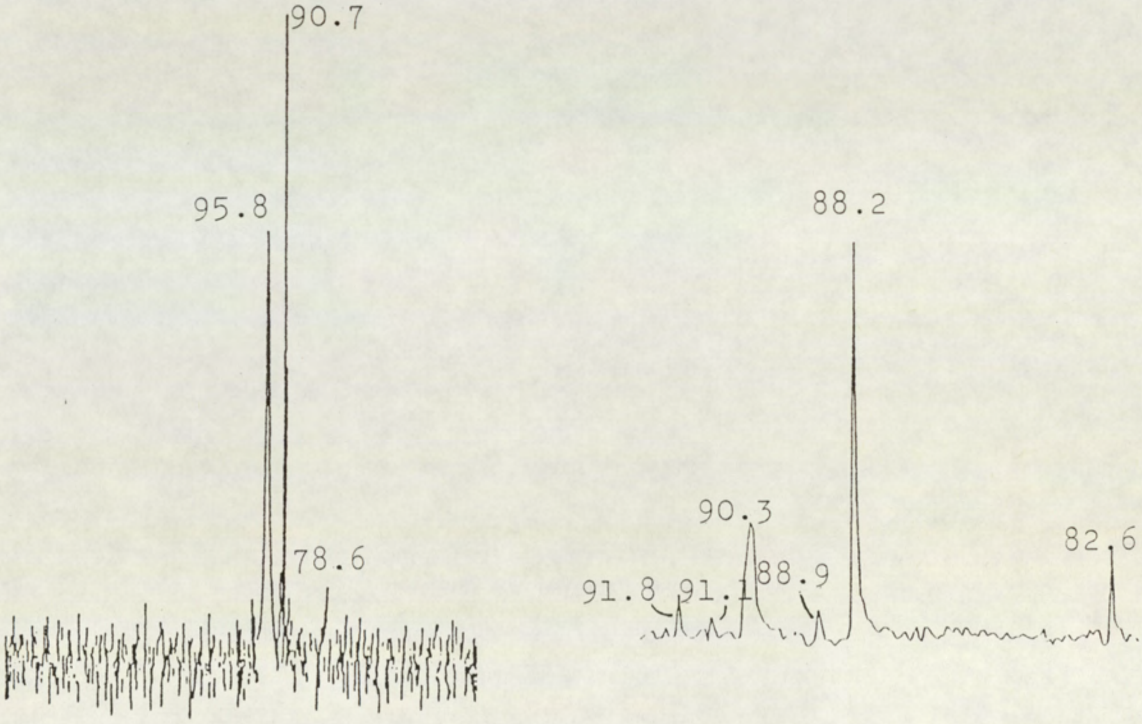


Figure 2.6 ^{31}P NMR spectra of attemted preparations of sulphides of dithiophosphonic acid.

2.1.3.10 Preparation of Dithiophosphates

Scheme 2.1 outlines the general preparation of dithiophosphates.

$$\begin{tikzcd}
P_2S_5 + 4ROH \arrow[r] & 2[(RO)_2PSSH] + H_2S\uparrow \arrow[d, "NH_3"] \\
& 2(RO)_2PSSNH_4 \arrow[d, "MCl_2"] \\
& NH_4Cl + [(RO)_2PSS]_2M
\end{tikzcd}$$

Scheme 2.1 General preparation of Dithiophosphates

2.1.3.11 Preparation of the Dithiophosphoric Acid(1)

44.4g (0.2 moles) phosphorus pentasulphide was gradually added to 59.2g (0.8 moles) isobutanol over a period of two hours at 80°C (see Scheme 2.1). The reaction was stirred and carried out in the presence of nitrogen gas. After addition of all the phosphorus pentasulphide the reaction was continued for a further 30 minutes to ensure reaction was complete. The hydrogen sulphide that was evolved was trapped by an aqueous solution of sodium hydroxide. The solution was then filtered to remove any unreacted phosphorus pentasulphide. The filtrate was treated with 5g of charcoal to remove black oily contaminents and filtered to give a green liquid.

Analysis

^{31}P NMR = 84.5 δ

F.T.I.R.

Functional group	Wave number(cm^{-1})
-P-O-C	960
-P=S	655
-P-SH	250

2.1.3.12 Preparation of Ammonium Dithiophosphate(1)

24.2g (0.1 moles) of the dithiophosphoric acid in hexane was treated with an excess of ammonia gas for 45 minutes with continuous stirring (see Scheme 2.1). The off white solid which formed was filtered, washed with hexane, and then recrystallised with benzene yielding white crystals. (Mpt 138°C)

2.1.3.13 Preparation of Nickel isobutyl Dithiophosphate(2)

23.8g (0.1 moles) of nickel chloride was dissolved in water and gradually added to a stirred solution of 51.8g (0.2 moles) of ammonium salt. A purple solid was filtered and washed thoroughly with water (see Scheme 2.1).

Analysis

^{31}P NMR = 93.2 δ

U.V. λ_{max} = 316 nm, 280 nm, 225 nm

F.T.I.R. Functional group	Wave number(cm^{-1})
-P-O-C	960
-P=S	665
-P-S-Ni	560
-Ni-S	350

2.1.3.14 Preparation of Cobalt isobutyl Dithiophosphate

23.8g (0.1 moles) of aqueous cobalt chloride was added dropwise to 51.8g (0.2 moles) of aqueous DTP ammonium salt with continuous stirring. The resulting green solution was extracted with chloroform and then dried with magnesium sulphate. The solvent was then removed yielding a brown fine powder.

Analysis

^{31}P NMR = 86.5 δ

2.1.3.15 Preparation of Zinc isobutyl Dithiophosphate

$$2(RO)_2PSSH \ + \ ZnO \longrightarrow [(RO)_2 \ PSS]_2Zn \ + \ H_2O \qquad 2.3$$

50g (0.207 moles) of the dithiophosphoric acid (slight excess) was added to 8.0g (0.099 moles) of zinc oxide in heptane, at 70°C under a nitrogen atmosphere over a period of two hours and 30 minutes. After addition of the acid, the solution was heated for a further 30 minutes to ensure completion of reaction. The solvent was then evaporated under vacuum and the resulting off white solid was recrystallised from heptane to give white crystals (Mpt 109-

110°C, Lit. 110-111°C [(3)]).

Analysis

^{31}P NMR = 98 75 δ

F.T.I.R.	Functional group	Wave number(cm^{-1})
	-P-O-C	992
	-P=S	660

2.1.3.16 Preparation of Iron (III) isobutyl Dithiophosphate

$$6(RO)_2PSSH + Fe_2O_3 \longrightarrow 2[(RO)_2PSS]_3Fe + 3H_2O \qquad 2.4$$

19.24g (0.08 moles) of the pure acid was dissolved in dry, distilled heptane and added dropwise to 2.4g (0.015 moles) iron oxide in refluxing heptane at 70°C. After addition, heating was continued for a further 30 minutes and the mixture was filtered hot to remove unreacted iron oxide. The solvent was then removed under vacuum leaving fine black needles.

Analysis

U.V. λ_{max} = 596 nm

F.T.I.R.	Functional group	Wave number(cm^{-1})
	-P-O-C	970
	-P=S	635

2.1.3.17 Preparation of Copper isobutyl Dithiophosphate(4)

25g of aqueous copper (II) sulphate was added to 24.2g (0.1 moles) of aqueous ammonium salt. The reaction mixture was stirred and a brown precipitate was formed. This was extracted with dichloromethane and the solvent removed under vacuum. The residue was recrystallised with methanol to give a pale yellow powder.

Analysis

^{31}P NMR = 100.5 δ

2.1.4. PURIFICATION OF REAGENTS

2.1.4.1 Purification of Cumene

Cumene (Koch Light) was distilled at 45°C under vacuum. The distillate was washed with aqueous sodium hydroxide to remove cumene hydroperoxide (CHP), and then dried with magnesium sulphate. Any traces of CHP still remaining were removed by passing the cumene through a column packed with activated alumina. The cumene was stored in a refrigerator.

2.1.4.2 Purification of Hydroperoxides

(a) Cumene Hydroperoxide

Cumene hydroperoxide (CHP) was purified by the method described by Kharasch and Co-workers(5). Commercially supplied cumene hydroperoxide (200 mls) in petroleum ether was added to 40 mls of concentrated NaOH at 0°C. A white precipitate (sodium salt) was formed which was filtered off and washed with petroleum ether. To liberate the CHP the sodium salt was treated with acetic acid. The ether layer was thoroughly washed with dilute sodium bicarbonate solution followed by further washings with water. The solution was dried with $MgSO_4$ and the petroleum ether removed using a rotary evaporator.The residual liquid was distilled under vacuum and the fraction boiling at 53°C (1mmHg) was collected. To test the purity of the CHP an iodiometric technique was employed. 2 mls of the above purified CHP was added to a solution of excess sodium iodide and acetic acid in 30 mls distilled isopropanol and refluxed for 10 minutes. Iodine was liberated and titrated against sodium thiosulphate.

$$ROOH + 2I^- + 2H^+ \longrightarrow I_2 + H_2O + ROH \qquad 2.6$$

$$I_2 + S_2O_3^{2-} \longrightarrow 2I^- + S_4O_6 \qquad 2.7$$

The purity of the CHP was found to be 98% and was stored in a refrigerator until required.

(b) Tertiary Butyl Hydroperoxide (TBH)

TBH, 70% in water as commercially supplied by Akzo Chemicals was purified by the procedure described in 2.1.4.2 (a)The fraction boiling at 55°C (10mmHg) was collected and found by iodiometric technique to be 97.5% pure and was stored at 0°C.

2.1.4.3 Purification of Solvents

Acetic acid, chlorobenzene and propan-2-ol were purified before use. Commercially available acetic acid was dried with $MgSO_4$, filtered off and distilled. The fraction boiling at 116°C was collected and stored in the dark.

Technical grade chlorobenzene was dried over phosphorus pentoxide, filtered and distilled. The fraction boiling at 132°C was collected.

Propan-2-ol was dried over $MgSO_4$ filtered and distilled. The fraction boiling at 82°C was collected.

2.1.4.4. Analysis of TPS

TPS was used as supplied by Exxon Chemicals Ltd.

^{31}P NMR 19.6δ

U.V. λ_{max} = 233 nm, 242 nm

F.T.I.R. Functional group	Wave number(cm^{-1})
-OH	3600
-P=S	679
-P-S	598

Elemental analysis

Calculated	C = 55.9%	H = 7.0%
Observed	C = 55.0%	H = 7.0%

2.2 COMPOUNDING AND FILM PREPARATION

2.2.1 Compounding using an Internal Mixer

All samples were processed using a Hampden RAPRA Torque Rheometer (6(a),6(b)). This is essentially a small mixing chamber containing two mixing screws contrarotating at different speeds. The speed of rotation can be adjusted from very slow to very fast. All the processings carried out in this work were done using a high speed of 60 rev/min. A continuous readout of both melt temperatures and torque is provided. The chamber may be operated closed or open to the atmosphere. During close mixing (CM) a full chamber using 35g of polymer charge is used whereas during open mixing (OM) the chamber stays partially full with 20g of polymer.

The polymer and additive were thoroughly mixed at room temperature by tumble mixing prior to charging into the torque rheometer. The processing temperature varies according to the nature of the polymer, in the case of polyethylene 160^{O}C and polypropylene 180^{O}C. The polymer and additive were processed for different specified time intervals. On completion of processing the polymer samples were removed and rapidly quenched in cold water to prevent further thermal oxidation.

For some synergistic systems a controlled oxidative processing was employed. Under these conditions, the polymer and additive were processed in an open chamber for ten minutes followed by addition of the synergist HOBP which was then processed for a further five minutes under closed mixing.

Concentrates of 2.4 % master batch (MB) of additives with polypropylene were also processed in both CM and OM conditions. NiDRPn master batch was then diluted with fresh unstabilised polypropylene under CM conditions.

2.2.2 Compounding using a Shaw Extruder

A Francis Shaw P 1 1/2 " extruder was fitted with a screw of 38 mm diameter, 18:1 L/D ratio, and a die of 5mm diameter. A temperature gradient from the barrel to the die tip can be obtained by adjusting the dials. In order to maintain a constant temperature water is continuously replenished.

Before extruding the sample under test the extruder was purged with fresh unstabilised polypropylene. The additive and polypropylene was hand tumbled in a polyethylene bag to get uniform dispersion, and then charged into the extruder hopper and stirred during operation. As the extrudate emerged from the die it was passed over a series of take off rolls. The extruder conditions used are as follows:-

	Zone	Set temp.(^{o}C)
Barrel	1	150
	2	170
Die head	3	210
Die tip	4	210

Screw speed 40 r.p.m.

2.2.3. Film preparation

Polymer films were prepared by compression moulding using an electric press. Polymer samples were placed between two stainless steel plates covered with special grade cellophane film used as a mould release. To obtain a standard thickness of 0.08 " (2 mm's) a fixed amount of polymer (about 7g) was placed between the cellophaned lined plates and inserted into the electric press whose plates had previously been heated to 180^{o}C. The sample was preheated for 90 seconds without applying any pressure. A pressure of 30 tonnes was then applied and immediately cooling of the press was commenced by running cold water through the plates. The full pressure was maintained until the temperature reached 80^{o}C, pressure was then released, and the plates removed. The films were stored in a freezer.

2.3 SOLVENT EXTRACTION OF PROCESSED POLYMER SAMPLES

Nickel dithiophosphonate and low molecular weight materials were extracted from the processed polymer sample by Soxhlet extraction using chloroform for a duration of 24 hours. A steady stream of nitrogen was bubbled throughout the extraction. At the end of the extraction a sample of the solvent was collected and its U.V. spectra recorded.

2.4 TESTING OF POLYMER SAMPLES

2.4.1 Ultra-Violet Irradiation of Polymer Films

All the film samples were irradiated in an ultra violet exposure cabinet. On the inside of the cabinet 28 fluorescent tube lamps (20 W) each are mounted in a cylindrical array. The lamps are symmetrically arranged to give a combination of one lamp type A1 (Westinghouse Sunlamps F1520) for every three lamps type C (Phillips Actinic Blue OS). Samples are mounted on a rotary drum fixed inside the cabinet and in this manner the light beam falls perpendicularly on the film samples. The distance of the sample from the light source is 10 cm and the temperature inside the cabinet with the light on is 30^{o}C. The combined distribution spectra of both types of lamps has shown (7) that the maximum in the relative intensity occurs within the range 280-370 nm. The intensity of the UV irradiation at the centre of the drum can be calculated (8(a),8(b)) and has been found to be 5.3 whm^{-3} . The exposure times are indicated on a counter clock.

2.4.2 Measurement of Embrittlement Times of Polymer Films

Embrittlement times (ET) were recorded as the time required to break the film when it is manually flexed onto itself i.e. through an angle of 180^{o}C. Each test was carried out in duplicate.

2.4.3 Thermal Ageing

The thermal ageing of polymer films were carried out in a Wallace oven at 140^{o}C in the presence of a steady flow of air (0.05 m^{3}/hr). Each polymer film was exposed in a separate cell to prevent cross contamination of additive by volatilisation. Each was examined in duplicate and the time required for the film to embrittle was noted.

2.4.4 Melt Flow Index

Melt flow index is the amount of polymer extruded through a standard capillary in a given time (usually 10 minutes), it is inversely related to molecular weight. The British Standard 2782 procedure was followed (9).

The melt stability was measured at 230°C for polypropylene samples, using a die of 0.0465" and a nominal force of 2.16 kg.

4g of the polymer sample to be extruded were cut into small pieces and charged into the barrel within 1 minute. After excluding trapped air the material was left to homogenise for four minutes, after which the 2.16 kg weight was placed on the piston and the extruded samples were cut at regular time intervals with a sharp edged knife. The first one or two cut offs were rejected and the next five extruded samples were taken e.g. at an interval of 30 seconds for weight measurement. The MFI was then calculated as the average weight extruded in 10 minutes.

2.4.5 Blooming of Additives from Polymer Films

The loss of additives from polymer films were examined using a Beckman U.V. spectrophotometer. Polymer film samples containing NiDiBuPn were allowed to bloom on standing at room temperature for varying periods of time. A U.V. spectra of each sample was taken immediately after it had been processed, and then again after 10, 20 and 30 days. Any surface bloom was dissolved with ether at room temperature prior to U.V. examination.

2.4.6 Screening efficiency of Additives

The screening efficiency of additives was determined by screening a polypropylene (PP) film with another PP film containing the additive under test. This was compared to a PP film screened with another unstabilised PP film (control). The embrittlement times for the screened PP films were recorded. The thickness of all films were maintained constant (0.08").

2.5 SPECTROSCOPIC ANALYSIS

2.5.1 Infra-red Spectroscopy

Infra-red spectra of polymer films were recorded on a Perkin Elmer 599 spectrophotometer and Perkin Elmer Fourier Transformer 1710 Infra Red Spectrophotometer (FTIR). Infra red spectroscopy is a useful technique for monitoring the degradation during thermal ageing and photo-irradiation. Functional groups such as carbonyl at 1710 cm^{-1} and hydroxyl at 3600 cm^{-1} were measured and calculated using the base line technique (10). This was carried out by drawing a tangential line between two adjacent shoulders of an absorption maxima. A perpendicular line was dropped to intersect the peak absorption base line. The distance between the tangential line and base line was taken as the absorbance which could be read directly from the chart paper.

The increase in carbonyl index during photo-irradiation of polymer films was calculated as follows.

$$\text{Carbonyl Index} = \frac{\text{log of carbonyl absorption at } 1710\text{cm}^{-1}}{\text{log of reference absorption at } 2720\text{cm}^{-1}}$$

The reference peak is used to minimise errors caused by deviations in film thickness.

2.5.2 Ultra Violet / Visible Spectroscopy

The ultra violet and visible spectra of polymer films and solutions were recorded using Beckmann DU7 spectrophotometer.

A particular λ_{max} was chosen depending on the nature of the additive. Absorbance(A) was read from the spectrum. Change in absorbance with increase in photo irradiation time for films or solutions were recorded.

2.5.3 Nuclear Magnetic Resonance

All spectra were recorded on a Jeol FX-90Q Fourier Transform Nuclear Magnetic Resonance Spectrometer, operating at 36.20 μHz. ^{31}P nuclear magnetic resonance spectroscopy (^{31}P NMR) was used to identify the phosphorous containing products. The accumulation time required to obtain a spectra was dependent on the phosphorous content of the sample. All spectra were measured with noise decoupling of the phosphorous-hydrogen received spin-spin coupling. Phosphoric acid (85%) was used as an external standard, to prevent any reaction occuring with other phosphorous compounds. The observed single phosphoric acid peak was set at zero and all other spectra recorded were relative to this peak. An estimation of the percentage of each species in any sample were calculated by assuming the total of all the intensities on any one spectrum to be 100%.

^{31}P NMR spectra for kinetic reactions were recorded at varying time intervals depending on the ratios of the reactants used. Reactions were carried out at 30°C, 100°C or 180°C.

2.6 <u>OXIDATION REACTIONS OF NiDiBuPn AND TBH</u>

(a) Various ratios of NiDTPn and TBH (1:4,1:10 and 1:20) were prepared in chloroform at room temperature and samples were collected at various time intervals throughout the reaction.

(b) A 1:4 ratio of NiDTPn:TBH was reacted in chlorobenzene under an atmosphere of nitrogen at 100°C. Samples were collected at varying time intervals for analysis.

(c) A 1:2 ratio of NiDTPn and TBH in methyl cyclohexane were exposed to U.V. light and samples of the solution were taken out over a period of time for analysis.

2.7 <u>THERMAL DECOMPOSITION REACTIONS OF NiDiBuPn</u>

Two kinetic reactions of nickel dithiophosphonate in p-dichlorobenzene at 180°C were carried out simultaneously one in the presence of air and the other in the presence of nitrogen.

2.8 ULTRA VIOLET EXPOSURE OF DITHIOPHOSPHONATES IN SOLUTION

The U.V. stability of the metal dithiophosphonates (Ni, Fe, Co) and the corresponding sulphide (TPS) were evaluated by continual irradiation of solutions (concentration 1×10^{-5} mol dm^{-3}) in cyclohexane at $25^{o}C$. Samples were withdrawn at suitable time intervals and their ultra violet / visible spectra recorded.

2.9 OXIDATIVE REACTIONS OF DITHIOPHOSPHONIC ACID

A 1:4 molar ratio of dithiophosphonic acid with TBH, the acid with excess isobutyl alcohol and the acid with excess water were each prepared in chlorobenzene and kinetically examined using ^{31}P NMR.

2.10 CONFIRMATORY REACTIONS USING TERTIARY AMINE

To each of the reactions described in 2.9 (above) an excess of triethyl amine was added. The reaction was kinetically followed using ^{31}P NMR.

2.11 HYDROPEROXIDE DECOMPOSITION

The decomposition of cumene hydroperoxide (CHP) by dithiophosphonates was studied in chlorobenzene (an inert non-oxidising medium) at $110^{o}C$ in a thermostated oil bath. The reaction apparatus is shown in Figure 2.7.

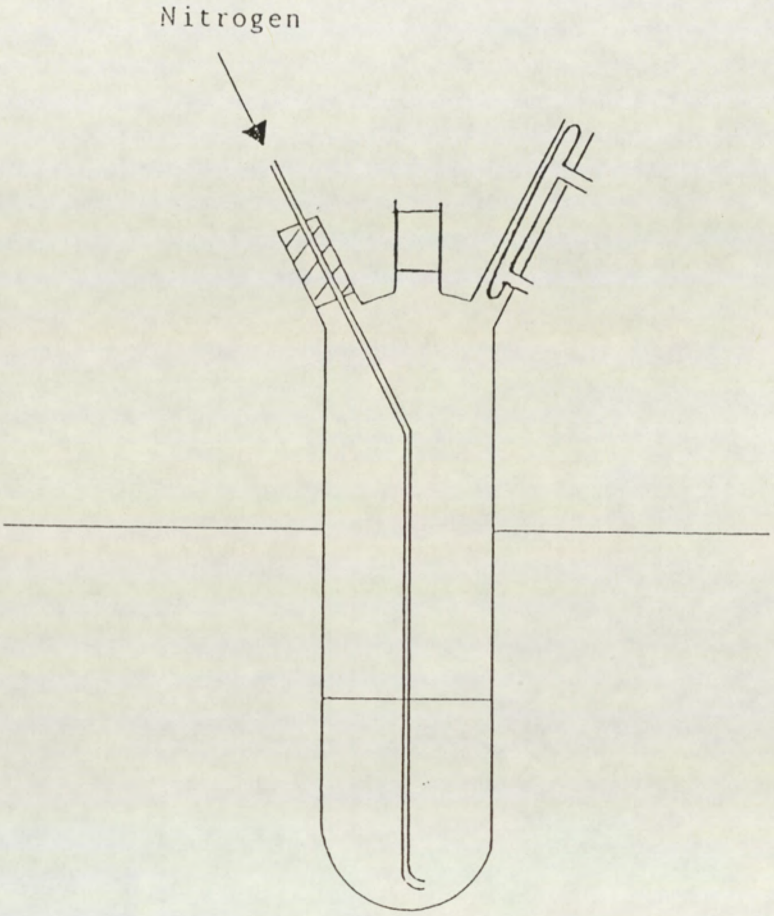


Figure 2.7 Hydroperoxide Decomposition Apparatus

The empty vessel was placed in the heated oil bath for 10 minutes prior to each experiment. A suitable volume of pure chlorobenzene was then introduced into the reaction vessel and left to equilibriate for 5 minutes after 5 mls of CHP ($8x10^{-2}$mol dm^{-3}) in chlorobenzene were added. The metal complex also in chlorobenzene ($4x10^{-3}$mol dm^{-3}) was then added after 5 minutes to obtain a total volume of 40 mls. A constant flow of nitrogen was maintained throughout the reaction using a manometer. Various ratios of the antioxidant and CHP were examined, this was achieved by varying the volume of chlorobenzene and additive. Initial time for the reaction was taken after the addition of the additive.

1 ml of the reaction mixture was pipetted at suitable time intervals into a flask already covered with aluminium foil, and containing 10 mls of 2.5 % v/v sodium iodide in propan-2-ol and 10 mls of 10 % v/v acetic acid in propan-2-ol. This reaction mixture was refluxed on a hot plate with vigorous stirring for 6 minutes and then cooled for a further 2.5 minutes. The aluminium foil was removed and 5 mls of distilled water were added to the contents (yellow) of the flask which were titrated against sodium thiosulphate solution (3.7×10^{-3} mol l^{-1}) to give a colourless solution which was taken as the end point.

The acetic acid in the final reaction mixture provides an acid medium for the oxidation of iodide to iodine by CHP.

$$\mathrm{ROOH} + 2\mathrm{I}^- + 2\mathrm{H}^+ \longrightarrow \mathrm{ROH} + \mathrm{I}_2 + \mathrm{H}_2\mathrm{O} \qquad 2.8$$

The iodine produced in reaction 2.8 reacts with sodium thiosulphate as shown :

$$2\mathrm{S}_2\mathrm{O}_3{}^{2-} + \mathrm{I}_2 \longrightarrow \underset{\text{colourless}}{\mathrm{S}_4\mathrm{O}_6{}^{2-}} + 2\mathrm{I}^- \qquad 2.9$$

In this procedure the concentrations have been calculated such that a 10 cm^3 titre is equivalent to 100 % CHP.

2.12 GAS LIQUID CHROMATOGRAPHY(11)

Gas liquid chromatography (G.L.C) was employed to identify the products arising from the decomposition of cumene hydroperoxide (CHP) by nickel dithiophosphonate and the sulphide, TPS. All work was carried out using a Pye-Unicam G.C.D chromatograph fitted with a flame ionisation detector. Dual glass columns packed with polyethylene glycol adipate on Chromosorb W were used. The temperature of the columns were maintained at 150°C until all the decomposition products had been eluted. A nitrogen flow rate of 30 cm^3 per minute was maintained.

A calibration curve was constructed for each of the possible decomposition products of CHP (Scheme 4.0) with the exception of acetone which due to its low boiling point would not be expected to remain in solution at the reaction temperature of 110°C used for the hydroperoxide determination experiments.

Several solutions of different concentration in chlorobenzene were prepared for each compound . A fixed amoumt of 1μdm^3 iodobenzene was injected into 1 cm^3 of each sample and 1μdm^3 of this solution was then analysed.

The areas of the sample peak and the iodobenzene peak in the resulting chromatogram were calculated by multiplying the peak height by the peak width at half height. A graph of peak area ratio verses molar ratio was then constructed. For each of the potential CHP decomposition products used a straight line was given.

The build up or decay of the various decomposition products of CHP (Scheme 4.0) was followed as a function of reaction time. At suitable reaction times, 1 cm^3 samples were withdrawn from the CHP decomposition experiments and rapidly frozen in dry ice/acetone to quench any further reaction. Prior to freezing an excess of triphenylphosphine was added to the sample in order to convert any unreacted CHP to α-cumyl alcohol as Bunn and co- workers have shown (11) that CHP on a GLC column may decompose to more than one product. The total yield of α-cumyl alcohol obtained needed to be corrected in order to allow for the contribution of that arising from the reaction of undecomposed CHP and triphenylphosphine. The amount of undecomposed CHP present at any time was determined from the hydroperoxide decomposition curves, and subtracted from the total yield to give the true yield of α-cumyl alcohol.

Each day samples were being analysed, a solution of $1x10^{-2}$ mol dm^{-3} CHP in chlorobenzene, having first been treated with excess triphenylphosphine, was run in order to find the peak area corresponding to a 100% yield of α-cumyl alcohol. Once this was known the area corresponding to a 100% yield of the other decomposition products, i.e. acetophenone, α-methyl styrene and phenol could also be determined from the calibration curves initially set up. Actual product yields were then calculated from the formula:-

$$\text{Actual Product yield} = \frac{\text{Peak area obtained}}{\text{100\% peak area}} \times 100\%$$

The retention volumes of the peaks due to chlorobenzene and α-methyl styrene were very similar, with the result that small yields of the latter were difficult to detect accurately.

2.13 OXYGEN ABSORPTION

A 5×10^{-4} mol dm^{-3} solution of azobisisobutyronitrile (AZBN) and 5×10^{-4} mol dm^{3} solution of the additive were prepared in purified cumene. Different aliquotes of AZBN solution and the additive were mixed to give a total volume of 10 mls prior to oxygen absorption testing. 5 mls of this solution was introduced into a 50 ml three necked flask magnetically stirred and heated at 55^{o}C by an oil bath. This flask was connected to another identical three necked flask, each fitted with a glass tap and a stopper. Both flasks were connected via side arms to a pressure transducer which in turn was connected to a chart recorder (see Figure 2.8). The sample flask was purged with oxygen through the glass tap and all joints thoroughly sealed to the atmosphere with silicone grease. As the oxygen in the sample flask warms up, the pressure increases slightly showing a decrease in chart reading. Therefore the initial reading is taken after 5 minutes to allow equilibration of pressure and temperature.

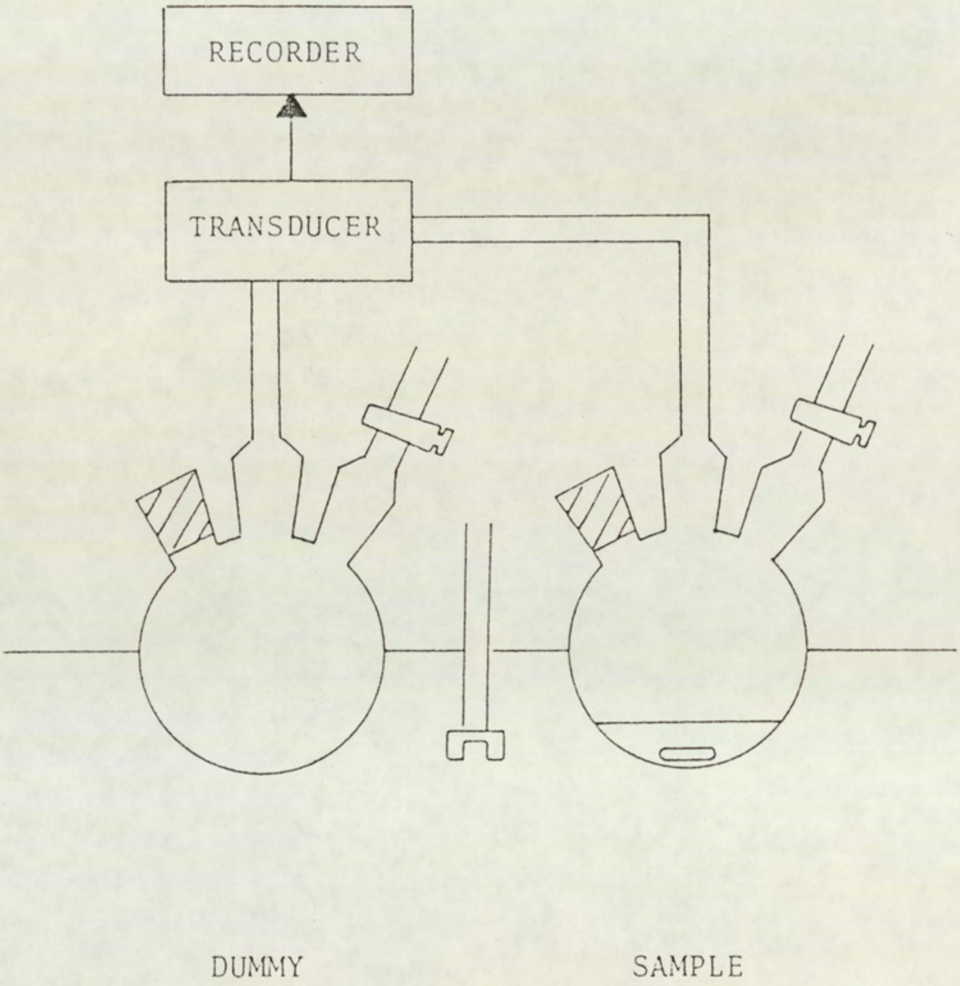


Figure 2.8 Oxygen Absorption Apparatus

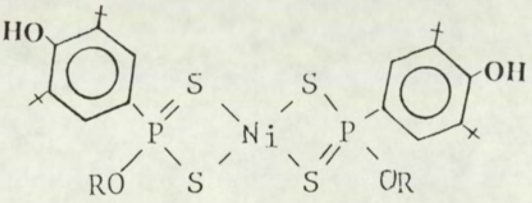
Oxygen absorption in the sample flask creates a pressure drop across the transducer and after calibrating this pressure difference can be interpreted as the number of mililitres of oxygen absorbed. For each sample, the chart reading was obtained as a continuous trace of chart deflection versus oxidation time. This deflection was converted to cm^3 oxygen absorbed by multiplying by a factor of 0.4 (as a deflection of 5 divisions = 2.0 cm^3 during calibration). A curve of oxygen absorbed versus oxidation time could then be plotted.

CHAPTER 3

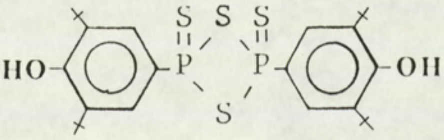
DITHIOPHOSPHONATES AS STABILISERS FOR POLYOLEFINES

3.1 OBJECT

The primary aim of the work described in this chapter is to evaluate dithiophosphonates (DRPn) as melt, thermal and photostabilisers in polypropylene when fabricated under different processing conditions. The dithiophosphonates examined were nickel (I), iron, cobalt and copper complexes (MDRPn) and a sulphide, TPS (II). The processing was carried out in a RAPRA-Hampden Torque Rheometer (Section 2.2.1) under conditions of limited (CM) or excess air (OM), and at different time intervals and concentrations. The oven ageing was carried out in a single cell oven at 140^{o}C with an air flow of 0.05 m^3/hr. Melt flow index was measured at 230^{o}C under a load of 2.16 Kg (for experimental details see sections 2.4.3 and 2.4.4) respectively). The synergistic effect of the dithiophosphonates with the commercial U.V. absorber 2-hydroxy-4-octyloxy-benzophenone (HOBP) was also investigated.



(I)



(II)

3.2 RESULTS AND DISCUSSION

3.2.1 Melt Stability

The main effect of a melt stabiliser is to maintain a constant viscosity during fabrication. Melt flow index (MFI) is a measure of viscosity change in the polymer and is inversely proportional to molecular weight.

A comparison of MFI values for various MDRPn's (M = Ni, Co, Fe, Zn, Cu) and TPS processed under (CM) and (OM) conditions is shown in Table 3.1 and Figure 3.1.

Table 3.1 Effect of processing conditions on MFI of PP containing various DRPn's

	MFI g/10mins	
Antioxidant	CM 10mins	OM 15mins
PP control	9.6	-
CuDiBuPn	2.3	2.2
NiDiBuPn	2.4	2.6
FeDiBuPn	2.1	2.3
ZnDiBuPn	2.4	2.3
CoDiBuPn	2.3	2.4
TPS	2.0	2.3

It is clear that the metal MDRPn's and the sulphide (TPS) are all very good melt stabilisers when compared with commercial controls such as Irganox 1010 and 1076 (c.f Table 3.2). Their high effectiveness may be attributed to a combination of chain breaking and peroxidolytic activity effects. The sulphur-phosphorus ligand is known to exert mainly peroxidolytic activity (and to a lesser extent exert a radical trapping ability) (1,2). On the other hand the hindered phenolic group has only chain breaking activity (3,4). The chain breaking (see Section 3.2.3(f)) and peroxide decomposing activity (see Section 4.2.1) of this class of compounds is examined closely in this work.

The nickel dithiophosphonate shows exceptionally good activity during U.V. irradiation (see Section 3.2.3) and oven ageing (see Section 3.2.2), its melt stability was therefore studied in more detail. Table 3.2 and Figure 3.2 compare the melt stability of nickel dithiophosphonate with that of other stabilisers. It is clear that NiDRPn is more effective even when compared to the hindered phenols,Irganox 1010 or 1076 which are good melt stabilisers due to their chain breaking activity(5). Peroxidolytic antioxidants such as phosphite esters and various sulphur compounds e.g. dithiophosphates which reduce hydroperoxides to alcohols by non-radical processes are effective melt stabilisers(1,2). The improved melt stability of NiDRPn when compared to the hindered phenols can therefore be attributed to a combination of the hindered phenol chain breaking activity and peroxidolytic activity of the phosphorus-sulphur ligands.

Table 3.2 Comparison of the MFI values of Controls with NiDRPn (0.4%)

Sample	MFI (g/10 mins) CM 10 mins
Unstabilised PP	9.6
Tinuvin 770*	4.3
HOBP*	4.0
Irganox 1076*	2.7
Irganox 1010*	2.5
NiDiBuP	3.1
NiDiBuPn	2.4

* For chemical structure see Table 2.1.

The effect of processing conditions on the melt stability of polypropylene containing Nickel dithiophosphonate is shown in Table 3.3 and in Figure 3.3. The results show little change in melt stability with increased processing time but there is a slight decrease in melt stability for samples that have been oxidatively processed. Under conditions of excess air (OM) both the peroxide concentration and the rate of chain scission increases (6).

Table 3.3 Effect of Processing variables on MFI values of PP containing NiDRPn (5×10^{-4} mol/100g)

NiDiBuPn	MFI g/10mins	
Processing time (mins)	CM	OM
10	2.4	2.6
20	2.4	2.6
30	2.5	2.6

The melt stabilising activity of the nickel dithiophosphonate is highly dependent on its concentration (Table 3.4, Figure 3.4). This is due to the increased concentration of the antioxidant function which becomes available in the polypropylene matrix.

Table 3.4 Effect of the concentration of nickel dithiophosphonate on the MFI value of Polypropylene

	MFI g/10 mins	
NiDiBuPn / conc.% (w/w)	CM 10 mins	OM 10 mins
0.2	2.8	2.9
0.3	2.5	2.8
0.4	2.4	2.6

It has previously been reported that the activity of most antioxidants is governed by volatility and solubility. Table 3.5 and Figure 3.5 show clearly that the higher alkyl, 2-ethyl hexyl (2-EH), nickel dithiophosphonate is a more effective melt stabiliser than the isobutyl (iBu) analogue, under both restricted (CM) and excess oxygen (OM) conditions. This is possibly due to the higher solubility (Figure 3.20(b)) of the 2-ethyl hexyl analogue which shows higher initial U.V. absorbance of the additive immediately after compression moulding into films of standard thickness.

Table 3.5 Effect of alkyl substituent on the MFI value of PP containing NiDRPn ($5x10^{-4}$ mol/100g)

	MFI (g/10mins)	
NiDRPn	CM 10mins	OM 10mins
iBu	2.4	2.6
2-EH	2.2	2.3

3.2.2 Thermal Stability

Thermal oxidation occurs when the solid polymer is exposed to air at elevated temperatures during use. Thermal degradation effects both physical and chemical properties of the polymer. The main parameters which control thermal stabilisation of an additive are volatility (7,8,10), solubility (11), diffusion rate (9) and the mode of activity of the stabiliser.

The thermal stability of MDRPn's and the sulphide, TPS, is shown in Table 3.6 and Figure 3.6. In each case metal dithiophosphonates show better thermal stabilising activity when the polymer is processed in the presence of excess air (OM) except for TPS which shows better activity under (CM) conditions. The decrease in activity of TPS during OM conditions may be due to volatilisation of the additive during processing, as it was found during thermogravimetric analysis that 19% weight loss ocurred at 180°C. This weight loss would obviously be considerably smaller under CM conditions.

Table 3.6 Oven ageing of PP films (at 140°C) containing dithiophosphonates and Irganox 1076

	Embrittlement time (hrs)	
Antioxidant (0.4%)	CM 10 mins	OM 15 mins
CuDiBuPn	16	22
FeDiBuPn	50	125
ZnDiBuPn	20	145
CoDiBuPn *	20	25
NiDiBuPn	1370	1810
TPS	160	50
Irganox 1076	480	-
Irganox 1010 (0.1%)	760	-

* Cobalt films are highly coloured see Section 3.2.3(e)

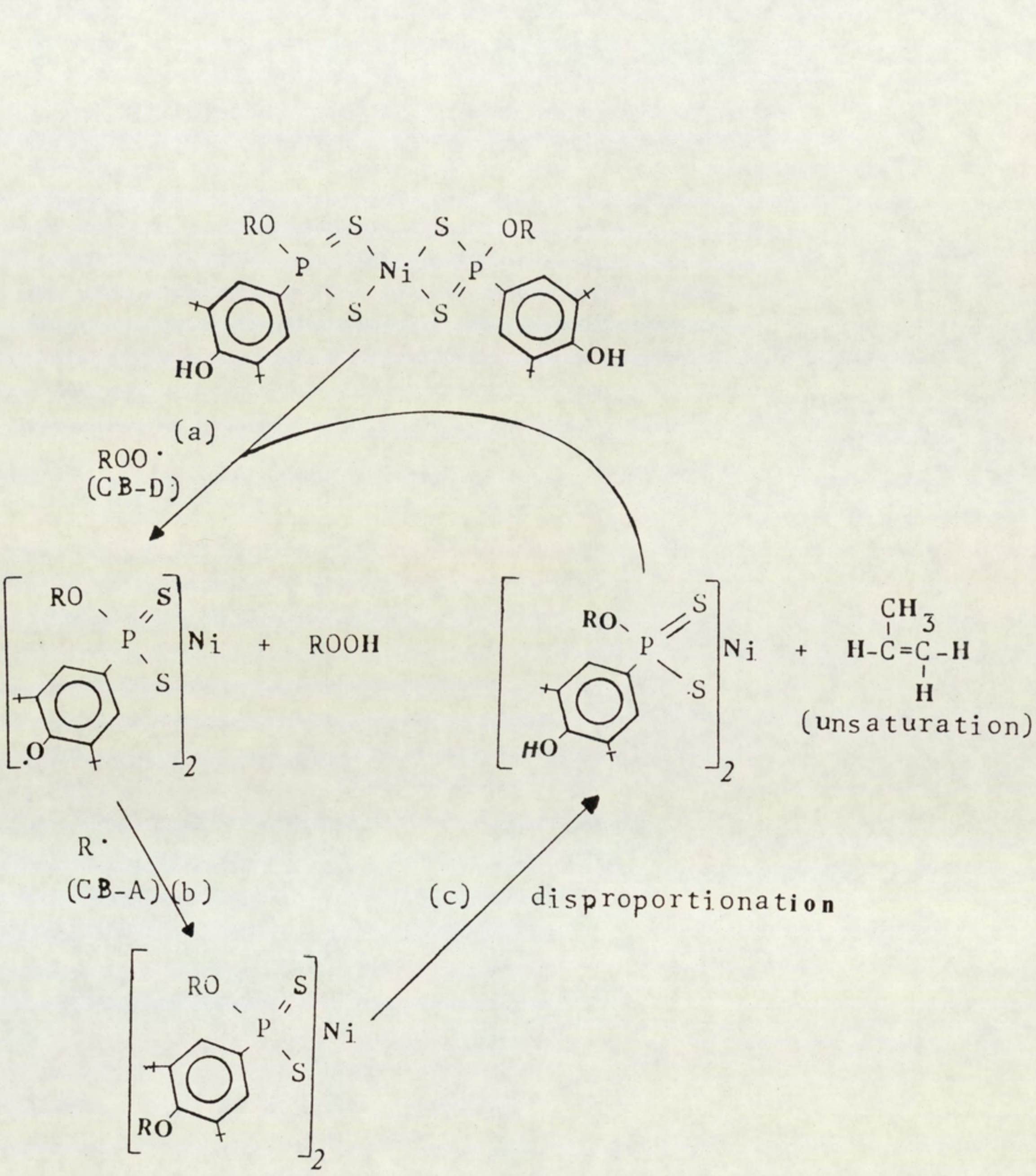
Sulphur containing hindered phenols are known to be effective thermal antioxidants (4,12,13) primarily due to their ability to act as catalysts for peroxide decomposition in addition to their normal chain breaking function. The nickel dithiophosphonates showed outstanding thermal stabilising activity (Table 3.6) and thus it was examined more closely. Table 3.7 and Figure 3.7 show that NiDiBuPn is much more effective than other nickel dithiolates, e.g. dithiophosphate and dithiocarbamate and is also superior to the hindered phenol, Irganox 1076. Dithiocarbamates (14) and dithiophosphates (15,16) attribute their activity mainly to a PD-C mechanism whereas Irganox 1076 to a chain breaking acceptor (CB-A) mechanism (17,18). The nickel dithiophosphonate, however, must exhibit both chain breaking (CB) and peroxide decomposing (PD) activity (See Section 4.2.1) as do other sulphur containing phenols (3,4,12,19) and hence its activity is probably due to autosynergism.

Table 3.7 Oven ageing (140°C) of PP films containing NiDRPn and controls

Antioxidant (0.4%)	Embrittlement time (hrs)
CM 10 mins	
NiDiBuC	162
NiDiBuP	42
Irganox 1076	480
NiDiBuPn	1370

No hydroperoxide formation was detected (during oven ageing) by IR spectroscopy in polypropylene containing dithiophosphonate although it is present in substantial amounts in a control film without additives under the same conditions. This may be due to the effect of the phenolic group of the nickel dithiophosphonate and the hydroperoxide decomposing activity of the sulphur - phosphorus moeity. The high induction period for carbonyl formation (Figure

3.8(a)) during thermal ageing of nickel dithiophosphonate is primarily attributed to the scavenging ability of radicals by the hindered phenol and complementary peroxide decomposition activity. Figure 3.8 (b) shows the persistence of the phenolic OH group for more than 900 hours instead of self sacrificial destruction of the hydroxyl group as in other hindered phenols (20). This can be explained on the basis that in nickel DRPn the para position of the hindered phenol is co-ordinated to a highly electronegative element, phosphorus, which forbids the formation of stilbene quinone which is formed in other hindered phenols such as BHT (see Section 1.3.1.1). It is well known (21) that the thermal stability of hindered phenols depends on the ease of formation of oxidised products such as stilbene quinone. Scott and Yusoff (20) have observed the formation of this product and the complete disappearance of the phenolic OH of BHT in only 10 minutes during the thermal ageing of BHT. On the basis of the observed results the enhanced thermal stability of NiDRPn must primarily be due to a cyclic regeneration of the hydroxyl group by a CB-D/CB-A mechanism (Scheme 3.0).



Scheme 3.0 Regenerative Mechanism of NiDRPn

The effect of processing time on the nickel dithiophosphonates is shown in Table 3.8 and Figure 3.9. It is known that during the processing of polypropylene, hydroperoxides are produced and that their concentrations increase with time (22,23). The presence of excess peroxides before thermal ageing leads to the rapid degradation of the polymer. The decrease in the thermal stability of the MDRPn's with the increase in processing time can therefore probably be attributed to an increase in peroxide concentration.

