Thematic course: Scientific Bases of Polymer Stabilization. Part I.

SYNTHESIS AND ANTIOXIDATIVE PROPERTIES OF ORGANOPHOSPHORUS COMPOUNDS.

© **Peter A. Kirpichnikov**, **Natalia A. Mukmenyeva**,*[+] and **Elena N. Cherezova***
Department of Technology of Synthetic Cautchouc. Kazan State Technological University.
K. Marx St., 68. Kazan 420015. Russia. E-mail: cherezov@cnit.ksu.ras.ru

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*Leader of the thematic course; [+]Corresponding author

Abstract

In this review the results of the studies on the synthesis and properties of organophosphorus compounds (the derivatives of three- and four-coordinated phosphorus) are analysed from the standpoint of correlation between their structure, antioxidizing properties and inhibitory efficiency, which is a scientific basis for searching and selecting highly efficient organophosphorus stabilizers of polymeric materials. The physical chemistry of potential and practically used organophosphorus compounds (**OPhC**) has been considered; the mechanisms of their inhibitory action have been discussed. The bibliography made up 46 references.

Introduction

The regular domestic studies in the field of organophosphorus stabilization of polymers begun at the end of 50-s in the Kazan Chemical Engineering Institute, now Kazan State Technological University, and is intensively developed nowadays [1-6].

Theoretical basis for using and researching organophosphorus compounds as stabilizers lies in the exclusive ability of phosphorus atom to enter into different types of electronic interactions. The presence of unoccupied orbitals and undivided electronic pair, high polarizability and polarity of phosphorus bonds allows designing practically any necessary structures of organophosphorus compounds [7].

As it has been established, the greatest antioxidative action is exhibited by aromatic and alkylaromatic esters of phosphorous acids, which are capable of showing a significant synergistic effect in mixtures with phenols, they are also capable of combining satisfactorily with polymers, have low volatility and oxidability with molecular oxygen. Qualitative model test estimations of the interactions of phosphites with hydroperoxide 1,1-diphenylethane [8] and stable diphenylpicrylhydrazyl radical [9] have allowed to relate phosphites to combined inhibitors. They destroy hydroperoxides suppressing degenerate branching, and can break off the chains in the reactions with peroxide radicals; on the other hand, they are cable of accepting catalytic admixtures of variable valency metals and to block "weak" spots (with regard to destruction) in polymer chain. The first data obtained on the basis of a variety of possible mechanisms of stabilizing action of organophosphorus compounds (**OPhC**), has been evolved in a number of later works. In these works the basic properties of organophosphorus compounds as stabilizers of polymeric materials have been established, the basic mechanisms of their inhibitory and color-stabilizing effect [2-6] have been formulated and proved.

I. Synthesis of Organophosphorus Compounds (OPhC).

This section presents a retrospective review, where the basic data on synthesis of potential and the most frequently used in practice organophosphorus inhibitors of oxidation of organic substrates, developed in the Kazan Chemical Engineering Institute, (now Kazan State Technological University), have been generalized and systematized.

While carrying out the investigations the peculiar ways of synthesis have been developed, as well as high-reactionary syntons have been found, which allowed to create a variety of **OPhC** structures. The choice of the directions of **OPhC** synthesis was based, on the one hand, on the empirical generalization of practical experience, and, on the other hand, on the achievements gained in studying the regularities and mechanisms of stabilizing action of **OPhC** in various oxidizable substrates (namely, low-molecular hydrocarbons and polymers).

The major groups of the synthesized **OPhC** are given below. Without going into detail of synthesis methods, let us just note that its choice essentially depends on the nature of substituents at phosphorus atom. The substituted acyclic and cyclic esters of phosphorous (mono-, di-, oligophosphites and oligophosphates) and amidophosphorous acids were obtained, mainly, by interaction of phosphorus halogen-derivatives with mono- and polyatomic alcohols, phenols, *bis*-phenols, aliphatic and aromatic amines, as well as by phosphite ester interchange reactions [10-23].

Glycidylphosphites have been synthesized by interaction of glycidol (2,3-epoxypropanol) with chloroanhydrides of the appropriate acids [29,30].

The majority of mono- and disubstituted esters of phosphorous acid have been obtained both by hydrolysis of appropriate chloroanhydrides [24-26], and diphenylphosphite re-esterification with hydroxycompounds.

Cyclic thiophosphorous acids have been isolated by the reaction of chloroanhydrides of octatomic cyclic *O,O'-bis*-phenylphosphites with hydrogen sulphide [26].

Dialkyl dithiophosphic and alkylene dithiophosphoric acids have been synthesized by interaction of appropriate alcohols, phenols or glycols with phosphorus pentasulfide [23].
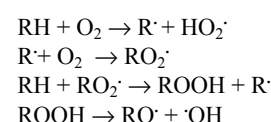
To synthesize sterically hindered dithiophosphonic acids and their derivatives the interaction of reactive synton - 2,4-*bis* (3,5-di-*tert*-butyl-4-hydroxyphenyl)-1,3-dithia-2,4-dithioxaphosphetane with mono- and polyatomic alcohols, as well as tertiary amines [27, 28, 31], has been carried out.

