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Reactions of RȮ, RṠ, and RȮ$_2$ Radicals with Phosphites and Phosphines

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The review deals with studies designed to elucidate the detailed mechanism and quantitative relations in the kinetics of the reactions of RȮ, RṠ, and RȮ$_2$ radicals with phosphites and phosphines. It is shown how the isotope tracer method has been used to prove the irreversible formation of the phosphoranyl radical—the primary intermediate in these radical reactions. The results of the study of the competition between the addition of RȮ and RṠ radicals to phosphites and phosphines on the one hand and their other reaction pathways (abstraction of a hydrogen atom from hydrocarbons, addition to a double bond, and monomolecular decomposition) on the other have been analysed. The last section discusses the mechanism of the inhibiting effect of aromatic phosphites in the thermo-oxidative degradation of polyolefins within the framework of the hypothesis that they terminate kinetic oxidation chains by radical exchange.
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I. INTRODUCTION

Organophosphorus compounds are involved in many free radical reactions[1-6]. The autoxidation of compounds such as phosphites and phosphines has a radical chain mechanism and constitutes a large and important class of organic reactions. The aim of the present review is to examine and analyse the kinetics and mechanisms of the elementary steps of the interaction of RȮ, RṠ, and RȮ$_2$ radicals with phosphites and phosphines, i.e. to examine all the reactions constituting the basis for the autoxidation processes of these compounds. There is in addition a practical aspect of the studies of these elementary radical reactions associated with the participation of phosphites in polymer stabilisation processes.

II. REACTIONS OF RȮ AND RṠ RADICALS

The reactions of RȮ radicals play an important role in the transfer of kinetic chains in the autoxidation of phosphites and phosphines. Before discussing the kinetics, we shall first examine the mechanism of the transfer reaction.

Trialkyl phosphites $(R'O)_3P$ readily interact with t-BuȮ radicals, forming the corresponding derivatives containing the phosphoryl group $\rangle P=O$:

$$(R'O)_3P + t\text{-}BuO \rightarrow (R'O)_3P{=}O + t\text{-}Bu\,.$$

These reactions take place with a high enthalpy change (the P=O bond energies are in the range 120—150 kcal mole^{-1} [5]). For example, the heats of reaction t-BuȮ

radicals with ethyl and butyl phosphites, which we estimated as the differences between the heats of formation of the final products and the initial reactants, are respectively 74 and 46.5 kcal mole^{-1}; the known values of ΔH_f^0 were employed[7-10].

Walling and Rabinowitz[11] studied by gas – liquid chromatography (GLC) and mass spectrometry the products of the interaction of triethyl phosphite with various oxy-radicals: in all cases triethyl phosphate and hydrocarbons were detected. The results of the quantitative analysis of the products are presented in Table 1.

Table 1. Products of the reactions of RȮ radicals with triethyl phosphite (in the absence of oxygen)[11].

Source of RȮ radicals	Type of RȮ radicals	Conditions of radical generation	No. of moles of phosphite per mole of peroxide	No. of moles of phosphate per mole of peroxide	No. of moles of hydrocarbon per mole of peroxide
Dicumenyl peroxide	$PhC(CH_3)_2\dot{O}$	Ultraviolet irradiation, 25°, 125°	5.4	2.16	0.46 (dicumene)
Ditto	ditto		5.4	1.87	0.71 (dicumene)
Di-t-butyl peroxide	$(CH_3)_3C\dot{O}$	Ultraviolet irradiation, 25°	3.6	2.08	0.31 (isobutane); 0.20 (isobutene); 0.035 (2,2,4-trimethylpentane); 0.080 (tetramethylbutane); 0.020 (2,2,4-trimethylpentane)
ditto	ditto	120°	3.4	2.2	Isobutane, isobutene tetramethylbutane (not determined quantitatively)

Table 1 shows that, firstly, the yield of phosphate is on average 2.0 moles per mole of peroxide and, secondly, the yield is independent of the source and type of RȮ radicals, the conditions of their generation, and also of phosphite concentration when the rates of thermal initiation by di-t-butyl and dicumenyl peroxides are almost equal (1.7×10^{15} and 2.2×10^{15} cm^{-3} s^{-1})†. This implies that phosphite molecules fully accept all the peroxy-radicals formed from the peroxide.

The following mechanism for the interaction of triethyl phosphite with RȮ radicals has been proposed on the basis of the composition of the reaction mixture[11]:

$$ROOR \rightarrow 2R\dot{O}, \quad (1)$$

$$R\dot{O} + R(OEt)_3 \rightarrow RO\dot{P}(OEt)_3, \quad (2)$$

$$RO\dot{P}(OEt)_3 \rightarrow \dot{R} + O{=}P(OEt)_3, \quad (3)$$

$$\dot{R} + \dot{R} \rightarrow \text{disproportionation products}, \quad (4)$$

$$\dot{R} + \dot{R} \rightarrow \text{recombination products}. \quad (5)$$

One may suppose that a similar mechanism will probably hold also for the reactions of tributyl phosphite with t-BuȮ radicals, where tributyl phosphate was detected as the main product by the ^{31}P NMR method[14].

Bentrude's data[15] derived from an analysis of the reaction product of another (aromatic) phosphite (triphenyl phosphite) conflict with this mechanism to some extent. Thus, in the stages involving the transfer of an oxygen atom [stages (2) and (3)], one should expect the formation of triphenyl phosphate; moreover, such a pathway is thermodynamically favourable (according to our estimate, the formation of the phosphate is exothermic to the extent of about 41 kcal mole^{-1}). However, in the experiment (130°C, di-t-butyl peroxide, chlorobenzene, no oxygen) only diphenyl phosphite, isobutene (1.0 and 0.5 mole per mole of triphenyl phosphite respectively), and phenol were detected[15]. This is because in the presence of triphenyl phosphite the elementary steps involving the substitution (exchange) of radicals mainly occur:

$$t\text{-}Bu\dot{O} + (PhO)_3P \rightarrow t\text{-}BuOP(OPh)_2 + Ph\dot{O}.$$

Furthermore, by hypothesis, the mixed phosphite, which is unstable under the experimental conditions, decomposes fully with formation of an olefin and diphenyl phosphite. This mechanism is confirmed also by the observation of the ESR spectrum of the phenoxy-radical under the conditions of the photolysis of di-t-butyl peroxide in the presence of triphenyl phosphite (–85°C, cyclopropane)[16].

