Mechanisms of Antioxidant Action: Nature of Transformation Products of Dithiophosphates. Part III. The Antioxidant Action of Dithio and Thio/Thionophosphoric Acids

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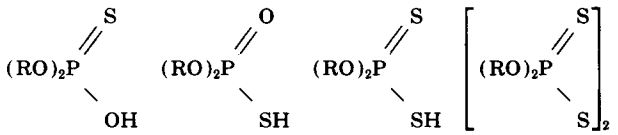
SYNOPSIS

The nature of transformation products of dithio- and thionophosphoric acids in the presence and absence of hydroperoxides and their role as transformation products formed during oxidation of thiophosphoryl disulfide at high temperatures is investigated. The major transformation product of dithiophosphoric acid was found to be the corresponding disulfide while thiophosphoric acid was the major oxidation product of the reaction of thionophosphoric acid with hydroperoxide. In the case of thiophosphoryl disulfide, it is shown that thionophosphoric acid was found to be one of the major transformation products in the presence of hydroperoxides, whereas no acids were formed in the absence of added hydroperoxides. © 1993 John Wiley & Sons, Inc.

INTRODUCTION

In Part II of this series,[1] we showed that the major transformation products of high-temperature reactions of thiophosphoryl disulfide (DRDS) with hydroperoxides in model compounds are thiophosphoric acid (DRTPA, chemical shift = 21 ppm) and thionophosphoric acid (DRTnPA, chemical shift = 63 ppm), in addition to mono- and polysulfides. In an earlier work, we showed that these acids are also formed from metal complexes of dithiophosphoric acids, notably, nickel[2,3] and zinc,[4] during their reactions with hydroperoxides at different temperatures. However, very little is known about the antioxidant activity (e.g., peroxide decomposition and radical trapping) of these acids. The object of the present investigation was, therefore, to examine the role of DRTPA as an antioxidant and the nature of its transformation products during high-temperature reactions with hydroperoxide and its activity will be compared with that of dithiophosphoric acid (DRDPA). Furthermore, the role of DRTPA and DRTnPA as transformation products formed during the oxidation of thiophosphoryl disulfide will be further investigated.



(DRTnPA) (DRTPA) (DRDPA) (DRDS)

EXPERIMENTAL

Materials

Dibutyl thiophosphoryl disulfide (DBDS) was prepared via the oxidation of ammonium dithiophosphate by iodine, as described previously.[3] Figure 1 shows the ^{31}P-NMR spectrum of the disulfide (δ = 85.2 ppm) used in this study, which indicates the presence of small concentrations of tetrasulfide (DBTeS, δ = 84.2 ppm) and monosulfide (DBMS, δ = 79 ppm) as impurities. Di-iso-butyl thionophosphoric acid (D^{i}BTnPA) was prepared by a pro-

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Journal of Applied Polymer Science, Vol. 50, 1823–1831 (1993)
 CCC 0021-8995/93/101823-09

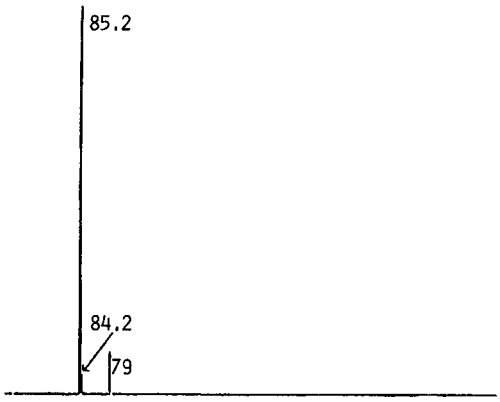


Figure 1 ^{31}P-NMR spectrum of DBDS. Nos. on peaks are chemical shifts in ppm.

cedure described by Foss[5] and its ^{31}P-NMR spectrum showed only one peak with a chemical shift of 63 ppm. The dihexyl dithiophosphoric acid was prepared from the reaction of *n*-hexanol (0.14 mol) with phosphorus pentasulfide (0.59 mol) at 80°C under a nitrogen atmosphere. The crude acid was purified by converting it to the ammonium salt (reaction with ammonia gas), which was then acidified back to the acid. The ^{31}P-NMR spectrum of the acid showed only one peak with a chemical shift of 85.6 ppm.

Technical-grade chlorobenzene, dichlorobenzene (ex. BDH), and dodecane (ex. Koch & Light) were used as substrates without further purification. Tertiary butyl hydroperoxide (ex. Koch-Light) was purified by a method described by Kharasch and coworkers.[6]

High-temperature Oxidative Reactions of DRDS, DRTPA, and DRTnPA and Their Product Analysis

The thermal reactions of DBDS in chlorobenzene and dodecane at 100°C were carried out in the internal cavity of the Bruker AC300 NMR spectrometer operating at 121.5 MHz that was connected to a computer-programmed stack plot designed to record data at time intervals. Phosphoric acid (85%) in $CDCl_3$ was used as an external reference and lock, and concentrations of reactants in the oxidation reaction were 0.5 *M* (DBDS) and 1.0 *M* (TBH). Preparation of the samples for ^{31}P-NMR measurements was as described in a previous publication.[1]

Higher-temperature oxidation reactions of DBDS in dichlorobenzene and in cumene were conducted in a three-neck round-bottom flask at 180°C (using a silicone oil bath) under reflux with continuous stirring and under a constant stream of air. Samples were withdrawn at the required time intervals and were immediately frozen in dry ice/acetone until subsequently analyzed by ^{31}P-NMR. The product analysis of the acid samples was carried out on a Jeol FX-90Q Fourier transform NMR spectrometer operating at 36.20 MHz as described previously.[1] Oxygen absorption measurements at 130°C were as described previously.[1]

RESULTS AND DISCUSSION

Effect of DRTnPA on the oxidation of Decalin at 130°C in the Absence and Presence of Hydroperoxide (CHP)