Dialkyl (3,5-di-*tert*-butyl-4-hydroxybenzyl)phosphonates have been obtained by the reaction of 3,5-di-*tert*-butyl-4-hydroxybenzylacetate with trialkylphosphites and sodium dialkylphosphites [32]; as well as by interaction of dialkylphosphorous acids with Mannich base (Mb) - *N,N*-dimethyl-(3,5-di-*tert*-butyl-4-hydroxybenzyl)amine [33]. *Tris*(3,5-di-*tert*-butyl-4-hydroxybenzyl)phosphine has been obtained by the reaction of the latter compound with phosphorous hydrogen [34].

The series of sterically hindered hydroquinonephosphates have been synthesized by interaction of 3,5-di-*tert*-butylbenzoquinone with dialkyl(aryl)phosphorous acids [35] (scheme 8).

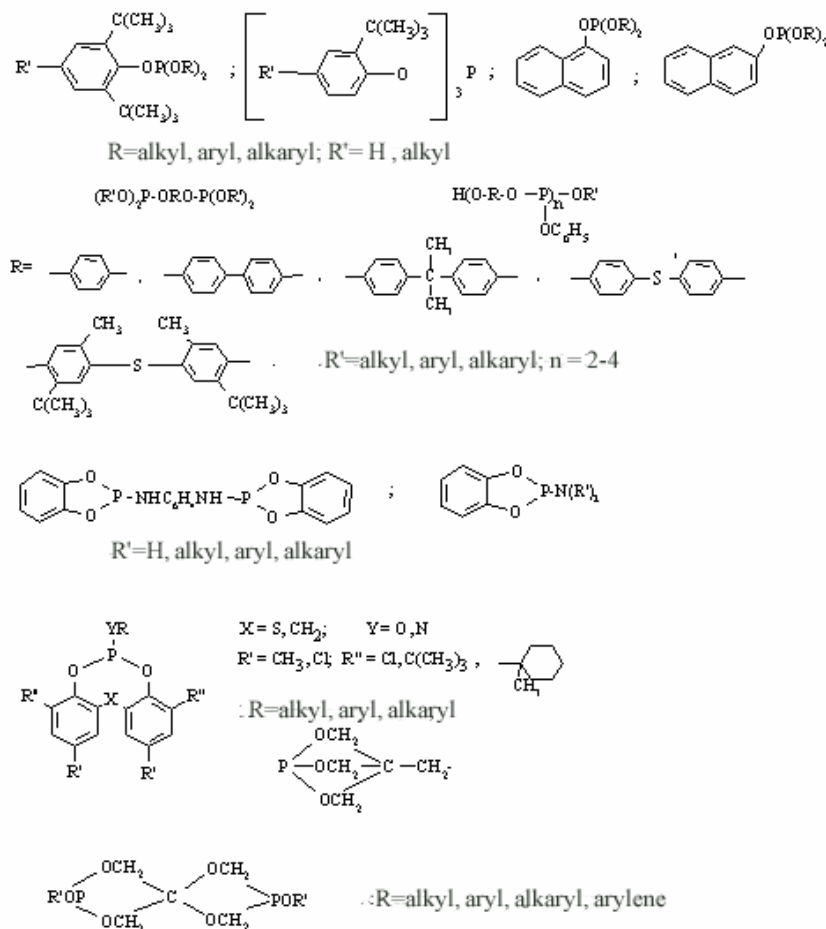### II. Antioxidative Properties of OPhC.

Antioxidative properties of organophosphorus compounds have been studied under model conditions of liquid-phase oxidation of hydrocarbons, which represents the chain reaction, including a number of stages [36]:

$$RH + O_2 \rightarrow R^{\cdot} + HO_2^{\cdot}$$
$$R^{\cdot} + O_2 \rightarrow RO_2^{\cdot}$$
$$RH + RO_2^{\cdot} \rightarrow ROOH + R^{\cdot}$$
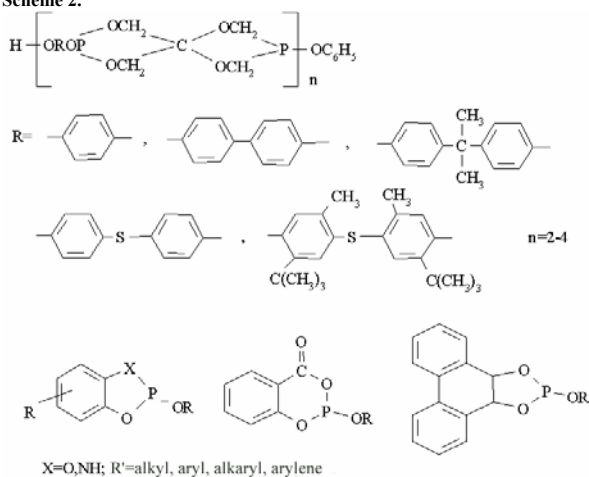$$ROOH \rightarrow RO^{\cdot} + {}^{\cdot}OH$$

III.1. Kinetics and Mechanism of OPhC Reactions with Hydroperoxides.

Reactions of hydroperoxides with completely substituted esters of phosphorous acids P(OR')(OR")(OR''') were investigated by kinetic polarography methods [37-38]. The reactions are characterized by the first order kinetic equation for each reactant; the numerical values of reaction constants, activation energies and preexponential factors are given in table III.1.1 [39]. As follows from this table, aromatic phosphites possess appreciablly greater activation energy value than the aliphatic ones.

