MECHANISMS OF ANTIOXIDANT ACTION. PHOSPHITE ESTERS

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ABSTRACT

Catechol phosphite esters are powerful stabilizers for polymers and appear to behave differently from simple alkyl or aryl phosphites in that they destroy hydroperoxides in a Lewis acid catalysed reaction. The effective catalyst is formed from the starting ester by reaction with hydroperoxides in a series of chemical reactions which during the initial stages involve the formation of free radicals. Some of the isolated reaction products do not show this behaviour and are themselves powerful thermal and u.v. stabilizer antioxidants.

Esters of phosphorous acid have become increasingly important in recent years as antioxidants and stabilizers. A long established use has been in the stabilization of uncured synthetic rubbers and tris-nonylphenylphosphite I(a) is still one of the favoured cheap gel inhibitors for styrene, butadiene rubber[1].

$$P(OR)_3$$

I

(a) $R = -\langle\bigcirc\rangle - C_9H_{19}$

(b) $R = \text{alkyl}$
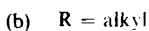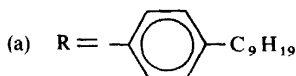
More recently, the alkyl phosphites I(b) and the mixed alkyl–aryl phosphites have assumed importance in polyolefins[2] and polyvinylchloride[3] as u.v. stabilizers. An important subgroup within the above general class of phosphite esters which has assumed particular importance in polyolefins is the catechol phosphite esters (II), which are particularly effective when R is hindered phenyl.

(a) $R = -CH(CH_3)_2$

(b) $R = -\langle\bigcirc\rangle$

(c) $R = $ (a hindered phenyl with t-Bu, t-Bu, Me substituents)
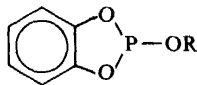
II
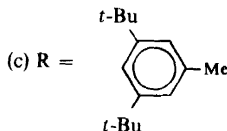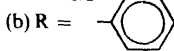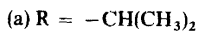
Extensive technological investigations have been carried out by Kirpichnikov and his co-workers, particularly in polyolefins[4–7], and in rubbers[8, 9] on the

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relationship between structure and activity. These workers have shown[7] that the hindered phenyl phosphite II, R = 2,4,6-tri-tert-butylphenyl was the most effective structure examined and that antioxidant effectiveness paralleled reactivity toward the 'stable' free radical diphenylpicryl hydrazyl. The high antioxidant efficiency of the catechol hindered-phenyl phosphites has been confirmed in the present studies (see later).
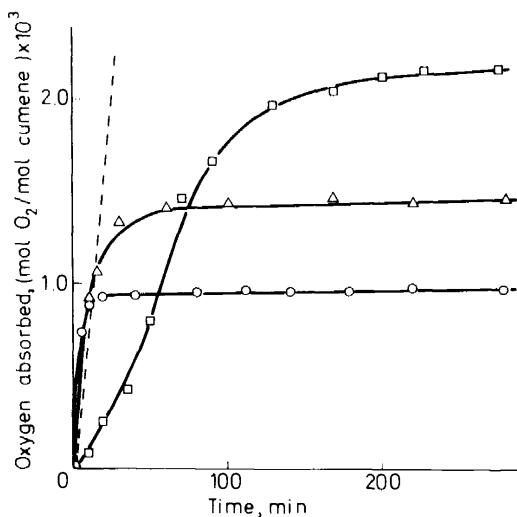

Figure 1. Inhibition of AZBN-initiated oxidation of cumene in oxygen at 50°C by 0.2M catechol phosphites. $[AZBN]_0 = 0.02M$: ☐ hindered phenyl phosphite: △ isopropyl phosphite: ○ phenyl phosphite - - - - no phosphite.

Rysavy and his co-workers[10, 11] have shown that in polypropylene, the aryl catechol phosphites (II, R = aryl) are more effective than the alkyl analogues (II, R = alkyl): however, there is some doubt as to whether these compounds are themselves responsible for the antioxidant activity or some hydrolysis product[12, 13].