The role of DRTnPA as an antioxidant was investigated in an oxidizable substrate, decalin, at 130°C. Figure 2 shows the effect of concentration of isobutyl-substituted DRTnPA on the extent of oxidation of decalin in the absence of added hydroperoxide. At low concentrations, e.g., 5×10^{-4} mol dm^{-3}, decalin oxidizes rapidly from the onset of the reaction, but at higher concentrations, above 2×10^{-3} mol dm^{-3}, the oxidation becomes autoretarded from the beginning of the reaction. The absence of an induction period during the oxidation of decalin by D^{i}BTnPA suggests that the acid is not a very effective antioxidant, but the autoretardation that occurs at higher concentrations (e.g., 2×10^{-3} mol dm^{-3}) suggests that it oxidizes to a very powerful antioxidant that is responsible for the effective inhibition. Figure 3 shows the effect of D^{i}BTnPA on the oxidation of decalin containing cumene hydroperoxide (CHP) at 130°C. It is clear that under these con-

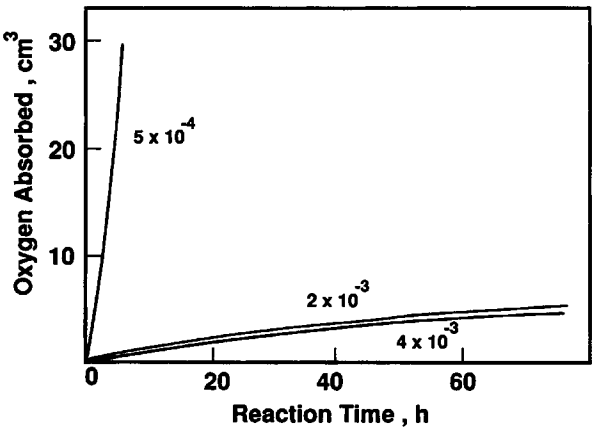


Figure 2 Effect of D^{i}BTnPA on oxidation of decalin at 130°C. Nos. on curves are DRTnPA concentrations in mol dm^{-3}.

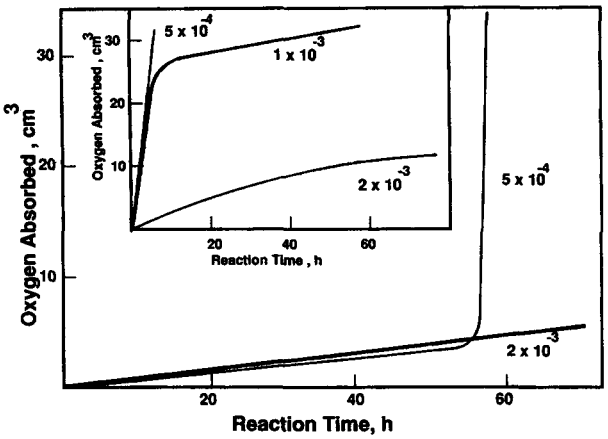


Figure 3 Effect of D^{i}BTnPA on oxidation of decalin at 130°C in the presence of 1×10^{-2} mol dm^{-3} CHP. Nos. on curves are D^{i}BTnPA concentrations in mol dm^{-3}. Inset shows the effect of the disulfide (DBDS) on oxidation of decalin at 130°C in the presence of 1×10^{-2} mol dm^{-3} CHP. Nos. on curves in inset are DBDS concentrations in mol dm^{-3}.

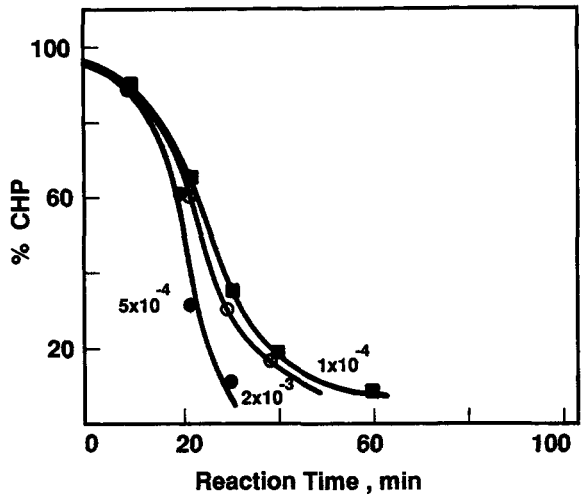


Figure 4 Decomposition of CHP (1×10^{-2} mol dm^{-3}) by D^{i}BTnPA in chlorobenzene at 110°C. Nos. on curves are D^{i}BTnPA concentrations in mol dm^{-3}.

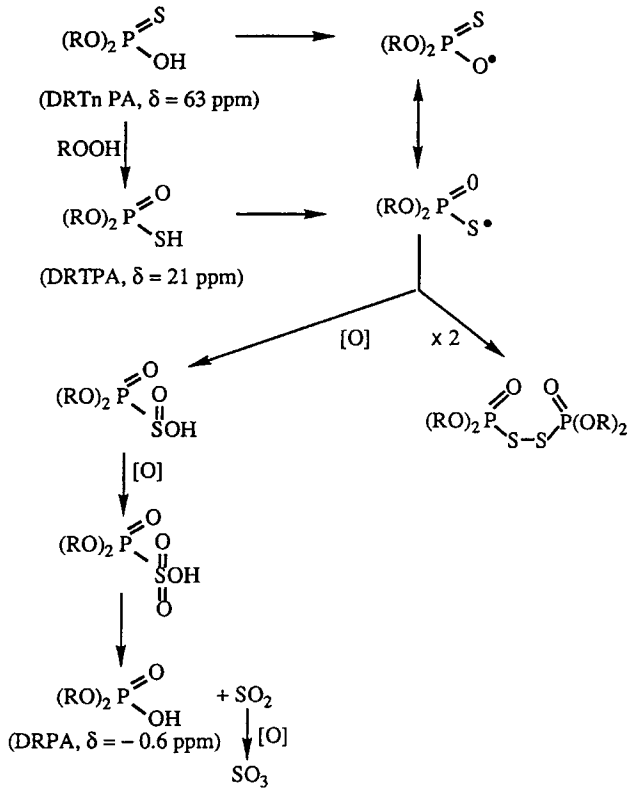
ditions even the small acid concentration of 5×10^{-4} mol dm^{-3}) autoretards the CHP-initiated oxidation of decalin (at least initially) in the same way as it does at higher concentrations (e.g., 2×10^{-3} mol dm^{-3}).

