MECHANISMS OF ANTIOXIDANT ACTION OF ORGANIC PHOSPHORUS COMPOUNDS
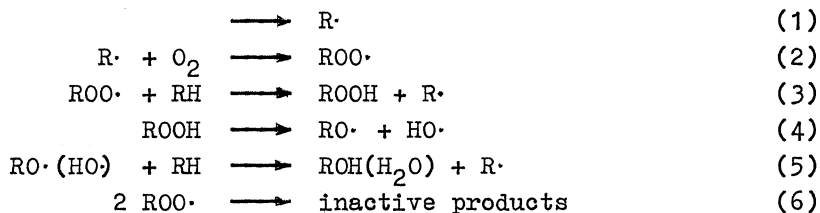
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Abstract- The antioxidative activity and the mechanisms of antioxidant action of alkyl, aryl, cyclic and sterically hindered phosphorous acid esters and amides have been studied. The chain-breaking efficiency of phosphites is shown to depend on the structure of both the phosphorus compound and the substrate to be stabilized. At moderate temperatures aryl phosphites act as primary antioxidants only in the autoxidation of substrates which are not very reactive towards peroxyl radicals. The chain-breaking efficiency is related to the nature of transformation products formed in the reactions of phosphites with alkylperoxyl and alkoxyl radicals. These products have been identified in some model reactions. All phosphorus(III) compounds destroy hydroperoxides and so are able to function as secondary antioxidants. o-Phenylene phosphite esters and amides react with hydroperoxides to give hydroxyphenyl phosphates which are efficient chain-breaking agents.

INTRODUCTION

Organophosphorus compounds, predominantly phosphite esters, have found a wide application as non-discolouring antioxidants in the stabilization of organic materials against ageing and degradation during processing. For the stabilization of polymers, such as rubber, polyolefines, ABS, and PVC, they represent a class of compounds whose importance is comparable with that of the sterically hindered phenols. Nevertheless, the detailed mechanisms of their antioxidant action have been studied far less thoroughly then those of phenols [1,2]. In particular, too little is known about the relationships between structure and antioxidant activity, the influences of different reaction conditions on them, and the nature and role of transformation products of the inhibitors in the stabilization process.

Phosphites are considered to act as antioxidants by several mechanisms depending on the modes they interfere with the autoxidation chain reaction of a compound RH.

$$\longrightarrow R\cdot \qquad (1)$$
$$R\cdot + O_2 \longrightarrow ROO\cdot \qquad (2)$$
$$ROO\cdot + RH \longrightarrow ROOH + R\cdot \qquad (3)$$
$$ROOH \longrightarrow RO\cdot + HO\cdot \qquad (4)$$
$$RO\cdot(HO\cdot) + RH \longrightarrow ROH(H_2O) + R\cdot \qquad (5)$$
$$2 ROO\cdot \longrightarrow \text{inactive products} \qquad (6)$$

Some phosphites are able to function as primary antioxidants competing with reaction steps (3) and (5) by trapping $RO_2\cdot$ and $RO\cdot$ radicals, so terminating the oxidation chain. All phosphites are secondary preventive antioxidants decomposing hydroperoxides in a non-radical way and so suppressing the chain branching step (4). Furthermore they act as metal complex forming agents blocking metal ions which cause chain initiation and branching by reaction with ROOH and RH.

The effects of several phosphites and amidophosphites in the autoxidation of isotactic polypropylene at 180 °C are shown in Fig. 1. All compounds studied inhibit the autoxidation showing induction periods and retarding effects after the induction period commonly greater than 2,6-di-tert-butyl-4-methyl-phenol (BHT).

PHOSPHITES AS CHAIN-BREAKING ANTIOXIDANTS

There is considerable disagreement in the literature concerning the chain breaking efficiency of phosphites in the autoxidation of hydrocarbons and polymers. Whereas some workers plead for a high radical scavenging activity of aryl phosphites [1,3], others deny their direct reaction with peroxyl radicals and relate the observed activity to their ability to release phenols in the course of autoxidation [4].