There appears to be no agreement as to whether these phosphite esters act by decomposing hydroperoxides or by removing chain propagating free radicals from the autoxidizing medium. Previous studies have shown[14] that a useful and sometimes diagnostic method of distinguishing between the two mechanisms is to compare the kinetics of hydrocarbon oxidation in the presence of an azo initiator and a hydroperoxide initiator. In general antioxidants which function exclusively as hydroperoxide decomposers are inactive in the former system.

In cumene initiated by azo-bis-iso-butyronitrile (AZBN) it was found that the phenyl ester II(b) rapidly reduced the rate of oxidation to zero after an initial pro-oxidant period (Figure 1). The iso-propyl ester II(a) was less effective and the hindered phenyl ester, II(c), required a large oxygen absorption before it became an effective antioxidant. By contrast, triphenylphosphite
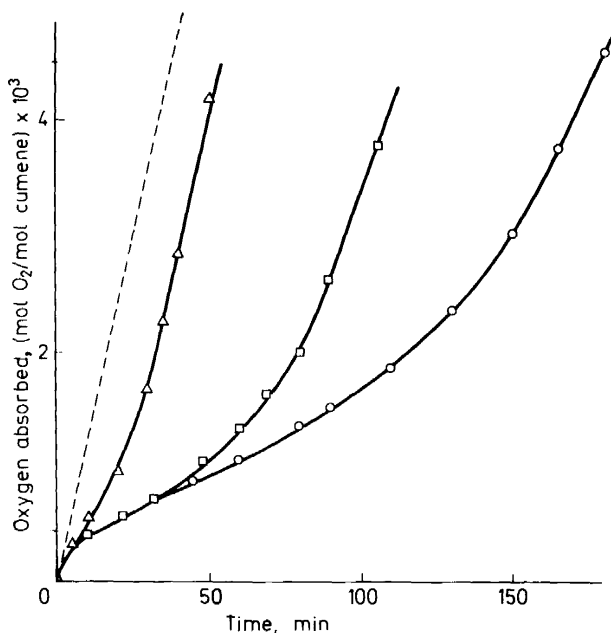
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Figure 2. Inhibition of AZBN-initiated oxidation of cumene in oxygen at 75°C by triphenyl phosphite. $[AZBN]_0 = 0.01M$: △ 0.022M: □ 0.035M; O 0.051M: – – – – no phosphite.

under the same conditions was auto-accelerating after a slight induction period (*Figure 2*).

With cumene hydroperoxide as initiator, more pronounced pro-oxidant effects were observed with the catechol hindered-phenyl phosphite (see *Figure 3*) which was selected for more detailed study because of its hydrolytic stability (see *Figure 4*). In addition gas evolution was observed with higher concentrations (*Figure 3*) and this behaviour was lacking in the case of triphenyl phosphite (*Figure 5*) which rapidly reduced the rate of oxidation to a constant value after an initial pro-oxidant effect. The gas evolution was shown to be associated with the reaction of hydroperoxide with phosphite since it also occurred in chlorobenzene which is inert to oxidation (see *Figure 6*). Gas evolution also occurred in the absence of oxygen (see *Figure 7*), and the fact that oxygen is absorbed by the oxidizable substrate (tetralin) indicates that free radicals are involved in its formation.

Comparison of the behaviour of the catechol phosphite esters with triphenyl phosphite led to the conclusion that whereas the latter was acting by stoichiometric destruction of hydroperoxide