CHP-initiated oxidation of decaline (at 130°C) by DRDS was shown[1] (under the same experimental conditions) to give an initial rapid oxidation of the substrate, followed by a second much slower oxidation stage (see inset in Fig 3). The absence of such a dramatic initial oxidation of the substrate in the case of DRTnPA suggests that the acid itself is a much more effective peroxide decomposer than is the disulfide. This is reflected in the rapid one-stage decomposition of hydroperoxide caused by all concentrations of D^{i}BTnTP examined (see Fig. 4).

^{31}P-NMR studies of the reaction of D^{i}BTnPA with excess CHP (CHP : D^{i}BTnPA = 2.5 : 1) in chlorobenzene at 110°C showed that, under these conditions, the DRTnPA (δ = 63 ppm) is almost quantitatively transformed to DRTPA (δ = 21 ppm) after only 3 min (Table 1 and Scheme 1, reaction a). After this short reaction time, the concentration of the formed DRTPA decreases slightly, giving rise mainly to phosphoric acid (DRPA, δ = −0.6 ppm) (see reaction, Scheme 1). The thiol isomer (DRTPA) forms from the thion isomer (DRTnPA) even at room temperature as long as there is hydroperoxide available. Figure 5 shows the almost quantitative formation of the thiol isomer (δ = 21 ppm) from DRTnPA (δ = 63 ppm) when a small concentration of tertiary butyl hydroperoxide (TBH) is added at room temperature. Kabachnick and coworkers[7] used DRTnPA to exemplify the thione–thiol tautomeric equilibrium that is applicable to most organophosphorus acids. They showed that the

Table I Products of Oxidation of D^{i}BTnPA During Its Reaction with CHP in Chlorobenzene at 110°C (DRTnPA : CHP = 1 : 25)

	Phosphorus Yield (%) (δ Values = ^{31}P Shifts) in ppm			
Reaction Time (min)	DRTnPA (63)	DRTPA (21)	$(RO)_3P{=}O$ (−0.1)	$(RO)_3P{=}S$ (64.8)
0	100	0	0	0
3	0	99	1	0
20	0	91	9	0
45	0	88	9	3



Scheme 1 Oxidation reactions of thionophosphoric acid (DRTnPA).

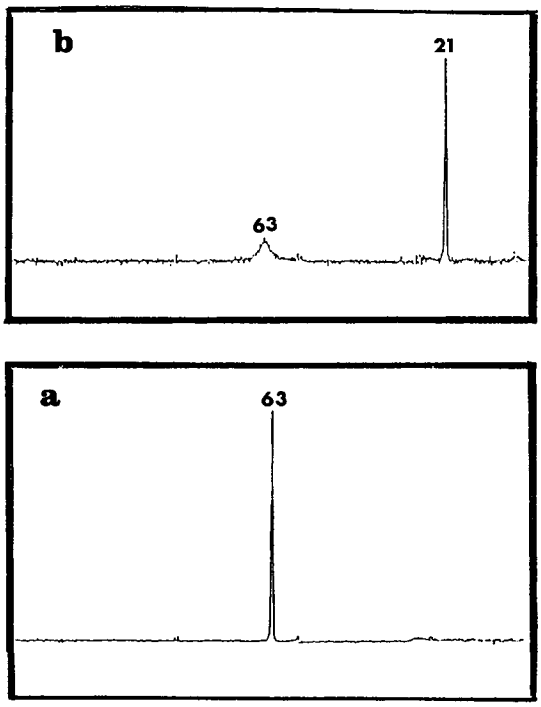


Figure 5 (a) The effect of addition of TBH to DRTnPA (at room temperature) on the ^{31}P-NMR chemical shift; (b) the NMR spectrum of the initial DRTnPA is also shown. Nos. on peaks are chemical shifts in ppm.

tautomeric equilibrium is dependent on the ratio of the ionization constant of the two forms (PSOH vs. POSH), which, to a great extent, depends on the nature of the reaction media and the structure of the tautomeric forms. This behavior explains the fact that the thiol isomer was shown[1,3] to be formed during the initial stages of all oxidation studies of DRDs when there is an abundance of hydroperoxide (see also Fig. 9 later), whereas the thione isomer (δ = 63 ppm) is observed only at the latter stages of the reactions when hydroperoxides have completely depleted.

Effect of DRDPA on the Oxidation of Decalin at 130°C in the Absence and Presence of Hydroperoxide (CHP)

Although more work about the antioxidant activity of DRDPA has been described in the literature,[8,9] its role as a catalyst responsible for the ionic decomposition of hydroperoxides in the presence of metal dithiophosphates remains controversial.[10–12] The oxidation of decalin by n-hexyl dithiophosphoric acid (DHDPA) at 130°C in the absence of added peroxides shows an initial induction period (length of which increases with increasing the acid concentration) followed by autoretarded oxidation, except for the very low concentration where a rapid oxidation takes place (see Fig. 6). Figure 7 shows that DHDPA is very effective inhibitor for the CHP-initiated oxidation of decalin even at very low concentration (5×10^{-4} mol dm^{-3}). Comparing the CHP-initiated oxidation of decalin by DRTnPA (Fig. 3) and DRDPA (Fig. 7) shows that the latter is more effective; even at low concentration, the oxidation rate of the substrate remained very low. Examina-

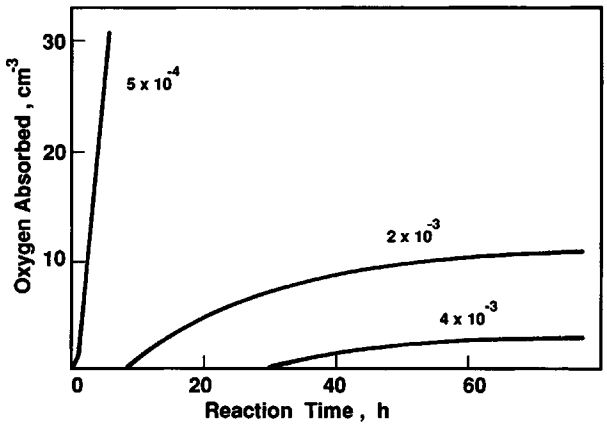


Figure 6 Effect of DHDPA on oxidation of decalin at 130°C. Nos. on curves are DHDPA concentrations in mol dm^{-3}.