In order to act as a primary chain breaking antioxidant, a stabilizer must fulfil two basic requirements: it must be able to compete effectively with the substrate RH for the $RO_2\bullet$ radicals, and it must form an efficient chain terminating agent in this reaction with $RO_2\bullet$ radicals.
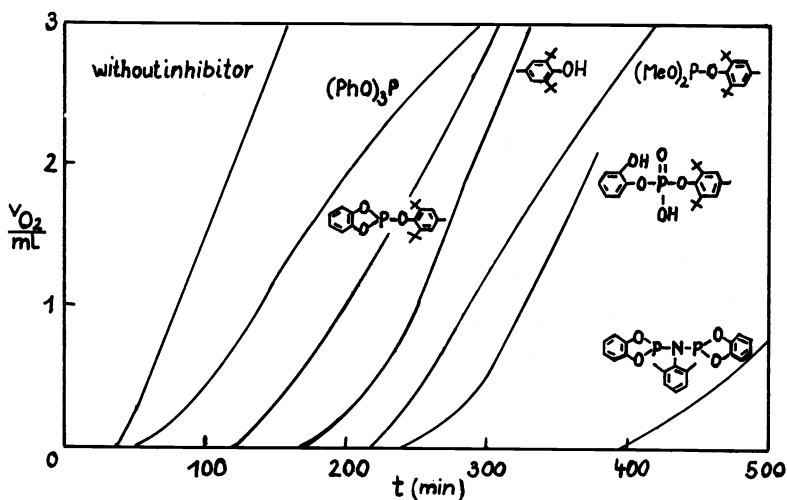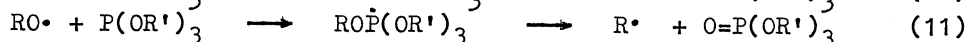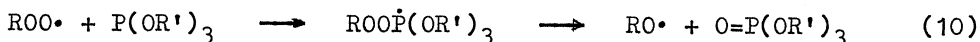

Fig. 1.   Oxidation of isotactic polypropylene in the presence of phosphorus compounds (0.05 mol/kg), 180 °C

Only aryl phosphites meet the second requirement. They react with simple alkylperoxyl radicals to give aroxyl radicals which are capable of terminating the autoxidation chain [5-7]:

$$ROO\bullet + P(OAr)_3 \longrightarrow ROO\overset{\bullet}{P}(OAr)_3 \longrightarrow RO\bullet + O{=}P(OAr)_3 \qquad (7)$$

$$RO\bullet + P(OAr)_3 \longrightarrow RO\overset{\bullet}{P}(OAr)_3 \longrightarrow ROP(OAr)_2 + \bullet OAr \qquad (8)$$

$$ROO\bullet + ArO\bullet \longrightarrow \text{inactive products} \qquad (9)$$
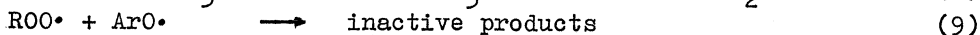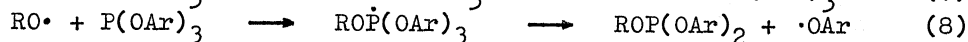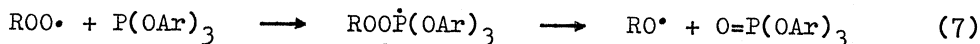
On the other hand, alkyl phosphites react with $RO_2\bullet$ radicals to form the corresponding phosphates in a rapid chain oxidation involving $R\bullet$ and $RO\bullet$ radicals [8,6] which are unable to terminate the autoxidation chain:

$$ROO\bullet + P(OR')_3 \longrightarrow ROO\overset{\bullet}{P}(OR')_3 \longrightarrow RO\bullet + O{=}P(OR')_3 \qquad (10)$$

$$RO\bullet + P(OR')_3 \longrightarrow RO\overset{\bullet}{P}(OR')_3 \longrightarrow R\bullet + O{=}P(OR')_3 \qquad (11)$$

The different activity of aliphatic and aromatic phosphites in the reaction with $RO_2\bullet$ is predominantly due to the different behaviour of the intermediate phosphoranyl radicals formed in the reaction of $RO\bullet$ radicals with the phosphites. Whereas alkoxyphosphoranyl radicals undergo ß-scission to give phosphates and $R\bullet$ radicals (eq. 11), aryloxyphosphoranyl radicals form an isomer phosphite and aroxyl radicals by α-scission (eq. 8) [7].

