EFFECT OF PROCESSING ON SULPHUR ANTIOXIDANTS IN POLYOLEFINS

by

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SUMMARY

The effects of processing on the antioxidant activity of sulphur-containing compounds, with particular reference to nickel dialkyldithiophosphates and their corresponding disulphides, were studied in polyolefins under melt, thermal and photo-oxidative conditions. These compounds were evaluated both at low (normal) and high(concentrates) concentrations.

In general, the dithiophosphates were found to be very efficient melt stabilisers at normal concentration levels, and compare quite favourably with the best commercially available systems. The nickel dithiophosphates were also found to be very efficient thermal stabilisers for polyolefins, but their activity is highly dependent on the alkyl substituent in the molecule. The corresponding disulphides on the other hand showed very little activity under thermal oxidative conditions, and this was attributed to their inefficiency in scavenging alkyl peroxyl radicals since both compounds possess similar peroxidolytic activity. Furthermore, the nickel dithiophosphates were found to be excellent photo stabilisers for mildly-processed polyolefins while the corresponding disulphides only offer slight protection to the polymer. Oxidative processing of the disulphide, however, results in a dramatic improvement in their photo antioxidant activity. Thionophosphoric acid, a major oxidation product of dithiophosphates,was also shown to have photo antioxidant activity similar to that of the disulphides.

A combination of a U.V. absober with the nickel complex and/or the disulphide resulted in a synergistic stabiliser system which was further augmented by oxidative processing. Moreover, the dilute analogues of such multicomponent stabiliser concentrates also showed excellent melt, thermal and photo-stabilising activity.

The mechanistic studies carried out on the nickel complex and the corresponding disulphide clearly identified the thionophosphoric acid as a major transformation product although various triesters were also formed as reaction intermediates. The mechanisms of the antioxidant action of the dithiophosphates, which are believed to involve a cyclical process similar to that shown for simple alkyl sulphides and nitroxyls, are discussed.

KEY WORDS:

Nickel dialkyl dithiophosphate
Thiophosphoryl disulphide
Thionophosphoric acid
Normal processing (CM)
Oxidative processing (OM)

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DECLARATION

The work described in this thesis was carried out at the University of Aston in Birmingham between February 1982 and August 1986. It has been done independently and submitted for no other degree.

M. R. S. COKER

IN MEMORY OF MY FATHER, SYLVANUS

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SUPPORTING PUBLICATIONS

1. M.S.S. Coker, G. Scott and H.A.A. Sweis
   Polym. Degr. and Stability, 4, (1982), p333.

2. S. Al-Malaika, M. Coker and G. Scott
   Polym. Degr. and Stability, 10, (1985), p173.

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CHAPTER ONE

INTRODUCTION

1.1 Autoxidation of Polyolefins

1.1.1 General Degradation Processes

Most polymers are subject to oxidative degradation by molecular oxygen during processing and on exposure to environmental conditions. In addition to the deleterious effects of oxygen, it has also been clearly established(1,2) that the degradation process is accelerated by other environmental influences such as heat, light, contamination by metal ions, ozone and mechanical deformation.

Degradation of polymers is generally considered to occur in two principal stages (3); the first is manifested during processing operations while the other occurs during the service life of the polymer artifact when subjected to relatively mild or intermittent oxidative attack. Thus during conversion of the polymer to fabricated end products (processing), they are subjected to high temperatures and high shearing forces in the polymer melt. Since it is impossible to exclude molecular oxygen completely from such procedures, important chemical modification inevitably occurs at this stage in the history of the polymer and this determines to a large extent its durability in service (2,4,5,6). Furthermore, the nature of the degradation reactions varies in rate and extent depending on the chemical structure(3,4) of the polymer, the presence of impurities(3,5,6,7) and the environment(1) to which they are exposed. For instance, the presence of a labile tertiary hydrogen on alternate carbon atoms in polypropylene accounts for its relative vulnerability to thermal as well as photo-oxidation. This is aggravated by the presence of impurities such as polymerisation catalyst residues (transition metal ions) and macro hydroperoxides which are in turn the precursors of macro carbonyl compounds.

Autoxidation is undesirable in the majority of cases because of the deterioration in properties of the polymeric materials. It is therefore necessary to stabilise polymers against the deleterious effects of atmospheric oxidation(8) and this is accomplished by the use of additives known as antioxidants.

1.1.2 Mechanism of Polymer Oxidative Degradation

Modern theories of the mechanism of oxidative degradation of polymers are primarily based on studies by Bolland and co-workers (9-12), who concluded that the central feature of autoxidation is the generation of hydroperoxides via the initial formation of free radicals ($R^\bullet$) .. The free radicals formed then reacts rapidly with oxygen to give an alkyl peroxyl radical ($ROO^\bullet$) which abstracts hydrogen to form hydroperoxides (Scheme 1.1.a-c).

$$\begin{array}{ll}
RH \longrightarrow R^\bullet + {}^\bullet H & \\
RH + O_2 \longrightarrow R^\bullet + {}^\bullet OOH & \text{Initiation (a)} \\
ROOH \longrightarrow RO^\bullet + {}^\bullet OH & \\
2ROOH \longrightarrow ROO^\bullet + H_2O + RO^\bullet &
\end{array}$$

$$\begin{array}{ll}
R^\bullet + O_2 \xrightarrow{(a)} ROO^\bullet & \\
ROO^\bullet + RH \xrightarrow{(b)} ROOH + R^\bullet & \text{Propagation (b)}
\end{array}$$

$$\begin{array}{ll}
2R^\bullet \xrightarrow{(c)} R{-}R & \\
ROO^\bullet + R \xrightarrow{(d)} ROOR & \text{Termination (c)} \\
2RO^\bullet \xrightarrow{(e)} \text{Inert products} & \\
2ROO^\bullet \xrightarrow{(f)} ROOR + O_2 &
\end{array}$$

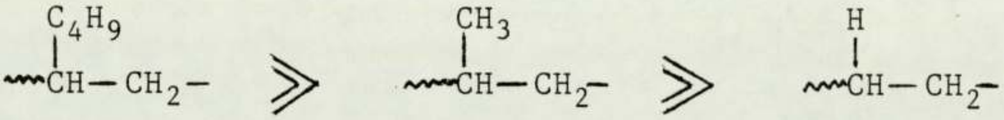
This free radical chain mechanism (Scheme 1.1), as postulated by these workers(9-12) for the autoxidation of model alkenes similar to natural rubber, has been found to hold for most hydrocarbon polymers. A considerable number of papers have been published by Scott and co-workers(13-19) to confirm that hydroperoxides are primarily responsible for initiation of the polymeric oxidative degradation process under melt, thermal and photo-oxidative conditions. This view is also supported by evidence provided by several other workers(6,20-22), and is now universally accepted. There seems no doubt, therefore, that the initial products of autoxidation are the polymer hydroperoxides while carbonyl compounds are secondary products formed from the decomposition of the hydroperoxides, and the initial rates of the degradative processes (melt, thermal and photo-oxidation) are primarily dependent on the concentration of the former (23,24). Since the initial propagation step (a) is a radical pairing process it has low activation energy and occurs with high frequency (4,25). The second step (b) on the other hand involves the breaking of a carbon-hydrogen bond and has a higher activation energy. Thus, in most polymers at normal oxygen pressures, the rate of the latter step (b) in the chain reaction determines the overall rate of oxidation. Under these circumstances the reaction rate then depends to a large extent on the chemical structure of the polymer (RH). The easier it is for hydrogen to be abstracted from RH, the higher will be the rate of oxidation, and the ease of hydrogen abstraction from different types of hydrocarbons has been shown (26) to increase in the following order:

Primary C-H < Secondary < Tertiary < Allylic < Benzylic

Furthermore, the structure of the autoxidising hydrocarbon (RH) and the oxygen concentration determine which of the termination steps lead to the removal of radicals from an autoxidising substrate. A practical consequence of the rate determining step (b) during propagation, is the predominance of alkyl peroxyl radicals in the substrate and termination occurs primarily by reaction of alkylperoxyl radical species (f). If, however, oxygen access is limited by diffusion, for example during processing of polymers in the barrel of a screw extruder or when the rate of initiation is high compared with the rate of diffusion of oxygen into the polymer as in U.V. irradiated oxidation or in mechano-chemical oxidation, termination steps (c) and (d) may assume greater importance(4a) .

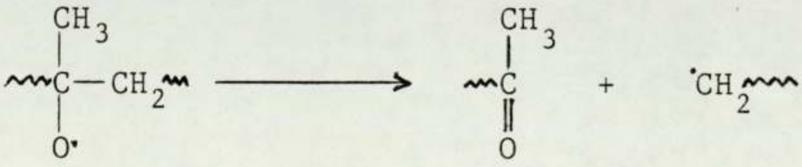
1.1.3 Melt Degradation During Processing

The industrial procedures used in the conversion of polyolefins to finished artifacts almost always encompass the use of a screw extruder or similar equipment to homogenise the molten polymer. Mechano-chemical scission occurs under these conditions (2,5a,26) and since a small amount of oxygen is always present either dissolved in the polymer or trapped in the polymer feed during extrusion processes and/or in the mixing chamber of a torque rheometer, the well-known initiation, propagation and termination sequences then take place as summarised in Scheme 1.1a-c. An important practical consequence of mechano-oxidation is therefore, the introduction of oxygen containing functional groups in the molten polymer. It is also an established fact that different hydrocarbons behave differently during processing as a result of the differences in chemical structure(4,5a,26). Thus although the mechano-chemical processes occuring in polyethylene (PE), polypropylene (PP) and poly-4-methyl pent-1-ene (P-4-MP) are similar(5a-b), the tendency towards scission increases with the positive inductive effect of the side chain(26) in the folowing order:



(P-4-MP) (PP) (PE)

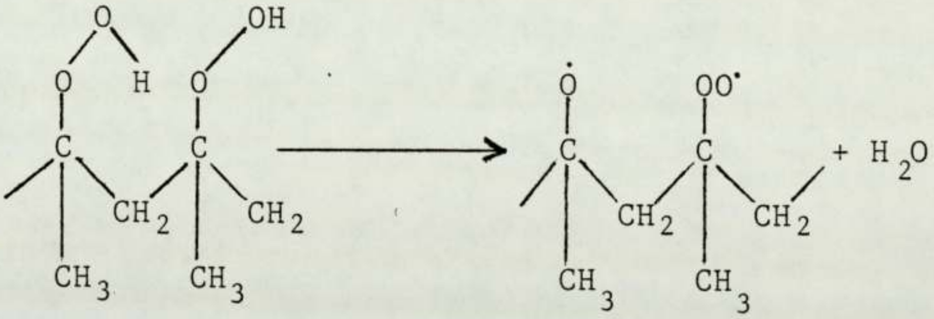
Nevertheless, the effects of processing are very evident in changes in melt viscosity or melt flow index (MFI) of these polymers(2,4,5a,16,26-27). The same workers have also shown that whereas the melt flow index of PE decreases during processing in a shearing mixer (due to crosslinking), PP undergoes an increase in MFI due to a reduction in molecular weight caused principally by fragmentation of the tertiary alkoxyl radical (RO$^\cdot$) to a ketone (reaction 1.1)



(RO$^\cdot$) (1.1)

The main difference in the behaviour of both polyolefins

(PE and PP) as was previously stated, lies in the difference in their chemical structure, and hence, the rate of the propagation step (b). Thus, the hydrogen bonding resulting from the vicinal hydroperoxide groups in PP, which is a direct consequence of the presence of tertiary carbon atoms in the polymer, is much less stable(5a) than isolated hydroperoxide groups as obtained in PE since the former undergo a facile intramolecular decomposition with concomitant increase in the rate of initiation (reaction 1.2).

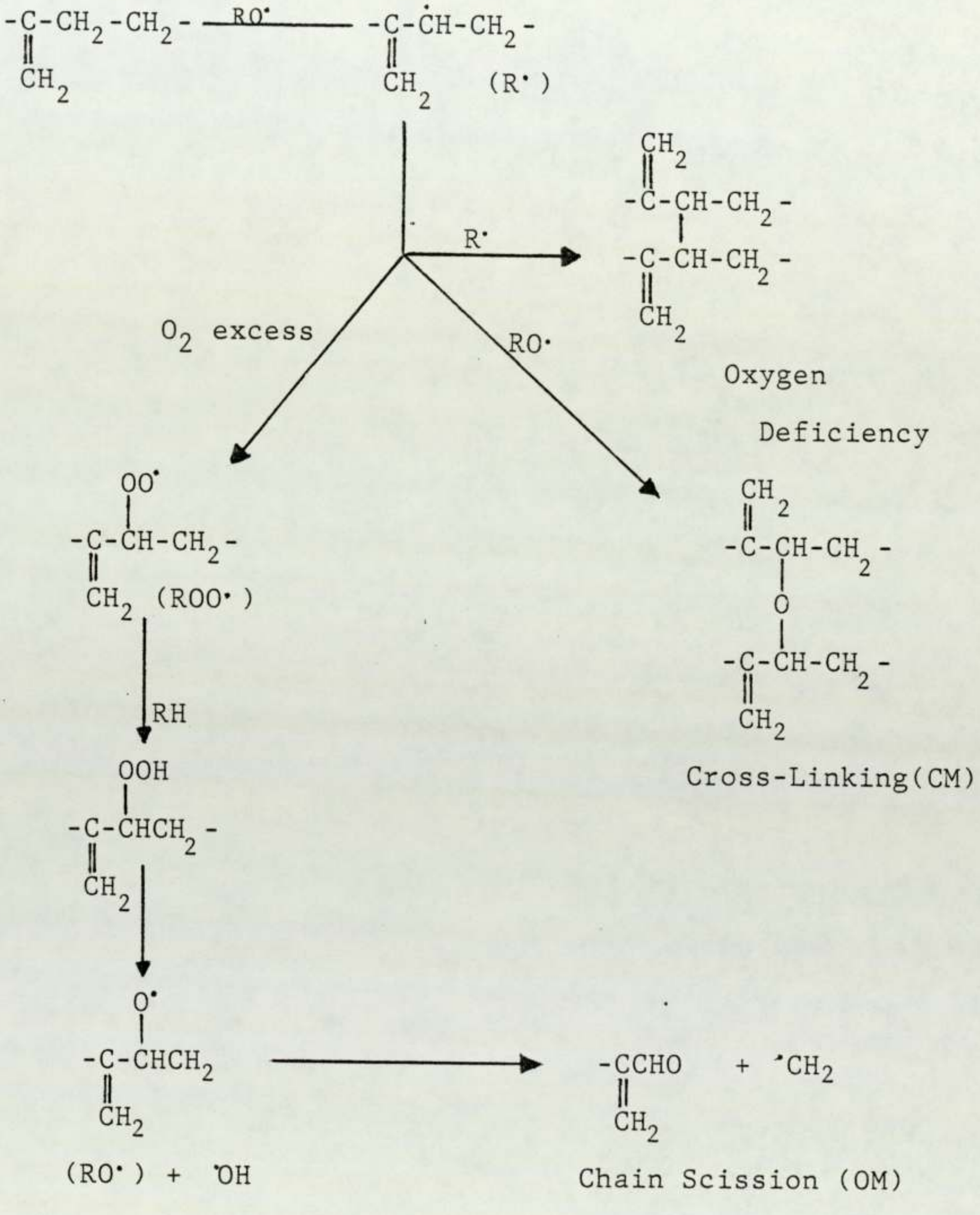


(1.2)

However, increasing the concentration of oxygen by deliberately allowing access of air leads to the predominance of chain scission in both polymers. Consequently, hydroperoxide concentration increases with processing time in both PE and PP, but much more rapidly in an open mixer (OM) than in a closed mixer(4,5a,16,23,27). The decrease in the melt flow index of PE is therefore associated with an upward shift in molecular weight distribution which in turn results from the formation of hydrocarbon-insoluble gel, and this behaviour (crosslinking) has been shown to occur only during processing under conditions of oxygen deficiency(5a,23) due to the relatively high concentration of alkyl radicals (Scheme 1.2). Furthermore, the pronounced increase in the melt flow index (MFI) with increasing processing severity (e.g OM) in PP is attributed(5a,27) to the presence of a high concentration of PP hydroperoxides, as compared to the less dramatic increase in the MFI observed during processing under conditions of oxygen deficiency.

The extent of the thermal oxidative treatment received during the processing stages is also known to have a profound effect on the service performance of the polymer artifact(2,4,5a,5b,6) since the final properties of the fabricated product depend largely on the molecular weight of the polymer. The conditions that exist during mechanochemical degradation of polyolefins as discussed in this section, also apply to some extent during service life under thermal oxidative conditions. During oven ageing tests, for instance, the presence of excess air leads to a high rate of hydroperoxide formation as is obtained during melt processing under similar oxidative conditions (OM), although this is not a normal industrial practice. Failure of the polymer article then results from thermolysis of in-chain hydroperoxides (ROOH) which finally leads to fragmentation of products of the hydroperoxide (RO$^•$) as shown in reaction 1.1 and scheme 1.2 for PP and PE respectively. A manifestation of the

Scheme 1.2 Competing chain-scission and cross-linking reaction occuring during processing of LDPE(5a)



(C-C) bond scission is the dimensional instability (creep) of the fabricated product and this limits the temperature at which most thermoplastic polymers are used(4,5a).

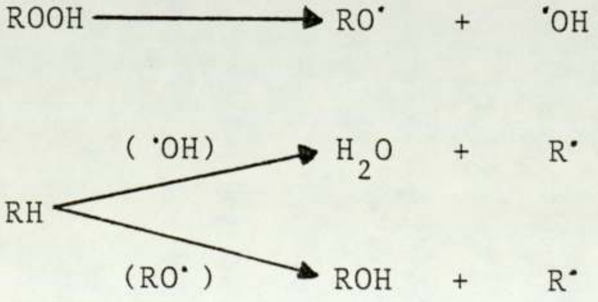
1.1.4 Photo-oxidative Degradation

Unlike pure hydrocarbons, commercially produced unprocessed polyolefins surprisingly absorb weakly at longer wave lengths of the sun's spectrum (> 285 nm). This is commonly attributed mostly to the presence of oxygen containing functional groups introduced during manufacture(5b), and the pioneering studies of Bateman and Gee(61) and later by Norrish and co-workers (62a-b) also confirmed the view that hydroperoxides, the primary products of autoxidation, absorb weakly up to 350 nm while the derived carbonyl compounds absorb much more strongly(18,19). Subsequent high temperature processing operations also lead to the formation of more hydroperoxides (Section 1.1.2.1) and carbonyl compounds which may then act as the photo-initiators at different stages of photo-oxidation.

The mechanism of photo-oxidation of polyolefins is basically similar to that involved in thermal oxidation, except for the rate of initiation which is much higher during photo-oxidation due to the much more rapid formation of hydroperoxides. This leads to higher radical concentrations and consequently shorter kinetic chains(5a,10,28). In addition to hydroperoxides and the derived carbonyl compounds, there is sufficient literature evidence(5b,29) to suggest that the photo-oxidation process can be initiated by certain chromophoric groups introduced during processing and environmental exposure. These include polymerisation catalyst residues, unsaturated products produced by side reactions during polymerisation, singlet oxygen, polynuclear aromatic compounds (PNA) and finally charge transfer complexes. However, the relative contribution of these chromophoric groups to the overall photo-initiation step is believed to be of little practical significance(5a) in the early stages of photo-oxidation when thermally formed hydroperoxides are present.

1.1.4.1 Photo-initiation Due to Hydroperoxide Photolysis

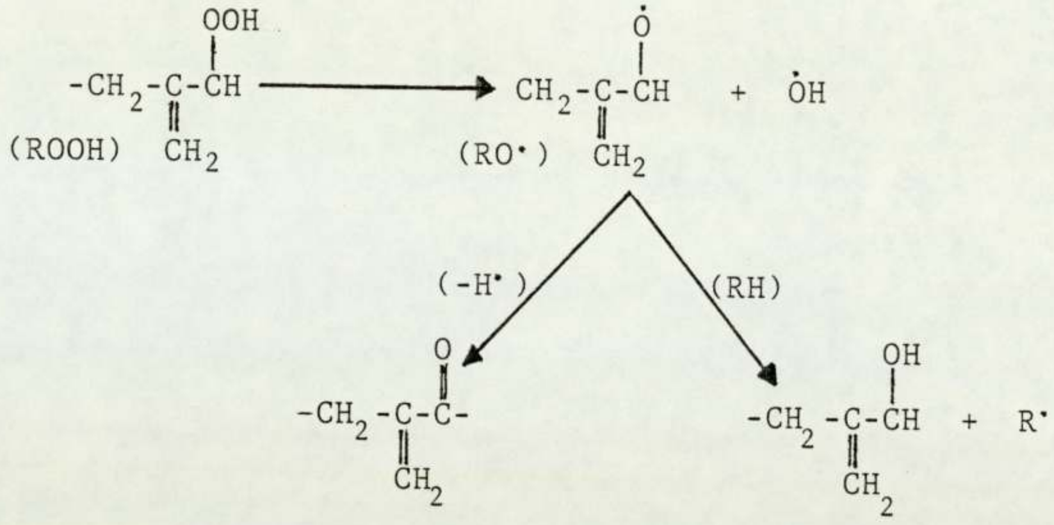
Hydroperoxides are considered to be the species responsible for initiation and subsequent chain scission during the early stages of photo-oxidation of polyolefins. The mechanism can be summarised as follows (reaction 1.3).



(1.3)

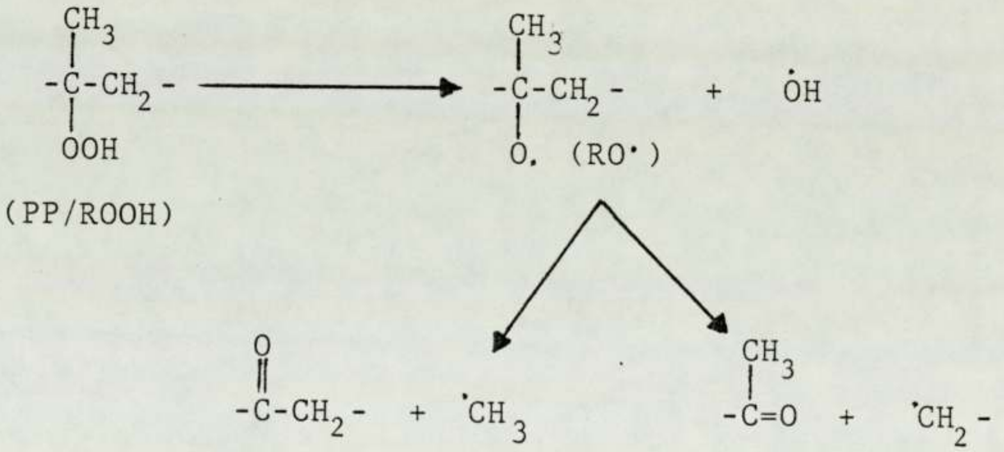
Scott and co-workers(3,6,17,23,24) have conclusively shown that whereas the rate of photo-oxidation of most polyolefins is related to the concentration of thermally formed hydroperoxides (during processing), there is no direct relationship between photo-oxidation rate and the concentration of carbonyl compounds formed in secondary processes. Although carbonyl compounds seem much less important than hydroperoxides during the initial stages of photo-oxidation, it has been suggested that the former may become involved as secondary photo-initiators during the latter stages of photo-oxidation(18,19). Thus, both species formed during fabrication process play an important role as photo-initiators at different stages of photo-oxidation.

Hydroperoxides undergo photolysis to alkoxyl radicals with concomitant formation of carbonyl species and alcohols (reaction 1.4). The radical formation has been shown(6,30) to be of high quantum yield ($\simeq 1$) due to the ready diffusion of the hydroxyl radical from the site of the reaction (cage), and the quantum efficiency of radical initiation for polypropylene hydroperoxide is much higher than it is for the derived carbonyl compounds.



(1.4)

These workers(6,30) postulated that photolysis of thermally formed PP hydroperoxides is a key step in the photo-oxidation and results in appreciable chain scission of the polymer chain (reaction 1.5)

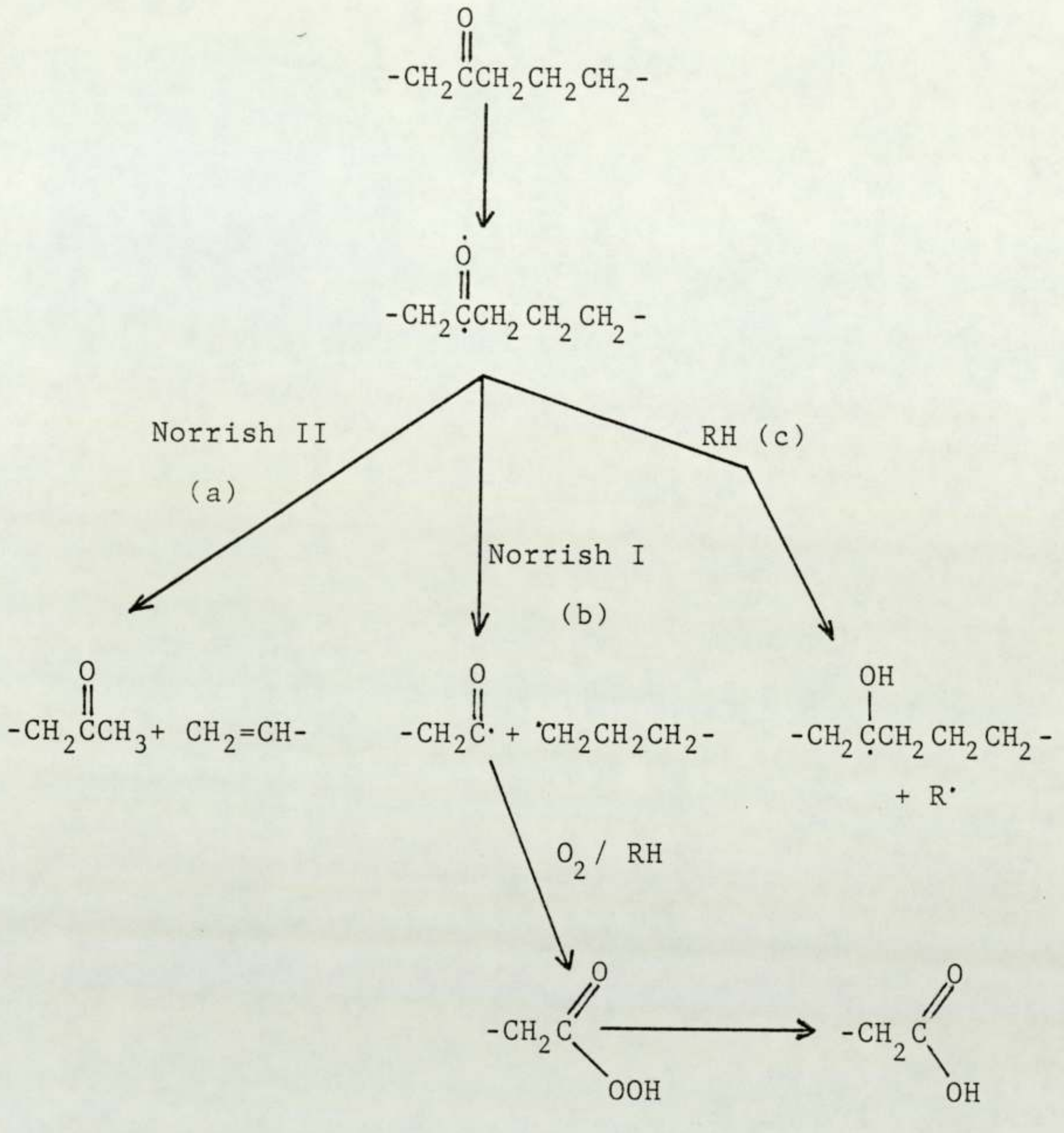


(1.5)

As the concentration of carbonyl compouonds builds up in the polymer, they in turn become the centre for further chain scission reactions by carbonyl photolysis.

1.1.4.2 Photo-initiation Due to Carbonyl Photolysis

Unlike hydroperoxides, carbonyl groups exhibit a strong ultra-violet absorbance in the 300 nm region and possess characteristic luminescence associated with excitation to the triplet excited state. The triplet states of the carbonyl compounds are highly reactive species(4) and it is now fairly well established that when these species are present in sufficient concentration in polyolefins, they undergo photolysis with reduction in molecular weight of the polymer(5b). Of the three different kinds of activity associated with these species during photo-oxidation, the Norrish II process is believed to occur predominantly in the early stages with the generation of vinyl unsaturation at the ends of broken chains (reaction 1.6a)(4,5b,31). Although carbonyl photolysis by this process is associated with chain scission of the polymer it does not give rise to free radicals and therefore cannot initiate further oxidative degradation. In contrast, photolysis by Norrrish I (reaction 1.6b) process results in the formation of free radicals which are potentially capable of initiating the autoxidation of the polymer. The low quantum efficiency associated with this process(4,5b,31) indicates that these radicals are formed in a 'cage' due to the high viscosity of the polymer in the solid state and the net result of this process is the formation of high concentrations of carboxylic acids as the ultimate products of photo-oxidation.



(1.6)

The hydrogen abstraction reaction (reaction 1.6c) which also gives rise to free radicals, has been suggested to be a secondary source of photo-initiation during the later stages of photo-oxidation(5b,19) since the alkyl radicals produced can react with oxygen as in the propagation step of chain reaction (Scheme 1.1b).

Similar Norrish I and II processes have also been postulated for the photolysis of carbonyl species in polypropylene(32) leading to the formation of free radicals (Norrish I) and molecular products (Norrish II) respectively. However, a great deal of evidence suggests(6,16,20-24) that hydroperoxides rather than carbonyls are the key photo-initiators during the early stages of photo-oxidation of polyolefins. Polypropylene differs from polyethylene in that the concentration of hydroperoxides is an order of magnitude higher in the former and also increases during photo-oxidation(16,21). Kinetic data from this study(16) not only indicate the dominant importance of hydroperoxides as the primary initiating species during the early stages of photo-oxidation, but also imply that carbonyl initiation contributes during the later stages.

In the light of such considerable evidence, it is, therefore, clearly evident that the severity of the processing condition will be reflected in the service performance of the polymer article(4,5a,5b,6).

1.1.5 Deterioration of Mechanical Properties During Oxidative Degradation of Polyolefins

It has been clearly shown in earlier sections that chain scission is one of the most important consequences of the autoxidation of polymers. It is also known that the most important properties of polymers result from their high molecular weights and since this is substantially reduced by chain scission, it therefore follows that some loss in the properties do occur during oxidative degradation of the polymer(4,6,33) . Thermolysis and photolysis of hydroperoxides which eventually results in chain scission, has been reported to occur predominantly in the oxygen-permeable amorphous phase(6,34) . The progressive oxidative chain scission therefore results in the restructuring of the amorphous phase as is evidenced by formation of surface crazes. In the case of polyolefins exposed to oxidative environments (light/heat), this phenomenon is manifested in a rapid reduction in residual elongation and tensile strengths with increasing exposure time. Scott(4) has suggested that the reduction in the impact resistance of semi-crystalline polymers during oxidative degradation is due to chemicrystallisation which results from the re-alignment of the broken chains in the crystalline domains.

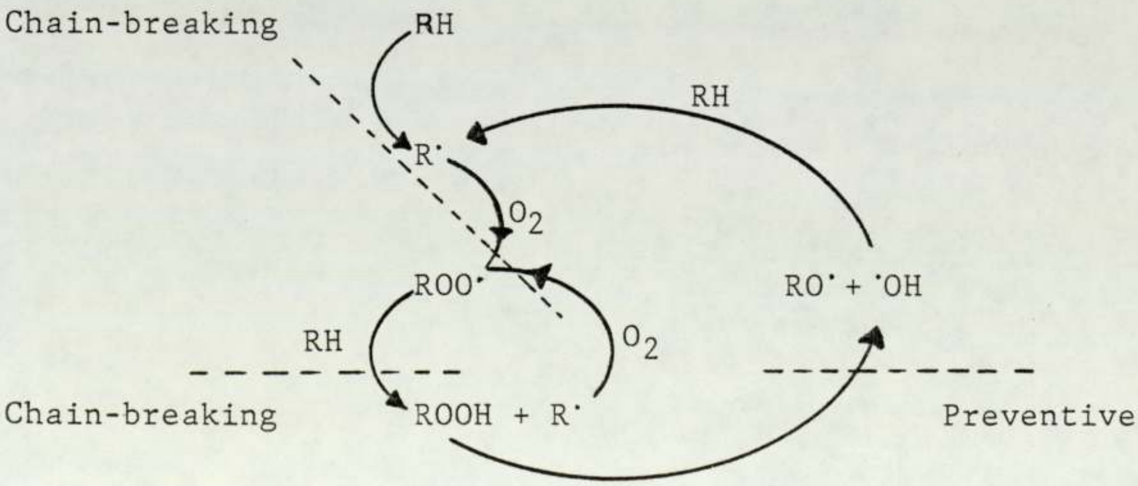
Finally, the extent of the thermal oxidative treatment received during the processing stage has a direct effect on changes in the mechanical properties of the polymer article during subsequent oxidative degradation. For instance, Carlsson and co-workers(6) have shown that drawn PP fibres produced under severe processing conditions are more susceptible to photo-oxidation than fibres produced under less severe conditions.

1.2 Antioxidant Mechanisms in Polyolefins

Antioxidants, by definition, are materials which are incorporated in polymers to inhibit oxidative degradation either during melt processing (melt stabilisers) or in service (e.g. thermal and photo stabilisers).

The autoxidation chain mechanism discussed in an earlier section (1.1.2) and summarised in Scheme 1.3, involves three inter-related processes. The first two processes represent the alkyl/alkylperoxyl chain reaction while the third involves the homolysis of hydroperoxides which feeds the chain reaction with new radicals.

Scheme 1.3 Essential features of the autoxidation chain mechanism

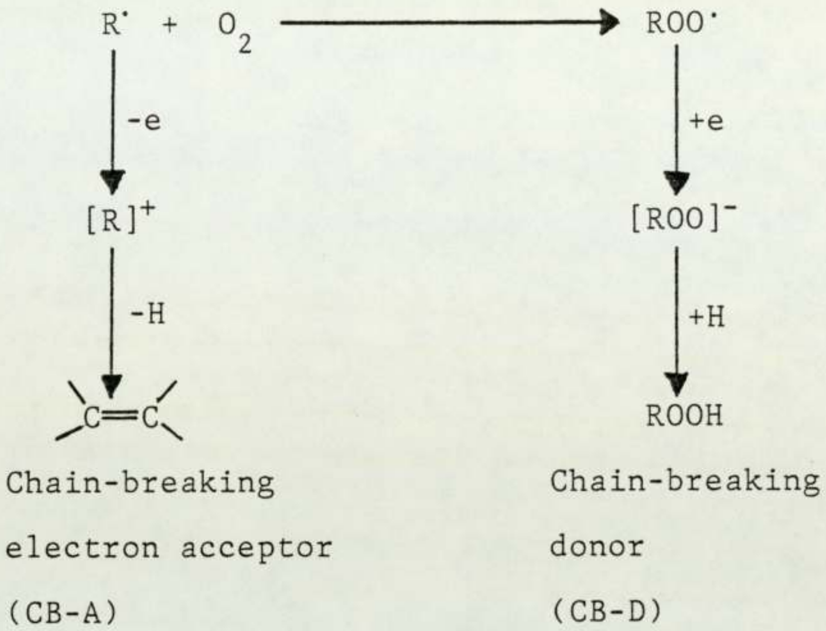


The main purpose of adding an antioxidant is, therefore, to prevent the attainment of a constant rate of oxidation by inhibiting or retarding the formation of hydroperoxides as long as possible (chain-breaking antioxidants). Since the latter species are both thermo and photo-labile giving rise to more free radicals which contribute to the autoxidation chain mechanism, a complementary process is therefore used to decompose the hydroperoxides into non-radical products (Preventive antioxidants).

1.2.1 Chain Breaking Antioxidants

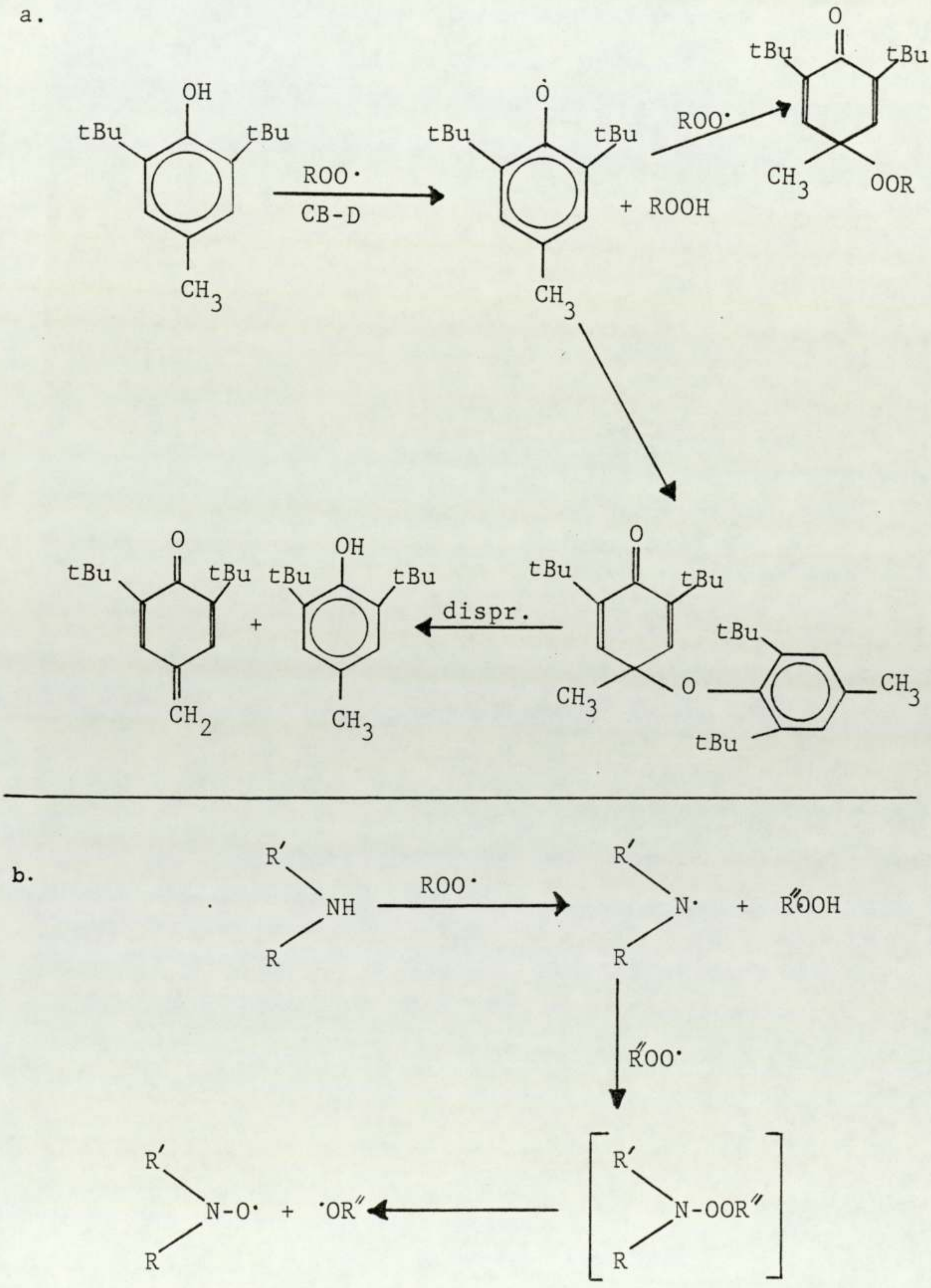
The scavenging of alkyl and alkyl peroxyl radicals are potential chain-breaking processes(8b). In the presence of an oxidising agent the alkyl radical, can be removed to give products such as olefins by elimination of a proton while the alkyl peroxyl radical can be reduced to form a hydroperoxide. Antioxidants which function by these two mechanisms are electron acceptors (oxidising agents) and electron donors (reducing agents) respectively, and are generally designated as CB-A and CB-D antioxidants(4b).

Scheme 1.4 Kinetic chain-breaking mechanisms



Hindered phenols and secondary amines are well known(8b,25,35,63) chain-breaking donor antioxidants in polymers. The antioxidant activity of these materials is associated with their abililty to deactivate alkylperoxyl radicals by electron donation (hydrogen atom). In the case of a hindered phenol, the phenoxyl radicals may either undergo mutual recombination or react with other alkyl peroxyl radicals (Scheme 1.5a); thus the stoichiometric coefficient (f) of the inhibitor is normally one or two. A typical member of this class of antioxidants is the material 2,6-di-tert-butyl phenol, normally referred to as butylated hydroxytoluene (BHT). Similar chain-breaking donor antioxidant mechanism have also been postulated for secondary amines and hindered piperidines (Scheme 1.5b)(25,35,63) .

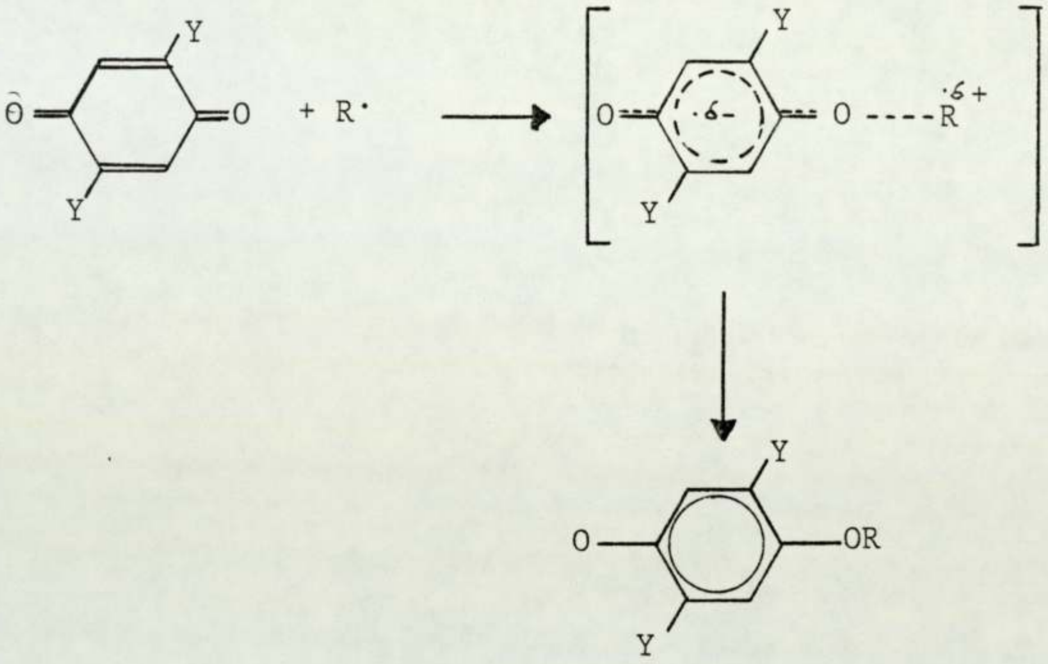
Scheme 1.5 Deactivation of alkyl peroxyl radicals by CB-D antioxidants



The presence of the reactive (O-H) or (N-H) functional group in these matierials, suggests that they compete with the polymer substrate for the alkyl peroxyl radical and thus terminate the propagation reaction by hydrogen transfer.

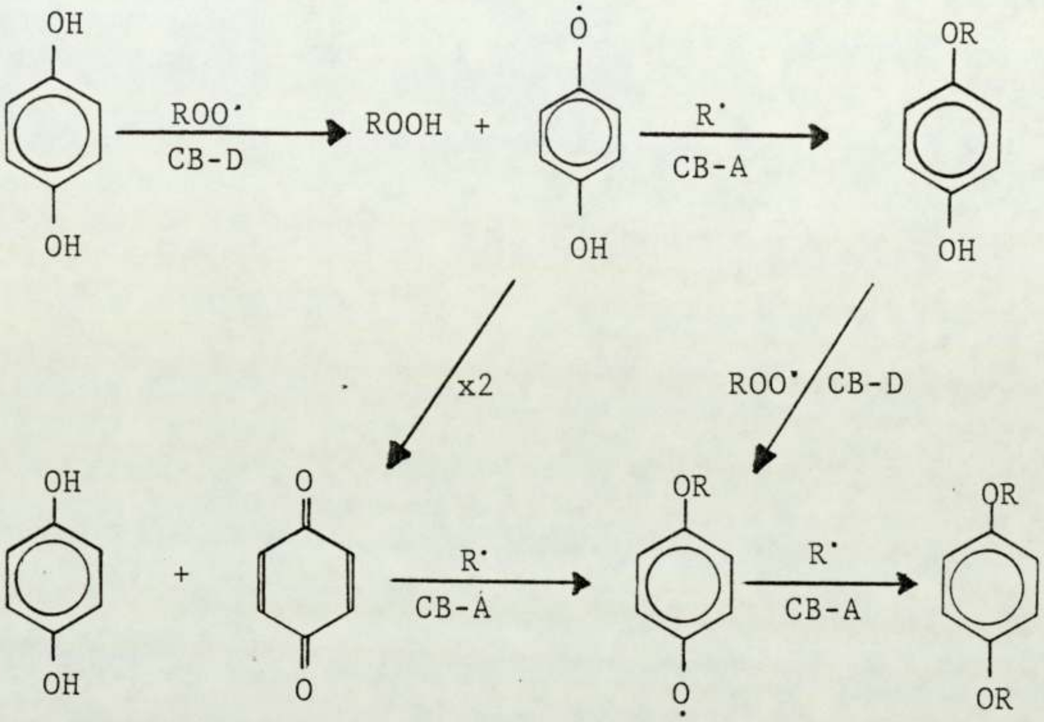
Antioxidants which function by oxidising or trapping alkyl radicals (CB-A) are generally used as inhibitors during polymerisation processes in the absence of oxygen(4b,25). Members of this class include quinones, nitro compounds, and a variety of stable radicals of which galvinoxyl and nitroxyls are the most important. Although quinones and nitro compounds are effective alkyl traps for rubber during processing, this ability is of little practical significance since their activity is considerably reduced in the presence of excess oxygen(25) However, the fact that quinones are widely used as antifatigue agents in rubber suggests that alkyl radical trapping plays an important part in their mechanism (Scheme 1.6) as antifatigue agents.

Scheme 1.6 Radical Trapping Activity (CB-A) Quinones



In the light of this discussion, it is clear that whereas CB-D antioxidants are most effective when the autoxidising system contains a high concentration of alkyl peroxyl radicals (oxygen excess), CB-A antioxidants operate best in oxygen deficient conditions or at high initiation rates. Since both alkyl and alkyl peroxyl radicals are present to some degree in most autoxidising processes, antioxidants which exhibit both kinds of activity are therefore superior to those operating by a single mechanism(25). The complementary antioxidant activity involving both CB-D and CB-A mechanisms is shown typically for hydroquinone (Scheme 1.7). This antioxidant is initially converted to the corresponding benzoquinone by CB-D mechanism and the latter then scavenges alkyl radicals by CB-A mechanism.

Scheme 1.7 Complementary CB-D/CB-A mechanisms involving hydroquinone and its derived products



The diaryl amines are also known to have the ability to alternate between the oxidised and reduced states and hence exhibit regenerative behaviour in a cyclical mechanism, under conditions where both alkyl and alkyl peroxyl radicals are present(25,36). Their activity as antifatigue agents in rubber is believed(25,36,37) to be due to their conversion to the corresponding nitroxyl radicals which then undergo a cyclical regenerative mechanism involving the hydroxylamines as intermediates.

These chain-breaking antioxidants do, however, suffer from some distinct disadvantages(39). First, they have no effect on the rate of chain initiation occuring by homolysis of the hydroperoxides (see Scheme 1.1a and also reaction 1.3), and secondly, hydroperoxides are formed in the slow rate controlling CB-D termination reactions (See Scheme 1.5 and 1.7). Clearly these antioxidants will lose their effectiveness under conditions where initiation by hydroperoxides and peroxide decomposition is important. Consequently, a second class of antioxidants was developed, and these are generally classified as preventive antioxidants(38,39).

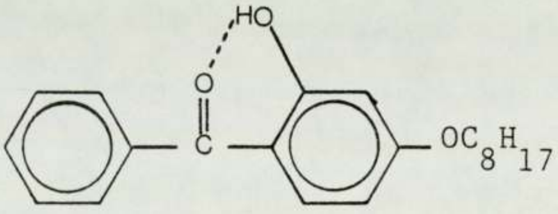
1.2.2 Preventive Antioxidants

These antioxidants interfere with generation of free radicals which feed back into the main autoxidation cycle (see Scheme 1.3). Hence materials which suppress the degradation rate by either physical processes (e.g U.V.-absorption, screening, quenching) or chemical processes (hydroperoxide decomposition) should effectively prevent the re-initiation of the chain reaction.

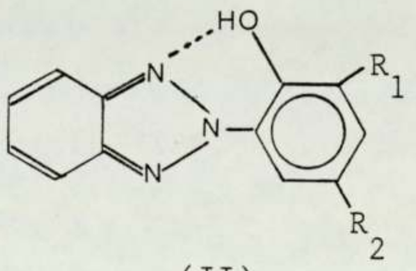
1.2.2a Physical Processes

This process involves the activity of compounds that absorb U.V. light(6). During photo-oxidation, light screens function either by absorbing damaging radiation before it reaches the polymer surface (e.g. coating as paints) or limiting its penetration into the polymer bulk (pigments). Carbon black is particularly successful in the latter category although its usefullness is limited by colour. Other less effective light-screening pigments such as titania are also frequently used (in combination with carbon black) in outdoor fittings such as PVC drain pipes$^{(4b)}$.

In recent years, research has led to the development of non-coloured U.V. filters which function essentially by protecting potential photosensitisers (hydroperoxides and carbonyl species) from the effects of light. Notable examples of this class of preventive antioxidants are the 2-hydroxybenzophenones (I) and the 2-hydroxyphenylbenzotriazoles (II)$^{(4b,6,29)}$. These compounds exhibit a strong U.V.absorption in the region 300-500nm and this is found to be associated with the hydrogen bonded interaction between the phenolic hydroxyl group and adjacent double-bonded groups (C=O and C=N).

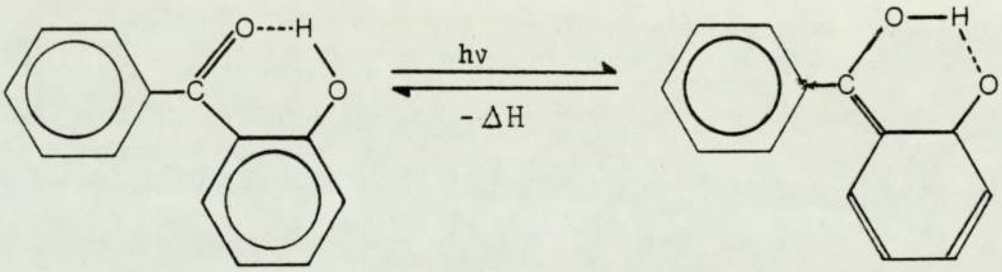


HOBP - (I)



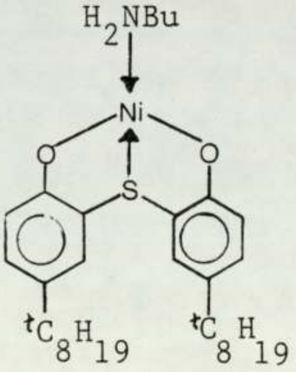
(II)

Thus, alkylation of the free hydroxyl group reduces the absorptivity substantially and these derivatives are not as effective as the precusors (I and II) which are much more U.V.-stable since they do not give rise to a triplet state on absorbing U.V. light(4b). For instance, the triplet state formed on absorption of light by the ketone group in (I) is internally deactivated by energy transfer from the hydrogen-bonded intermediate (reaction 1.7), which then undergoes tautomerism to the more stable hydroxybenzophenone with concomitant emission of the initially absorbed U.V. energy as heat(4b,18).

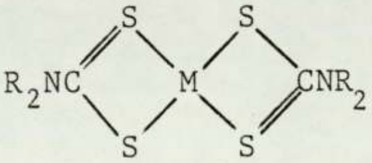


(1.7)

In common with (I) and (II), a variety of nickel chelates (e.g III and IV) also absorb strongly in the damaging region of the sun's spectrum, and hence function at least in part by U.V. screening and probably by quenching of



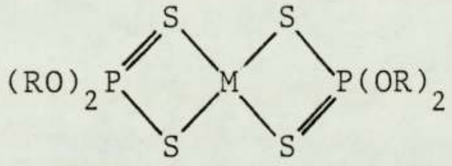
(III)

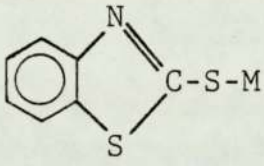


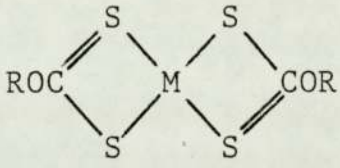
(IV)

(M = Ni or Co)

excited chromophoric groups(6,16,29) since they are able to dissipate absorbed U.V. radiation and emit it harmlessly as thermal energy. However, evidence suggests that U.V. screening plays only a minor part in the preventive antioxidant activity of dithiocarbamates (IV) and the structurally related dithiophosphates (V), xanthates (VI) and mercaptobenzothiazoles (VII), which is primarily associated with their peroxidolytic activity (Chemical processes).


(V)

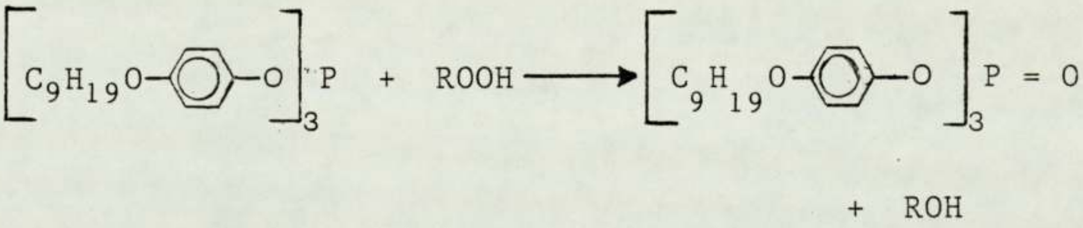

(VII)


(VI)

1.2.2b Chemical Process (Peroxide Decomposition [PD] Mechanism)

Since hydroperoxides are universally involved in autoxidation irrespective of the environment, its decomposition to non-radical products therefore represents the most important aspect of preventing mechanism. Hence, the hydroperoxide radical initiating mechanism (reaction 1.3) which may occur under melt, thermal or photo-oxidative conditions are interrupted (see also Scheme 1.3, hatched line).

Scott(25) has classified the function of peroxide decomposers (PD) in two main categories: the stoichiometric peroxide decomposers (PD-S) and catalytic peroxide decomposers (PD-C). The essential requirement of compounds which fall into the former class (PD-S) is the ability to reduce hydroperoxides to alcohols without substantial formation of free radicals as typically shown for the phosphite ester (reaction 1.8) which is widely used in rubber.



(1.8)

Of much more general applicability in polyolefins is the class of sulphur compounds which destroy hydroperoxides by a catalytic mechanism. These include dialkyl mono and disulphides, mercaptobenzthiazoles (VII), the metal thiolates (IV - VII) and their corresponding disulphides. The one thing these compounds have in common is the ability to destroy hydroperoxides through the formation of acidic products in a non—radical process, and in most cases, the antioxidant function is usually preceded by a pro-oxidant stage this being dependent on the structure of the sulphur compound(25). Thus, whereas the dialkyl mono and disulphides show pronounced initial pro-oxidant behaviour, this effect may only be transient in the case of the metal thiolates (IV - VII)(25).

Previous studies(4,5,13,41) on the dithiocarbamates(IV) and mercaptobenzthiazoles (VII) have indicated that an important factor of the peroxidolytic activity of these compounds is the formation of sulphur dioxide which is ultimately converted to sulphur trioxide. Analogous investigation into the mechanism of the dithiophosphates (V) and xanthates (VI) has led to similar conclusions(4,5,13,19,27,40b) since the elimination of the sulphur acids and sulphur dioxide are mechanistically similar. (see Scheme 1.9)

1.2.3 Review of Antioxidant Mechanisms of Dithiophosphates

Pioneering studies(64,65) on the antioxidant activity of metal dithiophosphates in autoxidising mineral oil had established the ability of these compounds to decompose hydroperoxide by ionic mechanism, this being attributed to the intermediates formed from the original complex.

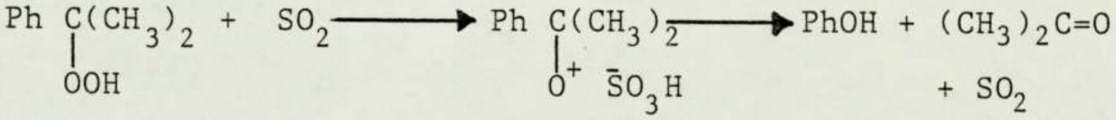
More recently, several groups of workers(43,66-70) have also demonstrated that most metal complexes, including the dithiophosphates, can scavenge alkylperoxyl radicals since they inhibited or retarded hydrocarbon autoxidation in the absence of hydroperoxide and at room temperatures where initiation by hydroperoxide homolysis was unimportant.

The ability of the dithiophosphates to function by both of the above mechanisms are discussed below.

1.2.3.1 Dithiophosphates as Peroxide Decomposers

The ablity of dithiophosphates to decompose hydroperoxides was first shown by Kennerly and Patterson(64) and on the basis of their studies, these workers proposed a catalytic mechanism for the decomposion of cumyl hydroperoxide to molecular products (acetone and phenol). Since there was no obvious mechanism for acid catalysed decomposition by the original complex, it was concluded that intermediates (such as the thiyl radicals) formed from the complex were responsible for ionic decomposition. They also noted that hydroperoxide decomposition in the presence of air resulted in a pro-oxidant effect, implying that free radical processes were also occuring.

Holdsworth, Scott and Williams(13) have observed the evolution of sulphur dioxide in tetralyl hydroperoxide catalysed oxidation of tetralin at 50°C, in the presence of zinc dinonyldithiophosphate and the structurally related dithiocarbamates and xanthates. The decomposition of cumyl hydroperoxide was also accompanied by the liberation of a gas along with the precipitation of the metal sulphate and marked auto-inhibition effect. The formation of mainly phenol and acetone as products of the decomposition of CHP in addition to the above evidence led these workers(13,41) to conclude that sulphur-containing antioxidants may be considered as potential reserviours for the production of sulphur dioxide which is a powerful peroxide decomposer according to the following rgenerative scheme (reaction 1.9).



$$\mathrm{Ph}\ \underset{\mathrm{OOH}}{\mathrm{C}}(\mathrm{CH_3})_2 + \mathrm{SO_2} \longrightarrow \mathrm{Ph}\ \underset{\mathrm{O^+}\ \bar{\mathrm{S}}\mathrm{O_3H}}{\mathrm{C}}(\mathrm{CH_3})_2 \longrightarrow \mathrm{PhOH} + (\mathrm{CH_3})_2\mathrm{C{=}O} + \mathrm{SO_2}$$

(1.9)

The observed initial pro-oxidant effect which is particularly important for nickel and cupric complexes, was attributed to the production of radicals by a homolytic reaction (reaction 1.10). Furthermore, this reaction assumed greater importance only when the

$$[(\mathrm{RO})_2\mathrm{PS_2}]\mathrm{M} + \mathrm{ROOH} \longrightarrow (\mathrm{RO})_2\mathrm{PS}_2^{\cdot} + \mathrm{HO{-}MS_2P(OR)_2} + \mathrm{RO}^{\cdot}$$

(1.10)

hydroperoxide: metal complex ratio was low while heterolytic products (phenol and acetone) predominate at high ratios (e.g. 100:1).

Burn, Cecil and Young(71) studied the decomposition of hydroperoxides by zinc dithiophosphates and confirmed the three-stage reaction first reported by Shorpov and co-workers(72). The three distinct stages observed include

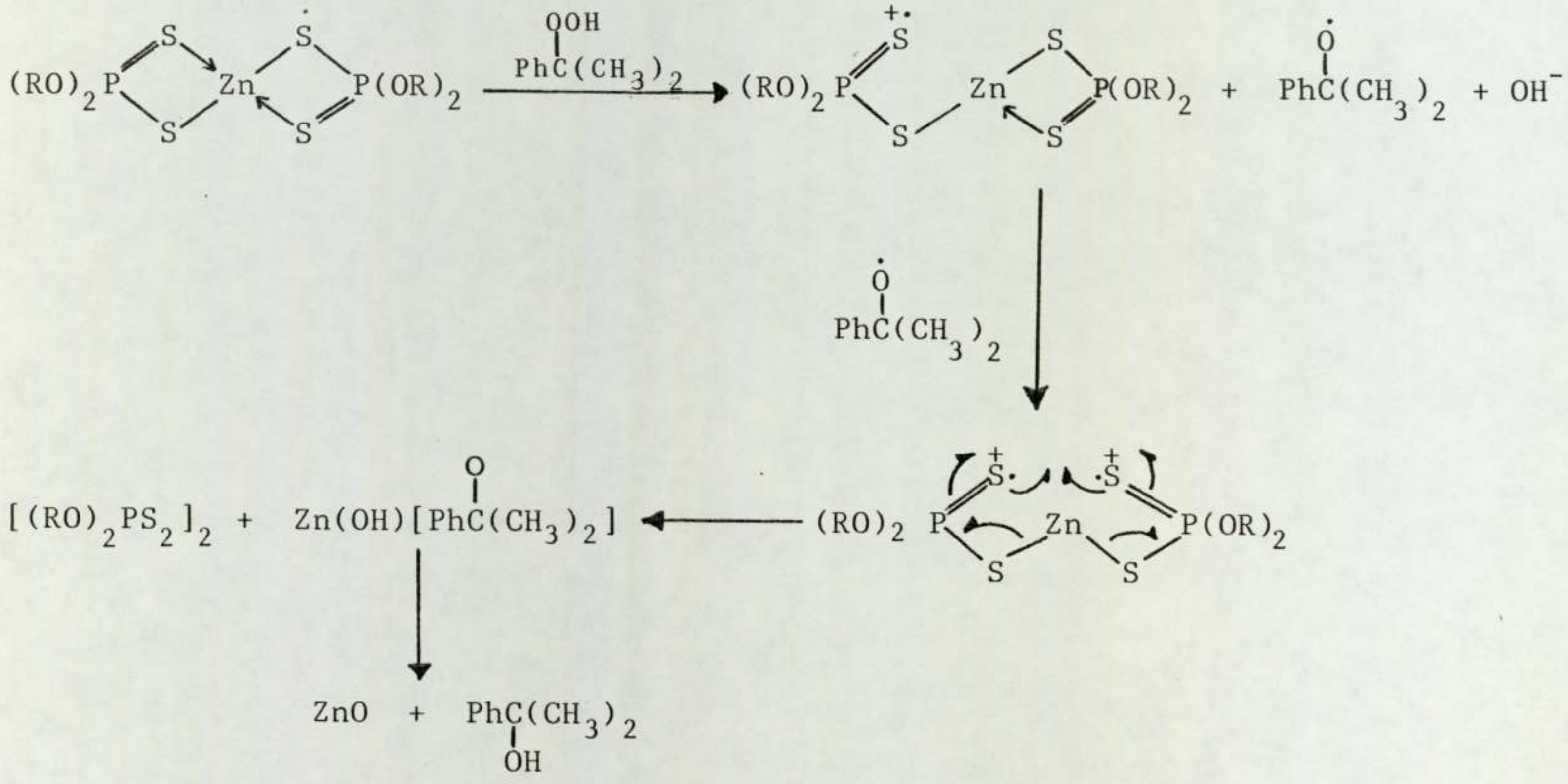
(a) An initial fast stage
(b) A slow stage or induction period
(c) A final fast stage

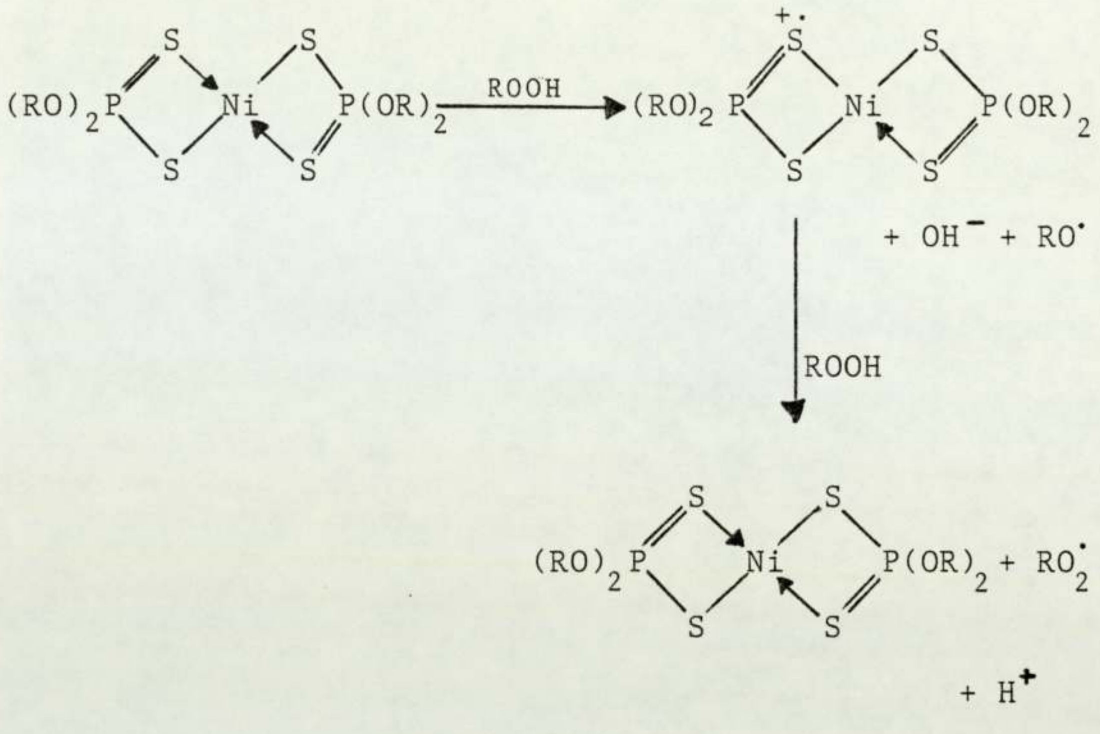
On the basis of these studies, Burn(71) originally proposed a mechanism to account for the initial free radical peroxide decomposition stage which results in concurrent formation of disulphide and α- cumyl alcohol (Scheme 1.8).

Other mechanisms were also postulated(71) to rationalize decomposition of more than one mole of CHP by each mole of complex. This mechanism appears to be substantiated by Ivanov and co-workers(70,73) who concluded from their work that most co-ordination complexes between zinc dithiophosphate and hydroperoxide contain two moles of hydroperoxide, and that these complexes decompose to give radical and molecular products.

In contrast to the behaviour of the zinc complexes, the initial reaction between nickel and cupric complexes with ROOH have been reported(39,68b) to be almost entirely homolytic and probably involves the redox cycle shown by the following reaction sequence (reaction 1.11).

Scheme 1.8 Initial reaction of zinc dithiophosphate with CHP.



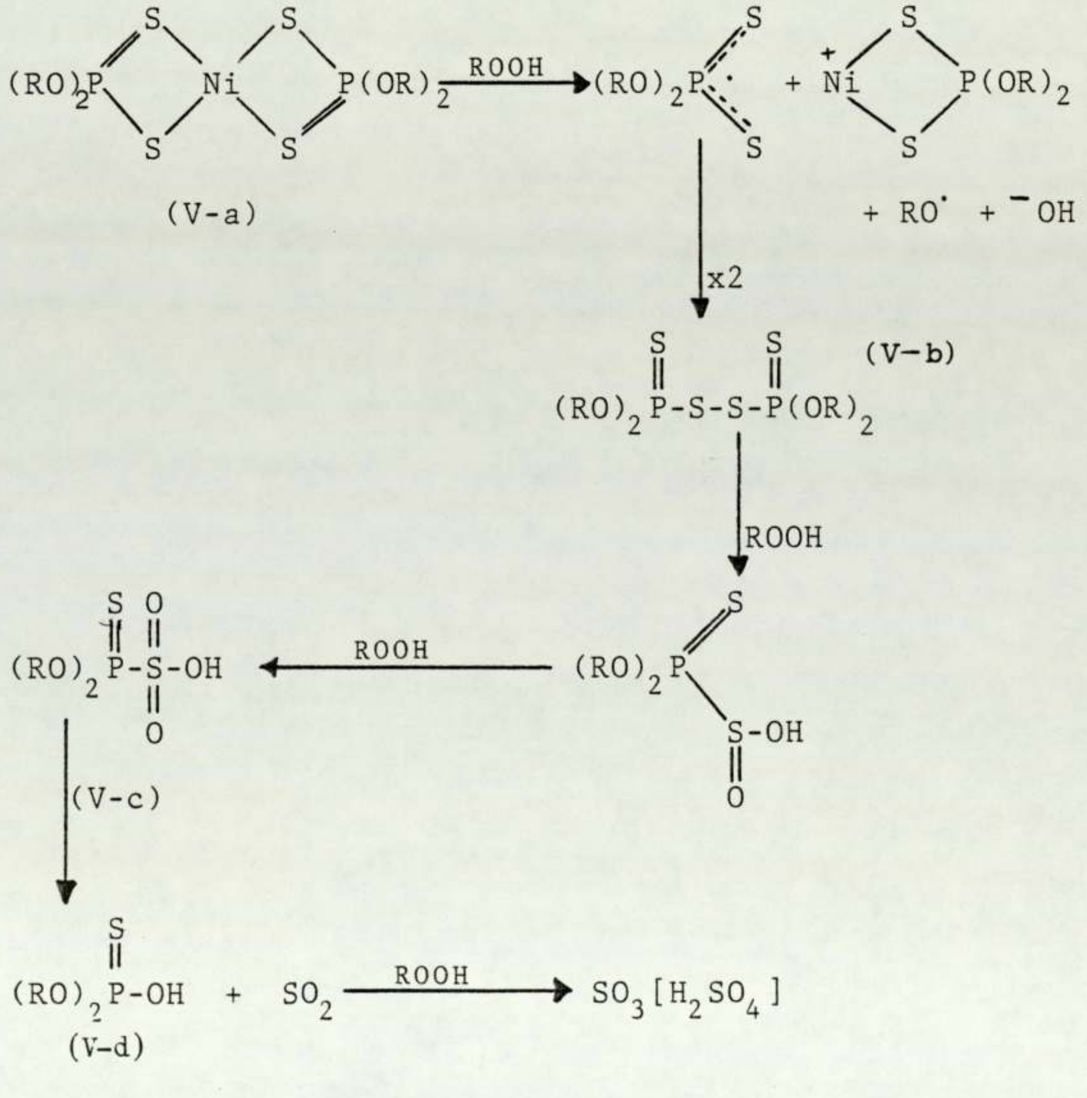


(1.11)

Thus, cumyloxy radicals formed (reaction 1.11) either abstract a hydrogen atom to give α- cumyl alcohol or undergo β- scission to form acetophenone.

The second stage or induction period that is observed in hydroperoxide decompositions at high ratios of ROOH:metal complex is believed(39) to be associated with the formation of the ionic catalysts from the oxidation products of the complex. This view is supported by the work of Al-Malaika and Scott(40b,74) who observed a similar three-stage process during decomposition of CHP by nickel dithiophosphates. Detailed product studies led these workers(40b,74) to conclude that the first rapid stage is associated with the formation of the disulphide (V-b) (see Scheme 1.9) which is then slowly converted, by further peroxide decomposition, to secondary nickel-free oxidation products. The most important of these products is believed to be the sulphonic acid (V-c) since it readily loses sulphur dioxide to give the relatively more stable thionophosphoric acid (V-d). Phenol, the product characteristic of ionic decomposition of CHP was not observed until the intermediate sulphonic acid (V-c) began to break down.

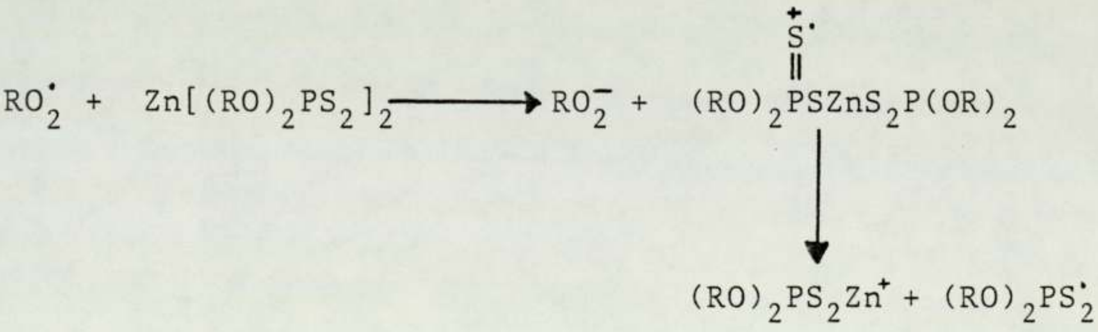
Scheme 1.9 Antioxidant Mechanism of Nickel dialkyl dithiophosphates



Although there still appears to be some controversy in published literature with regard to the nature of the catalysts responsible for the ionic peroxidolytic action of the metal dithiophosphates (V), Scott and co-workers(4,5,25,40,74) remain convinced that the fully oxidised protonic acids (SO_3, H_2SO_4) and the intermediate sulphonic acid (V-c) and the more stable thionophosphoric acid (V-d), are powerful candidates for this role.

1.2.3.2 Dithiophosphates as Radical Scavengers

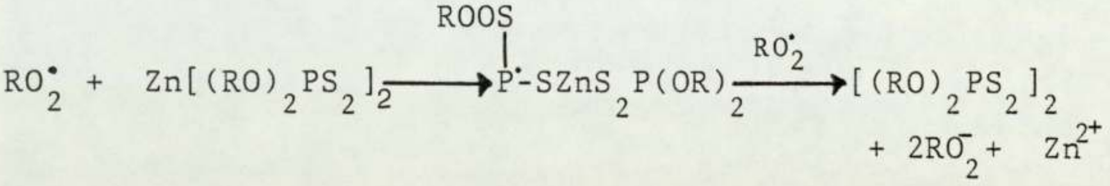
The ability of zinc dialkyl dithiophosphates to scavenge alkyl peroxyl radicals was first demonstrated by Colclough and Cunneen(43) who postulated an electron transfer mechanism in which an electron is abstracted from an electron rich sulphur atom in the ligand by the radical (reaction 1.12)



$$\begin{array}{l} RO_2^{\bullet} + Zn[(RO)_2PS_2]_2 \longrightarrow RO_2^{-} + (RO)_2\overset{\overset{\overset{+}{S}^{\bullet}}{\|}}{P}SZnS_2P(OR)_2 \\ \qquad\qquad\qquad\qquad\qquad\qquad\qquad\qquad\downarrow \\ \qquad\qquad\qquad\qquad\qquad\qquad (RO)_2PS_2Zn^{+} + (RO)_2PS_2^{\bullet} \end{array}$$

(1.12)

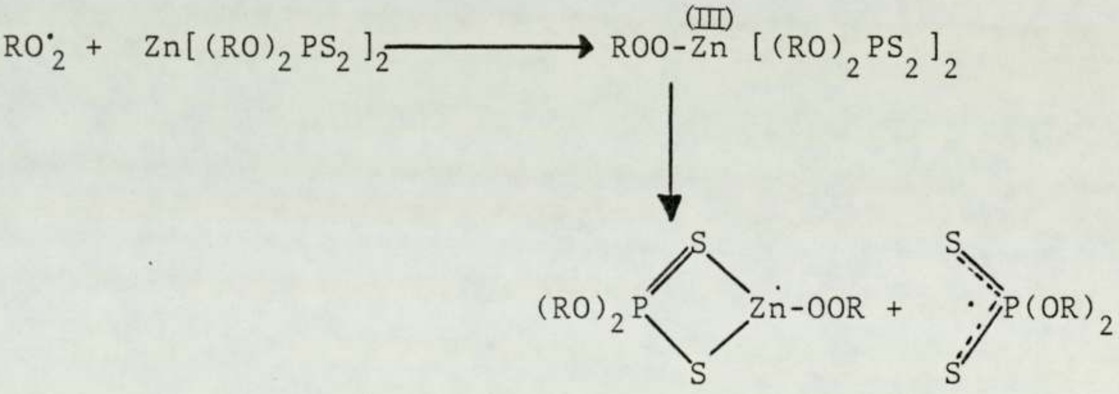
Burn(66) later proposed an alternative mechanism involving a stabilised peroxyl radical zinc complex intermediate which, on attack by a second peroxyl radical, leads to intramolecular dimerisation of the incipient thiyl radical to form the disulphide (reaction 1.13).



$$RO_2^{\bullet} + Zn[(RO)_2PS_2]_2 \longrightarrow \overset{ROOS}{\overset{|}{P^{\bullet}}}\text{-}SZnS_2P(OR)_2 \xrightarrow{RO_2^{\bullet}} [(RO)_2PS_2]_2 + 2RO_2^- + Zn^{2+}$$

(1.13)

It has been argued by Howard and co-workers(75) that alkyl peroxyl radicals react with zinc dithiophosphates and related complexes (IV and VI) at the metal centre either by the electron transfer mechanism (reaction 1.12) or by an S_H2 process (reaction 1.14) which involves a zinc (III) species as a transient intermediate.



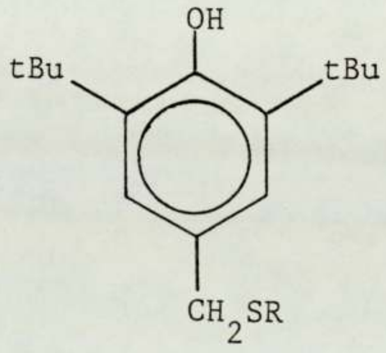
(1.14)

The main arguement in favour of this mechanism (reaction 1.14) is the inactivity of disulphides towards peroxyl radicals and the low pre-exponential factor observed for the reaction of the peroxyl radical with the metal complex.

The kinetic and product studies that have been performed on a variety of sulphur-containing transition metal complexes with particular reference to dithiophosphates (V) and dithiocarbamates (IV) have been comprehensively reviewed by Ivanov(70) and more recently by Howard(39). In conclusion, Howard(39) suggested that alkyl peroxyl radicals appear to react at the metal centre of dithiophosphates (V) to displace a ligand radical, while its interaction with the latter (IV) takes place at the electron rich sulphur atom.

1.2.4 Antioxidant Synergism and Antagonism

The autoxidation chain mechanism summarised in Scheme 1.3 indicates that the stabilisation process can be accomplished by a number of different and complementary ways. The co-operative interaction of antioxidants which function by different mechanisms is termed synergism(4b,5,22) and this not only leads to an overall antioxidant effect which is greater than sum of the individual effects, but also results in a much greater effectiveness than can be achieved by either antioxidant alone even at much higher concentrations. Thus, when a chain-breaking antioxidant (CB-A/D) is used in combination with a peroxidolytic antioxidant (PD-C), the primary function of the former is to reduce the amount of hydroperoxide formed in the autoxidising system while that of the latter is to reduce the concentration of radicals in the system (see Scheme 1.3). The net effect of this co-operative interaction between both types of antioxidants is manifested on the mutual protection of each other and hence prolong their independent, but complementary, activity in the polymer. The phenomenon of autosynergism is also known to occur$^{(18,40a)}$ when two antioxidant functions are present in the same molecule, and this phenomenon (hindered phenol, CB-D and sulphide, PD-C) is believed to be responsible for the enhanced effectiveness of the bisphenolic sulphides (VIII)$^{(18,40a,44)}$.



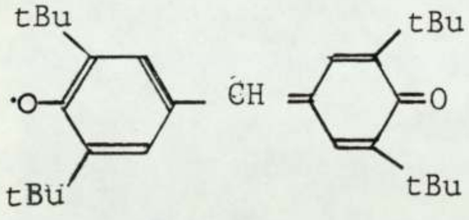
(VIII)

Conversely, when two antioxidants interact to decrease the sum of their individual effects, this is commonly referred to as an antagonistic effect. For instance, observed antagonistic effects between certain hindered phenols and some peroxidolytic antioxidants have been reported$^{(16,45)}$ to occur under photo-oxidative conditions, although they are synergists under thermal oxidative conditions.

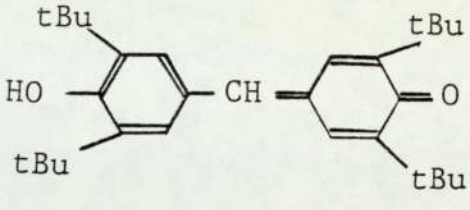
1.2.5 Stabilisation of Polyolefins During Fabrication and in Service

1.2.5.1 Melt Stabilisation

The primary function of a melt stabiliser is to inhibit the formation of hydroperoxides and other sensitising groups which would otherwise impair the durability of the fabricated polymer article during service life(4b,5a,5b). Since melt degradation of polymers is a primary consequence of chain scission (PP) or crosslinking (PE) reactions, the removal of macro-radicals and destruction of hydroperoxides should therefore be effective melt-stabilising processes. In practice, melt stabilisation is fairly readily achieved using a typical CB-D antioxidant such as the hindered phenol, BHT (see Scheme 1.5a) and the oxidation transformation products have been reported to be much more effective than BHT itself as melt stabilisers(2,4b,26,35). For instance, the 'stable' aryloxyl radical, Galvinoxyl (IX) has been shown(2,35) to be particularly effective in PP. It is rapidly reduced to hydrogalvinoxyl (X) followed by further regeneration of the former (IX) during the early stages of processing, and such complementary CB-A/CB-D activity is similar to that proposed for hydroquinone (see Scheme 1.7).

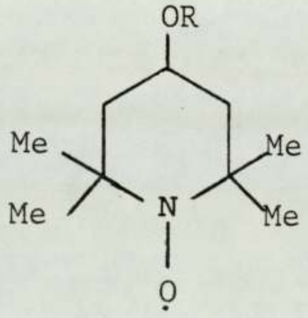


(IX)

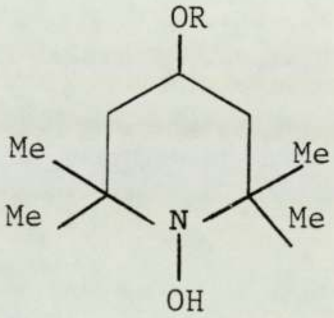


(X)

The high activity of these species as melt stabilisers for polymers during processing is therefore believed to be due to the existence of (IX) and (X) as a reversible redox couple under melt conditions. The hindered nitroxyl radical (XI) has been shown (2,35) to undergo a similar redox reaction involving the hydroxylamine (XII) under the same conditions.

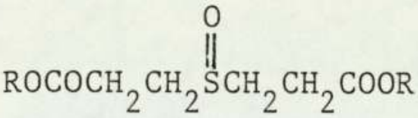


(XI)



(XII)

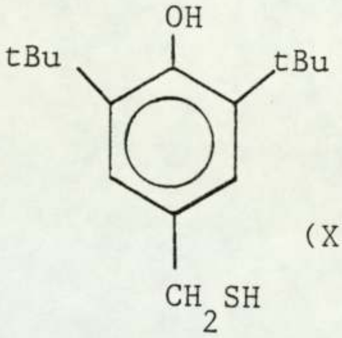
Peroxidolytic (PD) antioxidants are also very effective melt stabilisers for polyolefins. These include sulphoxides (XIII) derived from dialkyl dipropionate esters, metal dithiolate complexes of which the dithiocarbamates (IV) and dithiophosphates (V) are well known, their corresponding disulphides and the phenolic thiol (XIV)(2,4b,5a,27,40a-b).



$$ROCOCH_2CH_2\overset{\overset{O}{\|}}{S}CH_2CH_2COOR$$

(XIII)

$R = C_{12}H_{25}$ or $C_{18}H_{37}$

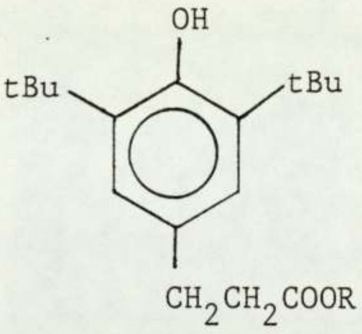


(XIV)

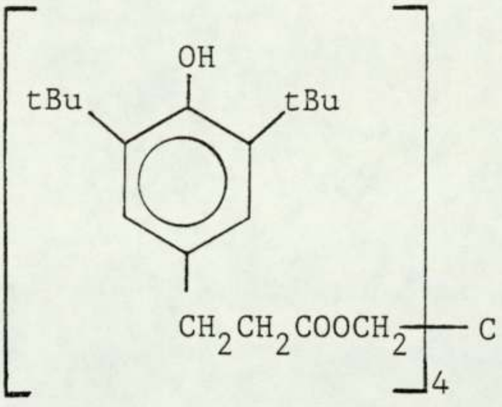
The salient features of the Chemistry of the sulphur containing melt stabilisers, as summarised for dithiophosphates (Scheme 1.9), is shown to involve a complex series of oxidation reactions culminating in the formation of the sulphur acids which are catalysts for the decomposition of hydroperoxides. In the case of the sulphoxide (XIII), the intermediate sulphenic acid (RSOH) has been reported (4b,40a,46) to be a powerful trap for both alkyl and allkylperoxyl radicals and it is believed that a cyclical regenerative process may be involved in this activity. Similarly, the effectiveness of the metal dithiolates (IV and V) as melt stabilisers in polyolefins is due in part to their peroxidolytic activity and also their ability to scavenge alkyl peroxyl radicals.

1.2.5.2 Thermal Oxidative Stabilisation

Chain-breaking donor (CB-D) antioxidants generally form the basis of heat-stabilising systems for polyolefins and the high molecular mass hindered phenols (XV and XVI) are widely used in this respect (4b,5a) in view of low volatility of the molecules.



$R=C_{18}H_{37}$ (XV)



(XVI)

Most sulphur-containing compounds are also efficient thermal antioxidants for polyolefins by virtue of their peroxidolytic activity, although they are not as effective as the hindered phenols. However, synergistic mixtures of these compounds (e.g. IV, V or XIII) with the hindered phenols (XV or XVI) have been widely reported (4b,5a,40a-b) to result in improved performance under thermal-oxidative conditions and this is attributed to the fact that the two types of antioxidant augment each other by virtue of their differnt mechanisms (PD-C/ CB-D). Furthermore, it has been shown (40a) that antioxidants which contain both PD-C and CB-D functions in the same molecule (e.g. VIII) are twice as effective on a molar basis as compared to structurally related hindered phenol (XV) which does not contain the peroxidolytic sulphide function.

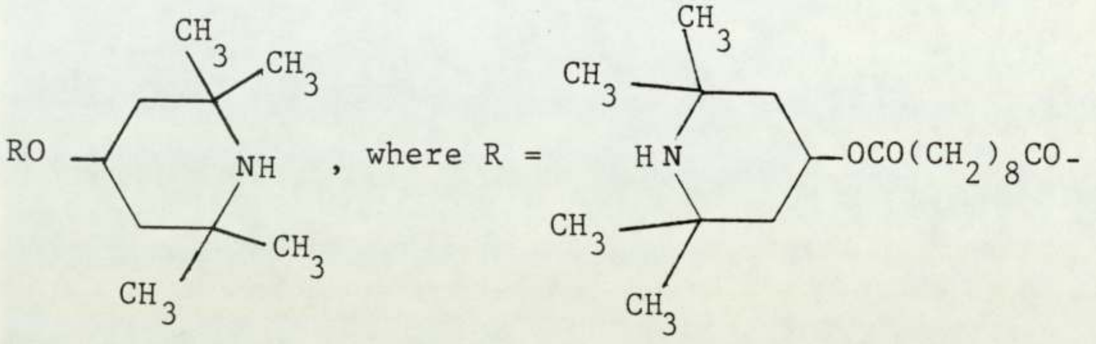
1.2.5.3 Photo-oxidative Stabilisation

Since polymer photo degradation under normal conditions of environmental exposure is essentially a light-initiated autoxidation process, the most frequently used U.V. stabilisers is based on the principle of screening the polymer from the damaging influence of U.V. light.

Compounds such as ortho-hydroxybenzophenones (I) and benzotriazoles (II) are well known U.V. absorbers although they have also been reported(4b,35,47) to behave as weak CB-D antioxidant. 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(16,23b,40b,47).

Some transition metal thiolates such as the dithiocarbamates (IV), dithiophosphates (V) and xanthates (VI) are excellent U.V. stabilisers since they not only decompose hydroperoxides to non-radical products, but also absorb light strongly in the 330nm region of the spectrum and are consequently very photo-stable(2,4b,5b,27,40a-b). It is the latter characteristic which distinguishes some metal complexes, notably nickel chelates, from others (e.g. zinc) which are effective thermal antioxidants but are not U.V. stabilisers. The nickel bisphenolate (III) is also U.V. stable by virtue of the strongly absorbing nickel complex and it has been suggested that this compound may act as 'quencher' for excited states of polymer chromophores.

The hindered piperidines (XVII) are unique among the effective U.V. stabilisers since they do not absorb U.V. light.



(XVII)

Moreover, they are rapidly transformed, partially during processing and completely during the early stages of photo-oxidation, to the corresponding nitroxyl radical (XI) and hydroxylamine (XII) which are more effective as photo antioxidants than the parent amine (XVII). Their activity is believed(2,4b,5b,6,35) to be associated with the same regenerative cycle involving the redox nitroxyl-hydroxylamine couple as is obtained under melt conditions (Section 1.2.4a).

Most photo antioxidants (CB or PD) synergise effectively with U.V. absorbers and hence reinforce one another by complementary mechanisms(4b,5b,18,27,40a-b). This represents an important trend in U.V. stabilisation technology toward multicomponent systems and 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. For instance, the metal thiolate antioxidants (IV - VI), including the zinc complex which is relatively inefffective as a U.V. stabiliser in its own right, have been widely reported (4b,5b,18,40a-b) to become highly effective in combination with the orthohydroxy benzophenone U.V. stabiliser (I) (40b,47), and it has been suggested (23b) that quenching of photo excited states of the dithiolate may be involved in the synergism. However, combination of metal dithiolates with phenolic CB-D antioxidants (e.g. XV) which are normally used as synergists during thermal oxidation (Section 1.2.4b), results in antagonism during photo-oxidation due to the photolytic destruction of the dithiolate by oxidation products of the phenol leading to a decrease in their effectiveness (23b,40b,45)

1.2.5.4 Physical Factors of Polymer Stabilisation

The design and selection of stabilisers for use in polymers is complicated by conflicting antioxidant requiremnts which determine their effectiveness during processing and in service. In addition to the intrinsic antioxidant activity, other physical factors which are known to influence antioxidant performance include their substantivity and solubility in the polymer, and the morphology, orientation state and surface-to-volume ratio of the polymer sample (4b,5b,6,34,40a). Since most polyolefins are semi crystalline in nature, the non-uniform distribution of stabilisers which leads to an increase in their concentration in the amorphous region is highly beneficial because this region is most sensitive to degradation.

However, high migration rates and low solubility of the stabiliser in the polymer leads to physical loss by exudation of the stabiliser to the surface (i.e blooming) Conversely, when the migration rates are too low and become rate controlling, the effectiveness of the stabiliser may be limited by diffusion (5b).

Polyolefins are being increasingly used in environments which are hostile to their long-term durability. High temperatures lead to loss of many antioxidants from the polymer and consequently, volatility factors then dominate antioxidant performance and this has been reported (4b) to account in part for the effectiveness of the high molecular mass phenolic antioxidants (e.g. XV and XVI) as thermal stabilisers for polyolefins. Furthermore, the poor U.V. stabilising performance of the low molecular mass phenols has been attributed not only to the formation of sensitising products, but also to the rapid physical loss of the antioxidant from the polymer (5b,6). In the recent past, however, molecularly dispersed polymer— bound antioxidants which cannot be physically lost from the substrate have been shown(4b,5b) to be resistant to physical loss by either volatility or leaching when in aggressive media such as lubricating oils, dry cleaning solvents or detergents.

1.2.6 Scope and Object of the Present Work

Both thermal processing and enviromental exposure result in the formation of hydroperoxides which are in turn the precursors of macro — carbonyl compounds. Since hydroperoxides are the most important source of initiatiating radicals during autoxidation, its decomposition to non-active products is therefore essential in the stabilisation process.

The ability to destroy hydroperoxides catalytically is a general feature of sulphur antioxidants and it has been shown(4,5,25,40) that these compounds are converted by oxidation to the sulphur acids which are more effective than their precursors.

The object of the present work was primarily to investigate the effect of processing on sulphur antioxidants in polyolefins, with particular reference to nickel dialkyldithiophosphates and their corresponding disulphides. Since these compounds are partially converted to oxidation products at elevated temperatures, it is therefore, of both theoretical and practical interest to evaluate their effectiveness in the polymer under various processing conditions. Processing of the polymer (PP and PE) in the presence of the sulphur compounds will be carried out not only under conditions of restricted oxygen (closed mixer), but also in the presence of excess oxygen (open mixer), although the effects of controlled oxidative processing of the additive in the presence of a hydroperoxide will also be assessed. Furthermore, the effectiveness of dithiophosphates as antioxidants in polyolefins will be evaluated both at normal (low) concentration levels and as concentrates which will subsequently be diluted to normal concentration levels in fresh unstabilised polymer.

The melt, thermal and U.V.-stability of the stabilised polymer samples will be assessed and compared with the best available commercial heat and light stabilising systems. Moreover, synergistic combinations of the dithiophosphates with existing U.V. stabilisers will be examined and their stability optimised. The possibility of mechano chemical binding of the antioxidant species to the polymer chain will be examined by extracting the processed samples and comparing their performance before and after extraction. The solvent extracts will also be analysed by techaniques such as IR, U.V. and ^{31}P NMR.

On the basis of the results obtained in the polymer, analogous mechanistic studies on the dithiophosphates will be carried out in oxidisable and non-oxidisable substrates under similar conditions, with the aim of identifying the major oxidation products which may be responsible for their antioxidant activity. In this instance, product analysis will be carried out by the use of analytical techniques such as IR, U.V. HPLC and ^{31}P NMR.

CHAPTER TWO

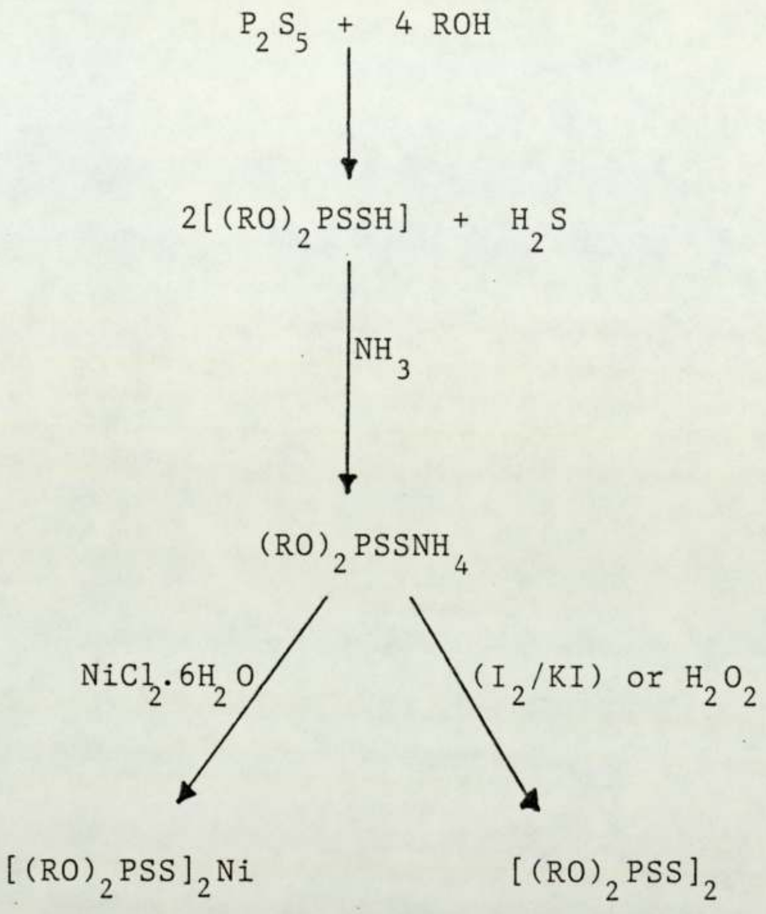
GENERAL EXPERIMENTAL METHODS

2.1 Synthesis and Characterisation of Additives

Scheme 2.1 outlines the general route used for the preparation of dithiophosphates (nickel complexes and the corresponding disulphides) evaluated as antioxidants for polyolefins (Chapter 3.4).

This section also deals with the synthesis of other phosphorus containing additives such as di-n-butyl thiono phosphoric acid (DnBTA), the triester O,O,S-tri-n-butyl thionophosphate (O,O,S - TBTP), bis-di-n-butyl thiophosphoryl polysulphide (S = 2-4) and finally, a reaction product of bis-n-hexyl thiophosphoryl disulphide (DHDS) and 2,4-di-hydroxy benzophenone (HBP). These compounds were primarily used for confirmation of the identity of observed oxidation products formed both in the polymer after processing and during U.V. exposure (Chapter 4) and also during model compound studies in organic substrates (Chapter 5), although the sulphur acid (DnBTA) was also evaluated as a potential antioxidant for polyolefins.

Scheme 2.1 Preparation of dithiophosphates(48-51)



The O,O-dialkyl dithiophosphoric acids and their ammonium salts were prepared according to the method of Wystrach et al(48). The appropriate nickel salts were prepared by metathetical exchange reactions from the ammonium salts using nickel chloride(49) while the corresponding disulphides were prepared by oxidation of the ammonium salts with an aqueous solution of iodine-potassium iodide(50). While technical grade solvents were used for all syntheses and were distilled when required for recrystallisation, analar and spectroscopic grades were used for all operations involving spectral studies of additive solutions.

2.1.1 Di-n-butyl dithiophosphoric Acid (DnBDTA)(48)

$$4\ C_4H_9OH + P_2S_5 \longrightarrow 2(C_4H_9O)_2PSSH + H_2S \qquad (2.1)$$

333g (1.5 moles) phosphorus pentasulphide was added in portions to 444g (6 moles) n-butanol over a period of three hours at 80°C under an atmosphere of nitrogen. Heating was continued for a further 30 minutes after which the stirred solution was cooled to 60°C and treated with 20g charcoal to remove some black-oily contaminant, and then filtered giving 621.4g of a pale green liquid.

Throughout the reaction, the solution was stripped of hydrogen sulphide which was subsequently trapped by passing the nitrogen flow through an aqueous solution of sodium hydroxide.

Analysis (Figure 2.1a)

I.R. Spectrum (CsI liquid film)

1060 - 900cm^{-1}	(very intense)	-(P)-O-C
875 - 730cm^{-1}	(strong)	-P-O-(C)
650cm^{-1}	(strong)	-P=S
580 - 450cm^{-1}	(strong)	-P-S-Sn; P-S-(H)
2600 - 2300cm^{-1}	(strong)	-(P)-S-H

2.1.2 Ammonium Salt(48)

$$(n\text{-}C_4H_9)_2PSSH + NH_3 \longrightarrow (n\text{-}C_4H_9O)_2PSS^- \ NH_4^+ \qquad (2.2)$$

269g (1 mole) of the crude acid (as prepared above) was dissolved in 500 ml hexane and treated with excess ammonium gas bubbled under the surface of the stirred solution. The solid product was isolated and washed with hexane giving 178g (66.2% yield) white powder which was recrystallised from toluene to give 160g white platelets Figure 2.1b shows the infra-red spectrum of the ammonium salt.

I.R. Spectrum (KBr disc.)

3300 - 3060cm^{-1}	$-NH_4^+$
1070 - 900cm^{-1}	-(P)-O-C
890 - 730cm^{-1}	-P-O-(C)
720 - 600cm^{-1}	-P=S
560cm^{-1}	$-PSS^-$

2.1.3 Di-n-butyl thiophosphoryl disulphide (DnBDS)(50-52)

$$2(n\text{-}C_4H_9O)_2PSSNH_4 + I_2 \longrightarrow [(n\text{-}C_4H_9O)_2PSS]_2 + 2NH_4I \qquad (2.3)$$

30g(0.12 moles) recrystallised ammonium di-n-butyldithiophosphate was dissolved in $100cm^3$ distilled water and the solution boiled with charcoal (Darco) and filtered, in order to remove a small amount of a black oily impurity that was present.

A solution of 20.3g (0.16 moles) iodine in $200cm^3$ 25% aqueous potassium iodide was added dropwise to a stirred solution of the ammonium salt at room temperature until the iodine colour persisted. The organic layer was extracted with diethyl ether(3 x $30cm^3$) and the extracts were washed with sodium thiosulphate aqueous solution (0.1M) in order to destroy the excess iodine. The resulting dried ($MgSO_4$), filtered solution was stripped under vacuum to leave a yellow viscous liquid. Successive recrystallisation of the starting material (ammonium salt) resulted in the production of very pure disulphide (see inset to Figure 2.2b and 2.2c).

Analysis (Figure 2.2a-c)

(a) I.R. Spectrum (CsI) liquid film)

$1060 - 900cm^{-1}$	-(P)-O-C
$875 - 730cm^{-1}$	-P-O-(C)
$650cm^{-1}$	-P=S
$580 - 450cm^{-1}$	$-P-S-S_n-$ (n=2-4)

(b) ^{31}P NMR Spectrum (solution in chloroform)

Chemical Shift (ppm)

85.1	$[(n\text{-}C_4H_9O)_2PSS]_2$
79.2	$[(n\text{-}C_4H_9O)_2PS]_2S$ - slight impurity

(c) HPLC Spectrum (neat)

Retention time (mins.)

19.04	$[(n\text{-}C_4H_9O)_2PSS]_2$
16.50	$[(n\text{-}C_4H_9O)_2PS]_2S$ - impurity

The disulphide sample prepared by H_2O_2 method was used as supplied by Synthetic Chemicals Ltd(54) and this material was found to be generally less pure than that prepared by I_2/KI) method as described above. The effect of purity of the disulphide on the antioxidant activity is discussed in great detail in Chapter 4.

2.1.4 Nickel bis-di-butyl dithiophosphate (NiDnBP)

$$2\ (n\text{-}C_4H_9O)_2PSSNH_4 + NiCl_2.6H_2O \longrightarrow [(n\text{-}C_4H_9O)_2PSS]_2Ni + 2NH_4Cl \qquad (2.4)$$

This material was prepared by a modified version of the procedure described by Chamberlain and Drago(49). 30g (0.11 moles) recrystallised ammonium di-n-butyl dithiophosphate was dissolved in 100 cm^3 distilled water and the solultion boiled with charcoal in order to remove a small amount of black oily contamitant.

An aqueous solution of nickel (II) chloride hexahydrate (30g, 0.13 mol) was added dropwise to a stirred solution of the ammonium salt at room temperature, until the mixture turned purple. The organic layer was extracted with diethyl ether (2 x $30cm^3$) and the solvent removed under vacuum, leaving 22g of the crude purple liquid (m.pt. 16°C)

Analysis (Figures 2.3a-c)

(a) I.R. Spectrum (KBr thin film)

Characteristic I.R. bands include those at:-

$1060 - 900cm^{-1}$	-(P)-O-C
$875 - 730cm^{-1}$	-P-O-(C)
$660cm^{-1}$(D)	-P=S
$560cm^{-1}$	-P-S-Ni
$350cm^{-1}$	-Ni-S

(b) ^{31}P NMR Spectrum (solution in chloroform)

Only one peak, having a chemical shift of 94 ppm, was observed.

(c) U.V. Spectrum (solution in hexane)

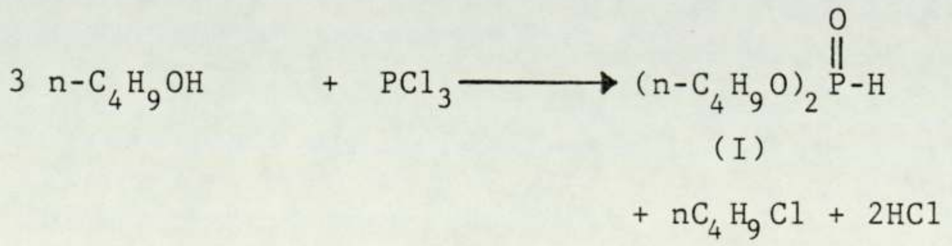
One major absorbance with maximum at 316 nm was observed in addition to two other minor bands of lower extinction coefficient at 225 nm and 280 nm.

The lower and higher alkyl homologues (R = C_2, C_6 and C_8) of the materials described above were prepared in a similar manner.

2.1.5 Di-n-butyl thiophosphoric Acid (DnBTA)

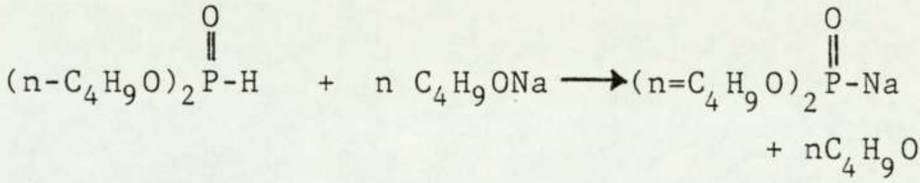
The preparation of this material was patterned after that described by Foss(53), and involves three distinct stages as shown by the following equations.

(a)



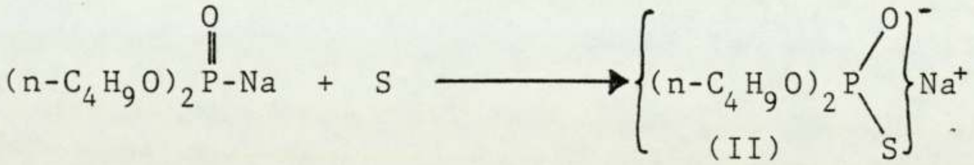
$$3\ n\text{-}C_4H_9OH + PCl_3 \longrightarrow \underset{(I)}{(n\text{-}C_4H_9O)_2\overset{\overset{O}{\|}}{P}\text{-}H} + nC_4H_9Cl + 2HCl \qquad (2.5)$$

(b)



$$(n\text{-}C_4H_9O)_2\overset{O}{\overset{\|}{P}}\text{-}H + n\ C_4H_9ONa \rightarrow (n{=}C_4H_9O)_2\overset{O}{\overset{\|}{P}}\text{-}Na + nC_4H_9OH$$

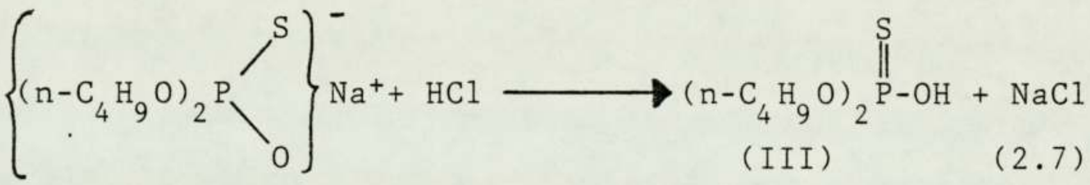
(2.6a)



(II)

(2.6b)

(C)



(III)

(2.7)

2.1.5a Preparation of Di-n-butyl hydrogen phosphite (I)

41.3g (0.3 moles) phosphorus trichloride in 50cm^3 chloroform was added dropwise to 66.6g (0.9 moles) n-butanol in 75cm^3 chloroform over a period of 60 minutes. The mixture was refluxed (80°C) for 30 minutes and then cooled for a further 60 minutes under nitrogen. The solvent was stripped off under vacuum, followed by vacuum distillation of the residue to give 46g of a colourless liquid, b.pt. 78-82°C (5mm Hg). Characteristic infra-red bands include those at 2420(w) (-P-H), 1255(S) (-P=O) and 975(S) (-P-O-C) cm^{-1}(Figure 2.4a).

2.1.5b Preparation of Sodium di-n-butyl thiophosphate(II)

4.6g (0.20 moles) sodium was added to 100cm^3 n-butanol and the resultant solution added to 39g (0.201 moles) of the hydrogen phosphite as prepared above (Section 2.1.5a). 100cm^3 diethyl ether was added to the resulting solution, followed by the addition, in portions, of 6.4g (0.2moles) sulphur. The thio-salt crystallised on cooling and was then filtered. The filtrate was stripped under reduced pressure until almost dry, leaving a wet solid which was washed with 40/60 petroleum ether and allowed to dry under vacuum.

2.1.5c Acidification of Sodium di-n-butyl thiophosphate

The white solid obtained (Section 2.1.5b) was dissolved in water, and dilute hydrochloric acid (2 M) was added. The oily layer which seperated out on shaking was washed several times with water, dried over magnesium sulphate and filtered to give a pale yellow liquid (Figure 2.4b-d)

Analysis

(a) IR Spectrum (liquid film)

1060 - 900cm^{-1}	-(P)-O-C
870 - 730cm^{-1}	-P-O-(C)
660cm^{-1}	-P=S

3700 - 3000cm^{-1}	-P-OH
2400 - 2100cm^{-1}(w)	-P-SH

(b) ^{31}P NMR Spectrum (solution in chloroform)

Only one peak, having a chemical shift of 63 ppm, was observed.

(c) HPLC Spectrum (neat)

Only one peak, having a retention time of 7.6 minutes, was observed.

2.1.6 Attempted(54) Preparation of Bis(di-n-butyl thiophosphoryl) tetrasulphide (DnBTe)

52g (0.2 moles) ammonium di-n-butyl dithiophosphate was dissolved in 150mls distilled water to which 5mls ammonia solution (SG. 0.880) was added. 13.5g (0.1 mole) sulphur monochloride was added dropwise over 60 minutes at 25°C.

The organic layer which seperated out was extracted with dichloromethane (3 x 100 cm^3). The combined extracts was washed several times with water, dried over sodium sulphate and stripped of the solvent (under vacuum) to give 46.0g of a red oil. Analysis (Figure 2.5a-b) indicates that the major component of the product is the tetrasulphide (DnBTe) with a significant quantity of the disulphide (DnBDS) and some trisulphide (DnBtr).

Analysis

(a) IR Spectrum (KBr liquid film)

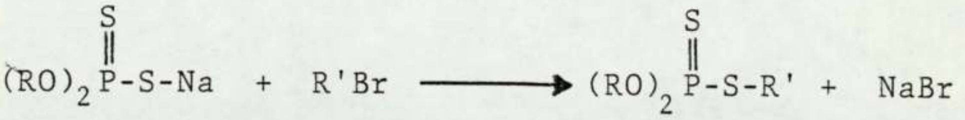
The infra-red spectrum (Figure 2.5a) of the sample is very identical to that of the disulphide (Figure 2.2a) except for absorption in the lower frequency region of 580 - 450 cm^{-1} attributed to the P-S-S linkages$^{(82)}$. The IR spectrum of this sample shows two distinct absorption bands at 530(S) (-P-S_2/ -P-S_4) and 470(S) (-P-S_3) cm^{-1}

(b) ^{31}P NMR Spectrum (solution in carbon tetrachloride)

Chemical shift(ppm)	Component	% Yield
85.0	$[(n\text{-}C_4H_9O)_2PSS]_2$	24.2
84.1	$[(n\text{-}C_4H_9O)_2PSS]_2S_2$	58.5
83.8	$[(n\text{-}C_4H_9O)_2PSS]_2S$	14.2

Figure 2.5b

2.1.7 Preparation of O,S,S-tri-n-butyl thionophosphate (O,O,S-TBTP)



$$(RO)_2\overset{\overset{\displaystyle S}{\|}}{P}\text{-S-Na} + R'Br \longrightarrow (RO)_2\overset{\overset{\displaystyle S}{\|}}{P}\text{-S-}R' + NaBr \qquad (2.8)$$

This material was prepared by the alkylation of sodium dialkyl dithiophosphate with an alkyl bromide(55a,55b).

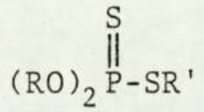
Sodium di-n-butyl dithiophosphate (20g, 0.075 mol) was dissolved in 150ml ethanol. The solution was heated to reflux and 8g(0.058) of 1-bromo-butane was added dropwise over a period of 30 minutes. The mixture was then refluxed for a further seven hours before being cooled, and the sodium bromide removed by filtration. The solvent was stripped off under vacuum at room temperature to give 12.5g of light brown oily liquid.

Analysis (Figure 2.6a-b)

(a) IR Spectrum (liquid film)

1030 - 900cm^{-1}	-(P)-O-C
875 - 730cm^{-1}	-P-O-(C)
660cm^{-1}	-P=S
600 - 500cm^{-1}	-P-S-C

(b) ^{31}P NMR Spectrum (solution in CCl_4)

Chemical shift (ppm)	Component
96.9	 $(RO)_2\overset{\overset{S}{\|}}{P}\text{-}SR'$
96.4	
95.5	

The multiplicity of the ^{31}P NMR peaks (Figure 2.6b) may be due to isomerisation of the alkyl group in the molecule.

2.1.8 Product of Reaction between Bis-(di-n-hexyl thiophosphoryl) disulphide (DHDS) and 2,4-dihydroxy benzophenone (HBP)(54)

A mixture of DHDS (14.9g, 0.025 moles) and HBP (21.4g, 0.1 mole) in 100ml Shellsol AB was heated under reflux to 180°C ± 5°C over a period of two hours under a steady stream of air. The product (deep red) was extracted with petroleum ether and the solvent decanted. The product residue was repeatedly washed with further petroleum ether, filtered, and dried over magnesium sulphate.

The U.V. analysis of this product in toluene (Figure 2.7) showed three distinct absorption bands with maxima at 283, 325 and 400 nm.

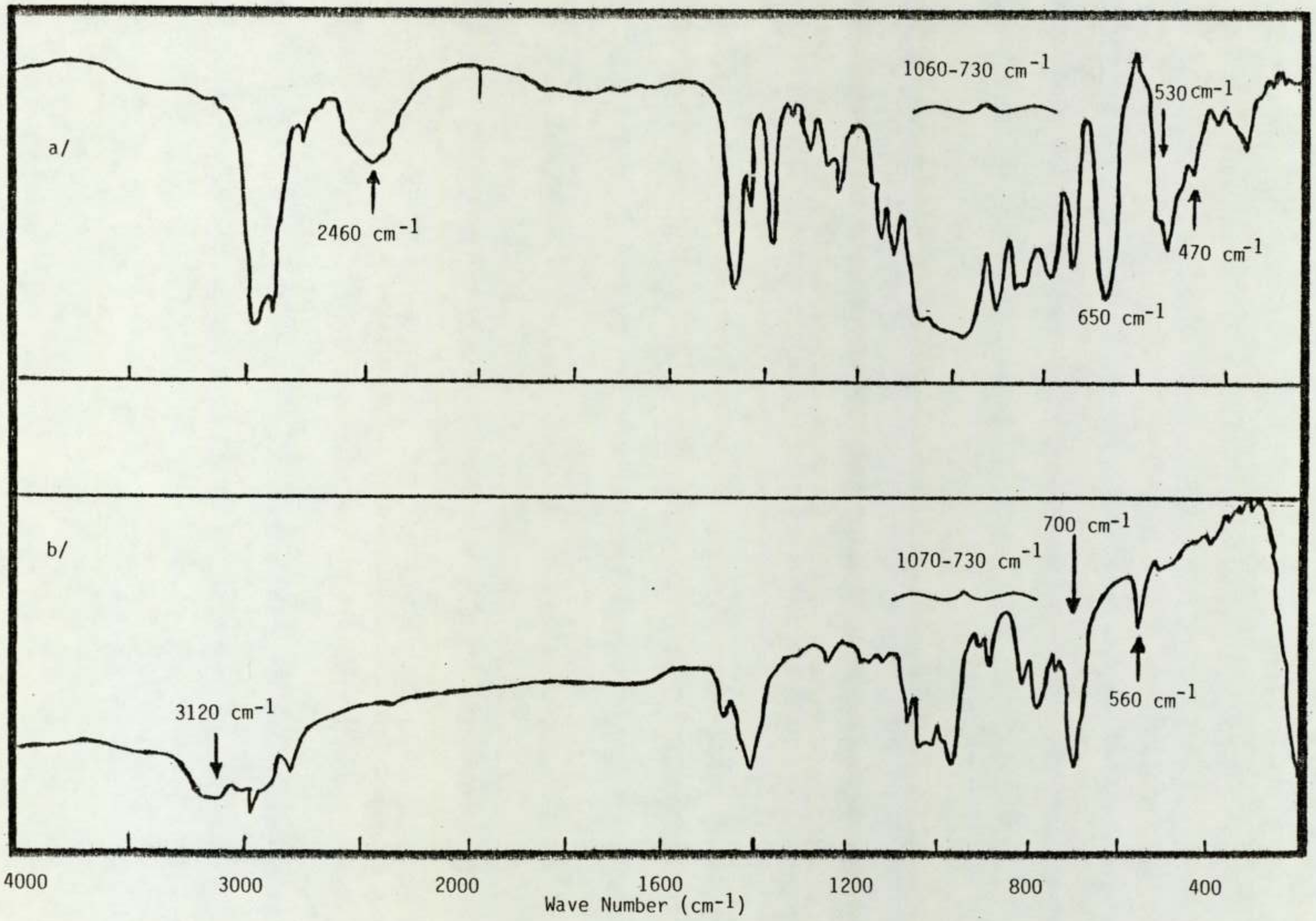


Figure 2.1 Infra-red spectra of (a) Di-n-butyl dithiophosphoric acid (DnBTA) and (b) Ammonium di-n-butyl dithiophosphate

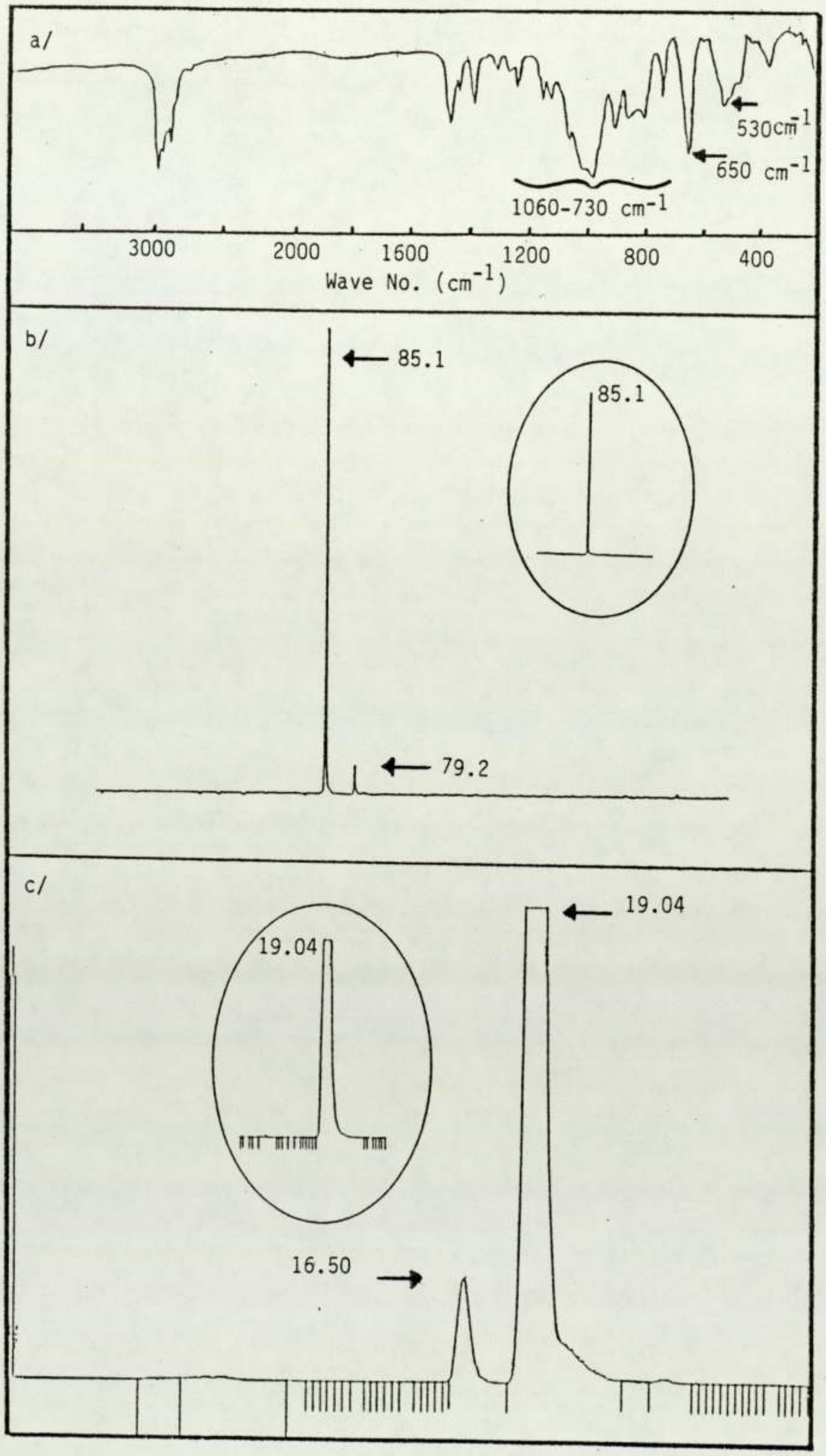


Figure 2.2 IR(a), ^{31}P NMR(b), and HPLC(c) spectra of bis-(di-n-butyl thiophosphoryl) disulphides(DnBDS)

Numbers on ^{31}P NMR spectrum (b) refer to the chemical shifts in ppm, while those on the HPLC spectrum (c) are the retention times in minutes. Inset in Figure 2.2b and 2.2c are the spectra of the pure sample.

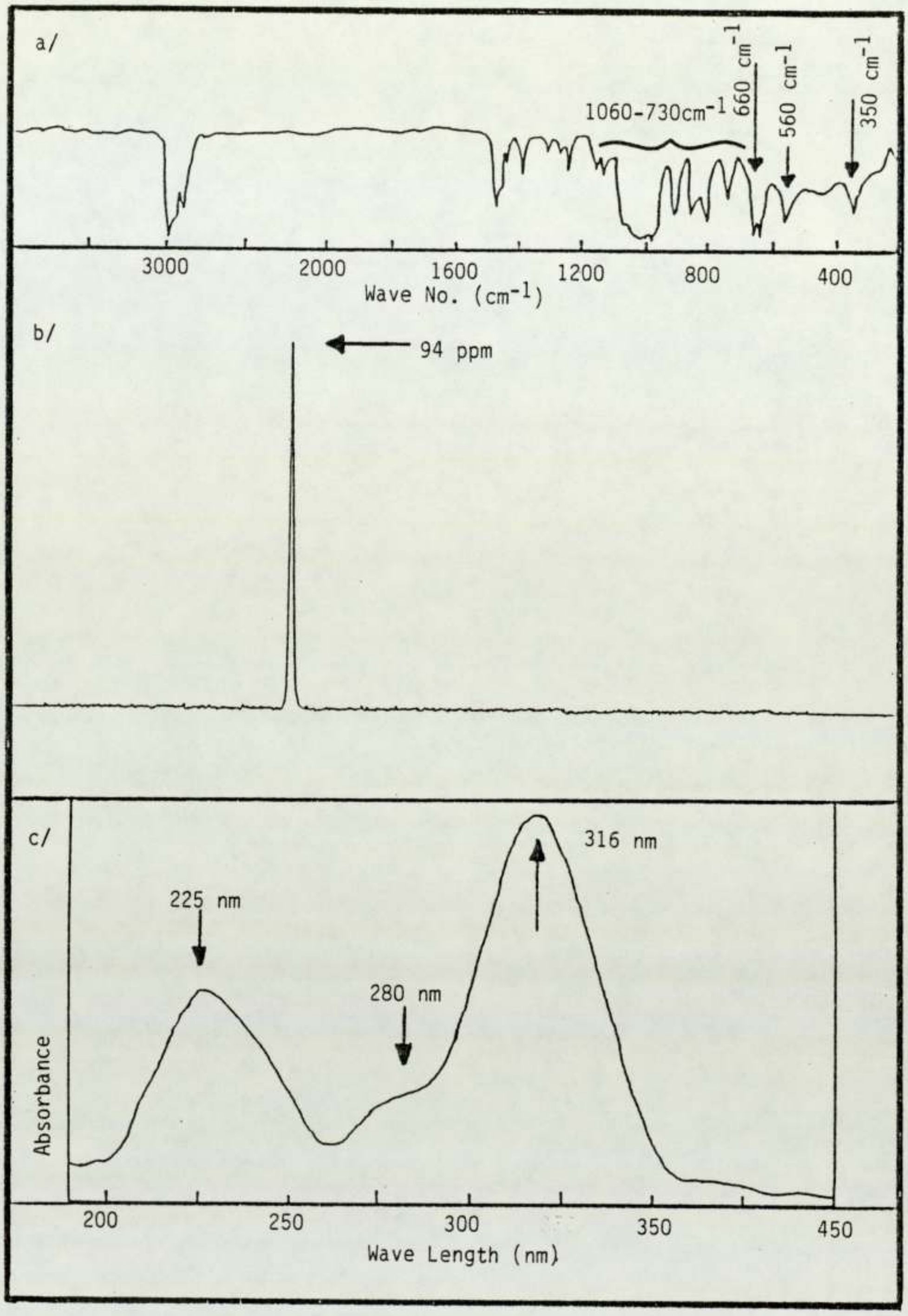


Figure 2.3 IR (a), ^{31}P NMR (b) and UV (c) spectra of Nickel bis(di-n-butyl dithiophosphate) (NiDnBP).