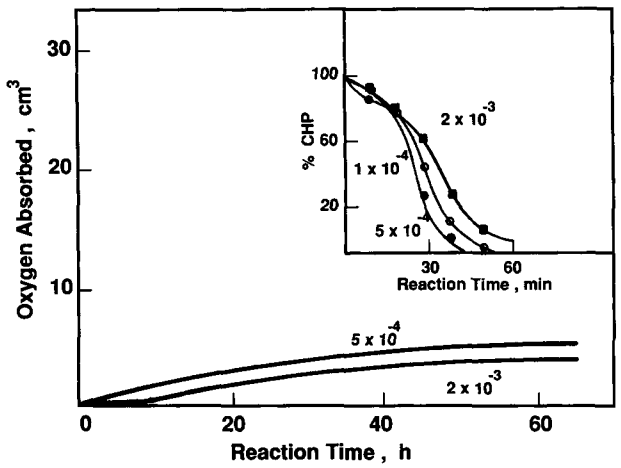


Figure 7 Effect of DHDPA on oxidation of decalin at 130°C in the presence of 1×10^{-2} mol dm^{-3} CHP. Nos. on curves are DHDPA concentrations in mol dm^{-3}. Inset shows CHP (1×10^{-2} mol dm^{-3}) decomposition curves by varying concentrations (nos. on curves) of DHDPA at 110°C.

tion of the CHP decomposition by DHDPA at 110°C shows that at all acid concentrations used (covering molar ratios of CHP/DHDPA of 2–100) there is a rapid one-stage CHP decomposition (see Fig. 7 inset).

The retarded oxidation shown in Figures 6 and 7 and the nature of the transformation products of the reactions of DRDPA with hydroperoxides reveal that the acid must be subsequently oxidized to more effective catalysts for peroxide decomposition. Figure 8 shows changes in the concentration of DHDPA and transformation products formed during its reaction with excess CHP (DHDPA : CHP = 1 : 2.5) at 110°C as measured by ^{31}P-NMR. It is clear that the acid is fully transformed, very early in the reaction, to further oxidation products, mainly to the corresponding disulfide (DRDS, 90% yield after 2 min) in addition to smaller concentrations of tetrasulfide (DRTeS) and thiophosphoric acid (DRTPA). The formation of disulfide from oxidation of DRDPA (reaction 1) has also been shown by other workers.[10,12] In the case of the reaction of the disulfide with CHP, it was shown[1] that the transformation products are mainly DRTeS, DRTPA, and DRTnPA (DRTPA is formed in the earlier stages of the reaction). The latter two products (DRTeS and DRTPA) that are formed from the DRDPA/CHP reaction are most likely, therefore, to be derived from the initial transformation product, the disulfide (see Fig. 8; decay of the disulfide after first 2 min of the reaction is paralleled by an increase in concentration of DRTeS and DRTPA). These powerful transformation products are then responsible for the effective inhibition of the CHP-initiated oxidation of hydrocarbons by DRDPA (Fig. 7):

$$2(RO)_2PSSH + ROOH \rightarrow [(RO)_2PSS]_2 + ROH + H_2O \quad (1)$$

It is clear from the above discussion that the overall behavior of DRTnPA and DRDPA in the CHP-initiated oxidation of decaline is similar. The fact that the former is less effective at low concentration during the later stages of the reaction (cf. curve 5×10^{-4} Fig. 3, and curve 5×10^{-4} in Fig. 7) may be due to the formation of fully oxygenated acids, e.g., DRPA, from DRTnPA, which cannot oxidize further (see Scheme 1), whereas the corresponding products in the case of DRDPA can oxidize to further antioxidant species.

DRTPA and DRTnPA as Transformation Products Formed During Oxidation of DRDS

The reaction of DRDS with hydroperoxides (e.g., TBH) in a nonoxidizable substrate (chlorobenzene) at high temperature (100°C) was shown[1] to give tetrasulfide (DBTeS) as the main product, in addition to DRTPA (the products were monitored during the reaction by ^{31}P-NMR using a Jeol FX-90Q Fourier transform NMR spectrometer operating at 36.20 MHz). The reaction was conducted for 8 h only, and during this period, the disulfide concentration decreased by about 60% of its original value. In an earlier work[3] on the antioxidant effect of DRDS in polyolefins, it was shown that DRTnPA

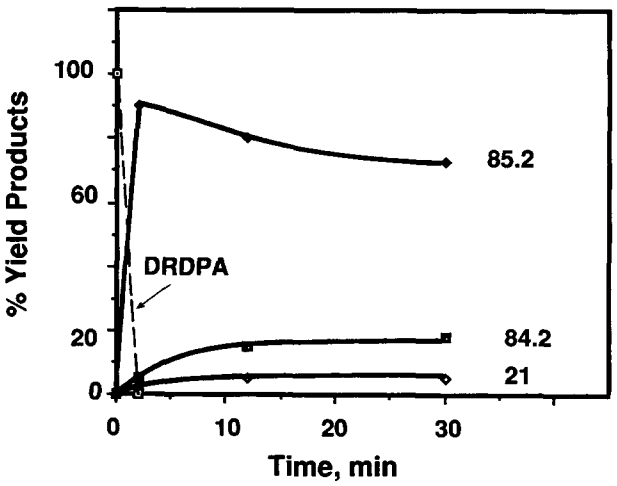


Figure 8 Kinetics of product formation during the reaction of DHDPA (0.2 mol dm^{-3}) with CHP (0.5 mol dm^{-3}) in chlorobenzene at 110°C. Nos. on curves are chemical shifts in ppm.