Table 3.8 Thermal Stabilising Activity (140^{o}C) of Nickel Dithiophosphonate (5x10^{-4} mol/100g) in PP at 140^{o}C and Varying Processing Times

NiDiBuPn	Embrittlement time (hrs)	
Processing time (mins)	CM	OM
10	1370	1640
20	1010	1580
30	820	1290

The effectiveness of additives within an analogous series has been found to depend strongly on its solubility in the polymer(11). Table 3.9 and Figure 3.10 show that the isobutyl is not as effective as the 2-ethyl hexyl analogue as a thermal stabiliser. This must be due to the higher solubility (Figure 3.20 (b)) and lower volatility of the 2-EH substituted nickel complex in the polymer. The volatility of the additive from the polymer is studied on the basis of blooming (see Section 2.4.5) which is shown in Figure 3.20 (a). The less soluble dithiophosphonate (iBu) began to bloom more rapidly from the polymer than the 2-ethyl hexyl analogue. The latter complex exhibited a much lower initial loss which is in agreement with results found for metal dithiocarbamates by earlier workers (11) Table 3.9 also illustrates that when NiDiBuPn is processed under excess oxygen (OM) it exhibits higher stability than under restricted oxygen (CM). This is observed in Figure 3.8 which shows that the rate of decay of NiDiBuPn processed in excess oxygen (OM) is considerably lower than when the complex is processed under restricted oxygen (CM). In addition a higher molar extinction coefficient (Figure 3.20 (b)) and a higher phenolic -OH index (Figure 3.8) is observed for oxidatively processed (OM) samples which is directly related to the higher solubility of the complex in the polymer. These results suggest that the cyclic regenerative mechanism (Scheme 3.0) is more efficient under conditions of excess oxygen (OM). This is further supported by Figure 3.8 which illustrates that the rate of decay of the phenolic -OH is much lower in OM than in CM samples.

Table 3.9 Thermal Stabilising effect of NiDiBuPn versus NiDEHPn (0.4 %) in PP

	Embrittlement time (hrs)	
NiDRPn	CM 10 mins	OM 10 mins
iBu	1370	1640
2-EH	1620	2010
Irganox 1076	480	-

As the concentration of the nickel dithiophosphonate is increased in polypropylene the embrittlement time also increases (See Table 3.10 and Figure 3.11). This is because the effective stabilising groups in the polypropylene are also increasing (see Figure 3.20 (c)).

Table 3.10 Effect of Concentration on the Thermal Stabilising Action of NiDiBuPn in PP

	Embrittlement time (hrs)	
NiDiBuPn (%)	CM 10mins	OM 10mins
0.2	750	1025
0.3	980	1375
0.4	1370	1810

Copper dithiophosphonate is a good melt stabiliser (Section 3.2.1) and photo-stabiliser (Section 3.2.3) but a very poor thermal stabiliser. It was therefore synergised with Irganox 1010 (as shown in Table 3.11) in an attempt to improve thermal stability of PP. It is clearly evident from this table that the thermal antioxidant activity of Irganox 1010 is drastically reduced in the presence of the copper complex. However, the activity of this complex has increased form 16 hours to 40 hours. This result seems to suggest that the copper ion interferes with the normal activity of the hindered phenols. It is quite likely that copper alternates between Cu^{2+} and Cu^{+} state. The copper (I) ion may abstract hydrogen from the phenol whereby the Irganox 1010's normal antioxidant mechanism(21) is interrupted and thus peroxyl radicals will build up in the polymer at a faster rate during thermal ageing.

Table 3.11 Thermal Stabilising Activity of Irganox 1010 and CuDRPn

Sample (CM-10mins)	Embrittlement time (hrs)
0.4% CuDRPn + 0.1% Irganox 1010	40
0.4% CuDRPn	16
0.1% Irganox 1010	760

3.2.3 Photo-Stability

One of the most harmful effects on the durability of polymers is caused by sunlight which causes oxidative chain scission and finally leads to total deterioration. The evidence suggests (24-26) that hydroperoxides are the most important initiators for the photo-oxidation of polyolefines. Thus, any peroxide decomposing agent would be a good stabiliser under these conditions.

3.2.3 (a) Dithiophosphonates as photostabilisers in Polypropylene

Nickel dithiophosphonate is a better photo-antioxidant than the other metal complexes when compared on both a weight and molar basis under CM and OM conditions. The order of their activity as photostabilisers compared on a weight basis (Figure 3.12) is as follows:-

CM Ni > Cu > Fe > TPS > Co > Zn

OM Ni > Cu > Co > Fe > Zn > TPS

When compared on a molar basis, however, (Figure 3.13) the order of activity is slightly changed such that both iron and cobalt DRPn's show better activity than the copper complex:-

CM Ni > Fe > Co > Cu > Zn

OM Ni > Co > Fe > Cu > Zn

The improved activity of the iron and cobalt complexes when compared to copper DRPn is clearly due to the presence of a much higher concentration of the former in the polymer matrix in view of the size of their molecules since the comparison in Figure 3.12 was carried out on a weight basis. The order of photo-stability of the dithiophosphonates observed on both a weight and molar basis during oxidative processing is in agreement with the rate of decay of each complex in solution after photo-irradiation (c.f Figure 3.14) and shows that the lower the rate of decay the higher the photostabilising antioxidant activity. This high photostabilising activity of the nickel complex will be discussed in the next section. It is also interesting to note that the sulphide, TPS, is less active when processed under oxidative conditions (cf. Figure 3.12 (a) and 3.12(b)) whereas the reverse is found for most metal dithiophosphonates. It is known (27) that the volatility of metal complexes during processing is low whereas volatility is high for low molecular weight compounds such as sulphides. It has been observed in this work that a 19% weight loss of TPS was found to occur at 180°C during thermogravimetric analysis. This weight loss would obviously be much smaller under close mixing conditions.

A comparison of the photo-antioxidant activity of the structurally related metal dithiophosphates (MDRP) on a molar basis (Figure 15) also shows that the nickel DRP is much better than other complexes under close mixing conditions. The order of the activity is as follows:-

CM Ni > Co > Cu > Fe > Zn

OM Co > Ni > Cu > Fe > Zn

When processed under oxidative conditions, however, it is shown clearly (Figure 3.15 (b)) that the activity of the NiDRP is almost halved. It has previously been reported (28,29) that increased processing severity (oxidative processing), result in a reduction of the nickel DTP's activity as a photostabiliser This difference in the activity of the nickel complexes of dithiophosphate and dithiophosphonate, especially under oxidative processing conditions, suggest that these two complexes must operate via different mechanisms. Both contain nickel and sulphur moieties which contribute to U.V. screening as well as peroxide decomposing activity. NiDiBuPn, however, has an additional hindered phenolic group which may scavenge alkyl peroxyl and alkyl radicals by a cyclic regenerative mechanism (see Scheme 3.0).

3.2.3 (b) Nickel Dithiophosphonates as a Photostabiliser in Polypropylene

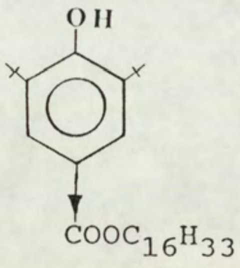
An in depth investigation was carried out for nickel dithiophosphonate as it exhibited enhanced photostabilising activity. Photo-irradiaton of NiDiBuPn (Figure 3.14) showed that the complex was highly stable to U.V. light. Thus the mode of action of the nickel complex must, at least initially, involve the whole molecule rather than its breakdown products. This contrasts with other phosphonates such as iron, cobalt and TPS which disappear much more rapidly from the system during photolysis (Figure 3.14). The results of iron dithiophosphonate during this study are surprising since iron complexes of any nature act as photo pro-oxidents (30). The rapid disappearance of the iron dithiophosphonate during photolysis (Figure 3.14) does not agree with the far greater overall photostabilisation activity of the complex (Figures 3.12 and 3.13). This clearly suggests that the original iron complex decomposes and the transformation products which are more photostable (probably do not absorb in the U.V. region) act as photo antioxidants. It is quite likely to assume that the iron complex undergoes redox reaction and the breakdown of ligands and formation of other organic ligands (iron free). This iron free organic molecule seems to act as a photostabiliser. However, much more work is required to confirm this view.

Table 3.12 shows that the nickel complex acts in part as a U.V. screen, but in addition a cyclic regenerative mechanism has been proposed (Scheme 3.0).

Table 3.12 Screening Efficiency of Nickel and Copper Dithiophosphonates and Controls Processed at 180°C (CM 10mins)

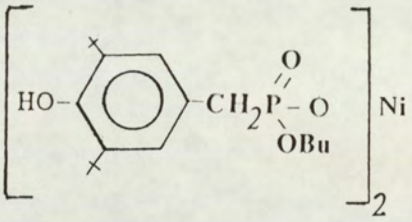
	Embrittlement time (hrs)	
Additive (0.4%)	As normal additive	As a screen
PP (Control)	95	110
NiDiBuPn	1390	285
CuDiBuPn	880	170
HOBP	1250	400

The evidence obtained by infra-red spectroscopy for the cyclic regenerative mechanism is shown in Figure 3.3 4(a) where a slow and steady decrease in the phenolic -OH (3636 cm^{-1}) group is observed, in addition an increase in absorption at 1645 cm^{-1} may be due to the development of unsaturation (Figure 3.3.4(b)) during photo-irradiation. It is well known that a hindered phenol is a self sacrificial stabiliser in which the phenolic -OH group decreases rapidly to form quinonoidal compounds (21). This rapid decrease in the phenolic -OH group was found to be only 8 minutes for BHT (20). The activity of the hindered phenol also depends on the electron withdrawing or donating ability of the substituent in the para position. If an electron withdrawing group is present it hinders the formation of dimerised and oxidised products such as in the case of (I) U.V. 2908 (a U.V. stabiliser). Another example is (II) Irgastab 2001 (30) which also contains a hindered phenol that is photostable because it is attached to a nickel complex and it contains a highly electronegative element phosphorus which is electron withdrawing. If, however, an electron donating group is present, e.g BHT or (III) Irganox 1076 it facilitates the formation of quinonoid products.



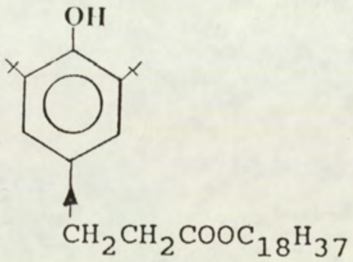
UV 2908
(UV stabiliser)

I



Irgastab 2001
(UV stabiliser)

II



Irganox 1076
(thermal stabiliser)

III

In dithiophosphonates the para position of the hindered phenol group is co-ordinated to phosphorus which is electron withdrawing and thus the formation of quinonoid products is not possible.

The contrasting photostabilising activity (Figure 3.16 (a) and (b)) of the nickel complex under conditions of excess oxygen (OM) and limited air (CM) is probably a consequence of the higher stability and solubility of the additive, during OM processing in the polymer. The rate of formation of alkyl ($R^{\cdot}$), alkyl peroxyl ($ROO^{\cdot}$) and hydroperoxides (ROOH) is critical during photo-oxidation of NiDRPn. The optimum time found for closed mixing is 10 minutes (Figure 3.16 (a)). This may be explained by the fact that at this time oxygen is at its highest concentration and thus a higher concentration of alkyl peroxyl radicals ($ROO^{\cdot}$) which are required for the regenerative cycle to take place. With increasing processing time though, the concentration of the alkyl radicals ($R^{\cdot}$) increases and as there is only limited oxygen in the system the concentration of alkyl peroxyl radicals ($ROO^{\cdot}$) is much lower. This low level of alkyl peroxyl radicals slows down the rate of the regenerative CB-D/CB-A cycle. During oxidative processing an optimum processing time was found to be 15 minutes (Figure 3.16 (b)). This must be a critical time for when alkyl peroxyl and alkyl ($ROO^{\cdot}/R^{\cdot}$) radicals are at the most favourable ratio for the regenerative cycle to take place.

The most successful U.V. stabiliser based on the peroxidolytic mechanism are the nickel complexes of dithiol acid (1). It was shown that in these cases the effective peroxidolytic antioxidants are not the parent metal complexes themselves but their transformation products which are primarily sulphur acids (1,31). In this work mechanistic studies on nickel dithiophosphonate revealed that it was a good peroxide decomposer (Section 4.2.1). In addition ^{31}P NMR studies have shown (Section 4.2.3.2(c)) that sulphur acids are produced but after prolonged U.V. irradiation.

A comparison of NiDRPn and controls (Figure 3.17 (b)) under OM conditions show nickel to be the best stabiliser, whereas processing under limited air (CM) (Figure 3.17 (a)) shows a change in trend as follows:-

OM NiDRPn > Tinuvin 770 > NiDRC > NiDRP > HOBP > Irg 1010

CM NiDRC > NiDRP > Tinuvin 770 > NiDRPn > HOBP > Irg 1010

The reason why NiDRPn is better than other antioxidants under OM conditions (Figure 3.17(b)) may be due to the different mechanisms by which each antioxidant performs. Tinuvin 770 functions by a non sacrificial CB-D/CB-A cyclic mechanism, NiDRC and NiDRP are both screeners and peroxide decomposing agents and to a lesser extent radical scavengers. HOBP is known as a good U.V. screener and Irganox 1010 stabilises by a self sacrificial CB-D mechanism. However, the NiDRPn operates via all these mechanisms.

The relationship between the decay of the nickel complex and the photo-induction period in polypropylene is illustrated in Figure 3.18. The length of the induction period roughly corresponds to the time for the disappearance of the nickel complex. Under conditions of excess oxygen (OM) the decay of the complex takes longer than under CM conditions which is reflected in a longer embrittlement time, and suggests higher stability of the nickel complex in open mixing.

It has been previously reported (32) that increasing the alkyl chain length in nickel dithiophosphates also increases their solubility in organic substrates. Similarly, in nickel dithiophosphonate the longer alkyl (2-EH) analogue exhibits better photostabilising performance than the shorter alkyl (iso butyl) nickel complex (c.f Figures 3.16 and 3.19). It has also been suggested (11) that U.V. stabilisers are extremely sensitive to their state of dispersion in polymers. Since many of them (including NiDRPn see earlier) behave in part as U.V. filters or screens, it is reasonable to assume that their effectiveness depends partly on the molar absorptivity and hence their U.V. absorbance in the polymer, which in turn depends on their solubility. This supposition is confirmed in Figure 3.20 (b) where the 2-EH analogue has a higher initial U.V. absorbance than the iBu analogue. A comparison of Figure 3.16 and 3.19 show that the NiD2-EHPn to be a better photostabiliser than the shorter chain length NiDiBuPn.

The photostabilising activity of NiDRPn increases with concentration (Figure 3.21) which is due to the increase in effective stabilising groups which is clearly observed in Figure 3.20(c) where an increase in the nickel complex concentration shows an increase in the characteristic 325 nm peak.

Nickel dithiophosphonate also absorbs light strongly in the most critical region of the solar spectrum (290-350nm) which is in common with the commercial U.V. absorber HOBP(33). Due to the high extinction coefficient of NiDRPn (Figure 2.4(b)) in this region (and its inherent deep purple colour) it is therefore expected to behave in part as a U.V. screen. U.V. screens are able to absorb U.V. radiation and emit it harmlessly as thermal energy (33). The effectiveness of NiDRPn as a U.V. screen (see Section 2.46) for experimental details) is shown in Table 3.12 which shows that a contribution is made by Ni DRPn screening on the overall U.V. stabilisation mechanism but not to the same extent as HOBP. The U.V. stabiliser HOBP is shown to be a more effective screen for polypropylene. This compound has been shown to operate primarily by absorbing the U.V. light and re-emitting it as vibrational (thermal) energy although it has also been reported to scavenge radical species(11,34,35,36).

3.2.3 (c) Copper Dithiophosphonate as a Photostabiliser in Polypropylene

The initial studies of dithiophosphonates as photo-antioxidants (Figure 3.12) showed that the nickel complex was the best followed by the corresponding copper complex and hence its photo-antioxidant activity was also examined.

Oxidatively processed (OM) copper dithiophosphonate (Figure 3.22 (b)) shows slightly better photostabilising activity than when processed under CM conditions (c.f Figure 3.22 (a&b)). Figure 3.23 shows that as the concentration of CuDRPn is increased, under both restricted and excess oxygen conditions its photostabilising activity increases. The effect of pressing temperature (180°C - 230°C) on the photostabilising activity of copper dithiophosphonate was evaluated (Figure 3.24) and it is clear that it decreases with increase in temperature. This may be due to an increase in the concentration of hydroperoxides at a higher temperature of pressing as it is now generally accepted (30,35,37,38) that polymer hydroperoxides produced during thermal processing operations are the most important photo-initiators during the early stages of U.V. irradiation. Table 3.12, shows that the screening ability of copper dithiophosphonate is only small compared to the total antioxidant activity of the molecule.

3.2.3.(d) Synergism of Nickel or Copper DRPn's with HOBP in Polypropylene

Combination of U.V. absorbers and peroxidolytic agents usually leads to synergism (39). HOBP can neither inhibit the formation of hydroperoxide during processing nor destroy them harmlessly during photo-oxidation (23,40). Consequently, HOBP is an indifferent antioxidant during processing and appears to behave essentially as a screen during the early stages of photo-oxidation when hydroperoxides are the primary initiators (41). In the later stages of the photo-oxidation, when carbonyl photolysis is the main photodegradation process (42) it has been shown that the U.V. stabiliser is sacrificially destroyed in the process of protecting the carbonyl group (36).

Nickel and copper dithiophosphonates show a high degree of synergism with the U.V. absorber HOBP. This is clearly illustrated in Table 3.13. The synergistic combination of these metal complexes with HOBP amalgamates the desirable features of both stabilisers, that is, the well defined induction period of the peroxide decomposition and the lower post induction period rate of the U.V. absorber. This synergistic action shows that the additives protect each other during thermal processing and U.V. exposure and hence lengthen the period of their independent but co-operative reaction. Table 3.13 and Figures 3.25 & 3.26 show that the synergistic effect varies with the molar ratio of the two types of stabilisers at a constant total concentration. Higher synergism is observed when the HOBP concentration is increased compared to the nickel complex. This indicates that the protection of the peroxide decomposing agent against photolysis is the major role of the synergist.

Table 3.13 Synergistic Effect of HOBP with Nickel or Copper Dithiophosphonate at 180°C in Polypropylene

		Embrittlement time/hrs		%Synergism*(43)	
Anti-oxidant	Conc	CM 10mins	OM 10mins	CM 10mins	OM 10mins
NiDiBuPn	0.2%	750	900	-	-
	0.3%	1200	1300	-	-
	0.4%	1580	1650	-	-
CuDiBuPn	0.2%	630	760	-	-
	0.3%	780	850	-	-
	0.4%	880	1000	-	-
HOBP	0.2%	600	300	-	-
	0.3%	890	450	-	-
	0.4%	1250	610	-	-
NiDiBuPn + HOBP					
0.4% + 0.2%		3000	3200	96	99
0.3% + 0.3%		3500	3900	162	188
0.2% + 0.4%		4000	4300	242	294
CuDiBuPn + HOBP					
0.4% + 0.2%		2200	-	141	-
0.3% + 0.3%		3400	-	230	-
0.2% + 0.4%		3800	-	254	-

$$^{*}\ \%\ \text{Synergism} = \frac{[Es - Ec] - [E1 - Ec] + [E2 - Ec]}{[E1 - Ec] + [E2 - Ec]} \times 100$$

where
Es = Embrittlement time of synergist
Ec = Embrittlement time of control
E1 = Embrittlement time of antioxidant 1
E2 = Embrittlement time of antioxidant 2

Figure 3.27 shows that the rate of decay of the combined absorption due to NiDiBuPn and HOBP (curve (c)) is much slower than NiDiBuPn or HOBP alone (curves (a) and (b) respectively). The decay of the characteristic absorption of NiDiBuPn at 325 nm is effectively reduced by the presence of HOBP at equimolar concentrations. The disappearance of NiDiBuPn from the system corresponds to the end of the induction period during carbonyl formation in both cases. The post-induction period rate, however, is much lower when HOBP is present than when it is absent. The slower rate of decay of the synergistic mixture when compared to HOBP used alone suggests that a product formed from the dithiophosphonate must be responsible for the protection of the HOBP. This is certainly due to the removal of the peroxide (by the metal complex) from the system which would otherwise cause the destruction of the HOBP.

On the basis of these results the synergistic action shown by the nickel complex with HOBP may be explained as due to the independent and co-operative action of additives. The mutual protection of the additives thus lengthen the period of their antioxidant activity. The NiDiBuPn therefore protects HOBP from destruction by peroxides during processing and U.V. exposure. In turn HOBP may protect the nickel complex from photolytic destruction both by the screening of U.V. light and by removing photo-excited reactive species from the dithiophosphonates during irradiation.

3.2.3 (e) Colour Development in Cobalt and Nickel Dithiophosphonates

The colour an additive produces in the polymer is of vital importance commercially. Ideally, the processed polymer should be colourless so manufacturers can add any pigment to achieve any colour they require.

The results found for nickel and cobalt dithiophosphonates after processing with polypropylene are shown in Table 3.14. The 2-EH dithiophosphonate analogues in both cases gave similar results.

Table 3.14 Colour of Nickel and Cobalt Dithiophosphonates Polymer after Processing at Various Time in a Torque Rheometer at 180°C

<table>
<tr><th></th><th colspan="2">NiDiBuPn</th><th colspan="2">CoDiBuPn</th></tr>
<tr><th>Processing time mins</th><th>CM</th><th>OM</th><th>CM</th><th>OM</th></tr>
<tr><td>0 (initial)</td><td>Purple</td><td>Purple</td><td>Orange</td><td>Orange</td></tr>
<tr><td>10</td><td>Pale Purple</td><td>Pale Purple</td><td>Green</td><td>Blue</td></tr>
<tr><td>20</td><td>Green/Black</td><td>Pale Purple</td><td colspan="2">Dark Green</td></tr>
<tr><td>30</td><td>Black</td><td>Pale Purple</td><td colspan="2">Dark Green</td></tr>
</table>

Non uniform films were produced on pressing polypropylene films containing cobalt or nickel dithiophosphonate ie. with patchy dark and light areas. However, the oxidatively (OM) processed samples produced slightly more uniform and paler films than those processed under restricted oxygen (CM). U.V. absorption spectra of NiDiBuPn processed under CM conditions **produced** a lower characteristic λ_{max} 325 nm peak than the OM sample at the same concentration Similarly, when two different areas (light and dark) of the same film were examined a clear peak (λ_{max} 325nm) was observed in the lighter area (Figure 3.28 (a)) whereas it was difficult to detect in the dark area (Figure 3.28 (b)). When the photostability of the coloured films were examined a remarkable difference was observed. This is illustrated in Figure 3.29, which clearly shows that oxidatively processed samples exhibited enhanced activity probably because those films were more uniform and less coloured than films produced under restricted oxygen (CM).

During processing under restricted oxygen (CM) as the processing time is increased the NiDiBuPn samples get darker in colour, whereas no large colour difference was observed after oxidative processing (OM) (see Table 3.14). All samples, however, (CM and OM) produced non-uniform films though CM films were darker and inferior to the OM films.

To compare the amount of NiDiBuPn detectable after processing in CM and OM, extraction studies (Section 2.3) were carried out using chloroform as solvent under a blanket of nitrogen. The samples processed for thirty minutes were selected, because under these conditions CM processing gave a black polymer whereas OM gives a pink polymer. The U.V. absorption spectrum of each extract is shown in Figure 3.30

which shows that the samples processed under restricted oxygen (CM) had a much lower NiDiBuPn peak (λ_{max} 325 nm) intensity. This illustrates that the blackening effect observed is caused by destruction of some of the original nickel complex. The same colour of processed polymer (fleshy pink/brown) was observed after extraction of both polymer samples (CM and OM) which indicates that the substance causing the blackening effect was extracted.

It was thought that the darkening and non-uniformity of the films may be due to a temperature effect during processing and pressing. Hence, low density polyethylene was selected as it is processed and pressed at a lower temperature and in addition it is a less readily oxidised polymer. The resulting films were of better quality than those processed with polypropylene but were still non-uniform and had dark and light patchy areas.

Attempts were made to change the mode of pressing to try and improve the quality of the films. The initial pressing method for all films was a cycle of one and a half minutes pre-heating and one and a half minutes at full pressure and temperature. The optimised pressing cycle was found to be one and a half minutes pre-heating after which the platens were cooled under full pressure (see Section 2.2.3). This method for pressing improved the colour of the films dramatically. The nickel (iBu) and (2-EH) dithiophosphonates all produced colourless films irrespective of their processing history. The cobalt films, however, only improved slightly, they were still coloured and had areas of dark green. The photo-stability of the nickel and cobalt complexes were again examined after modification of the pressing method and compared with the results for the previous pressing method. The results are shown in Table 3.15.

Table 3.15 Embrittlement Times of Nickel and Cobalt (iBu) dithiophosphonates processed in PP under different Pressing conditions

	Embrittlement time (hrs)			
Additive (0.4%)	Original method		Modified method	
	CM 10mins	OM 10mins	CM 10mins	OM 10mins
NiDiBuPn	450	1480	1560	1650
CoDiBuPn	320	410	450	790

An increase in the photostability of the NiDiBuPn processed under restricted oxygen (CM) was observed after modification of the method of pressing, whereas the change was not as apparent in oxidatively processed (OM) samples. This is because samples processed in excess air (OM) and pressed by the first method were all ready more uniform and less coloured with the light area of the film taken for analysis. Samples processed under restricted oxygen (CM), however, had extremely poor films at first but after modification of the pressing method the films improved dramatically. Additionally the films that had been oxidatively processed (OM) were less coloured and hence a better photostability was exhibited by these samples (see Table 3.15). Polypropylene was extruded (Section 2.2.2) with cobalt and nickel dithiophosphonate to see if a change in the processing technique would effect the colour of the polymer. Both complexes produced black extrudates.

Other methods to reduce the blackening effect included the processing of polypropylene with NiDiBuPn and tertiary butyl hydroperoxide (TBH) and the nickel complex with triphenyl phosphite ester. Each were processed for thirty minutes under restricted oxygen (CM) as these were the conditions which produced the darkest films.

It is well known [22,23] that the formation of peroxides is high when the polymer is processed for a longer time and under excess air (OM). Thus, it was thought that these peroxides may be playing a role in reducing the colour of the OM samples compared to the CM conditions. Hence TBH was added during processing but the resulting polymer was still found to be black.

The only case where the addition of nickel dithiophosphonate (0.4%) to polypropylene was successful (CM 30 mins) was when triphenyl phosphite ester was added at a ratio of 1:10 (phosphite:nickel). Aromatic and alkyl aromatic phosphites have been shown to preserve the original colour of the polymer under the conditions of their processing and use. This is thought to be closely related to the ability of the phosphites to inhibit the initiation and propagation steps in polymer degradation. They decompose hydroperoxides thereby depressing degenerated chain branching and by reaction with peroxyl radicals (44). In addition they are able to complex catalytic mixtures of metals of variable valency and to block weak links in polymer chains. It has been shown that aromatic phosphites have the ability to form a co-ordination complex with transition metal (including nickel) acetyl acetonates in polypropylene (44). Thus in our studies during processing of the nickel dithiophosphonate and phenyl phosphite ester a co-ordinated nickel complex may be forming which is more stable than the original compound and hence no blackening of the polymer is observed.

3.2.3 (f) Effect of U.V. Irradiation on I.R. Characteristic Absorption Bands of NiDiBuPn

The Perkin Elmer FT-IR spectrophotometer was used to follow changes in the characteristic absorption bands of the Ni DiBuPn during irradiation of the polypropylene (PP) films containing high concentrations of the additives (2.5% master batches). It has been previously reported (29) that the overall photostabilising activity of PP films containing metal complexes is directly related to the decay of the characteristic absorption bands of the additive. Figure 3.31 compares portions of the I.R. spectrum of PP films containing both the copper (CuDiBuPn) and nickel NiDiBuPn dithiophosphonates. It is seen clearly that the major characteristic absorption bands such as the phenolic OH group (3635 cm^{-1}), P=S (643 cm^{-1}), M-S-P (576 cm^{-1}) and M-S (354 cm^{-1}) are of much higher intensity for the PP films stabilised with NiDiBuPn compared with CuDiBuPn. This is even more interesting since both are compared on a weight basis, which should have resulted in a much higher concentration of the copper complex in view of its lower molecular weight. It is therefore not surprising that as shown previously (Figures 3.12 and 3.13) the photo-oxidative stability of PP films containing NiDiBuPn is superior to similar samples containing CuDiBuPn on molar and weight basis. The fact that the I.R. absorption intensity of bands due to the additive is much higher for NiDiBuPn as compared to CuDiBuPn suggests that the copper complex is more susceptible to thermal decomposition during processing. Thus, a comparatively lower amount of CuDiBuPn is left undecomposed after processing and this in turn appears to be related to the photo-oxidative stability of the film.

This relationship between the I.R. absorption intensity of the major characteristic bands present in the polymer film after processing and the photo-antioxidant activity of the stabilised PP films is also true for NiDiBuPn samples processed under both open mixing (OM) and close mixing (CM) conditions. The results obtained indicate that the initial I.R. absorption intensities of all the major bands are higher for the oxidatively processed (OM) master batch (Figure 3.32) and thus the decay of these bands during photo-oxidation is slower than a similar master batch processed under restricted air conditions (cf. Figures 3.33 (a) and (b)). This is shown clearly for the phenolic OH group (Figures 3.34 (a)) and the metal sulphur bands (Figure 3.34 (b)) which are directly related to the rate of formation of carbonyl species (Figure 3.34 (a)) and polymer unsaturation (Figure 3.34 (b)).

It is also of great interest to monitor the formation of any intermediate products during U.V. irradiation of the master batch films. A comparison of Figures 3.33 (a) and (b) clearly indicate the formation of a new absorption band (665 cm^{-1}) after 700 hours. This absorption band is believed to arise from the P=S vibrational modes of an intermediate product, probably an ester of the type observed during the oxidation studies on NiDiBuPn and TBH (Chapter 4 Section 4.2.3.2). During U.V. irradiation of the master batch films this new band is seen to increase gradually and then reduce after passing through a maxima. This phenomena is similar for samples processed under both close mixer and open mixer conditions, although the rates at which this product is formed is higher for the sample processed under limited air (CM). This is illustrated in Figure 3.34 (c) which not only shows that the rate of decay of the P=S band due to the antioxidant (643 cm^{-1}) is slower for the oxidatively processed sample but also clearly indicates that the rate of formation of the P=S vibrational mode of the intermediate product (665 cm^{-1}) is equally slower. The P=S stretching vibration in various dithiophosphorus esters of the type $(RO)_2P(S)SR$ and $(RO)_2P(S)Ar$ have been reported (45) to show high intensity absorption in the region of 670 - 656 cm^{-1}, while a frequency range (P=S) of 668 - 625 cm^{-1} is suggested for the free acids $(RO)_2PSSH$ and their metal salts. This suggests that the rate of decomposition of the antioxidant during processing is higher under limited amounts of air in view of the higher rate of shear involved when compared to oxidative processing. Consequently, the concentration of antioxidant remaining after processing is higher for oxidatively processed master batches and this accounts for the higher intensity of the characteristic bands of the nickel complex.

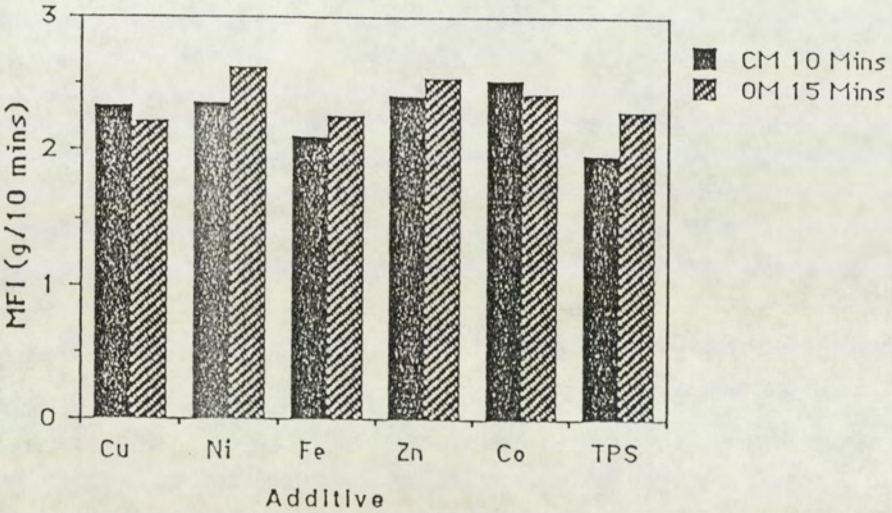


Figure 3.1 Effect of CM and OM processing on MFI of PP containing various DRPn's ($5x10^{-4}$ mol/100g)

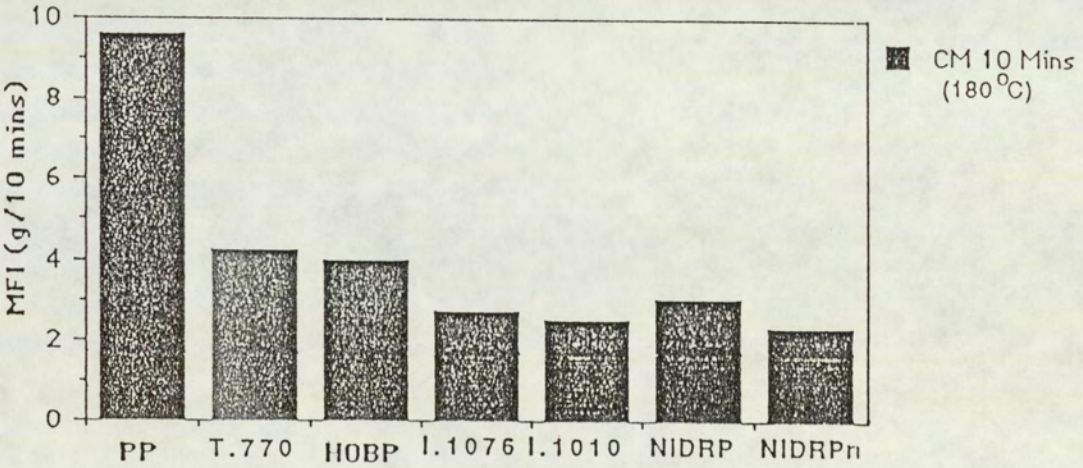


Figure 3.2 Comparison of the MFI (230^{O}C) values of various controls with NiDiBuPn (all at 0.4% conc.) in PP

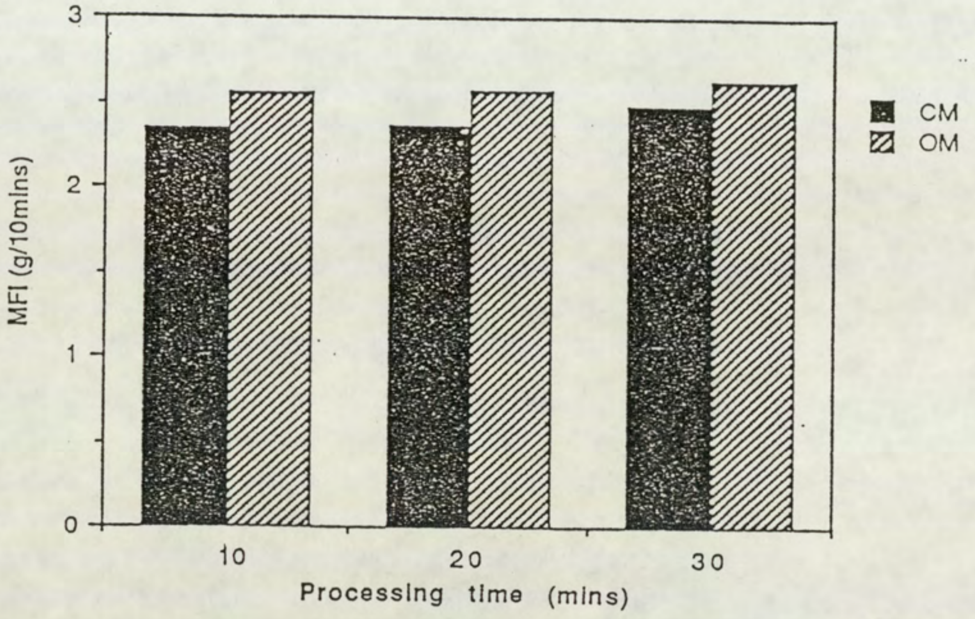


Figure 3.3 Effect of Processing conditions (CM, OM, time) on the MFI of PP containing NiDiBuPn (5×10^{-4} mol/100g)

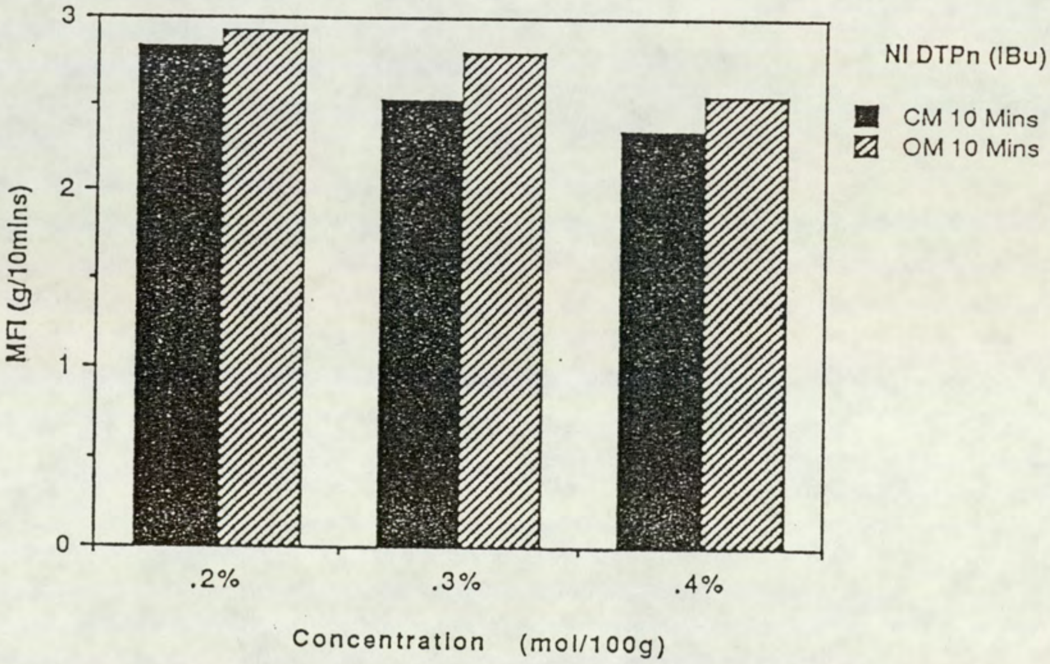


Figure 3.4 Variation of MFI with change in NiDiBuPn (in PP) concentration

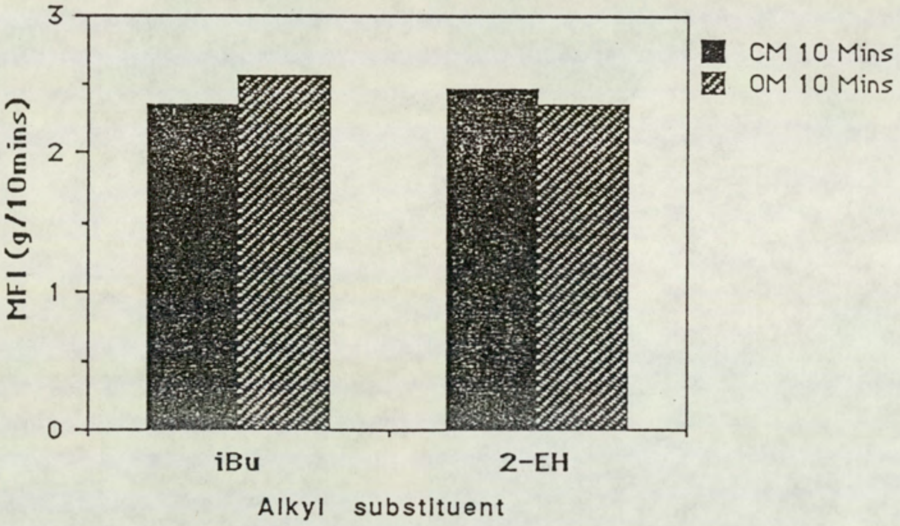


Figure 3.5 Effect of alkyl substituent on the MFI values of NiDRPn ($5x10^{-4}$mol/100g) in PP

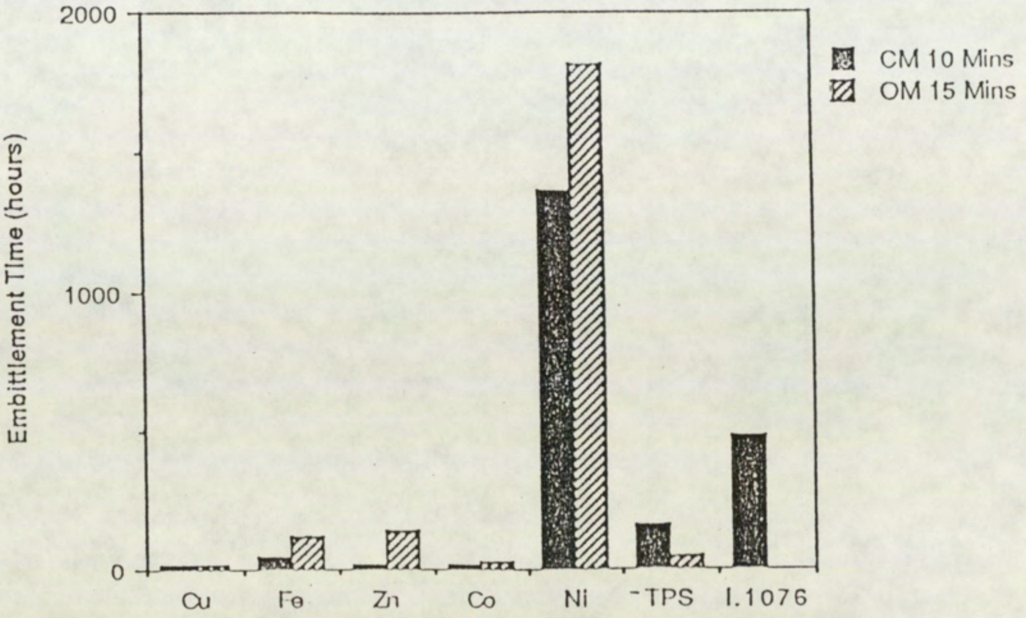


Figure 3.6 Comparison of Irganox 1076 with Dithiophosphates (0.4%) during oven ageing at 140^{O}C

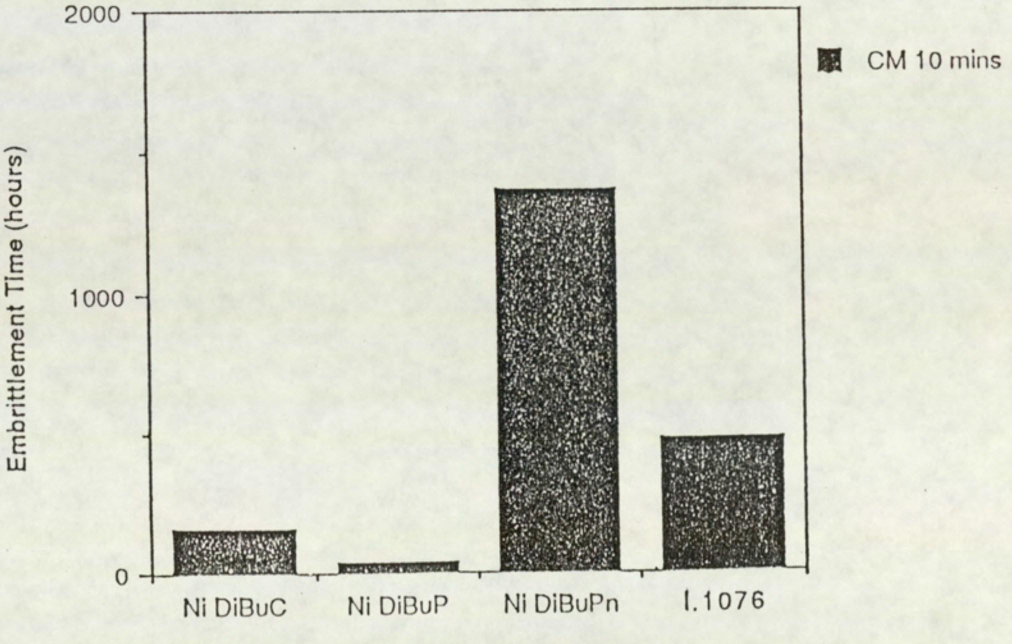


Figure 3.7 Comparison of NiDiBuPn and various controls (0.4%) during oven ageing at 140^{O}C

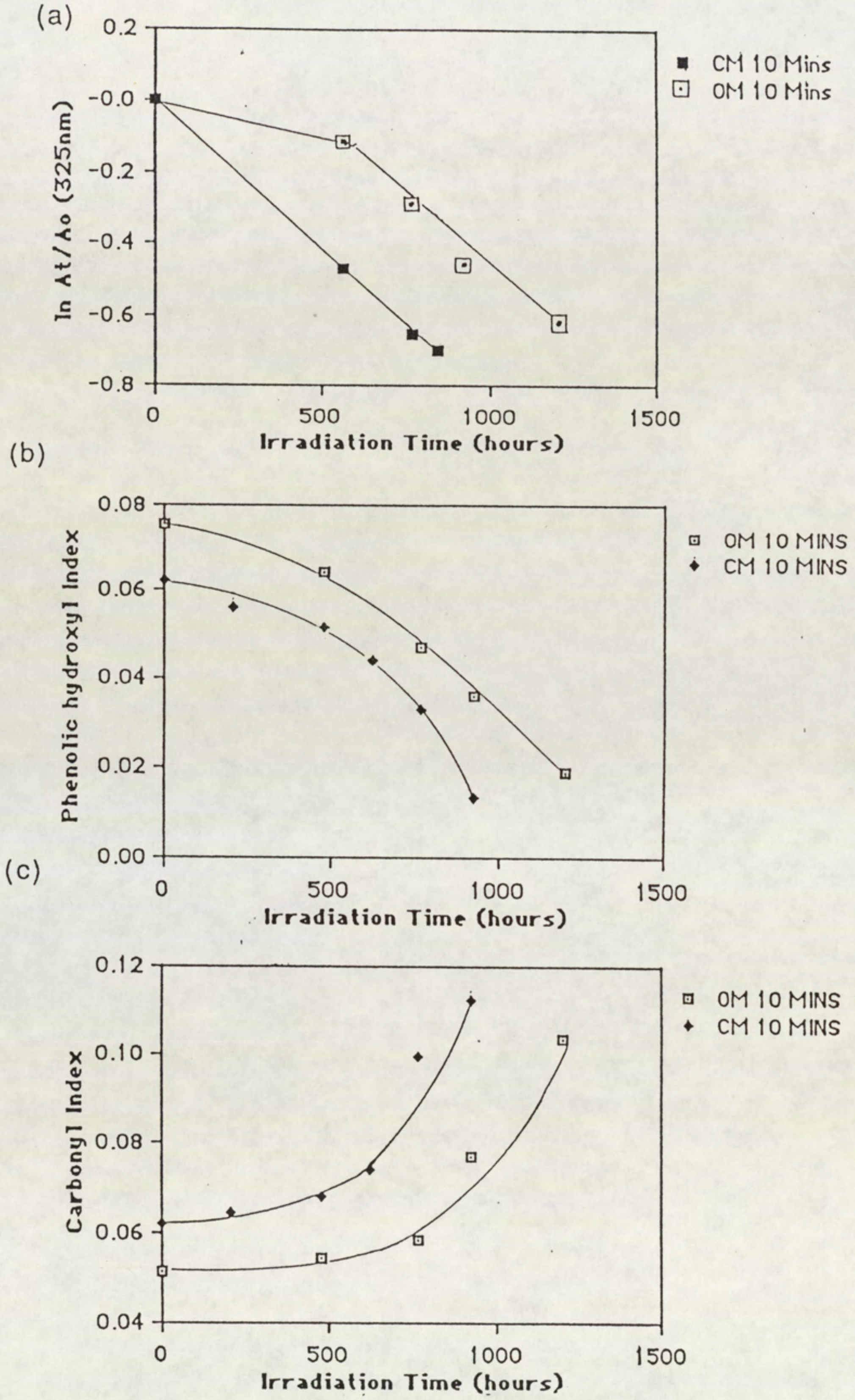


Figure 3.8 IR and UV spectral changes during oven ageing test on NiDiBuPn
(a) Decay of characteristic 325nm absorbtion of NiDiBuPn
(b) Decay of Phenolic hydroxyl of NiDiBu
(c) Carbonyl formation