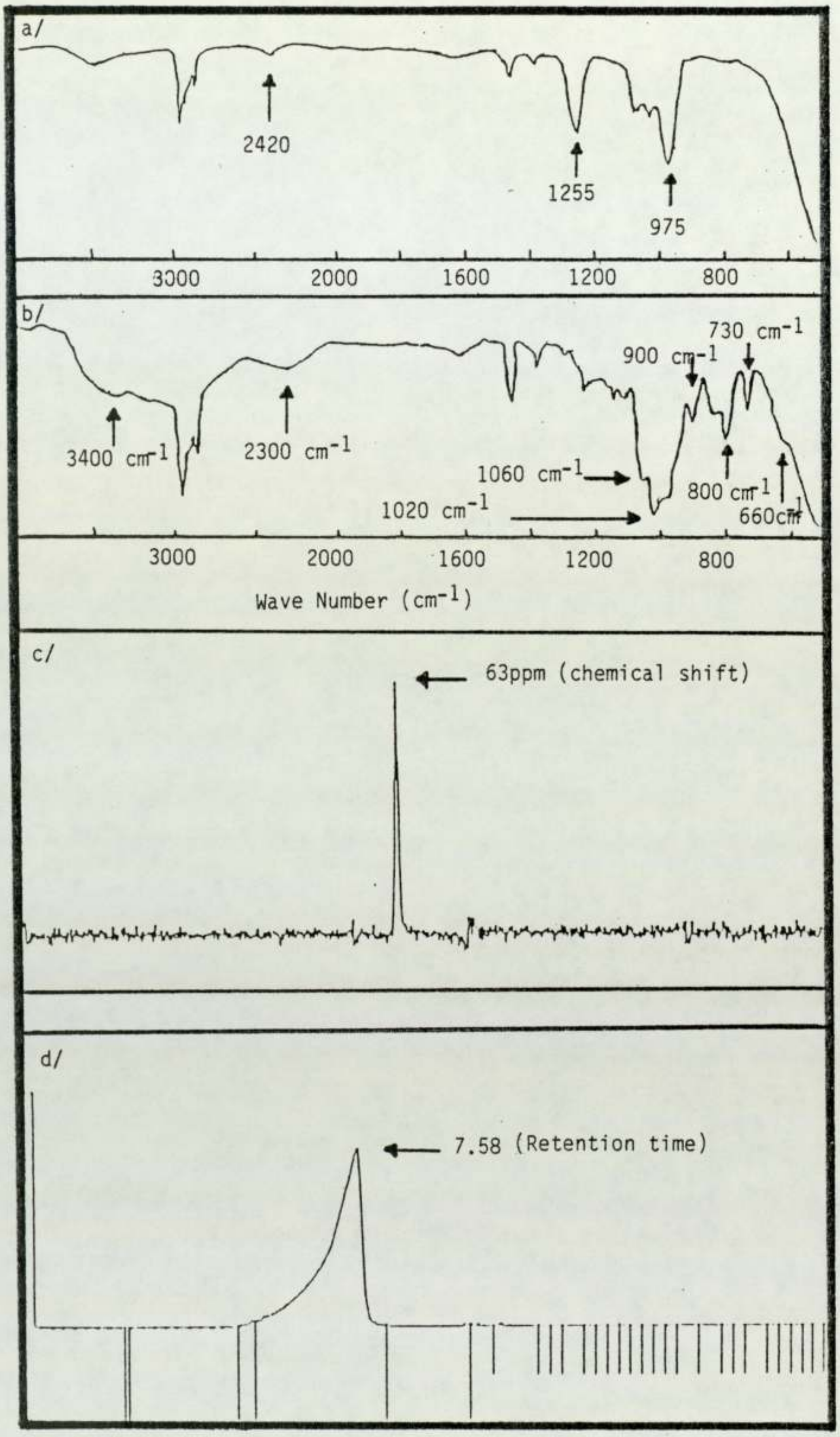


Figure 2.4 IR spectrum of di-n-butyl hydrogen phosphite(a); IR(b), ^{31}P NMR (c) and HPLC (d) spectra of di-n-butyl thionophosphoric acid (DnBTA).

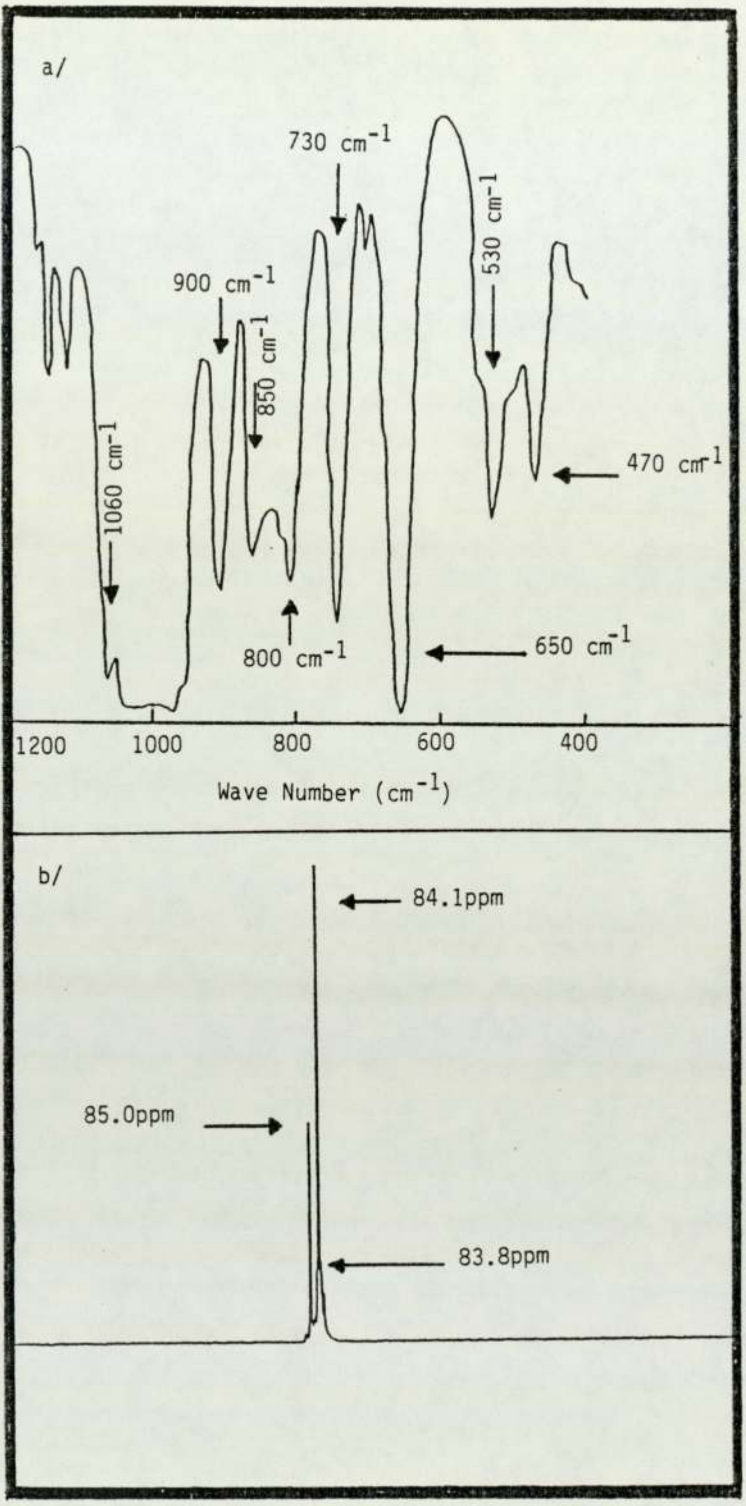


Figure 2.5 IR (a) and ^{31}P NMR (b) spectra of a mixture of bis-(di-n-butyl thiophosphoryl) polysulphides.

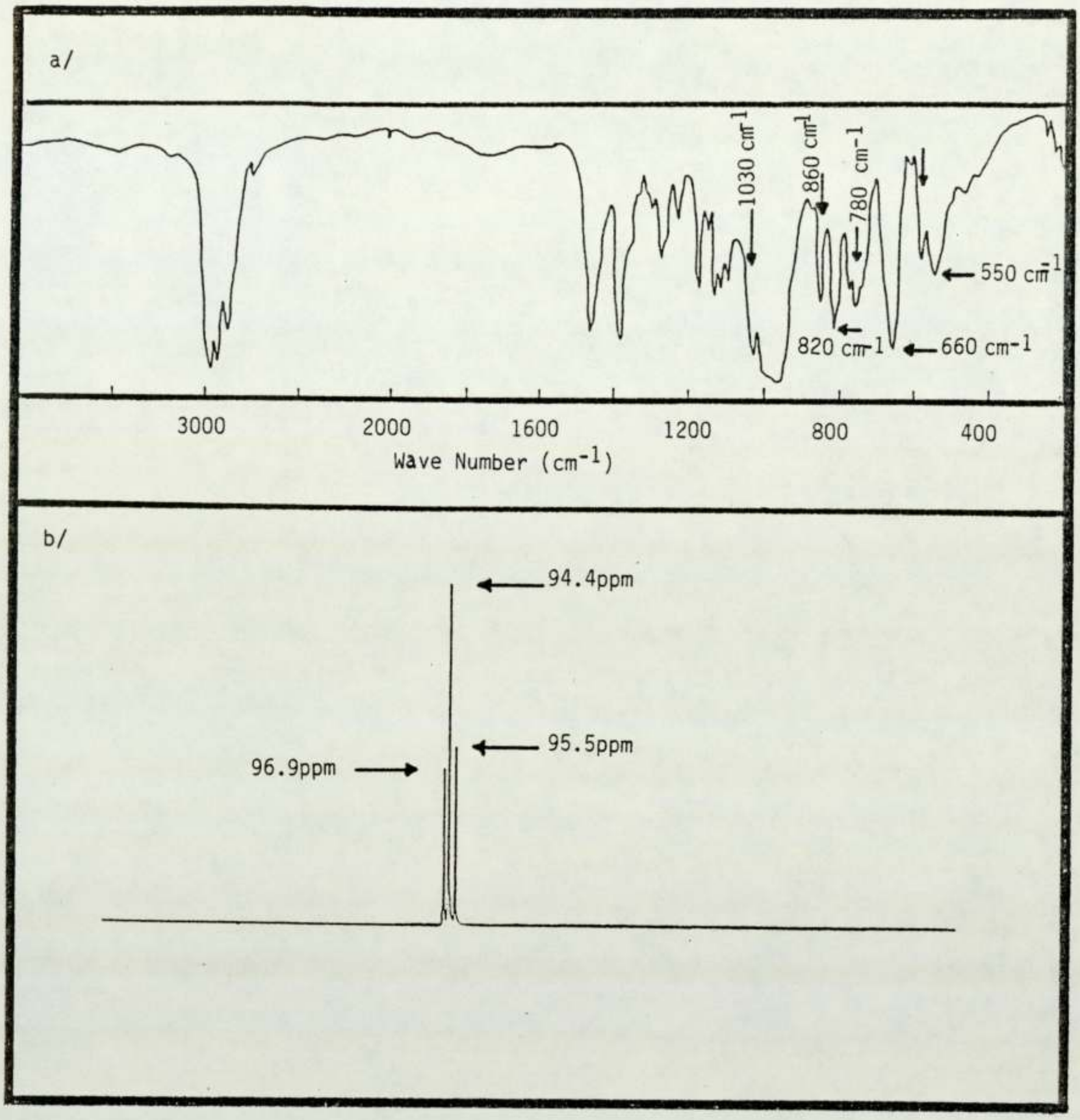


Figure 2.6 IR (a) and ^{31}P NMR (b) spectra of O,O,S-tri-n-butyl thionophosphate (O,O,S-TBTP)

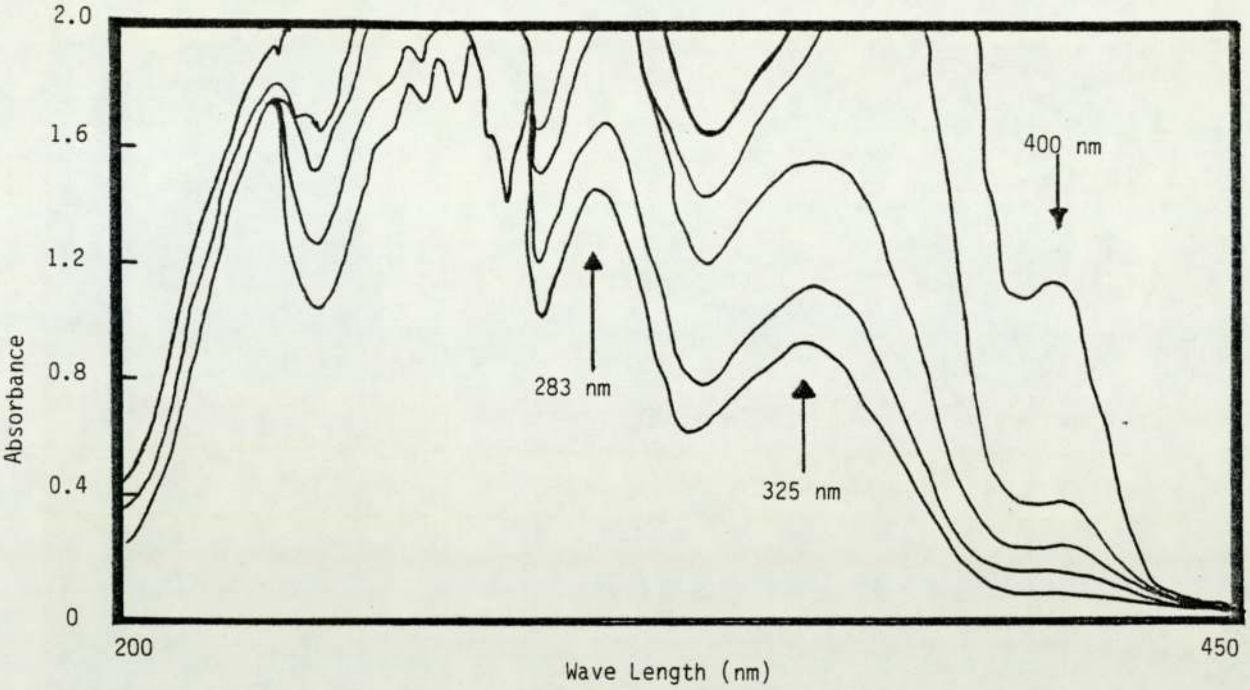


Figure 2.7 UV spectrum of product of the reaction between bis-(di-n-hexyl thiophosphoryl) disulphides (DHDS) and 2,4.dihydroxy benzophenone (HBP) in toluene at different concentrations.

2.2 General Processing Techniques

2.2.1 Polymer Materials

The polymers used were:

(1) Unstabilised polypropylene in powder form identified as "Propathene" HF-22, supplied by Imperial Chemical Industries (ICI), Plastics Division Limited.

(2) Untablised low density polyethylene (LDPE) in powder form (for compressing-moulded films) identified as "alkathene" polyethylene and supplied by Imperial Chemical Industries (ICI) Limited.

(3) BP low density polyethylene in granular form, identified as DYNH-3 natural, was used for film blowing (flat tubular films) operations. The polymer had a nominal density of $0.916 g/cm^3$ and a melt flow rate of 2.0

(4) Ethylene propylene diene polymer (EPDM) identified as VISTALON 6505; ENB-9%, supplied by Esso Chemical Limited.

(5) Purging material:- High impact polystyrene.

2.2.2 Processing Equipment

2.2.2.1 RAPRA Torque Rheometer (56a-b)

Most samples were processed in a RAPRA torque rheometer which is essentially a small mixing chamber containing two mixing screws contra-rotating at different speeds. A continuous readout is provided for both melt temperature and the torque required for mixing. The chamber may be operated either open to the atmosphere or sealed by a pneumatic ram. A full charge consists of 35g of polymer when the chamber is sealed (close mixer), but when it is desired to process in the presence of oxygen, a charge of 20g is employed and the chamber left open to atmosphere.

2.2.2.2 Francis Shaw P1½" Extruder

This equipment was used in the extrusion processes for melt flow measurements and also for the preparation of plaques used in subsequent thermal ageing and U.V. irradiation tests. The Shaw laboratory extruder is fitted with a 38 mm dia. screw of 18:1 L/D ratio and the die size was 5 mm in diameter. The production line consists of the extruder, a 150cm long water bath, and an Iddon sheet take off rolls. A set of rollers fitted to the bath is designed to keep the extrudate below the surface before take off. In order to maintain a constant temperature in the bath, the water is continuously replenished by means of a series of in and out pipes connected to the mains and drains respectively.

2.2.2.3 Humboldt HE 45 Extruder

The Humboldt extruder was employed for the production of flat tubular films of LDPE. The extruder is fitted with a 45 mm dia. screw of 20:1 L/D ratio and a 7.6 mm diameter die. This is connected to a Barand tubular film blowing equipment which comprises a tubular film die-head, cooling/blower accessory, and haul-off towers with take off rolls of infinitely variable speed. The film thickness is usually controlled by the die geometry and the temperature distribution over the die area. However once an extrusion line is running satisfactorily, it forms a very stable system such that ultimate thickness of the films can only then be controlled by making adjustments to the blow ratio and haul-off speed.

2.2.2.4 Edgwick Screw Injection Moulding Machine

The preparation of plaques was also accomplished using the Edgwick 1214-Hy type screw injection moulding machine fitted with a a 41 mm diameter screw, which provides a maximum shot volume of 15.2 cm^3. The cylinder barrel and nozzle are heated by resistance type heaters which are individually controlled by thermostats, plasticisation and injection being performed in two stages. The injection moulding conditions are given in Section 2.3.2.2.

2.3 Procesing Procedures

In general, stage one processing for most samples was carried out in the torque rheometer, and of particular importance is the preparation of masterbatches (concentrates) some of which were also diluted using the same equipment. During processing, the times and particularly temperatures of mixing is usually dependent on the nature of the polymer; typical examples are 180°C for polypropylene and 150°C for pol yethylene. A constant shear rate (rotor speed of 60 RPM) was maintained throughout the processing operation in the torque rheometer.

2.3.1 Additive Concentrate Preparation (Ct)

Since the method by charging the polymer/additive mixture into the torque rheometer is governed by the processing technique to be utilised, these may be summarised as follows.

2.3.1.1 Mild Processing (CM/NS)

The preweighed polymer/additive mixture (35g total) was charged into the mixing chamber and processed for a specified time with the ram down (closed to the atmosphere).

2.3.1.2 Severe Processing (OM)

In this method, the additive was mixed with the polymer (20g total) and processed with the mixer left open to the atmosphere throughout the operation.

2.3.1.3 Controlled Oxidative Processing (COM)

The polymer/additive mixture (35g total) was processed in the mixer with the ram down for most of the mixing period, but for a short interval during which time the mixer was opened to the atmosphere
to facilitate the introduction of synergists into the stabilised polymer melt. The ram was then brought down (closed to atmosphere) and the mixing continued for a set period of time.

Another form of controlled oxidative processing involved the use of a radical generator (TBH) as oxidant. This is incorporated into the stabilised polymer melt at some stage during processing, which was carried out under a slow, steady stream of nitrogen.

At the end of processing of each concentrate or sample, the polymer resin was rapidly removed from the mixing chamber and quenched in cold water to prevent further thermal oxidation.

2.3.2 Dilution of Concentrates (DCt.)

The dilution of the concentrates (Ct.) prepared in the torque rheometer with fresh unstabilised polymer was carried out using the various equipments described under Section 2.2, this being dependent on the tests to be carried out.

2.3.2.1 Multiple Extrusions

The dilution of some polypropylene concentrates for the purpose of melt flow determinations, was carried out using the shaw laboratory extruder (see Section 2.2.2.2). During extrusion, the preweighed Ct./polymer mixture in polyethylene bag was hand tumbled until uniform dispersion is attained. The contents of the bag was then charged into the extruder hopper and was stirred during the operation to maintain uniform dispersion of the mixture. Each extrudate on emerging from the die, was passed directly through the water bath in order to avoid possible volatilisation of the additives, and taken off using the Iddon sheet take off rolls. The extrudates were fed (by means of a feed conveyor system) into a "MASKIN AB RAPID" four-blade granulator fitted with a screen containing 8 mm dia. holes and the granules used for re-charging the extruder hopper for the next pass. Samples collected after each pass were then used for the melt flow measurements. The extruder conditions are as follows:

Screw speed - 40 rpm

Extrusion temperature:

	Zone	Set temp.(°C)	Observed temp(°C)
Barrel	1	150	170
	2	170	185
Die head	3	210	225
Die tip	4	210	220

As illustrated above, the temperature was continously monitored during extrusion and was found to show some increase in all zones, when compared to set conditions.

2.3.2.2 Preparation of Plaques

Some polypropylene concentrates were also diluted using the Edgwick screw injection moulding machine (see Section 2.2.2.4) is produce of plaques of size 10cm x 10cm and a nominal thickness of 1.0 mm. During dilution, the hand-tumbled (preweighed) Ct./polymer mixture was hopper-fed directly unto the screw and transferred to the nozzle end of the cylinder through a non-return valve which allows pressure on the polymer resin to be maintained during injection. The injection moulding conditions are given below:-

Injection pressure - 70.4 kg cm^2
Screw speed - 50 rpm
Temperature :- front heater
centre heater 220°C
nozzle heater
mould heater 30°C

The plaques so produced were then subjected to both thermal ageing and U.V.-stability tests using the Fissons environmental cabinet and the U.V.-exposure cabinet respectively.

2.3.2.3 Lay Flat Tube Extrusion (Film Blowing)

The Humboldt extruder described in Section 2.2.2.3 was primarily used for the production of LDPE tubular films of a nominal thickness of approximately 200μm (0.19 mm - 0.24 mm). As with the previous processes, the Hand-tumbled preweighed Ct/polymer mixture or additive/polymer mixture, as the case may be, was hopper-fed into the extruder. During operation, the cylinder of molten polymer on leaving the die was inflated to the required diameter by air pressure. The film was then cooled and collapsed between nip rolls prior to being wound-up.

Extruder conditions

Screw speed - 50 rpm
Take-off roll speed- 2 m min^{-1}

Extrusion temperature:-
Feed hopper zone 1 - 105°C
Barrel zone 2 - 115°C
zone 3 - 120°C
Die middle zone 4 - 120°C
Die tip zone 5 - 120°C

Film areas of uniform thickness were then exposed to U.V.-irradiation, and the growth in carbonyl formation followed using the Perkin-Elmer infra-red spectrophotometer model 599. Changes in the tensile properties of the polymer films during irradiation were also monitored on an Instron Tensile Tester as described in a subsequent section (Section 2.4.3.2)

In addition to the production of flat tubular films, polypropylene and polyethylene films of approximately the same thickness (200 µm) were also compression moulded using a 25 ton press with electrically heated platens. During moulding, the polymer resin (6g - 7g) was wrapped in layers of cellophane sheets and compression moulded using stainless steel glazing plates. At the end of the pressing period, the platens were cooled to approximately

40°C before removal of the films. Sections of uniform thickness were then selected as test films for thermal ageing and U.V.-exposure.

2.3.3. Extraction of Stabilised PP and PE Films

An electrically heater Soxhlet apparatus was used for continuous hot solvent(50°C) extraction of the stabilised polymer films. Samples were mounted on cellulose extraction thimbles and continuously extracted (methanol, hexane) under a steady stream of nitrogen for 24 hours or more, as the case may be, in order to ensure total extraction of unbound additives.

After extraction, the samples were dried under vacuum at 30°C for 24 hours. The solution extracts were then collected in small flasks and stored in the freezer for subsequent analysis.

2.4. Technological Testing Methods

2.4.1 Processing Stability Measurements (MFI)

The Melt Flow Index (MFI), defined as the mass of molten polymer extruded through a standard die in a given time (usually 10 mins.), is a measure of the melt viscosity of the polymer which in turn is related to the molecular weight.

The Davenport Polythene Grader which was employed for this measurement, is designed primarily for the determining the melt viscosity of polyethylene although the melt flow properties of other thermoplastics can also be determined by varying the temperature, die size and load. A strict relationship between the Melt Flow Index and the molecular weight only applies to polymers of the same chemical constitution and is equally restricted to polymers of the same density since this affects melt viscosity(57).

Since thermal oxidation brings about changes in the molecular weight of the polymer by virtue of such rections as chain scission, cross-linking etc., these are expected to be reflected in the melt flow values. The melt stability was measured(58a) at 230°C (for polypropylene) using a 2.095 mm (± 0.005) diameter die and a nominal force of 2.16kg (± 0.01).

An updated version(58b) of this test was also carried out on extruded polypropylene samples in the form of granulates. In common with conventional MFI measurements, the apparatus and test procedures are intended for measuring the fluidity, in arbitrary units, of molten thermoplastics under specified conditions of temperature and applied force. The fluidity determined in accordance with this method is expressed in terms of"melt flow rate" (MFR), as a mass flow in specified period, usually grams per 600 seconds. Given below, are the test conditions used for determining the melt flow rates of some polypropylene samples.

Nominal force - 10.0kg (± 0.04)
Die bore diameter - 2.095mm (± 0.005)
Test temperature - 190°C
Reference time - 600 seconds

The results are expressed as the Melt Flow Rate (MFR) in grams per reference time, by the formula:

$$\mathrm{MFR}\ (T,F) = \frac{S \times m}{t}$$

Where T = test temperature
F = test force (N or kg)
S = reference time (sec.)
m = average mass (in g) of the cut-off
and t = cut-off time interval (in sec.)

2.4.2 Accelerated Thermal Oxidation

Both the Wallace test equipment and the Fisons environmental cabinet were used for the thermal stability of polymer samples.

The Wallace heat ageing oven conforms to the British standards for the thermal testing of polymer films of thickness approximately 200μm. The oven consists of a cast aluminium block containing seven individual cylinderical cells, each of 7.5 cm diameter and 30.5 cm long(83). Air (2.5 cu.ft/hr-corresponding to seven complete changes of air per hour(84)) pre-heated to the appropriate temperature (140°C for PP and 110°C for PE) is forced into the bottom of each cell through a calibrated orifice from a common pre-heat chamber. This ensures even distribution of air through the seven cells and temperature variation in each cell is controlled to within ±1°C. The air is exhausted through the covers at the top of each cell to eliminate feedback contamination. During measurements, tests pieces were suspended from specimen racks within the cells.

Ageing at elavated temperatures for polypropylene plaques of nominal thickness between 0.5 mm - 3.0 mm were carried out in a Fis ons environmental cabinet with air circulation. Temperature of test was 150°C and specimens were simply hung upon open grill shelves. Since ageing at elevated temperatures leads not only to changes in the morphology of the polymer as a result of physical ageing, but also to changes in the chemical composition of the sample, these usually results in development of colour within the sample. In view of this fact, small pieces were taken from thermally aged specimens at time intervals, wrapped immediately in paper and stored in the freezer for subsequent schematic display.

2.4.3 Ultra-violet Exposure

Ultra-violet irradiation of the polymer samples (films and plaques) was carried out in the U.V. exposure cabinet, which comprises of a metal cylinder of about 110 cm in outer diameter, and having a concentric circular rotating sample drum whose circumference is 15cm from the periphery of the metal cylinder. 28 fluorescent tube lamps (20 **W** each) are mounted in a cylindrical array on the inside of the cabinet to provide radiation source. These consists of 21 lamps type C (Phillips Actinic Blue 05) and seven lamps type A1 (Westinghouse Sunlamps F/S20). The lamps are thus, symmetrically arranged to give a combination of one lamp type A1 for every three lamps type C, and during operation, the light beam from the radiation source is perpendicularly incident on samples mounted on the rotating drum. The combined distribution spectra of both types of lamps has shown(59) that the maximum in the relative intensity occurs within the range 280 - 370 nm. Exposure times are indicated on a counter clock while temperature inside the cabinet is usually maintained at about 30°C since the entire upper and lower sides (of the cabinet) is open to the atmosphere.

In order to maintain long-term uniform spectral distribution inside the cabinet, the lamps are replaced sequentially every 200 hours of operation in addition to periodical radiation output measurements as described below.

2.4.3.1 Measurement of Radiation Output in U.V.-Cabinet

The radiation output in the U.V. exposure cabinet was monitored sequentially every six months in order to maintain long term uniform spectral distribution inside the cabinet, and also to detect positional variations in output.

This measurement is based on the use of polysulphone films as dosimeters. The principle in this method is to relate the degree of deterioration of the films, usually in terms of changes in their spectroscopic properties, to the incident radiation dose(60a,60b). The suitability of polysulphone as U.V. monitors is a direct consequence of their photosensitivity below 320 nm, and this in turn is due to the high aromatic content of the material which results in optical density increases on exposure to U.V. radiation. The increase in U.V. absorbance at 330 nm of polysulphone film resulting from exposure to a U.V.source can then be expressed in terms of an equivalent dose of 305 nm monochromatic radiation necessary to produce the same increase in absorbance(60a,60b)

2.4.3.1.1 Procedure

(a) Preparation of film

The U.V.-monitoring technique was carried out with polysulphone granules manufactured by Union Carbide. The film was prepared by casting a 15% chloroform solution of the polymer (15g/100ml) between two flat glass plates with an appropriate former (of cellophane sheet) designed to produce a dry film 35-40 microns thick. The film was removed from the plates, dried overnight in a vacuum oven at 60°C and stored in the dark (freezer) before use.

(b) Exposure of film in U.V. cabinet

Samples (usually in triplicates) taken from the cast polysulphone film were arranged in a half frame film mount, and the initial U.V. absorbance at 330 nm (A_{330}) measured with reference to air on a Beckman Du-7 U.V.-visible computing spectrophotometer.

Films with initial A_{330} in the range 0.15 - 0.25 were then irradiated in the U.V. cabinet for 20 minutes and the A_{330} remeasured on the U.V. spectrophotometer. The exposure period chosen was such that increase in the U.V. absorbance of the films (A_{330}) is within the range 0.1 - 0.3 in accordance with ISO standard$^{(60b)}$.

(c) Calculation of intensity

An appropriate conversion table(60a,60b) was then used to convert the observed A_{330} of each film to the equivalent dose of 305 nm radiation (d). The average value of this dose (d) was determined for the set of films, and the corresponding mean intensity (I) in Whm^{-2} calculated using the following equation:

$$I = 60\,d/t$$

where I = Radiation output (intensity)
d = Equivalent dose of 305 nm radiation for A_{330}
t = Exposure time.

Figure 2.8a shows the sensitivity of a polysulphone film to wavelengths below 400 nm while Table 2.1 and Figure 2.8b depict the vertical distribution of radiation (Relative % U.V.) as is generally obtained in the U.V. cabinet.

It is seen (Figure 2.8b) that the fall off in intensity was more noticeable in the lower half of the rotating drum. For this reason, it was deemed necessary to rotate test specimens on a regular basis between the upper, middle and lower positions on the rotating drum in order to even out the total doses of the incident radiation.

Table 2.1 Effect of specimen position on incident U.V in U.V.-exposure cabinet (20 min. exposure)

Speciman Position(cm)	UV-output(Whm^{-2})	Relative UV (%)
23 above centre	3.9	71
15 above centre	4.8	87
7.5 above centre	5.3	96.5
0 (centre)	5.5	100
7.5 below centre	5.2	94.5
15 below centre	4.4	80
23 below centre	3.3	60
Mean Value	4.6	

Furthermore, it has been reported(60a) that intensities of the order of 4 Whm^{-2} have been measured outdoors with polysulphone when the sun is directly overhead and under clear sky conditions. Thus, the mean U.V. output (4.6 Whm^{-2}), as determined periodically (subject to sequential replacement of fluorescent tube lamps) is therefore close to the limiting outdoor value.

The stability of PP and PE films exposed to U.V.-irradiation in the U.V.-exposure cabinet was determined by monitoring the formation and growth of carbonyl species at time intervals, using the Perkin Elmer Infra-red Spectrophotometer Model 599. Changes in the tensile properties of the film samples under irradiation were also monitored on an Instron Tensile Tester. Crazing of exposed PP plaques on the other hand, was assessed with the aid of an optical microscope and complete crazing was taken to be when the surface crazes caused the sample to be non-transparent,colour permiting.

2.4.3.2 Tensile Measurements

Tensile force/extension measurements made at room temperature, provide a simple, reliable and descriptive method of monitoring the effects of ageing on properties. The changes in tensile properties caused by U.V.-irradiation were folowed using the Instron Tensile Tester (Model TMSM). Specimens were loaded at a constant rate of cross-head movement (5cm min^{-1}) and the usual force / elongation curves were produced by the chart recorder using a similar rate (5 cm min^{-1}). From the stress/strain curves obtained, parameters such as ultimate tensile strength and elongation at break were calculated thus(76)

$$\text{Ultimate tensile strength (UTS)} = \frac{\text{Force at break}}{\text{Cross-sectional area}}$$

$$\text{\% Elongation at break (\% EAB)} = \frac{\text{Chart length x crosshead speed}}{\text{Chart speed x gauge length}} \times 100$$

Sample Dimensions

Length	-	5.0 cm
Width	-	0.35cm
Thickness	-	variable (0.019 - 0.024 cm)
Gauge length	-	3.0 cm
Temperature of rest	-	21 ± 1°C

2.4.3.3 Flexural Test

This is essentially a destructive test method. Embrittle-ment Times (EMT) were estimated for U.V.-exposed films by noting the time required for the film to break when flexed manually through 180°C. This test can serve as a guide to the durability of the films, and the reproducibility of the results was found to be acceptable. Samples were tested in duplicates and the variation from the mean value was found to be of the order of ±5%.

2.5 Analytical Techniques

2.5.1 Infra-red Spectroscopy (IR)

The infra-red spectra of polymer films were recorded on a Perkin Elmer Infra-red Spectrophotometer Model 599. This method has been widely used to determine the nature of oxidation products and the rate of formation of these products during thermal and photo-oxidation. It is a non-destructive test which is particularly useful for quantitative purposes since the same test sample can be used repeatedly(77). Since thermal and photo-oxidation of polymers results in the build up of several oxidation products (such as hydroxyl, carbonyl, carboxyl, vinyl etc.), the formation and growth of these functional groups as irradiation proceeds, have been followed by observing the changes in the characteristic absorption bands which are assigned accordingly.

The base line technique was used to calculate the optical density or absorbance due to the various functional groups(77,78). As illustrated in Figure 2.9a, this is accomplished by drawing a straight line (base line) tangential to the adjacent absorption maxima or shoulders, then erecting a perpendicular through the analytical wavelength until it intersects the base line. The absorbance values were calculated using the Lambert-Beer equation:

$$A = \log I_o / I$$

where A = Absorbance

I_o = Intensity of incident radiation (point A)

I = Intensity of transmitted radiation (point B)

To minimise errors due to variation in film thickness as well as errors due to the instrument, an internal standard, a characteristic absorption band of the polymer was used (2720 cm^{-1} for PP and 1895 cm^{-1} for PE) for all index calculations. This (index) is defined as the ratio of the absorbance of the functional group peak to that of the reference peak, as illustrated below for the carbonyl index in PP.

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

2.5.1.1 Estimation of Binding Efficiency

The binding efficiency of dithiophosphoryl concentrates in PP and PE after exhaustive extraction (hexane, methanol) extraction of the polymer films was also estimated using the infra-red spectrophotometer (see Figure 2.9b). A specific wave number corresponding to a strong characteristic absorption band of the additive (e.g 650cm^{-1}-P=S) was chosen, and the percentage binding determinded by the following equation:

$$\%\ \text{Binding} = \frac{A_2 - A_1}{A_3 - A_1} \times 100$$

where A_1 = Absorbance of unstabilised polymer film.

A_2 = Absorbance of stabilised polymer film after extraction.

A_3 = Absorbance of stabilised polymer film before extraction

2.5.2 Ultra-violet Spectroscopy (U.V.)

The ultra-violet spectra of stabilised polymer films and solvent extracts were recorded using the Unicam SP 800 U.V.-visible spectrophotometer and the Beckman DU-7 U.V.-visible computing spectrophotometer. These instruments were used to monitor the decay of stabilisers during ageing by observing the characteristic U.V.-absorption bands of the additives. An unprocessed additive-free polymer film of identical thickness was used as reference to compensate for the polymer.

In the case of solution studies, spectra were recorded using quartz cells of 1 cm path length with the pure solvent serving as external reference. As is the case in all spectroscopic practice, quantitative anlysis in these studies was based on the Lambert Beer equation$^{(77,78)}$:

$$A = \log_{10}(I_o/I) = \varepsilon c l$$

where A = Absorbance

I_o = Intensity of incident radiation

I = Intensity of radiation transmitted through sample

ε = Molar absorptivity (mol dm^{-3}cm^{-1})

With the latter instrument (Beckman DU-7), the kinetics of the formation of new bands or the disappearance of original bands due to ageing, was followed by using a kinetic programme where kinetics of changes in the absorbance are recorded and plotted when required.

2.5.3 Nuclear Magnetic Resonance Spectroscopy (NMR)

^{31}P nuclear magnetic resonance spectroscopy (^{31}P NMR) was used to identify the phosphorus-containing soluble decomposition products arising from the thermal oxidation of dithiophosphates under oxidative conditions in various forms (see Section 2.6.3). This method was also used for the product analysis of solvent extracts of PP films containing concentrates of thiophosphoryl disulphide. In this instance, the effects of the processing condition on the type and amount of phosphorus-containing products formed in the polymer, can reasonable be assessed. Furthermore, this method was used for the estimation of purity of the thiophosphoryl disulphides (Section 4.2A.6)

All spectra were measured on a Jeol FX-9Q Fourier Transform Nuclear Magnetic Resonance Spectrometer operating at 36.20 MHz . In order to improve sensitivity and also to accommodate the number of samples to be measured, additive concentrations used were in the range 0.3 - 0.5 M. Thus, the accumulation time needed to obtain a spectrum was considerably reduced. The solvent extracts of the stabillised polymer films were also similarly concentrated before analysis by stripping off most of the extractive solvent.

All spectra were measured with noise decoupling of the phosphorus-hydrogen spin-spin coupling, and all chemical shifts weere also referenced to an external standard of 85% phosphoric acid. This is expressed as parts-per-million (ppm/δ) of the observed frequency, with positive shifts appearing low field of the reference. The phosphoric acid was used as an external instead of internal standard in order to prevent the possibility of any reaction occuring with other phosphorus-containing species present.

During anlysis, the standard was initially measured, and the position of the single peak observed in the spectrum was noted and set at 0 ppm. By measuring all subsequent samples under similar conditions, the peaks arising from the phosphorus-containing oxidation products were then referenced to the standard phosphoric acid peak which was originally set at 0 ppm. Approximate quantitative estimation of each specie in any one sample (% yield) was based on the normalization of all "Peak Areas" or" % Intensities" to 100%. However, it must be emphasised that the data quoted for the series of oxida ton studies (Section 5.2.1 - 5.2.3) are percentage phosphorus yields rather than percentage product yields since this can only be calculated if the identity of all the products formed were definitely known. The actual concentration levels of decomposition products containing only one phosphorns atom per molecule were therefore higher than those reported (Section 5.2.1 - 5.2.3) as being detected product yields (% yield). In some cases, absolute structural assignments to the ^{31}P NMR signals were accomplished on the basis of their identity with synthesised authentic standards.

2.5.4 High Pressure Liquid Chromatography (HPLC)(54)

The high pressure liquid chromatography was used primarily for the identification of phosphorus containing products formed during thermal-oxidation of thiophosphoryl disulphide (DnBDS) in dichlorobenzene under a steady stream of air (see Section 2.5.6.2). As with ^{31}P NMR, the high pressure liquid chromatography was also used for the estimation of purity of disulphide samples. Thus the major impurities of interest can be isolated and positively identified by synthesis of the appropriate authentic standards.

During analysis, the chromatographic procedure generally involves initial calibration of the instrument, followed by the injection of 50µl of sample diluted to approximately 7 mls with eluent mixture. The HPLC conditions were as follows(54):

Column : 5µm Spherisorb - ODS (25cm x 0.64)
Injection: 10µl Rheodyne valve
Detector : U.V.-225nm wavelength
Eluent : 25% deionised water/75% HPLC grade isopropanol
Flow rate: 1ml/min. Pressure 4,600 psi

In the absence of any calibration, as was the case during analysis of mixtures of DnBDS thermal oxidation products, the computer print out represents peak area normalization only and therefore cannot be used quantitatively because of the widely different absorbance values of the various oxidation products. However, this analytical method was particularly useful in the identification of the thiophosphoryl polysulphides (e.g.tri-and tetrasulphides) which not only are primary impurities in most disulphides samples, but also assumed greater importance as the major intermediates formed during the early stages of the oxidation reactions as described in the subsequent sections (see also Sections 5.2.1. - 5.2.3).

2.6 Analytical Procedures

2.6.1 Determination of Unsaturation

Polyolefins in general exhibit infra-red bands due to diverse unsaturated groups. For polyethylenes, IR bands at 1640cm^{-1}(all types of olefinic bonds), 909 and 990cm^{-1} (vinyl groups), 965cm^{-1}(in-chain olefinic groups) and at

$888cm^{-1}$(vinylidene groups) all indicate the presence of unsaturation. Polypropylene also exhibits IR bands at $1640cm^{-1}$ and $1685cm^{-1}$ due to olefinic unsaturation and conjugated carbonyl respectively.

The chemical procedure used for the determination of unsaturation formed in the polymer after processing and during U.V.-irradiation, is based on the reaction of the polymer unsaturation with iodine in the presence of mercuric acetate and trichloroacetic acid. This method has has been found (79) to give results which are twice as reproducible as those obtained with Wijs iodine chloride reagent.

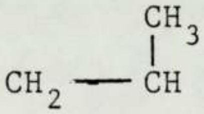
2.6.1.1 Procedure

A 0.5g sample of polymer film (weighed to about 0.002g) was cut into small pieces and swollen in 100ml of anhydrous carbon tetrachloride for 24 hours in a conical flask. 5ml of 20% trichloroacetic acid in carbon tetra-chloride was added and an equal amount of trichloroacetic acid solution also added to sample-free 100ml of anhydrous carbon tetrachloride to serve as a blank. 25ml of 0.1N iodine solution (in distilled water) were then added,with gentle swirling, to both the sample and blank and followed by 25ml of mercuric acetate solution(30 grams of mercuric acetate per litre of glacial acetic acid). After allowing to stand in the dark for at least two hours in a stoppered flask, 75ml of 7.5% potassium iodide solution (in distilled water) were poured into each flask and the mixture vigorously agitated. The excess iodine was then titrated with standard 0.1N thiosulphate employing the customary starch end point which is observed in the aqueous layer.

The mole percent unsaturation, defined as the mole percent of monomer units containing double bonds, was calculated as follows.

$$\text{Mole \% unsaturation} = \frac{(B-S)\,(N)\,(M)\,(100)}{(\text{grams of sample})\,(3000)}$$

Where B = ml of thiosulphate for blank
S = ml of thiosulphate for sample
N = normality of thiosulphate
M = molecular weight of structural unit of polymer

PP	42	 $CH_2 — \overset{CH_3}{CH}$
LDPE	28	$CH_2 — CH_2$

2.6.2 Peroxide Determination

Although peroxide groups in polyolefins may be determined as in low molecular weight compounds, by iodimetric titration, the procedure used was adapted from Bocek(80) and is based on the colour reaction of the peroxide with

Fe^{2+} and phenanthroline.

2.6.2.1 Procedure

A 0.5g sample of polymer film (very small pieces) was swollen in 25ml of de-aerated chloroform for 24 hours in a conical flask fitted with a rubber seal. 1ml of de-aerated 0.004M phosphoric acid (in MeOH) was added followed by 2ml of de-aerated solution of 0.005M ammonium ferrous sulphate in methanol. Both reagents were added using syringes to prevent contamination by oxygen.

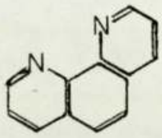
After allowing to stand in the dark for four hours, 1ml of 0.5% solution of 1,10 phenanthroline in de-aerated benzene was added, and the reaction mixture left to stand for 30 minutes after swirling. 5ml of the reaction mixture free of polymer was carefully withdrawn and its absorption in the visible region (490-520 nm) measured against the blank reference. Peroxide concentration was then read off using a calibration curve.

2.6.2.2a Calibration (U.V. method)

A blank sample was prepared in the same way with pure benzene in place of the sample. The difference between the absorbance of the blank sample and the analytical sample gave the quantity of divalent iron that had been oxidised by the hydroperoxide.

Variations in the amounts of added hydroperoxide caused equal variation in the amount of oxidised ferrous ion and enabled a calibration graph to be constructed (Figure 2.10a). The effect of additive Concentration (%) on the amount of hydroperoxide formed in the polymer at the end of processing, and hence the amount of coloured complex formed during analysis, is illustrated (Figure 2.10b) for DnBDS concentrates in PP.

$$ROOH + 2Fe^{++} + 2H^{+} \longrightarrow 2\,Fe^{+++} + ROH + H_2O$$

$2Fe^{+++}$ +  $\longrightarrow$ coloured products

2.6.2.2b Calibration by IR Method

Since the redox-type estimation (U.V. method) was reported$^{(81)}$ to be inconsistent especially in cases where the concentration of the sulphur containing additive is high relative to the peroxide concentration, the infra-red spectroscopy (Section 2.5.1) was used to monitor the decay in hydroperoxide concentration during oxidation studies (see Section 2.6.3) and also to identify products of the decomposition of the hydroperoxides.

This method involves the preparation of a series of chloroform solutions containing increasing concentrations of tertiary butyl hydroperoxide (TBH), and measuring the infra-red spectrum of each solution. A calibration graph of the absorbance at 3520cm which is due to oxygen-hydrogen stretching frequency of the hydroperoxide, was then plotted against concentration TBH (Figure 2.10c). The calibration graph was used as a basis for quantitative estimation of the rate of decomposition of the hydroperoxide.

2.6.3 Thermal Oxidative Reactions of Dithiophosphates

This section outlines the procedures used for the oxidation of bis-di-n-butyl thiophosphoryl disulphide (DnBDS) and the corresponding nickel complex (NiDnBP).

2.6.3.1 Materials

(I) Chlorobenzene

This was fractionated from phosphorus pentoxide and the fraction boiling at 132°C collected (760 mm). The solvent was primarily used for dilution purposes during product analysis

(II) Cumene (oxidisable substrate)

Technical grade cumene (EX BDH) was washed with concentrated sulphuric acid, water, sodium bicarbonate and water again before being fractionally distilled under nitrogen. The fraction boiling at 152°C (760 mm) was collected and stored under nitrogen.

(III) p-Dichlorobenzene (non-oxidisable substrate)

Analytical grade p-dichlorobenzene (EX BDH) was used without further purification (m.pt. 54-56°C; b.pt. 173°C; 97% pure).

(IV) n-Hexane/Cyclohexane

Standard laboratory reagent grade (Fisons) hexane was used without further purification while spectroscopic grade (Fisons) cyclohexane was used.

(V) Tertiary butyl hydroperoxide (TBH)

Mixture with water (70% peroxide content). This was used as supplied by the manufacturer, Akzo Chemie, without any further purification.

2.6.3.2 Thermal Oxidation of DnBDS in the Presence of Air

Oxidation of DnBDS was carried out in both an oxidisable (cumene) and a non-oxidisable (dichlorobenzene) substrate as described below.

A solution of DnBDS (0.5M) in dichlorobenzene was prepared by dissolving the additive in the substrate (40°C) with vigorous stirring (room temperature for cumene). The mixture was transferred to a 100ml 3-neck round bottom flask immersed in a silicon oil bath maintained at 185°C (180°C for cumene). The reaction mixture was refluxed under a slow, steady stream of air. Approximately 7ml samples were removed from the reaction mixture at time intervals using a syringe with a long needle. The samples collected were quenched in dry ice and stored in the freezer for subsequent product analysis (IR, ^{31}P NMR and HPLC).

2.6.3.3 Thermal Oxidation of DnBDS in the Presene of TBH

The ratios of TBH : DnBDS studied were 1:1 and 2:1 in dichlorobenzene while only one ratio (2:1) was studied in cumene.

(a) Dichlorobenzene as Substrate

The prepared solutions of DnBDS (0.5M) in the substrate were transferred to 100ml 3-neck round bottom flasks immersed in silicone oil baths maintained at 100°C. Pre-weighed solutions of TBH (0.5M and 1.0M) in the substrate were added dropwise over a period of 10 minutes. The reactions were then refluxed under a slow, steady stream of nitrogen and samples extracted at time intervals as described in the previous section. Products of the oxidation of the disulphide were determined by IR(Section 2.5.1) and ^{31}P NMR (Section 2.5.3), while the decay in the hydroperoxide concentration was monitored by IR analysis (Section 2.6.2.2b)

(b) Cumene as Substrate (In-situ ^{31}P NMR Experiment)

Only one TBH:DnBDS ratio (2:1) was studied in this substrate and the reaction was carried out inside the Joel FT NMR spectrometer at 100°C over an extended period (17 hours). Initially, the preweighed mixture of TBH (0.1M) and DnBDS (0.5M) was introduced into the NMR tube which contain 5mls of the substrate (cumene). The mixture was purged with nitrogen before being covered and placed in the instrument, originally programmed for a stacking run at 100°C. Thus, data were recorded at time intervals and the spectra was obtained at the end of the experiment.

2.6.3.4 Oxidation of NiDnBP by TBH

Studies of the oxidation of NiDnBP by TBH were carried out in spectroscopic grade cyclohexane at room temperature.

Solutions of TBH (0.3M - 3.0M) in cyclohexane were added to already prepared 0.3M solutions of NiDnBP in cyclohexane, such that the ratio of TBH:NiDnBP was varied between 1 and 10. The reaction in each case was very rapid, with concomitant precipitation (quantitative) of a green solid. At the end of each reaction (24 hours), the mixture was filtered to remove the precipitate which was then throughly washed with n-hexane and finally dried in a vacuum oven at room temperature. The soluble portion (filtrate) was stored in the freezer for subsequent product analysis (IR and ^{31}P NMR) and the precipitate was also subjected to infra-red and other chemical analysis.

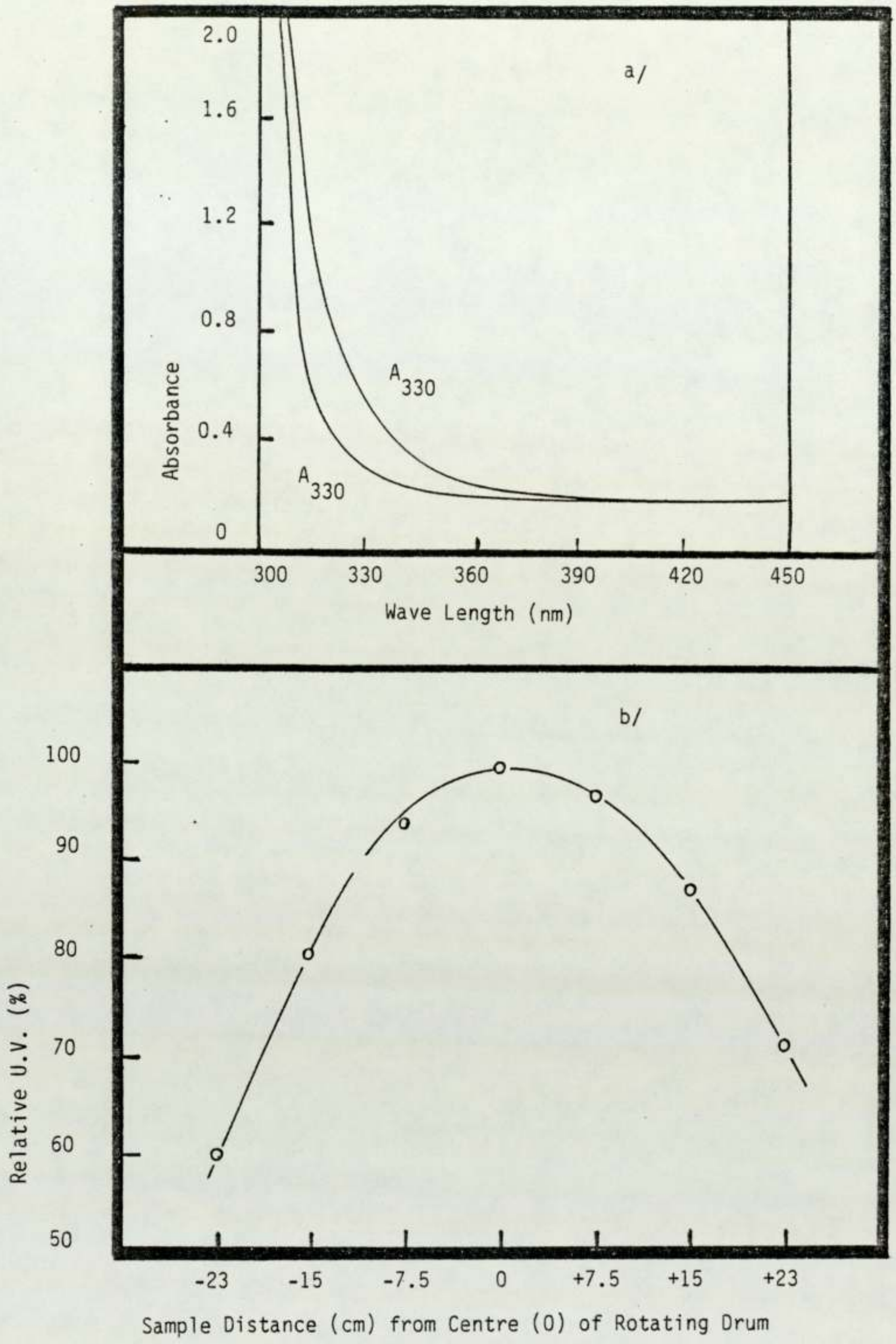


Figure 2.8 (a) Changes in optical density of polysulphone film after 20 minutes exposure in the UV cabinet

(b) Vertical positional variations in the U.V. out put in the U.V. cabinet.

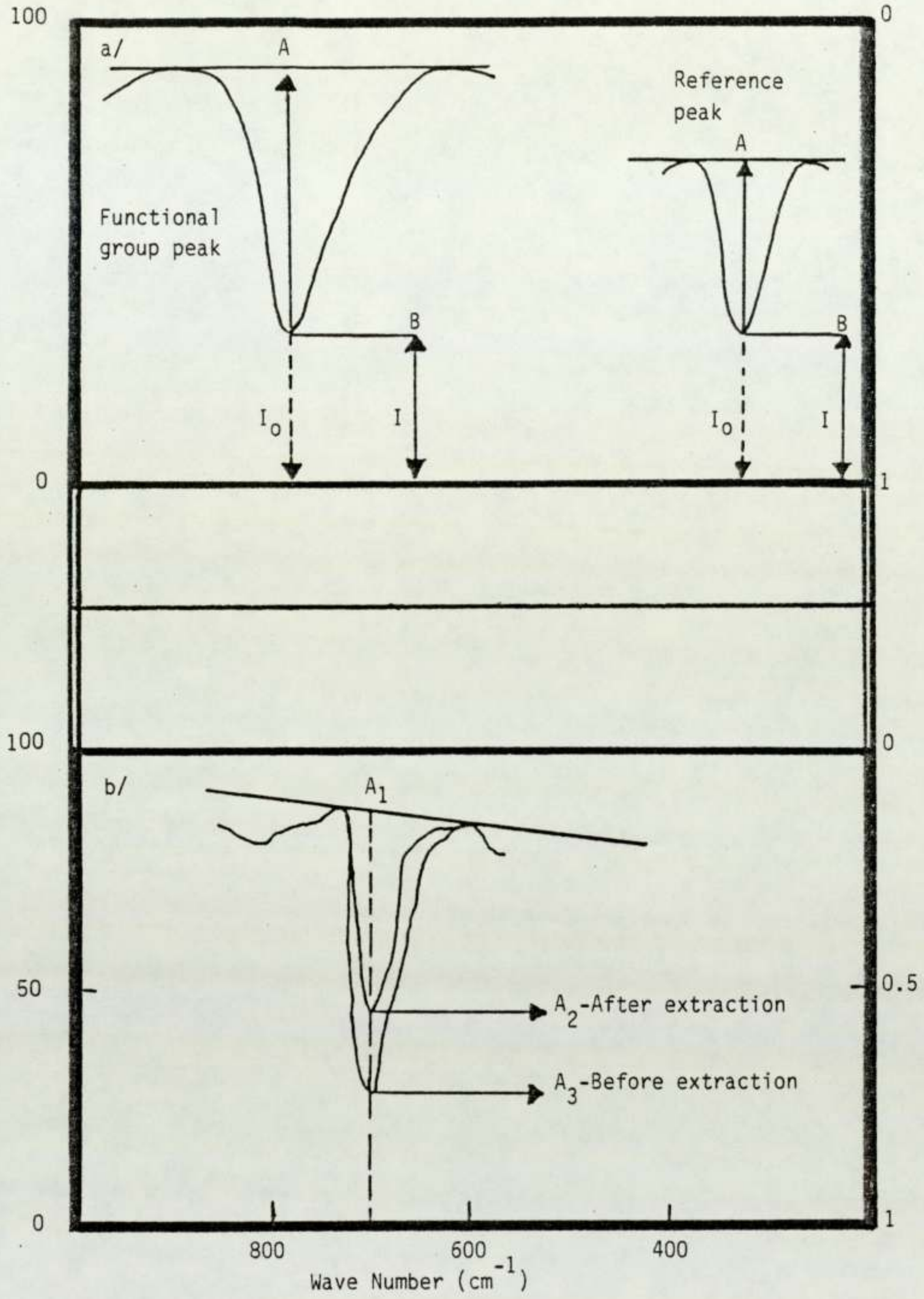


Figure 2.9 Infra-red spectra of PP films showing

(a) Functional group index measurement by base line technique and

(b) Estimation of binding by functional group measurement.

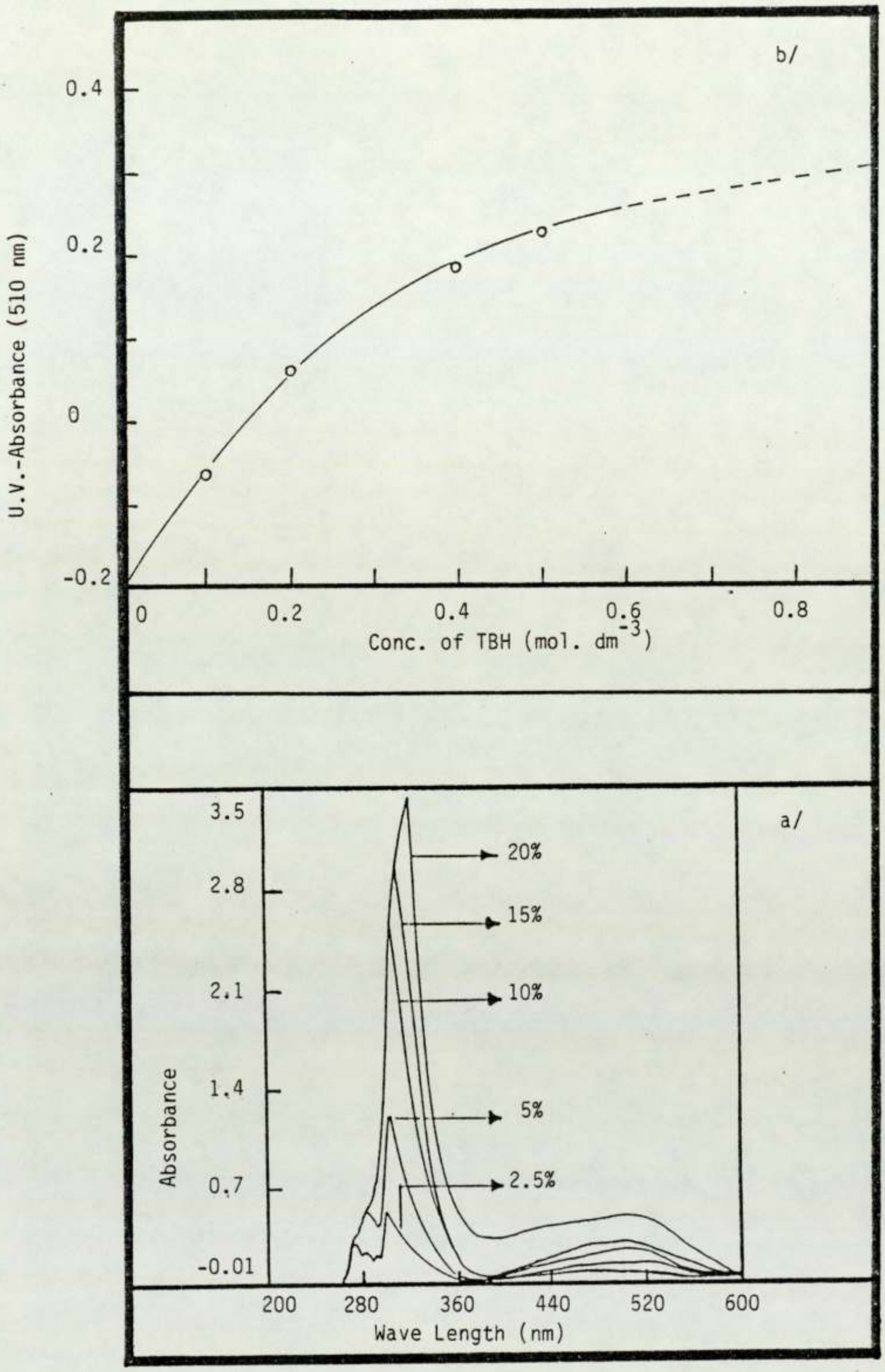


Figure 2.10 (a) UV spectra of the coloured complex formed during hydroperoxide determination of PP films of DnBDS concentrates(%)

(b) Calibration graph for the determination of tert butyl hydroperoxide (TBH) based on the colour reaction of the peroxides with ferrous ion(Fe^{++}) and phenanthroline - UV method.

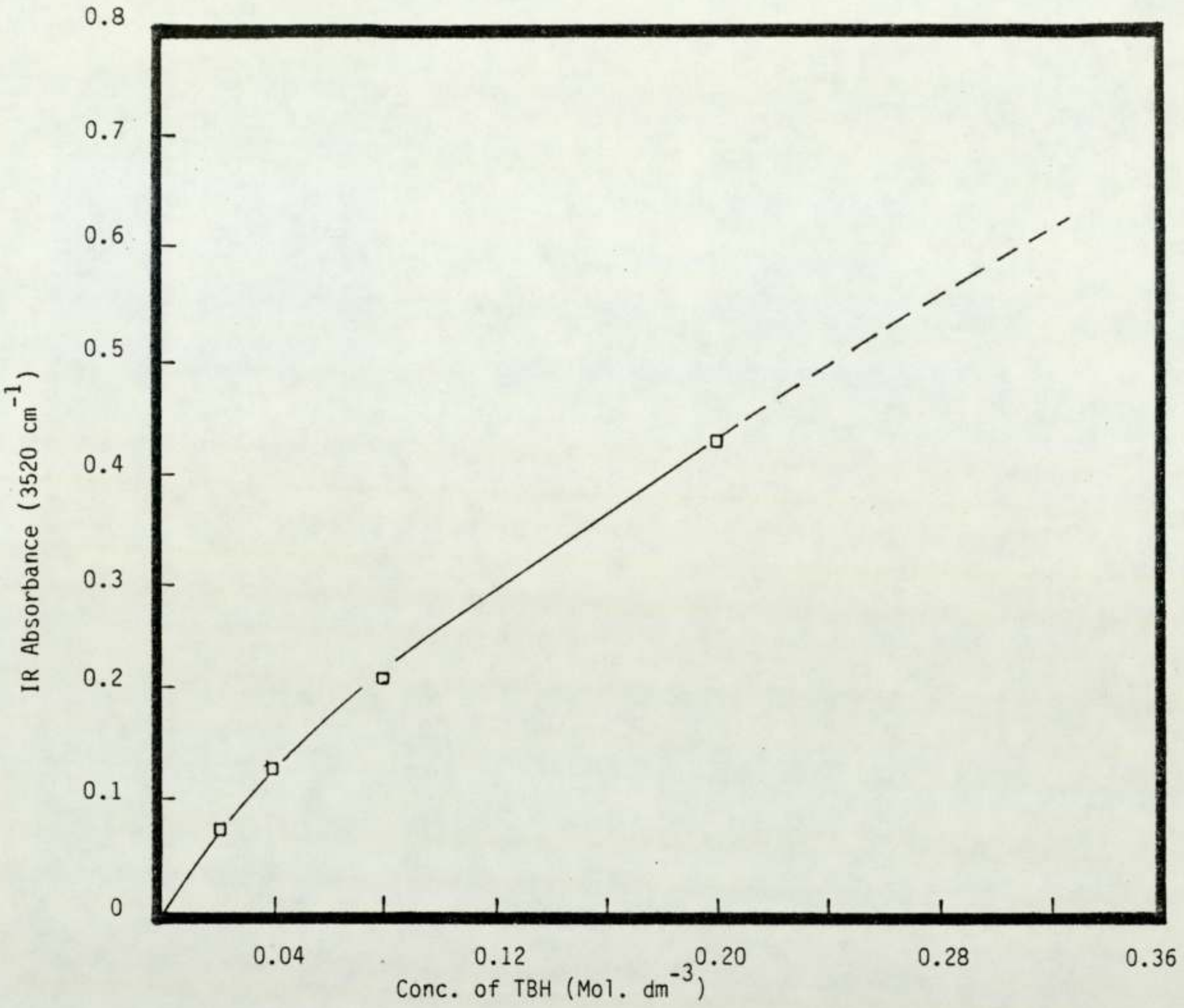


Figure 2.10c Calibration graph for the determination of tert-butyl hydroperoxide in chloroform - IR method

CHAPTER THREE

STABILISATION OF POLYOLEFINS BY NORMAL PROCESSING PROCEDURES (NS)

3.1 Object

It is now clearly established that auto-oxidation of polyolefins involves three inter-related oxidation cycles (see Section 1.1.2 and also scheme 1.1 and 1.3)

The first two involve the formation of alkyl ($R^{\bullet}$) and alkyl peroxyl ($ROO^{\bullet}$) radicals, while the second leads to the formation of radical generators, the most important of which are the hydroperoxides. These polymer hydroperoxides have also been identified(5a,5b,19,27) as the most important source of the main initiating radicals.

The auto-oxidation cycles can therefore in theory be interrupted in any one of the following steps:

$$RH \xrightarrow{XH} R^{\bullet} \xrightarrow{O_2} ROO^{\bullet} \xrightarrow{RH} ROOH \qquad 3.1$$

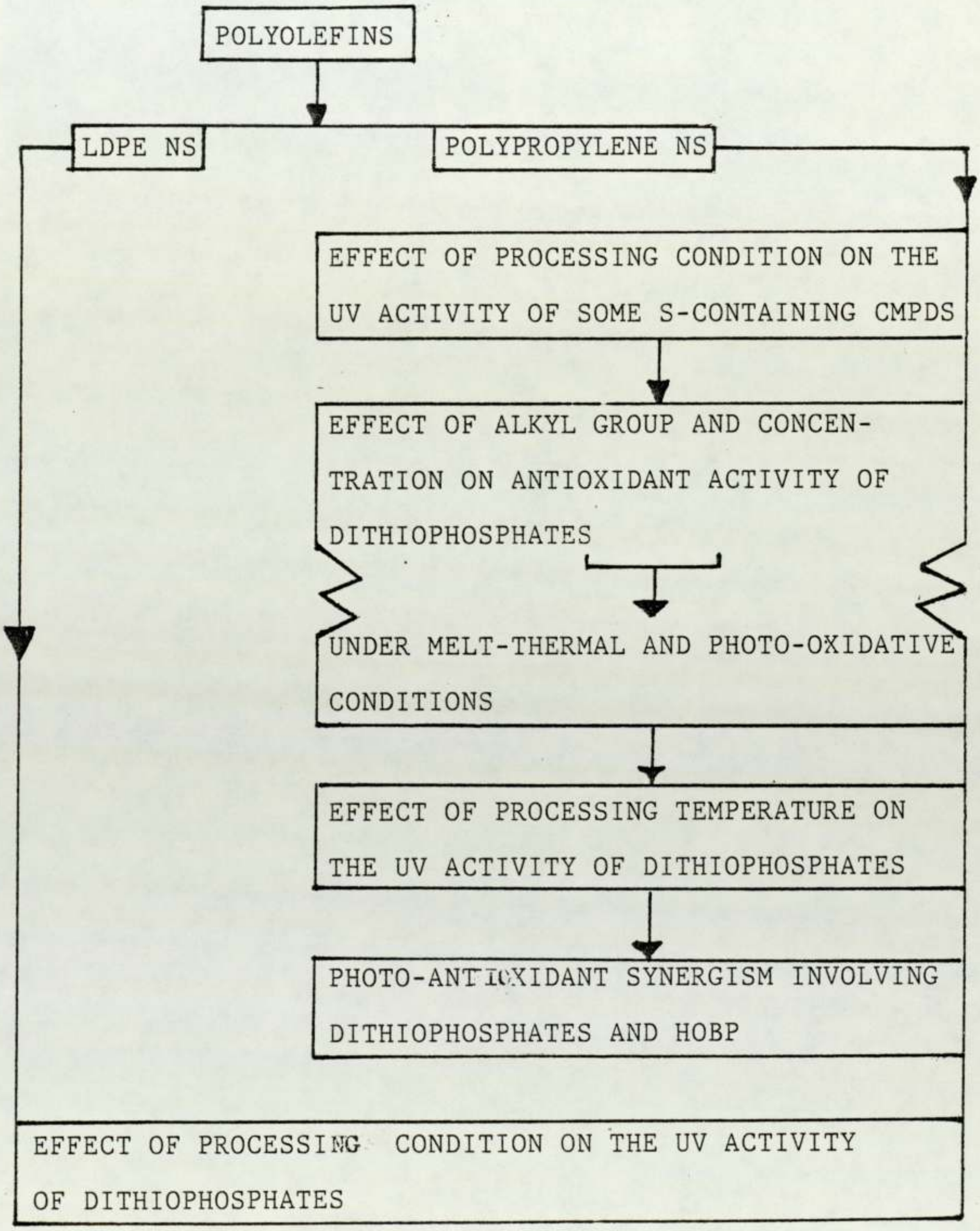
In view of the universal nature of hydroperoxides as the main source of initiating radicals, their decomposition to nonradicals products no doubt represents a significant in hibition process which cannot be overemphasised.

The protective action of sulphur antioxidants has been shown[(27,40a,40b)], in model compounds, to be due to their high peroxide-decomposing (PD-C), activity which is super imposed on the chain-breaking (CB-D and CB-A) activity.

This chapter deals with the effectiveness of dithiophosphates as photo, thermal and melt stabilisers in polyolefins. In order to establish or confirm the mechanisms involved in the antioxidant activity of these compounds, differing conditions were utilised during polymer processing (see Section 2.3 for full exptal. details). The effect of different alkyl substituents in the nickel dithiophosphates and the corresponding disulphides is also discussed in addition to the synergistic effects of the dithiophosphates and the U.V. absorber 2-hydroxy-4-octyloxy benzophenone (HOBP).

A schematic representation of the work described in this chapter is shown in Scheme 3.1.

Scheme 3.1 Stabilisation of polyolefins by normal processing procedures (NS)



A comprehensive list of the sturucture, chemical name and code of the stabilsers used in the work described in this chapter and chapter 4; is given in Table 3.1

Table 3.1 Structures of stabilisers

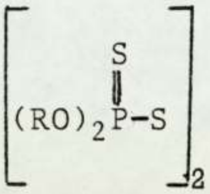
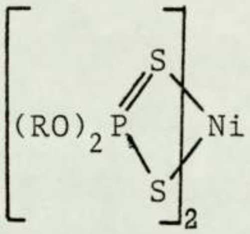
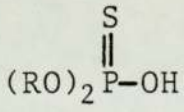
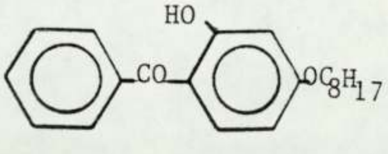
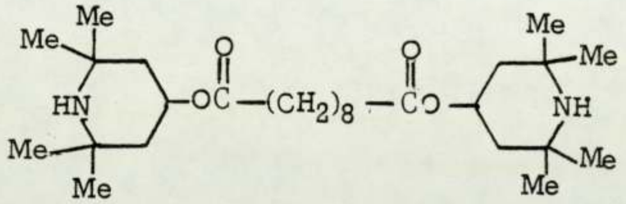
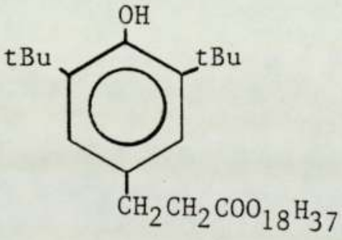
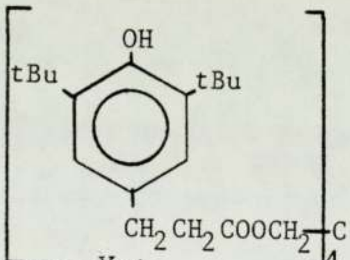
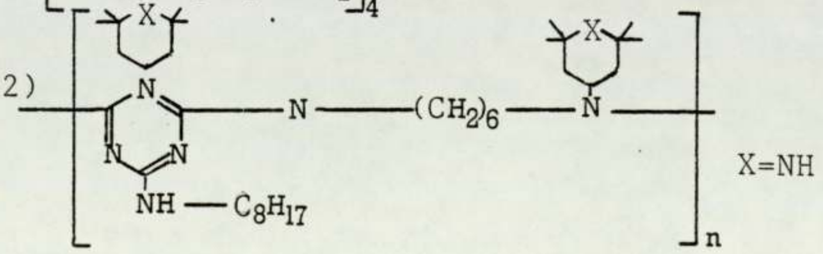
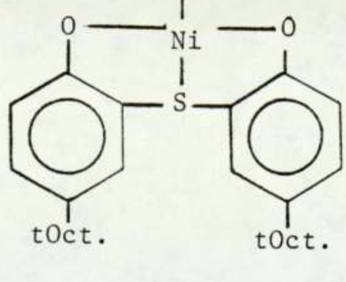
	STRUCTURE	NAME	CODE
(1)	 $\left[(RO)_2\overset{S}{\overset{\|}{P}}-S\right]_2$	Dialkyl thiophosphoryl disulphide	DRDS
		R = C_4	DnBDS
		R = C_6	DHDS
		R = C_8	DODS
(2)		Nickel dialkyl dithiophosphate	NiDRP
		R = C_4	NiDnBP
		R = C_6	NiDHP
		R = C_8	NiDOP
		R = C_9	NiDNP
(3)	 $(RO)_2\overset{S}{\overset{\|}{P}}-OH$	Di-n-butyl thionophosphoric acid	DnBTA
(4)	$(t\text{-}Bu)_2S_2$	Di-tert.butyl disulphide	DTBD
(5)	$(t\text{-}Dodecyl)_2S_2$	Di-tert. dodecyl disulphide	DTDD
(6)	$\left[(CH_3)_2NCS\right]_2S$	Tetra methyl thiuram monosulphide	TMTM
(7)	$(ROCOCH_2CH_2)_2S$ R = $C_{12}H_{25}$	Di-lauryl thio-dipropionate	DLTP

Table 3.1 (continued)

STRUCTURE	NAME	CODE
(8) 	2-hydroxy-4-octyloxy benzophenone	HOBP
(9) 	Bis-(2,2,6,6-tetramethyl-4-piperidinyl)-sebacate	Tinuvin 770
(10) 	Stearyl (3,5-di-tert-butyl-4-hydroxyphenyl)propionate	Irganox 1076
(11) 	Pentaerythrityl tetrakis-(3,5-di-tert-butyl-4-hydroxy phenyl)propionate	Irganox 1010
(12) 		Chemassorb 944
(13) 	2,2-thiobis(4-tert-octyl-phenolato)-butylamino nickel	Cyasorb 1084

3.2 Results

3.2A PP Normal Samples (NS)

The term 'normal samples' is used in this study to denote polymer samples processed under simulated normal commercial processing conditions, i.e in a closed chamber (CM) of the RAPRA torque rheometer under restricted amounts of oxygen at 190°C. In the context of this chapter, the term (NS) also applies to oxidatively processed samples (OM), the common factor here being the relatively low concentration of additives used in both processes (0.1-0.4% by weight of additive). Detailed processing procedures are described in Section 2.3.

3.2A.1 Effect of Processing on the Photoantioxidant Activity of some Sulphur-containing Compounds

This section is concerned with the effect of processing on the photo-oxidative stability of PP films containing the simple alkyl sulphides,di-tert butyl disulphide(DTBD) and di-tert. dodecyl disulphide (DTDD) as compared to other sulphur compounds such as tetra methyl thiurum monosulphide (TMTM), bis-di-n-butyl thiophosphoryldisulphide(DnBDS), and nickel di-n-butyl dithiophosphate(NiDBP).

Table 3.2, which compares the effectiveness of these sulphur compounds as photostabilisers in PP, also includes a DnBDS sample processed in the presence of tert-butyl hydroperoxide (TBH) and another sample containing di-n-butyl thionophosphoric acid (DnBTA) which is a major oxidation product (see Chapter 5, Section 5.3.1-5.3.4). It is clear from this table that all the sulphides show similar photo antioxidant activity when processed under restricted amounts of oxygen (CM) since the U.V. embrittlement times (EMT) fall within the same range (200-250h). Table 3.2 also indicates that whereas TMTM and DnBDS afford better U.V. protection to the polymer when oxidatively processed, this processing method (OM) only serves to reduce the antioxidant activity of the alkyl sulphides (DTBD and DTDD).

The much improved activity afforded by oxidative processing of DnBDS is confirmed by both the sample processed in the presence of TBH and that containing the oxidation product (DnBTA).

In contrast to DnBDS, NiDnBP is a much more effective U.V stabiliser although oxidative processing causes a reduction in its photoantioxidant activity (Table 3.2).

Table 3.2 Effect of processing 180°C on the U.V. stability of PP films containing sulphur antioxidants (0.2% by weight)

		EMBRITTLEMENT TIME (h)	
ADDTIVE	SULPHIDE TYPE	CM,5 min.	OM,5 min.
None	-	90	40
DTBD	ALKYL	215	205
DTDD	ALKYL	230	200
TMTM	THIURAM	235	290
DnBDS	THIOPHOSPHORYL	250	320
* DnBDS+TBH	,,	500	-
**DnBTA	,,	300	-
NiDnBP	,,	1350	750

All samples were synthesised via KI/I_2 method.

* sample contains 0.2% by weight of each component.

** CM,5 min/N_2 processing condition.

3.2A.2 Effect of Alkyl group and Concentration on the Antioxidant Activity of Dithiophosphates

This section deals with the melt, thermal and photostability of polypropylene normal samples processed under restricted amounts of oxygen (CM) at 190°C.

3.2A.2.1 Melt Stability During Processing

Table 3.3 compares the changes in melt flow index (MFI) of DnBDS and DODS – stabilised PP with that of other commercial melt stabilisers on successive passes in an extruder at 260°C (die temperature).

The effect of different alkyl substiituents in nickel dithiosphates and thiophosphoryl disulphides on the melt flow rates (MFR) of extruded PP (230°C) is also shown in Table 3.4 which clearly shows that the disulphides are better melt stabilisers than the nickel dithiophosphates or dithiocarbamates, and are comparable to one of the best commercial melt stabilisers (Irganox 1010).

Table 3.3 Comparison of MFI's(g/10 min) of dithiophosphates with other commercial antioxidants as melt stabilisers for PP.

(sucessive extrusions at 260°C, conc. of add.0.2%)

Antioxidant	MFI (190°C:2.16Kg: g/10min)		
	Extrusion Passes		
	1	2	3
None	1.2	3.9	7.8
IRGANOX 1010	0.38	0.49	0.68
IRGANOX 1076	0.36	0.52	0.76
DLTP	0.72	1.72	2.48
DNBDS ($R=C_4H_9$)	0.34	0.46	0.66
DODS ($R=C_8H_{17}$)	0.38	0.62	0.78

MFI for PP powder, 0.22

Table 3.4 Effect of alkyl group in dithiophosphates (0.4g/100g) on the Melt Flow Rates (MFR) of extruded (230°C) PP.

Antioxidant	* MFR (190°C: 10Kg: g/600s)	
	DRDS	NiDRP
R = nC_2H_5	24.0	28.9
R = nC_4H_9	23.2	28.2
R = nC_6H_{13}	23.7	29.1
R = nC_8H_{17}	23.9	30.0
R = nC_9H_{19}	25.0	31.0
NiDnBC, R = C_4H_9	31.5	
IRGANOX 1010	23.5	
IRGANOX 1076	23.2	
NONE	35.0	

* BS 2782 method 720A.

3.2A.2.2 Thermal Antioxidant Activity

Table 3.5 compares the effect of the alkyl group in the nickel dithiophosphates (NiDRP) and thiophosphoryl disulphides (DRDS) on the thermal stability of PP films in an air oven at 140°C. This table also includes the hindered phenol (Irganox 1076) compared at the same concentration (0.4g/100g) as that of dithiophosphates.

It is clear that the nickel dithiophosphates are effective thermal stabilisers in PP, where as the disulphides show very little activity.

The effect of the alkyl substituents in NiDRP on the thermal stability of polypropylene at different concentrations is also shown in Table 3.6 which indicates that the thermal antioxidant activity of NiDRP is highly dependent on the alkyl substituent in the additive.

Table 3.5. Effect of alkyl group in dithiophosphates on their thermal antioxidant activity in PP at 140°C (air oven)
(All samples processed in the torque rheometer in CM for 10 min. at 190°C)

Antioxidant	Embrittlement time (h)	
(0.4g/100g)	DRDS	NiDRP
R = C_2H_5	2	12
R = C_4H_9	6	150
R = C_6H_{13}	10	360
R = C_8H_{17}	15	500
R = C_9H_{19}	12	380
Irganox 1076, R = $C_{18}H_{37}$	550.0	
NONE	0.5	

Table 3.6. Effect of alkyl group in NiDRP on their thermal antioxidant activity in PP films at 140°C (air oven) (CM,10/190°C)

Antioxidant	Embrittlement Time (h) / Concentration (%)		
	0.1	0.2	0.4
NiDEP, R = C_2H_5	8	9	12
NiDBP, R = C_4H_9	50	90	150
NiDHP, R = C_6H_{13}	90	170	360
NiDOP, R = C_8H_{17}	140	260	500
NiDNP, R = C_9H_{19}	110	200	380

3.2A.2.3 Photo-stabilising Actvity

Tables 3.7 and 3.8 show the effect of the alkyl substituents in dithiophosphates (DRDS and NiDRP) on the U.V. stability of polypropylene samples at different concentrations. Tables 3.7 clearly indicates that the photo antioxidant activity of the disulphides is concentration dependent where as the type of alkyl substituent in the additive shows little effect on its activity. In contrast to DRDS, the U.V. activity of NiDRP is shown (Table 3.8) to be highly dependent on both the concentration and the type of alkyl group.

The effect of the alkyl group in NiDRP on the screening efficiency of the additive is shown in Table 3.9, which also indicates that the screening activity is dependent on the concentration of the additive. This table also includes data for the commercial U.V. absorber HOBP.

Table 3.7 Effect of alkyl group in DRDS* on the UV lifetimes of PP films. (CM,10/190°C)

Antioxidant	Embrittlement time (h) / Concentration			
	0.1%	0.2%	0.4%	3×10^{-4} mol/100g
DnBDS, $R=C_4H_9$	130	195	295	165
DHDS , $R=C_6H_{13}$	153	204	295	228
DODS, $R=C_8H_{17}$	145	190	298	220
DNDS, $R=C_9H_{19}$	135	185	295	205

* All DRDS additives were synthesised via the H_2O_2 method, so the data may vary at same concentration from those given for a similar DRDS synthesised via KI/I_2 method (Table 3.1).

Table 3.8 Effect of alkyl group in NiDRP on the ultraviolet lifetime (h) of polypropylene films (CM10/190°C).

Additive	Concentration			
	0.1	0.2	0.4	3×10^{-4} mol/100g
NiDEP, $R=nC_2H_5$	400	820	1550	700
NiDnBP, $R=nC_4H_9$	800	1400	2200	950
NiDHP, $R=nC_6H_{13}$	500	1250	1950	1150
NiDOP, $R=nC_8H_{17}$	530	850	1500	950
NiDOP, $R=nC_9H_{19}$	400	650	1250	750

Table 3.9 Comparison of the effectiveness of NiDRP and HOBP as U.V. screens for unstabilised polypropylene (CM,10/190°C)

Additive	Concentra. (mol/100g)	Embrittlement time (h)		Screening Contrbn.	Extinction Coeffici.(ε) $3x10^{-4}$ mol^{-1} (Hexane)
		Additive Film	Screened PP		
* NONE	-	110	135	-	-
HOBP	$3x10^{-4}$	310	270	87%	15000(285nm)/10,700(375nm)
HOBP	$6x10^{-4}$	520	450	87%	-
NiDEP	$3x10^{-4}$	700	240	34.3%	17,100 (316nm)
NiDnBP	$3x10^{-4}$	950	320	33.6%	19,200 (316nm)
NiDHP	$3x10^{-4}$	1150	360	31.3%	19,400 (316nm)
NiDOP	$3x10^{-4}$	950	330	34.7%	17,300 (316nm)
NiDNP	$3x10^{-4}$	750	260	34.6%	16,900 (316nm)
NiDnBP	$6x10^{-4}$	1500	480	32%	

* Unstabilised (unprocessed) PP

3.2A.3 Effect of Processing Temperature on the Antioxidant Activity of Dithiophosphates (closed chamber processing)

This section is concerned with the effect of the thermal history(processing temperature) on the thermal and photo-antioxidant activity of DnBDS and NiDnBP (0.2/100g). It is clear from Table 3.10 that whereas the antioxidant activity of DnBDS is relatively unaffected by the processing temperature, the U.V. stabilising activity of NiDRP is highly sensitive to the thermal history although the thermal antioxidant activity remains unchanged.

Table 3.10 also shows the effect of the oil (processing) temperature on the torque generated during processing of these samples.

Table 3.10 Effect of processing temperature on the antioxidant activity of dithiophosphates (0.2% CM.10)

Processing Temp. (°C)	Initial Melt Temp.(°C)	Final Melt Temp.(°C)	Initial Torque Tmax	Final Torque Tmin*	Embrittlement Time(h)	
					DnBDS	NiDnBP
180	165.5	176.5	120	16	185	1300
190	175	184.5	74	14	195	1400
200	182.5	191	55	9	175	900

* After 10 minutes processing in a closed chamber

3.2A.4 Synergism between Dithiophosphates and U.V Absorbers

The photo antioxidant synergism between dithiophosphates and the U.V absorber HOBP in polypropylene is reported in this section. Table 3.11 not only shows that DnBDS which is a relatively ineffective U.V stabiliser on its own right, becomes effective in combination with HOBP, but also clearly indicates that exceptionally high level of synergism is achieved with NiDnBP.

The effect of the alkyl substituent in NiDRP on the synergistic effect is shown in Table 3.12 which also strongly suggests that a combination of DnBDS and NiDnBP alone only show antagonistic effect in polypropylene.

Table 3.11 Synergistic effects of dithiophosphates and HOBP on photostability of polypropylene (CM.10:190°C) (conc. 6×10^{-4} mol/100g)

Stabiliser	Concentration	U.V. EMT (h)	% Synergism
DnBDS	$6\text{x}10^{-4}$	225	
HOBP	"	520	
NiDnBP	"	1500	
DnBDS+HOBP	5 + 1 ($\text{x } 10^{-4}$)	420	147
" "	4 + 2 "	480	177
" "	3 + 3 "	600	205
" "	2 + 4 "	700	221
NiDnBP+HOBP	5 + 1 "	1950	63
" "	4 + 2 "	2650	128
" "	3 + 3 "	2050	122
" "	2 + 4 "	1600	117

Table 3.12 Synergistic and antagonistic effects on U.V stability of polypropylene films (CM.10/190°C)

Antioxidant	Concen. %	Embrittlement Time (h)		
		Observed	Calculated Effect	% Synergism
None	-	90	-	-
DnBDS	0.2	195	-	-
NiDnBP	0.2	1400	-	-
NiDHP	0.2	1250	-	-
NiDOP	0.2	850	-	-
NiDNP	0.2	650	-	-
Tinuvin 770	0.2	1200	-	-
HOBP	0.2	520	-	-
NiDnBP+HOBP	0.2+0.2	3300	1920	134
NiDHP+HOBP	0.2+0.2	3200	1770	150
NiDOP+HOBP	0.2+0.2	2950	1370	227
NiDNP+HOBP	0.2+0.2	2550	1170	235
Tin770+HOBP	0.2+0.2	2900	1720	138
*DnBDS+NiDnBP	0.2+0.2	850	1595	-
**DnBDS+NiDnBP	0.2+0.2	850	1650	-

* Antigonistic Effect

** OM,15 min.

3.2A.4.1 U.V Screening Efficiency of Synergistic Systems

Table 3.13 shows the role of the U.V. absorber on the screening activity of the synergistic systems in PP. It is clear from these results that whereas the screening efficiency of the DnBDS:HOBP systems is entirely dependent on the concentration of HOBP, this is not the case in the NiDnBP:HOBP systems since both additives are good U.V. screens in PP.

Table 3.13 A comparison of the effectiveness of synergistic systems as U.V. screens for unstabilised polypropylene

Antioxidant	Concentration (mol/100g)	Embrittlement Time(h)	
		Additive Film	Screened PP
None	-	*110	135
DnBDS	$6x10^{-4}$	290	150
NiDnBP	"	1500	480
HOBP	"	520	450
DnBDS+HOBP	5 + 1 ($x\ 10^{-4}$)	420	260
DnBDS+HOBP	4 + 2 "	480	285
DnBDS+HOBP	3 + 3 "	600	350
DnBDS+HOBP	2 + 4 "	700	390
NiDnBP+HOBP	5 + 1 "	1950	400
NiDnBP+HOBP	4 + 2 "	2650	400
NiDnBP+HOBP	3 + 3 "	2200	460
NiDnBP+HOBP	2 + 4 "	1700	400

* Unstabilised (unprocessed) PP.

3.2B Polyethylene Normal Samples (PE/Ns)

Having carried out an extensive study of the antioxidant activity of dithiophosphates in polypropylene, it was deemed necessary to undertake a somewhat limited evaluation of their effectiveness in the less oxidisable low density polyethylene (LDPE). In accordance to the work carried out in polypropylene, the term 'normal samples' is also used to denote samples processed both in an oxygen defficient atmosphere (CM) and in the presence of excess oxygen (OM), the common factor being the relatively low concentration of stabilisers used (<0.4%).

3.2B.1 Effect of Processing at 150°C on the Photo-antioxidant Activity of Dithiophosphates

Table 3.14 shows how the effectiveness of dithiophosphates as U.V stabilisers in LDPE is influenced by the processing technique. It is clearly shown that whereas the photo-stabilising activity of the thiophosphoryl disulphide (DnBDS) is improved when oxidatively-processed (OM), the activity of the nickel complex (NiDsBP) seemed to be relatively unaffected by the processing severity. Table 3.14 also shows that severe processing improves the stabilising activity of the hindered piperidine derivative, Tinuvin 770, and this contrasts with the decreased activity of the U.V absorber, HOBP under similar conditions.

The photoantioxidant synergism involving thiophosphoryl disulphides (DnBDS) and DODS) and the U.V absorber, HOBP is shown not only to be highly effective in LDPE, but is also considerably improved with increasing processing severity.

Table 3.14 Effect of processing severity on the U.V activity of various stabilisers in LDPE (0.2g/100g)

Antioxidant	Time (h) to a Constant Carbonyl Index Value of 10	
	CM, 10 min	OM,10 min.
None	950	850
DnBDS	1250	1500
NiDsBP	1600	1600
HOBP	2600	2200
Tin. 770	2000	2400
DnBDS+HOBP(0.1%:0.2%)*	4200	5000
DODS+HOBP (0.1%:0.2%)*	4600	5500

*0.3g/100g

3.3 Discussion

3.3A PP Normal Samples (PP/NS)

3.3A.1 Effect of Processing Technique on the Photo-antioxidant Activity of Sulphur Compounds

The photo-stabilisation afforded by the various sulphur compounds in polypropylene is shown in Table 3.1,and Figure 3.1 which also demonstrates the effect of the processing techniques on their antioxidant activity. The results clearly show that the simple alkyl sulphides (DTBD and DTDD) give very similar photoantioxidant activity to the thiuram monosulphide (TMTM) and the thiophosphoryl disulphide (DnBDS) when processed under normal commercial conditions (CM). However, oxidative processing (OM) of TMTM and DnBDS leads to improved photo-oxidative stability of the polymer whereas this processing technique only serves to reduce the effectiveness of the simple alkyl sulphides DTBD and DTDD, in the polymer.

The reason for the reduced effectiveness of the simple alkyl sulphides when oxidatively processed may be due to rapid volatilisation of the additive and/or the oxidation products during thermal processing. It is known(5b,18,40b) that the simple alkyl sulphides function via their oxidation products by PD-C mechanism, but are weak U.V stabilisers on account of their photolytic instability.

It has also been reported(18,85) that the intermediate sulphoxide from these sulphides is very sensitive to light and, like carbonyl compounds, dissociates to free radicals as shown in Scheme 3.1 (reaction c.) for thiodipropionate esters.

Scheme 3.2 Antioxidant mechanism of alkyl sulphides

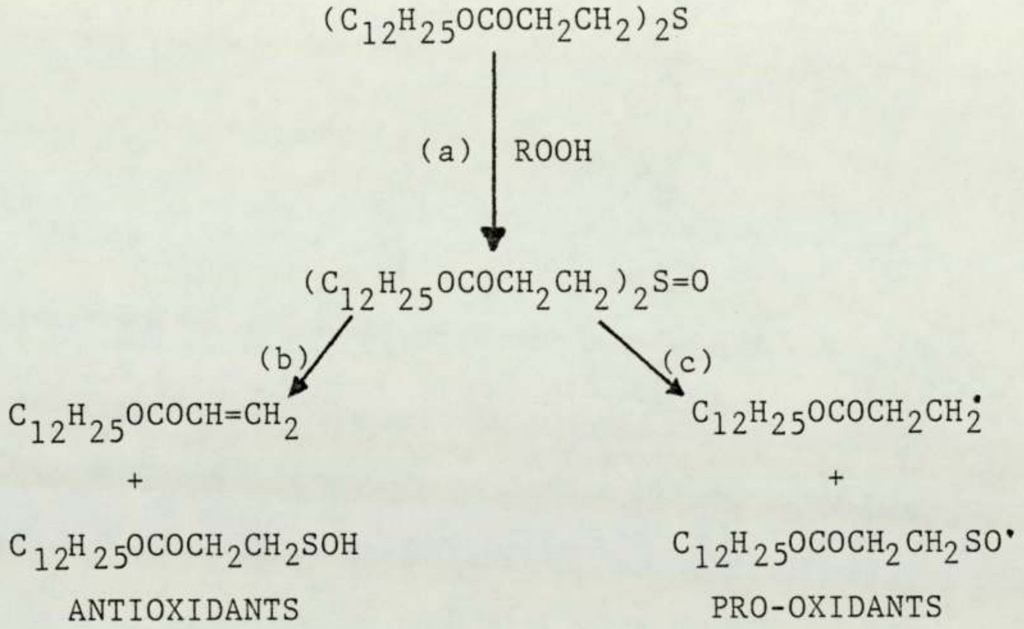
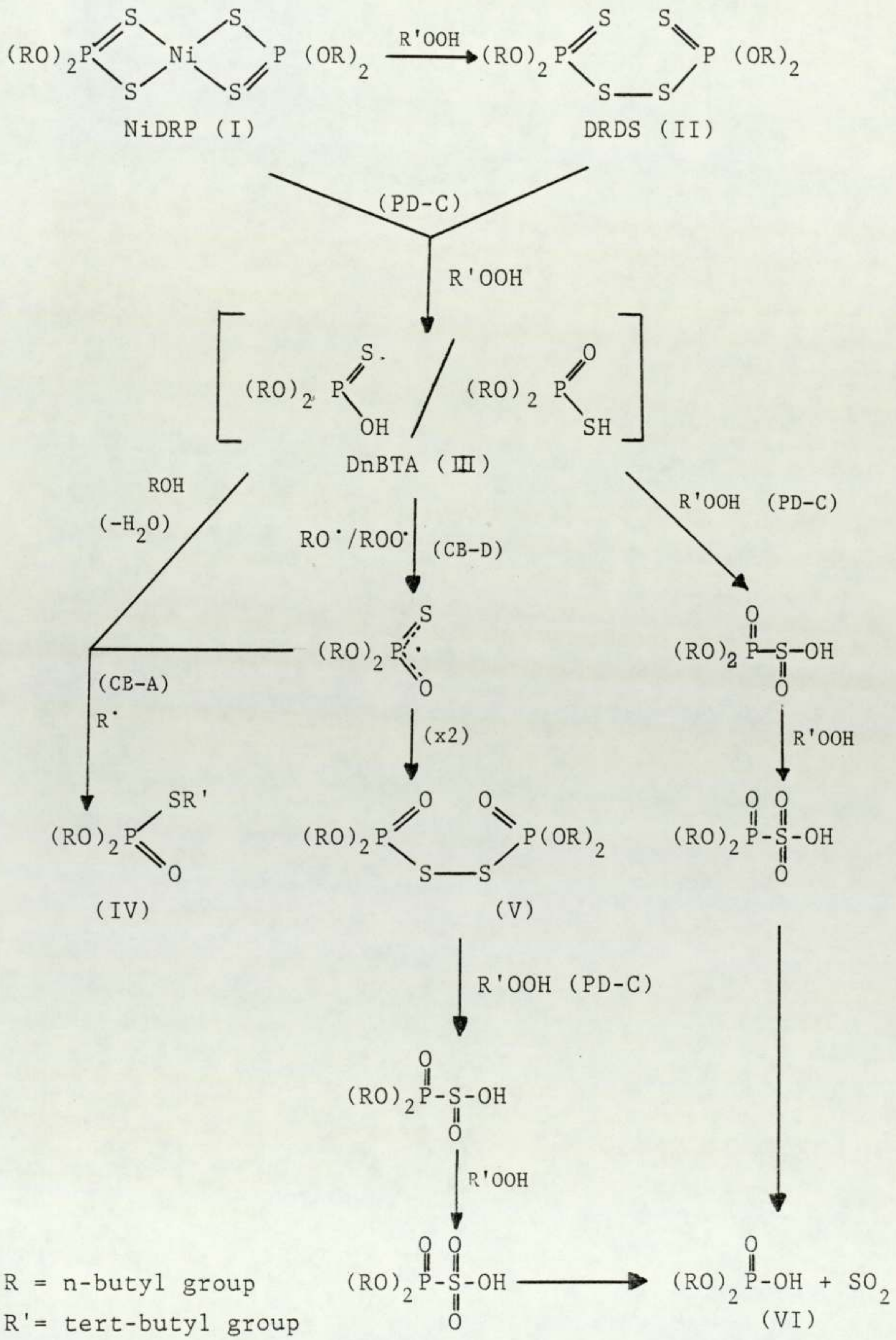


Table 3.2 and Figure 3.1 also clearly illustrate the large improvement in the photostabilising activity of TMTM and DnBDS when oxidatively processed in the presence of excess oxygen or a hydroperoxide (TBH) under nitrogen.

It has been previously shown(22,26,86) that the inhibitory role of disulphides during autoxidation of model compounds is mainly due to their oxidation products, with the primary function of the parent sulphide being that of a reservoir from which the active inhibitor can be generated as required. It is therefore not surprising that the additive DnBTA, which is a major oxidation product of dithiophosphates (see Chapter5, Section 5.3.1-5.3.4) shows a photo antioxidant activity only surpassed by oxidatively processed DnBDS.

The results (Table 3.2 and Figure 3.1) also demonstrate the detrimental effect of thermal oxidative processing (OM) on the efficiency of NiDnBP as a U.V stabilliser in polypropylene. In contrast to the sulphides, the nickel dithiophosphate (NiDnBP) is a much more effective U.V stabiliser due to its much higher U.V stability, and its ability to liberate the ionic catalysts for peroxide decomposition over a much longer period of time(5b,18,27). However, oxidative processing results in almost 50% reduction in the photoantioxidant activity of NiDnBP, presumably due to the partial conversion of the nickel complex to the corresponding disulphide (DnBDS) which has been shown (Table 3.2) to be relatively ineffective in stabilising PP against photo-oxidation. It is worth pointing out that this assumption has been confirmed in model compound studies involving NiDnBP and TBH (Chapter 5, Section 5.3.3) from which both DnBDS and DnBTA, amongst other species, were identified as major oxidation products by ^{31}P NMR analysis. This also validates the findings in a previous work(90) regarding the formation of DnBDS and DnBTA during the reaction of NiDnBP with cumene hydroperoxide at elevated temperatures. Scheme 3.3 which outlines further decomposition pathways of



Scheme 3.3 Possible antioxidant mechanisms of thion-/thiolphosphoric acid (DnBTA)

R = n-butyl group

R'= tert-butyl group

DnBTA clearly indicates that the triesters (IV), the phosphoryl disulphide (V) and the inorganic phosphoric acid (VI) largely represent the ultimate oxidation products of dithiophosphates and these products were positively identified by ^{31}P NMR during model compound studies (see Chapter 5, Section 5.3.1 - 5.3.3).

Although severe processing has been shown to have a deleterious effect on the photoantioxidant activity of the nickel dithiophosphates (see Table 3.2 and Figure 3.1), it has equally been shown that as might be expected from Scheme 3.3, the oxidative processing of DnBDS or the incorporation of an oxidising agent(e.g TBH) during processing, has a beneficial effect on the U.V stabilising activity of the disulphide in view of the antioxidant potential of the subsequent oxidation products.

3.3A.2 Effect of Alkyl Group and Concentration on the Antioxidant Activity of Dithiophosphates

3.3A.2.1 Melt Stability During Processing

Polypropylene, in the absence of a melt stabiliser, undergoes rapid chain scission during extrusion or closed chamber processing in a torque rheometer. A proportion of the alkyl radicals ($R^{\bullet}$) resulting from such mechano scission, react with oxygen to form alkyl peroxyl radicals ($RO_2^{\bullet}$). These are converted to hydroperoxides (ROOH), which in turn undergo thermolysis to give hydroxyl (·OH) and alkoxyl (RO·) radicals. In polypropylene, the reduction in molecular weight or increases in the melt flow index (MFI) is therefore a direct consequence of the fragmentation of the tertiary alkoxyl radicals(2,5a,26).

In table 3.3 and Figure 3.2,the melt stabilising activity of the thiophosphoryl disulphides (DnBDS and DODS) is shown to be very similar to that of the hindered phenols (Irganox 1076 and 1010) after three successive processing operations in an extruder at 260°C. It has been variously reported(40b,68a,68b,70,74)that the dithiophosphates are very effective melt stabilisers not only by virtue of their ability to reduce hydroperoxides to alcohols by non-radical processes but also via their radical trapping activity (R· and ROO·).

Furthermore, it has been demonstrated in model compound studies (Chapter 5, Section 5.3.1 - 5.3.3) that the intermediate radicals formed from the decomposition of dithiopphosphates, seem to be very efficient alkyl (R·) and alkoxyl (RO·) radical scavengers. The peroxidolytic activity (PD-C) which is super-imposed on the chain-breaking (CB) activity accounts for the slight changes in melt flow index observed during extrusion.

The effect of the different alkyl substituents in nickel dithiophosphates and thiophosphoryl disulphides on the melt flow rates (MFR) of extruded polypropylene (230°C) is illustrated in Figure 3.3. These results, which are also shown in Table 3.4, clearly indicate that the disulphides are superior to the nickel dithiophosphate in stabililsing the polymer against thermal degradation during processing. Since both possess high peroxidolytic and radical scavenging activity, this superiority (of DRDS over NiDRP) must therefore be associated with the relative ease of formation of the effective antioxidants from the disulphide during processing. Thus, the oxygenated oxidation products (e.g sulphoxides and acidic species) are expected to be formed rapidly from the disulphide under the high temperature conditions used during extrusion (230°C) and such intermediates have been known(5a,40a,85) to be powerful traps for both alkyl and alkylperoxyl radicals.

From Table 3.4 and Figure 3.3,it is clear that increasing the alkyl chain length in the dithiophosphates ($R=C_2$- C_9) only show a slight change in the melt stabilising effectiveness of the series. For both compounds however, the butyl analogue ($R=C_4$) is shown to be the most effective, whereas the melt stabilising activity reduces slightly as the chain length is increased beyond this optimum. This is clearly due to the dilution of the antioxidant function in the molecule by the inert alkyl chain whose function is to increase solubility in the polymer, since the concentration of all additives is based on weight percentage as opposed to molar concentration. The results also suggest that antioxidant loss by volatilization is much less important during processing of dithiophosphates in view of the very slight changes in the melt flow rates (MFR) on increasing the alkyl chain length (R=$C_2$to C_8). A comparison of the dithiophosphates with the dithiocarbamate (NiDBC) and the traditional hindered phenols (Irganox 1076 and 1010) under identical conditions (Table 3.4), also clearly confirms the very effective melt stabilising activity of the disulphides.

The nickel dithiophosphates have been known(5a,27,35) to function primarily as light-stable reservoirs for oxidatively-derived antioxidants. It therefore follows that since these species are partially formed during processing in the presence of a trace amount of oxygen, nickel dithiophosphates are effective melt stabilisers in polypropylene, and it has also previously been reported(5a,35) that no hydroperoxide can be detected in the polymer during the MFI induction period.

3.3A.2.2 Thermal Antioxidant Activity

In addition to the efficient melt stabilising activity of the dithiophosphates as shown in the previous section, these compounds have also been known(5a,18,27) to be effective thermal stabilisers in polypropylene and their activity under thermal conditions, as in melt, constitutes the ionic decomposition of hydroperoxides (PD-C) which is super imposed on the chain breaking mechanisms.

Figure 3.4 illustrates the effect of the alkyl group in the nickel dithiophosphates (NiDRP)and the thiophosphoryl disulphides (DRDS) on the thermal oxidative stability of PP films. In contrast to the behaviour of these compounds as melt stabilisers in PP, the nickel dithiophosphates are shown to be superior to the disulphides during thermal oxidation (air oven) of polypropylene, irrespective of the alkyl substituent attached to the antioxidant function. As with their U.V activity, the higher effectiveness of the nickel dithiophosphates is attributed(87) to the presence of the metal centre which apparently enhances the stability of the molecule. Such higher thermal stability of the NiDRP molecule therefore facilitates the controlled liberation of the oxidation products (Scheme 3.3) including DRDS, over a much longer period.

The presence of excess air (as obtained in oven tests micht be expected to promote the formation of alkyl peroxyl radicals (ROO$^\bullet$) and it has been previously reported(39,70) that the nickel dithiophosphates are capable of deactivating alkyl peroxyl radicals by a variety of mechanisms, the most probable of which is electron transfer from the metal ion or sulphur atom of the chelate to the active radical. Ranaweera and Scott(67) have also demonstrated the importance of hydroperoxide decomposition by nickel-chelate based light stabillisers such as the dithiocarbamates and these have been shown to act both as radical scavengers and, more effectively, as catalytic hydroperoxide decomposers.

Another important feature in Figure 3.4 and Table 3.5-3.6 is that the thermal antioxidant activity of the dithiophosphate function depends on the alkyl substituents attached to it. These results clearly indicate that the thermal antioxidant activity increases with decreasing volatililty (R= C_2- C_9) and/or increasing solubililty in the polymer since the higher alkyl analogues (R= C_6- C_9) are much more effective even on weight percentage basis (0.4%). For both DRDS and NiDRP, the optimum chain length for maximum thermal stabilisation is shown to be the octyl derivative (R=C_8), and increasing the chain length beyond this optimum only reduces the thermal antioxidant activity.

The effect of the alkyl substituent in NiDRP on their thermal antioxidant activity as discussed above is clearly illustrated in Figure 3.5a-b, which also shows that increasing the concentration of NiDRP results in a linear increase in stabilisation effectiveness as reflected by the improvement in the embrittlement times. In the light of this discussion, it is therefore not surprising that the thermal antioxidant activity of the higher alkyl analogues of nickel dithiophosphates (R=C_8), parallels that of the traditional hindered phenol Irganox 1076 as shown in Table 3.5. In contrast to the behaviour observed in the melt stabilising activity of the dithiophosphates, the results discussed in this section clearly suggests that antioxidant loss by volatilisation or increasing solubility, is much more important during thermal-oxidative tests in an air oven.

3.3A.2.3 Photo-stabilising Activity

The efficient photo-stabilising activity of dithiophosphates (the nickel complex and its corresponding disulphide) have been shown (scheme 3.3) to be primarily due to their ability to decompose hydroperoxides in addition to the radical scavenging potential possesed by subsequent oxidation products. Although the thiophosphoryl disulphides (DRDS) have been reported to be fairly weak U.V stabilisers in polypropylene (Section 3.3.1.1), their activity seems to be relatively unaffected by changes in the alkyl substituent attached to the antioxidant function. This is shown in Figure 3.6 which also illustrates the effect of different concentrations (weight percentage) on their U.V activity as well as the behaviour of the nickel dithiophosphates (NiDRP) under similar conditions. Hence Figure 3.6 clearly indicates that whereas the activity of NiDRP, which is a much more effective U.V stabiliser, is highly dependent on both alkyl substituent and concentration effects, the activity of the corresponding disulphide (DRDS) is only slightly altered by these variables. These facts are also illustrated in Figure 3.7-3.8 which show the effect of the alkyl chain length on the stabilising effectiveness in PP, of DRDS and NiDRP on molar concentration basis (Figure 3.7), and the effect of concentration on the U.V activityof the butyl derivatives on a weight percentage basis (Figure 3.8) respectively.

It has been previously reported$^{(87)}$ that increasing the alkyl chain length in nickel dithiophosphates also increases their solubility in organic substrates. Figure 3.9 which compares the photoantioxidant activity of NiDRP at concentrations 0.2% and $3x10^{-4}$ mol.$(100g)^{-1}$, clearly shows that NiDnBP ($R=C_4$) is the most effective on a weight percentage basis, whereas the higher homologues are less effective. This behaviour, shown to be consistent over a range of concentrations (Figure 3.6) has been attributed to the dilution of the antioxidant function in the molecule by the inert alkyl chain whose primary role is to increase solubility in the polymer(87) However, comparison on a molar basis indicates that the optimal chain length for maximum photo antioxidant activity in the nickel dithiophosphates corresponds to the hexyl derivative ($R=C_6$) as reflected by the U.V embrittlement times (Figure 3.7 and 3.9).

It has previously been suggested(88) that U.V stabilisers are extremely sensitive to their state of dispersion in polymers. Since many of them (including NiDRP) behave in part as U.V filters or screens,it is therefore reasonable to assume that their effectiveness depends partly on their molar absorptivity and hence their U.V absorbance in the polymer, which in turn depends on their solubility This supposition is confirmed in Figure 3.10 which illustrates the relationship between the photoantioxidant effectiveness of the nickel dithiophosphates (weight % basis) and their initial U.V absorbance (316nm) in the polymer. Figure 3.11 also shows that on a molar basis, the molar absorptivity (316nm) of NiDRP in hexane roughly parallels their U.V absorbance (316nm) in PP, and hence their overall U.V activity as reflected by the embrittlement times for the stabilised PP films. This clearly suggests that, as in melt processing, the antioxidant loss by volatilisation is much less important during U.V exposure whereas other factors such as solubility and equilibrium concentration of the antioxidant function play a much more important role. Optimum photoantioxidant activity of the nickel dithiophosphates as shown in these results, therefore involves a compromise between chemical and physical effects(87), and it is seen that a balance exists between the butyl (NiDnBP) and the hexyl (NiDHP) derivatives when compared on both a weight percentage (Figure 3.10) and a molar (Figure 3.11) basis i.e $R=C_4-C_6$

In common with the commercial U.V. absorber HOBP, the nickel dithiophosphates absorb light strongly in the most critical region of the solar spectrum (190-350nm) and are consequently very photo-stable(4b,40b,87). Figure 3.12 shows that the induction period to photo-oxidation of polypropylene stabilised with NiDRP is directly related to the time taken for the photo-destruction of the complexes in the system. This implies that once the metal complex has been destroyed by the photo-oxidative reactions occuring in the polymer,it loses its effectiveness and the polymer is destroyed by oxidation(4b.40). It can therefore be seen that the higher activity of NiDHP ($R=C_6$) within the homologous series is due to its higher U.V. stability, which is in turn a direct consequence of its higher molar absorptivity and U.V. absorbance.

Since the ratio ($R^{\cdot}/ROO^{\cdot}$) during photo-oxidation is expected to be high due to the slow rate of oxygen diffusion, this provides the necessary conditions for the operation of the chain breaking (CB-A/CB-D) antioxidant mechanism. The above discussion has illustrated the well established fact that a very important function of the nickel dithiophosphate (NiDRP) is to act as light-stable precusors of the effective catalytic decomposers(5b,19,27). There is also sufficient data in the literature(5b,39,70) to suggest that a subsidiary function is to scavenge chain propagating radicals which are the photolysis products of hydroperoxides. These two main antioxidant modes of activity, as shown in Scheme 3.3, have been confirmed in model compound studies on NiDnBP and its corresponding disulphide (DnBDS) with a hydroperoxide (Sec. 5.3.1-5.3.3). A prominent oxidation product of the dithiophosphates (DnBTA) have been reported (Sec.3.3.1.1) to show a fair amount of photoantioxidant activity in polypropylene. Evidence from model compound studies suggests that not only is the thionophosphoric acid (DnBTA) an excellent peroxide decomposer, but that its mode of activity also involves both CB-A and CB-D processes. As shown in Scheme 3.3, the presence of the acid hydrogen is necessary for antioxidant activity of the protonic acid under oxidative conditions involving both radicals (R$^\cdot$,RO$^\cdot$ ROO$^\cdot$) and hydroperoxides. A simple CB-D activity followed by, and associated with both CB-A and PD-C activities, is proposed to account for the formation of the triester (IV), the phosphoryl disulphide (V) and the phosphoric acid (VI) in the very late stages of the oxidation of NiDnBP and/or DnBDS by TBH(Sec. 5.3.2-5.3.3). The proposed mechanistic pathways is therefore a clear reflection of the complimentary antioxidant mechanisms (PD and CB) involved in the activity of the nickel dithiophosphates.

Since the nickel dithiophosphates have a high absorbance in the critical region of the solar spectrum (290-350nm), they are then able to dissipate absorbed U.V. radiation and emit it harmlessly as thermal energy$^{(4b)}$ .In view of their high extinction coefficient within this region (Fig 3.11), in addition to the inherent deep purple colour, these complexes are therefore expected to behave in part as U.V. screens. A comparison of the effectiveness of HOBP and NiDnBP as U.V. screens for unstabilised PP (Fig. 3.13) not only suggests that U.V. screening makes only a minor contribution to the overall U.V. stabilising

function of the nickel complex, but also clearly indicates that the U.V. screening activity is fairly, but not linearly, dependent on the concentration of the complex. In contrast to the nickel complexes, the 2-hydroxybenzophenone U.V. stabiliser (HOBP) is shown to be a very effective screen for polypropylene. This compound has been known to operate primarily by absorbing U.V. light and re-emitting it as vibrational(thermal)energy although it has also been reported to scavenge radical species(18,19,47,88)
From Table 3.9 Figure 3.13, it can be seen that the contribution of U.V. screening to the overall stabilizing activity of HOBP is almost 90% while that of NiDnBP is only about 34%. It is clear from these results that like the 2-hydroxybenzophenone U.V. stabiliser, NiDnBP has a moderately efficient method of internally deactivating the absorbed light.

It has been shown (Fig. 3.11)that on increasing the alkyl chain length in the nickel dithiophosphates, their molar absortivity (316nm), and hence molar U.V. stabilizing activity in polypropylene was found to increase. Figure 3.14 clearly indicates that this relationship is also closely associated with the screening efficiency of the nickel complexes, although its contribution to the overall stabilising activity remains the same for all the alkyl substituents ($R=C_2$to C_9).

In th light of this discussion, it is therefore clear that U.V. screening plays a minor part in the U.V. stabilizing function of the nickel complexes (NiDRP), which is primarily associated with their peroxidolytic (PD-C) activity in addition to some chain breaking antioxidant activity.

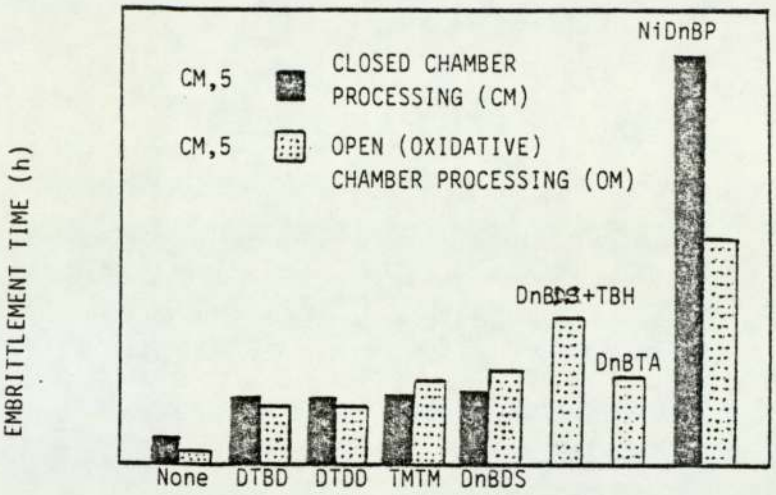


Figure 3.1. Effect of processing technique on photoantioxidant activity of sulphur compounds (concentration of all additives, 0.2g/100g).

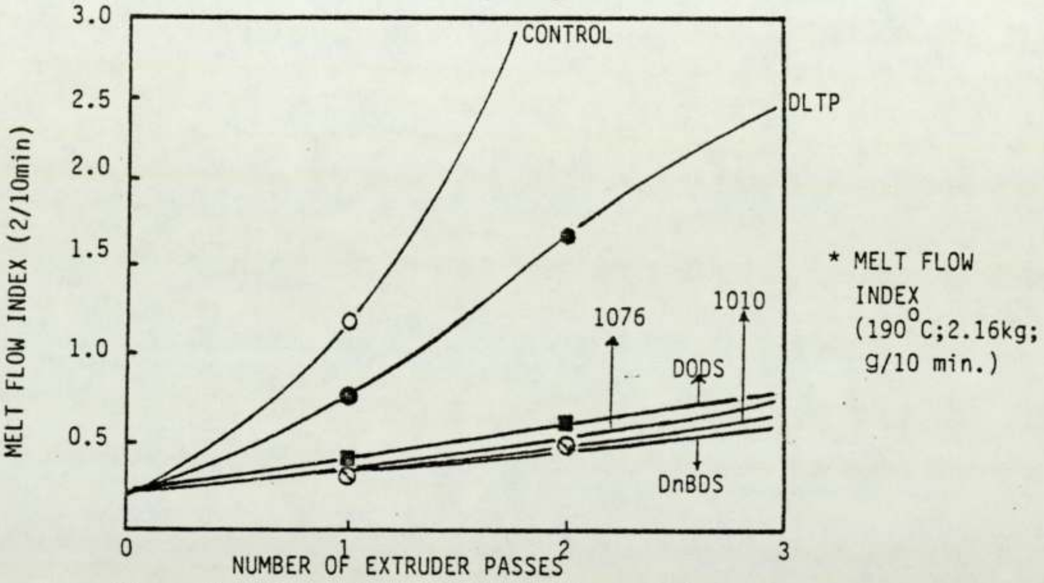


Figure 3.2 Comparison of disulphides and hindered pnenols as reprocessing stabilisers for polypropylene at 260°C (0.2g/100g)

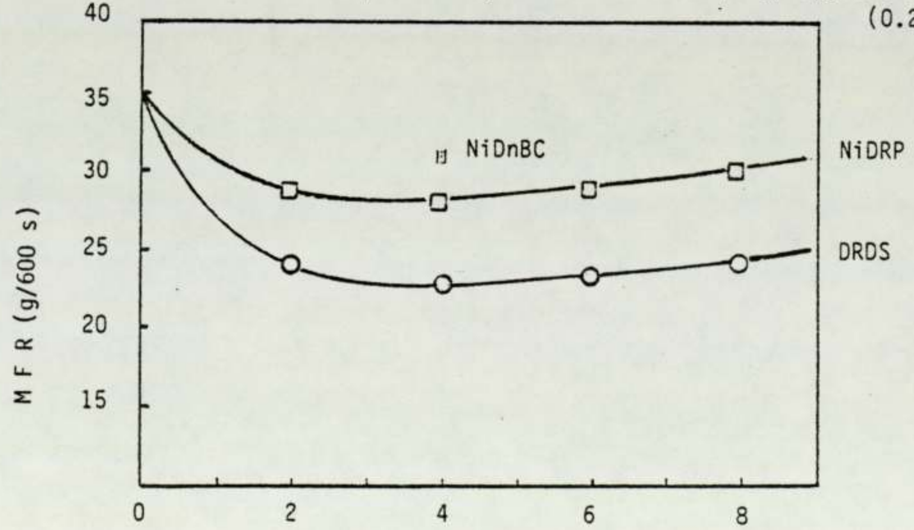


Figure 3.3. Effect of alkyl group in dithiophosphates on the melt stability of extruded (230°C) polypropylene (0.4g/100g).
MFR (190°C; 10kg; g/600 s)

Fig. 3.5a.

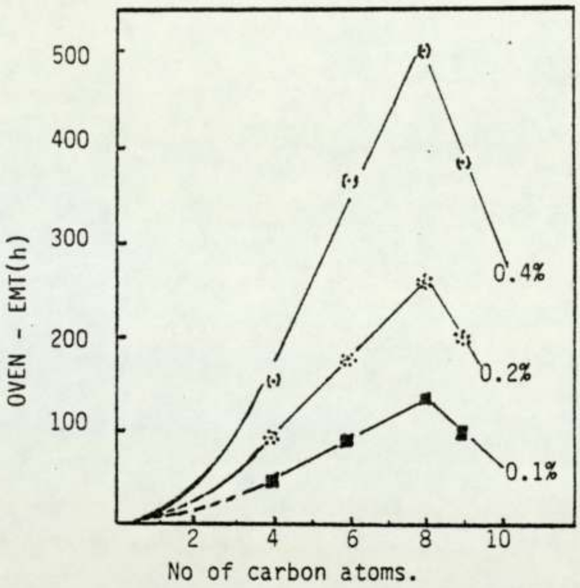


Fig. 3.5b.

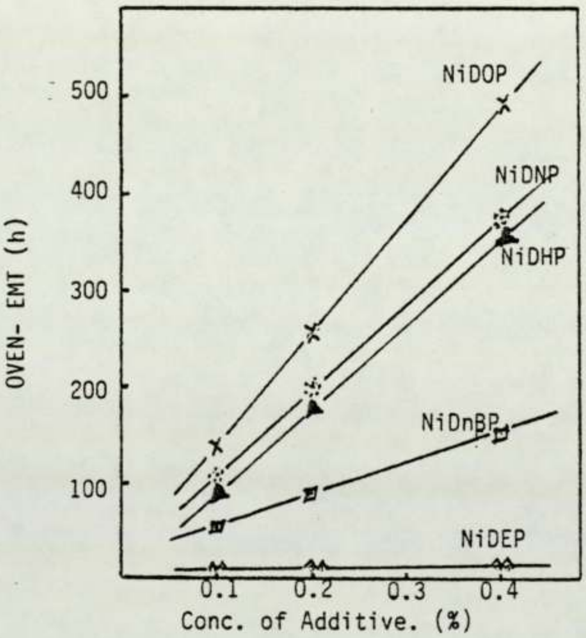


Fig. 3.4.

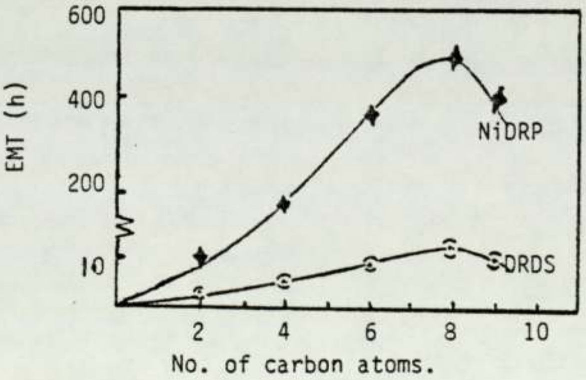


Fig. 3.5a. The effect of alkyl group on the thermal stability (CM, /190°C) Of PP films.

