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Catalytic decomposition of organic and organoelemental peroxides in the presence of electron donors and electron acceptors

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ABSTRACT. The main characteristics (the kinetics and mechanism) of the radical decomposition of organic and organoelemental peroxides in the presence of active electron-donor and electron-acceptor components in alkanes and polymerising media are discussed. The decisive role of the formation of complexes of peroxides with active catalytic components and olefins in these processes is shown. The formation of triple complexes of monomer–Lewis acid–olefin plays an important part in the initiation of radical polymerisation. Examples of the practical application of the initiating systems peroxide–electron donor and peroxide–electron acceptor are given.
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I. Introduction

During the last 15–20 years research into radical polymerisation has undergone a real transformation; new ideas and possibilities have appeared, adding fresh impetus to this well-known process.[1–4]

One of the current and future trends is radical-complex polymerisation using chemical activation agents that participate in radical polymerisation.[4–11] Radical-complex polymerisation in essence consists of the directed change in reactivity of monomers and growing radicals that participate in chain propagation by using complexing agents (Lewis acids, proton acids), which results in catalytic acceleration (or selective inhibition) of this stage of the radical chain process.

In 1957 it was found[5] that the rate and degree of radical polymerisation of acrylonitrile (AN) increased in the presence of small quantities of LiCl. The increase in rate of the reaction was attributed to the interaction of the nitrile group in the AN monomer and radical with LiCl. It was recorded in subsequent studies[6–12] that there was an increase in the rate of radical homo- and co-polymerisation of the vinyl monomers methyl methacrylate (MMA) and AN in the presence of inorganic salts (LiCl, $MgCl_2$, $ZnCl_2$, $AlCl_3$, $AlBr_3$, $SnCl_4$) that are capable of forming coordinate complexes with functional groups (C=O and C≡N) in the reacting monomers and radicals.

Another trend of research is to improve the polymerisation processes by means of the chemical action of effective initiators on the fundamental initiation stage.[1,2] This idea consists of the possibility of controlling the reactivity of the initiator through its specific interaction with active donor or acceptor components which accelerate the radical decomposition of the initiator and cause it to be effective over a required range of temperature. Olefins, amines, phosphates, phosphites, sulphides, and other compounds have been used as electron donors while Lewis acids, PCl_3, and SO_2Cl_2 have been used as electron acceptors. The formation of complexes between peroxides and electron donors or electron acceptors leads to a change in the electronic configuration of the peroxide and hence its capacity to generate radicals.[13–16]

II. Effect of electron donors on the decomposition of peroxides and initiation of radical polymerisation

Binary donor–acceptor systems which have an organic peroxide as one of the components have attracted the attention of research workers for a long time because of the possibility of using them as effective initiators of radical polymerisation.[17–22] A necessary condition for such a system to function is its ability to generate radicals within the required range of temperature at a rate desirable for the process. A sufficient condition is high activity of the radicals formed, capable of initiating a radical process. It has been shown by various methods[13–16,19,20] that at the primary stage a complex is formed with charge transfer between the components of the donor–acceptor system.

A general mechanism for the radical initiation of polymerisation of different monomers by the system organic peroxide–amine (A) with low degrees of conversion[18] may be given by the following scheme:

$$P \rightleftarrows [R^{\cdot}\,R^{\cdot}] \rightarrow 2R^{\cdot},$$

$$P + A \rightleftarrows [P...A] - \begin{cases} \longrightarrow [R^{\cdot}...A] + R^{\cdot} \\ \longrightarrow \text{heterolysis} \end{cases}$$

$$[R^{\cdot}...A] - \begin{cases} \longrightarrow R^{\cdot} + A \\ \xrightarrow{M} RMA^{\cdot} \\ \xrightarrow{H} RH + A^{\cdot} \end{cases}$$

$$R^{\cdot} + M \rightarrow RM^{\cdot},$$

M – monomer

The formation of complexes between amines and peroxides was demonstrated by UV, IR and NMR spectroscopy in the same study.[18] From a quantitative study of the effect of acids and bases on the kinetics of the decomposition reactions of peroxide in the presence of amines in different media it was proposed that a complex

of amine–peroxide–solvent was formed. Amines (aminoacids) have a considerable effect on the kinetics of radical polymerisation of vinyl monomers, namely, on the rate of initiation and the ratio of chain growth constant to chain termination constant ($k_g/k_t^{1/2}$). When aromatic amines interact with organic peroxides the primary reaction in the initiation system peroxide–amine is formation of a complex between the components.[20–22] The complexing agent activates the peroxide molecule and assists the generation of radicals at a high rate within the required range of temperature. A primary complex was detected in benzoyl peroxide–aromatic amine systems at 243–253 K. The formation of benzoate free radicals was established by means of EPR using a spin trap (phenyl t-butyl nitrone).

