Mechanisms of Antioxidant Action: Nature of Transformation Products of Dithiophosphates. II. Antioxidant Action of Thiophosphoryl Disulphides

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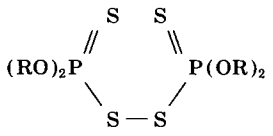
SYNOPSIS

The nature of transformation products of high-temperature reactions of thiophosphoryl disulphides with hydroperoxides in the absence and presence of oxidisable substrates and the role of the disulphide in the overall antioxidant mechanism was investigated using a range of techniques such as oxygen absorption, ^{31}P nuclear magnetic resonance (NMR), gas–liquid chromatography (GLC), and peroxide determination. The major transformation products of the above oxidation reactions were found to be the thio- and thiono-phosphoric acids, in addition to mono and polysulphides. At high molar ratios of peroxide to disulphide (>10), these oxidation products are the main catalysts for peroxide decomposition, while at lower ratios the disulphide itself was found to play a major role in the antioxidant mechanism.

INTRODUCTION

Examination of the antioxidant role of dialkyl thiophosphoryl disulphides [DRDS, relation (1)] is important since they have been identified as transformation products from reactions of many metal dithiophosphate complexes (e.g., Zn, Ni) with hydroperoxides, both in polymers and in hydrocarbon model systems.[1-6] Thiophosphoryl disulphides were



(1)

shown[2,7] to act predominantly as peroxidolytic agents; heterolytic decomposition predominate at all molar ratios of peroxide to disulphide while radical scavenging contribution is only minor. Much less work has been done on the nature of intermediates formed during the antioxidant action of these compounds, and questions remain as to the details of the mechanism of action, e.g., identity of oxidation products, extent of contribution of each of the above processes to the overall mechanism, and whether the disulphide itself, or its oxidation products, are the main catalysts for the ionic decomposition of hydroperoxides. It is also important to point out that the experimental conditions used in different laboratories for carrying out these mechanistic studies are quite varied, giving rise to different data and interpretations and apparent discrepancies in the details of the mechanisms.

In polyolefins, we have shown previously[8] that processing of polymers in the presence of the disulphide under oxidative conditions (presence of air or hydroperoxides) offers much higher stabilising effect than when processed under normal mild conditions (restricted access of oxygen). This has led to the development of very effective stabilisation systems based on a controlled oxidation of thiophosphoryl disulphide in the presence of other dithiophosphate metal complexes.[9] The importance of oxidation/transformation products of the disulphide, under polymer processing conditions, therefore, cannot be overemphasised. The main object of this article is to investigate the nature of transformation products

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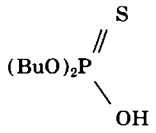
formed during high-temperature reactions of thiophosphoryl disulphide with hydroperoxides in model hydrocarbon systems, conditions closely related to those used for polymer processing. The role of the disulphide itself as an antioxidant and its contribution as the initial transformation product during the oxidation of metal dithiophosphate complexes is also examined.

EXPERIMENTAL

Materials

Dibutyl thiophosphoryl disulphide (DBDS) was prepared via the ammonium salt of dithiophosphoric acid as described previously,[10] and ^{31}P nuclear magnetic resonance (NMR) of the pure compound showed only one peak with a chemical shift of 85 ppm. Dibutyl thionophosphoric acid [DBTnPA, relation (2)] was prepared according to a procedure described by Foss,[11] and ^{31}P NMR spectrum of this compound showed only one peak with a chemical shift of 63 ppm.



(2)

Technical-grade cumene (e.g., BDH) was purified by washing with concentrated sulphuric acid, water, sodium bicarbonate, and water again before being fractionally distilled under nitrogen (BP 152°C/760 mm Hg). Technical-grade decalin was purified as follows: It was distilled under vacuum in a nitrogen-purged flask and a 90% centre cut fraction was taken, BP 35°C (1 mm Hg). The decalin was shaken with several portions of 10% sulphuric acid until no darkening occurred in either the aqueous or the organic phase. The hydrocarbon was then washed several times with water, 10% sodium hydroxide solution, and water again, and was then dried over calcium sulphate. The decalin was redistilled under vacuum under nitrogen atmosphere. A 90% centre cut BP 35°C (1 mm Hg) was again taken. Immediately prior to use, the decalin was passed through a column of activated silica to remove any traces of hydroperoxide. Technical white mineral oil was supplied by Esso Chemicals as Marcol 172; it is predominantly paraffinic in origin and a highly refined product.[12] Cumene hydroperoxide (CHP), e.g., BDH, and tertiary butyl hydroperoxide (TBH), e.g., Koch-Light, were purified by a method described by Kharasch and coworkers.[13] Dichlorobenzene (e.g., BDH) and chlorobenzene (puris, e.g., Koch and Light) were used without further purification.