Fig. 3.5b. The effect of alkyl group on the thermal stability of PP

Fig. 3.4. Effect of alkyl group in dithiophosphates on the thermal stability of PP in an air oven at 140°C (CM,10 ; 0.4%)

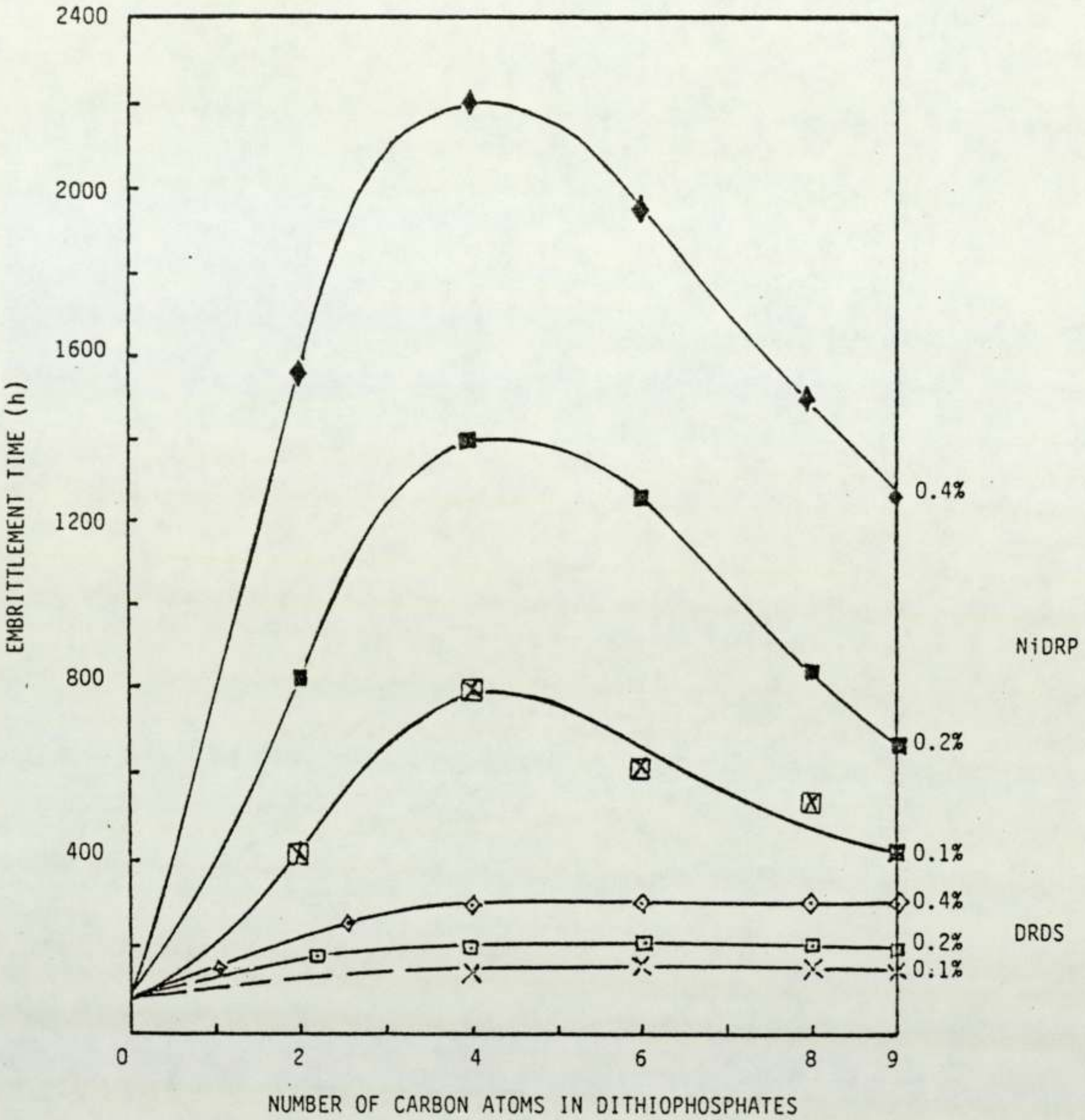


Figure 3.6 Effect of alkyl chain length and concentration (wt.) on the photo stabilizing efficiency of dithiophosphates (CM,10, 190°C)

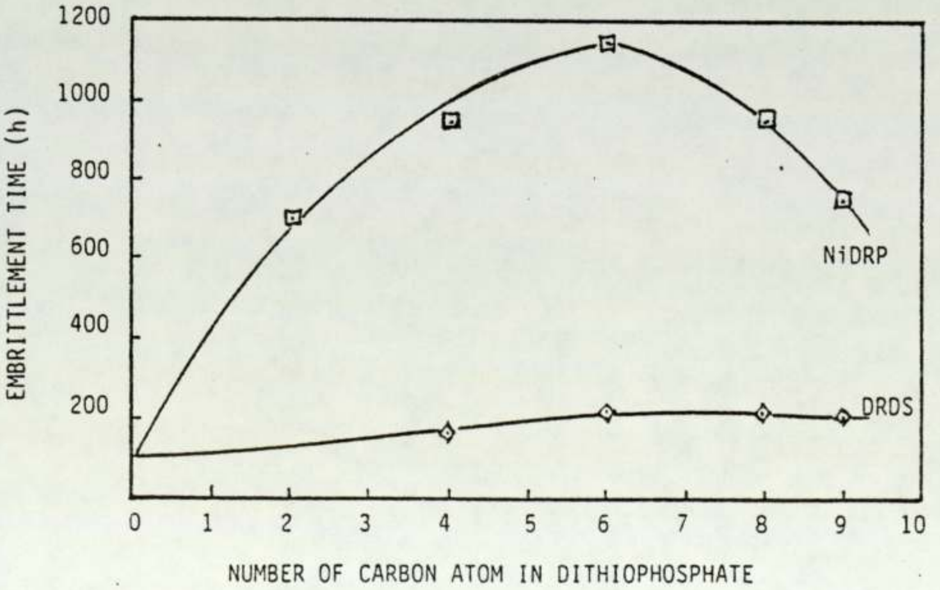
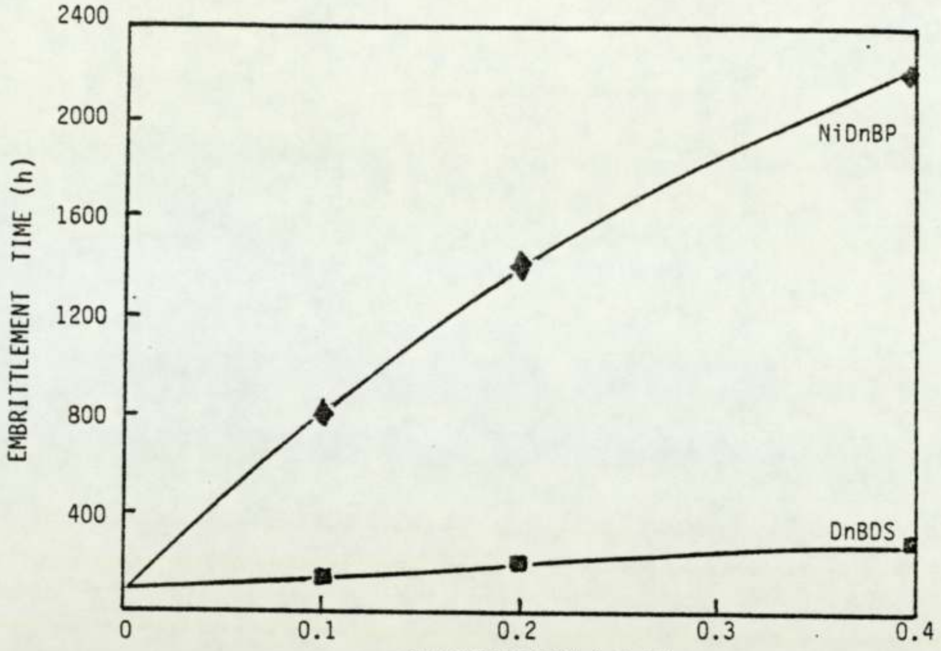
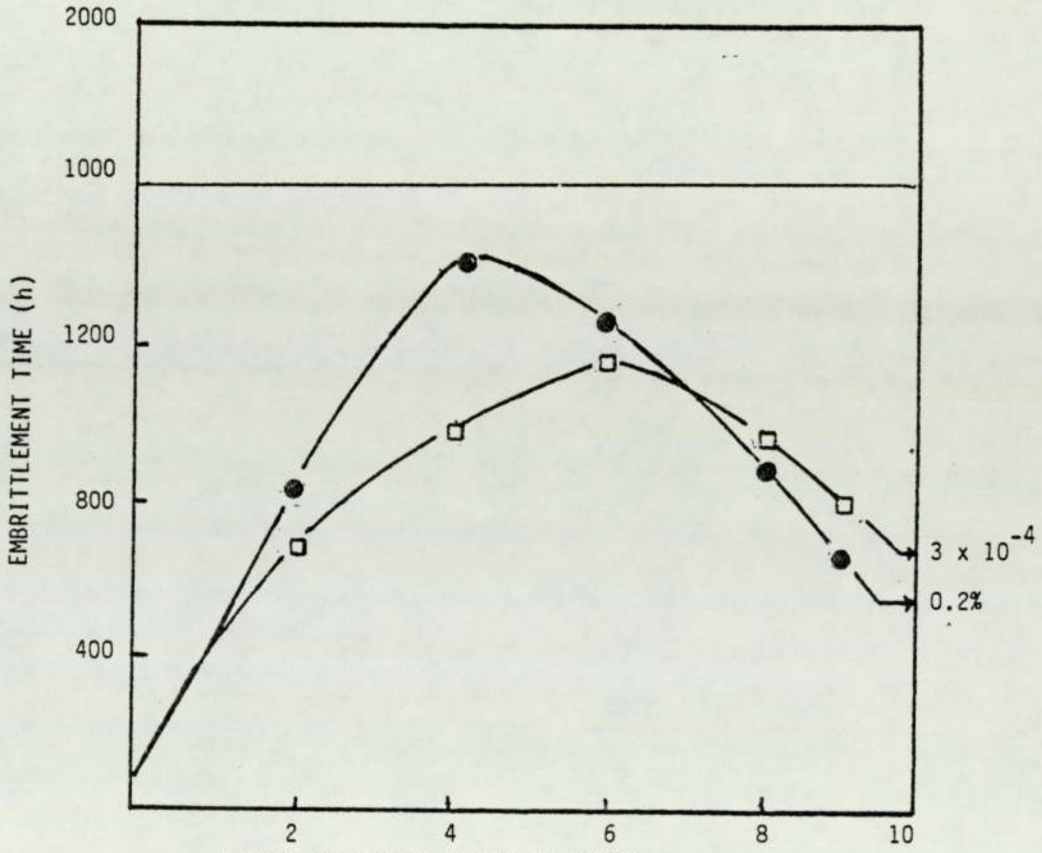


Figure 3.7 U.V. stabilising activity of dithiophosphates in PP (3×10^{-4}) as a function of the alkyl group (CM,10/190°C)



CONCENTRATION (wt %)

Figure 3.8 Effect of concentration of DnBDS and NiDnBP on the U.V. stability of PP



NUMBER OF CARBON ATOMS IN NiDRP

Figure 3.9 Effect of alkyl chain length on the U.V. stabilizing efficiency of NiDRP at concentrations 0.2% and 3 x 10^{-4} mol$(100g)^{-1}$

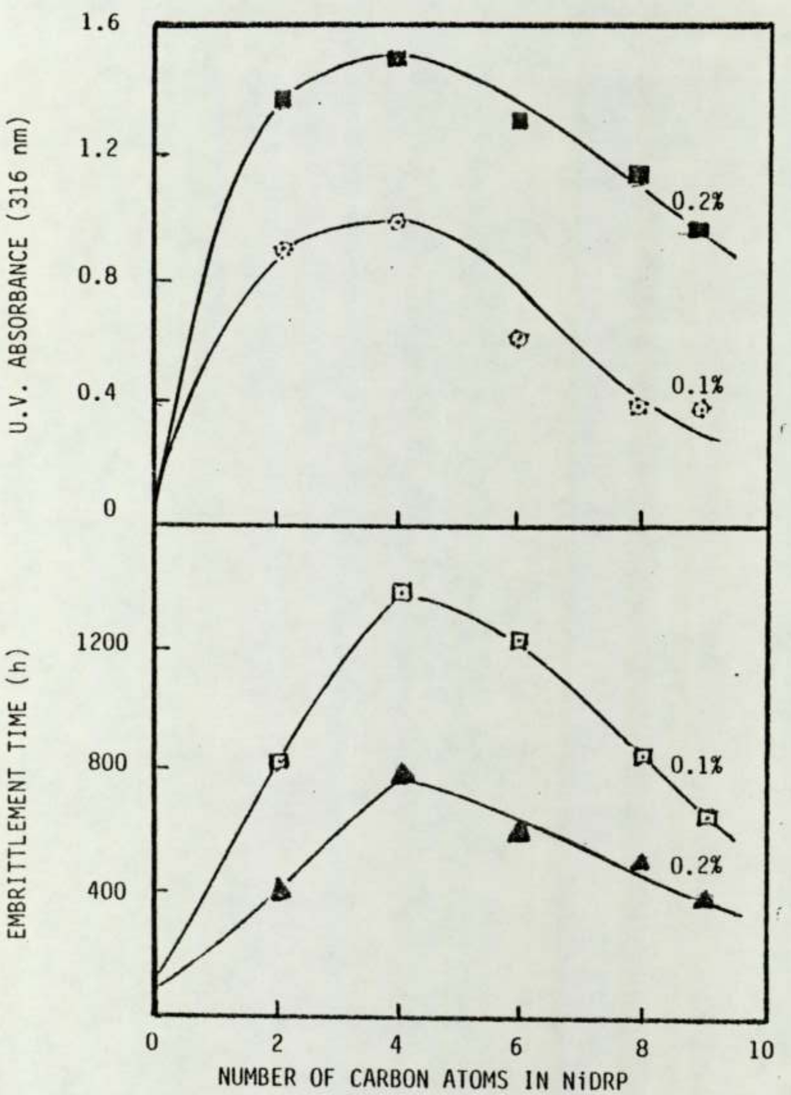


Figure 3.10 Relationship between U.V. absorbance (316 nm) and embrittlement times (h) of NiDRP in polypropylene (wt. %)

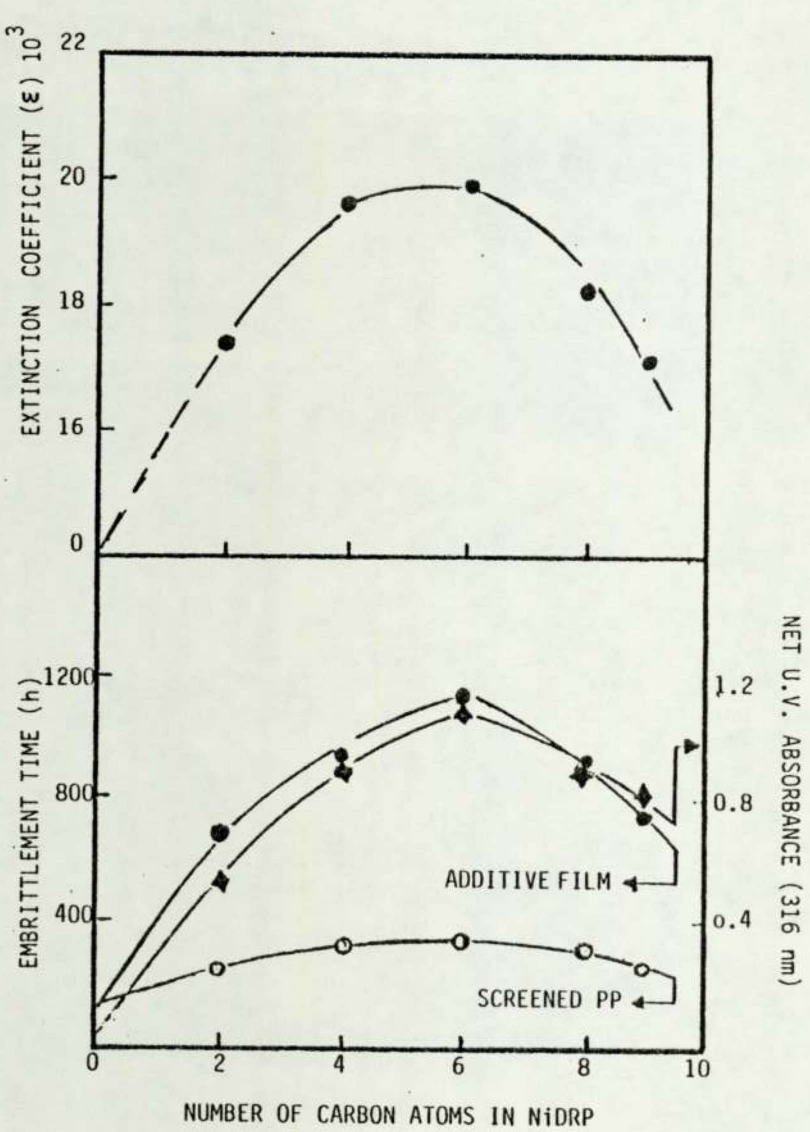


Figure 3.11 Relationship between (a) the molar absorptivity in hexane (316 nm), and (b) the net U.V. absorbance (316 nm), screening efficiency and the embrittlement times of NiDRP-stabilised PP films (3×10^{-4} g/100g) (concentration of NiDRP in hexane, 3×10^{-4} mol $^{-1}$)

Figure 3.12

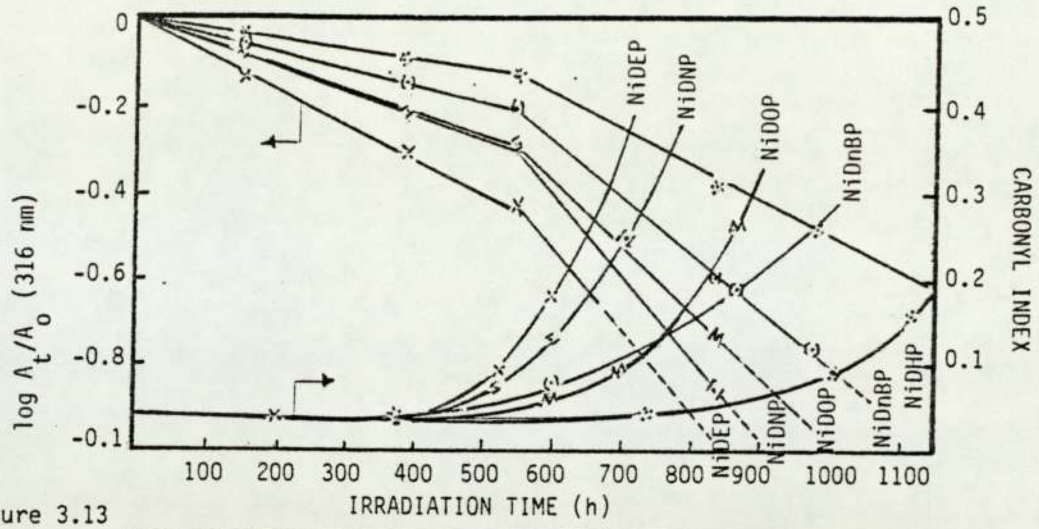


Figure 3.13

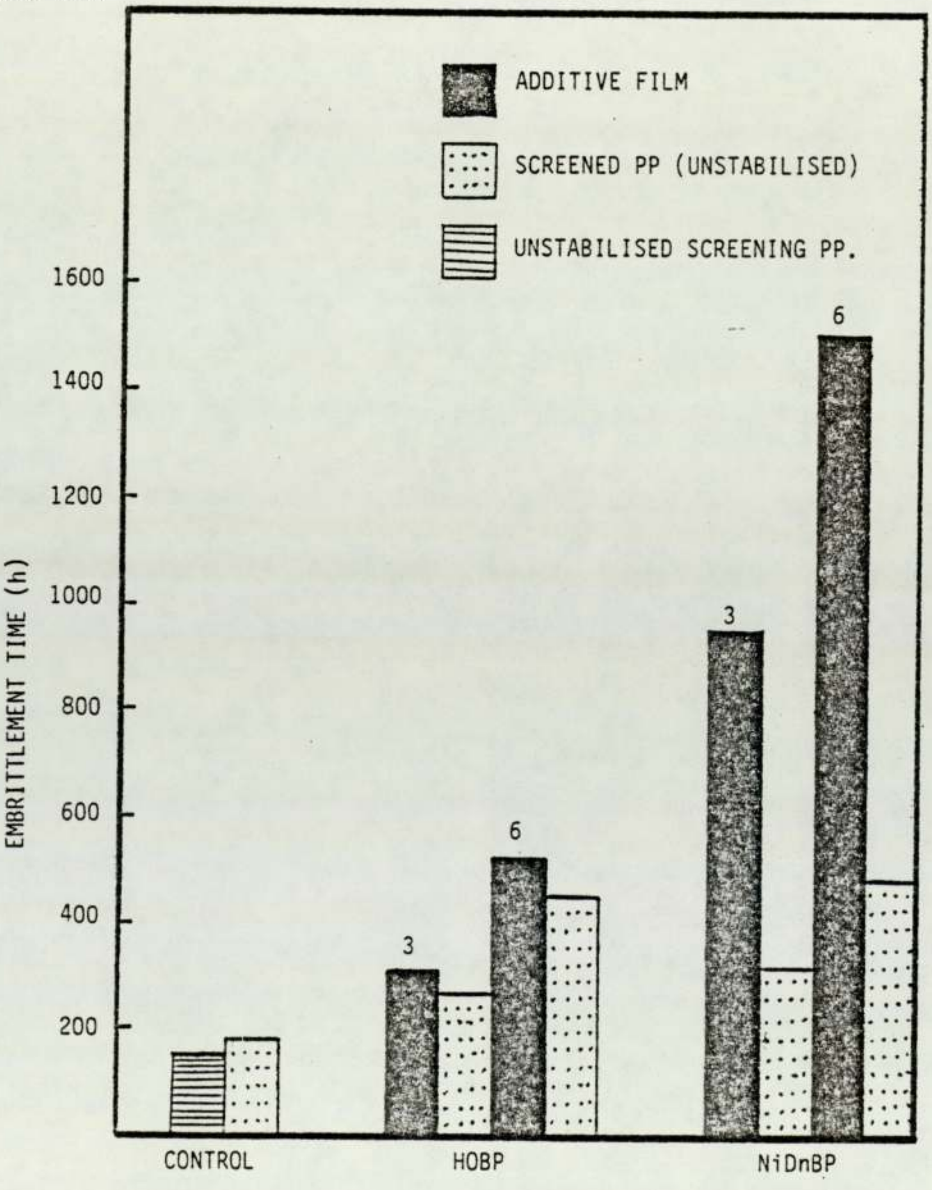


Figure 3.12 Correlation of U.V absorbance of NiDRP (316nm) in poly propylene with photo-oxidation induction period. Initial additive concentration, 3 x 10^{-4} mol/100g

Figure 3.13 Comparison of the U.V. screening efficiency of HOBP and NiDnBP (numbers on histogram are conc. x 10^{-4} mol.100g)

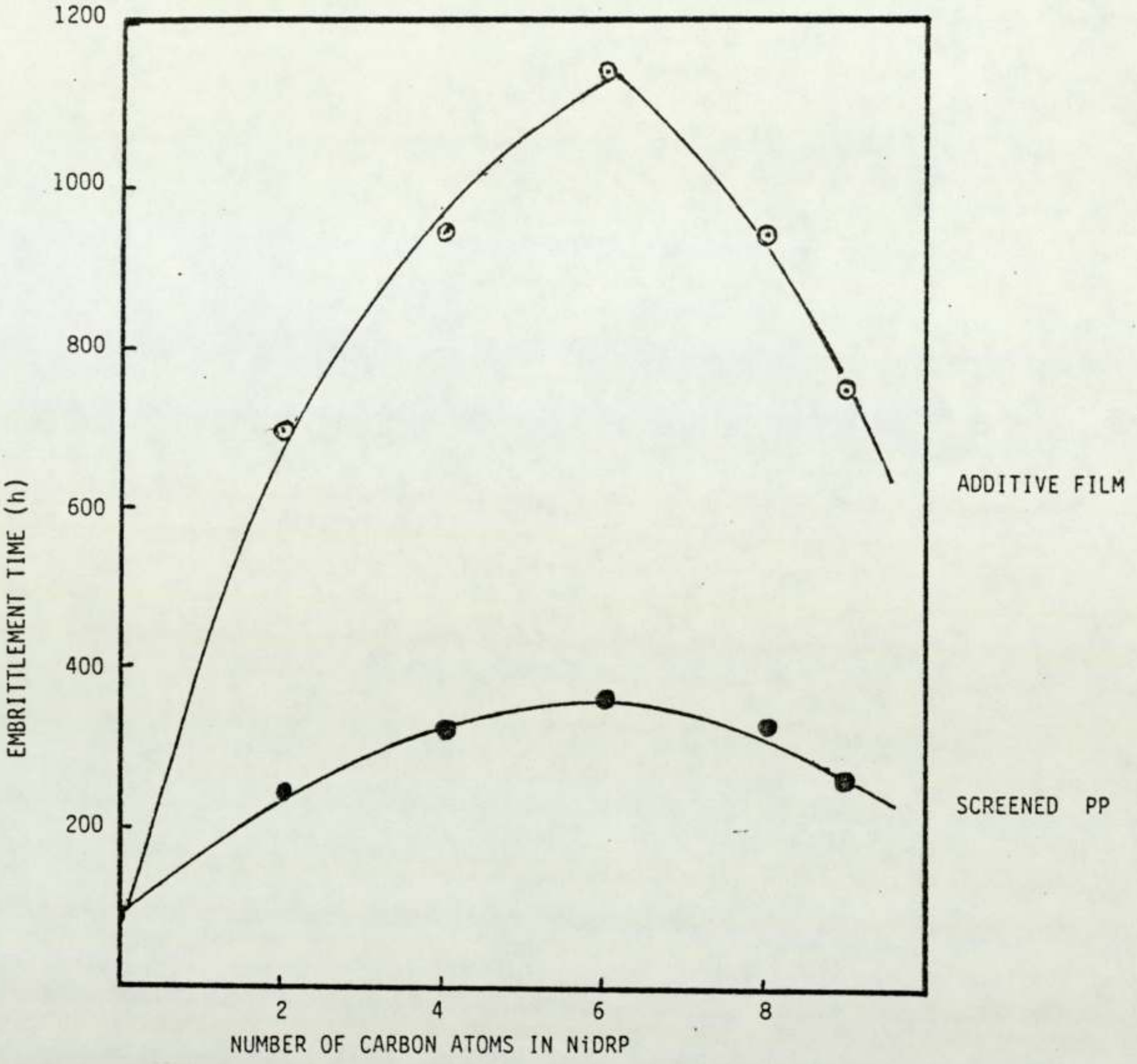


Figure 3.14 Relationship between the screening efficiency and the U.V. stabilising activity of NiDRP in polypropylene (3×10^{-4} mol/100g)

3.3A.3 Effect of Processing Temperature on the Antioxidant Activity of Dithiophosphates

It is now generally accepted(2,5b,19,35) that polymer hydroperoxides produced during thermal processing operations are the most important photo-initiators during the early stages of U.V. irradiation. The polymer hydroperoxides so formed undergo photolysis to alkoxy radicals with concomitant chain scission to form the carbonyl compounds as the secondary products. An important practical consequence of the thermal processing of polypropylene is the introduction of oxygen-containing functional groups which profoundly affect the service performance of the polymer.

It has been shown(2,5a,5b) that the pronounced increase in MFI (decrease in melt viscosity) observed with increasing processing severity (processing in the presense of excess oxygen or excessive temperatures) results from thermolysis of the in-chain hydroperoxides which then leads to chain scission. The effect of the thermal history on the photo-oxidative stability of unstabilised PP have also been shown (5b) to be detrimental in cases where severe processing conditions have been used.

The effect of processing temperature on the antioxidant activity of dithiophosphates was conveniently evaluated using DnBDS and NiDnBP at 0.2% mass concentration in poly propylene (CM, 10min). It is clearly seen from Fig. 3.15 that whilst the U.V. activity of the disulphide (DnBDS) is low compared to the nickel complex, its effectiveness is shown to be relatively unaffected by the processing temperature. The nickel complex, which is a much more effective U.V. stabiliser,is shown (Fig. 3.15) to be very sensitive to the effects of the processing temperature although the thermal antioxidant activity remains unaffected. This behaviour of the nickel complex, as has been extensively discussed in the previous section (3.3A.2.3),can be explained in terms of both the physical and chemical parameters which govern the antioxidant activity of most compounds. The most important of these are compatibility (solubililty) of the additive with the polymer and loss of additive either through volatilization or due to some chemical transformation during processing. Fig. 3.15 clearly indicates that the photoantioxidant activity of the nickel complex (NiDnBP) in PP is most effective when processed at 190°C(torque rheometer)whereas further increases in the processing temperature(200°C) only serves to reduce its effectiveness. This confirms the findings in a previous work done at much higher extrusion temperatures (220°C-270°C) regarding the high sensitivity of NiDnBP to changes in the processing temperature, as compared to DnBDS(91). At this point, it is important to report the existence of a temperature lag at each of the processing temperatures used (Fig. 3.16) due to heat lost (to the atmosphere) between the heater and the mixing chamber. Hence the actual melt temperatures after 10 minutes processing are somewhat lower than the heater temperatures. Thus whilst a heater temperature of

180°C only results in melt temperature of 176.5°C at the end of processing, the final melt temperatures observed at the higher processing temperatures of 190°C and 200°C are 184°.5°C and 191°C respectively (see also Table 3.10) The changes in the torque generated during processing (Fig. 3.16) is a clear reflection of the differences in the melt temperatures (3.5°C-9°C),hence it is conceivable that the solubility of the nickel complex in the polymer at higher melt temperatures may be more efficient than at the lower melt temperatures. This is confirmed in Figure 3.17 which shows the U.V. absorption spectra of the stabilised PP films and it is seen that the net U.V. absorbance (316nm) is highest for the sample processed at 190°C, this being a direct consequence of the solubility of the nickel complex in the polymer.

Since it has been shown (Sec. 3.3A.2.3) that the U.V. activity of the nickel complexes is highly dependent on their U.V. absorbance at 316nm, it is therefore not surprising that the best stabilizing effectiveness is shown by the sample processed at the higher temperature of 190°C (net A=1.20) as compared to that processed at 180°C (net A=0.93). The net U.V. absorbance of the sample processed at 200°C is shown to be only slightly higher (0.95) than that processed at 180°C despite the fact that the solubility of NiDnBP in PP is expected to be more efficient at the higher temperature (200°C). Furthermore the photoantioxidant activity of this sample (200°C,Anet= 0.95) is shown (Fig. 3.15) to be much less than that processed at 180°C (Anet = 0.93) and this phenomenon is attributed to the fact that higher amounts of the oxidation products (e.g DnBDS and DnBTA)are formed during processing at such high temperatures (200°C).

These transformation products have been known (5b,19,40a) to be weak U.V. stabilisers and may therefore catalyse rather than inhibit the photo-oxidation process on account of their photolytic instability. Figure 3.17 clearly illustrates the partial conversion of the nickel complex to the oxidation products, notably the disulphide (DnBDS) and the acidic species DnBTA both of which show very similar U.V. absorption spectrum with maxima between 275nm and 250nm.(inset to Fig. 3.171). More interestingly it is seen (Fig. 3.17) that the U.V. absorption band in the 275nm-250nm region which is similar to that shown by DnBTA (inset), is significantly more pronounced for the sample processed at 200°C as compared 190°C and 180°C.

It has previously been shown (5a,5b,18) that the rate of formation of hydroperoxides in polymers during processing is higher as the processing temperature is increased, although its concentration in a closed chamber processing is much less than during oxidative processing. It is therefore envisaged that the concentration and rate of formation of polymer hydroperoxides is higher during processing at 200°C compared to 190°C and 180°C. Consequently,the reduced activity of NiDnBP processed at 200°C as discussed previously, is clearly due to the formation of higher amounts of the photolytically unstable oxidation products via their interaction with the polymer hydroperoxides formed during processing (Figure 3.17).

In the light of the considerable evidence shown in this section, it is therefore apparent that the prior thermal history of NiDRP-stabilised PP does, to a major extent, determine their subsequent photo-oxidative performance. It has been clearly shown that the processing severity (increasing temperature) has a large effect on the equilibrium concentration of the nickel complex in PP, this being in turn dependent on its relative solubility in the polymer. The U.V. activity of NiDnBP has also been shown (Figure 3.15)to be related to these parameters and this is consistent with literature evidence(88) which suggests that molecularly-dispersed antioxidants are more effective than less soluble antioxidants. However, it is quite interesting to note that although increased processing severity has an adverse effect on the U.V.activity of the nickel complex, the thermal antioxidant activity remains altered (Fig. 3.15). This evidently suggests that the oxidation products formed at the higher processing temperatures (190°C-200°C) are themselves good thermal stabilisers.

Since it has been shown (3.3A.2.3) that the stabilisation of PP by nickel dithiophosphates is partly due to their screening contribution (30%) which is only secondary to their somewhat regulated peroxidolytic activity. It is therefore of utmost importance that appropriate conditions are chosen during processing in order to avoid any loss in the concentration of the complex through untimely conversion to the oxidation products which may be photolytically unstable during U.V. exposure.

3.3A.4 Photoantioxidant Synergism between Dithiophosphates and HOBP

The nickel dithiophosphates have been shown to be very effective U.V. stabilisers in polypropylene while the corresponding disulphides are much less effective, and their antioxidant activity is known (19,27,40b) to be primarily associated with the decomposition of hydroperoxides, provided they are U.V. stable.

The dithiophosphates show very powerful synergistic effects with the U.V. absorber, HOBP and this is clearly illustrated for both DnBDS and NiDnBP in Table 3.11 and Figure 3.18-3.19. It is seen from these results that the synergistic effect varies with the molar ratio of the two types of stabilisers at a constant total concentration ($6x10^{-4}$mol/100g). The thiophosphoryl disulphides which have been shown to be weak U.V. stabilisers in PP when used alone improves in activity when synergised with HOBP For these stabiliser systems (DnBDS+HOBP), it is quite clear that the photoantioxidant activity and the % synergism is increased proportionately as the concentration of the U.V. absorber is increased (Table 3.11), and at a 2:1 ratio of HOBP to DnBDS, the stabiliser system is more than thrice as effective as DnBDS alone or almost twice as effective as HOBP alone at the same total concentration ($6x10^{-4}$).

These result clearly suggest that a major function of the disulphide (DnBDS) is to protect the U.V. absorber from destruction by peroxides during processing and on U.V. exposure. The U.V. absorber on the other hand protects the disulphide from photolytic destruction both by screening of U.V. light and by sacrificially quenching the photo-excited reactive species formed from the disulphide during irradiation(19,40b)

However, the systems containing NiDnBP and HOBP show a different behaviour altogether since the synergistic effect attains a maximum at a 1:2 ratio of HOBP to NiDnBP. This indicates that in contrast to the previous system (DnBDS:HOBP), the nickel complex not only protects the U.V. absorber from destruction by peroxides during processing and on subsequent U.V. exposure, but also complements the screening effect of the U.V. absorber, HOBP, during U.V. exposure. This illustrates an important trend in U.V. stabilisation technology toward multicomponent systems of antioxidants and U.V. stabilisers which reinforce one another by complementary mechanisms. It is an established fact (19,40b,47) that HOBP is unable to destroy or inhibit the formation of hydroperoxides during processing and on subsequent U.V.exposure which of course contrasts with the peroxidolytic activity of the dithiophosphates. The synergism resulting from the combination of the peroxide decomposers (DnBDS & NiDnBP) with the U.V. absorber, HOBP, is therefore in part due to minimisation of the deleterious effects of hydroperoxides formed during processing on HOBP. Thus HOBP is able to exert its effect during U.V.irradiation by prolonging the presence and hence the activity of the dithiophosphate.

The relationship between the first order decay of the nickel complex in the synergistic systems (NiDnBP:HOBP) and the photo-oxidative induction period in polypropylene is illustrated in Figure 3.20. That the length of the induction period roughly corresponds to the time for the disappearance of the nickel complex from each system clearly indicates that the U.V. activity of these systems is highly influenced by the nickel complex, although the inclusion of HOBP in the system is absolutely vital in order to prolong the presence of the former in the polymer. Some typical U.V. absorption spectra of the changes occuring in these systems during photo-oxidation is shown in Figure 3.21.

The effect of the alkyl substituent in the nickel complex on the photoantioxidant effectiveness of these synergistic systems is shown in Table 3.12 and Figures 3.22-3.23. These results clearly illustrate the exceptionally high level of synergism that can be achieved with these systems, and the mechanism of the synergistic action as discussed previously, involves the mutual protection of each other during processing and on U.V. exposure and hence lengthen the period of their independent but complementary action. From Fig. 3.22, it is seen that the trend in the photoantioxidant activity of the synergistic systems roughly parallels that of the nickel complexes alone at the same total concentration (weight%) and this is attributed to the dilution of the antioxidant function in the NiDRP molecule by the inert alkyl chain. This is also reflected on the trend in % synergism within the series since this is seen to increase with increasing chain length of the alkyl group (see table 3.12),and this interestingly is associated with the reduced U.V activity of the nickel complex on its own (without HOBP).

Another interesting feature of this work is that a combination of the nickel complex (NiDnBP) and its corresponding disulphide (DnDBS) alone (without HOBP) show antagonistic rather than synergistic effect during U.V. irradiation. This is illustrated in Table 3.12 and Figure 3.23. This behaviour may be due to the presence of a high concentration of photo-excited reactive species formed from both additives during U.V. irradiation. It is a well established fact$^{(27,40b,86)}$ that the disulphide (DnBDS) is one of many oxidation products of the nickel complex (NiDnBP), most of which are known to be photolytically unstable. It is therefore reaso nable to assume that the processing of NiDnBP in the presence of additionalDnBDS shall undoubtedly result in the formation of a rather higher than usual concentration of the photolytically-unstable intermediates which may catalyse rather than inhibit the photo-oxidation process in PP.

It must however be pointed out that this antagonistic behaviour between DnBDS and NiDnBP in PP may be less probable if processed in a less oxidisable substrate such as LDPE, in view of the slower rate of formation and concentration of hydroperoxides in this polymer.

3.3A.4.1 Screening Efficiency of the Synergistic Systems in PP

The role of the U.V. absorber, HOBP, on the screening efficiency of the synergistic systems is clearly illustrated in Table 3.13 and Figures 3.24 - 3.25.

In accordance with their effectiveness in stabil ising PP against photo-oxidation, the screening efficiency of the

[DnBDS:HOBP) systems is entirely dependent on the concentration of HOBP in the system. This behaviour is not surprising since HOBP is the only component with the ability to screen U.V. light, hence the activity of these systems as U.V. screens for unstabillised PP is seen to improve with concomittant increase in the concentration of HOBP in the system (Figure 3.24).

The role of HOBP on the screening efficiency of [NiDnBP : HOBP] systems is not as straight forward as is obtained in the previous system and this is simply due to the fact that both components possess the ability to screen U.V. light. It has been shown (Section 3.3A.2.3) that U.V. screening plays a minor part (30%) in the overall U.V. stabilising function of the nickel complexes, which of course is primarilly associated with their peroxidolytic (PD-C) activity. Table 3.13 shows that the screening efficiency of these systems is most effective of equimolar ratio of both components,although this is not necessarily the best ratio for overall photo-stabilising activity of these systems. This clearly suggests that the U.V. screening activity of these systems is a direct consequence of the combined, and yet independent, screening capabilities of both components.

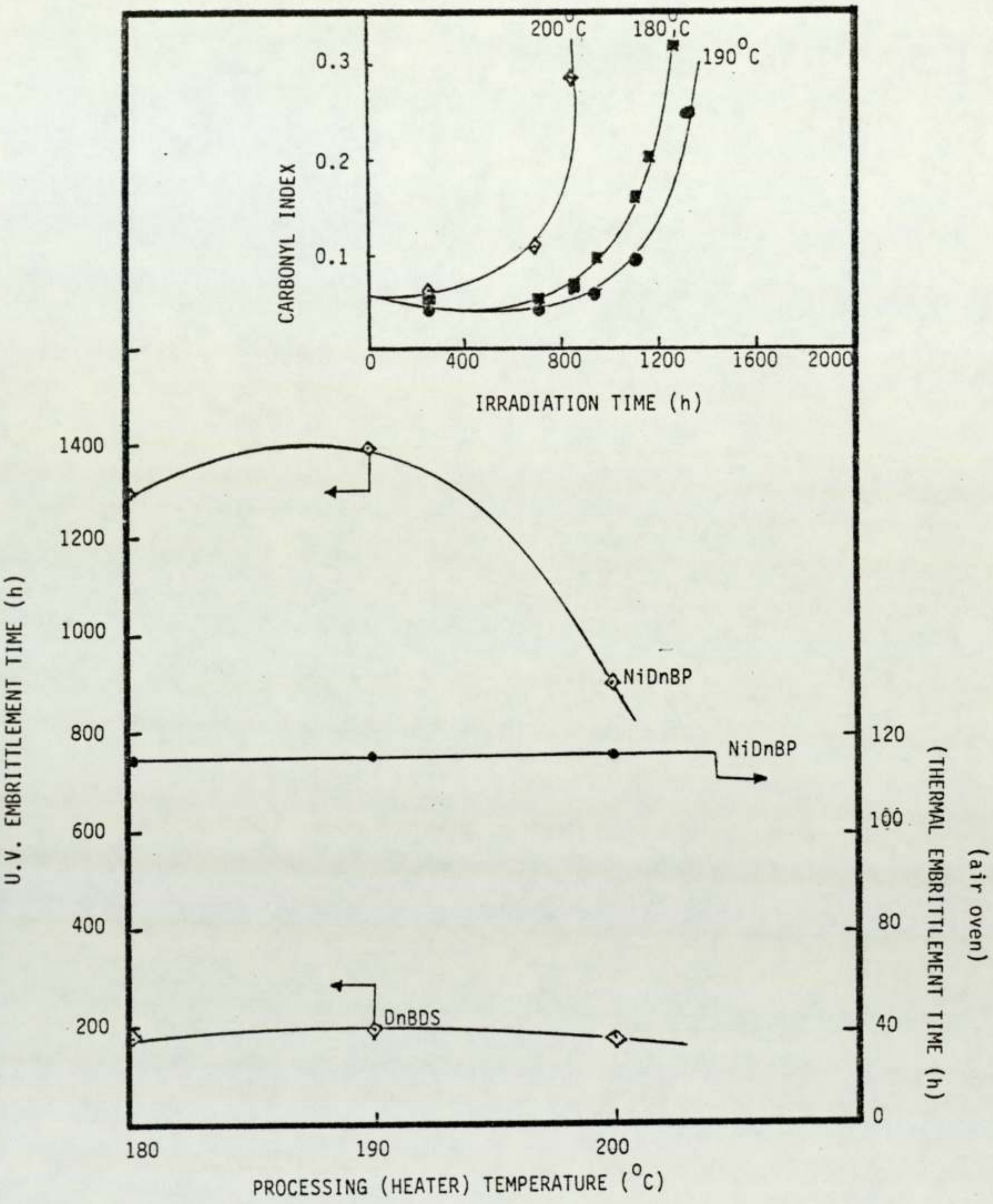


Figure 3.15 Effect of processing (heater) temperature on the thermal and U.V.-stabilising effectiveness of dithiophosphates (closed mixer 10 min; 0.2g/100g). in PP . Inset compares the rate of carbonyl formation during U.V. irradiation of PP films containing NiDnBP

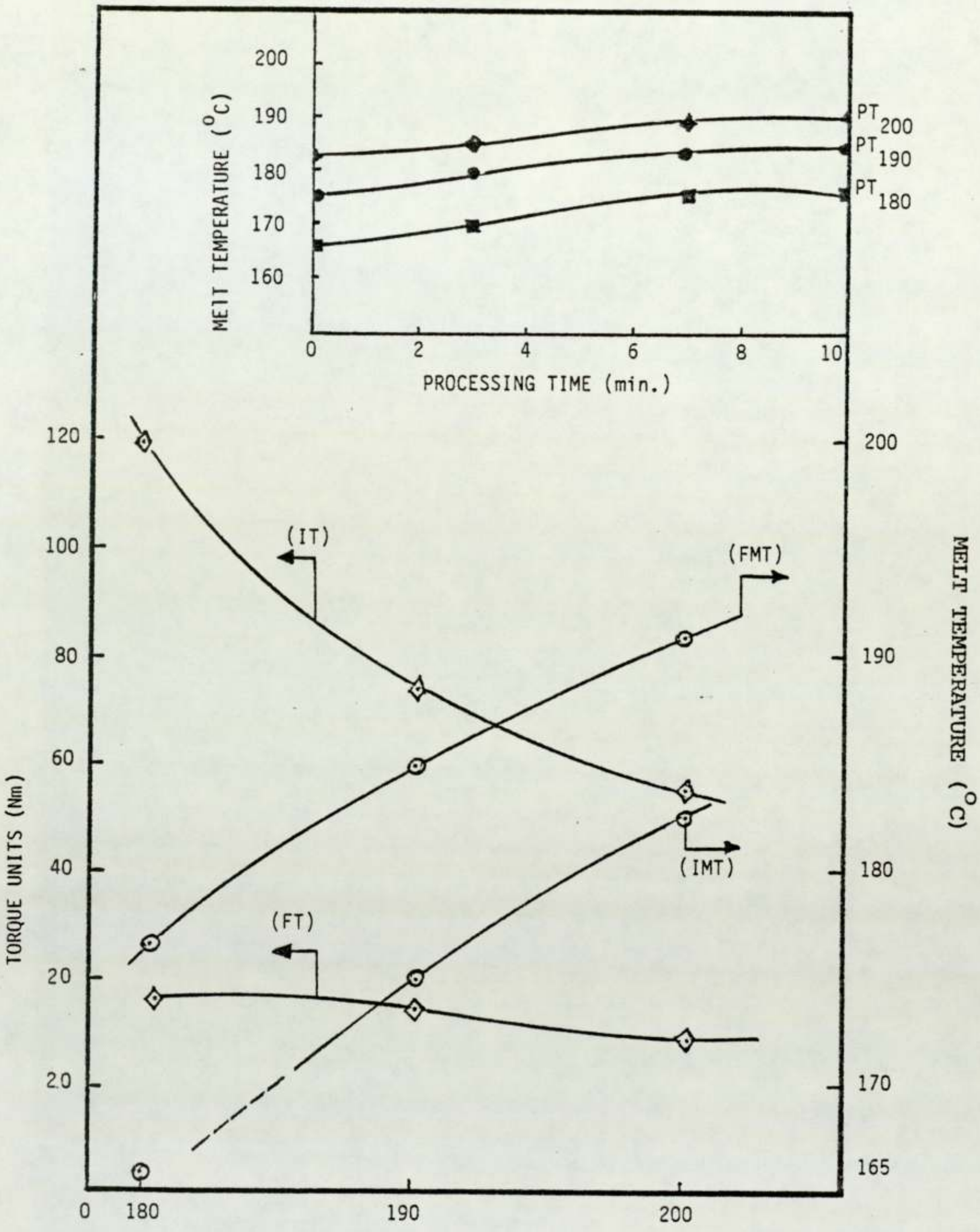


Figure 3.16 The effect of processing (heater) temperature in the torque rheometer on the melt temperature and torque generated during processing of dithiophosphates. Inset shows rate of increase in melt temperature as a function of the processing time (CM,10)

(IT) - Initial torque
(FT) - Final torque
(IMT) - Initial melt temperature
(FMT) - Final melt temperature

Figure 3.17

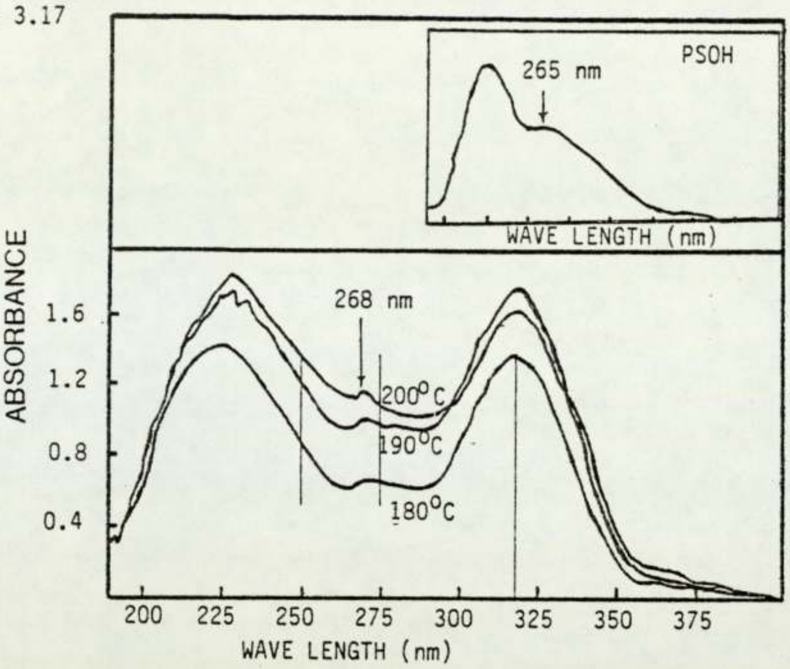


Figure 3.18

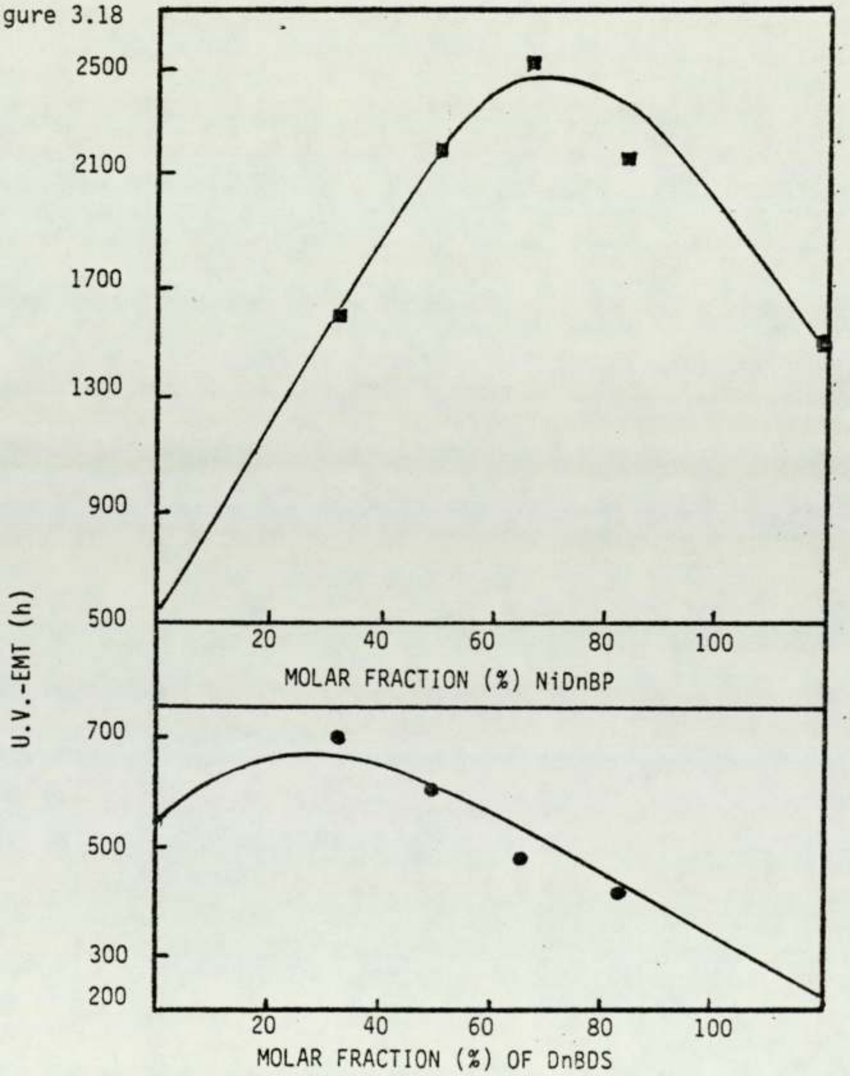


Figure 3.17 Effect of the processing(heater)temperature on the U.V. absorbance (316 nm) of NiDnBP in polypropylene. Inset shows the U.V. spectrum of thionophosphoric acid (DnBTA). Numbers on the spectra are processing (heater) temperatures (^{o}c)

Figure 3.18 Synergism between dithiolates and HOBP during U.V.-irradiation of polypropylene films. Total conc. of additives, 6 x 10^{-4}mol/100g

Figure 3.19

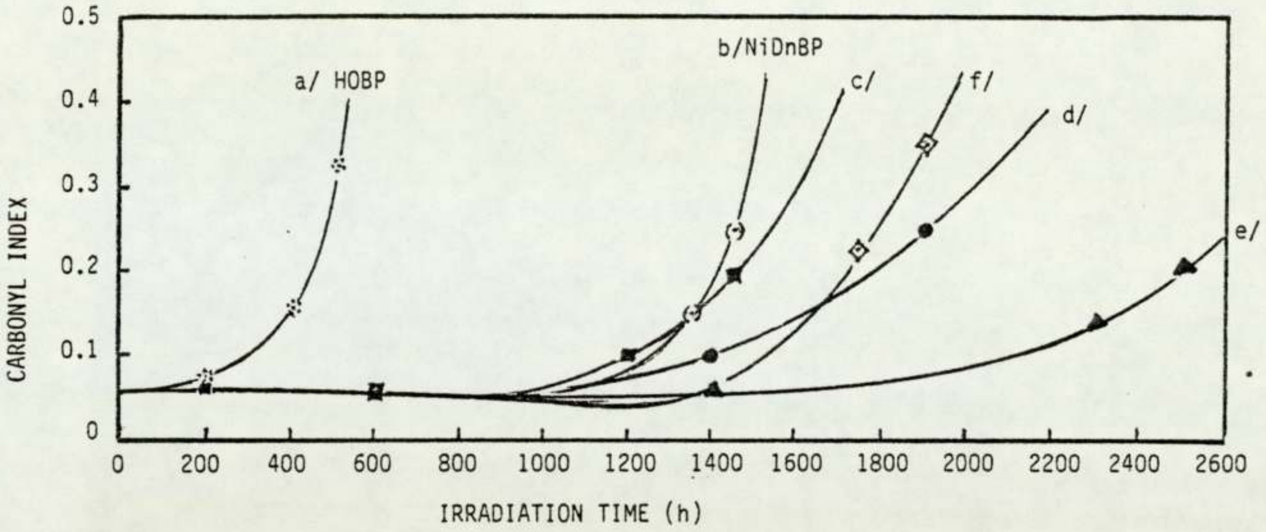


Figure 3.20

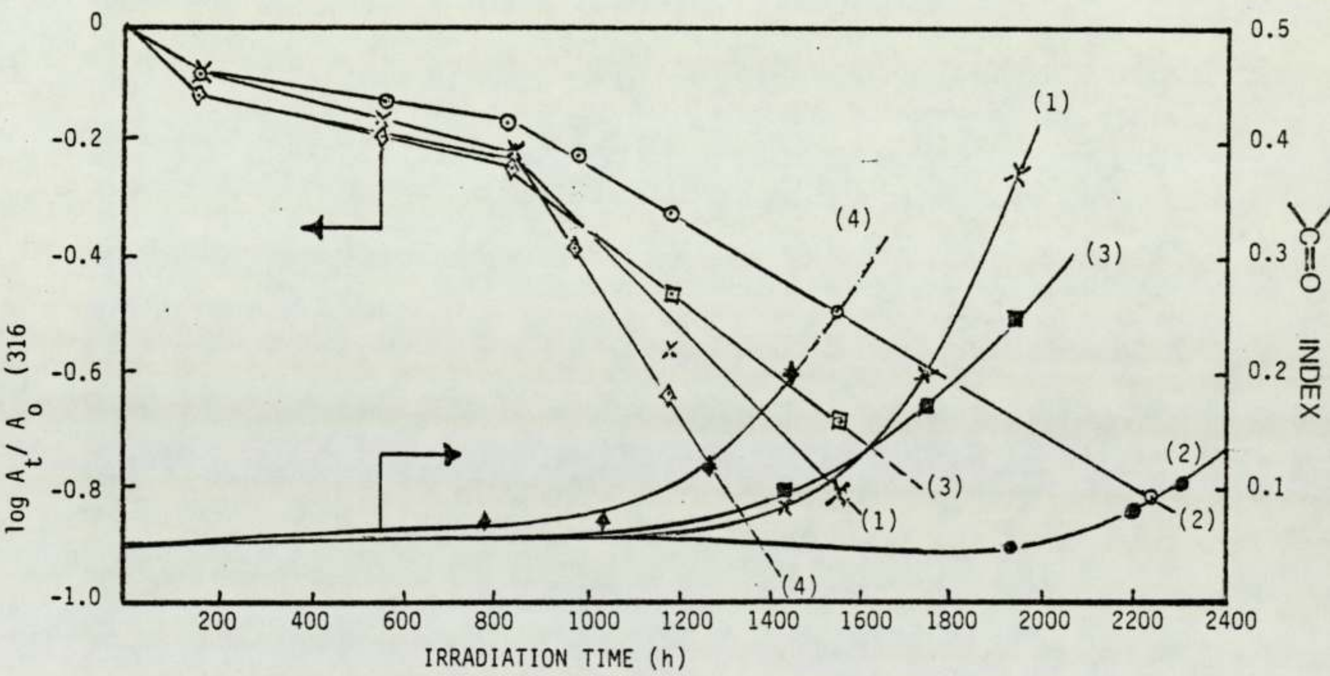


Figure 3.19 Synergism B/W NiDnBP and HOBP on photostabilisation of polypropylene Total additive concentration - 6 x 10^{-4} mol/100g (190°C)

	EMT (h) ± 50
a/ HOBP	520
b/ NiDnBP	1550
c/ NiDnBP + HOBP 2 x 10^{-4} + 4 x 10^{-4})	1600
d/ NiDnBP + HOBP 3 x 10 + 3 x 10)	1050
e/ NiDnBP + HOBP 4 x 10^{-4} + 2 x 10^{-4})	2650
f/ NiDnBP + HOBP 5 x 10^{-4} + 1 x 10^{-4})	1950

Figure 3.20 Relationship between the first order decay of 316 nm band of NiDNBP in [NiDnBP:HOBP] systems and photo-oxidative induction period in polypropylene (CM,10)

(1) 5:1 ratio (2):1 ratio (3) 1:1 ratio (4) 1:2 ratio (Total concentrations 6 x 10^{-4} mol/100g)

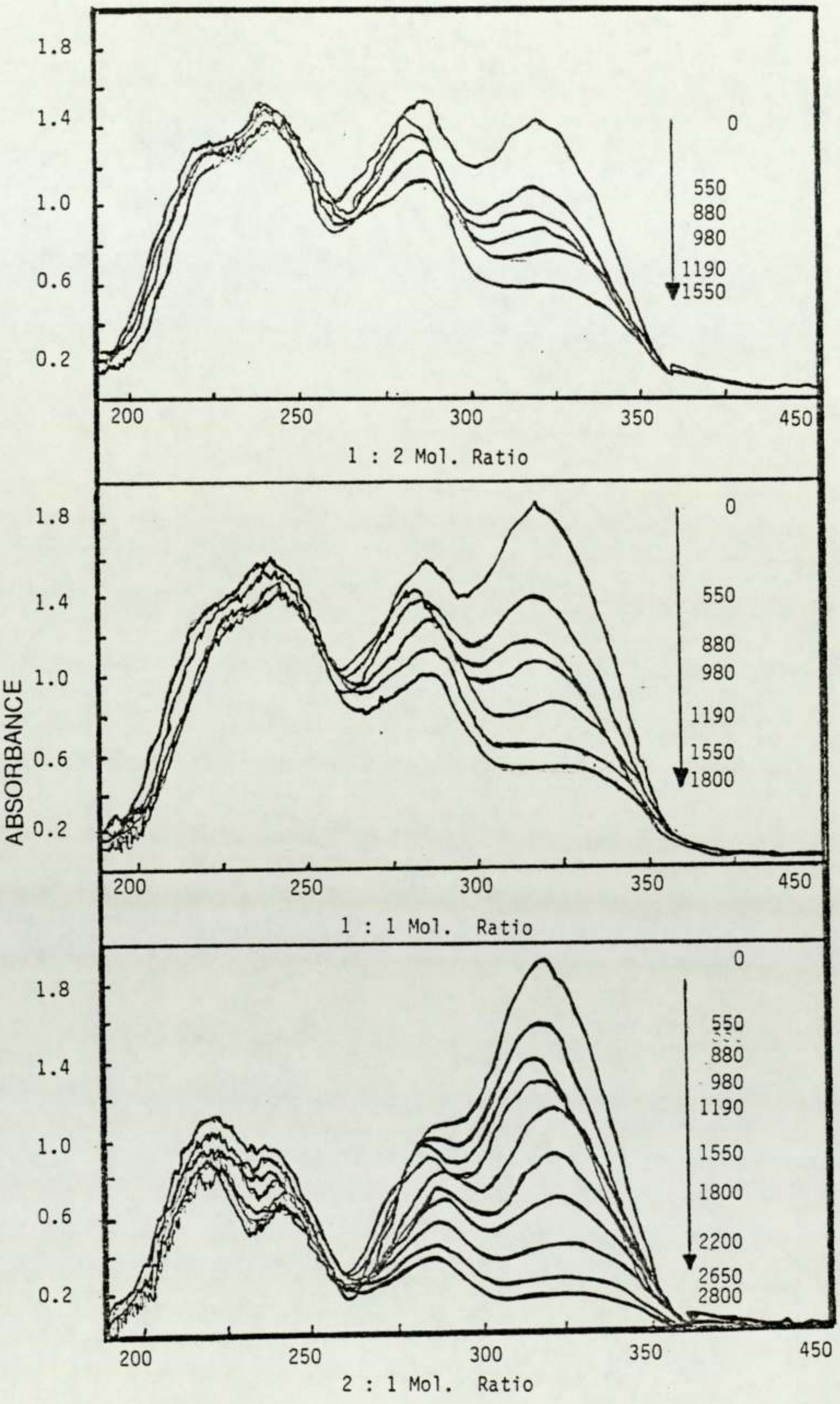


Figure 3.21 Typical U.V. spectra of changes occuring during U.V. irradiation of [NiDnBP : HOBP] synergistic systems. Numbers on the spectra represent the U.V. irradiation times in hours.
Total concentration in all systems = 6×10^{-4} mol/100g

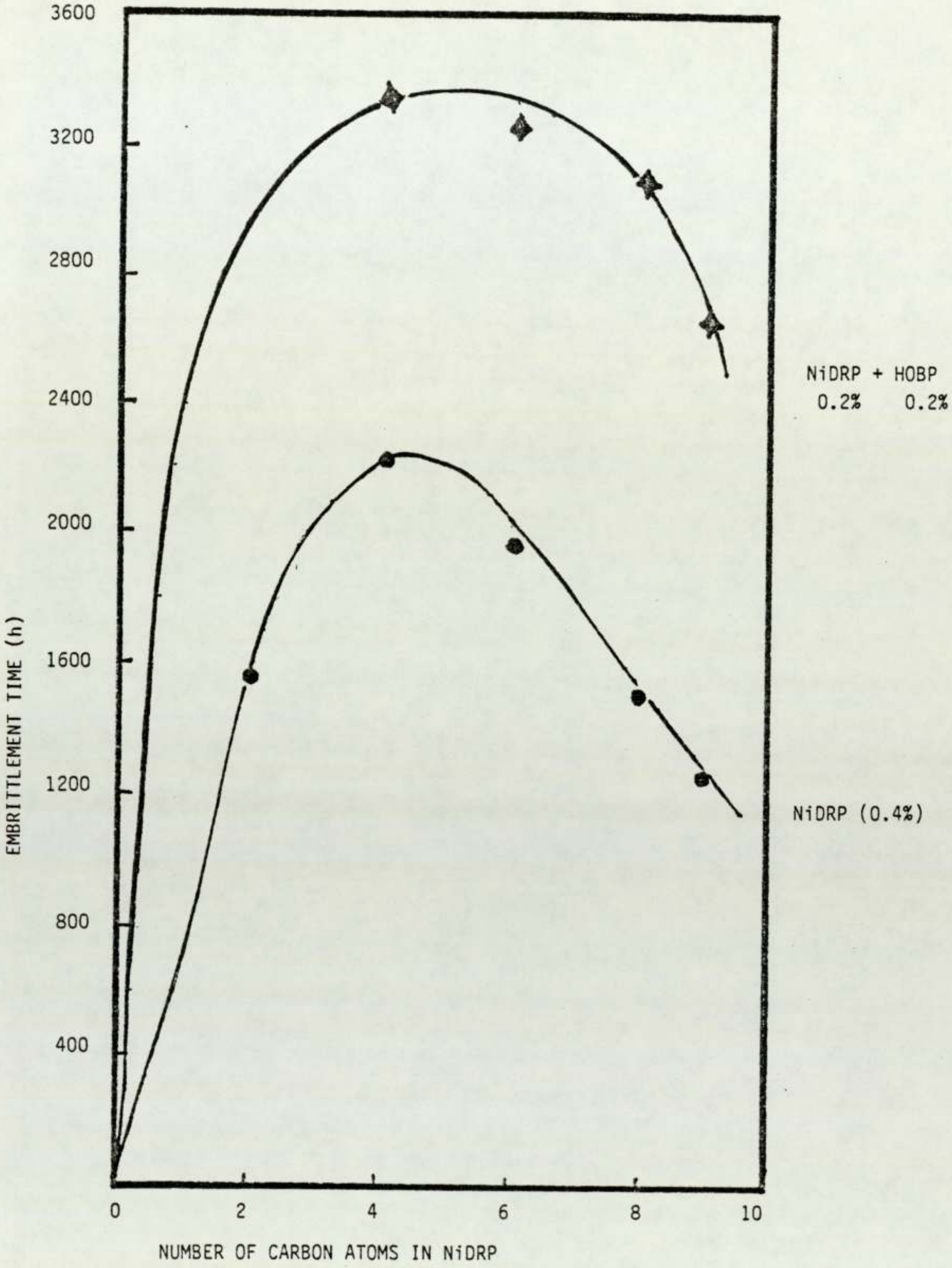


Figure 3.22 Effect of alkyl group in NiDRP on their photoantioxidant synergism with HOBP in polypropylene (CM,10/190°C)

	(1) NiDnBP	+	HOBP	3350
	(2) NiDHP	+	HOBP	3250
	(3) NiDOP	+	HOBP	3125
	(4) NiDNP	+	HOBP	2650
	(5) TIN 770	+	HOBP	2900
CM,10 —	(6) NiDnBP	+	DnBDS	850
OM,15 —	(7) NiDnBP	+	DnBDS	850

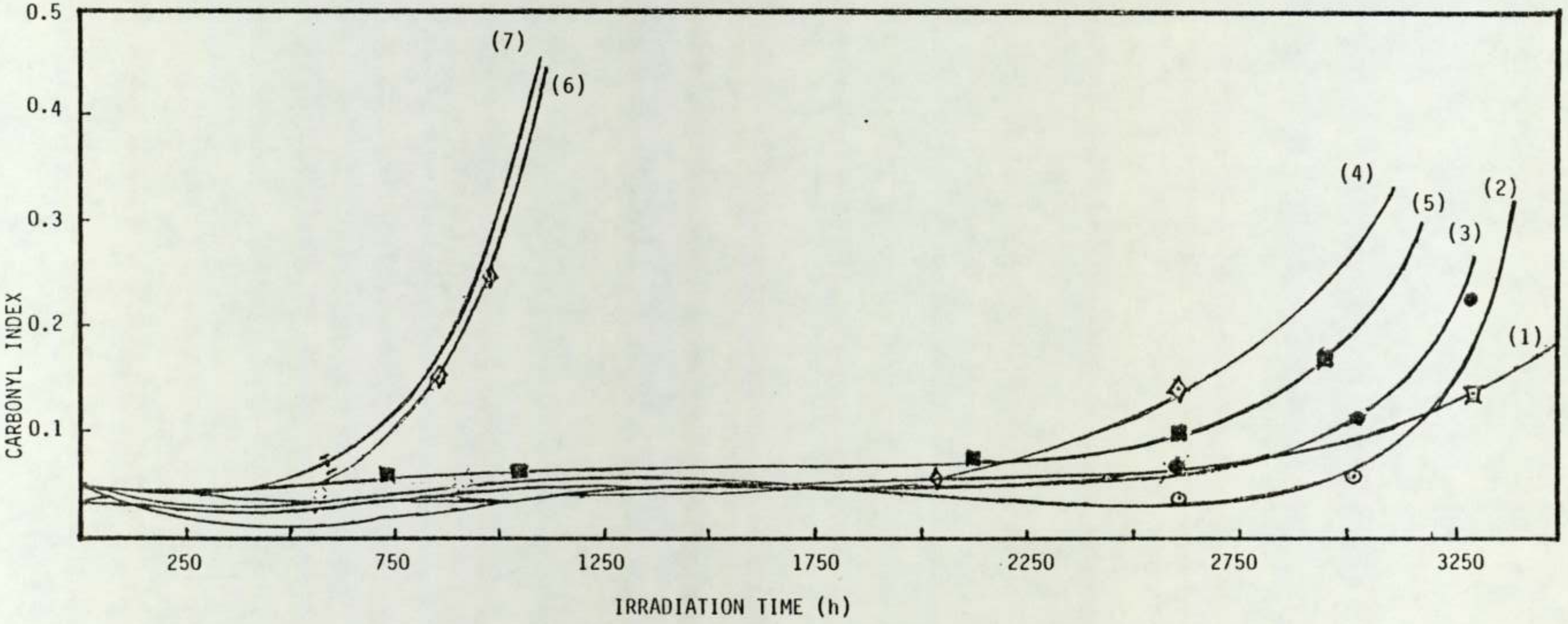


Figure 3.23 Synergistic and antagonistic effects on U.V. stability of polypropylene (CM,10/190°C)

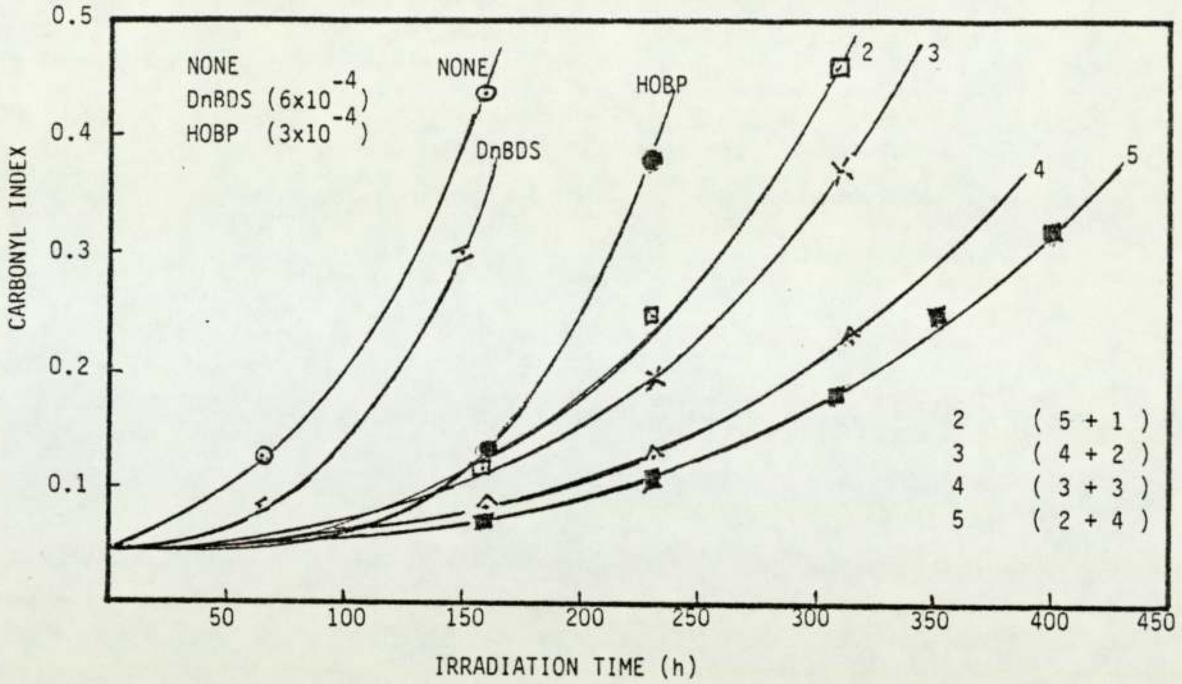


Figure. 3.24. DnBDS + HOBP (conc. x 10^{-4} mol/100g)

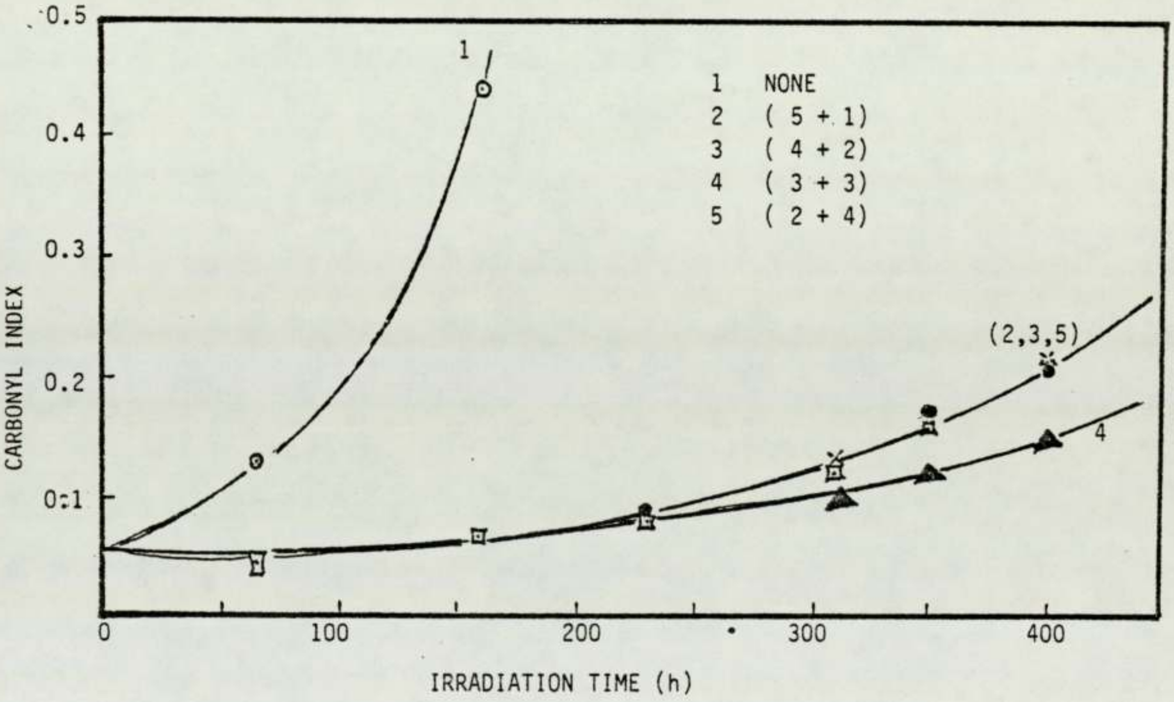


Figure. 3.25. NiDnBP + HOBP (conc. x 10^{-4}mol/100g)

Screning efficiency of synergistic DTP| HOBP systems in PP.

3.3B LDPE Normal Samples

As previously mentioned, the work done in LDPE as normal samples represents only a limited evaluation of the effectiveness of the dithiophosphates as U.V. stabilisers in LDPE compared to other commercially-available U.V. stabilisers.

It is an established fact the LDPE is inherently much more flexible (less crystalline) than polypropylene and this is reflected on their much higher intrinsic photo-oxidative lifetimes(6). A direct consequence of the low crystallinity is the common observation that the carbonyl index of irradiated LDPE films often reaches extremely high values (>40) before actual physical embrittlement occurs, and as will be shown in a later section (Chapter 4, Sec. 4D.2) the time to 50% loss of the original elongation (T.50) generally occurs at relatively low carbonyl index values (<10). In the light of these facts, the irradiation time when the carbonyl index reaches a constant value (>C=0,10) is compared for the different systems studied in this section in order to maintain a consistent means of evaluation in the absence of any measurements on the mechanical properties during U.V. exposure.

3.3B.1 Photoantioxidant Activity of Dithiophosphates(CM.10)

The stabilisation of LDPE by dithiophosphates alone (nickel complex and corresponding disulphides) is shown in this study (Table 3.14) to be inferior to that of the commercial U.V. stabilisers, Tinuvin 770 and HOBP at the low concentration used (0.2%). This behaviour greatly contrasts the activity of the same additives in PP since the superiority of the nickel dithiophosphates over the commercial U.V. stabilisers was clearly illustrated (Sec. 3.2A). The relatively poor performance of the dithiophosphates alone (DnBDS & NiDsBP) in LDPE as compared to Tinuvin 770 and HOBP, is also illustrated in Figure 3.26

which, however, does indicate that the nickel complex is most effective during the early stages of photo-oxidation (>600h) when hydroperoxides are the primary photo-initiators. This is reflected in the slower byild-up in the concentration of the carbonyl species for the sample containing NiDsBP, during the early stages.
Since it is now well established that the dithiophosphates function primarily as peroxide decomposers, it is therefore reasonable to assume that they are likely to be much more effective in PP than in LDPE, the difference being mainly as a result of the more rapid formation of hydroperoxides in the former under normal processing conditions. The concentration of PP hydroperoxides formed during processing has been shown (5a,19,45) to be much higher than that found in LDPE under identical conditions, and a very significant difference between both polymers is that the hydroperoxides present in the former are mainly of the highly unstable intramolecularly bonded types whereas the latter contains only isolated hydroperoxide groups which are much less effective as photo-initiators.This also accounts for the much improved activity of the U.V. absorber HOBP in the stabilisation of LDPE since it is well known that this additive is incapable of destroying or inhibiting the formation of hydroperoxides during processing and on subsequent U.V. exposure (5a,27,45). The reduced effectiveness of the nickel complex as U.V. stabiliser in LDPE may therefore be associated with its inability to function appropriately in view of the apparent deficiency of hydroperoxides in the substrate, as compared to its activity in PP (Figure 3.28)

However, the thiophosphoryl disulphides, DnBDS and DODS ($R=C_4$ and C_8 respectively) do show exceptionally high levels of synergism with the commercial U.V. absorber HOBP in LDPE, in a manner similar to that observed in PP. The synergism resulting from such a combination of peroxide decomposers and the U.V. absorber, as has previously been discussed for PP (Sec. 3.3A),is therefore partly due to the protection of the disulphides (or their oxidation products) from photolysis with concomittant protection of HOBP from photo-oxidative destruction in the presence of peroxides (45).

3.3B.2 Effect of Processing on the Photoantioxidant Activity of Dithiophosphates

The effect of increasing the processing severity on the photo-stabilising activity of the dithiophosphates and the commercial U.V. stabillisers in LDPE is illustrated in Table 3.14 and Figure 3.27. It has previously been shown (5b,23a) that the concentration of initially-formed hydroperoxides in LDPE is higher with increasing processing severity and this is reflected on the U.V.lifetimes As has been shown consistently in PP, it is clear from Table 3.14 and Figure 3.27, that the photo stabilising activity of the thiophosphoryl disulphide in LDPE is improved with increasing oxygen availability in the mixer (OM) although the activity of the nickel complex is relatively unaffected. This behaviour, which contrasts the observed processing of the nickel complex in PP(Table 3.2),is attributed to the difference in the concentration of hydroperoxides formed during processing as previously discussed. Al-Malaika et al (45) have clearly shown (by U.V. absorption measurements) that when processed at the same concentration and under similar conditions, only a small portion of the nickel complex (NiDBP) is consumed during processing in LDPE compared to that in PP. The same workers also reported that although less than half the originally added nickel complex survived the processing operation in PP, the length of the photo-oxidative induction period provided by the remaining complex(NiDBP) is roughly the same as that for LDPE stabilised with the same initial concentration of NiDBP, which as was previously shown, remained almost intact after processing. Such reduced activity of the nickel complex in LDPE as has been discussed earlier, is obviously a direct consequence of the intrinsic stability of the substrate. The difference in the concentration of the initially-formed LDPE hydroperoxides after only 10 minutes processing under both oxygen deficient and oxidative conditions is somewhat insignificant, hence the lack of any observed effect on the stabilising activity of NiDsBP. However, a fair amount of hydroperoxides in the substrate appears to be a desireable criteria if the additive is to function more effectively.

The commercial U.V. stabilisers, on the other hand, show conflicting activity in LDPE when oxidatively processed. For Tinuvin 770, it is seen that oxidative processing results in improved photo-stabilising activity of the additive (Table 3.14 and Figure 3.27), and this improved performance appears to be associated with the transformation products (nitroxyl radicals) rather than the parent additive. Although the hindered piperidines are not catalysts for peroxide decomposition, they have been reported to react with hydroperoxides in a stoichiometric radical generating process(5b,87) to form the corresponding nitroxyl radicals which are powerful trapping agents for alkyl radicals. Furthermore, it has been shown(5b,89) that the combination of Tinuvin 770 and a peroxide decomposer are antagonistic and this suggests that the presence of hydroperoxides in the polymer during processing, is desir able in order to improve the activity of the hindered amine. In contrast to the effect of severe-processing on the activity of Tinuvin 770, the effectiveness of the U.V. absorber HOBP is decreased and this is attributed to the partial destruction of the additive by hydroperoxides formed during processing and on subsequent U.V. exposure(5b,27,89).

Although the activity of HOBP is reduced when LDPE is processed under oxidative conditions (Fig.3.27), it is also clearly illustrated that the photoantioxidant synergism involving the U.V. absorber and the thiophosphoryl disulphides (DnBDS and DODS) is powerfully augmented by the very same oxidative processing. Such high levels of synergism involving DRDS and HOBP is currently receiving much attention in technological media, and the addition of small amounts of the nickel complex to the system will be shown in a latter section (Chapt. 4)to further improve their performance.

It must however, be emphasised that the high activity of HOBP as presented in this section, is in sharp contrast to that reported in previous publications(27,40b,88,89). Although there is no adequate reason for this discrepancy, the findings in this study clearly suggests that HOBP is quite effective in LDPE as compared to the nickel complex and Tinuvin 770.

3.4 Conclusion

In general,the dithiophosphates have been shown to be very effective in stabilising PP under a range of conditions. The thiophosphoryl disulphides show excellent melt stabilising activity in PP, but are not effective in protecting the polymer against both thermal-(air oven) annd photo-oxidative degradation. Although they are relatively ineffective as U.V. stabilisers in PP, their activity is not only markedly improved when oxidatively processed, but is also relatively unaffected by parameters such as changes in the alkyl substituent, concentration, and processing temperature.

The nickel dithiophosphates, like their corresponding disulphides, are effective melt stabilisers in polypropylene although they are inferior to the latter in this respect. They are also very efficient thermal and photo-stabilisers in view of their high peroxidolytic activity and U.V. stability. In contrast to the disulphides, their activity as melt, thermal and photo-stabilisers in polypropylene is highly dependent on changes in the alkyl substituent, concentration and processing severity. This broad spectrum activity of the dithiophosphates, particularly the nickel complexes in PP, is a clear reflection of the fact that they are able to neutralise hydroperoxides which are the primary agents responsible for all three types of oxidative degradation.

In contrast to the high U.V. activity of the dithiophosphates in PP, these compounds are much less effective in stabilising low density polyethylene (LDPE) against photo oxidative degradation at the low concentrations (<0.4%)

used in the context of normal samples. This behaviour is particularly noticeable with LDPE-stabilised samples containing the nickel complex (NiDsBP), and it is suggested that this apparent inactivity of the additive in LDPE is as a result of the much lower concentration of hydroperoxides formed in the polymer during processing and also during subsequent U.V. exposure.

Although the rate of formation and concentration of hydro peroxides are much more important in the photo-oxidation process in polyolefins than other chemical processes(5b,19,27). it is interesting to note that this can be used beneficially to convert the antioxidant precusor to the effective antioxidant species during processing. In the case of the nickel dithiophosphates which function primarily as the precusors of the effective catalytic peroxide decomposers, the results therefore clearly suggest that the presence of some hydroperoxide (critical amount) is desireable in the substrate for maximum U.V. activity. This obviously accounts for the much higher U.V. activity of NiDsBP in a more oxidisable substrate as illustrated in Figure 3.28, which shows that the length of the photo-oxidative induction period (PIP) for both PP and LDPE stabilised with the same initial concentration of NiDsBP under similar processing condition (temperature excepted) is roughly the same.

Finally, the dithiophosphates also show extremely high level of synergism with the U.V. absorber HOBP in both PP and LDPE, although a combination of the dithiophosphates alone (NiDRP+DRDS) in polypropylene is antagonistic on U.V. exposure.

Fig. 3.26.

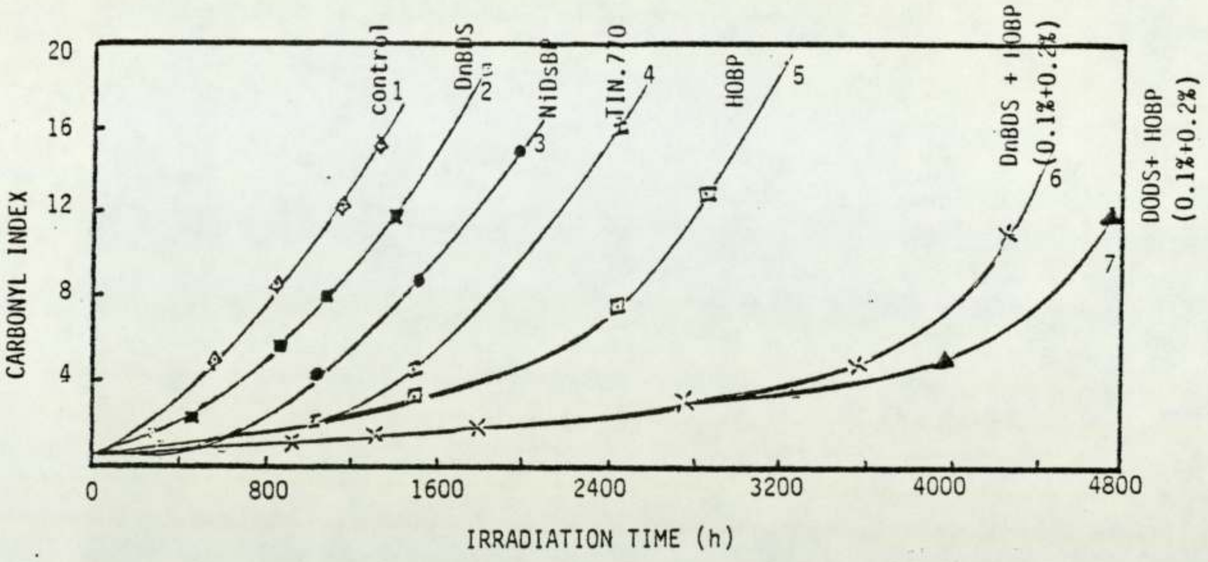


Fig. 3.27.

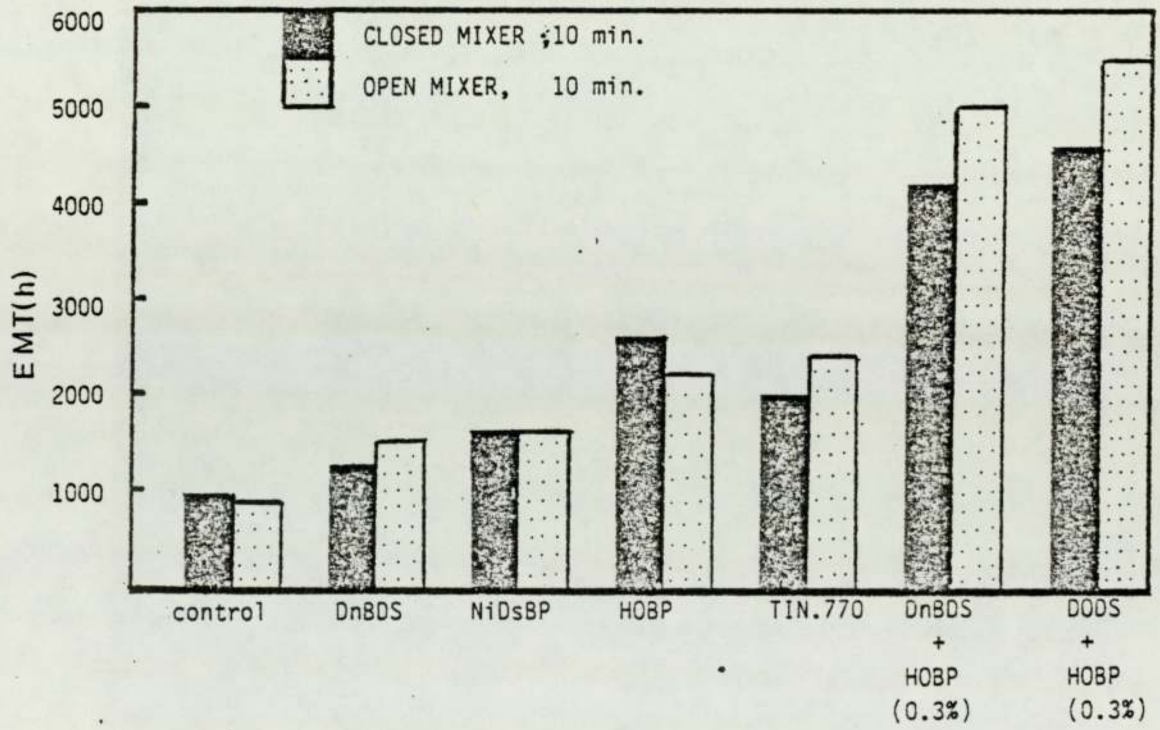


Fig. 3.26. Comparison of antioxidants as UV stabilisers in LDPE (0.2g/100g: CM, 10)
(Unless stated otherwise conc. of all additives, 0.2g/100g: and processing times are 10 min. in a closed mixer at 150°C)

Fig. 3.27. Effect of processing severity on the uv. activity of various stabilisers in LDPE.
(Unless stated otherwise conc. of all additives, 0.2g/ 100g)

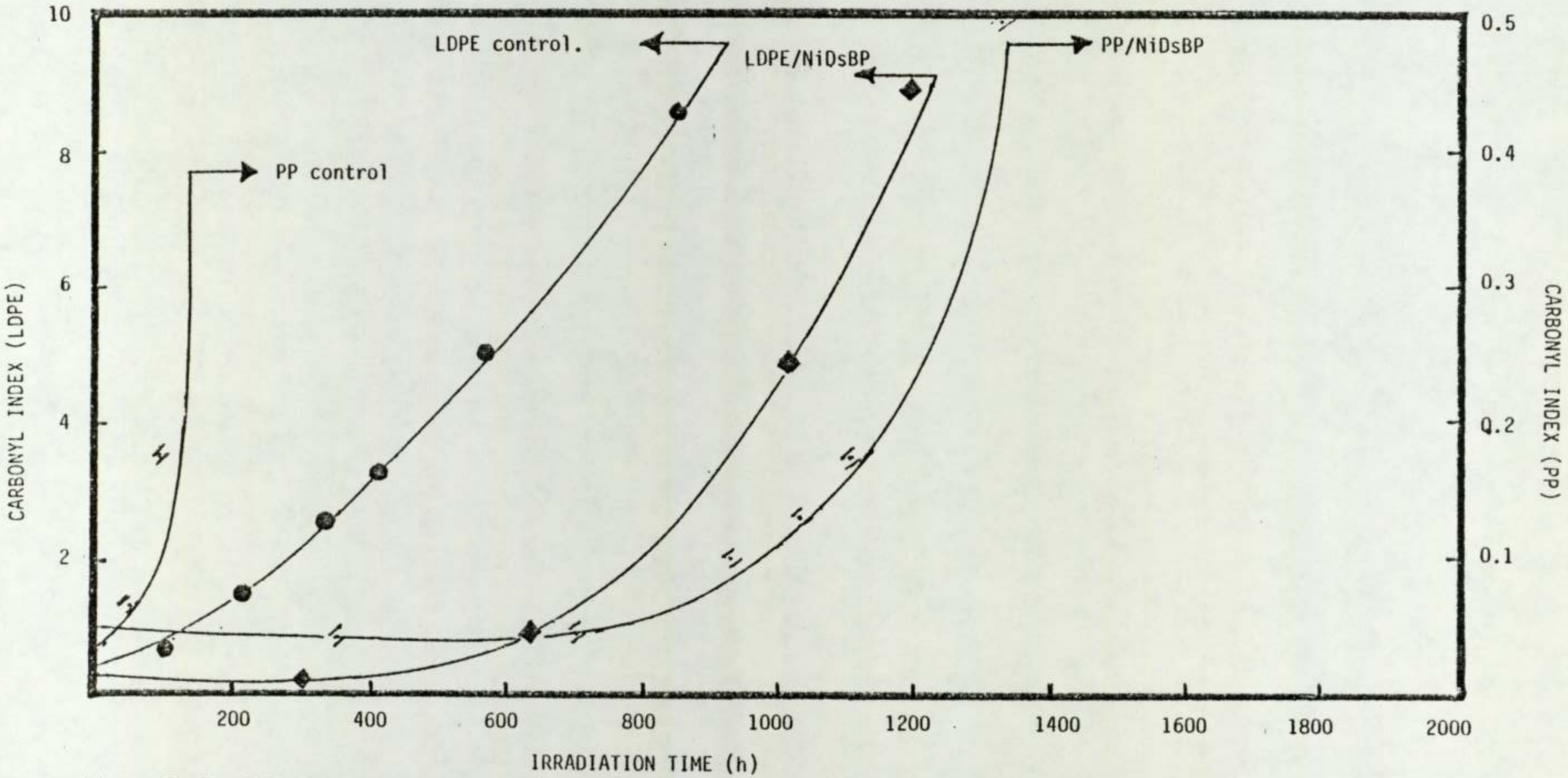


Figure 3.28. Effect of nickel complex (NiDsBP) on the length of the photo-oxidative induction period in PP and LDPE when processed in a closed chamber (CM,10) at a mass concentration of 0.2g/100g.

concentration) in polyolefins effectively improves their photo antioxidant activity. In view of this fact, it is therefore expected(86) that the incorporation of small amounts of pre-oxidised antioxidant concentrates to fresh unstabilised polymer may reduce the extent of oxidative degradation during the conventional mixing operation (dilution processing).

The aim of the work described in this chapter is therefore to evaluate the photo antioxidant effectiveness of high concentrates of thiophosphoryl disulphides (DRDS), the corresponding nickel complex (NiDRP) and their synergistic combinations with the U.V. absorber HOBP, in polyolefins. The processing of these concentrates was carried out under both mild (restricted oxygen) and severe (excess oxygen) conditions in various forms, while their dilution with fresh unstabilised polymer was accomplished under mild processing condition. Although detailed experimental procedures for the preparation and subsequent dilution of the concentrates are described in an earlier section (Section 2.3) a glossary of the abbreviations which will be used throughout this chapter is outlilned as follows:

a. Ct - Additive concentrate ($\geqslant 2.5\%$)
b. DCt - Dilute additive concentrate ($\leqslant 0.6\%$)
c. CM - Mild (closed mixer) processing under oxygen deficient conditions.

CHAPTER FOUR

STABILISATION OF POLYOLEFIN CONCENTRATES

The work in this chapter describes the effect of oxidative processing on the effectiveness of concentrates (high concentrations) of mainly thiophosphoryl disulphide (DnBDS) in PP and LDPE at 190°C and 150°C respectively. These concentrates may then be diluted down to normal additive concentrations (0.2% - 0.6%) with fresh unstabilised polymer under normal processing conditions in the presence of a second and/or third component as the case may be.

4.1 Object

It has, in the past, been amply demonstrated(5a,5b,19) that adequate stabilisation is essential for plastics products because of the formation, during processing, of hydroperoxides which are chiefly responsible for subsequent polymer degradative reactions. Furthermore, it is known(5a-b,18,19,22,40b,86) that most sulphur antioxidants are partially converted to oxidation products at elevated temperatures, and some of these oxidation products have been shown to be more effective antioxidants than their precusors (Section 3.3.1). It has also previously been shown that oxidative processing of thiophosphoryl disulphides as "normal samples" ($<$ 0.4% additive

d. OM - Severe (open mixer) processing in the presence of excess oxygen.

e. CM/N_2/TBH - Oxidative processing in the presence of a hydroperoxide(TBH). A mixture of the antioxidants and TBH is charged into a mixing chamber previously purged with nitrogen and processed in total absence of air.

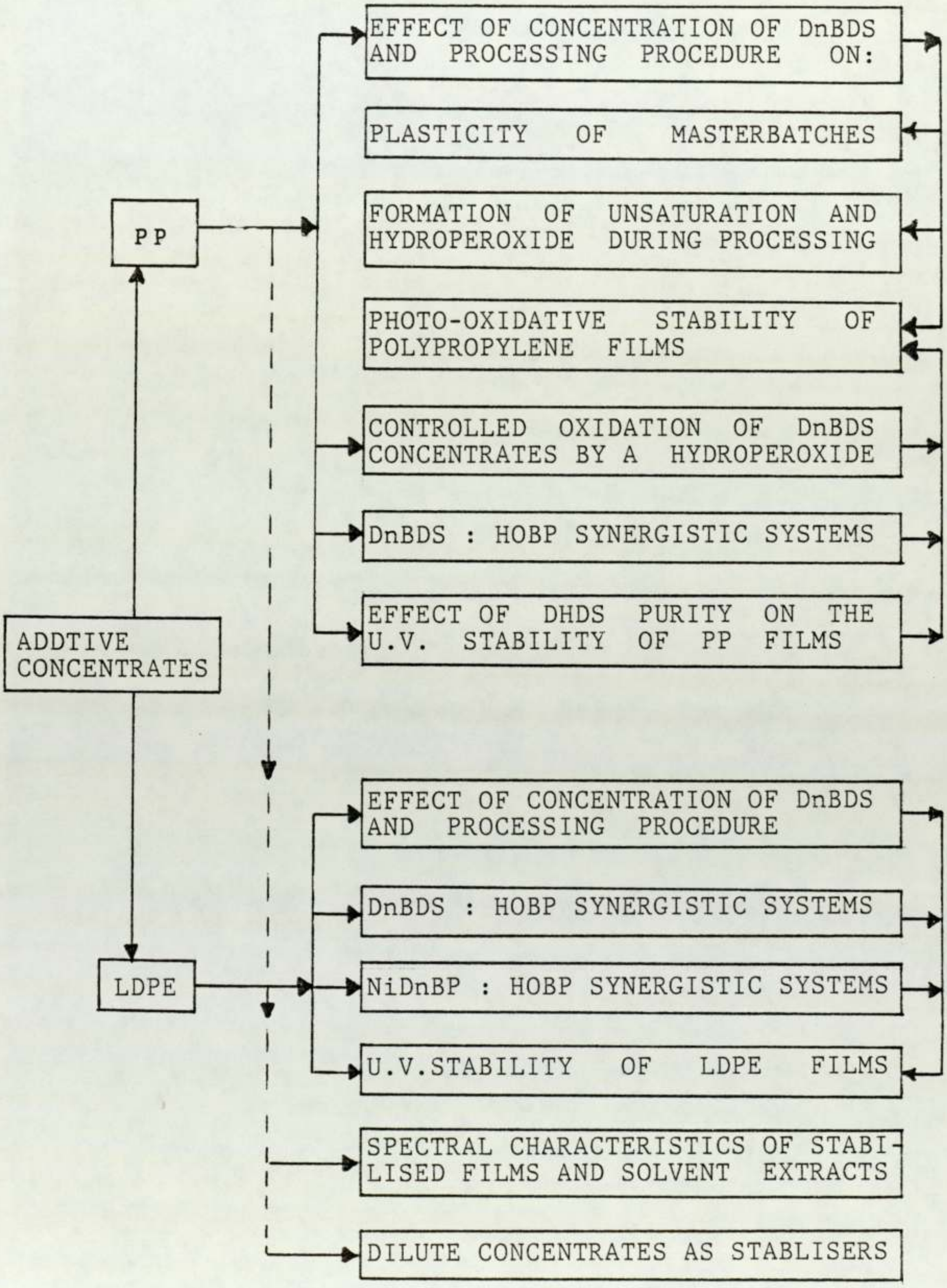
f. COM - Controlled oxidative processing with air as oxidant. The disulphide (DRDS) is initially processed under closed chamber (5 mins.), which is then opened to the atmosphere (30 sec.) to facilitate the addition of the synergists (HOBP & NiDRP) and finally closed for the rest of the processing period (3.5 mins.).

g. COM/TBH - Controlled oxidative processing with hydroperoxide as oxidant. The disulphide is charged into a mixing chamber previously purged with nitrogen and processed initially for five minutes. The mixing chamber is then opened (< 30 sec. under N_2) to permit the addition of TBH and closed for a further three minutes processing. The mixing chamber is opened once again (< 30 sec.) for the addition of the synergists (HOBP & NiDRP), and finally closed for the rest of the processing period (3 min.)

At this point, it is worth emphasising that no spectroscopic examination was carried out on the latter two 3-component concentrates containing DRDS, HOBP and NiDRP (controlled oxidative processing, COM and COM/TBH) because of their highly coloured nature. These concentrates are, therefore, primarily designed for dilution in fresh unstabilised polymer, and the antioxidant activity of the dilute analogues is discussed in Section 4.2D and 4.3D.

Scheme 4.1 shows a schematic representation of the work described in this chapter.

Scheme 4.1 Stabilisation of polyolefin concentrates



4.2 Results

4.2A Polypropylene Additive Concentrates (PP/Ct)

4.2A.1 Effect of Concentration of DnBDS (in PP) and Processing Procedure on the Plasticity of the Concentrates.

This section compares the effect of the concentration of DnBDS (2.5%-20% by weight of DnBDS) on the plasticity of the concentrates when processed under conditions of restricted oxygen (CM, 5 min) and under oxidative conditions (OM, 15 min) at 190 °C. The plasticity was evaluated by following changes in the torque generated during processing and it is clearly shown in Figures 4.1-4.2 that for both procesing procedures and at all concentrations, there is an initial sharp increase in the torque when the polymer/additive mixture is charged into the mixing chamber. On passing through the maximum, the torque then decreases until a constant level is attained which corresponds to a constant melt viscosity in each of the concentrates.

Figures 4.1 - 4.2 also indicate that increases in the concentration of DnBDS (2.5% - 20%) is associated with a reduction in both the maximum and minimum torque generated during processing. The inset in Figure 4.2 not only indicates that the torque levels (maximum & minimum) for oxidatively-processed concentrates are only about 25% of that of the normally-processed concentrates (CM), but also that the lubricating effect of the higher concentrates is common for both processing procedures.

4.2A.2 Effect of Concentration of DnBDS (in PP) on the Amount of Unsaturation and Hydroperoxides Formed After Processing

Tables 4.1 - 4.2 clearly indicate that the concentration of unsaturation and hydroperoxides formed during processing of PP/DnBDS concentrates is highly dependent on both the concentration of the additive and the processing procedure. The polymer unsaturation was measured by a modified version of the method used by Gallo et. al.(79) while the method used for the hydroperoxide determination was adapted from Bocek(80) (see Section 2.6.1 and 2.6.2).

Table 4.1 not only shows that increasing the concentration of DnBDS up to a critical level (15%) results in an increase in the % mole unsaturation formed after processing, but also clearly indicates that this behaviour is apparently unaffected by the processing procedure. The % mole unsaturation is also seen to be consistently higher for concentrates processed under restricted amounts of oxygen (CM). Table 4.1 also shows that further increases (15% - 20%) in the concentration of DnBDS results in a reduction in the amount of unsaturation formed for both processing procedures.

Table 4.1 Effect of DnBDS concentration on amount of polymer unsaturation formed after processing of PP (190°C).

DnBDS Concentrate (g / 100g)	% Mole Unsaturation CM,5	OM,15
CONTROL	0.195	0.12
2.5	0.75	0.34
5.0	1.20	0.80
10.0	1.98	1.62
15.0	2.80	2.44
20.0	1.88	1.88

In contrast to the polymer unsaturation, the concentration of hydroperoxides formed after processing tends to be higher for oxidatively-processed DnBDS concentrates. This is shown in Table 4.2 which also indicates that for both processing procedures, the hydroperoxide concentration in the polymer is progressively increased with increasing DnBDS concentration, and this increase is much more rapid at concentration of DnBDS in excess of 15% (15 g / 100 g) as illustrated in Figure 4.3

Table 4.2 Effect of DnBDS concentration in PP on the amount of hydroperoxides formed after processing (190°C).

DnBDS concentrate (g /100g)	Hydroperoxide concentration ($mol\,g^{-1}$) CM.5	OM,15
CONTROL	0.195	0.22
2.5	0.16	0.18
5.0	0.21	0.24
10.0	0.23	0.34
15.0	0.25	0.52
20.0	1.90	2.20

4.2A.3 Effect of DnBDS Concentration on the Photo-Oxidative Stability of PP Films

Table 4.3 and Figure 4.4 show how the effectiveness of DnBDS concentrates as U.V. stabilisers in polypropylene varies with increasing mass concentration of the additive. It is clear that the photo-oxidative stability of these concentrates is highly dependent on the concentration of DnBDS since it can be seen that embrittlement time increases with concomitant increase in the concentration of the additive. This behaviour is similar for both processing procedures although the embrittlement times for oxidatively-processed concentrates (OM) are generally slightly less than those for the normally-processed concentrates (CM), except at the highest concentration (20%) which shows the opposite trend. It must, however, be pointed out that the performance of most PP concentrates was determined as time required to reach fixed carbonyl index during U.V. irradiation ($T_c=0$).

Table 4.3 Photo-oxidative stability of PP/DnBDS concentrates (190°C)

DnBDS Concentrate (g/100g)	$T_{C=0}$ / 0.25 (h) CM,5	OM,15
CONTROL	90	40
2.5	1500	1300
5.0	2580	2300
10.0	2900	2900
15.0	3600	3400
20.0	3300	3900

This was necessary in view of the difficulty associated with accurate embrittlement time determination (physical fracture)which is a direct consequence of the lubricating effect of the additives at such high concentrations. Figures 4.5 - 4.6 illustrate the variation of carbonyl index with irradiation time for both the closed mixer

(CM) and open mixer (OM) concentrates.

4.2A.4 Photo Antioxidant Activity of DRDS / TBH Concentrates in Polypropylene (Hydroperoxide System)

The controlled oxidation of the thiophosphoryl disulphide, DnBDS during processing of PP at 180°C was achieved by varying the concentration of the hydroperoxide (TBH) in each concentrate containing DnBDS at a constant concentration (2.5%). Processing was carried out under nitrogen as described in Section 2.3.1.3

Table 4.4 compares the photo antioxidant activity of these systems with that of conventional 'normally'-processed (CM,5 & OM,15) DRDS concentrates of the same concentration. It is clear that the most stabilising effectiveness is obtained at equimolar ratio of both components, as reflected by the U.V. embrittlement times for the DnBDS ($R=C_4$) series and also for the DHDS ($R=C_6$) series. These results are also clearly illustrated in Figures 4.7 - 4.8 which show the variation of carbonyl index with irradiation time for both systems.

Table 4.4 A comparison of the photo antioxidant activity of DRDS / TBH concentrates in polypropylene (CM,5 ; N_2; 180°C)

Concentrate	concentration (g / 100g)	Molar Ratio DnBDS : TBH	Embrittlement Time (hours)
DnBDS/CM,5	2.5	-	1030
DnBDS/OM,15	2.5	-	940
DnBDS + TBH	2.5 + 0.117	4 : 1	550
DnBDS + TBH	2.5 + 0.234	2 : 1	430
DnBDS + TBH	2.5 + 0.468	1 : 1	1350
DnBDS + TBH	2.5 + 0.936	1 : 2	1200
DHDS / CM,10	2.5	-	840
DHDS / OM,10	2.5	-	620
DHDS + TBH	2.5 + 0.38	1 : 1	1050

4.2A.5 Effect of Processing Procedure on the photo antioxidant synergism of DnBDS/HOBP Concentrates in PP

Table 4.5 and Figure 4.9 compares the photo antioxidant activity of DnBDS/HOBP concentrates processed under both oxygen deficient (CM) and oxidative conditions.(OM). It is clear that at such high concentrations employed (5% - 7.5% total), the observed effect is not strictly synergistic since this is less than the sum of the individual effects of the two components.

More interesting still is the fact that oxidative processing either in the presence of excess oxygen or a hydroperoxide reduces the photo antioxidant activity of the concentrates in polypropylene.

Table 4.5 Effect of processing severity on the embrittlement times of PP films containing DnBDS : HOBP Concentrates.

Concentration(%) DnBDS + HOBP	Processing Condition	$T_{C=0}$ / 0.3 (h) Observed	*Calculated Effect
DnBDS (2.5%)	CM,5	1500	--
DnBDS (2.5%)	OM,15	1300	--
HOBP (2.5%)	CM,10	4120	--
HOBP (5%)	CM,10	4800	--
[DnBDS + HOBP]			
(2.5% + 2.5%)	CM,5	4400	5620
(2.5% + 2.5%)	OM,15	3850	5400
(+ 0.234% TBH)	CM,5/N_2	4000	5400
(+ 0.468% TBH)	CM,5/N_2	4000	5400
[DnBDS + HOBP]			
(2.5%+ 5%)	CM,5	4800	6300
(2.5%+ 5%)	OM,15	4400	6100

* calculated as the sum of the individual effects.

Fig. 4.1.

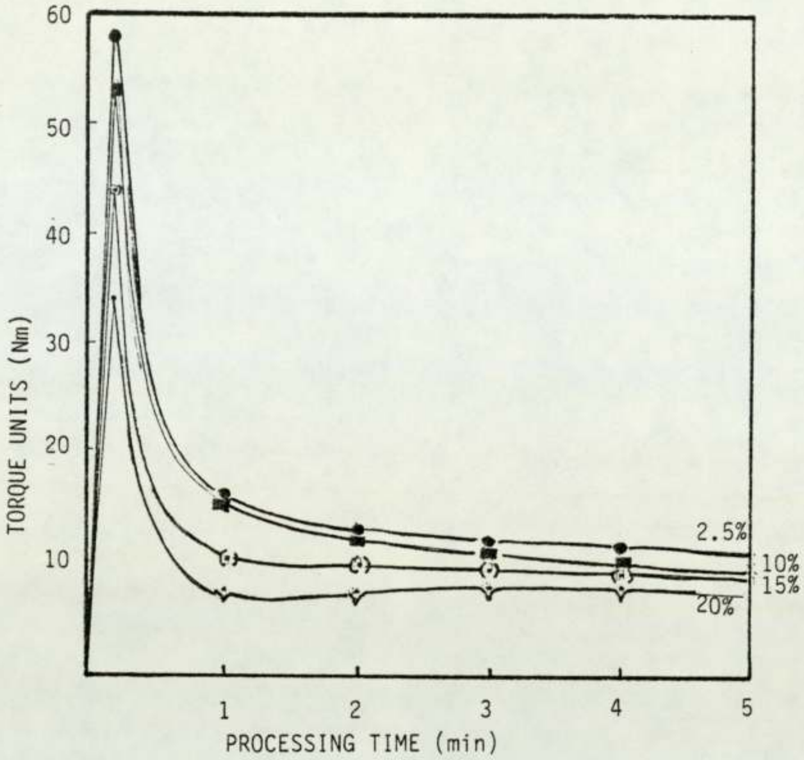


Fig. 4.2.

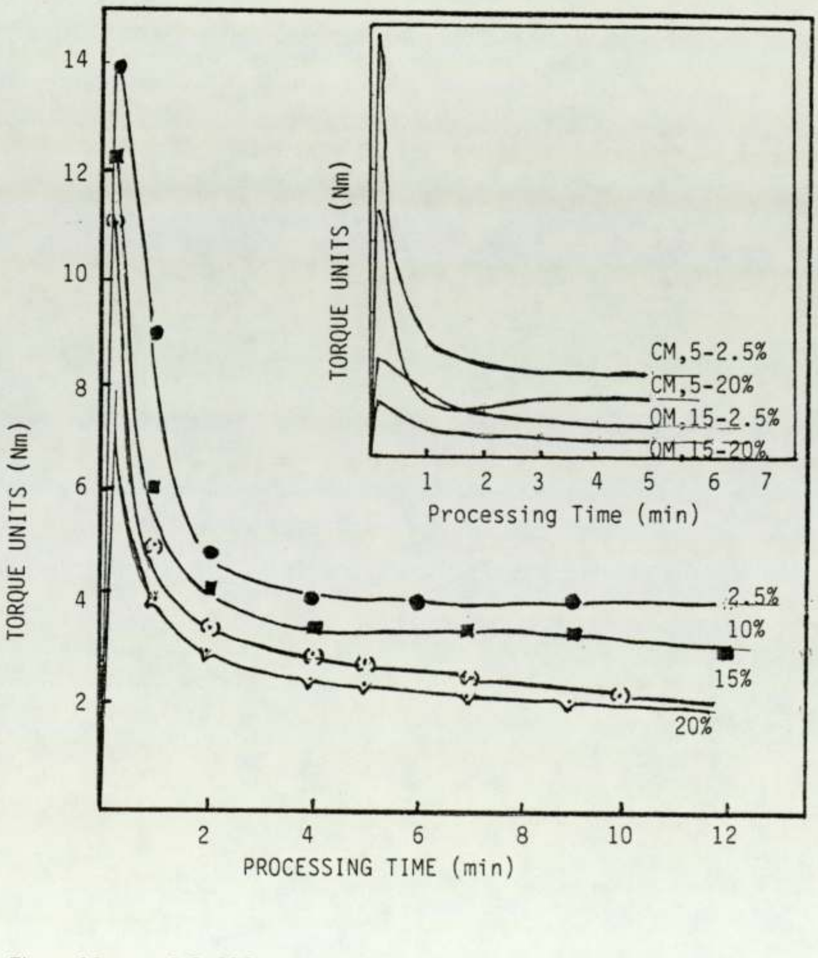


Fig. 4.1. The effect of DnBDS conctration on the Torque generated during mild processing (190°C) Of PP concetrates (CM,5)

Fig. 4.2 The effect of DnBDS conc. on the torque generated during oxidasive processing (190°C) of PP of concentrates (OM,15). Inset compares the torque generated during both mild and oxidative processing of the concentrates at conc. 2.5% and 20%.

Figure 4.3

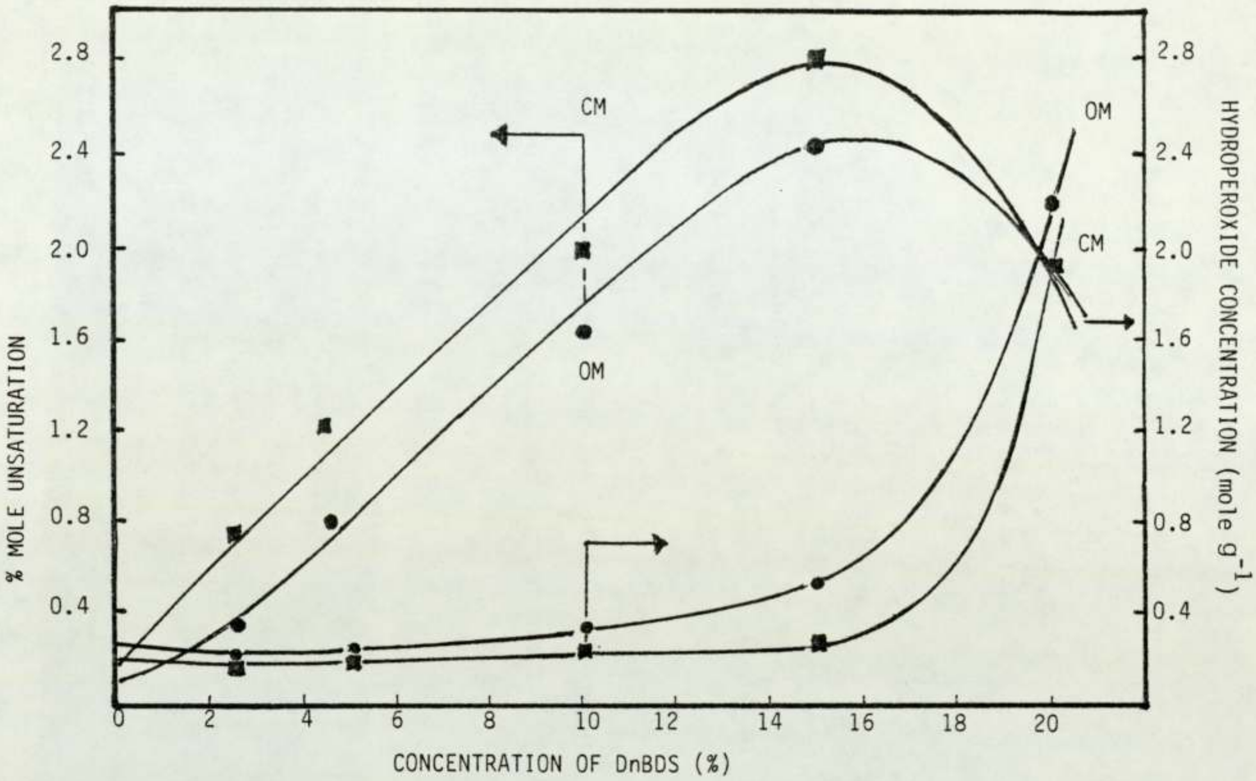


Figure 4.4.

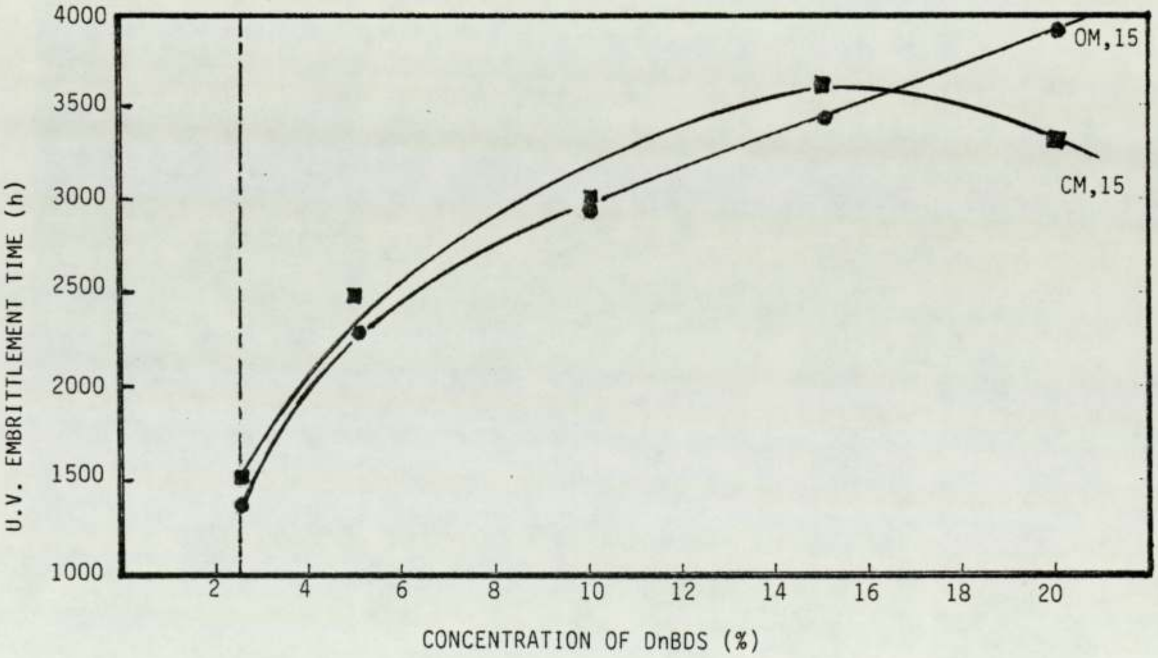


Figure 4.3 Effect of DnBDS concentration in polypropylene on the amount of unsaturation and hydroperoxides formed after processing (190°C)

Figure 4.4 Effect of DnBDS concentration (190°C) on U.V. stability of PP films.