Scheme 1

R=alkyl, aryl, alkaryl; R'= H , alkyl

R'=alkyl, aryl, alkaryl; n = 2-4

R'=H, alkyl, aryl, alkaryl

X = S, CH$_2$;   Y= O ,N
R' = CH$_3$, Cl; R" = Cl, C(CH$_3$)$_3$,

: R=alkyl, aryl, alkaryl

:R=alkyl, aryl, alkaryl, arylene

Scheme 2.

n=2-4

X=O,NH; R'=alkyl, aryl, alkaryl, arylene

Scheme 3.

R= R' = alkyl, phenyl
R = alkyl
R' = phenyl

R = alkyl, aryl

Scheme 4.

$(RO)_2P(O)H, (C_6H_5O)_2P(O)H, (\pi\text{-}C_9H_{19}\text{-}C_6H_4O)_2P(O)H$

R'=alkyl, aryl, alkaryl, arylene; R' = H, CH_3, C(CH_3)_3

X = S, CH_2

X= S, CH_2, C(CH_3)_2 ;

R'=alkyl

Scheme 5.

$X = CH_2$, S ; $R = C(CH_3)_3$

Scheme 6.

R=C_2H_5, C_3H_7-i, C_8H_17-i, C_6H_5, -CH_2CH=CH_2; R'=C_3H_6, C_4H_8;

R = CH_3, C_3H_7, i-C_3H_7, C_6H_5,

R' = CH(CH_3)CHCH_3 , CH(CH_3)CH_2CH_2 , CH_2C(CH_3)_2CH_2

R = alkaryl

Scheme 7.

R = alkyl, aryl, alkaryl; X= O,S

R' =

Scheme 8.

R = alkyl, aryl, alkaryl

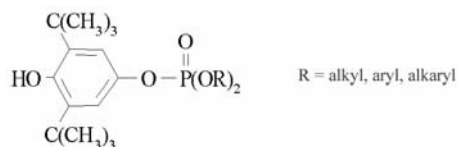**Table III.1.1.** Reaction constants (K), activation energies (E), preexponential factor (A) and steric Rs-constants of phosphorus atom substituents for the reaction of phosphite (scheme 9) with cumene hydroperoxide (benzol, 20° C).

Number of phosphite	$K \cdot 10^3$, $1 \cdot (mol \cdot c)^{-1}$	E, kJ/mol	A, $1 \cdot (mol \cdot c)^{-1}$	$Rs(P)$	$-lg K$	Number of phosphite	$K \cdot 10^3$, $1 \cdot (mol \cdot c)^{-1}$	E, kJ/mol	A, $1 \cdot (mol \cdot c)^{-1}$	$Rs(P)$	$-lg K$
I	851.00			4.14	0.07	XIV	1.29	45.6	$3.2 \cdot 10^5$	9.65	2.89
II	83.30	24.7	$3.2 \cdot 10^3$	5.46	1.08	XV	3.80	58.5	$2.4 \cdot 10^8$	7.96	2.42
III	77.90	25.5	$3.8 \cdot 10^3$	6.36	1.11	XVI	3.30			13.55	2.48
IV	45.00			3.10	1.35	XVII	0.79	57.5	$3.8 \cdot 10^7$	14.20	3.10
V	34.30			3.41	1.46	XVIII	0.80	58.5	$5.8 \cdot 10^7$	14.35	3.22
VI	19.51			4.18	1.71	XIX	2.88	45.0	$1.26 \cdot 10^{28}$	15.49	2.54
VII	26.04			3.81	1.57	XX	5.01	43.0	$7.94 \cdot 10^7$	5.57	2.30
VIII	30.22			3.43	1.52	XXI	16.60	61	$1.00 \cdot 10^5$	5.80	1.78
IX	14.51	34.7	$1.2 \cdot 10^4$	6.08	1.84	XXII	1.58			11.50	2.80
X	6.03			7.50	2.22	XXIII	3.02			10.26	2.52
XI	11.40			7.80	1.94	XXIV	5.25			11.50	2.28
XII	1.66			9.14	2.78	XXV	1.20			11.95	2.92
XIII	5.01	37.6	$4.9 \cdot 10^4$	7.50	2.30						

Reactions of hydroperoxide with acid esters having general formula $(RO)_2P(O)H$, for which there exists the tautomeric equilibrium with another reactive form - $(RO)_2P$-OH, were investigated. The reactions are of the first order on acid and of the second order on hydroperoxide [40].

As it follows from the table III.1.2, the observable decrease of reactivity of phosphorus cyclic acids occurs with the ring expanding from penta- to octa-membered cycle, which is related to the considerable decrease of proton-donor action of the acids. The strong acids of phosphorus are capable of catalytic decomposing of hydroperoxide, which is proved by the consumption of an acid during its stepwise adding to the reaction system, as well as by the greater values of stochiometric factors of the reaction.

On comparing the dissociation constants, determined by potentiometric titration, it is possible to conclude, that the acids characterized by great pKa values (pKa > 8) are inert with cumene hydroperoxide; CHP can only be decomposed by the strongest acids of the series stated above (pKa < 8). This indicates qualitative participation of tautomeric P(III)-containing form of the investigated acids containing P(III) in CHP decomposition reaction as reactive particles, catalysing the reaction. This conclusion is proved by NMR ^{31}P spectra for phenylene phosphorous acid (I) (table III.1.3) (δ^{31}P = +129, 126 p.p.m.). The existance of two peaks is due to availability of two conformers containing trivalent phosphorus atom [40].

Kinetic investigations of CHP reactions with the series of dithiophosphoric and dithiophosphonic acids have shown, that this process is characterized by great values of ν (table III.1.3), which indicates superstoichiometric (catalytic) CHP destruction in the presence of both types of acids [41-42].