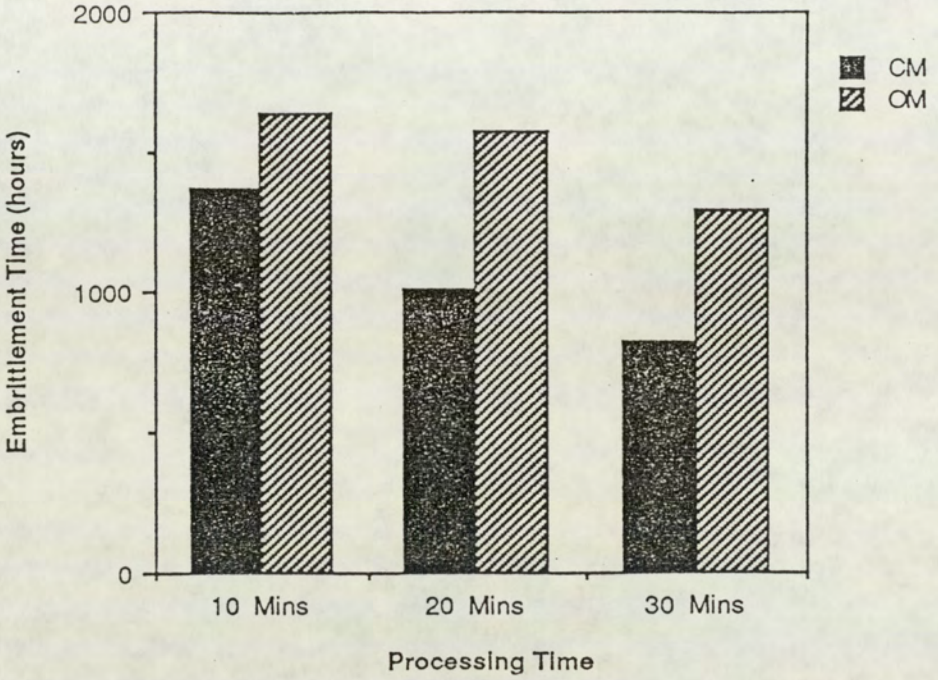


Figure 3.9 Thermal stability of PP containing NiDiBuPn at varying processing time (5×10^{-4}mol/100g)

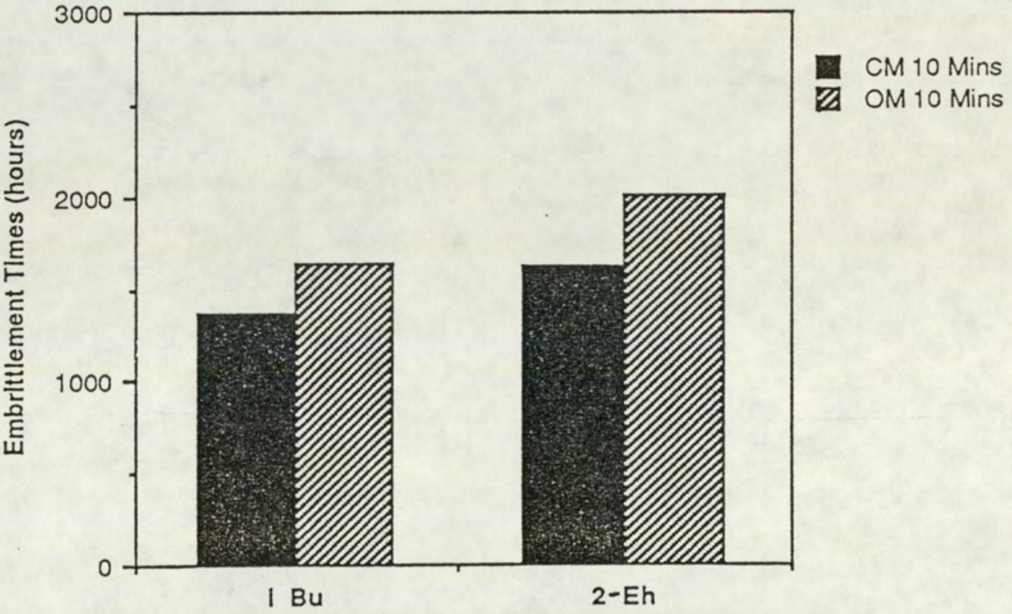


Figure 3.10 Comparison of the Thermal stability of PP containing NiDiBuPn or NiDEhPn (0.4%)

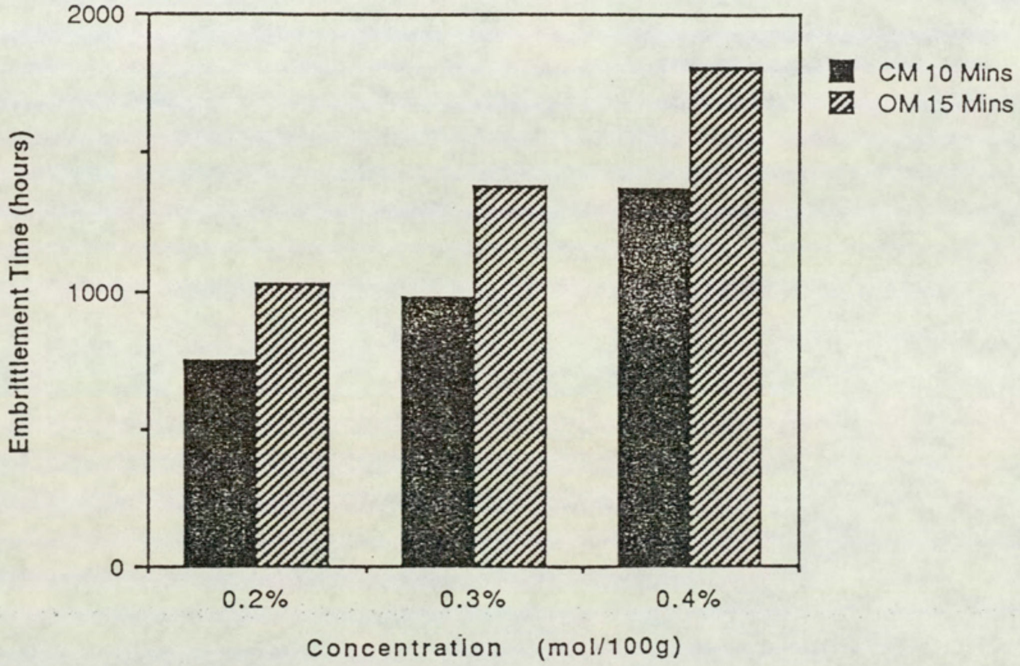


Figure 3.11 Effect of NiDiBuPn concentration in PP during oven ageing at 140°C

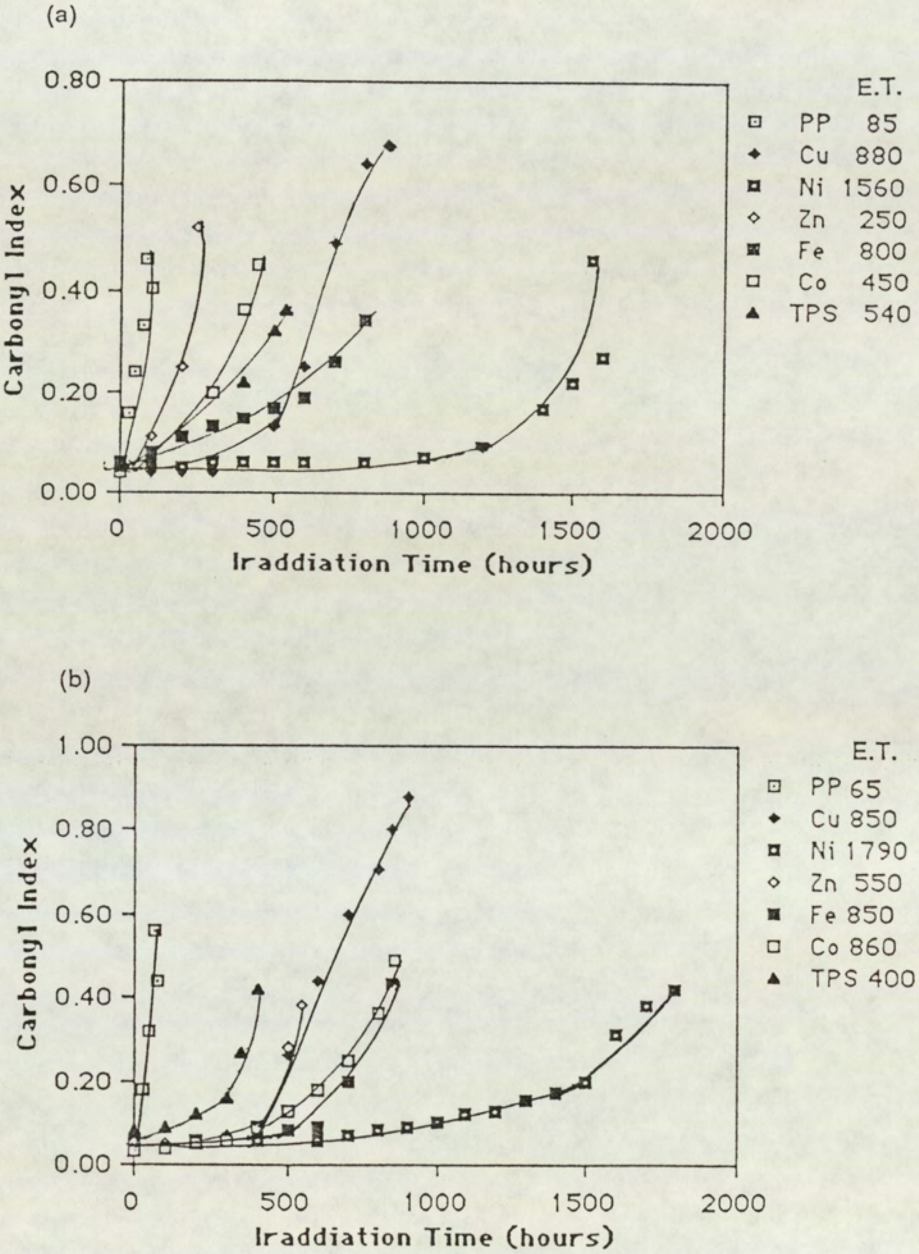


Figure 3.12 Dithiophosphonates as photostabilisers in PP (0.4%) (a) CM 10 mins (b) OM 15 mins

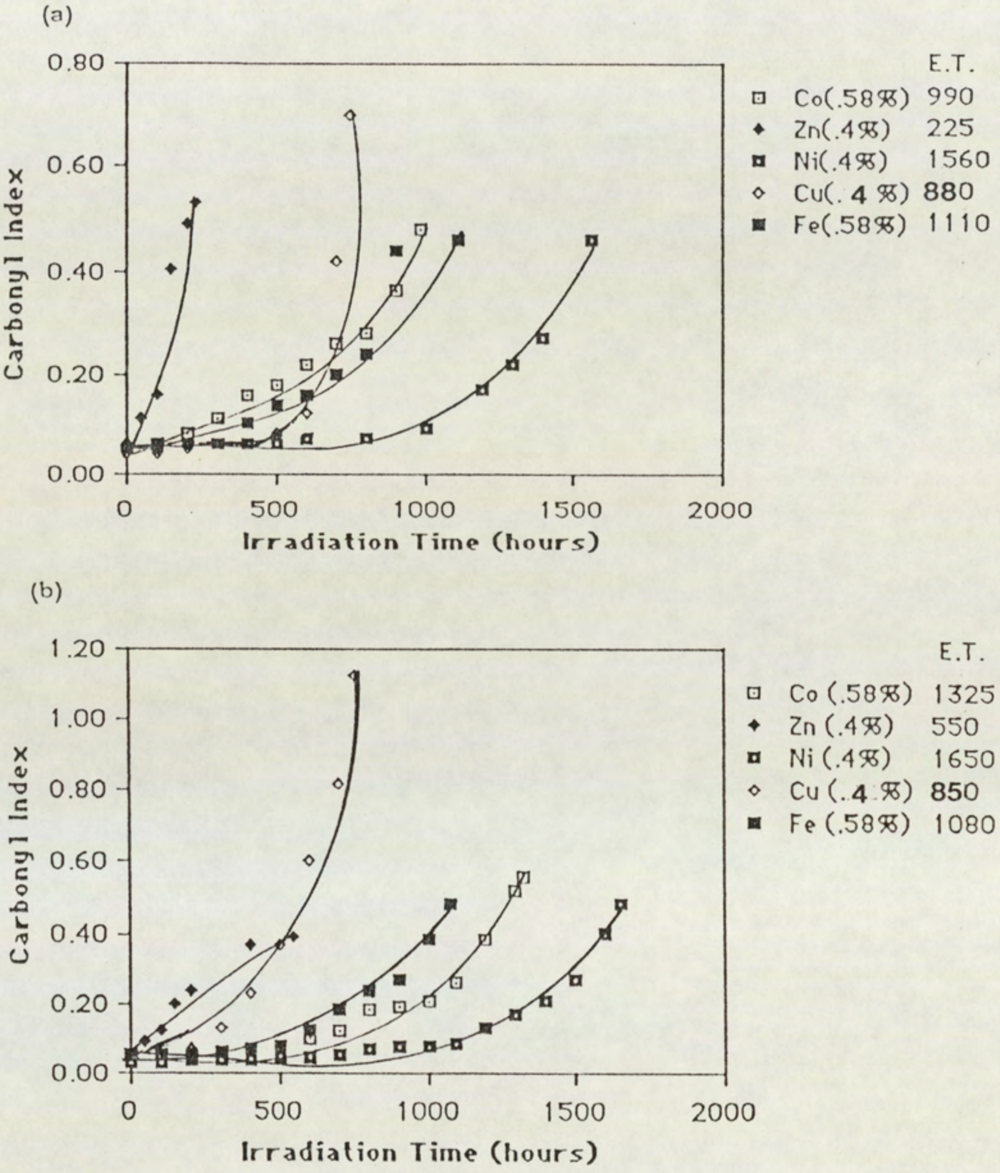


Figure 3.13 Dithiophosphonates ($5x10^{-4}$mol/100g) as photostabilisers in PP (a) CM 10 mins (b) OM 15 mins

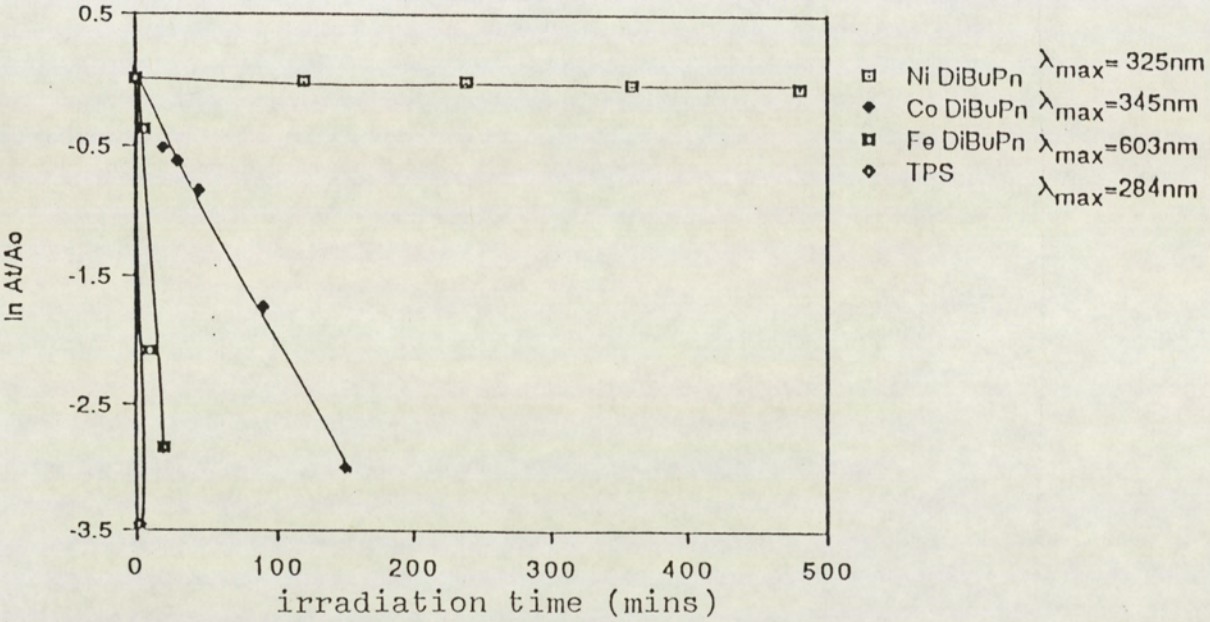


Figure 3.14 Decay of characteristic uv absorbtion bands of various dithiophosphonates in cyclohexane.

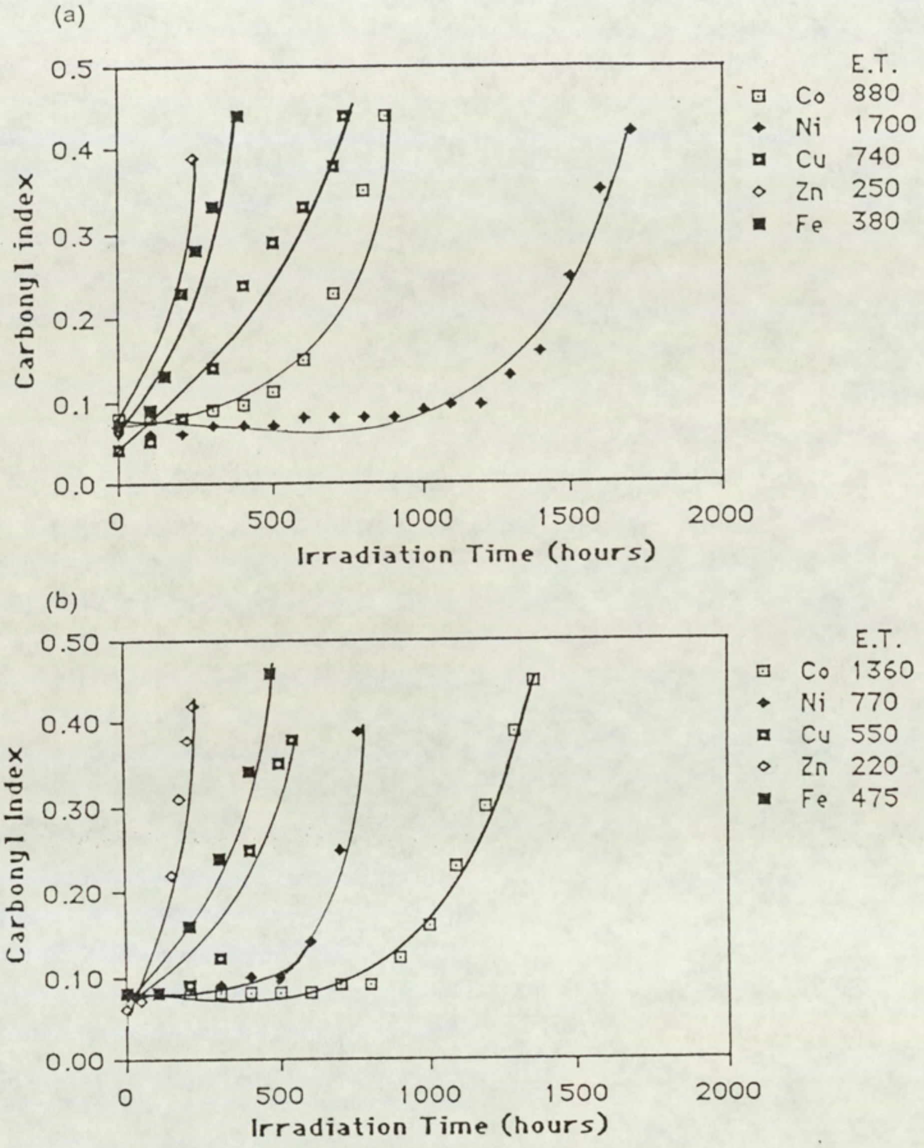


Figure 3.15 Dithiophosphates ($5x10^{-4}$mol/100g) as photostabilisers in PP (a) CM 10 mins (b) OM 10 mins

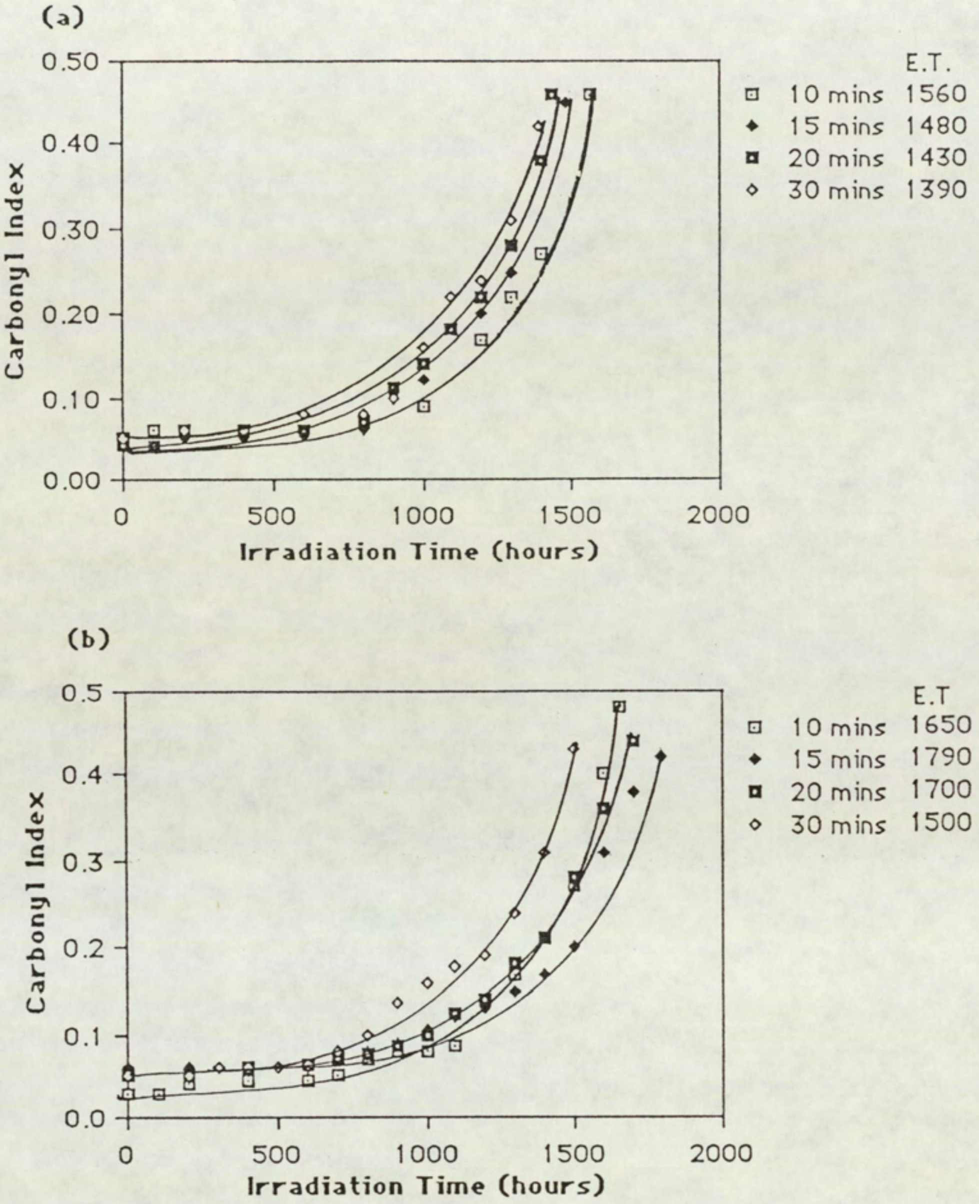


Figure 3.16 Effect of processing time on the photostabilising activity of NiDiBuPn ($5x10^{-4}$mol/100g) in PP (a) CM (b) OM

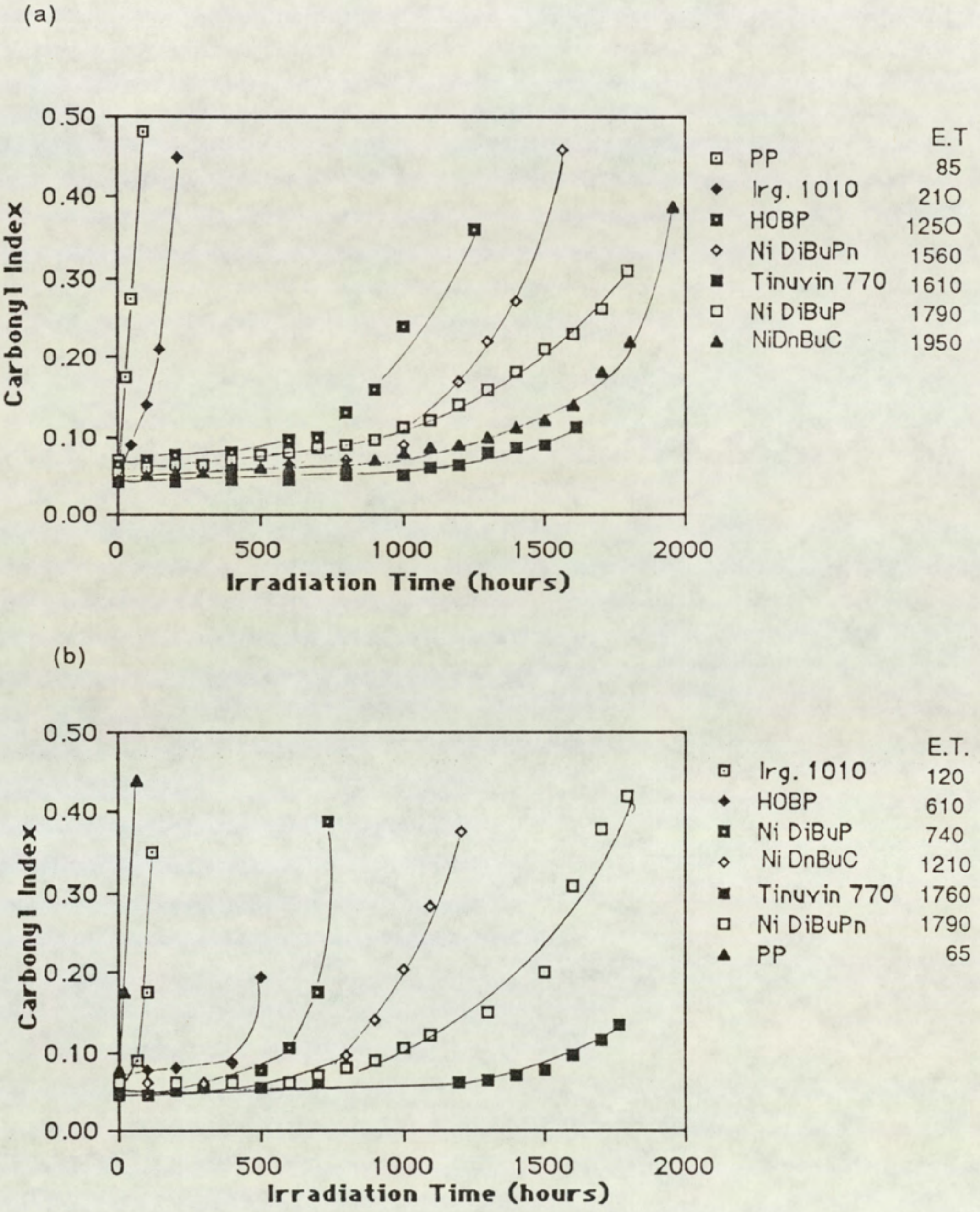


Figure 3.17 Comparison of NiDiBuPn and various controls as photostabilisers (0.4%)in PP (a) CM 10 Mins (b) OM 15 Mins

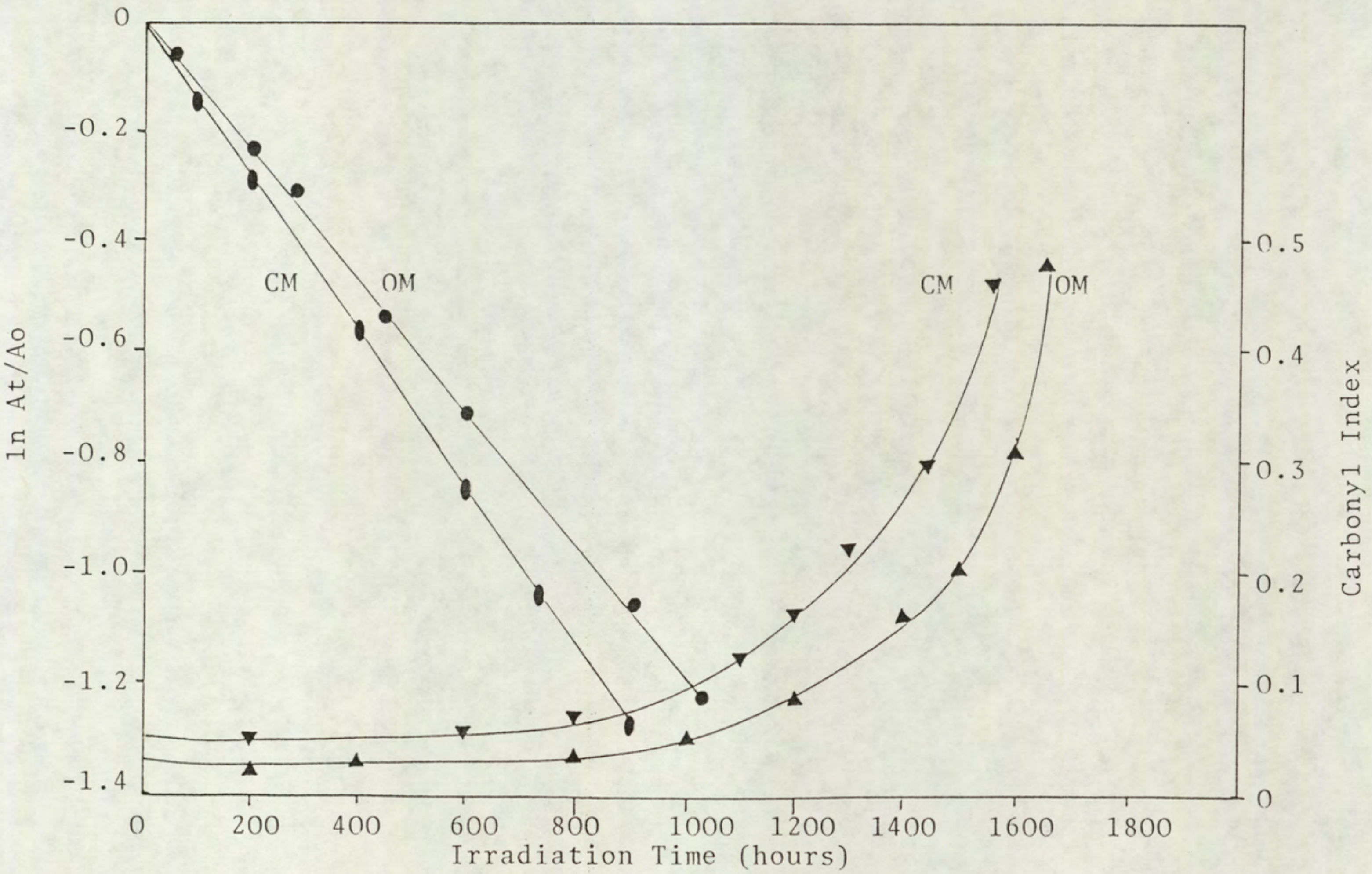
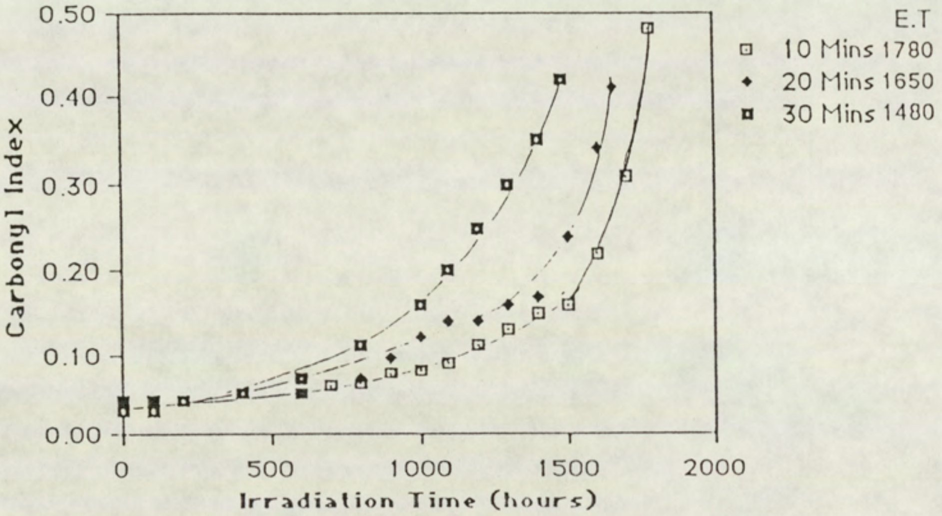


Figure 3.18 Decay of characteristic uv peak (325nm) of NiDiBuPn (0.4%) and the build up in carbonyl (1710 cm^{-1}) of PP during thermal ageing at $140^{o}C$. (CM 10 mins., OM 15 mins.)



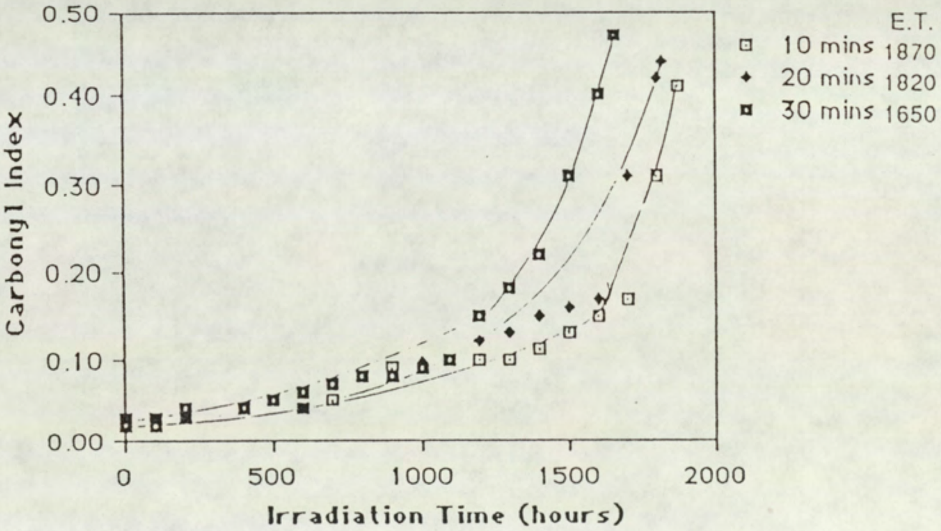


Figure 3.19 Effect of processing time on the photostabilising activity of NiDEhPn ($5x10^{-4}$mol/100g) in PP (a) CM (b) OM

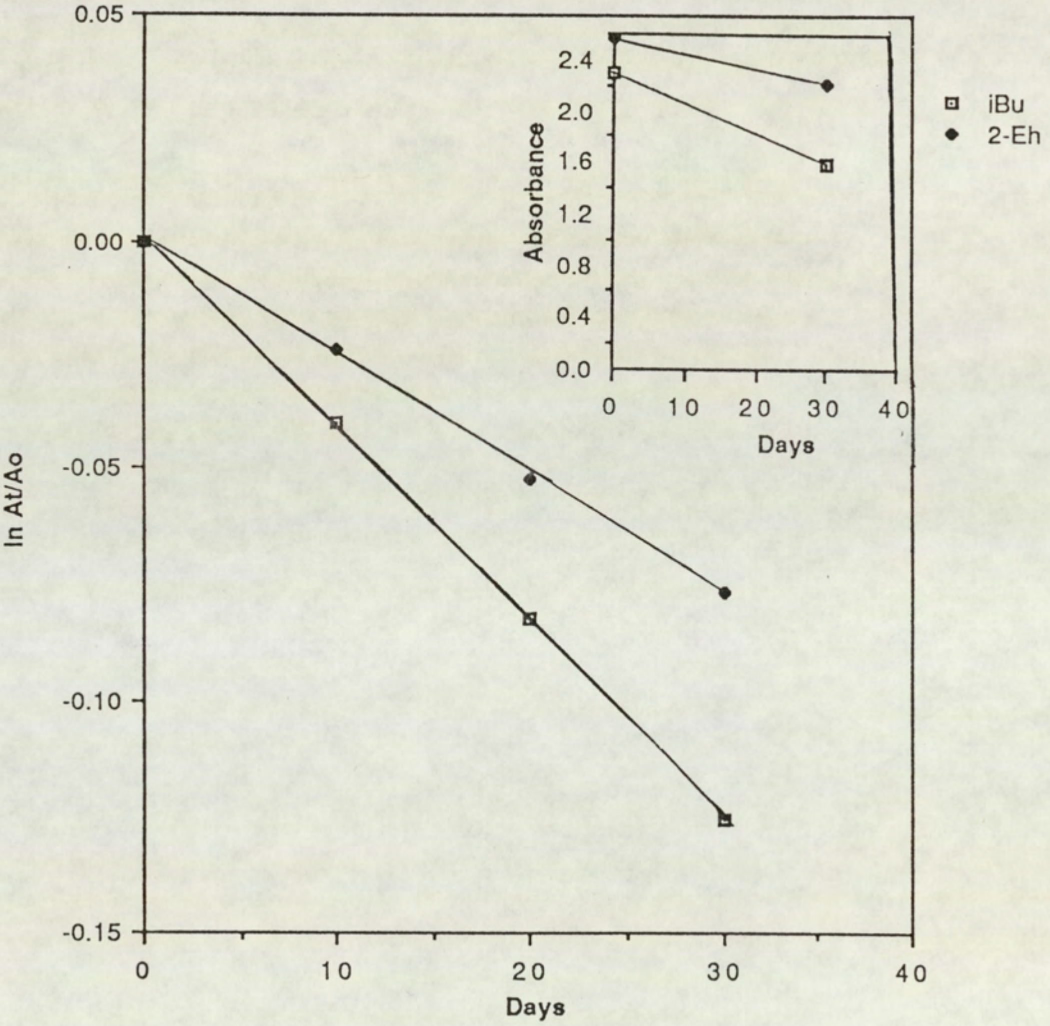


Figure 3.20(a) Blooming of NiDiBuPn and NiDEhPn ($5x10^{-4}$ mol/100g, OM 10mins) in PP.

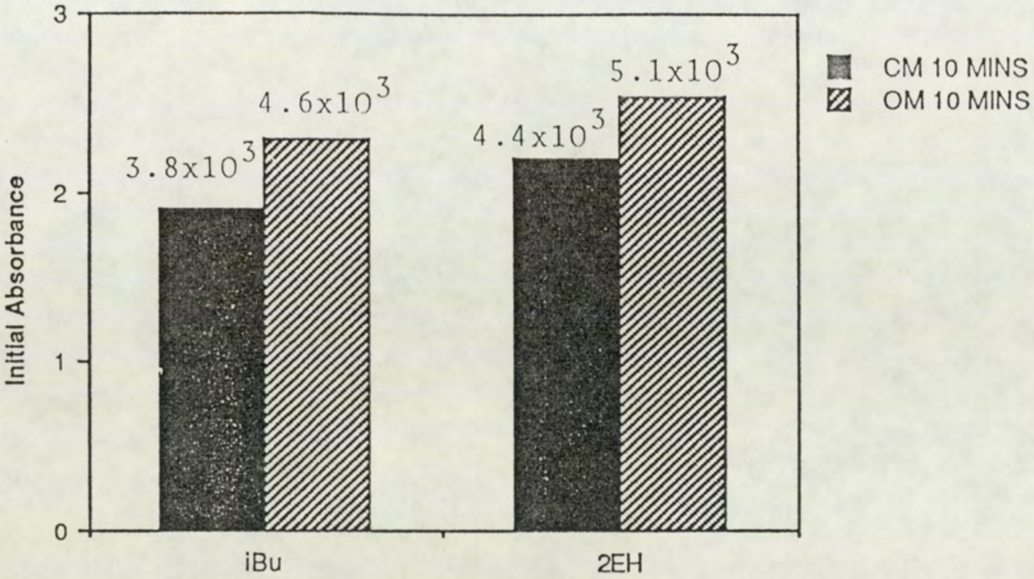


Figure 3.20(b) Initial uv absorbance (λ_{max} 325nm) of NiDiBuPn and NiDEhPn ($5x10^{-4}$mol/100g, CM 10mins). Figures on bars represent ϵ(molar extinction coefficient)

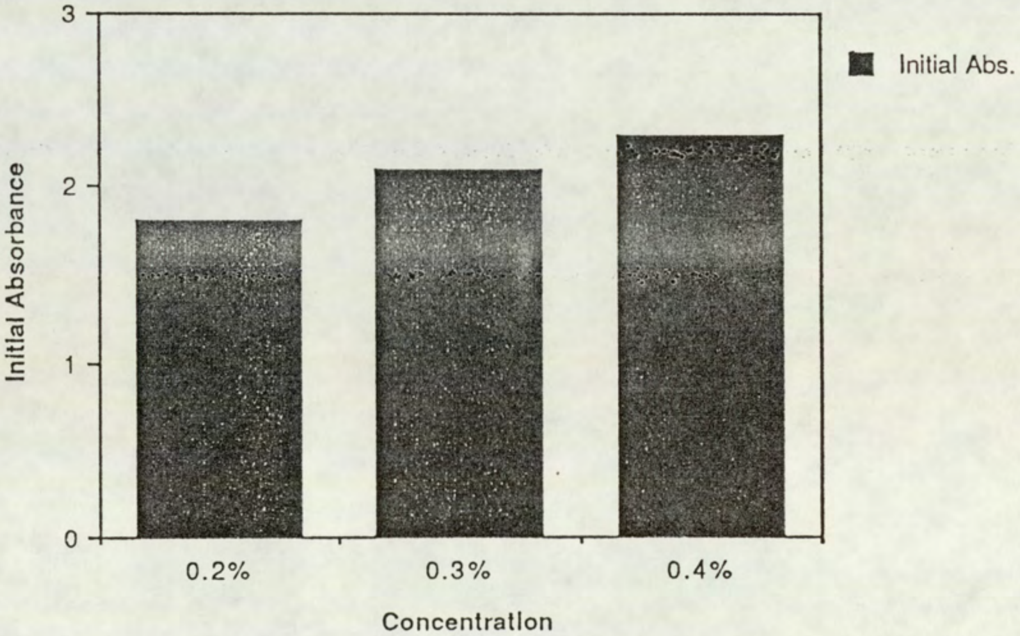


Figure 3.20(c) Effect of concentration on the initial uv absorbance (λ_{max} 325nm) of NiDiBuPn (CM 10mins).