$$(PhO)_3P + ROOH \rightarrow (PhO)_3P = O + ROH$$
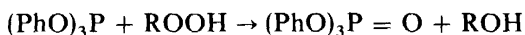
the former, or products derived from them, appeared to destroy hydroperoxides in a catalytic manner. This was unexpected since only the stoichiometric reaction of hydroperoxides with phosphite esters has previously been
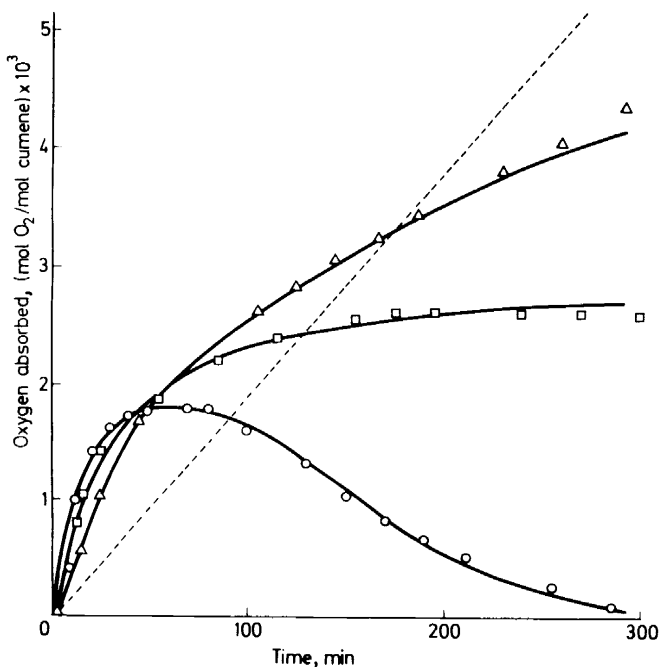
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Figure 3. Inhibition of cumene hydroperoxide-initiated oxidation of cumene in oxygen at 75°C by catechol hindered-phenyl phosphite. $[CHP]_0 = 0.2M$: $\triangle$ $2 \times 10^{-3}M$; $\square$ $1 \times 10^{-2}M$; $\bigcirc$ $2 \times 10^{-2}M$; – – – – no phosphite.

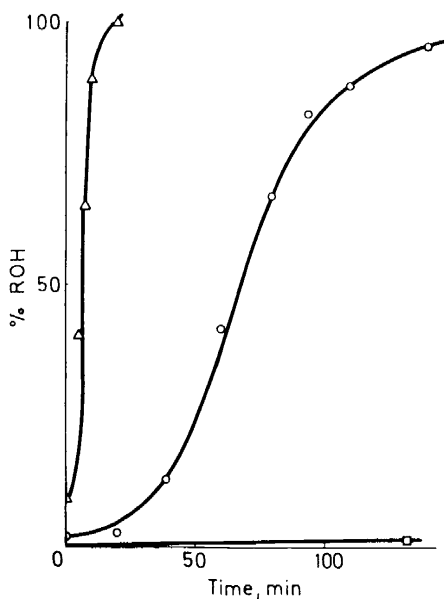*Figure 4.* Hydrolysis of catechol phosphites (0.02M) in 95% (v/v) aqueous ethanol at 75°C. $\square$ catechol hindered-phenyl phosphite; $\triangle$ catechol phenyl phosphite; $\bigcirc$ catechol isopropyl phosphite.
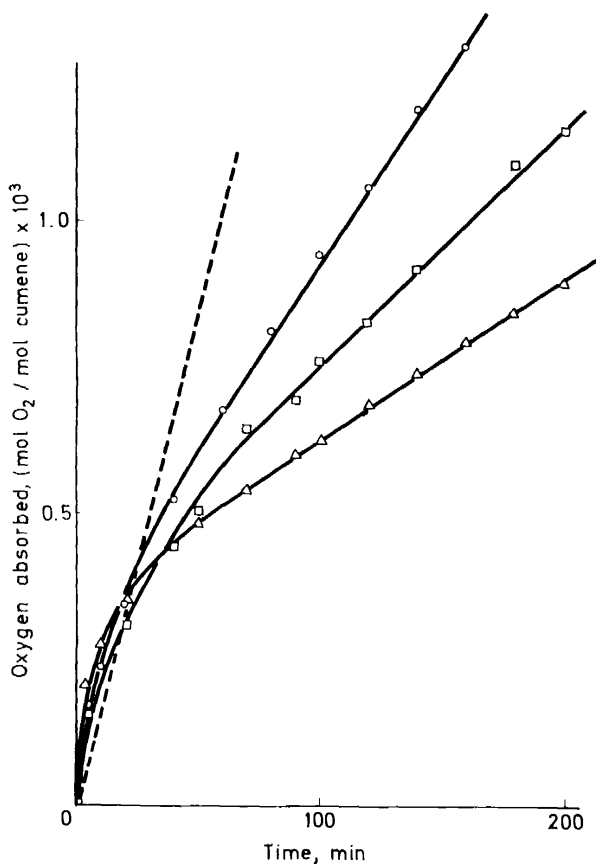
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Figure 5. Triphenyl phosphite-inhibited oxidation of cumene initiated by 0.2M CHP in oxygen at 75°C. ○ 0.01M; ▢ 0.02M; △ 0.03M phosphite; – – – – no phosphite.