The substitution of t-BuȮ radicals, accompanied by the dissociation of the P – C bond in the phosphoranyl radicals and less probable from the thermodynamic point of view, was also observed when these radicals were allowed to act on tri-n-butylphosphine (130°C, no oxygen)[17]. Quantitative study of the reaction products of the phosphine yielded an estimate of the probability of this reaction: the yield of t-butyl di-n-butylphosphinite, which can only be obtained in the substitution step

$$t\text{-}Bu\dot{O} + n\text{-}Bu_3P \rightarrow t\text{-}BuOP(n\text{-}Bu)_2 + n\text{-}B\dot{u},$$

amounts to about 80%; the fraction of phosphine oxide, formed in the step involving the transfer of an oxygen atom, is significantly lower (20%).

Thus there is a definite kinetic control of the relative amounts of the products of addition to phosphines and aromatic phosphites. At the present time it is difficult to interpret this phenomenon unambiguously; its possible causes may be different distributions of unpaired electron density in the P – O and P – C bonds of phosphoranyl radical and also the differences between the energies of the bonds undergoing dissociation.

In an interesting recent study[16], where the intermediate radical products of the oxidation by t-BuȮ radicals of a large class of trialkyl phosphines and trialkyl phosphites were investigated by ESR, showed that in all cases alkyl radicals are present. The authors demonstrated by special experiments that, in the absence of organophosphorus compounds, in the photolysis of di-t-butyl peroxide (between –70° and –90°C, cyclopropane), only t-BuȮ radicals are formed, while in the presence of such substances alkyl radicals are detected immediately; the ratio of the line intensities in the hyperfine structure and the proton hyperfine coupling constants (HCC) are consistent with this interpretation of the ESR spectra. Thus, in the reactions of triethyl-, tri-isopropyl-, tri-isobutyl-, and tricyclohexyl-phosphines, the observed ESR spectra were assigned respectively to $CH_3\dot{C}H_2$, $(CH_3)_2\dot{C}H$, $(CH_3)_2CH\dot{C}H_2$ and $\dot{C}_6H_{11}$ radicals, probably formed by a substitution mechanism‡:

$$R'_3P + \dot{O}C(CH_3)_3 \rightarrow R'_2P{-}OC(CH_3)_3 + \dot{R}'. \quad (6)$$

† According to the literature[12,13], the rate constants for the decomposition of the peroxides are $k = 10^{15.1} \exp(-36\,000/RT)$ for di-t-butyl peroxide and $k = 10^{14.6} \exp(-34\,500/RT)$ (s^{-1}) for dicumenyl peroxide.

‡ Adams and Ingersoll[18] succeeded in detecting by the ESR method the alkyl radicals $CH_3\dot{C}H_2$, $CH_3(CH_2)_2\dot{C}H_2$, and $CH_3(CH_2)_6\dot{C}H_2$ formed under simpler conditions: in the photolysis of iso-octane solutions of the same peroxide in a flow system (20°C, trialkylphosphines).

The behaviour of trialkyl phosphites (trimethyl, triethyl, and tri-isopropyl phosphites) in relation to t-BuO· radicals is fundamentally different from that of the trialkylphosphines: in all cases only the t-Bu· radicals were detected; they are probably formed by a mechanism in which an oxygen atom is transferred:

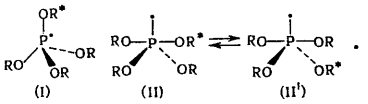
$$(R'O)_3P + \dot{O}C(CH_3)_3 \rightarrow (R'O)_3P{=}O + \dot{C}(CH_3)_3 \ . \qquad (7)$$

This result (see also Hudson and Hussain[19]) may be regarded as confirmation of the mechanism of the interaction of trialkyl phosphites with t-BuO· radicals proposed[11] on the basis of chemical analysis of non-radical products.

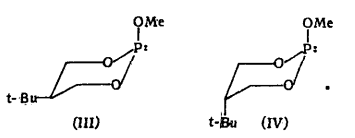
The problem arises whether the phosphoranyl radical [$R'_3\dot{P}OR$ or $(R'O)_3\dot{P}OR$] is a kinetically independent species or whether it is a form of transition state for the transfer of an oxygen atom or for substitution via mechanisms (6) and (7). Other experimental data, which allow a choice to be made, will be considered next.

Bentrude and Wielesek[20], who studied the decomposition of di-t-butyl hyponitrite, labelled with the ^{14}C isotope in the methyl groups, in deoxygenated benzene solution at 65°C in the presence of tri-t-butyl phosphite, showed that the phosphite is quantitatively converted into phosphate. It was demonstrated that, firstly, the fraction of labelled phosphate is independent of the concentration of phosphite and of the phosphite/hyponitrite ratio, secondly, the ^{14}C label is hardly incorporated into the unreacted phosphite or phosphate added before the reaction, and, finally, the fraction of labelled phosphate is constant (about 75%).

These results are important; they imply that all t-Bu*O· radicals, which have emerged from the [Bu*-O· O· — Bu-t] cage, are entirely captured by acceptor (phosphite) molecules and that the formation of the phosphoranyl radical $[(t\text{-BuO})_4\dot{P}]^*$ as an intermediate is irreversible. Bentrude and Wielesek[20] suggested that a statistical distribution of the ^{14}C label in the phosphoranyl radical becomes possible if the radical has the structure of an equilateral pyrimid (I) where all four alkoxy-groups are configurationally equivalent or it can obtain in a trigonal-bipyramidal structure (II) as a result of the pseudorotation of configurationally non-equivalent groups; by hypothesis, such rotation takes place at a frequency higher than that of the decomposition of radical (II):



However, it has been shown[21] that stereospecific transfer of an oxygen atom from t-BuO· radicals to a mixture of geometrical isomers—six-membered cyclic *cis*(III)- and *trans*-(IV)-phosphites—and also to the optically active methylphenyl-n-propylphosphine $\{[-\alpha]_D\}$ takes place with retention of the configuration at the phosphorus atom. The results of a stereochemical study of the free-radical oxidation at the tervalent phosphorus atom are presented in Table 2.



The retention of the configuration at the phosphorus atom in a radical reaction (stereospecificity, retention of the sign of optical rotation) implies that the pseudorotation of the substituents at the phosphorus atom in the radical with structure (II) is impossible, since it should lead to the inversion of the sign of optical rotation or to the isomerisation of the phosphite.

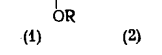
Thus a reasonable explanation of both the statistical distribution of the ^{14}C label and the retention of the configuration at the phosphorus atom in the oxidation by t-BuO· radicals can be obtained only within the framework of the model where the phosphoranyl radical has structure (I).

Table 2. Oxidation of an optically active phosphine and a mixture of isomeric phosphites by t-BuO· radicals.