Figure 4.5

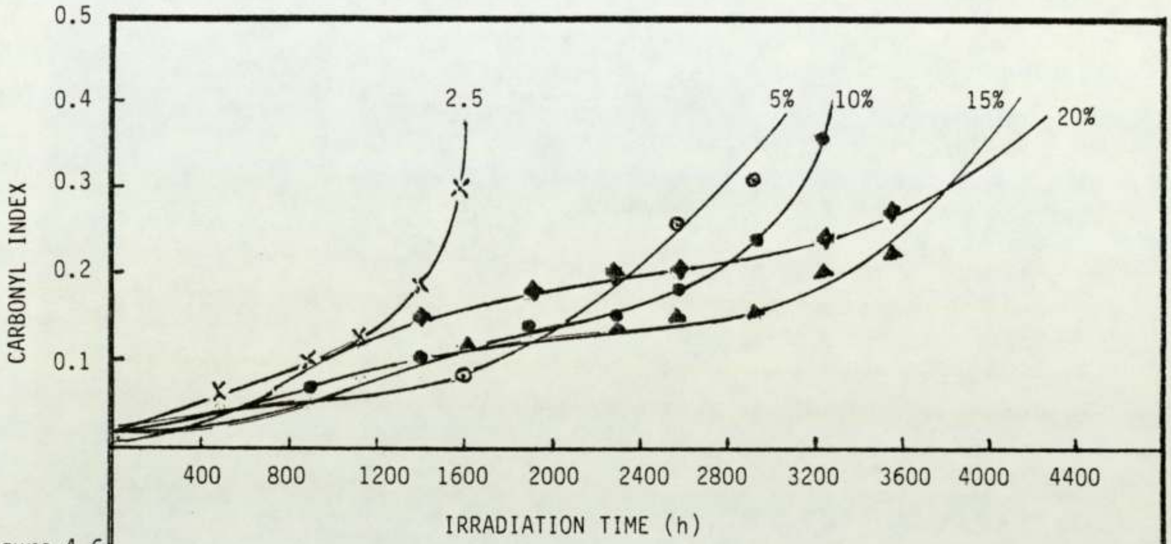


Figure 4.6

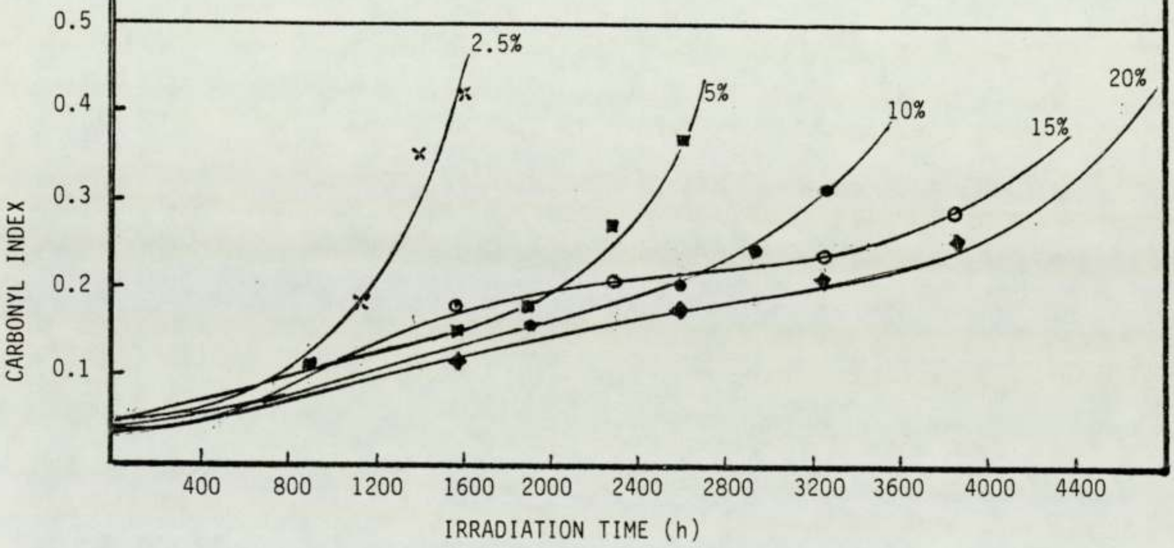


Figure 4.5 Effect of DnBDS concentration on the photo-oxidative stability of polypropylene films (CM,5; 190°C)

Figure 4.6 Effect of DnBDS concentration on the photo-oxidative stability os polypropylene films (CM,15; 190°C)

Figure 4.7

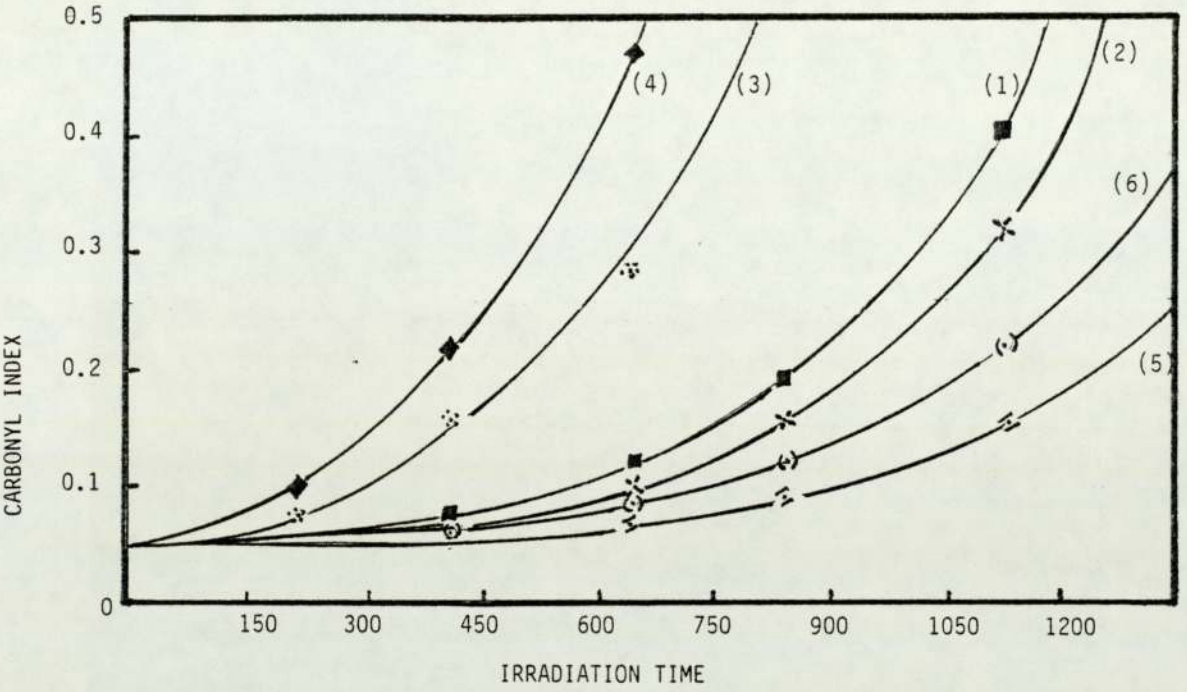


Figure 4.8

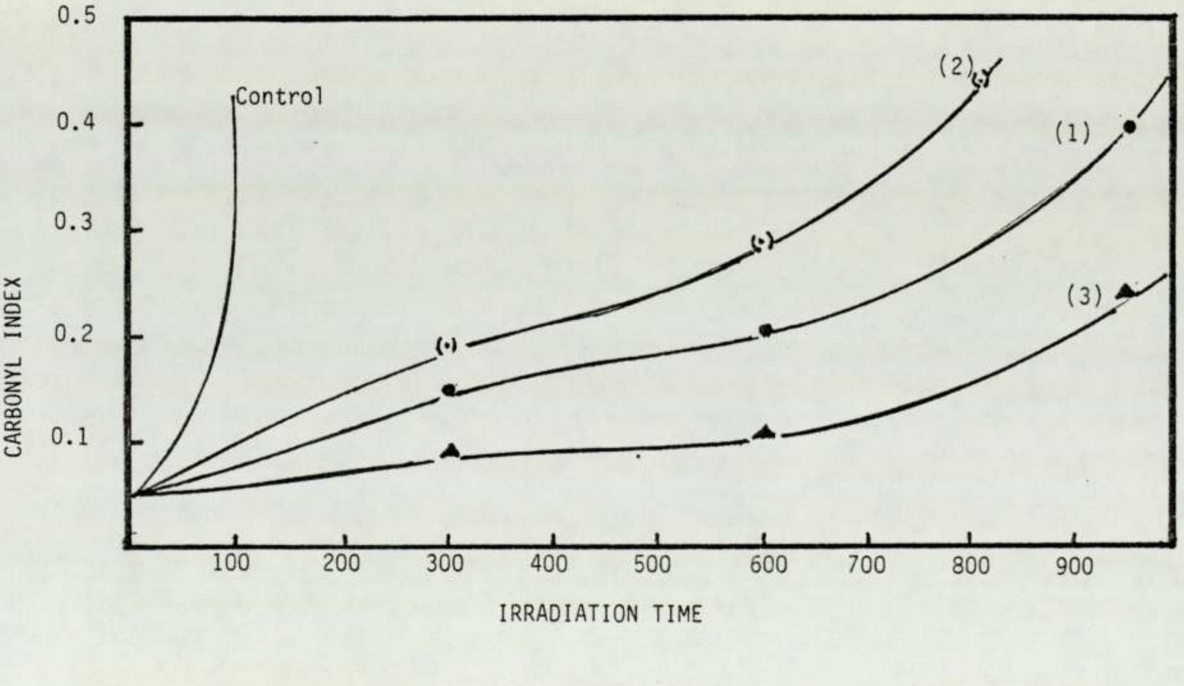
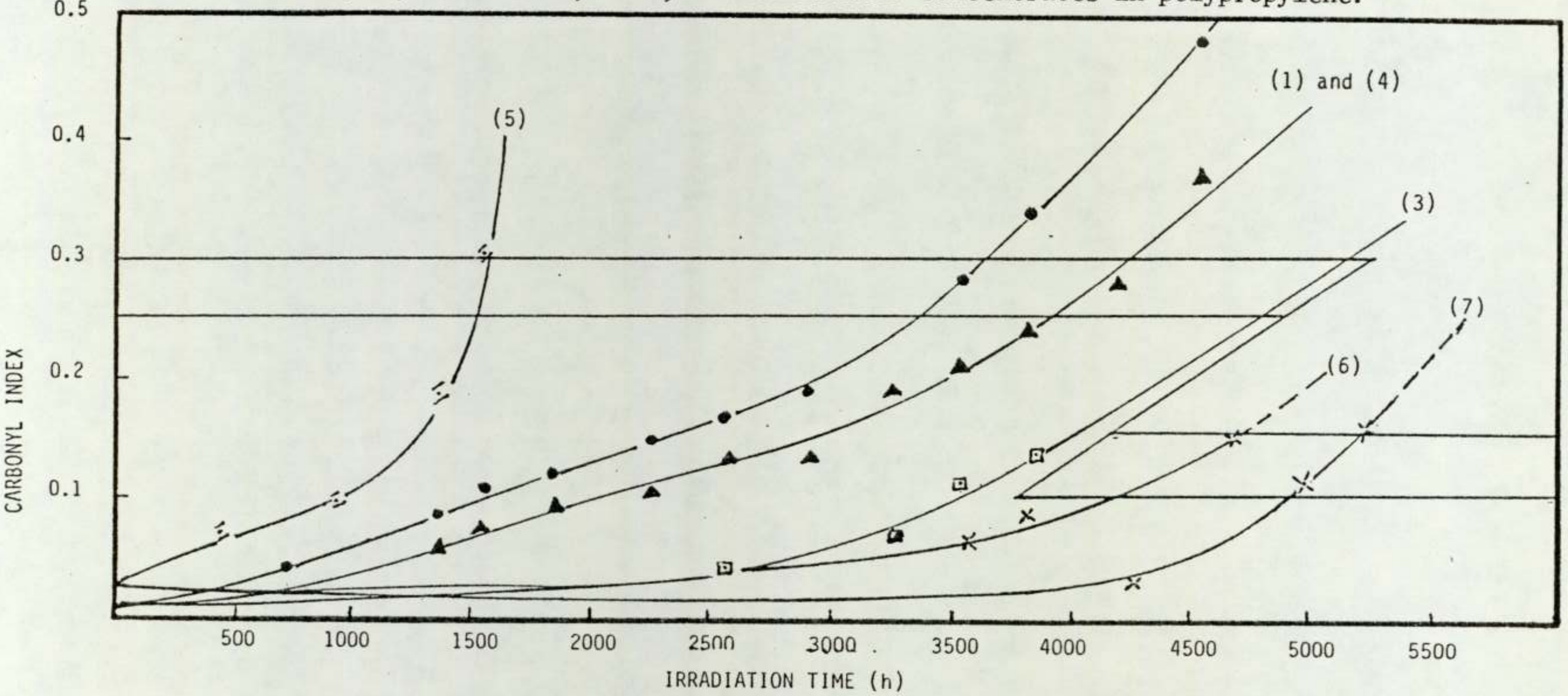


Figure 4.7 The effect of TBH concentration on the U.V.- stability of PP/DnBDS MB films (180^{0}C). Concentration of DnBDS in all MBs = 2.5% (1) OM,15; (2)CM,15; (3) + 0.117% TBH; (4) + 0.234% TBH; (5) + 0.468%; (6) + 0.936% TBH . Samples (3) - (6) wereprocessed under nitrogen for 5 minutes

Figure 4.8 Effect of processing severity (180^{0}C) on the photo-stabilising activity of DHDS concentrates. (1) CM,10; (2) OM,10; (3) + 0.38% TBH - CM,10/N_2 Concentration of DHDS in all concentrates, 2.5%

Figure 4.9 The effect of processing severity(190^{o}C) on the photostabilising activity of DnBDS, HOBP, and DnBDS:HOBP concentrates in polypropylene.



PP/MB		EMT (h)		>C=0 [0.30]	
(1) DnBDS + HOBP (2.5% + 2.5%)	- C_5	3800	>C=0 [0.25]	4250	
(2) DnBDS + HOBP (2.5% + 2.5%)	- 0_{15}	3250		3625	
(3) DnBDS + HOBP (2.5% + 5%)	- C_5	4750		5000	
(4) DnBDS + HOBP (2.5% + 5%)	- 0_{15}	3800		4250	
(5) DnBDS (2.5%)	- C_5	1500		1500	
(6) HOBP (2.5%)	- C_5	4120	>C=0 [0.10]	4620	>C=0 [0.15]
(7) HOBP (5%)	- C_5	4800		5130	

4.2A.6 Effect of Impurity Level in DRDS on their Photo-Stabilising Activity in PP (R = hexyl)

The preparation of bis(O,O - dialkyl thiophosphoryl) disulphides (DRDS) from the corresponding phosphorodithioic acids can be accomplished via the oxidation of the ammonium salts by either hydrogen peroxide (H_2O_2) method) or iodine (I_2 /KI method) as described in the experimental chapter (Section 2. 1. 3). The latter of these two methods generally gives a pure and visually clear (light yellow) product although a poor colour (yellow —— brownish) is usually indicative of the presence of impurities, which may also accumulate in a pure sample with increasing storage time.

Figure 4.10 compares the ^{31}P NMR spectra of different samples of di-n-hexyl thiophosphoryl disulphide (DHDS) containing various levels of impurities, while the nature and percentage of these impurities is given in Table 4.6a. Sample (a) which is a very pure I_2/KI product shows a sharp ^{31}P NMR signal with a chemical shift of 85 ppm whereas as the typical H_2O_2 product (sample b) contains additional ^{31}P NMR signals with chemical shifts of 83.8 ppm, 79.2 ppm and 72.8 ppm due to impurities. These same impurities are also present in the visually poor (cloudy yellow) I_2/KI product, sample (c) and in the partly-decomposed (190°C/5 min./air) product, sample (d) although the additional ^{31}P NMR signals (δ = 96.1 and

52.6) in these latter two samples clearly indicates the presence of more impurities.

Table 4.6a Structural assignments to impurities present in samples of DHDS as measured by ^{31}P NMR

Sample	% of sample (δ = chemical shifts in ppm)						
	δ	96.1	85.0	83.8	79.2	72.80	52.6
	Structure	$(RO)_2(RS)PO$	$[(RO)_2PSS]_2$	$[(RO)_2PSS]_2S$	$[(RO)_2PS]_2S$	$(RO)_3PS$	$(RS)_2(RO)PO$
a. (I_2/KI)		-	>99.9	-	-	-	-
b. (H_2O_2)		-	89.6	2.6	6.1	1.74	-
c. (I_2/KI)		2.2	75.0	8.8	11.1	2.70	-
d. (partly decom)		4.2	65.0	21.8	-	3.50	5.4

The photo-oxidative stability of polypropylene films containing these samples in the form of concentrates processed under various mixing conditions at 190°C, is shown in Table 4.6b.

Table 4.6b Effect of impurity leval in DHDS on the U.V. stability of polypropylene films (2.5g/100g : 190°C)

Sample	% Purity (DHDS)	Embrittlement Time(h) CM,10	OM,10	CM,10/TBH/N_2*
a.(I_2/KI)	>99.9	840	620	1050
b.(H_2O_2)	89.6	780	680	950
C.(I_2/KI)	75.0	1060	780	- **
d.(heated in air)	65.0	720	600	600

* Concentration of TBH, 0.38g/100g.(1:1 molar ratio of DHBDS to TBH)

** Sample insufficient for this processing procedure.

It is clear from Table 4.6b and Figure 4.11 that the level of impurity [samples (a) - (c)] in DHDS does affect their photo antioxidant activity in polypropylene, but not necessarily in favour of the pure sample (a). Sample (c) which is only about 75% pure is most effective under conditions of both oxygen deficiency (CM) and excess oxygen (OM) although, this sample was insufficient for further examination (with TBH). However, oxidative processing in the presence of excess oxygen (OM) is shown to be detrimental to the U.V. stabilising activity of all

Fig. 4.10

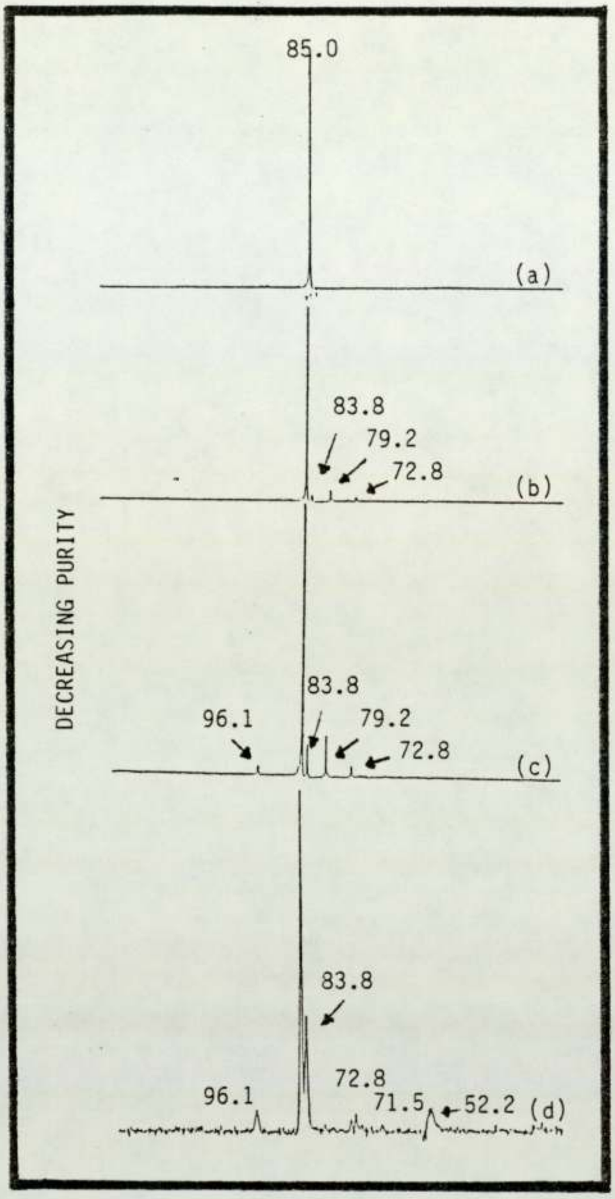
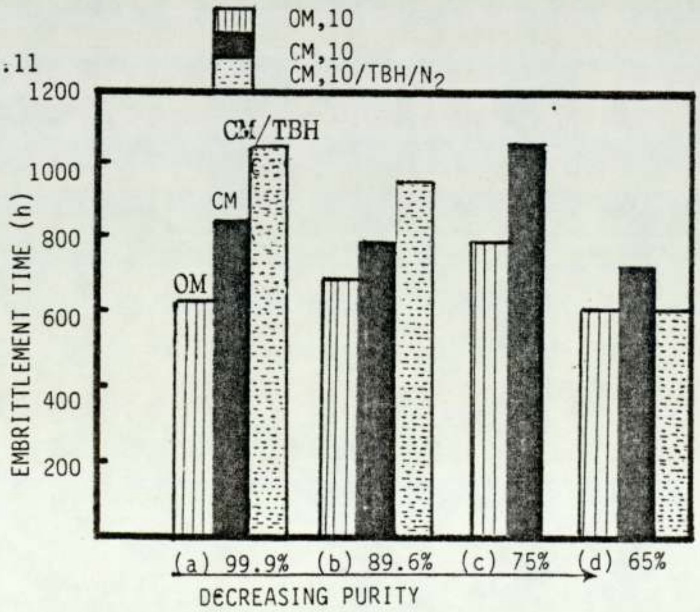


Fig. 10 31P NMR spectra showing the level of impurities in different samples of di-n-hexyl thiophosphoryl disulphide (DHDS).
(a) Pure (> 99%) I_2/KI Product (b) Typical H_2O_2 product; (c) Visually-poor I_2/KI product; (d) partly-decomposed [190°C/5min./air] product

Fig. 4.11



4.11 Effect of impurity level in DHDS (2.5g|100g) on the U.V. stability of polypropylene films (processed at 190°C) the samples while the use of TBH as oxidant clearly improves the activity of the samples of higher purity (> 70%). It is also interesting to note that the partly-decomposed sample (65% purity) is only effective as a U.V.stabiliser in PP when processed under conditions of restricted oxygen. The result on this particular sample must however be treated with extreme caution since the initial thermal decomposition reaction of the disulphide was carried out in a hydro-carbon solvent of suspect stability (Shellsol AB). The extremely rapid change in the colour of the reaction mixture (light yellow - dark brown) after only five minutes (190°C) decomposition, clearly suggests that the substrate is highly oxidisable and may therefore generate a considerable amount of chain propagating species (RO$^{\cdot}$, ROO$^{\cdot}$).

4.2B Low Density Polyethylene Additive Concentrate (LDPE / Ct)

4.2B.1 Effect of Concentration of DnBDS and Processing Procedure (150°C) on the U.V. Stability of LDPE

Figure 4.12 compares the effects of processing procedure on the U.V.stabilising effectiveness of DnBDS concentrates in LDPE at concentrations 2.5g/100g and 5g/100g. This figure not only shows that the antioxidant activity is increased with increasing concentration of DnBDS , but also indicates that the effect of the processing procedure on the photo antioxidant behaviour is very similar at both concentrations. In both cases, the behaviour is clearly associated with an initially slow auto-acceleration step in the early stages of photo-oxidation (< 1000 hrs.) followed by a much more rapid, but continuously auto-retarding oxidation.

It is also interesting to note that the increased retardation effects expected from the oxidative processing of the DnBDS concentrates is only apparent during the later stages of photo-oxidation (> 2400 hrs). A comparison of curves (1), (2) and (3), (4) for concentrations 2.5g/100g and 5g/100g respectively, indicates that the photo antioxidant behaviour of DnBDS concentrates in LDPE is relatively unaffected by the processing procedure during the early stages of photo-oxidation although oxidative processing affords a greater auto-retardation effect during the later stages. This behaviour is a clear reflection of their performance (Table 4.7), defined as the time(h) required to reach a fixed carbonyl index value ($T_{C=O}$).

Table 4.7 Effcct of processing procedure (150°C) on the U.V. stabilising activity of LDPE / DnBDS concentrates

DnBDS Conc. (g /100g)	Processing procedure	Time (h) to Fixed Carbonyl value T(>C=0,10)	T(>C=0,16)
Control	(CM,10)	960	1340
Control	(OM,15)	850	1160
2.5	(CM,10)	2100	3200
2.5	(OM,15)	2100	3500
5.0	(CM,10)	2700	3700
5.0	(OM,15)	2800	4200

4.2B.2 Photo antioxidant Synergism of Dithiophosphate/ HOBP Concentrates in LDPE

Figure 4.13 compares the photo-stabilising activity of LDPE-Ct films containing DnBDS (curve 1), HOBP (curves 2 and 3), NiDnBP (curve 4), the synergistic combinations DnBDS:HOBP (curves 5 and 6) and NiDnBP:HOBP (curve 7). It is clear that the activity of NiDnBP alone (curve 4) is characterised by extensive photo-oxidative induction period (PIP) followed by a rapid increase in the carbonyl index. A slightly similar PIP is also evident, albeit to a much lesser extent, in the behaviour of the synergistic NiDnBP:HOBP concentrate (curve 7) before showing auto-retarded oxidation. In contrast to this, the synergistic DnBDS:HOBP concentrates(curves 5 and 6)exert a pronounced auto-retardation during the early stages of photo-oxidation folowed by a much more rapid, but continuously auto-retarding phase, as illustrated in the inset to Figure 4.13. Furthermore, the U.V. activity of the DnBDS:HOBP concentrate (curve 5) appears to be augmented by severe processing (curve 6) only up to a certain point (10,000 hrs) after which the carbonyl index starts to increase.

When compared on the basis of the time required to reach a fixed carbonyl index value (Table 4.8), the effectiveness of the stabiliser-concentrate films increases in the following order:

NiDnBP:HOBP > DnBDS:HOBP > NiDnBP > HOBP > DnBDS

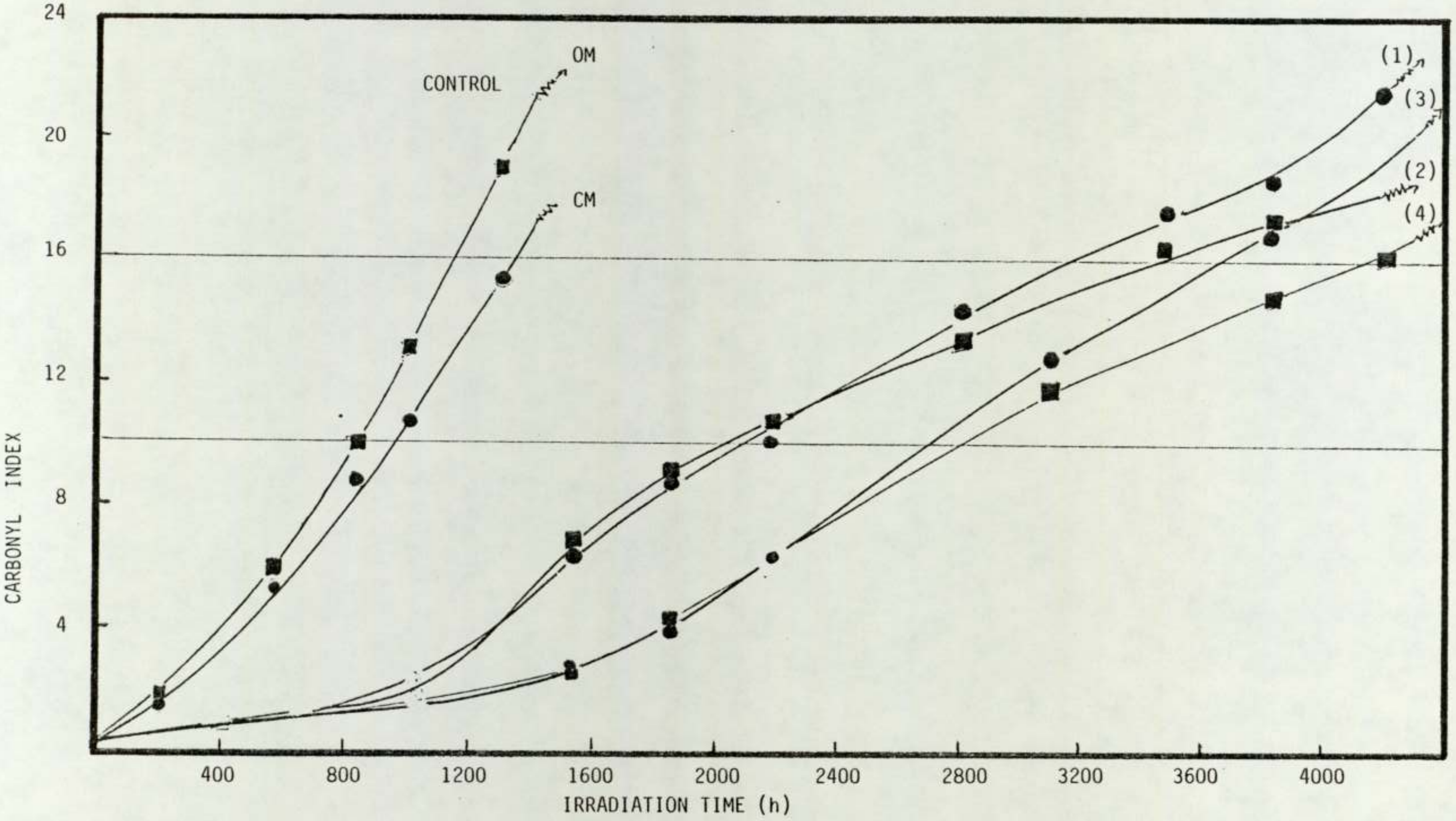


Figure 4.12 Photo-oxidative stability of LDPE films containing DnBDS concentrates processed at 150°C

(1) 2·5%-CM,10; (2) 2.5%-OM,15; (3) 5%-CM,10; (4) 5%-OM,15

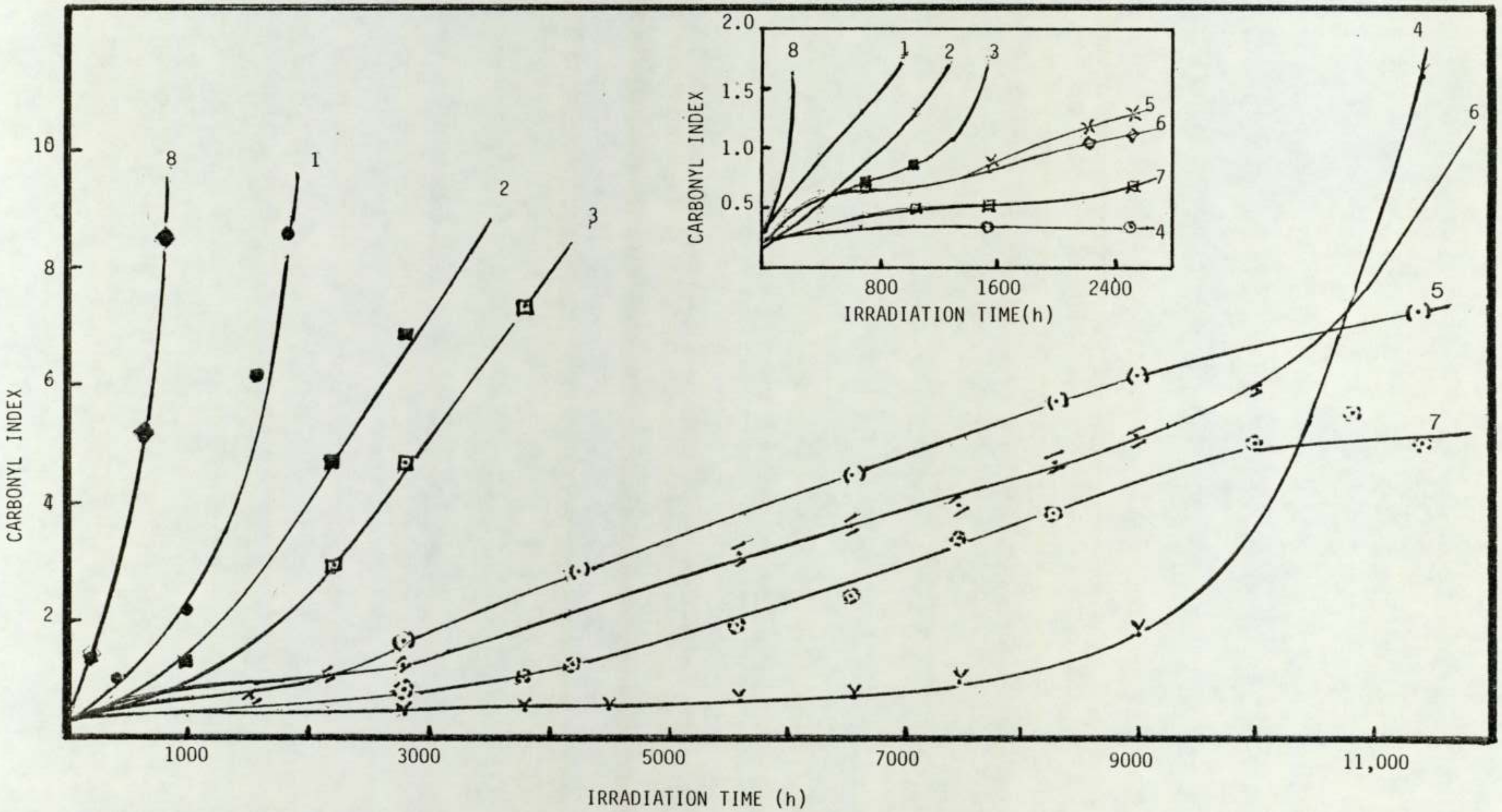


Figure 4.13 Effect of additives (2.5%) on the photo-oxidative stability of LDPE. films. (1) DnBDS, (2) HOBP, (3) HOBP - 5% (4) NiDnBP, (5) DnBDS:HOBP, (6) DnBDS:HOBP/OM,15, (7) NiDnBP:HOBP, (8) Control without additive. All samples except (6) were processed CM,10 at 150°C. Inset compares the initial photo-oxidative behaviour of the samples (using an expanded axis).

Table 4.8 Effect of additives (2.5%) on the photo-oxidative stability of LDPE concentrates (CM,10 / 150 °C)

Antoxidant concentrate	Time (h) to Fixed Carbonyl value T(>C=0 , 10)
Control(without addtive)	960
DnBDS	2100
HOBP	4000
* HOBP	5000
NiDnBP	11200
DnBDS : HOBP	>12000
** DnBDS : HOBP	11700
NiDnBP: HOBP	>12000

* concentration, 5%

** severe processing (OM,15)

4.2C Spectral Characteristics of Concentrate (Ct) Films

The presence of additives in the polymer at such concentrate levels (> 2.5%) can be accurately detected by spectroscopic methods such as IR and U.V. These can also be used to monitor the changes in the absorption characteristics of the additives during the ageing process of the stabilised polymer films or polymer extracts in solution.

4.2C.1 DnBDS and NiDnBP Concentrate Films

Figures 4.14a - 4.14c compare the IR spectral regions of PP and LDPE films prepared from DnBDS concentrates (2.5%) with the CsI disc spectrum of the pure additive. The major characteristic absorption bands of DnBDS are clearly observed in the concentrate films except in cases where these are obscured by absorption bands due to the polymer. For example, of the P-O-(C) stretching modes at 895-730 cm , only that at 730 cm is observed in PP because of the large number of wagging and bending vibrations exhibited by the polymer, which interestingly also obscured the absorptions due to P-S-S linkages (550-400 cm^{-1}). In contrast to PP, most of the characteristic absorption bands of DnBDS are clearly evident in LDPE except for the P-O-(C) stretching vibration (730 cm^{-1}) which is obscured by the strong band in the same region (730 cm^{-1}) due to CH_2 rocking vibrations of the polymer. In view of these facts, some of the characteristic absorption bands of the additive were therefore monitored during photo-oxidation of the concentrate films since the decay in the intensity of these absorption bands was found to be closely related to the photo antioxidant behaviour of the additive during the ageing process. The use of IR spectroscopy for the identification and quantification of additives in the polymer after processing, is clearly illustrated in Figure 4.15 which shows the effect of increasing DnBDS concentration in PP concentrates on the intensity of the P-O-(C) (730 cm^{-1}) and the P=S (645 cm^{-1}) stretching vibration.

Figure 4.16 illustrates the relationship between the P=S index (645 cm^{-1}) and the photo-oxidative stability of PP films containing DnBDS:TBH concentrates (see also Table 4.4). It can be seen that the addition of increasing amounts of TBH to a 2.5% DnBDS concentrate, increases the P=S index due to the additive and this is shown to be closely associated with improved photo antioxidant activity of the systems.

Figure 4.17 shows changes in the relative concentration of the various functional groups during photo-oxidation of LDPE/DnBDS concentrate (2.5%) film. The initial autoretarded oxidation of the stabilised film is shown to be associated with reduction in the intensities of both the P-O-(C) stretching vibrations (895 cm^{-1}) and the P-S-S linkages (520 cm^{-1} and 460 cm^{-1}). It is clearly shown that the end of absorption due to these functional groups not only coincides with the onset of the second auto-retarding stage, but also roughly coincides with the formation of some oxidation products of the additive with absorption bands at 490 cm^{-1} and 585 cm^{-1}. This phenomenon is also illustrated in Figure 4.18b. which shows the infra-red spectra of the stabilised polymer film.

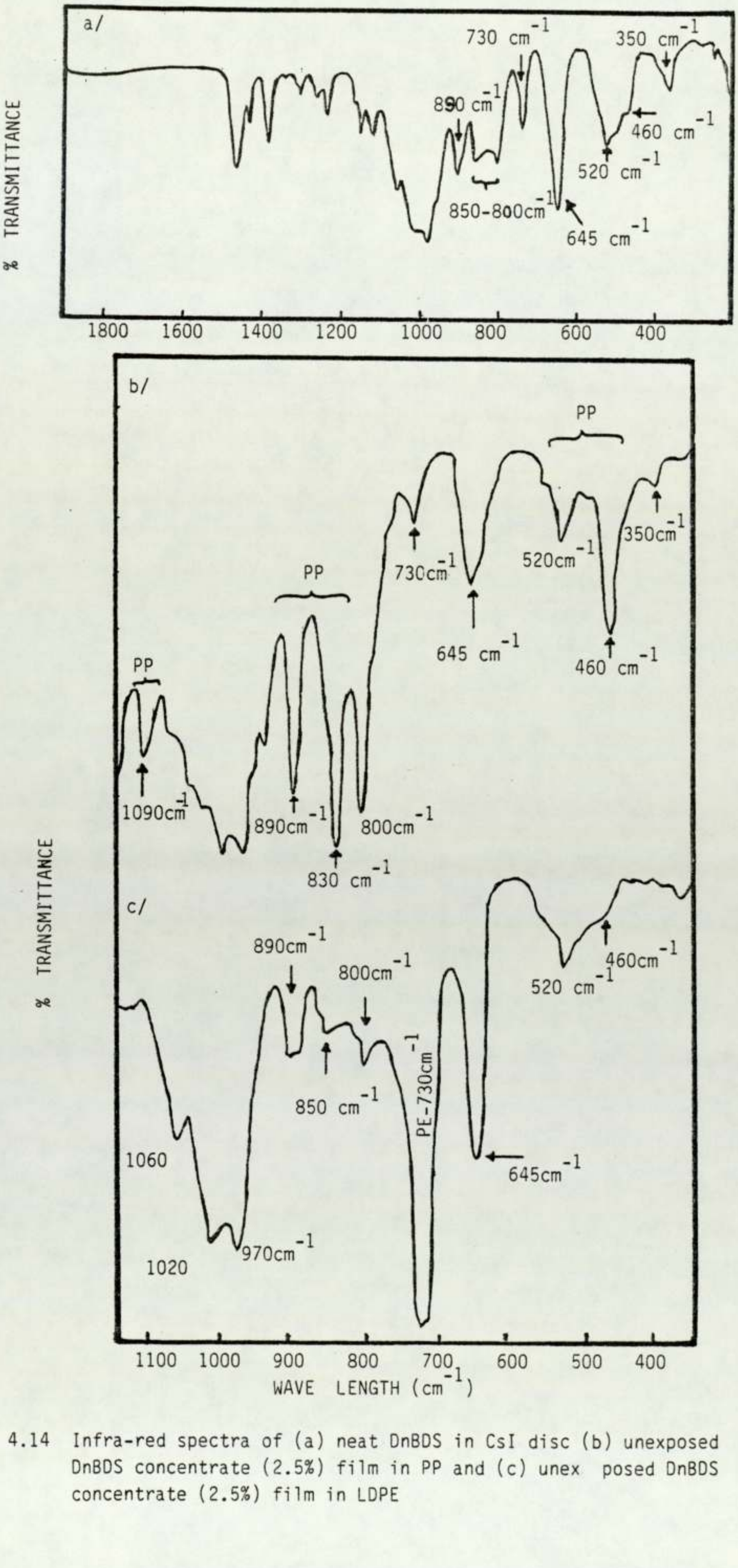


Figure 4.14 Infra-red spectra of (a) neat DnBDS in CsI disc (b) unexposed DnBDS concentrate (2.5%) film in PP and (c) unexposed DnBDS concentrate (2.5%) film in LDPE

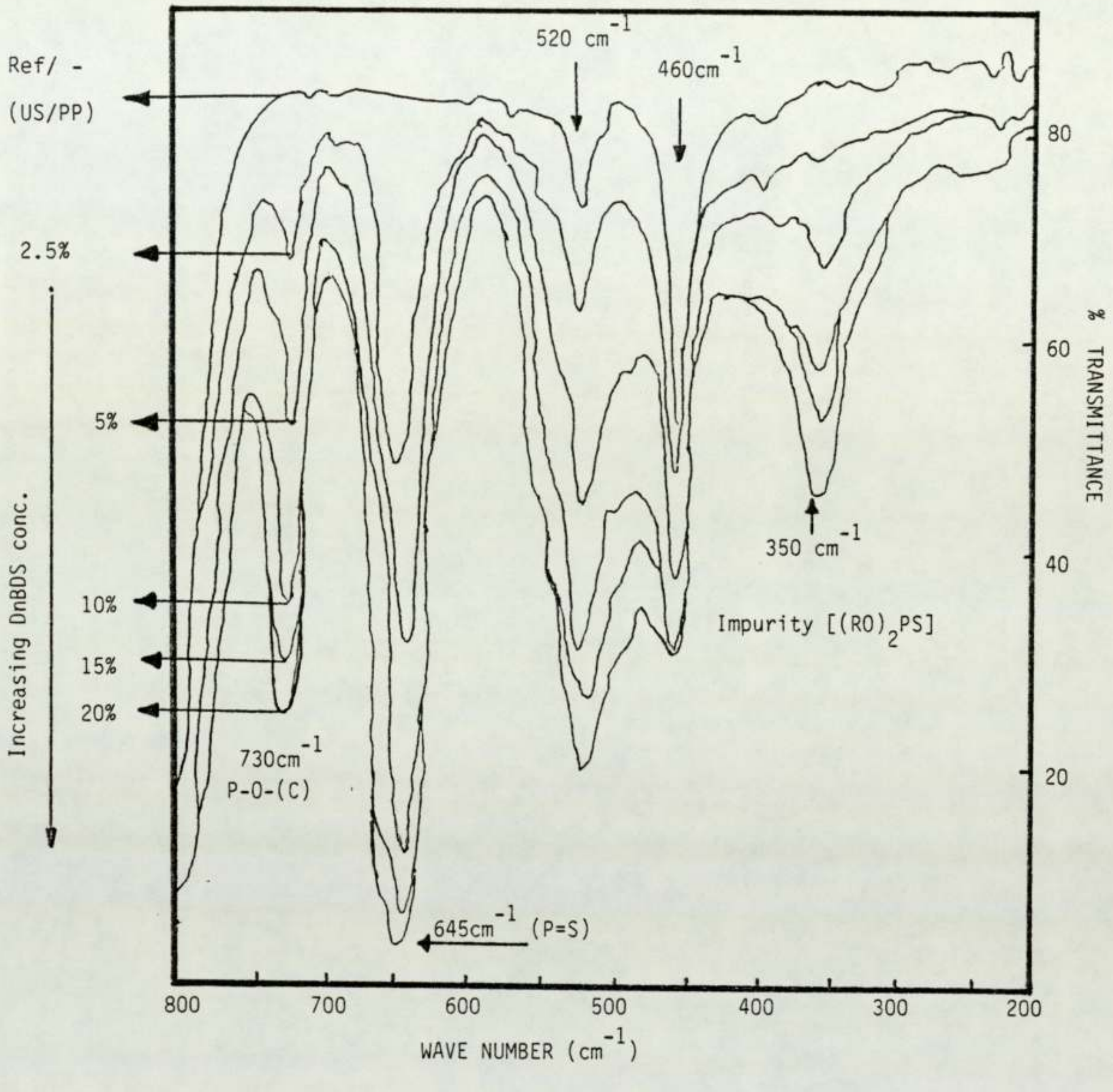


Figure 4.15 Infra-red spectra of DnBDS Concentrates in PP

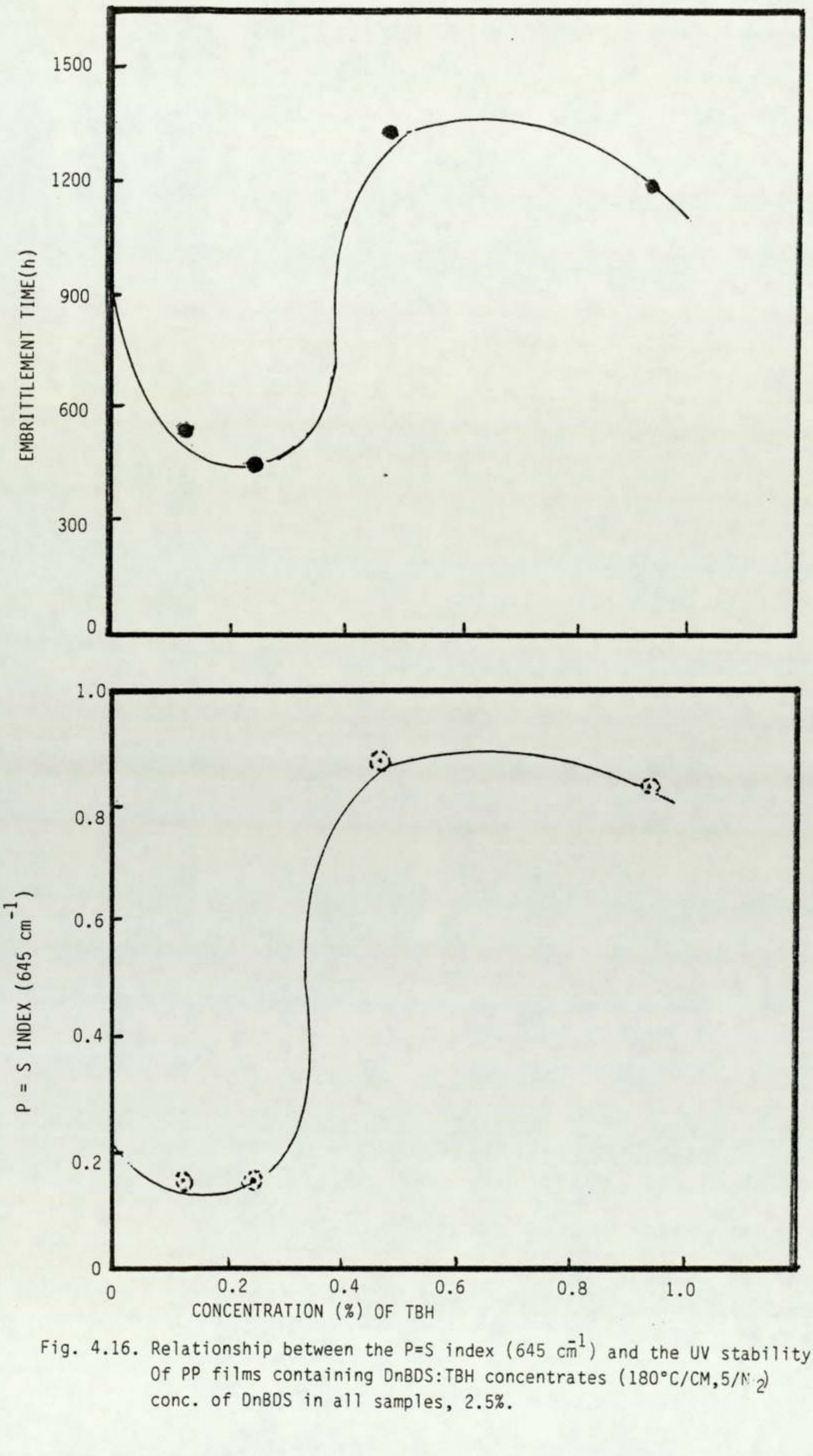


Fig. 4.16. Relationship between the P=S index (645 cm^{-1}) and the UV stability Of PP films containing DnBDS:TBH concentrates (180°C/CM,5/N$_2$) conc. of DnBDS in all samples, 2.5%.

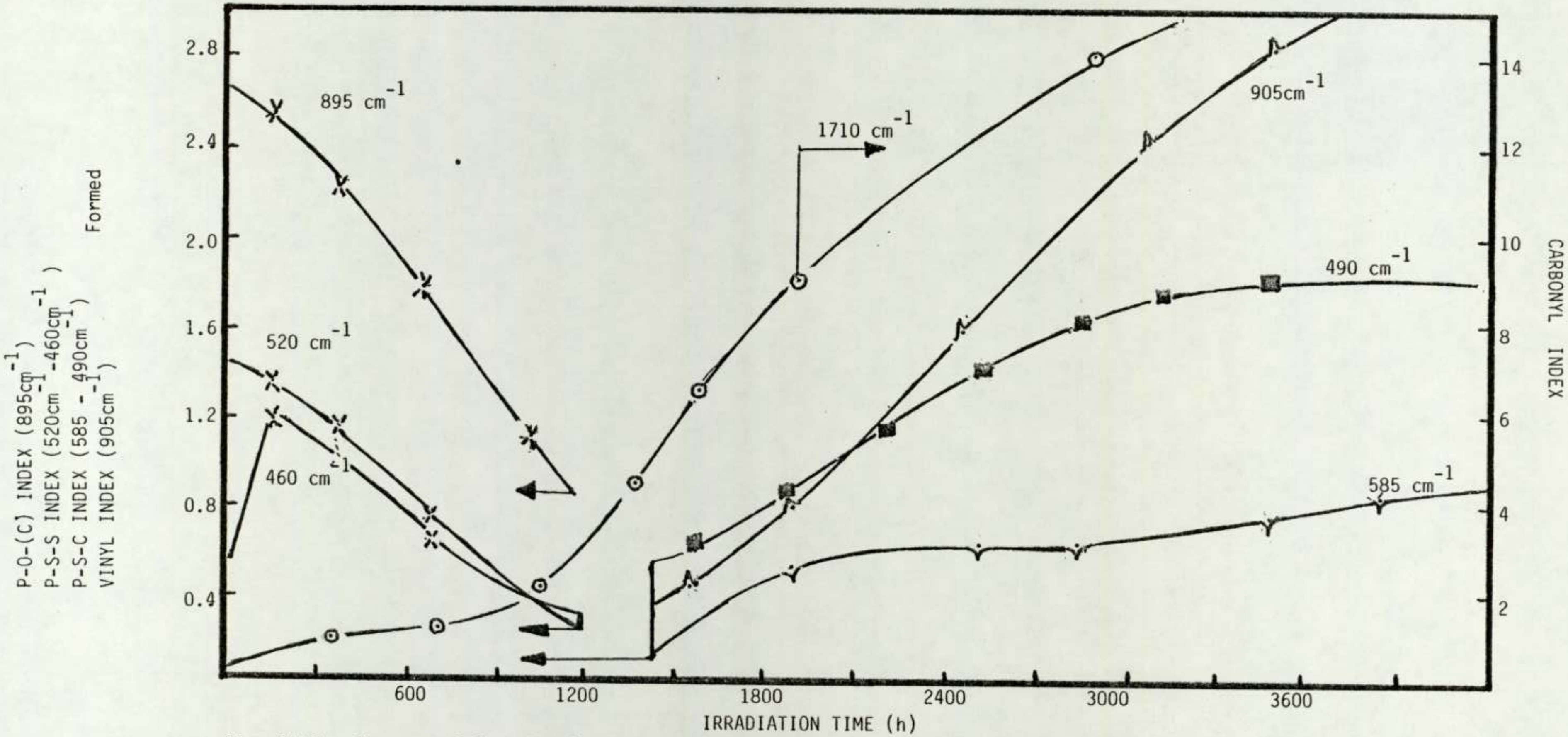


Fig. 4.17. Changes of functional groups during photo-oxidation of LDPE/DnBDS concentrate (2.5%) processed CM,10 at 150°C

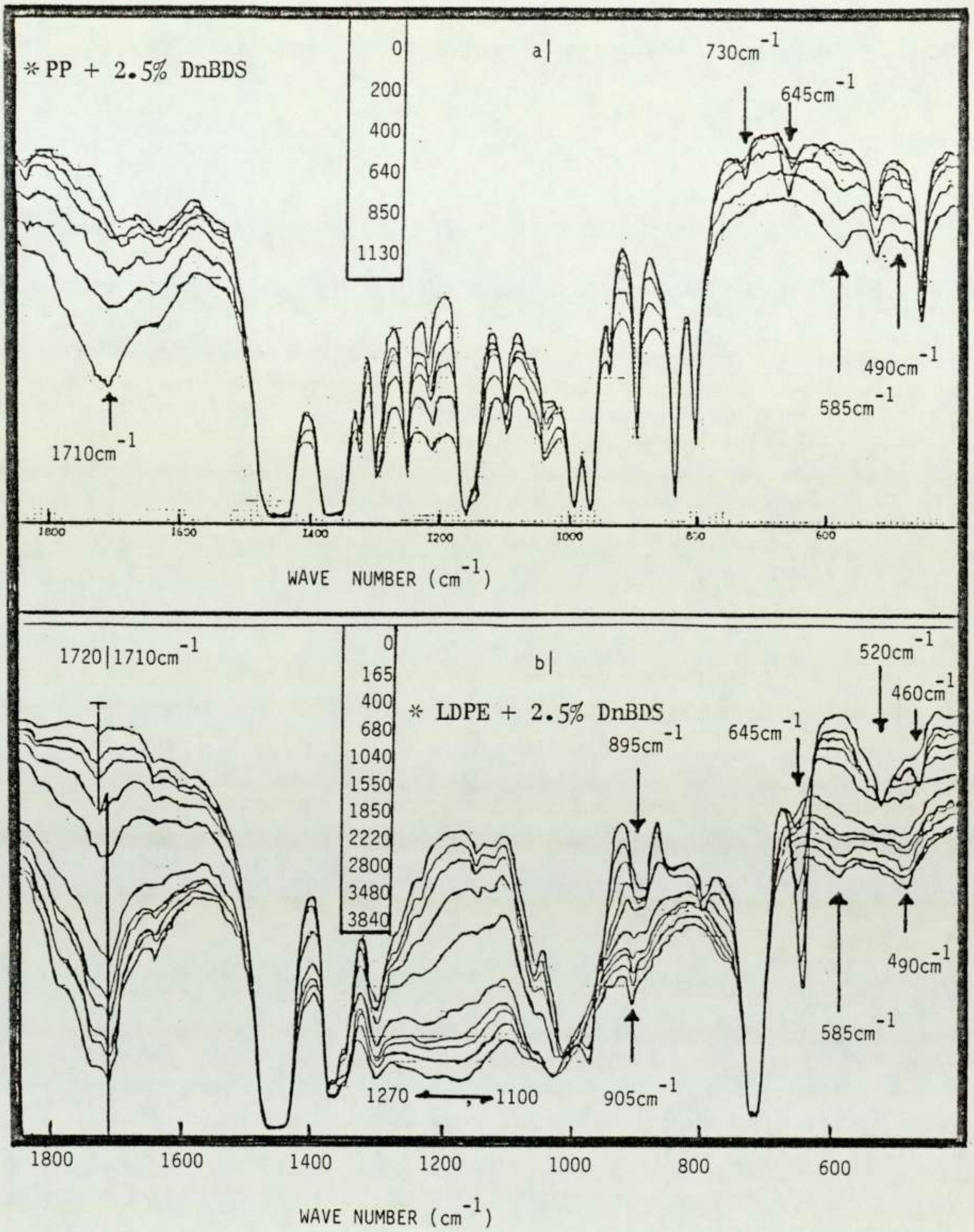


Figure 4.18 IR spectra of PP (a) and LDPE (b) DnBDS concentrates showing changes of functional groups during photo-oxidation of the stabilised films. (Exposure times are shown in hours).

* concentration of DnBDS.

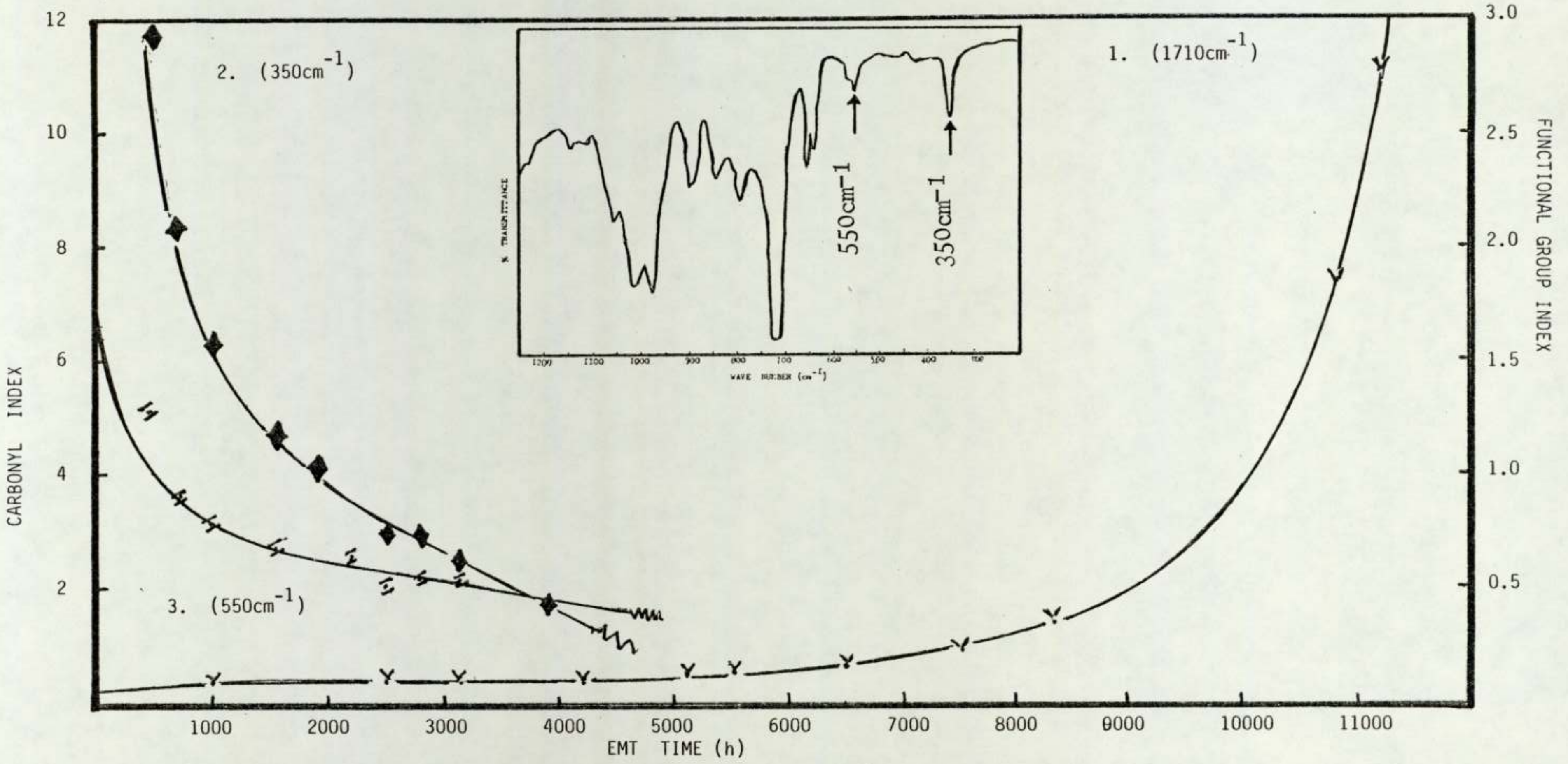


Figure 4.19 Changes of functional groups during photo-oxidation of LDPE|NiDnBP concentrate (2.5%) processed CM,10 at 150°C
(1) Formed C=O, (2) Ni-S stretching vibr., (3) P-S-Ni stretching vibr .

Furthermore, a similar relationship between the decay in the intensity of some IR absorption bands of the additive and the photo-oxidative stability of the stabilised polymer film was also observed during photo-oxidation of LDPE films containing NiDnBP Ct. (2.5%) processed CM,10 at 150 C. Figure 4.19 which displays the IR spectrum of the unexposed LDPE/NiDnBP concentrate film (inset), also shows that the persistence of the absorption bands at 550 cm^{-1} (P-S-Ni) and 350 cm^{-1} (Ni-S) amongst others, is clearly associated with the initial photo-oxidative induction period (PIP) observed during the early stages of photo-oxidation. As with the DnBDS-stabilised film (Figure 4.17), the almost complete decay of the functional groups in the NiDnBP concentrate film roughly coincides with the onset of the auto-acceleration stage (Figure 4.19).

4.2C.2 Synergistic DnBDS:HOBP Concentrate Films

An interesting feature of the synergistic DnBDS : HOBP combinations in PP and LDPE, is the probable formation of a product of their reaction because of the occurence of a new U.V. absorption band around 400 nm HOBP in its own right exhibits three U.V. absorption bands at 240 nm, 285 nm and 325 nm (Figure 4.20; curve 3) whereas the DnBDS:HOBP concentrate films show the new band at 400 nm in addition to the three bands of HOBP. In view of the opacity to U.V. light below 370 nm of films prepared from

DnBDS:HOBP concentrates (Figure 4.20; curve 1), a 0.6% dilute analogue of this concentrate (curve 2) is therefore used to illustrate this fact (Figure 4.20). The new absorption band (400 nm) is clearly evident in films prepared from both mildly - processed (CM,5) and severely-processed (OM,15) concentrates although the U.V absorbance of this band in the latter is much higher than that in the former. This is illustrated in Figure 4.21a-b which shows the U.V. absorption spectra of PP films prepared from DnBDS:HOBP concentrates processed under both mild and severe conditions, and also at two different additive ratios (2.5% + 2.5% and 2.5% + 5%). Another interesting feature of these concentrates is the observation that the intensity of the IR absorption bands (645 cm^{-1}) associated with P=S stretching vibrations (see Figures 4.21c-d), is distinctly lower for severely-processed concentrates. This is clearly a direct consequence of the greater rate of consumption of DnBDS during severe processing (OM) to form the species responsible for the 400 nm U.V.absorption band since the concentration of this species is shown (Figure 4.21a-d) to be higher for these concentrates (OM), as compared to the mildly-processed analogues. Under photo-oxidative conditions, the 400 nm band decreases rapidly in intensity to a minimum in less than 30 hours for concentrates processed under severe conditions and eight hours for mildly-processed concentrates, although no change was observed in the other absorption bands.

Figure 4.20a

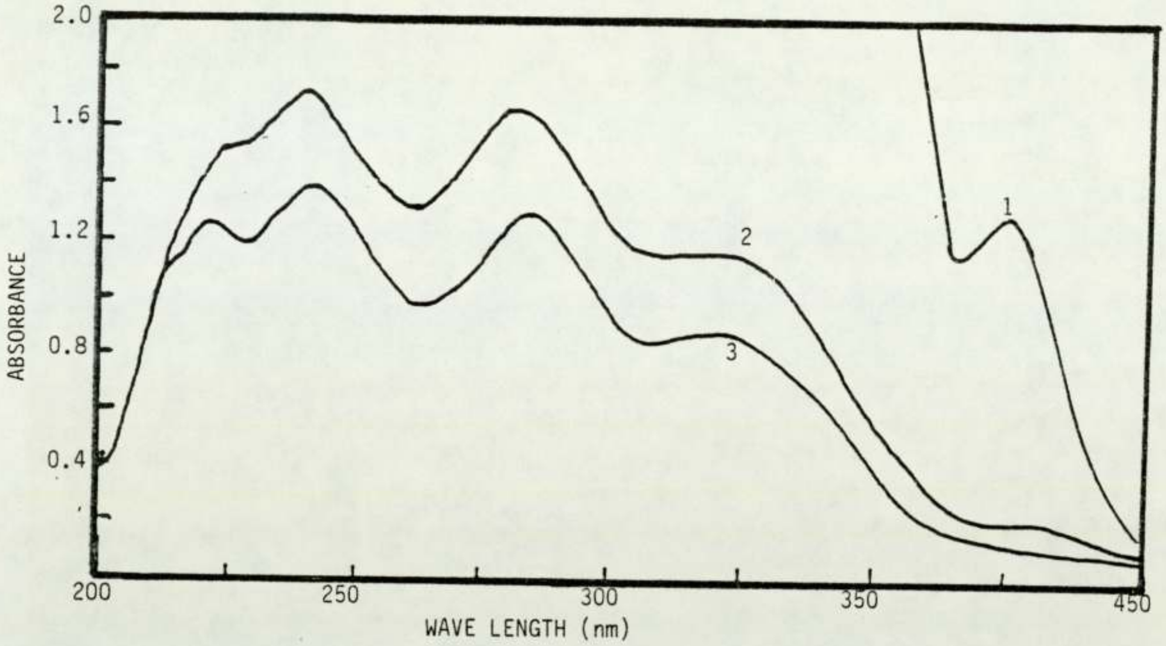


Figure 4.20b

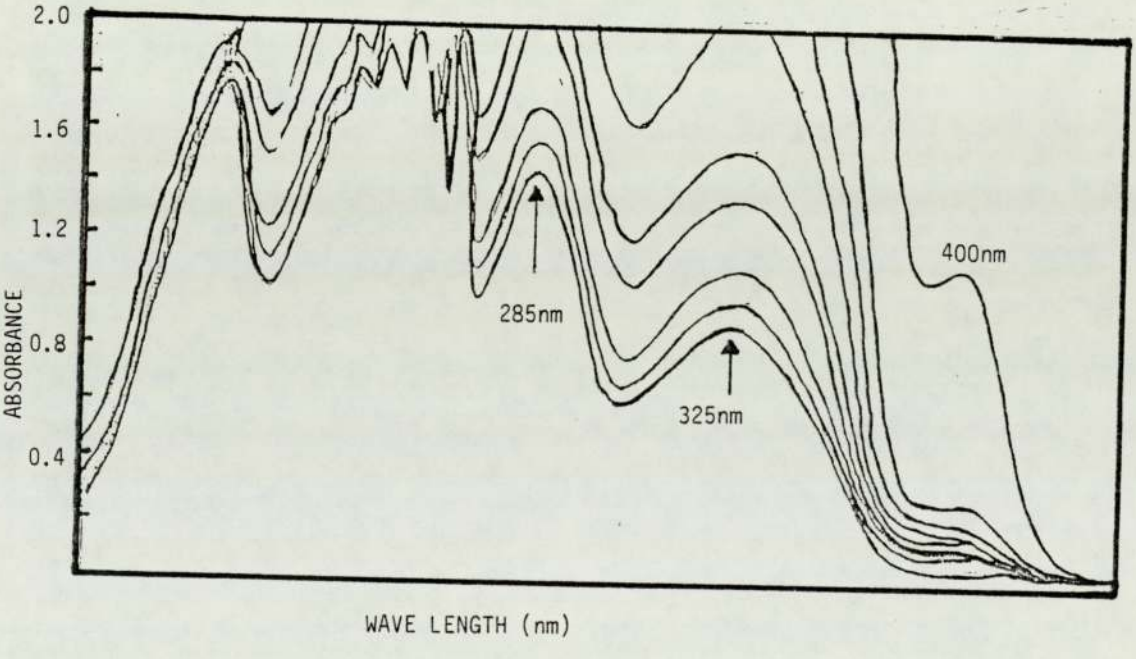


Figure 4.20a U.V.-absorption spectra of (1) PP film of severely processed DnBDS:HOBP concentrate at 1:1 ratio (conc. of DnBDS=2.5%, (2) 0.6% DCt of same concentrate, (3) 0.15% HOBP processed CM,10.

Figure 4.20b U.V.-absorption spectrum of toluene solution of the synthesised product of Bis-di-n-hexyl benzophenone. Absorption at higher concentrations is is also shown

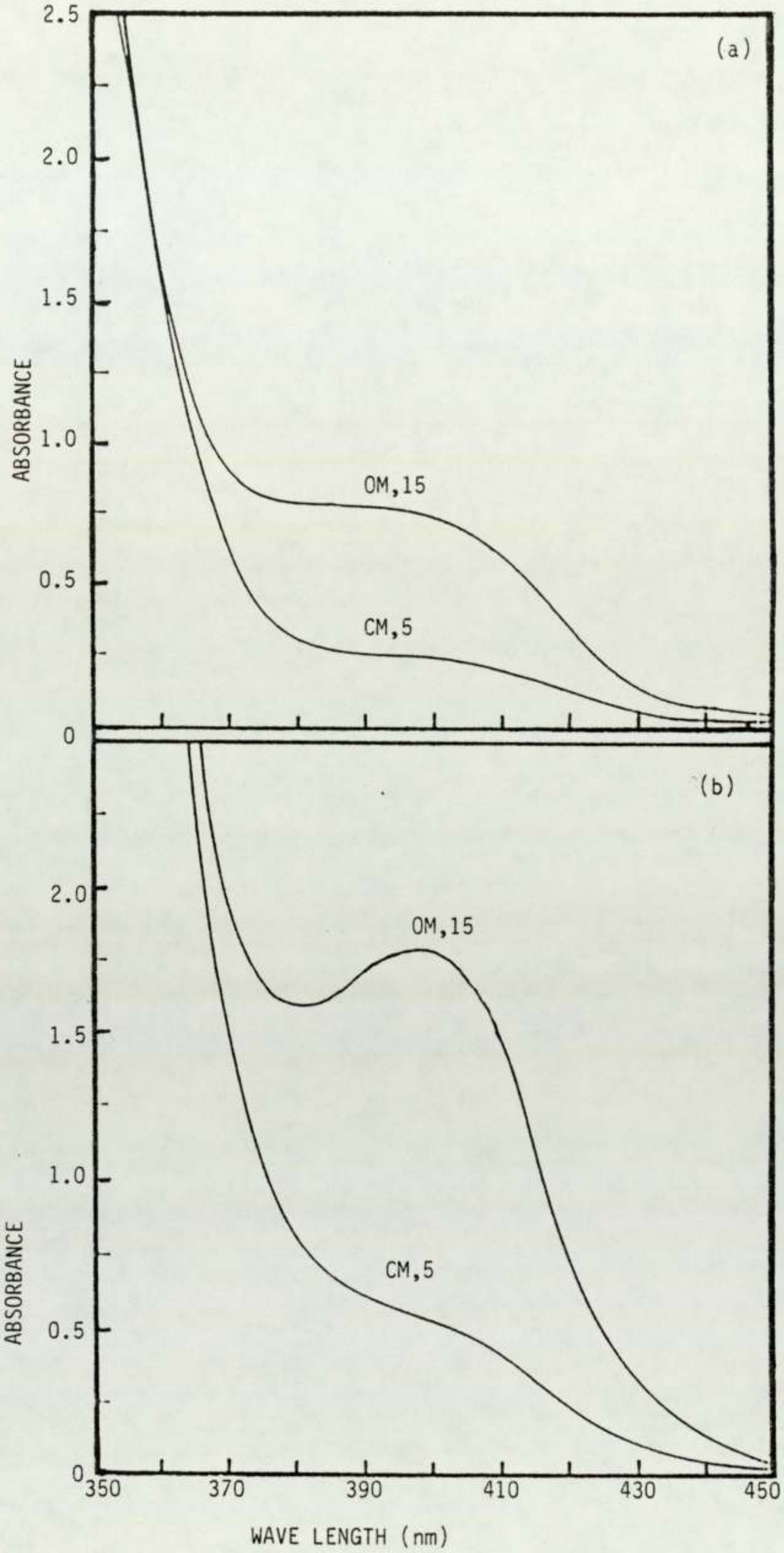
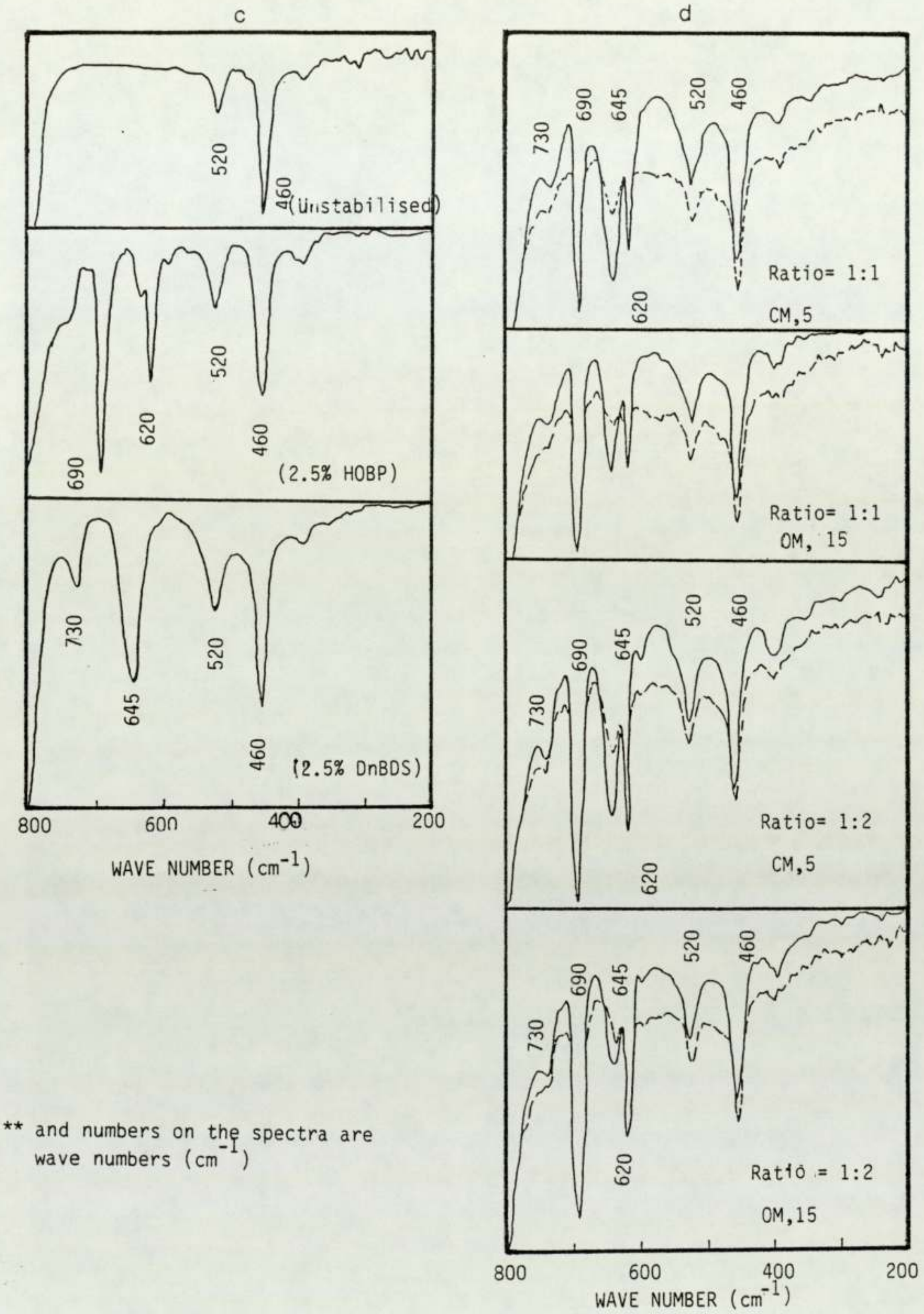


Figure 4.21.U.V. absorption of PP films containing DnBDS:HOBP concentrates (190°C) at concentrations (a) 2.5% : 2.5% and (b) 2.5% : 5%



** and numbers on the spectra are wave numbers (cm^{-1})

Figure 4.21b. Low freq. IR spectral region of PP films containing (C) 2.5% each of HOBP and DnBDS concentrates (CM/10) and (d), [DnBDS:HOBP] concentrates at different ratios (1:1 & 1:2). Dotted line represents IR spectra of same film after 3000 hrs U.V. irradiation. (Concentration of DnBDS in each concentrate, 2.5%)

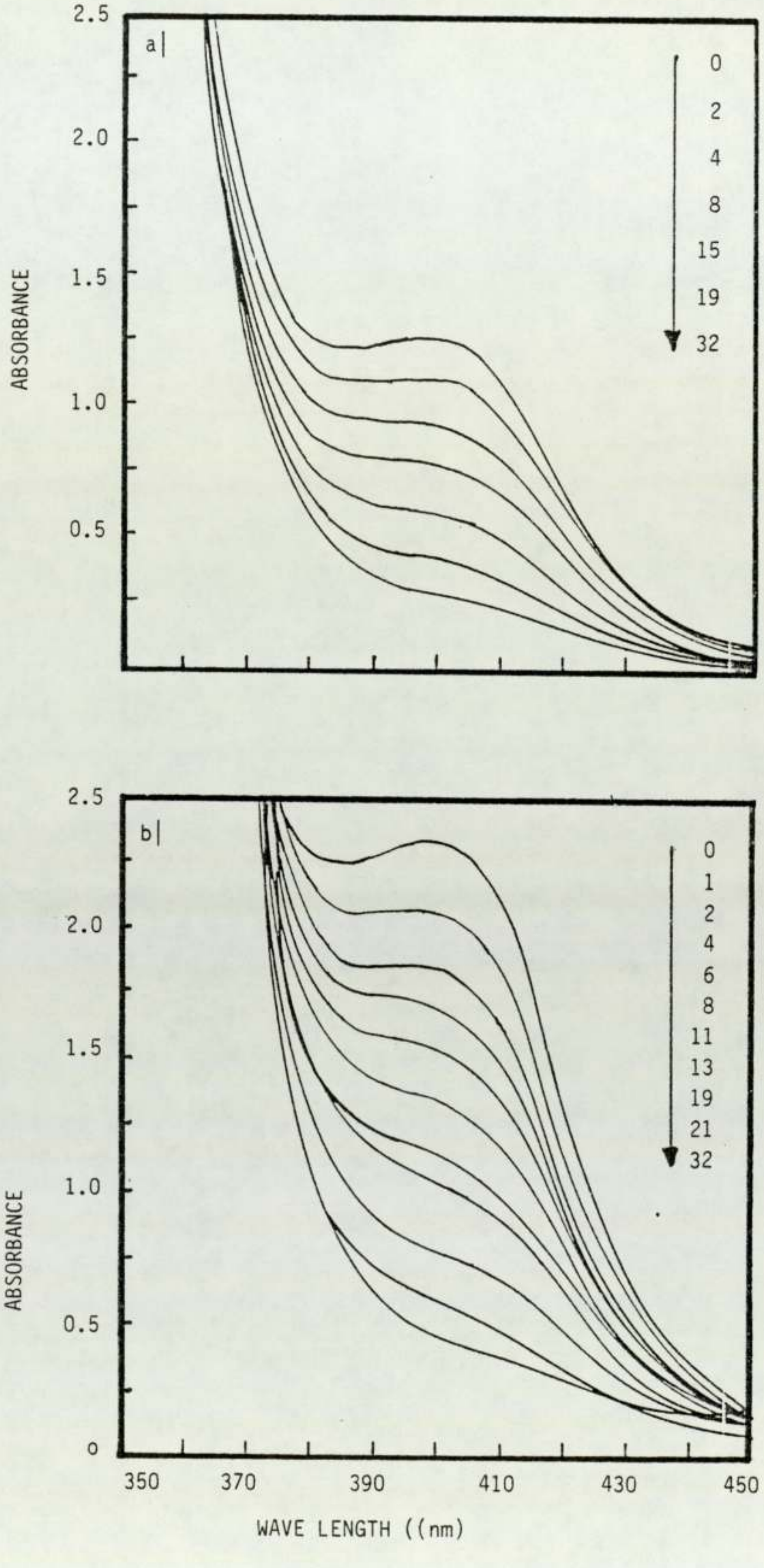


Figure 4.22 Changes in the intensity of the 400 nm band following photolysis (30°C) in the U.V. cabinet of PP films prepared from severely-processed (OM,15|190°C) DnBDS:HOBP concentrates at additive ratio (a) 1:1 and (b) 1:2 (U.V. exposure times are shown in hours, and conc. of DnBDS = 2.5%)

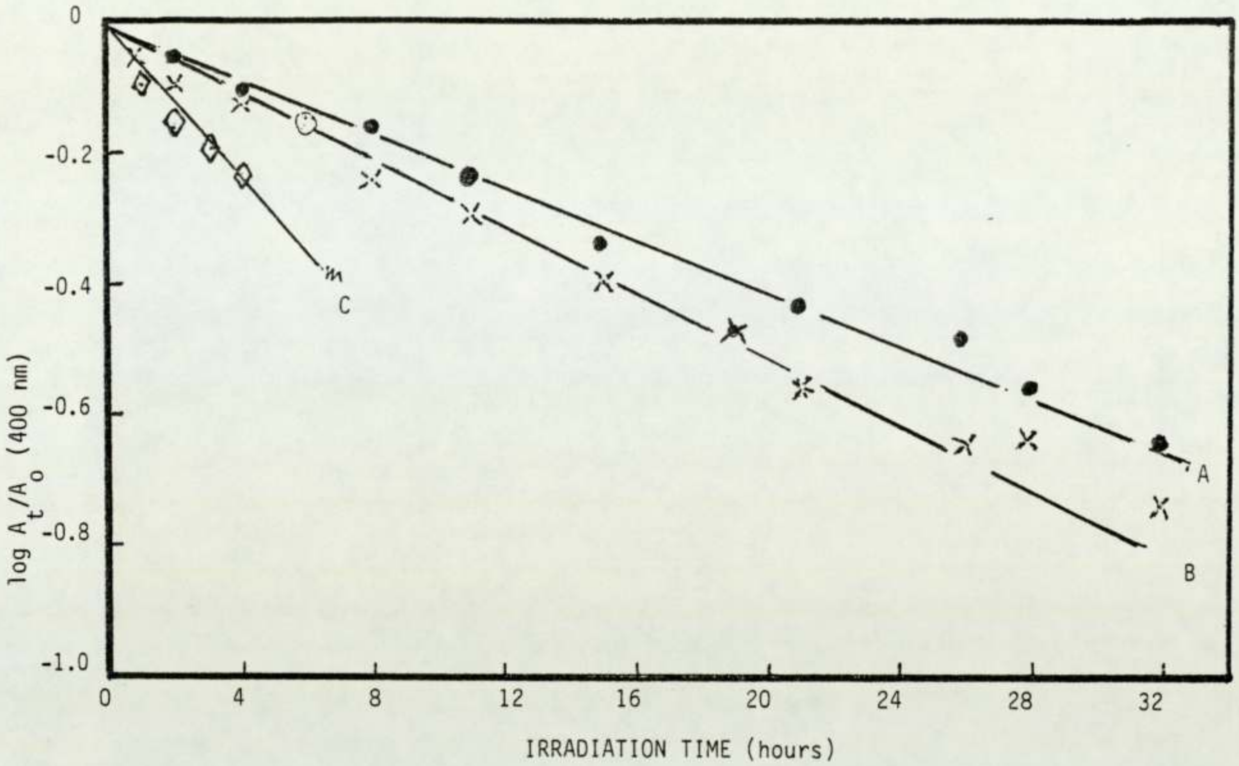


Figure 4.23 Kinetics of disappearance of 400nm band of PP films prepared from severely-processed (OM,15/190°C) DnBDS:HOBP concentrates (2.5% DnBDS) at additive ratios (a) 1:1 and (b) 1:2; and (c) mildly-processed concentrates at both ratios

Changes in the 400 nm band of the concentrate films following periods of photolysis in the U.V. cabinet is shown in Figure 4.22 for the severely-processed concentrates (OM,15), while the kinetics of the disappearance of the band is shown in Figure 4.23. It is clear that at both additive ratios, the 400 nm band of the mildly-processed (CM) concentrates is relatively much more unstable to U.V. light compared with that of the severely-processed concentrates (OM). Similarly, a comparison of the severely-processed concentrates clearly indicates that the photolytic instability of the 400 nm band is more pronounced for the 1:2 ratio (DnBDS:HOBP) concentrates as shown in Figure 4.23.

4.2C.3 Spectral Features of Extracted Concentrate Films and Solvent Extracts

Figure 4.24 shows the infra-red absorption spectra of unextracted and extracted PP and LDPE films containing DnBDS concentrate (2.5%) processed under oxidative conditions. It is clear that hot methanol extraction (at 50°C) effectively removes the various antioxidant species responsible for the spectral features of the stabilised film. A similar effect was observed not only for the mildly-processed (CM,5) concentrates, but also when a different solvent such as hexane is used. Furthermore, Figure 4.25 clearly shows that hot methanol extraction (50°C) of LDPE film containing NiDnBP concentrate (2.5%)

also results in complete removal of all the antioxidant species from the film.

This phenomenon is confirmed in Figure 4.26 which shows the ^{31}P NMR spectra of solvent (methanol) extracts of PP film containing (a) mildly-processed DnBDS concentrate and (b) severely-processed DnBDS concentrate (2.5%). The ^{31}P NMR spectra of the extracts indicate that very identical products are formed during processing of DnBDS concentrates under both mild (CM) and severe (OM) conditions as reflected by the ^{31}P NMR signals with chemical shifts of 98.8 ppm, 96.4 ppm, 94 ppm, 63 ppm and 53 ppm (all chemical shifts are referenced to a H_3PO_4 standard). However, the ^{31}P NMR spectra of the extract of the severely-processed concentrate film (b) also contains additional signals with chemical shifts of 85 ppm and 84.1 ppm.

Solvent (methanol at 50 ^{o}C) extraction of PP and LDPE films containing the synergistic combinations revealed that all the species responsible for the original spectral features were completely extracted since the extracted films showed similar IR and U.V.spectrum to the unstabilised control films. Furthermore, the extracts of the DnBDS:HOBP concentrate films also showed very identical U.V.spectral features to the stabilised films. Figure 4.27a-b, illustrates the changes in the intensity of the 400 nm band of methanol extracts of PP films containing both mildly-processed (a) and severely-processed (b) DnBDS:HOBP concentrate films, following periods of photolysis in the U.V.cabinet. Changes in the intensity of the 400 nm band of the product of DHDS and 2,4-di-hydroxybenzophenone in methanol under similar conditions is also shown in Figure 4.27c. The kinetics of the disappearance of this band in both the polymer extracts and the synthesised product (Figures 4.28a and 4.28b respectively) clearly confirms the high photolytic instability of this band as was shown for the stabilised polymer films (Figures 4.22 - 4.23). Similarly, the 400 nm band of extracts of the mildly-processed concentrate films at both additive ratios (Figure 4.28a curves (1) and (3)) seem to be more unstable to U.V. light compared to that of the severely-processed concentrate films (curves (2) and (4))and this appears to be in good agreement with the findings reported for the stabilised films (Figure 4.23). Moreover, Figures 4.28a-4.28b clearly demonstrate the highly stable nature of the 400 nm band under thermal conditions since the kinetics revealed that the intensity of this band in both the extracts and the synthesised product in toluene actually shows an increase following periods of thermolysis in an oil bath. (105 C).

In contrast to the susceptibility to extraction by organic solvents of DnBDS concentrates in PP and LDPE, preliminary examination of a DnBDS 2.5% concentrate in

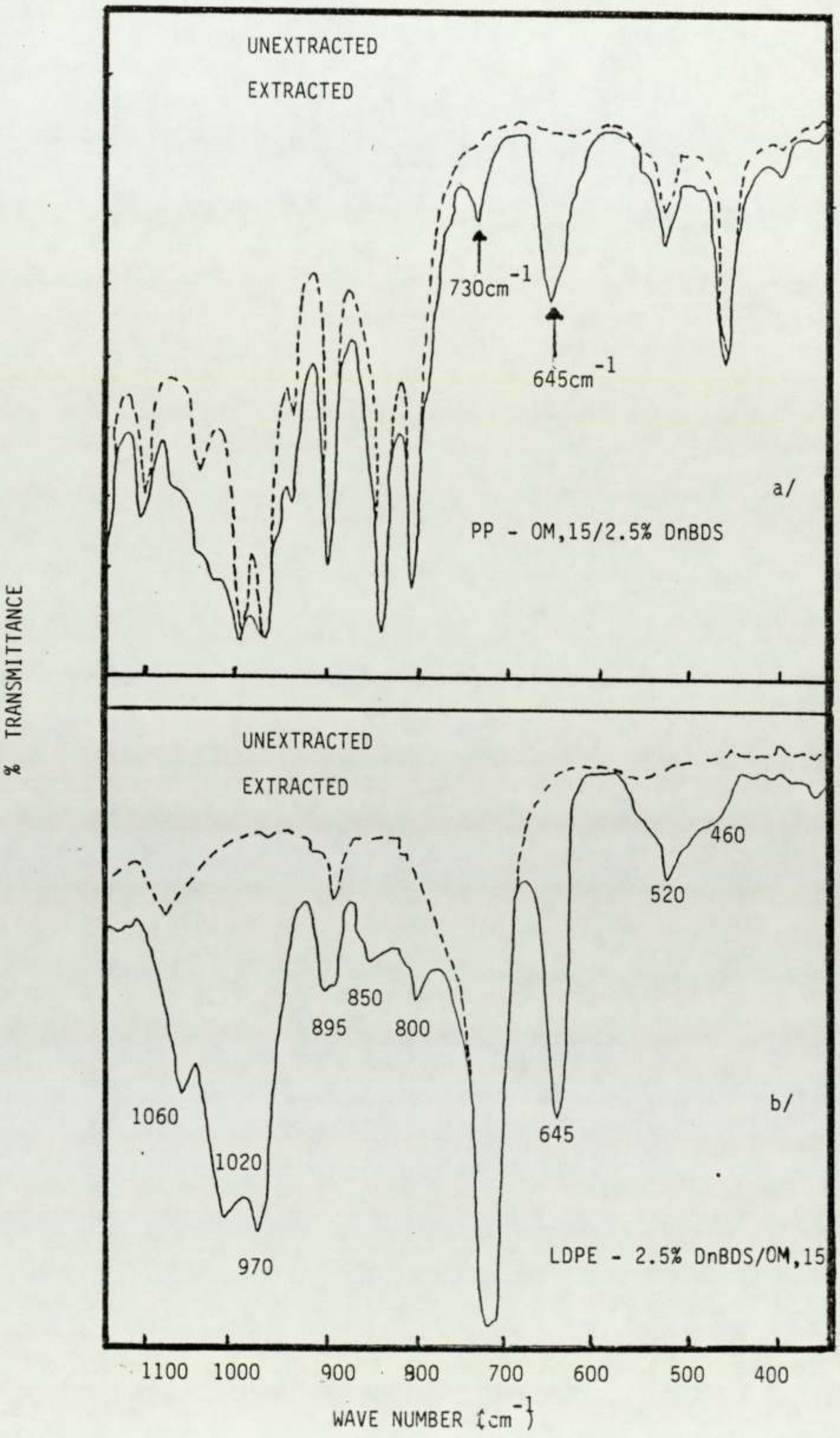


Figure 4.24 Infra-red spectra of DnBDS (2.5%) concentrates in PP (a) and LDPE (b) before (——) and (----) extraction after

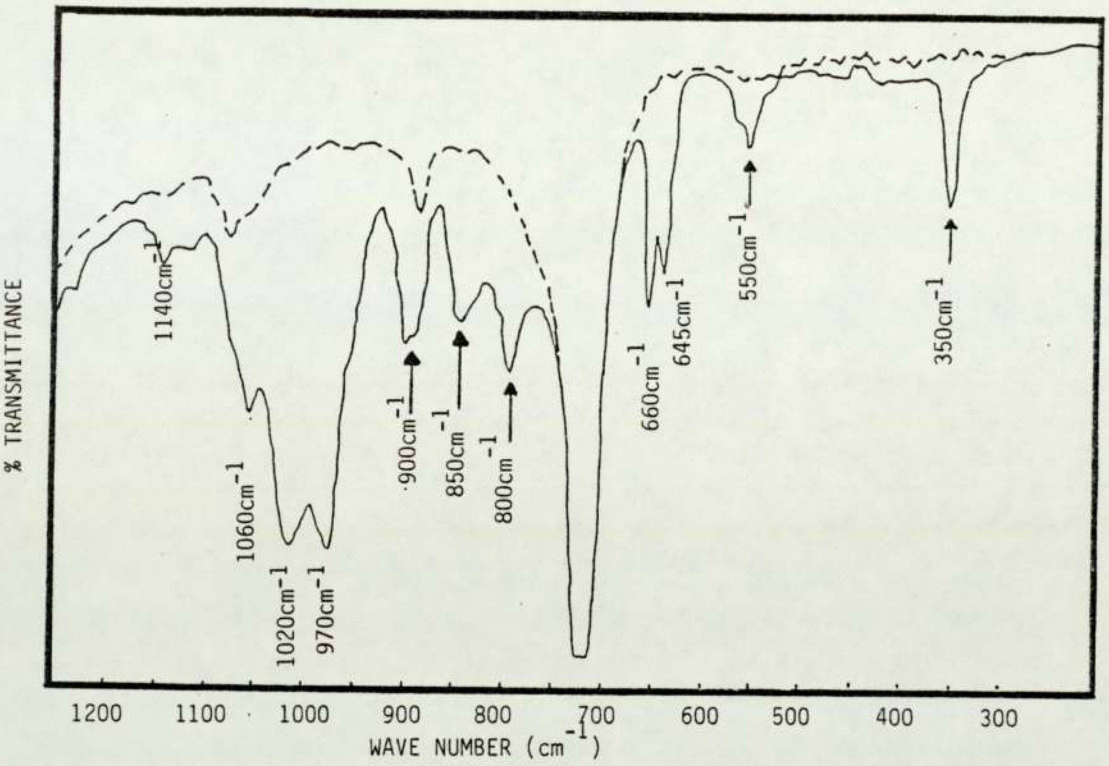


Figure 4.25 IR - spectra of extracted (-----) and unextracted (——) LDPE film containing 2.5% NiDnBP concentrate (CM,10/150°C).

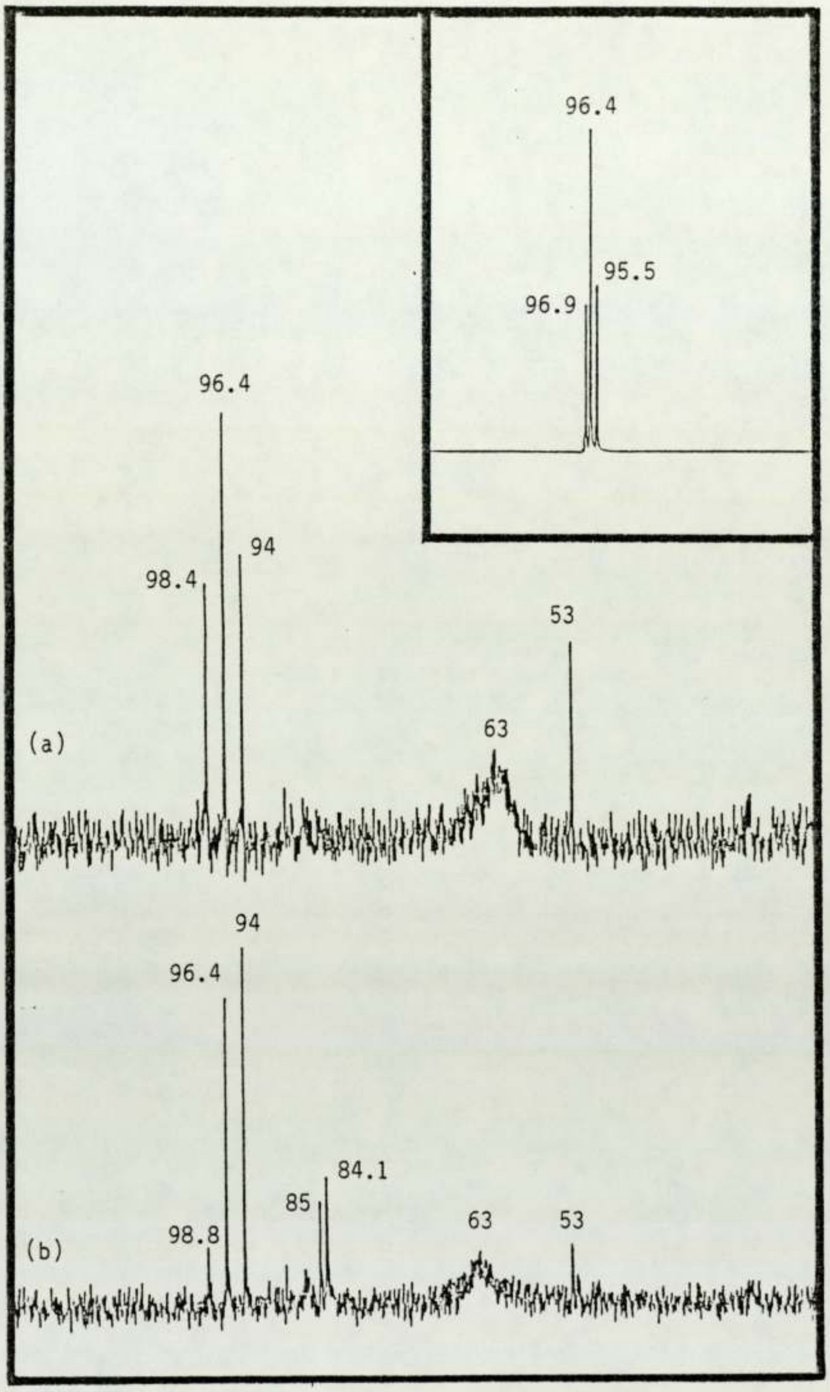


Figure 4.26 ^{31}P NMR spectra of solvent extracts of PP films containing 2.5% DnBDS concentrates processed under conditions of both restricted oxygen (a) and excess oxygen (b). Inset shows the ^{31}P NMR spectrum of a synthesised sample of di-n-butyl thiolphosphate $[(RO)_2(RS)PS]$

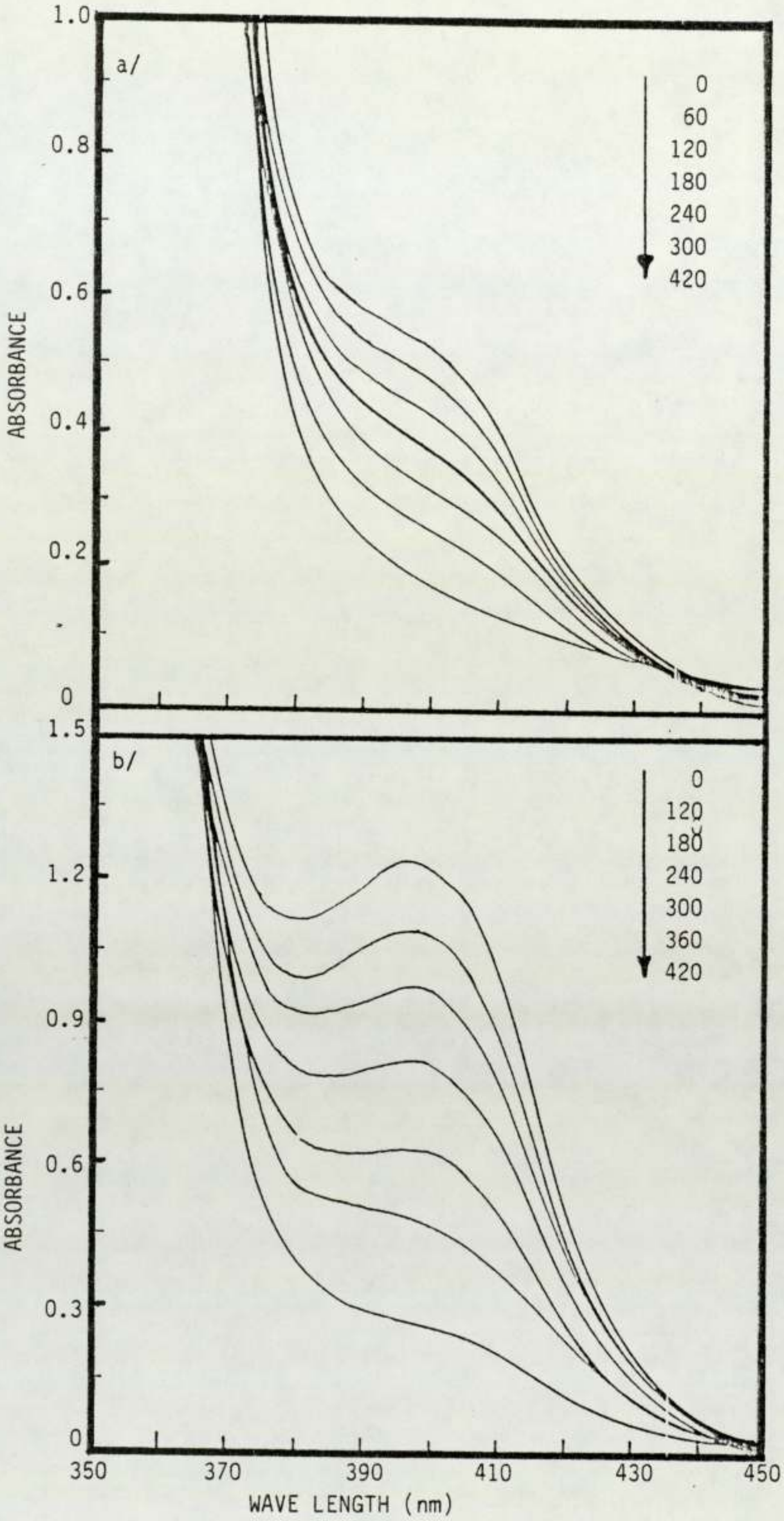


Figure 4.27 Changes in the intensity of the 400nm band following photolysis in the U.V. cabinet of methanol extracts of PP/Ct films of DnBDS;HOBP (2.5%+2.5%) processed (a) CM,5 and (b) OM,15. (U.V. exposure times are shown in minutes).

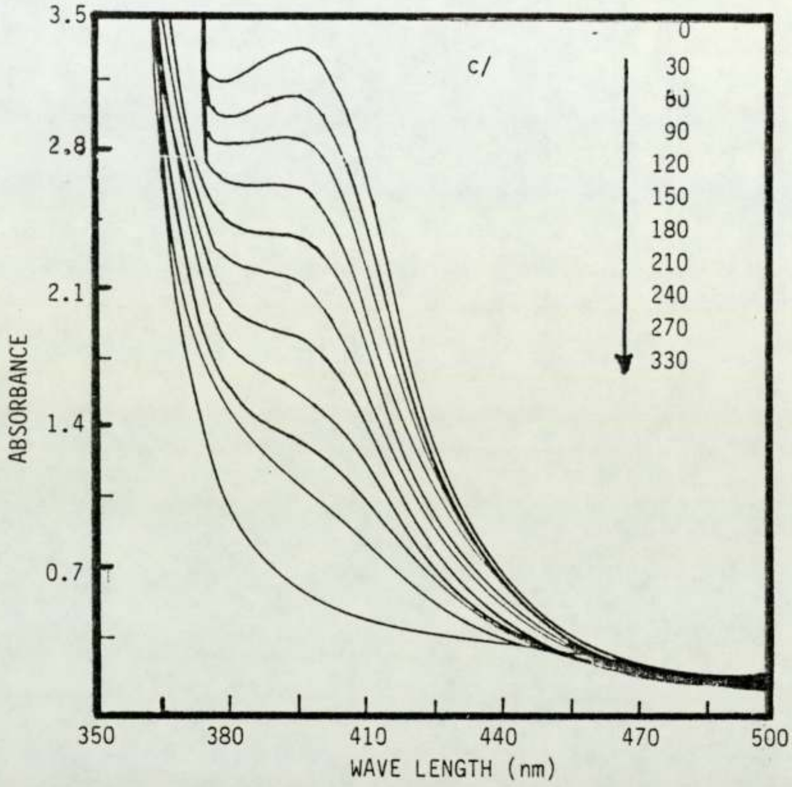


Figure 4.27 Changes in the intensity of the 400 nm band of the synthesised sample of DHDS and 2,4-di-hydroxy benzophenone in methanol, following photolysis in the U.V. cabinet. (U.V. exposure time are shown in minutes).

Fig. 4.28a.

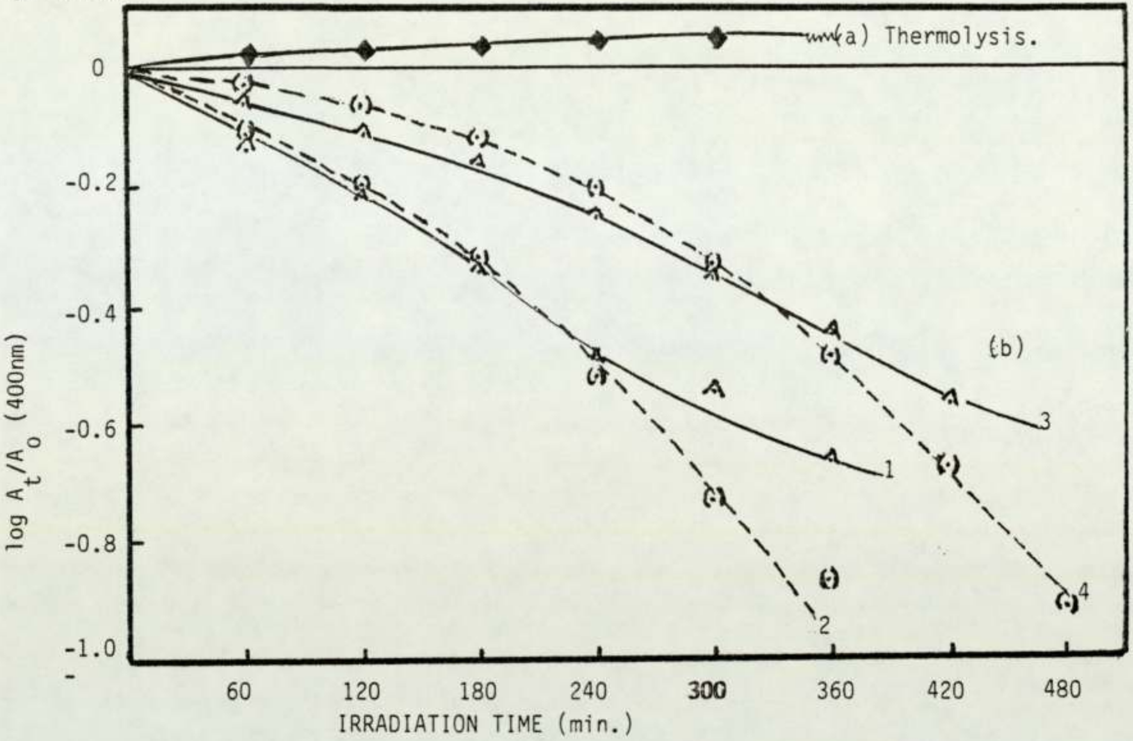


Fig. 4.28b.

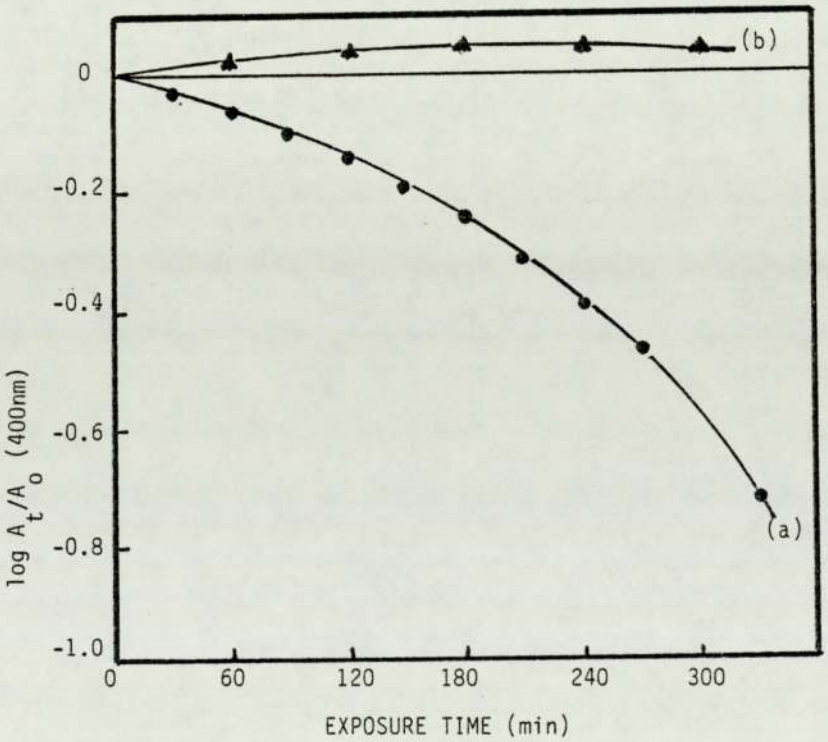


Figure 4.28a Kinetics* of the disappearance of 400nm band following periods of thermolysis (a) and photolysis (b) of methanol extracts of PP films containing DnBDS:HOBP concentrates at ratios:- (1) 1:1, CM-5, (2) 1:1 OM-15, (3) 1:2, CM-5 and 1:2, OM-15 (2.5% DnBDS)
* Thermolysis carried out on toluene extracts at 105°C

Figure 4.28b Kinetics of the disappearance of 400nm band of the synthesised product of DHDS and 2,4-di-hydroxybenzophenone in (a) methanol during photolysis in the U.V. cabinet and (b) toluene during thermolysis in an oil bath (105°C).

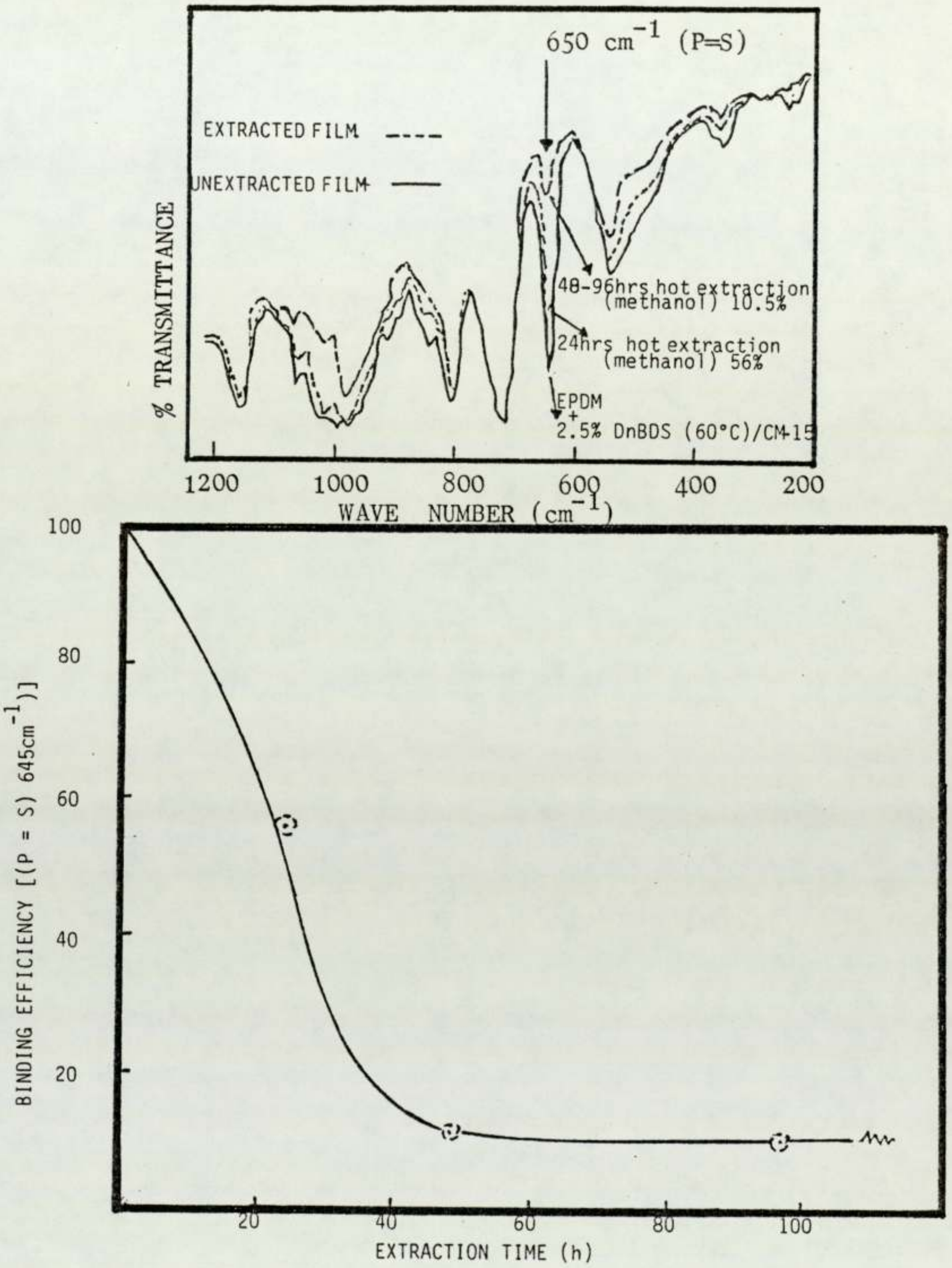


Figure 4.29 Mechanochemical binding of thiophosphoryl species to the polymer chain during processing of 2.5% DnBDS concentrate in EPDM (CM,15/60°C)
Inset shows changes in the IR spectral region of unextracted and extracted EPDM thin film containing 2.5% DnBDS concentrate.

EPDM processed under mild conditions (CM,15/60°C) reveals a significant departure from the previous results on PP and LDPE concentrates. The inset to Figure 4.29 illustrates the resistance to extraction by methanol (50°C) of an EPDM thin film containing the concentrate (DnBDS). Figure 4.29 clearly indicates that some thiophosphoryl species may be chemically bound to the polymer chain during processing, hence the persistence of the P=S stretching vibrations (645 cm^{-1}) after exhaustive (96 hours) solvent extraction.

4.2D Dilute Concentrates (DCt) as Stabilisers

This section deals with the overall antioxidant activity of dilute concentrates (0.2% - 0.6%) in PP and LDPE. The dilution of the original concentrates of [DRDS] and [DRDS:HOBP] in fresh unstabilised polymer was carried out in the presence of a second and/or third component (HOBP and/or NiDRP) as the case may be, although results are also shown for a considerable number of dilute concentrates derived from the controlled oxidatively-processed 3-component concentrates (COM and COM/TBH) as summarised in Section 4.1.

4.2D.1 PP Dilute Concentrates (PP/DCts)

4.2D.1.1 Melt Stability During Processing

Table 4.9 and Figure 4.30a compare the changes in melt flow index (MFI) of thiophosphoryl dilute concentrates in PP with that of other commercial melt stabilisers at the same concentration (0.4%), on successive passes in an extruder at 260 °C. The original thiophosphoryl concentrates were initially severely-processed (OM,COM) in a Banbury mixer at 200°C for 10 minutes and subsequently diluted with fresh unstabilished PP in the absence of any additional component during the extrusion process. The commercial additives on the other hand were extruded as normal samples.

Table 4.10 and Figure 4.30b also compare the melt stability of a series of dilute concentrates derived from severely-processed concentrates with that of some commercial stabilisers in the form of dilute concentrates. Thus, all the stabiliser concentrates (including the commercial stabilisers) were initially processed in the torque rheometer at 180 °C and subsequently diluted down to 0.6% concentration with fresh unstabilised PP during the extrusion process. The melt stability was determined in the context of multiple extrusions at 230°C and the melt flow measurements in this case involves the use of a 10 kg weight nominal force (BS 2782 : Method 720A)

Table 4.9 Comparision of DCts with commercial antioxidants (0.4%) as reprocessing stabilisers for PP on sucessive extrusions at 260°C (MFI for PP powder, 0.22)

Antioxident	MFI (190°C);2.16Kg;g/10min.)		
	Extrusion Passes		
	1	2	3
NONE	1.20	3.90	7.80
DLTP:HOBP (0.2% + 0.2%)	0.62	1.02	2.00
1084:HOBP (0.2% + 0.2%)	0.56	0.90	1.52
1076:HOBP (0.2% + 0.2%)	0.36	0.54	0.80
*DODS:HOBP (OM) (0.15% + 0.25%)	0.36	0.50	0.78
IRGANOX 1076 (0.4%)	0.32	0.42	0.60
*DnBDS:HOBP:NiDsBP(COM) (0.1% + 0.2% + 0.1%)	0.32	0.44	0.52

* DCts derived from severely-processed concentrates (OM,COM)

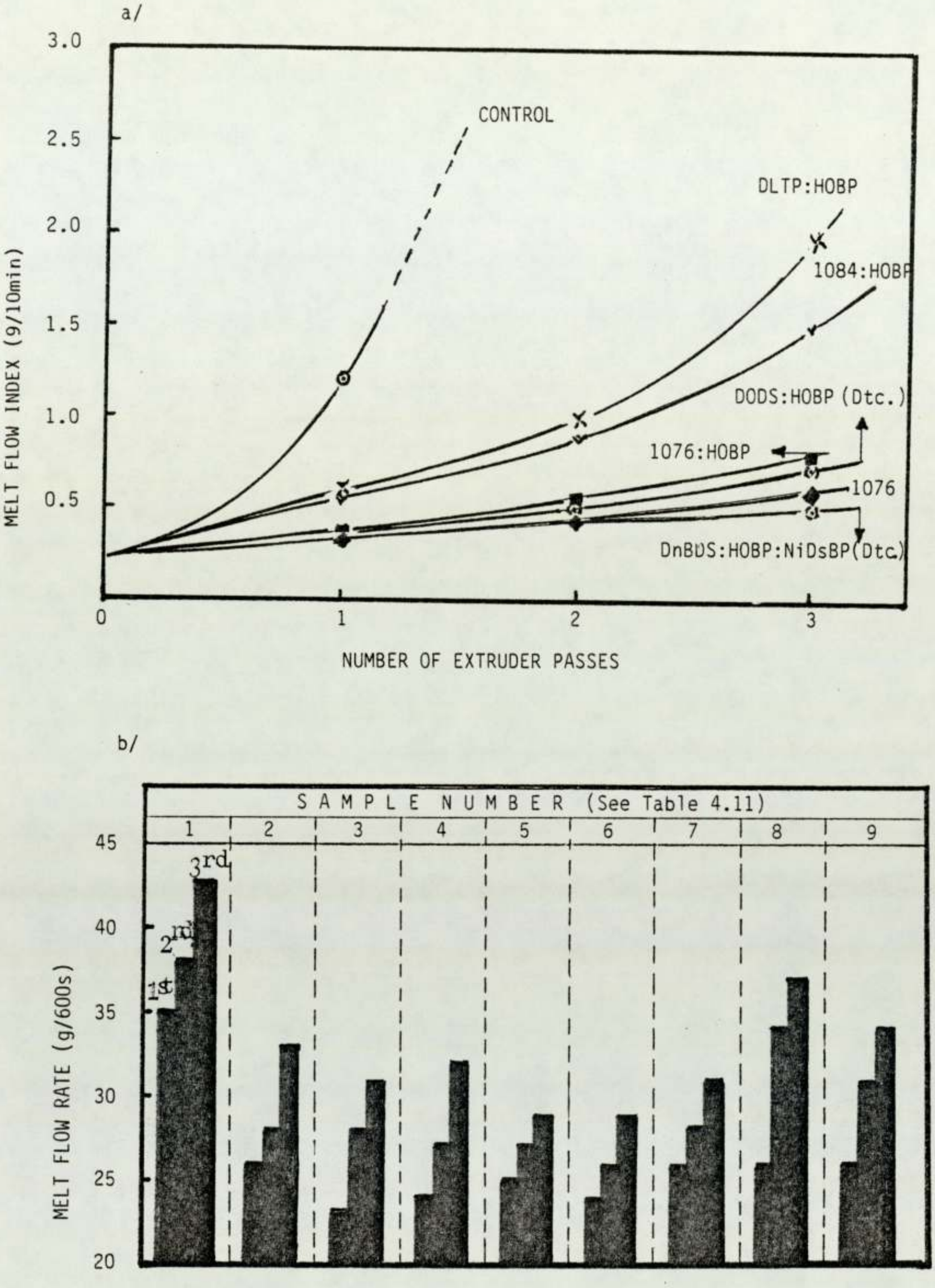
The results shown in Tables 4.9 - 4.10 and Figure 4.30 clearly illustrate the superior melt stability of PP containing thiophosphoryl dilute concentrates over that of the commercial stabilisers.

Table 4.10 Comparison of the melt flow rates (MFR) of dithiophosphoryl DCt's with that of other DCt's (0.6%) containing commercial stabilisers on sucessive extrusions at 230°C (MFR for PP powder,33)

Sample No.	Antioxidant: Concentration(%) of Components in Ct	Processing Methods (of Ct)	MFR (190°C;10Kg ;600s) Extrusion Passes 1	2	4
1	NONE -	-	35	38	43
2	DHDS : HOBP : NiDHP 2.5 : 5 : 2.5	COM / TBH	26	27	33
* 3	DHDS : HOBP : NiDHP 2.5 : 5 : 2.5	COM / TBH	23	27	31
4	DnBDS : HOBP : NiDnBP 2.5 : 5 : 2.5	COM / TBH	24	27	33
5	NiDnBP: HOBP 2.5 : 2.5	CM	25	28	29
**6	DHDS : HOBP : NiDHP 1 : 5 : 2.5	COM / TBH	24	26	29
7	DnBDS : HOBP : NiDsBP 2.5 : 5 : 2.5	COM	26	28	31
8	TIN.770 : IRG.B215 2.5 : 1.25	CM	26	34	37
9	IRG 1010: DLTP 1.5 : 2.5	CM	27	32	34

* This sample was prepared with a disulphide (DHDS) of very high purity (> 99.9%)

** This sample (6) is the same as sample (2) and (3) except for the difference in the relative proportion of the additives. Thus sample (6) contains a higher proportion of NiDHP relative to DHDS when compared to samples (2) and (3)



** 1st, 2nd and 3rd refer to number of extrusion passes.

Figure 4.30 Comparison of dithiophosphoryl Dtcs with other commercial stabilisers in the form of (a) normal samples (0.4%) and (b) Dtcs (0.6%) as reprocessing stabilisers for PP during extrusion at 260°C and 230°C respectively

4.2D.1.2 Thermal Antioxidant Activity

Table 4.11 illustrates the contribution of the nickel dithiophosphates to the thermal stability of PP films containing thiophosphotyl dilute concentrates. The original DODS:HOBP (5%:10%) concentrate was severely-processed (OM,15) in the torque rheometer at 180°C and subsequently diluted down to 0.4% with fresh unstabilised PP. Further dilutions of the concentrate to progressively lower concentrations (0.3%;0.24% and 0.17%) were prepared in the presence of increasing amounts of NiDOP (0.1%;0.16 and 0.23%) such that the total concentration of stabilisers in each dilute concentrate remains constant (0.4%). This table also includes the hindered phenol (Irganox 1076) compared at the same concentration as that of the dilute concentrates. The results which are also illustrated in Figure 4.31 clearly demonstrate the superior thermal antioxidant activity(air oven at 140°C) of dilute concentrates containing higher proportions of the nickel complex.

Figure 4.32 compares the thermal stability of PP plaques containing thiophosphoryl DCt's with that of some commercial stabilisers also in the form of DCt's in an air oven (Fissons) at 150°C. The original concentration are the same as those described in section 4.2D.1.1. and shown in Table 4.10 and plate 1 . The concentrates were subsequently diluted down to 0.6% concentration with

Table 4.11 Effect of increasing amounts of NiDOP in DCts on the thermal stability of PP films in an air oven at 140°C. Original DODS:HOBP(2.5%:5%) concentrate was processed OM,15 at 180°C)

Additive Proportions(%) in Dilute Concentrate DODS	HOBP	NiDOP	Embrittlement Time (h) (air oven at 140°C)
	None		0.5
0.15	0.25	-	20.0
0.10	0.20	0.1	300.0
0.08	0.16	0.16	450.0
0.057	0.114	0.229	720.0
Irganox 1076 (0.4%) / CM,10			550.0
NiDOP (0.4%) / CM,10			500.0

fresh unstabilised PP in the injection moulding machine; to produce plaques of nominal thickness 0.5 mm, 1 mm and 3 mm (see plate 1). Numbers on the histogram (Figure 4.32) correspond to DCt analogues of the concentrates shown in Table 4.10 and Plate 1.

These results not only indicate, with some exception (samples 5 and 6), that the thermal stability of PP plaques is improved with increasing specimen thickness, (Original DODS:HOBP (5% + 10%) concentrate processed OM,15 at 180°C)

* [No nickel]

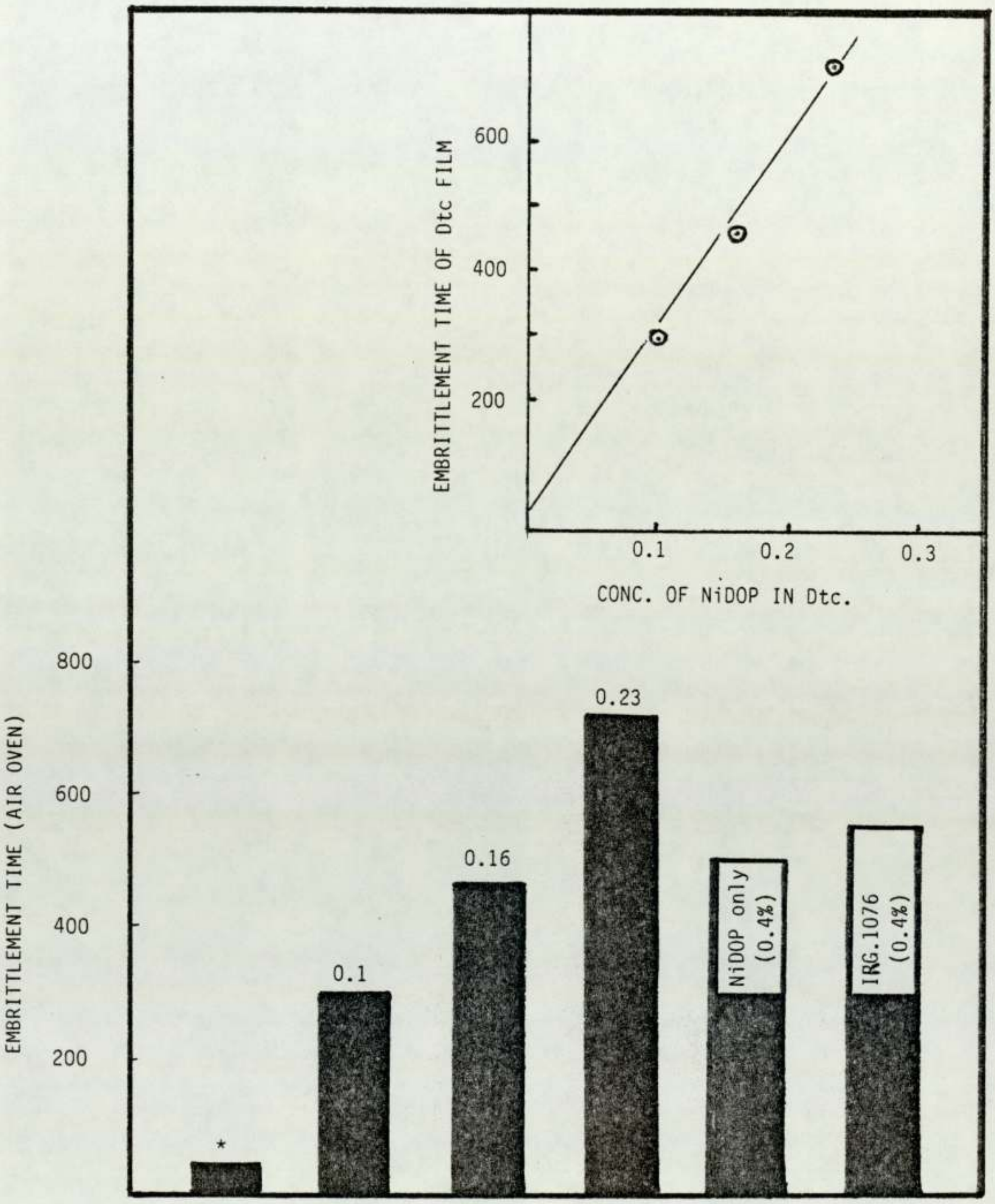


Figure 4.31 Effect of increasing amounts of NiDOP in Dtcs on the thermal stability of PP films in an air oven at 140°C. Number on each histogram refer to the concentration of NiDOP (%) in the various Dtcs containing DODS:HOBP:NiDOP at a total concentration of 0.4%. Inset also shows the contribution of NiDOP on the thermal stability of PP films containing the Dtcs.