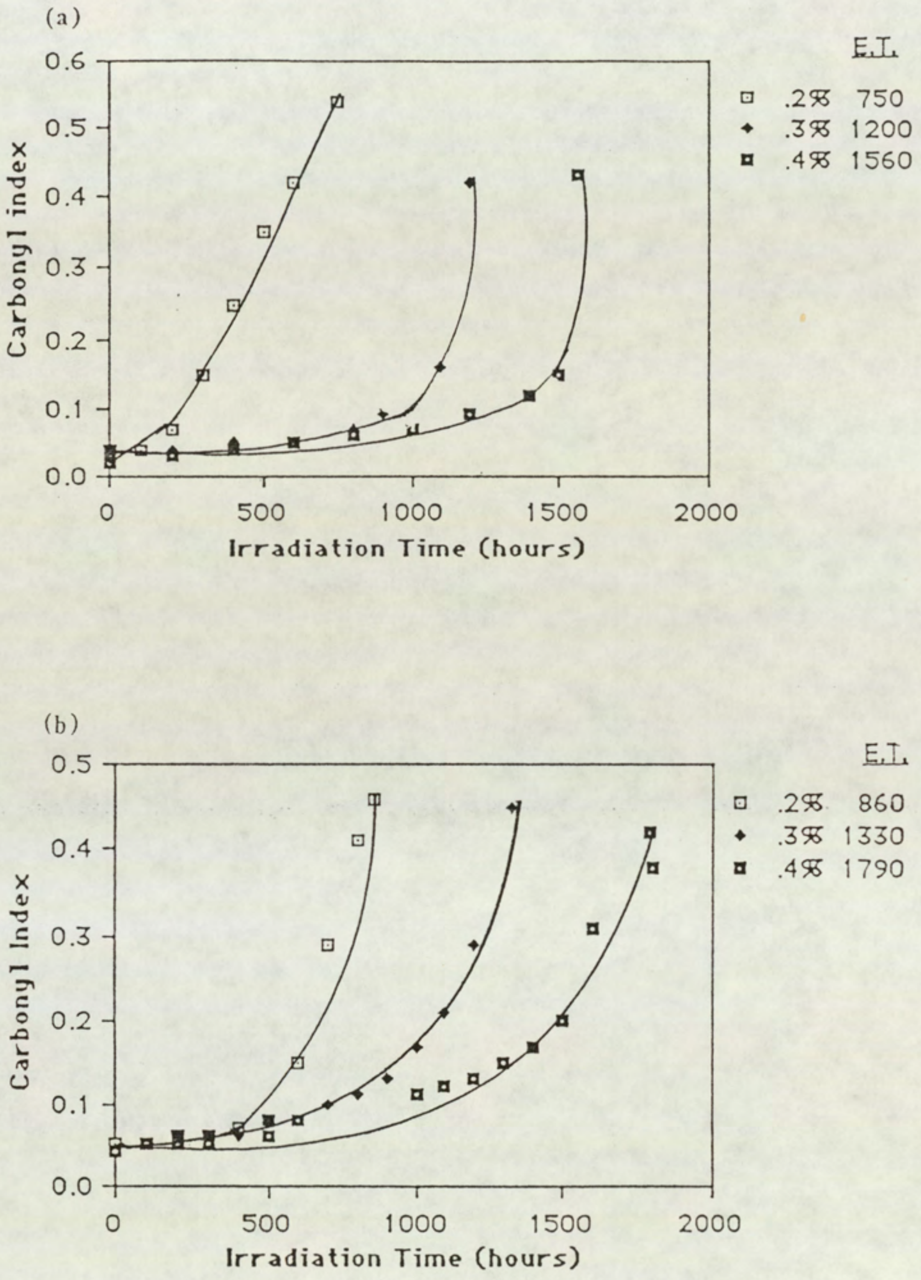


Figure3.21 Variation of photostabilising activity with change in concentration of NiDiBuPn in PP (a) CM 10 mins (b) OM 15 min

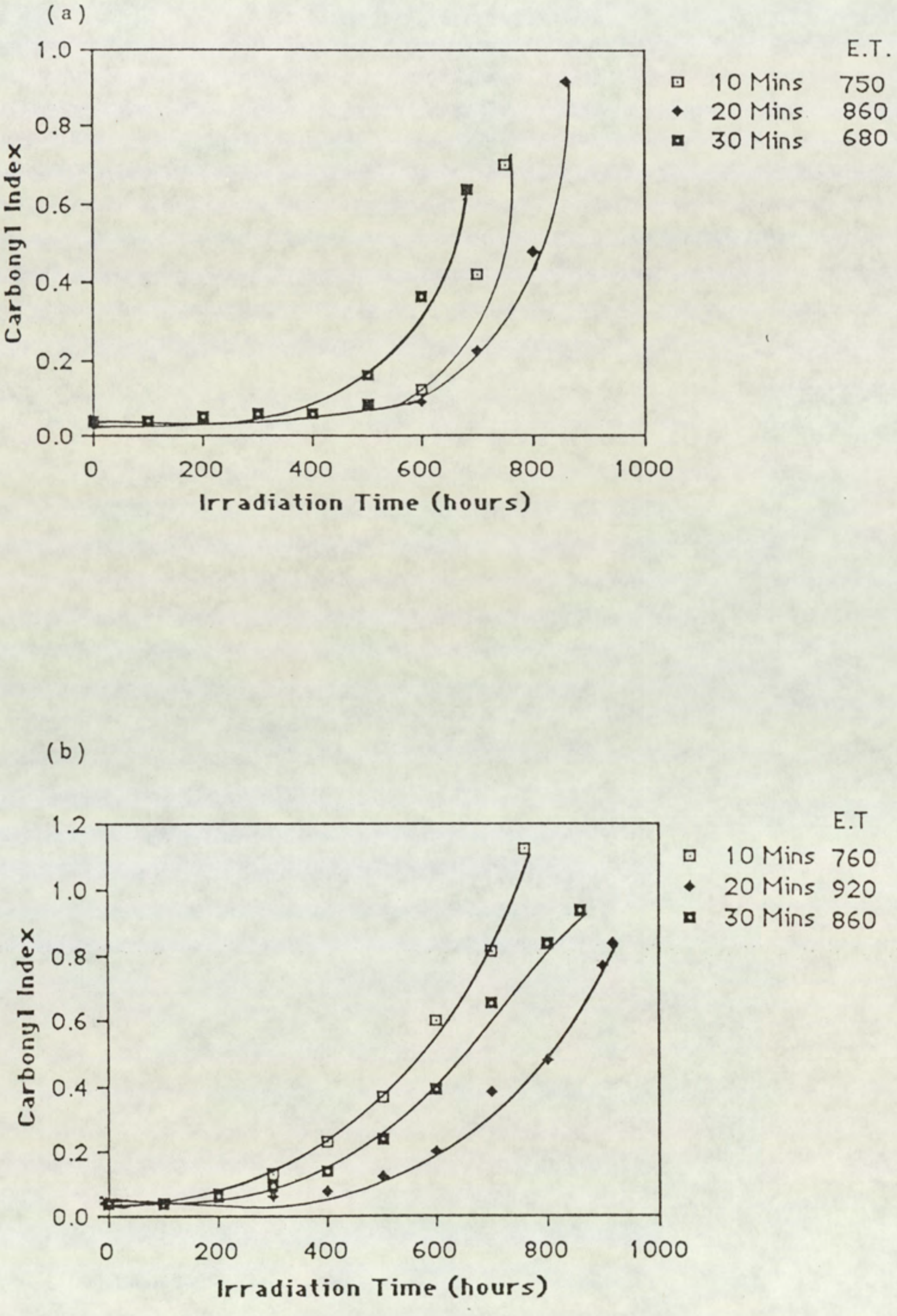
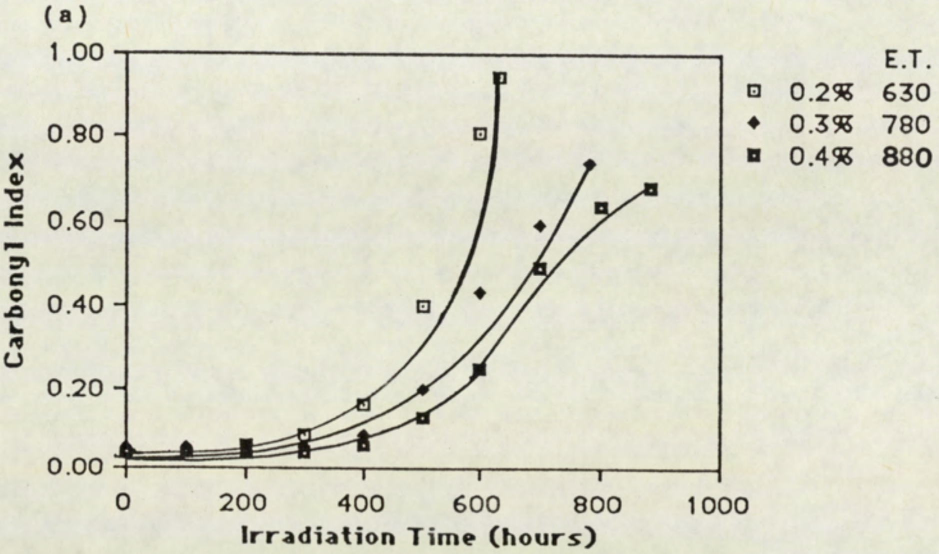


Figure 3.22 Effect of processing time on the photostabilising activity of CuDiBuPn ($5x10^{-4}$ mol/100g) in PP (a) CM (b) OM



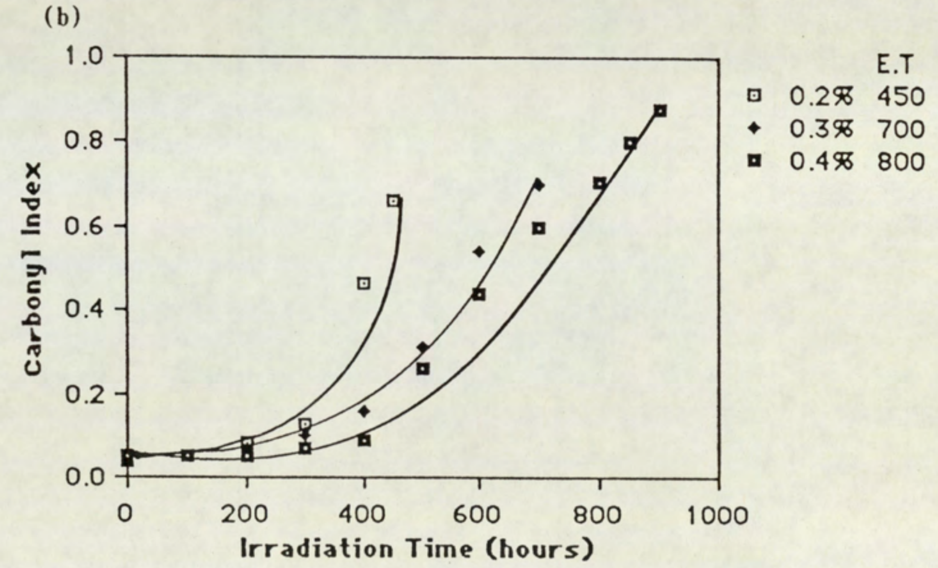


Figure 3.23 Photostabilising activity of CuDiBuPn at various concentration in PP (a) CM 10 mins (b) OM 15 mins

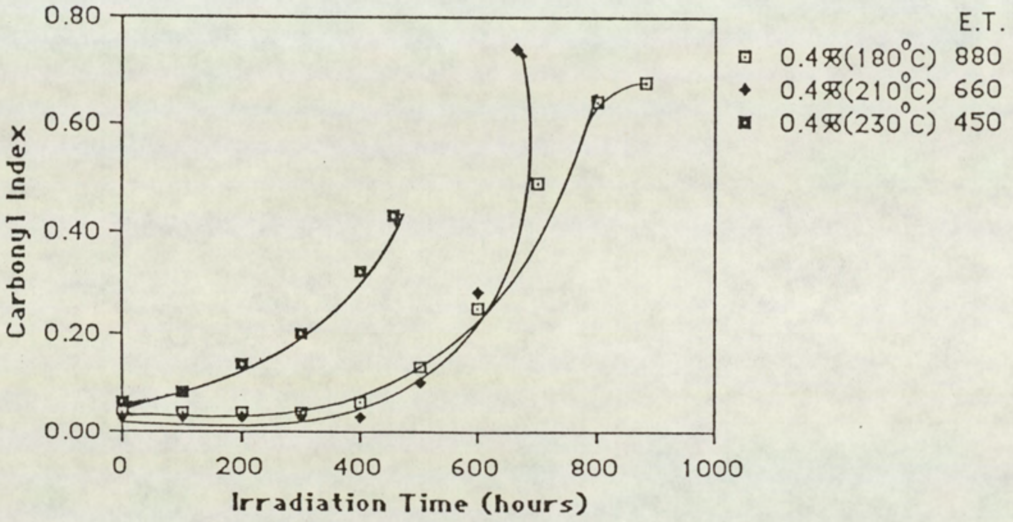


Figure 3.24 Effect of pressing temperature on the photostabilising activity of CuDiBuPn in PP (0.4%, CM 10 mins)

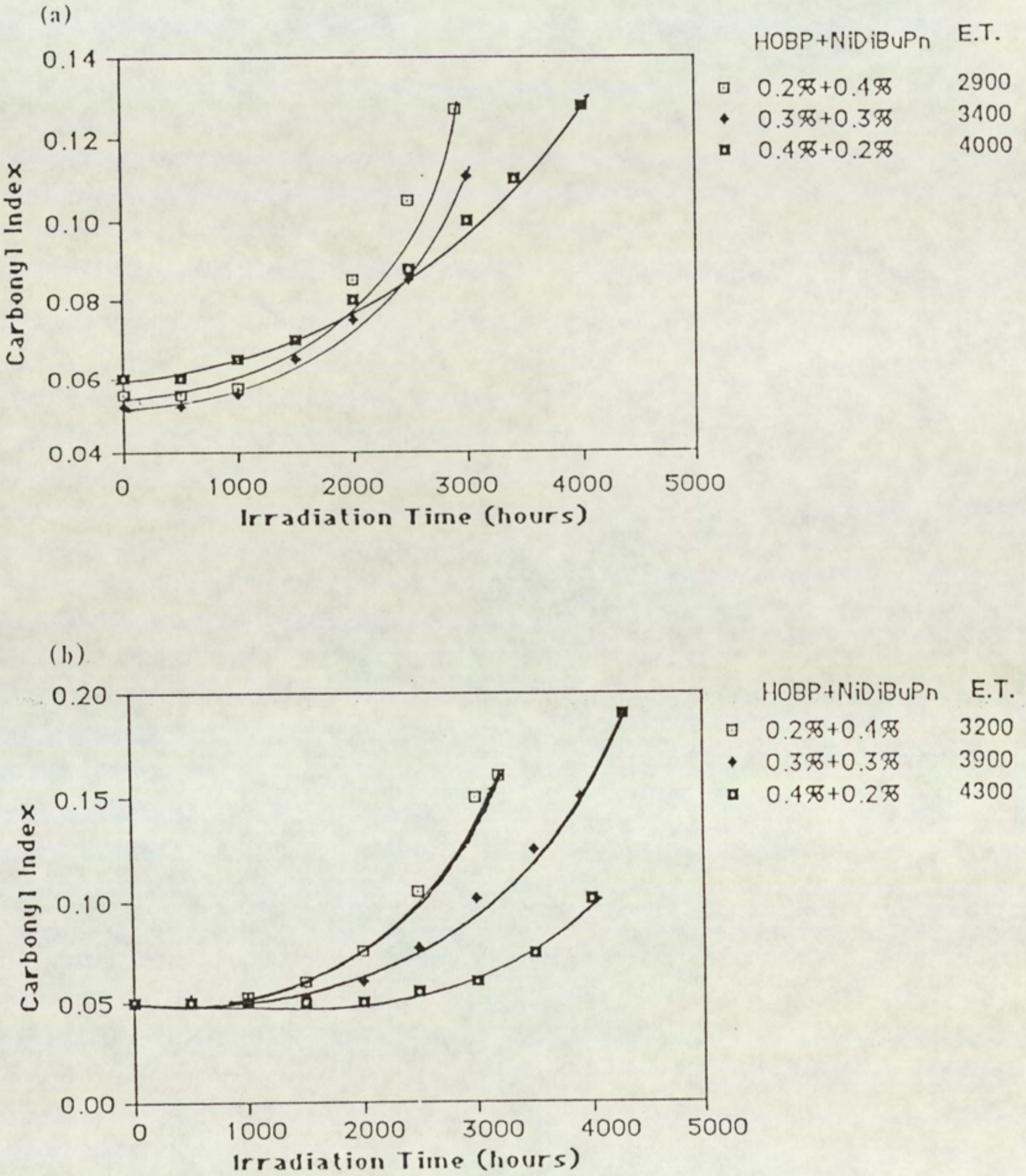


Figure 3.25 Synergistic combinations of NiDiBuPn and HOBP in PP (a) CM 10 mins (b) OM 10mins

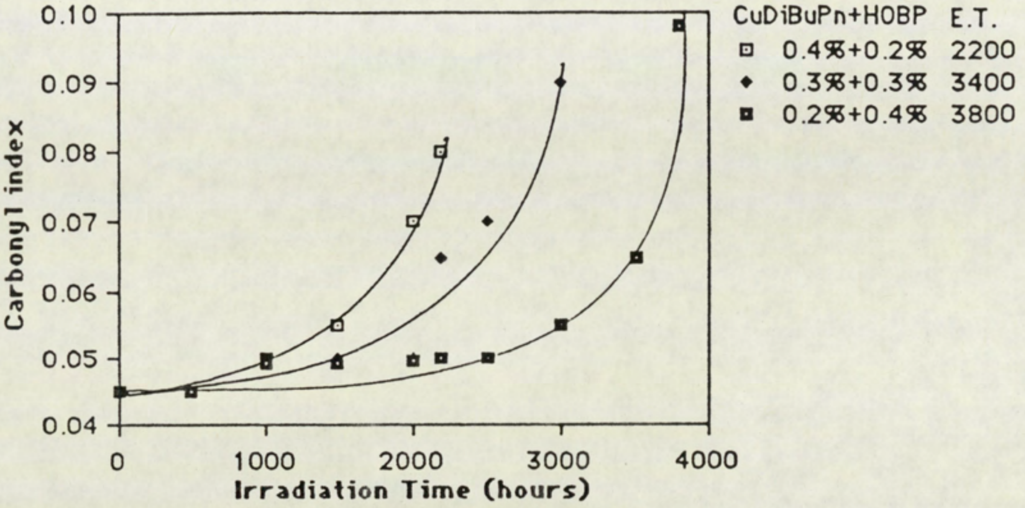


Figure 3.26 Synergistic combinations of CuDiBuPn and HOBP in PP (CM 10 mins)

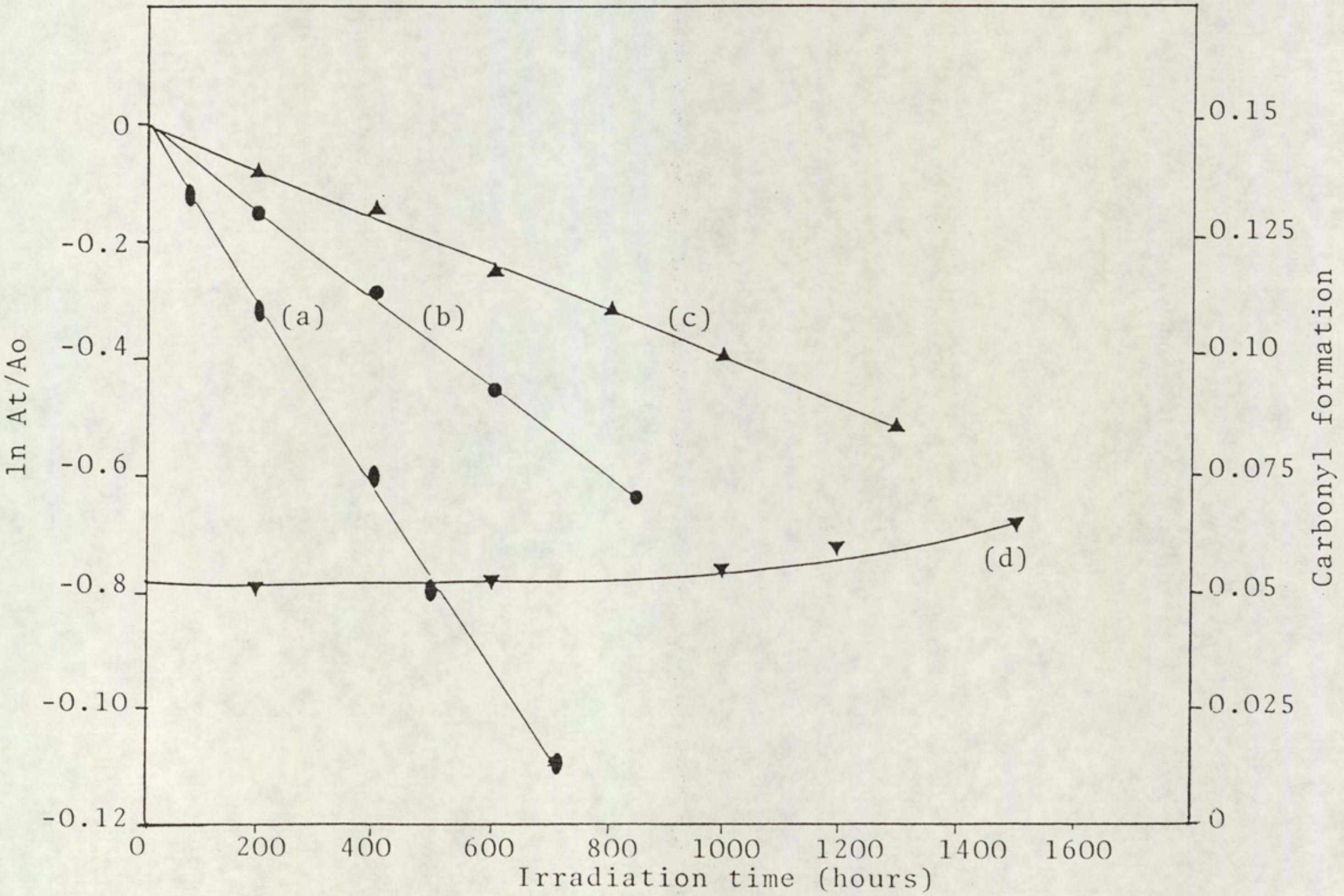
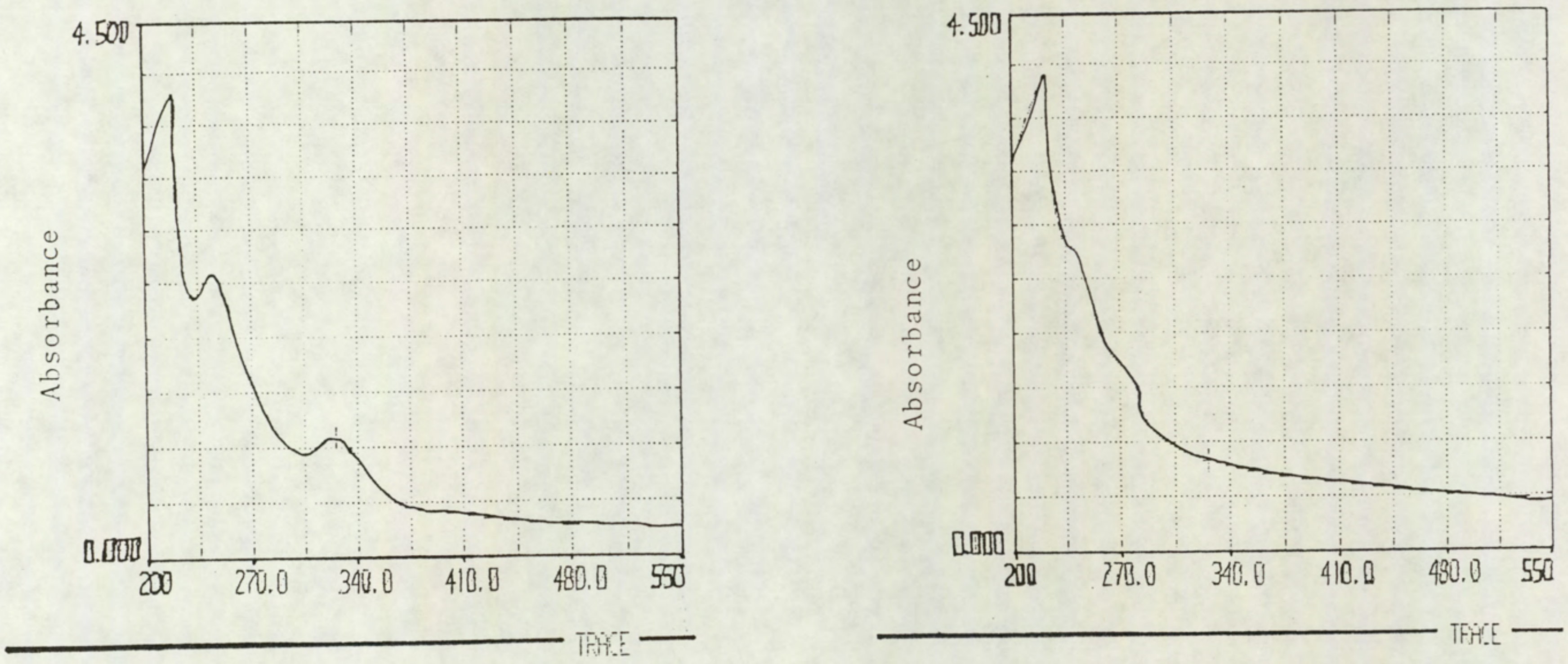


Figure 3.27 Decay of characteristic λ_{max} 325nm peak during uv irradiation of samples processed in PP CM 10 mins (a) NiDiBuPn (b) HOBP (c) NiDiBuPn and HOBP (conc. of each 0.3%). Carbonyl formation in PP containing 0.3% NiDiBuPn and 0.3% HOBP (d)


(a) Light area of film

(b) Dark area of film

Figure 3.28 Comparison of UV spectra of two NiDiBuPn samples taken from the same PP film (processed CM 10 mins, conc. 0.4%)

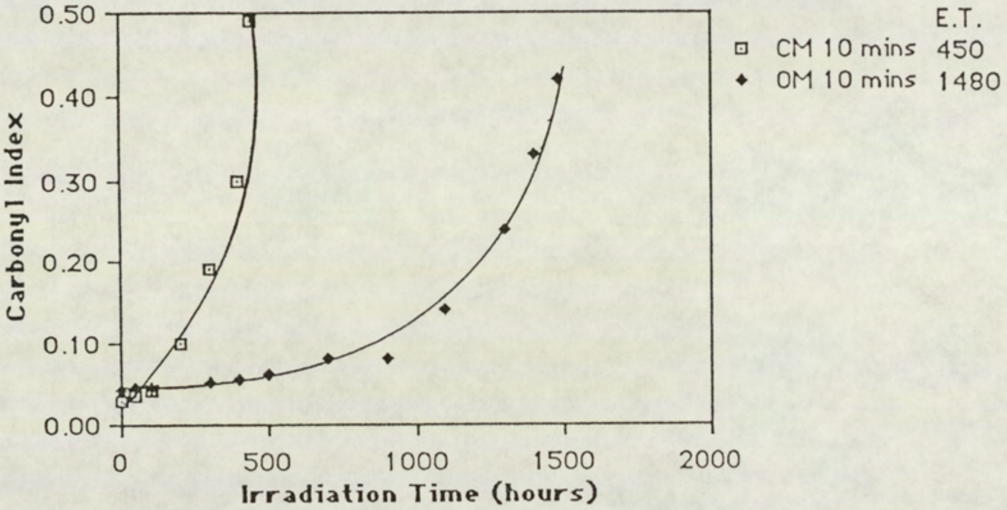


Figure 3.29 Photostabilising activity of NiDiBuPn in PP (0.4% unmodified pressing method)

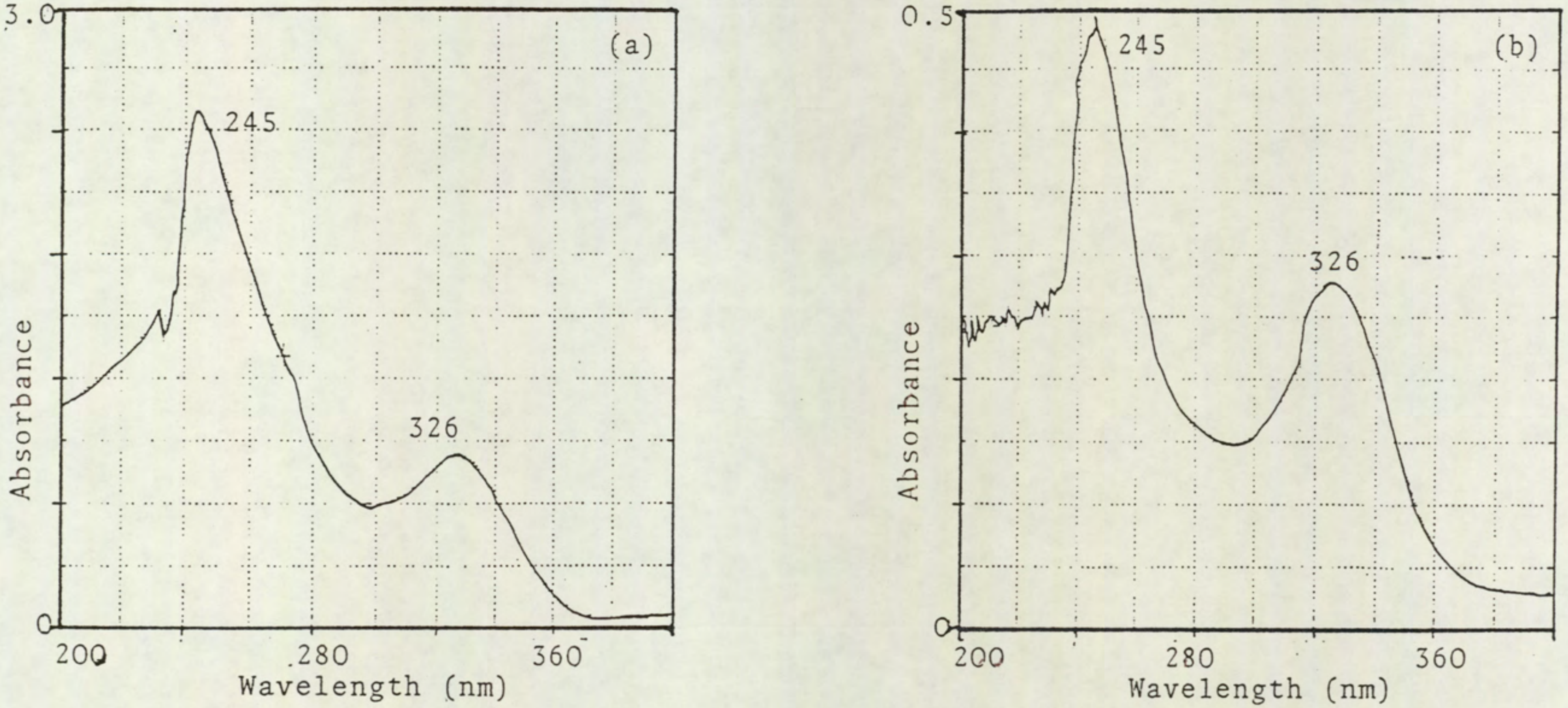


Figure 3.30 UV absorption spectra* of NiDiBuPn in PP extracted with chloroform
(a) OM 30mins (pink polymer) (b) CM 30 mins (black polymer)
[*Spectra is of extractant and not of polymer]

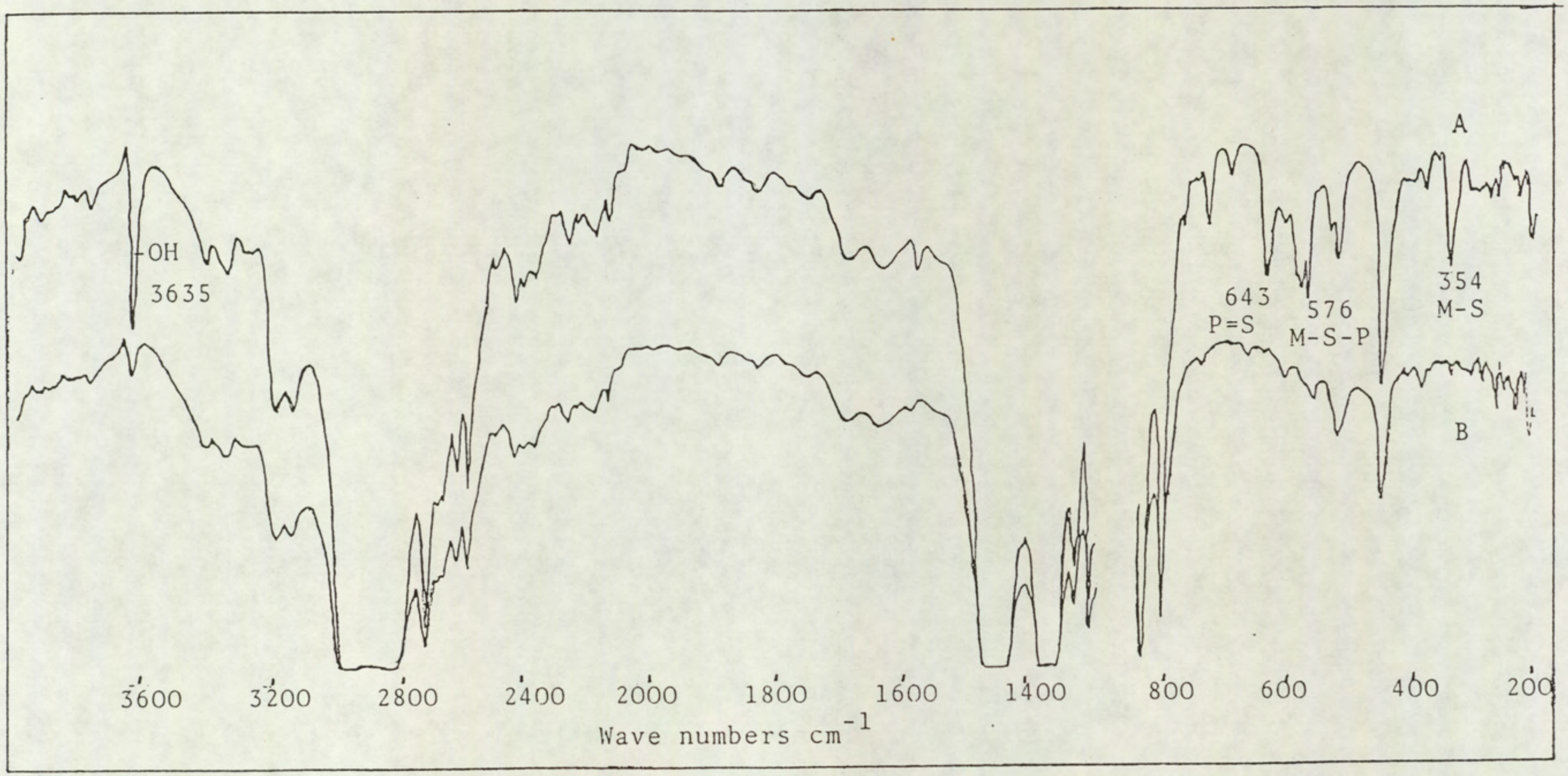


Figure 3.31 Comparison of the IR spectra of MB samples (2.5%, CM 10 mins)of NiDiBuPn (A) and CuDiBuPn (B).

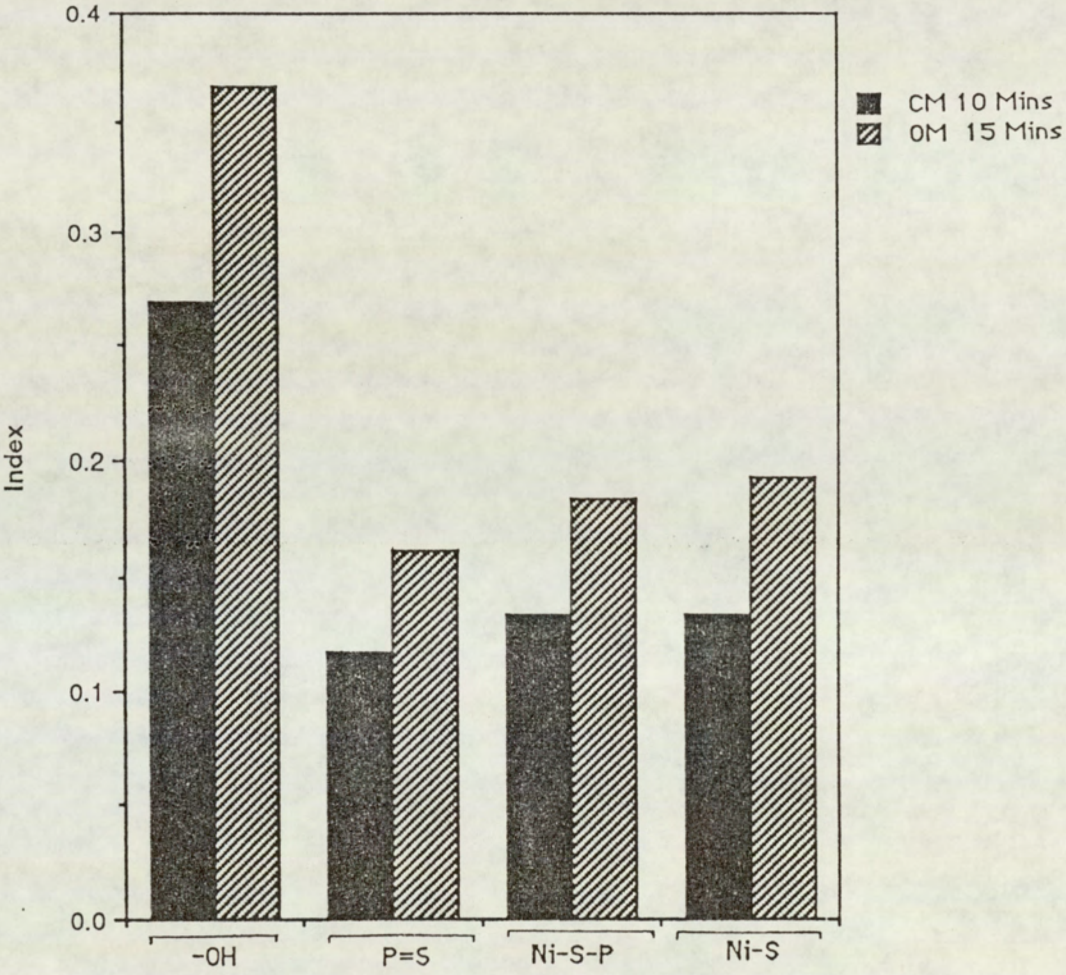


Figure 3.32 Comparison of major IR charateristic absorbtion bands of NiDiBuPn in PP (2.5% MB)

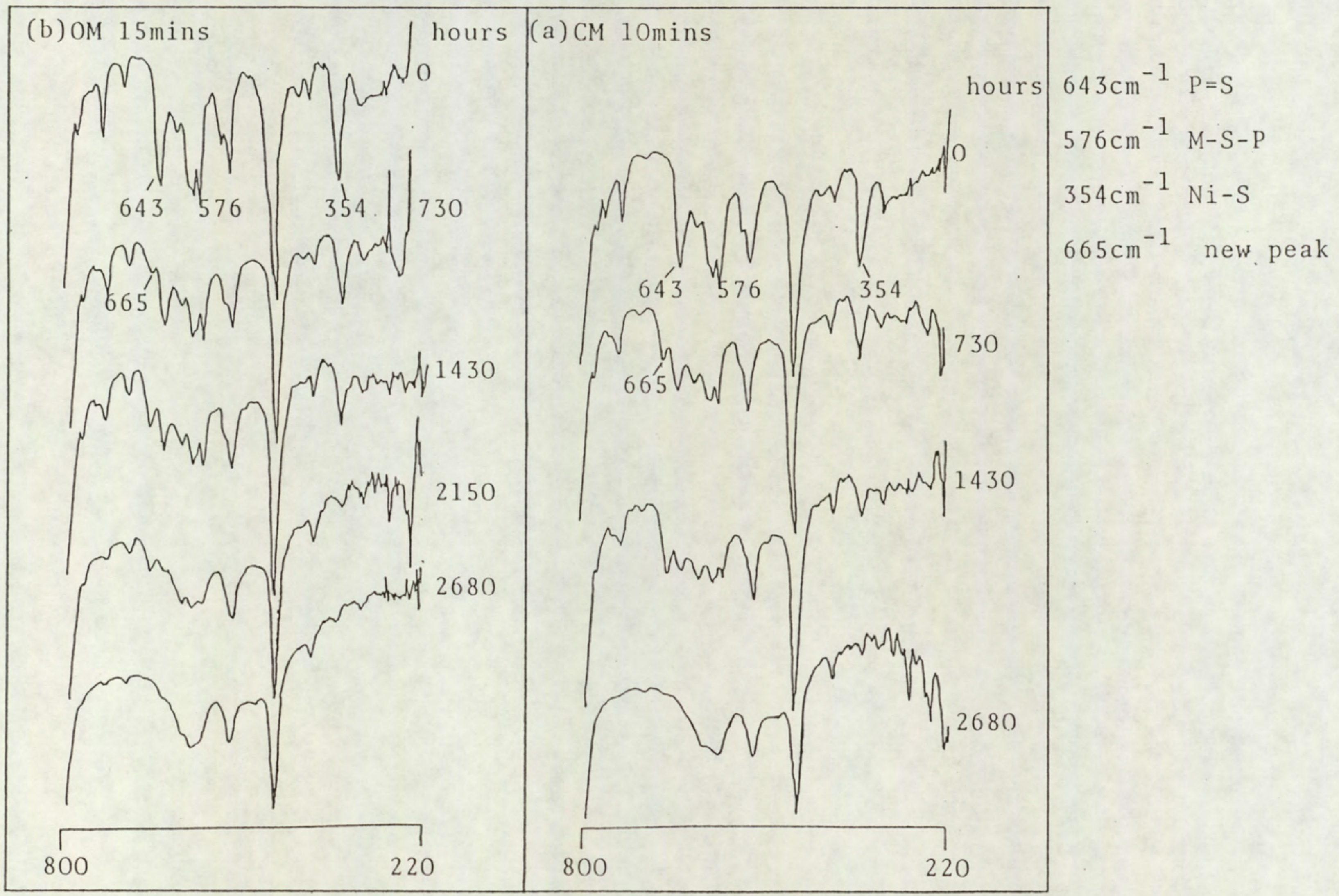


Figure 3.33 Dissapearance of characteristic IR absorption bands of 2.5% MB of NiDiBuPn between wavenumbers 220 - 800 cm^{-1}

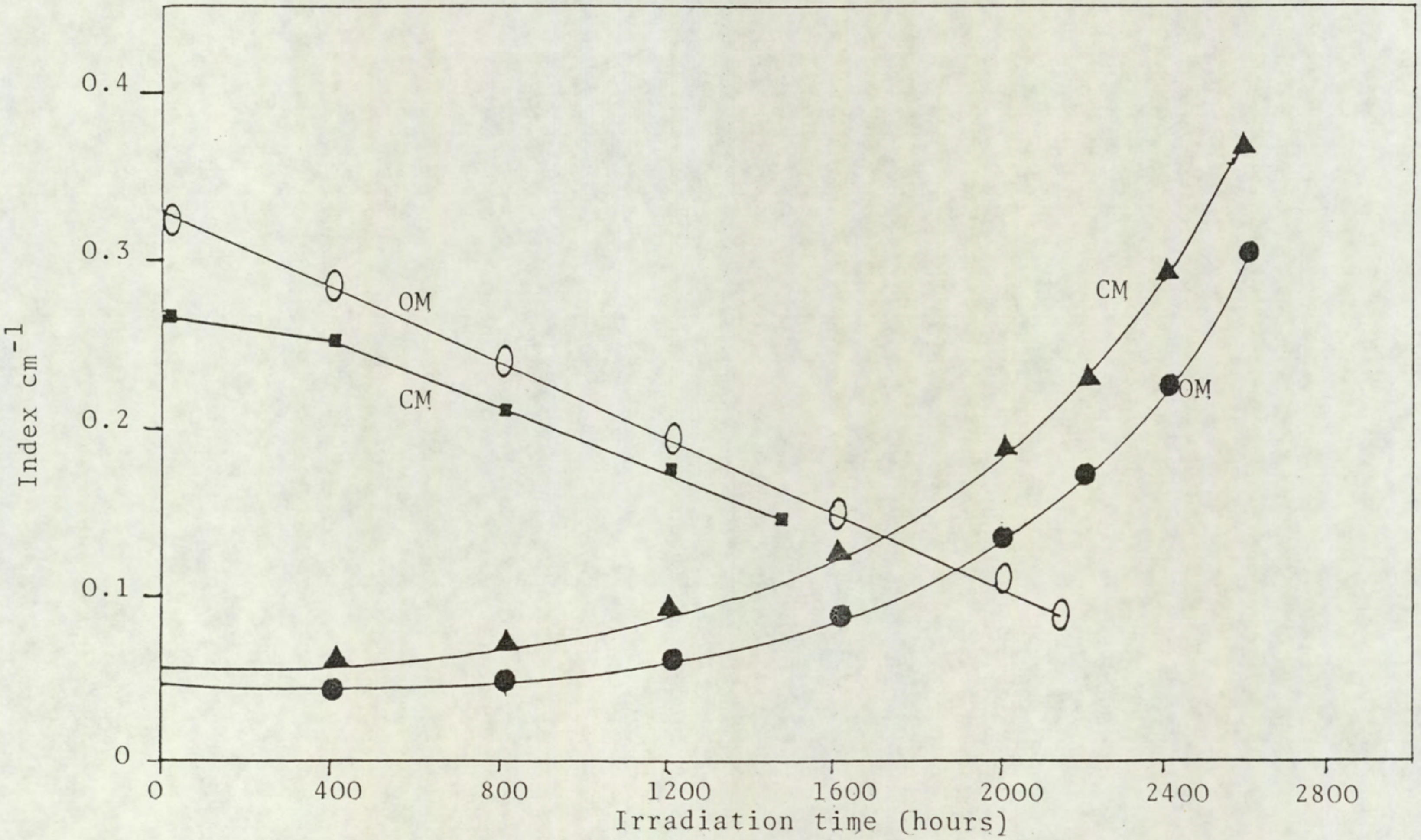


Figure 3.34 (a) Decay of phenolic -OH (3636 cm^{-1}) and increase in carbonyl formation (1710 cm^{-1}) during uv irradiation of 2.5% MB samples of NiDiBuPn in PP.