High-Temperature Oxidative Reactions of DBDS

Reactions of DBDS with CHP were carried out in decalin and white oil in the oxygen absorption cell (described in the next section) at 130°C and in chlorobenzene at 110°C as described previously.[2] Oxidative reactions of DBDS with TBH [molar ratio (TBH)/(DBDS) = 2] in cumene were carried out inside the NMR spectrometer cavity over an extended period of time at 100°C as follows: A preweighed mixture of TBH (1.0*M*) and DBDS (0.5*M*) in cumene was introduced into the NMR tube. The mixture was vigorously shaken, purged with nitrogen before being covered, and placed in the NMR spectrometer, which was originally programmed for a stacking run at 100°C. Thus, data were recorded at time intervals and all spectra obtained at the end of the experiment. Higher-temperature oxidation reactions of DBDS by TBH in the presence of oxidisable (cumene) and nonoxidisable (dichlorobenzene) substrates were conducted at 180°C (using silicon oil bath) in three-neck round-bottom flasks. The reaction mixture was refluxed with continuous stirring under a constant stream of nitrogen. Samples were withdrawn at the required time intervals and immediately frozen in dry ice/acetone until subsequently analysed by ^{31}P NMR.

Product Analysis and Oxygen Absorption

The fate of thiophosphoryl disulphide and the build up of transformation products during its high-temperature reactions with hydroperoxides in the presence or absence of oxidisable substrates were examined by ^{31}P NMR spectroscopy using a Jeol FX-90Q Fourier Transform NMR spectrometer operating at 36.20 MHZ. All spectra were measured with noise decoupling of the phosphorus–hydrogen spin–spin coupling and chemical shifts (ppm) were referenced to an external standard of 85% phosphoric acid. Products formed were identified by their ^{31}P chemical shift values, which were compared either with those obtained from authentic samples or with literature data, and product percent yields (relative abundance) are based on the normalisation of all peak signals to 100%. Infrared spectroscopy (using Perkin-Elmer 599) and gas–liquid chromatography (GLC) analysis (using Pye-Unicam GCD Chromatograph fitted with flame ionisation detector) were also used to support the identification of

products formed during the reactions from the disulphide and hydroperoxides used.

Oxygen absorption measurements were carried out in a number of "cells" immersed in oil baths at the required test temperature. Each cell consisted of two identical three-necked round-bottom flasks (50 cm^3), each fitted with a glass tap and a stopper and connected via side arms to a Pye-Ether pressure transducer (range 5 psi), which in turn was wired to a 24-channel chart recorder (Leeds Northrup Speedomax). The sample flask contained a glass-sheathed bar magnet and the whole cell was placed in a thermostatted bath of silicone oil (130 ± 0.5°C) such that the sample flask was in close proximity to an external horseshoe magnet attached to an overhead stirrer. Before oxygen absorption measurements were conducted, the cell was calibrated by removing a fixed amount of air from the sample flask that corresponded to a certain deflection on the chart recorder (hence, sensitivity of recorder was adjusted accordingly) that enables it to measure the absorption of a certain volume of oxygen corresponding to oxidation up to a 1% (weight by weight) uptake of oxygen. Decalin was mixed with all the other components used for the test reaction and introduced into the sample flask via a pipette such

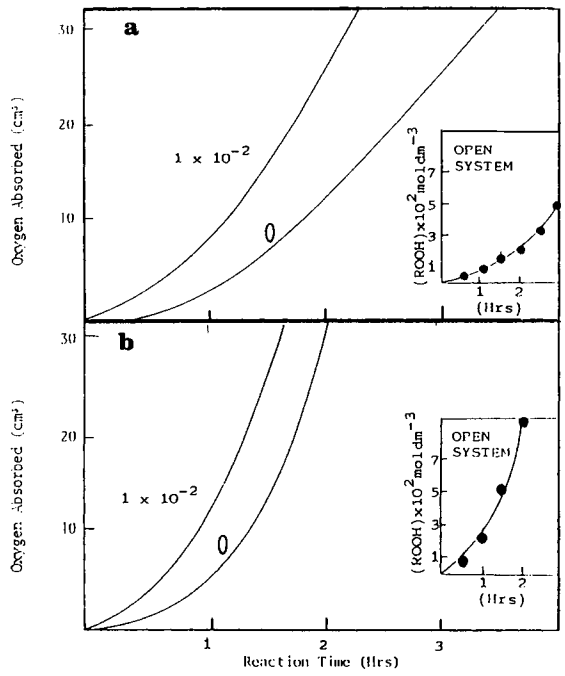


Figure 1 Thermal oxidation of (a) white oil and (b) decalin at 130°C in the absence and presence of CHP. Numbers on curves are CHP concentrations in mol dm^{-3}. Insets show hydroperoxide build up during oxidation of the substrates.