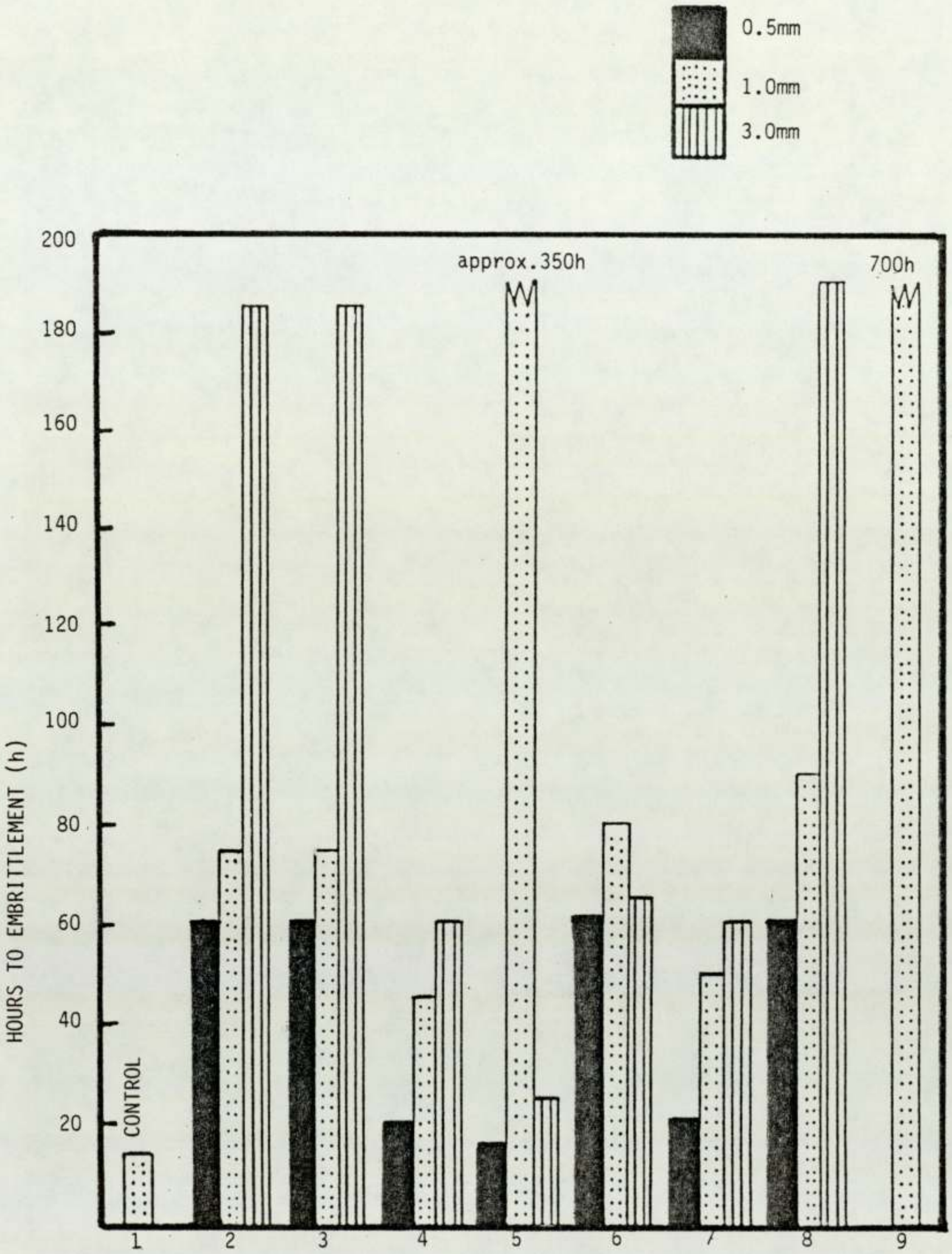
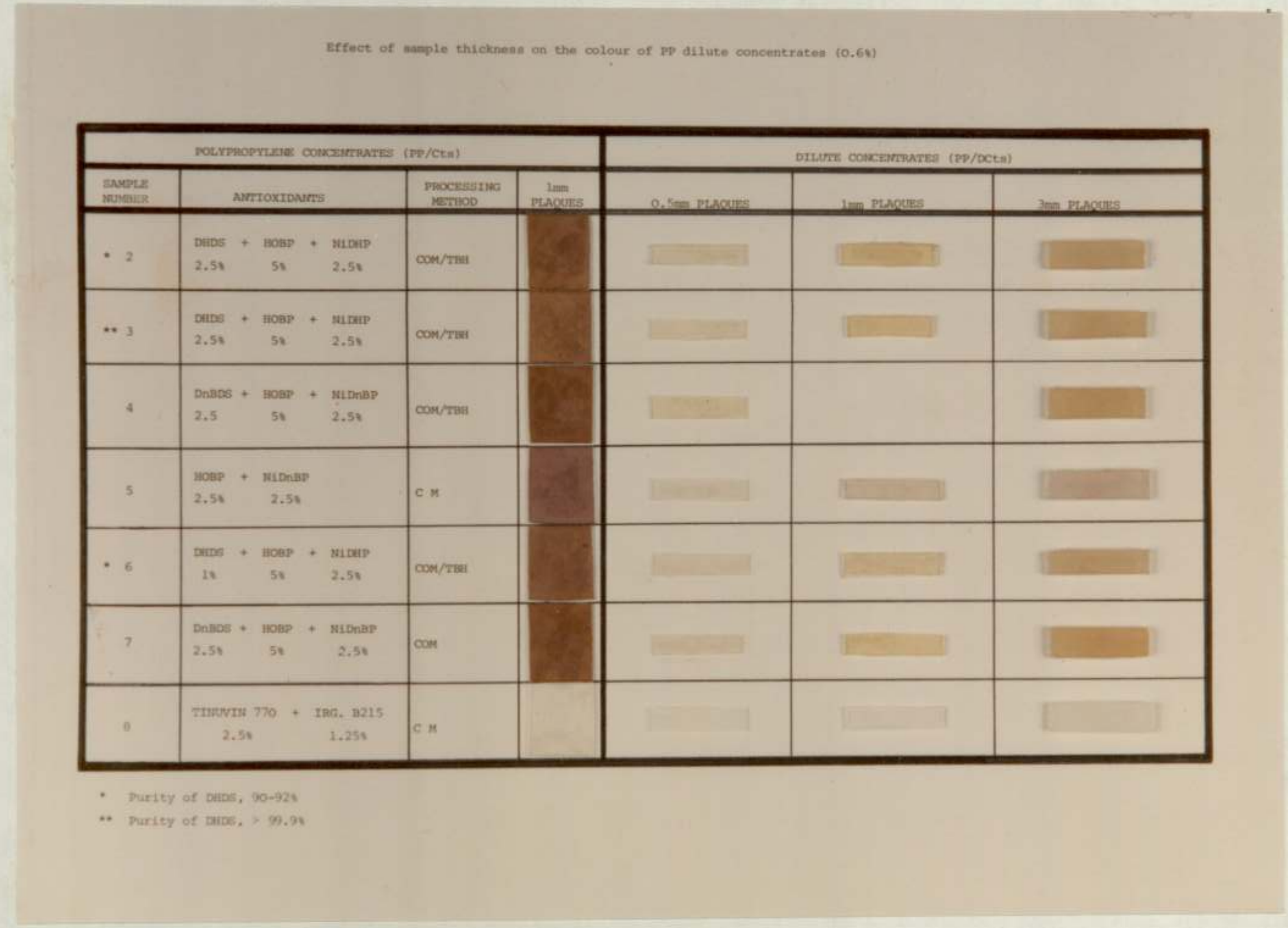


Figure 4.32 Comparison of the thermal stability of PP plaques containing dithiophosphoryl Dtcs (2-7) with that of Dtcs of some commercial stabilisers (8-9) in an air oven at 150°C. Numbers on the histogram refer to the stabiliser combinations shown in Table 4.10 and Plate 2.



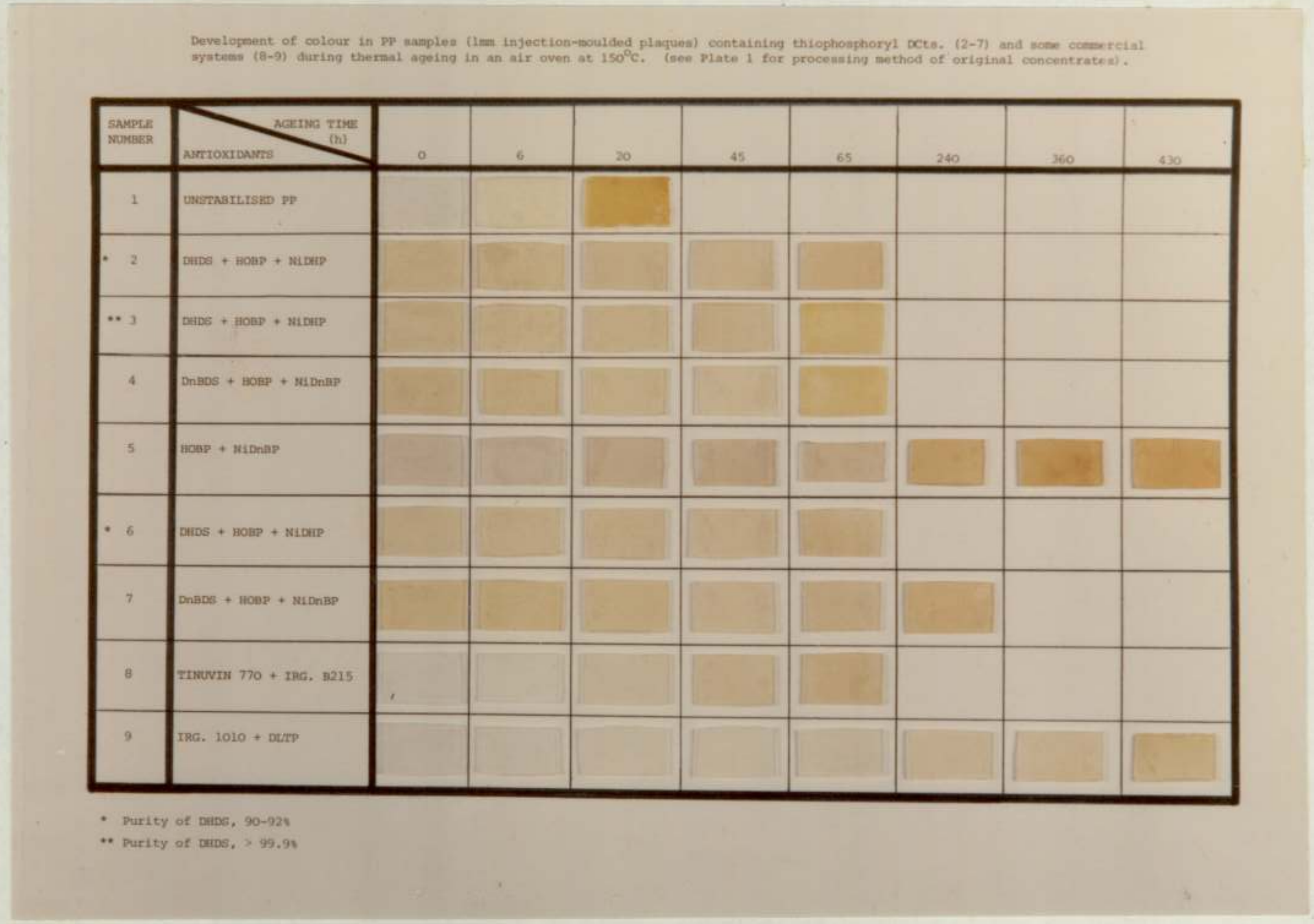
Effect of sample thickness on the colour of PP dilute concentrates (0.6%)

POLYPROPYLENE CONCENTRATES (PP/Cts)				DILUTE CONCENTRATES (PP/DCts)		
SAMPLE NUMBER	ANTIOXIDANTS	PROCESSING METHOD	1mm PLAQUES	0.5mm PLAQUES	1mm PLAQUES	3mm PLAQUES
* 2	DHDS + HOBP + NiDHP 2.5% 5% 2.5%	COM/TBH				
** 3	DHDS + HOBP + NiDHP 2.5% 5% 2.5%	COM/TBH				
4	DnBDS + HOBP + NiDnBP 2.5 5% 2.5%	COM/TBH				
5	HOBP + NiDnBP 2.5% 2.5%	C M				
* 6	DHDS + HOBP + NiDHP 1% 5% 2.5%	COM/TBH				
7	DnBDS + HOBP + NiDnBP 2.5% 5% 2.5%	COM				
8	TINUVIN 770 + IRG. B215 2.5% 1.25%	C M				

* Purity of DHDS, 90-92%

** Purity of DHDS, > 99.9%

Plate 1. Effect of sample thickness on the colour of PP dilute concentrates (0.6%).



Development of colour in PP samples (1mm injection-moulded plaques) containing thiophosphoryl DCts. (2-7) and some commercial systems (8-9) during thermal ageing in an air oven at 150°C. (see Plate 1 for processing method of original concentrates).

SAMPLE NUMBER	AGEING TIME (h) / ANTIOXIDANTS	0	6	20	45	65	240	360	430
1	UNSTABILISED PP	▨	▨	▨					
* 2	DHDS + HOBP + NiDHP	▨	▨	▨	▨	▨			
** 3	DHDS + HOBP + NiDHP	▨	▨	▨	▨	▨			
4	DnBDS + HOBP + NiDnBP	▨	▨	▨	▨	▨			
5	HOBP + NiDnBP	▨	▨	▨	▨	▨	▨	▨	▨
* 6	DHDS + HOBP + NiDHP	▨	▨	▨	▨	▨			
7	DnBDS + HOBP + NiDnBP	▨	▨	▨	▨	▨	▨		
8	TINUVIN 770 + IRG. B215	▨	▨	▨	▨	▨			
9	IRG. 1010 + DLTP	▨	▨	▨	▨	▨	▨	▨	▨

* Purity of DHDS, 90-92%

** Purity of DHDS, > 99.9%

Plate 2. Development of colour in PP samples (1mm injection-moulded plaques) containing thiophosphoryl DCts. (2-7) and some commercial systems (8-9) during thermal ageing in an air oven at 150°C. (see Plate 1 for processing method of original concentrates).

but also clearly shows that the thiophosphoryl DCts are all effective thermal stabilisers in PP. With respect to the effect of specimen thickness however, samples containing little or no disulphide (5 and 6) appear to be most effective at a nominal thickness of 1 mm, while increases up to 3 mm thickness only show a negative effect on their thermal antioxidant activity. The development of colour within the samples during oven ageing tests is shown in Plate 2.

4.2D.1.3 Photo-stabilising Activity

The effect of processing conditions of the original DnBDS concentrates on the photo-stability of PP films containing 0.2% dilute concentrates is shown in Table 4.12 which also includes a dilute concentrate of DnBTA at the same concentration. It is clear that the photo-antioxidant activity is higher when the original concentrate is severely-processed (OM,15) as compared with the mildly-processed concentrate (CM,5). It must however be emphasised that the photo-oxidative stability of PP films containing the original mildly-processed concentrate (2.5%) is higher than that of the oxidatively-processed concentrate (Section 4.2A.3; Table 4.3). Table 4.12 also indicates that the dilute concentrate of the oxidation product, DnBTA is equally very effective in stabilising PP against phto-oxidation.

Table 4.12 Photo-oxidative stability of PP-DCt's (0.2%) of DnBDS and DnBTA (All DCt's processed CM,10)

Processing Method of Original Concentrate (2.5%)	Embrittlement Time (h)		
	Unstabilised PP	DnBDS	DnBTA
CM, 5	90	250	260
OM,15	40	290	-

Figure 4.33 which shows the effect of the processing severity of the original concentrate on the photo-antioxidant activity the dilute analogues prepared in the presence of HOBP and NiDnBP, also illustrates the excellent U.V.stabilising activity of a dilute concentrate (curve 7) based on the sulphur acid (DnBTA) instead of the disulphide (DnBDS) as shown below.

(0.1% DnBDS/DnBTA DCt) + 0.2% HOBP + 0.1% NiDnBP

It can be seen that the U.V. stabilising activity of the sample prepared from the severely-processed DnBDS concentrate (curve 3) is superior to that prepared from the analogous but mildly-processed concentrate (curve 2). However, increases in the proportion of NiDnBP in the DCt with concomitant reduction in the amounts of DnBDS and HOBP, shows a marked improvement in the photo antioxidant activity (compare curve 3 with curves 4 and 5). A similar behaviour was also observed for the dilute concentrates containing DODS, HOBP and NiDOP. It has previously been shown (Table 4.11 and Figure 4.31) that increasing amounts of NiDOP in the sample improves the thermal antioxidant activity and the same effect is also clearly evident under photo-oxidative conditions (Figure 4.34).

Table 4.13 compares the photo antioxidant activity of samples derived from both mildly-processed (CM,5) and severely-processed concentrates of [DnBDS:HOBP] in various forms (OM,15 and CM,5/N_2 /TBH). The original concentrates, as shown in Table 4.5 were subsequently diluted down to 0.6% with fresh unstabilised PP in the absence of any additional component (NiDnBP). It is clear that the photo antioxidant activity of the DCt's is roughly consistent with the findings observed for the original concentrates (Table 4.5) since the U.V.stability of PP films containing stabilisers derived from OM,15-processed concentrates are inferior to the mildly-processed analogues (CM,5) at both additive ratios (cf curves (3) and (7)/CM,5 with curves (4) and (8)/OM,15 in Figure 4.35). However, the samples prepared from both severely-processed concentrates containing TBH show highly improved photo antioxidant activity as compared to those derived from CM,5- and OM,15- processed concentrates. Furthermore, it can be seen that contrary to the finding in the concentrate series (Table 4.5), the expected photo antioxidant synergistic effect is much more evident at normal additive concentrations.

Table 4.13 Effect of processing condition (of original concentrate) on the embrittlement time of PP films of the dilute analogues (0.6%)

Antioxidant Concentrate		Embrittlement times (h)	
Conc. (%)	Processing Method	Observed	Calculated Effect
DnBDS (2.5%)	CM,5	280	-
HOBP (0.3% NS)	CM,10	800	-
HOBP (2.5%)	CM,10	1300	-
[DnBDS : HOBP]			
(2.5% : 2.5%)	CM,5	1750	1080
(2.5% : 2.5%)	OM,15	1550	530
(+0.234% TBH)	CM,5/N_2	2500	530
(+0.468% TBH)	CM,5/N_2	3000	530
[DnBDS : HOBP]			
(2.5% : 5%)	CM,5	4400	1580
(2.5% : 5%)	OM,15	3625	530
HOBP (0.3% NS)	OM,10	250	-

Table 4.14 compares the photo-oxidative stability of PP plaques of nominal thickness 0.5 mm and 1 mm containing thiophosphoryl DCt's with that of some commercial

stabilisers. A colour profile of the various plaques as a function of sample thickness (mm) is shown in Plate 1 which also depicts the intense colour of the thiophosphoryl concentrates. In view of the difficulty associated with the flexing of thick specimens, the time to formation of surface crazing on the exposed faces, as observed under the microscope, was therefore used as an additional test criteria upon which the performance of the samples are assessed.

Surprisingly, thin samples (0.5 mm) show approximately 30-40% better performance than the thick samples and this not only seem to be the case for the time required for onset of surface crazing but also for the time at which actual physical embrittlement was observed. Table 4.14 also clearly indicates that the photo antioxidant activity of the dithiophosphates are certainly superior to that of the commercial stabilisers when diluted from concentrates.

A closer examination of the dithiophosphoryl series clearly indicates that the least effective sample is that without any disulphide (NiDnBP:HOBP) while the most effective is that containing a higher proportion of the nickel complex (NiDHP) relative to DHDS. However, unexpected results such as that of DCt (2), as compared to the closely similar DCt (3), could well have been a consequence of poor dispersion since effective mixing of

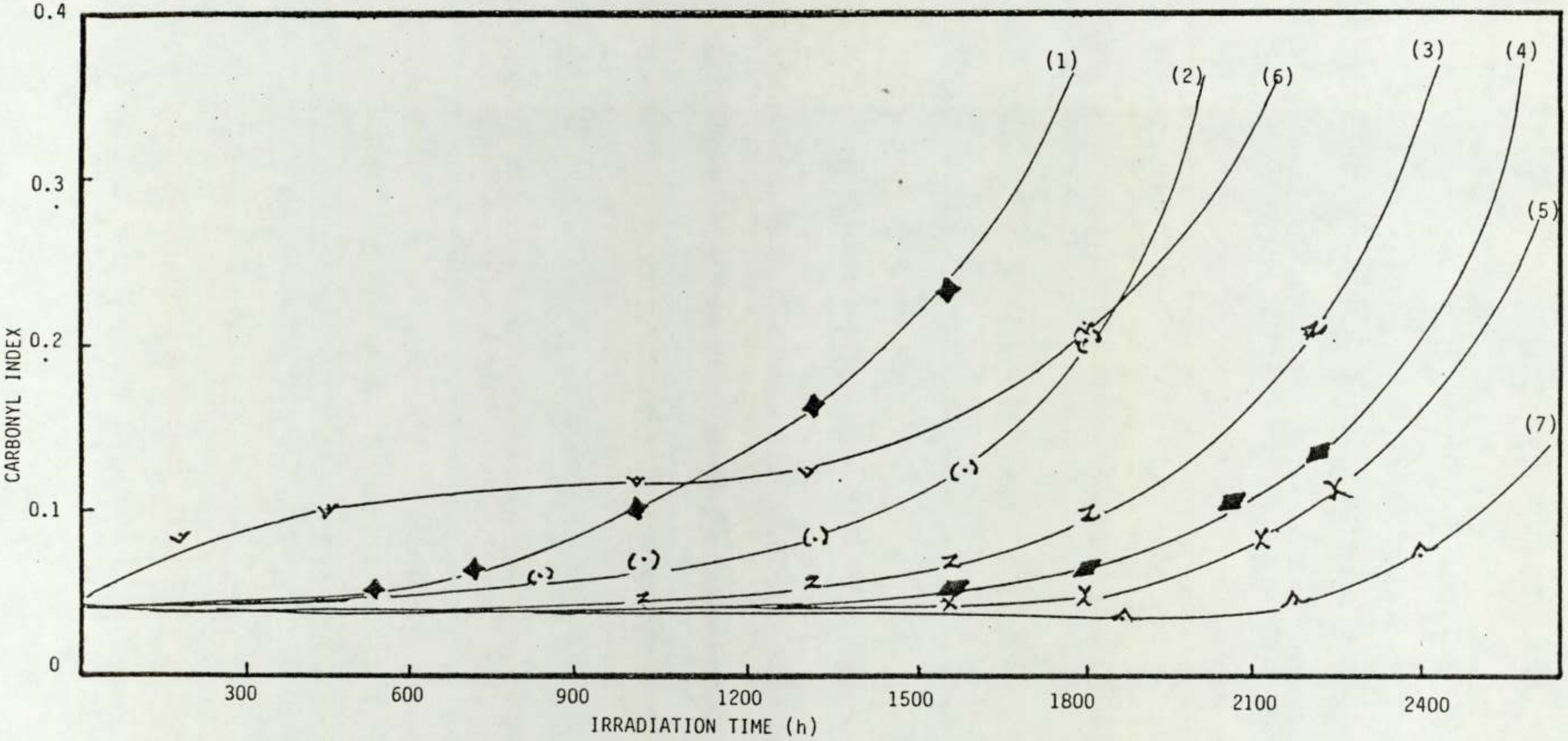


Figure 4.33 Comparison of the photostability of PP films containing various dithiophosphoryl DCt's at a concentration of 0.4% total.

Sample No.	Dilute Concentrate(DCt.)			Original Concentrate(Ct.)
	DnBDS :	HOBP :	NiDnBP (%)	
1.	0.15	0.25	–	2.5% DnBDS + 5% HOBP / OM,15
2.	0.1	0.2	0.1	2.5% DnBDS / CM,5
3.	0.1	0.2	0.1	2.5% DnBDS / OM,15
4.	0.08	0.16	0.16	" "
5.	0.057	0.114	0.229	" "
6.	Tinuvin 770 -- 0.4% NS			----
7.	DnBTA → 0.1	0.2	0.1	2.5% DnBTA / CM,5

For samples (2) - (5) and (7), the synergists were added during dilution of the original concentrates(DnBDS or DnBTA) and all samples were processed at 190°C.

Fig. 4.34. Effect of increasing amounts of NiDOP in dilute concentrates on the UV - stability of PP films.

		DODS	HOBP	NiDOP(%)
	1.	0.15	0.25	-
*	2.	0.1	0.2	0.1
*	3.	0.08	0.16	0.16
*	4.	0.057	0.114	0.229
	5.	0.1	0.2	0.1

Samples (1) - (4) were derived from a 5% DODS + 10% HOBP/OM,15 concentrate, while sample (5) was diluted from a 3-component concentrate incorporating the nickel complex thus:

2.5% DODS + 5% HOBP + 2.5% NiDOP / COM,9

* NiDOP added during dilution.

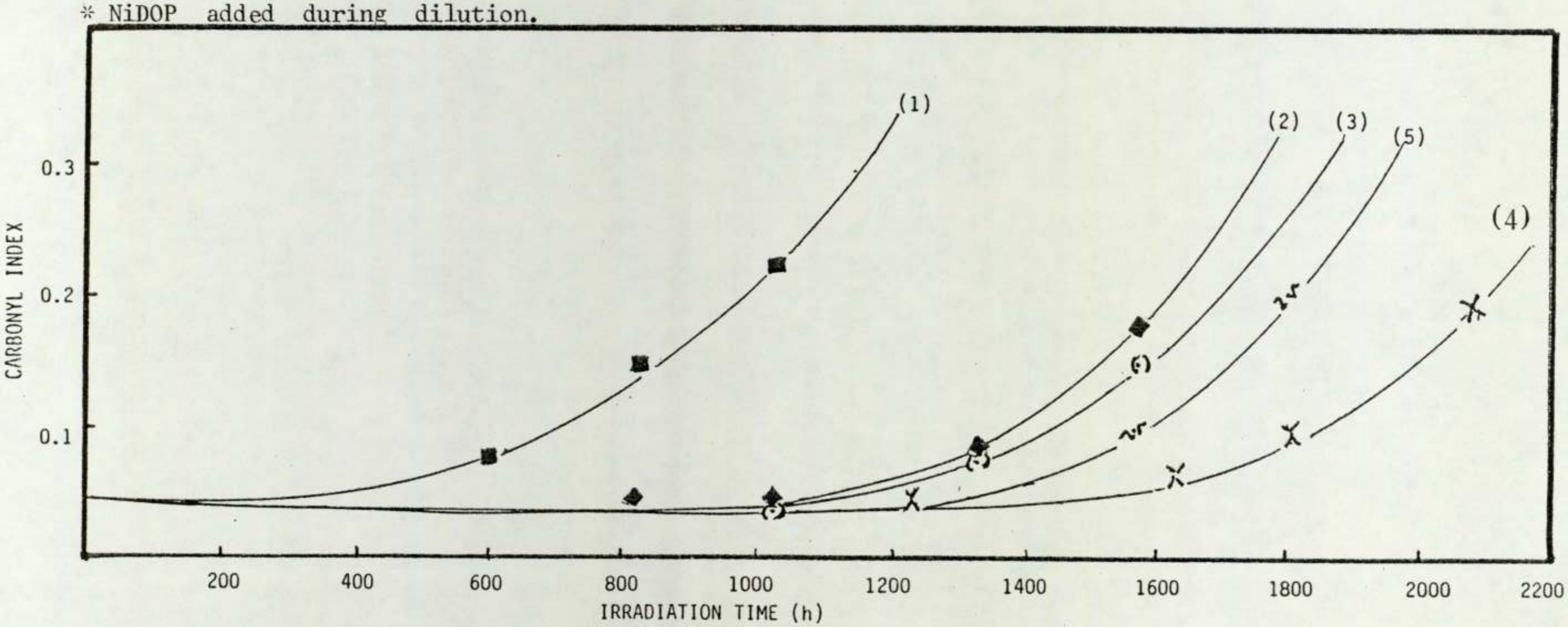


Fig. 4.35. Effect of processing severity at 190^{o}C on the photoantioxidant stability of PP films containing dilute analogues(0.6% DCt.) of DnBDS(2.5%), HOBP(2.5%), and the synergistic DnBDS:HOBP(2.5%:2.5% and 2.5%:5%) concentrates. Processing conditions shown refer to that of the original concentrates.

(1) DnBDS/CM,5; (2) HOBP/CM,10; (3) DnBDS:HOBP ratio = 1/CM,5; (4) ratio = 1/OM,15; (5) ratio = 1(+ 0.234% TBH); (6) ratio = 1(+ 0.468% TBH); (7) ratio = 2/CM,5 and (8) ratio = 2/OM,15. See Table 4.13.

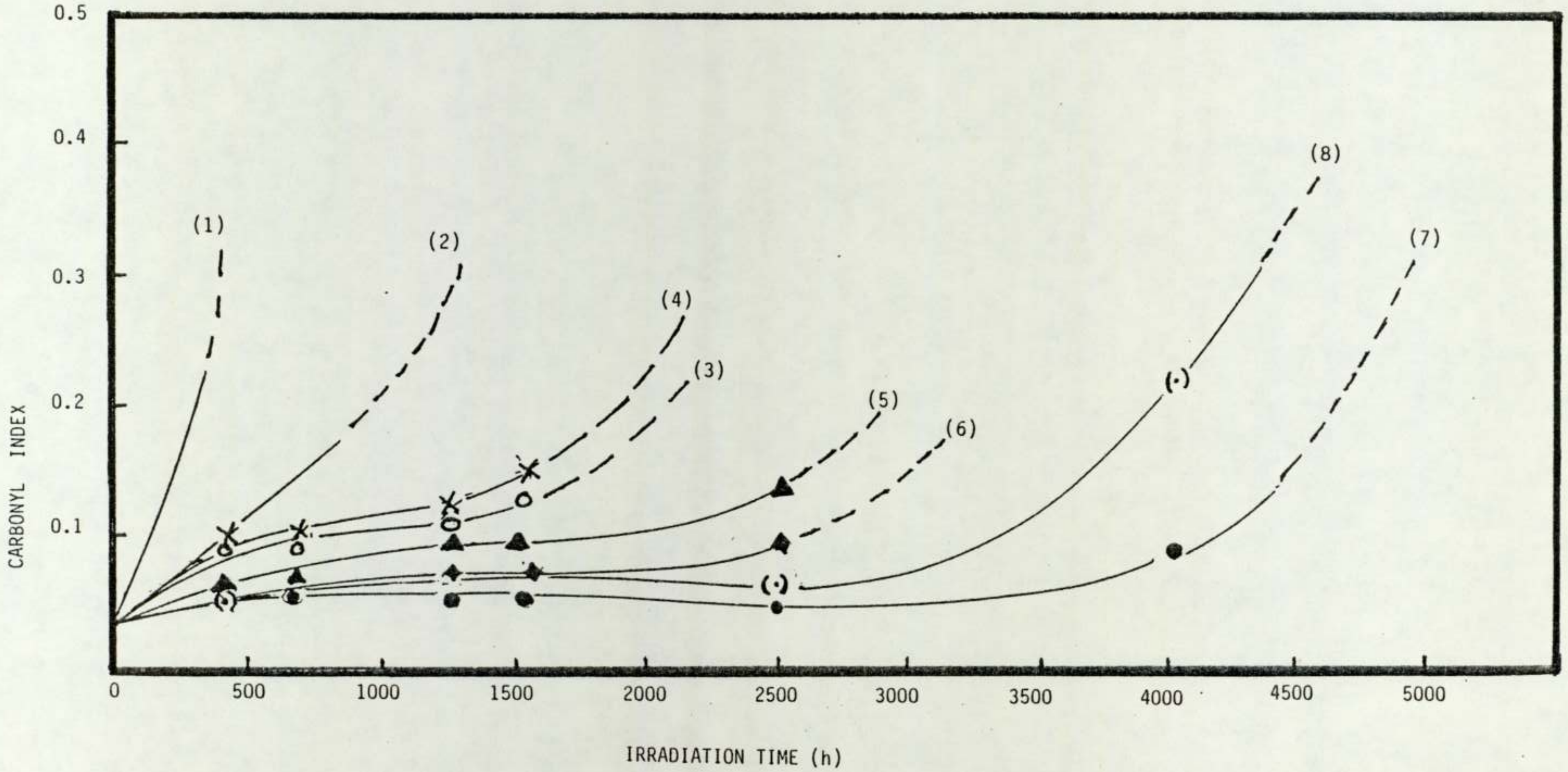


Table 4.14 Photo-oxidative stability of PP plaques of dithiophosphoryl DCt's and the DCt's of some commercial stabilisers (0.6%)

	*	Processing Method	Sample	Hours To	
Sample No	Antioxidant	of Original Ct	Thickness(mm)	Craze Formation	Embrittlement
1	NONE		1.0	-	290
2	DHDS:HOBP: NiDHP (2.5: 5 : 2.5)	COM / TBH	0.5	3720	4320
			1.0	2640	2840
** 3	DHDS:HOBP:NiDHP (2.5: 5 : 2.5)	COM / TBH	0.5	4320	5040
			1.0	2880	4080
4	DnBDS:HOBP:NiDnBP (2.5 : 5 : 2.5)	COM / TBH	0.5	4320	5040
			1.0	2880	4080
5	NiDnBP:HOBP (2.5 : 2.5)	CM	0.5	3360	4320
			1.0	2400	3600
*** 6	DHDS:HOBP:NiDHP (1 : 5 : 2.5)	COM / TBH	0.5	4800	5500
			1.0	3600	2320
7	DnBDS:HOBP: NiDsBP (2.5: 5 : 2.5)	COM	0.5	4080	4800
			1.0	2640	3840
8	Tin 770 : Irg B125 (2.5 : 1.25)	CM	0.5	1100	2800
			1.0	850	2100
9	Irg 1010: DLTP (1.5 : 2.5)	CM	1.0	750	900

* Also includes the concentration (%) of the components in the original concentrates.
** Prepared from DHDS of very high purity (99.9%).
*** Contains less DHDS as compared to sample (2) and (3).

the peroxide (TBH) and the stabilisers is critical in such systems.

4.2D.2 LDPE Dilute Concentrates as Stabilisers

This section deals primarily with the photo-oxidative stability of LDPE films (200 μm) and the associated changes in the tensile properties during the photo-oxidation process.

4.2D.2.1 Photo-stabilising Activity (of DCts) in Compression Moulded Films

Figure 4.36 shows the effect of processing condition of the original additive concentrates on the U.V.stability of LDPE films of the dilute analogues. The photo-antioxidant activity of 0.2% DnBDS DCt's is seen to be most effective when the original concentrate (2.5%) is severely-processed (OM,15 > OM,30 > CM,10). A comparison of the dilute concentrates (0.3%) derived from 1:2 ratio DnBDS:HOBP concentrates also illustrates the fact that the activity of the synergistic systems is augmented by oxidative processing of the original concentrate, with the activity decreasing in the following order: OM,15 > OM,30 > CM,10. The addition of 0.1% of NiDnBP to the 0.3% DnBDS : HOBP DCt's (during dilution of original concentrates) effectively improves their performance, and the photo antioxidant synergism is most favourably pronounced when the original concentrate is processed under extremely-severe condition (OM,30). The effectiveness of the DCt's in the presence of the nickel complex decreases in the following order:

OM,30 > OM,15 > CM,10.

Figure 4.37 illustrates the effect of processing severity of the original DnBDS concentrates (2.5%) on the changes in % elongation and % mole unsaturation during photo-oxidation of LDPE films containing 0.4% DnBDS dilute concentrates. It is clear that the oxidatively-processed-derived DCt (OM,15) is superior to the mildly-processed analogue with respect to the photo-oxidative behaviour, as reflected by the changes in the % elongation of the films, the carbonyl index and the % unsaturation formed in the films during U.V.irradiation.

4.2D.2.2 Photo-stabilising Activity (of DCt's) in Flat Tubular (Blown) Films

Table 4.15 and Figure 4.38 compare the U.V stability of LDPE films containing dithiophosphoryl DCt's with that of some commercial stabilisers. Whereas the original dithiophosphoryl concentrates were initially oxidatively-processed in the torque rheometer at 150 °C and subsequently diluted with fresh unstabilised LDPE during the film blowing operation, flat tubular films of LDPE samples 3-5 were produced without any concentrate preparation. These results clearly illustrate the effectiveness of the dithiophosphoryl DCt's in stabilising the polymer against photo-oxidation when compared with the commercial systems although the latter were processed as normal samples (NS) during the film blowing operation.

Table 4.15 Photo-oxidative stability of LDPE flat tubular films of dithiophosphoryl DCt's and some commercial stabilisers

Sample No	Antioxidant DCt/NS (%)	Processing Method of Original Ct.	Hours to Carbonyl Index 8.0
* PE-1	DHDS + HOBP + NiDHP 0.15 0.3 0.15	COM / TBH	7000
* PE-2	DnBDS + HOBP + NiDnBP 0.15 0.3 0.15	COM / TBH	7200
**PE-3	HOBP + NiDnBP 0.2 0.2	NS	5400
**PE-4	Cy. 1084 + HOBP 0.2 0.2	NS	4200
**PE-5	Irg. 1076 + Chim.944 0.1 0.2	NS	3500
* PE-6	DnBDS + HOBP + NiDsBP 0.15 0.3 0.15	COM	6300

* See Table 4.14, sample numbers 2,4 and 7, for the proportion of additives in the original concentrates. These were subsequently diluted(0.6% total) during the film blowing operation.

** Prepared as normal samples (NS) during the film blowing operation.

In addition to the carbonyl index measurements, the loss in the tensile properties of the films under irradiation was also monitored in accordance with BS 2782: methods 326A to 326C (Section 2.4.3.2). The results are presented as % retention of the original property (tensile/EAB) since this provides a reliable yardstick by which the relative effectiveness of the various systems may be assessed.

Figure 4.39 which illustrates the residual tensile strength of the samples during U.V.irradiation clearly indicates that the dithiophosphates (PE 1, 2 & 6) are superior to the commercial systems with respect to the retention of the original property. This superiority is confirmed in Figure 4.40 which shows the residual elongation of the various samples as a function of exposure time. Figure 4.41 provides clear evidence that a 50% loss in elongation of the DCt samples (1,2 &6) can be delayed for a much longer period as compared to the commercial systems.

The relationship between the carbonyl index and the time (hours) to 50% loss of the original elongation (T 50) is shown in Table 4.16. This evidently suggests that even at relatively low carbonyl index values, a 50% loss in flexibility has already occurred in all the samples under examination, although this value (carbonyl index) represents over 500% increase in the concentration of

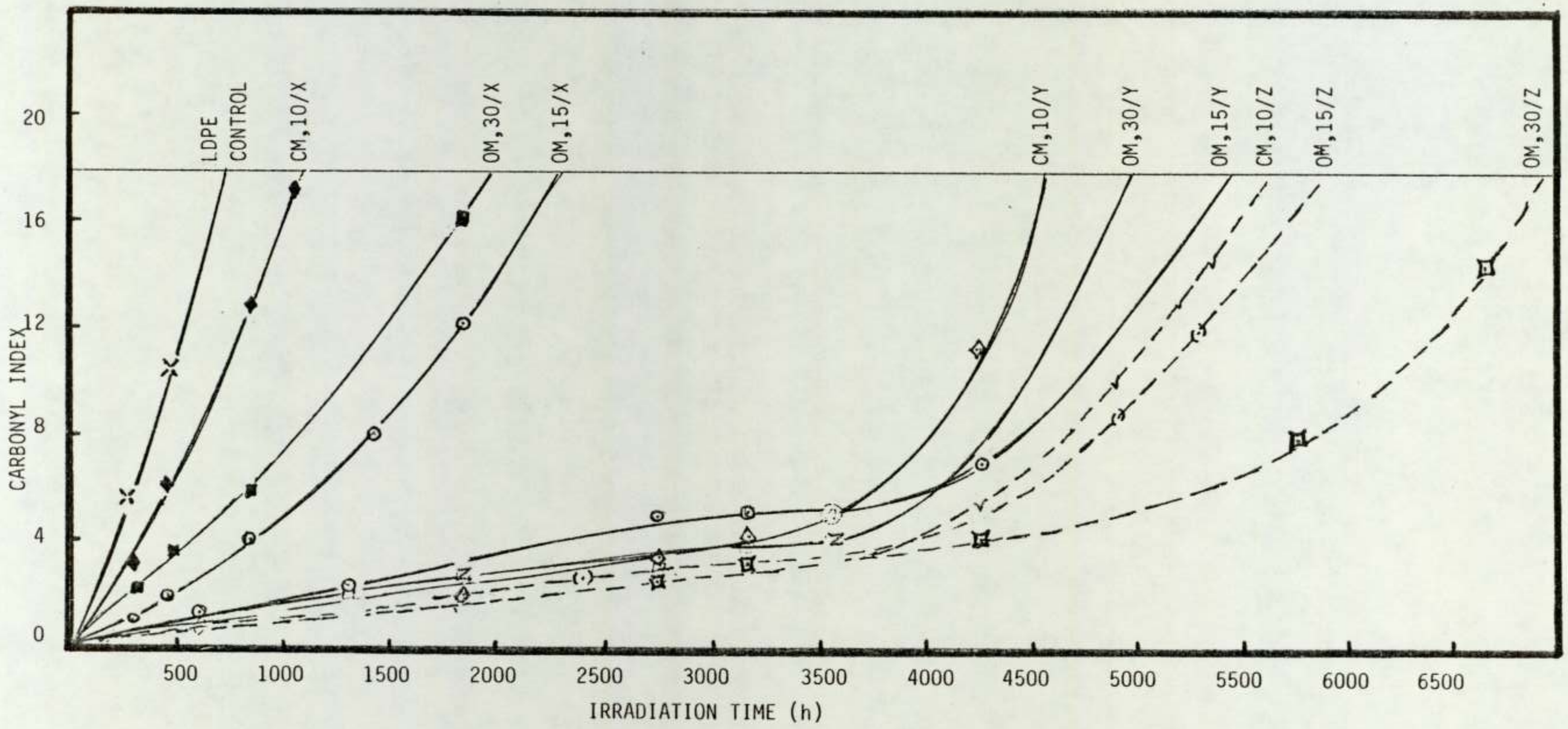


Figure 4.36 Effect of processing severity (150°C) of the original DnBDS (2.5%) and DnBDS:HOBP (2.5%:5%) concentrates on the photo-oxidative stability of LDPE films of the dilute concentrates (DCt's) prepared in the absence and presence of NiDnBP. Curves x,y and z refer to 0.2% DnBDS DCt, 0.3% DnBDS:HOBP DCt. and 0.3% DnBDS:HOBP DCt. + (0.1% NiDnBP) respectively.

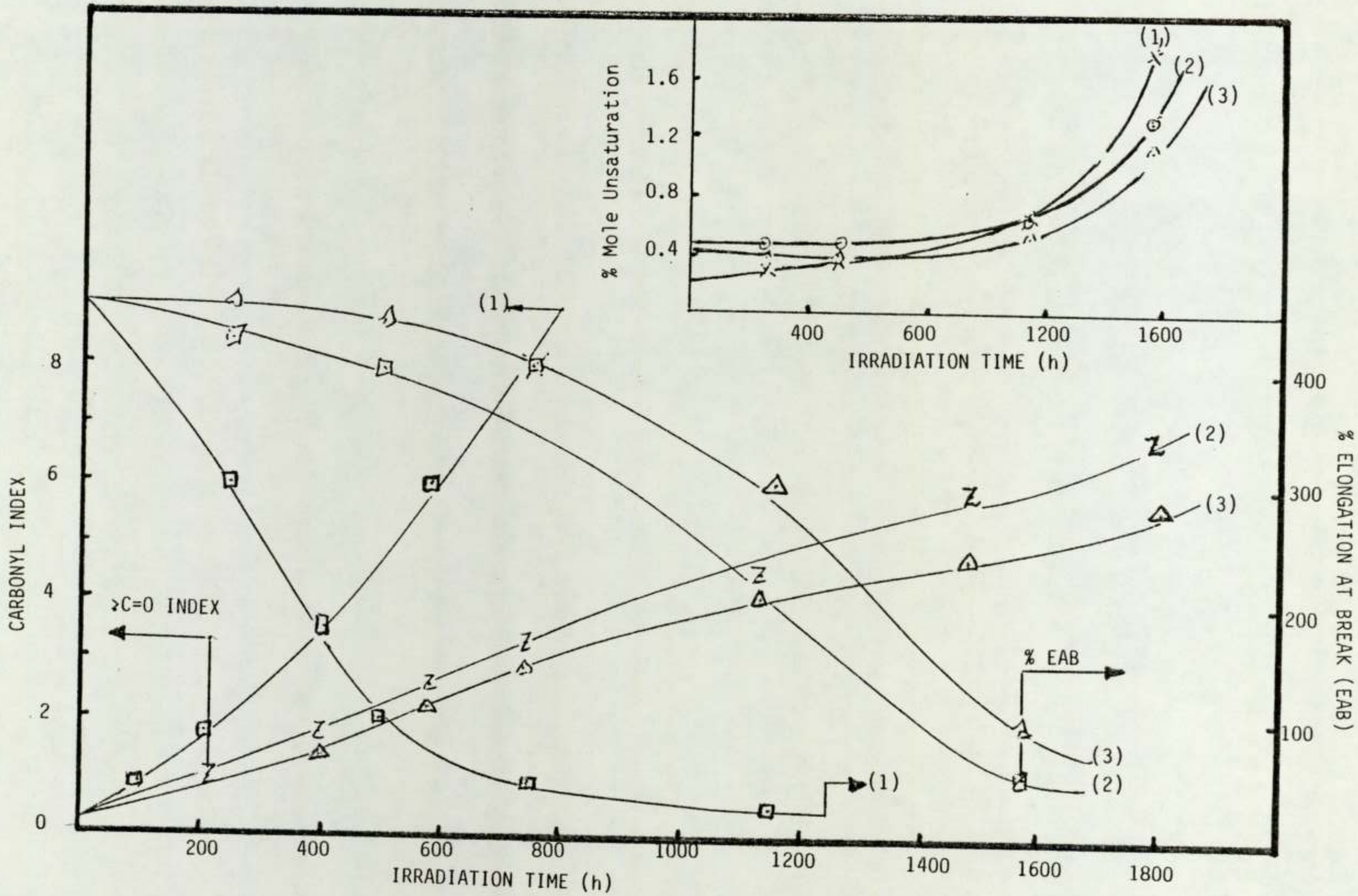


Figure 4.37 Effect of processing condition (CM,10 and OM,15) of original DnBDS concentrate (2.5%) on the changes in the carbonyl index, % elongation and % mole unsaturation (inset) during photo-oxidation of LDPE films containing 0.4% dilute concentrates (DCts) (1) control (no additive), (2) CM,10/DCt, (3) OM,15/DCt. (all dilute concentrates processed CM,10 at 150^{o}C)

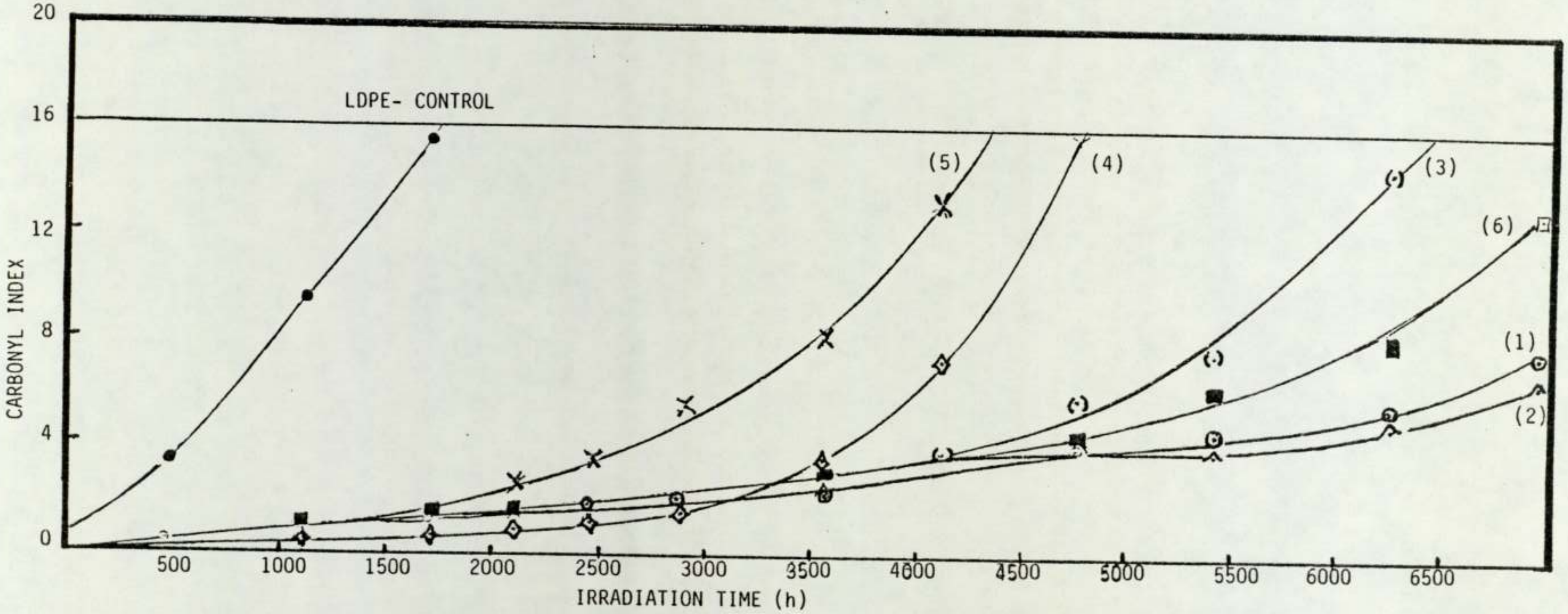


Figure 4.38 Comparison of the photo-oxidative stability of LDPE blown films containing thiophosphoryl DCts. (Curves 1,2 and6) of severely-processed concentrates (COM) with that of normal samples (NS) of (3) NiDnBP:HOBP (4) 1084:HOBP and (5) 1076:944(see Table 4.15).

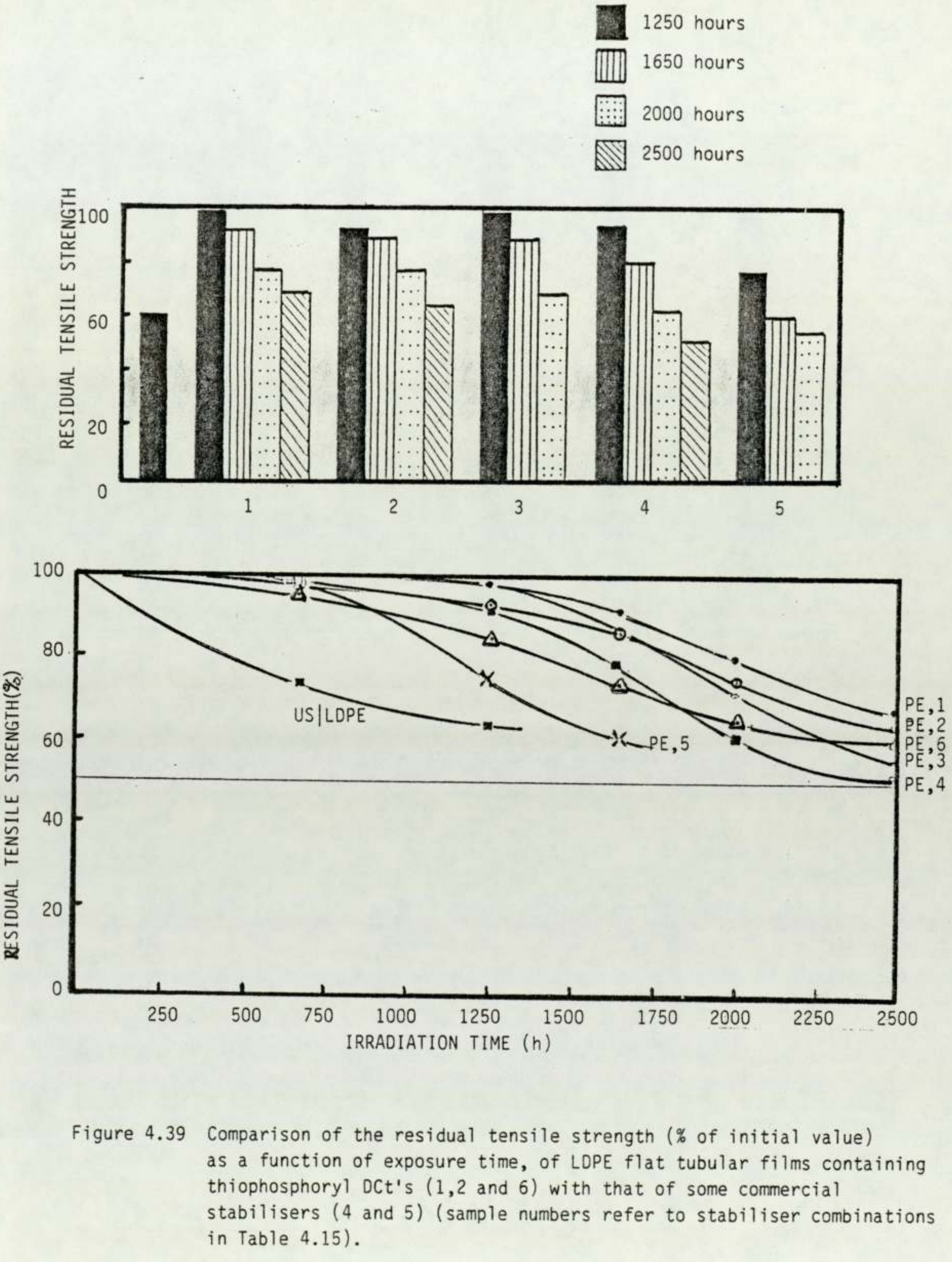


Figure 4.39 Comparison of the residual tensile strength (% of initial value) as a function of exposure time, of LDPE flat tubular films containing thiophosphoryl DCt's (1,2 and 6) with that of some commercial stabilisers (4 and 5) (sample numbers refer to stabiliser combinations in Table 4.15).

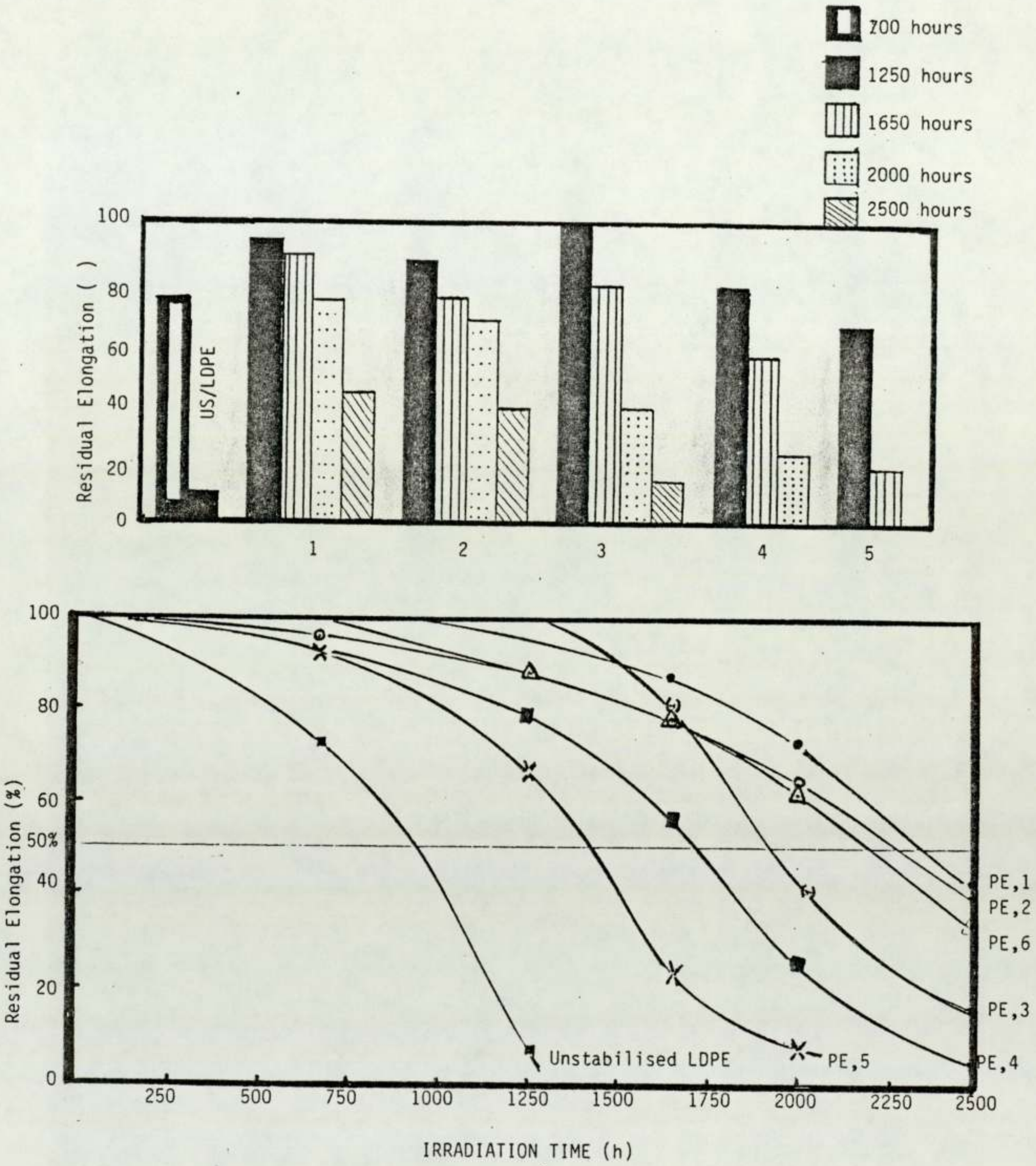


Figure 4.40 Comparison of the residual elongation (% of the initial value) as a function of exposure time of LDPE flat tubular films containing dithiophosphoryl DCt's (1,2,and 6) with that of some commercial stabilisers (4 and 5) (Sample numbers refer to stabiliser combinations in Table 4·15.

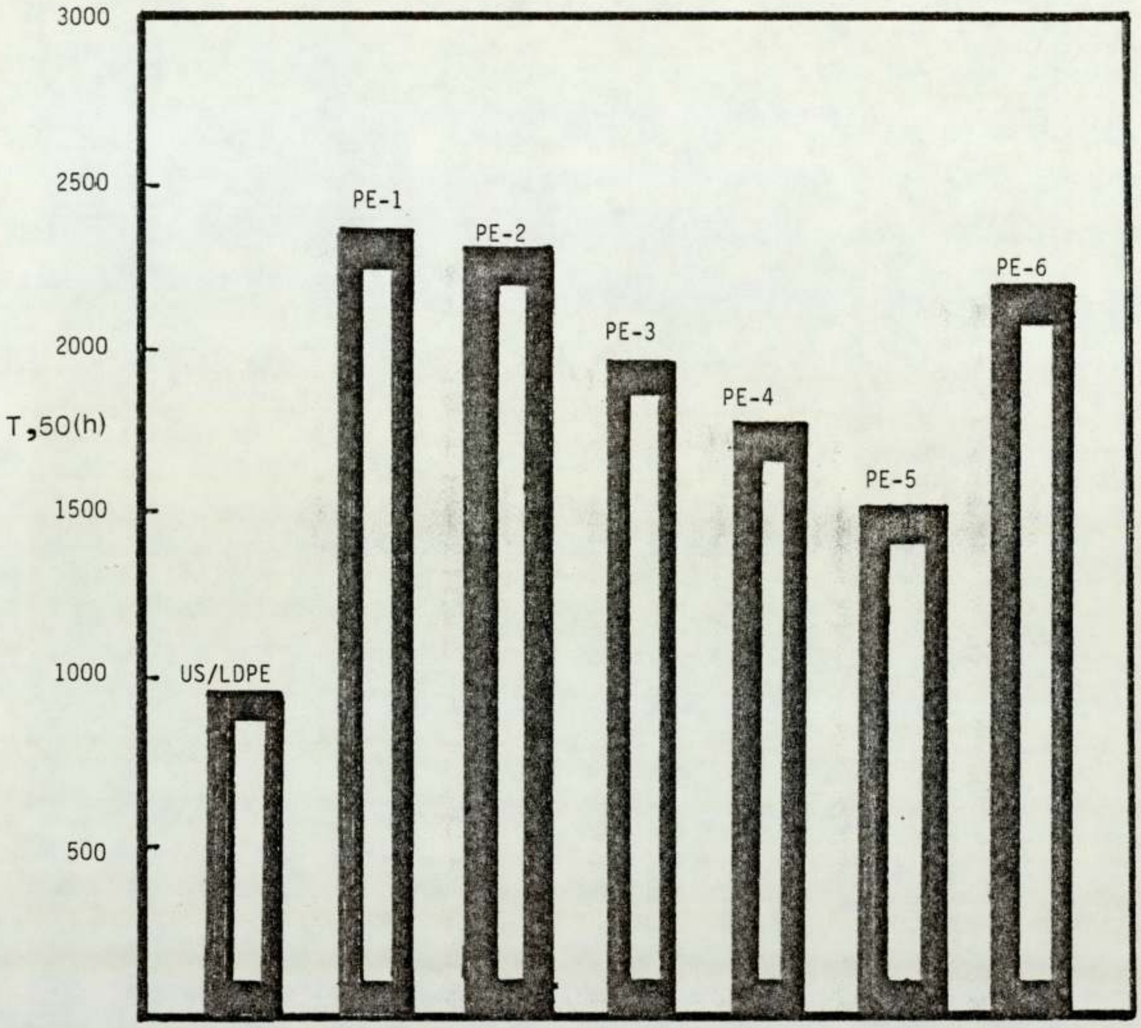


Figure. 4.41. Hours to 50% retained elongation (T,50) during UV- irradiation of LDPE flat tubular films. (see Table 4.15).

carbonyl species e.g. 0.15 - 1.5 carbonyl index.

Table 4.16 Relationship between T,50 and carbonyl index

Sample No	T,50 (h)	Carbonyl Index(at T50)
Unstabilisd LDPE	900	7.0
PE-1	2350	1.75
PE-2	2300	1.75
PE-3	1900	1.65
PE-4	1700	0.75
PE-5	1450	1.75
PE-6	2200	1.70

4.3 Discussion

4.3A Prolypropylene Additive Concentrates (PP/Ct)

4.3A.1 Effect of Concentration of DnBDS (in PP) and Processing Procedure on the Plasticity of the Concentrates.

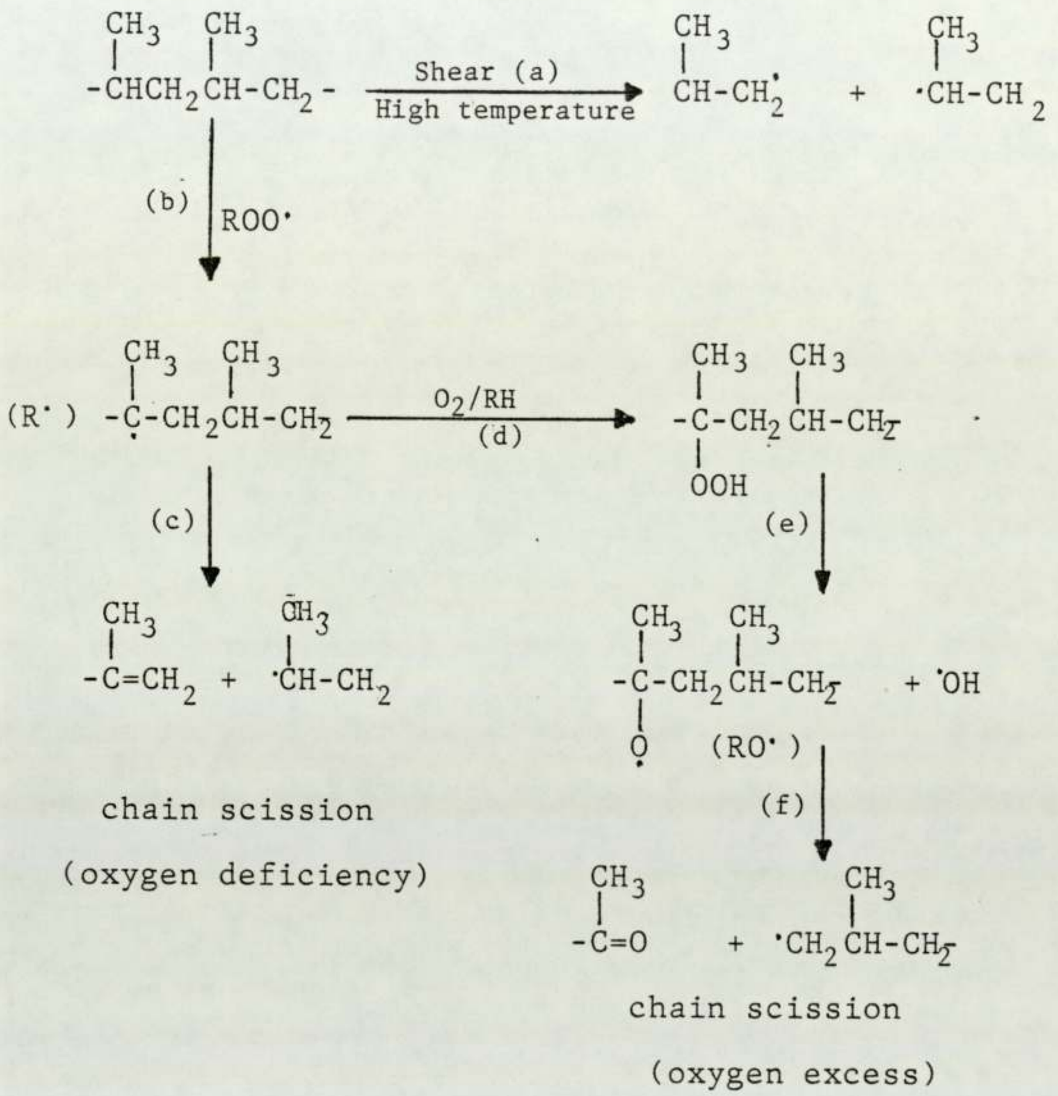
The plasticity of PP concentrates, as measured by following changes in the torque generated during processing is shown for both mildly-processed (Figure 4.1) and severely-processed (Figure 4.2) DnBDS concentrates. It is a well established fact (56a,56b) that most materials possess characteristically shaped torque-time curves, from which changes in the consistency due to heat and shear can be determined. The initial high torque, as seen in Figures 4.1 - 4.2 for the various concentrates processed under both mild and severe conditions, corresponds to the time when the polymer is passing from the solid state, through the rubbery state to the viscous liquid state(2,56a,56b). It is also evident that increases in DnBDS concentration (2.5% - 20%) results in a reduction of both the initial high torque generated during processing and the final torque observed at the end of processing. Such reduced torque levels may be due to the lubricating effect of the additive (DnBDS) when present in a super — saturated state. The consequences of the lubricating effect observed when high concentrations of DnBDS is used (10% - 20%), as measured by the torque generated during processing, is two-fold. Firstly, a much higher amount of the stabilised polymer resin was required during compression moulding of the films, as compared to the lower DnBDS concentrates (2.5% - 5%). Secondly, additive loss by exudation to the film surface was clearly evident for the higher concentrates (10% - 20%). It has previously been reported(5b,34) that equilibrium concentration of stabilisers in polyolefins at ambient temperatures is normallly very low and amounts in excess of this concentration exude to the surface.

In the light of these facts, the phenomenon of super saturation in the polymer is not entirely unexpected in view of the high concentrations of DnBDS involved, and this is clearly reflected on the torque generated during processing of the concentrates under both mild and severe conditions (Figure 4.1 - 4.2).

4.3A.2 Effect of Concentration of DnBDS (in PP) on the Amount of Unsaturation and Hydroperoxides Formed After Processing

An understanding of the changes which occur during the processing of PP containing DnBDS concentrates is essential if the mechanism of their antioxidant action is to be clarified. It has been well established that the degradation of polymers in a shearing mixer involves a high rate of radical formation by mechanical scission of the polymer backbone(2,4,5a,5b). Once an alkyl radical is formed, it will react with oxygen to give alkyl peroxyl radical which abstracts hydrogen to form a hydroperoxide and this in turn, will cleave to alkoxyl radical. The effect of the mechano-oxidative breakdown of PP during processing, as outlined in Scheme 4.2 has been reported(2,4a,5a,5b,27) to account for the rapid decrease in melt viscosity (increase in MFI) of the polymer.

Scheme 4.2 Mechano-chemical degradation of PP during Processing

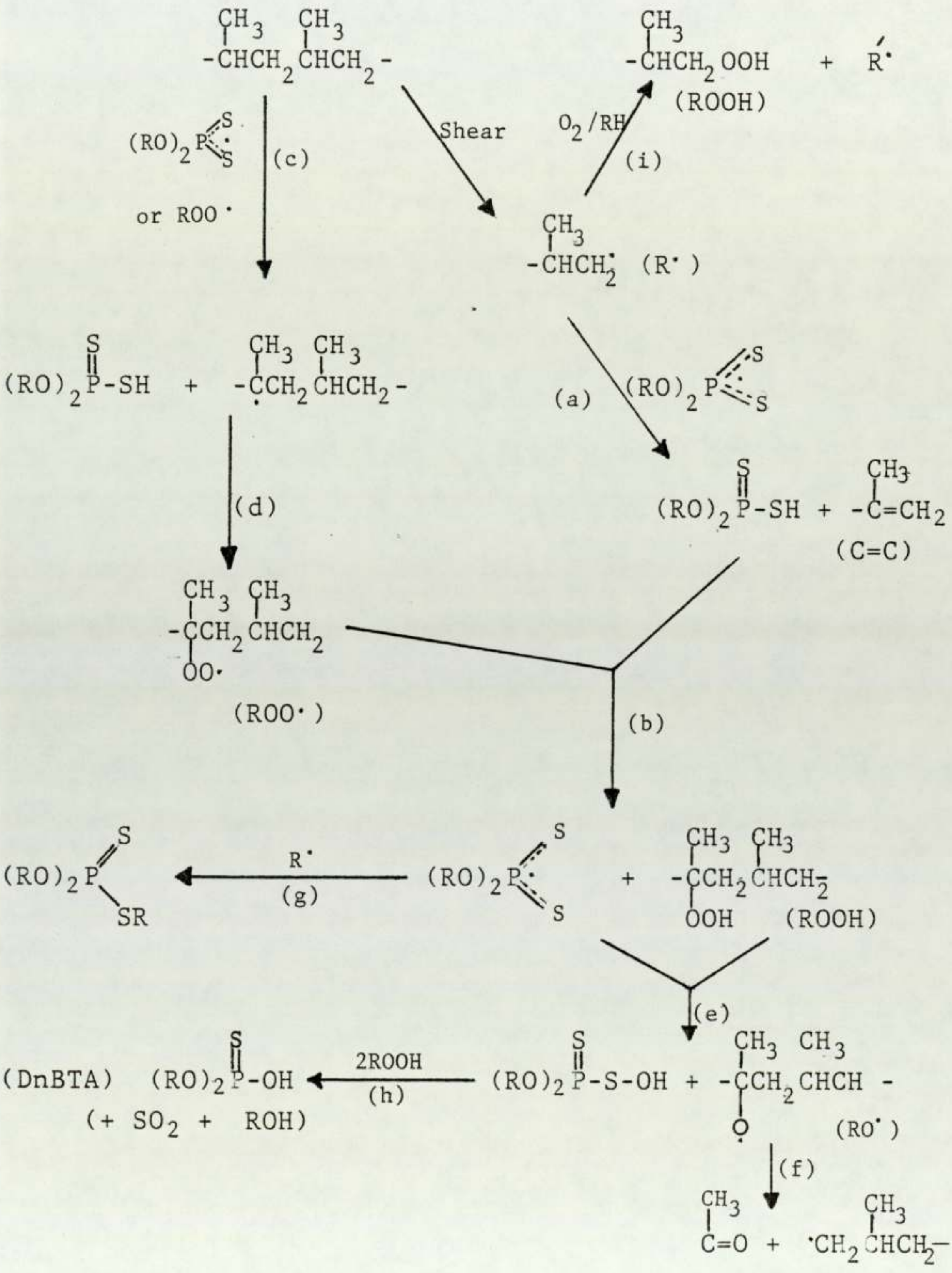


Furthermore, it has been shown (see Section 5.3.1 Scheme 5.1) that the thermal oxidative decomposition of DnBDS may result in the formation of the thiyl $(RO)_2PSS\cdot$, perthiyl $(RO)_2P\text{-}\overset{S}{\overset{\|}{S}}\text{-}S\cdot$ and the phosphorus – centred $(RO)_2\dot{P}S$ radicals. The conditions that exist during the thermal processing of DnBDS concentrates in PP are therefore ideal for the operation of the chain-breaking acceptor

(CB-A) and donor (CB-D) antioxidant mechanisms, and both mechanisms have been shown (see Section 3.3A.2.1, Scheme 3.3) to account for the melt stabilising activity of the thiophosphoryl disulphides.

The behaviour of the thiyl radicals during processing appears to involve the oxidation of macro alkyl radicals ($R^{\cdot}$), followed by further regeneration of the thiyl radical. An essential feature of the CB-A/CB-D antioxidant mechanism of DnBDS in PP (Scheme 4.3) is the formation of more unsaturation and hydroperoxide than can be accounted for from the thermal oxidative degradation of unstabilised PP alone, and this is clearly illustrated in Figure 4.3. This is convincing confirmation of the view that the macro-alkyl radicals generated by shearing of the polymer chain (Scheme 4.3 reaction (a)) undergo β-hydrogen abstraction by thiyl radicals to give vinyl groups which can no longer participate in the chain reaction. It is known$^{(4a)}$ that the strength of a β—C...H bond in an alkyl radical is only about 40% of that of the corresponding alkane and hence this reaction (reaction (a)) is kinetically favoured over other hydrogen abstraction reactions (e.g. reaction (c)). Scheme 4.3 also shows that the oxidation of the dithiophosphoric acid $(RO)_2PSSH$ by alkyl peroxyl radicals ($ROO^{\cdot}$) formed in the parallel reaction of alkyl radicals with oxygen, results in the formation of a hydroperoxide (ROOH) and the regeneration of both redox couples [reaction (b) and (f)]

Scheme 4.3 Catalytic antioxidant mechanism of thiyl radicals during thermal processing of polypropylene



Higher amounts of unsaturation in the closed mixer concentrates (CM) as compared to the oxidatively-processed concentrates (OM) indicates a higher rate of termination reactions (Scheme 4.3 reaction (a)) due to the interaction of thiyl radicals with macro alkyl radicals which are present in high amounts as a result of the high shearing force in the mixer (CM). It is also seen (Figure 4.3) that increasing the concentration of DnBDS also results in an increase in the unsaturation (see also Table 4.1) and this obviously is a direct consequence of an increase in the concentration of the thiyl radicals. However, when processing is carried out under oxidative conditions (OM), it is clearly evident that the reduced unsaturation and increased hydroperoxide levels in the concentrates (as compared to mildly-processed concentrates) is a direct consequence of the inability of the thiyl radicals to compete with oxygen for macro alkyl radicals (compare reaction (a) and (i) in Scheme 4.3). This factor may also account for the reduction in unsaturation level when concentration of DnBDS is increased up to 20% for both mildly and oxidatively-processed concentrates (Table 4.1 and Figure 4.3) since the slow diffusion of oxygen into the mixer removes both components of the redox couple. More interesting still is the fact that the reduction in unsaturation (20% concentrates) roughly parallels the rapid increase in the concentration of hydroperoxides in the concentrates (see Figure 4.3). At such high concentrations of DnBDS, the thiyl radicals formed may therefore interact with the macro alkyl radicals (R$^\cdot$) to form the triester $(RO)_2PSSR$ (reaction g), or may decompose polymer hydroperoxides to form the acidic specie $(RO)_2PSOH$ (reaction h) and both species have been identified in model compound studies (see Chapter 5, Section 5.3.1 - 5.3.2) as major oxidation products of DnBDS. Furthermore, the ^{31}P NMR analysis of extracts of DnBDS concentrates (Figure 4.26) clearly identifies these species (triesters and sulphur acid) as the major products formed from the disulphide during processing.

4.3A.3 Effect of DnBDS Concentration on the Photo-Oxidative Stability of PP Films

The effect of increasing DnBDS concentration on the photo-oxidative stability of PP films is shown in Table 4.3 and Figures 4.6. The results clearly show that the mildly-processed (CM) concentrates (2.5% - 15%) perform slightly better than the oxidatively-processed (OM) analogues as reflected by the U.V.embrittlement times. This may be due to the higher rate of termination reactions occuring during processing in a closed mixer (CM) as compared to oxidative processing (OM). A direct consequence of these reactions is the formation of vinyl groups (unsaturation) which can no longer take part in the chain reaction as shown in Scheme 4.3, reaction (a) . However, the effect of the higher hydroperoxide levels in the oxidatively-processed concentrates cannot be under estimated since the high potency of hydroperoxides as photo initiators is well known(5a,5b,18,19,27). Figure 4.4. also shows that the oxidatively-processed 20% DnBDS concentrate is superior to the mildly-processed analogue. The reason for this reversal in photo antioxidant activity within the series is not clear, although it is seen (Figure 4.3) that both the mildly-processed (CM) and oxidatively-processed (OM) concentrates contain the same level of unsaturation, and hence similar chain terminating activity (Scheme 4.3 reaction (a)). The higher activity of the severely-processed (OM) 20% DnBDS concentrate may therefore be due to the fact that the peroxide decomposing mechanism (reaction (e) and (h)) predominates over the chain breaking acceptor mechanism as typified by reaction (g) in Scheme 4.3.

It is now well established(5b,19,23a,23b,40) that not only is the rate of photo-oxidation a direct function of the initial (thermally produced) hydroperoxide concentration, but the rate of photo-oxidation is proportional to [ROOH] during the initial stages of U.V. irradiation(6,40b) . This is confirmed in Figures 4.5 - 4.6 which show the rate of carbonyl formation during photo-oxidation of PP films of both the mildly-processed (Figure 4.5) and severely-processed (Figure 4.6) concentrates. It is clear that the extent of the autoretarded oxidation exhibited by the stabilised PP films is closely related to the initial (thermally produced) hydroperoxide concentration in the DnBDS concentrates (see Figure 4.3). For both processing conditions, pronounced auto-retardating effects were observed as the concentration of DnBDS is increased (Figures 4.5 - 4.6) and it has also been shown that the hydroperoxide concentration is increased with concomitant increase in DnBDS concentration (Figure 4.3).

There is absolutely no doubt that the sulphur acids (e.g. DnBTA) formed from DnBDS during processing or on subsequent U.V. irradiation, are excellent peroxide decomposers (93). The formation of this specie from DnBDS has been confirmed in systems in which hydroperoxides could be formed in situ (cumene) and which could exhibit distinctive features associated with co-oxidation phenomena (see Chapter 5, Section 5.3.1 - 5.3.2). Furthermore , the photo antioxidant efficiency of this acidic species (DnBTA) in PP have also been shown (Section 3.3.1) to be identical not only to that of DnBDS, but also to a sample of DnBDS processed in the presence of added tert-butyl hydroperoxide at normal sample concentrations (0.2%). It therefore seems that a critical concentration of this oxidation product is necessary for effective antioxidant activity, since it was previously shown (Section 3.3.1) that severely-processed (OM) DnBDS samples are superior to the mildly-processed analogues at low concentrations (0.2%). The inferior performance of the severely-processed concentrates as compared to the mildly-processed analogues (Figure 4.4) may in part be due to the formation of an extremely high concentration of the oxidation products/intermediates which may be photolytically unstable. For example, the intermediate sulphoxide formed from dipropionate esters is known(18,40a) to be very sensitive to U.V light and, like carbonyl compounds, dissociates to free radicals. The accumulation of such reaction intermediates on the film surface due to exudation may therefore nulify the excellent peroxidolytic activity of the main oxidation products.

In the light of this discussion, it is clear that the photo antioxidant activity of mildly-processed (CM) and severely-processed (OM) DnBDS concentrates suggests a delicate interplay of the following three factors:-

(i) Exudation of light sensitive oxidation intermediates to the film surface.

(ii) Rate of chain termination activity (unsaturation).

(iii) Peroxide decomposing activity.

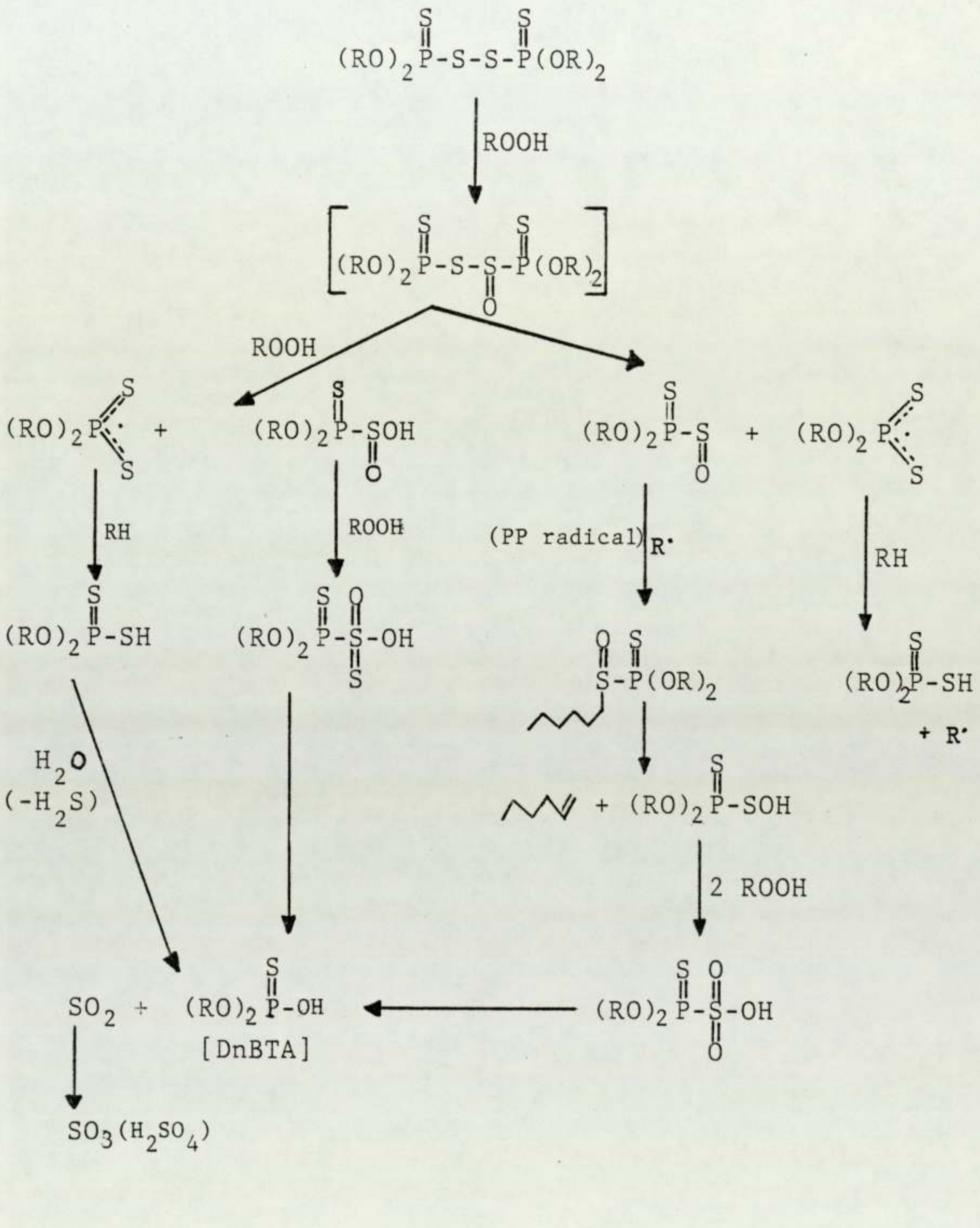
4.3A.4 Photo antioxidant Activity of DRDS / TBH Concentrates in PP

It has long been established(85,86,92-97) that the higher oxidation levels of sulphur-based antioxidants formed either during processing of polyolefins or from natural rubber sulphur vulcanisates, are the actual inhibitors of auto-oxidation rather than the parent sulphur compounds. An extension of this principle which involves the processing of DnBDS in PP in the presence of tert-butyl hydroperoxide (TBH) have been shown(27,8b) to result in improved photo-antioxidant activity (see also Section 3.3.1).

Table 4.4 and Figure 4.7 which compare the photo-antioxidant activity of DnBDS concentrates (2.5%) processed in the presence of varying amounts of TBH in PP indicates that the best stabilising effectiveness is obtained when an equimolar ratio of both components is used. Table 4.4 clearly shows that a 2-4 molar excess of DnBDS is highly detrimental to the U.V. activity of the stabilised PP films and this may be due to the formation of mainly the photolytically unstable oxygenated intermediates. This no doubt is a direct consequence of incomplete oxidation of the additive since not only is the hydroperoxide level low, but processing was also carried out under a blanket of nitrogen. At higher TBH levels however (equimolar ratio & 2-fold molar excess of TBH), it is seen that the photo antioxidant activity is markedly superior to that of DnBDS without any added hydroperoxide. In contrast to the nature of the products formed when a molar excess of DnBDS is used, the oxidation of DnBDS in the presence of such high levels of TBH is expected to result in the eventual formation of the sulphur acids during processing and on subsequent U.V irradiation (Scheme 4.4).

A similar behaviour is also observed when DHDS (R = hexyl) is processed in the presence of TBH under similar conditions as those used for DnBDS (R = n-butyl). It can be seen from Table 4.4 and Figure 4.8 that the photo-antioxidant activity of an equimolar ratio DHDS:TBH sample is clearly superior to that of both the mildly-processed (CM,10) and severely-processed (OM,10) DHDS concentrates at the same concentration. This behaviour, as has been described for DnBDS, is obviously a direct consequence of the controlled oxidation of the disulphide in the polymer which results in the generation of a critical concentration of the effective peroxidolytic antioxidants in situ. Scheme 4.4 outlines the reaction pathways involved in the formation of the effective peroxidolytic antioxidant (DnBTA) from DnBDS in polypropylene.

Scheme 4.4 Oxidation of DnBDS by TBH in polypropylene



Scheme 4.4. clearly shows that the acidic species DnBTA, is a major oxidation product and this has been confirmed in model compound studies on the oxidation of DnBDS by TBH in cumene (Section 5.3.2).

The sulphonic acid intermediate has also been identified by Al-Malaika and co-workers(27,40b) in studies involving the oxidation of the nickel complex NiDBP by cumene hydroperoxide. Furthermore, the acidic specie DnBTA has been shown (Section 3.3.1) to be effective in stabilising PP against photo-oxidation and its activity has been proposed to involve both chain breaking (CB-A/CB-D) and peroxidolytic (PD-C) mechanisms (see Section 3.3.1, Scheme 3.3) resulting in the formation of triesters and inorganic phosphates amongst others, all of which are effective antioxidants.

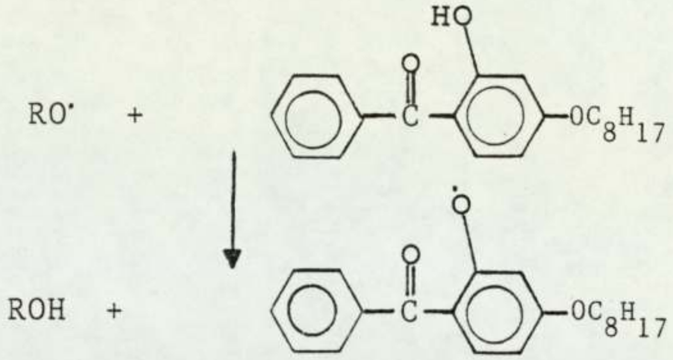
The results described in this section therefore provide clear evidence that controlled oxidation of DnBDS by TBH can be put to beneficial use provided the right ratio (of both components) is adopted.

4.3A.5 Effect of Processing Procedure on the Photo antioxidant Synergism of DnBDS / HOBP Concentrates in PP

In contrast to the observed photo antioxidant synergism between DnBDS and the U.V. absorber HOBP in PP at normal sample concentrations (see Section 3.3A.3), the behaviour of this combination in the form of concentrates cannot be described as being strictly synergistic. Table 4.5 clearly shows that the observed photo antioxidant activity of DnBDS:HOBP concentrates is less than the sum of the individual effects of the two components. Although the reasons for this behaviour is not yet clear, it may well be due to a combination of the following factors.

(i) The exudation (blooming) of additives to the film surface was clearly evident, and at such high concentrations used the high amount of transformation products present at the film surface may, on U.V. irradiation, photolyse faster than should be the case had the additives remained inside the matrix.

(ii) The destruction of HOBP by hydroperoxides formed during processing and on subsequent U.V. irradiation. Literature evidence (47) suggests that HOBP behaves as a sacrificial antioxidant by removing chain initiating radicals formed from hydroperoxides (reaction 4.1)



(4.1)

The loss in the activity of HOBP may therefore result from dimerisation of such reaction product following photolysis of the species when present at the film surface.

Table 4.5 and Figure 4.9 also clearly indicate that oxidative processing either in the presence of air or tert-butyl hydroperoxide, has a detrimental effect on the photo antioxidant activity of the concentrates. This implies that the sacrificial destruction of HOBP (reaction 4.1) by hydroperoxides proceeds at a higher rate during oxidative processing. The photolysis of this specie (reaction 4.1) and/or that of its reaction products with a thiyl radical $(RO)_2PSS^{\cdot}$, may therefore be responsible for the poor performance of the severely-processed concentrates. An examination of the U.V. absorption spectra of DnBDS:HOBP concentrates (Figure 4.20) clearly indicates the formation of a new reaction product in view of a new U.V. absorption band at 400 nm. The mechanisms involved in the formation of such a reaction product and its relevance to the overall stabilising activity of these concentrates in PP will be discussed in detail in Section 4.3C.1 and 4.3C.2

4.3A.6 Effect of Impurity Level in DRDS on Their Photostabilising Activity in PP (R = hexyl)

It has been shown (see Chapter 2, Section 2.1.3) that although purity of bis(O, O'- dialkyl thiophosphoryl) disulphides (DRDS) is dependent on the method of preparation, impurities have been known to accumulate in a pure sample with increasing storage time. Figure 4.10 which compares the ^{31}P NMR spectra of different samples of DHDS (a-c) containing various levels of impurities, clearly shows that not only is the nature of the impurities similar in all three samples, but also that the partly decomposed (190°C /5 min./air stream) sample contains a higher proportion of these impurities relative to the disulphide. The pure disulphide (a) shows a sharp ^{31}P NMR signal with chemical shift of 85 ppm, while the various impurities contained in the other samples show ^{31}P NMR signals having chemical shifts of 83.8 ppm, 79.2 ppm, 72.8 ppm, 96.1 ppm and 52.6 ppm. The signals due to these impurities are assigned (98) to the trisulphide DHTR, the monosulphide DHMS and the triesters O,O,O-THTP ($(RO)_3PS$), O,O,S-THDTP ($(RO)_2(RS)PS$) and O,S,S-THDTP ($(RS)_2(RO)PO$) respectively. That these impurities are merely oxidation products of the disulphide have been demonstrated (Section 5.3.1 - 5.3.2) in model compound studies on the thermal oxidation of DnBDS under a wide range of conditions.

*

		δ
[DHTR]	Bis(O,O-di-n-hexyl thiophosphoryl) trisulphide	83.8
[DHMS]	Bis(O,O,-di-n-hexyl thiophosphoryl) monosulphide	79.2
[O,O,O-THTP]	O,O,O-tri-n-hexyl thiophosphate	72.8
[O,O,S-THDTP]	O,O,S-tri-n-hexyl dithiophosphate	96.1
[O,S,S-THDTP]	O,S,S-tri-n-hexyl dithiophosphate	52.6

It is distinctly clear (Table 4.6 and Figure 4.11) that the presence and concentration of impurities in DHDS does influence its effectiveness as a U.V. stabiliser in PP although the effect is not necessarily in favour of the pure sample (a). The relative ability of the impurities to participate in the photo-stabilising process is best illustrated by sample (c) which is only about 75% pure DHDS. This sample is shown (Table 4.6 and Figure 4.11) to be the most effective under conditions of both mild-processing (CM) and oxidative-processing in the presence of air (OM) although it was insufficient for any further assessment with TBH. This behaviour is not surprising since literature (70) evidence suggests that esters of dithiophosphoric acid are effective stabilisers for PP under both thermal and photo-oxidative conditions. Sanin et. al.(99) have also demonstrated the effectiveness of some triesters (O,O,S-TETP and O,O,O-TETP) in inhibiting hydrocarbon oxidation. The detrimental effect of severe-processing in the presence of air (OM), is clearly reflected on the photo-stabilising activity of all the samples, although a closer scrutiny of the data (Table 4.6b and Figure 4.11) clearly indicate that the beneficial effect of oxidative processing in the presence of TBH is more pronounced with the sample of highest purity (> 99.9%). However, it must be emphasised that similar improvements may be achieved with the less pure DHDS samples provided the molar ratios (DHDS:TBH) are adjusted accordingly, since a high level of impurity is diagnostic of an equally high oxidation state of the disulphide (see also Section 5.3.1 - 5.3.2). The detrimental effect of oxidative processing on the photo-antioxidant performance of the partly-decomposed DHDS sample (65% purity) in PP, may be associated with the activity of any chain propagating species (RO· /ROO·) present in the sample (see Section 4.2A.6). This probably accounts for its reduced effectiveness in PP as compared to the other samples (b and c) with similar, but slightly lower level, of impurities (Table 4.6).

The photo-stabilising activity of the various impurities, notably the triesters can be interpreted in terms of their ability to retard the oxidation process(99). The thiolphosphate esters have also been widely recognized as effective thermal antioxidants in polyolefins. The mechanism of their antioxidant activity is not very clear, but it has been postulated(100) that their decomposition results in the formation of simple alkyl sulphides and inorganic phosphates (see Section 5.3.2 ; Scheme 5.9). Since the auto-oxidation inhibition activity of the alkyl sulphides and disulphides is attributed to products formed from them as hydroperoxides accumulate in the substrate(25,85,86,92,94-97) it is therefore fairly reasonable to assume that these transformation products are able to complement the activity of the thiophosphoryl disulphide, by virtue of their peroxide decomposing activity. In addition to their ability to decompose hydroperoxides, the sulphenic acids (RSOH) derived from the intermediate sulphoxides, have also been reported(22,85,108) to function in part as chain breaking antioxidants.

In the light of this discussion, it is quite clear that the presence of these impurities in a disulphide sample may therefore enhance its antioxidant activity, this being clearly dependent on the prevailing auto-oxidative conditions.

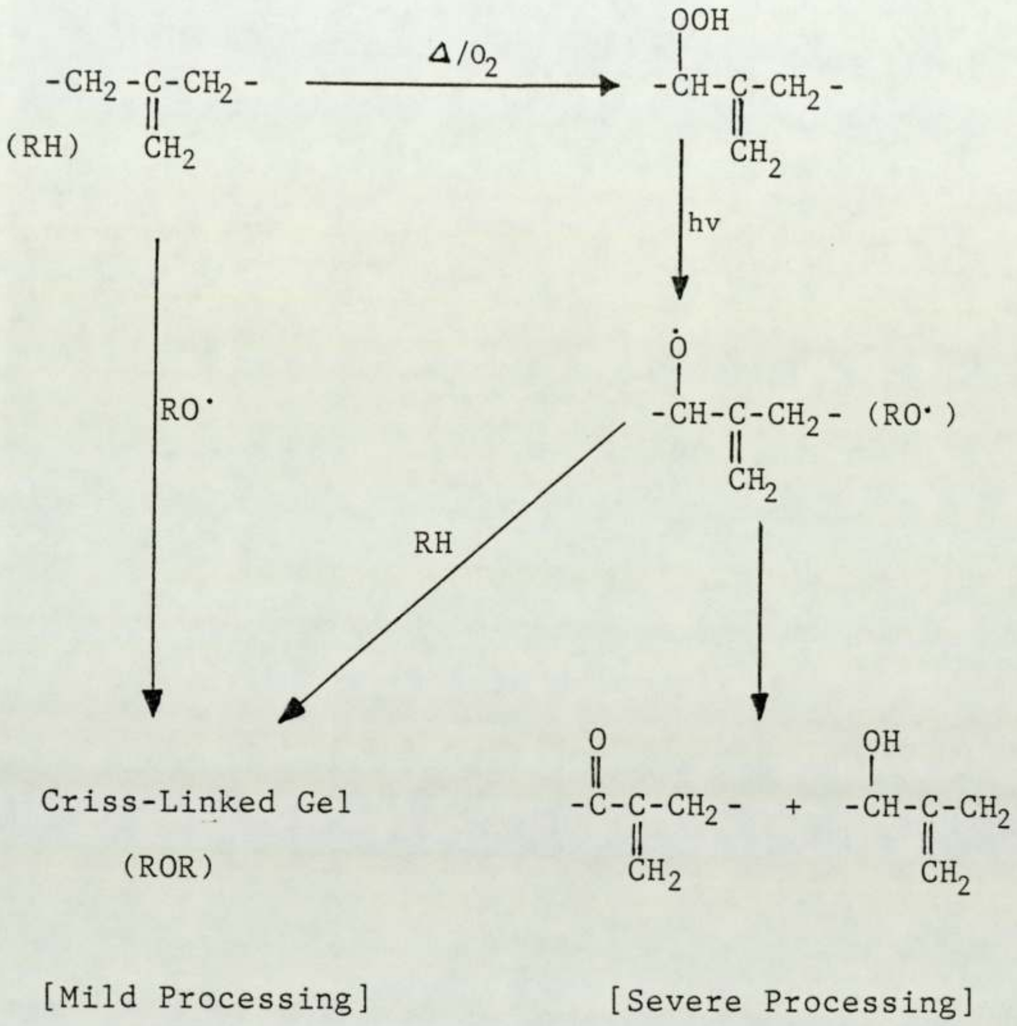
4.3B LDPE DnBDS Concentrates (LDPE/Ct)

4.3B.1 Effect of Concentration of DnBDS and Processing Procedure (150°C) on the U.V. Stability of LDPE

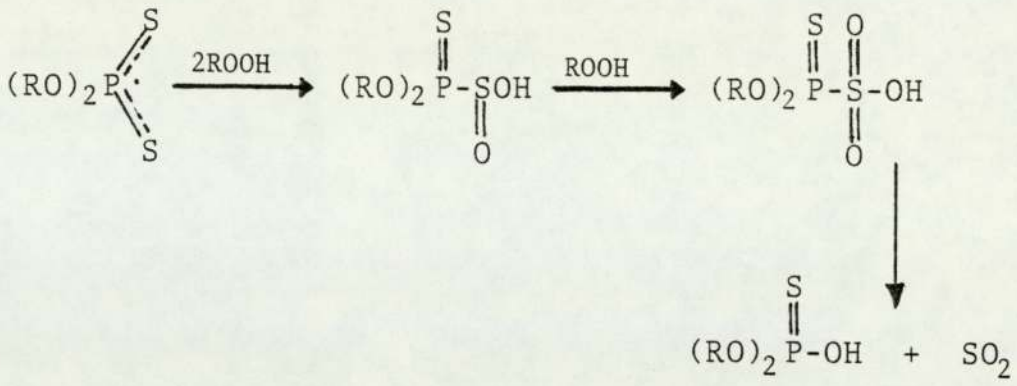
In contrast to the observed slight detrimental effect of severe-processing (OM) on the photo-antioxidant activity of DnBDS 'concentrates' in PP, its activity in the less oxidisable LDPE is relatively unaffected by the processing procedure during the early stages of photo-oxidation (Figure 4.12). This implies that the rate of consumption of DnBDS, and hence the rate of formation of the effective peroxidolytic antioxidant during the early stages of photo-oxidation, appear to be similar for both processing conditions (CM and OM). However, the improved auto-retarding oxidation of the severely-processed sample is clearly indicative of the presence of a higher proportion of the catalytic peroxide decomposers which then exert their effect during the later stages of photo-oxidation.

It is now well established(5b,6,19,23a,23b) that a small concentration of unsaturation (mainly vinylidine) formed by side reactions during polymerisation of LDPE results in the formation of hydroperoxides during processing. The same workers(6,23a,23b) have also clearly demonstrated that a proportionately higher concentration of hydroperoxides is formed during severe processing (OM) while cross-linked gel formation is favoured by mild processing (CM) according to Scheme 4.5, which also briefly outlines the subsequent reactions of the hydroperoxide during photolysis.

Scheme 4.5 Thermal formation and photo-chemical breakdown of hydroperoxide Groups in LDPE



As would be expected from scheme 4.5, the high peroxide concentration formed during severe-processing of DnBDS therefore provides an ideal condition for the formation of the effective peroxidolytic antioxidants (reaction 4.2).

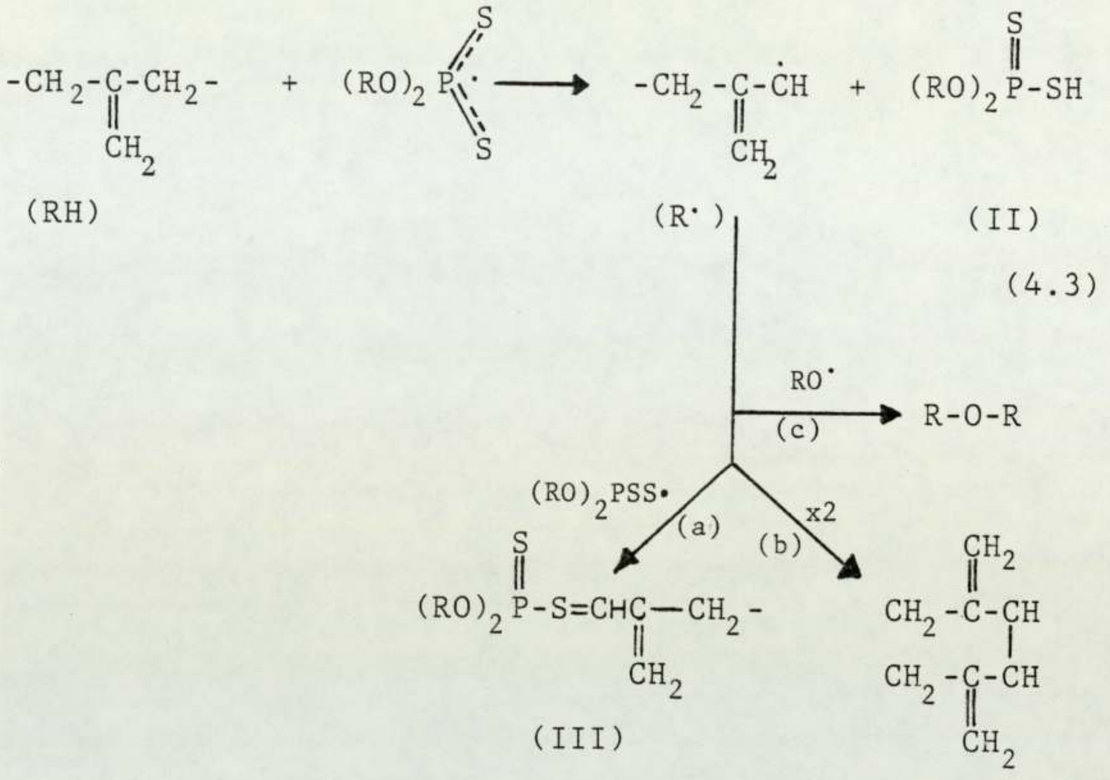


(I)

(4.2)

The accumulation of these species during processing and on subsequent U.V. irradiation is responsible for the observed extensive auto-retarded oxidation (Figure 4.12). The initial auto-retarded effect may also be attributed to hydrogen abstraction from allylic groups in the polymer (reaction 4.3) to create a radical which may either interact with a thiyl radical to form an ester (reaction 4.4a) or crosslink with other propagating species (R˙/ RO˙) resulting in the formation of insoluble gel (reaction 4.4b-c).

The lack of any direct evidence for the formation of the dithiophosphoric acid (II) may be attributed to the fact that they either readily undergo hydrolysis to form thionophosphoric acid (I), or regenerate the thiyl radical by virtue of their CB-D activity (see reaction 4.5a-b). In contrast to the acidic specie, there is unequivocal evidence for the presence of the thiophosphate ester (III) during the later stages of

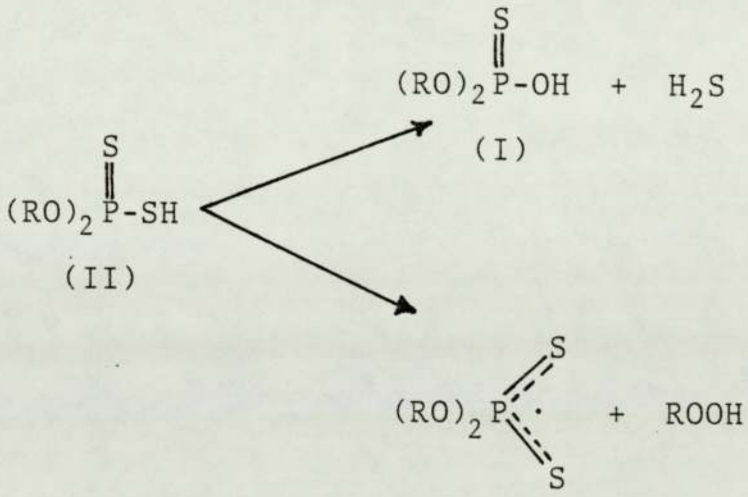


(4.3)

(4.4)

photo-oxidation as is evidenced by the formation of IR absorption bands due to P-S-C linkages at 585 cm^{-1} (see Figures 4.17 and 4.18b). Similarly, the formation of a strong IR absorption band within the range 1270 cm^{-1} - 1100 cm^{-1} during the later stages of photo-oxidation suggests the presence of C-O-C linkages (see Figure 4.18) although absorptions due to single bond (C-O) vibration within the carbonyl group in carboxylic acid may also absorb in this region.

Although the photo-initiated free radical addition reactions of thionophosphoric acid (I) to olefins have been reported$^{(100)}$ to occur more readily than that of the corresponding dithiophosphoric acid (II), the findings in this study (Section 4.3C.2) clearly suggest that the thiyl radicals (from (II) are equally as effective in the formation of ester groups. However, these may also be formed via a series of alkylation - dealkylation reactions involving the ambident thiyl or thione radicals ($(RO)_2PSS^{\cdot}$ or $(RO)_2PSO^{\cdot}$) as shown in Chapter 5; reactions 5.5a - 5.9. A detailed review of the implications of these reactions on the overall photo-stabilising activity of the disulphide will be discussed in Section 4.3C.1 - 4.3C.2.



(4.5)

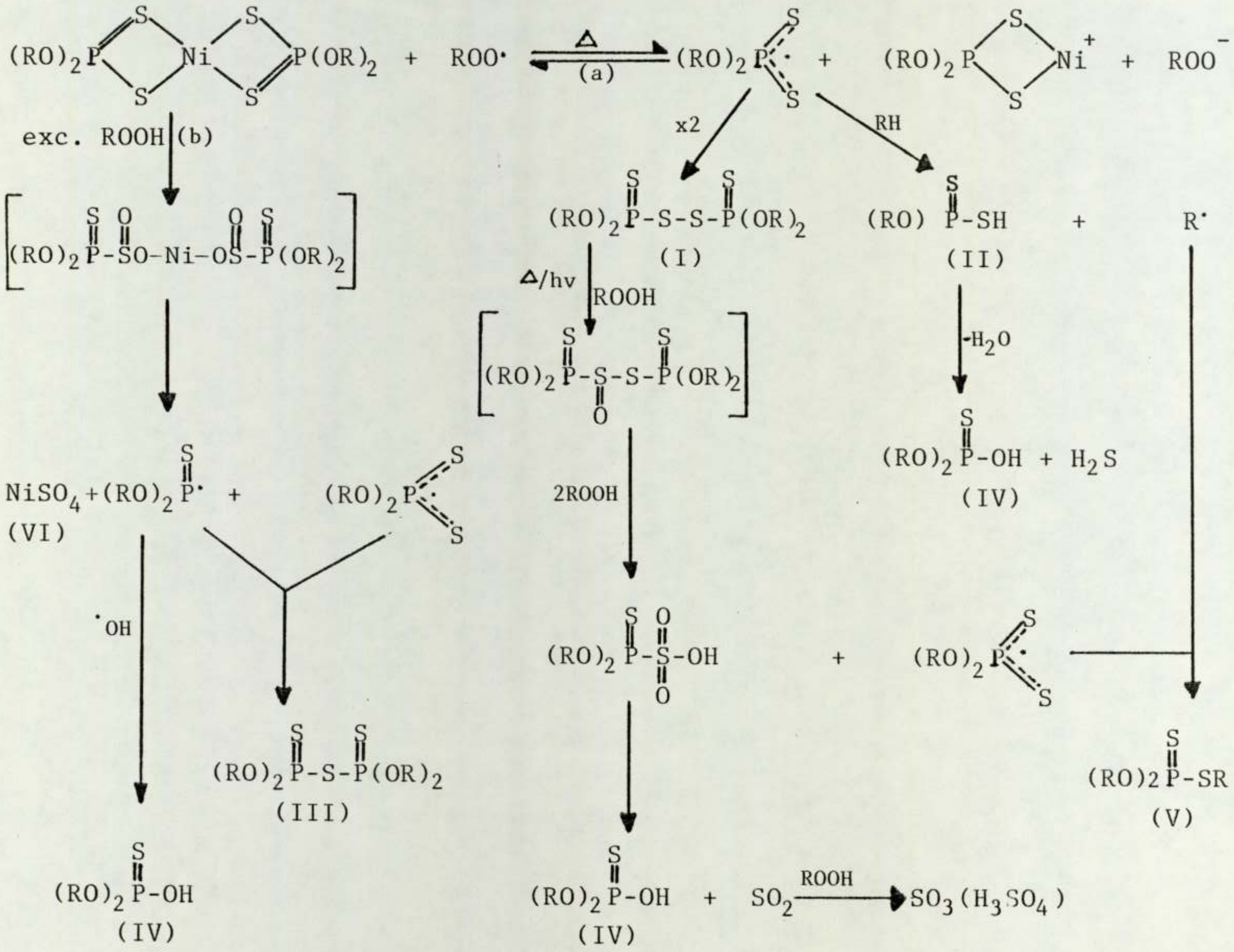
4.3B.2 Photo antioxidant Synergism of Dithiophosphate/HOBP Concentrates in LDPE

The photo antioxidant synergism between DnBDS and HOBP at normal sample concentrations (< 0.4%) in LDPE has already been demonstrated in a previous chapter (Section 3.3B.2), and it was clearly shown that the synergistic effect is augmented by severe-processing. The concentrate films are shown in the present chapter to exhibit similar photo-oxidative stability when processed under identical conditions (Table 4.8 and Figure 4.13), although the beneficial effects of severe-processing in this instance is only evident up to a certain point (10,000 hr) after which the photo-oxidative behaviour becomes auto-catalytic (Figure 4.13 curve 6). This implies that the destruction of some HOBP by hydroperoxides formed during oxidative processing of the synergistic combination in LDPE, as described for PP (Section 4.3A.5), does occur and may therefore result in the formation of light unstable species. The new U.V. absorption band of 400 nm, as shown for PP (Figure 4.20), was only observed in the severely-processed LDPE concentrate and this appears to be closely associated with the photo-stabilising behaviour of the systems when processed under both mild (CM) and severe (OM) conditions (cf. curves 5 and 6 in Figure 4.13).

It is known that the activity of HOBP decreases markedly when the polymer is processed under oxidative conditions(5b,23b,27), and its activity has also been reported(47) to involve the removal of chain initiating radicals formed from hydroperoxides (see also reaction 4.1). This behaviour is therefore a direct consequence of the oxidisability of the substrate and the subsequent formation hydroperoxides which destroy the stabiliser under conditions of U.V.irradiation. It is therefore not surprising that the extent of such a reaction is much higher in the more oxidisable PP, such that the expected synergistic phenomenon is completely nullified. There seems little doubt, however, that the better auto-retardation effect exhibited by the severely-processed LDPE concentrate during the early stages of photo-oxidation (up to 10,000 h), is due to the greater protection afforded to HOBP by the oxidatively-produced peroxidolytic antioxidants (cf. curves 5 and 6 in Figure 4.13).

In contrast to a DnBDS sample and the synergistic DnBDS:HOBP samples, the NiDnBP-stabilised LDPE film shows and extensive photo-oxidative induction period (PIP) followed by a rapid auto-catalytic stages (cf. curves 1-3, 5 and 6 with curve 4 in Figure 4.13). The pronounced auto-retarded oxidation exhibited by the latter samples during the early stages of photo-oxidation, is only slightly distinguishable in the NiDnBP concentrate film (see inset to Figure 4.13). This behaviour can be explained in terms of the limited significance of hydrogen abstraction reactions of the initially formed thiyl radicals (reaction 4.3), since the macro radicals which may be created are quite capable of propagating the oxidation process by acting as sites for oxygen uptake. The prolonged photo-oxidative induction period of the NiDnBP concentrate film may therefore be attributed to the controlled liberation of the various antioxidant species [from the nickel complex] during processing and on subsequent U.V. irradiation. It is now well established(5b,19,27,40b,70) that the effective U.V. stabilising activity of the nickel dithiophosphates is not only due to their high U.V. stability, but also a direct consequence of their ability to liberate the peroxidolytic antioxidants over a long period of time. Scheme 4.6,which outlines the different reaction pathways involved in the antioxidant mechanism of NiDnBP, clearly shows that a significant feature of the two processes indicated (a and b) is the formation of the sulphur acid (IV). The activity of this specie as a peroxide decomposer (93) and as an effective U.V. stabiliser (Section 3.3A.1) has been demonstrated. However, the formation of the various products outlined in this scheme (Scheme 4.6) has been confirmed in model compound studies (Section 5.3.3) on the oxidation of NiDnBP by TBH at room temperature (2-10 molar excess of TBH). In this study ^{31}P NMR analysis shows that the initial oxidation products at low TBH/NiDnBP ratios (1-4) are mainly the disulphide (I) and the monosulphide (III) while higher TBH ratios (4-10) leads to the formation of not only the thionophosphoric acid (IV),but also the formation of more monosulphide (III). This confirms the view that both processes (processes a and b in Scheme 4.6) may be involved in the antioxidant activity of NiDnBP, thus the various antioxidant species formed are then able to exert their effect as photo-oxidation proceeds. An additional factor responsible for the effectiveness of the nickel dithiophosphates (NiDRP) is their ability to scavenge alkylperoxyl radicals (ROO·). Several mechanisms have been proposed(25,28,39,43,70), most of which involve an electron transfer process whereby an electron is abstracted from an electron rich sulphur atom in the ligand by the radical (ROO·). The resulting thiyl radicals may therefore either undergo mutual combination to form the disulphide (I) or abstract hydrogen from the polymer back bone with the generation of dialkyldithiophosphoric acid (II) as shown in Scheme 4.6 (reaction pathway (a)). Howard(39) has reviewed the various mechanisms proposed for the interaction of metal thiolates with alkyperoxyl radicals, and concluded that alkylperoxyl radicals appear to react at the metal centre of dithiophosphates to displace a ligand radical. The auto-catalytic trend observed during the latter stages of photo-oxidation may be due to photolysis of the light unstable species formed from the decomposition of the thiolphosphate esters (V), and this stage is usually preceded by complete breakdown of the nickel complex (Figure 4.19). The decomposition of the thiolphosphate esters have been known(100) to result in the formation of inorganic phosphates and simple alkyl sulphides (see also Scheme 5.9). Further oxidation of the sulphides will most likely give rise to the intermediate sulphoxide and these, like the carbonyl compounds, are known(18,40a) to be

Scheme 4.6 Alternative Antioxidant Mechanism of NiDnBP



very sensitive to U.V. light and may dissociate to free radicals which will then propagate the photo-oxidation process.

The initial auto-retarded oxidation, as shown for the synergistic DnBDS:HOBP concentrate films (curve 5 and 6 in Figure 4.13) is also clearly evident, albeit to a much lesser extent, in the behaviour of the synergistic NiDnBP:HOBP concentrate film (curve 7). This confirms the view that auto-retardation is not only associated with dithiophosphoryl radical formation from the dithiophosphate, but also with the probable destruction of some HOBP by hydroperoxides during processing and on subsequent U.V irradiation. The new U.V.absorption band at 400 nm was also observed although this band is very much less than that reported for the DnBDS:HOBP concentrates processed under similar conditions. This implies that the nickel complex affords a better protection to HOBP during processing when compared to the role of the disulphide in this respect, and this is equally reflected on the auto-retardation behaviour of the samples (Figure 4.13 and Table 4.8). Please refer to Sections 4.3C.2 - 4.3C.3 for a detailed discussion on the product associated with the 400 nm band and its relevance to the overall stabilising activity. However, the excellent auto-retarded oxidation of the NiDnBP:HOBP film clearly indicates the mutual participation of both components in the photo-stabilization process. In this instance, the nickel complex protects the U.V. absorber from the destruction effects of hydroperoxides during processing and photo-oxidation, while HOBP exerts its effect during photo-oxidation by prolonging the presence and hence the activity of NiDnBP.

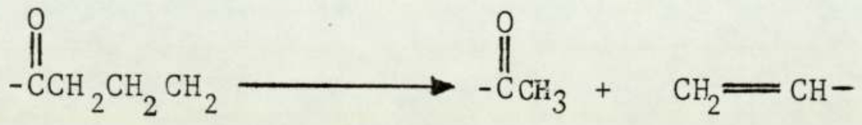
4.3C Spectral Characteristics of Concentrate Films

4.3C.1 DnBDS and NiDnBP Concentrate Films

The major IR characteristic absorption bands of the additives are easily observed in the concentrate films although some of these may be obscured by absorption bands of the polymer (see Section 4.2C.1). It can be seen (Figure 4.15) that the intensity of both the P-O-(C) (730 cm^{-1}) and P=S (645 cm^{-1}) stretching vibrations in PP is proportionately increased with concomitant increase in the concentration of DnBDS. Although the origin of the absorption band at 350 cm^{-1} is not clear, this band was found to be present in most synthesised DnBDS samples (see Figure 4.14a) and the intensity of the band was also observed to increase with increasing storage time. This evidently suggests that the 350 cm absorption band may be due to an impurity in the disulphide, possibly a thiophosphate ester of the type shown (Figure 4.11) to be present in some DHDS samples (see Section 4.3A.6) with a ^{31}P NMR chemical shifts of 72.8 ppm. There is literature evidence(82,101) to suggest that this specie ($(RO)_3PS$) not only shows an infra-red absorption band in the range 540-490 cm^{-1}, but that there is also absorption(101) (weakly) within 260-360 cm^{-1} region. It seems likely therefore, that this absorption band (350 cm^{-1}) is due to the thiolphosphate ester O,O,O TBTP, and the presence of this impurity in most DnBDS samples have been amply demonstrated by ^{31}P NMR analysis (Sections 4.3A.6, 5.3.1-5.3.2). The significance of the functional groups to the overall stabilising activity of the additives, is clearly illustrated in Figure 4.16 which shows the relationship between the P=S index (645 cm^{-1}) of DnBDS:TBH concentrates and their photo-antioxidant activity in PP. Figure 4.16 not only shows that the incorporation of increasing amounts of TBH to several 2.5% DnBDS concentrates leads to an increase in the P=S index, but also clearly indicates that the P=S index of the unexposed samples are directly related to their U.V. stabilising activity. In contrast to PP, LDPE was found to be an ideal matrix for a study of the changes in the relative concentration of the various functional groups in DnBDS, during photo-oxidation. It was also possible to monitor the formation of the thiolphosphate esters formed from the interaction of thiyl radicals with macro alkyl radicals (reaction 4.4a). It is shown (Figure 4.17) that the initial auto-retarded behaviour of the DnBDS concentrate film is clearly associated with the breakdown of the disulphide molecule, as reflected by the decay in the intensity of the absorption bands at 520 cm^{-1} and 460 cm^{-1}

assigned to the disulphide (P-S-S-P) and the trisulphide (P-S-S-S-P) respectively (see Section 2.1.6). The trisulphide (460 cm^{-1}) has been shown to be present as an impurity in most DRDS samples (Section 4.3A.6 and also Figure 4.14a) and this impurity (DnBTr) was also identified as a major reaction intermediate during the thermal oxidation of DnBDS at 180 °C in the presence of air and also at 100 °C in the presence of TBH (Section 5.3.1 - 5.3.2). During the course of these reactions, the trisulphide was shown to increase rapidly in the early stages and then decays as the reaction proceeds. A similar behaviour is clearly evident in the polymer since the absorption band at 460 cm^{-1} is seen to increase rapidly during the early stages of photo-oxidation before decaying (Figure 4.17). It is also clear that the reduction in the intensity of the P-O-(C) stretching vibrations (895 cm^{-1}) roughly parallels that of the P-S-S linkages (550 - 400 cm^{-1}). More interesting still is the fact that the complete decay of these functional groups roughly coincides with the second auto-retardation stage during which time the thiolphosphate esters began to form. The P-S-(C) vibrational modes of these esters 585 cm^{-1} and 490 cm^{-1})(82) is shown (Figures 4.17 - 4.18) to increase in intensity during the latter stages of photo-oxidation. Figure 4.17 also illustrates the formation and increase in the concentration of vinyl unsaturation during the latter stages of photo-oxidation, coincident with the increase in carbonyl concentration.

This confirms the view(5b,6,18,19) that the carbonyl groups formed from photolytic decomposition of hydroperoxides undergo further photolysis initially by Norrish II process giving vinyl unsaturation as the major product (reaction 4.6)



$$-\overset{\overset{O}{\|}}{C}CH_2CH_2CH_2 \longrightarrow -\overset{\overset{O}{\|}}{C}CH_3 + CH_2{=}CH-$$

(4.6)

In the case of the NiDnBP-stabilised concentrate films, a similar relationship was found to exist between the decay in the intensity of the absorption bands of the additive and its photo-stabilising activity in LDPE. It is clearly shown (Figure 4.19) that the reduction in the intensity of the IR absorption bands at 550 cm^{-1} and 350 cm^{-1} corresponds to the decomposition of the nickel complex. These bands are respectively assigned to the Ni-S and P-S-Ni stretching vibrations, and as previously postulated (Section 4.3B.2) the prolonged photo-oxidative induction period exhibited by this sample is partly due to the conversion of the nickel complex to the various antioxidant species (See Scheme 4.6) which are constantly used up in the decomposition of hydroperoxides. The fact that the complete decay of these absorption bands roughly coincides with the onset of the autocatalytic stage confirms the view that the nickel complexes are the precursors of the effective catalytic peroxide decomposers since the decay of the complex is seen to herald the failure of the sample.

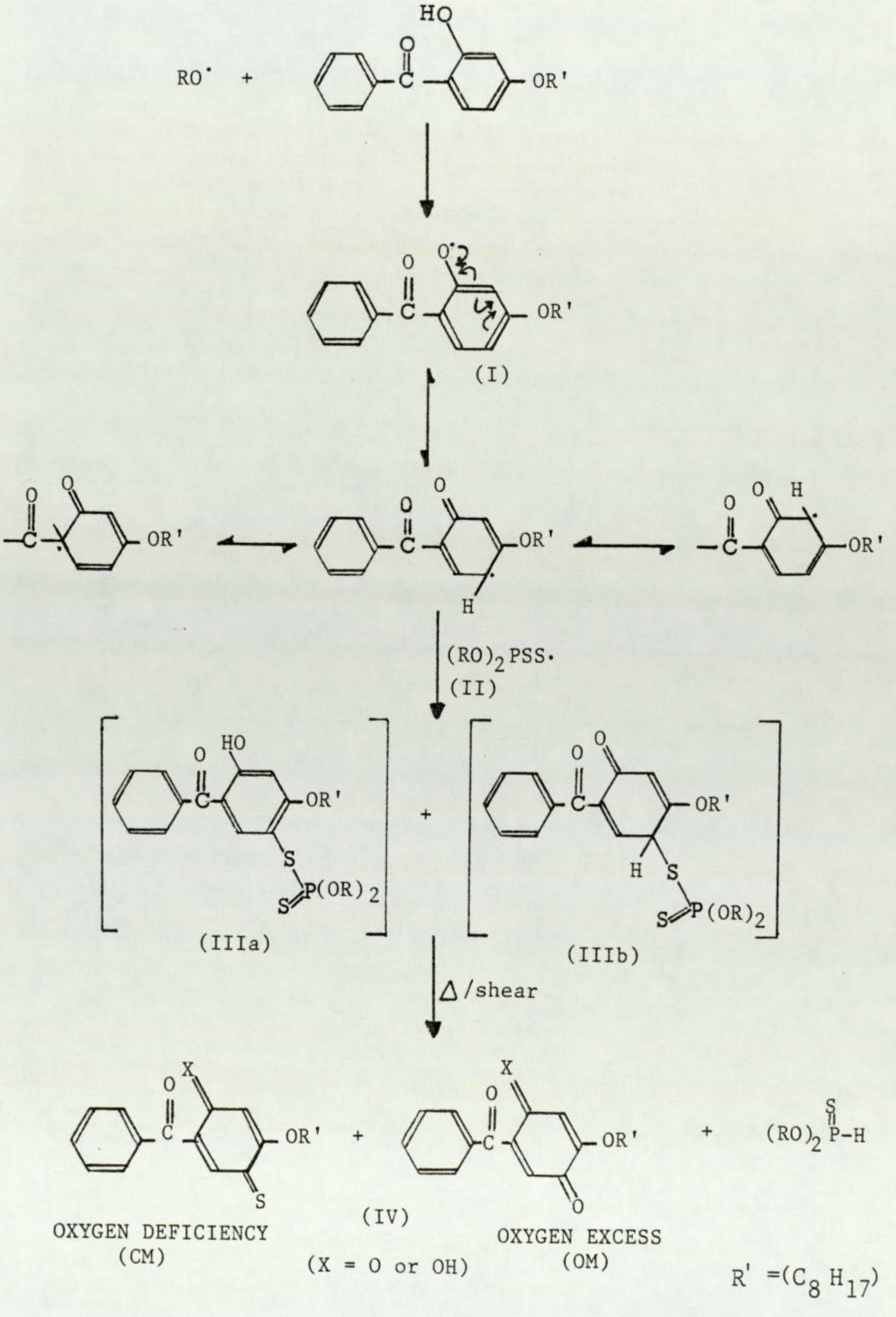
In the light of this discussion,it therefore follows that a study of the several IR characteristic absorption bands of the dithiophosphates during photo-oxidation, can be conveniently used to elucidate the antioxidant mechanism of the compound.

4.3C.2 Synergistic DnBDS:HOBP Concentrate Films

During processing of the synergistic DnBDS:HOBP concentrates, it was observed that in addition to the original U.V.absorption bands of HOBP (240 nm, 285 nm and 325 nm), a new band around 400 nm was observed in the compression moulded films (Figure 4.20). This band was first observed by Al-Malaika(59) who studied its behaviour under both photo- and thermo-oxidative conditions although the exact identity of the specie responsible for the 400 nm band was not resolved. In the present study, however, the intensity of this band in severely-processed concentrates (in both PP and LDPE) is much higher that in the midly-processed concentrates (Figure 4.21a-b) and the polymer melt also appeared to be intensely coloured. During U.V.irradiation, however, the 400 nm band disappeared very rapidly while the original peaks due to HOBP seemed to be fairly stable (Figure 4.22). This behaviour clearly suggests that the disulphide interacts in some way with HOBP during processing to form a coloured compound which is responsible for the 400 nm absorption band. The mechanism involved in the formation of this new product is not very clear, but it is quite unlikely that the octyloxy group of HOBP is cleaved since available evidence(103) so far suggests that HOBP is thermally stable up to 300°C. A probable reaction pathway may arise from the initial destruction of some HOBP by hydroperoxides formed during processing. It has previously been postulated(47) that the destruction of HOBP during processing may result in the formation of a benzophenone radical (reaction 4.1). The new product may therefore be formed via the interation of the benzophenone radical(1) with a thiyl radical (II) formed from homolytic decomposition of the disulphide (Scheme 4.7). However, the addition product of this reaction (III) would not be very stable to withstand the processing temperature and time. Consequently sulphur/phosphorus bond may break with the eventual formation of a quinone-type compound (IV), particularly in the presence of excess oxygen (OM).