Catalyzed by dithiophosphoric acid CHP decomposition apparently proceeds according to proton catalysis scheme and can be described by the second order kinetic equation in relation to CHP and the first order – in relation to an acid.

As stated above, the tendency is for stoichiometric factors of CHP decomposition to be in interrelation with pK values of acids. Thus, the greatest values are observed for diphenyl-, 2,3-butylene-, diisopropyldithiophosphoric acids, which are the strongest among the investigated acids (their pKa in benzol are less than 4).

In the case of diisopropyl- and di(4-oxy-3,5-di-*tert*-butylphenyl)dithiophosphoric acids the CHP reactions were investigated in detail by identifying the reaction products and using NMR ^{31}P and ^{1}H spectroscopy by means of regular spectrum recording [41]. As it has been shown, it takes only a few minutes for the basic process of oxidation of dithioacids to disulphides to take place under these conditions;

bis(diisopropylthiophosphoryl)disulphide has been isolated and characterized.

Sulfuric acid can be formed as a by-product of oxidation of dithio- and thiocompounds of phosphorus in the reaction mixture.

Thus, the reactivity of various phosphorus acids in the reactions with hydroperoxide is related to their acidity, and apparently all acids formed in the course of reaction make their contribution to catalytic decomposition of hydroperoxide.

III.2. The Correlation Analysis of Reactivity of OPhC in the Reactions with Cumene Hydroperoxide

The quantitative estimation of OPhC reactivity in the reactions with CHP has been carried out by comparing lgν values and reaction constants (K), on the one hand, and steric constants of substituents at the phosphorus atom, on the other hand. This calculation has been carried out on the basis of steric model taking into account the atomic radii, standard bond lengths and valence angles, at both phosphorus atoms (for complete phosphites) and at each sulfur atoms - carbothionic and carbothiolic (for dithioacids of phosphorus) [39,42].

For complete phosphites the total steric constants Rs(P) were calculated, which well describe steric shielding at phosphorus atom produced by all three substituents (table III.1.1).

The correlation analysis data obtained for the studied phosphite series (table III.1.1) in coordinates lgK - Rs was shown to break up to 5 reaction series.

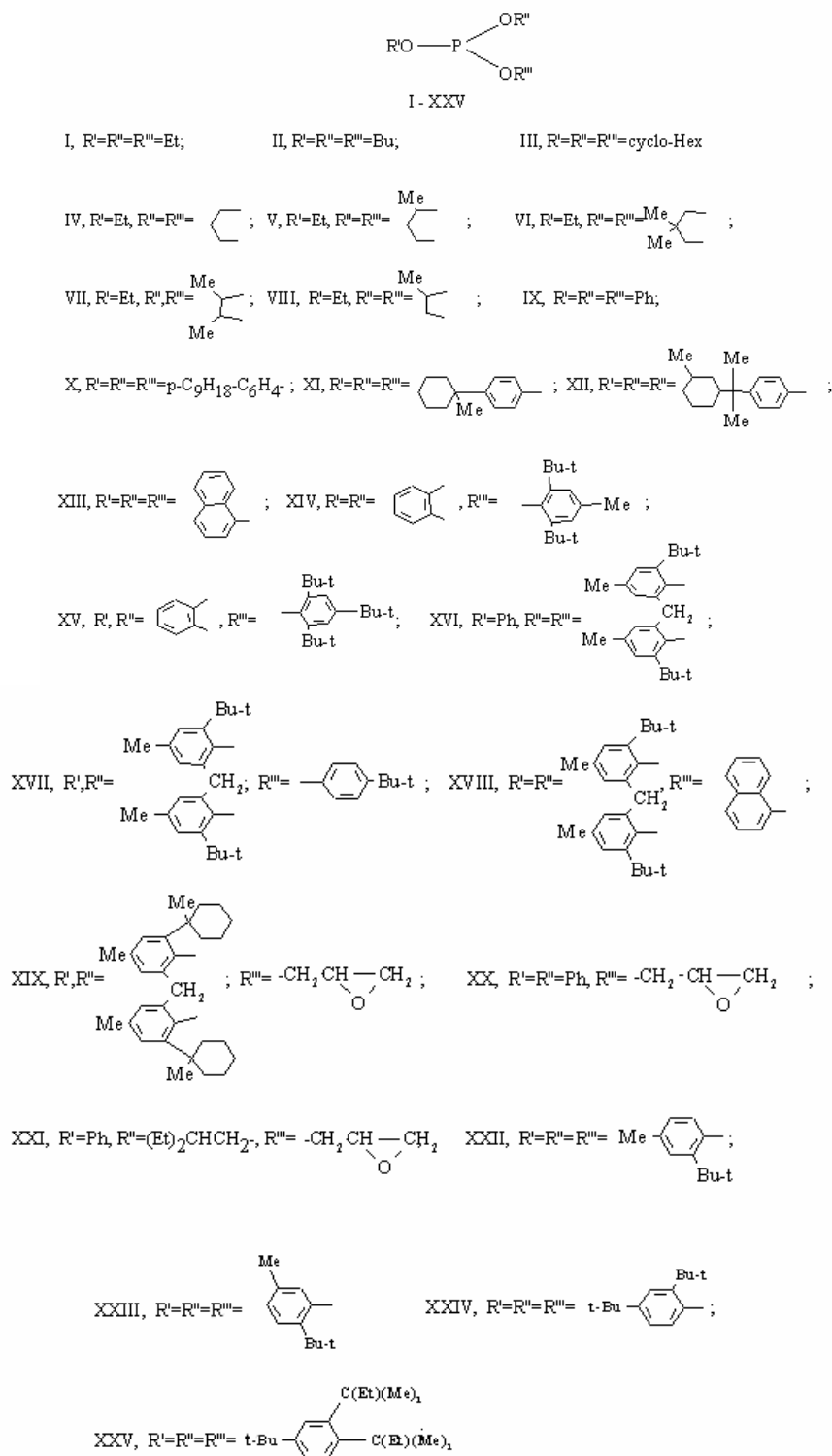**A-series** includes trialkylphosphites (**I-III**) and is described by correlation equation (1):