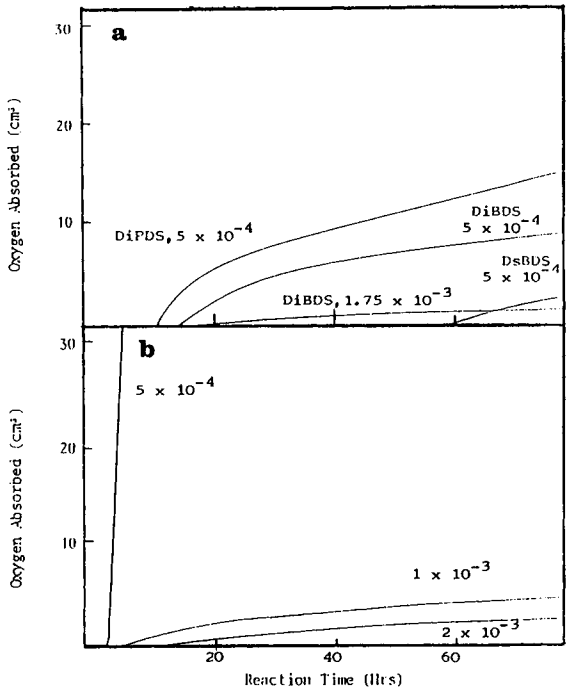


Figure 2 Effect of DRDS on oxidation of (a) white oil and (b) decalin at 130°C. Numbers on curves are DRDS concentrations in mol dm^{-3}.

that the total volume of the oxidisable substrate used was, in all cases, 5 cm^3. Once the sample was introduced, a stream of pure oxygen was passed into the flask for 20 s, after which the sample flask was stoppered and the overhead stirrer activated. Each system studied was evaluated at least three times and an average curve, based on average volume of oxygen absorbed at various oxidation times, was taken; experimental error was within 15%.

RESULTS

Oxidation of DBDS by CHP in Decalin and White Oil at 130°C

The role of thiophosphoryl disulphide as an antioxidant was investigated in two hydrocarbon substrates of different oxidisability. Figure 1 compares the extent of oxidation of white oil and decalin in the absence and presence of CHP at 130°C. The higher oxidisability of decalin is clearly illustrated by the absence of an induction period and the higher concentrations of peroxides that build up during its oxidation [c.f. Fig. 1(a) and (b)]. Figures 2 and 3 compare the effect of DBDS on the oxidation of these two substrates in the absence (Fig. 2) and presence (Fig. 3) of CHP at the same temperature

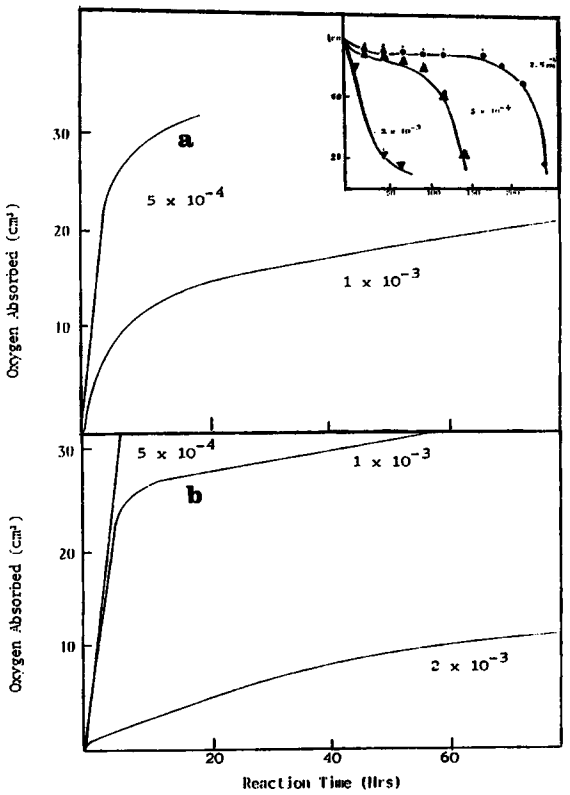


Figure 3 Effect of DRDS on oxidation of (a) white oil and (b) decalin at 130°C in the presence of 1×10^{-2} mol dm^{-3} CHP. Inset shows the decomposition of CHP (1×10^{-2} M) by DRDS in chlorobenzene at 110°C. Numbers on curves are DRDS concentrations in mol dm^{-3}.