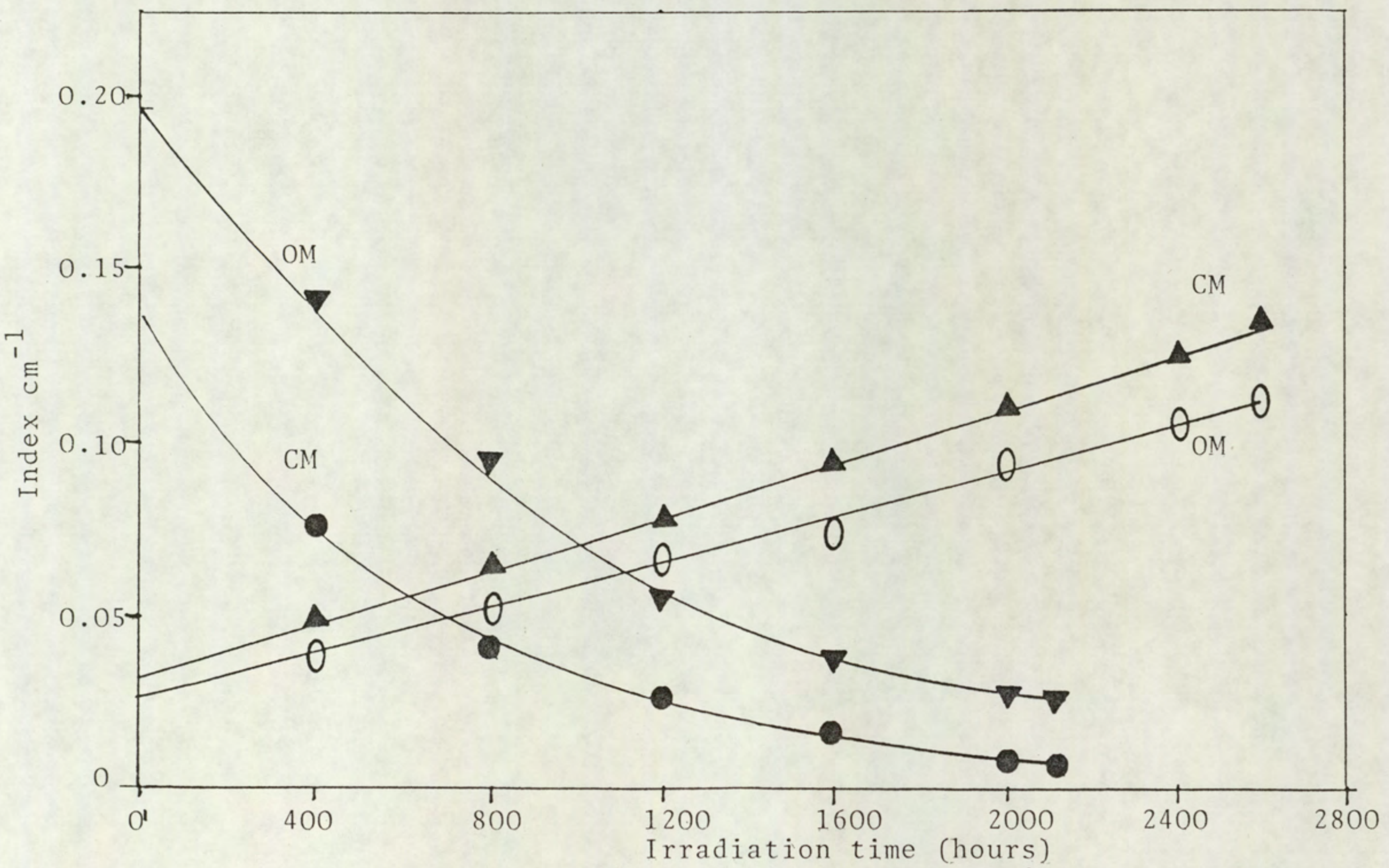


Figure 3.34 (b) Decay of IR absorption band of Ni-S (354 cm^{-1}) and increase in 1645 cm^{-1} (possibly polymer unsaturation) during uv irradiation of 2.5% MB samples of NiDiBuPn in PP.

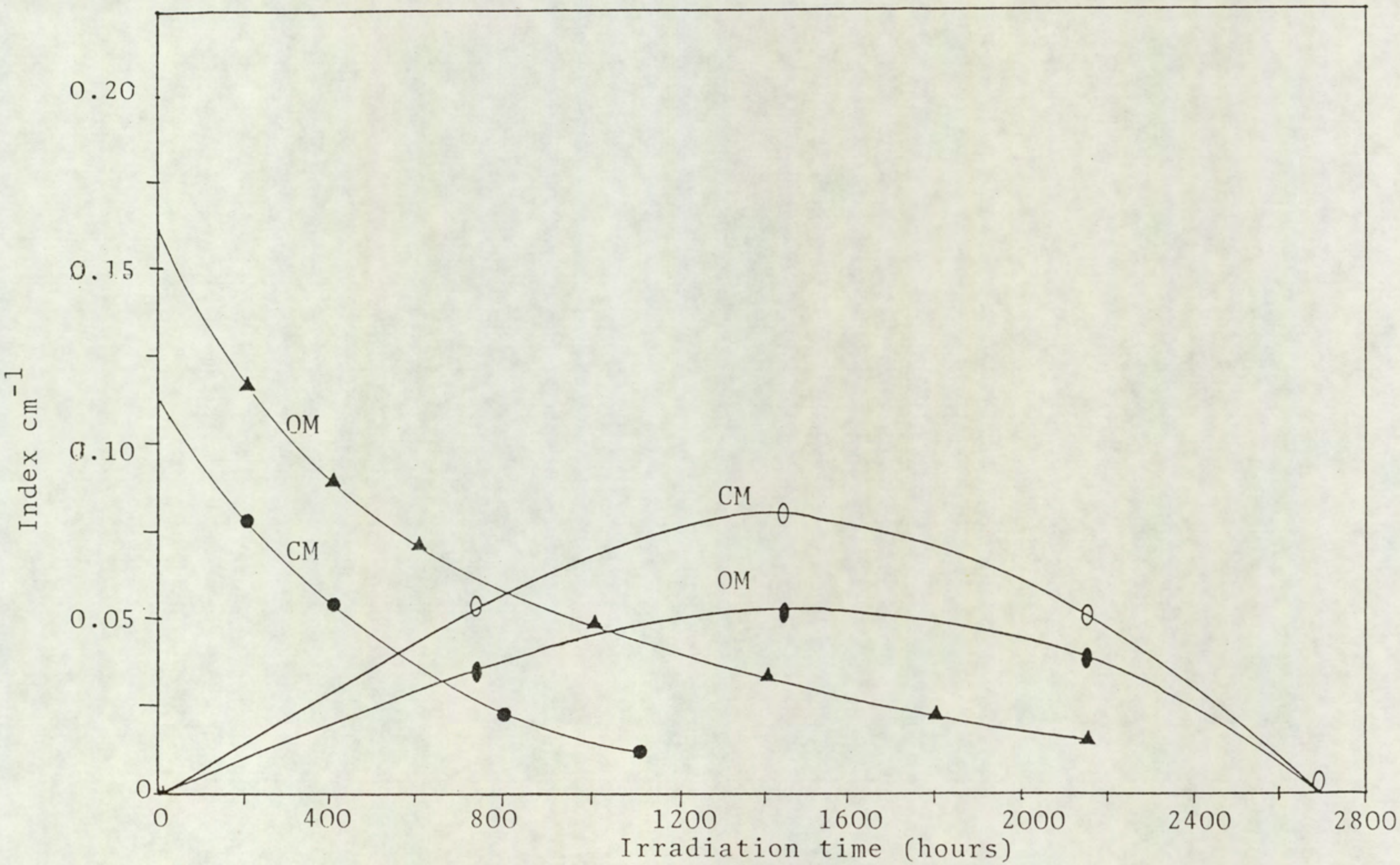


Figure 3.34 (c) Decay of IR absorption bands of P=S (643 cm^{-1}) and formation of intermediate (665 cm^{-1}) during uv irradiation of 2.5% MB samples of NiDiBuPn in PP.

CHAPTER 4

MECHANISTIC STUDIES

4.1 OBJECT

The dithiophosphonates in general have been shown (Chapter 3) to be very effective stabilisers for polypropylene under melt, thermal and photo-oxidative conditions. Their mode of antioxidant activity is believed to include both chain breaking and peroxide decomposing mechanisms. It is also known (1,2) that during fabrication sulphur compounds in general are transformed into oxidation products which are capable of protecting the polymer.

The aim of the work described in this chapter is therefore to elucidate the mode of antioxidant mechanism of the dithiophosphonates by evaluating their peroxidolytic activity (hydroperoxide decomposition), radical trapping activity (oxygen absorption) and also by identifying the nature of the transformation products using ^{31}P NMR, after a series of oxidation studies.

A description of the materials, substrates and experimental methods utilised during these studies is given in Sections 2.6 - 2.13, and also briefly summarised in the appropriate sections.

4.2 RESULTS AND DISCUSSION

4.2.1 Dithiophosphonates as Hydroperoxide Decomposers

The decomposition of cumene hydroperoxide ($1x10^{-2}$ mol dm^{-3}) in the presence of nickel isobutyl dithiophosphonate and the sulphide TPS is measured as a function of time by the hydroperoxide decomposition method (see Section 2.11) at 110°C under nitrogen. Analysis of the decomposed cumene hydroperoxide products was carried out by gas-liquid chromatography (see Section 2.12). In order to establish the reaction mechanism, various concentration ratios of the additive to cumene hydroperoxide were studied.

4.2.1.1 Decomposition of Cumene Hydroperoxide by NiDiBuPn

The rate of decomposition of cumene hydroperoxide by nickel isobutyl dithiophosphonate (NiDiBuPn) at various concentrations is shown in Figure 4.1. It is clearly evident that as the concentration of the nickel complex decreases the reaction time for the decomposition of cumene hydroperoxide increases. A three stage decomposition is observed at a NiDiBuPn:CHP ratio of 1:5. An initial fast stage is followed by a slower second stage and then finally by a slightly faster third stage. A similar three stage decomposition of cumene hydroperoxide by NiDRP (3) and ZnDRP (4-8) has also been reported.

The build up of products arising from the decomposition of CHP by NiDiBuPn at a molar ratio of 1:5 (NiDiBuPn:CHP) is shown in Figure 4.2. The products initially formed are acetophenone and α-cumyl alcohol. Although the concentration of acetophenone continues to rise throughout the reaction, the concentration of α-cumyl alcohol rises initially and slightly decreases as the reaction progresses. Both these products are characteristic of the homolytic decomposition of CHP (Scheme 4.0)(9). The large amount of acetophenone formed from the decomposition of CHP by a relatively high concentration of the nickel complex is in agreement with previously reported work on the related nickel dithiophosphate complexes(3). The yields of α-cumyl alcohol arising from the use of NiDiBuPn however is much lower than the high values (>40%) reported when CHP is decomposed by other transition metal dithiophosphates when tested under similar conditions (4,5,7,10-12). The build up of phenol and α-methyl styrene during the early second stage shows that acid catalysed reactions are occurring. Phenol is formed from the ionic decomposition of CHP by Lewis acids (Scheme 4.0 (9) and 4.1 (13)) and α-methyl styrene from the degradation of α-cumyl alcohol which is also catalysed by acidic species (9) (Scheme 4.2 (14)). The nature of these acidic species are discussed in Section 4.2.3. The initial homolytic decomposition leading to the generation of free radicals is responsible for the pro-oxidant and thus fast first stage observed. The subsequent slower second step is caused by the ionic decomposition of hydroperoxides by sulphur acids formed by the interaction of the nickel complex and the CHP during the first stage. During the final stage the nickel complex decomposes CHP at a faster rate than in the second stage, this may be due to a reduction of the antioxidants (sulphur acids) present.

At a higher ratio of peroxide to nickel complex (1:20) the reaction is predominantly ionic (Figure 4.3). Initially a high level of α-cumyl alcohol is detected which then decreases throughout the reaction. Acetophenone increases up to 45 minutes and then levels off up to 200 minutes after which it can not be detected anymore. These two products are characteristic of the homolytic (free radical) decomposition of CHP. Phenol (the ionic product) is the most predominant species formed in this reaction. It rises rapidly and levels up at a high value throughout the reaction. A low concentration of α-methyl styrene is also formed, which increases slowly throughout the reaction. The increase in α-methyl styrene parallels the decrease in α-cumyl alcohol. The rapid first stage which is due to the homolytic decomposition of CHP generates free radicals. The subsequent generation of sulphur acids by the interaction of NiDiBuPn and CHP is responsible for retarding the hydroperoxide decomposition at a later stage. This two stage behaviour was reported by Rossi and Imperato (4) and by Burn and co-workers for dithiophosphates (5).

Very little decomposition of CHP was achieved by NiDiBuPn at a low concentration (1:100) as can be seen in Figure 4.4. At the beginning of the reaction α-cumyl alcohol and acetophenone were observed. The acetophenone decreases rapidly after the initial sharp build up. The three products acetophenone, α-cumyl alcohol and α-methyl styrene all indicate homolytic cleavage. After 10 mins. acetophenone decreases very rapidly whilst phenol formation starts to increase. This clearly indicates that after a short period of homolytic decomposition the reaction undergoes predominantly an ionic decomposition mechanism. The inability of the nickel complex at low concentration to decompose CHP may be due to the low availability of sulphur acids (which have an autoretarding effect) in the reaction mixture.

On the basis of the evidence obtained during ^{31}P NMR studies (Section 4.2.3 (b)) of NiDiBuPn and TBH (studied at a molar ratio of 1:4) at 100°C the nickel complex produces dithiophosphonic acid (See reaction 1 and 2) and it is likely that this acid is the catalyst for hydroperoxide decomposition.

$$[RO(Ar)PS_2]_2\ Ni + R'OOH \longrightarrow [RO(Ar)PS_2]\ Ni(OH) + [RO(Ar)PS_2^{\cdot}] + R'O^{\cdot} \qquad (1)$$

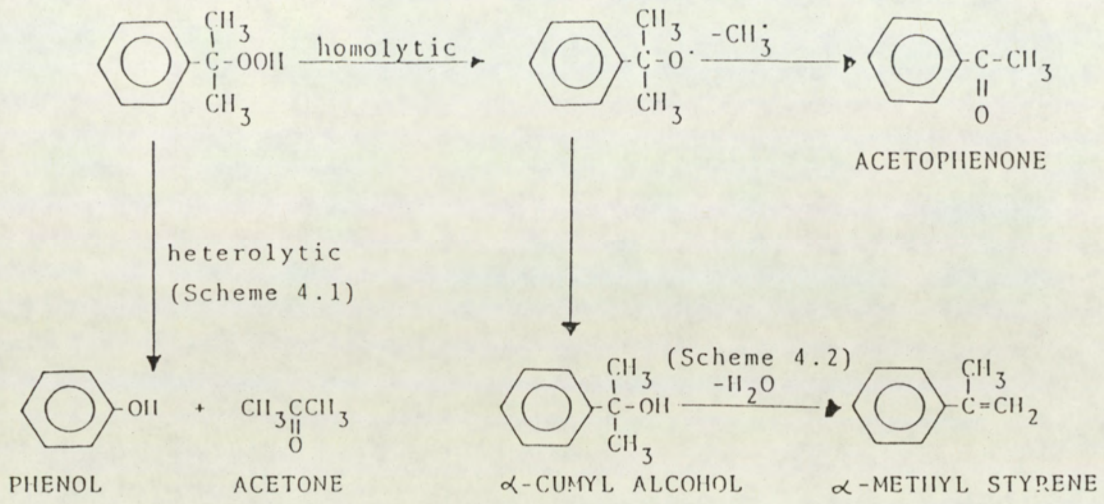
$$[(RO\ (Ar)PS_2^{\cdot}] + R''OOH \longrightarrow [(RO)(Ar)PS_2H] + R''O_2^{\cdot} \qquad (2)$$

The formation of the acid may take place by reaction of the thiyl radical with hydroperoxide (Reaction 2). Similar work by Sexton (15) and Burn et al. (5) has suggested this role for thiyl radicals in the case of the related dithiophosphates. Other workers (10,16-18) have shown, however, that the thiyl radical recombines and forms the corresponding disulphide. No disulphide was detected during studies of the nickel dithiophosphonate and hydroperoxide at a 1:4 molar ratio at 100°C. When high molar ratios of nickel dithiophosphonate and hydroperoxide (1:10 and 1:20) are used at room temperature some disulphide is detected by ^{31}P NMR studies (see Section 4.2.3.2(b)). This disulphide, however, was found to be produced after the acid (See Section 4.2.3.1 (b) and 4.2.3.1 (c)). This contrasts to the low molar ratio (1:4) reaction at room temperature where the disulphide is detected at the same time as the acid and in higher concentration than the acid (See Section 4.2.3.1 (a)).

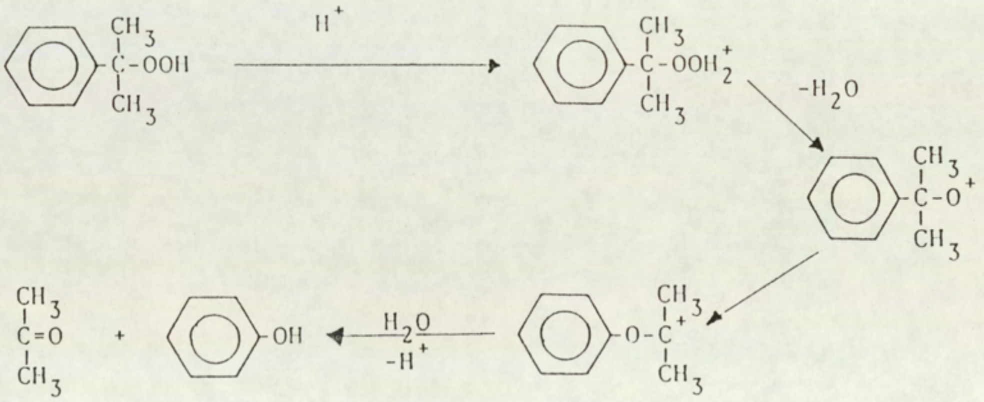
4.2.1.2 Decomposition of Cumene Hydroperoxide by TPS

The decomposition of Cumene hydroperoxide (CHP) by TPS (a sulphide) was examined in chlorobenzene at two different molar ratios of [TPS]/[CHP] of 1:5 and 1:20 at 110^{o}C under nitrogen and is shown in Figure 4.5. At higher concentrations of peroxide, the rate of decomposition is slower. The products formed during the decomposition of CHP by TPS at a molar ratio of [TPS]/[CHP] of 1:5 is shown in Figure 4.6. During the initial stages of the reaction the predominant species are α-cumyl alcohol and acetophenone which indicate a homolytic (free radical) mechanism. After 60 minutes phenol starts to form and by the end of the reaction it is the most predominant species, indicating an ionic mechanism. The decomposition of CHP is occurring by a two stage mechanism. The first rapid stage is predominantly homolytic and free radicals are produced. During the second slower stage sulphur acids are produced. These sulphur acids are responsible for decreasing the rate of decomposition of CHP. Similar observations of dithiophosphetanes producing acids that have an inhibitory effect towards hydroperoxide decomposition have previously been reported. (19)

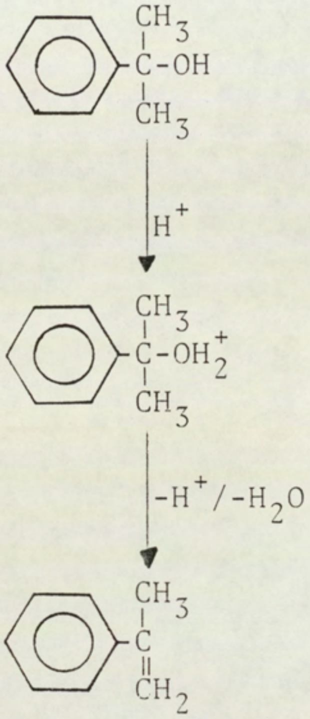
At a higher ratio of CHP (1:20) the reaction proceeds by a predominantly ionic mechanism (Figure 4.7) which is clearly shown by the steady increase in the phenol concentration. α-cumyl alcohol forms at the beginning of the reaction, but at a much lower concentration than phenol and at later stages a small amount of acetophenone and α-methyl styrene were also observed, indicating a small contribution by a homolytic mechanism.



Scheme 4.0(5) Homolytic and heterolytic decomposition products of CHP



Scheme 4.1(13,15) Lewis acid catalysed ionic decomposition of CHP



Scheme 4.2(14) Dehydration of α-cumyl alcohol by Lewis acids

4.2.2. Dithiophosphonates as Radical Trapping Agents

The promotion of oxidation takes place by catalysis of the decomposition of hydroperoxides to free radicals, whereas stabilisation occurs by radical trapping, and in the case of some antioxidants, by catalysis of the decomposition of hydroperoxides to non-radical products. The method used to determine the effectiveness of these compounds as radical traps is the oxygen absorption technique (20,21) described in Section 2.12. The effect of the additive at 55°C is determined in the presence of cumene an oxidisable substrate and Azo-bis-isobutyronitrile (AZBN) a radical initiator.

The uninhibited oxidation, that is, with AZBN and no additive occurred immediately with a rapid oxygen uptake and no induction period (Figure 4.8). This auto accelerating nature of the uninhibited oxidation is expected on consideration of the general auto-oxidation scheme outlined in Section 1.1.. During the initial stages of the oxidation the free radical concentration and consequently the hydroperoxide concentration is low. These hydroperoxides are the main chain initiators and thus chain initiation of the oxidation reaction is restricted initially. As the oxidation proceeds via a chain reaction the hydroperoxide concentration and consequently the oxidation rate increases rapidly. The control AZBN had no induction period and thus the existence of an induction period before oxidation suggests that the additives themselves must be responsible, at least initially for the inhibition observed. The induction period for the metal dithiophosphonates and the sulphide, TPS, varied considerably as can be seen in Table 4.1 and Figure 4.8.

Table 4.1 Induction Period during Oxygen Absorption of Various Additives in the presence of AZBN (1×10^{-2} mol dm^{-3}) at 55^{o} C

Additive	Induction Period (hrs)	Conc.(10^{-4} mol dm^{-3})
CuDiBuPn	2.5	8
CoDiBuPn	13.0	4
FeDiBuPn	12.5	4
ZnDiBuPn	4.0	4
NiDiBuPn	11.0	4
TPS	13.0	4
DtBP	2.5	2

As all additives have at least one hindered phenol, di-tertiarybutyl phenol (DtBP) was also examined. DtBP had a short induction period of 2.5 hours and the subsequent rate of oxidation was faster than that observed with the other metal complexes and TPS. It must be remembered, however, that a lower concentration (2×10^{-4} mol dm^{-3}) had been used to assess the contribution of one hindered phenol. Effectively DtBP may in actual fact be better than copper dithiophosphonate (Figure 4.8). Both DtBP and the copper complex have an induction period of 2.5 hours, and although copper has a slower rate of oxidation its concentration

(8×10^{-4} mol dm^{-3}) is four times that of DtBP.

The effectiveness of the dithiophosphonates on the AZBN initiated oxidation of cumene during the first 20 hours, is shown in Figure 4.8 and in decreasing activity is as follows:

TPS > Fe > Zn > Ni > Co > Cu

this order is somewhat altered as the reaction continues (Figure 4.9):

Fe > Ni > Zn > TPS > Co > Cu

Copper dithiophosphonate has a short induction period of 2.5 hours which is followed by a rapid and autoaccelerating uptake of oxygen. The short induction period suggests that the original copper must be used up very quickly by reaction with the radicals generated by AZBN.

Cobalt dithiophosphonate (Figure 4.9) has a long induction period of 13 hours, very similar to the induction period of 12.5 hours for iron dithiophosphonate. The cobalt and iron complexes differ only by their metal ion and thus any difference in the rate of oxidation must be due to the strength of the metal sulphur linkage. The cobalt molecule has been shown (Figure 3.14) under U.V. irradiation to decompose at a slower rate than the iron complex. It has previously been found (2) that the transformation products of sulphur-containing stabilisers (mainly acidic species) are the active antioxidants rather than the original molecule. Thus as iron decomposes at a higher rate than cobalt it may be producing effective antioxidants at a faster rate.

Figure 4.9 also illustrates that cobalt and iron show autoretarding oxidation behaviour, but is more enhanced in the case of iron. This suggests that iron must undergo further reaction to form more and more powerful antioxidants. The cobalt forms antioxidants that are good inhibitors (induction period 13 hours) but they are consumed rather quickly. Iron also forms good antioxidant inhibitors (induction period 12.5 hours) which are consumed at a much slower rate than cobalt. Iron was the best radical trapping agent examined, this must partially be due to the three hindered phenolic groups it contains. It has already been seen from Figure 4.9 that DtBP (a hindered phenol) scavenges radicals and thus it is logical to assume that as the phenolic groups are increased in a molecule its radical trapping ability will also increase.

Nickel and zinc dithiophosphonate differ only in their metal centre and thus this must play a role in their small difference in activity. The short induction period of zinc suggests that the zinc complex must be consumed very quickly by reaction with the radicals generated by the AZBN. The antioxidants produced after this reaction must be very powerful as shown by the autoretarding oxidation. Nickel dithiophosphonate has much longer induction period, after which the nickel complex reacts with the radicals to produce sulphur acids (Section 4.2.3) which are the powerful antioxidants. This is clearly shown by the autoretarding oxidation shown in Figure 4.8.

TPS has a long induction period of 13 hours which is followed by an autoretarding oxidation. TPS like nickel and zinc dithiophosphonate has two hindered phenolic groups in its molecule but has no metal centre, however nickel and zinc are better inhibitors for oxidation which suggests that the metal may play a role in decreasing the rate of oxidation at later stages.

The oxygen uptake of metal dithiophosphonates in the presence of cumene as a substrate, and AZBN as an initiator, has been shown, in this study, to increase in the following order:

Cu > Co > Zn > Ni >Fe

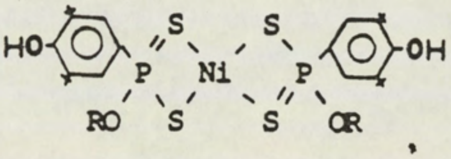
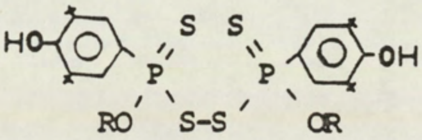
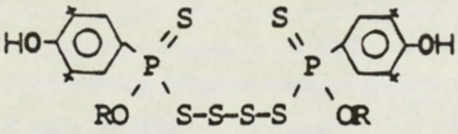
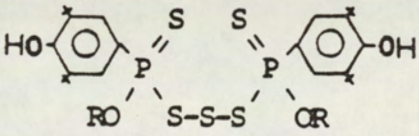
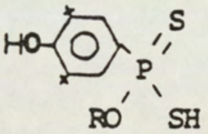
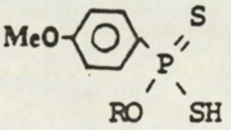
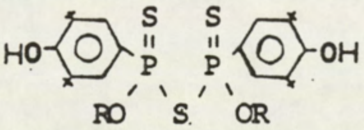
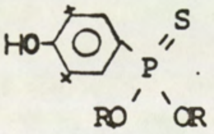
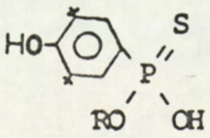
4.2.3 ^{31}P NMR Studies of Dithiophosphonates

The object of the work described in this section is to obtain a better understanding of the mode of antioxidant action of the dithiophosphonates, by studying the reaction intermediates and products obtained from a series of experiments carried out in pure solvents. The experiments are designed to represent a model system which could be related to the conditions employed during the processing of these materials in polypropylene. All product percentage yields are based on the normalisation of all peak areas to 100%. In the absence of sufficient literature data, the structural assignments to some ^{31}P NMR signals, notably the esters and the acids, are based on products obtained from other secondary reactions involving the intermediate free acid (PSSH) and their behaviour in the presence of other reagents (see Section 4.2.5). All products are referenced to 85 % phosphoric acid.

4.2.3.1 Oxidation of Nickel Dithiophosphonate at 25°C in the presence of Tert-Butyl Hydroperoxide.

The oxidation of nickel dithiophosphonate (NiDiBuPn) was carried out directly in the Jeol FX90Q NMR spectrometer. Three different molar ratios of the nickel complex and TBH were examined, 1:4, 1:10, and 1:20. Table 4.2 summarises the possible structural assignments to ^{31}P NMR signals of the products formed during these reactions. The dithiophosphonic acid and the sulphides were assigned on the basis of their identity with that of authentic samples prepared in this work. The dithiophosphonic acid (see Section 2.1.3.2) and the corresponding monosulphide (see Section 2.1.3.6.) as prepared were pure compounds since only one ^{31}P NMR peak was obtained. On the other hand, the preparation of the di, tri and tetra sulphides gave rise to a mixture of products (see Section 2.1.3.7 - 2.1.3.9).

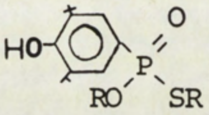
Table 4.2 Possible ^{31}P NMR Assignments for transfomation Products found during this study

CHEMICAL SHIFT	POSSIBLE STRUCTURAL ASSIGNMENT	ABBREVIATION
102δ		NiDiBuPn* R = iBu
93.3δ		S_2* R = iBu
91δ		S_4* R = iBu
90δ		S_3* R = iBu
88.4δ		PSSH* R = iBu
86.5δ		R = C_2H_5 Lit. (22)
84δ		S_1* R = iBu
82δ		P(S)OR R = iBu
72-78δ		P(S)OH R = iBu

' * ' Synthesised

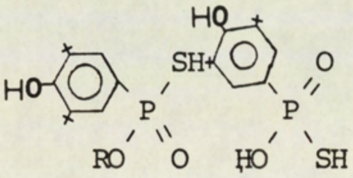
Table 4.2 cont.

44-41.5δ



R = iBu

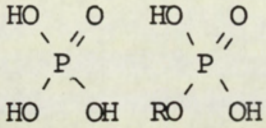
21-25δ



-P(O)SH

R = iBu

0.8-4δ



R = iBu

4.2.3.1(a) [NiDiBuPn]/[TBH] 1:4 Molar Ratio at Room Temperature

The ^{31}P NMR spectral changes occurring during the 1:4 molar oxidation of NiDiBuPn by TBH is illustrated in Figure 4.10 whilst Table 4.3 gives the relative abundance of the oxidation products. This is also shown in Figure 4.11 which depicts the decay in the abundance of the starting material (102 s) and the formation of various products with time.

It is quite clear from these results that after only 5 hours oxidation the relative abundance of NiDiBuPn is reduced to less than 50%. This is accompanied by the formation of various products which can be identified from Table 4.2. The principal products are the dithiophosphonic acid (s =88 ppm) the mono (84 ppm), di (93.4 ppm), tri (90.6 ppm) and tetra (91.6) sulphides. The identity of the products giving rise to the ^{31}P NMR signals with chemical shifts in the region of 86.5 ppm is possibly an acid product$^{(22)}$, however the identity of the species giving rise to shifts in the region of 44.3 - 41.5 ppm is not clear at the present time. The fact that these signals seem to persist in most of the oxidation studies suggest that they are most possibly due to major transformation products, possibly esters. It is seen, however, that with increasing reaction time, the relative abundance of the various

Table 4.3 Products of the Oxidation of NiDiBuPn by TBH in chlorobenzene (1:4 molar ratio) at 25°C

Reaction time (hrs.)	0	5	15	26	37	48	68
Chemical shift (ppm) and assignment	RELATIVE ABUNDANCE (%)						
102.2 (NiDRPn)	100	47.1	37.9	31.7	19.7	21.5	11.6
93.4 (S_2)	-	9.2	8.1	5.4	8.6	6.4	6.6
91.5 (S_4)	-	-	2.3	3.2	4.3	4.9	4.0
90.6 (S_3)	-	6.0	7.2	11.0	10.8	15.9	18.4
88.7 (-PSSH)	-	2.3	6.9	10.0	13.9	11.8	15.4
86.5	-	9.5	10.4	12.9	11.7	8.5	12.4
84.1 (S_1)	-	5.1	3.8	6.3	3.8	5.9	5.2
82.2 (-P(S)OR)	-	2.2	1.6	-	-	-	-
72.1 (-P(S)OH)	-	1.2	2.0	-	-	-	-
44.3	-	1.1	1.4	1.6	1.4	2.1	1.8
41.5	-	2.5	3.3	3.0	7.8	8.0	8.9
21.1 (-P(O)SH)	-	-	-	1.4	1.5	2.9	2.1
Others*	-	13.8	15.1	13.5	16.5	12.1	13.6

* Very low intensity (<2% each) signals of uncertain origin (δ = 65 - 62 ppm, 55 -53 ppm 47 ppm and 38 - 27 ppm) which appeared intermittently during the course of the reaction. Possible structural assignments to ^{31}P NMR signals are given in Table 4.2.

products continued to increase whilst that of the starting material (NiDiBuPn) decreases rapidly. Hence, by the end of the experiment (68 hours) only about 12% of the nickel complex remained undecomposed. The presence of the thiolphosphonic acid (δ = 21 ppm) must be noted here as this is one of the major products in later reactions (Section 4.2.3.1(b) - 4.2.3.1(c)).

4.2.3.1(b) [NiDiBuPn]/[TBH] 1:10 Molar Ratio

Table 4.4 summarises the oxidation products obtained during the 1:10 molar ratio oxidation of NiDiBuPn with TBH. At the higher ratio of TBH the oxidation is much faster, such that after only 3 hours the NiDiBuPn has completely disappeared and this contrasts with the previous 1:4 molar ratio reaction. The products formed in this reaction are very similar to those identified in the previous reaction, the main difference being the rate at which they are formed. It is also seen that the formation of the acidic species (δ = 72 and 21 ppm) seems to be favoured at such high concentrations of TBH. This reaction however, was stopped after 15 hours due to the very low signal to noise ratio available. The major products formed after 15 hours reaction are the free acid (δ = 88 ppm) and probably a similar acid (22) (86 ppm), mono sulphide (84 ppm), trisulphide (90 ppm) and the acidic product with a chemical shift of 21 ppm (thiol isomer). It must be observed that the identity of the signals of chemical shifts of 100, 98, 78, 49-41 ppm were unconfirmed. These signals are thought to be due to various phosphonate esters since similar products have been reported (22) to give rise to signals having chemical shifts in the same region.

Table 4.4 Products of the Oxidation of NiDiBuPn by TBH (1:10 Molar Ratio) in chlorobenzene at 25°C

Reaction time (hrs)	0	0.25	3	6	9	12	15
Chemical shift(ppm) and assignments	RELATIVE ABUNDANCE (%)						
102.1 (NiDRPn)	100	84.4	-	-	-	-	-
100.2	-	-	7.2	8.7	8.8	8.3	8.9
98.7	-	-	8.3	8.4	8.9	7.2	5.0
93.8 (S_2)	-	-	-	-	4.3	-	-
90.3 (S_3)	-	-	-	7.0	-	5.2	12.3
88.4 (-PSSH)	-	15.6	8.3	7.0	9.6	11.9	11.3
86.5	-	-	26.5	18.3	20.9	14.1	20.6
84.2 (S_1)	-	-	19.5	9.9	8.4	8.0	5.7
78.2	-	-	13.4	20.4	15.3	13.9	15.0
72 -75 (-P(S)OH)	-	-	6.3	-	6.2	4.0	-
43.9	-	-	5.7	4.8	6.3	5.4	4.1
41.7	-	-	-	-	-	4.5	4.2
21.2 (-P(O)SH)	-	-	6.9	12.1	5.3	4.3	8.7
Others	-	-	-	0.4	6.0	13.2	4.2

4.2.3.1(c) [Ni DiBuPn]/[TBH] 1:20 Molar Ratio

The distribution and nature of the products formed at an even higher ratio (1:20) is shown in Table 4.5 and the structural assignment (Table 4.2) to the ^{31}P NMR signals are the same as in the previous ratios (1:4), (1:10) since the signals have similar chemical shifts.

Table 4.5 Products of the Oxidation of NiDiBuPn by TBH (1:20 Molar Ratio) in chlorobenzene at 25°C

Reaction time (hrs)	0	0.2	5	15	30	40	50	90
Chemical Shift(ppm) and assignment	RELATIVE ABUNDANCE (%)							
102.0 (NiDRPn)	100	82.2	-	-	-	-	-	-
99.9	-	-	8.8	9.8	6.0	-	-	3.7
98.5	-	-	10.0	10.4	-	-	-	4.2
94.1 (S_2)	-	-	11.8	5.3	-	-	-	1.6
91.3 (S_4)	-	-	17.0	-	-	-	-	3.2
90.1 (S_3)	-	-	-	-	6.8	5.0	5.9	4.6
88.7 (-PSSH)	-	9.7	3.6	9.0	15.4	30.4	23.5	6.5
86.5	-	-	3.8	10.9	6.5	-	5.3	5.9
84.2 (S1)	-	-	13.1	14.7	31.0	11.7	7.3	2.3
82.4 (-P(S)OR)	-	-	-	4.6	-	-	5.6	-
77.5 - 79.5	-	8.1	16.1	4.7	9.0	8.1	11.3	-
72.0 - 75.0	-	-	6.7	5.1	-	4.4	-	-
48.2	-	-	-	-	-	-	-	7.7
43.9	-	-	2.9	3.8	-	5.5	5.0	17.6
21.5 (-P(O)SH)	-	-	-	5.6	25.2	17.7	18.1	11.1
16.4	-	-	-	-	-	-	-	8.9
0.0 - 4.0	-	-	-	5.4	-	-	6.4	10.9
Others	-	-	6.2	10.7	0.1	17.2	11.6	10.8

The spectral changes occurring during this reaction are qualitatively illustrated in Fig. 4.12 whilst the changes in the relative abundance of the various transformation products are shown in Figure 4.13. In common with the 1:10 molar ratio reaction, the reaction rate in this instance was fast as complete decomposition of the metal thiolate (NiDiBuPn) occurred in less than 3 hours. The ^{31}P NMR data (Table 4.5) clearly indicate that the reaction mixture after 5 hours comprises of mono, di and tetra sulphides (s = 84, 93 and 91 ppm respectively). Other transformation products include the dithio-acid (PSSH) and the thiono phosphonic acids (PSOH/POSH) with chemical shifts in the range 88 ppm and 72-75/21 ppm respectively, and phosphonate esters in various forms (100-97 ppm, 48-44 ppm). With the increase in the reaction time however, large fluctuations in the relative abundance of these transformation products were observed. The di and tetra sulphides (Table 4.5) which form part of the major reaction intermediates in the initial period (5 hrs) disappeared completely whilst the monosulphide and sulphur acids increased sharply. This increase of the latter species is probably as a result of the hydroperoxide decomposition of the initially formed di and tetra sulphides. Other secondary reactions between these predominant products and more hydroperoxides would account for the observed fluctuations (Figure 4.13). Ultimately, the gradual decay in the relative abundance of these transformation products (monosulphides and sulphur acids) is paralleled by a corresponding increase in the formation of the thiophosphonate ester (44 ppm) and the completely oxygenated species (0.5, 0.4 ppm).

In each of the reactions carried out (4.2.3.1 (a) - 4.2.3.1 (c)) a gradual colour change from deep purple to yellow was observed with increasing reaction time. Furthermore, each reaction was associated with the precipitation of a turquoise solid which was identified as hydrated nickel sulphate ($NiSO_4.nH_2O$) on the basis of its identity with an authentic sample (Figure 4.14(a)). The precipitate also showed a positive result on the barium sulphate test for sulphates, and decomposes at temperatures >300°C.

4.2.3.1(d) Overview of the Oxidation of NiDiBuPn by TBH at Room Temperature

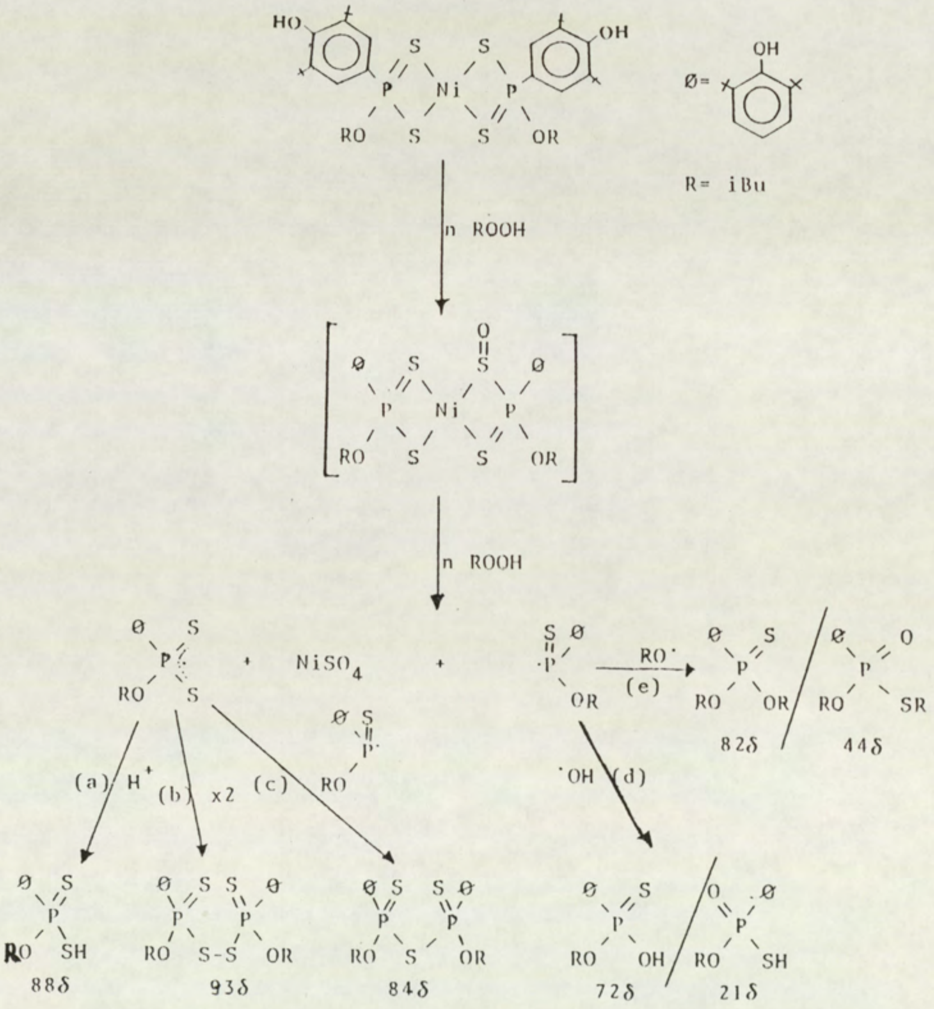
It is clear from the results presented that the oxidation of nickel dithiophosphonate results in the formation of the corresponding dithiophosphoryl sulphides (S_1 - S_4), the sulphur acids and phosphorus esters in various forms. In all cases the monosulphide and the sulphur acids feature as major transformation products. It is also observed that increases in the [NiDiBuPn]/[TBH] ratio from 1:4 to 1:20 not only results in a faster rate of decomposition of the metal thiolate but also gives rise to a corresponding increase in the relative proportions of the major products (Table 4.6).

Table 4.6 Comparison of the Relative Abundance of Products Formed after the Oxidation of NiDiBuPn by TBH in chlorobenzene at room temperature after 15 hours reaction

[NiDiBuPn]/[TBH] Molar ratio	1:4	1:10	1:20
Chemical shift(ppm) and assignment	RELATIVE ABUNDANCE (%)		
102.2 (NiDRPn)	37.9	-	-
100.2	-	8.9	9.8
98.7	-	5.0	10.4
93.4 (S_2)	8.1	-	5.3
91.5 (S_4)	2.3	-	-
90.1 (S_3)	7.2	12.3	-
88.7 (-PSSH)	6.9	11.3	9.0
86.5	10.4	20.6	10.9
84.1 (S_1)	3.8	5.7	14.7
82.2 (-P(S)OR)	1.6	-	4.6
78.2	-	15.0	4.7
72 - 75(-P(S)OH)	2.0	-	5.1
44.3	1.4	4.1	3.8
41.5	3.3	4.2	-
21.0 (-P(O)SH)	-	8.7	5.6
0.4	-	-	5.4
Others	15.1	4.2	10.7

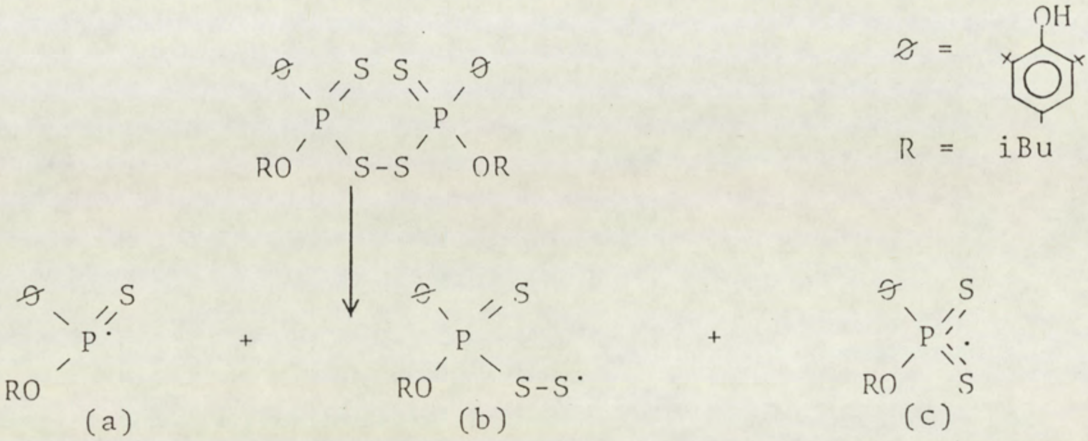
The results are strikingly similar to literature (15,23,24) data on the transformation products of structurally related metal dithiophosphates. The formation of dialkyl(aryl) dithiophoric acid as a major product of the oxidation of various metal thiolates have previously been proposed by Sexton (15). Similarly the formation of large amounts of monosulphide, the thio acids and completely oxygenated species have also been reported during the oxidation of nickel dithiophosphate by a molar excess of hydroperoxide (23). Furthermore, these (23) and other workers (24) clearly identified the precipitate formed in these reactions as hydrated nickel sulphate. It is therefore evident that the results obtained in this work (room temperature) on NiDiBuPn is in agreement with that reported (15,23,24) for the structurally related dithiophosphates.

On closer examination of Tables 4.3 -4.5 it can be seen that the formation of the higher sulphides (di, tri and tetra) is much more prevalent at lower [NiDiBuPn]/[TBH] ratios with higher molar ratios favouring the formation of the monosulphide, sulphur acids, phosphonate esters and inorganic phosphates. The only exception to this trend is the free acid (PSSH) which is favoured in appreciable quantities even at the lowest molar ratios (1:4). The behaviour can only be explained by the participation of a complementary chain breaking donor (CB-D) mechanism where an antioxidant molecule donates a hydrogen to stabilise a thiyl radical (Scheme 4.3 reaction (a)). Scheme 4.3 shows possible reaction pathways for the formation of the disulphide (reaction (b)), monosulphide (reaction (c)), the thio acids (reaction (d)) and the phosphonate esters (reaction (e)). The latter three products, as mentioned above, are usually present in large quantities when the hydroperoxide molar ratio is high since they are diagnostic of the complete breakdown of the metal thiolate.