Source of t-BuO· radicals	Optical activity of phosphine oxide	(III):(IV) ratio	(III)-oxide:(IV)-oxide ratio
t-BuO—N=N—OBu-t- (65°, CH_3CN, without O_2)	−16.7±0.2	15:85 91:9	21:79 96:4

The formation of phosphoranyl radicals was first observed directly by Kochi and Krusik[16] and by Davies et al.[22] Thus, Kochi and Krusik[16] observed in the oxidation of trimethylphosphine by t-BuO· radicals (photolysis of di-t-butyl peroxide, cyclopropane, temperature between −70° and 90°C) an ESR spectrum with a doublet splitting of 619 G, which was assigned to hyperfine interaction involving the ^{31}P nuclei in the $t\text{-BuO}\dot{P}(CH_3)_3$ radical. According to Davies et al.[22], the addition of t-BuO· radicals to triethyl phosphite (photolysis of di-t-butyl peroxide, cyclopentane, −85°C) is accompanied by the appearance of the ESR spectrum of the phosphoranyl radical $t\text{-BuO}\dot{P}(OC_2H_5)_3$ with an HCC constant a_P = 891 G and g = 2.008; it is noteworthy that this was the first determination of the g-factor of the phosphoranyl radical.

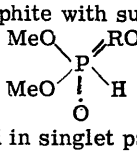
Another striking example illustrating the possibility, in principle, of the formation of the phosphoranyl radical as a kinetically independent species is the observation[14] of the chemically induced nuclear polarisation of ^{31}P (CINP-31P), which arises in the thermal decomposition of di-t-butyl and dibenzoyl peroxides in the presence of triethyl, tributyl, or triphenyl phosphite (110 — 190°). Since the appearance of CINP in chemical reactions implies that they take place with formation of radical pairs[23,24], the negative sign of the chemically induced nuclear polarisation of ^{31}P suggests that the CINP in phosphate molecules is solely a result of the elementary step involving the disproportionation of the radical



in singlet radical pairs [$a_P > 0$; $\Delta g = (g_1 - g_2) > 0$; the g_2-factor of the majority of hydrocarbon radicals is 2.0024 — 2.0025,[25] while according to the literature[22] the g_1-factor of the phosphoranyl radical $t\text{-BuO}\dot{P}(OC_2H_5)_3$ is 2.008]§; previously this type of disproportionation of phosphoranyl radicals was examined by Davidson[26] on the basis of the chemical analysis of the non-radical products.

§ Disproportionation in triplet pairs is unlikely since it leads to the formation of a phosphate molecule in an electronically excited triplet state.

Thus the study of the chemically induced nuclear polarisation of ^{31}P is extremely promising from the standpoint of the identification or refining of the mechanism of the elementary radical reactions of organophosphorus compounds.

For example, analysis[27] of the sign of the CINP involving ^{31}P nuclei (emission) in the dicyclohexyl peroxydicarbonate (or dilauryl peroxide) — dimethyl phosphite systems (75 — 110°C, tetrachloroethane) led us to the conclusion that of the two kinetically equivalent mechanisms of the formation of the polarised product (phosphate)—via the abstraction of a hydrogen atom and the recombination of the $(MeO)_2\dot{P}{=}O$ and $R\dot{O}$ radicals ($a_P > 0$ $\Delta g > 0$; absorption by ^{31}P expected in "random" pairs) or via the "adhesion" of the $R\dot{O}$ radicals to the double bond of the phosphite with subsequent disproportionation of the radicals  and $O\dot{R}$ ($a_P > 0$, $\Delta g > 0$; emission expected in singlet pairs)—the second mechanism actually obtains.

The above analysis shows that the composition of the intermediate and final products of the reactions of $R\dot{O}$ radicals with phosphites and phosphines has been investigated fairly completely; only one other aspect of the mechanism needs to be refined, namely the reaction kinetics. However, so far there are no experimental data obtained by direct determination of the elementary rate constants; the only source of information on this problem is kinetic analysis of the competition between the reactions involving the abstraction of a hydrogen atom from the hydrocarbon by $R\dot{O}$ radicals and their addition to phosphites and phosphines.

Table 3. Ratios of the rate constants for the reactions of t-Bu$\dot{O}$ radicals with triethyl phosphite and triphenylphosphine (130°C, hydrocarbon).

Hydrocarbon	k_{ph}/k_{RH}	
	$(EtO)_3P$	Ph_3P
Cyclohexane	610±10	7.0±0.2
Cyclohexene	440±10	7.4±0.2
Cyclopentene	610±10	7.4±0.2
Cumene	730±10	10.3±0.5
2,3-Dimethylbutane	1100±100	9.8±0.7

Thus Walling and Pearson[28] investigated the competition between the addition to triethyl phosphite or triphenylphosphine of t-Bu$\dot{O}$ radicals (the radicals were generated by the thermal decomposition of di-t-butyl peroxide at 130°C in sealed tubes) and the abstraction by them of a hydrogen atom from various hydrocarbons (cyclohexane, cyclohexene, cyclopentene, cumene, and 2,3-dimethylbutane). The results of the kinetic analysis are presented in Table 3; the ratios of the rate constants for the reaction of the phosphite k_{ph} to that for the reaction of the hydrocarbon k_{RH} were estimated from the composition of the products—a phosphate and an alcohol).

Table 3 shows that triethyl phosphite reacts 82 ± 20 times faster with t-Bu$\dot{O}$ radicals than does triphenylphosphine and that even the abstraction of a hydrogen atom from hydrocarbons cannot compete effectively with these two reactions.

Since the study under consideration[28] is unique as regards the quantitative kinetics of the reactions of $R\dot{O}$ radicals with phosphines, we believe it is useful to supplement its results with an approximate calculation of the activation energy for the reaction of t-Bu$\dot{O}$ radicals with triethyl phosphite on the basis of the quantitative data of Walling and Pearson.