(130°C). The presence of the induction periods observed during the oxidation of both hydrocarbon substrates suggests that, initially, the disulphide itself is able to decompose hydroperoxides, and its effect as an antioxidant at this stage increases in the presence of a less oxidisable substrate [longer induction period in white oil, Fig. 2(a) and (b)]. In the presence of CHP, on the other hand, oxidation of the hydrocarbon substrates occurs immediately (without an induction period), as illustrated by the rapid uptake of oxygen, leading to a second much slower oxidation stage (Fig. 3). The extent of oxidation in the first stage depends on the molar ratio of peroxide to disulphide. It is important to point out here that in the case of the more oxidisable substrate (decalin vs. white oil) higher concentrations of disulphide are needed to achieve the same effect, as illustrated, for example, in the large difference in the extent of the initial prooxidant stage in the two substrates at [DBDS] of 1×10^{-3} M [c.f. curves 1×10^{-3} in Fig. 3(a) and (b)]. This initial prooxidant stage indicates the inability of the disulphide to inhibit the hydrocarbon oxidation in the presence of excess hydroperoxides. However, the presence of the second autoretarding oxidation stage suggests clearly that, under these conditions, the DBDS must be oxidised during the first step to more powerful catalysts, which are responsible for the autoretarded oxidation in the second stage. This is supported by the two-stage decomposition process observed for hydroperoxides [see Fig. 3(a) inset]: An initial induction period involving no (or very little) peroxide decomposition during which the disulphide is oxidised to more powerful products responsible for the second rapid catalytic stage.[1,5,6]

Oxidation of DBDS by Hydroperoxides (CHP, TBH) in Presence (Cumene) and Absence (Dichlorobenzene) of Oxidisable Substrate at 100–180°C

To clarify the question of whether thiophosphoryl disulphide itself (in addition to its transformation products) plays a direct role in the decomposition of hydroperoxides, ^{31}P NMR was used to follow the fate of the disulphide and the formation of transformation products during its reactions with hydroperoxides (e.g., TBH or CHP at 100 and 110°C, respectively) and at high molar ratios of hydroperoxide to sulphur compound (e.g., ratios of 1 to 5). Figure 4 shows the kinetics of product formation and disappearance of the disulphide during its reaction with TBH (molar ratio of peroxide to disulphide of 2) in dichlorobenzene at 100°C. Table I gives products of oxidation of DBDS during its reaction with CHP (molar ratio of peroxide to disulphide of 5) in chlorobenzene at 110°C. It is clear from both Figure 4 and Table I that at these high disulphide concentrations (e.g., 1×10^{-1} M) in the absence of an oxidisable substrate the disulphide itself is responsible for the initial peroxide decomposition since almost no transformation products were observed during the decomposition of the initial 80% of the peroxide, during which period the concentration of the disulphide decreased only very slightly. After this initial period of very slow changes in disulphide concentration, there is a sharp fall in its concentration that is paralleled by a rise in the concentration of the oxidation products during a second stage of slow peroxide decomposition (Fig. 4). The main oxidation products formed during this reaction were found to be the tetrasulphides [DRTeS, relation (3)] and trisulphides [DRTS, relation (4)], in addition to thiophosphoric [DRTPA, relation (5)] and thionophosphoric [DRTnPA, relation (2)] acids (see Fig. 4).