reported[15]. Detailed studies have confirmed this. *Figure 8* shows the effect of the three catechol phosphite esters in the decomposition of cumene hydroperoxide. All are catalysts for hydroperoxide decomposition and show good first order kinetics although the hindered-phenyl phosphite, II(c) appears to exhibit more complex behaviour initially. The apparent first order rate constants are listed in *Table 1*.

Table 1. Apparent first order rate constants for the decomposition of 0.2M cumene hydroperoxide in nitrogen at 75° by 0.02M catechol phosphites (II)

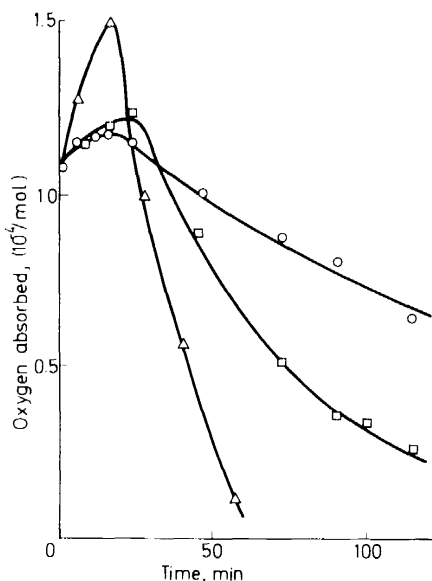| Phosphite	II (a)	II(b)	II(c)
k, S^{-1}	8.0×10^{-4}	2.5×10^{-3}	6.7×10^{-5}

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Figure 6. Gas evolution during reaction of catechol hindered-phenyl phosphite with 0.2M cumene hydroperoxide in chlorobenzene at 75°C. ○ 0.0095M; □ 0·021M; △ 0.04M.

The rate constant for the catechol hindered-phenyl phosphite was found to depend on the initial concentration of phosphite and plotting log k against log phosphite concentration gave a straight line of unit slope (*Figure 9*) indicating that the reaction is first order with respect to a species (P) formed
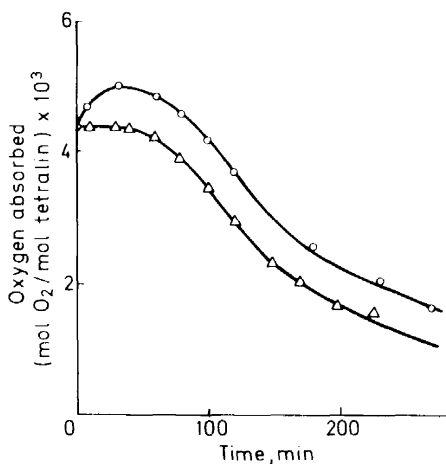

Figure 7. Gas evolution during reaction of catechol hindered-phenyl phosphite (1.25×10^{-2}M) with tetralin hydroperoxide (0.25M) in tetralin at 50°C. △ in nitrogen; ○ in air.