To meet the first requirement for chain-breaking antioxidant action, phosphites must be able to react with peroxyl radicals faster then the substrate RH, $k_7[P(OAr)_3]$ must be larger then $k_3[RH]$. Because k_7 is relatively small (about $10^2 M^{-1}s^{-1}$ for arylphosphites at moderate temperatures, see Table 2), this holds only when the substrate RH is not very reactive towards $RO_2\bullet$ radicals, as in the case of saturated aliphatic hydrocarbons and polyolefins, or when the phosphite concentration is rather high. In Table 1 are given those concentrations which have at least to be used in order to act triphenyl phosphite as a chain-breaking antioxidant.

TABLE 1.   Triphenyl phosphite concentration at which
$k_7[P(OPh)_3] \approx k_3[RH]$ (30 °C) [1]

RH	$k_3/M^{-1}s^{-1}$	$[P(OPh)_3]$ /M
2,4,6-Trimethylheptane	0.052	0.003
Cumene	0.18	0.01
Methyl isopropyl ketone	0.36	0.03
Di-isopropyl ether	0.4	0.03
Oct-1-ene	1.0	0.06
Ethylbenzene	1.3	0.1
Tetralin	6.4	0.5
Styrene	41	4

1) k_3 from the compilation of J.A. Howard, Adv. Free
   Radical Chem. 4, 49-173 (1972); k_7 from Table 2.

Towards the more reactive araliphatic and olefinic hydrocarbons, phosphites cannot operate as primary antioxidants, as it is seen in Fig. 2 which demonstrate the ineffectualness of aryl phosphites in the autoxidation of tetralin. The behaviour of the sterically hindered p-phenylene phosphite is exceptional in that it shows a pronounced retarding effect in the later stages of the reaction. This is because transformation products with high chain-breaking activity arise from the phosphite in the course of oxidation (see below).
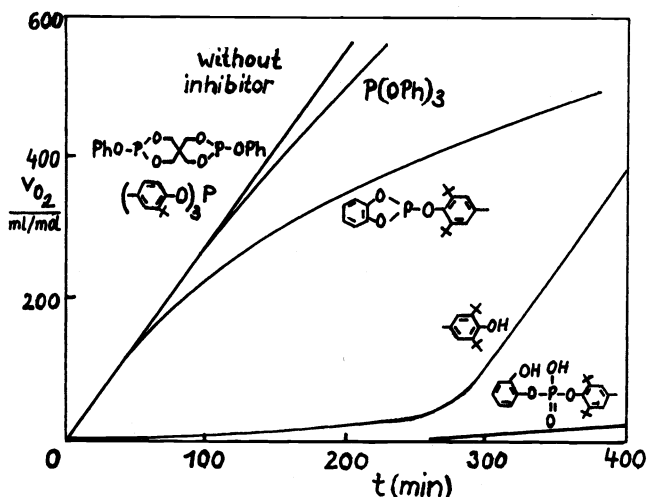
Fig. 2   Oxidation of teralin at 60 °C in the presence of
phosphorus compounds ($[P]$ = 5 x 10^{-4} M, $[AIBN]$ = 5 x 10^{-3} M)

Towards the less reactive cumene, on the other hand, sterically hindered phosphites in moderate concentrations act as chain breaking antioxidants.

Reports in the literature demonstrating the chain breaking efficiency of aryl phosphites in tetralin and styrene autoxidation are possibly due to phosphites contaminated with phenols from the preparation procedure.

In order to verify the given interpretations, we have studied the kinetics and mechanisms of the reactions of phosphites with $RO_2\cdot$ and $RO\cdot$ radicals generated by thermal degradation of azo-bis-isobutyronitrile (AIBN) in the presence of oxygen
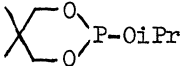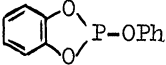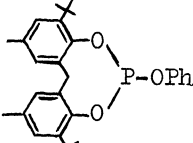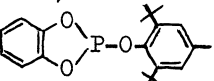
$$AIBN \xrightarrow[-N_2]{+O_2} 2a \ NC-\underset{\underset{Me}{|}}{\overset{\overset{Me}{|}}{C}}-O-O\cdot \qquad (12)$$

and of di-tert-butyl peroxalate (DTBPO)