The presence of a heteroelement in organoelemental peroxides of composition $R_{n-1}EOOR'$ makes them have a greater tendency to coordinate compared with organic peroxides. Their conversion routes in an inert solvent or polymer systems are much more complex than for organic peroxides. Reactions (1)–(7) are possible conversion routes for organoelemental peroxides in radical polymerisation processes:

$$R_{n-1}EOOR' \rightarrow R_{n-1}EO^{\cdot} + {}^{\cdot}OR', \quad (1)$$

$$R_{n-1}EOOR' \rightarrow R_{n-2}E(OR)OR', \quad (2)$$

$$R_{n-1}EOOR' \rightarrow R_{n-1}EOH + R'_{-H}O, \quad (3)$$

$$R_{n-1}EOOR' \rightarrow [R_{n-2}E{=}O] + R'OH \text{ (if one of } R = H), \quad (4)$$

$$R_{n-1}EOOR' + SH \rightarrow R'OH + [\overbrace{R_{n-1}EO^{\cdot}\ {}^{\cdot}S}] \quad (5)$$

$$\downarrow \qquad\qquad \downarrow$$

$$R_{n-1}EOS \qquad R_{n-1}EO^{\cdot} + S^{\cdot}$$

$$R_{n-1}EOOR' + D \rightleftarrows [R_{n-1}EOOR'.D] \rightarrow [R_{n-1}EO^{\cdot}.D] + {}^{\cdot}OR', \quad (6)$$

$$R_{n-1}EOOR' + R''_nE' \rightarrow R''_{n-1}E'OR' + [\overbrace{R_{n-1}EO^{\cdot}\ {}^{\cdot}R''}] \quad (7)$$

$$\downarrow \qquad\qquad \downarrow$$

$$R_{n-1}EOR'' \qquad R_{n-1}EO^{\cdot} + {}^{\cdot}R''$$

SH – solvent, D – donor.

Reaction (1) is the homolytic decomposition of peroxide to radicals that are responsible for initiating radical processes. An actual polymerisation or vulcanisation system is a complex multi-component mixture in which the peroxide can participate not only at the stages of initiation and chain growth but also in side reactions. For example, reactions of spontaneous non-radical conversion of peroxides[23–25] [reactions (2)–(4)] are in a number of cases fundamental for organoelemental peroxides, and the initiator then has little effect on radical polymerisation.

Reactions (5)–(7) are processes for generating radicals in bimolecular reactions with the solvent,[26] donor electrons,[13,14] or organoelemental compounds[27–30] when the latter are present in the reaction system.

During polymerisation of MMA, butyl methacrylate (BMA), or styrene, some complexing agents—electron donors—can produce a substantial change in initiating activity of organoelemental peroxides, accelerate radical polymerisation or copolymerisation, and also have an effect on the composition of the copolymer.[31–33] The activation effect on the decomposition of organoelemental peroxides in olefins is due to the formation of a donor–acceptor complex of olefin–organoelemental peroxide, which decomposes to radicals at a higher rate than does pure peroxide in an inert solvent.

$$R_{n-1}EOOR' + \rangle C{=}C\langle \underset{k_{-1}}{\overset{k_1}{\rightleftarrows}} \left[\rangle C{=}C\langle \cdots R_{n-1}EOOR' \right] \xrightarrow{k_2} \left[\rangle C{=}C\langle \cdots R_{n-1}EO^{\cdot} \right] + R'O^{\cdot}$$

Organosilicon peroxides $R_{4-n}Si(OOBu\text{-}t)_n$, where n = 1–4, R = Me, CH_2 = CH, form similar complexes with acrylic monomers. Coordination occurs between the unshared electron pair of the carbonyl oxygen in the monomer an the vacant *d* orbital of silicon in the peroxide.

The formation of a complex of $Me_3SiOOBu\text{-}t$ with MMA and BMA in hexane and benzene in the temperature range 193–293 K was demonstrated by ^1H NMR spectroscopy from the change in chemical shifts of the protons of the MeO groups in MMA or the *cis*-protons of the $CH_2{=}C$ group in the monomers on changing the concentration of peroxide.[15] By measuring the chemical shifts of the protons it was possible to determine the equilibrium constants and enthalpies (ΔH) of complex formation. The displacement of the proton signals downfield is an indication that the monomers act as electron donors in the complex.

It should be noted that even t-butyl peroxide (TBP) forms a complex with MMA or BMA.[34] Measurements were made by monitoring the variation in the difference between the chemical shifts of the *cis*- and *trans*-olefinic protons in MMA (internal chemical shift ν). The concentration of TBP was varied at a fixed concentration of MMA. Addition of peroxide caused a decrease in ν in MMA by a value of Δ. The latter is dependent on the concentration of peroxide (C_n):[35]

$$\frac{1}{\Delta} = \frac{1}{K\Delta_c}\frac{1}{C_n} + \frac{1}{\Delta_c},$$

where K is the equilibrium constant for formation of complex, Δ_C is the chemical shift of complex.