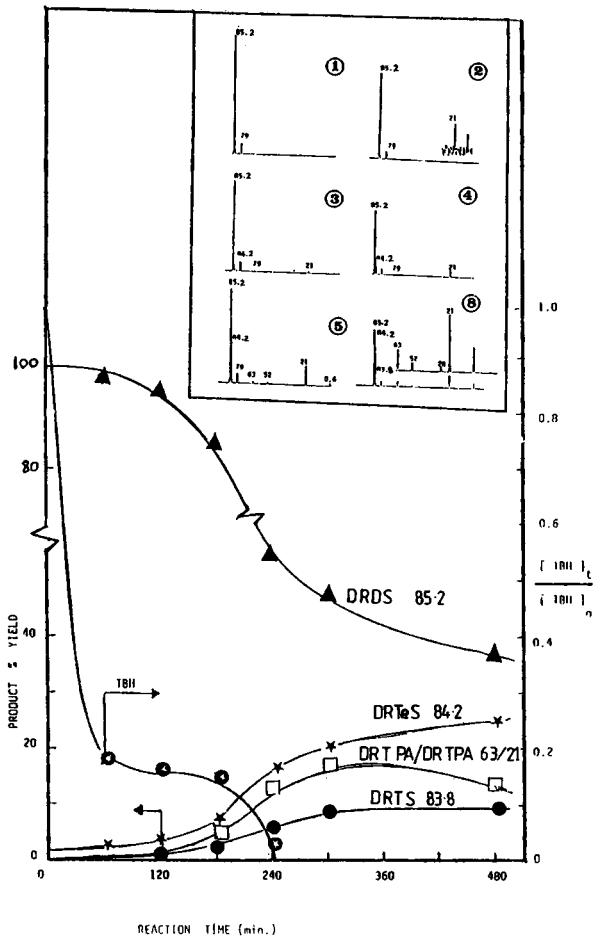


Figure 4 Kinetics of product formation during the reaction of DBDS (0.5*M*) with TBH (1*M*) in chlorobenzene at 100°C. The percent yield values were calculated from NMR signal peak intensities. Inset shows ^{31}P NMR spectra of this reaction. Encircled numbers are reaction times in hours. Numbers on the NMR peaks are chemical shifts in ppm.

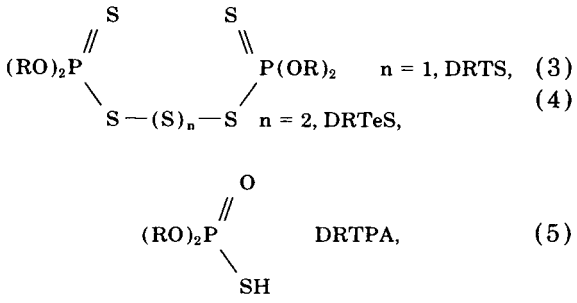
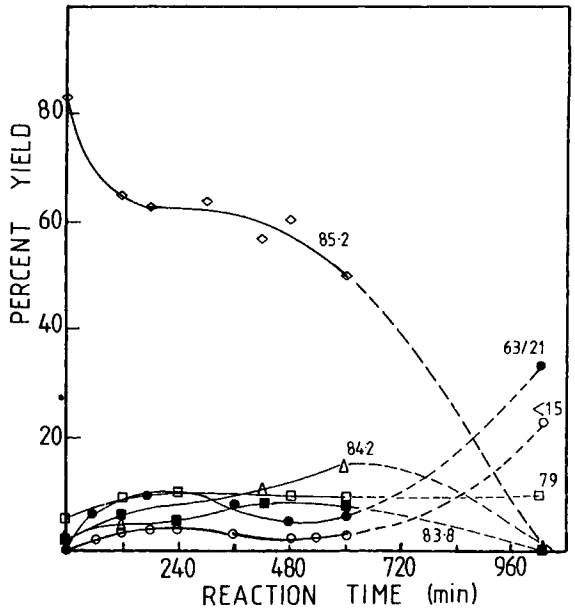
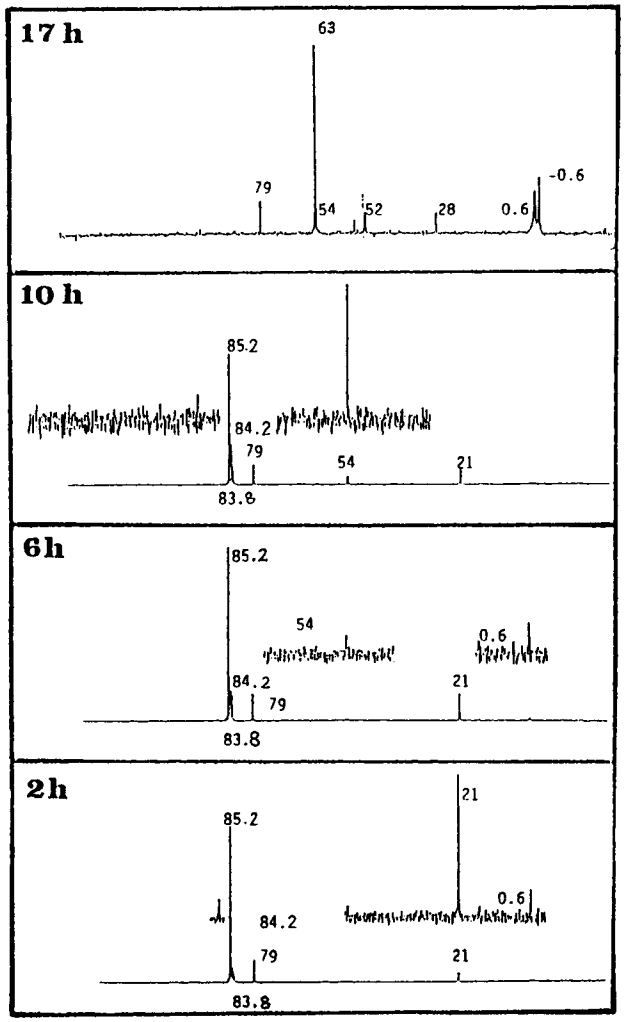