The activation energy for the competing reaction with cyclohexene is approximately 3 kcal mole^{-1}.[29] The main reaction (the addition to the phosphite) can occur at a rate comparable to that of the competing reaction only if its activation energy is equal to or somewhat less than 3 kcal mole^{-1}. The activation energy for the reaction of $(EtO)_3P$ with t-Bu$\dot{O}$ radicals can be estimated approximately in the following way. In Walling and Pearson's experiments[28], the concentration of peroxide molecules was 6×10^{23} cm^{-3} and the rate constant for the decomposition of the peroxide at 130°C was $k_{decomp} = 4.0 \times 10^{-5}$ s^{-1} (we obtained this value from other literature data[12,13]). Therefore the rate of initiation under these conditions is

$$W_i = 2 \cdot 4.0 \cdot 10^{-5} \cdot 6 \cdot 10^{23} = 4.8 \cdot 10^{19} \text{ cm}^{-3}\text{ s}^{-1},$$

so that the steady-state concentration of t-Bu$\dot{O}$ radicals may be determined as follows:

$$[\text{t-Bu}\dot{O}]_{st} = \frac{4.8 \cdot 10^{19}}{k_{RH}[RH] + k_{ph}[(EtO)_3P]} = \frac{4.8 \cdot 10^{19}}{A} \text{cm}^{-3}.$$

Next the rate constant k_{RH} for the abstraction of a hydrogen atom from cyclohexane, which we estimated from Walling's data[29], is

$$10^{-13}\exp\left(\frac{-3000}{RT}\right) = 2.4 \cdot 10^{-15} \text{ cm}^{-3}\text{ s}^{-1}$$

then the rate of abstraction becomes

$$W_{RH} = 2.4 \cdot 10^{-15}\frac{4.8 \cdot 10^{19}}{A} 12 \cdot 10^{23} = \frac{13.8}{A} \cdot 10^{28} \text{ cm}^{-3}\text{ s}^{-1},$$

where 12×10^{23} is the concentration of hydrocarbon molecules.

Since the concentration of phosphite molecules was 12×10^{23} cm^{-3}, then, in terms of the activation energy for the reaction of the phosphite E_{ph}, its rate at 130°C should be

$$W_{ph} = 10^{-13} \cdot 10^{-E_{ph}/4.57 \cdot 403} \cdot 12 \cdot 10^{23}\frac{4.8 \cdot 10^{19}}{A} =$$

$$= \frac{5.76}{A} 10^{30} \cdot 10^{-E_{ph}/4.57 \cdot 403} \text{ cm}^{-3}\text{ s}^{-1}.$$

For the reaction of the phosphite with t-Bu$\dot{O}$ radicals to proceed at an inappreciable rate, it must amount to not more than 1% of W_{RH}, i.e.

$$\frac{5.76}{A} 10^{30} \cdot 10^{-E_{ph}/4.57 \cdot 403} \leqslant \frac{13.8}{A} 10^{26}$$

or

$$10^{30} \cdot 10^{-E_{ph}/4.57 \cdot 403} \leqslant 2.4 \cdot 10^{26}.$$

Hence it follows that the activation energy for the reaction of triethyl phosphite with t-Bu$\dot{O}$ radicals is $E_{ph} \geqslant 3.62 \times 4.57 \times 403 = 6.7$ kcal mole^{-1}¶. Evidently this value of E_{ph} is higher than the activation energy for

¶ In the calculation of E_{ph} a typical value was adopted for the pre-exponential factor for the reaction of t-Bu$\dot{O}$ radicals with molecules, namely 10^{-13} cm^3 s^{-1};[30] it can be easily shown that with the pre-exponential factor equal to the bimolecular collision frequency ($10^{-10} - 10^{-11}$ cm^3 s^{-1}), E_{ph} should be even higher.

the reaction of the active hydrocarbon. Using it, it is possible to show that only in the presence of a 100-fold excess of the phosphite can the competing reaction with the hydrocarbon be supressed. This conclusion, albeit in fact inconsistent with the conclusions of Walling and Pearson, makes it necessary to treat with a certain amount of caution the earlier estimate of the relative reactivity of triethyl phosphite[28].

Walling and Pearson employed the method of competing reactions also for the determination of the relative reactivities of the triethyl phosphite — triphenyl phosphite, tri-n-butylphosphine — triphenylphosphine, and triethyl phosphite — tri-n-butylphosphine pairs in relation to t-BuȮ radicals. Kinetic analysis (the reactivities were estimated from the degree of consumption of the reactant) led to the following relative reactivity series for the compounds investigated (at 130°C):

$$Bu_3P : (EtO)_3P : (PhO)_3P : Ph_3P = 1.9 : 1.6 : 1 : 0.78\dagger .$$

It is useful to estimate the ratio of the rate constants for the reactions of triethyl and triphenyl phosphites (k_1/k_2) from an approximate calculation of the activation energies for the two reactions. Thus, for the overall decomposition of di-t-butyl peroxide in the presence of triphenyl phosphite, one can postulate a competition between the decomposition of the t-BuȮ radical:

$$(CH_3)_3C\dot{O} \xrightarrow{k_d} \dot{C}H_3 + CH_3COCH_3$$

and its addition to the phosphite:

$$(CH_3)_3C\dot{O} + (PhO)_3P \xrightarrow{k'_{ph}} (CH_3)_2C{=}CH_2 + HOP(OPh)_2 + Ph\dot{O} .$$

In Bentrude's experiments[15] (in this investigation a detailed study was made of the reaction products of triphenyl phosphite), the concentration of t-BuȮ radicals was (130°C, in chlorobenzene)

$$[t\text{-}Bu\dot{O}]_{st} = \frac{2 \cdot 4 \cdot 10^{-5} \cdot 2.4 \cdot 10^{20}}{k'_{ph}[(PhO)_3P] + k_d} = \frac{2 \cdot 10^{16}}{B} \quad cm^{-3}$$

where 4×10^{-5} s^{-1} is the rate constant for the decomposition of the peroxide and 2.4×10^{20} cm^{-3} is the concentration of peroxide molecules, while the rate constant for the decomposition of the radicals $k_d = 10^{11.5} \exp(-10\,600/RT) = 5.6 \times 10^5$ s^{-1}.[31] Therefore the rate of decomposition of t-BuȮ radicals is

$$W_d = 5.6 \cdot 10^5 \cdot \frac{2 \cdot 10^{16}}{B} = 1.1 \cdot \frac{10^{22}}{B} \quad cm^{-3}\, s^{-1}.$$

Since the concentration of triphenyl phosphite molecules was 5×10^{20} cm^{-3}, the rate of reaction of triphenyl phosphite with t-BuȮ radicals at 130°C should be

$$W'_{ph} = 10^{-13} \cdot 10^{-E'_{ph}/4.57 \cdot 403} \frac{2 \cdot 10^{16}}{B} \cdot 5 \cdot 10^{20} = \frac{1}{B} 10^{24} \cdot 10^{-E'_{ph}/4.57 \cdot 403} \quad cm^{-3}\, s^{-1}$$

Using the kinetic condition for the supression of competition by the phosphite which we derived above, one can show that

$$\frac{10^{24}}{B} \cdot 10^{-E'_{ph}/4.57 \cdot 403} \leqslant 1.1 \cdot \frac{10^{20}}{B} .$$

Hence it follows that the activation energy for the reaction of triphenyl phosphite $E'_{ph} \geqslant 3.96 \times 4.57 \times 403 = 7.3$ kcal $mole^{-1}$.