Scheme 4.3 Possible reaction pathways for the formation of major transformation products during the oxidation of NiDiBuPn by TBH

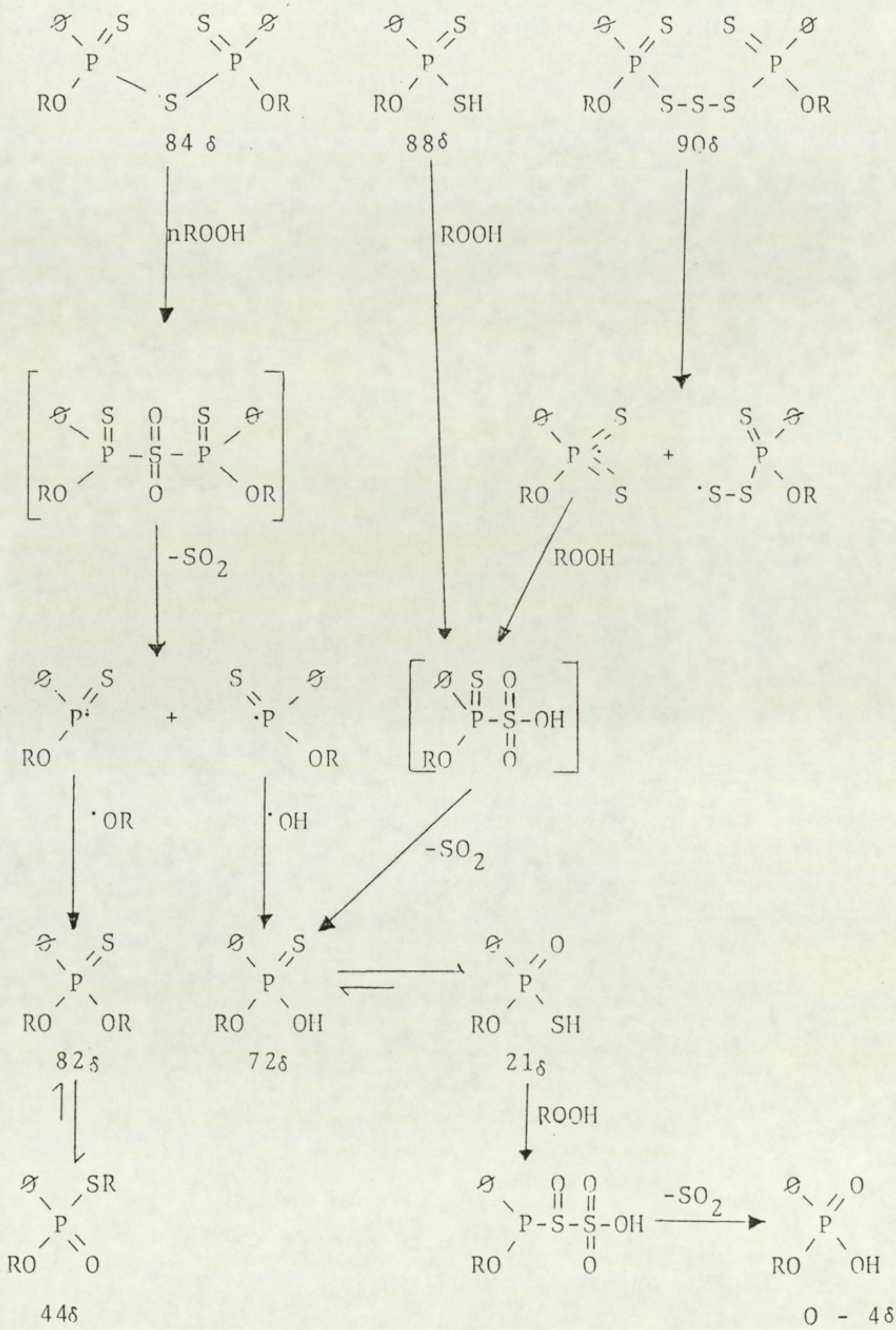
In contrast the formation of the tri and tetra sulphides which persist only at lower molar ratios may result from induced decomposition of the disulphide. By analogy with related thiophosphonyl disulphides (25), the decomposition of the thiophosphonyl disulphide may give rise to a mixture of the thiyl, perthiyl and phosphorus centred radical. It can be seen from Scheme 4.4 that further interaction between these radicals may account for the formation of not only the mono but also the tri and tetra sulphides. Radicals of a similar nature have been identified(25) by E.S.R studies of irradiated thiophosphonyl disulphide at very low temperatures (190-300K). Furthermore, it has been shown from recent studies on the oxidation of the related nickel dithiophosphate by TBH at room temperature (23) and the oxidation of the corresponding disulphide by TBH at 100°C (23), that the tri and tetra sulphides feature prominently as major reaction intermediates. The fact that these polysulphides are, more predominant at lower [NiDiBuPn]/[TBH] ratios and are only present at the initial periods when molar ratios are high (Table 4.3 - 4.6) suggests that they are merely reaction intermediates and do decompose with time to form other products. This no doubt accounts for the predominance of transformation products with only one phosphorus atom (See Scheme 4.3) as typified by the sulphur acids and esters.



(a)	+	(c)	Mono-sulphide
(b)	+	(c)	Tri—sulphide
(b)	+	(b)	Tetra-sulphide

Scheme 4.4 <u>Possible reaction pathways for the formation of sulphides</u>

As stated previously the structural assignment to some of the ^{31}P NMR signals is uncertain in view of the lack of ^{31}P NMR literature data on dithiophosphonates and the lack of time to prepare authentic samples. These are assumed, however, to be due to a variety of phosphonates esters in the absence of any other bibliographic data. The formation of completely oxygenated species which also appears to increase with increasing reaction time (0-4 δ) undoubtedly results from the subsequent decomposition of the various products (Figure 4.13) such as monosulphide (84 S) and acids (88,86,72 S). This is illustrated clearly in scheme 4.5 for the three major products which exhibited great fluctuations in the behaviour of their relative abundance. It is seen that the possible reaction pathways shown in scheme 4.5 not only accounts for the decay in major transformation products (Figure 4.13 and Table 4.5) but also gives rise to the liberation of sulphur dioxide. In the light of these results it is clearly evident that most of the transformation products of nickel dithiophosphonates are efficient peroxide decomposers.



Scheme 4.5 <u>Hydroperoxide decomposing activity of major transformation products formed during the oxidation of NiDiBuPn by TBH</u>

4.2.3.2 Thermal and Photo-reactions of NiDiBuPn

4.2.3.2.(a) Thermolysis of NiDiBuPn at 180°C

This study involved two simultaneous reactions carried out in a non oxidisable substrate (p-dichlorobenzene), one under a constant stream of nitrogen and the other in air. The reaction was carried out for a duration of 12 hours (see Section 2.7), and samples withdrawn at various time intervals were analysed by I.R., U.V. and ^{31}P NMR techniques.

The analytical results obtained from these studies (Table 4.7) not only exemplifies the high thermal stability of the nickel complex, but also indicates that its rate of decomposition may be marginally faster under nitrogen. This deduction is based on the differences observed in the colour of the mixture during the course of the reactions. The small amount of black precipitate observed at the end of both reactions appeared to be slightly higher for the reaction carried out under nitrogen. Both IR and ^{31}P NMR spectroscopic methods, however, revealed no changes in the characteristic absorption for the nickel dithiophosphonate complex even after 12 hours thermal decomposition, although a small decrease in the characteristic U.V. absorption (λmax = 325nm) of the complex was observed during U.V. study.

Table 4.7 Changes observed during thermal decomposition of NiDiBuPn under Air and N_2 atmosphere (180°C) using p-Dichlorobenzene as substrate over a period of 12 hours

Analysis	N_2	Air
Colour	Purple ⟶ dark purple/ brown	Purple ⟶ dark Purple
U.V.	Small decrease in 325 nm peak	Very small decrease in 325 nm peak
NMR	Only 102 δ peak observed	Only 102 δ peak observed
Black ppt.	Small amount visible* at the end of reaction	Less ppt visible than under N_2
I.R.	No apparent change	No apparent change

* Precipitate thought to be inorganic due to its lack of solubility in common organic solvents. The I.R. spectrum is shown in Figure 4.14 (b).

Nevertheless, there is enough evidence (Table 4.7) to suggest that the nickel thiolate is less thermally stable under conditions of limited air as compared to conditions of excess air. This behaviour correlates with the findings observed (Chapter 3 Section 3.2.3 (b)) in the overall antioxidant activity of the NiDiBuPn since its effectiveness as a stabiliser in polypropylene is improved when processing is carried out under oxidative conditions (OM) as opposed to processing in limited air (CM).

4.2.3.2(b) Thermal Oxidation of NiDiBuPn by TBH at 100°C

The thermal oxidation of NiDiBuPn (0.05 M) in the presence of tert-butyl hydroperoxide (molar ratio 1:4) gave rise to a variety of identifiable products which contrasts sharply to the findings discussed in the previous section 4.2.3.2 (a). The rate of decomposition of NiDiBuPn was faster even though a lower temperature was used. For example when compared at the same reaction time of 12 hours only one peak (nickel complex) was observed in the reaction at 180°C in the absence of TBH (4.2.3.2 (a)), which suggests that 100% of the nickel complex still remained, although after 12 hours in this reaction (in presence of TBH) only 70% of the metal complex remained undecomposed.

Table 4.8 (which shows the distribution of the products formed in this study), clearly indicates that under these conditions the corresponding trisulphide (90 δ), the free acid (88 δ) and the ester species (82 δ) constitute the initial transformation products. With the increase in reaction time, however, the relative abundance of the ester species is seen to increase progressively to reach a maxima whilst no trace of monosulphide or free acid was detected. The disappearance of the ester species (82 δ) after only 9 hours roughly coincides with the formation of the thiol acid (22 δ) which continued to increase with time. Thus, at the end of the reaction time (120 hours) about 60% of the NiDiBuPn remained undecomposed, the major transformation products being the thiol acid (22 δ) at 24% and small amounts of the dithioic acid (88 δ) at 7%. The identity of the product giving rise to the ^{31}P NMR signal with a chemical shift of 111 ppm is unknown but is possibly due to an ester species by analogy with the structurally related dithiophosphates $^{(26)}$. Furthermore, some workers $^{(27)}$ have also assigned similar ^{31}P NMR signals (102 δ, 103 δ, 110 δ) to phosphonotrithioc esters. The mere persistence of this species suggests that it may be an important transformation product.

Table 4.8 Thermal Oxidation of NiDiBuPn (0.05M) by TBH in p-dichlorobenzene at 100°C (molar ratio 1:4)

Reaction time (hrs)	5mins	1hr	2hrs	5hrs	12hrs	30hrs	60hrs	100hrs	120hrs
δ (ppm)*	RELATIVE ABUNDANCE (%)								
112	-	-	-	-	-	12.7	8.4	5.8	7.9
102	94.2	91.1	90.0	82.0	69.0	67.4	66.5	62.9	57.3
90	2.7	0.9	-	-	-	-	-	-	-
88	3.1	2.1	-	-	-	-	4.9	6.0	6.7
82	-	5.9	10.0	18.0	21.0	-	-	-	-
22	-	-	-	-	10.0	19.9	20.1	25.2	24.1

* For structural assignments see Table 4.2

Although the rate of thermal oxidation of the nickel complex has been shown to be much faster in the presence of TBH as compared to the thermal studies (4.2.3.2 (a)) under nitrogen and air, significant differences are observed between this study and that carried out at room temperature using the 1:4 molar ratio of nickel and TBH (4.2.3.1 (a)). A comparison of the data in Tables 4.3 and 4.8 indicate clearly that the room temperature oxidation of NiDiBuPn by TBH (Table 4.3) gives rise to a considerably faster reaction rate as can be seen by the residual NiDiBuPn observed at a similar reaction time. It has been shown (Table 4.8) that about 60% of the nickel complex remained undecomposed even after 120 hours thermal oxidation by TBH (at a 100°C) whereas only 11% remained after 70 hours during a similar reaction but at room temperature (Table 4.3). A direct consequence of this difference in the rates of oxidation of the parent nickel complex is the formation of a wide range of products at room temperature as compared to much fewer products observed at the higher temperature. Although the rate of oxidation is slower at high temperature, the formation of the phosphonothioic acid (22 δ) as a predominant product appears to be much more favourable under these high temperature conditions, whereas at room temperature this was only found to be the case at high molar ratios and not at a 1:4 nickel to TBH ratio. In addition no monosulphide (84δ) was detected in this study whilst it was at the same ratio at room temperature. In general the predominant products at the end of the 1:4 room temperature reaction were the sulphides (mono, di, tri and tetra) and phosphonodithioic acid (88 δ) with only a small amount of the phosphonothioic acid (22 δ). These findings are illustrated in Figure 4.15 which shows that the rate of oxidation of NiDiBuPn by TBH is faster at room temperature and consequently a higher concentration of transformation products are observed.

4.2.3.2 (c) Photolysis of NiDiBuPn in the presence of TBH at 30°C

It has previously been shown (Figure 3.14) that NiDiBuPn is highly resistant to photolysis in the absence of TBH when compared to other metal dithiophosphonates (e.g. Fe, Co). Thus the photolysis of the nickel complex (0.05 M) in the presence of TBH ([NiDiBuPn]/[TBH] = 1:2) was carried out (see Section 2.6(c)) in methyl cyclohexane at 30°C. The ^{31}P NMR spectral changes occurring during this reaction are qualitatively illustrated in Figure 4.16. In common with thermal studies a small decrease was observed in the λ_{max} of 325nm which is a characteristic peak of the nickel complex. Again, as in the previous sections (4.2.3.2 (a) - 4.2.3.2 (b)), the nickel complex is shown in this study to be highly stable under photo-oxidative conditions. Even after 190 hrs. U.V. exposure about 85% of the NiDiBuPn still remained undecomposed and the other 15% was found to be dithiophosphonic acid with a chemical shift in the region of 88 δ. This species has also been found to be a major transformation product in all the oxidative reactions carried out. Samples from both photolysis and thermal decomposition reactions were examined by E.S.R. at varying intervals of time throughout each study to attempt to find a phenoxyl radical to support the cyclical regenerative mechanism proposed (Scheme 3.0) but none were detected.

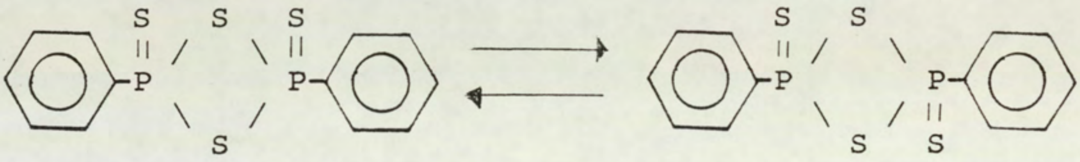
From the evidence collected, it is clear that NiDiBuPn is extremely stable under both thermal and U.V. conditions. There seems no doubt that this behaviour accounts for the excellent overall antioxidant activity of this compound in polypropylene under melt, thermal and photo-oxidative conditions (Chapter 3).

4.2.3.3 Thermal Oxidation of TPS in the Presence of Air

TPS was heated using p-dichlorobenzene as substrate in the presence of air at 180°C. Samples were withdrawn at various time intervals and examined using NMR. Prior to analysis chlorobenzene was added to withdrawn samples in order to form a solution as p-dichlorobenzene alone is a solid at temperatures below 40°C.

Figure 4.17 illustrates (using NMR spectra) the changes observed during thermal oxidation of TPS. It is clear that the TPS (18.7 δ) is being transformed into many new products which have very similar chemical shifts (70.1-76.9 δ), the most prominent of which is at 73.5 δ. These new products must contain very similar environments around the phosphorus atom as they differ so little in chemical shift.

Phenyl phosphonodithioic anhydride $(C_6H_5PS_2)_2$ which has a similar structural formula to TPS (except that TPS has a hindered phenolic group) varies considerably in reported chemical shifts from 13 ppm (28) to 15.4 ppm (29,30) and to 72 ppm (31). It has not been established, however, whether such a large variation is associated with the presence of dimers, trimers and polymers or with the existence of an equilibrium in solution between the cis and trans isomers (Reaction 1).



Cis Trans (1)

This phenyl anhydride has been reported (27) to be a dimer after molecular weight determinations by ebullioscopic measurements as opposed to a trimer as had previously been reported (32). Colclough (33) has shown using mass spectrometry that TPS is polymeric.

With regard to the structure of organophosphonothioic anhydrides $(RPOS)_n$, once again there is no unanimous opinion in the literature. Trimeric phenyl phosphonothioic anhydride has a chemical shift of 70 ppm (34), other similar anhydrides $(RPOS)_n$ have been regarded as pentamers (35), trimers (36,39), dimers (37) and monomers (38). On the whole more authors (34,36,39) have reported the trimeric structure $(RPOS)_3$ which would consist of alternating phosphorus and oxygen atoms, three of each and there are three thionic sulphur atoms. Thus, in the light of this literature evidence we can postulate that signals in the range 70.1-76.9 δ (shown in Figure 4.17) may be due to various organophosphonothioic anhydrides $(RPOS)_n$.

4.2.3.4 Oxidation of Phosphonodithioic acid by TBH at Room Temperature

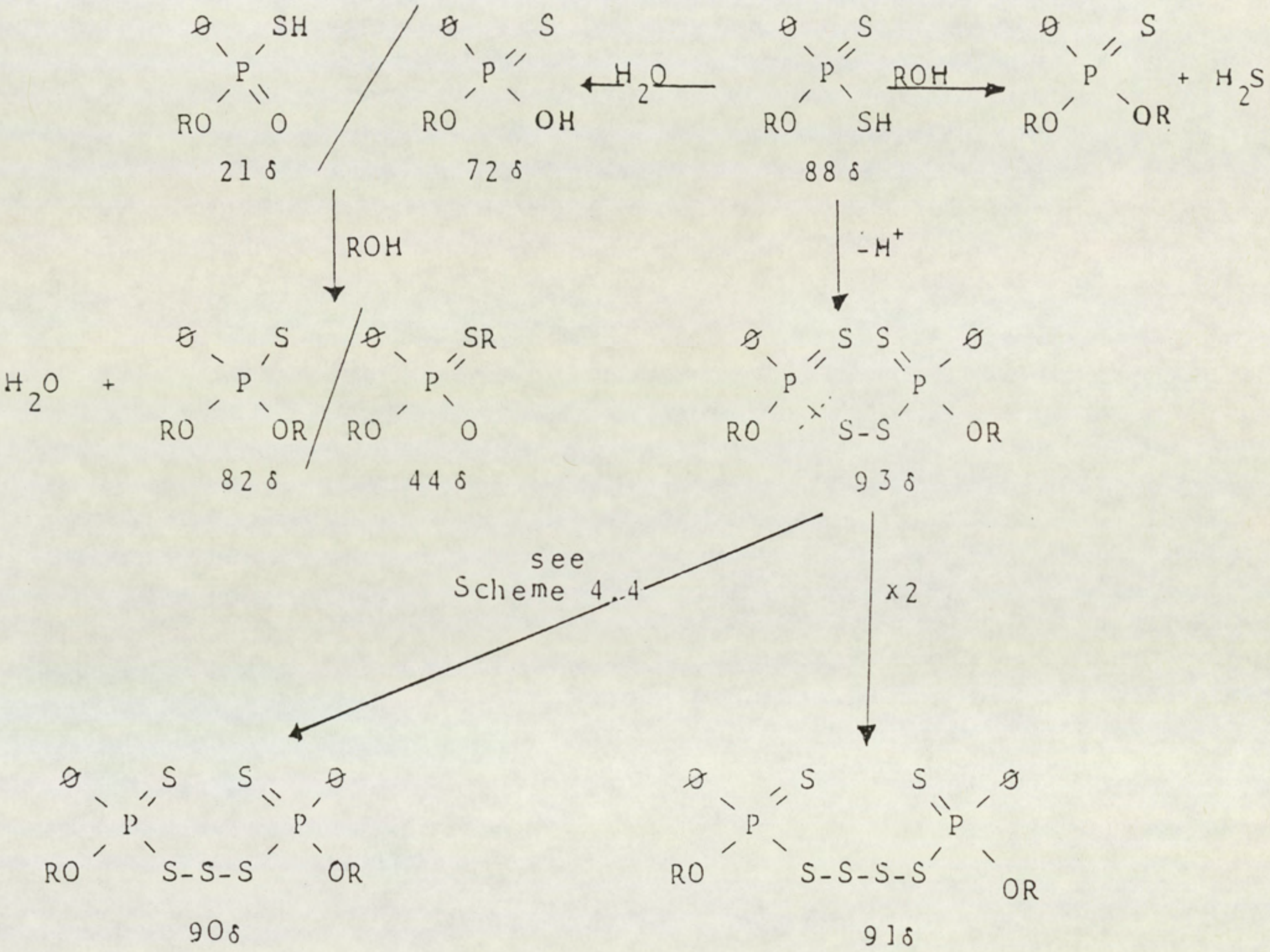
The distribution of the products formed during the room temperature (25°C) oxidation of phosphonodithioic acid (0.05M) by TBH at a molar ratio of 1:4 is shown in Table 4.9, whilst Figure 4.18 illustrates the changes occurring during the ^{31}P NMR analysis. The original starting material (88 δ) contained about 6% impurity which gave rise to an absorption at 82 ppm. This impurity is assigned to an ester species (See Table 4.2) and seems to increase in abundance with storage time.

The results obtained in this work indicate clearly that the initial major transformation product of the dithioic acid is the corresponding disulphide (93.3 ppm). It can be seen (Table 4.9) that over 60% of the dithioic acid is decomposed after only 1 hour of reaction whilst the disulphide constitute the major product at almost 40%. Other minor products formed at this stage include the tri (4.9%) and tetra-sulphide (4.6%), various esters giving rise to signals in the region of 42-48 ppm (~12%) and a small amount of the inorganic acid (0.8%). Very little change was observed in the relative abundance of the various species up to 45 hours reaction which clearly suggests that the hydroperoxide appears to have been used up in the first hour of the reaction. It has also been observed (Table 4.9) that some dithioic acid is regenerated after 40 hours although the proportions of the other products remained somewhat stable. At longer reaction times (40 hours), however, it is seen that further decomposition of the dithioic acid and the corresponding disulphide results primarily in the formation of large amounts of the trisulphide (90 S) and the ester species with a chemical shift of 44 ppm. These results are also illustrated in Figure 4.19 which clearly indicates that the initial major product of the oxidation of dithioic acid is the corresponding disulphide which then undergoes further decomposition to form other products as outlined in Scheme 4.6.

Table 4.9 Oxidation of Phosphonodithioic acid by TBH in chlorobenzene at room temperature

Reaction time (hrs)	0hrs	1hr	3hrs	5hrs	42hrs	840hrs
δ (ppm) *	RELATIVE ABUNDANCE (%)					
93.3 (S_2)	-	39.0	32.6	30.1	31.3	16.6
91.0 (S_4)	-	4.6	5.1	6.2	4.4	6.5
90.4 (S_3)	-	4.9	6.9	7.6	4.8	17.6
88.4 (-PSSH)	94.1	32.2	31.5	33.2	47.9	27.3
82.3	5.9	2.2	-	-	-	-
48.2	-	2.6	1.9	2.1	0.9	-
44.3	-	0.6	5.0	6.2	2.8	18.1
42.2	-	7.5	7.3	6.7	5.6	3.6
21.1 (-P(O)SH)	-	0.8	2.2	1.6	1.2	5.1
0.8	-	-	-	-	-	0.9
Others	-	5.6	7.5	6.3	1.1	4.3

* For other structural assignments see Table 4.2



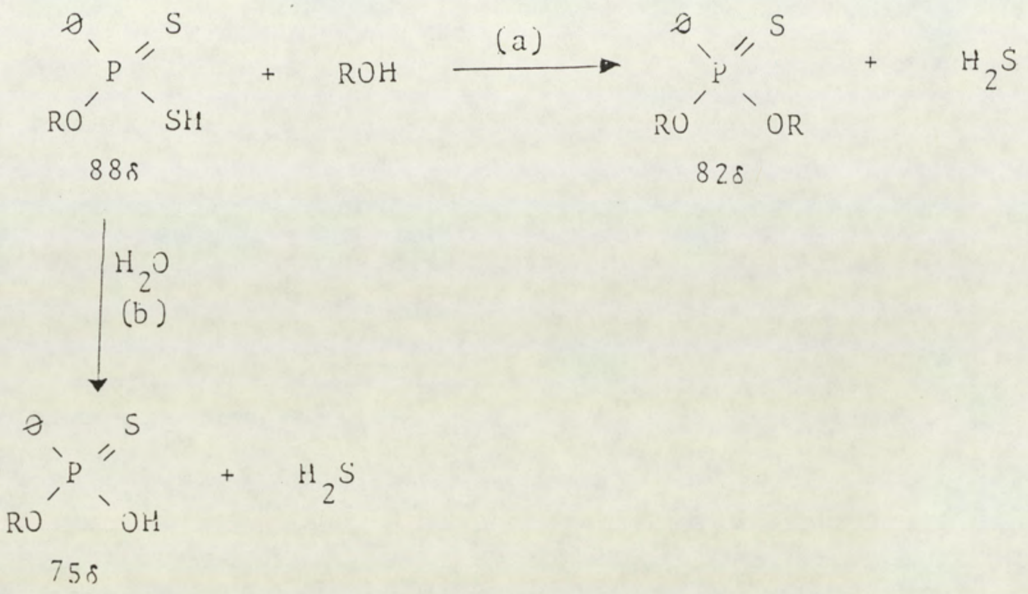
Scheme 4.6 <u>Oxidation products formed during the reaction of Phosphonodithioic and TBH at 25°C.</u>

4.2.4 CONFIRMATORY STUDIES

This section describes some simple experiments which are designed as a means of aiding the assignment of some of the ^{31}P NMR signals observed during the oxidation studies, with particular reference to the ester species and the thioic acids.

4.2.4.1 Esterification of Phosphonodithioic Acid (PSSH)

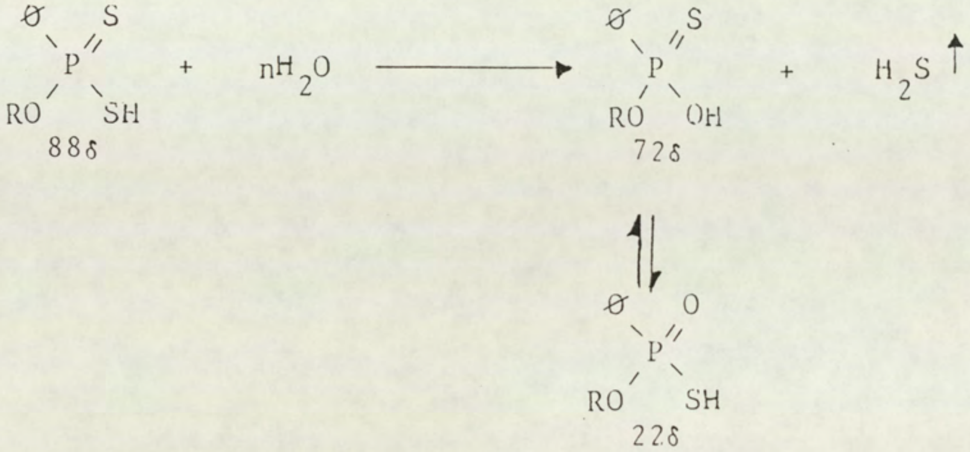
The distribution of products formed during the esterification of dithioic acid (excess of isobutyl alcohol added to acid) at room temperature is qualitatively represented in Figure 4.20 which shows the ^{31}P NMR spectral changes occurring during the reaction. The results show clearly that the interaction of isobutyl alcohol with the dithioic acid results mainly in the formation of the ester species (s=82). Although this ester is shown to be present as an impurity in the original material (Figure 4.20) it is seen to increase at a dramatic rate, such that at the end of the reaction (850 hours), only one other minor product (thioic acid) was detected (Figure 4.21). The formation of the thioic acid (PSOH) is believed to result from a secondary reaction between the dithioic acid and any water present in the mixture (see Scheme 4.7).



Scheme 4.7 Esterification of Phosphonodithioic acid

4.2.4.2 Hydrolysis of Phosphonodithioic Acid

The ^{31}P NMR spectral changes taking place during the hydrolysis of the dithioic acid (excess of water added to acid) at room temperature is shown in Figure 4.22 whilst the distribution of products is graphically illustrated in Figure 4.23. As the hydrolysis reaction progresses, the results (Figures 4.22 - 4.23) show clearly that in addition to the formation of thioic acid (P(S)OH - 72 δ), an appreciable quantity of the ester species (82 δ) is also formed during the reaction and H_2S was clearly detected (by smell). The possible reaction pathway for both products is shown in Scheme 4.8 although it is somewhat surprising that the ester is formed in such high quantities.



Scheme 4.8 Hydrolysis of Phosphonodithioic Acid

Nevertheless these results are consistent with literature data (40) on the hydrolysis of the structurally similar phosphorodithioic acid. These workers showed that the thionic acid (-P(S)OH) is the predominant product although small quantities of ester species are also formed. Their findings are in accordance with the results obtained in this work except that large quantities of the ester species appear to have been formed in this instance. The isomerisation of the thionic acid (72 δ), however, to the thiol form (22 δ) is clearly illustrated (Figure 4.23) and is also shown in Scheme 4.8. This is in accordance with the established principles (41) which govern the thiono-thiol equilibrium in most organophosphorus acids. A similar behaviour has also been observed (42) with thio acids formed from the structurally related dithiophosphates.

4.2.4.3 The Use of Triethylamine as an Assignment Aid During ^{31}P NMR Analysis

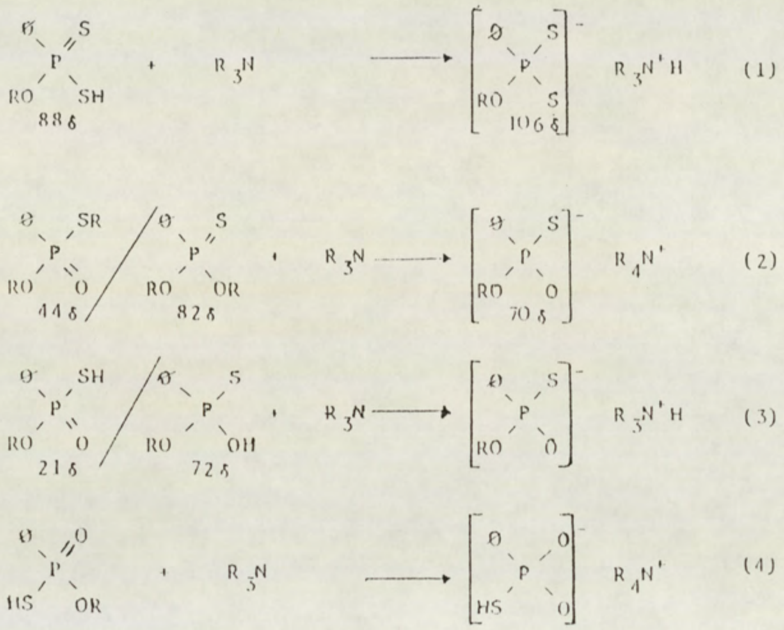
The use of a tertiary amine as an aid to the assignment of some ^{31}P NMR signals has been previously documented (33,42). The principle involved in the utilisation of this method is based on the conversion of unionised acid groups to the ionised salt forms which is reflected by a shift in the ^{31}P NMR absorption after reaction.

The effect of the triethylamine (excess of amine added to acid) on the chemical shift of phosponodithioic acid (Section 2.10) is shown in Table 4.10 and Figure 4.24.

Table 4.10 Reaction of Dithiophosphonic acid with Triethylamine at room temperature

ACID		ACID + R_3N(10 mins)	
δ ppm	% Yield	δ ppm	% Yield
88.5	88	106.7	88
82.2	12	70.4	12

The dithioic acid as prepared gives a sharp absorption at 88.5 δ and shows the presence of an ester species (82 δ) as an impurity. The addition of excess amine to a solution of the sulphur acid moved the original absorption at 88.5 δ to 106.7 ppm. The absorption due to the ester impurity was moved upfield to 70 δ. It is clear that the interaction of the amine with both species results in quantitative conversion of the species to the respective amine salts as shown in Scheme 4.9.



Scheme 4.9 Reaction of R_3N with Acid and Ester Species

Whilst the shift in the original absorption of the dithioic acid is clearly due to the conversion of the unionised group to the ionised salt form (Reaction 1), the exact product due to the interaction of the ester species with the amine is not clear at the present time. The shift in the ester absorption may be due to quaternization of the amine as shown in Scheme 4.9 (Reaction 2). This appears to be in accordance with literature data on the alkylation of amines by thiophosphates and the quaternization of tertiary amines during the phosphonylation of alcohols with dithiophosphates(43).

The effect of the addition of triethylamine on the chemical shift of a mixture of transformation products formed during the oxidation of phosphonodithioic (PSSH) acid by TBH at room temperature (see Section 4.2.3.4) is shown in Table 4.11 and Figure 4.25.

Table 4.11 Reaction of Triethylamine with a mixture of Transformation Products Formed during the Oxidation of Phosphonodithioic Acid by TBH at Room Temperature

Amine reaction time (hrs)	0hrs	4hrs	18hrs	54hrs
Chemical Shift (ppm)	RELATIVE ABUNDANCE (%)			
106.5	-	7.3	16.8	33.8
95.5	-	1.4	8.8	4.2
93.3 (S_2)	16.6	22.1	7.3	1.9
91.0 (S_4)	6.5	2.3	-	-
90.3 (S_3)	17.6	2.8	-	-
88.6 (-PSSH)	27.3	26.1	11.5	-
70.3	-	28.1	32.6	37.1
44.4	18.1	-	-	-
42.1	3.6	-	-	-
21.3 (-P(O)SH)	5.1	-	-	-
14.3	-	1.5	7.0	9.3
11.4	0.8	-	2.8	3.9
0 - 4	0.9	1.1	2.5	2.4
Others	3.6	7.5	10.7	7.5

At the end of the oxidation reaction of the dithioic acid and TBH (see Section 4.2.3.4) the ^{31}P NMR reaction mixture indicated the presence of a fair amount (27.3%) of residual dithioic acid (88.5 δ) and moderate amounts of other transformation products which include the di, tri and tetra sulphides (93, 91 and 90 δ respectively), the thioic acid (21 δ) and the ester species with a chemical shift of 44 δ (see Table 4.9). On addition of excess triethylamine to this mixture the ^{31}P NMR signals due to the thioic acid (21δ) and the ester species (44δ) were completely replaced by a signal with a chemical shift of 70 δ after only 4 hours. This is not surprising as it is observed (Scheme 4.9 reactions 2 and 3) that the phosphorus containing anions which result from the interaction of these species with tertiary amines are identical. The conversion of some of the residual dithioic acid (88.5 δ) to the ionised salt (106 δ) is also clearly evident after 4 hours amine reaction. This signal (106 δ) is seen to increase with reaction time in parallel with a corresponding reduction in the intensity of the signal due to the unionised dithioic acid at 88.5 (Figure 4.25). The fact that the relative abundance of the amine salt (at 106 δ) is much higher after 54 hours reaction than can be accounted for on the basis of the original quantity of the dithioic acid clearly suggests that this acid is regenerated via the desulphuration of the polysulphides (tri and tetra) during the course of the reaction. It is believed that the desulphuration of the polysulphide not only results in the formation of dithioic acid (88 S) which is simultaneously converted to the amine salt (106 S), but also gives rise to a slight increase in the relative abundance of the disulphide (93 S) which eventually decays to a minimum. The desulphuration of polysulphides by tertiary amines and phosphines is known (44,45) to occur in the presence of hydrogen sulphide, and it has also been suggested (46) that the resultant amine salt is responsible for the dark red colour of the solution as was observed in these studies. These results are consistent with the findings reported (42) for the interaction of triethylamine with the structurally related thiophosphoryl polysulphides. Other minor products observed at the end of the amine reaction (54 hours) include an ester species (95.5 S) and some completely oxygenated species (14 - 0.8 S).

Similarly the effect of triethylamine on the chemical shifts of transformation products observed during the room temperature hydrolysis of the dithioic acid is shown in Figure 4.26 and Table 4.12. The major transformation products of the hydrolysis of phosphonodithioic acid (see Section 4.2.4.2) are the ester species (82 S) and both isomers of the thioic acid (72 and 21 S).

The addition of excess triethylamine to this mixture gave rise (after 10 minutes) to the instantaneous conversion of the species present to their respective amine salts.

Table 4.12 Effect of Triethylamine on the Transformation Products Formed after the Hydrolysis of Dithiophosphonic acid (912 hrs)

WATER + ACID (912 hrs)			WATER + ACID + R_3N (10 minutes)	
Assignment	s	% Yield	s	% Yield
-P(S)OR	82	52	70	73
-P(S)OH	72	24	53	8.3
-P(O)SH	21	24	14.6	15.6
			10.7	2.9

By analogy with the findings previously discussed in this section, the interaction of the amine with all three species present (82, 72 and 22 s) should give rise to just one ^{31}P NMR signal (70 s) since the phosphorus containing anion in all cases is similar (Scheme 4.9 reaction 2 and 3). The fact that the two additional ^{31}P NMR absorptions (53 and 14.6 s) were observed suggests that other secondary reactions may be occurring. For instance the absorption with the chemical shift of 53 s may be due to the formation of amine salts of slightly different structure (Scheme 4.9 Reaction 4). The origin of the absorption with a chemical shift of 14.6 s is not clear at the present time but the position of this signal suggests it to be due to a highly oxygenated species, possibly pyrophosphonates (P-O-P linkages).

In the light of this discussion it is fairly clear that the structural assignment to most of the ^{31}P NMR absorptions observed during various oxidation studies is somewhat justified in view of the data obtained from the confirmatory reactions.

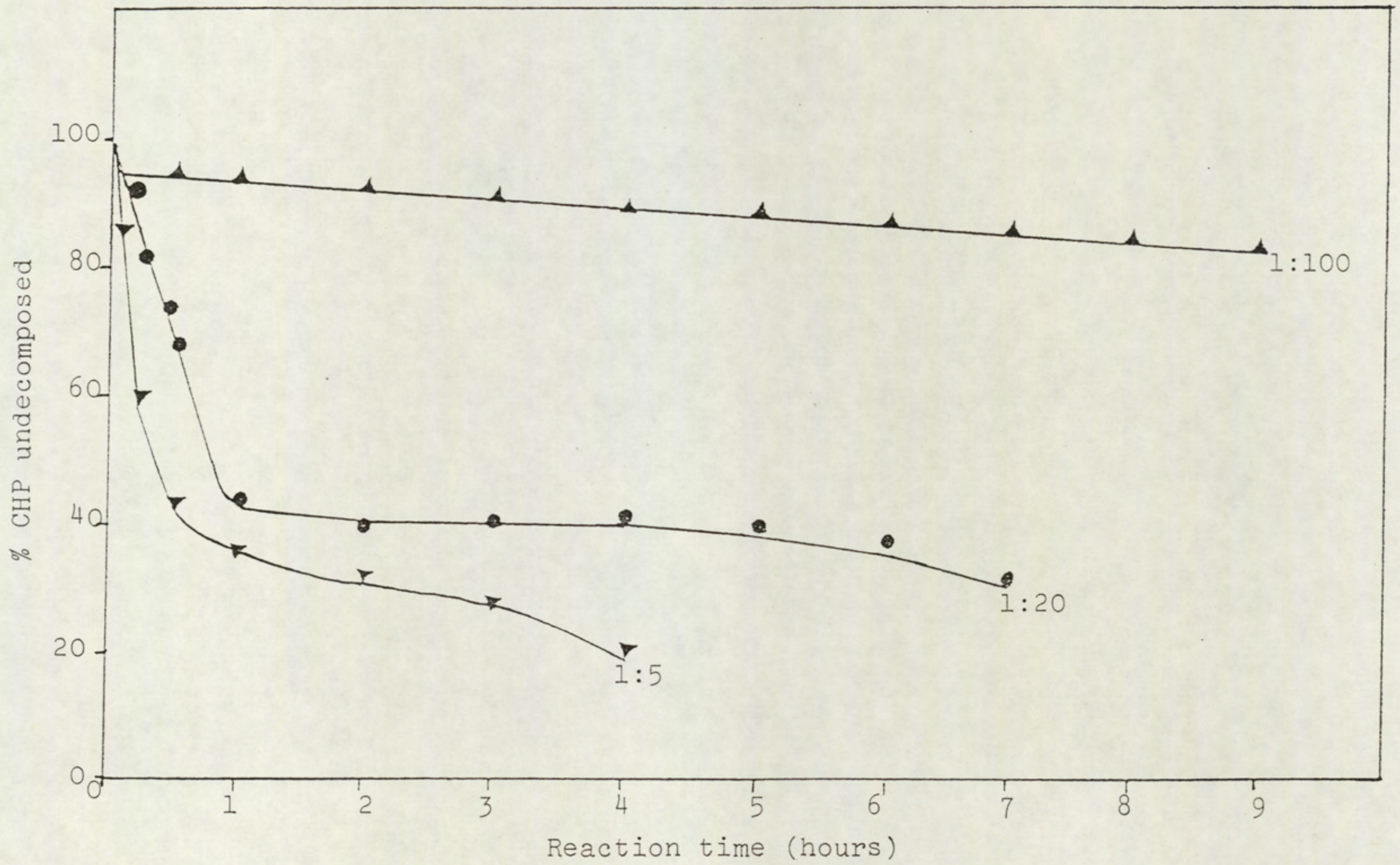


Figure 4.1 Decomposition of CHP by NiDiBuPn at 110°C, numbers on curves represent molar ratio of NiDiBuPn:CHP (concentration of CHP= 1×10^{-2} mol dm^{-3}).

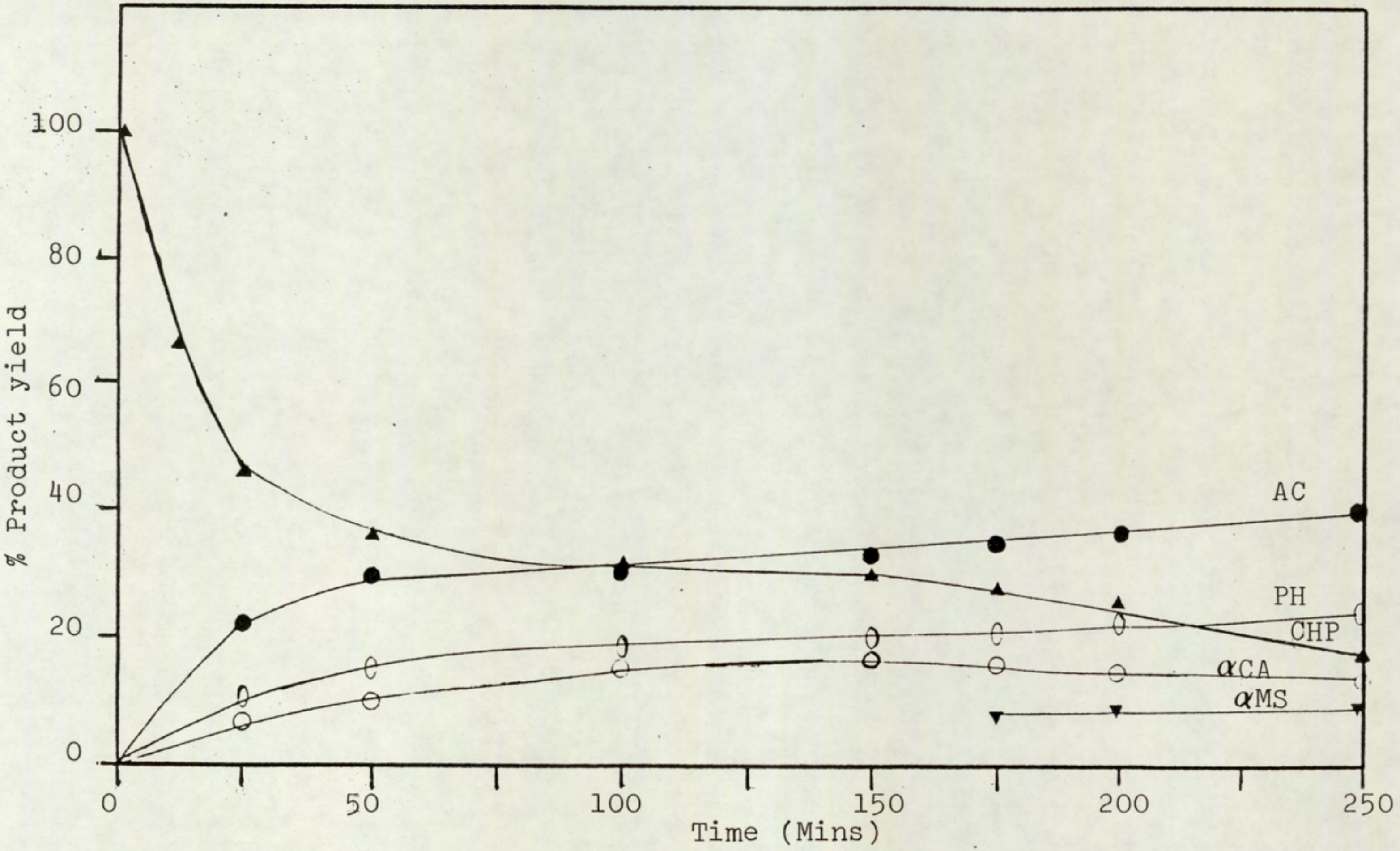


Figure 4.2 Decomposition of CHP by NiDiBuPn at 110°C and its products of decomposition (molar ratio NiDiBuPn to CHP 1:5), where CHP concentration = 1×10^{-2} mol dm^{-3}.

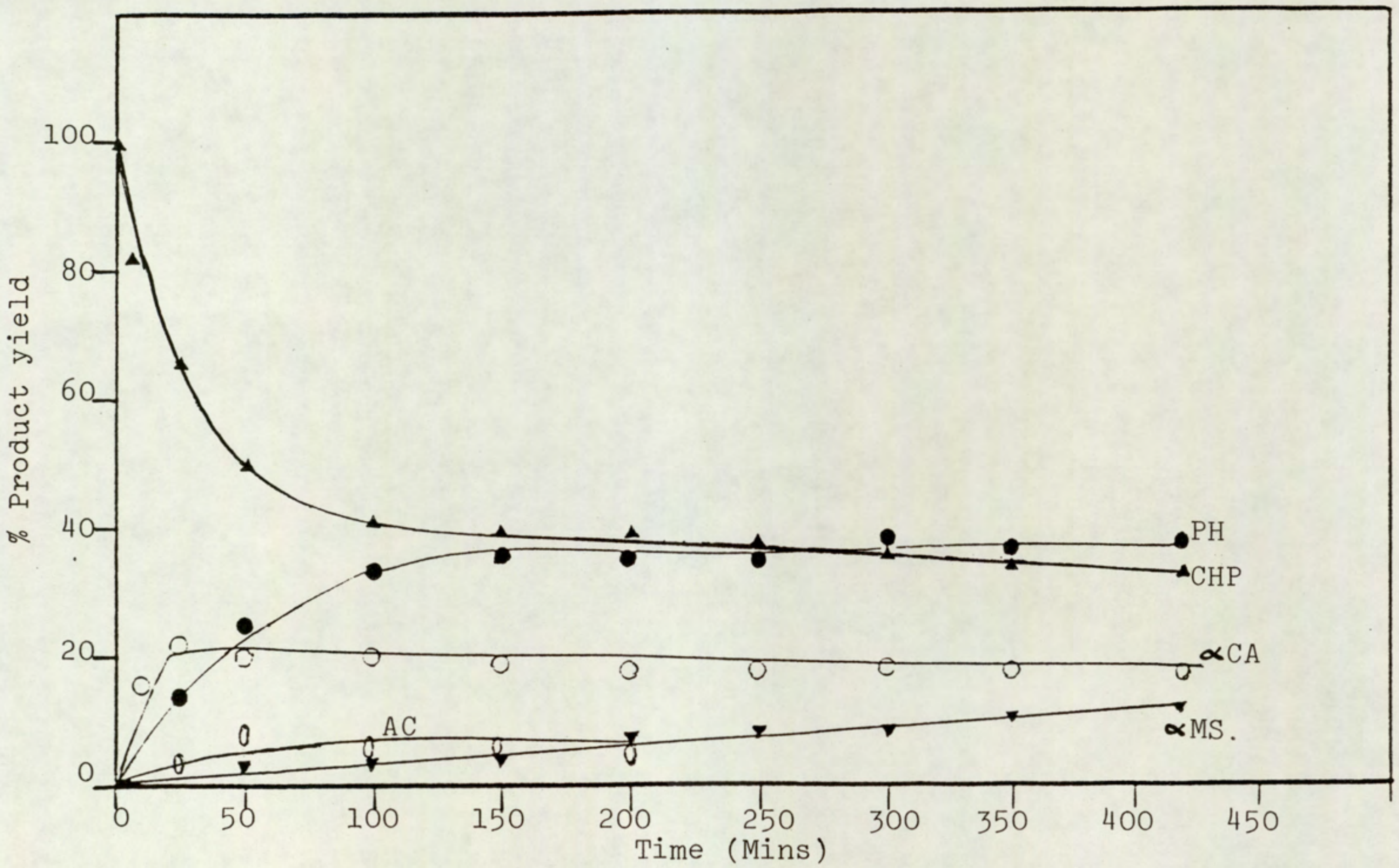


Figure 4.3 Decomposition of CHP by NiDiBuPn at 110°C and its products of decomposition (molar ratio NiDiBuPn to CHP 1:20), where CHP concentration = $1x10^{-2}$mol dm^{-3}.