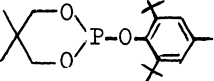$$tBu-O-O-\underset{\underset{O}{\|}}{C}-\underset{\underset{O}{\|}}{C}-O-O-tBu \xrightarrow{-CO_2} 2 \ tBu-O\cdot \qquad (13)$$
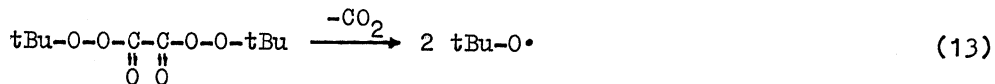
As expected, aliphatic phosphites react with AIBN and oxygen via <u>cyanoiso-propylperoxyl radicals</u> completely according to equations (10) and (11) to give the corresponding phosphates in a rapid chain reaction ($r/r_i > 100$), whereas the reaction of sterically hindered aryl phosphites results initially in the formation of an equimolar mixture of phosphate and phosphite $>P-O-CMe_2CN$ according to equations (7) and (8) in a slow non-chain process ($r/r_i \approx 1^2$) (Table 2). Non sterically hindered aryl phosphites give the phosphates in a short chain reaction!

TABLE 2. Initial rates (r_o) and products of reaction of phosphites (0.2 M) with oxygen and AIBN at 65 °C ($-R = -CMe_2CN$)

$>P-OR'$	$>P{<}^O_{OR'}$ mole-%	$>P-OR$	$10^8 \times r_i$ M s^{-1}	$10^6 \times r_o$ M s^{-1}	$\dfrac{r_o}{r_i}$	$10^{-2} \times k_7$ M^{-1}s^{-1}
$P(OEt)_3$	100	–	2.26	36	1600	18
$P(OiPr)_3$	100	–	2.26	22	970	11
$P(OtBu)_3$	100	–	2.26	14	620	7
⤷P-OiPr	100	–	226	178	80	9.4
$P(OPh)_3$	100	–	226	35	16	1.8
⤷P-OPh	100	–	226	11	5	0.6
⤷P-OPh	100	–	226	8.9	3.9	0.5
$P(O-⟨⟩-)_3$	69	31	226	4	2	
⤷P-O-⟨⟩	53	47	226	3.2	1.4	
⤷P-O-⟨⟩	48	52	226	3	1	

Using the rate laws

$$r = -d[P]/dt = (2 \ r_i/k_4)^{1/2} k_7 [P]$$

$$r_i = 2a \ k_{12} [AIBN]$$

which results from a reaction scheme involving the equations 12, 10, 11, and 6 with $k_4 = 5 \times 10^6$ l mol^{-1}s^{-1} [9], k_7, the rate constants of reaction (7),

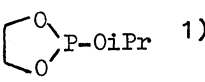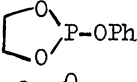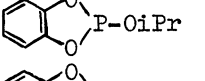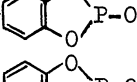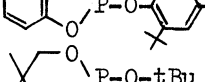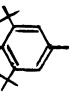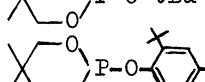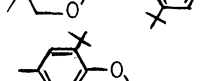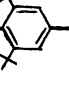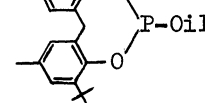can be calculated (Table 2). For alkyl phosphites the values of k_7 are in the order of those expected by other methods [10], for phenyl phosphites they are approximately tenfold smaller. For the sterically hindered aryl phosphites, a reaction scheme involving the equations 12, 7, 8 and 9 leads to the rate law

$$r = - d\,[P]/dt = r_i$$

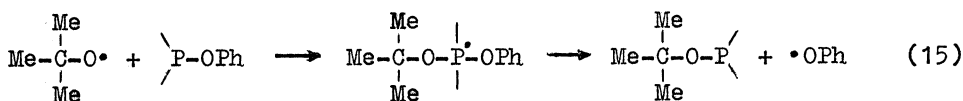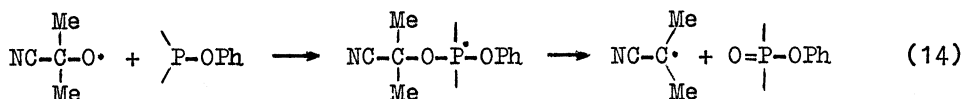which also is observed experimentally and from which k_7 cannot be evaluated.