† It follows from the data in Table 3 that the relative reactivity of triphenylphosphine should be 0.020; this finding confirms yet again the contradictory nature of the results in Table 3.

Since this is lower than the activation energy for the decomposition of t-BuȮ radicals, triphenyl phosphite can accept these radicals to an appreciable extent‡. Next, assuming that the reactions of triethyl and triphenyl phosphites have the same pre-exponential factor (about 10^{-13} $cm^3\, s^{-1}$), it is possible to estimate the ratio of the rate constants for these reactions; k_1/k_2 is found to be 2.1. This is close to the value of 1.6 found by Walling and Pearson[28] from experimental kinetic data for the joint consumption of triethyl and triphenyl phosphites in the decomposition of di-t-butyl peroxide, which illustrates the internal consistency of the estimates of activation energy quoted here.

In conclusion of the discussion of the kinetics of the reaction of RȮ radicals with phosphite and phosphines, one should also point out that the level of the quantitative kinetics of these radical reactions is fairly low. For the majority of elementary reactions, there are no quantitative data and treatment has to be restricted to approximate estimates of activation energies and rate constants. For example, by studying the rate of consumption of reactants under various experimental conditions (different rates of initiation, temperatures, radical sources, relative amounts of the reactants, etc.) and using the kinetic procedures of the method of competing reactions, it is possible to determine, in principle, the rate constants for elementary radical reactions. So far no experimental studies on these lines have been made.

We shall now consider the experimental data on the mechanism and kinetics of the reactions of RṠ radicals with phosphites and phosphines. Like those of the RȮ radicals, these reactions are of interest from the standpoint of the determination of the mechanism of the formation of phosphoranyl radicals; moreover, they are suitable for the generation of alkyl radicals of known structure from mercaptans and disulphides.

Walling et al.[11,32] established by gas — liquid chromatography that the main molecular products of such interaction are the phosphorothionates $(R'O)_3P{=}S$ and phosphine sulphides $R'_3P{=}S$ as well as hydrocarbons or sulphides; their formation is greatly accelerated by ultraviolet irradiation, azobisisobutyronitrile (AIBN), and di-t-butyl peroxide; this implies that the reaction involves kinetic chains. The following mechanism has been proposed on the basis of the composition of the reaction products of triethyl phosphite, for example:

$$R\dot{S} + P(OEt)_3 \rightarrow RS\dot{P}(OEt)_3 \rightarrow \dot{R} + S{=}P(OEt)_3 ,$$
$$\dot{R} + RSH \rightarrow RH + R\dot{S}$$

or

$$\dot{R} + RSSR \rightarrow RSR + R\dot{S} .$$

Many facts support the above mechanism of the interaction of RṠ radicals with phosphites or phosphines[11,32]. For example, Kochi and Krusik[16] detected by the ESR method the $(CH_3)_3\dot{C}$ radical, which is formed in the photolysis of di-t-butyl disulphide in the presence of tri-isopropylphosphine (−90°C, cyclopropane) probably by the reaction

$$(CH_3)_3C\dot{S} + [(CH_3)_2CH]_3P \rightarrow (CH_3)_3\dot{C} + [(CH_3)_2CH]_3P{=}S.$$

Subsequently Kavun et al.[33] demonstrated by the ESR method that the alkyl radicals formed in thermal decomposition of di(trichlorophenyl) disulphide (60 — 100°C, benzene, no oxygen) in the presence of triphenylphosphine combine with stable nitroxide radicals as acceptors; the

‡ Indeed hardly any acetone was detected in the mixture of products[15].

kinetic behaviour of the acceptor then reflects accurately the kinetics of the rate-limiting stage—monomolecular decomposition of the disulphide bond. The following mechanism has been proposed for the decomposition of a disulphide in the presence of a phosphine:

$$RSSR \rightarrow 2R\dot{S};$$
$$R\dot{S} + R'_3P \rightarrow RS\dot{P}R'_3 \rightarrow \dot{R} + S{=}PR'_3;$$
$$\dot{R} + \text{acceptor} \rightarrow \text{stable product.}$$

This mechanism is confirmed by the kinetics of reactions in which radicals combine with acceptors.

Finally Bentrude et al.[21] established that the stereospecific transfer of the sulphur atom from BuS· radicals to a mixture of geometrical isomers (III) and (IV) (see p. 557) takes place, as for t-BuO· radicals, with retention of the configuration at the phosphorus atom.

This result and also the direct detection of alkyl radicals and their combination with stable nitroxide radicals as acceptors illustrate the common features of the interaction of RO· and RS· radicals with phosphites and phosphines, which take place via the formation of an intermediate phosphoranyl radical; in this sense the reactions of RO· and RS· radicals have common properties and features.

Only one study has been made[28] on the kinetics of the reactions of RS· radicals, in which the ratio of the rate constants for the interaction of n-BuS· radicals (from n-BuSH) with triethyl phosphite and styrene, initiated by AIBN at 70°C, was measured. By hypothesis, the following reactions occur under experimental conditions:

$$\text{AIBN} \xrightarrow{k_0} \overline{\dot{r} + N_2 + \dot{r}} \begin{cases} \xrightarrow{fk_2} \dot{r} + N_2 + \dot{r} \\ \xrightarrow{(1-f)k_2} r{-}r + N_2 \end{cases},$$
$$\dot{r} + RSH \xrightarrow{k_1} rH + R\dot{S},$$
$$R\dot{S} + P(OEt)_3 \xrightarrow{k_2} \dot{R} + S{=}P(OEt)_3,$$
$$\dot{R} + RSH \xrightarrow{k_3} RH + R\dot{S},$$
$$R\dot{S} + CH_2{=}CHPh \xrightarrow{k_4} RSCH_2{-}\dot{C}HPh,$$
$$RSCH_2{-}\dot{C}HPh + RSH \xrightarrow{k_5} RSCH_2{-}CH_2Ph + R\dot{S},$$

where f is the probability of the emergence of the radicals from the "cage".

Since the sulphide $RSCH_2CH_2Ph$ was obtained only by the reaction with styrene and the phosphorothionate $S{=}P(OEt)_3$ by the reaction with a phosphite, the rate constant ratio k_4/k_2 is determined by analysing the products for an olefin and phosphite:

$$\frac{d[\text{olefin}]}{d[\text{phosphite}]} = \frac{d[\text{sulphide}]}{d[\text{phosphorothionate}]} = \frac{k_4[\text{olefin}]}{k_2[\text{phosphate}]}.$$

The average value of this ratio was found to be 3.2. On the basis of a study by Sivertz[34], who showed that RS· radicals add to the styrene molecule with a diffusional rate constant of 1.3×10^{-12} cm^3·s^{-1}, Walling and Pearson[28] determined the absolute rate constant $k_2 = 0.4 \times 10^{-12}$ cm^3 s^{-1}; this value implies that the reaction of RS· radicals with triethyl phosphite should occur with an almost zero activation energy.