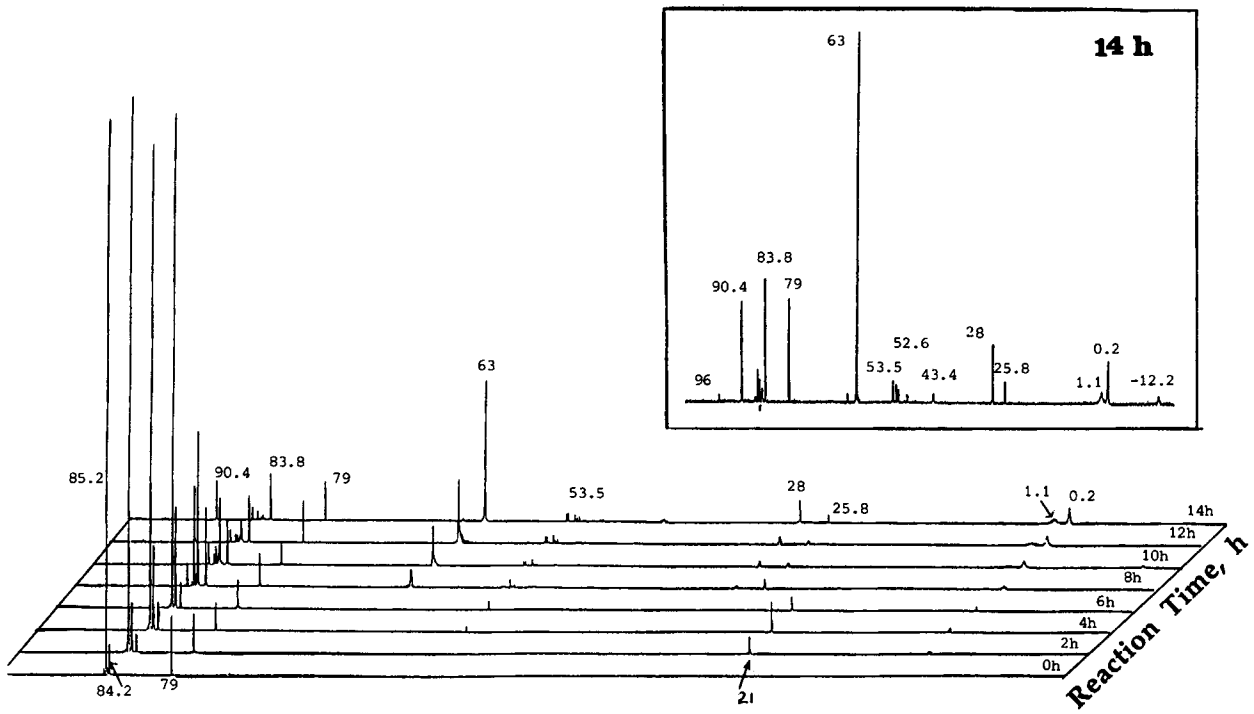


Figure 9 ^{31}P-NMR spectra of the reaction of DBDS (0.5 mol dm^{-3}) with TBH (1.0 mol dm^{-3}) in chlorobenzene at 100°C at different time intervals. Inset reproduces the NMR spectrum at the end of the reaction (after 14 h). Nos. on peaks are chemical shifts in ppm.

is one of the transformation products formed from disulfide during polymer (PP) processing. In the above model reaction, no DRTnPA was formed (instead, DBTeS and DRTPA formed). This was thought to be due to the incomplete decomposition of the disulfide (about 40% disulfide was still in the reaction mixture at the end of the experiment). In this investigation, therefore, this model reaction was repeated but the reaction time was extended until all the disulfide had decomposed (14 h). The transformation products formed during the course of this reaction were then monitored by ^{31}P-NMR using a Bruker AC300 NMR spectrometer operating at 121.5 MHz.

Figure 9 shows the rate of DBDS disappearance and distribution of transformation products formed during its reaction with TBH in chlorobenzene at 100°C. As was shown previously,[1] the major product during the early stages of the reaction is the corresponding DRTeS (δ = 84.2 ppm) in addition to smaller concentrations of the trisulfide and DRTPA (δ = 21 ppm). However, at later stages of the reaction (e.g., 10 h and over), the polysulfide concentration starts to decrease and DRTPA (δ = 21 ppm) is converted to DRTnPA (δ = 63 ppm) (see Fig. 10), which becomes the major product (~ 40% of total) at the end of the reaction in addition to a variety of phosphorous esters (δ = 90.4, 53.5, 28, and 25.8 ppm), inorganic phosphoric acids (e.g., δ = 1.1 and 0.2 ppm), and monosulfide δ = 79 ppm) (see also Fig. 9 inset).

Oxidation of DRDS in the absence of added peroxides has, however, led to very different products.

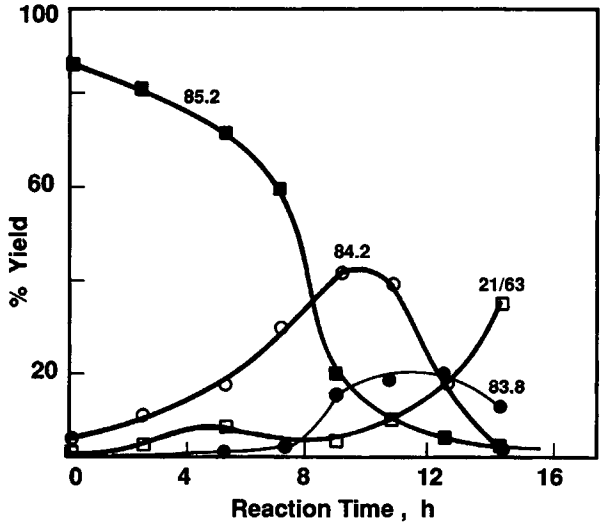


Figure 10 Kinetics of product formation during the reaction of DBDS (0.5 mol dm^{-3}) with TBH (1.0 mol dm^{-3}) in chlorobenzene at 100°C; the % yield values were calculated from the NMR signal peak intensities. Nos. on curves are chemical shifts in ppm.