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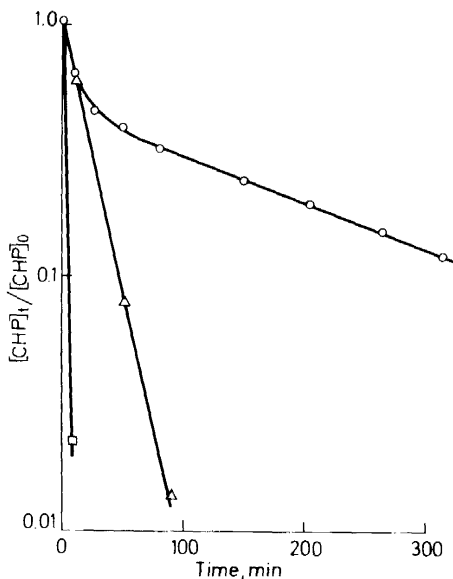
Figure 8. First order plot for the decomposition of 0.2M cumene hydroperoxide in cumene (in nitrogen) at 75°C by 0.02M catechol phosphites. O hindered-phenyl phosphite: △ isopropyl phosphite: ⬚ phenyl phosphite.

from the phosphite which must be the effective catalyst for hydroperoxide decomposition. This was confirmed by adding more hydroperoxide at the end of the experiment when it was found (see *Figure 10*) that the rate of hydroperoxide decomposition was the same (within experimental error) as

Figure 9. Logarithmic plot of pseudo first order rate constants for the catalytic decomposition of cumene hydroperoxide by catechol hindered-phenyl phosphite in chlorobenzene at 75°C.

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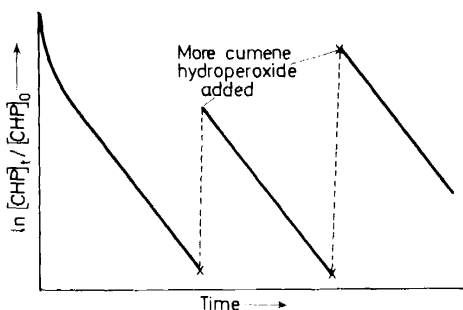
Figure 10. Catalytic activity of the products formed in the reaction between cumene hydroperoxide and catechol hindered-phenyl phosphite.

the original first order rate. Several hundred fold of hydroperoxide could be destroyed in this way. By contrast, the reaction of triphenylphosphite with cumene hydroperoxide was strictly stoichiometric (see *Table 2*).

Table 2. Stoichiometry of the reaction between triphenylphosphite and cumene hydroperoxide

$[(PhO)_3P]$ (mol. l^{-1})	[CHP] destroyed (mol. l^{-1})	$(PhO)_3P/[CHP]$
0.0235	0.025	1/1.06
0.0478	0.053	1/1.07
0.1003	0.104	1/1.03
0.2050	0.200	1/1.02

Extrapolation of the straight line portion of the first order plot of hydroperoxide decomposition to zero time (*Figure 8*) over a range of concentration ratios of phosphite and hydroperoxide indicated a constant stoichiometry of 4:1 (hydroperoxide:phosphite) for the non-linear part of the decomposition curve, suggesting that four molecules of hydroperoxide are involved in the formation of the catalytic species. The phosphate ester (III) was identified as