It is noteworthy that there are no serious grounds for regarding this conclusion as unambiguous; this follows from the following considerations. Firstly, analysis of the experimental results of Walling and Pearson[28] in Table 4 showed that, with an approximately constant $[\text{styrene}]_0/[\text{phosphite}]_0$ ratio, the rate constant ratio k_4/k_2 varies in parallel with the increase of the concentration of the mercaptan (by a factor of 2); such an increase can probably be explained either by the fact that at the concentrations indicated in Table 4 there is not sufficient time for the mercaptan to accept all the cyanoisopropyl radicals ṙ emerging from the initiator "cage" into the bulk of the solvent or by the occurrence of side reactions where the olefin is alkylated, which were disregarded by the authors in the kinetic treatment of the experimental results.

Table 4. Ratios of the rate constants for the addition of n-BuS· radicals to triethyl phosphite (AIBN, 70°C, n-BuSH, styrene, no oxygen).

$10^3[\text{n-BuSH}]_0$, M	$\frac{k_4}{k_2}$	$\frac{[\text{olefin}]_0}{[\text{phosphite}]_0}$	$10^3[S{=}P(OEt)_3]$, M	$10^3[\text{sulphide}]$, M	$\frac{k_4}{k_2}\left(\frac{[\text{olefin}]}{[\text{phosphite}]}\right)_{av}$
4.1	1.9	1.0	1.6	2.5	1.71
4.3	2.3	0.8 av 0.9	1.3	1.9	2.07
9.5	4.9	0.9	0.43	1.02	4.4
4.5	2.3	0.47	1.9	1.5	1.22
9.5	4.4	0.6 av 0.53	0.52	1.37	2.33

Secondly, according to the same authors' estimate, the difference between the reactivities of n-BuS· and t-BuO· radicals in relation to various phosphites and phosphines is almost independent of the structure of the radicals and lies in the range 0.1 — 1.0; this means that the reaction of n-BuO· radicals, like that of t-BuO·, with phosphites probably involves an appreciable activation energy.

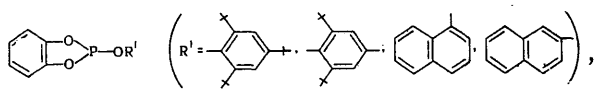
III. REACTIONS OF RO_2· RADICALS

In the previous section evidence was presented demonstrating that RO· and RS· radicals interact effectively with phosphites and phosphines under any conditions either by a radical exchange (substitution) mechanism or via a sulphur or oxygen atom transfer.

At first sight this has the consequence that the kinetics of the reactions of RO· and RO_2· radicals should be determined only by the reactivity of the phosphites (phosphines) and should not be sensitive to the type of the oxygen-containing radical. However, many facts contradict this conclusion.

In liquid-phase chain oxidation of hydrocarbons, the intensity of the chemiluminescence associated with the exothermic elementary step (recombination of peroxy-radicals) decreases appreciably in the presence of certain phenolic and amine inhibitors[35]; this is explained by postulating that the rate of linear chain termination by the inhibitor becomes higher than the rate of quadratic termination (via the recombination of RO_2· radicals). However, Khloplyankina et al.[36], who studied the AIBN-initiated oxidation of ethylbenzene at 60°C by a chemiluminescence method, showed that the introduction of tri-isopentyl phosphite, tri-isopentyl phosphate, and diethylphosphorous acid has almost no effect on the luminescence intensity I: their relative reactivities in the reaction with RO_2· were found to be respectively 1×10^{-5}, 2×10^{-3}, and 1×10^{-5}, i.e. the rate of this reaction is zero or very low.

When an aromatic phosphite,



is introduced into the reaction mixture, the chemiluminescence intensity decreases slightly. It was then found that the rates of consumption of these phosphites, calculated from the kinetic luminescence data, are on average higher by one- two powers of 10 than the specified rate of initiation, while the quantity $[d(I/I_0)/dt]_{max}$ (the maximum slope of the kinetic curve), which characterises the capacity of the inhibitor molecules to react with peroxy-radicals[35], remained almost constant and was usually equal to the corresponding quantity measured in experiments with free phenols (catechol and substituted phenols), which may be obtained by the hydrolysis of phosphites, i.e. may be present as impurities.

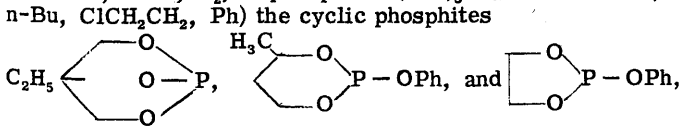
All these characteristics of the quenching of chemiluminescence by aromatic phosphites may be accounted for by adopting a mechanism in which a single kinetic oxidation chain is terminated either by 10 — 100 phosphite molecules or by a single phenol molecule (for an impurity/phosphite ratio of 0.1 — 0.01). The agreement between the slopes of the kinetic luminescence curves for the consumption of the phosphite and its hydrolysis products is evidence that the second mechanism obtains, i.e. aromatic phosphites, like aliphatic phosphites, hardly react with RO_2 radicals at 60°C.

Walling and Rabinowitz[11] were the first to draw attention to the fact that at higher temperatures (about 130°C) the oxidation of aliphatic phosphites by alkoxy-radicals in the presence of O_2 becomes autocatalytic (an excess superstoichiometric amount of phosphate is formed). They also explained the autocatalysis on the hypothesis that at 130°C the peroxy-radicals, into which the alkyl radicals $\dot{R}$ (t-BuO) were converted at 130°C under the influence of molecular oxygen (see p. 556 for the mechanism of the formation of $\dot{R}$), rapidly oxidise new phosphite molecules, regenerating at the same time the active centres of the kinetic chains—the $R\dot{O}$ radicals:

$$\dot{R} + O_2 \rightarrow R\dot{O}_2,$$
$$R\dot{O}_2 + P(OR')_3 \rightarrow RO_2\dot{P}(OR')_3,$$
$$RO_2\dot{P}(OR')_3 \rightarrow O{=}P(OR')_3 + R\dot{O},$$
$$R\dot{O} \rightarrow \text{stages (2) and (3).}$$

It should be noted that this mechanism does not include the termination of the kinetic chains; the oxidation continues until the complete consumption of the phosphite.