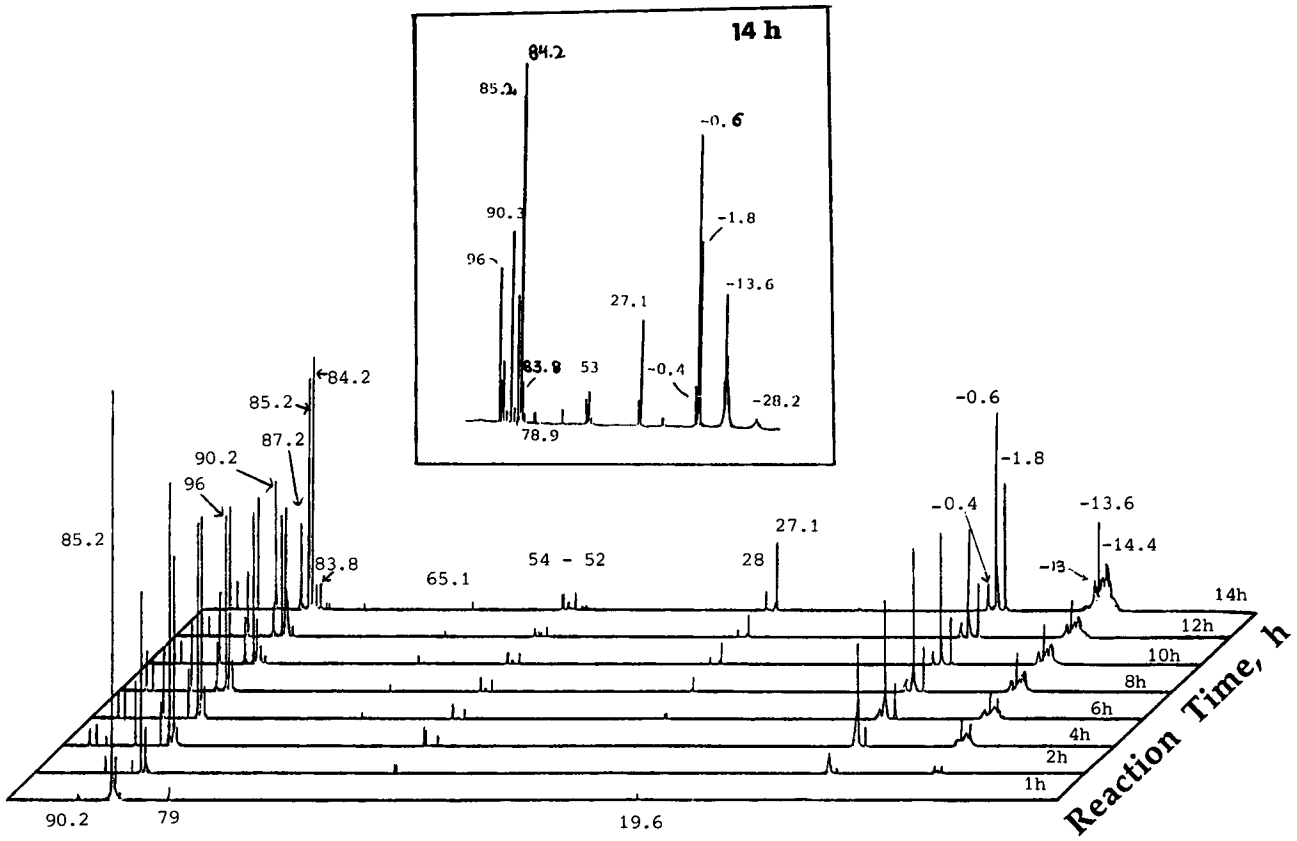


Figure 11 ^{31}P-NMR spectra of thermal decomposition of DBDS in dodecane under nitrogen atmosphere at 100°C at different time intervals. Inset reproduces the NMR spectrum at the end of the reaction (after 14 h). Nos. on peaks are chemical shifts in ppm.

Figure 11 shows the distribution of products formed from the oxidation of DBDS in dodecane under nitrogen atmosphere at 100°C. After 14 h reaction time, about 14% of the disulfide remains in the reaction mixture and the predominant products at the end of the reaction were mainly DRTeS (δ = 84.2 ppm), triester species (with chemical shifts of 96, 90.3, 53, and 27 ppm, see Fig. 11 inset), and inorganic phosphates (with clusters of progressively enhanced signals in the regions −0.4 to −1.8 ppm and −13 to −14.4 ppm). An important difference between the oxidation of the disulfide in the absence and presence of peroxides is, therefore, the fact that no DRTPA or DRTnPA are formed when the oxidation takes place in the absence of added peroxides (cf. Figs. 9 and 11). Similarly, oxidation of the disulfide in an inert substrate (dichlorobenzene) but at higher temperature (180°C) and under a stream of air did not give these acids and the products were mainly phosphorous triesters and highly sulfurated triesters (e.g., chemical shifts of 139, 112, 96, 94, 54, and 19 ppm) (Fig. 12 and Table II).