$$lg\ k = -(1.868 \pm 1.098) + (0.492 \pm 0.203)Rs, \quad r = 0.9243, S_0 = 0.0319, N = 3 \qquad (1)$$

B-series unites, mainly, sterically non-overloaded trialkylphosphites, containing no more than one substituted aryl (**IX-XV**). They have lower reactivity in comparison with trialkylphosphites, which is obviously caused by electron-deficient nature of aryl substituents and is described by the equation (2):

$$lg\ k = (0.052 \pm 0.360) + (0.296 \pm 0.046)Rs, \quad r = 0.9979, S_0 = 0.030, N = 7 \qquad (2)$$

Scheme 9 for table III.1.1.

$$R'O - P \overset{OR''}{\underset{OR'''}{}}$$

I - XXV

I, R'=R''=R'''=Et;   II, R'=R''=R'''=Bu;   III, R'=R''=R'''=cyclo-Hex

IV, R'=Et, R''=R'''= ; V, R'=Et, R''=R'''= ; VI, R'=Et, R''=R'''= ;

VII, R'=Et, R'',R'''= ; VIII, R'=Et, R''=R'''= ; IX, R'=R''=R'''=Ph;

X, R'=R''=R'''=p-C_9H_{18}-C_6H_4- ; XI, R'=R''=R'''= ; XII, R'=R''=R'''= ;

XIII, R'=R''=R'''= ; XIV, R'=R''= , R'''= ;

XV, R',R''= , R'''= ; XVI, R'=Ph, R''=R'''= ;

XVII, R',R''= CH$_2$; R'''= -Bu-t ; XVIII, R'=R''= , R'''= ;

XIX, R',R''= CH$_2$; R'''= -CH$_2$CH$-$CH$_2$; XX, R'=R''=Ph, R'''= -CH$_2$-CH$-$CH$_2$;

XXI, R'=Ph, R''=(Et)$_2$CHCH$_2$-, R'''= -CH$_2$CH$-$CH$_2$ XXII, R'=R''=R'''= Me ;

XXIII, R'=R''=R'''=   XXIV, R'=R''=R'''= t-Bu ;

XXV, R'=R''=R'''= t-Bu

Introduction of cyclic dioxyalkylene substituents (**series B**) into phosphorus atom (**IV-VIII**), which, as it is well known, possesses a considerable acceptor effect, greatly reduces the reactivity of phosphite in the reaction with CHP that is described by correlation equation (3):

$$\lg k = (0.170 \pm 0.082) + (0.378 \pm 0.021)Rs, \ r = 0.9941, \ S_0 = 0.041, \ N = 6 \qquad (3)$$

A very interesting thing is observed for compounds (**XXII-XXV**), united in **G-series**. These trialkylphosphites have ortho-substituents at each of their three aryls which distinguishes them from the representatives of **B series**. This results, first of all, in appreciable steric repulsion of three ortho-substituents of aryl groups in a triarylphosphite molecule. It is inevitable that such repulsion should lead to magnification of O-P-O valence angles in phosphite molecule and, as a result, to changes of hybridization of atomic orbitals of phosphorus from p- (valence angle - 90°) to p^3-status (valence angle - 109°). In its turn, such increase of p-character of non-divided electronic pair of phosphorus atom results in the increase of its nucleophility and reactivity of phosphite. Thus, we have a classical manifestation of stereoelectronic effect, and three ortho-substituent radicals behave as donor groups as compared to regular aryls.

$$\lg k = (0.146 \pm 0.168) + (0.231 \pm 0.015)Rs , \ r = 0.9959, \ S_0 = 0.019, \ N = 4 \qquad (4)$$

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Table III.1.2. Kinetic parameters of the decomposition reaction of cumene hydroperoxide (CHP) (scheme 10) under the action of arylenephosphorous acids, their dissociation constants and $\delta^{31}P$ values.

Number of acid	CHP, ν_{cp}	100 °C k, $l^2 \cdot mol^{-2} \cdot c^{-1}$	pKa, propanol	$\delta^{31}P$, p.m. (J_{PH}, Hz)
I	100.0	210.0	4.19 10.57	129 126
II	28.0	3.0	-	5 (680)
III	15.0	0.4	10.68	6 (720)
IV	0.5	-	12.54	2 (735) 5 (700)
V	30.0	1.2	8.54	20 (705)
VI	11.0	0.6	11.46	4 (740) 0 (746)

Scheme 10 for table III.1.2.
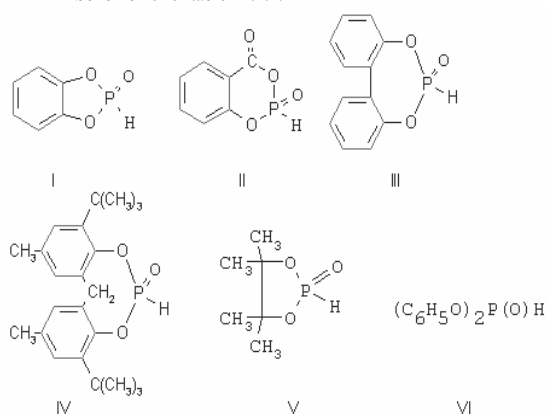
Table III.1.3. Stoichiometric factors (ν) of the reactions of dithiophosphoric acids $R^1R^2P(S)SH$ with cumene hydroperoxide, steric and electronic constants of the substituents.