As might be expected from Scheme 4.7, the formation of the new U.V. absorption band at 400 nm may be due to increased conjugation within the molecule of the reaction product (IV). The higher concentration of the quinone-type product in the severely-processed concentrates may

Scheme 4.7 Possible mechanism of the formation of reaction product of DnBDS and HOBP during processing at 180°C

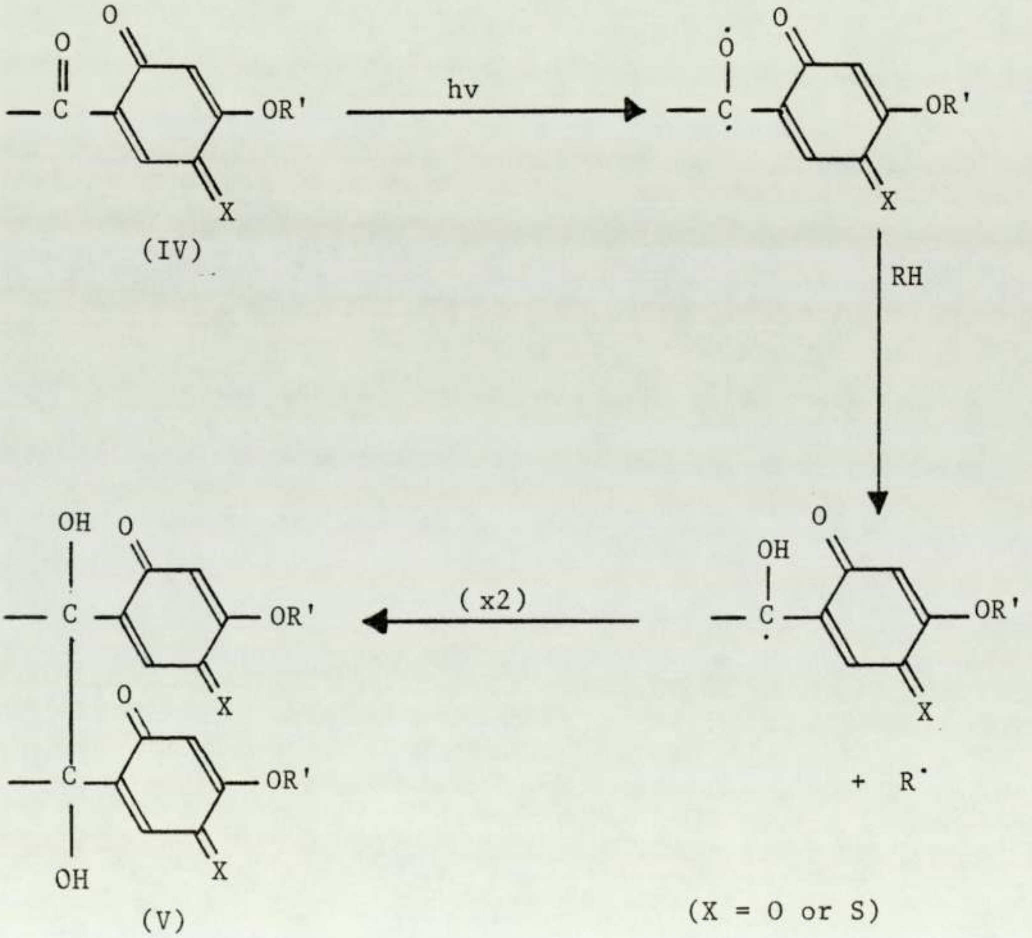


therefore be responsible for the observed lower photo-oxidative stability of the films, as compared to the mildly-processed analogues. Furthermore, the fact that this behaviour is much more pronounced in PP (Table 4.5 and Figure 4.9) than in LDPE (Table 4.8 and Figure 4.13) clearly confirms the view that the thermally formed hydroperoxides, and hence the oxidisable nature of the substrate, is crucial to the formation of the new product. However, the IR spectra of the concentrate films failed to reveal the presence of the quinonoid product since its absorption bands may be obscured by the strong characteristic absorption bands of HOBP with maximum at 1620 cm^{-1} (carbonyl) and 1570 cm^{-1} (skeletal ring vibration). Quinonoid compounds of the types shown in Scheme 5.7 are known(109a) to have carbonyl stretching vibrations within the same range as HOBP (1650 - 1550 cm^{-1}). Similarly, there is no direct IR evidence for the formation of the other by-product, the dialkyl hydrogen thiophosphate (Scheme 5.7), which is characterised(109b) by a P-H stretching vibration of medium intensity in the range 2460 - 2270 cm^{-1}. This again may be due to some interference from absorption bands of the polymer in the same region. Confirmation of the interaction between HOBP and the disulphide (DRDS) can, however, be deduced from the low frequency regions of the IR spectra of the concentrate films (See Figures 4.21c - 4.21d). HOBP exhibits two strong bands at 690 cm^{-1} and 620 cm^{-1} due to mono-substituted aromatic rings while the disulphide is characterised by both the P-O-(C) and P=S stretching vibrations at 730 cm and 645 cm^{-1} respectively (Figure 4.21c) within the same region. The most distinguishable feature of the [DnBDS:HOBP]concentrate films is provided in the 645 cm IR region which is associated with the P=S stretching vibrations, and it is distinctly shown (Figure 4.21d) that the intensity of this band is higher for the mildly-processed concentrates as compared to the severely-processed analogues at both additive ratios used [(2.5% + 2.5%) and (2.5% + 5%)]. This absorption band is clearly due to the P=S stretching vibrations of DnBDS which survived the processing operation, although it may also include absorption from the thiophosphoryl adducts of the type postulated in the reaction intermediate in Scheme 5.7 (III). This implies that severe processing (OM) results in a much higher consumption of DnBDS in the formation of the quinonoid product (IV) in view of an equally higher rate of destruction of HOBP by thermally formed hydroperoxides. It is also possible that the rate of fragmentation of the adduct intermediate (III) during processing is higher in the presence of excess oxygen (OM). A direct consequence of both reactions is the reduced intensity of the band due to P=S stretching vibrations (Figure 4.21d) in severely-processed concentrates and this, interestingly, is clearly associated with the higher concentration of the quinonoid product (IV) as is evidenced by the increased intensity of the 400 nm U.V. absorption band of these concentrates (Figures 4.21a-b). It is also clearly evident (Figure 4.21d) that the intensity of the P=S absorption band (645 cm^{-1}) after 3000 hours U.V. irradiation is proportionately higher for the mildly - processed concentrates and this is reflected on their higher photo-stabilising activity as compared to the severely processed analogues (see Table 4.5 and Figure 4.9).

The rapid disappearance of the 400 nm band during photo-oxidation (see Figures 4.22 - 4.23) can be explained in terms of the ability of the quinonoid species (IV) to abstract hydrogen from the polymer in a photo-sensitized reaction (Scheme 4.8).

The photo-sensitized reactions of quinones have been known[(104)] to involve their carbonyl groups and the ring double bonds, so the dimer product (V) shown in Scheme 4.8 is by no means the end product since further photo sensitized reactions could occur via the ring double bonds. Quinones have also been known to be very effective compounds for the photo-degradation of most poly-olefins by virtue of their photolytic instability . The polymer macro radicals resulting from these reactions will no doubt propagate the photo-oxidation process and this is reflected on the photo-oxidative behaviour of the synergistic DnBDS:HOBP concentrates. It is also shown (Figure 4.23) that the mere persistence of this quinone-type product in the concentrate film (400 nm band) is clearly associated with the reduced activity of the severely-processed concentrates in both PP and LDPE. It is also conceivable that the much higher proportion of this new product as obtained in PP, is responsible for the apparent loss in the expected photo-antioxidant synergism (see Table 4.5).

Scheme 4.8 Photosensitized reactions of product formed during processing of synergistic DnBDS:HOBP concentrates at 180°C



(X = O or S)
($R' = C_8H_{17}$)

4.3C.3 Spectral Features of Extracted Concentrate Films and Solvent Extracts

It is evident from the results that hot solvent extraction of the polymer films (PP and LDPE) containing DnBDS (Figure 4.24) and NiDnBP (Figure 4.25) effectively removes the various antioxidant species responsible for the IR spectral features of the stabilised films (see also Figure 4.26).

There seems little doubt that very similar products are formed under both mild and severe conditions since the thiol-phosphate esters are the predominant products in both cases with ^{31}P NMR chemical shifts of 98.8 ppm [$(RO)_2P(S)SSR$], 96.4 ppm [$(RO)_2P(S)SR$](98,105a,106), 94 ppm [$(RS)_3PS$](93,105a) and 53 ppm [$(RS)_2P(O)OR$](93,98,106). The assignment of the signal having a chemical shift of 96.4 ppm is confirmed by virtue of its identity with that of an authentic sample (see inset to Figure 4.26). A some what broad signal with a chemical shift of 63 ppm is also clearly evident in both extracts and this is assigned to thionophosphoric acid [$(RO)_2P(S)OH$], on the basis of its identity with that of an authentic sample (Section 5.3.4). The additional signals (85 ppm and 84.1 ppm) observed in the extract of the severely-processed concentrate are assigned to the disulphide (DnBDS) and the tetrasulphide (DnBTe) respectively, and this indicates that a fair amount of the original additive (DnBDS) still remains undecomposed at the end of processing or reformed by mutual combination of the thiyl radicals. This fact may also be responsible for the slightly higher proportion of oxidation products observed in the extract of the mildly-processed concentrate since no ^{31}P NMR signals due to either the disulphide or the tetrasulphide was observed in this extract. The mechanisms resulting in the formation of the various products observed in the extracts, have been clearly illustrated (Scheme 4.4) and also demonstrated in model compound studies (Section 5.3.1 - 5.3.3).

There is no doubt that the dithiophosphoryl moieties do graft unto the polymer backbone, in view of the various triesters observed in both the stabilised polymer films (Figures 4.17 - 4.18) and solvent extracts (Figure 4.26). However, the ease of extraction of these species suggests that the antioxidant moieties are only bound to low molecular weight macro alkyl radicals which are then readily extracted. Alternatively, the decrease in binding efficiency could possibly be due to the oxidation of the sulphur containing adducts which leads to heat or shear induced fragmentation of the antioxidant moieties from the polymer backbone (see also Scheme 4.4.).

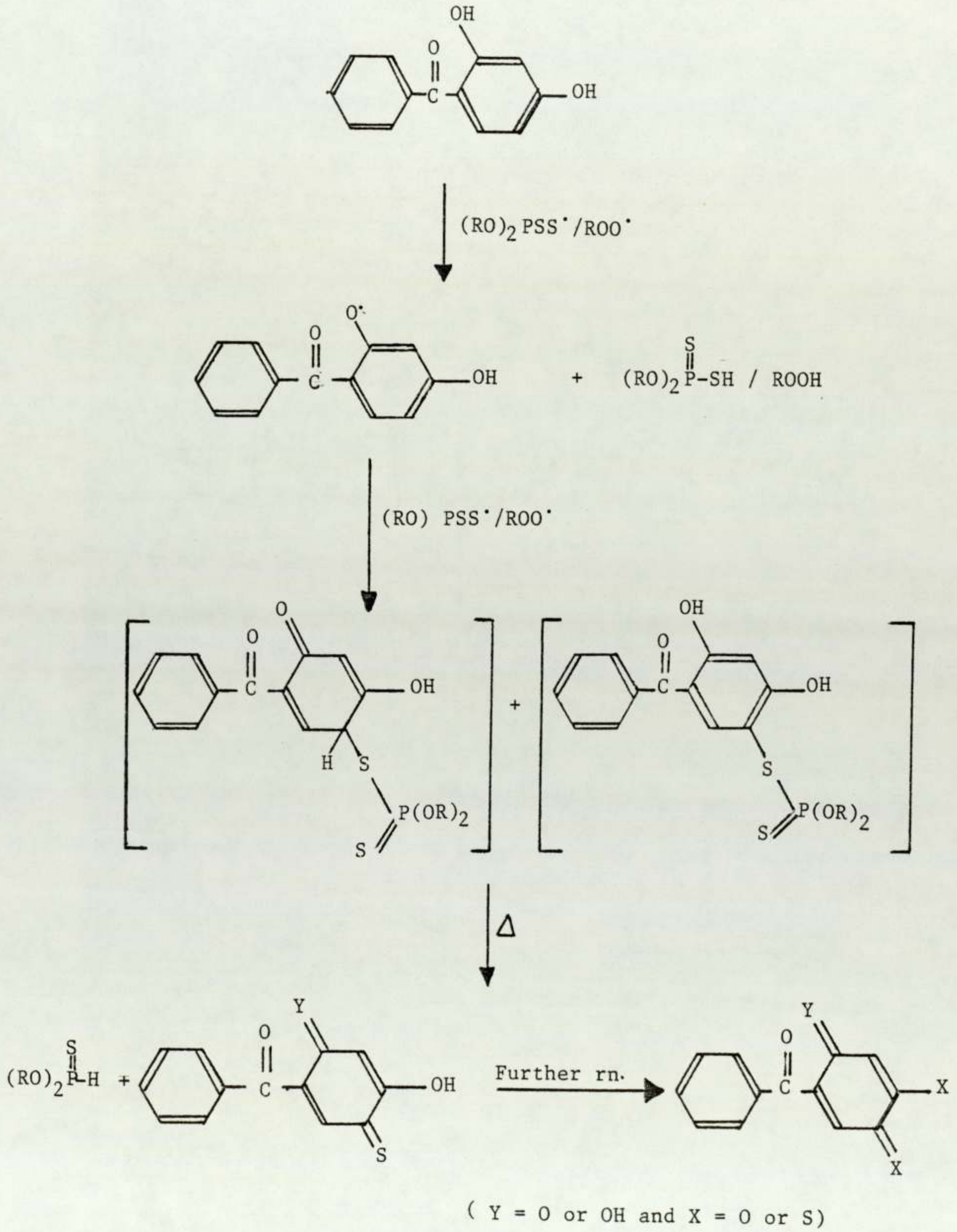
The U.V spectra of solvent extracts of DnBDS:HOBP concentrates and changes in the intensity of the 400 nm band following photolysis in the U.V cabinet (Figure 4.27

a - b), are strikingly similar to that reported for the stabilised polymer films (see Figure 4.22). An identical behaviour is also evident during photolysis of a methanol solution of a synthesised sample of bis-di-n-hexyl thiophosphoryl disulphide (DHDS) and 2,4-di-hydroxybenzophenone in the presence of air at 180 C ± 5°C(see Section 2.1.8). The product of this reaction, as postulated in Scheme 4.9 (Figure 4.20b), seems to be the same as that formed in the polymer (Scheme 4.7) in view of the similarity observed not only in their U.V.-spectral features, but also in their behaviour under photo-oxidative conditions (Figure 4.27 a - c).

By analogy with the behaviour observed in the polymer films (Section 4.3C.2), the rapid disappearance of the 400 nm band of both the solvent extracts and the synthesised product (see Scheme 4.9) during U.V. irradiation, can be explained in terms of the photo-sensitized reactions(104) of the species which may involve their carbonyl groups and the ring double bonds (see Scheme 4.8).

It can be seen (Figure 4.28a-b) that the photo oxidative instability of this specie, which is associated with the gradual disappearance of the original colour, contrasts with it stability under thermo-oxidative conditions. During thermolysis (105 °C) of both extracts and the synthesised product in toluene, there was neither any

Scheme 4.9 Product of the reaction of DHDS and 2,4 - dihydroxybenzephenone at 180°C



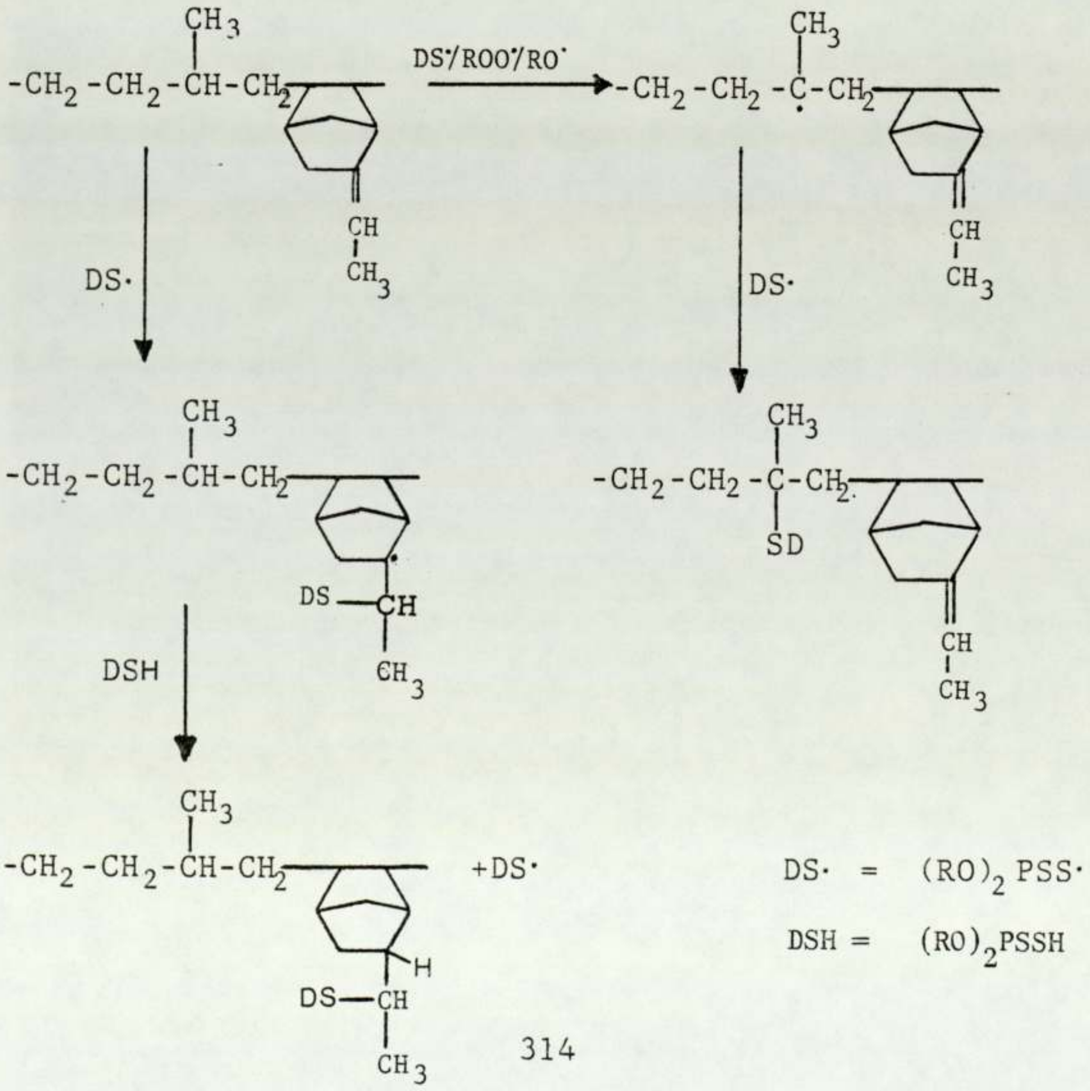
(Y = O or OH and X = O or S)

change in the colour of the compound nor in the intensity of the 400 nm band. The behaviour of this species under thermal conditions is not surprising since quinones are generally known (25,26,35) to be effective melt stabilisers in polyolefins. The same authors (25,26,35) have clearly established that several quinonoid products formed by oxidation of the hindered phenol (BHT) are much more effective than the hindered phenol itself as melt stabilisers in polypropylene, and their activity was postulated to involve the chain breaking antioxidant (CB-A) mechanism.

A close examination of an EPDM thin film containing a 2.5% DnBDS concentrate revealed (Figure 4.29) that the antioxidant adducts bound to the polymer backbone are highly resistant to extraction by organic solvents. The binding efficiency, as evaluated by the persistence of the P=S index (645 cm^{-1}) in the thin film, is seen to decrease with increasing extraction time until a limiting level is attained after 48 hours extraction. Further extraction of the same film showed no changes in the P=S index, indicating that some thiyl radicals $(RO)_2PSS$ or their oxidised forms $(RO)_2$ PSSO remain chemically bound to the polymer, even after exhaustive extraction. The improved binding efficiency observed in EPDM, as compared to PP and LDPE, is a direct consequence of the diene content in the terpolymer (2-methylene norborn -5-ene) which provides additional unsaturation in a side chain (107).

The amount of unsaturation in EPDM is therefore considerably higher (9%) than that present in either PP or LDPE (< 3%), hence more sites are available for subsequent adduct formation. During processing, the thiyl radicals (DS•) formed from the decomposition of the disulphide may then either add to the double bonds on the side chain or react with macro radical on the polymer backbone (Scheme 4.10).

Scheme 4.10 Mechanism of thiophosphoryl adduct formation in EPDM during processing under closed mixer at 60°C.



The addition of radicals of dialkyl dithiophosphoric acids $(RO)_2PSSH$ to strained cyclic olefins such as norbornene has been known to occur readily (100) in solution with the resultant formation of mainly thiolphosphate esters.

The persistence of these antioxidant adducts in EPDM after exhaustive extraction seems to suggest that apart from the beneficial effect of the additional site for grafting, other parameters such as processing temperature and processing procedure may have contributed to the improved binding efficiency. Thus, temperature induced fragmentation of the polymer backbone which may result in the formation of low moleculer weight thiolphosphate esters, is less likely to occur in EPDM (processed at 60°C), as compared to the higher processing temperatures of PP (180 °C) and LDPE (150°C). The higher binding efficiency of dithiophosphates in EPDM is therefore clearly due to the combined effects of the processing temperature, and higher amount and site of unsaturation. However, no attempt was made to optimise the conditions necessary for improved binding in EPDM in view of time limitations.

4.3D Dilute Concentrates (DCts)

4.3D.1 PP Dilute Concentrates (PP/DCts)

4.3D.1.1 Melt Stability During Processing

The excellent melt stabilising activity of the nickel dithiophosphates(NiDRP) and the corresponding disulphides (DRDS) at normal sample concentrations (< 0.4%) in PP has already been demonstrated (Section 3.3A.2.1), and it was clearly shown that their activity is quite comparable to that of well known commercial melt stabilisers such as hindered phenols. The thiophosphoryl dilute concentrates are shown in the present chapter to exhibit similar melt stabilising activity at concentrations 0.4%, for conventional MFI measurements (Figure 4.30a) and 0.6% for MFR measurements (Figure 4.30b).

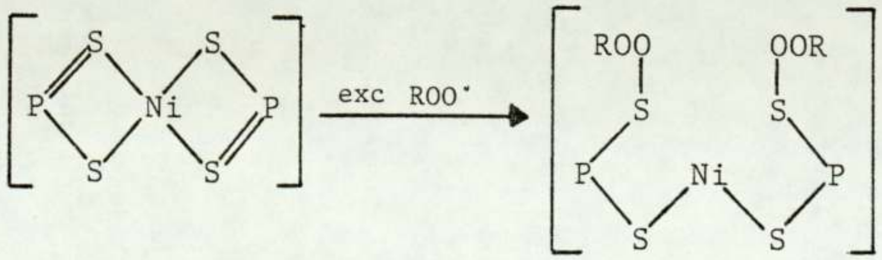
It is known(2,5a,27) that the effects of processing are evident in the changes in melt viscosity or melt flow index of polyolefins. Thus, the rapid increase in MFI is a direct consequence of the thermolysis of in-chain hydroperoxides which results in (C-C) bond scission to generate free radicals. These conditions are not only ideal for the operation of peroxidolytic activity (PD-C) but also for the chain breaking (CB-A/CB-D) mechanisms, and the ability of the dithiophosphates to function effectively under such conditions have been clearly illustrated (see Scheme. 3.3). This accounts for their effective melt stabilising activity since it can be seen (Figure. 4.30a) that the melt flow index of the thiophosphoryl DCts is not significantly affected by increasing extruder passes, as compared to other commercial melt stabilisers. More interesting still, is the fact that the incorporation of the U.V. absorber HOBP in the systems during concentrate preparation under oxidative conditions (OM/COM) known to be deleterious to HOBP(5a,19,27,47) does not detract from the melt stabilising ativity of the DCts.

The melt stability of some thiophosphoryl DCts derived from severely-processed concentrates (COM and COM/TBH) is also shown (Table 4.10 and Figure 4.30b) to compare quite favourably with other DCts derived from some commercial systems, at a total concentration of 0.6%. The estimation of melt stability in this instance(MFR), involves the use of a nominal force of 10 kg wt.(58b), as compared to the nominal force (2.16 kg.wt) generally used for conventional MFI measurements (Table 4.9). The results also clearly indicate (Table 4.10 and Figure 4.30b) that the best stabilising effectiveness is exhibited by the DCt (see Table 4.10; sample (6)) containing higher proportion of the nickel complex (NiDHP) relative to the disulphide (DHDS). The reason for this behaviour is not very clear, but may be as a result of the greater control exercised by the slightly higher amount of NiDHP (as compared to DHDS) in the release of the effective peroxidolytic antioxidants on successive extrusions. This is to be expected since the nickel complexes are known(5a,5b,18,19) to possess the ability to liberate the ionic catalysts for peroxide decomposition over a much longer period of time. Alternatively, the improved activity of this sample is most likely a direct consequence of the ability of the nickel complex (NiDHP) to scavenge alkyl peroxyl radicals (ROO$^{\cdot}$).

However, the thiophosphoryl dilute concentrates are shown (Figure 4.30a-b) to be marginally better than the well known commercially available melt stabilisers not only in the form of normal samples (NS), but also in the form of dilute concentrates (DCts).

4.3D.1.2 Thermal Antioxidant Activity

The beneficial effects of increasing the proportion of the nickel complex (NiDRP) in the DCt. at the expense of the other components (DRDS and HOBP), is strikingly evident under thermo-oxidative conditions in an air oven at 140 C. It is clearly shown (Table 4.11 and Figure 4.31) that increases in the proportion of NiDOP (R=octyl) in the dilute concentrates roughly parallels similar increases in the thermal stability of PP films containing the samples. The inability of the thiophosphoryl disulphides in protecting PP against thermal oxidation has previously been shown although the nickel complexes were found to be effective thermal stabilisers in PP (Section 3.3A.2.2). Since the U.V. absorber, HOBP is known to be ineffective as a thermal stabiliser in PP, it is therefore of interest to note that a synergistic mixture of the three components (DODS:HOBP:NiDOP) results in excellent thermal stabilising activity, provided the right proportions and ratio of the additives are used. It can be seen that the sample containing a higher proportion of the nickel complex (NiDOP) relative to DODS, affords a much better protection to PP, as compared to both the hindered phenol (IRG. 1076) and the nickel complex alone at the same total concentration as the DCt. The fact that the concentration of NiDOP in this dilute concentrate (0.23%) is only about half of that present in the NiDOP sample (0.4%), clearly suggests that the improved performance of the DCt cannot be accounted for by the activity of NiDOP alone. It may be argued that since the disulphide (DODS) is initially used to decompose the thermally formed hydroperoxide during concentrate processing, the sulphur acids (DRTA;R=Octyl) formed are therefore available for similar peroxidolytic activity during the dilution process, when the nickel complex is added. The sulphur acids produced in the initial operations are therefore used efficiently in prolonging the life time, and hence, the activity of NiDOP during subsequent thermal oxidative tests in the air oven. It is quite probable that the three major antioxidant mechanisms (PD-C, CB-A and CB-A) could be involved in the thermal stabilisation of PP with the dilute concentrates. Since the oxygen molecule is a powerful radical scavenger, it is expected to compete effectively with thiyl radicals (CB-A activity) for the alkyl radicals at ambient oxygen pressures (oven ageing). However, there is a higher probability of efficient collisions between the macro alkyl radicals and oxygen, as compared to the thiyl radicals and as a result of this, alkyl peroxyl radicals (ROO$^{\cdot}$) are formed predominantly. The presence of an effective CB-D antioxidant such as the sulphur acid, which is constantly been generated during both processing operations and on subsequent thermal oxidation of the DCt film, can therefore be put to beneficial use in terminating propagating species. The effectiveness of the sulphur metal complexes as thermal stabilisers is known to be due in part to their very rapid reaction with hydroperoxides(4a,5a,19,25,70) but a secondary function is their ability to trap allkyl peroxyl radicals(5a,25,28,39,70). This latter ability (reaction 4.7) may account for the much improved thermal antioxidant activity of DCts containing higher proportions of the nickel complex (NiDOP).



(4.7)

The thermal antioxidant activity of thiophosphoryl DCts is also clearly evident in PP plaques under thermal-oxidative conditions in a circulating air oven at 150°C. It can be seen that their activity is improved with increasing sample thickness, the only exception being the samples (plaques) containing little or no disulphide (i.e. samples 5 and 6 in Figure 4.32). The latter samples appear to be most effective at a nominal thickness of 1 mm while further increases in sample thickness only serves to reduce their thermal stabilising activity. The reason for the drastic loss in activity of these DCts in thick sections is not very clear, but may be a direct consequence of a slower rate of migration of the nickel complex (NiDRP) to the surface. It is widely assumed(34) that oxygen diffusion during oxidation is much more important for thick samples than for thin samples hence virtually all the oxidation will take place close to the surface. This therefore implies that only a small proportion of the uniformly dispersed stabiliser can be used effectively unless it is able to diffuse to the surface with reasonable speed. Since this behaviour is peculiar only to DCts containing little or no disulphide (Samples 5 and 6 in Figure 4.32), it can therefore be explained in terms of the reduced mobility of the nickel complex as compared to the corresponding disulphide. However, at a nominal thickness of 1 mm these samples become more effective than similar DCts containing higher amounts of the disulphide. The best thermal stabililsing activity is shown by the hindered phenol and this is clearly due to the fact that in thick sections and at high temperatures (during oven ageing), antioxidant loss by volatility becomes more important. It is therefore not surprising that the thermal antioxidant activity of the thiophosphoryl DCts ($R=C_4-C_6$) is only slightly inferior to that of the hindered phenol ($R = \dot{C}_{18}$).

Since ageing at elevated temperatures leads not only to changes in the morphology of the polymer as a result of physical ageing, but also to changes in the chemical composition of the sample, these usually result in development of colour within the sample. This is typically illustrated in plate 2 which depicts the chemical transformations taking place within the sample. It can be seen that such development of colour within the thiophosphoryl DCts, particularly with the sample containing no disulphide (i.e NiDnBP + HOBP), is clearly associated with the formation of the oxidation products from the nickel complex during thermal oxidation. Similar colour changes is also reported (Section 5.3.1) to occur during thermal oxidation of DnBDs in dichlorobenzene at 185°C in the presence of air. In this study, the changes in the original colour of the reaction mixture is attributed to the decomposition of the initially-formed reaction intermediates and a similar analogy can be drawn in this instance.

4.3D.1.3 Photo-stabilising Activity

Although the photo antioxidant activity of severely-processed 2.5% DnBDS concentrate was shown to be slightly inferior to the mildly - processed analogue (Section 4.3A.3), this was attributed to the presence of a much higher concentration of light unstable oxygenated intermediates in the former which may accelerate the photo-oxidation process. On subsequent dilution, however the dilute concentrates (0.2%) derived from the severely-processed concentrate is shown to possess a higher photo antioxidant activity as compared to that derived from the mildly processed analogue (Table 4.12). A probable reason for this behaviour may be the presence of a much lower concentration of the light sensitive reaction intermediates in the dilute concentrates, as compared to the concentrates. It has been shown that increasing oxidation not only leads to greater amount of sulphur acids which are catalysts for hydroperoxide decomposition (Section 5.3.1 - 5.3.3), but also to an equally greater amount of the light sensitive intermediates which must precede the formation of the former. It appears, therefore, that the peroxidolytic activity of the sulphur acids supersedes any photo-sensitized reaction of the light unstable intermediates since only small amounts of both species are present in the dilute concentrates. The observation that the dilute concentrate of the synthesised sulphur acid (DnBTA) shows similar photo antioxidant activity as the disulphide derived dilute concentrates (CM/OM), clearly confirms the view that the inhibitory role of the disulphides during auto-oxidation cannot be attributed to the disulphides themselves but rather to their oxidation products, notably the sulphur acids(22,27,85,86,94-96). Furthermore, it has previously been confirmed (Section 3.3.1 and 4.3A.4) that oxidative processing of DnBDS in the presence of a hydroperoxide (TBH) leads to improved photo-antioxidant activity provided specific ratios are adhered to.

Similarly, it is clearly shown (Figure 4.33) that the dilution of the severely-processed DnBDS concentrate (0.1%) in the presence of HOBP (0.2%) and NiDnBP (0.1%) also results in a much better photo-stabilising activity as compared to an identical sample derived from the mildly-processed DnBDS concentrate. The photo antioxidant activity of the sample prepared from the severely-processed concentrate is further improved as the proportion of the nickel complex in the sample is increased, while maintaining the same level of concentration in the DCt (0.4%). Since increases in the proportion of NiDnBP in the sample is allied to corresponding reduction in the amounts of DnBDS and HOBP, it therefore follows that the photoantioxidant activity of these synergistic systems (DCt's) can be optimised by adjusting the ratio of the components appropriately. This behaviour is also clearly evident in dilute concentrates prepared from dithiophosphates with higher alkyl substituents such as octyl. Thus, increase in the concentration of NiDOP with concomitant reduction in the amount of DODS and HOBP, markedly improves the photo-stabilising activity of the dilute concentrate (Figure 4.34) and a similar effect has also been clearly demonstrated under thermo-oxidative conditions (see Table 4.11 and Figure 4.31). Furthermore, it can be seen (Figure 4.33) that the dilution of the sulphur acid (DnBTA) concentrate in the presence of HOBP and NiDnBP, results in a much better photo-stabilising activity as compared to DCt's derived from the disulphide. This implies that the sulphur acid may be actively involved in protecting the other components from destruction by hydroperoxides during processing and on subsequent U.V. irradiation since it is continuously being generated via the decomposition of the nickel complex. The extensive photo oxidative induction period is therefore not only due to the peroxidolytic activity of the sulphur acids, but also due in part to the role of HOBP in protecting the antioxidants (DnBTA and NiDnBP) from photolysis by screening of U.V. light and probably by quenching of photo-excited states of the dithiophosphates, as was previously suggested for dithiocarbamates(5b,18,23b,40b).

It was previously shown (Section 4.3A.5) that the loss in photo antioxidant synergism between DnBDS and HOBP in concentrate forms is due to a combination of factors, the most important of which are the blooming phenomenon and the probable formation of a light sensitive quinonide type product (See Section 4.3C.1 - 4.3C.2) during processing. The latter effect was also shown to be a direct consequence of the oxidisability of the polymer (PP). However, it can be seen (Table 4.13) that subsequent dilution of the concentrates to lower concentrations (0.6%) practically restores the photo antioxidant synergism between the additives, although the overall photo antioxidant activity of the DCts is roughly consistent with the behaviour observed for the original concentrates (Table 4.5), with respect to the effects of the processing condition of the original concentrates. It is also clearly shown (Table 4.13 and Figure 4.35) that the DCts derived from TBH assisted oxidatively-processed concentrates imparts greater photo-stability to the polymer as compared to similar DCts derived from the mildly-processed (CM) and the air— assisted oxidatively processed (OM) concentrates. In view of the excellent photo antioxidant synergism exhibited by these dilute concentrates (DnBDS+HOBP), it is fairly reasonable to assume that the addition of small concentrations of the nickel complex to the DCts during dilution, would result in exceptionally high photo-antioxidant activity. More interesting still, is the fact that the DCts derived from concentrates containing a 2-fold excess of HOBP (DnBDs:HOBP ratio, 1:2) show almost similar U.V. activity as compared to the original concentrates. This is clearly an arguement in favour of the reported detrimental effects of both the blooming phenomenon and the relatively high amount of the light sensitive quinonide type product as observed in the concentrates. The restoration of photo antioxidant synergism in the DCts, is therefore attributed to the negligible effect of those factors responsible for the poor photo-antioxidant activity of the concentrates.

The superiority of the thiophosphoryl dilute concentrates over most commercial systems during photo-oxidation of PP plaques is clearly illustrated in Table 4.14. The most important observation deduced from this study is the fact that the photo-oxidation process leads to changes in the morphology of the polymer, as reflected by the formation of surface crazing on exposed faces of the plaques. Clearly this is indicative of chain scission within the polymer matrix since it is shown that formation of surface crazing generally precedes actual physical embrittlement of the plaques (Table 4.14). It has previously been reported(5b) that surface crazes and crack initiation, which eventually leads to failure of polymer artefacts, are a manifestation of the amorphous phase following chain scission under prolonged oxidative exposure. The photo-antioxidant activity of all the thiophosphoryl DCts is shown to be much better than similar synergised commercial systems in the form of DCts and this is seen to be the case for both thick and thin samples with respect to the U.V. irradiation times required for onset of surface crazing and actual physical embrittlement. However, it is worth emphasising that the best photo-stabilising activity is shown by the DCt containing a higher proportion of the nickel complex relative to the disulphide. This does not necessarily imply that the total exclusion of the disulphide in the DCt shall result in better photo-stabilising activity, because it is clearly shown (Table 4.14) that a DCt containing all three components (DnBDS+HOBP+NiDnBP) exhibits better U.V. activity as compared to the DCt containing only the nickel complex and the U.V.absorber (cf sample numbers (4) and (5) in Table 4.14). Moreover, it has clearly been shown in this chapter that increases in the proportion of the nickel complex, with concomitant reduction in the amounts of both the disulphide and the U.V. absorber, results in the formulation of a DCt with high antioxidant activity not only under photo-oxidative conditions, but also under both melt (4.3D.1.1) and thermal oxidative (4.3D.1.2) conditions.

4.3D.2 LDPE Dilute Concentrates

4.3D.2.1 Photo-stabilising Activity (of DCts) in Compression Moulded Films

The beneficial effects of oxidative processing of thiophosphoryl disulphides (DRDS) on their photo antioxidant activity in LDPE has been demonstrated for both the 'normal samples' (Section 3.3B.1) and additive concentrates (Section 4.3B.1). In the present chapter, the 0.2% DnBDS dilute concentrates are also shown (Figure 4.36) to be more effective when the original concentrate is severely-processed (OM) compared to the mildly-processed (OM) analogue. There seems no doubt that the improved activity of the severely-processed derived DCt over that of the mildly-processed analogue, is due to a higher rate of conversion of the disulphide to the sulphur acids (DnBTA). The same effect is also clearly evident in synergistic dilute concentrates containing DnBDS and HOBP (2-fold excess of HOBP) at a total concentration of 0.3%, since it can be seen that the activity of the synergistic system is augmented by oxidative processing (OM) of the original concentrate. In this instance, it appears that during oxidative processing of the original concentrate the greater amounts of the active species formed from the disulphide are able to afford greater protection to HOBP, by preferentially destroying hydroperoxides during the dilution operation and on subsequent photo-oxidation. Thus, the U.V. absorber is then able to exert its effect during photo-oxidation by protecting the antioxidants from photolysis. Such complementary mechanisms have been widely known(5b,18,40b) to account for the excellent photo antioxidant synergism between peroxide decomposers and U.V. absorbers. The addition of only a small amount

(0.1%) of the nickel complex to the 0.3% dilute concentrate (during dilution) is shown (Figure 4.36) to synergise the system effectively and this behaviour is more pronounced when the original DnBDS:HOBP concentrate is processed under very extreme oxidative conditions (OM 30). Although oxidative processing of the nickel complex in PP have been shown to be detrimental to its photo antioxidant activity (Section 3.3.1), it has also been suggested that its activity in LDPE may be enhanced by some oxygen availability during processing since this polymer is intrinsically more stable compared to the former (Section 3.3B.1). The present results therefore represent a very good arguement in favour of the view that controlled oxidative processing of the nickel dithiophosphates in LDPE may lead to exceptional photo antioxidant activity.

It is known(33) that the photo-oxidation of polyolefin films leads to a comparatively rapid deterioration of the mechanical properties, and it has also been reported(5b) that the severity of the processing method has a direct effect on these changes. As can be seen from Figure 4.37, the rapid loss in the relative elongation of the unstabilised LDPE film roughly parallels the increase in the concentration of carbonyl species in the sample. This is clearly a manifestation of chain scission of the polymer backbone by Norrish I and II processes. By comparison, the 0.4% DnBDS dilute concentrates substantially increases the life times of LDPE films, as distinctly shown in figure 4.37. It can be seen that the retarded loss in relative elongation of the DCt films is a clear reflection of the auto-retarted photo-oxidative behaviour exhibited by these samples, this being more pronounced with the sample derived from the severely processed concentrate. Furthermore, the rate of formation of unsaturation in the samples during the latter stages of photo-oxidation (inset to Figure 4.37) roughly coincides with their respective photo-oxidative behaviour since it is seen that a lower rate is shown by the dilute concentrates despite the fact that the initial level of unsaturation in the unexposed films is higher than that present in the unstabilised LDPE films. Since the rapid rate of formation of unsaturation during the latter stages of photo-oxidation appears to be directly associated with an equally rapid decline in the relative elongation of the samples, there seems little doubt therefore that this is a direct consequence of the Norrish II process(2,5b,6,18). Thus, the better performance of the dilute concentrate derived from the severely-processed DnBDS concentrate is a striking example of the advantages of oxidative processing of the thiophosphoryl disulphides.

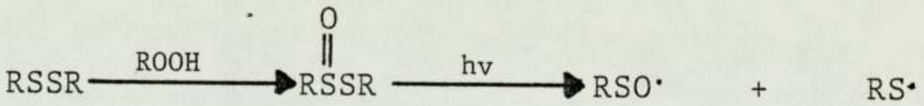
4.3D.2.2 Photo-stabilising Activity (of DCts) in Flat Tubular (Blown) Films

The beneficial effects of controlled oxidative processing of thiophosphoryl concentrates in LDPE is distinctly reflected on the photo-stabilising activity of the DCts fabricated in the form of flat tubular films. It is clearly shown (Table 4.15 and Figure 4.38) that the photo oxidative behaviour of the thiophosphoryl DCts is characterised by very extensive auto-retarded oxidation compared to the commercial controls. As indicated in the previous section (Section 4.3D.2.1), the changes observed in the mechanical properties of polyolefin films is directly associated with their photo-oxidative behaviour. This is seem to be the case with all the samples under examination since it is clearly shown that the photo-oxidative behaviour of these films (Figure 4.38) is manifested on the changes observed in their mechanical properties (Figures 4.39-4.40) during U.V. irradiation. These results clearly indicate that the oxidatively-processed dilute concentrates are definitely superior to the commercial controls with respect to the loss in both the tensile strength and the flexibility (elongation) of the films during photo-oxidation. For instance, a 50% loss in the flexibility of the Dct samples can be delayed for a much longer period as compared to the commercial systems (see Figure 4.41).

Furthermore, it is apparent (Table 4.16) that the time (hours) to a 50% loss in the flexibility of the stabilised films is attained at relatively low carbonyl index values (< 2). This illustrates the importance of measuring the mechanical properties of the films during photo-oxidation, instead of relying solely on carbonyl index measurements. This criterion (T.50) clearly represents a more reliable means of evaluating polymer artefacts which may be used in applications where durability is very important.

4.4. Conclusions

The photo-antioxidant activity of concentrates of thiophosphoryl disulphides (DRDS) in PP have been shown to be highly dependent on a number of factors, the most important of which are the concentration of unsaturation and hydroperoxides present in the film, this being in turn dependent on the previous thermal history of the concentrate. Thus oxidative processing (OM) is clearly detrimental to the photo-antioxidant activity of DRDS concentrates as compared to the mildly-processed (CM) analogues, and this has been attributed to the lower levels of unsaturation and higher levels of hydroperoxides present in the former (severely-processed concentrates). Consequently, a greater number of termination reactions occur during mild processing (CM) while severe processing (OM) leads to greater amounts of oxidation products including the sulphur acids which are catalysts for hydroperoxides decomposition. However, activity of the sulphur acids may be of little technological importance in this instance since the intermediate sulphoxides present at the film surface may dissociate under photolysis to give free radicals and thus propagate the photo-oxidation process as illustrated for a simple alkyl disulphide (reaction 4.8).



$$\mathrm{RSSR} \xrightarrow{\mathrm{ROOH}} \mathrm{R}\overset{\mathrm{O}}{\overset{\|}{\mathrm{S}}}\mathrm{SR} \xrightarrow{h\nu} \mathrm{RSO}^{\cdot} + \mathrm{RS}^{\cdot} \qquad (4.8)$$

In contrast to PP, severe processing (OM) of DRDS concentrates results in a higher level of photo-stabilising activity in LDPE. This is believed to be a reflection of the relative ease of oxidation of PP compared with LDPE, which is known to give relatively higher concentration of hydroperoxides in the more oxidisable polymer (PP). The principle of a hydroperoxides — assisted controlled oxidation of DRDS concentrates during processing have therefore been used to develope U.V. stabilising systems of very high activity in PP. Furthermore, it has been clearly established that the impurities present in most DRDS samples has no adverse effect on their photo antioxidant activity. On the contrary, a critical impurity level appears to enhance the photo-stabilising activity of the disulphide, and this is attributed to the fact that these impurities which mainly constitute the thiolphosphate esters do possess antioxidants properties in their own right. Thus, they are able to complement the activity of the disulphide and therefore extend the service life of the polymer.

Similarly, the photo antioxidant synergism between the disulphide and the U.V. absorber HOBP in concentrate films has been shown to be dependent not only on the severity of the processing condition, but also more importantly, on the oxidisability of the polymer. It was clearly established that severe processing (OM) of these concentrates in PP results in lower photo-stabilising activity as compared to the mildly-processed (CM) analogue and this is believed to be due to the subsequent photo-sensitized reactions of certain quinonoid products formed during processing of the concentrates (DRDS+HOBP). The poor photo-stabilising activity of the severely-processed concentrates is clearly due to the presence of a significantly higher concentration of the quinonoid products, and their activity during photo-oxidation is also believed to be responsible for the total loss in photo-antioxidant synergism between both components in PP. In LDPE, however, the concentration of these products is almost negligible since this polymer is intrinsically much less oxidisable compared to PP. Thus, processing of DRDS:HOBP concentrates in LDPE results in a high level of photo — antioxidant synergism and the activity of this system is powerfully augmented by oxidative processing. The exceptionally high level of synergism that can be achieved with concentrates of the nickel complex (NiDRP) and HOBP was also clearly demonstrated in LDPE.

Although there was no direct evidence of binding during processing of dithiophosphates, a ^{31}P NMR analysis of solvent extracts of DRDS concentrates indicates that the thiolphosphate esters are predominantly formed during processing while the sulphur acids account for only a small proportion of the products. This implies that the mechano chemical grafting of thiophosphoryl moieties unto the polymer backbone occurs only with low molecular weight macro alkyl radicals to form thiolphosphate esters, which are then readily removed from the matrix by solvent extraction.

The photo — antioxidant activity of DRDS dilute concentrates was shown to be higher in both PP and LDPE when the original concentrate is oxidatively-processed as compared to mild processing. In PP the improved performance of dilute concentrate analogue of the severely-processed DnBDS concenterate is believed to be due to presence of a significantly lower concentration of the light unstable intermediates. The peroxidolytic activity of the sulphur acids therefore supersedes any photo-sensitized reactions of these unstable intermediates during photo-oxidation. However, the dilution of the DnBDS:HOBP concentrates in PP results in the restoration of the photo antioxidant synergism although the activity of the DCt derived from severely-processed concentrate still remains inferior to that of the mildly-processed analogue, this being consistent with the photo-oxidative behaviour of the original concentrates. The addition of small concentrations of the nickel complex during dilution of oxidatively-processed DRDS/HOBP concentrate was found to synergise the system effectively. An important feature of this system is that, in addition to its excellent photo and thermal antioxidant activity, it also stabilises the polymer in the melt (during processing) and it has been clearly established that the activity of the dilute concentrates under these conditions is markely improved in samples containing a higher proportion of the nickel complex (NiDRP) relative to that of DRDS and HOBP. Furthermore, the photo antioxidant activity of a dilute concentrate of the sulphur acid (DnBTA) was shown to be as effective as that derived from the disulphide and this clearly identifies this acidic product (and other related products) as the primary species responsible for the long term oxidative stability of hydrocarbon polymers containing them. This is supported by the fact that this oxidation product (DnBTA) shows exceptionally high level of synergism with HOBP and NiDRP, even more so than that shown by synergistic systems containing the disulphide. In LDPE on the other hand, the beneficial effects of oxidative processing of the original concentrates is distinctly reflected on the photo-oxidative behaviour of the dilute derivatives in all respects. Thus, the photo antioxidant activity of all thiophosphoryl dilute concentrates (single or multicomponent) is powerfully augmented by oxidative processing. Finally, the importance of monitoring changes in the mechanical properties of the polymer films during oxidation process has been clearly established.

The chemistry of the antioxidant mode of activity of the dithiophosphates have been fully described in this chapter; and the products formed during processing have also clearly been shown to be similar to those identified during model compound studies in pure organic solvents (see Sections 5.3.1 - 5.3.4). Besides the fully protonic sulphur acids which are primarily responsible for the effective non-radical decomposition of hydroperoxides, the intermediate thiyl radicals formed from the decomposition of the disulphide also appear to play a part in trapping of macro alkyl radicals (see Schemes 4.3 and 4.6). Since these species are partially formed during polymer processing in the presence of a trace amount of oxygen, the primary function of the nickel complexes therefore remains that of the light stable reserviour for oxidatively derived antioxidants(5a,5b,19,25,27,39,70,86) in addition to its abililty is scavenge alkyl peroxyl radicals ($ROO^{\cdot}$).

CHAPTER FIVE

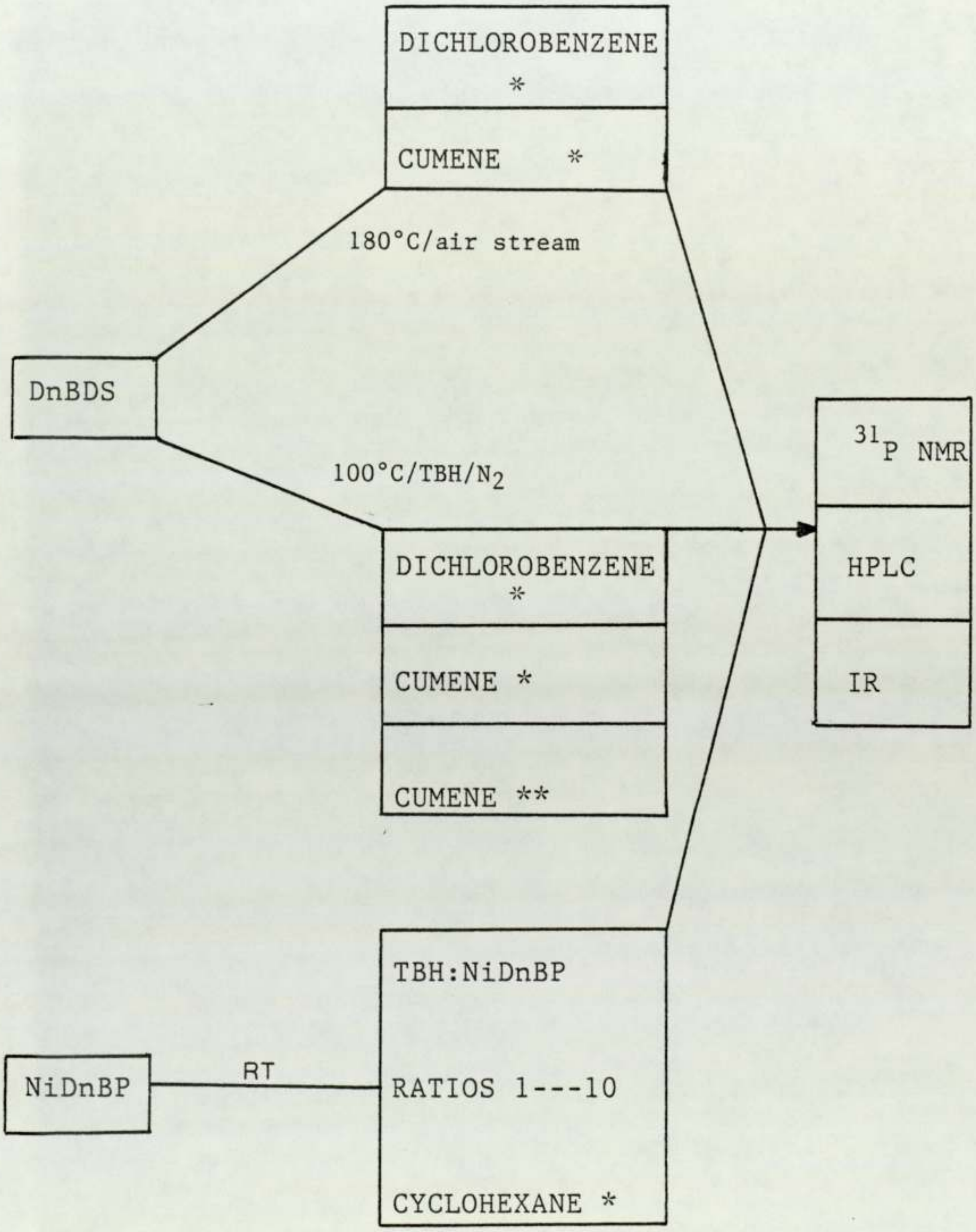
THERMAL OXIDATIVE REACTIONS OF DITHIOPHOSPHATES

5.1 Object

The mechanism involved in the antioxidant activity of dithiophosphates have been well documented(5a,13,45,68b) in which a number of suggestions were made as to the identify and origin of the reaction intermediates. Although there is a fair amount of agreement with respect to the nature of the transformation products and reaction pathways involved, areas of some controversy still exist. This may be accounted for by the differences in the experimental conditions and techniques employed by the various workers. For instance, the thermal and oxidative decomposition intermediate and/or products of these compounds have been analysed by methods such as chromatography,(90,111) IR spectroscopy,(90) mass spectroscopy(110) and ^{31}P NMR(105a,106). In each of these studies, which covers a wide range of experimental conditions, product analysis has shown that the oxidation of dithiophosphates results largely in the formation of various triesters and sulphur acids amongst others. In some cases, positive identification was accomplished by synthesis of the appropriate standards.

The object of the work described in this chapter is to obtain a better understanding of the mode of antioxidant action of the dithiophosphates, by studying the reaction intermediates and products obtained from a series of experiments carried out in pure organic solvents. The experiments are designed to represent a model system which could be directly related to the conditions employed during processing of these materials in polyolefins, with particular reference to oxidative processing procedures (see Chapter 2, Section 2.3.). The oxidation of the nickel complex by tert-butyl hydroperoxide was carried out in cyclohexane at room temperature, while that of the corresponding disulphide, bis-di-n-butyl thiophosphoryl disulphide at different temperatures (100°C-185°C), was carried out in both an oxidisable (cumene) and non-oxidisable (para-dichlorobenzene) substrates in the presence of air and/or tert-butyl hydroperoxide. Scheme 5. outlines a simple schematic representation of these oxidation studies. (for experimental details see Chapter 2 Section 2.6.3) Product analysis was carried out by ^{31}P NMR (Chapter 2 Section 2.5.3), HPLC (Chapter 2 Section 2.5.4) and IR (Chapter 2 Section 2.5.1). However, it is important to emphasise the fact that the oxidation studies on the thiophosphoryl disulphide (DnBDS) were carried out on a sample synthesised via KI/I_2 method (96% pure) although the purity was seen to decrease with storage time (see tables 5.1, 5.4, 5.6 and 5.8).

Scheme 5. DnBDS/NiDnBP Oxidation Studies



* substrate

** insitu ^{31}P NMR experiment

5.2 Results

5.2.1 Thermal Oxidation of DnBDS in the Presence of Air

5.2.1(a) Dichlorobenzene as Substrate

Products formed during thermal oxidation (185 °C, air stream) of DnBDS, as measured by ^{31}P NMR are shown in Table 5.1 and the peak assignments are given in Table 5.2. Figures 5.1 - 5.3 also show the ^{31}P NMR, HPLC and IR spectral changes occuring during the above thermal oxidation studies. Furthermore, changes in the relative abundance are quantitatively presented in Figures 5.4 (^{31}P NMR) and 5.5 (HPLC). It is clear that the phosphorus-containing species formed throughout the reaction have chemical shifts at low and high field when compared to the starting material, DnBDS (see Fig. 5.1). This is indicative of both highly sulphurated (high field) and equally highly oxygenated (low field) species (see Tables 5.1 - 5.2). The primary reaction intermediates however, were identified as the trisulphide with a chemical shift of 83.9ppm and a triester with chemical shift of 54ppm (see Tables 5.1 - 5.2 and Figures 5.1 and 5.4). HPLC analysis of the same reaction mixtures also provided further evidence as to the identify of these primary reaction intermediates (see Table 5.3, Figures 5.2 and 5.5), and the identification of some of the products was further supported by synthesising the authentic samples. Table 5.3 which shows the distribution of various sulphides of dithiophosphoric acid formed during the oxidation of DnBDS, also includes data for an unidentified specie which elutes well before the sulphides (see Figure 5.2). The exact identity of this specie (R=2.1) amongst others all of which elute before the sulphides (retention times 2 min. - 8 min.), is not very clear at the present time. However, these HPLC signals with retention times between 2 minutes and 8 minutes (Figure 5.2) may, by analogy with the ^{31}P NMR results (Table 5.1 - 5.2 and Figure 5.1), be due to various triesters. This is confirmed by the HPLC analysis of a synthesised triester, and it can be seen (inset to Figure 5.2a)that this sample elutes well before the disulphide. Although retention times (RT) are not reproducible over a period of time, the elution time for this sample is roughly equivalent to 6-8 minutes on the original chromatograms (Figure 5.2b).

Table 5.1 Product distribution of DnBDS thermal oxidation at 185°C in dichlorobenzene in the presence of a steady stream of air

Reaction Time (min)	Product % yield (δ values= ^{31}P chemical shifts in ppm)*																
	δ 139	123	112	102	96	94	91	85.1	83.9	79	74	67	58.9	54	36.5	31	19	7
0	0	0	0	0	0	0	0	95.5	0	3.9	0.6	0	0	0	0	0	0	0
60	0	0	0	0	0	0	0	95.1	0	4.1	0.5	0.3	0	0	0	0	0	0
120	0	0	0	0	1.0	0	0.3	83.3	6.5	5.1	0.5	0.95	0	1.8	0	0	0	0
180	0	0	0	0	4.4	0	0.96	53.3	20.8	7.7	2.8	1.3	0	8.0	0	0	0	0
240	0	0	0	0	6.1	0	0.6	38.2	28.1	7.7	4.1	0.82	0	12.2	1.4	0	0	0
300	0	0	2.5	0	9.4	0	1.7	15.4	32.8	6.9	3.7	0.81	0	21.6	4.5	0	0	0
360	9.2	2.8	14.7	3.2	8.1	4.4	1.0	5.5	7.1	1.4	1.7	1.6	0.7	21.4	6.1	0.8	5.3	5.1

*All Signals are referenced to 85% H_3PO_4 external standard

Table 5.2 Assignments to peaks shown in Table 5.1

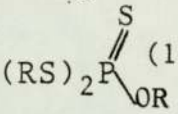
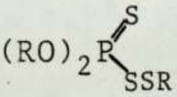
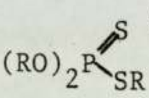
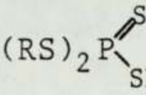
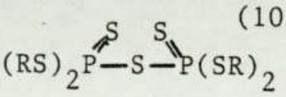
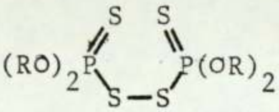
Chemical Shifts(ppm)	Assignments	Comments: %Yield at End of Reaction (6 hours)
139	$(RO)_3\ P:$ (119)	Trivalent phosphorus species. Only formed at the end of reaction 9.2%
123	$(RS)_3\ P:$ (105a,119)	Ditto - 2.8%
112	 $(RS)_2P(=S)OR$ (105a)	Only formed in the later stages (5h) and showed considerable increase in yield at the end of reaction. 14.7%
102	 $(RO)_2P(=S)SSR$	Only formed at the end of the reaction. 3.2%
96	 $(RO)_2P(=S)SR$ (105a,106)	Formed in the early stages (2h) and builds up with time before showing signs of decay. 8.1%
94	 $(RS)_2P(=S)SR$ (105a,119)	Only formed at the end of the reaction. 4.4%
91	 $(RS)_2P(=S){-}S{-}P(=S)(SR)_2$ (105a)	Formed in the early stages (2h) and builds up slowly with time before showing signs of decay 1.0%
* 85.1	 $(RO)_2P(=S){-}S{-}S{-}P(=S)(OR)_2$ [DnBDS]	Decreased in yield after initial induction period 5.5%

Table 5.2 (continued)

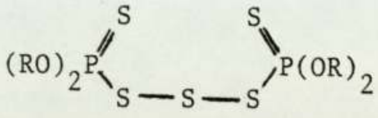
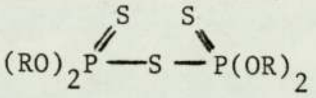
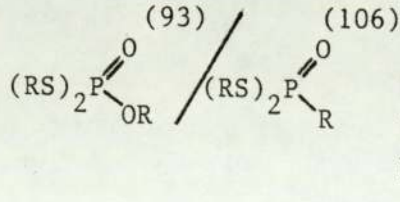
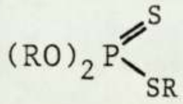
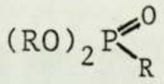
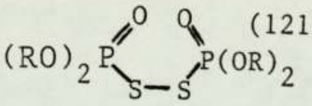
Chemical Shifts(ppm)	Assignments	Comments: %Yield at End of Reaction (6 hours)
* 83.9	 [DnBTr]	Formed in the initial stages (1h). Continued to build up at a very fast rate before decaying. 7.1%
* 79		Present in original material as impurity. Builds up slowly and then shows signs of decay. 1.4%
74	$(RO)_3P = S^{(106,120)}$ $(C_6H_5)Cl_2PS^{(119)}$	Impurity in original material. Builds up slowly after initial induction period before showing signs of decay. 1.7%
67	$(RS)_3P = O^{(106)}$	Formed in the initial stages (1h) and builds up slowly. Remained at very low level throughout reaction. 1.6%
58.9	?	Of uncertain origin-partially oxygenated & only formed at the end of reaction. 0.7%
54		Formed in the early stages and builds up at a very fast rate throughout reaction. Major product at end of reaction. 21.4%

Table 5.2 (continued)

Chemical Shifts(ppm)	Assignments	Comments: %Yield at End of Reaction (6 hours)
36.5	 $(RO)_2P(=S)SR$ $(C_6H_5)Cl_2PO$ (119)	Formed in the later stages (4h)and continues to build up 6.1%
31	 $(RO)_2P(=O)R$ (119)	Only formed at the end of reaction. 0.8%
19	 $(RO)_2P(=O)\text{–}S\text{–}S\text{–}P(=O)(OR)_2$ (121)	Ditto - 5.3%
7	$[(RO)_3P]_2O$ (93) pyrophosphates	Ditto - 5.1%

* Assigned on the basis of its identity with that of an authentic specimen.

Table 5.3 Distribution of primary reaction intermediates formed during the oxidation of DnBDS in dichlorobenzene at 185°C in the presence of air (RT refers to HPLC retention times in minutes)

Reaction time (min.)	Product % yield (based on normalization of peak areas to 100%)				
	$(RS)_2P(O)OR$	$[(RO)_2PS]_2S$	$[(RO)_2PSS]_2$	$[(RO)_2PSS]_2S$	$[(RO)_2PSS]_2S_2$
	RT=2.1	RT=8.5	RT=10.2	RT=11.2	RT=12.9
0	2.6	5.3	88.1	4.0	trace
60	4.0	5.3	76.4	14.4	1.0
120	5.6	5.6	63.8	22.6	2.4
180	16.2	5.1	33.9	34.8	9.8
240	17.0	8.2	20.7	36.9	17.5
300	33.6	8.4	11.8	32.2	14.1
360	>10	<5	<10	<10	<5

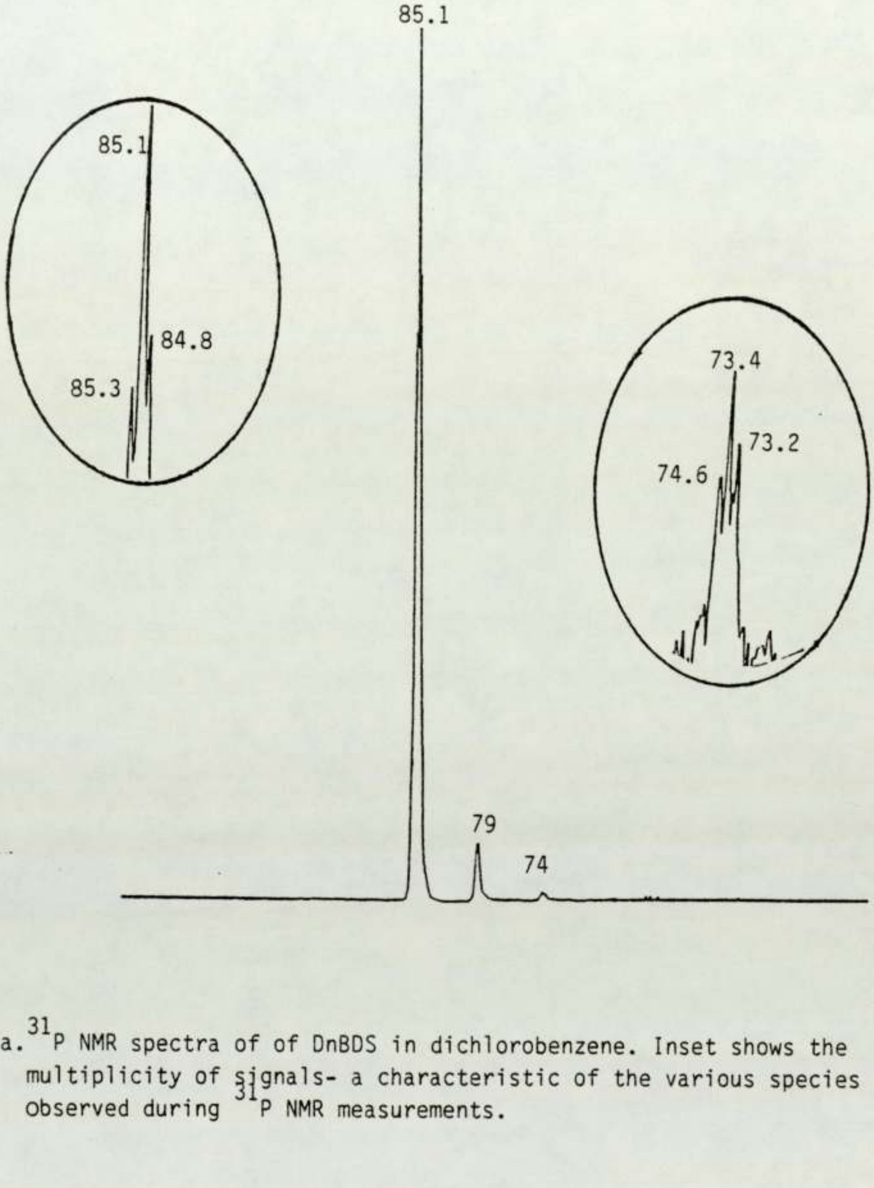


Figure. 5.1a. ^{31}P NMR spectra of of DnBDS in dichlorobenzene. Inset shows the multiplicity of signals- a characteristic of the various species Observed during ^{31}P NMR measurements.

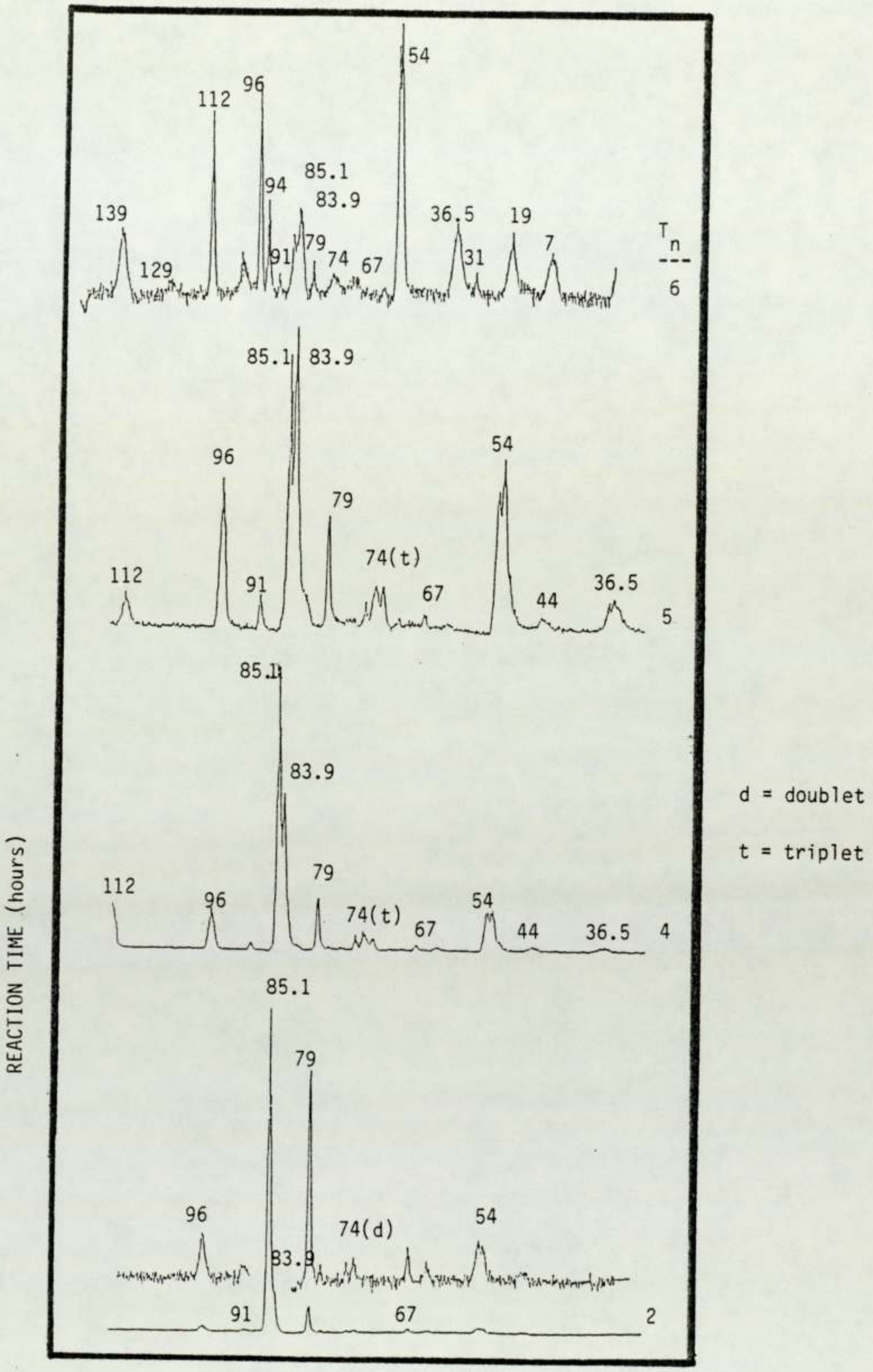


Figure 5.1b ^{31}P NMR spectra of the thermal-oxidation of DnBDS in dichlorobenzene at 185°C in the presence of air stream. Numbers on signals are chemical shifts in ppm. and Tn is reaction time in hours

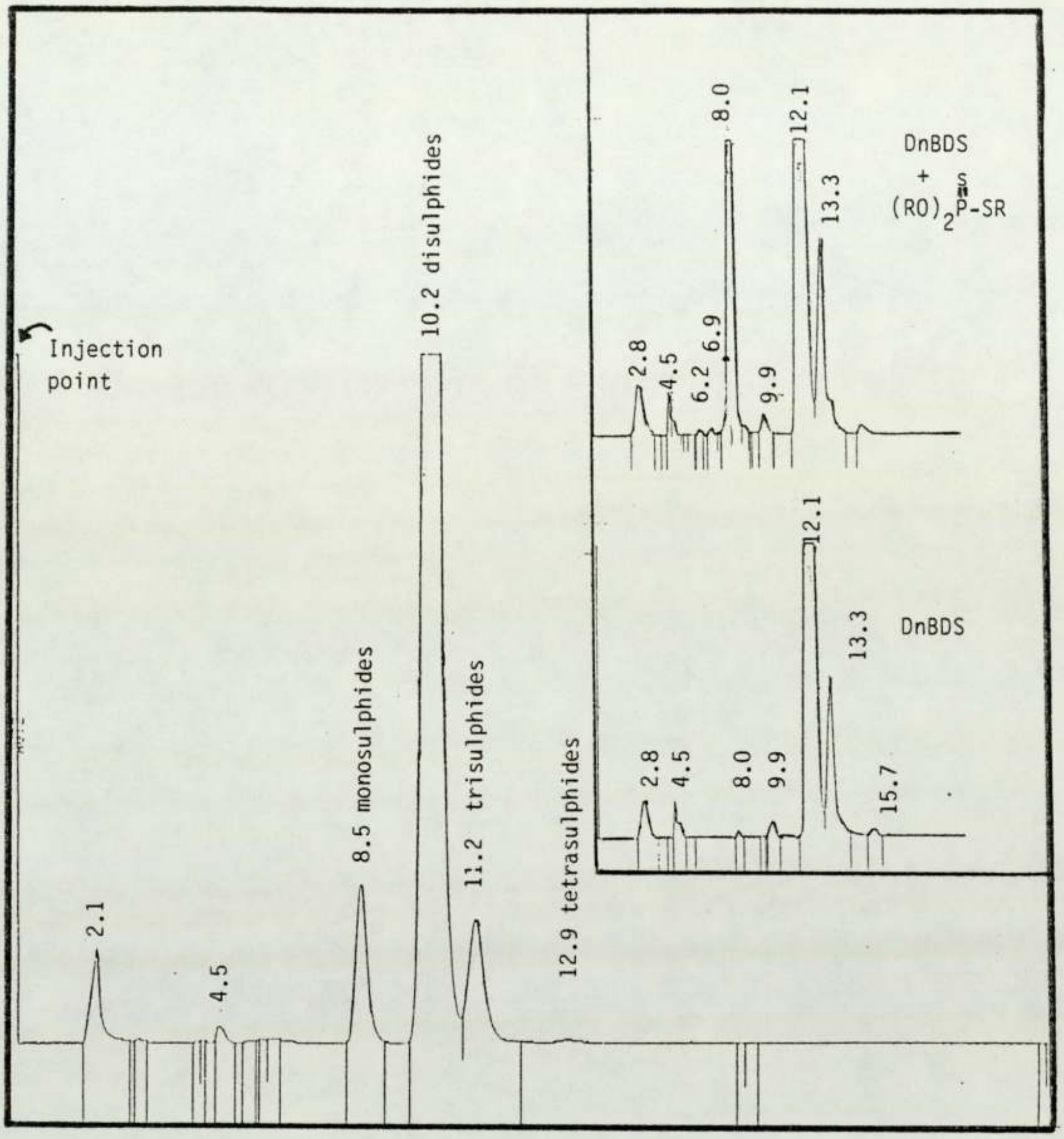


Figure 5.2a HPLC spectrum of neat DnBDS (4500 psi, 1ml/min, 225 nm). Inset shows the chromatogram of a sample mixture of DnBDS and triester O,O,S-TBDTP (RT=8.0). Numbers on peaks are retention times in minutes

Analysis of sample shown in the inset was carried out several times after that of the original sample hence the difference in RT values

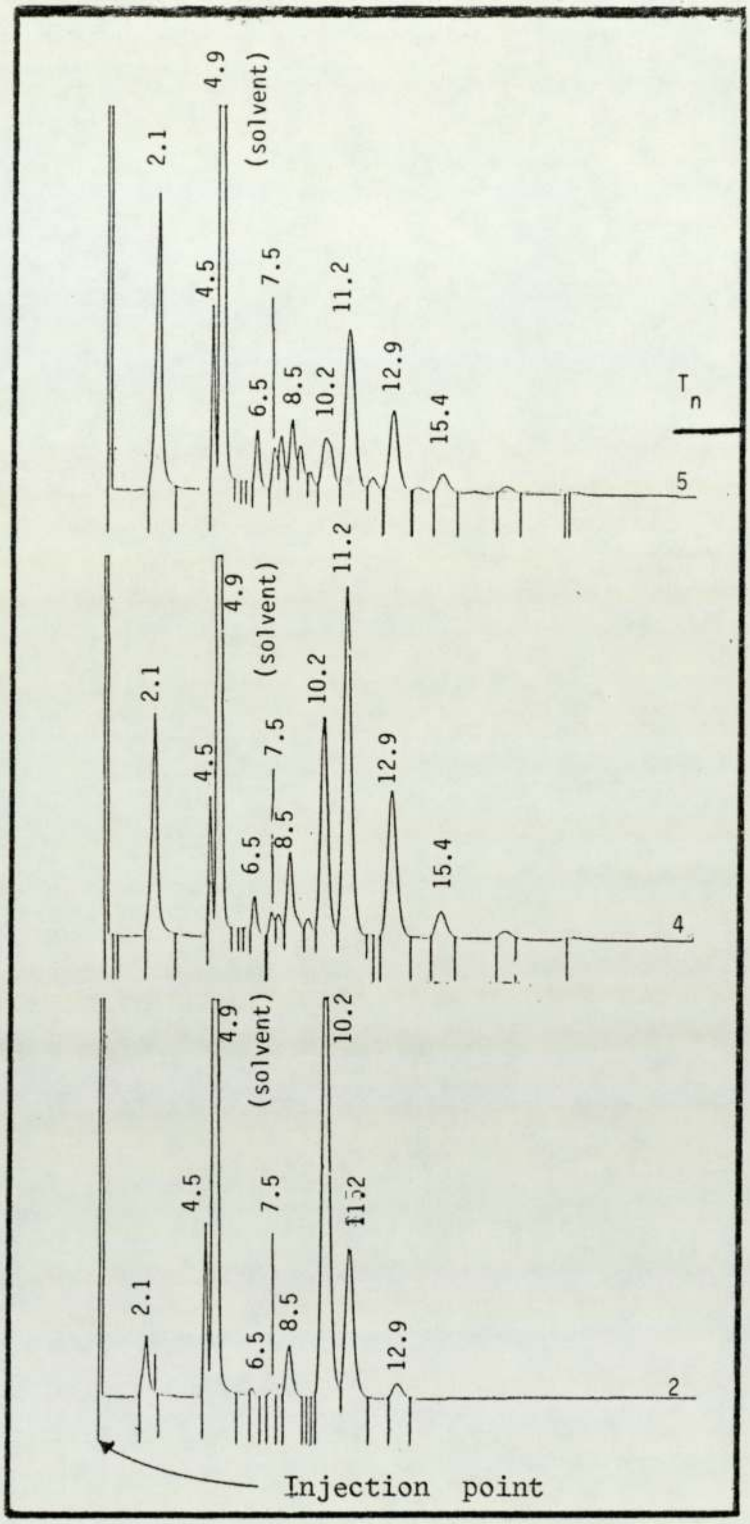


Figure 5.2b HPLC chromatograms of the thermal oxidation of DnBDS in dichlorobenzene at 185°C in the presence of air stream (4500 PSI, 1ml/min., 225nm).
Numbers on peaks are retention times in minutes and Tn refer to reaction time in hours.

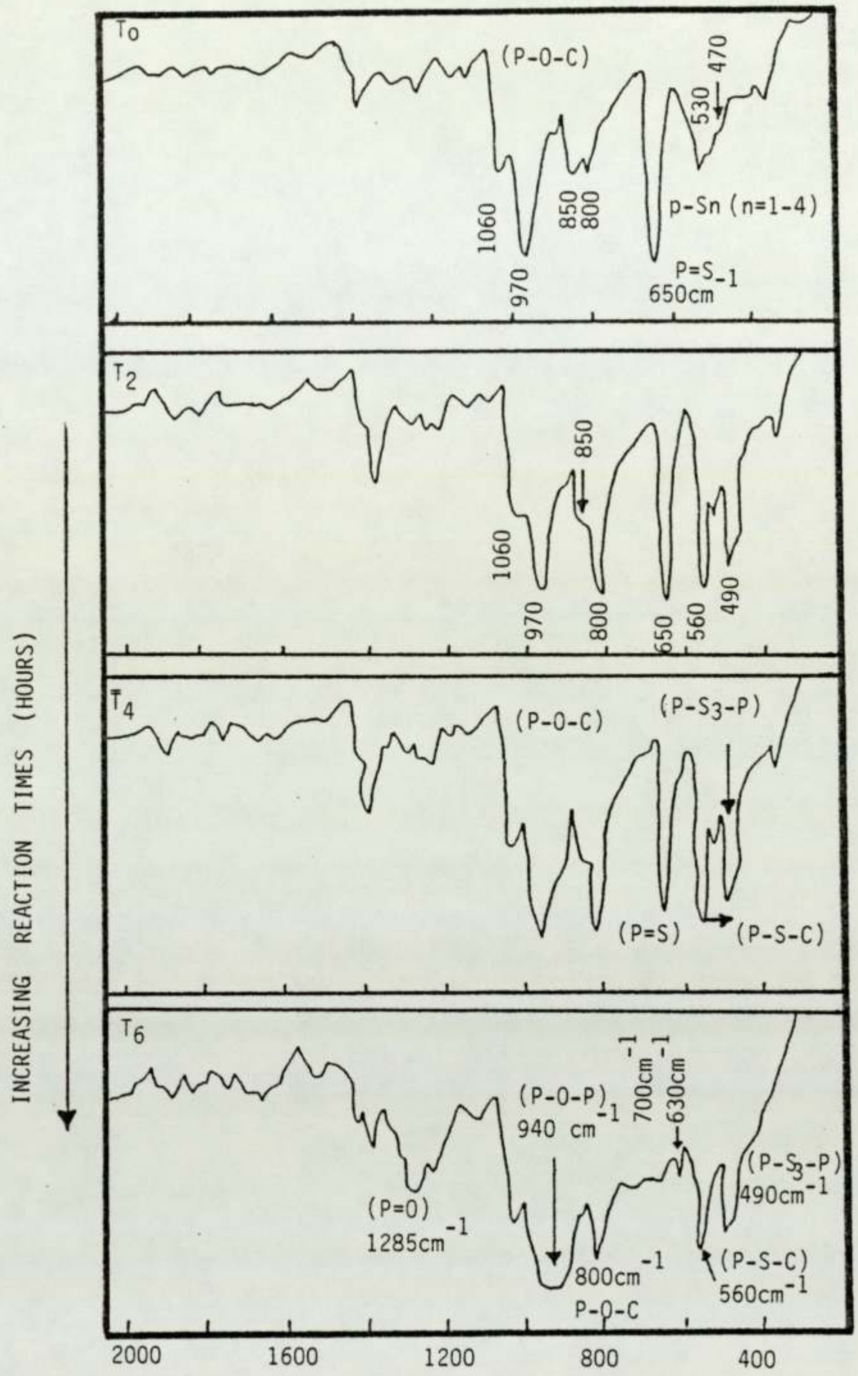


Figure 5.3 Infra-red spectra of products formed during oxidation of DnBDS in dichlorobenzene at 180°C. Values of T on the spectra are the reaction time in hours.

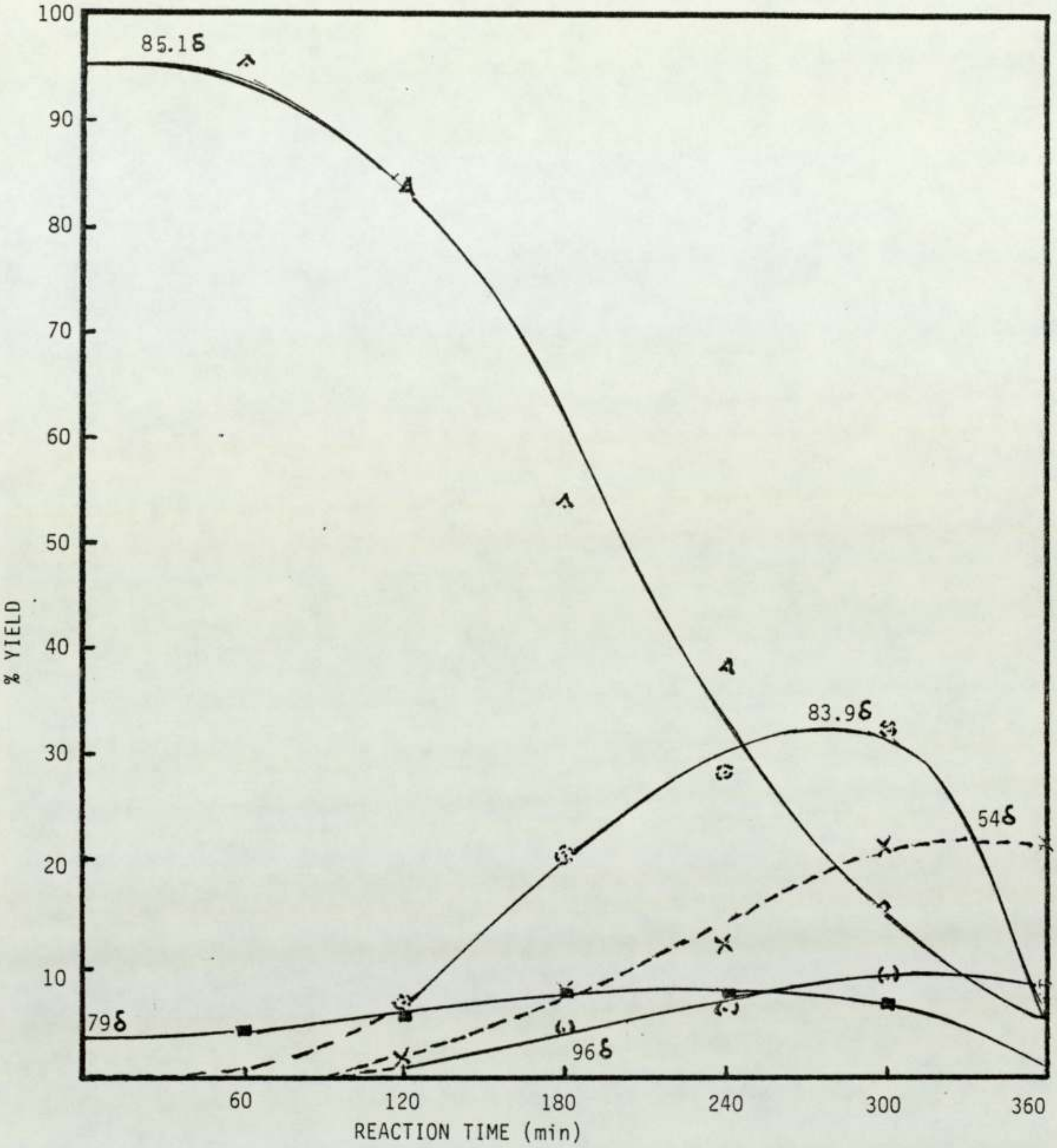


Figure 5.4a Product distribution of DnBDS thermal oxidation in dichlorobenzene at 185°C in the presence of air; as measured by ^{31}P NMR.

Figure. 5.4b.

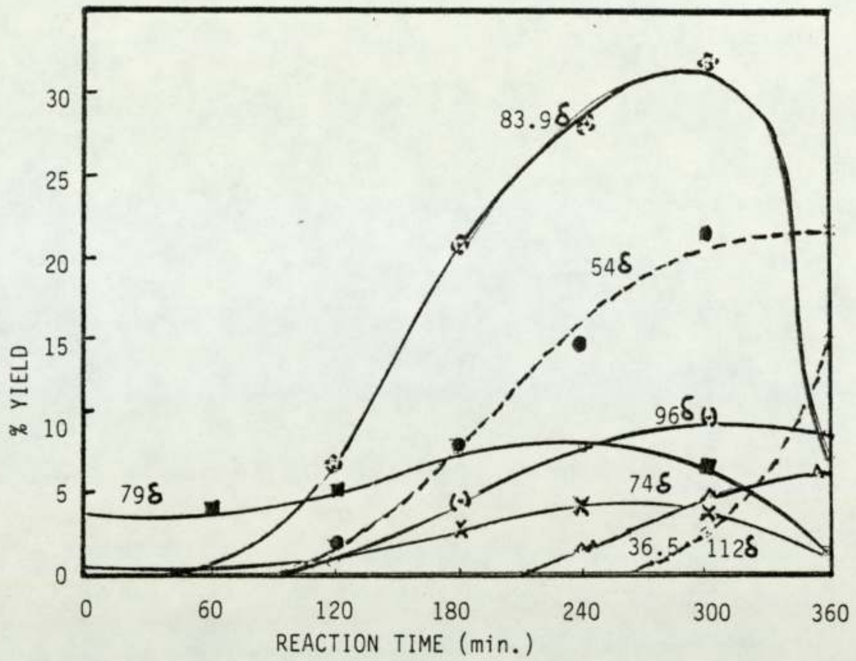


Figure. 5.4c.

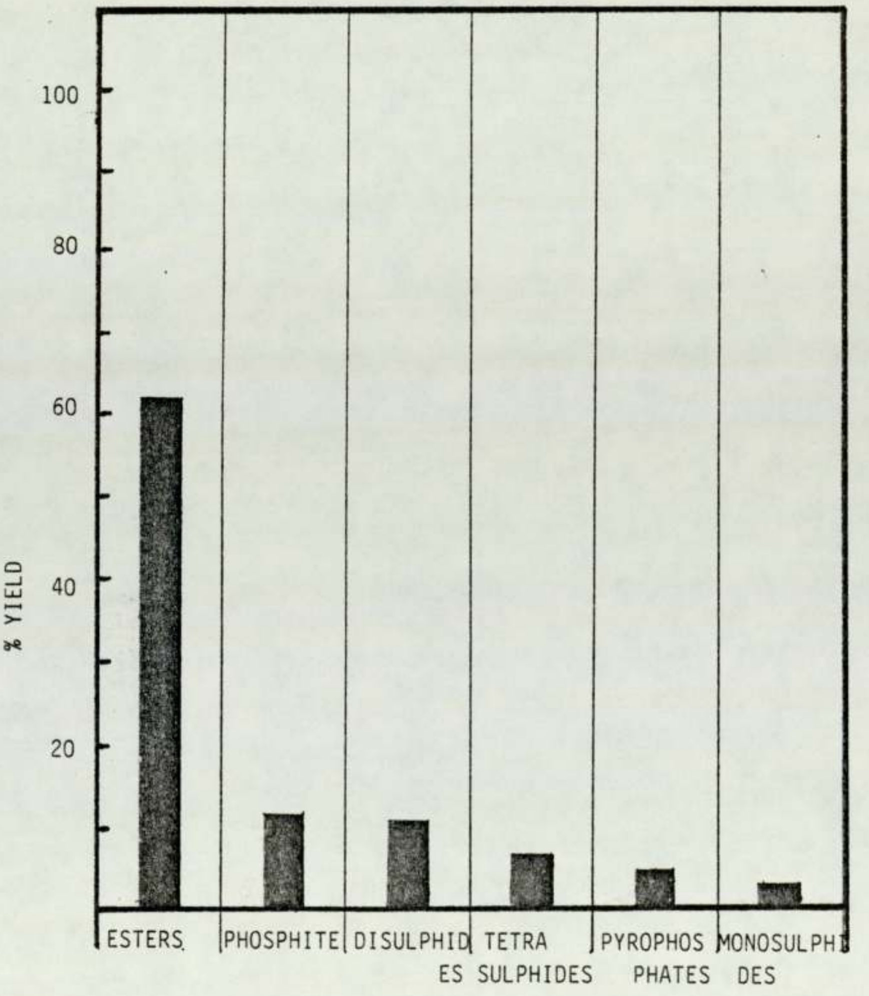


Figure 5.4b Product distribution of DnBDS thermal oxidation in dichlorobenzene at 185°C in the presence of air; as measured by ^{31}P NMR

Figure 5.4c Final product distribution after 6 hours DnBDS thermal oxidation reaction in dichlorobenzene at 185°C in the presence of a steady stream of air as measured by ^{31}P NMR.

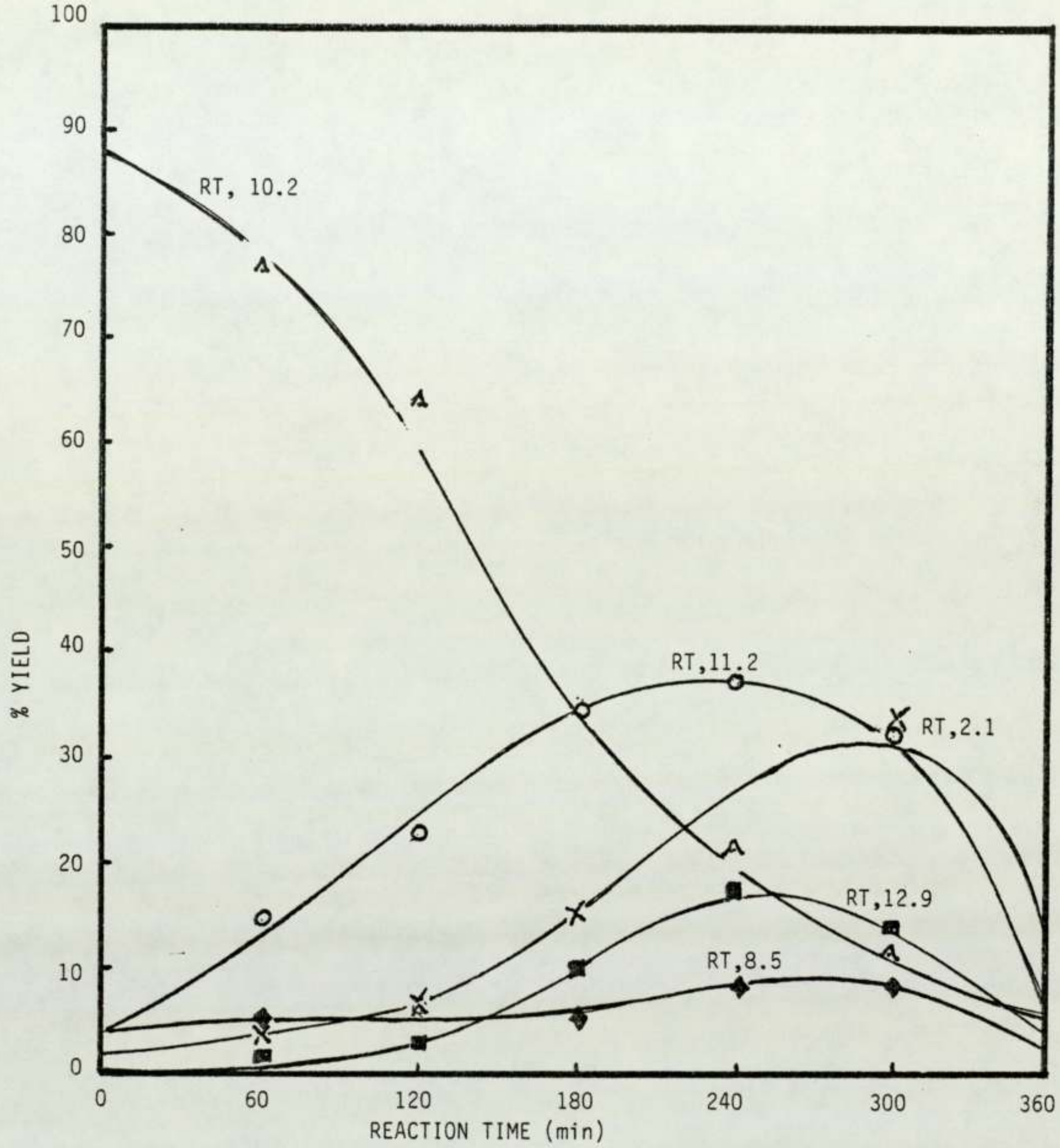


Figure 5.5 Distribution of some DnBDS thermal oxidation products in dichlorobenzene at 180°C in the presence of air stream

Numbers on the curves are retention times in minutes

5.2.1(b) Cumene as Substrate

The distribution of products formed during thermal oxidation of DnBDS in cumene at 180 °C under a constant stream of air, as measured by ^{31}P NMR is shown in Table 5.4 and the peak assignments are given in Table 5.5 Figure 5.6 shows the ^{31}P NMR spectra of products formed during the oxidation process, and the relative abundance of the various products as a function of the reaction time is shown in Figure 5.7. In contrast to the thermal oxidation of DnBDS in dichlorobenzene(Section 5.2.1a),the rate of DnBDS oxidation in cumene was slower (a slightly lower temperature of 180°C was used in the latter) although the products were quite similar, with P NMR chemical shifts both at low and high field compared to the starting material (Figure 5.6). A white crystalline precipitate was formed at the end of the reaction (after six hours). This was isolated and shown by infrared (Figure 5.8) analysis to be composed mainly of alkyl or aryl sulphides and the corresponding sulphoxides and/or sulphones.

Table 5.4 Distribution of DnBDS thermal oxidation products in cumene at 100°C and under a constant stream of air

Reaction time(min)	* Product % yield (δ values= ^{31}P chemical shifts in ppm)													Other signals of variable intensity of ocurrence
	δ − 96	89.1	85.5	84.96	84.1	83.8	79	63	54.8	53.1	52.3	50.6	29	
0	0	0	2.9	85.5	2.8	2.1	5.8	0	0	0	0	0	0	72 0.95%
60	0.6	0	3.9	77.6	4.2	6.4	5.5	1.0	0	0.4	0	0	0	72 0.4%
120	1.3	0	2.2	70.4	3.9	11.8	5.3	3.5	0	1.1	0	0	0	21.6 0.4%
180	2.9	0.7	1.7	57.7	6.1	13.4	6.1	5.8	0	2.0	0.7	0	1.0	77.1 0.8% ;-11 0.4%
240	3.9	1.0	1.5	53.0	8.3	17.3	5.0	4.9	0	2.1	0	0	1.0	141.2 0.5% ; 77.2 1.0% ; 0.4 0.4%
300	5.4	1.8	1.9	42.4	9.0	18.6	5.2	4.4	1.6	2.6	1.9	1.8	1.2	129.9 0.4% ; 86.5 0.6% ; 77.2 0.8% ;18.3 0.5%
360	10.0	2.9	1.96	31.1	9.4	19.1	5.3	4.6	3.7	5.9	2.4	2.1	0.8	68.8 0.6% ;

* Normalization of the % intensities for all signals to 100%

Table 5.5 Assignments to peaks shown in Table 5.4

Chemical shifts (ppm)	Assignments	Comments
	Reference	% yield at the end of reaction (6 hours)
96.0	$(RO)_2(RS)PS$ (106,105a,119)	Formed in the early stages (1h) and builds up with time. (10%)
89.1	$(RS)_2(R)PS$ (106)	Only formed after three hours reaction and continues to build up with time. (2.9%)
85.5	?	Impurite in original material. Remains throughout the reaction at roughly the same level. (2%)
84.96	* $[(RO)_2PSS]_2$ (DnBDS)	Decreased steadily in yield throughout the reaction. (31.1%)
84.1	* $[(RO)_2PSS]_2S_2$	Impurity in original material. Continues to build up throughout reaction. (9.4%)
83.8	* $[(RO)_2PSS]_2S$	Impurity in original material. Tremendous build-up throughout the reaction. (19.1%)
79.0	* $[(RO)_2PS]_2S$	Impurity in original material. Remains throughout the reaction at roughly the same level. (5.3%)
63.0	* $(RO)_2PSOH$	Formed in the early stages (1h) and builds up to a maximum after three hours before showing signs of decay. (4.6%)

Table 5.5 (continued)

Chemical shifts (ppm)	Assignments	Comments
	Reference	% yield at the end of reaction (6 hours)
54.8	$(RS)_2(R)PO$(106)/$(R)_3PS$(119) $(p\text{-}CH_3C_6H_4O)_3PS$(119)	Only formed in the later stages (5h) and builds up with time. (3.7%)
53.1	$(C_6H_5O)_3PS$(119)	Formed in the early stages (1h) and builds up with time. (5.9%)
52.3	$(O\text{-}CH_3C_6H_4O)_3PS$(119)	Only formed after three hours reaction and continues to build up with time. (2.4%)
50.6	$(R)_2(RO)PO$ (119)	Only formed in the later stages(5h) and builds up with time. (2.1%)
29.0	$(RO)_2(RS)PO$(106,114,119)	Only formed after three hours and remains throughout the reaction at roughly the same level. (0.8%)

* Assigned on the basis of its identity with that of an authentic specimen.

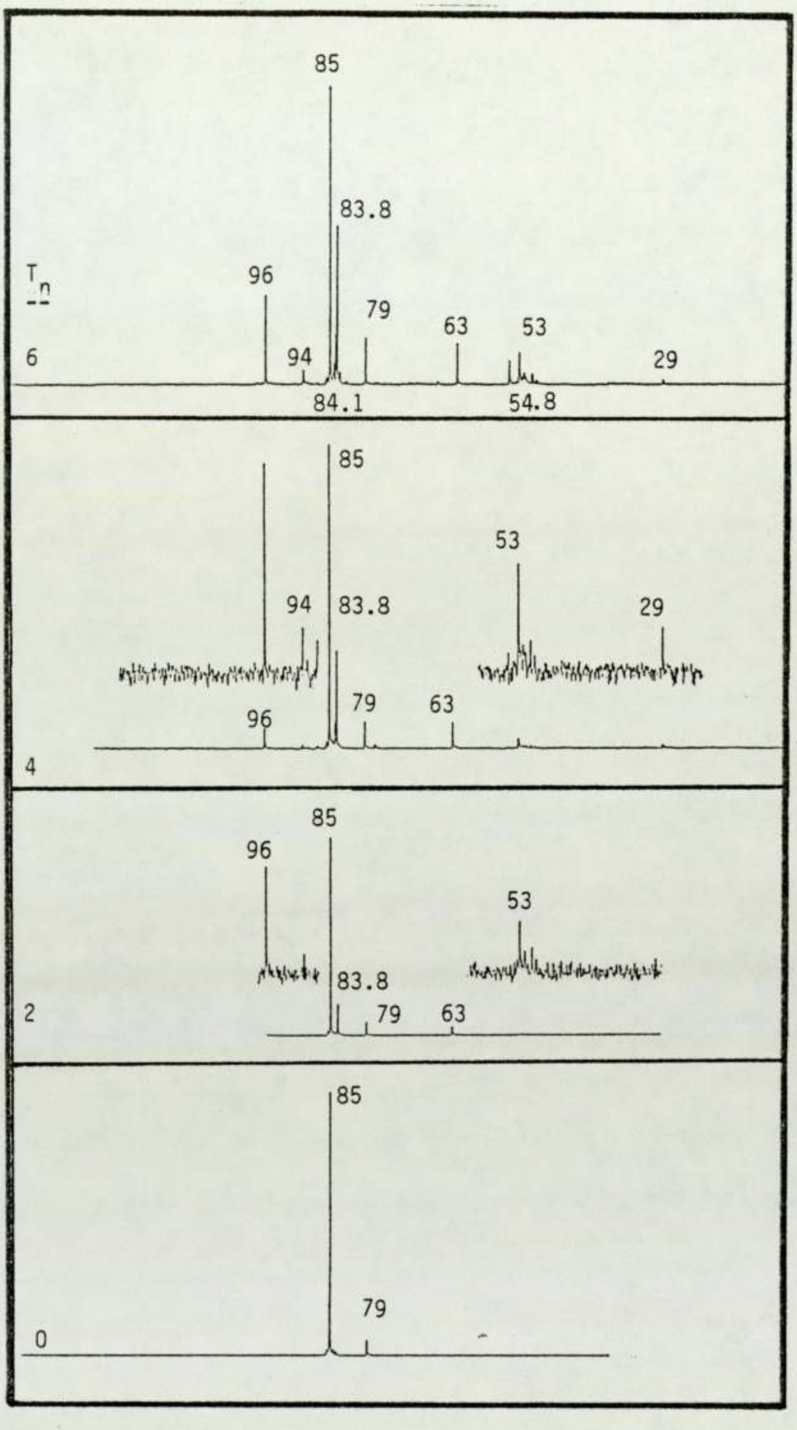


Figure 5.6 ^{31}P NMR spectra of products formed during thermal oxidation of DnBDS in Cumene at 180°C in the presence of air. Numbers on the signals are chemical shifts in ppm and Tn refers to reaction time in hours.

Figure. 5.7a.

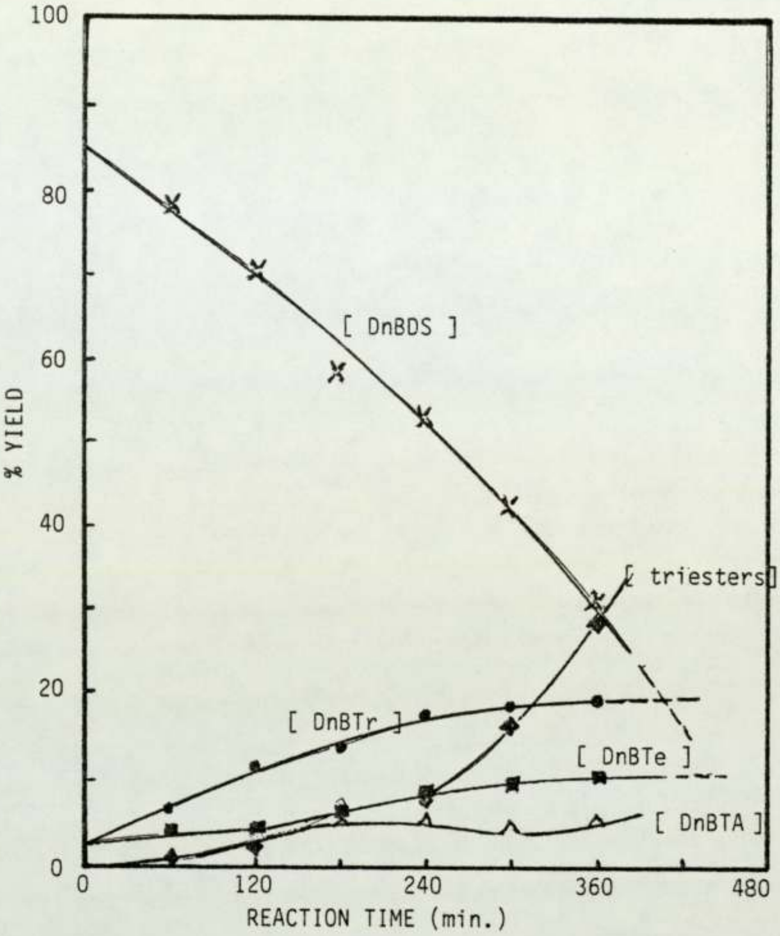


Figure. 5.7b.

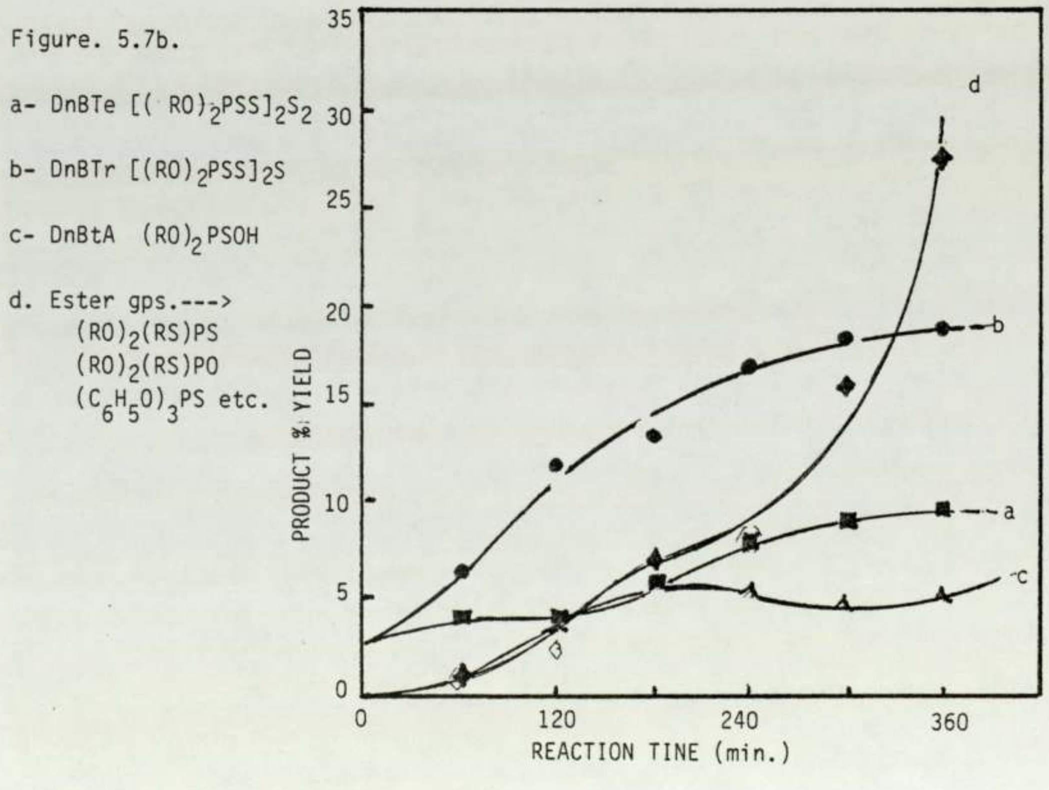


Fig. 5.7a. Products of DnBDS thermal Decomposition in cumene at 180°C under a constant stream of air.

Fig. 5.7b. Products of DnBDS thermal oxidative decomposition in cumene at 180°C under a steady stream of air.

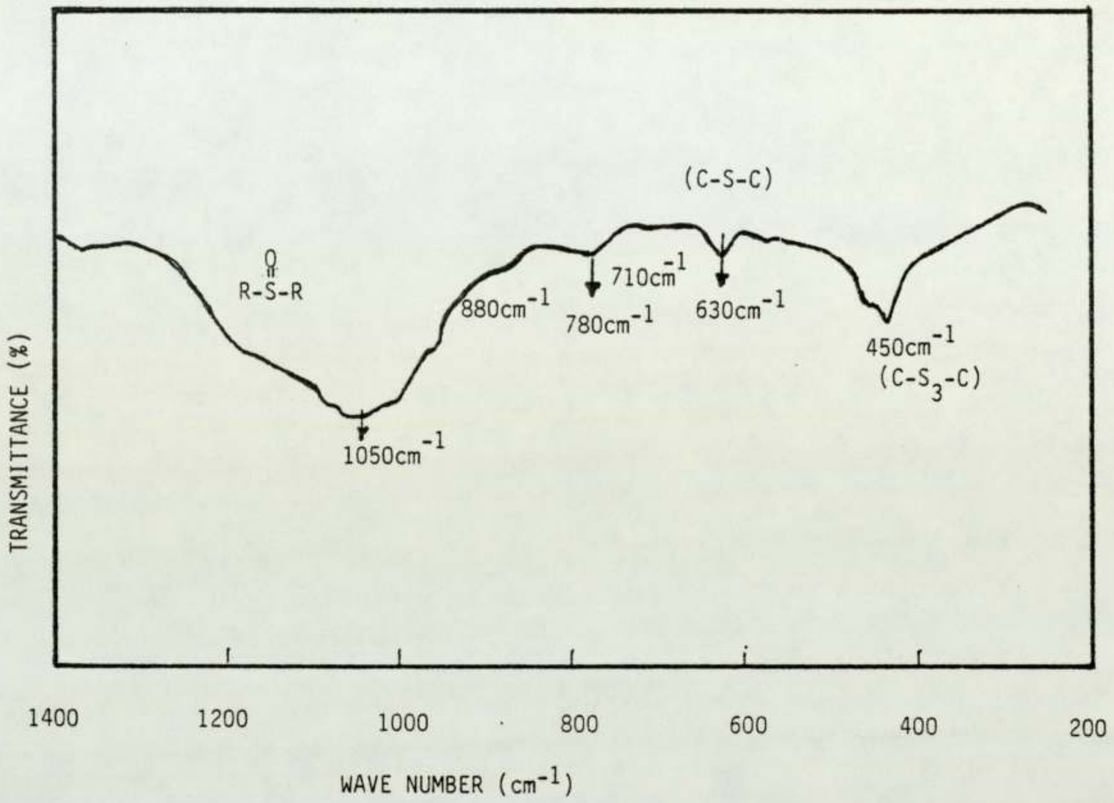


Figure 5.8 Infra-red spectrum of white precipitate formed after 6 hours thermal oxidation of DnBDS in Cumene at 180°C in the presence of air stream (KBr disc)

5.2.2 Thermal Oxidation of DnBDS at 100 °C in the Presence of Tert-butyl Hydroperoxide (TBH)

5.2.2(a) Dichlorobenzene as Substrate

Thermal oxidation of DnBDS by TBH (at two different molar ratios) in dichlorobenzene at 100°C was monitored by ^{31}P NMR, and changes in chemical shifts of products formed during the reactions are shown in Table 5.6. Structural assignments to the ^{31}P NMR, signals are given in Table 5.7. As in the previous studies, it is clear that the oxidation of DnBDS by TBH results in the formation of highly oxigenated phosphorus species having chemical shifts lower than that of DnBDS (Tables 5.6-5.7), although the tri- and tetra-sulphides, again, represent the primary oxidation intermediates in addition to the sulphur acid. Figures 5.9-5.11 show ^{31}P NMR and IR spectra of the reaction products at both ratios of TBH:DnBDS(0.5M DnBDS), and the relative abundance of the various species is shown in Figure 5.13.

For both TBH:DnBDS ratios studied, the oxygen-hydrogen stretching frequency of the hydroperoxide which gives a sharp infrared peak around 3520 cm^{-1}, was used as a basis for quantitative estimation of the rate of decomposition of the hydroperoxide (Figure 5.12). It is clear that almost all the original hydroperoxide has decomposed after 120 minutes at equimolar TBH:DnBDS ratio, and 240 minutes when a 2-fold excess of TBH is used (Figures 5.12-5.13). Figure 5.12 also shows that at equimolar ratio, the free OH vibration frequencies at $3645cm^{-1}$ and $3620cm^{-1}$ build-up during the reaction. This may be attributed to methanol and tert-butyl alcohol respectively which are products of the decomposition of TBH. Shoulders of both absorption bands are also fairly visible when a 2-fold molar excess of TBH is used, although they are slilghtly obscured by the broad absorption band ($3700cm^{-1}$-$3000cm^{-1}$) due to hydrogen bonding in dimeric forms.

Table 5.6 Products of the oxidation of DnBDS by TBH in chlorobenzene at 100°C

TBH:DnBDS ratio	Reaction time(min)	*Product % yield (δ values = ^{31}P chemical shifts in ppm)												
		δ-85.5	85	84.3	84.1	83.8	79	63	57	52	21	28	<10	>90
1:1	0	0.92	88.3	2.1	2.1	0	5.6	0	0	0	0	0	0	0
	60	0.71	79.9	1.1	5.9	2.1	6.0	0.13	0	0	3.4	0	0.35	0.38
	120	0.66	70.4	1.9	10.2	4.5	4.7	0	0	0.9	6.7	0	0	0
	180	0.60	61.6	1.1	15.9	6.2	3.7	0.53	0	0.8	7.5	0	0.85	0
	240	0.52	59.3	1.6	16.0	7.4	4.6	0.81	0	1.1	7.9	0	0.88	0
	480	1.60	58.5	1.9	17.6	5.3	3.4	1.20	0	1.4	5.8	0.4	1.94	0.64
2:1	60	0	86.3	0	2.7	0	7.1	0	0	0	0	0	2.1	1.4
	120	1.3	84.1	1.9	3.5	1.1	7.1	0	0	0	0.99	0	0	0
	180	1.0	74.4	1.8	6.4	2.2	7.7	0	0	0	4.90	0	1.1	0.6
	240	0.84	54.5	0	17.0	5.9	4.9	0	0	0.83	14.1	0	1.7	0.3
	300	0	47.4	2.7	19.7	8.9	4.3	0.8	0	1.10	13.1	0	2.0	0
	480	1.6	37.3	2.5	25.6	9.5	3.2	2.9	0	1.60	10.5	0.8	4.7	0

* Normalization of the % intensities for all signals to 100%

Table 5.7 Assignments to peaks shown in Table 5.6

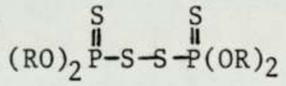
Chemical Shifts(ppm)	Assignments	Comments
> 90 1:1 146,133,95	$(RO)_3P$ (119) $(RO)_2(RS)PS$ (106,105a)	Predominantly trivalent phosphorus species.Only formed at vary low levels 1:1 ratio--▶Disappears completely after initial formation.
2:1 145,138,114	$(RO)_3P$: (119)	2:1 ratio--▶ Decays with reaction time
141,127,129	$(RS)_3P$: (105a,119)	
85.5	?	Present in original material as an impurity. Decayed steadily but remained throughout the reaction when ratio is equal to 1:1. With excess TBH, this species disappeared completely after one hour reaction,but was regenarated an hour later before decaying in latter stages. %yield--▶ 2:1 >> 1.1
* 85.0	 $(RO)_2\overset{S}{\overset{\Vert}{P}}-S-S-\overset{S}{\overset{\Vert}{P}}(OR)_2$ DnBDS	Steady decay in abundance during reaction. Showed a faster rate of decay when ratio = 1:1. At 2:1 ratio, initial rate of decay was slow indicating the presence of an induction period after which it became autocatalytic.

Table 5.7 (continued)

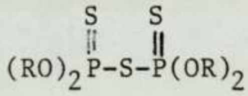
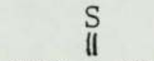
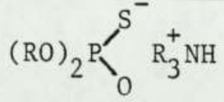
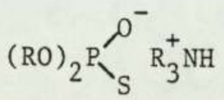
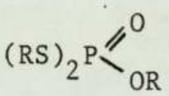
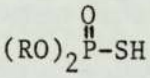
	Chemical Shifts(ppm)	Assignments	Comments
	84.3	?	originally present as an impurity.Remained throughout reaction at roughly the same leval.
*	84.1	$[(RO)_2PSS]_2S_2$ DnBTe	Originally present as an impurity. Intense build up during reaction,at both ratios. Became one of the major products at the end of reaction.
*	83.8	$[(RP)_2PSS]_2S$ DnBTr	Formed in the initial stages and continues to build up during the reaction. Of moderate yield at end of reaction
*	79.0	 $(RO)_2\overset{\overset{S}{\|}}{P}-S-\overset{\overset{S}{\|}}{P}(OR)_2$ DnBMS	Major impurity in original material. Builds up initially and then decays at a vary slow rate. Still present at end of reaction.
*	63.0	 $(RO)_2\overset{\overset{S}{\|}}{P}-OH$ DnBTA	Formed in the initial stages when ratio = 1:1, and builds up slowly. With excess TBH (2:1) this species is only formed in the later stages of the reaction.

Table 5.7 (continued)

Chemical Shifts(ppm)	Assignments	Comments
* 57.0	  (Ionised acid salt)	Formed via the conversion of the unionised acid groups to the salt forms, on addition of a tertiary amine.
52.0	 (93)	Formed in the later stages and continues to build up during the reaction. Rate of build up --▶ 2:1 >> 1:1
* 21.0	 $(RO)_2P(O)\text{-}SH$ DnBTA	Formed in the initial stages when ratio = 1:1 and builds up to a maximum at the end of reaction. With excess TBH this is only formed after two hours reaction and then builds up. Rate of build up---▶ 2:1 >> 1:1 % yield (after 4h)--▶ 2:1 >>1:1
1:1-▶ 10.3; 0.1, 0.6; 0.5 < 10 10.3,4.3,0.6 2:1-▶ -5.6, 12.2 0.6, -9.5	$(RO)_2P{=}O$, $[(RO)_3PO]_2$, $(RO)_2P(O)OH$, $[(RO)_2POOH]_2$, $(RO)R'_2P(O)$ etc. (19)	Formed in the initial stages at both ratios and builds up during reaction. Generally of very low yields particularly when ratio is = 1:1 Totally oxygenated groups.example phosphates, phosphites,and phosphinates etc.

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* Assigned on the basis of its identity with that of an authentic specimen.

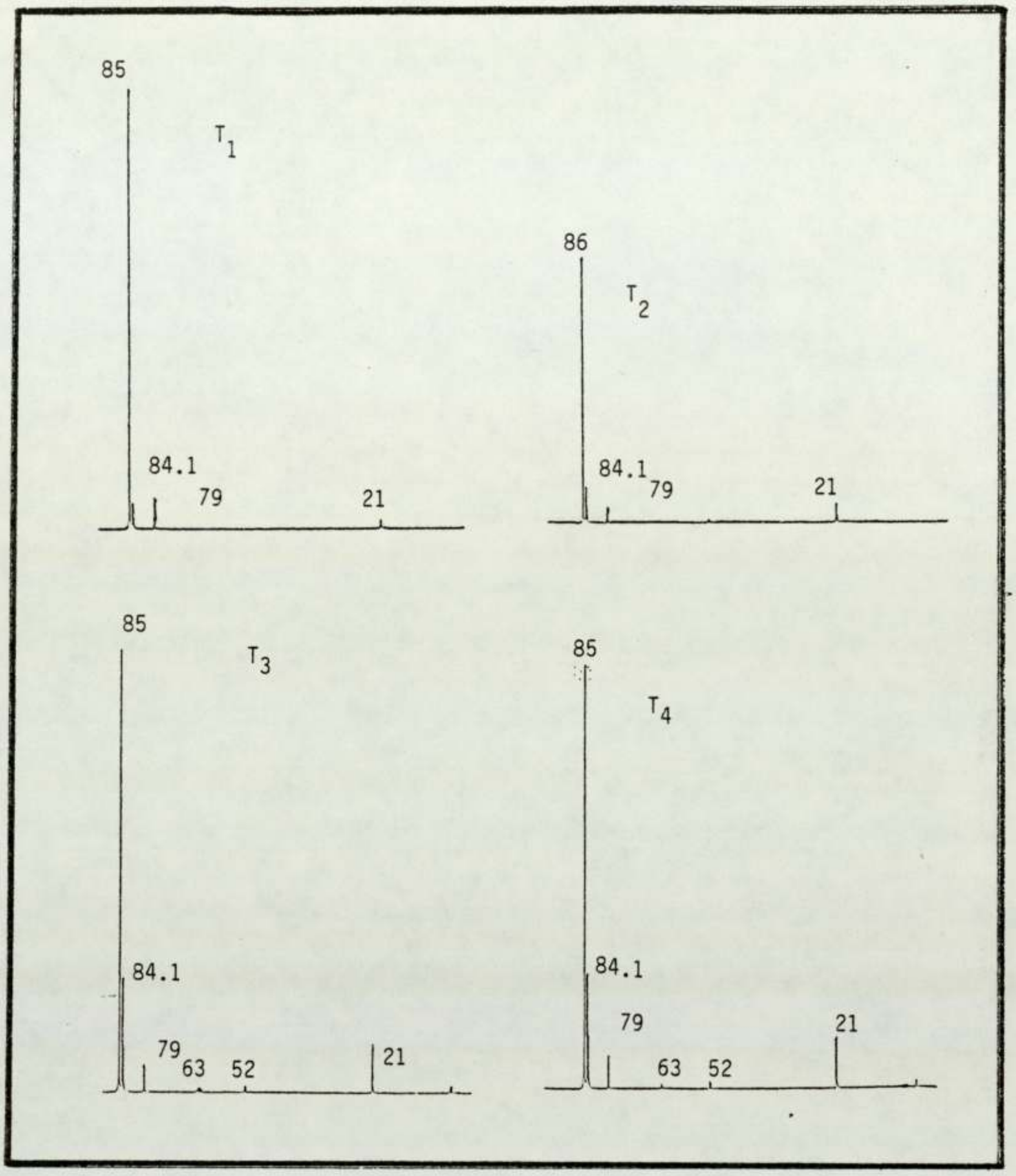


Figure 5.9 ^{31}P NMR spectra of the oxidation of bis-di-n-butyl thiophosphoryl disulphide (0.5M) by TBH in dichlorobenzene at 100°C. (T_0 - T_4) refer to reaction time in hours and [TBH]:[DnBDS] molar ratio = 1.