III

one of the products of the reaction. This was found to be a powerful catalyst for hydroperoxide decomposition and at the same concentration gave the same pseudo first order rate constant as the phosphite (*Figure 11*). Triphenyl phosphate on the other hand was inert as anticipated. In agreement with
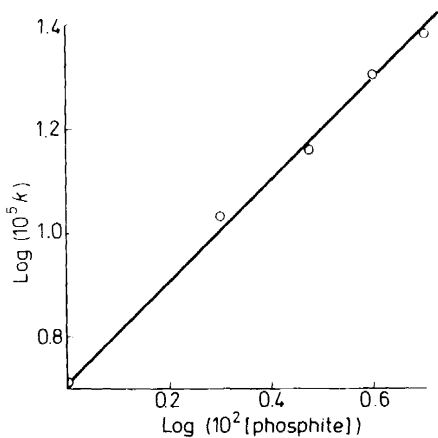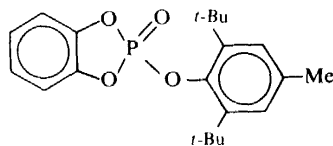
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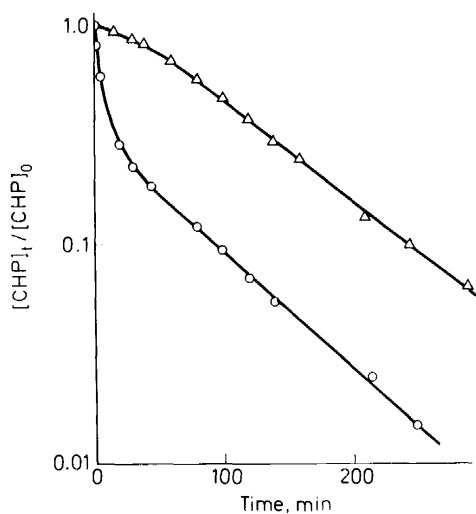
Figure 11. First order plot for the decomposition of 0.2 M cumene hydroperoxide in chlorobenzene at 75°C by: ○ 0.04 M catechol hindered-phenyl phosphite: △ 0.04 M catechol hindered-phenyl phosphite.
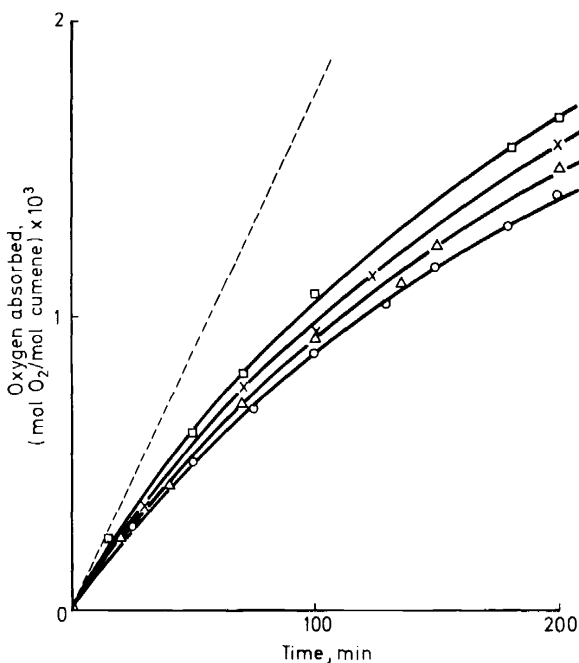

Figure 12. Inhibition of the cumene hydroperoxide-initiated oxidation of cumene in oxygen at 75°C, by catechol hindered-phenyl phosphate. $[CHP]_0$ 0.2M; ○ 0.005M; △ 0.01M; × 0.02M; □ 0.03M. (All curves are averages of four runs each.) - - - - no phosphate.

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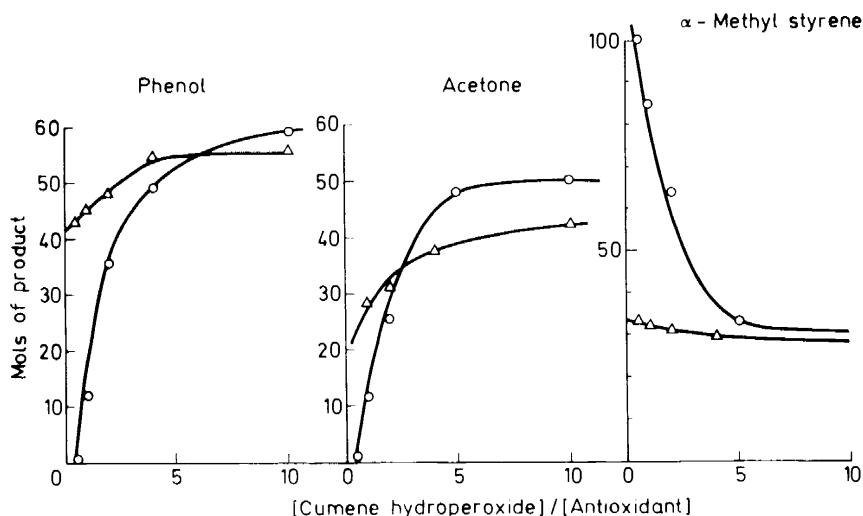
Figure 13. Cumene hydroperoxide decomposition products in chlorobenzene at 75 C. (Constant 0.2M hydroperoxide.) O Phosphite: △ phosphate.

this behaviour, the catechol hindered-phenyl phosphate is an effective anti-oxidant (*Figure 12*) but unlike the phosphite does not give an initial pro-oxidant effect and it is much slower in achieving full inhibition, particularly at higher concentrations due to the induction period before the active catalyst is produced. For this latter reason it appears unlikely that the phosphate is involved in the sequence of reactions leading to the antioxidant.