№	R^1	R^2	ν_{cp} 100°C	$-R_s(P)$ [a]	$-R_s(-S)$ [6]	$-R_s(=S)$ [в]	$\Sigma\sigma^*$
I	CH_3O	CH_3O	15000	2.06	3.00	3.17	3.46
II	C_3H_7O	C_3H_7O	18000	2.74	3.53	3.69	3.46
III	$i\text{-}C_3H_7O$	$i\text{-}C_3H_7O$	20000	3.03	3.78	3.87	3.46
IV	C_6H_5O	C_6H_5O	25000	3.36	4.13	4.07	4.72
V	ArO	ArO	10000	5.25	5.99	6.20	-
VI	CH(CH₃)	CH(CH₃)	22000	2.21	3.84	3.02	3.46
VII	ArO	C_2H_5O	1800	4.52	4.65	4.67	2.28
VIII	- " -	$i\text{-}C_3H_7O$	2000	4.85	4.92	4.89	2.28
IX	- " -	$i\text{-}C_8H_{17}O$	1500	5.25	5.27	5.20	-
X	- " -	cyclo-$C_6H_{11}O$	2500	5.20	5.12	4.97	2.28

Notice:
ArO = 4-oxy-3,5-di-*tert*-butyl-C_6H_4O-
a) steric effect of R^1 and R^2 substituents at phosphorus atom.
b) steric effect of R^1 and R^2 substituents at carbothiolic sulfur atom.
c) steric effect of R^1 and R^2 substituents at carbothionic sulfur atom.

Further magnification of shielding of reaction centre in heavily sterically overloaded molecules (**XVI-XIX**) leads to subsequent increase in the contribution of stereoelectronic effect by the mechanism described above, as well as results in appreciable distortion of structure of activated complex, which is expressed in sharp increase (approximately, threefold) of sensitivity of the reaction rate to steric effect of substituents.

$$\lg k = -(10.160 \pm 0.377) + (0.934 \pm 0.022)Rs \,, \quad r = 0.9996, \; S_0 = 0.016, \; N = 3 \qquad (5)$$

Thus, it has been shown that reactivity of complete phosphites in the reaction with cumene hydroperoxide is controlled by electronic and steric effects of the substituents at phosphorus atom, which forms the reaction centre. The increase of spatial volume and electron-deficient nature of substituents results in decreasing the reaction rate.

The complex of obtained data points to nucleophilic, from the standpoint of phosphorous reagent, mechanism of interaction of phosphites with cumene hydroperoxide, the limiting stage of them being the oxidation of phosphites to phosphates. For dithioacids of phosphorus the Rs-constants of the substituents have been calculated both at phosphorus atom, and at each sulfur atom (carbothionic and carbothiolic ones), as it cannot be stated for certain, with available data on the mechanism of the reaction of phosphorus dithioacids with hydroperoxides, which of these three atoms is the reaction centre. Theoretically, each of them could take part in the limiting stage of the process.

The correlation analysis carried out by the least-squares method has shown, that satisfactory correlations of lgv and lgK values with the structure of dithiophosphoric acids are observed only for Rs-constants, describing the steric effect of the substituents at carbothiolic sulfur atom P(S). It denotes that it is carbothiolic sulfur atom (or the S-H-group) that serves as the reactionary centre in the reaction. In lgv-Rs(S) coordinates dithiophosphonates and dithiophosphates form two separate dependences (6, 7) with close angular coefficients.

$$\lg v = (3.576 \pm 0.074) - (0.196 \pm 0.020)Rs(S) \,, \quad r = 0.9845, \; S_0 = 0.017, \; N = 5 \qquad (6)$$

$$\lg v = (1.865 \pm 0.043) - (0.297 \pm 0.088)Rs(S) \,, \quad r = 0.9586, \; S_0 = 0.029, \; N = 3 \qquad (7)$$

Statistical estimation of lgv values within the framework of two-parameter equation has been carried out:

$$\lg v = 3.826 + (0.391 \pm 0.106)\Sigma\sigma^* - (0.276 \pm 0.124)Rs(S), \quad r = 0.9513, \; S_0 = 0.085, \; N = 8 \qquad (8)$$

As follows from the above equation, there is an opportunity to describe the reactivity of both dithiophosphonates and dithiophosphates by common dependence. It follows from equations (6-8), that stoichiometric factor grows with the growth of steric effect of the substituents at carbothiolic sulfur atom and with the increase of their electron-accepting action. As to the constant of the interaction rate of dithioacids with cumene hydroperoxide, it, on the contrary, decreases with the increase of steric effect of substituents, and in this case both dithiophosphates and dithio-phosphonates are described by general one-parameter dependence (9) with an excellent coefficient of correlation.

$$\lg k = (2.821 \pm 0.162) + (0.431 \pm 0.330)Rs(S), \qquad r = 0.9912, S_0 = 0.064, N = 6 \qquad (9)$$

The data obtained are in agreement with the above assumption about the acid character of catalysis in the reactions of dithiophosphoric acids with hydroperoxides.