An illustration of the mechanism of the autoxidation of phosphites with AIBN as an initiator is provided by the data of Bentrude[15], who measured the yields of trialkyl and triallyl phosphates in the oxidation by $R\dot{O}_2$ radicals (benzene, 80°C, O_2) of phosphites $(R'O)_3P$ (where R' = Et, n-Bu, $ClCH_2CH_2$, Ph) the cyclic phosphites



and the mixed phosphite $(EtO)_2P(OPh)$: in all cases the yield was found to be close to 80 — 90% for the molar ratio phosphite/initiator = 10. It is noteworthy that, when di-t-butyl peroxide was employed as an initiator, the rate of initiation decreased under the experimental conditions (130°C, chlorobenzene) only by a factor of 2 (relative to AIBN), while the yield of cyclic and aromatic phosphates was less than 2.5 moles per mole of the peroxide; this can probably be accounted for by the occurrence of the competitive radical exchange reaction (see Section II).

The above example shows that, in order to conclude that a particular reaction is impossible (such a conclusion was arrived at by Neiman and Miller[37] for the reaction of RO_2 with phosphites on the basis of the results of Khloplyankina et al.[36]), it is insufficient to investigate this reaction at only one temperature; a comprehensive kinetic investigation is required.

Clearly the results of only one study[15] do not yield a complete picture of the kinetics of the reactions of $R\dot{O}_2$ with phosphites; in addition, it is necessary to have data which would make it possible to identify the oxidation conditions and to find the rate-limiting stage (from the effect of O_2 pressure, rate of initiation, phosphite concentration, etc. on the rate of formation of phosphates).

Buckler[17] observed the autocatalytic oxidation of tri-n-butylphosphine under the influence of O_2 to phosphine oxide and n-butyl di-n-butylphosphinite at 26°C in hexane solution in the absence of initiators. It was found that the catalysis is possible when the diffusion of oxygen is retarded and chain propagation

$$R\dot{O}_2 + PR_3 \rightarrow R\dot{O} + O{=}PR_3$$

is much faster than chain transfer

$$R\dot{O} + PR_3 \rightarrow \dot{R} + O{=}PR_3$$
$$R\dot{O} + PR_3 \rightarrow \dot{R} + ROPR_2.$$

Next it was discovered that the relative yields of phosphine oxide varies in parallel with the increasing polarity of the solvent. This finding implies that the polarisation of the P — O bond in the phosphoranyl radical $R - O\dot{P}R_3$ is probably the main cause of the formation of phosphine oxide (see also p. 556). Since in this investigation an initiator was not employed, the nature of the elementary chain initiation step remains obscure.

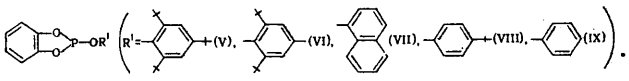
The above brief analysis shows that there are almost no quantitative data for the reactions of $R\dot{O}_2$ radicals with phosphites and phosphines although these reactions, like those of the $R\dot{O}$ and $R\dot{S}$ radicals, are important in the autoxidation of phosphites and phosphines and, as will be shown below, in polymer stabilisation processes. Quantitative kinetic criteria for such reactions are very necessary for practical purposes.

IV. THE ROLE OF RADICAL MECHANISMS IN THE OXIDATION OF POLYMERS INHIBITED BY PHOSPHITES

Hitherto the kinetics and mechanisms of the reactions of low-molecular-weight radicals $R\dot{O}$ and $R\dot{O}_2$ with phosphites and phosphines in the liquid phase were considered. The kinetics of the reactions of $R\dot{O}$ and $R\dot{O}_2$ macroradicals with phosphites are of exceptional interest for the theory of polymer stabilisation. Unfortunately, there are almost no quantitative data for the rates of these reactions in polymer melts and in the solid phase. Nevertheless, such data would be extremely significant. The point is that the idea of the involvement of aromatic phosphites in the termination of kinetic chains in the oxidation of polymers (in the melts) and the associated theory of the action of organophosphorus inhibitors (critical concentrations, linear relation between the induction period and phosphite concentration, etc.) are based on hypotheses concerning the reactions of low-molecular-weight $R\dot{O}$ and $R\dot{O}_2$ radicals (see Sections II and III); these hypotheses were developed by Levin[38,39] and confirmed by a number of investigators

in studies on the high-temperature (180 – 220°C) oxidation of polypropylene[38–43]. Initially we shall examine the available data in this field and then interpret them from the kinetic standpoint.

Levin and coworkers[39,40,43], who studied the oxidation of polypropylene at 200°C (i.e. in the melt) and at an oxygen pressure of 200 mmHg, observed a linear relation between the induction period in the oxidation process τ and the concentration of aromatic phosphites with the general formula



Comparison of several mechanisms for the inhibited oxidation of polypropylene in the presence of these phosphites shows that formally they all reduce to a linear relation between τ and the phosphite concentration.

Firstly, phosphites may inhibit degenerate branching:

$$RH + O_2 \xrightarrow{W_0} \dot{R} + HO_2^{\cdot},$$

$$\dot{R} + O_2 \xrightarrow{k_1} R\dot{O}_2,$$

$$R\dot{O}_2 + RH \xrightarrow{k_2} ROOH + \dot{R},$$

$$R\dot{O}_2 + R\dot{O}_2 \xrightarrow{k_3} \text{stable products},$$

$$ROOH + RH \xrightarrow[k_4]{O_2} \delta R\dot{O}_2,$$

$$ROOH + P(OR')_3 \xrightarrow{k_5} \text{stable products}.$$

Kinetic analysis of this mechanism (where δ is the probability of degenerate chain branching) in the steady state (with respect to $\dot{R}$, $R\dot{O}_2$, and ROOH) leads to the following relation between the rate of consumption of the phosphite and its concentration:

$$-\frac{d[P(OR')_3]}{dt} = \frac{k_2 k_5 [RH] W_0^{1/2} [P(OR')_3]}{k_3^{1/2}(k_4[RH] + k_5[P(OR')_3])}.$$