The behavior of the disulfide at 180°C under the same conditions as above but in the presence of an oxidizable substrate (cumene) (Fig. 13) is similar to its behavior at lower temperature (100°C) in the presence of hydroperoxide and an inert substrate, chlorobenzene (Fig. 9), in that both led to the formation of DRTnPA. Figure 13 shows the transformations of the oxidation of DRDS in cumene at 180°C in the presence of an air stream. Even though the reaction was not taken to completion and over 30% of the disulfide was still present in the reaction mixture, DRTnPA (δ = 63 ppm) is formed (cf. Figs. 9 and 13).

CONCLUSIONS

From the above discussion, the following conclusions can be drawn:

1. Both dithio- (DRDPA) and thionophosphoric acids (DRTnPA) are more efficient peroxide decomposers than are the corresponding disulfides. Comparison of the effect of low concentrations of the acids and the disulfide on the oxidation of decalin in the presence of CHP shows the presence of an

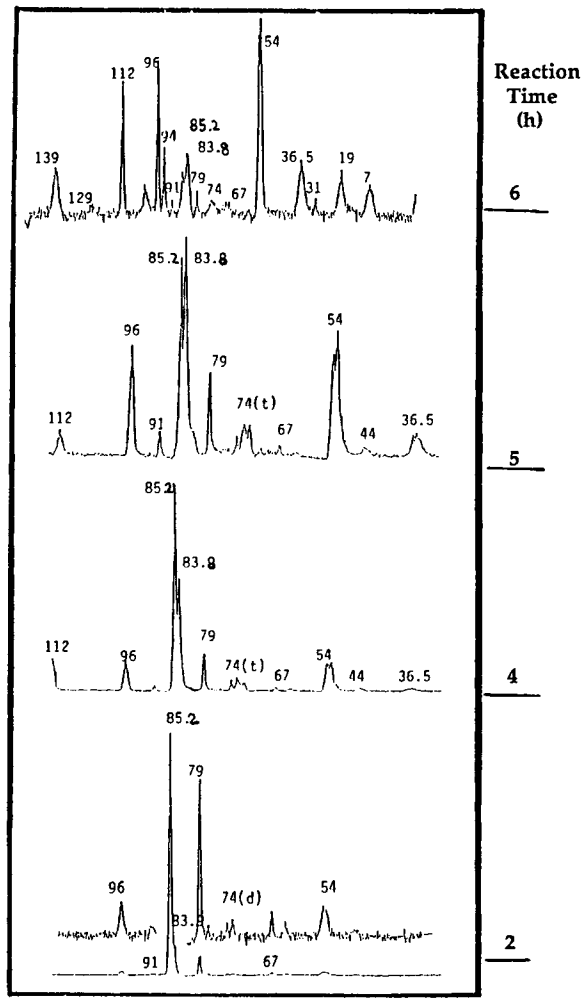


Figure 12 ^{31}P-NMR spectra of the thermal decomposition of DBDS in dichlorobenzene at 180°C in the presence of an air stream. Nos. on peaks are chemical shifts in ppm (*d* is doublet and *t* is triplet). The reaction time in hours is shown.

initial autoretarded oxidation in the former case, whereas the latter shows an initial fast oxidation before the onset of an autoretarded inhibition (cf. Figs. 3 and 7). This is further supported by the fact that the acids show a one-stage efficient peroxide decomposition, whereas the disulfide decomposes hydroperoxides in two stages; the initial induction period to peroxide decomposition is due to the rapid oxidation of the disulfide to more effective antioxidants that are responsible for the second rapid peroxide decomposition stage (see Fig. 3).

2. The early stages of oxidation of dithiophosphates led to the formation of thiophosphoric acid (DRTPA), whereas DRTnPA becomes the major product at the end of the reactions. DRTnPA is, in fact, quantitatively transformed to the DRTPA in the presence of hydroperoxides even at low temperatures.
3. One of the major transformation products formed in the oxidation of thiophosphoryl disulfide (DRDS), either in the presence of hydroperoxide or in the presence of an oxidizable substrate and a stream of air at high temperature, is the DRTnPA that is a powerful antioxidant. The significance of the latter set of conditions (oxidizable substrate, air, and temperature of 180°C) is that it stimulates an "unusual" controlled oxidative processing condition that we have developed for processing polyolefins with DRDSs.[18,19] Polymers processed under such conditions showed very high stabilization, much more effective than when the polymer was processed with the disulfide under the normal

Table II Summary of the Main ^{31}P-NMR Chemical Shifts Observed in Figures 9, 11, 12, and 13

Chemical Shift (ppm)	Structural Formula (Ref.)	Chemical Name	Code
139.0	$(RO)_3P$ (13)	*O,O,O*-Trialkyl phosphite	—
112.0	(RS)2(RO)PS (14)	*O,S,S*-Trialkyl trithiophosphate	—
96.0	$(RO)_2(RS)PS$ (13–15)	*O,O,S*-Trialkyl dithiophosphate	—
94.0	(RS)3PS (13, 14)	*S,S,S*-Trialkyl tetrathiophosphate	—
85.2	$[(RO)_2PSS]_2$[a]	Dialkyl thiophosphoryl disulfide	DRDS
84.2	$[(RO)_2PSS]_2S_2$[a]	Dialkyl thiophosphoryl tetrasulfide	DRTeS
83.3	$[(RO)_2PSS]_2S$[a]	Dialkyl thiophorphoryl trisulfide	DRTS
79.0	$[(RO)_2PS]_2S$[a]	Dialkyl thiophosphoryl monosulfide	DRMS
63.0	$(RO)_2PSOH$[a]	Dialkyl thionophosphoric acid	DRTnPA
54.0	$(RS)_2(RO)PO$ (13, 15, 16)	*O,S,S*-Trialkyl dithiophosphate	—
28.0	$(RO)_2(RS)PO$ (13, 15, 16)	*O,O,S*-Trialkyl thiophosphate	—
21.0	$(RO)_2POSH$[b]	Dialkyl thiophosphoric acid	DRTPA
19.0	$[(RO)_2POS]_2$ (17)	Bis-dialkyl phosphoryl disulfide	—

[a] Assigned on the basis of its identity with that of an authentic sample (prepared in this study).
[b] This is isomeric form of DRTnPA.