Thus, it has been established, that stoichiometric factors and rate constants of the reaction linearly depend on the steric effect of substituents in dithioacids of phosphorus. The found correlation equations have allowed to establish, that in reactions with cumene hydroperoxide the reactionary centre in dithioacids of phosphorus is carbothiolic sulfur atom.

III.3. Kinetics and Mechanism of the Initiated Oxidation of OphC.

Kinetic regularities of inhibition of free-radical processes of oxidation of various substrates by organic phosphites can be explained from the standpoint of the mechanism of their antioxidative action. The reactions of $RO^{\cdot}$ and $RO_2^{\cdot}$ radicals with phosphites are the classical objects for research in the field of homolytical chemistry of phosphorus [7].

It is known that trialkylphosphites are vigorously oxidized by alkylperoxide radicals at 130° C. This oxidation has the chain character and proceeds up to the complete exhaustion of phosphite ("autooxidation" process). For the purpose of revealing the basic tendencies of the "autooxidation" process the analysis of their chain oxidation rates (Wp) as a function of initiation rate (Wi) and concentration of phosphites [5, 37, 44] has been carried out.

It is essential that chain length of "autooxidation" appreciablly shortens at the transition from trialkylphosphites to aromatic phosphites (from ~104 to 5-130 units correspondingly), especially when introducing shielded phenoxyl fragments into phosphite molecule. Besides, at the transition from aliphatic to aromatic phosphites the observable $Wp \sim W_{il/2}$ dependence is substituted for $Wp \sim Wi$ dependence, which indicates the replacement of rapture mechanism for chain oxidation. Thus, the interaction of aliphatic phosphites with peroxide radicals proceeds with the formation of alkyl radicals actively participating in the process of chain oxidation:
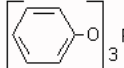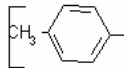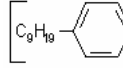

etc.
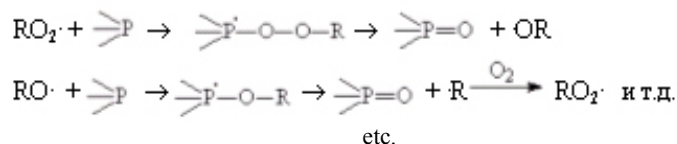
In the case of aromatic phosphites the bimolecular rupture of chains is substituted by linear one on the secondary phenoxyl radicals, which can be formed by the reactions of substitution from kinetically unstable phosphoalkyl radicals.

$$(ArO)_3P + {}^{\cdot}OR \rightarrow (ArO)_2POR + ArO^{\cdot} \xrightarrow{RO_2^{\cdot}} \text{chain rapture}$$

The data sited above are confirmed by detecting the chemical polarization of nuclei (ChPN) on oxidizing of triethylphosphite in the case of non-branched chain reaction (azoisobutyronitrile, O_2, 55° C), as well as by the absence of ChPN in the case of chain oxidation of aromatic phosphites. Introduction of sterically loaded phenoxyl groups in phosphite molecule leads, as a rule, to the growth of reaction constant of chain rapture (K_7 or K_7/K_2), the stoichiometric factor of inhibition grows too (table III.3.1).

Table III.3.1. Kinetic parameters of the reactions of peroxide radicals with phosphites.

Composition	$[C_6H_5{-}O]_3P$		$[CH_3{-}C_6H_4{-}O]_3P$		$[C_9H_{19}{-}C_6H_4{-}O]_3P$	
	f	$\lg K_7$	f	$\lg K_7$	f	$\lg K_7$
Styrene + chlorobenzene (50 vol. %)	0.010	4.86	0.063	4.62	0.27	4.76
Tetralin + chlorobenzene (50 vol. %)	0.015	5.00	0.049	5.49	-	-
Benzaldehyde (0.2 mol/l) + chlorobenzene	0.500	6.20	2.000	6.49	3.400	6.74

After the direct quantitative assessment of efficiency of phosphites has been carried out, the validity of notions about aromatic phosphites with sterically loaded substituents as more effective stabilizers of carbochain polymers has been convincingly proved.

The dependence between inhibitory properties and the nature of phosphorus atom substituents has been found for phosphorus acids. As the kinetic parameters of inhibition reactions (K_7 or K_7/K_2) indicate, the antioxidative properties of cyclic phosphorous acids lessen at the transition from penta- to hepta- and octa-membered cycles. In particular, the greatest efficiency, as follows from table III.3.2, is typical of phenylenephosphorous acid. At the transition from cyclic to acyclic acids of phosphorus the decrease of reactivity in the reactions with peroxide radicals is also observed [45].

At the same time, dialkylphosphorous acids catalyse styrene oxidation, which seems to be related to the formation of unstable radicals, bringing in the additional contribution to the development of chain processes of oxidation. The potential of the formation of phosphonyl radicals in this case is confirmed by this work, in which the EPR method and radical traps have been used for identifying phosphon-radicals, their structure-dependent stability has been shown.

Dialkyldithiophosphoric acids show antioxidative action, which can be related to the substitution of $RO_2^{\cdot}$ radicals, forming in oxidizing substrate, for inactive sulfur-centred $(RO)_2PS_2^{\cdot}$ - radical [46].