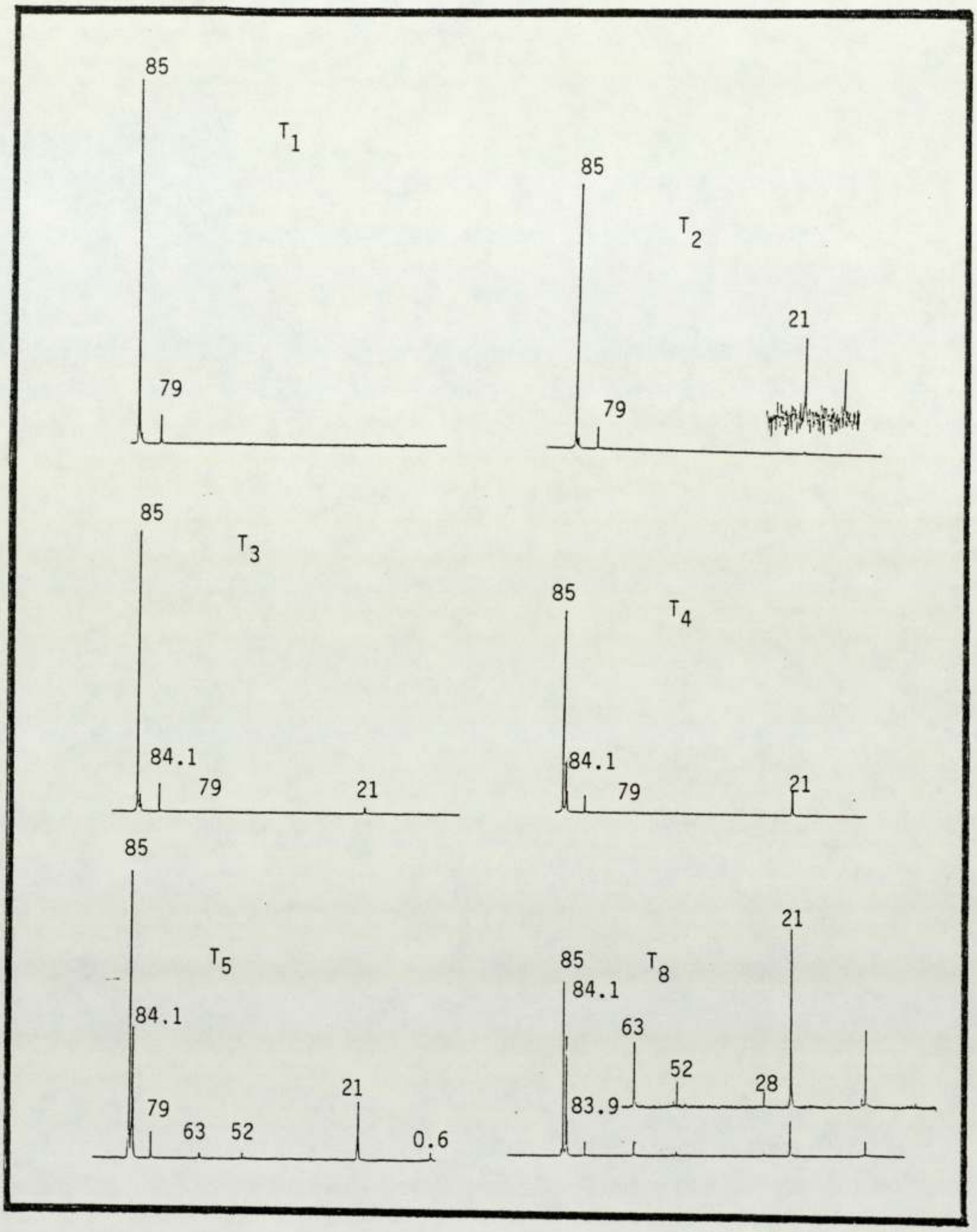


Figure 5.10 ^{31}P NMR spectra of the oxidation of di-n-butyl thiophosphoryl disulphide (DnBDS) by a 2-fold molar excess of TBH in dichlorobenzene at 100°C. (T_1 - T_8) refer to reaction times in hours

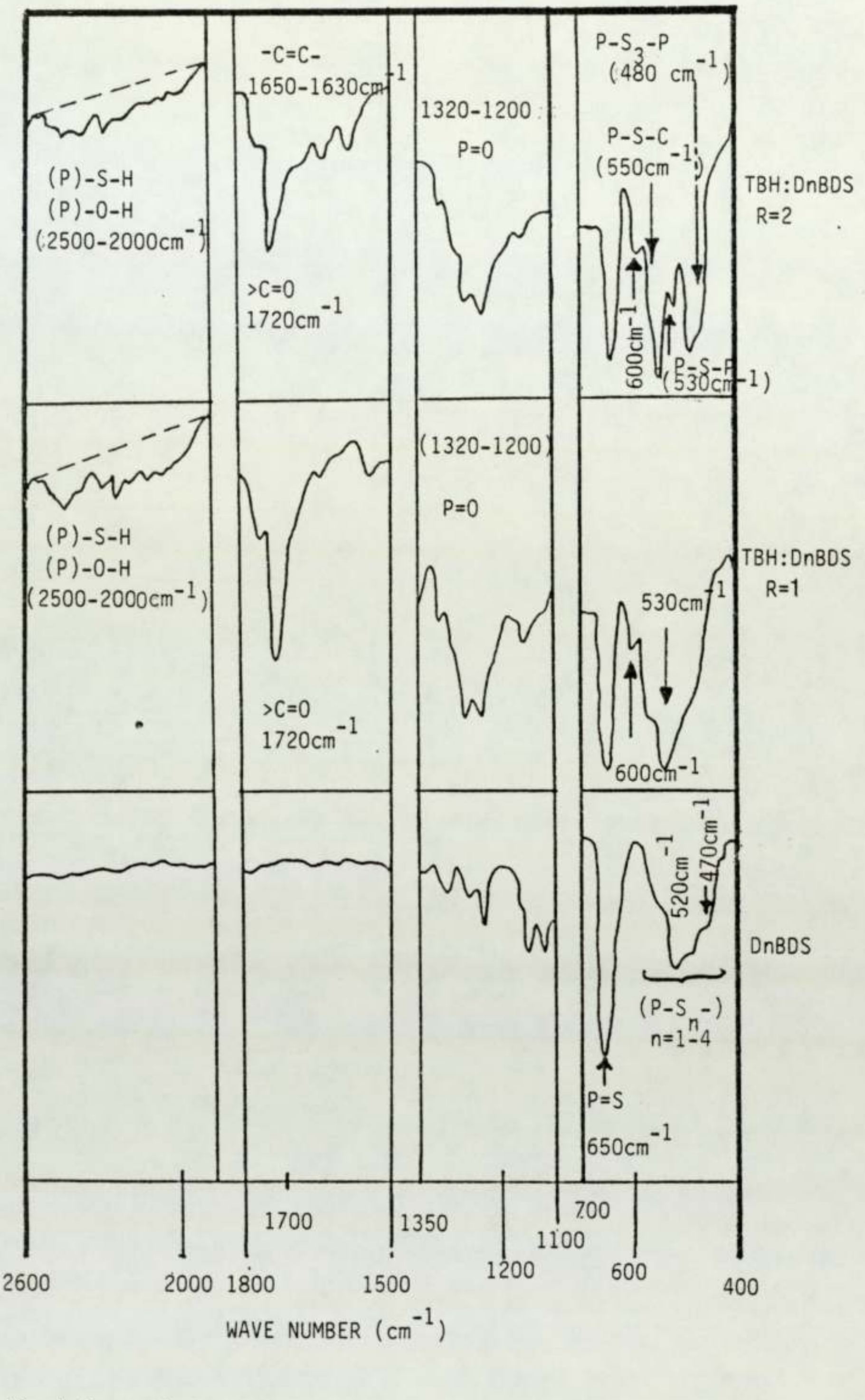


Figure 5.11 Infra-red absorption spectra of samples obtained after the eight hour oxidation of DnBDS by TBH in dichlorobenzene at 100°C

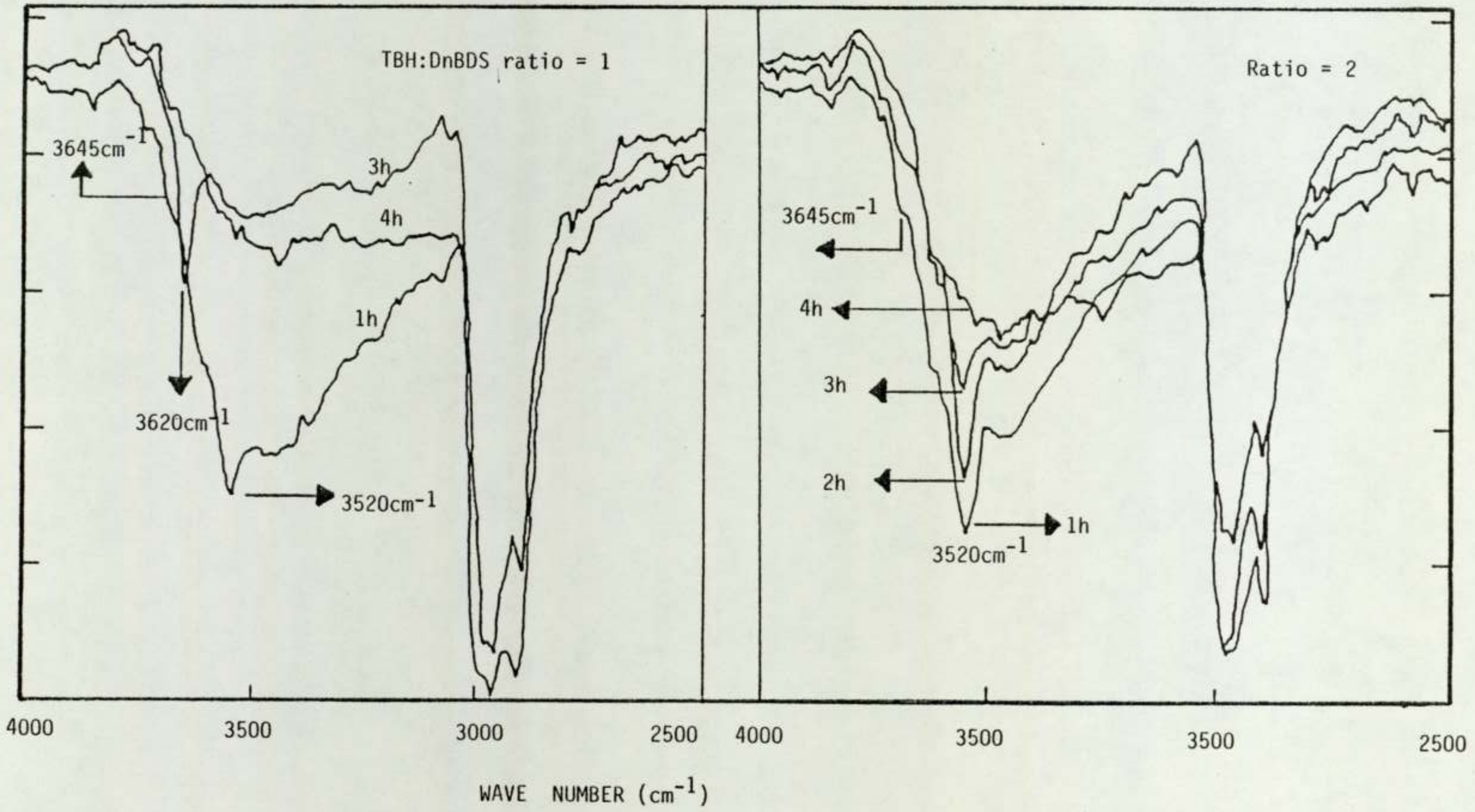


Figure 5.12. Qualitative representation of the decay in TBH conc. during oxidation of DnBDS by TBH in dichlorobenzene at 100°C.

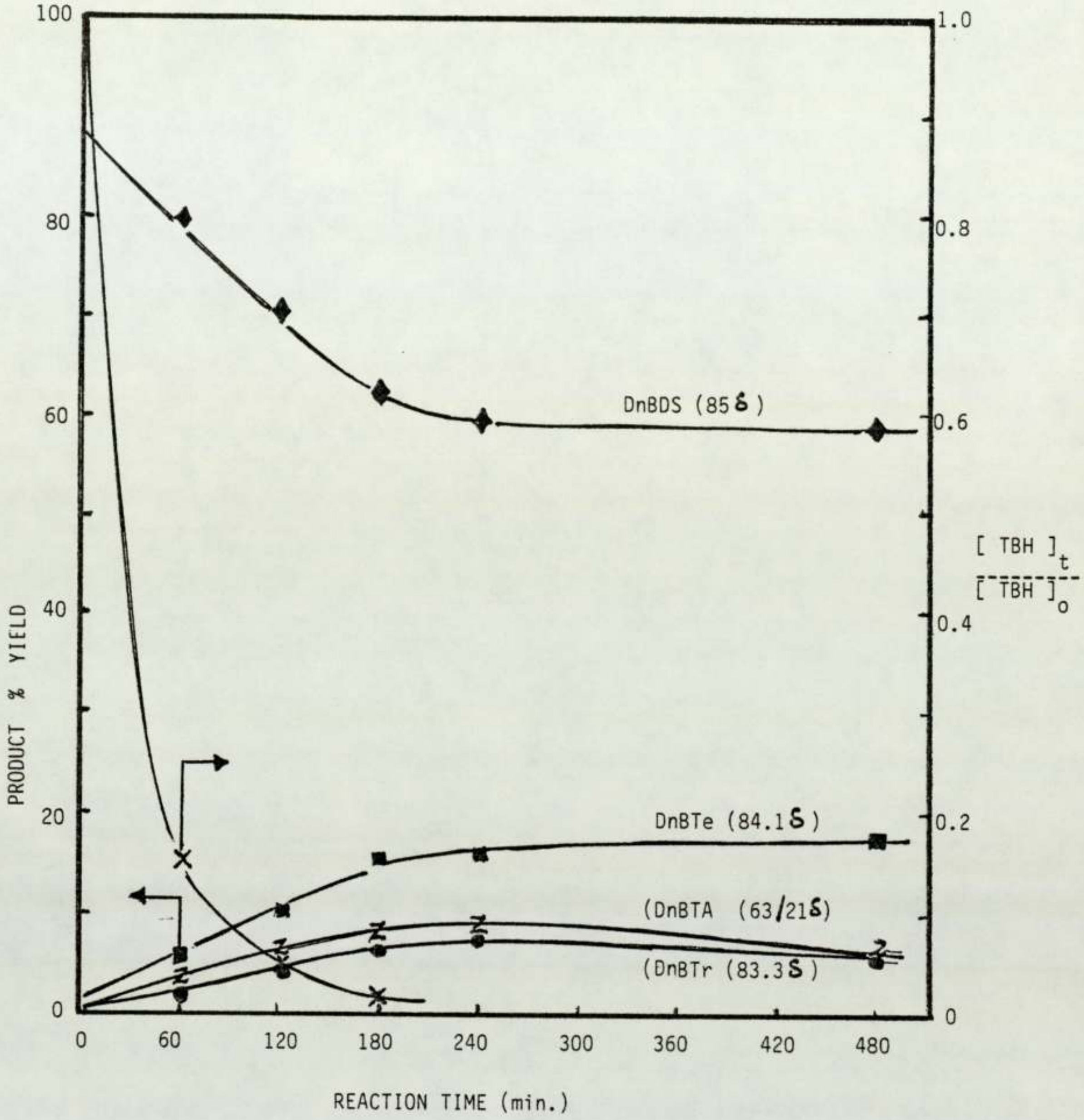


Figure 5.13a Products by ^{31}P NMR of the oxidation of DnBDS by TBH (equimolar ratio) in dichlorobenzene at 100°C.

Kinetics of TBH disappearance is also shown.

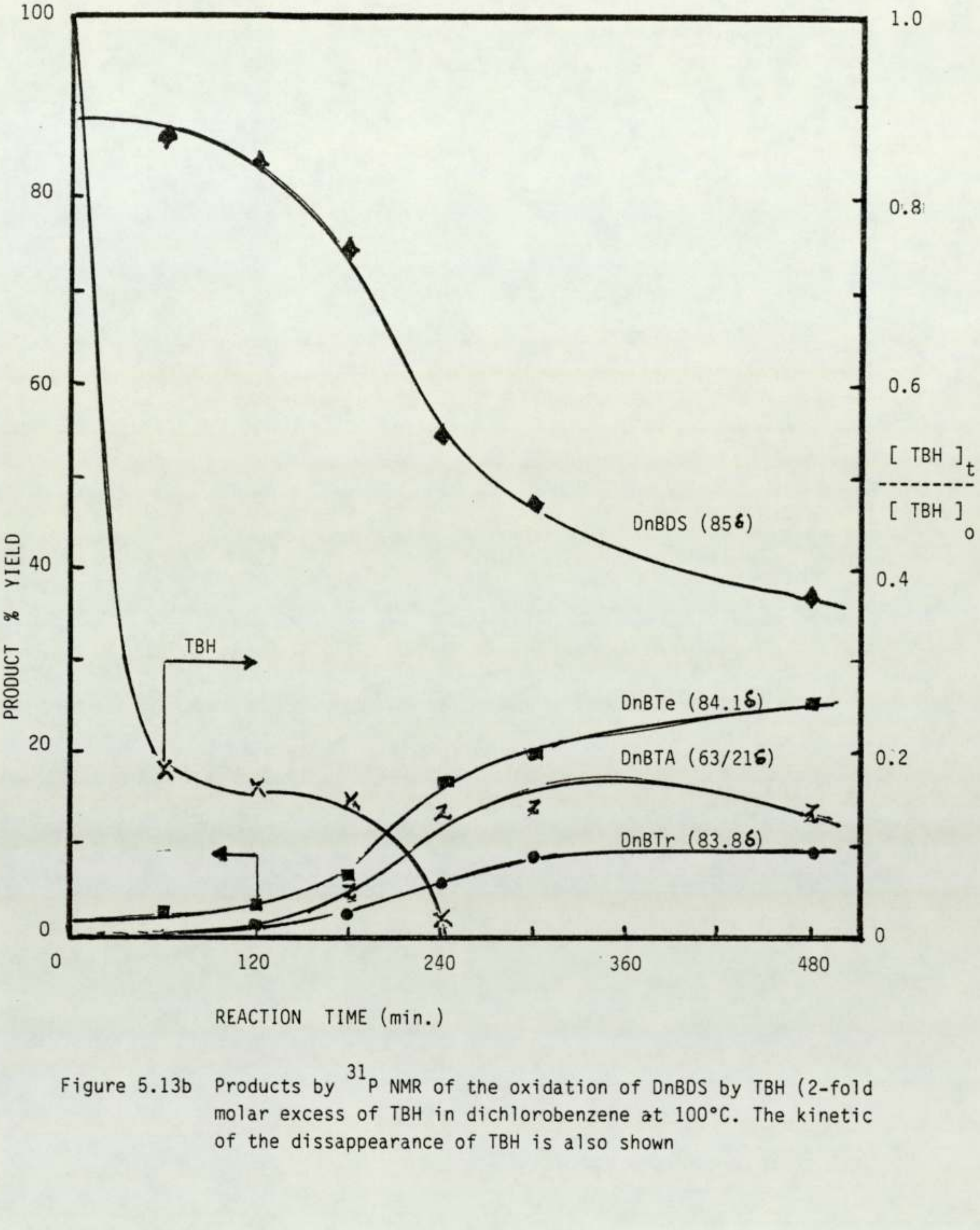


Figure 5.13b Products by ^{31}P NMR of the oxidation of DnBDS by TBH (2-fold molar excess of TBH in dichlorobenzene at 100°C. The kinetic of the dissappearance of TBH is also shown

5.2.2(b) Cumene as Substrate

In contrast to the previous oxidation studies, the oxidation of DnBDS by TBH(2-fold excess of TBH) in cumene was carried out directly in the JOEL NMR spectrometer, originally programmed for a stacking run at 100°C. The composition of the oxidation products is shown in Table 5.8, and the peak assignments are given in Table 5.9. It is evident (Table 5.8) that the initial oxidation products (<600 minutes), are very identical to those obtained in the past section (5.2.2a). At longer reaction times however (>600 minutes), all ^{31}P NMR signals in the immediate vicinity of the original DnBDS (80δ-86δ) decayed to a minimum, with concomittant emergence of other signals having chemical shifts far low field and far high field of the original DnBDS signal. The eventual positions of the various ^{31}P NMR signals at the end of the reaction (17 hours) is once again indicative of the formation of highly oxygenated phosphorus species. A ^{31}P NMR spectral representation of the chemical transformations occuring under these conditions is shown in Figure 5.14, while Figure 5.15 shows the distribution of the various products during the oxidation process.

At the end of the reaction (1020 minutes), the mixture was found to be composed of two different layers both of which were subsequently analysed; the top yellow layer by ^{31}P NMR (Figure 5.14,T =17) and the brown bottom layer by IR spectroscopy as a thin film on KBr disc (Figure 5.16).

Table 5.8 Distribution of products of the oxidation of DnBDS by TBH (2:1 molar excess of TBH)

in cumene at 100 °C

Reaction	*Product % yield (δ values = ^{31}P chemical shifts in ppm)													
time(min)	δ-96.0	85.5	85.0	84.1	83.9	79.0	63.3	52.0	28.0	21.0	19.0	>100	<15	Other signals of variable intensity of occurrence
0	X	2.9	85.4	2.8	2.1	5.8	X	X	X	X	X	X	X	XXX
60	X	2.8	64.5	5.8	4.6	10.4	X	X	X	6.9	X	X	0.8	(89.2δ,1.5%)
120	X	2.1	64.5	6.8	5.3	9.4	X	0.6	X	4.4	X	1.3	4.1	(89.2δ,0.73%) (59.7δ,0.54%) (33.1 ,0.42%)
180	0.6	1.9	62.3	6.9	4.8	9.4	X	X	X	7.5	0.5	1.7	4.2	(68.5δ,0.5%) (49δ,0.5%)
240	X	1.5	55.4	6.8	5.5	10.1	X	0.9	X	11.0	0.54	3.0	3.7	(44.5δ,1.1%)
300	1.1	2.3	64.7	8.6	6.2	6.2	X	X	X	6.5	X	1.7	1.96	XXX
360	0.61	1.5	54.7	9.7	8.5	8.8	X	X	X	8.6	X	2.3	3.2	(89.2δ,0.73%) (64.5δ,0.57%) (39.7δ,0.6%)
420	X	1.79	56.6	11.3	5.6	8.2	X	1.5	X	5.9	X	2.1	5.66	(45.5δ,0.57%) (41.3δ,0.64%)
480	X	1.5	60.8	11.0	8.7	10.0	X	1.1	X	4.8	X	X	1.04	(88.7δ,0.58%) (73.3δ,0.56%)
540	2.2	1.5	66.1	4.2	7.4	8.3	X	1.4	X	6.2	X	0.5	2.3	XXX
600	1.0	1.6	49.3	15.5	7.8	7.8	X	3.5	0.7	6.4	X	3.0	3.4	XXX
1020	2.9	X	X	X	X	9.9	32	4.9	8.2	X	X	13.3	24.9	(48.9δ,2.8%) (31.2δ,0.9%)
sample"1020" fraction a. (top layer)	1.8	X	X	X	X	7.8	41	3.6	5.0	X	X	6.8	26.8	(48.9δ,5.3%) (31.2δ,1.4%

---

* calculated from signal peak intensities

>100----> signals at 100 , 111 ,120 , 124 , 132 , 138 , and 140 δ.

<15----> signals at 15.0 ,13.3 , 12.8 , 10.0 , 5.2 , 0.65 and between -0.68 and -21 δ.

Table 5.9 Assignments to peaks shown in Table 5.8

chemical	Assignments	Comments
shifts (ppm)	reference	%yield at end of reaction(17h)
>100		Mixture of trivalent phosphours species and ester groups.Formed in early stages and remained throughout reaction at relatively low level. One of the major products after 17 hours (13.3%)
138	$(RO)_3P$	
132		
120	$(RS)_3P$	
111		
100	$(RS)_2(RO)$ PS	
95.5	$(RO)_2(RS)PS$	Only formed after three hours and remains throught reaction (2.9%)
85.5	?	Impurity in original material.Remains throughout the reaction (up to 600 minutes) then decays (X)
85.0	$[(RO)_2PSS]_2$ * (DnBDS)	Showed a 3-stage decomposition pattern. Initial rapid reduction in abundance, followed by long induction period before decaying. (X)
84.1	$[(RO)_2PSS_2S_2$ *(DNBTe)	Impurity in DnBDS. Built up rapidly before decaying. (X)
83.9	$[(RO)_2PSS]_2S$ *(DnBTr)	Impurity in DnBDS. Built up slowly before decaying. (X)
79.0	$[(RO)_2PSS]_2S$ *(DnBMS)	Impurity in DnBDS. Built up rapidly after one hour and remained at roughly the same level. (9.9%)
63.3	*$(RO)_2PSOH$	Only formed at the very later stages (>10h) Major product at end of reaction. (32%)

Table 5.9 (continued)

chemical shifts (ppm)	Assignments	Comments
	reference	%yield at end of reaction(17h)
58.0	$*(RO)_2PSO^-R_3NH^+$	Formed via the conversion of unionised acid groups $[(RO)_2PSOH]$ to the amine salt forms.
52.0	$(C_6H_5O)_3PS$	Formed in the early stages (2h) and continues to build up slowly throughout reaction. (4.9%)
28.0	$(RO)_2(RS)PO$	Only formed after 10 hrs and built up with time. (8.2%)
21.0	$*(RO)_2POSH$	Formed in the early stages (1h). Continues to build up before undergoing thermal isomerization. (X)
<15 $\begin{cases} 15, 13.3 \\ 5.2, 0.7 \\ 0.6 \text{ to} -21 \end{cases}$	$(RO)_3PO$ $(RO)_2P(O)OH$ $(RO)R'_2P(O)$	Totally oxygenated species. Formed in the early stages and remained throughout the reaction. Became one of the two major products. (24.9%)

*Assigned on the basis of its identity with that of an authentic specimen.

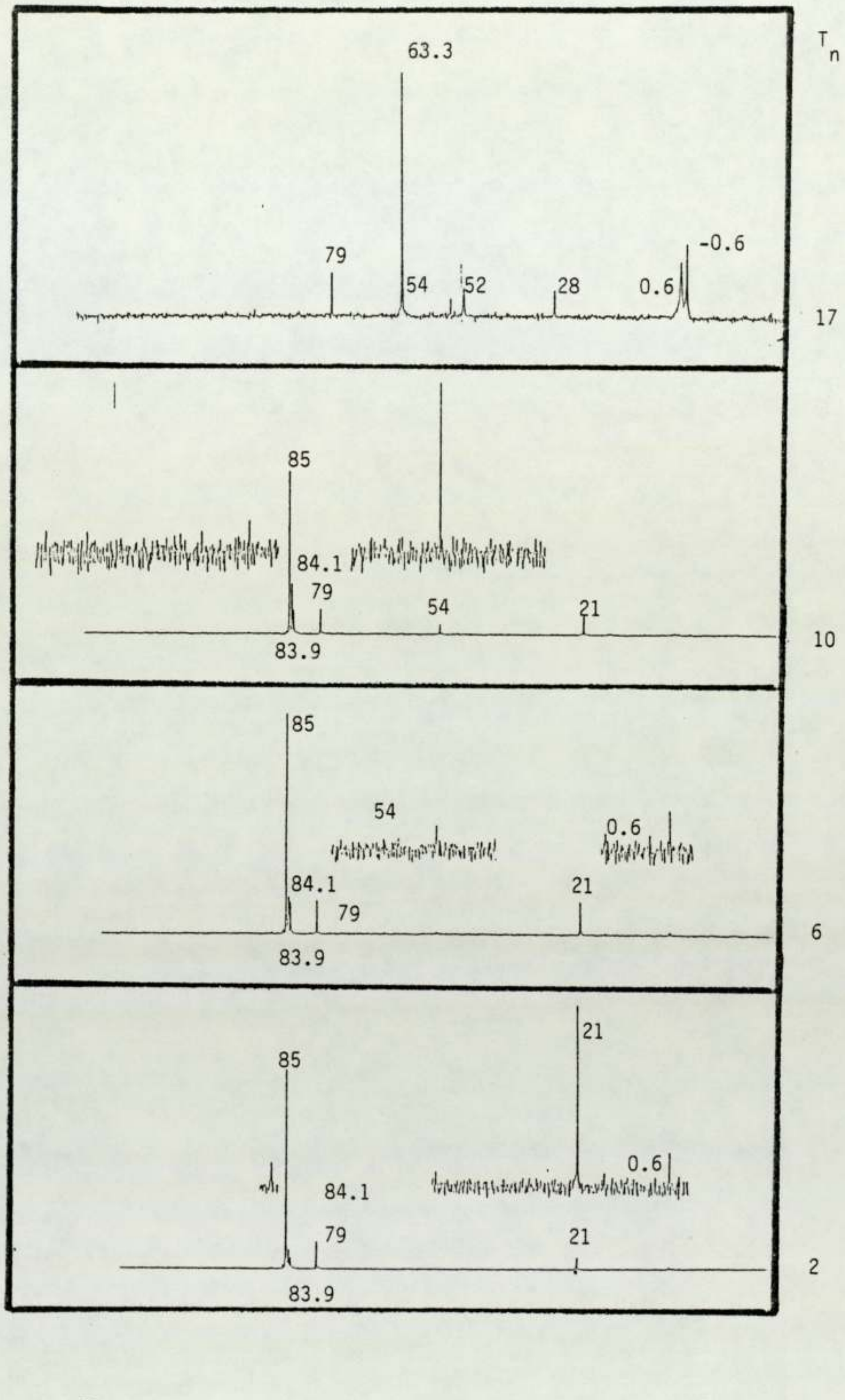


Figure 5.14 ^{31}P NMR spectra of products formed during the thermal oxidation of DnBDS by TBH in Cumene at 100°C. Numbers on the signals are chemical shifts in ppm; and Tn refer to reaction times in hours.

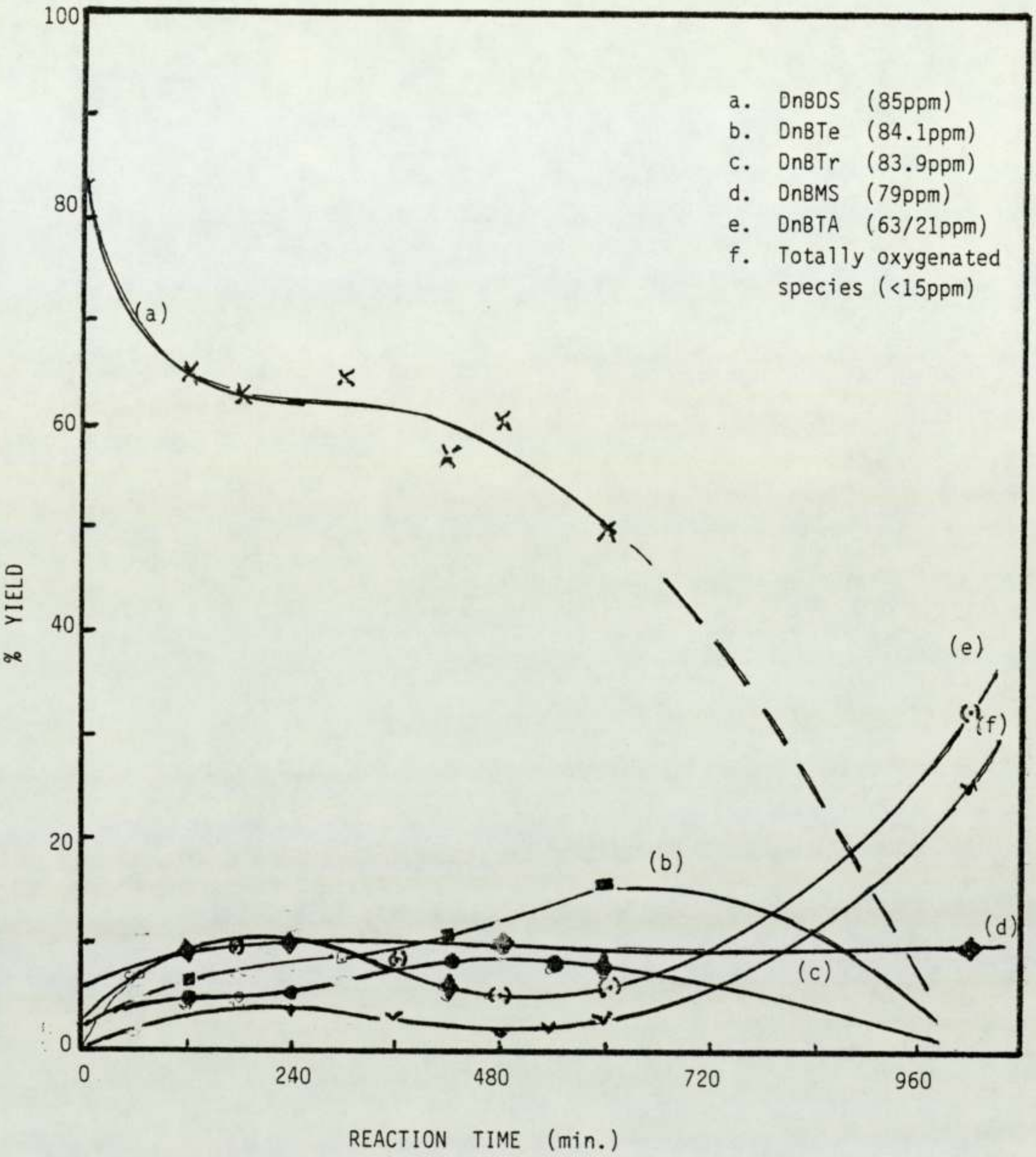


Figure 5.15a Products of the oxidation of DnBDS (0.5M) by TBH (1.0M) in cumene at 100°C . % yields were calculated from NMR signal peak intensities.

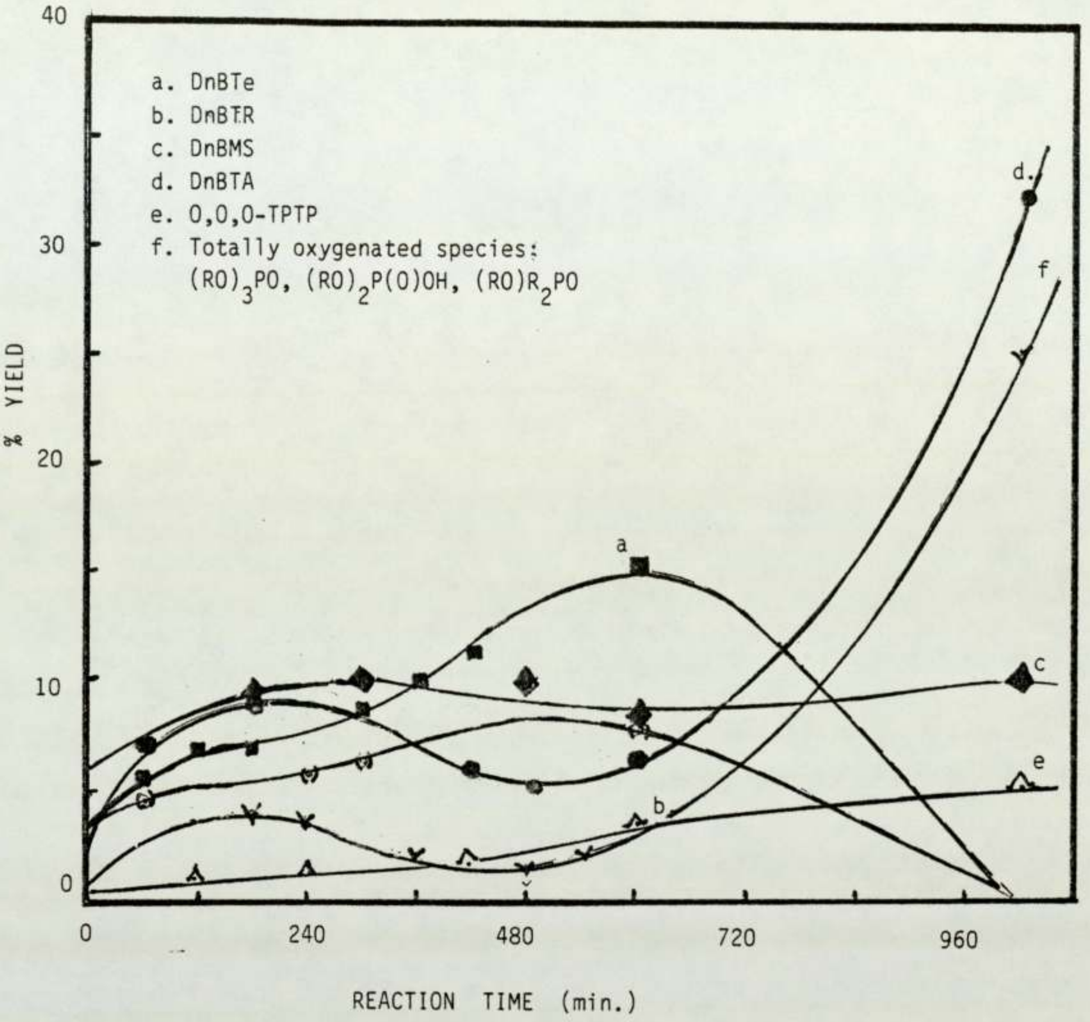


Figure. 5.15b. Products of the oxidation of DnBDS by TBH (2:1 molar excess of TBH) in cumene at 100°C.

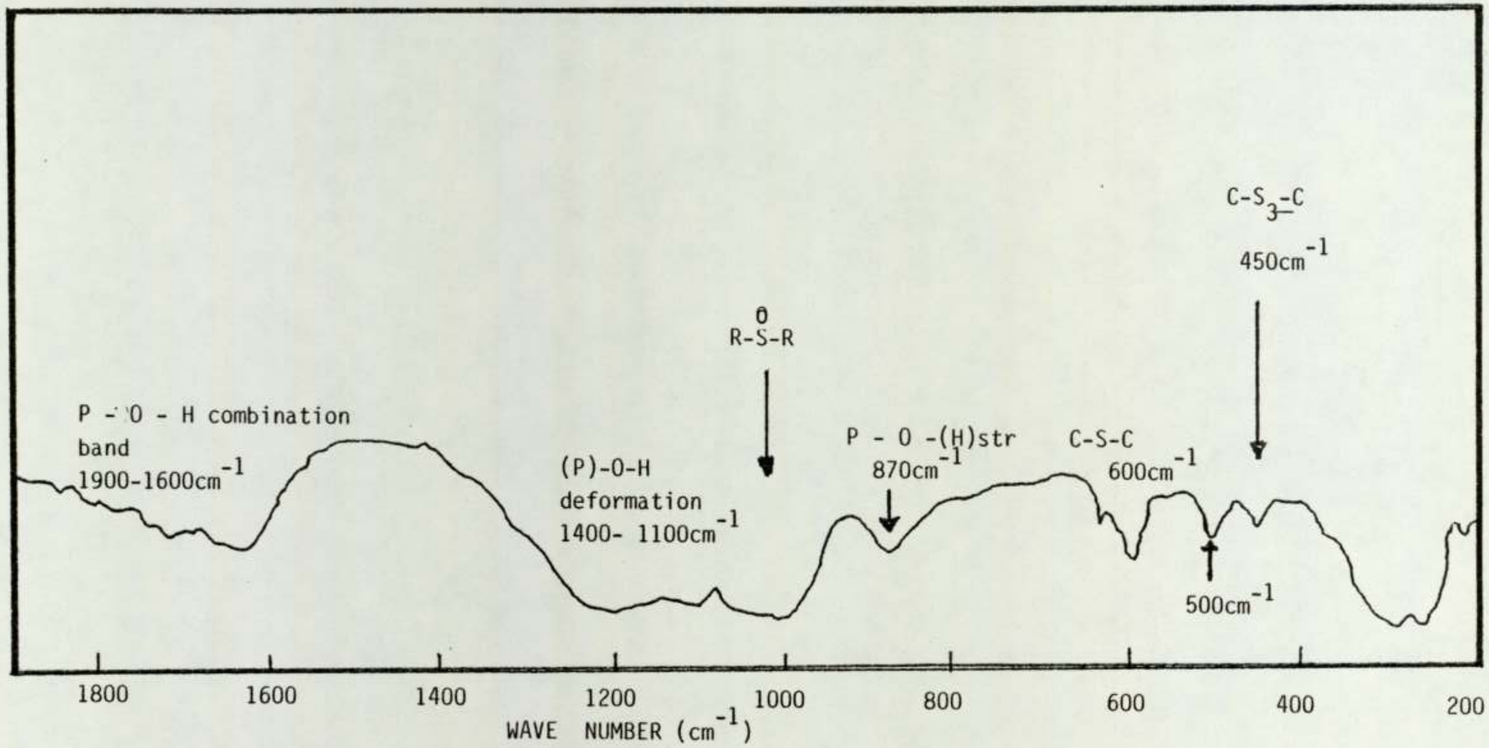


Figure 5.16 Infra-red spectrum of the brownish liquid isolated after 17 hours thermal oxidation of DnBDS by TBH in Cumene at 100°C (Thin film on KBr disc).

5.2.3 Oxidation of NiDnBP by TBH at 25°C

The composition of the soluble products of the oxidation of NiDnBP by TBH (at different molar ratios) in cyclohexane, as measured by ^{31}P NMR, is shown in Table 5.10 along with the peak assignments.

All the ^{31}P NMR signals listed in Table 5.10 with the exception of a few (**), were assigned on the basis of their identify with that of authentic samples prepared in this work.

A green precipitate was isolated after 24 hours reaction (Ratio=10) and was identified as hydrated nickel sulphate ($NiSO_4.nH_2O$) with melting point > 300°C ($-H_2O$,100°C). A positive sulphate analysis was accomplished via the precipitation of barium sulphate on addition of a barium chloride solution to an aqueous solution of the nickel sulphate.

Qualitative representations of the chemical changes occuring during each reaction as measured by both ^{31}P NMR and IR, are illustrated in Figures 5.17 and 5.18 while Figure 5.19 shows the relative abundance of the major products formed. The infrared spectrum of the green "insoluble product" isolated at the end of each reaction is also shown in Figure 5.20.

Table 5.10 Products of the oxidation of NiDnBP (0.3M) by TBH

TBH : NiDnBP	* Product % yield (δ values = ^{31}P chemical shifts in ppm)					
	δ – 94	85	79	63 60	21	Others
Mol. ratio	$[(RO)_2PSS]_2Ni$	$[(RO)_2PSS]_2$	$[(RO)_2PS]_2S$	$(RO)_2PSOH$ $(RO)_2P(H)S$	$(RO)_2POSH$	**
1	89.7	3.6	6.8	X	X	X
2	79.9	7.2	13.2	X	X	X
4	53.3	16.7	26.6	X	X	(54δ) 1.3%
6	50.1	25.8	20.6	1.5	X	(54δ) 2.0%
10	1.9	8.4	46.5	10.8	22.9	10

* Based on the normalization of all peak areas to 100%

Sample shows a signal at 60 ppm. The value due to this signal (2.5%) is included in the total value (10.8%) when TBH:NiDnBP ratio = 10.

** These include triesters such as $(RS)_2(RO)PO$-(54δ), and $(RO)_2(RS)PO$-29δ, the monosulphide $[(RS)_2PS]_2S$ – (91δ), the phosphoryl disulphide $[(RO)_2POS]_2$ – (17δ) and some inorganic phosphates, $(RO)_3PO$ with a chemical shift of 0.9 ppm.

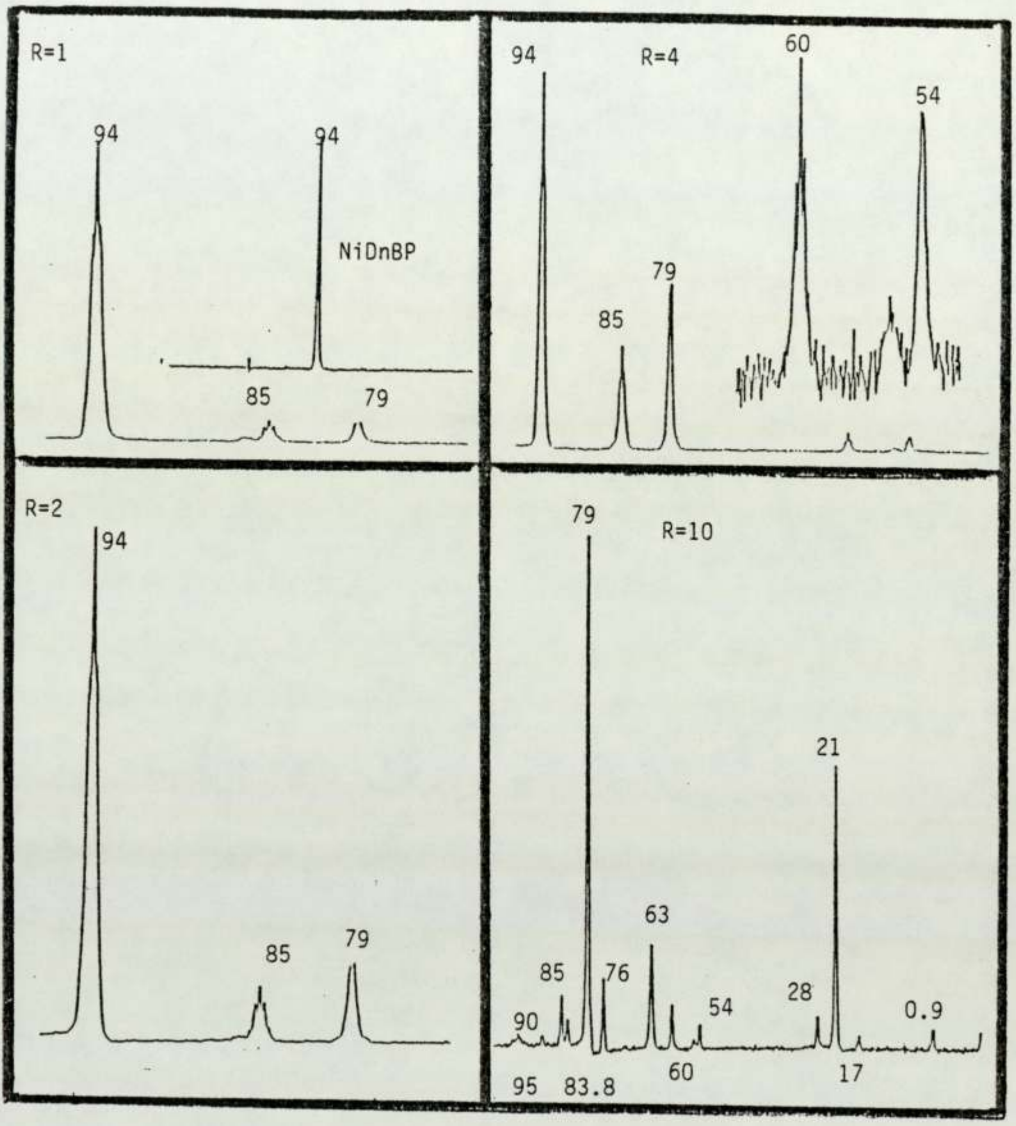


Figure 5.17a. ^{31}P NMR spectra of the oxidation of NiDnBP (0.3M) by TBH in cyclohexane at 25°C after 24 hours reaction. R - 1,2,4 and 10 represent TBH:NiDnBP molar ratios). Sample R = 10 was measured under a slightly different condition i.e XE 6024 Hz as against XE 3012 for samples R = 1 - 4.

Fig. 5.17b.

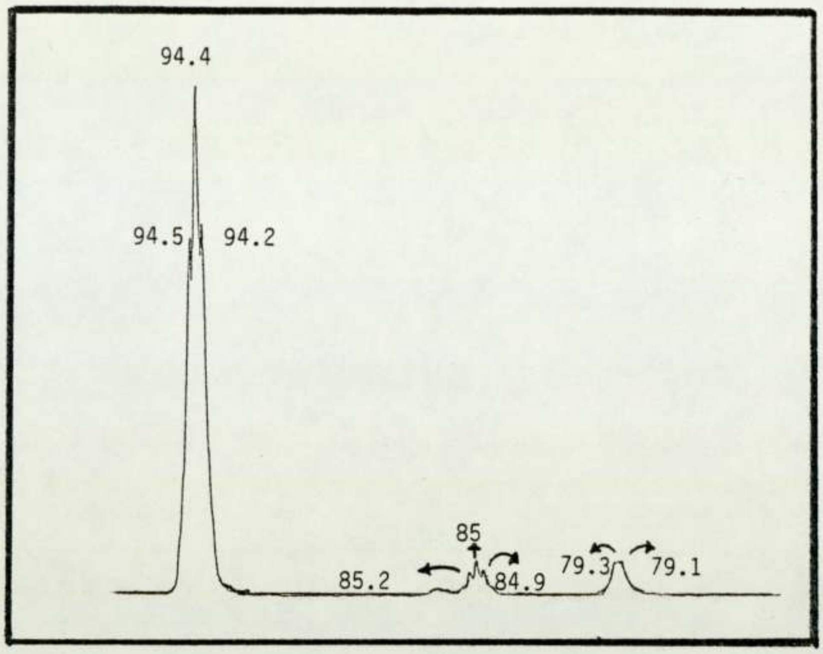


Fig. 5.18.

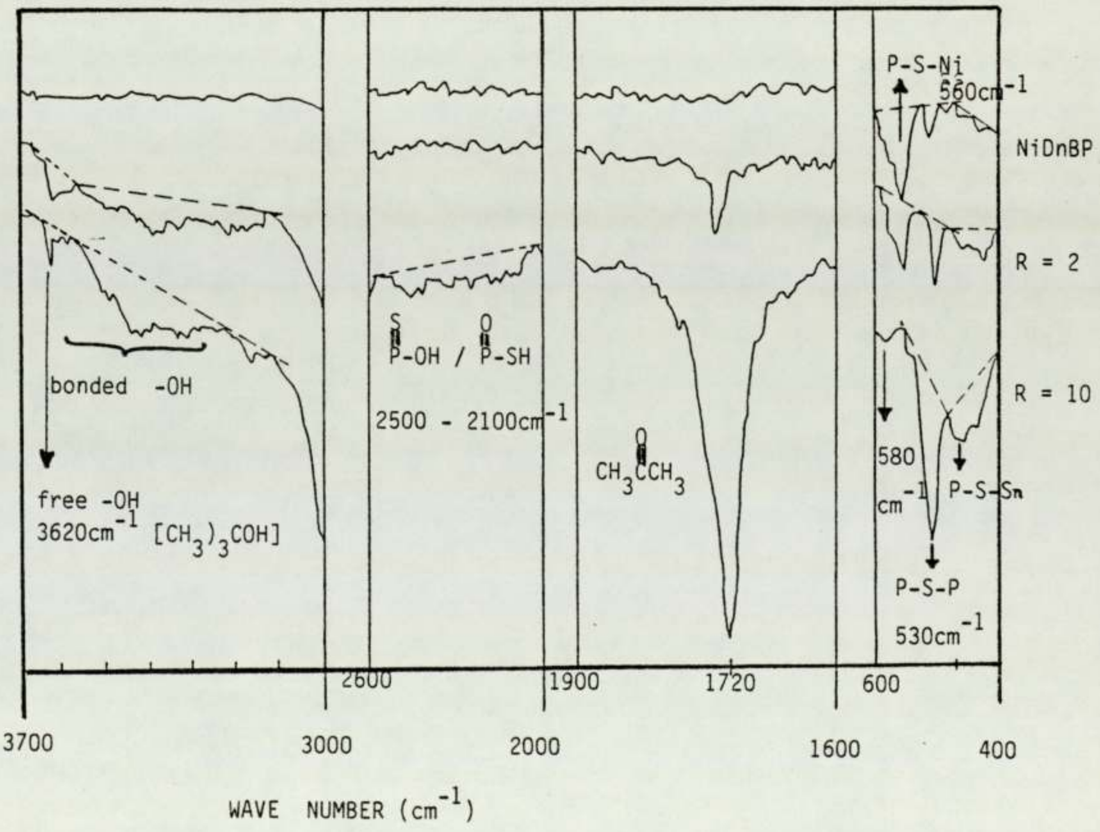


Figure 5.17b. ^{31}P NMR high gain spectrum of the oxidation of NiDnBP by TBH in cyclohyxane at 25°C. (TBH:NiDnBP ratio = 1). Spectrum shows the multiplicity of signals exhibited by the various species

Figure 5.18 Infra-red absorption spectra showing products obtained during the oxidation of NiDnBP by TBH in cyclohexane at 25°C. (TBH:NiDnBP ratios 2:1 and 10:1)

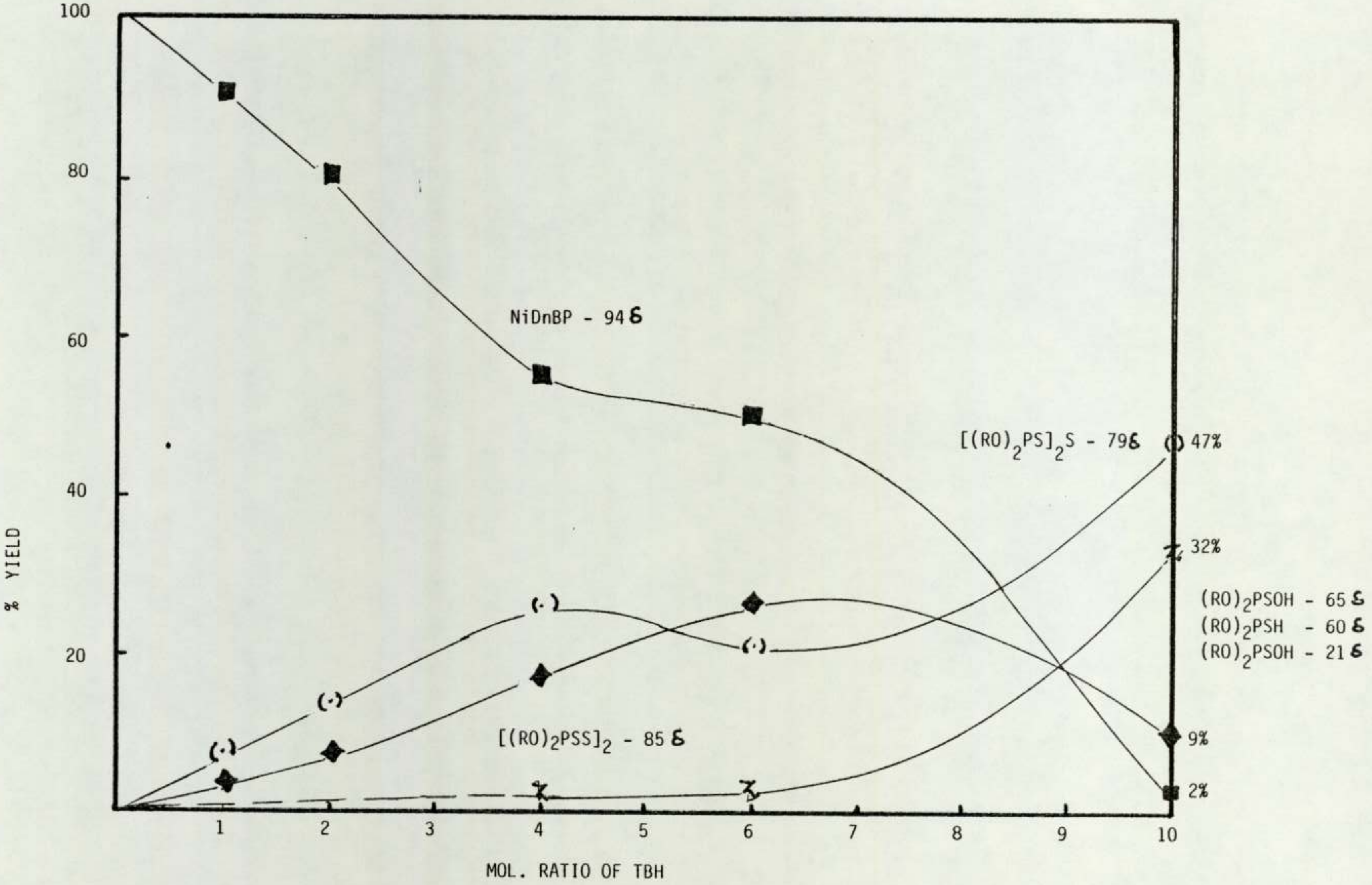


Figure 5.19 Major reaction products|intermediates obtained during the oxidation of NiDnBP by TBH in cyclohexane at 25°C

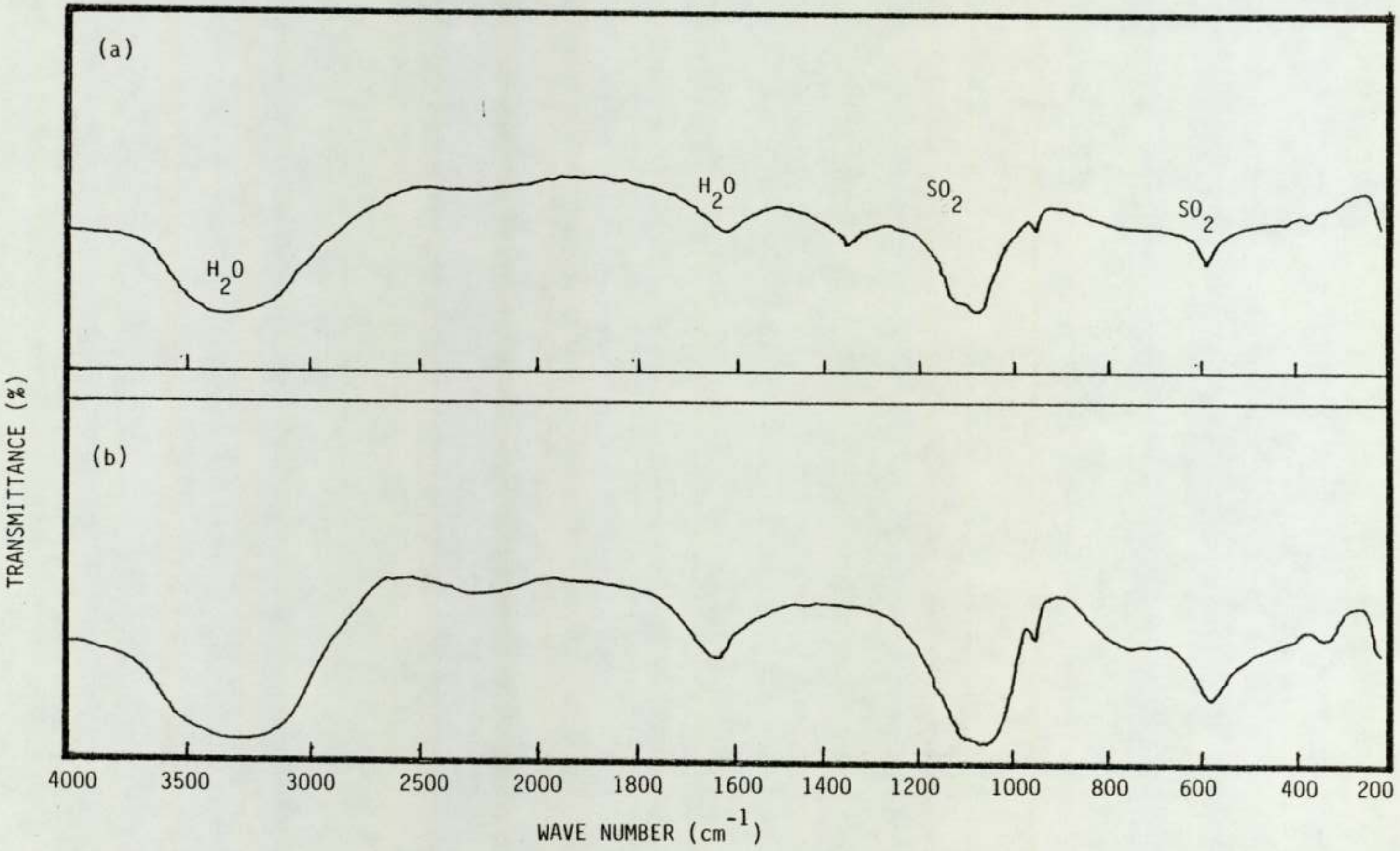


Figure 5.20 Infra-red spectra of (a) an authentic $NiSO_4.6H_2O$ sample and (b) the green "insoluble product" obtained from the oxidation of NiDnBP by TBH (at all ratios examined) in cyclohexane at room temperature (KBr. disc).

It is clear that the oxidation of NiDnBP by TBH leads to the formation of the transformation products having chemical shifts at low fields of the original NiDnBP. This is indicative of the formation of not only nickel-free phosphorus species, but also some equally highly oxygenated phosphorus species.

5.2.4 The use of Reagents as Assignment Aids During ^{31}P NMR Analysis.

The use of triethylamine (R_3N) and tert-butyl hydroperoxide(TBH) as ^{31}P NMR assignment aids was primarily employed for the confirmation of the assignments attributed to both the sulphur acid,DnBTA and the various thiophosphoryl mono-,di-,tri-,and tetra-sulphides (see Tables 5.1,5.2 and 5.4-5.10)

5.2.4(a) Effect of Triethylamine and Tert-butyl Hydroperoxide on the Chemical Shift of Thionophosphoric Acid (DnBTA)

The effect of triethyl amine (b) and tert-butyl hydroperoxide (c) on the chemical shift of a synthesised sample of di-n-butyl thionophosphoric acid (a) is shown in Figure 5.21a-c. It is clear that the interaction of triethyl amine with the sulphur acid (63 ppm) results in the formation of the amine salt (57 ppm) as reflected by the low field shift of the original ^{31}P NMR signal of the acid. The reaction between the acid and TBH also resulted in a low field shift of the original ^{31}P NMR signal. This is indicative of the conversion of the acid from the original thione form (63 . ppm) to the thiol form (21 . ppm) by analogy with assignments given in the previous tables. (Tables 5.4-5.10).

5.2.4(b) Effect of Triethyl Amine on the Chemical Shifts of Thiophosphoryl Polysulphides

The ^{31}P NMR spectra of a synthesised sample of di-n-butyl thiophosphoryl tretrasulphide indicates that the sample is mainly a mixture of di-tri- and tetrasulphides with the latter being the more predominant specie at 59% (see Figure 5.22, t=0). Table 5.11 and Figure 5.22 show products of the reaction between the polysulphide mixture (S_2, S_3, and S_4) and triethyl amine in carbon tetrachloride at room temperature (25°C).

It is clear that the reaction between the polysulphides and triethylamine results initially in incomplete disappearance of the original ^{31}P NMR signals assigned to the tetrasulphide (84.1 . ppm) and dithiophosphoric acid (84.5.ppm) after only five hours reaction. This is clearly associated with the increase in the relative abundance of the disulphide (85 . ppm), the trisulphide (83.8.ppm) and the formation of a new product with a chemical shift of 111.7 ppm assigned to the amine salt of

Table 5.11 Effect of tertiary amine on the chemical shifts of di-n-butyl thiophosphoryl polysulphides.

Reaction time(hrs)	% yield ($\delta = {}^{31}$P chemical shifts in ppm)				
	δ - 111.7	85.0	84.5	84.1	83.8
	$(RO)_2PS\bar{S}R_3NH^+$	$[(RO)_2PSS]_2$	$(RO)_2PSSH$	$[(RO)_2PSS]_2S_2$	$[(RO)_2PSS]_2S$
0	XX	24.2	3.1	58.5	14.2
5	14.8	45.8	XX	XX	40.2
600	42.0	49.0	XX	XX	9.0

the dithiophosphoric acid(93)(Table 5.11 and Figure 5.22). At longer reaction times (> 600 hours), the ^{31}P NMR signal due to the trisulphide (83.8 . ppm) is seen to reduce further while the signals with chemicals shifts of 85 ppm (disulphide) and 111.7 . ppm (amine salt) increased in intensity. The implications of these observations will be discussed in a latter section (Section 5.3.4b).

5.2.4(c) Reaction of Triethylamine with Mixtures of DnBDS/NiDnBP Oxidation Products

Table 5.12 shows the changes observed in the relative abundance and/or chemical shifts of products formed during the oxidation of DnBDS (0.5M) by TBH (1M) in dichlorobenzene (see Section 5.2.2a), when reacted with triethyl amine at room temperature. Table 5.12 and Figure 5.23 show the total disappearance of the signals with chemical shifts of 84.1ppm and 65ppm after only one hour reaction. This again is not only associated with the increase in the relative intensities of ^{31}P NMR signals having chemical shifts of 85 ppm and 83.8 ppm, but also with a reduction in the intensity of the signal with a chemicals shifts of 21 ppm. At the same time, an additional signal having a chemical shift of 57 ppm was formed. At longer reaction times (> 300 hours), the ^{31}P NMR signals having chemical shifts of 21 ppm and 83.8 ppm disappeared completely while the new signals with chemicals shifts of 57 ppm and 112 ppm increased in intensity. The intensity of the signal due to the original disulphide (85 ppm) also reduced. It can be seen that the effect of the tertiaryamine on both the sulphur acids (63 ppm) and 21 ppm) and the various thiophosphoryl polysulphides (85 ppm, 84.1 ppm and 83.8 ppm) formed during the oxidation of DnBDS by TBH (Table 5.12 and Figure 5.23), roughly parallels that shown for the authentic samples (Table 5.11 and Figures 5.21 and 5.22).

Figure 5.24 also shows the effect of triethyl amine on the chemical shifts of products formed after the insitu 17 hours oxidation of DnBDS by TBH in cumene at 100°C (see Section 5.2.2b,Table 5.8 and Figure 5.14). The total disappearance of the ^{31}P NMR signal with a chemical shift

Table 5.12 The effect of triethylamine(at 25^oC) on the products of the oxidation of DnBDS by TBH(1.2) in dichlorobenzene at 100^oC (5 hours oxidation reaction mixture)

Sample	product % yield (values = ^{31}P NMR chemical shifts in ppm)									
	δ 112	85	84.1	83.8	79	63	57	21	< 1.0	others
Reaction time(hours)	$[(RO)_2PSS]^- R_3\overset{+}{N}H$	$[(RO)_2PSS]_2$	$[(RO)_2PSS]_2S_2$	$[(RO)_2PSS]_2S$	$[(RO)_2[S]_2S$	$(RO)_2\overset{S}{\overset{\parallel}{P}}\text{-}OH$	$[(RO)_2P\overset{O}{\underset{S}{<}}]^- R_3\overset{+}{N}H$	$(RO)_2\overset{O}{\overset{\parallel}{P}}\text{-}SH$	$(RO)_3P{=}O$ $(RO)_2P(O)OH$	***
5h. oxidation sample+R_3N	XX	46.2	20.9	11.8	3.7	1.1	XX	9.2	2.2	4.9
1	XX	60.6	XX	15.5	3.8	XX	5.8	5.1	4.2	5.0
2	0.6	64.5	XX	5.3	4.1	XX	11.5	1.0	6.5	6.5
300	12.2	27.8	XX	XX	4.7	XX	32.4	XX	7.4	15.4

*** These include triesters with chemical shifts of 96, 93, 53, and 27ppm.

of 63.3 ppm and the formation of a new signal having a chemical shift of 57.5 ppm, is clearly in accord with the behaviour shown for the authentic sulphur acid (see Figure 5.21).

Table 5.13 and Figure 5.25 show that the addition of triethyl amine to the 10:1 ratio reaction mixture of TBH and NiDnBP results in almost quantitative conversion of the ^{31}P NMR signals due to both forms of the sulphur acid (21 ppm and 63 ppm) to that of the amine salt with a chemical shift of 57.3 ppm.

<u>Table 5.13 The effect of triethyl amine on the chemical shifts of thionophosphoric acid formed during the oxidation of NiDnBP (0.3M) by TBH(3M) in chclohexane at 25°C</u>

	% yield (values= chemical shifts in ppm)			
Sample	$(RO)_2PSOH$ 63δ	$(RO)_2POSH$ 21δ	$[(RO)_2P\overset{S}{\underset{O}{<}}]^- R_3\overset{+}{N}H$ 57.3δ	Others
TBH:NiDnBP soluble portion (R=10)	15.2	9.8	XX	75
+R_3N	XX	XX	24	76

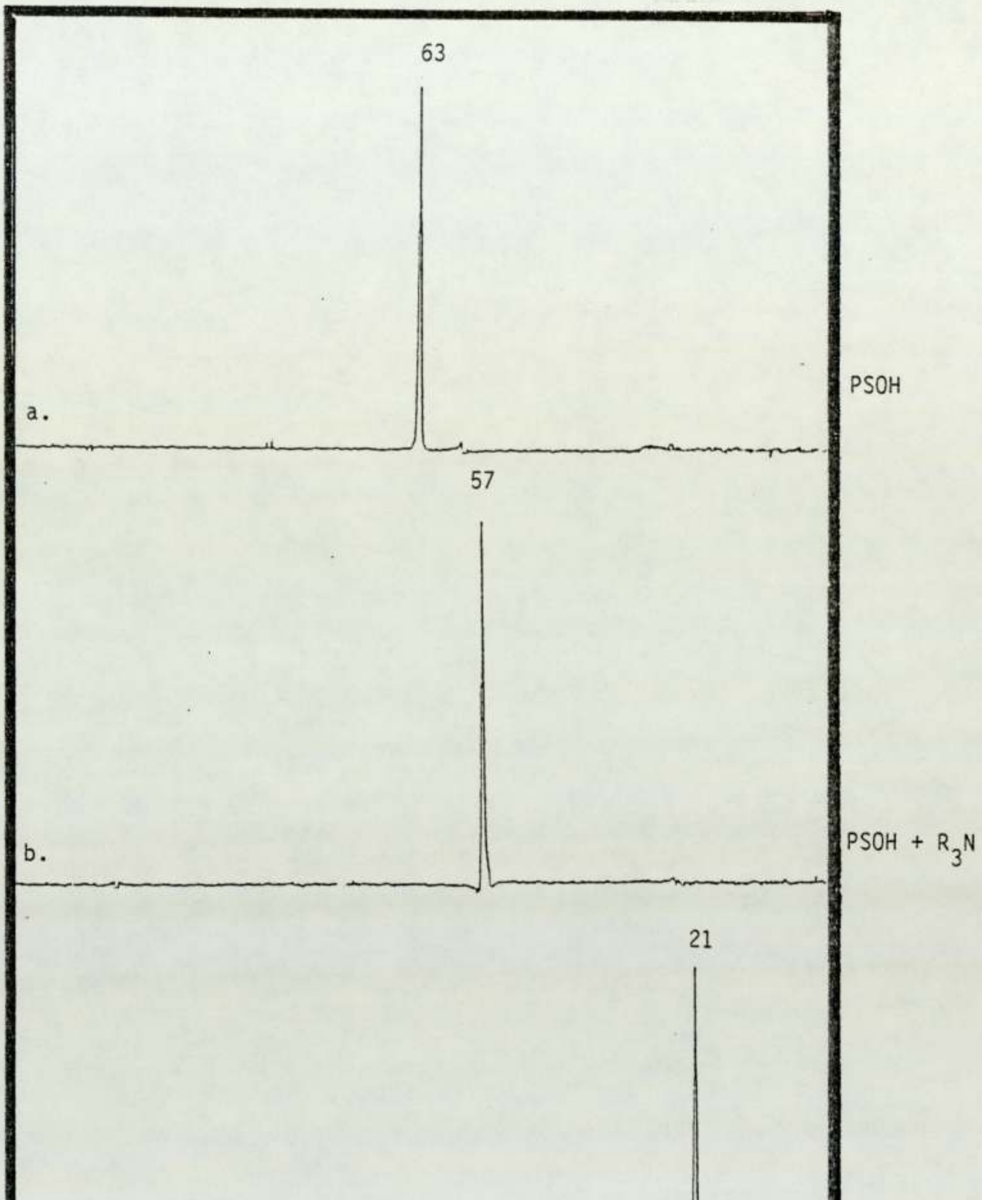


Figure 5.21 The effect of triethyl amine (b) and TBH (c) on the chemical shift of di-n-butyl thionophosphoric acid (a) in chloroform. Numbers on the signals are chemical shifts in ppm.

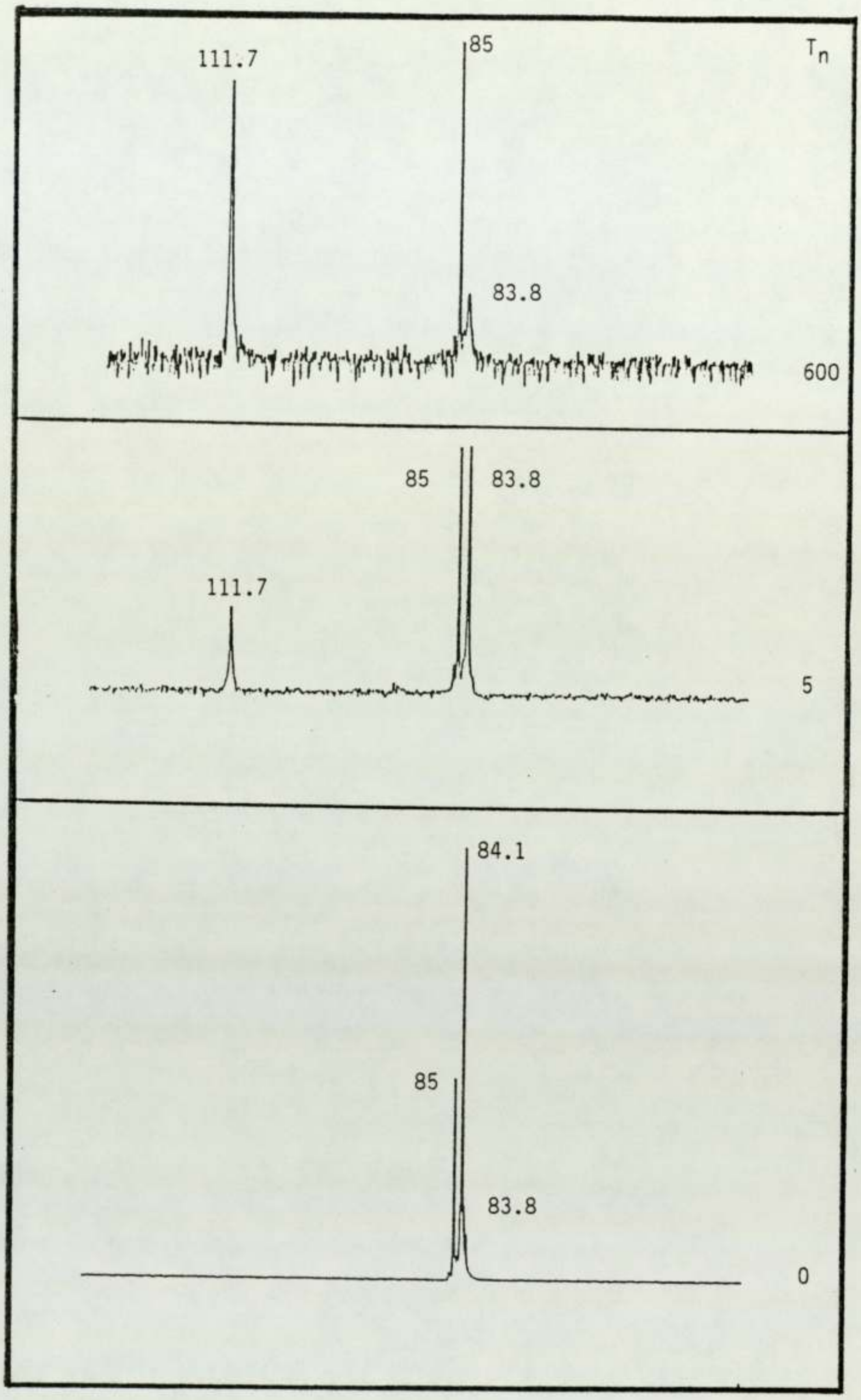


Figure 5.22 ^{31}P NMR spectra of a reaction between triethyl amine (R_3N) and a mixture of thiophosphoryl polysulphides (DnBDS, DnBTr and DnBTe). Assignments to these ^{31}P NMR signals are shown in Table 5.11. T_n refer to reaction times in hours while numbers on the signals are chemical shifts in ppm.

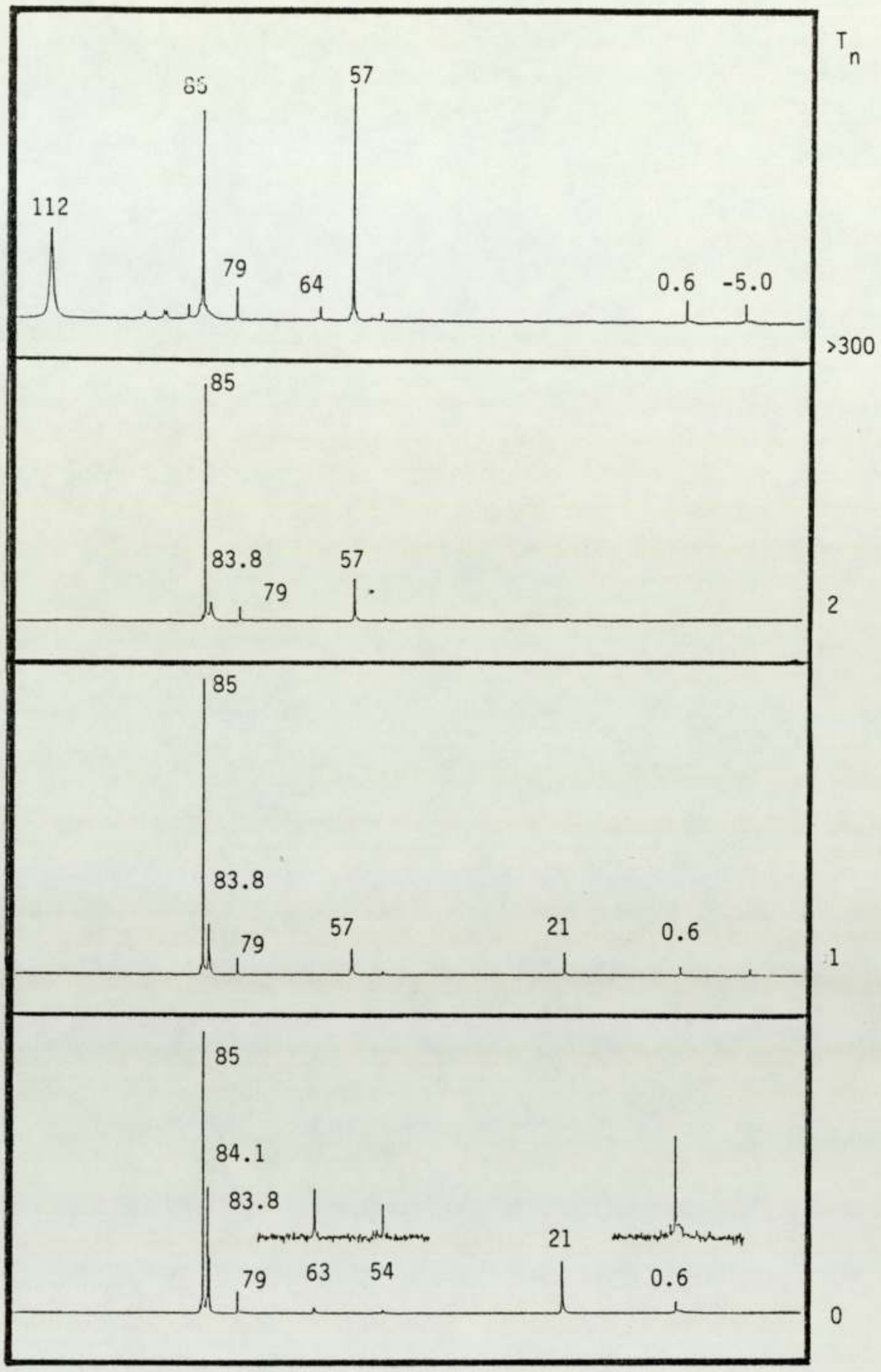


Figure 5.23 ^{31}P NMR spectra of the RT reaction between triethyl amine (R_3N) and the 5 hour TBH:DnBDS oxidation reaction mixture in dichlorobenzene at (100°C) [TBH:DnBDS ratio = 2]. T_n refer to reaction time in hours

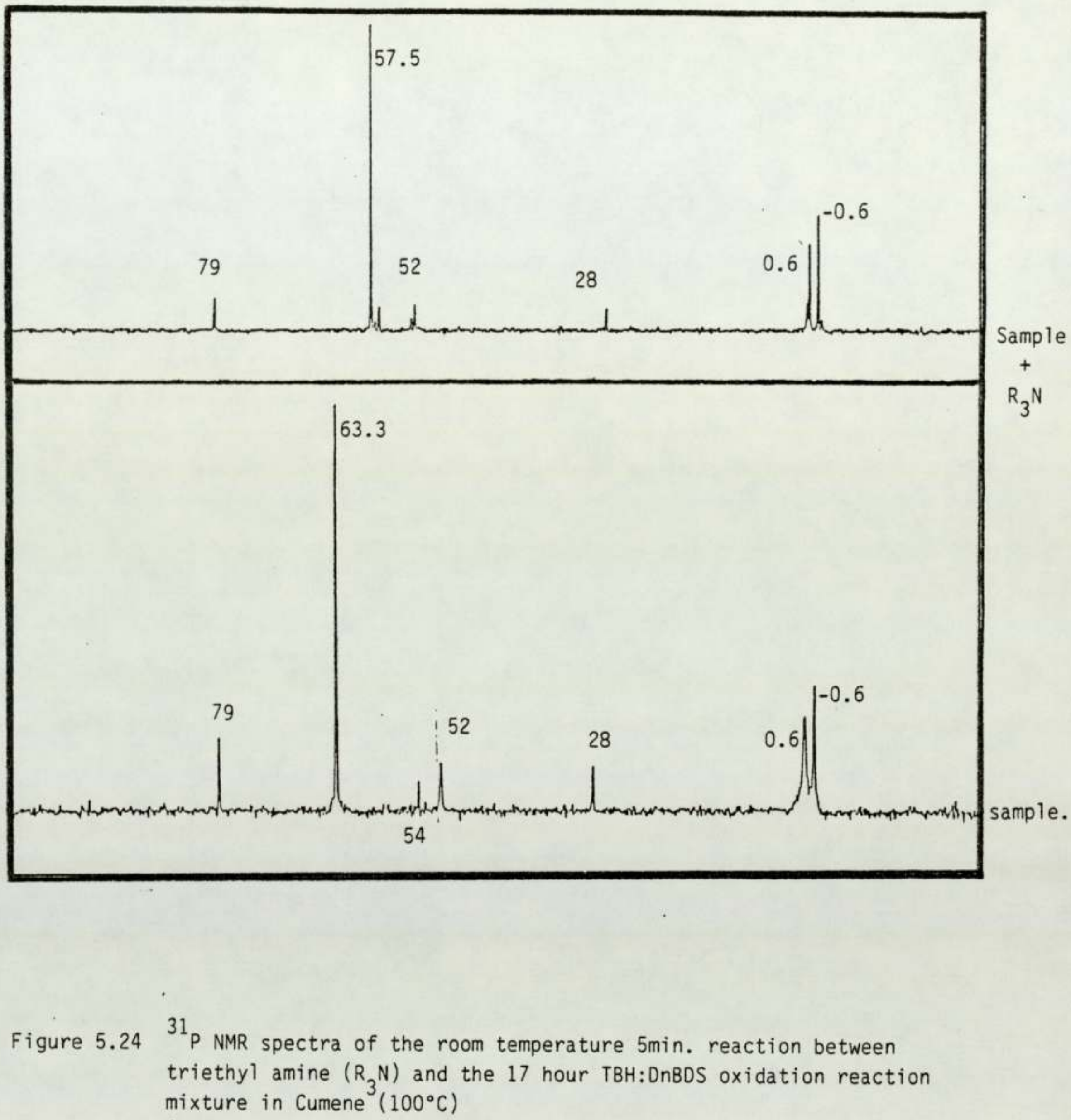
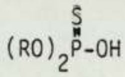
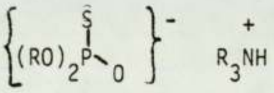


Figure 5.24 ^{31}P NMR spectra of the room temperature 5min. reaction between triethyl amine (R_3N) and the 17 hour TBH:DnBDS oxidation reaction mixture in Cumene (100°C)
(TBH:DnBDS ratio = 2)

63 ppm -

$(RO)_2\overset{S}{\overset{\|}{P}}-OH$

57 ppm -

$\left\{(RO)_2\overset{S}{\overset{|}{P}}\diagdown O\right\}^- \quad R_3\overset{+}{N}H$

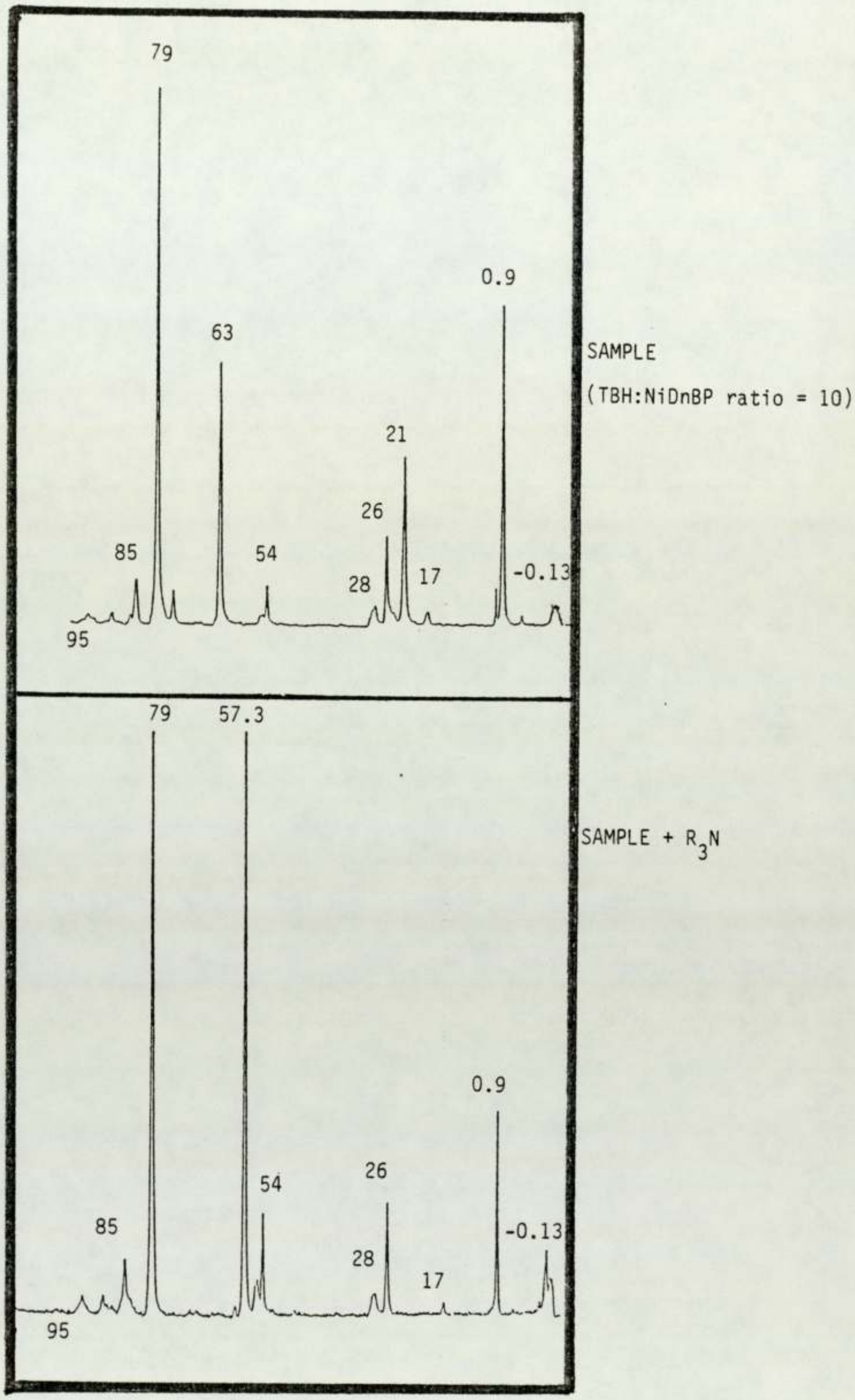
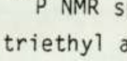
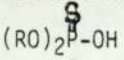


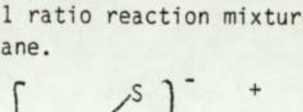
Figure 5.25 ^{31}P NMR spectra of the room temperature reaction of triethyl amine and the 10:1 ratio reaction mixture of TBH and NiDnBP in cyclohexane.



$(RO)_2\overset{S}{\overset{\|}{P}}-OH$ 63ppm



$(RO)_2\overset{O}{\overset{\|}{P}}-SH$ 21ppm



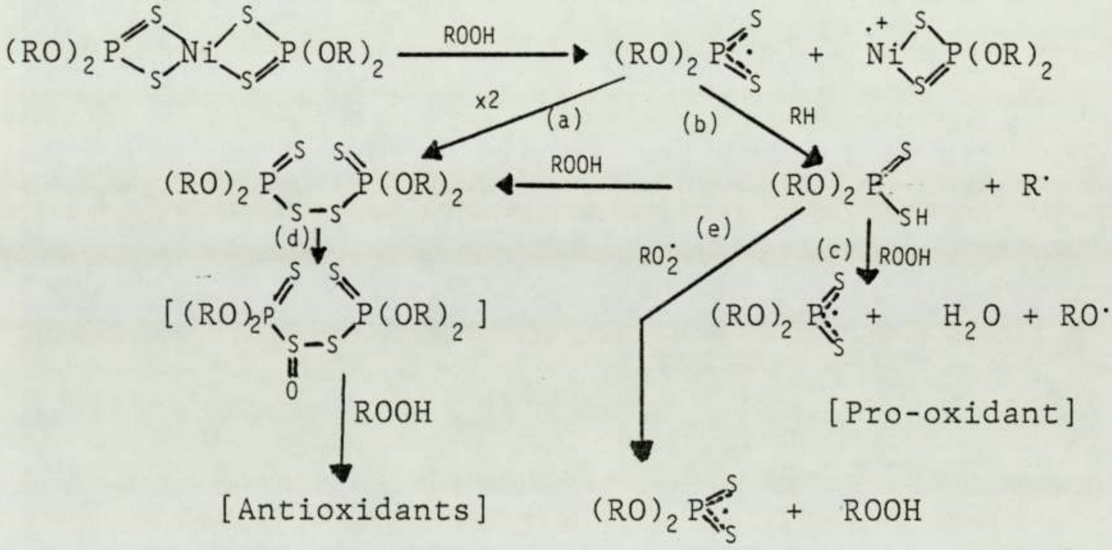
$\left\{(RO)_2P\langle{}^{S}_{O}\right\}^{-}\ \overset{+}{R_3NH}$

57.3ppm

5.3 Discussion

The mechanism involved in the antioxidant activity of dithiophosphates in polyolefins have been described and viewed(5a,45,90) in terms of a series of reactions culminating in the formation of the catalyst responsible for the decomposition of hydroperoxides. The results were interpreted in terms of the folowing reactions, which depicts the two main stages frequently shown by these compounds.

Scheme 5.1 Antioxidant and pro-oxidant mechanisms of DTPs



However, the pro-oxidant stage involving the dialkyldithiophosphoric acid (reaction c) may be only transient(25) since Howard(105b) has reported the ability of the free acid to inhibit auto-oxidation of styrene and cyclohexene in model systems. Its activity was explained in terms of the abstraction of the hydrogen attached to sulphur by an alkyl peroxy radical (ROO•), with the thiyl radical being less reactive than ROO• towards propagation

In the present studies the analysis carried out on the heated samples of oxidised DnBDS and NiDnBP (RT) (Section 5.2.1-5.2.3) showed that the oxidation products do not alter appreciably except in cases where experimental conditions differ, and, not surprisingly, the decomposition proceeds more rapidly as decomposition temperature is raised. However, the ^{31}P NMR analyses have proved very useful for the identification of several decomposition products some of which have not previously been identified. For brevity, a summary of the major products identified during this work and their abbreviations which will be used throughout the discussion section, is shown in Table 5.14. The assignments of some of the products in Table 5.14 is based on their identity with authentic samples, and this have been clearly shown in earlier tables.

5.3.1 Thermal Oxidation of DnBDS(185 C)in the Presence of Air

5.3.1(a) Dichlorobenzene as Substrate

The disulphide sample used in this study was only about 96% pure, as determined by ^{31}P NMR analysis (Table 5.1). The ^{31}P NMR spectra of this sample in dichlorobenzene (Figure 5.1a) contains a signal from the disulphide (DnBDS) at 85.1 ppm in addition to signals from

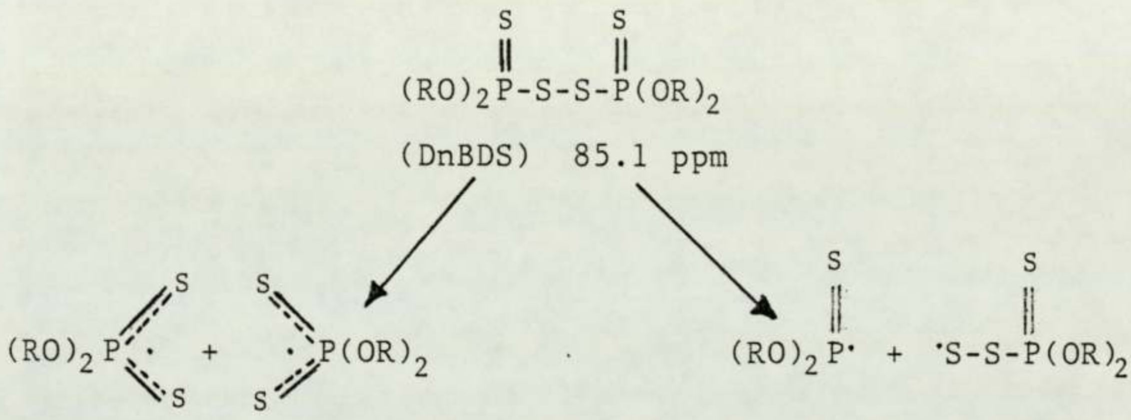
Table 5.14 A summary of DnBDS/NiDnBP decomposition products

Chemical shift(ppm)	structral formula	chemical name	abbreviation
139	$(RO)_3P:$	0,0,0-tri-n-butyl phosphite	0,0,0-TBP
123	$(RS)_3P:$	S,S,S-tri-n-butyl phosphite	S,S,S-TBP
112	$(RS)_2(RO)PS$	0,S,S-tri-n-butyl trithiophosphate	S,S,S-TBTTP
102	$(RO)_2\ (RO)PS$	0,S,S-tri-n-butyl trithiophosphate	0,0,S TBTTP
96	$(RO)_2(RS)PS$	0,S,S-tri-n-butyl dithiophosphate	0,0,S-TBDTP
94	$(RS)_3PS$	S,S,S-tri-n-butyl tetrathiophosphate	S,S,S-TBTP
91	$[(RS)_2PS]_2S$	S,S-bis-/di-n-butyl thiophosphoryl monosulphide	S,S-DnBMS
85	$[(RO)_2PSS]_2$	bis-/di-n-butyl thiophosphoryl disulphide	DnBDS
84.1	$[(RO)_2PSS]_2S_2$	bis-/di-n-butyl thiophosphoryl tetrasulphide	DnBTe
83.8	$[(RO)_2PSS]_2S$	bis-/di-n-butyl thiophosphoryl trisulphide	DnBDr
79	$[(RO)_2PS]_2S$	bis-/di-n-butyl thiophosphoryl monosulphide	0,0-DnBMS
74	$(RO)_3PS\ S$	0,0,0-tri-n-butyl thiophosphate	0,0,0-TBTP
74	$(C_6H_5)Cl_2PS$	dichloro-phenyl thiophosphate	DCPTP
67	$(RS)_3PO$	S,S,S-tri-n-butyl trithiophosphate	S,S,S-TBTTP
64	$(RO)_2PSOH$	di-n-butyl thionophosphoric acid	DnBTA
54	$(RS)_2(RO)PO$	0,S,S-tri-n-butyl dithiophosphate	0,S,S-TBDTP
54	$(R)_3PS$	tri-n-butyl thiophosphine	TBTP
53.1	$(C_6H_5O)_3PS$	0,0,0-tri-phenyl thiophosphate	0,0,0-TPTP
50.6	$(R)_2(RO)PS$	0-tri-n-butyl thiophosphinate	0-TBTP
36.5	$(RO)_2(RS)PO$	0,0,s-tri-n-butyl thiophosphate	0,0,S-TBTB
36.5	$(C_6H_5)Cl_2PO$	dichloro phenyl phosphate	DCPP
31	$(RO)_2(R)PO$	0,0-di-n-butyl alkyl phosphinate	0,0-DBP
28.5	$(RO)_2(RS)PO$	0,0,S-tri-n-butyl thiophosphate	0,0,S-TBTB
21	$(RO)_2POSH$	di-n-butyl thio-phosphoric acid	DnBDA
19	$[(RO)_2POS]_2$	bis-di-n-butylphosphoryl disulphide	DBD
7	$[(RO)_3P]_2O$	bis-tri-n-butyl pyrophosphate	0,0,0-TBPP

impurities at 79 ppm and 74 ppm, respectively assigned to the monosulphide (DnBDS) and a triester 0,0,0-TBTP. Although the relative importance of these impurities in the overall oxidation process is not very clear, both were still present at the end of the reaction (Figure 5.1b). The inset to Figure 5.1a also shows a high gain spectrum of the disulphide and the triester. The multiplicity of peaks as shown for both species is a constant feature of most of the oxidation products observed (see Figure 5.1b), and this phenomenon strongly suggests the isomerisation of the alkyl group even before (under storage) and during oxidation. It is worth mentioning that some workers(105a) have been able to isolate n-propanethiol from the decomposition of zinc di-isopropyl dithiophosphate at 180°C.

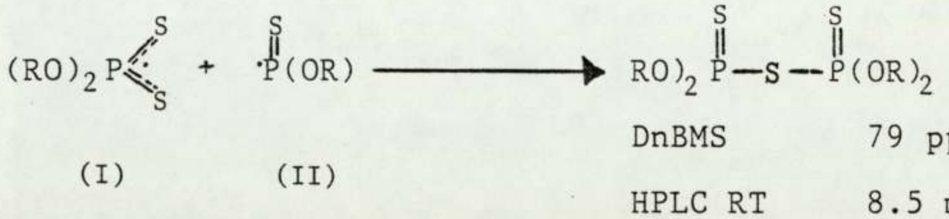
In addition to the impurities (DnBMS and 0,0,0,-TBTP) observed in the ^{31}P NMR spectra of the starting material (DnBDS), the HPLC analysis of a neat DnBDS sample also indicated the presence of the mono-, tri- and tetrasulphides (DnBMS, DnBTr and DnBTe), and two other peaks eluting well before the sulphides with retention times of 4.5 minutes and 2.1 minutes (see Figure 5.2a). Although these other two impurities have not been positively assigned to any particular species, they may well be due to the ester groups observed as impurities by ^{31}P NMR analysis with a chemical shift of 74 ppm (Figure 5.1a). The origin of these impurities can be explained in terms of reactions involving radicals that may have been generated in the disulphide (DnBDS) even at storage temperatures (scheme 5.2).

Scheme 5.2 Radicals formed during the decomposition of DnBDS



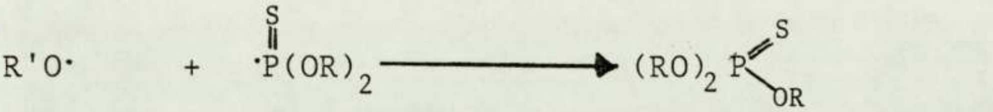
I II III

Radicals I-III (scheme 5.2) have been identified(112) by ESR studies of irradiated (1. KW mecury-xenon lamp/190-300K) bis-di-alkyl thiophosphoryl disulphide. Dudzik and Puppel(113) have also shown that with dithiocarbamates such as tetramethyl thiuram disulphide (TMTD), asymmetric decomposition of the molecule does take place at high temperatures resulting in the formation of a perthiyl radical (R_2 NC(S)SS·) as indicated for dithiophosphates above. Furthermore, it is highly likely that any remaining solvent in the disulphide sample may be oxidised to a hydroperoxide following intermittent exposure of the sample to air. Thus, the initial impurities as indicated by ^{31}P NMR (Figure 5.1a) and HPLC (Figure 5.2a) can therefore be formed via the folowing reactions.



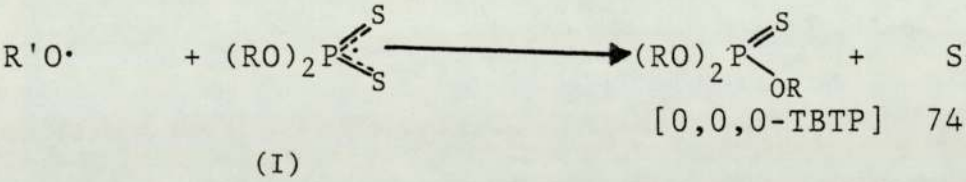
DnBMS 79 ppm (5.1)

HPLC RT 8.5 min.



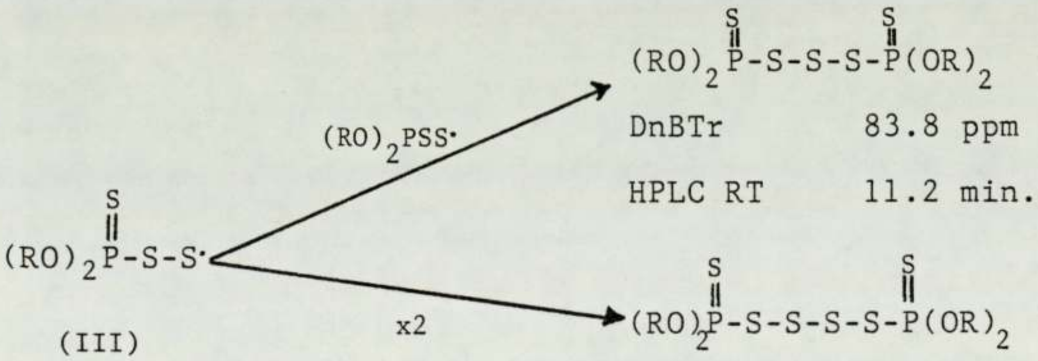
(5.2a)

0,0,0-TBTP 74 ppm



(5.2b)

[0,0,0-TBTP] 74 ppm



(5.3)

DnBTr 83.8 ppm

HPLC RT 11.2 min.

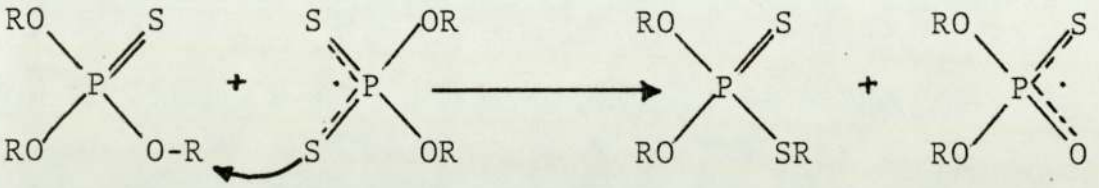
(5.4)

DnBTe 84.1 ppm

HPLC RT 12.9 min.

It should be noted that although the tri-and tetrasulphides were not positively identified as impurities by ^{31}P NMR in view of the multiplicity of peaks in the region (Figure 5.1a), the HPLC chromatogram of the disulphide sample (see table 5.3 and Figure 5.2a) clearly confirms the presence of these species as impurities, assigned on the basis of their identity with authentic standards. As shown above, the phosphorothionate impurity may originate either from an interaction between an alkoxy radical (from ROOH) and a phosphorus-centred radical (reaction 5.2a) or the displacement of a sulphur atom from a thiyl radical by the alkoxy radical (reaction 5.2b). Furthermore, the formation of these impurities (reaction 5.1-5.4) involve all radicals formed in the radical generating routes shown in scheme 5.2 which include both the symmetric and asymmetric decomposition of the disulphide.

After only two hours heating time there is clear evidence (Table 5.1, Figures 5.1b and 5.4) that a high proportion of the disulphide still remains undecomposed, although the ^{31}P NMR spectrum (Figure 5.1b) indicates the formation of major reaction intermediates with chemical shifts of 96,91,83.9,67 and 54 . ppm. These are assigned to O,O,S-TBDTP, S-S-DnBMS, DnBTr, S,S,S-TBTTP and O,S,S-TBDTP respectively. The formation of the trisulphide DnBTr has been shown (reaction5.3) to occur via a reaction between the thiyl (I) and perthiyl (III) radicals initially formed from DnBDS as shown in scheme 5.2. The triester O,O,S - TBDTP (96 . ppm) is most probably formed via an intermolecular alkylation-dealkylation reaction (reaction 5.5a) initiated by 0,0,0,-TBTP (74 ppm) which was clearly shown (Table 5.1, Figures 5.1b and 5.4) to be present as an impurity in the disulphide sample (see also reaction 5.2a-b).



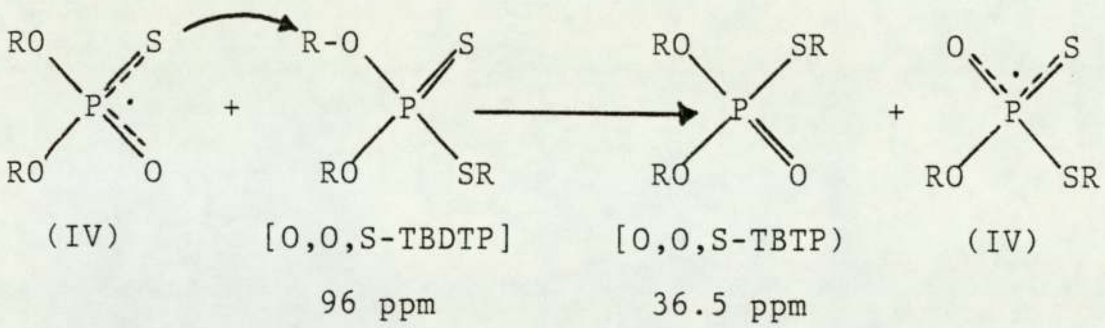
0,0,0-TBTP (I) 0,0,S-TBDTP (IV)
74ppm 96ppm

(5.5a)

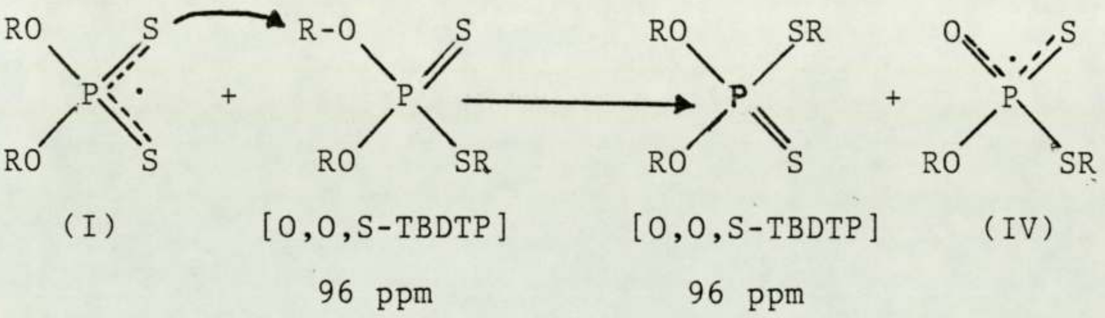
It is known that thiol,thione or dithio-phosphorus compounds which possess at least one alkoxy group exhibit alkylating properties, and the alkylating process consists of the heterolysis of the O-C bond by nucleophilic attack on the C-O carbon by an $S_N2(P)$ mechanism.(100,105b,141) In principle, the thiophosphoryl (P=S) and phosphoryl (P=O) groups have greatly differing reactivity as nucleophiles, which can be explained on the basis of the "hard" and "soft" acid and base concept. Thus, the thiophosphoryl (-P=S) group is a typical soft base, since the sulphur has a low overall nuclear charge (due to the low polarity of the P=S bond) and high polarizability (since the sulphur atom is large and diffuse.). The phosphoryl group (-P=O) on the other hand, is a typical hard base, since the oxygen atom carries a high nuclear charge (due to high polarity of the P=O bond) and a low polarizability (the oxygen atom being much smaller and less diffuse than the sulphur atom). Hence, where competition occurs, sulphur is alkylated in preference to oxygen where as oxygen and not sulphur reacts preferentially with tetrahedral phosphorus (105b). This is consistent with the general principle of the theory that soft acids preferentially react with soft bases (P=S), and hard acids with hard bases (P=O).

Since the resulting thiol ester O,O,S - TBDTP is a stronger alkylating agent than the thione ester O,O,S - TBTP, it may therefore either re-alkylate the thione radical (IV) or alkylate another thiyl radical (1) according to reaction 5.5b-c.

A similar, but ionic, mechanistic reaction sequence was previously postulated for the formation of various thiolphosphate esters during thermal degradation of zinc dialkyldithiophosphates (ZnDTPs) in white oil, under very identical conditions (180°C/air stream) as that used in this study. This is highly indicative of the co-existence of both radical and ionic mechanisms under such severe conditions.

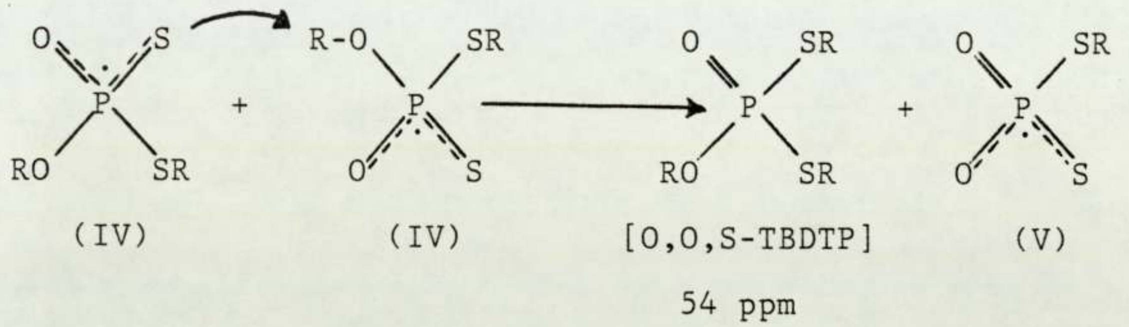


(5.5b)



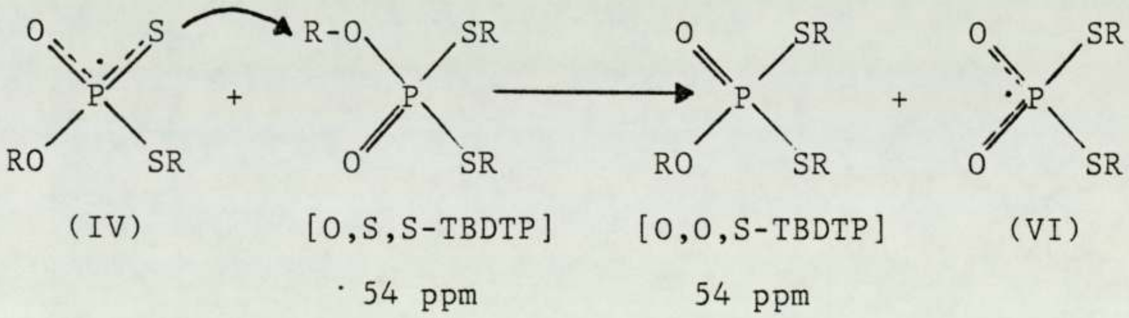
(5.5c)

There seems little doubt that the predominant pathway at this stage of the reaction (1-2 hours) is the alkylation of the thiyl radical (reaction 5.5c) since the product of the realkylation of the thione radical (reaction 5.5b) is the thiol isomer (O,O,S-TBTP) of the initial alkylating agent O,O,O-TBTP (74 ppm), and this product (36.5 ppm) was not observed by ^{31}P NMR until the later stages of the reaction (4-6 hours). The net result of reactions 5.5a-c is the migration of an alkyl group from oxygen to sulphur and this may become autocatalytic once the concentration of the triester O,O,S-TBDTP (96 ppm) has reached a finite level. In parallel with this reaction, the triester O,O,S-TBDTP (54 ppm) is simultaneously formed from a similar intermolecular alkylation - dealkylation reaction between the thione radical (IV), and it can be seen that this reaction sequence (reaction 5.6a-b) also results in the migration of a second alkyl group from oxygen to sulphur.



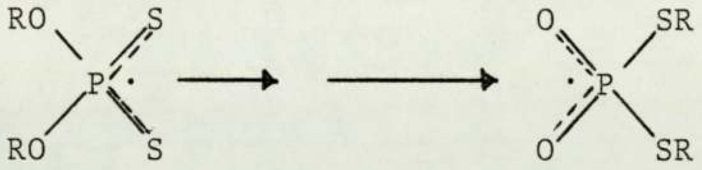
(5.6a)

The second migration is also expected(105b) to become autocatalytic as the concentration of the triester [O,S,S,-TBDTP] reaches a finite value, thus avoiding the generation of the polar thione radical (V) as shown in reaction 5.6b.



(5.6b)

The reaction of (IV) with (I) to give the triester plus a polar thiyl radical is also possible. Thus, the overall consequence of reactions 5.5-5.6 is a double alkyl migration from oxygen atoms to sulphur atoms (reaction 5.7) and this seems to account for the much higher rapid build-up in relative abundance of this triester with a chemical shift of 54 ppm compared to that (O,O,S-TBDTP) with a chemical shift of 96 ppm (see Table 5.1 and Figure 5.1b).

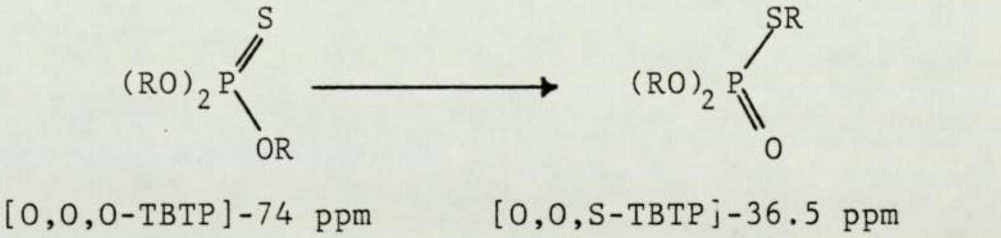


(5.7)

The build-up in relative abundance of these triesters [O,O,S-TBDTP and O.S.S-TBDTP] and the polysulphides DnBTr (83.8 ppm) and DnBTe (HPLC RT - 12.9 min.), all of which constitute the major reaction intermediates (3-5 hours), reached a maximum after five hours oxidation (Tables 5.1-5.3 and Figure 5.4) before showing signs of decay. Interestingly, the period of transition (5-6 hours), as distinctly illustrated in Figures 5.1b; 5.2b; 5.4; and 5.5; roughly coincides with the time at which the original colour of the DnBDS reaction mixture gradually changed from yellow to brown, during which time the disulphide content had also already reduced to less than 16%. The fact that the rapid decay of the polysulphides after five hours reaction roughly corresponds to the time during which the colour changes in the reaction mixture was observed, provides clear evidence that these components are merely decomposition intermediates which are subsequently further decomposed to yield more products. It must, however be pointed out that similar colour development have been reported (Section 4.3D.1.) to occur during thermal oxidative ageing(air oven at 150 °C of polypropylene 1 mm plaques containing thiophosphoryl dilute concentrates (see Plate 2)

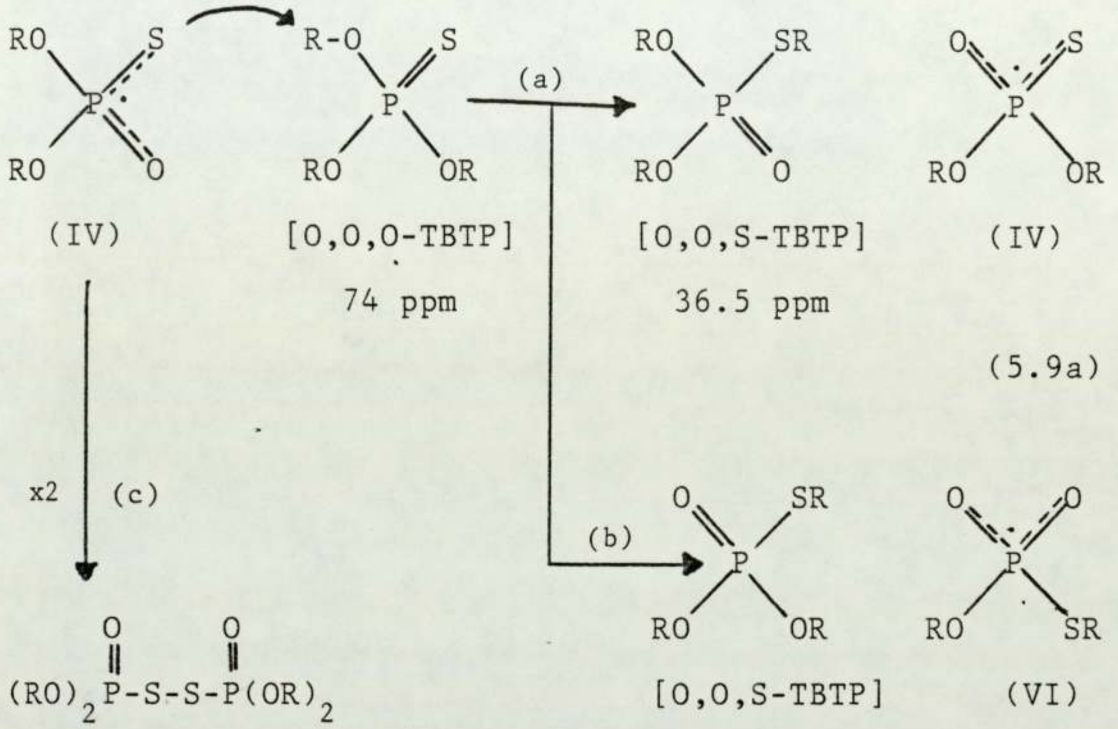
Further evidence regarding the migration of the alkyl functions from oxygen atoms to sulphur atoms, as typified by reaction 5.7 is illustrated in Figure 5.3 which shows the infra-red spectra of the reaction mixture at two hourly intervals. The very intense absorption bands at 560 cm^{-1} and 490 cm^{-1} confirms the strong presence of phosphorothioates(82) after only two hours reaction. Several authors(82) have assigned an overall range of 645 - 475 cm^{-1} to P-S-(C) vibrations in pentavalent phosphorus species and compounds of the type $(RO)_2PSSR$ 966, $(RS)_3PS$ - 946, $(RO)_3PS$ - 746, and $(RS)_2(RO)PO$ - 546 all show absorption bands within this range. The 490 cm^{-1} absorption band may also include absorption due to the polysulphides (DnBTr and DnBTe) which have been shown to absorb in the IR region of 470 cm^{-1} (see Figure 5.3 and also Chapter 2) . It is interesting to note that the formation of the P-S-(C)absorption bands roughly parallels the gradual decay of the P-O-(C) stretching modes at 900 cm^{-1} and 850 cm^{-1} , which eventually disappeared at the end of the reaction (Figure 5.3).

After four hours oxidation, a new ^{31}P NMR signal with chemical shift of 36.5 ppm was observed and assigned to O,O,S-TBTP. As proposed earlier (reaction 5.5b), the formation of this product may result from realkylation of the thione radical (IV) by the triester O,O,S-TBDTP (96. ppm). Alternatively, and most probably, the formation of this specie may arise from the thermal isomerisation of the thione analogue O,O,O-TBTP (74 ppm) which originally was present as an impurity in the DnBDS starting material (reaction 5.8).



(5.8)

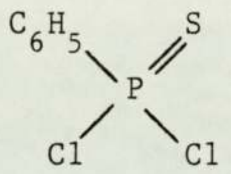
Such isomerisation reactions (reaction 5.8) of O,O,O-triesters of thiophosphoric acid with no nucleophilic centre have been known(141) to require temperatures of 120°C - 180°C for activation. There seems little doubt that the frequent isomerisation of this triester O,O,O-TBTP during alkylation of either a thiyl radical (reaction 5.5a) or the ambident thione radical (reaction 5.9), is a direct consequence of the previously stated principles involved in the chemistry of thiophosphate esters. Thus, the ambident O,O-dialkyl thiophosphate radical (IV)is first alkylated by the triester O,O,O-TBTP (74 ppm), with self-regeneration, to form the thiol ester O,O,S-TBTP (36.5 ppm).



(5.9a)

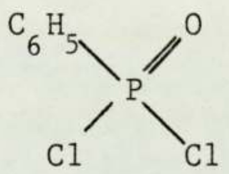
(5.9b)

The latter is then dealkylated (reaction 5.9b) by the same radical (IV) with generation of O,O,S-TBTP, to form the O,S-thiophosphate radical (VI), and in all cases the alkyl donors are always the alkoxy (-OR), never the alkyl thio (-SR) groups. However, it must be emphasised that the ^{31}P NMR chemical shift value quoted for this specie (36.5 ppm) is about 8 ppm higher than literature values (26-29 ppm)(106,114,119) There is no adequate explanation for this difference in values although it may well be solvent shifts due to other decomposition products(105a) or simply a function of the reaction enviroment. Muller and Goldenson(114) assigned ^{31}P NMR chemical shifts of 68.1 ppm and 26.4 ppm to similar species (when R = ethyl, i.e. O,O,O-TETP and O,O,S-TETP), although in the same work involving the ^{31}P NMR analysis of over fifty synthesized compounds, the ^{31}P NMR shifts of 74 ppm and 36.5 ppm as shown in reaction 5.8 were assigned to the following structures:



[DCPTP]-74.8 ppm

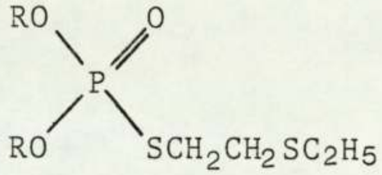
(VIIa)



(DCPP]-34.5 ppm

(VIIb)

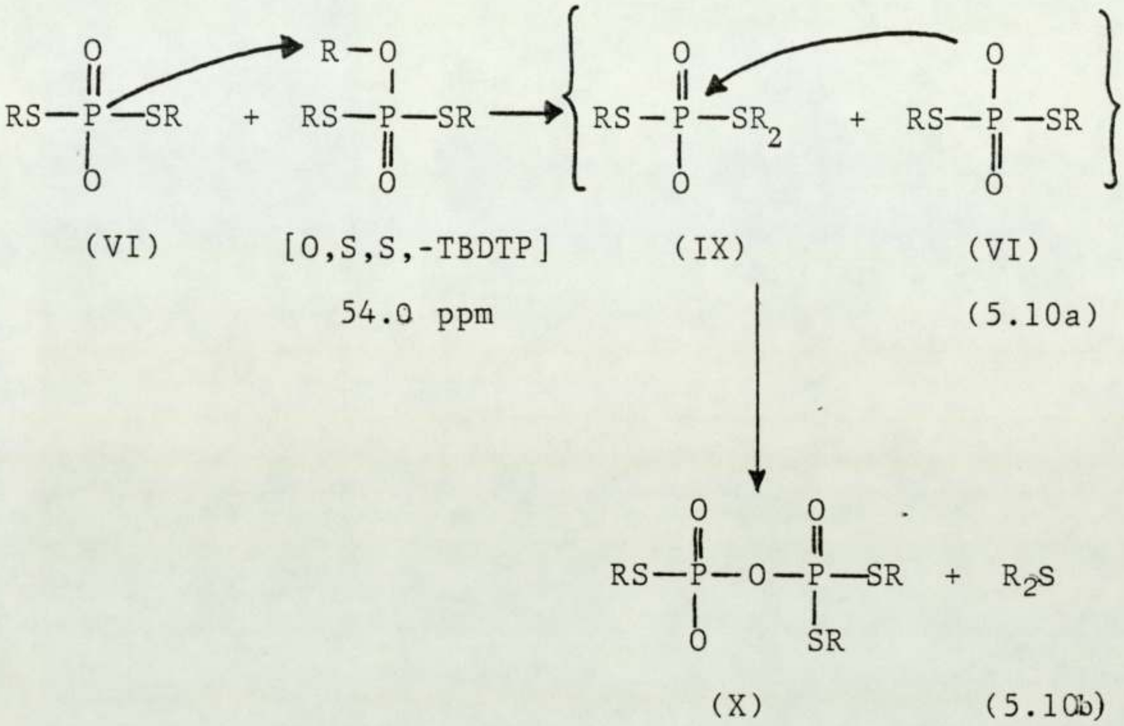
The formation of these products (DCPTP and DCPP) can reasonably be accounted for since the reaction substrate (dichlorobenzene) is only 97% pure and may contain impurities such as catalyst residues (Cl_2) and phenol which is formed as a byproduct during the preparation of dichlorobenzene. However, the isomerisation phenomenon is confirmed by the fact that the ^{31}P NMR signal with a chemical shift of 36.5 ppm builds up when that at 74ppm starts to decay after four hours reaction (see Figures 5.1b and 5.4b). The ethyl analogue of this triester, β-ethylthioethyl diethyl phosphorothiolate (VIII) and its thione isomer are well known insecticides and have been studied by many workers (114,115,116,117,141).



(VIII)

Muller and Goldenson(114) have shown that each of these molecules exhibits a single ^{31}P NMR signal and the difference between the magnetic field values (chemical shifts) obtained for the two signals was about 40 ppm. This is roughly in accordance with the values obtained in the present study, and it should also be noted that the alternative structural assignments to these ^{31}P NMR signals (DCPTP and DCPP) exhibit approximately the same difference in chemical shift values (74.8 ppm - 34.5 ppm) Further evidence regarding the thermal isomerisation phenomenon can easily be deduced from the infra-red spectra (Figure 5.3) of the oxidation mixture after four hours reaction. It has previously been reported(118) that the P=S absorption band at 650 cm^{-1} has been known to disappear during the isomerisation of phosphorothionates to phosphorothiolates (reaction 5.8) and this is an arguement in favour of the findings in the present study. It is distinctly shown (Figure 5.3) that the 650 cm^{-1} absorption band (P=S) remained almost constant up to four hours reaction, presumably in view of the relatively high abundance of the [P=S] fragment in the system. Thereafter, this absorption band decayed progressively (4-6 hours) to zero, with concomitant increase in the intensity of bands due to free P=O (1285 cm^{-1}).