Figure 5 shows the rate of disulphide disappearance and kinetics of formation of its products during a similar reaction with TBH (at 100°C) but in the presence of an oxidisable substrate, e.g., cumene; ^{31}P NMR spectra for this reaction at different time intervals are also shown [Fig. 5(b)]. Under these conditions, changes in the disulphide concentration follow different pattern from those shown above in the absence of oxidisable substrate (c.f. Figs. 4 and 5). The concentration decreases in a first rapid stage at the beginning of the reaction before passing through a slower stage (after 10 h reaction time only 50% of the disulphide is consumed), leading to the final consumption of the disulphide after long reaction times (e.g., 17 h). The initial decrease in the disulphide concentration is paralleled by an increase in concentration of its oxidation products, notably thiophosphoric acid (**V**) and poly- and monosulphides (see Fig. 5), while thionophosphoric acid (**II**) becomes the major final product at the end of the reaction (17 h) when the disulphide is completely consumed. It was shown recently[14] that addition of triethylamine to thionophosphoric acid converts it quantitatively to the ionised form (see reaction 1), hence moving the chemical shift from 63 down to 57 ppm. Addition of excess triethylamine to the pro-

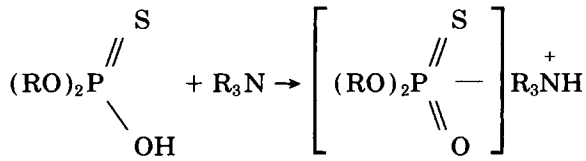
Table I Products of Oxidation of DRDS during its Reaction with CHP in Chlorobenzene at 110°C

DRDPA : CHP Molar Ratio	Reaction Time (min)	Phosphorous % Yield (δ Values = ^{31}P Shifts) in ppm			CHP Decomposed (%)
		DRDS 85.2	DRTeS 84.2	DRTPA 21	
1 : 5	0	100	0	0	0
	2	99	1	0	75
	10	92	6	3	90
	30	91	6	2	95





longed reaction product mixture (after 17 h) indeed has converted quantitatively all the acid to its ionised form (see change in chemical shift 63 to 57 in Fig. 6), while all other products remained unchanged as they were unaffected by this treatment.



63 ppm 57 ppm

(6)

To simulate the conditions of reactions of thiophosphoryl disulphide during melt processing (at 180°C) of polymers under oxidative (in the presence of excess air) conditions, which gave very effective stabilisation to the polymer,[8] the disulphide (DBDS) was oxidised in air in the presence and absence of oxidisable substrate at 180°C and transformation products of the reactions were monitored by ^{31}P NMR. In general, the results of these experiments showed quite similar relation between kinetics of the disulphide disappearance and formation of its transformation products to that observed at lower temperatures (e.g., 100°C) in the presence of a hydroperoxide as the oxidant; in the presence of nonoxidisable substrate, the disulphide concentration does not change at the beginning of the reaction and transformation products are not formed during this period, while the presence of an oxidisable substrate causes an immediate reduction in the concentration of the disulphide with concomitant increase in concentration of transformation products. The nature of transformation products under air oxidation is, however, much more complicated and will be the subject of a later communication.