It has been shown that considerable amplification of inhibitory properties can be obtained by introducing into a molecule sterically hindered phenoxyl fragments, having the properties of strong inhibitor of free-radical oxidation. Thus, stoichiometric factor of inhibition of the appropriate dithiophosphonic acids grows up to 1.5-2 units, and in the case of *bis*(dithiophosphonic) acids the efficiency of interaction with peroxide radicals is practically doubled.
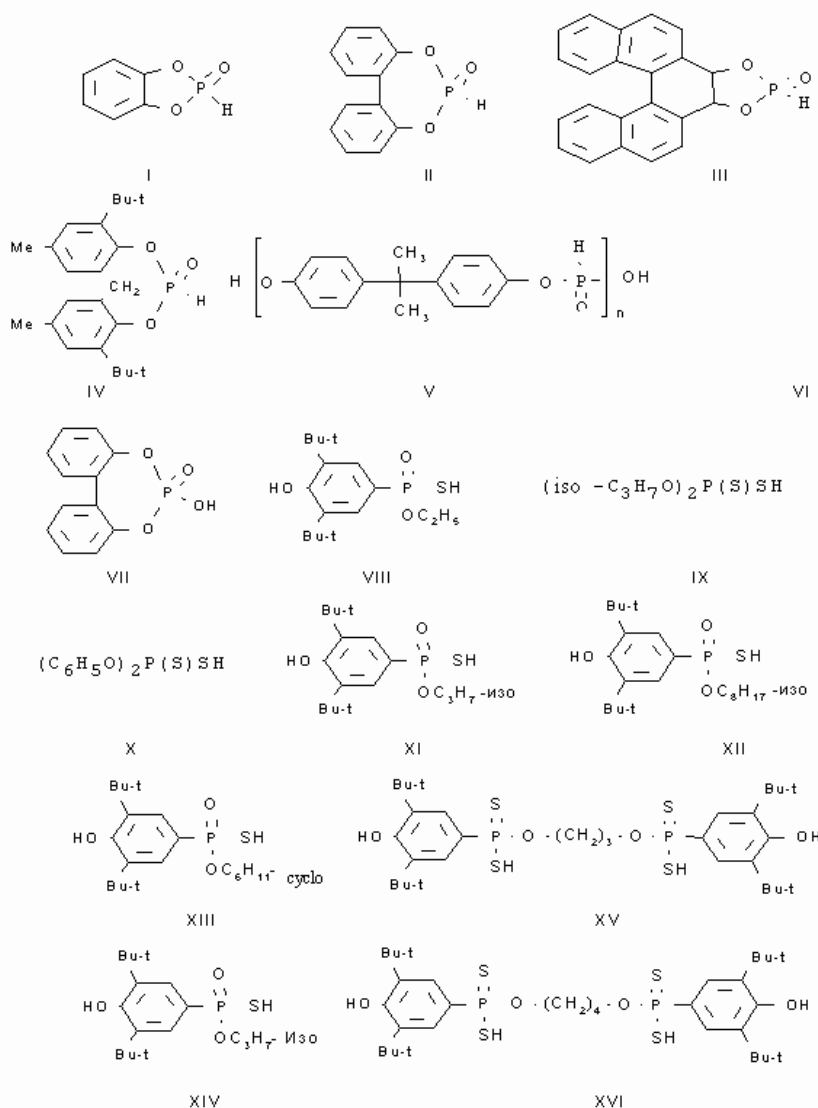
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Scheme 11 for table III.3.2.

Table III.3.2. Kinetic and stoichiometric parameters of inhibitory action of acids of phosphorus in the process of initiated oxidation of styrene and polypropylene (initiator - azoisobutyronitrile) [6, 42].

Number of acid	Styrene (50° C)			Polypropylene (85° C)		
	f	$K_7 \cdot 10^{-4}$, l/mol·c	$K_7/K_2 \cdot 10^{-2}$	f	$K_7 \cdot 10^{-3}$, kg/mol·c	$K_7/K_2 \cdot 10^{-3}$
I	1.35	81.00	70.43	-	5.85	39.00
II	1.33	1.40	1.22	1.20	3.38	22.52
III	1.35	4.60	4.00	1.20	3.81	25.31
IV	0.80	0.18	0.16	0.50	0.04	0.25
V	1.25	6.16	5.39	0.80	2.93	19.55
VI	0.60	0.71	0.62	0.60	2.70	18.00
VII	0.11	4.54	3.95	-	-	-
VIII	0.60	1.25	1.09	-	-	-
IX	0.35	120.00	104.35	0.30	8.69	57.93
X	0.22	70.00	61.65	-	-	-
XI	1.50	3.00	2.61	-	-	-
XII	2.00	3.78	3.29	1.20	2.34	15.60
XIII	2.00	1.30	1.13	1.00	0.84	5.62
XIV	1.65	2.21	1.92	-	-	-
XV	3.60	1.25	1.09	-	-	-
XVI	3.50	1.20	1.05	1.60	1.03	6.84

Conclusions

Thus, the complex of parameters, closely connected with each other, namely, the constants of inhibition rate K_7, and duration of inhibition, represents the specificity of action of organophosphorous compounds as oxidation inhibitors. Knowing these features of antioxidizing behaviour of OPhC, it is possible to predict the best modes of inhibition of oxidation of organic substrates, when "autooxidation" of phosphites will be suppressed, and the duration of their stabilizing action will be essentially increased.

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