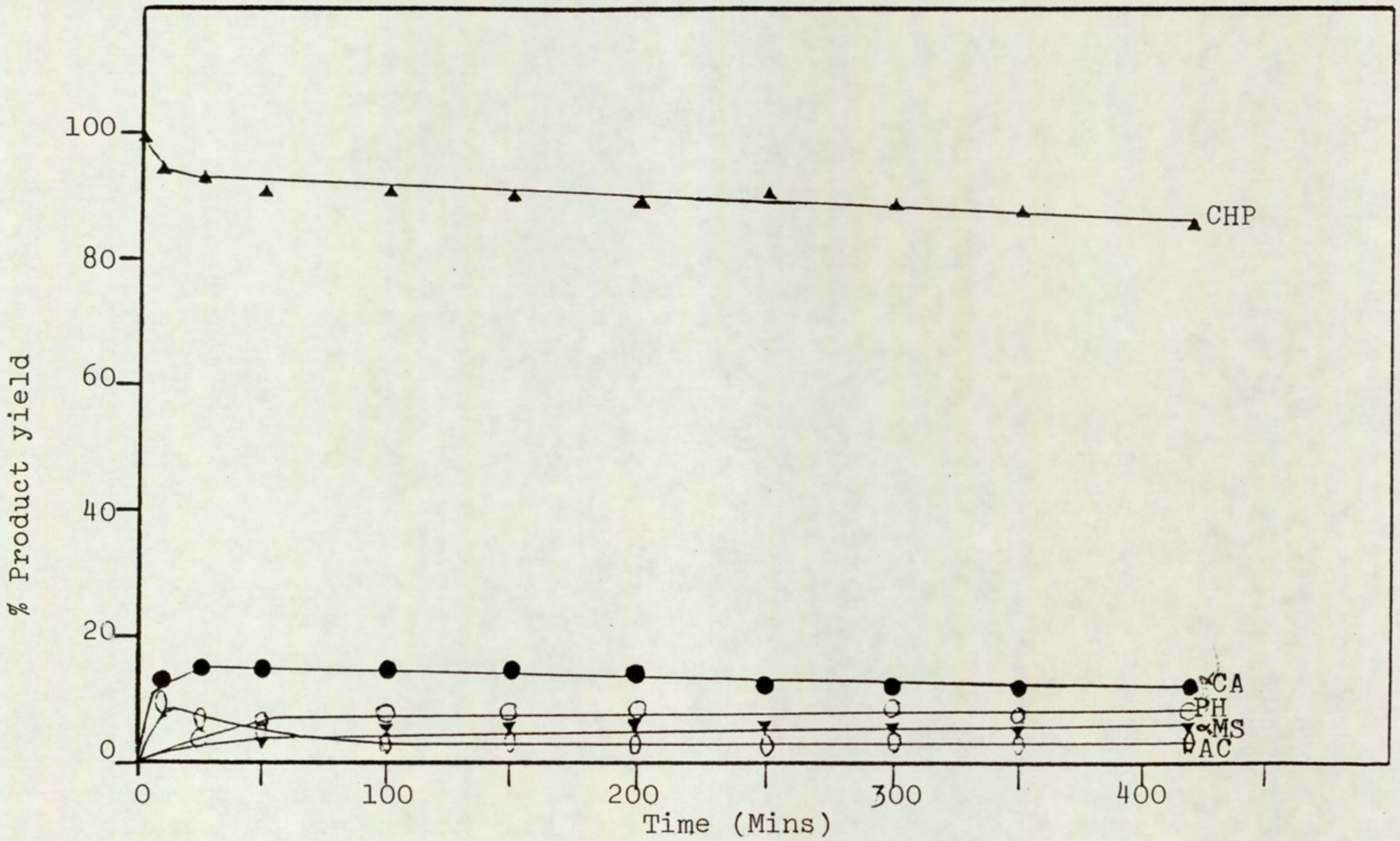


Figure 4.4 Decomposition of CHP by NiDiBuPn at 110°C and its products of decomposition (molar ratio NiDiBuPn to CHP 1:100), where CHP concentration = 1x10^{-2}mol dm^{-3}.

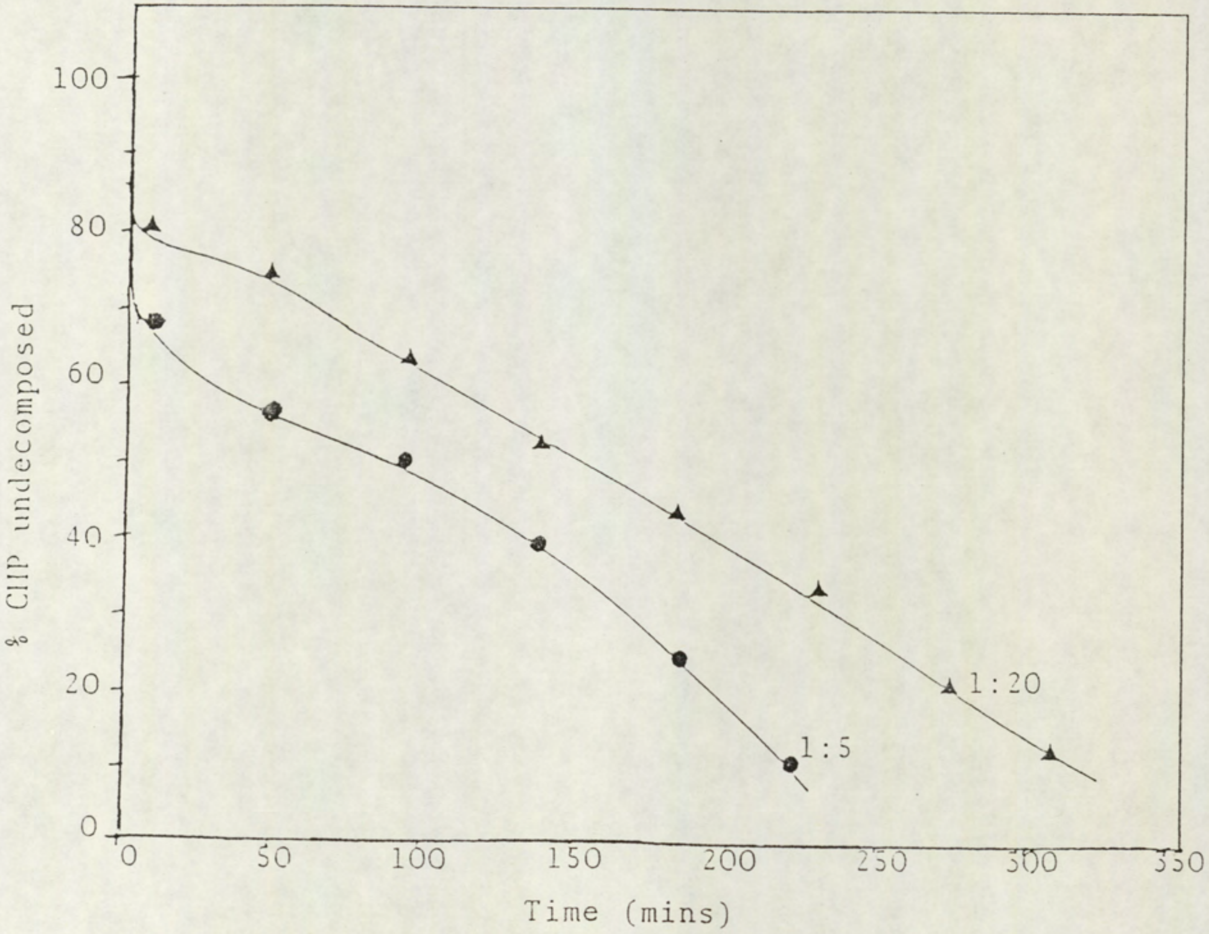


Figure 4.5 Decomposition of CHP by TPS at 110°C, numbers on curves represent molar ratio of TPS:CHP (concentration of CHP= 1×10^{-2} mol dm^{-3}).

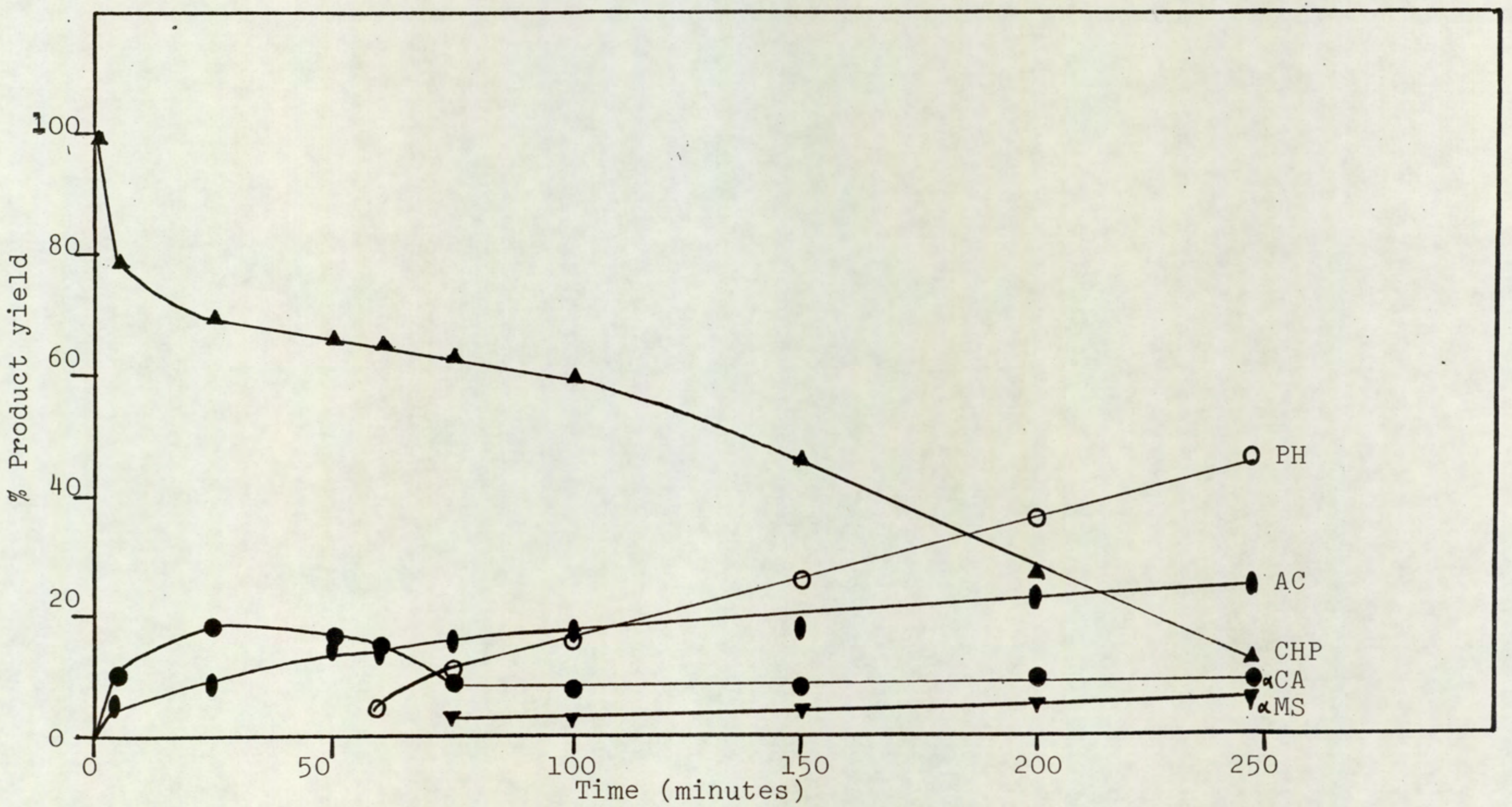


Figure 4.6 Decomposition of CHP by TPS at 110^{o}C and its products of decomposition (molar ratio TPS to CHP 1:5), where CHP concentration = 1x10^{-2}mol dm^{-3}.

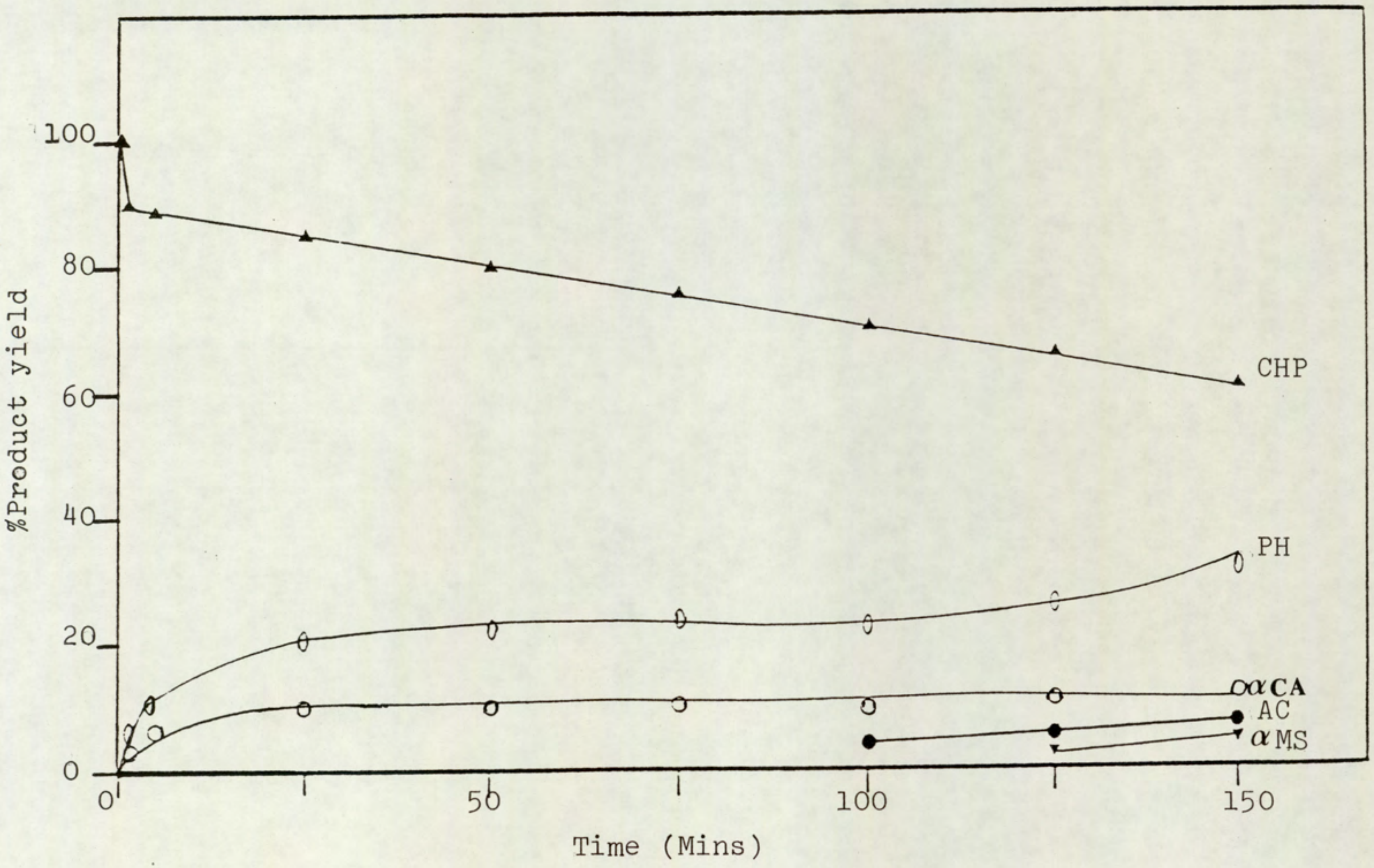


Figure 4.7 Decomposition of CHP by TPS at 110°C and its products of decomposition (molar ratio TPS to CHP 1:20), where CHP concentration = 1×10^{-2} mol dm^{-3}.

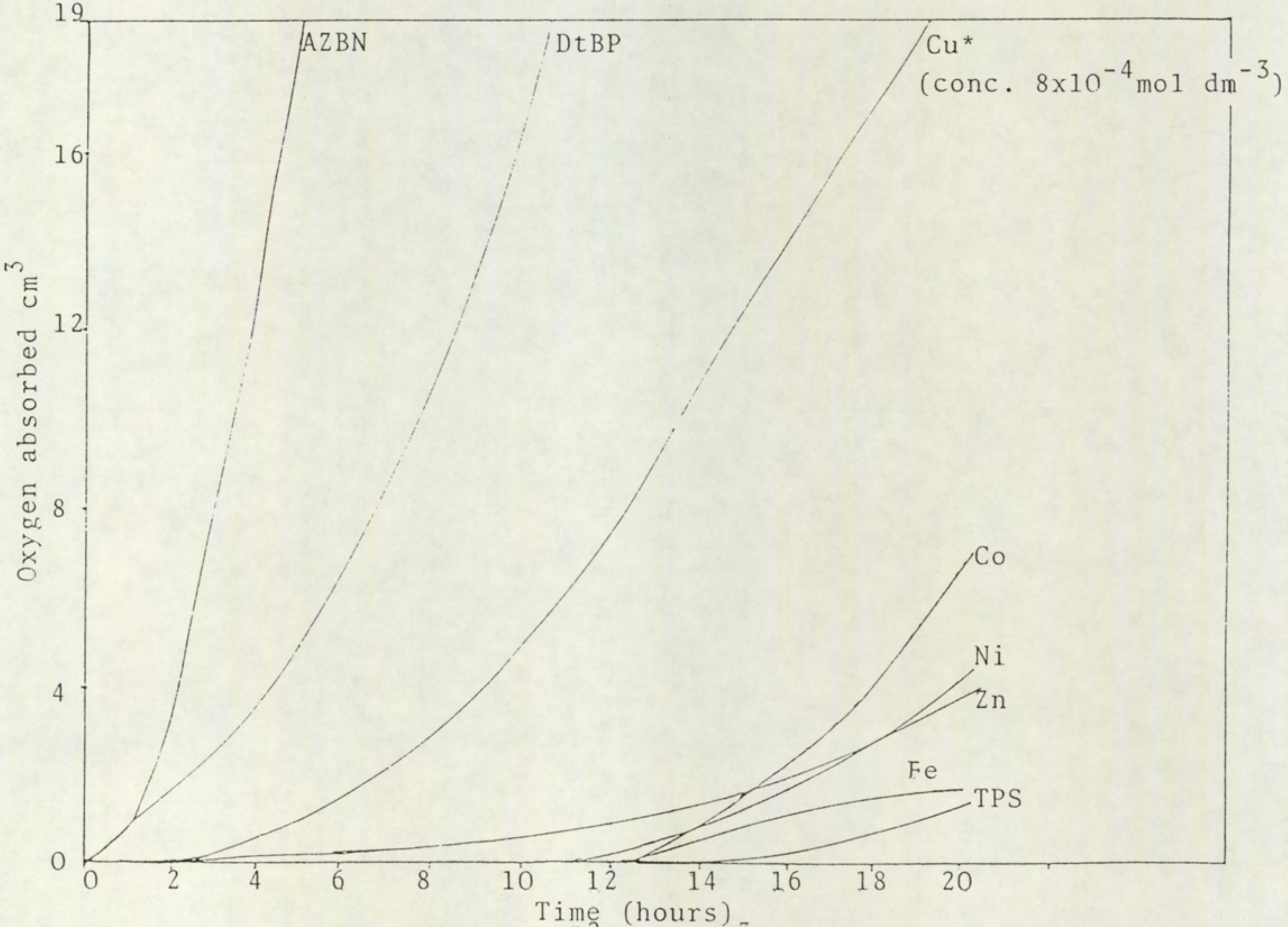


Figure 4.8 Initial stages of AZBN (1×10^{-2} mol dm^{-3}) initiated oxidation of cumene at $55^{o}C$ in the presence of 4×10^{-4} mol dm^{-3} dithiophosphonates *

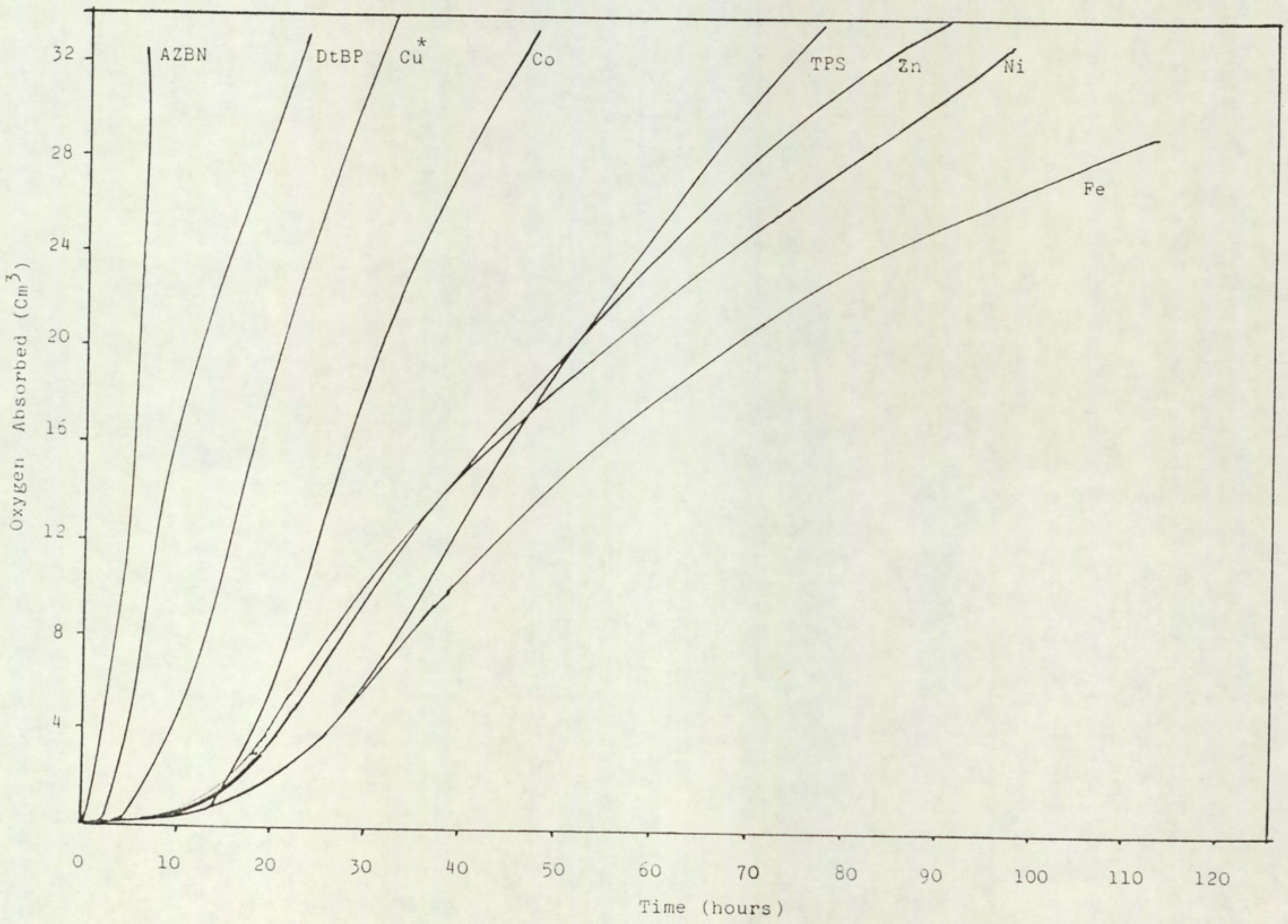


Figure 4.9 AZBN ($1x10^{-2}$mol dm^{-3}) initiated oxidation of cumene at 55°C in the presence of dithiophosphonates* ($4x10^{-4}$mol dm^{-3})

* Cu concentration $8x10^{-4}$mol dm^{-3}

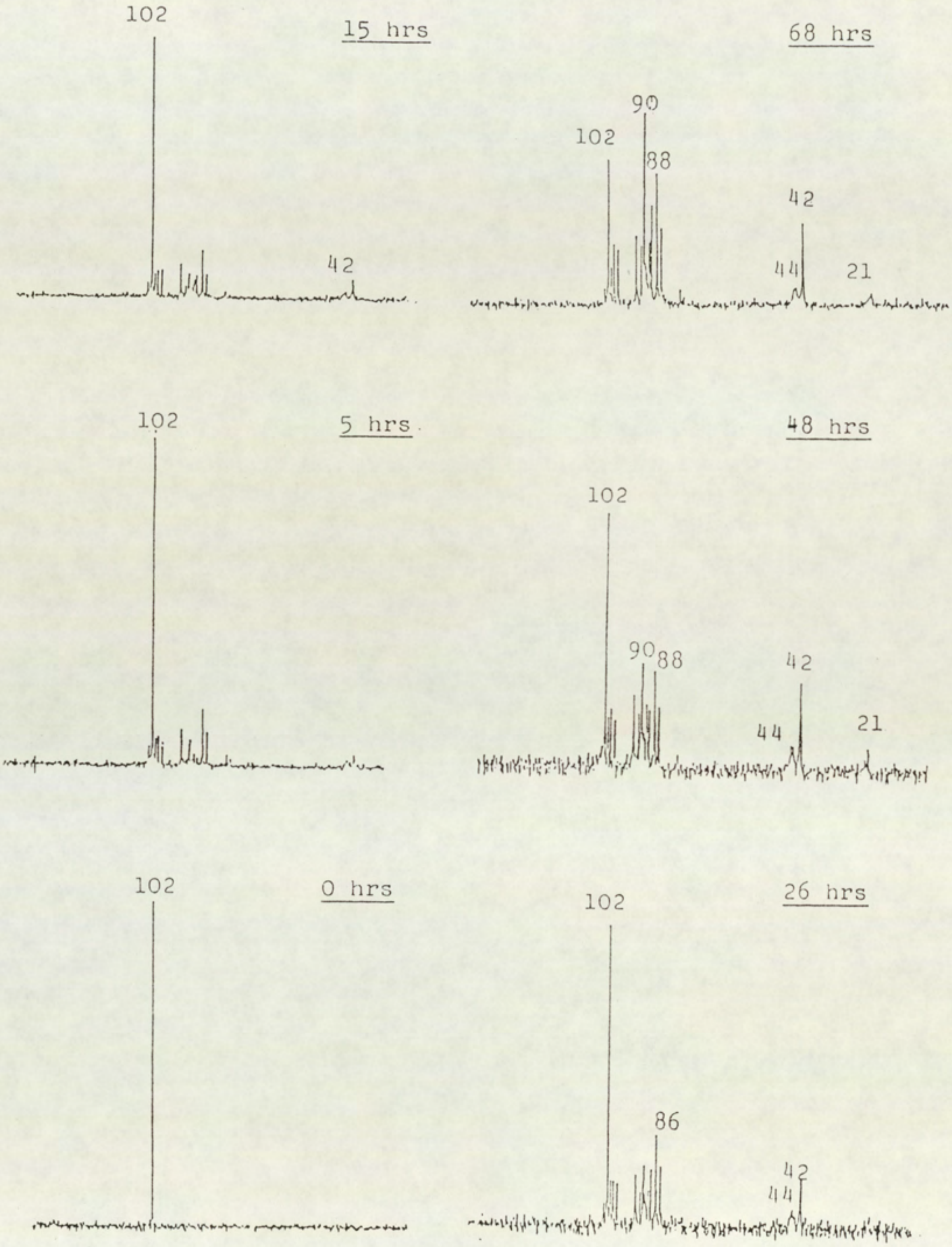


Figure 4.10 ^{31}P NMR spectral changes occuring during the 1:4 molar oxidation of NiDiBuPn by TBH at room temperature.

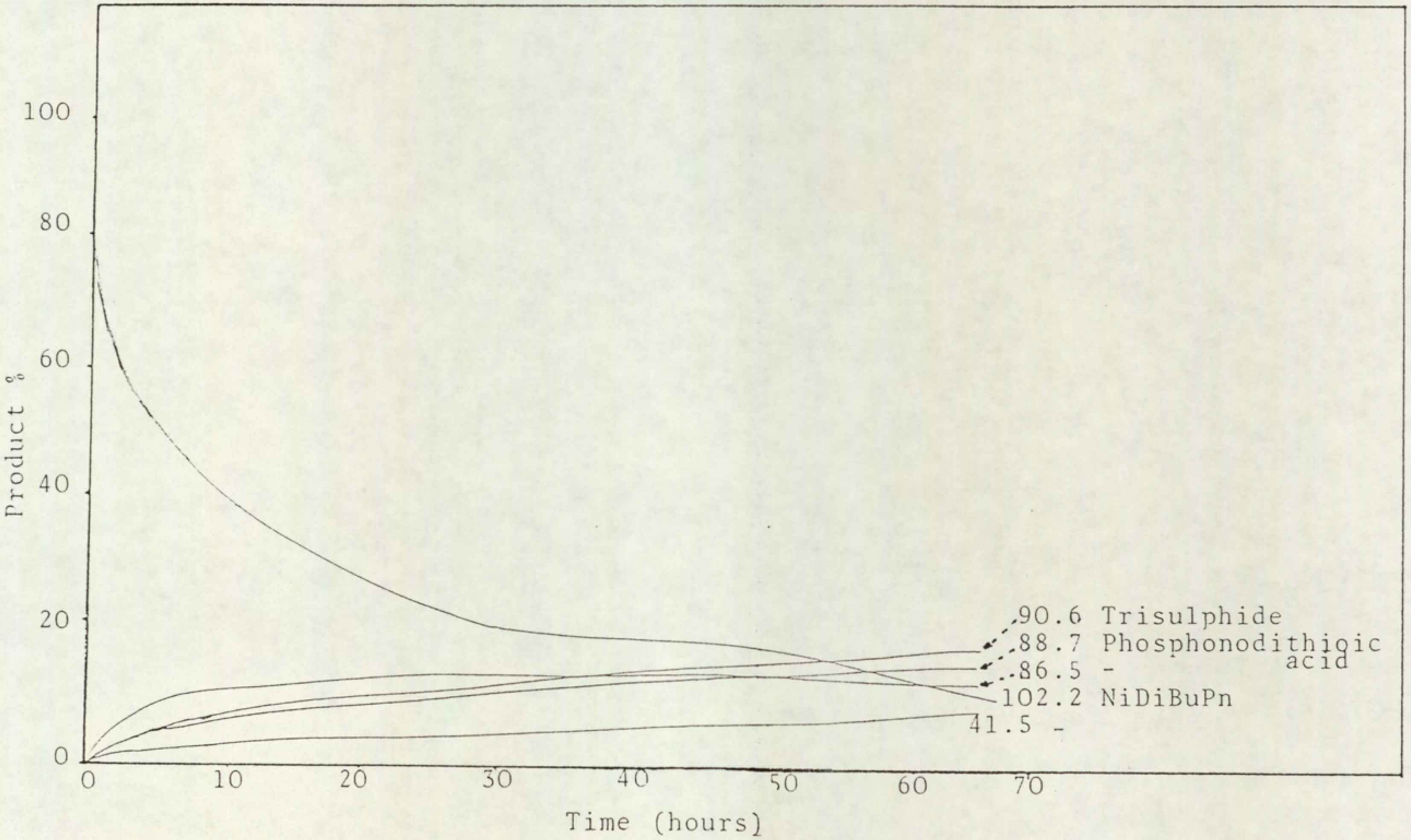


Figure 4.11 Decay of NiDiBuPn and formation of transformation products during a 1:4 molar ratio reaction of NiDiBuPn and TBH at room temperature.

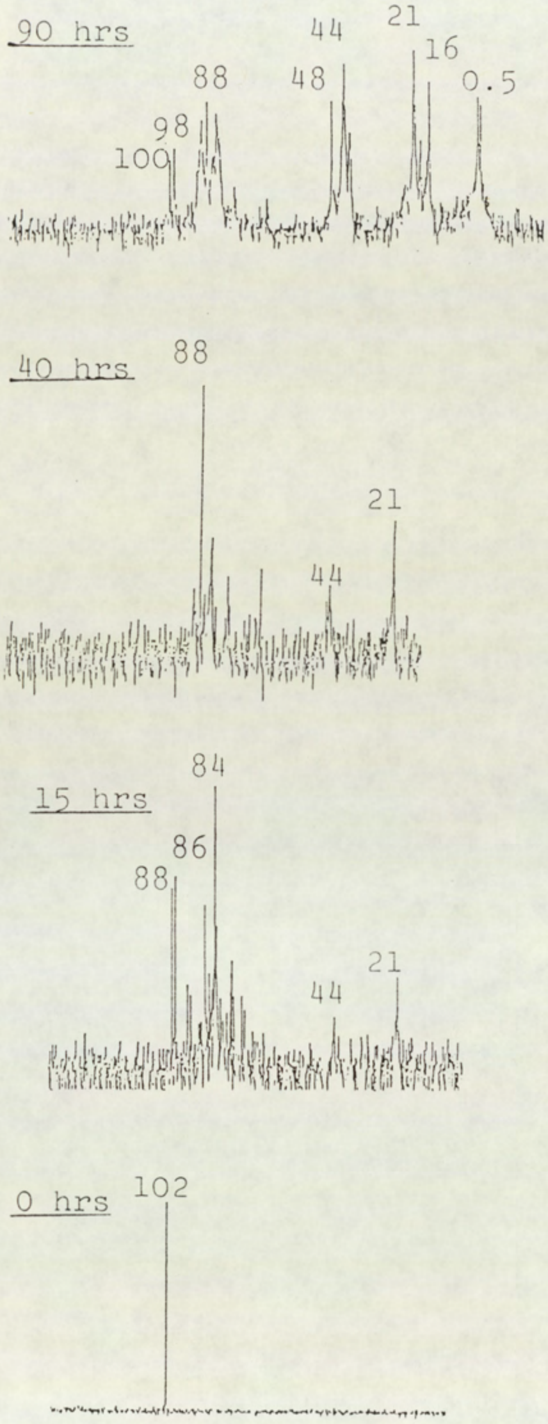


Figure 4.12 ^{31}P NMR spectral changes occuring during the 1:20 molar oxidation of NiDiBuPn by TBH at room temperature.

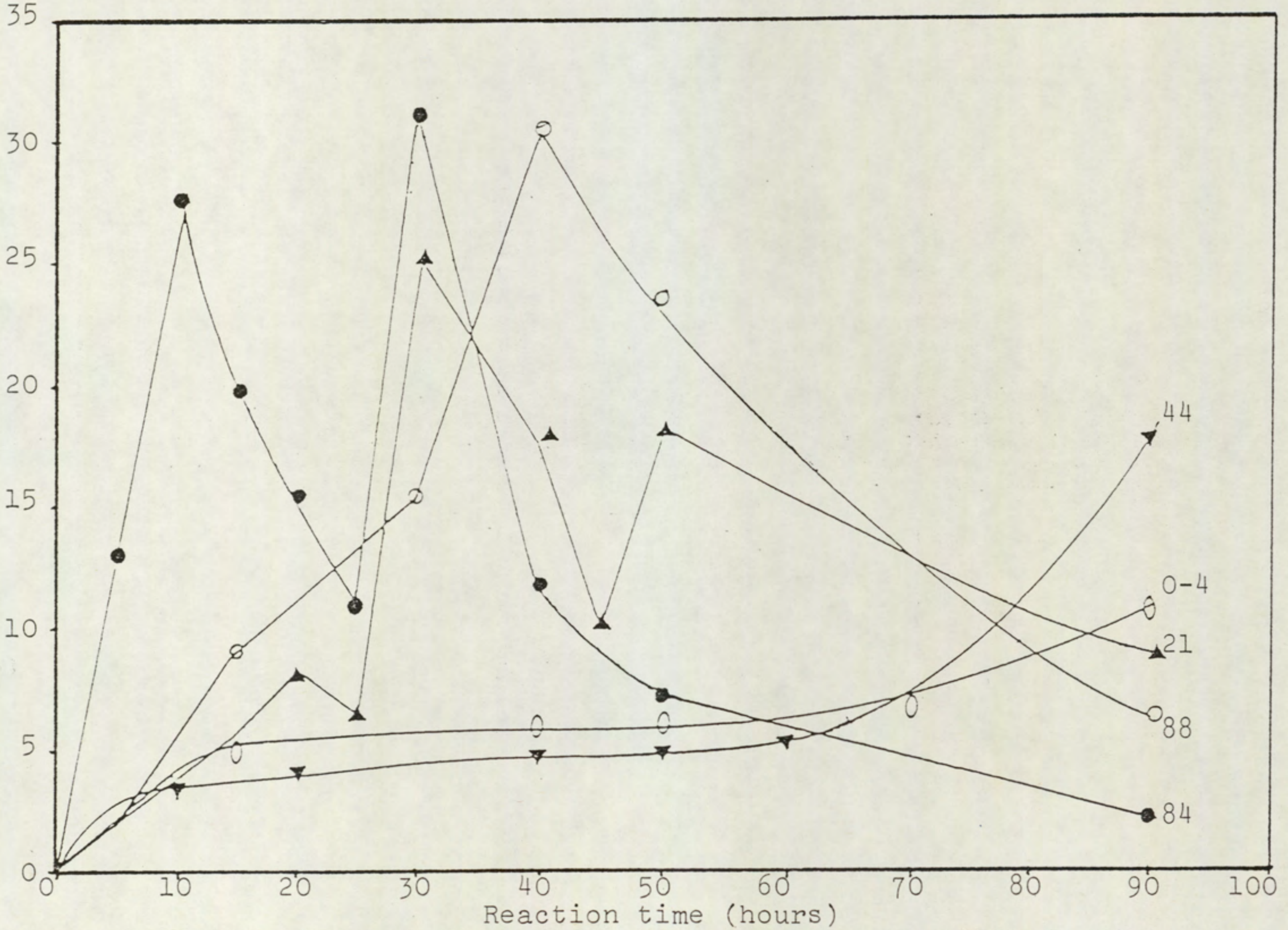


Figure 4.13 Distribution of transformation products of NiDiBuPn during its reaction with TBH at room temperature (molar ratio NiDiBuPn to TBH= 1:20). Numbers on curves are ^{31}P NMR chemical shifts.

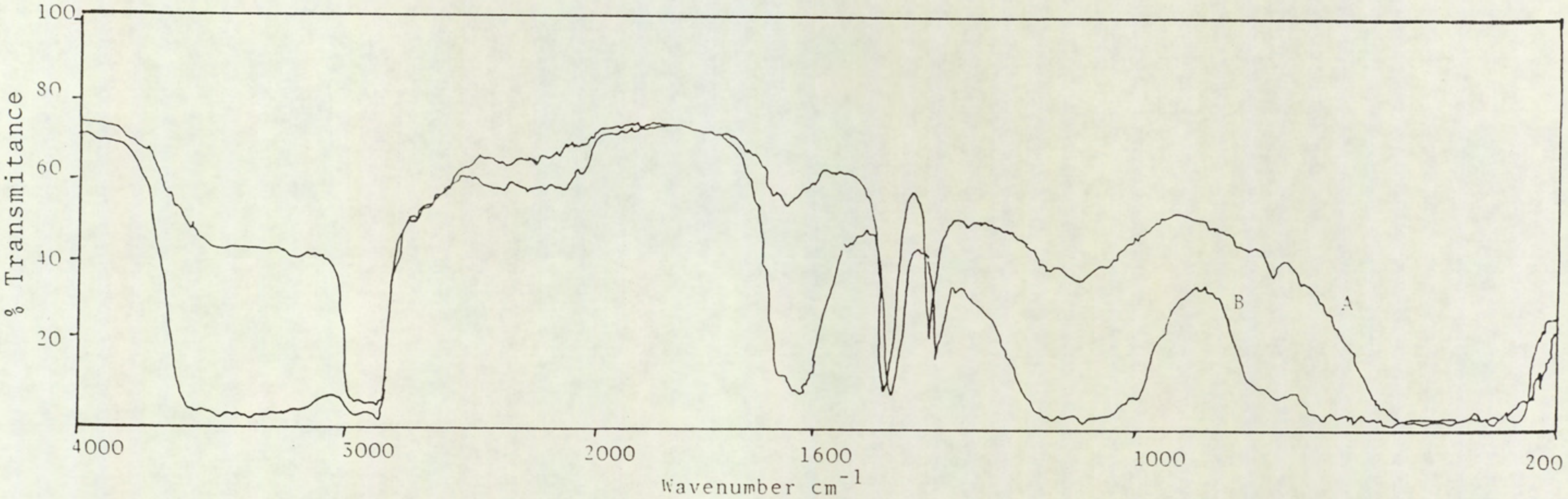


Figure 4.14 (a) Infra-red spectrum of $NiSO_4$ isolated during 1:20 molar ratio reaction of NiDiBuPn and TBH at room temperature (A) and Infra-red spectrum of authentic $NiSO_4$ (B).

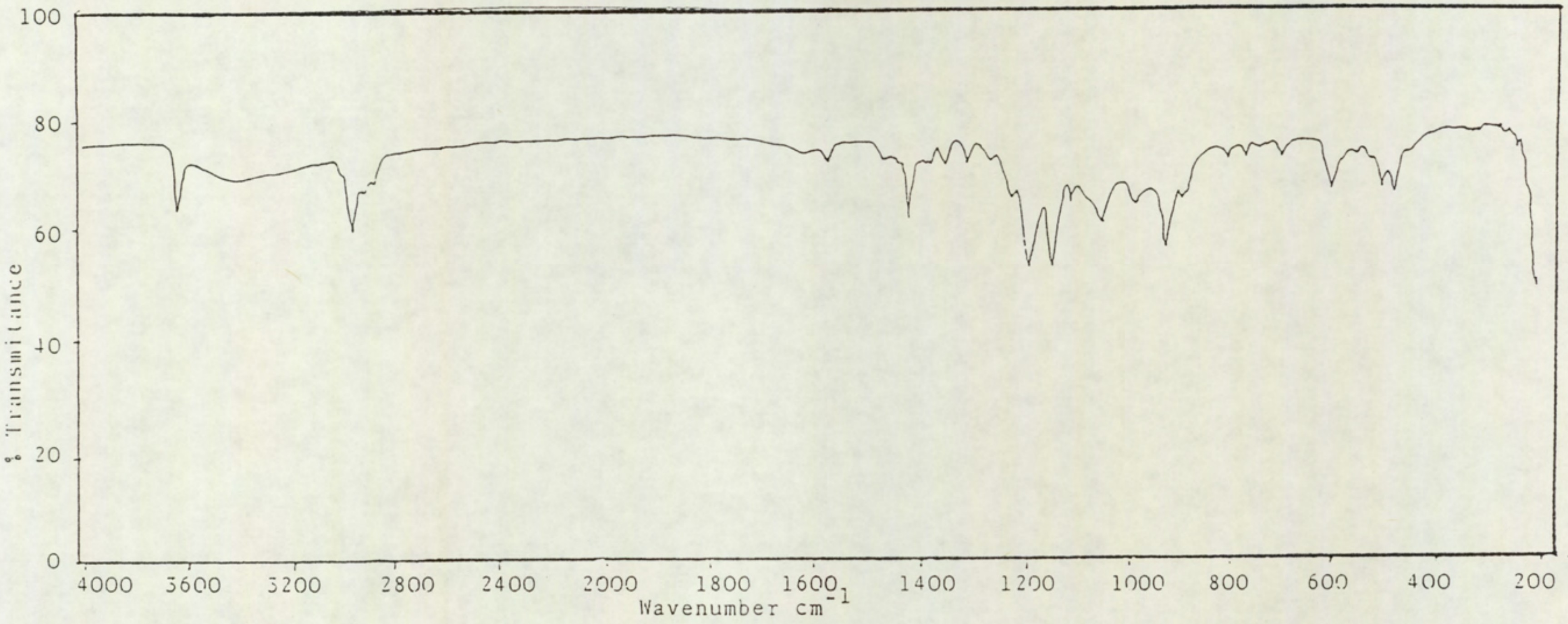


Figure 4.14(b) Infra red spectrum of the black substance isolated during thermal decomposition of NiDiBuPn at 180°C in p-dichlorobenzene

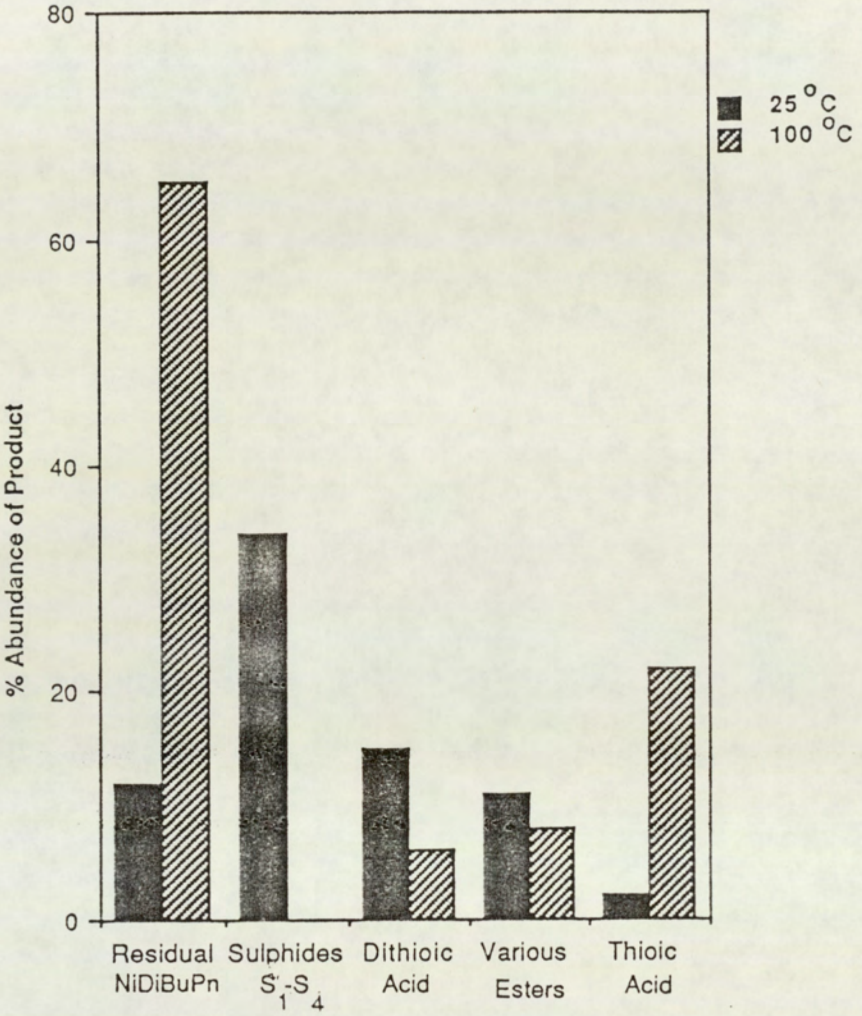


Figure 4.15 Relative Abundance of Major Transformation Products of the oxidation of NiDiBuPn by TBH (1:4 Molar ratio) after 70 hours reaction at room temperature (25°C) and 100°C.