DISCUSSION

Extensive mechanistic studies on sulphur-containing compounds have shown that their antioxidant stage is normally preceded by a radical generating prooxidant step, the importance of which is strongly

Figure 5 (**a**) Kinetics of product formation during the reaction of DBDS (0.5 mol dm^{-3}) with TBH (1 mol dm^{-3}) in cumene at 100°C. The percent yield values were calculated from NMR signal peak intensities. (**b**) ^{31}P NMR spectra of this reaction recorded at different time intervals. Numbers on the NMR peaks and curves are chemical shifts in ppm. (---), one interpolated region.

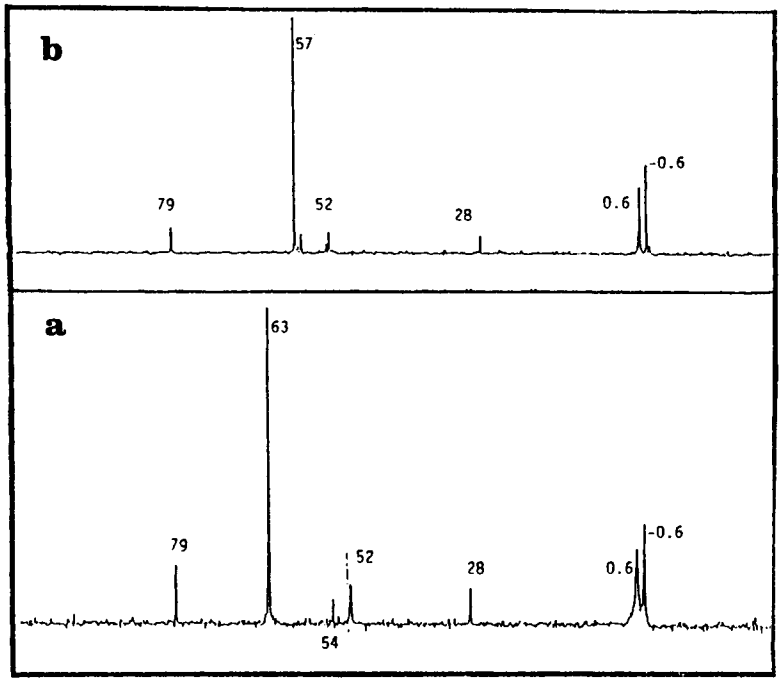
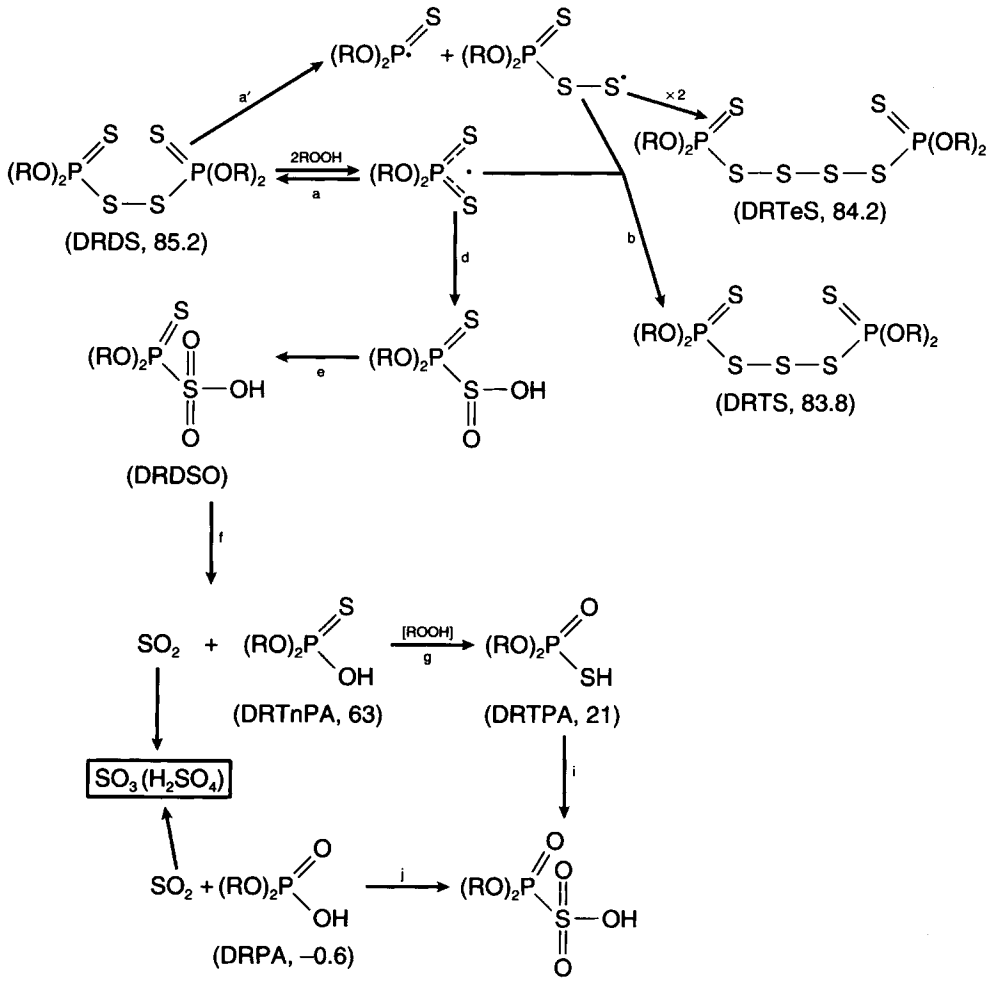