With tert-butoxyl radicals from DTBPO, aliphatic phosphites react to form the corresponding phosphates according to equation (11). The aryl phosphates give according to equation (8) preferentially the tert-butyl phosphite which is easily oxidized to form the tert-butyl phosphate (Table 3). It is worth noting that cyclic aromatic phosphites like the o-phenylene phosphites react mainly by ß-scission and not under ring opening of the intermediate phosphoranyl radicals as is typical for aliphatic phosphites!

TABLE 3. Initial rates (r_o) and products of reactions of phosphites (0.2 M) with DTBPO (0.1 M) in chlorobenzene at 55 °C

$\diagdown$P–OR'	$\diagdown$P$\diagup\diagdown$$^O_{OR'}$	$\diagdown$P–OtBu	$\dfrac{r_o}{r_i}$
	mole-%		
P–OiPr 1)	100	–	
P–OPh	–	100	0.6
P–OiPr	75	25	1.0
P–OPh	–	100	0.8
P–O–(aryl)	–	100	0.6
P–O–tBu	92	8	1.9
P–O–(aryl)	–	100	0.8
P–OiPr	75	25	

1) $[DTBPO]_o = 0.2$ M

As can be seen, phenyl phosphites react with cyanisopropoxyl and tert-butoxyl radicals in a different manner. With the former the corresponding phenyl phosphates are built up by ß-scission of the intermediate phosphoranyl radicals (eq. 14), whereas with the latter tert-butyl phosphites are formed by α-scission (eq. 15).
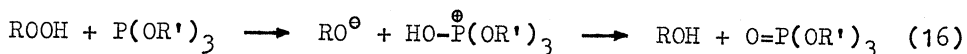
(14)

(15)

Obviously, this is because the $NC(Me)_2C$-O bond is weaker then the $(Me)_3C$-O bond and its breaking successfully competes with the scission of the P-OPh bond in the phosphoranyl radical.

Therefore, the chain-breaking efficiency of phenyl phosphites should depend on the chemical nature of the substrate to be stabilized. They should exhibit a pronounced primary antioxidant activity only in saturated aliphatic hydrocarbons and polyolefines, whereas in cyano or phenyl substituted compounds, such as polyacrylonitriles, polystyrenes and their copolymers (e. g. ABS), their chain-breaking efficiency should be low.
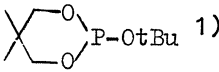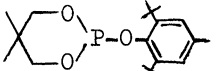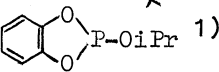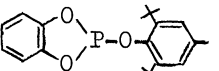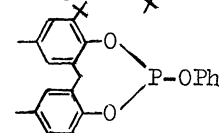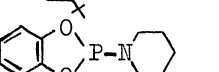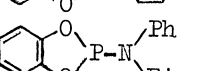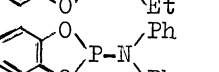
PHOSPHITES AND AMIDOPHOSPHITES AS HYDROPEROXIDE DECOMPOSERS

It is well known that organic phosphites react with hydroperoxides to form phosphates and alcohols obeying a second order rate law [8,11]. The reaction proceeds according to a non-radical mechanism, probably a S_N2-mechanism at the O-O bond with P as the nucleophile

$$ROOH + P(OR')_3 \longrightarrow RO^{\ominus} + HO-\overset{\oplus}{P}(OR')_3 \longrightarrow ROH + O{=}P(OR')_3 \quad (16)$$

The rate constants and activation parameters of the reactions of several phosphites and amidophosphites with <u>cumyl hydroperoxide</u> (CHP) are shown in Table 4. The reactivity of the phosphorus compounds is mainly governed by polar and steric effects of the groups bound to P: amidophosphites are more reactive then phosphites and the reactivity decreases in the order alkyl > aryl > sterically hindered aryl derivatives.