The antioxidant is a powerful Lewis acid as is shown by the decomposition products formed from cumene hydroperoxide by both the catechol hindered-phenyl phosphite and phosphate (*Figure 13*). At low hydroperoxide to phosphite ratios the product is primarily that expected from a homolytic breakdown of hydroperoxide, namely α-methyl styrene. This accords with the initial pro-oxidant effect on this system (see *Figure 3*) due to the formation of free radicals.

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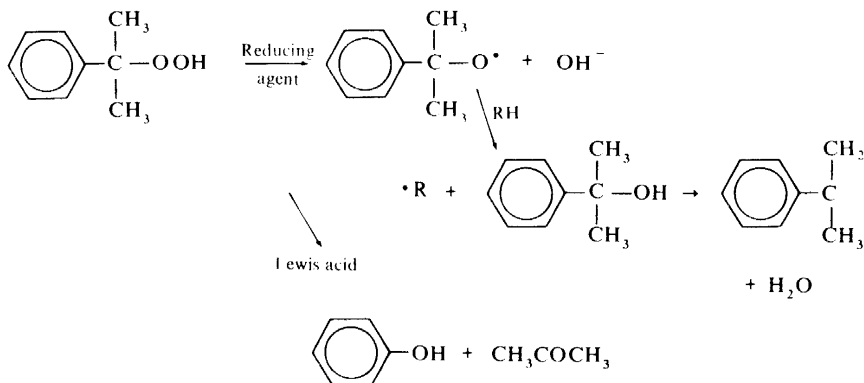
The catalyst which is formed acts predominantly, although not exclusively, as a Lewis acid (*Figure 13*). This dual characteristic is shown by the effect of the cumene hydroperoxide phosphite system in the polymerization of styrene. *Figure 14* shows that whereas cumene hydroperoxide alone exhibits the well known dependence of the rate of polymerization on the square root of the initiator concentration (lowest curve), there is no such simple
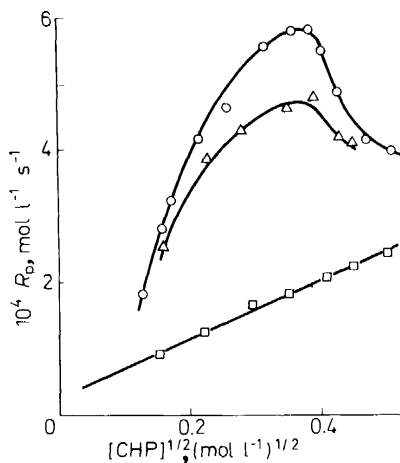

Figure 14. Dependence of rate of polymerization of styrene in oxygen on hydroperoxide concentration in the presence and absence (□) of catechol phosphites. ○ 0.01 M catechol hindered-phenyl phosphite; △ 0.01 M catechol isopropyl phosphite.

relationship in the presence of the catechol phosphites [II(a) and (c)]. Both systems show a maximum rate of polymerization and hence of radical formation at the same hydroperoxide:phosphite ratio. This is consistent with the view already expressed that the initial reaction between phosphite and hydroperoxide involves the formation of free radicals. This reaction has been found to be first order with respect to each component and radical generation in this stage is consistent with the mechanism proposed by Pobedimskii[16] who postulated a bimolecular reaction between hydroperoxide and phosphite to give a radical cage structure from which the radicals may escape to initiate free radical chain reactions or may undergo further reaction within the cage to give the ultimate reaction products. Measurement of the rate of the styrene initiation process indicates that escape from the cage is a minor reaction since the efficiency of radical generation is between five and ten per cent. The main rection leads to the formation of other products by a non-radical process and it is one or more of these products which lead to the formation of a powerful Lewis acid species which inhibits both autoxidation and styrene polymerization in the later stages of the reaction.