Figure 6 (**a**) ^{31}P NMR spectra of the 17-h reaction products of the TBH : DBDS oxidation reaction in cumene at 100°C reproduced from Fig. 5(b). (**b**) ^{31}P NMR spectra after treatment of the above reaction product mixture with triethylamine (R_3N) at room temperature for 5 min.

dependant on the ratio of hydroperoxide to sulphur compound.[2,7,15-21] Figure 3 demonstrates this clearly in the case of thiophosphoryl disulphide and shows that a much higher prooxidant effect is observed at higher peroxide to disulphide ratio (i.e., lower disulphide concentration), accounting for the much longer induction period to peroxide decomposition under these conditions. On the other hand, near to stoichiometric ratios, the induction period is not observed but is replaced by a rapid and effective decomposition from the beginning of the reaction, accounting for the much lower prooxidant effect observed under these conditions [c.f. Fig. 3(a) and inset]. The existence of a prooxidant stage (though only at a low extent) supports the finding that on examination of the product distribution of the peroxide decomposition reaction (using GLC) at such high disulphide concentrations [e.g., molar ratio of (CHP)/(DRDS) = 5] the hydroperoxide decomposition occurred initially via a homolytic process, with the ionic products building up to a high level only at the later stages of the reaction. Furthermore, we have shown previously[2] that although thiophosphoryl disulphide decomposes hydroperoxides mainly by an ionic process at all ratios, there is a small contribution of the homolytic process at both stoichiometric and catalytic ratios. This suggests that the further oxidation products responsible for the ionic decomposition must be produced during the initial homolytic process involving the disulphide and the hydroperoxide.

Figures 3 and 4 (and Table I) clearly illustrate that while the oxidation products are mainly responsible for the antioxidant effect of the disulphide when present in systems containing excess peroxides (high molar ratios) the disulphide itself plays the major antioxidant role in the initial stages of reactions in systems containing low molar ratios of peroxide to disulphide (i.e., high disulphide concentration). The direct contribution of the disulphide to initial peroxide decomposition, under these conditions, is further supported by the fact that, in the absence of added peroxides, oxidation of oxidisable substrates (e.g., white oil or decalin) is characterised by an initial induction period before the onset of slow autoretarding oxidation (Fig. 2). At these later stages, therefore, the oxidation products become ultimately responsible for the final decomposition of the peroxide. The extent of contribution of the disulphide to the overall antioxidant effect depends on the oxidisability of the substrate (c.f. Figs. 4 and 5).

The nature of oxidation products formed from the disulphide, which are responsible for ultimate



Scheme 1 Oxidation of thiophosphoryl disulphide in the presence of hydroperoxides. Numbers in the scheme are ^{31}P NMR chemical shifts.

decomposition of hydroperoxides, were shown to be mainly acids of different forms, the most important of which are the thio- [relation (5)] and thionophosphoric [relation (2)] acids, in addition to mono-, tri-, and tetrasulphides [relations (3) and (4)] (see Figs. 4 and 5). The concentration of the acids was found[14] to increase in the presence of excess hydroperoxides. Thionophosphoric acid (DRTnPA) has been identified[1,22] as one of the final transformation products of nickel and zinc dithiophosphates, both of which give the disulphide as the initial transformation product. The mechanism of antioxidant action of the disulphide is outlined in Scheme 1. It is worth mentioning here that in the case of polymer stabilisation the concentration of stabilisers (e.g., dithiophosphates) is normally quite low (of the order of 10^{-4} M) and under these conditions oxidation products of the disulphides, rather than the disulphides themselves, must play the major role in the stabilisation mechanism.

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