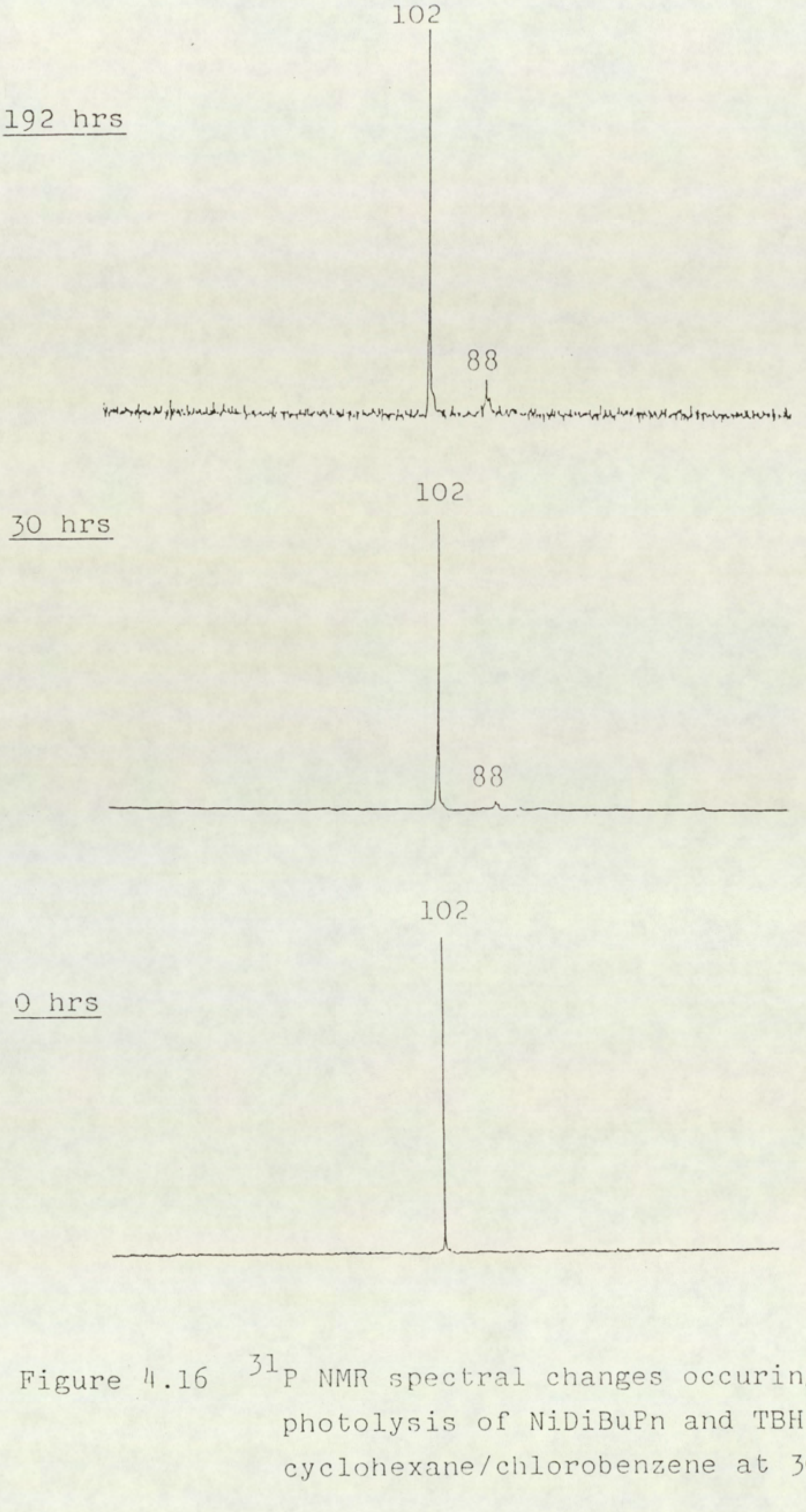


Figure 4.16 ^{31}P NMR spectral changes occuring during photolysis of NiDiBuPn and TBH in methyl cyclohexane/chlorobenzene at 30°C

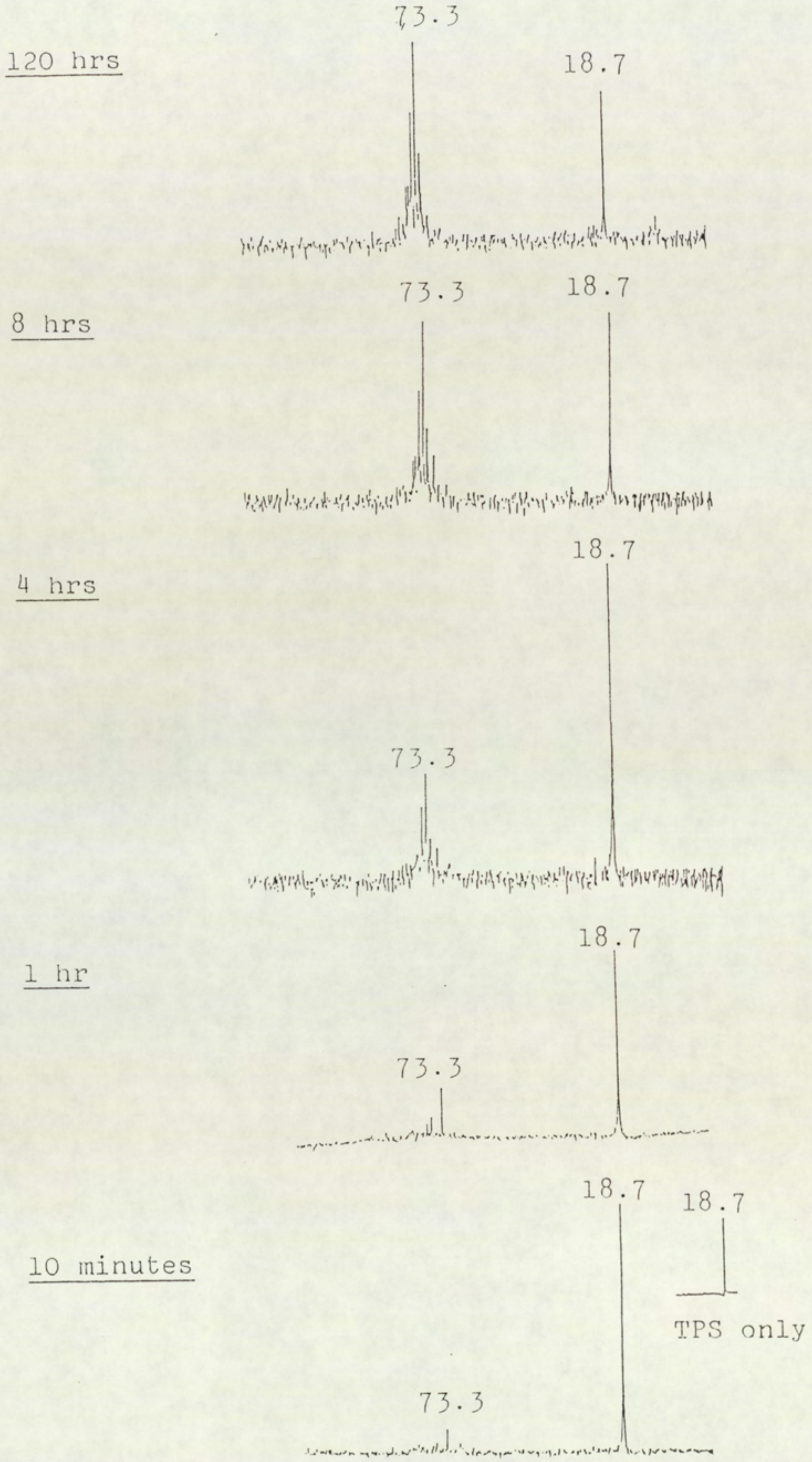


Figure 4.17 ^{31}P NMR spectral changes during thermal decomposition (180°C) of TPS.

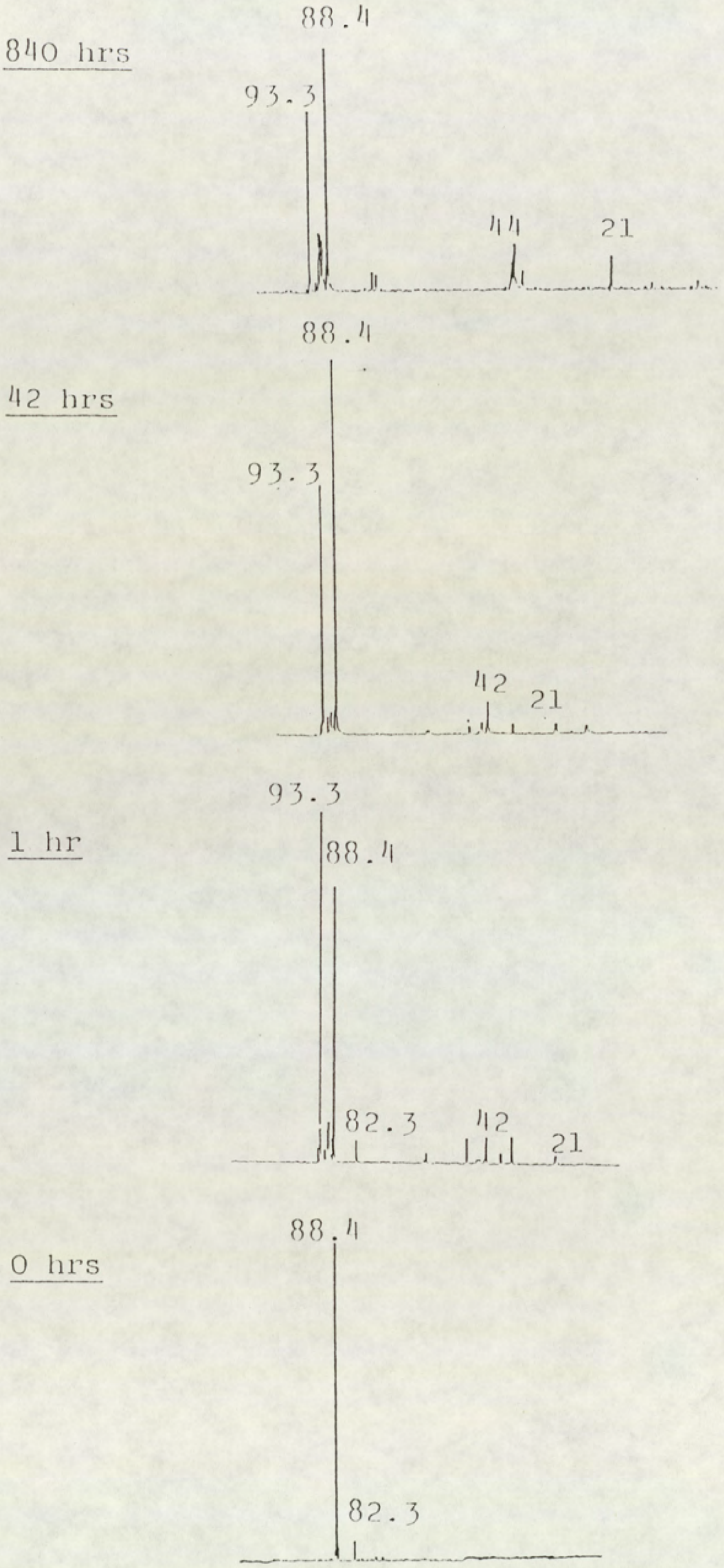


Figure 4.18 ^{31}P NMR spectral changes occuring during the oxidation of phosphonodithioic acid by TBH at room temperature.

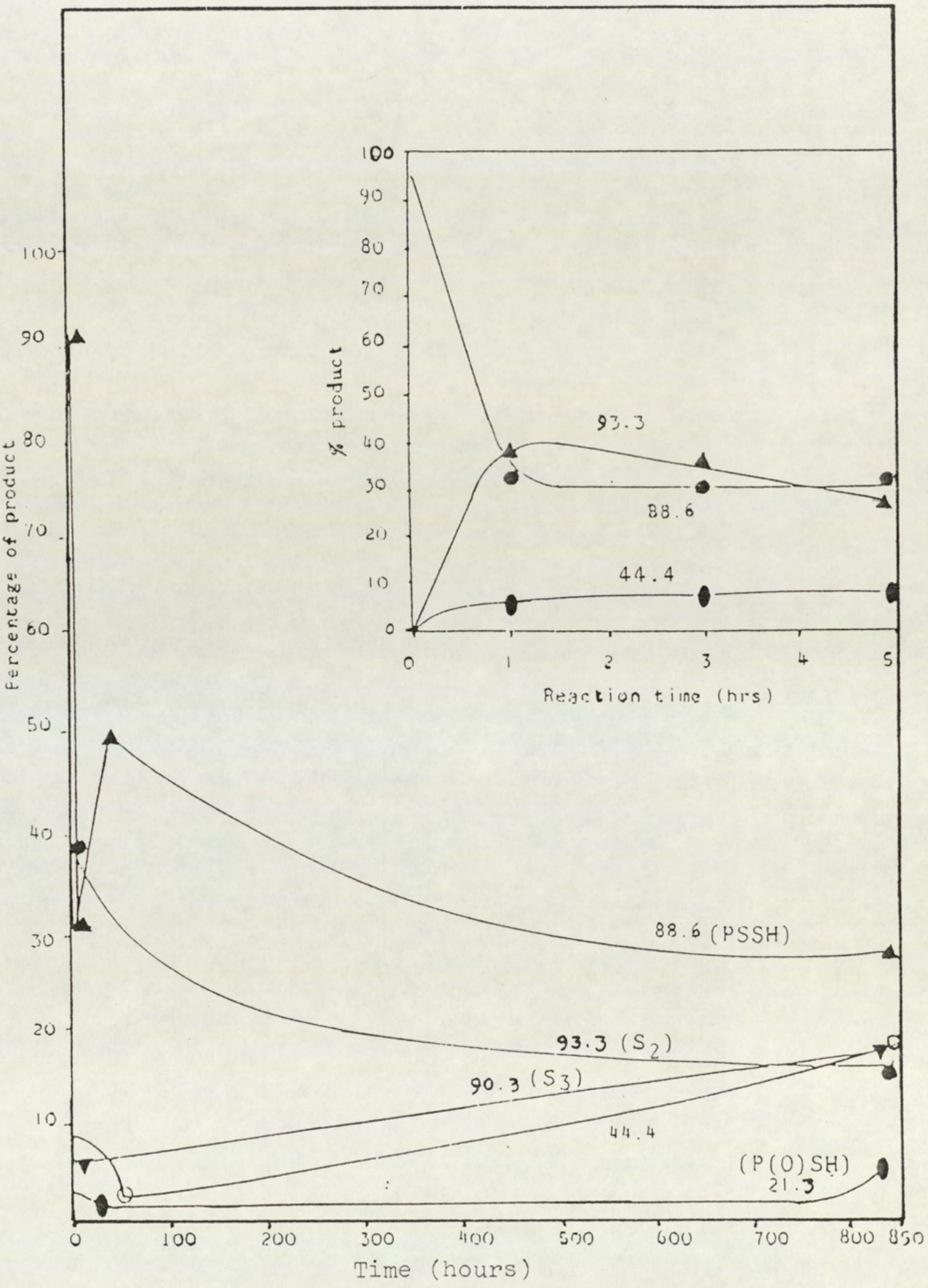


Figure 4.19 Major transformation products formed during a 1:4 molar ratio reaction of phosphonodithioic acid and TBH at room temperature.

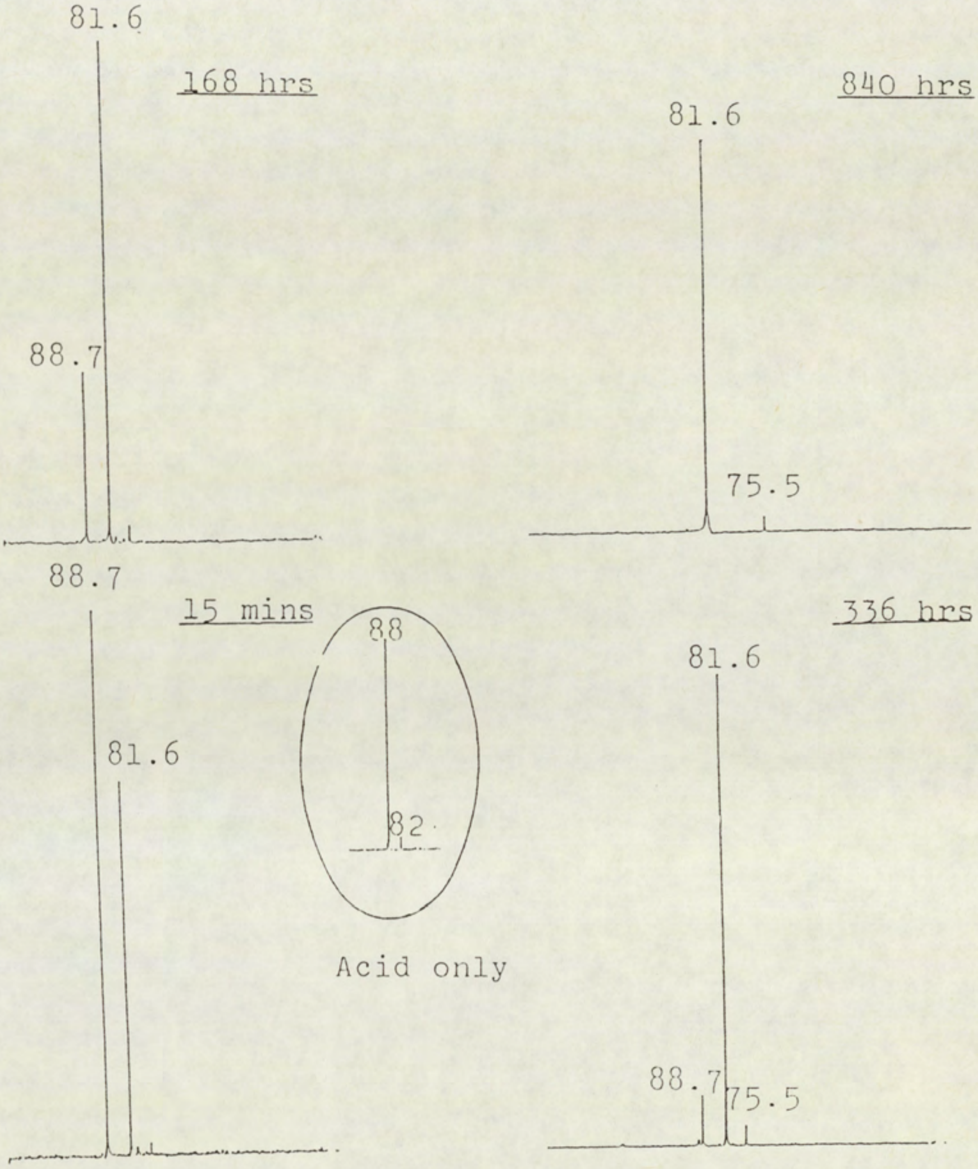


Figure 4.20 ^{31}P NMR spectral changes occuring during the esterification of phosphonodithioic acid with isobutyl alcohol at room temperature.

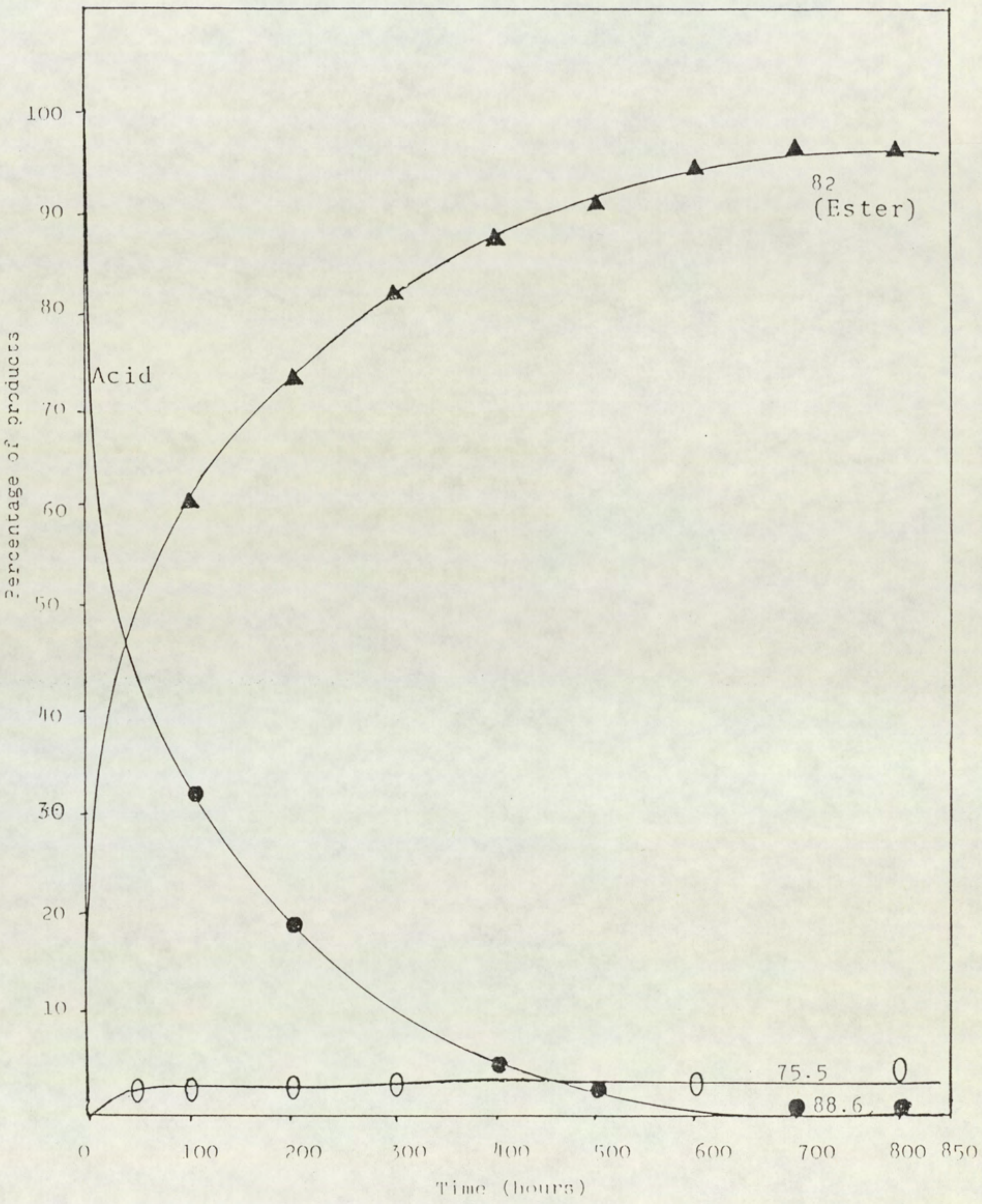


Figure 4.21 Reaction of Phosphonodithioic acid and excess isobutyl alcohol at room temperature

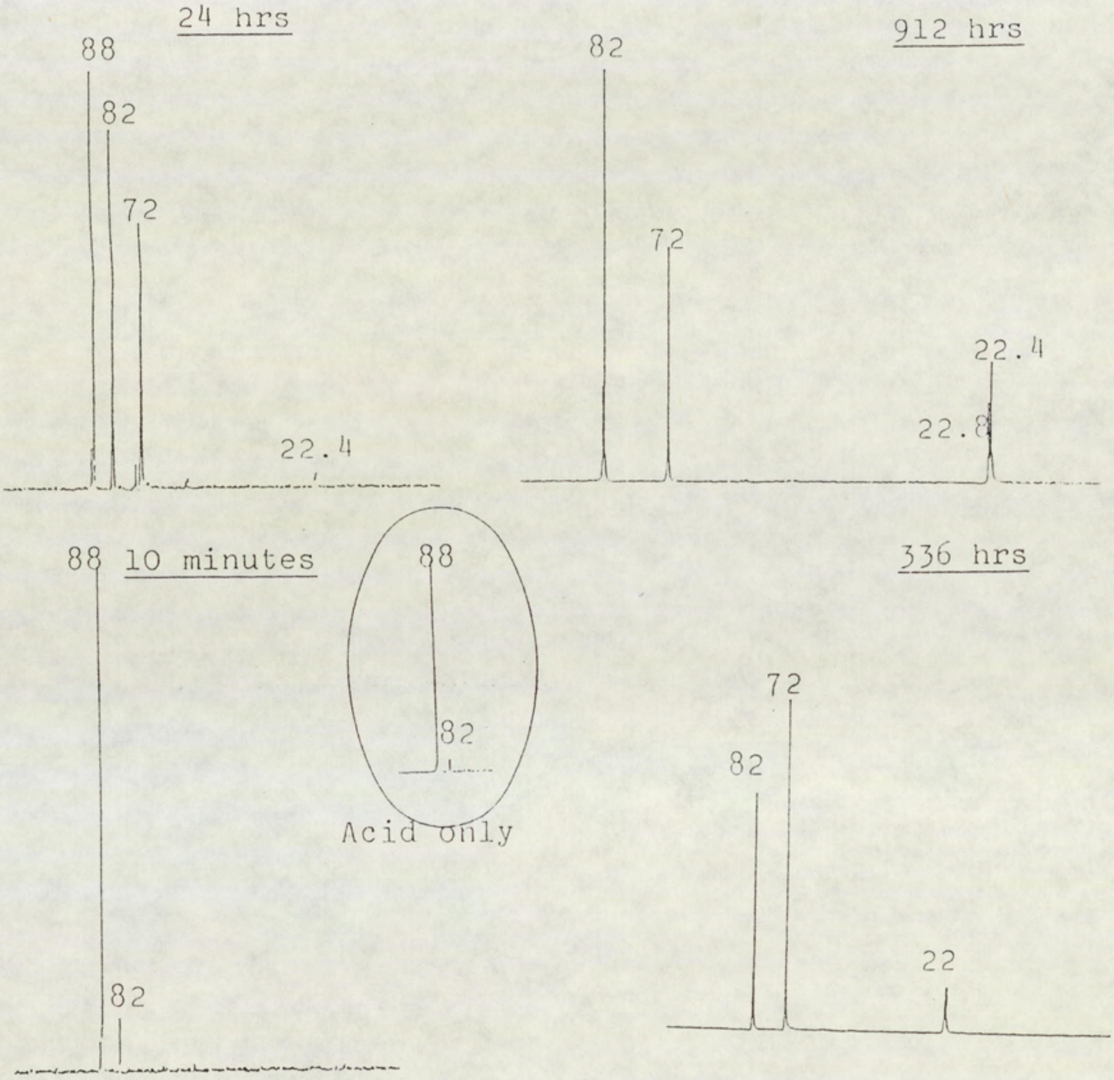


Figure 4.22 ^{31}P NMR spectral changes occuring during the hydrolysis of phosphonodithioic acid at room temperature.

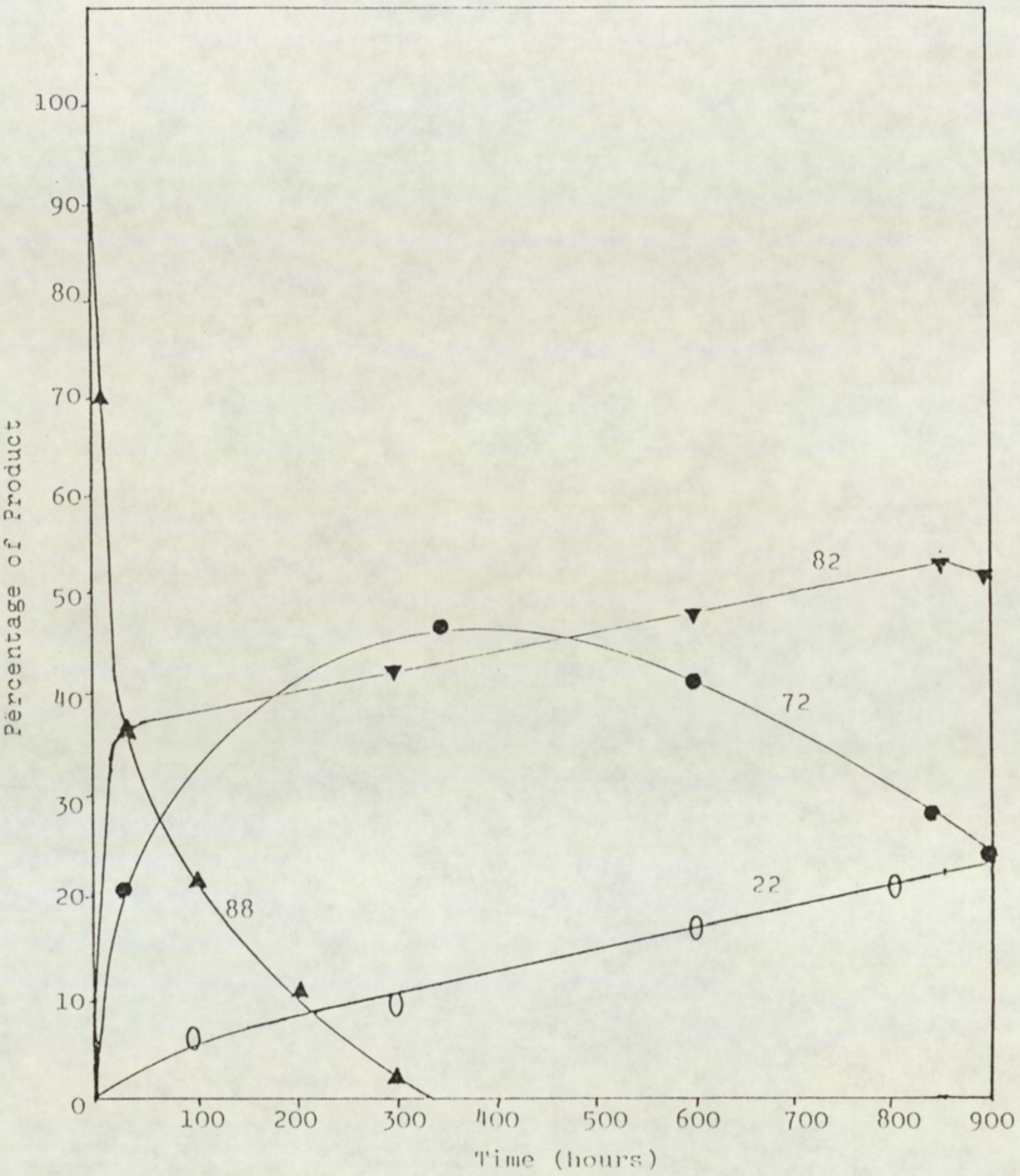


Figure 4.23 Reaction of dithiophosphonic acid with excess water at room temperature.

10 minutes

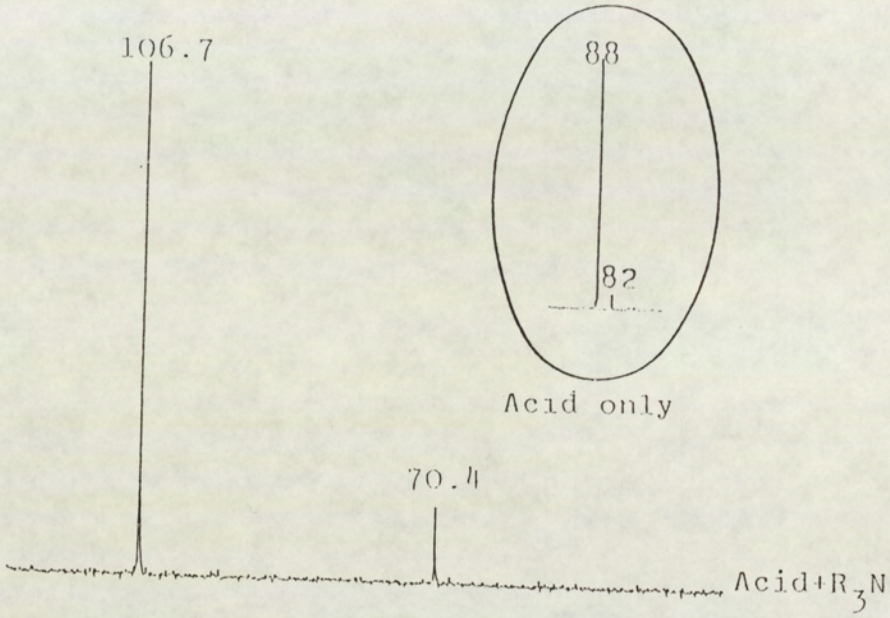


Figure 4.24 ^{31}P NMR spectra of dithiophosphonic acid before and after the addition of triethyl amine at room temperature.

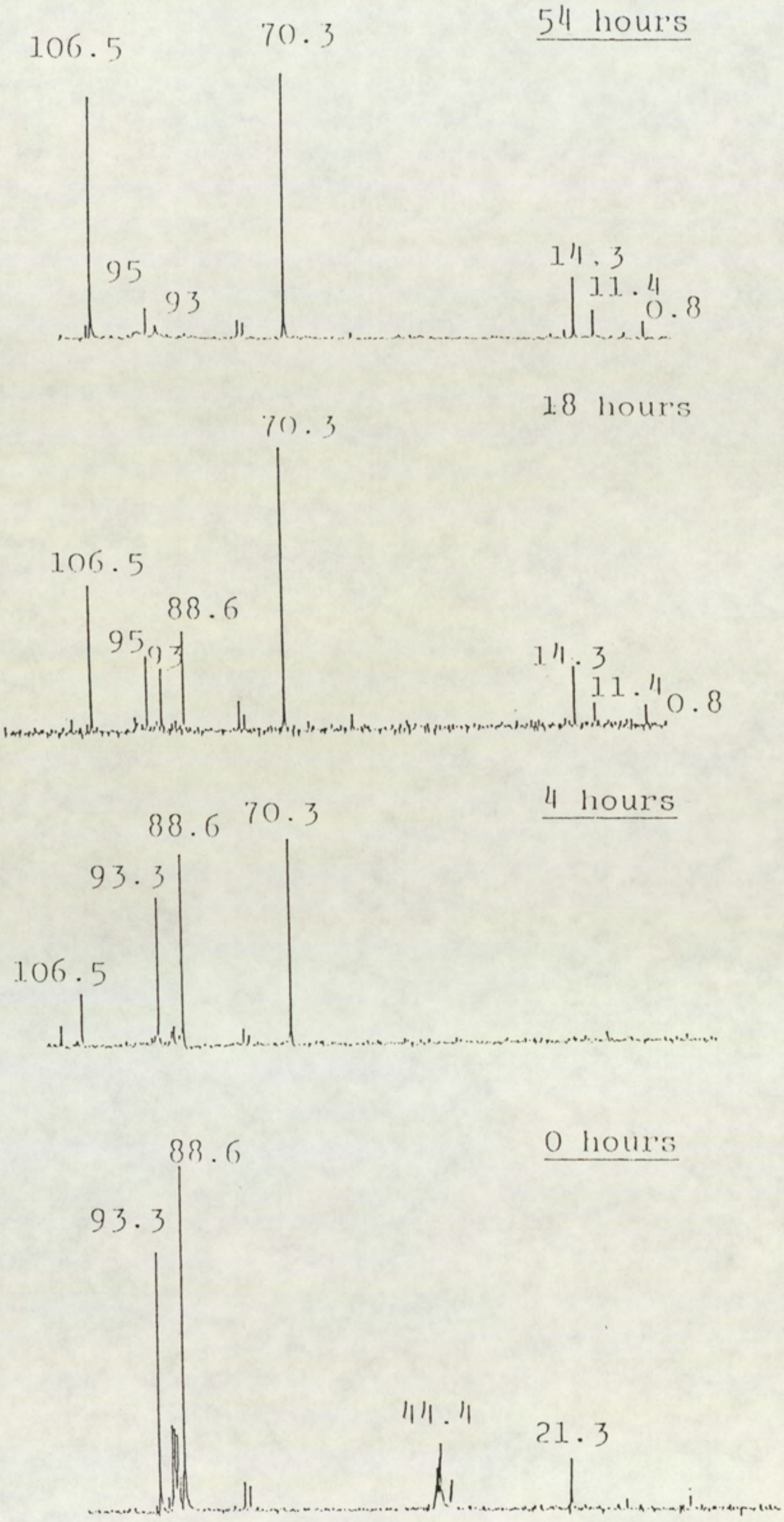


Figure 4.25 ^{31}P NMR spectral changes after the addition of triethylamine to the products of dithiophosphonic acid and TBH that had previously been reacted at room temperature.

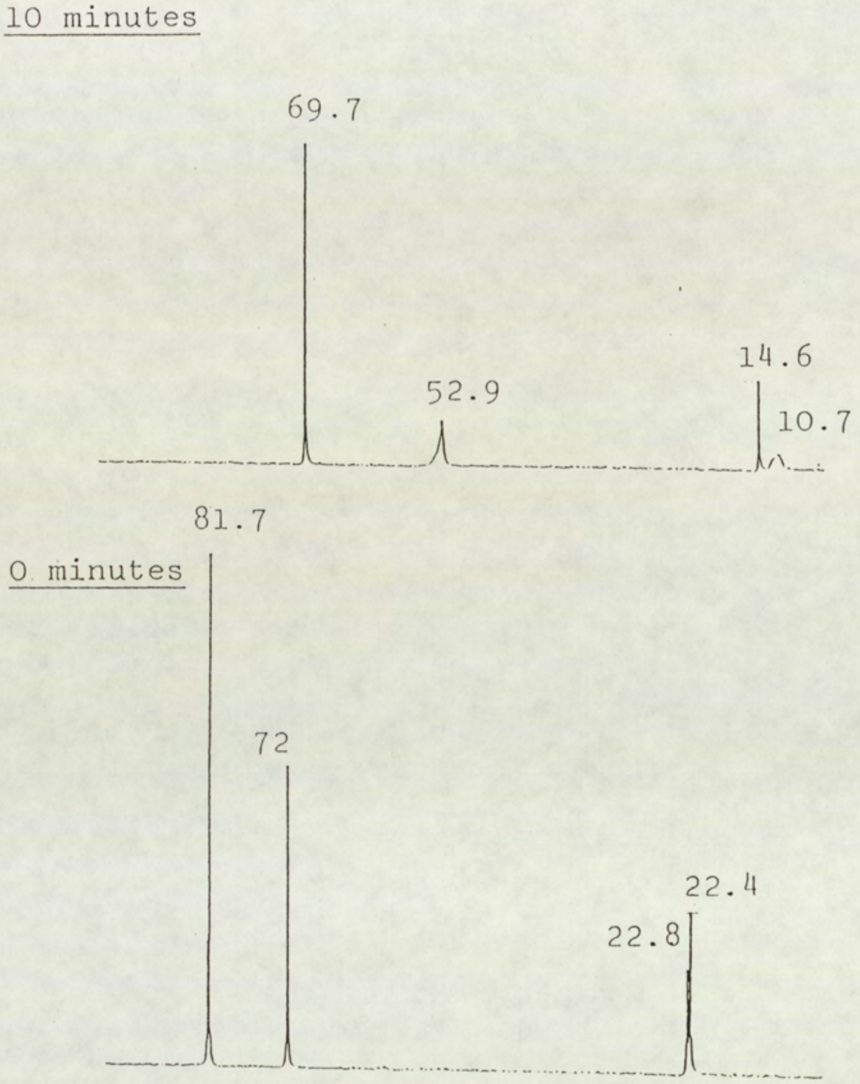


Figure 4.26 ^{31}P NMR spectral changes after the addition of triethyl amine to previously hydrolysed (912 hours) dithiophosphonic acid at room temperature

CHAPTER 5

CONCLUSION AND SUGGESTIONS FOR FURTHER WORK

5.1 CONCLUSION

The main conclusions that can be drawn from this study are as follows:

(1) All the dithiophosphonates examined (Ni, Cu, Zn, Fe, Co, TPS) were found to be excellent melt stabilisers for polypropylene when compared to hindered phenols (e.g. Irganox 1010) commercial controls.

(2) The thermal stability of the dithiophosphonates varied considerably depending on the metal centre in the antioxidant and the processing severity. CuDiBuPn was found to be a poor thermal stabiliser whilst NiBuDiPn was excellent when compared to Irganox 1076, which is a commercial hindered phenol control. The sulphide (TPS) was found to be more effective as a thermal antioxidant after it had been processed under limited oxygen conditions (CM) whilst the reverse is the case for the nickel complex. In addition the activity of NiDiBuPn in these highly volatilising environment (air oven) was found to be dependent on changes in concentration and alkyl substituent.

(3) The photostabilising activity of the dithiophosphonates in polypropylene, is also strongly dependent on changes in concentration, nature of alkyl substituent and the

processing severity. The NiDiBuPn shows the best performance as a photo stabiliser when compared to the other phosphonates studied on a molar and weight basis. Nickel and copper dithiophosphonate were found to synergise effectively with the U.V. absorber, HOBP, under photo-oxidative conditions. The activity of these synergistic mixtures were found to increase when an excess of the U.V. absorber was used.

(4) NiDiBuPn was found to be the most outstanding antioxidant of the dithiophosphonates examined. It showed excellent melt, thermal and photoantioxidant activity. Its high activity may be attributed to a regenerative radical scavenging mechanism (CB-A/CB-D), peroxide decomposing activity, screening ability and a very high stability towards U.V. light.

(5) Mechanistic studies of NiDiBuPn in the presence of peroxides (e.g. TBH) carried out at room temperature produced a wide range of products notably sulphides, acids and esters. These transformation products varied widely depending on the molar ratio of the nickel complex to the hydroperoxide.

At low NiDiBUPn to TBH ratios (1:4) the predominant products are the higher sulphides (di, tri and tetra) and the dithiophosphonic acid, that is, in general high field products which suggest sulphurated rather than oxygenated products. At higher molar ratios (1:20), however, the monosulphide, dithioic acid, thioic acid, esters and inorganic phosphates are favoured. These products generally have low field shifts and are more oxygenated products.

(6) In contrast to the room temperature work the oxidation of NiDiBuPn by TBH at high temperatures (100°C) gave rise to fewer transformation products principally the dithioic acid, thioic acid and small quantities of some ester species. The nickel complex, however, was found to be highly stable to thermolysis (180°C) when no hydroperoxide was used.

(7) A comparison of the metal complexes under photolysis as measured by U.V. spectroscopy clearly showed that the NiDiBuPn is extremely stable to U.V. light when compared to other phosphonates. A similar finding was also observed when the photolysis of NiDiBuPn was carried out in the presence of hydroperoxides.

(8) Dithiophosphonates have been found to be very interesting and effective new class of antioxidants. In particular the nickel complex demonstrates outstanding all round performance as a melt, thermal and photoantioxidant. The effectiveness of dithiophosphonates was shown to be due to a combination of mechanisms, a regenerative chain breaking

(CB-A)/(CB-D) and peroxide decomposing (PD-C) and U.V. screening.

5.2 SUGGESTIONS FOR FURTHER WORK

The following suggestions are recommended for further work:

(1) During this study NiDRPn was shown to be an excellent all round stabiliser. Only two alkyl substituents were examined, notably R = iBu and 2-EH, with varying performance. It would be of interest, therefore, to carry out a detailed investigation regarding the effects of various alkyl substituents on the antioxidant activity of the dithiophosphonate.

(2) Iron dithiophosphonate was found to have exceptional behaviour when compared to other iron complexes such as FeDRP. It shows melt, thermal and photoantioxidant activity in polypropylene, in addition to being the best radical trapping agent when compared to other dithiophosphonates during oxygen absorption studies. A more thorough investigation of this metal complex would be of interest.

(3) The dithiophosphonates show far superior thermal activity than the structurally similar dithiophosphates. This difference is thought to be due to the replacement

of some alkoxy groups in DRP by hindered phenols in the case of DRPn. It would be of academic interest to see if the replacement of all or more of the alkoxyl groups by hindered phenol substituents further improved the thermal stability of the polymer.

(4) Preliminary work has shown that the addition of a phosphite to NiDiBuPn helps retain the original colour of the additive in the polymer during processing. It would be advantageous from a technological point of view to optimise this combination and to study the effect it has on melt, thermal and photostabilising activity. In addition it would be important to identify more accurately the black substance which is formed during the processing of NiDiBuPn.

(5) Dilution of masterbatches (MB) which is often a normal commercial practice needs to be evaluated technologically as these often produce different results to samples processed normally.

(6) During mechanistic studies involving NiDiBuPn and TBH the dithiophosphonic acid and the monosulphide seemed to be major transformation products. It is of some importance to evaluate the antioxidant performance of these species in the polymer.

(7) Reactions of some of the intermediates with hydroperoxides such as the monosulphide needs to be investigated further to elucidate their role in the mode of antioxidant activity of dithiophosphonates.

(8) The synthesis of major transformation products such as esters and acids is necessary in order to identify more accurately the ^{31}P NMR absorptions due to these products.

(9) High temperature reactions of NiDiBuPn in an oxidisable substrate such as cumene (with and without TBH) needs to be carried out since this will correlate more appropriately with the technological performance of the additive in the polymer matrix.

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