After six hours reaction, the ^{31}P NMR spectrum (Figure 5.16) indicates that only a small proportion of the starting material remains undecomposed (6%) although some signals of moderately high intensity were observed. These include trivalent phosphorus species [$(RO)_3P$: 139 ppm and $(RS)_3P$:∽123 ppm], the triester [$(RS)_3PS$∽94 ppm], the oxygenated phosphoryl disulphide [DBD∽19 ppm] (see reaction 5.9c) and completely oxygenated species such as the pyrophosphate [O,O,O-TBPP ∽ 7 ppm]. The presence of the triesters O,S,S-TBTTP (112 ppm) which was observed after only two hours oxidation and increased to a very high level after six hours, and S,S,S-TBTP . (94 ppm) formed after six hours oxidation, indicates that there must be an overall disproportionation of the sulphur and oxygen atoms between different phosphorus atoms as shown in earlier reaction sequences (reaction 5.5a-c and 5.6a-b). The final stages of this reaction sequence is expected to result in the formation of not only the completely sulphurated specie S,S,S-TBTP (94 ppm), but also in the generation of species containing P-O-P bonds and considerable quantities of alkyl sulphides. The formation of the latter two species (P-O-P and R-S-R) is illustrated in reactions 5.10a-b which depicts the dealkylation of the triester O,S,S-TBDTP (54 ppm) formed in early alkylation reaction (reaction 5.6b) by the ambident S,S - dialkyl dithiophosphate radical (VI) [see also reaction scheme 5.9].


(VI) [O,S,S,-TBDTP] (IX) (VI)

54.0 ppm (5.10a)

(X) (5.10b)

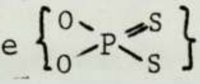
A similar mechanistic sequence was postulated(39) for the formation of identical products during thermal degradation of zinc dibutyl dithiophosphates (ZnDTP) and it was suggested that further nucleophilic attacks on the intermediate (X) by phosphoryl oxygen (see reaction 5.10b),leads to the elimination of a mercaptide (-SR) and the formation of the P-O-P linkages. Excellent confirmation for the formation of the latter is provided in Figure 5.3, which shows a strong P-O-P stretching vibration at 940 cm^{-1} ,associated with another weak band around 700 cm^{-1}. Literature value(125a) for P-O-P stretching modes is within the region 1050-850 cm^{-1} and 800-650 cm^{-1} Figure 5.3,in accordance with the ^{31}P NMR Figure 5.1b.and 5.4a-b also clearly indicates the reduction in relative abundance of the various triesters and the trisulphude (DnBTr) after six hours reaction.This implies that these species are in turn undergoing thermal decomposition to yield alkyl sulphides and disulphides which may further be oxidised to form the analogus sulpoxides and sulphones It is therefore not surprising that the photostabilising activity (in PP) of thiophosphoryl disulphides containing various triesters as impurities is better than that of very pure samples (see Chapter 4, Section 4.3A.6). This behaviour is attributed to the fact that the peroxidolytic activity of the thiophosphoryl disulphide is complemented by similar activity of the alkyl sulphides which are generated during the decomposition of the triester impurities.

In conclusion therefore, the thermal oxidation of DnBDS in dichlorobenzene at 185°C in the presence of a constant stream of air, leads to a series of competing and complicated reactions resulting in a general migration of the alkyl functions from oxygen atoms to sulphur atoms (i.e. P-O-R to P-S-R).Thisprocess leads to the formation of extended P-O-P systems, with concomitant loss of thioalkyl (-SR) functions bound to phosphorus as dialkyl sulphides (630 cm^{-1} band in Figure 5.3, T_6) and disulphides. The inset to Figure 5.2a which shows the HPLC chromatogram of a mixture of the triester (authentic sample) O,O,S-TBDTP and DnBDS, also indicates that the triester exhibits lower HPLC retention time (8 min.)

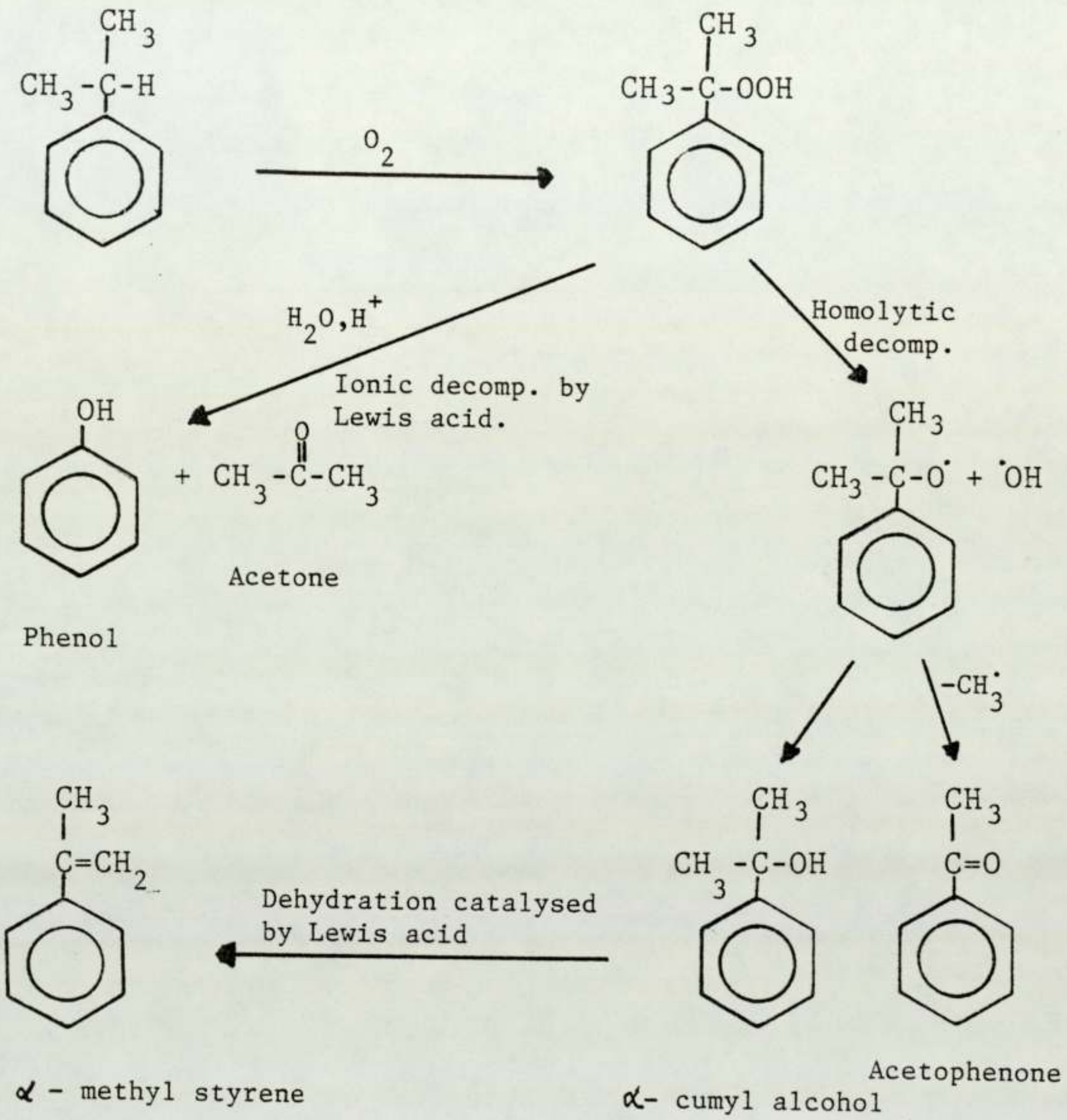
when compared to the thiophosphoryl sulphides. It is therefore reasonable to assume that the various triesters observed during ^{31}P NMR analysis of the heated samples (Figure 5.1b) may all elute before the sulphides, as reflected by the HPLC peaks with retention times below eight minutes (Figure 5.2b). A comparison of Figure 5.1b, 5.4a-b with Figures 5.2b and 5.5 clearly shows that the formation and increase in the intensity of the ^{31}P NMR signals assigned to the triesters roughly parallels the behaviour of the HPLC peaks of low retention times (< 8 mins.). As previously indicated, it is envisaged that further prolonged oxidation would result in the formation of completely oxygenated species and a high abundance of alkyl sulphides and disulphides (reaction 5.10) which may undergo further oxidation. At the end of the reaction, the major products (as measured by ^{31}P NMR) are the trivalent phosphites, phosphorothioates and inorganic phosphates, as illustrated in Figure 5.4c.

Although absolute structural assignments are difficult, some of these have been accomplished by synthesis (Chapter 2, Section 2.1.1-2.1.7), and previously recorded data(105a,110,111) on the thermal decomposition of DnBDS (MS/GC) and ZnDTP ('H NMR, ^{31}P NMR and TLC) have also been used as a guide.

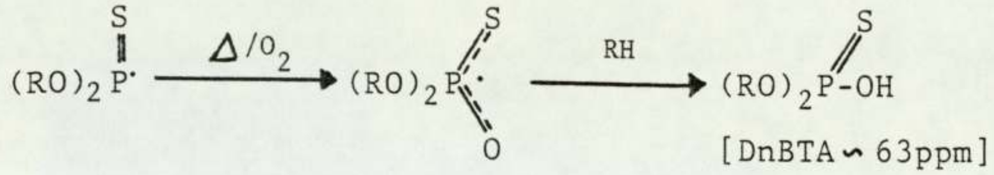
5.3.1(b) Cumene as Substrate

The products of the decomposition of DnBDS in an oxidisable substrate (cumene) at 180°C as measured by ^{31}P NMR, are quite similar to those obtained in a non-oxidisable solvent (dichlorobenzene), with only a few exceptions which will be pointed out in the course of this discussion. As in the previous study, the starting material (DnBDS) contains signals from DnBDS at 85 ppm plus signals due to impurities. These include DnBTe (84.1δ), DnBTr (83.8δ), DnBMS (79δ) and the triester O,O,O-TBTP (72δ). The origin of the impurity with a chemical shift of 85.5 ppm is presently uncertain, although the presence of this species in most of the oxidation studies strongly suggests that it is likely to contain the  grouping (Table 5.4). After one hour oxidation (Figures 5.6-5.7), the ^{31}P NMR spectra shows the formation of new signals at 96δ, 63δ and 53.1δ which are respectively assigned to O,O,S-TBDTP, DnBTA and O,O,O-TPTP. Of these three new products, only the former (O,O,S-TBDTP) was detected in the previous study (when QCl was used as substrate) according to reaction 5.5. The formation of the latter two products may arise from simultaneous oxidation of cumene to yield cumene hydroperoxide, which further decomposes to give the ionic products of phenol and acetone[(52,122)] according to Scheme 5.3

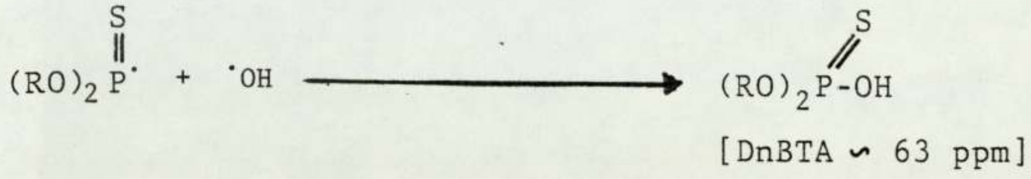
Scheme 5.3(52,122) Oxidation of cumene/decomposition of CHP



The formation of the acidic specie DnBTA (63 ppm) as shown in Figures 5.6 and 5.7, may result from several reaction pathways involving either hydrogen abstraction from the substrate by a thione radical (reaction 5.11a) and/or reaction of a phosphorus centred radical with the hydroxyl radical (·OH) obtained via the homolytic decomposition of CHP (reaction 5.11b).



(5.11a)

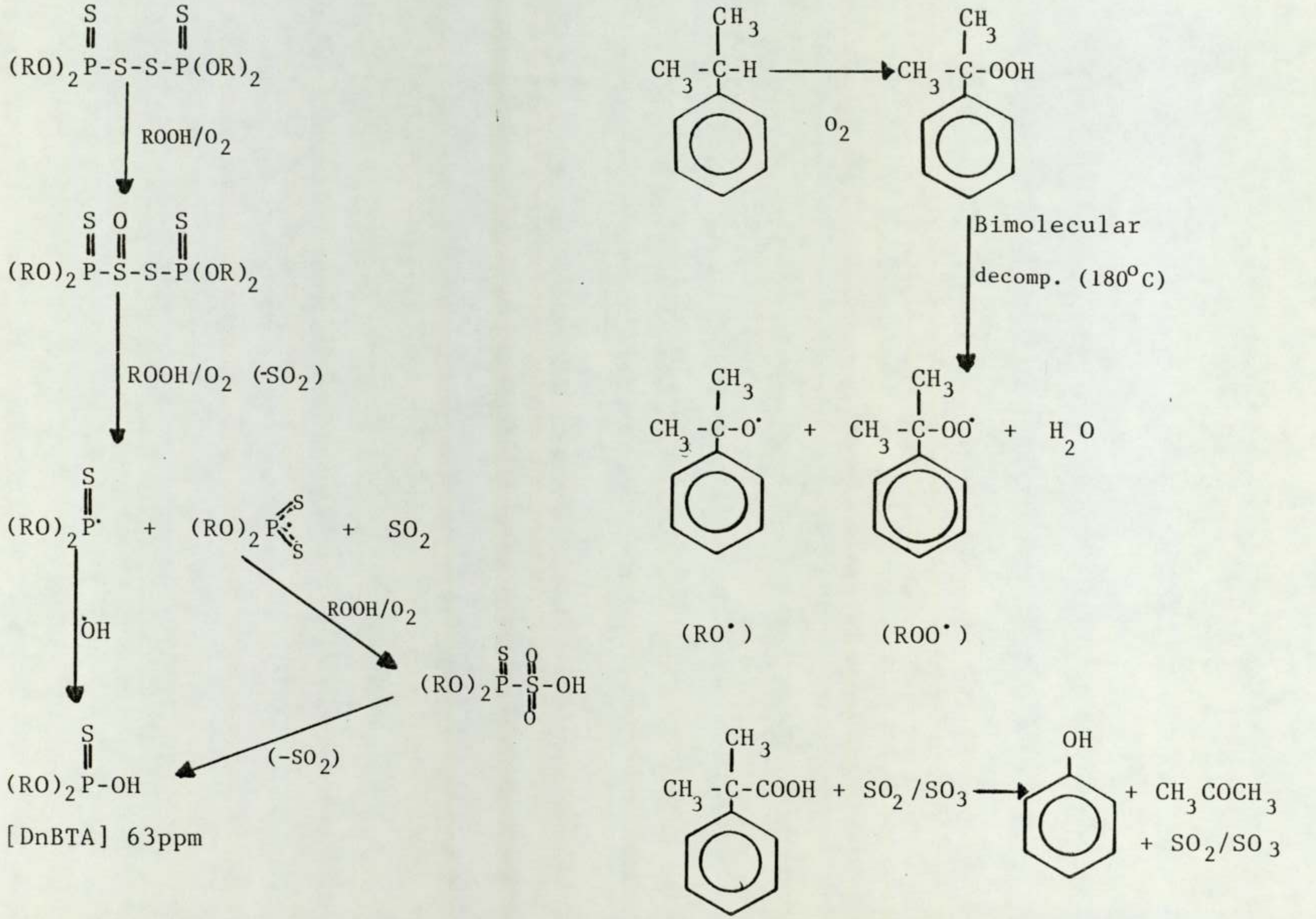


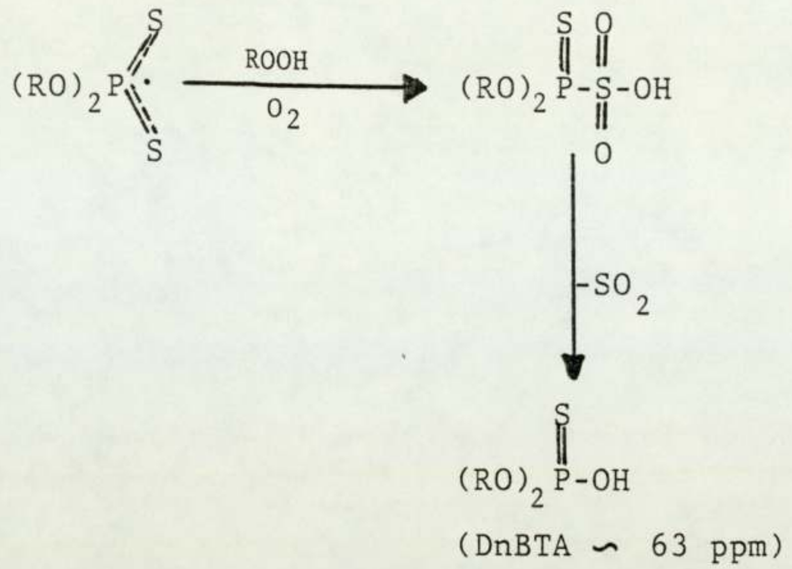
(5.11b)

It is highly unlikely that this acidic specie would result from direct oxidation of the thiyl $[(RO)_2P{<}^{S}_{S}\ ]$ or perthiyl $[(RO)_2\overset{S}{\overset{\|}{P}}\text{-S-S}\cdot]$ radicals since these are expected to be mostly consumed in the formation of the tri- and tetra-sulphides (DnBTr and DnBTe), in addition to the triester, O,O,S-TBDTP (reaction 5.2-5.5, Figure 5.7). However direct oxidation of the disulphide molecule and/or a thiyl radical by oxygen or cumene hydroperoxide may also result in the formation DnBTA (Scheme 5.4).

It is clear from Scheme 5.4 that the oxidation of the thiyl radical results in the formation of the acidic species (reaction 5.11c).

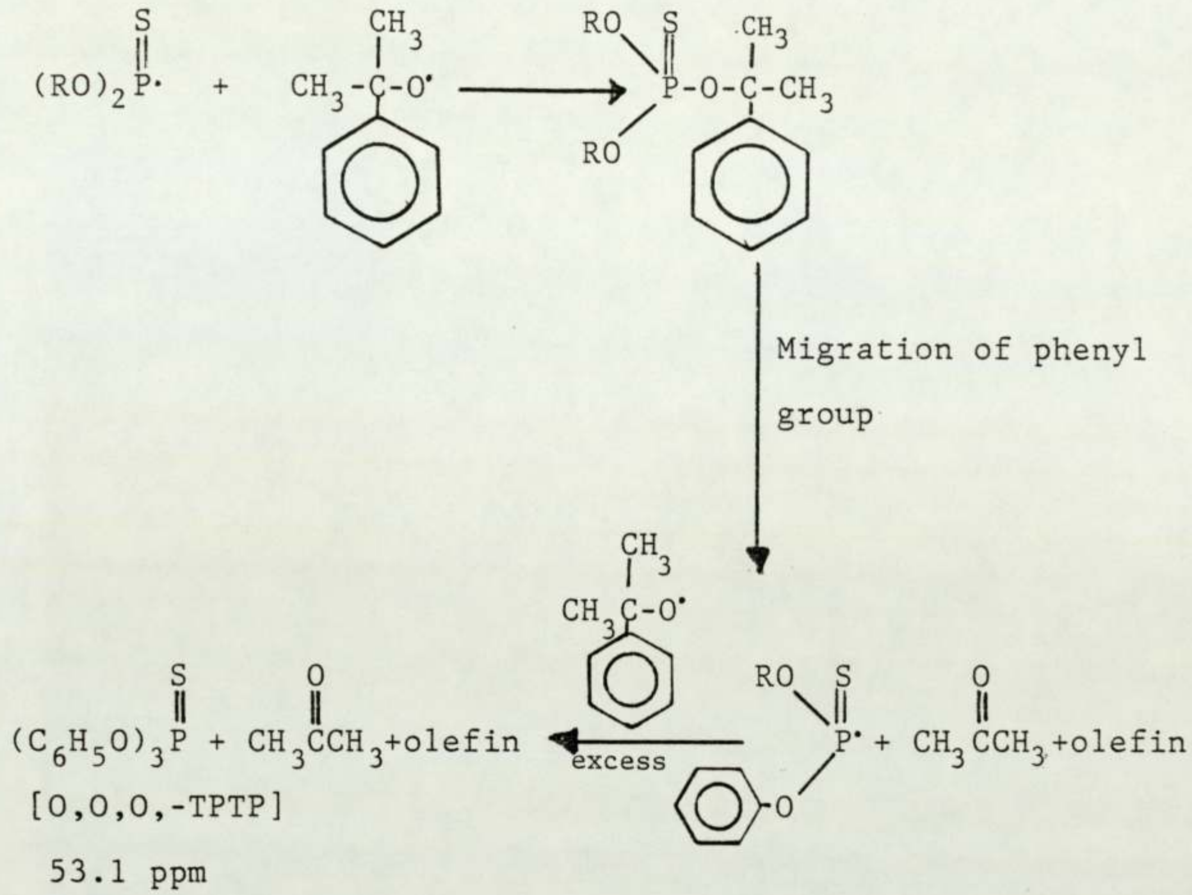
Scheme 5.4 Direct oxidation of DnBDS molecule





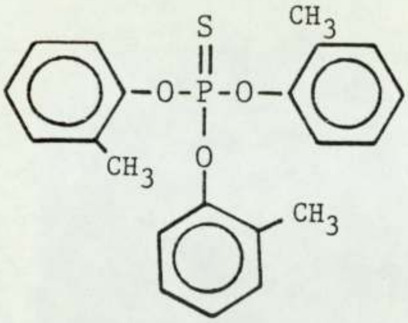
(5.11c)

It is also reasonable to assume that a reaction between the phosphorus-centred radical and an alkoxy or alkylperoxyl radical might result in the formation of the triester O,O,O-TPTP (53.1δ) with the elimination of a ketone and an olefin via an alkoxyl cleavage reaction (reaction 5.12).

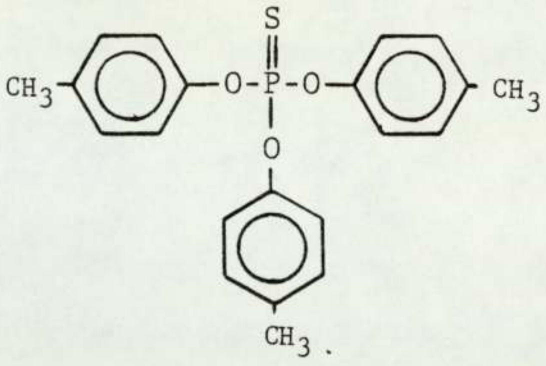


(5.12)

It is very probable that the various steps involved are simultaneous, the migrating phenyl group helping to push out the ketone and olefin in each step (reaction 5.12). The ^{31}P NMR spectra at the latter stages of the reaction also contains signals in the same region(54.8δ and 52.3δ) which have been tentatively assigned to the para- and ortho methyl substituted analogues of O,O,O-TPTP with the folowing structures.(119)



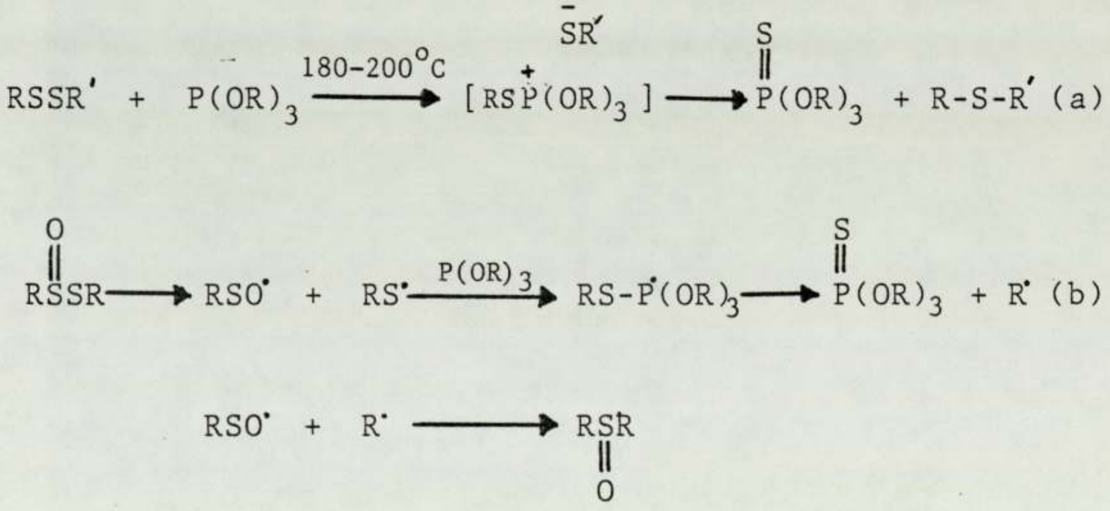
54.8 ppm



52.3 ppm

The formation of these triesters as shown in Table 5.5, have been assigned to these structures in the absence of any other bibliographical data. As in the previous study, the major reaction intermediates are the tri and tetrasulphides and the various ester groups, although the rate of formation of these products is slower in view of the slightly lower temperature used (185°C vs 180°C). At the end of the reaction only about 30% of the disulphide remained undecomposed. This is illustrated in Figure 5.7 which also includes the rate of formation of the various products.

The IR spectrum (Figure 5.8) of the precipitate isolated at the end of the reaction denotes the presence of alkyl sulphides, di-or trisulphides, mercaptans and definitely sulphoxides. Figure 5.8 shows a very strong band with a maximum at 1050 cm^{-1}, associated with four other bands at 780 cm (w), 710 cm^{-1} (w), 630 cm (w), and 450 cm^{-1} (s). Alkyl sulphides, disulphides and mercaptans all absorb within the range 800 cm^{-1} - 500 cm^{-1} (109c), with trisulphides absorbing below 500 cm^{-1}. For example, the C-S frequency for methyl mercaptan has been assigned(109c) at 705 cm^{-1} while the range 700-600 cm^{-1} has been proposed as an approximate frequency range for the C-S-C linkage. The formation of alkyl sulphide as indicated in the previous section (reaction 5.10), may arise via the thermal decomposition of the various ester species(115) . Furthermore, the decomposition of phosphorothioates is of interest in connection with the observations of mixed sulphide formation in the thermal reactions of trialkyl phosphites with disulphides(115,123) . Nucleophilic attack of the phosphite on the easily polarizable disulphide linkage displaces the mercaptide ion which is alkylated to produce the thioether (reaction 5.13a) or the sulphoxide (reaction 5.13b).



$$RSSR' + P(OR)_3 \xrightarrow{180\text{-}200^{\circ}C} \overset{\overset{-}{S}R'}{[RS\overset{+}{P}(OR)_3]} \longrightarrow \overset{\overset{S}{\|}}{P}(OR)_3 + R\text{-}S\text{-}R' \quad (a)$$

$$R\overset{\overset{O}{\|}}{S}SR \longrightarrow RSO^{\bullet} + RS^{\bullet} \xrightarrow{P(OR)_3} RS\text{-}\dot{P}(OR)_3 \longrightarrow \overset{\overset{S}{\|}}{P}(OR)_3 + R^{\bullet} \quad (b)$$

$$RSO^{\bullet} + R^{\bullet} \longrightarrow R\underset{\underset{O}{\|}}{S}R$$

(5.13)

It must be pointed out that some trivalent phosphorus species with chemical shifts between 120 ppm and 140 ppm [$(RS)_3P$ and $(RO)_3P$: where R= alkyl or aryl](98,105a,119) were observed in the later stages of the reaction (Table 5.4). The brief occurance of these transient products, along with other triesters of similar occurence (δ = 72 & 67) could account for the formation of the alkyl sulphides as shown in reaction 5.13.

As mentioned earlier, the very strong infra-red absorption band with a maxima at 1050 cm^{-1} (Figure 5.8) clearly suggests the presence of oxygenated sulphur compounds, possibly a mixture of sulphoxides and thiolsulphinates. The S=O frequency have been known to fall within the 1070 - 1035 cm^{-1} range for most alkyl and aryl sulphoxides.

In the light of the present results, the formation of at least some of the sulphide by the various reaction pathways shown cannot be ruled out, and these obviously will be oxidised to sulphur - oxygen compounds in the presence of excess oxygen.

5.3.2 Thermal Decomposition of DnBDS in the Presence of TBH (100°C)

5.3.2(a) Dichlorobenzene as Substrate

The oxidation of DnBDS by TBH under the conditions employed results in the formation of very similar products as those described in the previous sections (oxidation in the presence of air). However, product formation in the presence of a hydroperoxide tends to favour a predominance of the acidic specie DnBTA (δ= 21~ thiol isomer) in the early stages, in preference to the triesters. This is shown in Tables 5.6-5.7 from which it is equally clear that in accordance with the trend obtained when oxidation is carried out in the presence of air, the tri- and tetrasulphides (DnBTr and DnBTe) are the initial major transient products in addition to slightly lower yields of DnBTA.

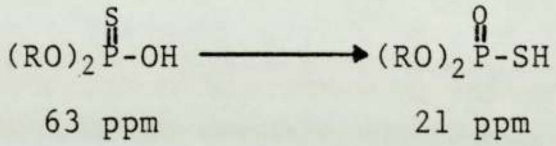
It is also interesting to note that the oxidation of DnBDS by TBH facilitates the formation of higher yields of DnBTE (δ = 84.1) than DnBTR (83.8δ) (see Figure 5.13a). This behaviour is exactly opposite to that observed when oxidation is carried out in the presence of air (see Figure 5.7a). The formation of these three major products is clearly ilustrated in Figures 5.13a-b, which also includes the decay in TBH concentration during each reaction.

The results can be interpreted in terms of the reactions shown in Scheme 5.5 which depicts the various reaction pathways shown during the oxidation of DnBDS by TBH at 100°C. Scheme 5.6 also shows the various products of the decomposition of the hydroperoxide.

The reaction pathways (reactions (a)-(c)) in Scheme 5.5 apply to both TBH:DnBDS ratios used since product formation during oxidation is extremely similar for both reactions (see Figures 5.13a-b). After eight hours reaction, the major products as measured by ^{31}P NMR, are DnBTe, DnBTr and DnBTA in decreasing order (DnBTe > DnBTr > DnBTA). Other products which make up only a small proportion of the total (< 10%) include triesters with chemical shifts of 52, 28 and 95 ppm, trivalent phosphorus species (δ = 127-141) and inorganic phosphorus species (δ = < 10); and these are only formed in the later stages of the reactions (Table 5.6).

As shown earlier (Section 5.3.1a-b), it is clearly evident that the disulphide molecule can and does undergo both asymmetrical and symmetrical decomposition (Scheme 5.5, Reaction (a) and (b)) since the three major products originate from radicals formed via both reaction pathways. Although it has been found(113,124) in many studies that radicals with a great number of sulphur atoms are relatively unreactive, the perthiyl $[(RO)_2\overset{S}{\overset{\|}{P}}\text{-}SS\cdot]$ radicals formed in this and in the previous studies have shown a great tendency to either dimerise or react with thiyl radicals [$(RO)_2P{\lessdot}^{S}_{S}$] to form DnBTe and DnBTr respectively (Scheme 5.5; reaction a_1 and a+b).

From Scheme 5.5, it is also very clear that the predominant reaction pathway is typified by reaction (a_1) ~ dimerisation of perthiyl radicals, folowed by reaction (a + b) to yield the trisulphide, and finally reaction of the phosphorus- centred radical with a hydroxyl radical ($^{\bullet}OH$) from the hydroperoxide to form the acidic specie DnBTa which is simultaneously converted to the thiol isomer in the presence of hydroperoxides, as shown in reaction 5.14.



$$\underset{63\ \text{ppm}}{(RO)_2\overset{S}{\overset{\|}{P}}\text{-OH}} \longrightarrow \underset{21\ \text{ppm}}{(RO)_2\overset{O}{\overset{\|}{P}}\text{-SH}}$$

(5.14)

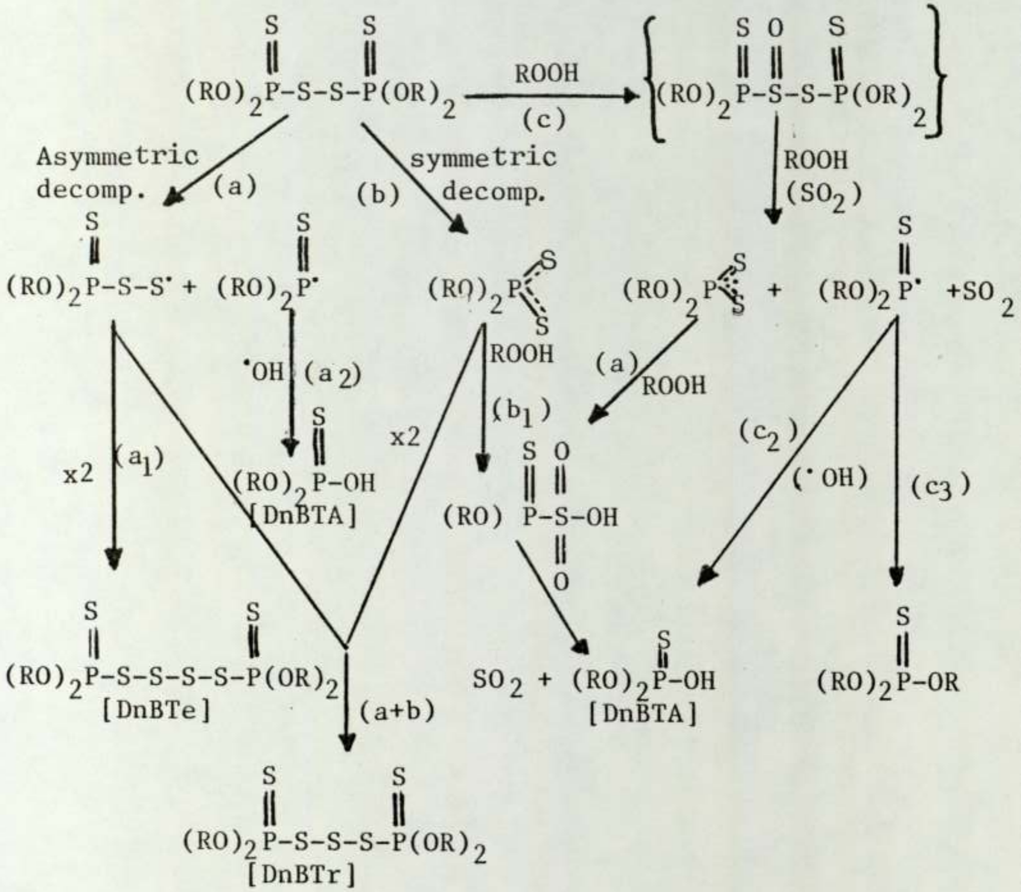
This tautomeric behaviour will be discussed in great detail in Section 5.3.4. The reaction pathways (b) and (c) [Scheme 5.5] which involves direct oxidation of the thiyl radical and the disulphide molecule have received much support from some workers(5a,13,40b). However, the results obtained in the present studies clearly indicates that all three reaction pathways are possible (Scheme 5.5, reaction (a), (b) and (c)), with the radical generating routes (reactions (a) and (b)) being more predominant since the major products are the tetrasulphide and the trisulphide. The presence of the acidic specie DnBTA [$(RO)_2$ POSH] in the initial stages would most likely catalyse the ionic decomposition of the hydroperoxide as shown in scheme 5.6 (proton from the ionisation of the DnBTA). The hydroperoxide decomposing activity of DnBTA have been clearly demonstrated by Smith(93) who ascribed the rapid disappearance of CHP as a consequence of acid catalysed heterolytic decomposition of the hydroperoxide.

The infra-red absorption spectra (Figure 5.11) of the eight hour reaction samples confirms the presence of the acidic specie DnBTA which shows a broad shallow band within the region 2500-2000 cm^{-1}. Absorption due to (P)-S-H linkage have been known(125a) to arise in the range 2400-2300 cm^{-1}) and a similar range have also been ascribed(109,125a) to (P)-O-H stretching modes in several organophosphours acids. This band is clearly associated with another very strong absorption in the region 1320-1200 cm^{-1}, attributed to P=O stretching frequences [in $(RO)_2\overset{O}{\overset{\|}{P}}SH$]. Figure 5.11 also provides excellent confirmation of the difference between the two ratios (of TBH) used. The near total breakdown of the disulphides when ratio of TBH : DnBDS = 2 clearly contrasts with that observed when ratio = 1. The strong broad absorption band within the region 580-450 cm^{-1} attributed to P-S-C , P-S-P and P-S-S linkages remains almost unchanged when TBH ratio = 1 where as with 2-fold excess of TBH, this band was completely broken down into four distinct bands at 600, 550,530 and 480 cm^{-1}. These bands have been assigned to C-S-C, P-S-C, P-S-P and P-S-S (n=2-4) groupings respectively, by analogy with previous study on the oxidation of DnBDS in the presence of air (see Section 5.3.1a).

The difference in the breakdown of the disulphide molecule as observed in the infra-red spectra (for both ratios) is also clearly illustrated in Figures 5.13a-b, which not only show the decay in the concentration of both reactants, but also unequivocally indicates that the rate of formation of the three major products (DnBTe, DnBTr and DnBTA) roughly parallels the rate of such decay. At equimolar ratio, the rapid decay of both the disulphide and TBH is closely related to an equally rapid rate in the formation of all three products. However, oxidation of the disulphide ceases once the TBH is used up (Figure 5.13a). At the end of the reaction the ^{31}P NMR data indicates that almost 60% of the disulphide still remains undecomposed.

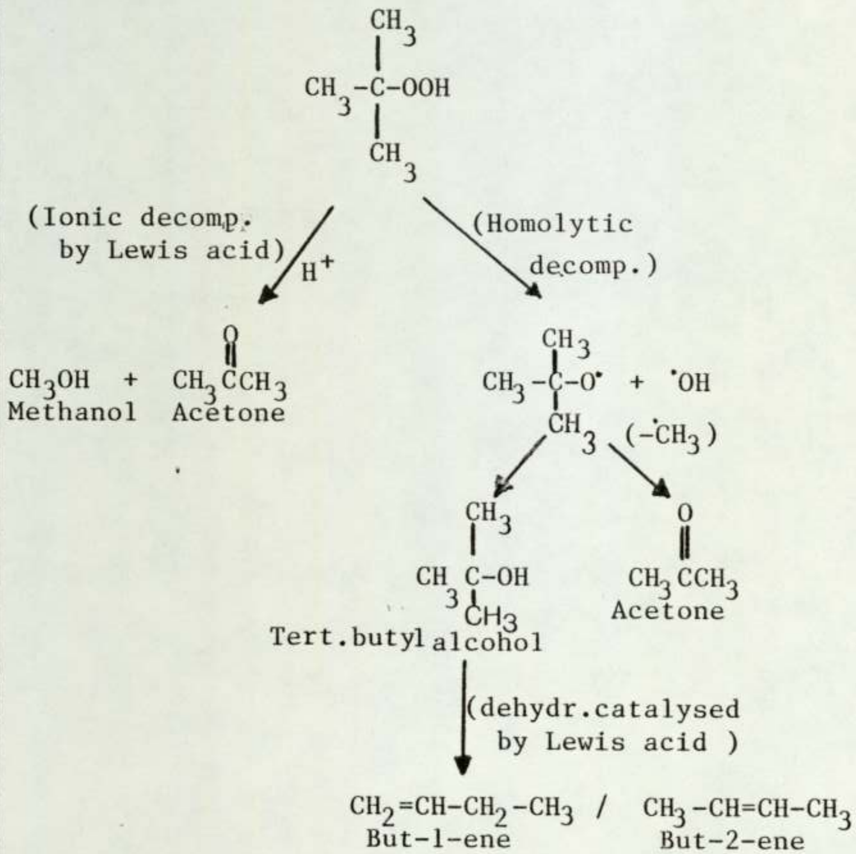
With excess TBH (ratio = 2), Figure 5.13b clearly indicates an initial induction period in both the rate of decay of DnBDS and the rate of formation of all three major products. This behaviour is concomitant with an initial rapid decay in TBH concentration, followed by an induction period during which time the products are being formed, and finally another rapid decay which also

Scheme 5.5 Oxidation of DnBDS by TBH at 100°C



Product formation After eight hours = DnBTe > DnBTr > DnBTA

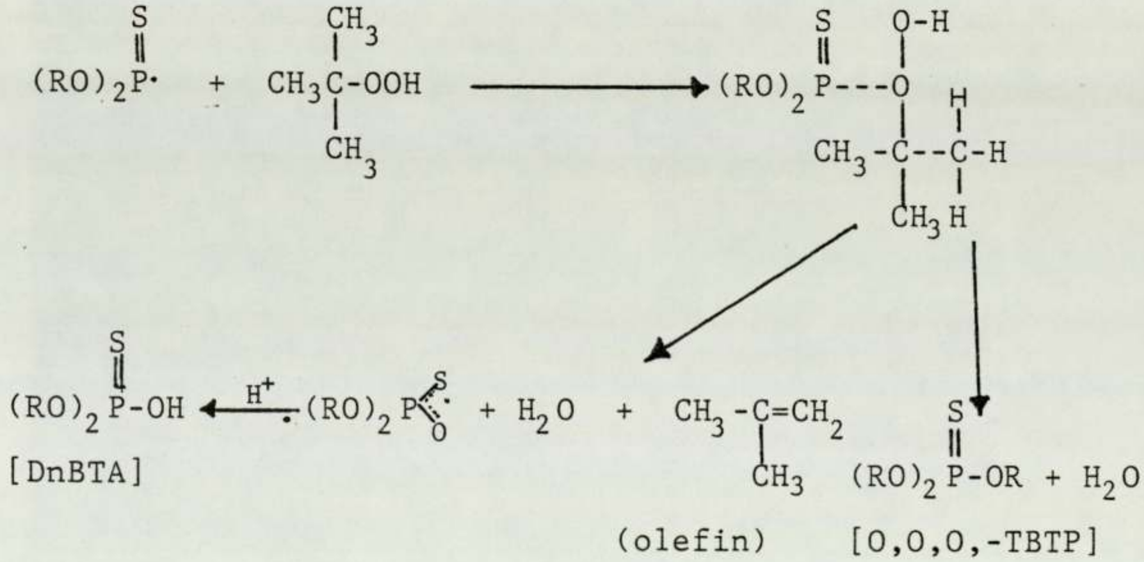
Scheme 5.6 Decomposition of tert-butyl hydroperoxide



interestingly corresponds to the third stage in DnBDS decomposition. At the end of the reaction, only about 38% of the disulphide is left. This 3-stage behaviour described, sharply contrasts the 2-stage process observed when TBH:DnBDS ratio = 1 (Figure 5.13a).

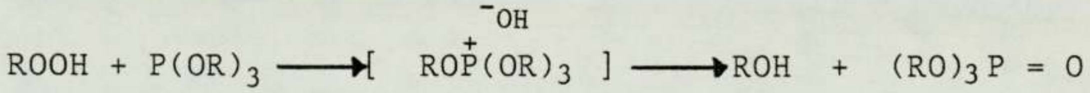
The reason for the induction period observed when excess TBH is used may be due to the formation of addition products of TBH and a thiyl or a phosphorus - centred radical as shown in Scheme 5.7.

Scheme 5.7 Addition products of TBH and a phosphorus centred radical



A similar addition product to the thiyl radical has also been reporated by Grishina(127). The decomposition of the addition product as shown results in the formation of water and an olefin as byproducts in addition to DnBTA by proton abstraction. Similar addition products have also been observed by some workers(126) for dialkyl sulphides. It is also worth noting that the presence of olefins was confirmed in the infra-red spectra (Figure 5.11) which shows absorption bands at 1650 cm^{-1} and 1630 cm^{-1}. This corresponds to C=C stretching vibrations in compounds which contain only an isolated double bond(109d) with the overall range covering the 1680-1620 cm^{-1} region.

Finally, some of the trivalent phosphites formed intermittently (particularly when TBH ratio = 2) during the reaction, with chemical shifts between 120 ppm and 141 ppm, could react with hydroperoxide to form addition products. Walling and Rabinowitz(123) have reported the deoxygenation of TBH by triethylphosphite to give tert-butyl alcohol and triethyl phosphate (reaction 5.15).



$$ROOH + P(OR)_3 \longrightarrow [\ RO\overset{^{-}OH}{\overset{+}{P}}(OR)_3\ ] \longrightarrow ROH + (RO)_3P = O \qquad (5.15)$$

The increase in the formation of these inorganic phosphates with chemical shifts < 10 ppm is clearly indicated in Tables 5.6 - 5.7, which also shows the intermittent occurence of the phosphites (> 90). Products of the decomposition of the hydroperoxide include tert-butyl alcohol, methanol, olefins and acetone. The formation of both alcohols is illustrated qualitatively in Figure 5.12 which shows the free OH frequency vibrations at 3620 cm^{-1} (tert-alcohols) and 3645 cm^{-1}(methanol) in addition to the broad OH stretching vibration of dimeric alcohols (after complete depletion of TBH). The OH deformation modes of the alcohols were also observed around 1150 cm^{-1}. The formation of acetone is clearly illustrated in Figure 5.11 which shows a very strong absorption band at 1720 cm^{-1}.

5.3.2(b) Cumene as Substrate (Insitu ^{31}P NMR Experiment)

The oxidation of DnBDS by TBH in cumene at 100°C was carried out directly in the Joel transform NMR spectrometer, already programmed for a stacking run at 100°C covering a wide range of time (17 hours).

This process therefore affords the opportunity in being able to positively identify the final products of the decomposition of DnBDS since the time range used facilitates complete decomposition of the various reaction intermediates observed in the previous studies; notably the tri- and tetrasulphides (DnBTr and DnBTe).

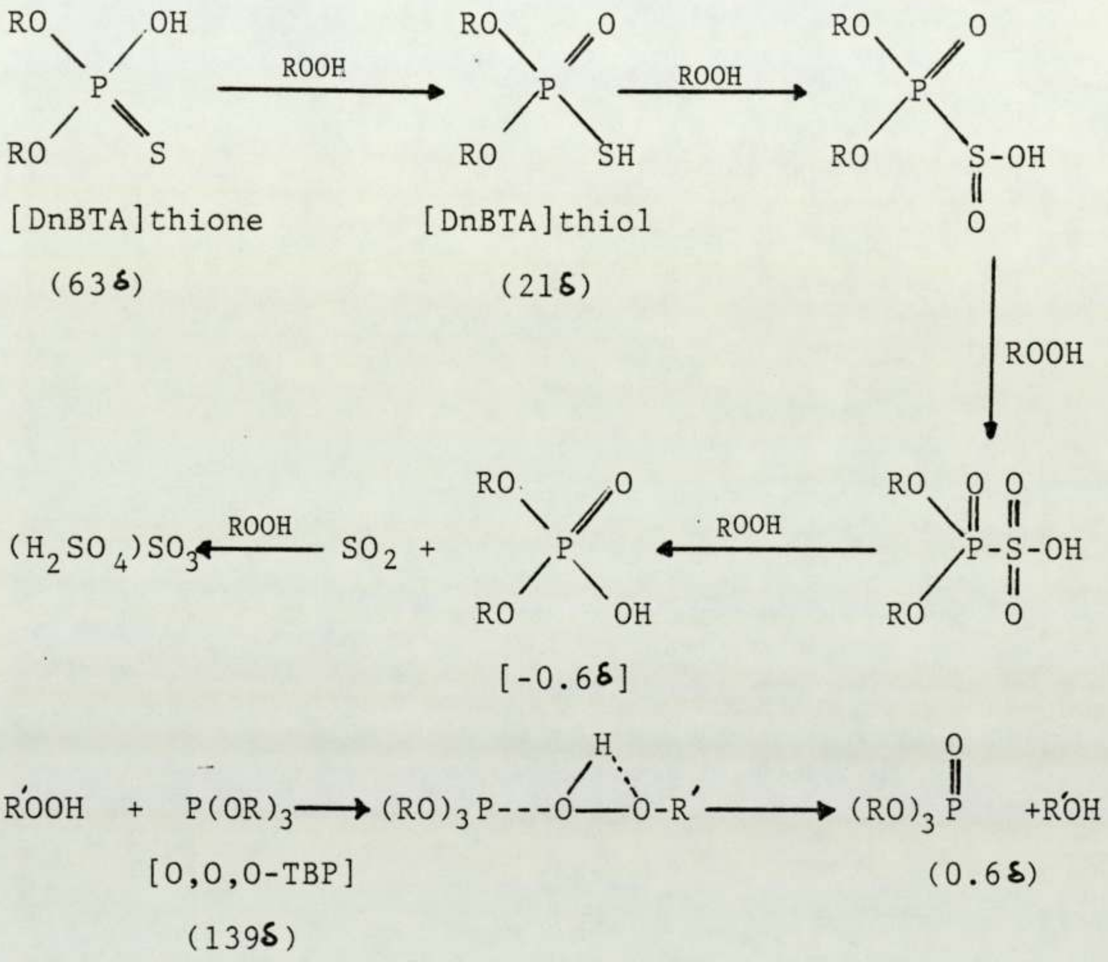
It is clear from Tables 5.8-5.9; that the initial decomposition products ($<$ 10 hours) are very identical to those described in the past section (5.3.2a). At longer reaction times however (10-17 hours), the trend in product formation changed distinctly such that DnBTe and DnBTr (and DnBDS) decayed to zero with a corresponding rapid increase in the abundance of the acidic specie DnBTA (thione isomer , 63δ) and a mixture of inorganic mono- and di-phosphates having chemical shifts at 15 - 21 ppm.

As with the oxidation of DnBDS by TBH in dichlorobenzene, the three major products (< 10hours) are DnBTe, DnBTr, and DnBTA (thiol isomer) with chemical shifts at 84.1δ , 83.9δ and 21 δ respectively although the thiophosphoryl monosulphide (DnBMS 79δ) also featured as a prominent reaction product in this study.

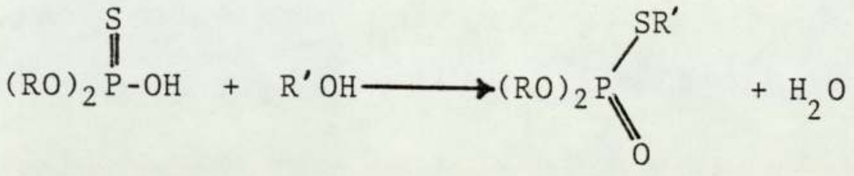
Figure 5.15 clearly indicates that the oxidation of DnBDS by TBH in cumene exhibits a similar 3-stage process as described in Section 5.3.2a with reference to the decay of the disulphide (DnBDS) and the formation of the various products. The relative abundance of the former two (DnBTe and DnBTr), both of which were originally present as impurities, reached a maximum after 10 hours decomposition before decaying sharply. The acidic specie DnBTA with a chemical shift of 21 . ppm (Table 5.8), was formed in the early stages and reached a maximum after only four hours oxidation before showing signs of slight decay, while still maintaining a respectable level (6%) after 10 hours (Figure 5.15). At the end of the reaction however (17 hours), the ^{31}P NMR spectra (Figure 5.14) shows that all the acidic specie (DnBTA 21δ) originally in the thiol form, including any more that may have been formed in the subsequent hours (10-17 hours), are converted to the thione isomer with a chemical shift of 63 ppm. This is highly indicative of the characteristic tantomeric behaviour of organo - thiophosphorus acids(128) which will be discussed in Section 5.3. After 17 hours decomposition, this specie (DnBTA) represents one of two major end products at 32 %, the other being a mixture of inorganic phosphates [$(RO)_3 P = 0$] and dialkyl phosphoric acids [$(RO)_2P(O)OH$] at 25%.

The formation of the inorganic phosphorus species is most likely (Scheme 5.8) via the hydroperoxide decomposition of DnBTA to form the phosphoric acid, and the deoxygenation of the hydroperoxide by a phosphite to form the phosphates as reported by Walling and Rabinowitz (123,129)

Scheme 5.8(93) Formation of inorganic phosphoric acids and phosphates



The continuous formation of trialkylphosphites having chemical shifts > 100 ppm (120 - 140δ) as shown in Table 5.8 is certainly an argument in favour of the formation of these inorganic phosphates. The same observation also does apply to the formation of not only the inorganic phosphoric acids, but also to the formation of the triester [$(RO)_2P(O)SR$] with a chemical shift of 28 ppm. It must be pointed out that this specie, which was only observed (Table 5.8) after 10 hours oxidation, can be formed(130) by an esterification reaction (reaction 5.16) between DnBTA and an alcohol.



$$(RO)_2P(=S)\text{-}OH + R'OH \longrightarrow (RO)_2P(=O)SR' + H_2O$$

[O,O,S-TBTP]

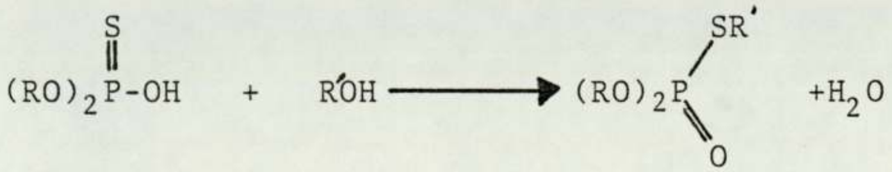
(5.16)

Another triester which was formed in a fairly reasonable level is O,O,O-TPTP [$(C_6H_5O)_3PS$] with a chemical shift of 52 ppm. This specie is thought to be formed via a reaction similar to that proposed in Section 5.3.1b (reaction 5.12) which deals with the oxidation of DnBDS in cumene at 180°C in the presence of air.

The relatively high participation of a hydroperoxide in most of the reactions can be explained by the assumption that in addition to the added TBH, the substrate is equally simultaneously oxidised to cumene hydroperoxide during the course of the reaction (section 5.3 - 5.4).

At the end of the reaction (17 hours), a very small brownish layer separated from the mixture and this was analysed by infra-red spectroscopy (Figure 5.16). Analysis was carried out as a thin film between two KBr discs in view of the immiscibility of the brownish portion in most of the organic solvents tried. As with the precipitate obtained when oxidation of DnBDS is carried out (in cumene) in the presence of air, the infra-red spectrum of this brownish portion (Figure 5.16) shows absorption bands at 600, 500 and 450 cm^{-1} assigned to alkyl sulphides, disulphides and trisulphides respectively. Cymerman and Wilis(131) have proposed that because of the symmetry of the S-S group, aliphatic and aryl disulphides show a weak band which occurs of 520-500 cm^{-1} and 500-430 cm^{-1} respectively, due to the stretching of the S-S bond. Other workers(109c) have also reported an approximate frequency range of 700-600 cm^{-1} for C-S-C linkages. Alternatively, the bands of 600 cm^{-1} and 500 cm^{-1} may be due to the scissoring and wagging modes of alkyl and/or aryl sulphones ($R-SO_2-R$), which is associated with the very strong S = O stretching frequency vibrations found in the regions 1400 - 1100 cm^{-1} and 1080 - 940 cm^{-1}. The presence of the strong and broad bands within the S = O frequency range is highly indicative of the formation of alkyl or aryl sulphoxides and sulphones since these species are known(109c,132) to absorb strongly over the frequency range of interest. Furthermore, the intense absorptions between 1400 - 1100 cm^{-1} is probably due to various (P)-O-H deformation modes, associated with not only the P-O-(H) stretching vibration of 870cm^{-1} but also with some P-O-H combination bands in the range 1900 - 1600 cm^{-1}.

The formation of the sulphides via the decomposition of the triesters (reaction 5.10) and/or through the various reactions of the phosphites, have been described in Section 5.3.1b (reaction 5.13). Although this reaction was carried out over an extended period (17 hours), the range of products obtained after 17 hours do not strictly represent the ultimate products of the oxidation of DnBDS. It is envisaged that had the reaction continued further, the trend in product formation will tend towards increased formation of more ester species and inorganic phosphates via the various reactions of the acidic specie DnBTA (63). As shown in Scheme 5.8 the production of more inorganic species through the reactions of DnBTA or the phosphite [O,O,O-TBP] with hydroperoxides is not feasible since the reaction media at this stage will be devoid of any hydroperoxide. The predominant reaction pathways may therefore involve the esterification(130) reaction of DnBTA and alcohols, as shown in reaction 5.16 or simple addition reaction(100) of the thiophosphoric acid (DnBTA) with olefins, some of which have been detected in these studies (Section 5.3.2a).



$$(RO)_2P(=S)\text{-}OH + R'OH \longrightarrow (RO)_2P(=O)SR' + H_2O$$

(DnBTA~ 636)

R/R' =alkyl or aryl

(5.16)

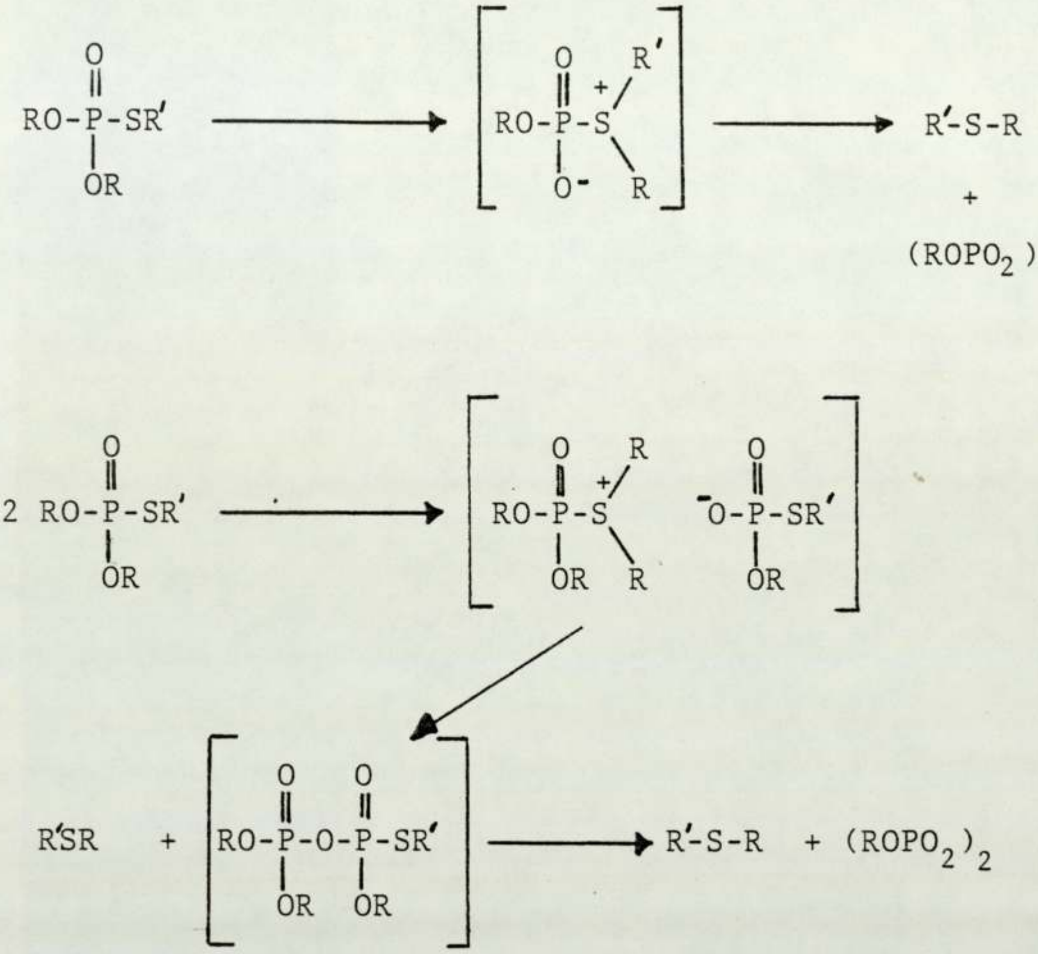
Such reactions of DnBTA will obviously result in an increase in the formation of the various ester species which variously account for about 20% (Table 5.8) of the total products after 17 hours, as shown below.

DnBTA - > INORGANIC PHOSPHATES > TRIESTERS > DnBMS
(63δ)33% (< 15δ)25% (96,28ppm)20% (79δ)10%

The trivalent phosphorus species TBP (> 100) make up the remaining 12%.

Simultaneous, decomposition of the ester groups is therefore likely to occur via an alkoxide cleavage reactions (reaction 5.10). The thermal decomposition of thiolphosphate esters(100) is regarded as an autoalkylation reaction, followed by the cleavage of the transalkylated part of the molecule, the reaction occuring via an intra- or intermolecular mechanisam as shown in scheme 5.9.

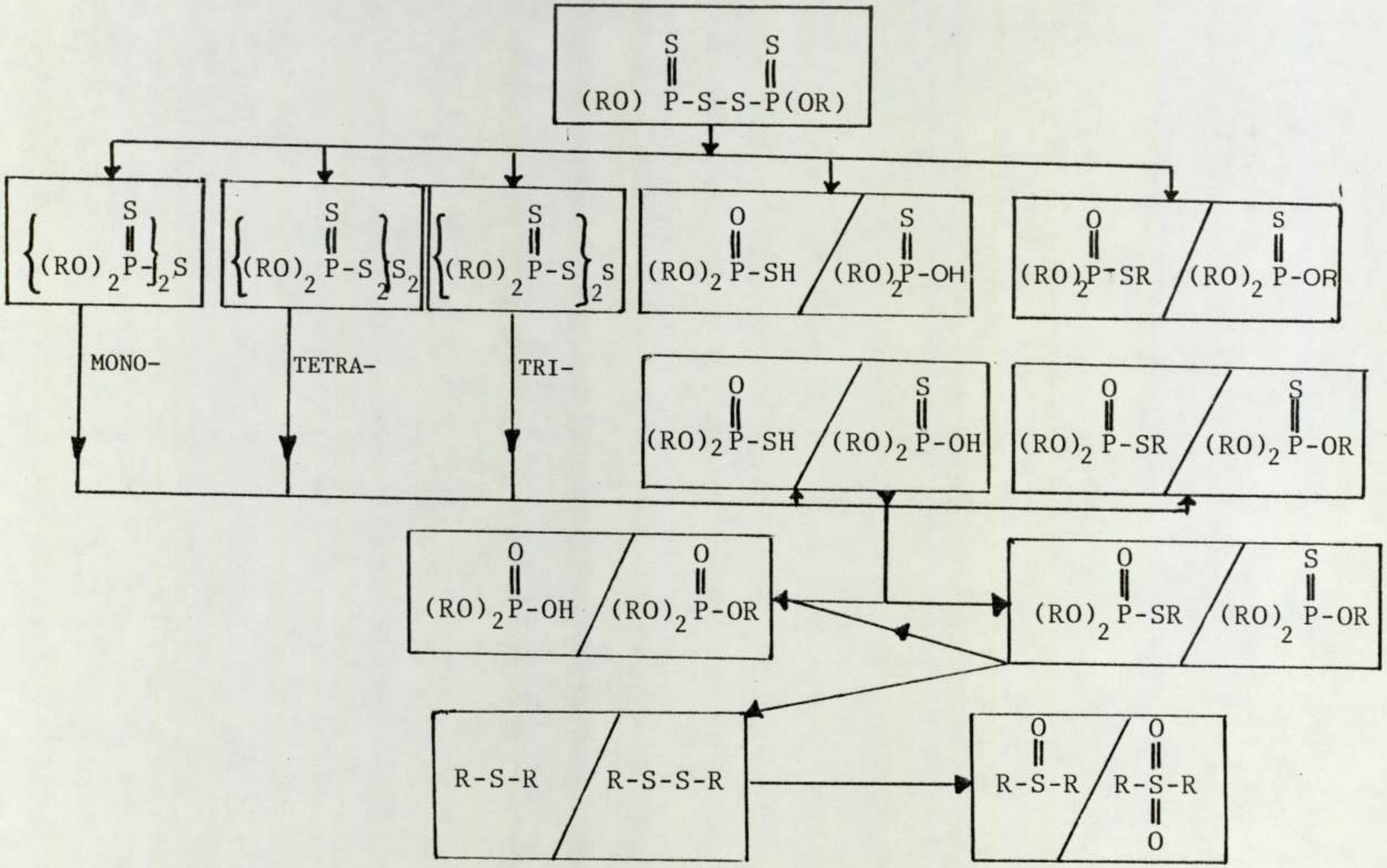
Scheme 5.9 Autoalkylation of thiophophorus esters(100)



From Scheme 5.9,it is therefore reasonable to assume that the formation of more sulphides and inorganic polyphosphates cannot be ruled out. On subsequent oxidation, the sulphides are then expected to form alkyl sulphoxides and possibly the sulphone and these have equally been identified by infra-red analysis.(Figure 5.16)

The thermal oxidative decomposition of di-n-butyl disulphide (DnBDS), with particular reference to the various reaction products, is therefore summarised in Scheme 5.10.

Scheme 5.10 Products of the thermal-oxidative decomposition of DnBDS

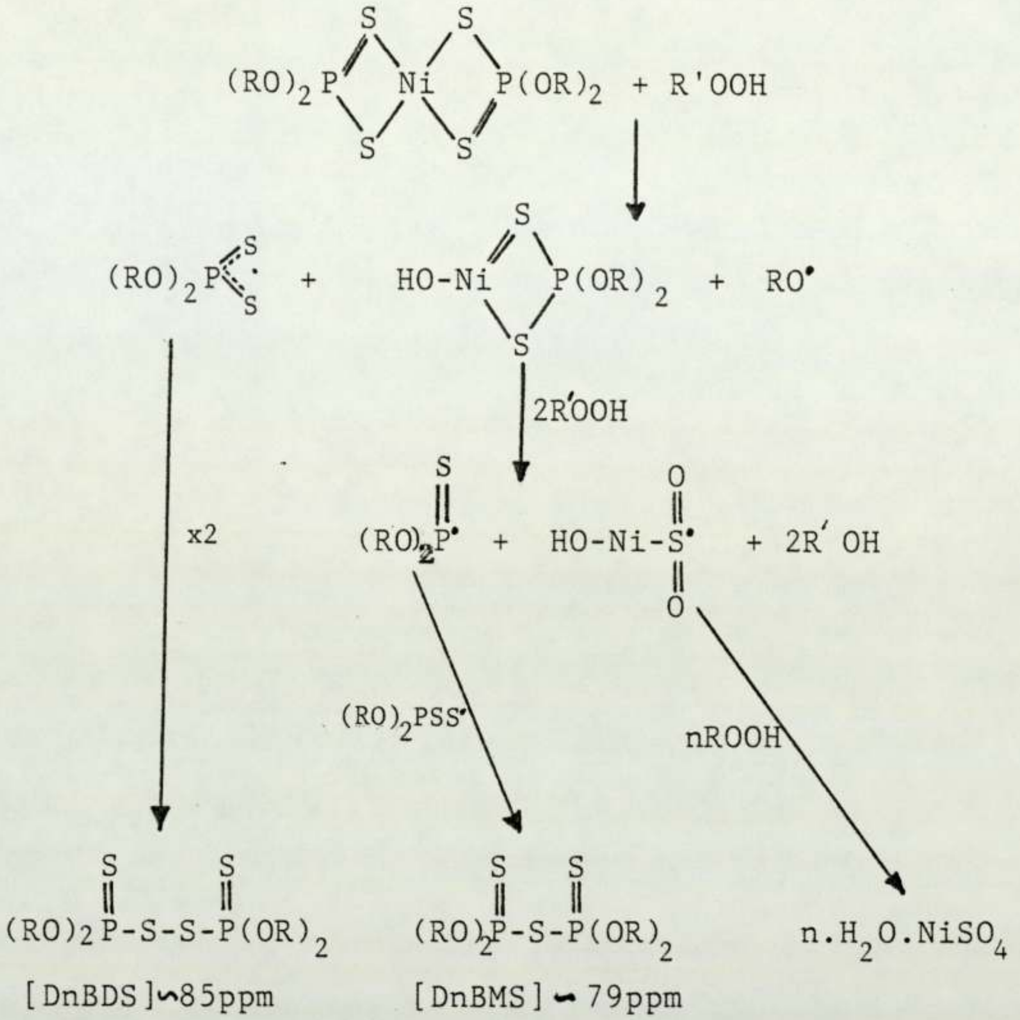


It is clear from Scheme 5.10 that the inorganic phosphates may be considered as the final stable products since these,particularly the dialkylphosphoric acids have been shown(133) tobe inactive towards hydroperoxides.

5.3.3 Reaction Products of the Oxidation of NiDnBP by TBH

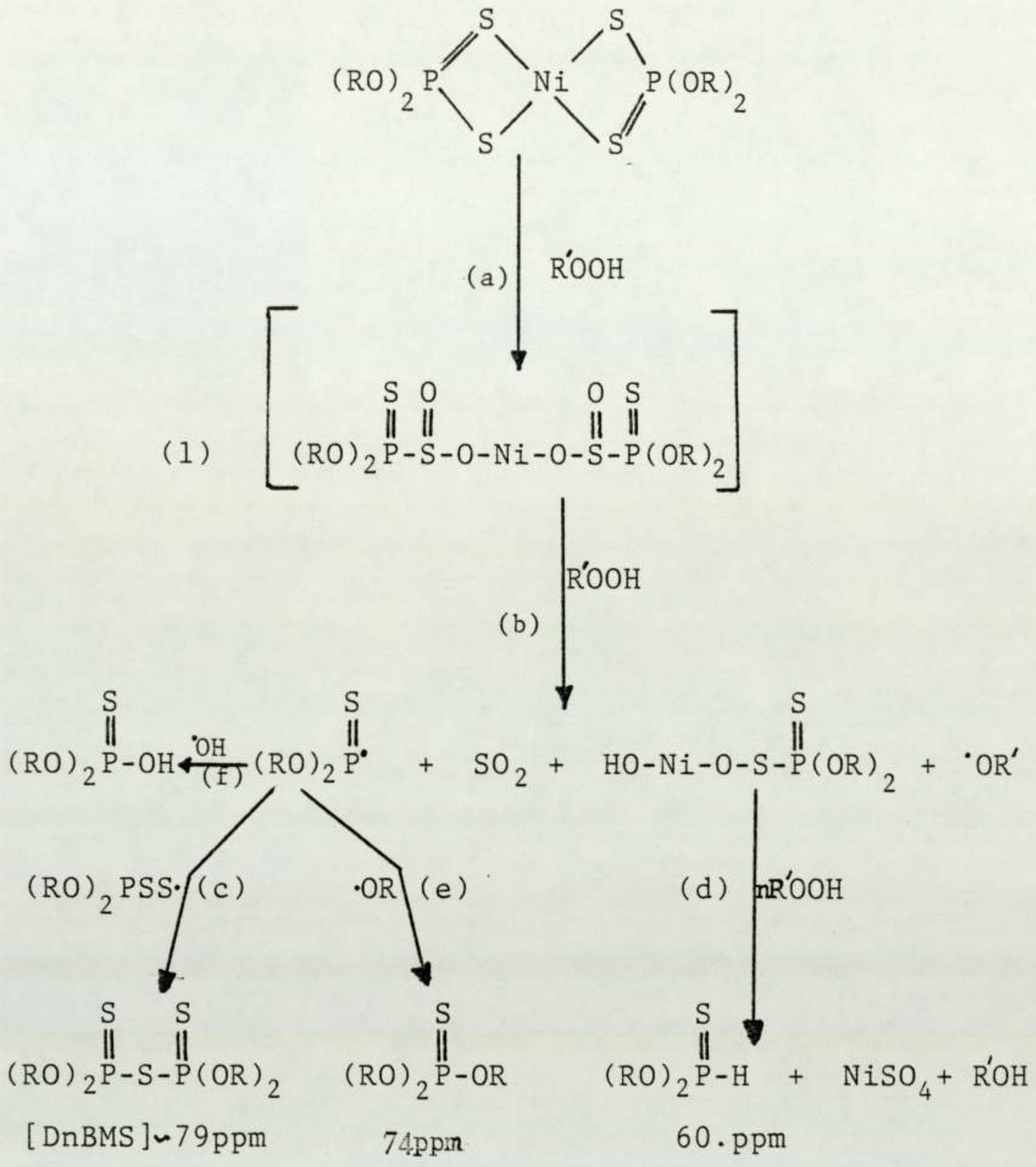
As described in section 5.2.3 highly concentrated solutions of TBH (0.3M-3.0M) in cyclohexane were reacted with previously prepared 0.3M solutions of NiDnBP at room temperature. After 24 . hours, the insoluble green precipitate formed early in each reaction (quantitative) was analysed and identified as hydrated nickel sulphate (see Figure 5.20). The major soluble reaction products derived from the nickel complex for a range of TBH ratios are summarised in Table 5.10.

An examination of the soluble portions by ^{31}P NMR clearly indicates that at low molar [TBH] : [NiDnBP] ratios (R = 1-2), the only products identified are the corresponding disulphide (DnBDS) and monosulphide (DnBMS) with chemical shifts of 85 . ppm and 79. ppm respectively (see Table 5.10 and Figure 5.17). The formation of these products can be explained in terms of the following reaction sequence (reaction 5.17) which continuously generates ketones and alcohols as products of homolytic decomposition of hydroperoxide.



(5.17)

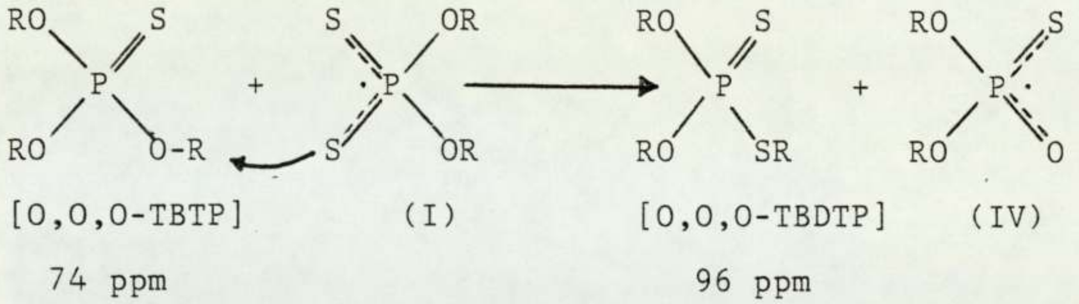
The fact that hydrocarbon auto-oxidation is initiated by mixtures of nickel complex and alkyl hydroperoxides(39,68b) indicates a high efficiency of free radical production from the initial homolytic reaction between the reactants. In parallel with this reaction (reaction 5.17), an oxidation process between NiDnBP and TBH (reaction sequence 5.18) is also possible since the reaction mixtures contain more monosulphide than can be accounted for by reaction 5.17 alone.



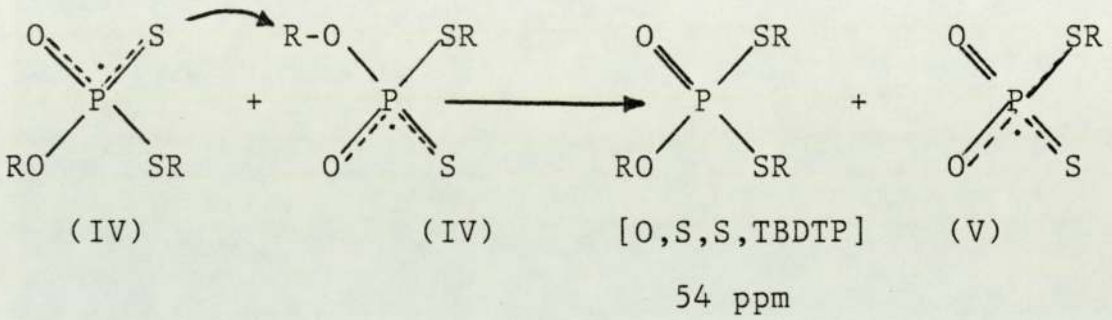
(5.18)

Intermediate sulphinates analogous to (1) have previously(134) been isolated from low molar ratio reaction of TBH and ZMBT/NiMBT. The addition of a low concentration of the sulphinate (ZMBT/NiMBT) to cumene initiated with CHP in oxygen absorption studies(134), gave a very marked pro-oxidant effect and this is an arguement in favour of the radical generating reactions postulated in reactions 5.17 - 5.18.

At higher [TBH]:[NiDnBP] molar ratios (R = 4-6), however, the disulphide and monosulphide still constitute the predominant products (> 40%) although the ^{31}P NMR analysis also indicates the formation of small quantities (3.5% total) of the hydrogen thiophosphate and the triester O,S,S-TBDTP with chemical shifts of 60 ppm and 54 ppm respectively (see Table 5.10 and Figure 5.17). It is clear that the decomposition of the intermediate sulphinate(1) as shown in reaction sequence 5.18, results not only in the formation of the hydrogen thiophosphate (60 ppm) and nickel sulphate (reaction . d), but also in the formation of the triester O,O,O-TBTP (reaction . e). The fact that no ^{31}P NMR signal was observed for this specie (74 ppm) clearly suggests that it is probably dealkylated by a thiyl radical (I) to form a thione radical (IV), which on further alkylation-dealkylation reaction with a similar specie, results in the formation of O,S,S-TBDTP (54 . ppm). These alkoxide cleavage reactions of the thiophosphate esters have been illustrated in an earlier section (Section 5.3.1a, reaction 5.5 - 5.6).



(5.5a)

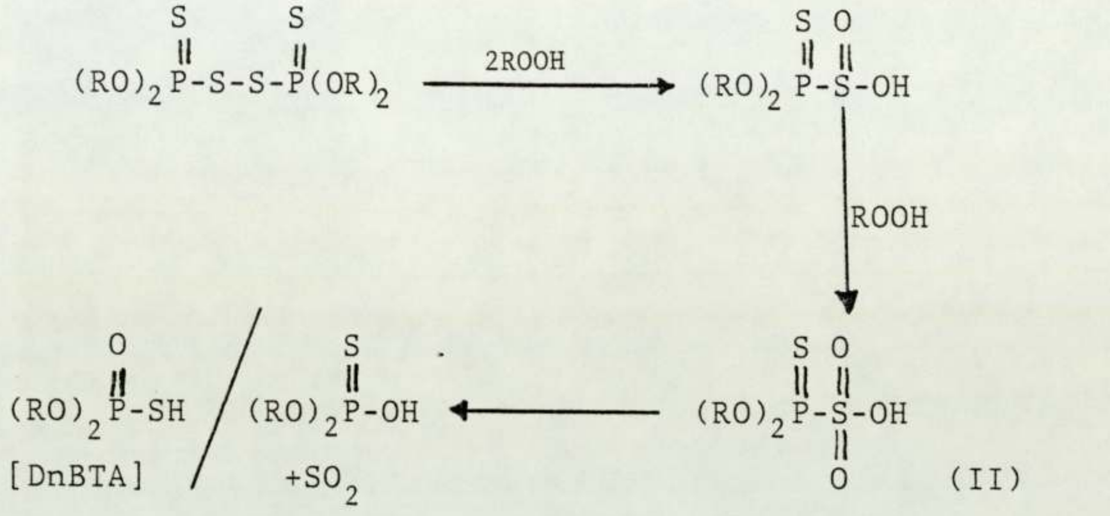


(5.6a)

Furthermore, the isomerisation of the triester O,O,O-TBTP to the thiol isomer O,O,S-TBTP (see reaction 5.9) is known(141) to be autocatalytic in the presence of polar solvents and the net result of these reactions is the migration of the alkyl function from oxygen to sulphur. The thiolisomer O,O,S-TBTP have been reported(106,114,124) to show a signal in the region 25-29 ppm, and the formation of this specie is clearly shown in Figure 5.17a when TBH:NiDnBP ratio = 10. The infra-red spectra in Figure 5.18 also provides clear evidence of the presence of the various ester groups which normally show a P-S-(C) absorption band around 580cm^{-1}(82). This figure also illustrates the gradual decay of the P-S-Ni band at 560cm^{-1}, concomitant with the increase in the P-S-P and

P-S-S vibration modes at $530cm^{-1}$ and $500 - 400cm^{-1}$ respectively. The former band is assigned to the monosulphide (DnBMS) while the latter range is certainly due to a mixture of di-tri-and/or tetrasulphide since the ^{31}P NMR signal (when R = 10) clearly shows a signal of 83.8 ppm which has previously (Section 5.3.2a) been assigned to the trisulphide. The formation of the acidic species at higher TBH ratios (R = 6-10) is also indicated in Figure 5.18 by virtue of the broad shallow band between $2500-2000cm^{-1}$. As indicated in section 5.3.2a, absorption due to (P)-S-H linkages and (P)-O-H stretching modes have been known(109b,125a) to arise in the region $2500-2000cm^{-1}$ for several organophosphorus acids.

The rapid increase in the formation of the acidic species with chemical shifts of 63 ppm and 21 ppm for the thione and the thiol isomer respectively, is very much in evidence when TBH:NiDnBP ratio equals 10. It must however be pointed out that the mere existence of this acid in predominantly (Table 5.10 and Figure 5.17a) the thiol form ($\sim 21\delta$) clearly suggests that some of the hydroperoxide still remains undecomposed. This is consistent with the findings reported in previous sections regarding the tautomeric behaviour of organo-thiophosphorus acids(128), and will be discussed in Section 5.3.4. These acidic species (DnBTA) could either be formed via the decomposition of the sulphinate (1) as shown in reaction 5.18(f) or more likely through the instant oxidation of the disulphide as they are formed, as favoured by Al-Malaika and co-workers(5a,40b)(reaction 5.19)



(5.19)

This is not surprising since the loss in the relative abundance of DnBDS at higher TBH:NiDnBP ratios, roughly parallels the rapid increase in the formation of DnBTA (Figure 5.19) and DnBMS via reaction pathways 5.17-5.18. The other products identified by ^{31}P NMR when TBH:NiDnBP ratio = 10, include inorganic phosphates $[(RO)_3PO]$ with a chemical shift of 0.9 ppm, the phosphoryl disulphide $[(RO)_3POS]_2 \sim 17$ ppm and the completely sulphurated monosulphide $[(RS)_2PS]_2S \sim 90$ ppm which may result from intermolecular sulphur transfer reactions (reaction 5.5 - 5.9). The origin of the new ^{31}P NMR signal having a chemical shift of 76 ppm when TBH:NiDnBP ratio = 10, is presently uncertain. The position of this signal implies that this specie is a monosulphide with a lower alkyl group rather than butyl (e.g. ethyl). Alternatively, the alkyl group may be s-butyl since the primary alkyl derivatives of dithiophosphates have been known(93) to show ^{31}P NMR chemical shift which are approximately 3 ppm higher than the secondary alkyl analogues. The origin of the previously-mentioned products with chemical shifts of 0.9 ppm, 17.ppm and 90 . ppm have all been fully discussed in sections 5.3.1 - 5.3.2 (thermal-oxidative decomposition of DnBDS).

The products of the decomposition of the hydroperoxide (TBH) include tertiarybutyl alcohol and acetone. Figure 5.18 shows the free OH frequency vibrations of the alcohol at $3620cm^{-1}$ associated with the broad OH stretching vibrations of dimeric alcohols. The OH deformation modes of the alcohol was observed(at $1150cm^{-1}$) but not shown in this figure, which also clearly illustrates the strong presence of a ketone, probably acetone at $1720cm^{-1}$.

As mentioned in section 5.2.3, the green crystalline solid isolated from the 10:1 ratio reaction was analysed by infra-red spectroscopy (KBr disc). A comparison of the infra-red spectrum of this solid with that of an authentic nickel sulphate ($NiSO_4 . 6H_2O$) sample shows that this solid is largely nickel sulphate (Figure 5.20).

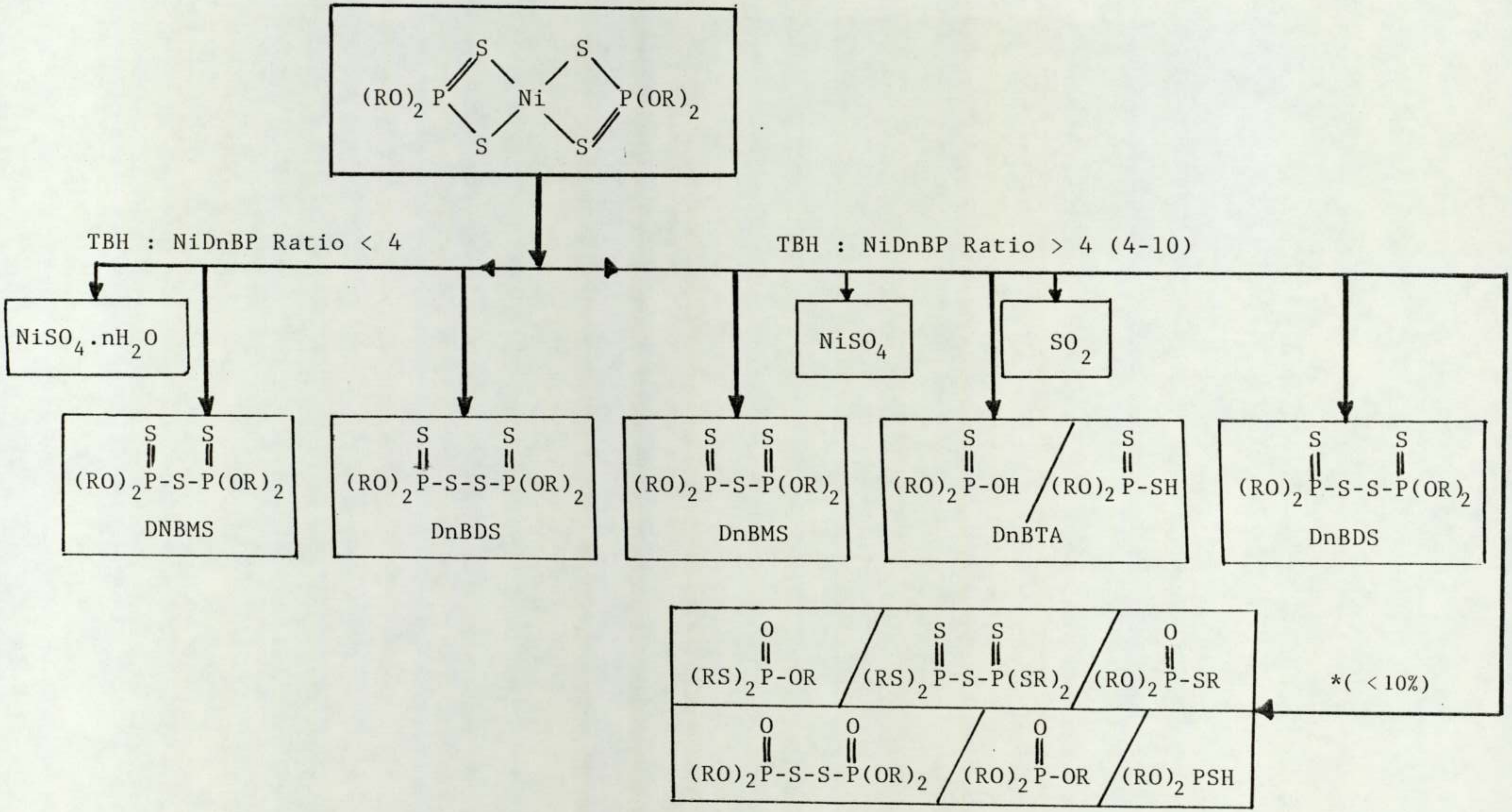
In conclusion therefore,the oxidation of NiDnBP by TBH at

[TBH]:[NiDnBP] molar ratios of 1 - 10, results largely in the formation of di-n-butyl thiophosphoryl monosulphide (DnBMS) as the predominant product. This is closely associated with the formation of a mixture of di-,tri-, and/or tetra-sulphides (mainly disulphide) which reached a maximum at 6:1 ratio. At much higher TBH:NiDnBP ratios however (10:1), the acidic species DnBTA are formed at the expense of the disulphide, although the monosulphide still features as the major product. These findings are distinctly shown in figures 5.17 - 5.20, and the formation of the sulphur acids (DnBTA) in high yields at the expense of the disulphide (when R = 10) seems to confirm the view that both radical and non-radical generating mechanisms apply, with the latter being less predominant of low molar [TBH]:[NiDnBP] ratios. The strong presence of the monosulphide even at such a high ratio (R = 10) also appears to support this view. It is, therefore, clearly evident that the sulphur acid results from a non-radical generating mechanism (reaction 5.19) involving direct oxidation of the disulphide molecule in earlier radical generating routes (reaction 5.17 - 5.18). This conclusion appeared to be substantiated by Al-Malaika and co-workers(13,40b) who previously reported that peroxide decomposition by the nickel dithiophosphates is charaterised by the formation of the corresponding disulphide in the first rapid stage and that this is then slowly converted to the unstable sulphonic acid (II) which readly loses SO_2 to form the stable sulphur acid

(DnBTA). Furthermore, it was clearly shown(40b) that, although the hydroperoxide (CHP) is decomposed from the begining of the reaction, phenol, the product of the ionic decomposition of CHP, is only formed when the intermediate sulphonic acid (II) starts to break down. This clearly identifies the antioxidant activity of the dithiophosphates with the sulphur acids formed by hydroperoxide oxidation, and the effective photo-stabilising activity (in PP) of the sulphur acid (DnBTA) and the disulphide processed in the presence of TBH, has shown this to be the case (see Sections 3.3.1 and 4.3A.4). The quantitative production of nickel sulphate also appears to support the mechanisms proposed in this section since several workers(13,68b,105b) have in the past arrived at similar conclusions.

The products of the oxidation of NiDnBP by TBH at room temperature (25°C) are summarised in scheme 5.11.

Scheme 5.11 Products of the oxidation of NiDnBP by TBH in cyclohexane at 25°C



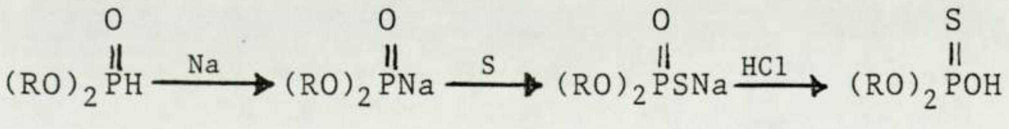
* of total yield

5.3.4 The Use of Certain Reagents as Assignment Aids During ^{31}P NMR Analysis

It has been reported(93) that additional information on ^{31}P NMR data can be accomplished by observing the effects of adding certain reagents such as an amine, to mixtures of dithiophosphate oxidation products. The use of this method has led to some ^{31}P NMR signals being assigned with a high degree of certainty since the observed effect of the reagents on the oxidation products directly parallels that of synthesised standards.

5.3.4(a) Effect of Tertiary Amine and a Hydroperoxide on the Chemical Shift of Thionophosphoric Acid (DnBTA).

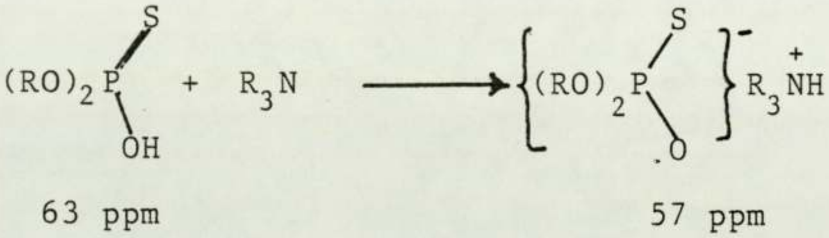
Di-n-butyl thionophosphoric acid $(RO)_2$ PSOH was obtained by treating sodium di-n-butyl thiophosphate with a mineral acid, the former being in turn, synthesised by sulphur addition to di-n-butyl hydrogen phosphite in the presence of sodium metal as folows



$$(RO)_2\overset{\overset{O}{\|}}{P}H \xrightarrow{Na} (RO)_2\overset{\overset{O}{\|}}{P}Na \xrightarrow{S} (RO)_2\overset{\overset{O}{\|}}{P}SNa \xrightarrow{HCl} (RO)_2\overset{\overset{S}{\|}}{P}OH$$

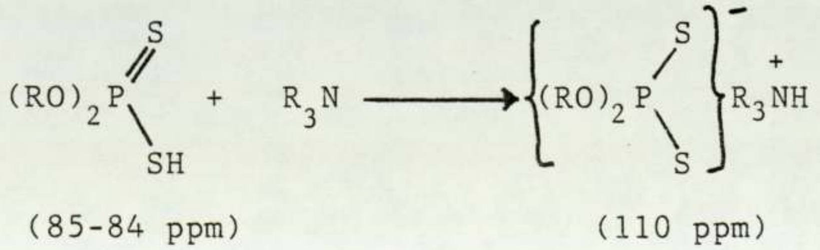
(5.20)

A detailed procedure is given in the experimental chapter (Section 2.1.5). The effects of triethyl amine (R_3N) and tertiary butyl hydroperoxide (TBH) on the chemical shift of the acid is shown in Figure 5.21a-c. The pure acid as prepared shows a sharp ^{31}P NMR signal at 63 ppm which when reacted with triethyl amine, shifts to 57 ppm due to the conversion of the unionised acid groups to the ionised salt forms thus: (reaction 5.21)



(5.21)

The same effect is equally applicable to the thiol isomer, as will be shown in the course of this discussion. It is also worth mentioning that a similar effect has been observed(93) in reactions of the amine with Di-alkyl dithiophosphoric acids $(RO)_2$ PSSH which normally show a ^{31}P NMR signal in the region of 85 ppm. This reaction results in the formation of the amine salt with a chemical shift of 110 ppm (reaction 5.22).

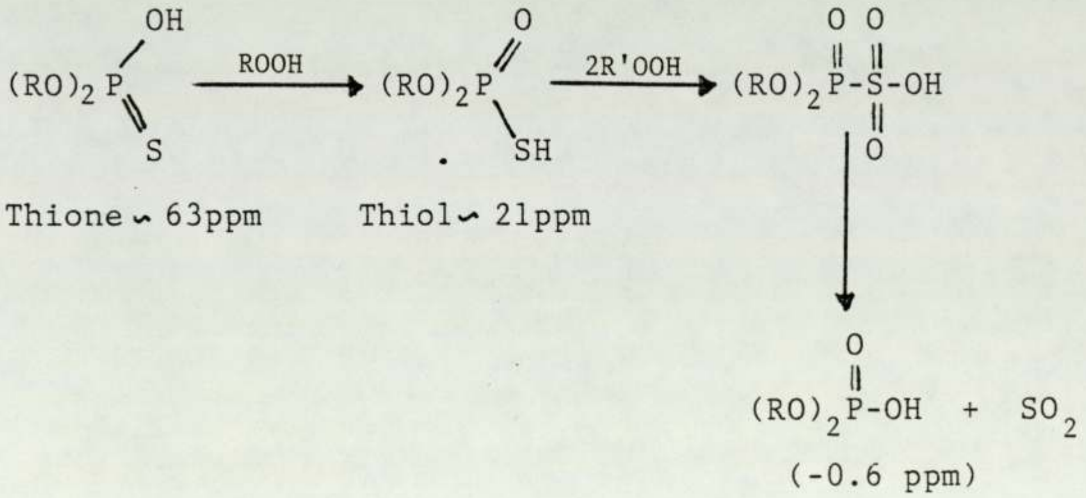


(5.22)

The reaction of the acid (DnBTA) with TBH on the other hand produces a much larger effect on the chemical shift of the original acid. On addition of the hydroperoxide to the acid, the original chemical shift at 63 ppm was replaced by a new signal of approximately equal intensity with a chemical shift of 21 ppm. This signal is assigned to the thiol isomer by analogy with the hydroperoxide decomposition mode of the acid as shown in Section 5.3.2b, Scheme 5.8.

The fact that this acid (PSOH) is an excellent hydroperoxide decomposer have been shown(93) in great detail by Smith, who postulated a reaction scheme involving the thiol isomer (POSH) as the initial reaction intermediate.

Scheme 5.8



Kabachnick and co-workers(128) have previously used the same specie $(RO)_2PSOH$ to exemplify the thione-thiol tautomeric equilibrium which is equally applicable to several organo-phosphorus acids. Their findings shows that the tautomeric equilibrium is determined by the ratio of the ionization constants of the forms (PSOH vs POSH), which to a great extent depends on the nature of the solvent/reaction media and the structure of the tautomeric forms.

Figure 5.21c also indicates that all the added hydroperoxide have been decomposed since the ^{31}P NMR still shows the original signal for the thione isomer (63δ) which clearly suggests that a trace amount of the original acid (PSOH) is still present in the mixture. This behaviour (dependency on reaction media) is consistent with the results obtained in these oxidation studies. From tables 5.6 and 5.8, it is seen that during the oxidation of DnBDS by TBH at 100 °C (in both dichlorobenzene and cumene respectively), the thiol isomer with a chemical shift of 21 ppm is always formed in the initial stages while there is still hydroperoxides present in the system. The thione isomer (63 ppm) is only observed in the latter stages of the reactions, this being highly indicative of the tautomeric behaviour of the acid. A striking example is provided in table 5.8 and figure 5.14 in a previous section which shows complete conversion of all the thiol form (POSH) to the thione form (PSOH) at the end of a 17 hour reaction.

5.3.4(b) Effect of Tertiary Amines on the Chemical Shifts of Thiophosphoryl Polysulphides.

As previously stated (Section 5.2.4b), the assignment of certain ^{31}P NMR signals was confirmed or extended by the use of both hydroperoxide and amine treatment.

The chemical shifts of di-alkyl dithiophosphoric acid $(RO)_2PSSH$ and the corresponding di-or polysulphides $[(RO)_2PS]\ Sn$ (n=2-4) practically coincide since all show their ^{31}P NMR signal within the range 85.2-83.8 ppm. They can however be differentiated by treatment with a tertiary amine as was shown for the acid in reaction 5.23. In contrast to the effect of the tertiary amine on the chemical shift of the acidic species, it has been claimed(93) that the disulphide does not react with tertiary amines although no comments were made regarding reactions between the tertiary amines and the polysulphides. During the course of these oxidation studies however, the addition of triethyl amine to mixtures of the oxidation products led to the decay of certain signals originally assigned to the tri- and tetrasulphides with chemical shifts of 84.1 and 83.8 ppm respectively. In order to confirm these assignments, an authentic synthesized polysulphide sample (Chapter 2, section 2.1.6) was subjected to similar amine treatment.

The attempted preparation(54) of di-n-butyl tetrasulphide and the trisulphide from the ammonium salt and sulphur chlorides (S_2Cl_2/SCl_2) resulted in a mixture of sulphides. This is consistent with the findings of Kende and co-workers(29) who only obtained yields of 40-50% in their attempted preparation of methyl tetrasulphide and the difficulty in obtaining high yields was attributed to the high thermal instability of the polysulphide linkage.

It is very clear from Table 5.11 that the reaction of triethyl amine (R_3N) with the polysulphides results in complete decomposition of all the tetrasulphide ($\delta = 84.1$) within five hours, with concomitant increase in the relative (%) yields of both the disulphide (DnBDS) and trisulphide (DnBTr). It is also evident that the reaction mixture after five hours, contains more amine salt ($\delta = 111.7$) than can be accounted for by the conversion of the dithiophosphoric acid ($\delta = 84.5$) which was originally present as a small impurity. This suggests that in parallel with the formation of di- and trisulphides via radicals obtained from the decomposition of the tetrasulphide, some dithiophosphoric acid is equally formed by simple proton abstraction by a thiyl radical, and simultaneously converted to the amine salt.

After 600 hours reaction time, the ^{31}P NMR spectra (Figure 5.22 and Table 5.11) shows that the decomposition of the trisulphide results largely in the formation of the dithiophosphoric acid which as described above, is simultaneously converted to the amine salt; although some disulphide is also formed in the process.

The precise mechanism involved in these reactions is not clear, but may be related to the catalysis of sulphur reactions by amines. This behaviour is analogous(135) to the action of piperidine at room temperature on various dialkyl tetrasulphides in removing a considerable proportion of the poly-sulphidic sulphur in the form of a complex, the tetrasulphite being largely converted to the disulphide. The reaction of triethyl amine and the thiophosphoryl polysulphides may be regarded as a desulphuration process involving the formation of sulphurated nitrogenous compounds. It is worth mentioning that(135) in reactions between triethyl amine and sulphur at 140°C, compounds such as NN-diethylthioacetamide ($CH_3CS\text{-}NEt_2$) have been isolated.

Similarly, Hodgson and co-workers(136) have established (by ESR analysis) that the radicals in amine solutions of sulphur are the result of homolytic scission of S-S bonds in the amine complex (N,N'-polythiobisamines) which are formed by step wise nucleophillic attack on S_8 rings by the amine (reaction 5.24a).

$$\underset{2^{\circ}\text{Amine}}{2\,RR'NH} + S_x \longrightarrow \underset{(I)}{(RR'N)_2S_{x-1}} + H_2S \qquad (5.23a)$$

The hydrogen sulphide may then react further with the formation of amine polysulphides.

$$2\ RR'NH\ + H_2S\ +\ S_x \longrightarrow (RR'NH_2)_2^+\ S_{x+1}^-$$

(5.23b)

Hodgson, et al$^{(136)}$have suggested that the initial complex N'N-polythiobisamines (I) is responsible for the colour of the solutions, while the dark red oil deposited by piperidine solutions of sulphur is equally such a salt. This is consistent with the findings in the present study since the colour of the amine/polysulphide solution progressed from light orange (original sample solution) to dark red. In over a period of days, the solution separated into two layers, an upper light orange layer and a lower dark red layer. A similar separation have been demonstrated by these workers$^{(136)}$ by passing hydrogen sulphide into a freshly prepared solution of sulphur in piperidine.

The presence of radicals as described in this study must be considered in connection with the catalysis of a broad variety of sulphur reactions by amines. For instance, Bartlett, et al$^{(137,138)}$ have reported that tertiary phosphines (trialkylphosphine) reacts vigorously with sulphur to yield trialkyl phosphine sulphide on a quantitative basis. They also found that pure triethyl amine alone did not catalyse this reaction although powerful catalytic effects were observed in the presence of hydrogen sulphide and sulphur dioxide.

In view of these considerations, it is therefore not surprising that in the oxidation studies described in this chapter (see Section 5.3.1 - 5.3.3), the addition of triethylamine to mixtures of the oxidation products results not only in the conversion of any unionised acid group present in the mixture to the ionised salt form, but also to the catalytic desulphuration of the thiophosphoryl polysulphides in general. This behaviour was, however, found to be time - dependent particularly in the case of the trisulphide as shown for the authentic sample described previously (Table 5.11 Figure 5.22).

5.3.4(c) Reaction of Triethyl Amine (R_3N) with Mixtures of DnBDS/NiDnBP Oxidation Products (Effect on Chemical Shifts)

The striking similarity between these reactions (Tables 5.12 - 5.13) and those obtained with the authentic specimens is responsible for the high degree of accuracy employed for the structural assignment of some of the ^{31}P NMR signals, with particular reference to the polysulphides and acidic species.

Table 5.12 shows the changes observed in the relative abundance and/or chemical shifts of compounds formed during the oxidation of DnBDS by TBH at 100°C (TBH:DnBDS ratio = 2), when reacted with triethyl amine. The ^{31}P NMR data in Table 5.12 clearly shows the quantitative conversion of the thiono-thiol phosphoric acids with chemical shifts of 63. and 21. ppm respectively, to the amine salt (δ = 57) with the latter being time dependent. The complete desulphuration of the tetrasulphide (δ = 84.1) after only one hour amine treatment is also clearly indicated, and this roughly parallels the increase in the relative abundance of both the disulphide (δ = 85) and trisulphide (δ = 83.8). It is equally evident that further amine reaction (2 hrs) results in the desulphuration of the trisulphide to yield mainly the disulphide, and some inorganic phosphorus species with chemical shifts < 1.0. Some dithiophosphoric acid may also have been formed and simultaneously converted to the amine salt. After 300 hours reaction, Table 5.12 clearly indicates that in addition to the reactions of the amine with the various species contained in the mixture, further oxidation is also occuring in view of the rapid decay of the disulphide (δ = 85). The dramatic loss in the disulphide content is not surprising since such oxidation may be catalysed by any one of, or a combination of the various compounds present in the mixture such as amines, hydroxy compounds, hydrogen sulphide, oxygen, sulphur dioxide etc. The importance of these compounds either singly or collectively, in the decomposition of the disulphide cannot be ruled out. Since some of these have been widely shown(137) as effective redistributors of sulphur.

However, this decay in the disulphide content after 300 hours amine reaction, roughly concides with the formation of the amine salts of both the thiophosphoric (57δ) and the dithiophosphoric (112δ) acids. There is no doubt that the formation of these amine salts of the respective acids (PSOH and PSSH), is an arguement in favour of the assumption that the disulphide decomposes to form the acids which are in turn simultaneously converted to their amine salts. Table 5.12 also shows that during the course of these series of reactions, more triesters and inorganic phosphorus species are formed. These results are also illustrated in Figure 5.23.

Further confirmation of the assignment to both tautomeric forms of the thiophosphoric acid is provided in Figures 5.24 - 5.25 which illustrate the formation of amine salts of the acidic groups formed in the oxidation reactions of TBH with DnBDS in cumene, and NiDnBP in cyclohexane respectively.

It was shown earlier (Section 5.3.2b) that the 17 hour oxidation of DnBDS by TBH in cumene at 100°C results largely in the formation of thionophosphoric acid (DnBTA 63.3 δ) as the major product. Figure 5.24

depicts the total conversion of this acid to the ionised salt form after a five minute reaction of the sample with triethylamine at room temperature. This phenomenon is also shown in Table 5.8 which clearly indicates that the amine salt is formed quantitatively.

The ^{31}P NMR spectra of the soluble portion of the 10:1 molar ratio TBH:NiDnBP reaction in cyclohexane at room temperature (Section 5.3.3) also shows the thiophosphoric acids as one of two major products. The mere presence of both isomers however suggests that some hydroperoxide still remains undecomposed, since the thiol isomer (POSH) has previously been shown (Section 5.3.4a) to exist only in the presence of hydroperoxides. As with the TBH:DnBDS oxidation reaction sample, the amine treatment of this sample (TBH:NiDnBP) results in a quantitative conversion of the acidic groups to the ionised salt forms. This behaviour is illustrated in Table 5.13 and Figure 5.25. It must however be emphasised that the ^{31}P NMR data on the original sample (R = 10) as presented in Table 5.13 and Figure 5.25 are completely different from those shown in Table 5.10 and Figure 5.17a, since the ^{31}P NMR analysis of the amine reaction was carried out several days after the initial analysis. A direct consequence of this lapse in the ^{31}P NMR measurement, is the reduced % yield of the thiophosphoric acids, which may have decomposed some of the hydroperoxide still present in the mixture. It is therefore not surprising that some of the thiol isomer (21 ppm) have been converted to the thione form (63 ppm) due to the reduced peroxide content in the mixture.

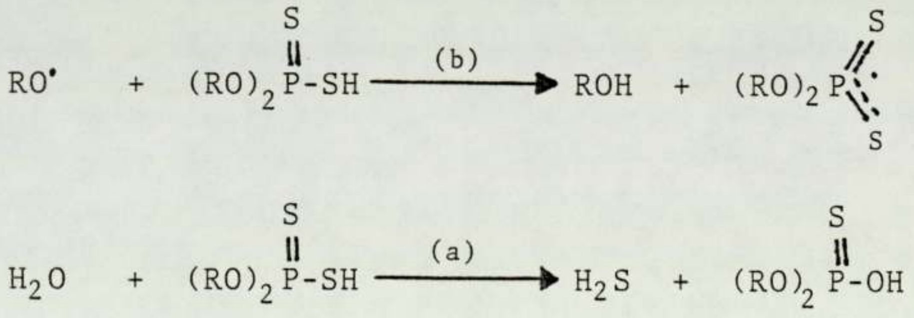
It is undeniably clear from these discussion that the structural assignments to the ^{31}P NMR signals of importance observed in the course of these studies (Section 5.3.1 - 5.3.3) have been proven beyond doubt.

5.4. Overview of the Oxidation / Thermal Oxidative Decomposition of NiDnBP and DnBDS

The oxidation of nickel di-n-butyldithiophosphate at room temperature and the thermal-oxidative decomposition of bis-di-n-butyl thiophosphoryl disulphide under a variety of conditions, have been studied (Section 5.3.1-5.3.3) in great detail. In both cases, the oxidation products and/or reaction intermediates have been identified with a high degree of certainty and this has provided an insight into the detailed mechanism of the antioxidant function of these materials.

(1) In Section 5.3.3, the interaction between NiDnBP and TBH at room temperature have been shown (Figure 5.19) to involve two distinct catalytic stages. The first which is favoured by a low TBH:NiDnBP molar ratio (< 4), gives rise to free radical products, mainly the thiophosphoryl monosulphide (DnBMS) and the thiophosphoryl disulphide

(DnBDS). The second catalytic stage which is preceded by an induction period, occurs at higher TBH:NiDnBP ratios and this stage appears to be coincident with the formation of the thiophosphoric acid (DnBTA) which may be regarded as an ionic product. These results are consistent with the findings of Al-Malaika et al(40b) who concluded by kinetic studies that the nickel complex is always destroyed before the onset of the secondary catalytic stage of the hydroperoxide decomposition. It must be pointed out however, that there was no evidence (by ^{31}P NMR analysis) for the formation of the dithiophosphoric acid $(RO)_2PSSH$ as was suggested by Sexton(139) for zinc dithiophosphates. The difficulty experienced in identifying the ^{31}P NMR signal from the acid may be due to their ease of hydrolysis(130) and their ability to generate thiyl radicals(13) by their reaction with peroxides thus: (reaction 5.24).



$$RO^{\bullet} + (RO)_2\overset{S}{\overset{\|}{P}}\text{-SH} \xrightarrow{(b)} ROH + (RO)_2P\overset{S}{\underset{S}{\cdot\cdot}}$$

$$H_2O + (RO)_2\overset{S}{\overset{\|}{P}}\text{-SH} \xrightarrow{(a)} H_2S + (RO)_2\overset{S}{\overset{\|}{P}}\text{-OH}$$

(5.24)

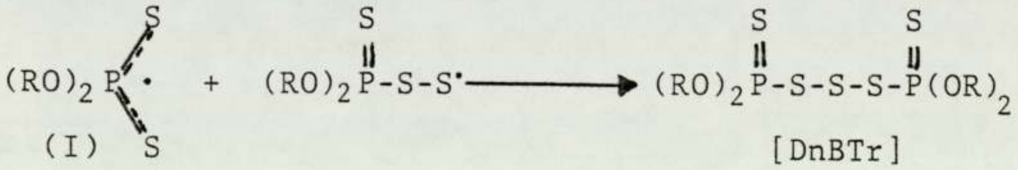
The major products formed when TBH:NiDnBP molar ratio = 10 are DnBMS, DnBTA and DnBDS in decreasing order. Other minor products (< 10%) include triesters in various forms and inorganic phosphorus species.

(2) The thermal decomposition of DnBDS under a variety of conditions have been shown (Section 5.3.1 - 5.3.3) to involve very similar reaction intermediates/products in the early stages of oxidation, with particular reference to the thiophosphoryl tri - and tetrasulphides (DnBtr DnBTe), the thiophoshoric acid (DnBTA) and the triesters in various forms. The formation and distribution of these products is equally similar in both reaction media used (dichlorobenzene and cumene), although certain differences are clearly in evidence when the nature of the oxidant is changed (air vs TBH). The main distinguishing features of these oxidation studies are as follows:

a) When the oxidation of DnBDS is carried out under a constant stream of air at 180 °C (in both substrates) the major reaction intermediates as mentioned earlier are the trisulphide (DnBTr), tetrasulphides (DnBTe) and the triesters in various forms. In the early stages of oxidation, all available evidence (^{31}P NMR & HPLC) clearly indicates a predominance of the trisulphide over the tetrasulphide (DnBTr > DnBTe) although various triesters are continuously being formed throughout each reaction. However, it is worth mentioning that the thionophosphoric acid (DnBTA) is only formed when an oxidisable substrate (cumene) is used since this is simultaneously oxidised to the hydroperoxide in the presence of oxygen.

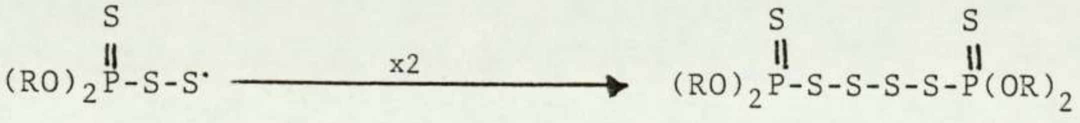
b) The use of a hydroperoxide (TBH) as the oxidant at 100 °C, results in a predominance of the tetrasulphide over the trisulphide (DnBTe > DnBTr) although both tautomeric forms of the thiophosphoric acid (DnBTA) are formed, presumably at the expense of triesters which are only formed in the very later stages of each reaction.

The differences regarding the trends in product formation can be accounted for by a mechanism involving the co-existence of both symmetric and asymmetric decomposition of the disulphide molecule to yield the thiyl [$(RO)_2P\overset{S}{\underset{S}{<}}$] perthyl [$(RO)_2\overset{S}{\overset{\|}{P}}-S-S\cdot$] and the phosphorus - centred radical [$(RO)_2\overset{S}{\overset{\|}{P}}\cdot$] all of which undergo various reactions to form the various products thus:



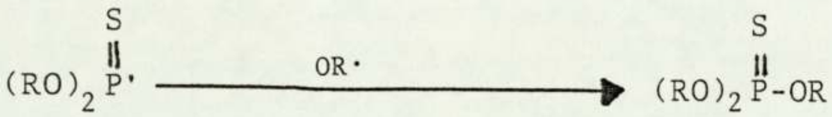
$$(RO)_2P\overset{S}{\underset{S}{<}}\cdot + (RO)_2\overset{S}{\overset{\|}{P}}-S-S^{\cdot} \longrightarrow (RO)_2\overset{S}{\overset{\|}{P}}-S-S-S-\overset{S}{\overset{\|}{P}}(OR)_2$$

(I) [DnBTr] (5.3)



$$(RO)_2\overset{S}{\overset{\|}{P}}-S-S^{\cdot} \xrightarrow{x2} (RO)_2\overset{S}{\overset{\|}{P}}-S-S-S-S-\overset{S}{\overset{\|}{P}}(OR)_2$$

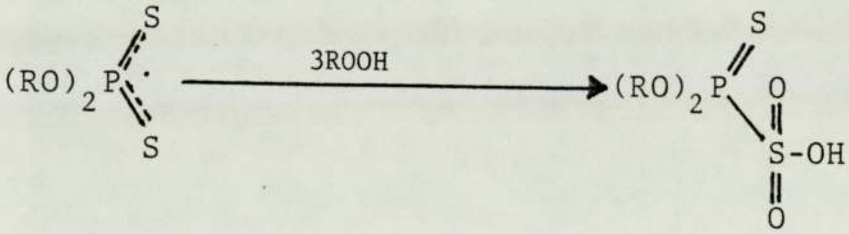
(II) [DnBTe] (5.4)



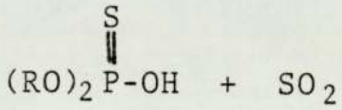
$$(RO)_2\overset{S}{\overset{\|}{P}}\cdot \xrightarrow{OR\cdot} (RO)_2\overset{S}{\overset{\|}{P}}\text{-}OR$$

(III) [ester] (5.2)

The reactions shown above represent the formation of the various product in the presence of air. In the presence of hydroperoxide however, dimerisation of radical (II) becomes more frequent since the tetrasulphide (DnBTe) is the predominant product. The formation of DnBTe as described is obviously enhanced by the limited availability of radical (I) since some of these (thiyl radicals) may be oxidised by the hydroperoxide to form the sulphonic acid which subsequently decomposes to yield the thionophosphoric acid thus:



(sulphonic acid)



$$(RO)_2\overset{S}{\overset{\|}{P}}\text{-}OH + SO_2$$

(DnBTA)

(5.11c)

The utilisation of some of the thiyl radicals in the formation of the acidic specie at the expense of the trisulphide (reaction b) is certainly an arguement in favour of the predominance of the tetrasulphide (DnBTe) over the trisulphide (DnBTr). The same arguement also applies to the limited formation of the triesters from the phosphorus-centred radical (III) since this radical easily undergoes a reaction with a hydroxyl radical ($\cdot$OH) to form the thionophosphoric acid (DnBTA).

In conclusion therefore, prolonged oxidation of the disulphide have been shown to result largely in the formation of the thionophosphoric acid and inorganic phosphorus species as the major products. This confirms the fact that all the previous products (DnBTe, DnBTr triesters) are merely reaction intermediates which in turn decompose to form alkyl sulphides and corresponding sulphoxides, some of which were isolated and positively identified. This view is confirmed by the fact that ^{31}P NMR analysis of solvent extracts of PP films stabilised with the disulphide (DnBDS), distinctly suggests that the major products formed after processing are the triesters and the sulphur acid (see Chapter 4, Section 4.3c.2).

CHAPTER SIX

CONCLUSIONS AND SUGGESTIONS FOR FURTHER WORK

6.1 Conclusions

In general, nickel dithiophosphates (NiDRP) and the corresponding disulphides (DRDS) were found to be very effective in stabilising polyolefins over a range of conditions although their activity is profoundly influenced in varying degrees by parameters such as the processing variables, changes in the alkyl substituent, concentration, and the level of impurities in the additive. The salient features of their antioxidant activity is summarised as follows:-

(1) Both compounds (NiDRP and DRDS) are efficient melt stabilisers for polypropylene during processing, when assessed at normal (low) concentration levels either singly (designated as normal samples- NS) or as multi-component synergistic stabiliser systems containing the U.V.-absorber, HOBP (designated as dilute concentrates-DCt.). Although the melt stabilising activity of thiophosphoryl disulphides is slightly better than that of the nickel complexes when assessed as normal samples, increases in the proportion of the latter (NiDRP) at the expense of the former (DRDS) in dilute concentrates leads to an increase in activity.

Furthermore, in contrast to the behaviour of DRDS when processed singly (NS), the activity of the corresponding nickel complexes is susceptible to changes in the alkyl substituent. Finally, the melt stabilising activity of these compounds under highly demanding conditions (e.g. successive extrusions) is comparable with that of well known commercial melt stabilisers based on the hindered phenols (e.g. Irganox 1076).

(2) The nickel dithiophosphates (NiDRP) show excellent thermal antioxidant activity in PP,in highly volatilising environments (air oven) in which less stable stabilisers are lost. Thus, whereas their activity in this instance is strongly dependent on changes in the alkyl substituent in the molecule, and concentration, changes in the processing temperature has no noticeable effect on their performance.

The corresponding disulphides (DRDS) on the other hand, are not effective in protecting the polymer against thermal oxidative degradation and are therefore much less affected by changes in the above parameters.

Furthermore, the thermal stabilising activity of multi-component synergistic systems (DCt) based on the higher alkyl homologues (e.g. octyl) is also comparable with that of the commercial thermal stabiliser, Irganox 1076, and the performance of these synergistic systems is markedly improved with increases in the proportion of the nickel complex relative to the disulphide within the system (i.e. NiDRP > DRDS).

(3) The nickel dithiophosphates are very effective in stabilising polyolefins (PP and PE) against photo-oxidation in view of their high U.V. stability and their ability to release the ionic catalysts for peroxide decomposition over a long period of time. Their photo antioxidant activity in PP is however, strongly dependent on changes in the alkyl substituent, concentration and processing severity. When assessed at normal (low) concentration levels, the butyl substituent is superior to its higher homologues on a weight basis while the hexyl derivative is most effective on a molar basis. An analogous behaviour is also shown by the corresponding thiophosphoryl disulphides although these are not very effective as photo antioxidants.

(4) The effect of thermal processing on the photo antioxidant activity of the nickel dithiophosphates and the corresponding disulphides in both PP and PE was found to be profoundly dependent on the amount of oxygen in the mixer. Processing in the presence of variable amounts of oxygen (severe processing), although not a part of normal industrial processing practice, causes a reduction in the photo antioxidant activity of the nickel complexes due to their partial conversion to the oxidation products,

notably the disulphides.

In contrast, severe processing has a beneficial effect on the U.V. stabilising activity of thiophosphoryl disulphide in PP only when processed at normal (low) concentration levels (NS and DCt.) although it has a deleterious effect when high concentration levels are used (concentrates-Ct.) due to the formation of a high concentration of light unstable intermediates. However, controlled oxidative processing of DRDS concentrates in the presence of a hydroperoxide (e.g.TBH) imparts greater photo stability to the polymer when compared to its performance under mild (limited oxygen) and severe (excess oxygen) processing conditions. A significant feature of controlled oxidative processing is the production of a critical amount of the effective peroxidolytic antioxidant in situ. Thus, thionophosphoric acid (DnBTA), a major oxidation product of dithiophosphates (NiDRP and DRDS) shows a U.V.stabilising activity (in PP) which is similar to that of the disulphides.

In the less oxidisable LDPE, however, severe processing has a beneficial effect on the U.V. activity of thiophosphoryl disulphides when assessed either at normal (low) concentration levels (NS and DCt.) or as concentrates (Ct.).

(5) The effect of impurity level in thiophosphoryl disulphides on their photo antioxidant activity is strongly dependent on the level of impurity and processing procedure. DRDS samples containing low levels of impurity (<25% impurity) impart greater photo stability to PP under mild processing condition when compared to DRDS samples of very high purity (>99%). Oxidative processing of such impure samples (>75% purity) also improves the U.V. stabilising activity although this depends on the severity of processing.

(6) Dithiophosphates (NiDRP and DRDS) synergise effectively with the U.V. absorber, HOBP under photo-oxidative contitions, but synergism is most marked when the additives are added at normal (low) concentration levels. Furthermore, the U.V.-synergistic system containing DRDS and HOBP is powerfully augmented by oxidative processing, particularly in LDPE. A notable feature of this system is the loss in synergism particularly in PP when high concentrations of additives are used. This is attributed to the formation of a high concentration of light-unstable quinonoid products from the reaction of the disulphide and HOBP. However, the dilution of such concentrates to normal (low) concentration levels (DCt.) restored the photo antioxidant synergism, and this is further improved by the addition of a small amount of the nickel complex (NiDRP). A significant feature of the multicomponent synergistic systems (DCt.) is that, in

addition to its excellent performance as a melt and thermal stabiliser, it also stabilises the polymer against photo-oxidation.

(7) Although there is clear evidence that some thiophosphoryl adducts become bound to the polymer matrix during processing, these are believed to undergo further thermal and/or shear-induced fragmentation to give low molecular weight analogues which are readily extracted under exhaustive conditions.

However, processing of thiophosphoryl disulphides in EPDM results in a much higher level of binding efficiency. This is primarily due to the presence of additional sites for binding in the terpolymer, this being in turn due to the higher level of unsaturation.

(8) Analogous mechanistic studies in solution clearly identified the sulphur acid as the major oxidation product formed from both the nickel dithiophosphate and their corresponding disulphides. The oxidation of thiophosphoryl disulphide in the presence of oxygen or a hydroperoxide results mainly in the formation of the corresponding tri- and tetrasulphides and various triesters as the major reaction intermediates. These then undergo further reaction to form what may be assumed as the ultimate products; namely the thionophosphoric acid (DnBTA), several inorganic phosphorus species and the

simple alkyl mono- and di-sulphides and derived oxygenated species.

The nature of products formed from the oxidation of the nickel dithiophosphate by a hydroperoxide (TBH) at room temperature is markedly dependent on the molar ratio of the hydroperoxide to the nickel complex (i.e. TBH:NiDRP ratio). At low TBH:NiDRP ratios ($< 6:1$), the primary products of the nickel complex are the corresponding mono- and di-sulphides. At higher molar ratios, however (e.g. 10:1), the major products identified are the thiophosphoryl monosulphides and the thionophosphoric acid which is formed concomitantly from the oxidation of the initially formed disulphide.

(9) In the light of all data accumulated in this study, it is clear that the mechanisms involved in the antioxidant action of dithiophosphates not only includes catalytic peroxidolysis (PD-C) which is their primary function, but may also involve some radical scavenging activity (CB-A/CB-D). The scavenging of alkyl peroxyl radicals (CB-A) is believed to be partly responsible for the high thermal stabilising activity of the nickel complexes. However, products formed from the nickel complex and the corresponding disulphide (e.g.the sulphur acid intermediates) appear to have the ability to alternate between the oxidised and reduced states and hence exhibit regenerative behaviour under conditions

where both alkyl and alkyl peroxyl radicals are present during processing and subsequent thermal and photo-oxidation.

6.2 Suggestions for Further Work

In view of the observations and conclusions reached in this study, the following suggestions are recommended for further work.

(1) The beneficial effects of severe processing on the photo antioxidant activity of thiophosphoryl disulphides can be optimised in PP by reducing the degree of severity (i.e. processing time). This may improve the activity of the concentrates since the concentration of the light-sensitive intermediates may be reduced.

(2) Although severe processing was found to have a detrimental effect on the U.V. stabilising activity of the nickel dithiophosphates, it is of both practical and mechanistic interest to investigate its effect on the thermal antioxidant activity. The same principle also applies to the thionophosphoric acid which was shown to possess some U.V. stabilising activity. Such an investigation will no doubt clarify the source and contribution of alkyl peroxyl radical scavenging to the overall antioxidant activity.

(3) The quinonoid product either formed during oxidative processing of synergistic DRDS:HOBP concentrates or synthesised by a reaction between DRDS and 2,4-di-hydroxy benzophenone (HBP), was shown to be highly unstable to U.V.-light, although preliminary studies indicate that this compound is thermally stable. It is, therefore, important to assess its performance in the polymer under thermal-oxidative (air oven) conditions.

(4) Throughout this work, there were indications that oxidative processing of nickel dithiophosphates may improve their photo antioxidant activity in LDPE which is intrinsically more stable than PP. Alternatively, concentrates of the nickel complex can be prepared in LDPE and then diluted down to normal (low) concentration levels in the presence of HOBP only. It is believed that an investigation in this direction will lead to the production of highly synergistic stabiliser mixtures whose activity may be superior to that of existing systems.

(5) The oxidation studies carried out on the thiophosphoryl disulphides revealed that the corresponding monosulphides which are minor oxidation products are highly stable to thermal oxidation although their contribution to the overall antioxidant activity is still ill-defined. It would be useful to examine the antioxidant activity of an authentic sample of the thio-

phosphoryl monosulphide in the polymer, with particular reference to thermal oxidation (air oven).

(6) It is also of paramount importance to investigate the antioxidant activity (in the polymer) of authentic samples of the various reaction intermediates (notably the thiophosphate esters and the thiophosphoryl tri-and tetra-sulphides) identified during the oxidation studies on NiDRP and DRDS. A comprehensive evaluation of these species in the polymer will no doubt clarify their contribution to the overall antioxidant activity of the dithiophosphates.

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