TABLE 4. Reaction of phosphorus compounds with cumyl hydroperoxide in chlorobenzene ($[P]_0 = 0.1$ M, $[CHP]_0 = 0.2$M)

Phosphorus compound	$10^3 \times k$ / $M^{-1}s^{-1}$		$\Delta H^{\ddagger}$	$\Delta S^{\ddagger}$
	0 °C	30 °C	kJ mol^{-1}	J mol^{-1}K^{-1}
$P(OtBu)_3$	3.7	220		
$P(OPh)_3$	1.3	31		
(structure) P-OtBu [1)		57		
(structure) P-O-(aryl)		37	52	−105
(structure) P-OiPr [1)		190		
(structure) P-O-(aryl)	0.3	3.3	69	−62
(structure) P-OPh [1)		4.6	74	−42
(structure) P-N⟨⟩	38	350	48	−93
(structure) P-N⟨Ph,Et⟩	25	170	41	−122
(structure) P-N⟨Ph,Ph⟩	60			

1) $[P]_0 = 0.2$ M, $[CHP]_0 = 0.2$ M

Five-membered cyclic phosphites are capable of decomposing cumyl hydroperoxide catalytically to give phenol and acetone [12]. The catalytic decomposition is preceded by a fast reaction stage in which the catalytically active species is formed. We observed by HPLC and ^{31}P-NMR two phosphates during the course of the reaction of 2,6-di-tert-butyl-4-methylphenyl-o-phenylene phosphite (1)(Fig. 3). The first (2) ist going through a maximum
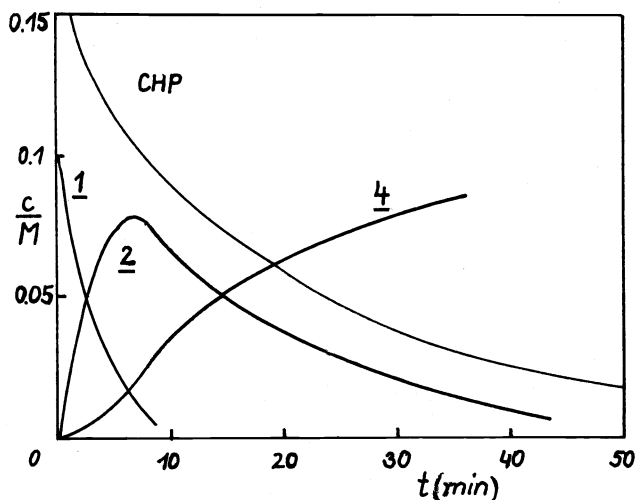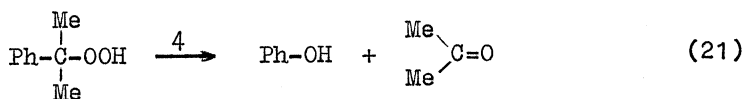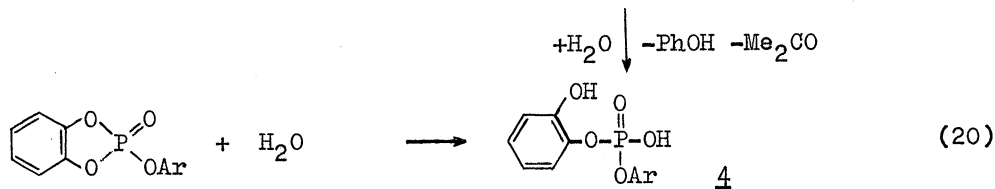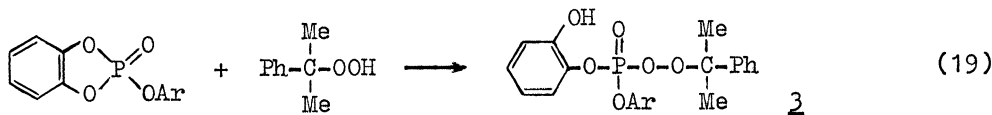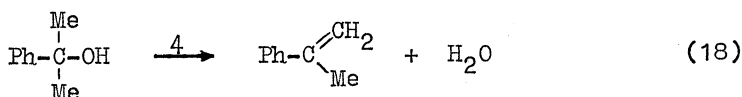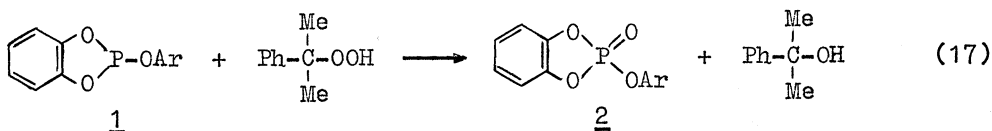
Fig. 3. Reaction of 2,6-di-tert-butyl-4-methylphenyl o-phenylene phosphite with cumyl hydroperoxide in chlorobenzene at 50 °C
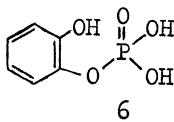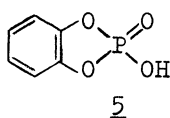
of concentration. It forms the second phosphate (4) in two ways, rapidly by reaction with water (from reaction 18 and moisture) and more slowly with the hydroperoxide giving a peroxy phosphate (3) which is unstable and decomposes to form 4 and phenol and acetone. The open-chained phosphate 4 is the acidic catalyst in the catalytic stage of the reaction (21).