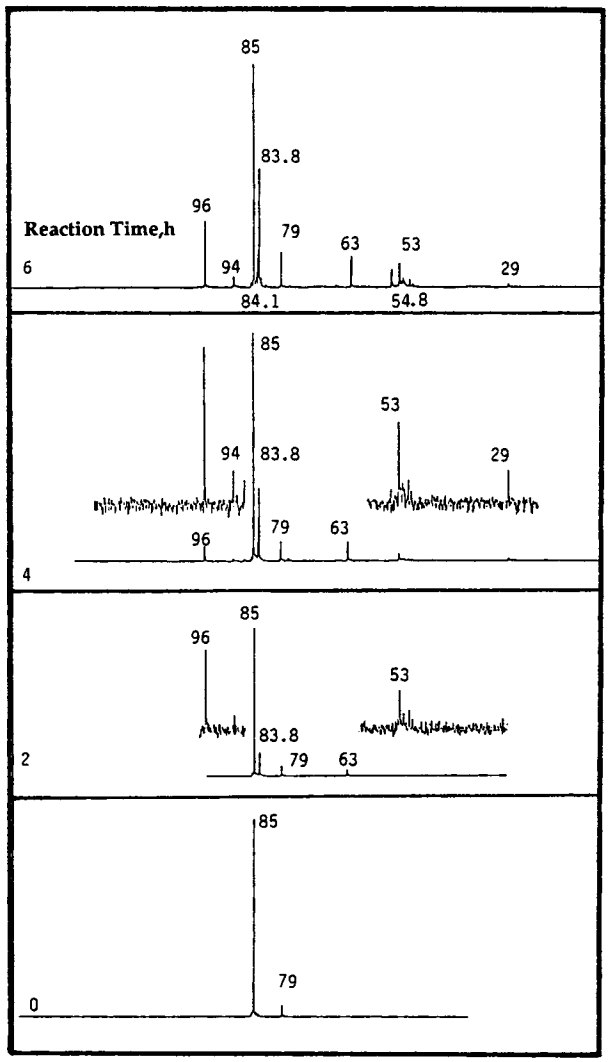


Figure 13 ^{31}P-NMR spectra of the reaction of DBDS in cumene at 180°C in the presence of air stream. Nos. on peaks are chemical shifts in ppm and reaction time in hours is shown.

restricted oxygen access conditions. The results from the model work described here shows clearly that under conditions similar to those used in polymer stabilization the DRTnPA that is formed is a powerful peroxide decomposer. The high stabilization effect of the disulfide when oxidatively processed in polyolefins[13] must, therefore, be associated with the formation of acidic species that are themselves effective antioxidants. However, in the absence of added peroxides or the presence of an oxidizable substrate, the acids are not formed and the products are mainly esters of a different nature.

Financial support from Synthetic Chemicals, Exxon Research Centre, and SERC is gratefully acknowledged. Thanks are also due to Dr. T. Colclough for discussion on ^{31}P-NMR; Dr. M. Perry for his help with running the NMR; and Drs. J. H. Young and F. S. Yates, Mr. L. S. Fuller, and Mrs. E. A. J. Earle for discussions, synthesis, and identification of mono-, tri-, and tetrasulfides that were used as authentic samples for NMR analysis.

REFERENCES

1. S. Al-Malaika, M. Coker, P. J. Smith, and G. Scott, *J. Appl. Polym. Sci.*, **44,** 1297 (1992).
2. S. Al-Malaika and G. Scott, *Polym. Commun.*, **23,** 1711 (1982).
3. S. Al-Malaika, M. Coker, and G. Scott, *Polym. Degrad. Stab.*, **22,** 147 (1988).
4. S. Al-Malaika, P. J. Smith, and G. Scott, unpublished work.
5. U. Foss, *Acta Chem. Scand.*, **1,** 8 (1947).
6. M. Kharasch, A. Fono, and W. Nudenburg, *J. Org. Chem.*, **16,** 113 (1951).
7. M. I. Kabachnick, T. A. Mastrukova, A. E. Shipov, and T. A. Melentyera, *Tetrahedron,* **9,** 10 (1960).
8. S. Ivanov and I. Kateva, *Neftekhimiya,* **18,** 417 (1978); *Chem. Abstr.,* **89,** 146540k (1978).
9. S. Korcek, L. Mahoney, M. Johnson, and W. Siegl, Technical Paper 810014, Society of Automotive Engineering, 1981.
10. M. Johnson, S. Korcek, and M. Zinbo, Technical Paper SP-558, Society of Automotive Engineering, 1983, p. 71.
11. A. Bridgewater, J. Dever, and M. Saxton, *J. Chem. Soc. Perkin Trans.*, **11,** 1006 (1980).
12. O. Grishina and V. Bashinova, *Neftekhimiya,* **14,** 142 (1974); *Chem Abstr.,* **80,** 145654c (1974).
13. N. Muller, P. C. Lanterbur, and J. Goldenson, *J. Am. Chem. Soc.,* **78,** 3557 (1956).
14. R. C. Coy and R. B. Jones, in *Proceedings of the ASLE/ASME Lubrication Conference,* Dayton, Oct. 1979, p. 77.
15. G. L. Marshall, in *Proceedings of the Institute of Petroleum London* (Petro anal. 81), 1982, p. 409.
16. M. M. Crutchfield, C. H. Dungan, T. H. Letcher, V. Markand, and J. R. Wazer, *Compilations of ^{31}P NMR Data,* Topics in Phosphorous Chemistry, vol. 5, Interscience, New York, 1967, p. 35.
17. E. Kranczyk and A. Skowronska, *Phosphorus Sulphur,* **9,** 189 (1980).
18. S. Al-Malaika, *Br. Polym. J.,* **16,** 301 (1984).
19. S. Al-Malaika and G. Scott, U.K. Pat. Appl. GB2117779A (1983).

Received February 22, 1993
Accepted April 17, 1993