$$(RO)_3P + R'OOH \rightarrow [(RO)_3P \text{---} O\text{---}R']$$
$$\downarrow \quad | \atop OH$$

$$(RO)_3P{=}O \qquad \leftarrow [(RO)_3\dot{P}\text{--} OH\ \dot{O}R]$$
$$+ ROH$$
$$\Big| (<10\%)$$
and further $\qquad \downarrow$
oxidation products $\quad (RO)_3\dot{P}\,OH + \dot{O}R$

As has already been indicated, the phosphate (III) is almost certainly not the powerful antioxidant species, although it is quite as effective as an anti-oxidant for polypropylene as the parent phosphite ester and both are con-siderably more effective on a weight basis than one of the best commercial

Figure 15. Induction periods to oxidation of polypropylene at 150 C stabilized by: O catechol hindered-phenyl phosphite; △ catechol hindered-phenyl phosphate; ⊓ 3:1 of DLTP: Irganox '1010'.

synergistic stabilizing systems (see *Figure 15*). Other products identified in the reaction, the catechol hydroxy phosphate (IV) and its hydrolysis product (V), appear to be much more likely candidates.

IV

V

The former destroys hydroperoxides at a faster rate than any of the other products identified from this reaction (see *Table 3*) and, more important from the point of view of the mechanistic reaction sequence, unlike the catechol hindered-phenyl phosphate (III) neither IV nor V exhibits an initial slow stage before the onset of the pseudo first order reaction.

Table 3. Pseudo first order rate constants for the decomposition of cumene hydroperoxide by catechol hindered-phenyl phosphite II(c) and derived products in chlorobenzene at 75°C
$[CHP]_0 = 0.2M$, $[P]_0 = 0.02M$

p k_1, S^{-1}	II(c) 1.1×10^{-4}	III 1.2×10^{-4}	IV 84×10^{-4}	V 2.5×10^{-4}

In confirmation of this both the hydroxyphosphate (IV) and its hydrolysis product (V) which are formed as minor byproducts from the oxidation of the catechol phosphites have been found to be powerful antioxidants in model systems. *Figure 16* shows that the catechol hydroxy phosphate (IV) causes very rapid cessation of oxygen absorption in cumene initiated by cumene hydroperoxide and not only is no pro-oxidant effect evident but an immediate gas evolution occurs at a more rapid rate than in the case of the catechol hindered-phenyl phosphite at the same molar concentration (see
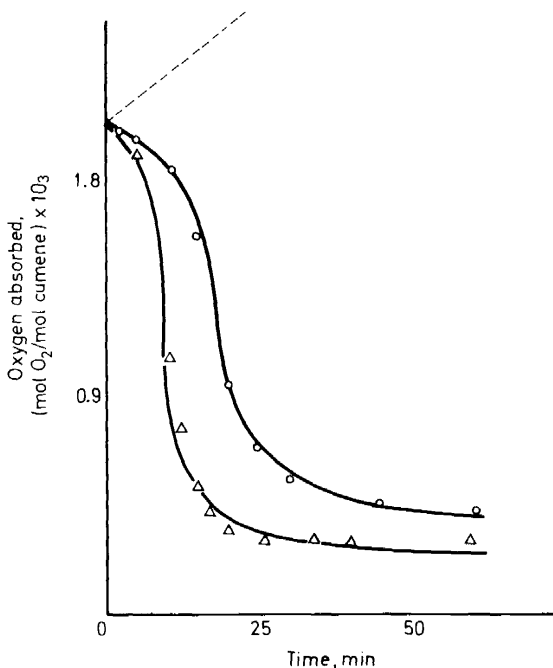

Figure 16. Gas evolution during the reaction of 0.02M catechol hydroxy phosphate with 0.2M cumene hydroperoxide in cumene at 75°C. O in oxygen; Δ in nitrogen. – – – no phosphate.

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Figure 3). This additive is also an effective thermal and u.v. stabilizer for polypropylene as might be expected from its peroxide decomposing activity. Comparative studies of the effects of these compounds as u.v. stabilizers will be discussed in another paper at this conference.

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