4 is also formed in the reaction of 1 with other hydroperoxides, e. g. tert-butyl hydroperoxide and tetralin hydroperoxide. It is a very efficient chain-breaking antioxidant and responsible for the inhibiting activity of 1 in the later stages of the initiated oxidation of hydrocarbons (cf. Fig. 2).
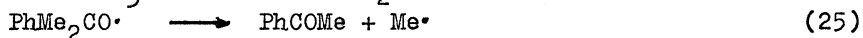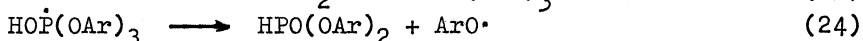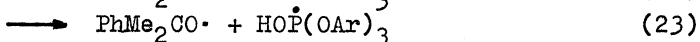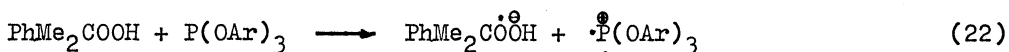
Higher (six, seven, eight) membered cyclic phosphites do not react with
CHP catalytically but only in a stoichiometric 1:1 reaction, because the
corresponding phosphates are very much more stable against peroxidolysis
and hydrolysis than the five-membered derivatives.

Of the o-phenylene amidophosphites, the aliphatic derivatives react with
cumyl hydroperoxide in a 1:1 reaction, whereas the arylamidophosphites
decompose the hydroperoxide catalytically giving phenol and acetone. The
amidophosphates formed in the first instance are removed in the later
stages of the reaction giving a great number of new phosphates. As main
products the compounds 5 and 6 could be identified.

These are the acid catalytically active species for the decomposition of
the hydroperoxide by arylamidophosphites.

Radical side reactions. The heterolytic mechanism of hydroperoxide decom-
position by phosphites and amidophosphites is accompanied by a homolytic one
in a minor proportion. The phosphite-hydroperoxide system exhibit ^{31}P-CIDNP
[14,15], initiate oxidation and polymerisation reactions [12,13], and inter-
mediate radicals can be trapped with stable nitroxyl radicals [1]. We were
able to detect the 2,6-di-tert-butyl-4-methylphenoxyl radical by ESR in the
reactions of 1 with CHP and tert-butyl hydroperoxide [16]. In the reactions
of amidophosphites with CHP, nitroxyl radicals can be observed by ESR [16]
and ^{31}P-CIDNP also is a common feature. The homolytic side reactions
possibly follow a mechanism proposed by Pobedimskii and Buchachenko [17]
shown in the following scheme:

$$PhMe_2COOH + P(OAr)_3 \longrightarrow PhMe_2C\overset{\cdot}{O}\overset{\ominus}{O}H + \cdot\overset{\oplus}{P}(OAr)_3 \qquad (22)$$

$$\longrightarrow PhMe_2CO\cdot + HO\overset{\cdot}{P}(OAr)_3 \qquad (23)$$

$$HO\overset{\cdot}{P}(OAr)_3 \longrightarrow HPO(OAr)_2 + ArO\cdot \qquad (24)$$

$$PhMe_2CO\cdot \longrightarrow PhCOMe + Me\cdot \qquad (25)$$

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