At fairly high phosphite concentrations, we obtain

$$-\frac{d[P(OR')_3]}{dt} = \frac{k_2[RH] W_0^{1/2}}{k_3^{1/2}}.$$

and

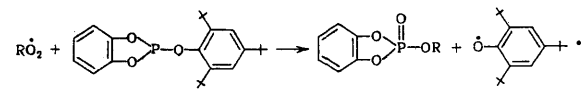
$$\tau = \frac{k_3^{1/2}}{k_2[RH] W_0^{1/2}} [P(OR')_3]_0.$$

i.e. τ varies linearly with $[P(OR')_3]_0$. In addition, it is possible to show that, under the experimental conditions (200°C, typical inhibitor concentration $10^{-1} - 10^{-2}$ mole kg^{-1}), the phosphite (V) is in fact capable of suppressing degenerate branching, since

$$\frac{W_5/[ROOH]}{W_4/[ROOH]} = \frac{0.4 \cdot 10^{-12} \exp(-14\,000/RT)(10^{-1} - 10^{-2})}{1.6 \cdot 10^{-12} \exp(-25\,000/RT) \cdot 23} = 1.2(10^3 - 10^4).$$

The rate constant for the bimolecular decomposition of polypropylene hydroperoxide was obtained by ourselves from the results of Pudov and Neiman[44] and the "liquid-phase" rate constant for the reaction of tri-t-butylphenyl *o*-phenylene phosphite with 1,1-diphenylethyl hydroperoxide (this hydroperoxide can serve as a model of polypropylene hydroperoxide) extrapolated to 200°C was taken from Mukmeneva[45]; the inhibitor and polymer concentrations were $10^{-1} - 10^{-2}$ and 23 mole kg^{-1}. However, the finding that the effectiveness of the phosphites (V) – (IX) investigated is not correlated with the rates at which they decompose 1,1-diphenylethyl hydroperoxide in the liquid phase at 25°C cannot be accounted for within the framework of this mechanism[39,45,46].

Secondly, phosphites can terminate kinetic oxidation chains probably by replacing the active macroradicals $R\dot{O}_2$ by relatively inactive resonance-stabilised phenoxy-radicals[38] (see also Section II):



In this case the general mechanism of the inhibited oxidation can be represented as follows:

$$RH + O_2 \xrightarrow{W_0} \dot{R} + H\dot{O}_2,$$

$$\dot{R} + O_2 \xrightarrow{k_1} R\dot{O}_2,$$

$$R\dot{O}_2 + RH \xrightarrow{k_2} ROOH + \dot{R},$$

$$R\dot{O}_2 + P(OR')_3 \xrightarrow{k_p} O{=}P(OR')_2(OR) + Ar\dot{O},$$

$$ROOH + RH \xrightarrow[k_4]{O_2} \delta R\dot{O}_2.$$

Assuming steady-state concentrations of $\dot{R}$, $R\dot{O}_2$, and ROOH, it is possible to obtain the following expression for the rate of consumption of phosphite:

$$-\frac{d[P(OR')_3]}{dt} = \frac{k_p[P(OR')_3] W_0}{\delta k_2[RH] + k_p[P(OR')_3]}.$$

At fairly low values of δ (it has been shown in a review[47] that, at oxygen pressures ranging from 0 to 200 mmHg, δ varies in the range $17 \times 10^{-3} - 0.8$, i.e. is less than unity), this expression simplifies:

$$-\frac{d[P(OR')_3]}{dt} = W_0 \text{ and } \tau = \frac{1}{W_0}[P(OR')_3]_0;$$

i.e. in this case τ depends linearly on $[P(OR')_3]_0$. This mechanism is confirmed by the critical concentrations of the phosphites investigated[40–42] (observed in kinetic experiments), i.e. concentrations above which the oxidation process passes from a non-steady state to a steady state (hypotheses concerning the critical concentrations of inhibitors of different types have been developed by Neiman and Shlyapnikov[48,49]). Evidently an unambiguous and direct demonstration of the elementary kinetic chain termination stage in oxidation by aromatic phosphites in the polymer melt and in the solid phase would be of fundamental importance for the theory of the stabilisation of polymers by these compounds; hitherto such a demonstration has not been achieved in any of the experimental studies.

Thirdly, a linear relation of the type $\tau \cong [P(OR')_3]_0/W_0$ may be obtained on the hypothesis[37] that aromatic phosphites inhibit the oxidation of polypropylene via their hydrolysis products, which are formed in the course of the oxidation process. Indeed, the formation of water molecules in the induction period of the oxidation reaction becomes the rate-limiting stage in this case and therefore the hydrolysis of the phosphite is of zero order with respect to the phosphite. However, from the standpoint of these hypotheses about phosphites as sources of catechol and other stabilisers, one cannot explain the finding that the phosphites investigated (except phosphites with the substituents  and ) have a critical concentration, while all theoretically conceivable products of their hydrolysis (phenols, catechol, *o*-phenylenephosphorous acid, phosphorous acid, and others) do not exhibit such a concentration[41].

Thus the existence of a linear relation between the induction period and the concentration of aromatic phosphites can be explained unambiguously by adopting the mechanism in which the kinetic oxidation chains are

terminated by radical exchange. This mechanism probably obtains in polymer melts; on the other hand, the presence of critical phosphite concentrations can serve as a kinetic criterion of its validity. Moreover, such a mechanism makes it possible to deal more rigorously and on a sounder basis with the selection of phosphites for which an inhibiting effect may be predicted.

It is noteworthy that the extensive data on the effectiveness of aromatic phosphites in polymer oxidation products in melts can be hardly used for solid-phase reactions of $R\dot{O}_2$ radicals with phosphites; this follows from the kinetic characteristics of solid-phase radical reactions (see the review on radical polymer degradation and stabilisation reactions[47]). We may note that, in order to determine the effectiveness of the phosphites in the termination of kinetic chains in the oxidation of a solid polymer (100 – 130°C), it is necessary to know not only the rate constant and the elementary mechanism of the interaction of the $R\dot{O}_2$ macroradical with the phosphite (which characterises the kinetic stage) but also the diffusion coefficient of the phosphite in the solid polymer (the macrodiffusion stage).

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This review has dealt with the most important radical reactions of phosphites and phosphines, their role in autoxidation processes in the liquid phase and in the inhibited oxidation of polymers in melts has been assessed, and their quantitative kinetic characteristics have been given.

It is noteworthy that the quantitative data for many reactions are extremely contradictory; frequently this applies not only to kinetic constants but even to the mechanisms. For example, the mechanism of the termination of kinetic chains in the oxidation of polypropylene by aromatic phosphites via radical exchange is valid provided that the phenoxy-radical is not involved in the propagation of the $Ph\dot{O} + RH \rightarrow PhOH + \dot{R}$ chains but recombines with a second peroxy-radical. Calculation shows that 200°C the rate via the first pathway for the disappearance of phenoxy-radicals is comparable with the rate via the second pathway; one can only suppose that phenoxy-radicals disappear via disproportionation to low-molecular-weight products. The solution of these problems constitutes an important step in the creation of a theoretical basis for the stabilisation of polymers by organophosphorus compounds.

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