It was possible to determine complexes of TBP and $Me_3SiOOBu\text{-}t$ with MMA and BMA at temperatures below 253 K.[15,34] The equilibrium constants for formation of these complexes are small, and for the MMA–TBP complex they vary from 0.22 to 0.1 over the temperature range 193–253 K while for the MMA–$Me_3SiOOBu\text{-}t$ complex the variation is 1.3 to 0.25 over the temperature range 213–253 K. The values of δH for these complexes are equal to 6.0 ± 0.3 and 23 ± 3 kJ mol^{-1} respectively. Hence organosilicon peroxides form stronger complexes with monomers than do organic peroxides, which is due to the presence in the organosilicon peroxides of an active acceptor site on the silicon atom (vacant *d* orbital).

The complexing agent activates organoelemental peroxides (the peroxide band is weakened), and the rate constant for decomposition of the peroxide bonded to the monomer in the complex is increased. For example, $Me_3SiOOBu\text{-}t$ decomposes in nonane at 373 K with a rate constant (k) equal to 2×10^{-9} s^{-1} (calculated from published data[36]), whereas in BMA the value of k increases by a factor of 1000 and has a value of 2.4×10^{-6} s^{-1}.[37] The energy of activation of the decomposition processes on changing from nonane to BMA falls from 159 to 75 kJ mol^{-1}. A similar pattern occurs for all organoelemental peroxides of the series $Me_{4-n}Si(OOBu\text{-}t)_n$ on changing from an inert solvent to a polymerisable olefin (MMA, BMA).

The formation of a donor–acceptor complex of monomer with an organoelemental peroxide is responsible for the increase in rate of decomposition of the peroxide and hence an increase in the rate of initiation of polymerisation. In one study[15] the rate of polymerisation of different vinyl monomers initiated by organosilicon peroxides is given. As the number of peroxide groups in organosilicon initiator molecule increases, the rate of polymerisation of the vinyl monomers MMA, BMA and styrene increases disproportionately to the number of peroxide groups, which is an indication of the different reactivity of the latter in the $Me_{4-n}Si(OOBu\text{-}t)_n$ molecule.

The polymerisation of vinyl monomers initiated by organosilicon peroxides is a radical process since its rate is proportional to the concentration of initiator to the power 0.5, and when the stable radical 2,2,6,6-tetramethyl-1-piperidinoxyl [$C_0 = 1-6 \times 10^{-5}$ mol litre^{-1}] is introduced into the polymer system, inhibition that is typical for a radical process occurs, the magnitude of the induction period being proportional to the concentration of the inhibitor.

Thus, organosilicon peroxides that generate radicals in an inert solvent at 423–473 K, owing to the formation of a complex with monomer, are capable of initiating radical polymerisation within the temperature range 353–373 K.

The ability of organoelemental peroxides to form complexes with olefins, as shown above, led to the assumption that they had a potential effect on the composition of copolymers during copolymerisation.[15,16] It was shown that the relative reactivities of monomers vary when copolymerisation is carried out in the presence of organosilicon peroxides. This could be accounted for by the formation of complexes of silicon peroxides not only with monomers but also with the growing radicals, while the latter effect is probably more important because of the small quantity of peroxide in the reaction system.

Table 1. Stability constants and enthalpies of formation for 1 : 1 R_3EOOR'·ligand complexes at 298 K.[32]

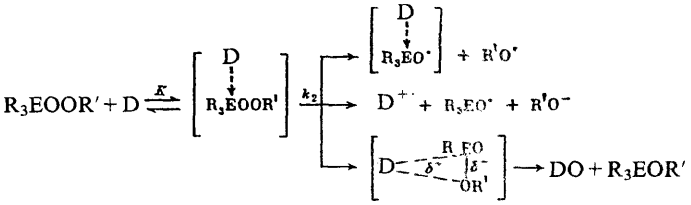
Peroxide	Ligand	$-\Delta H$, kJ mol^{-1}	K^*
$Si(OOBu\text{-}t)_4$	C_5H_5N	29.06	1.96
$Et_3(SnOOBu\text{-}t)$	C_6H_{12}	6.99	0.054
	$Ph_2C{=}CH_2$	11.40	0.055
	$PhCH{=}CH_2$	10.80	0.052
	$CH_2{=}C(Me){-}C(Me){=}CH_2$	10.55	0.084
	C_6H_5N	16.11	0.18
$Et_3SnOOCMe_2Ph$	C_5H_5N	21.5	0.88

*Solution with concentration 1 mol litre^{-1} chosen as the standard state.

It is not only the monomer itself that is capable of activating organic peroxides or organoelemental peroxides to form donor–acceptor complexes with them but other electron donors (amines, ethers, phosphates, sulphides) can also accelerate the decomposition of peroxides and increase the proportion of homolytic cleavage of the peroxide bond. In a number of studies[14,16,31–34,38–45] kinetic and activation parameters are given for the decomposition of organic peroxides and organoelemental peroxides of silicon, germanium, and tin in the presence of various donors (D). It was established by kinetic, thermochemical, and ^{1}H NMR spectroscopic methods[31,32,38–45] that the primary stage of the decomposition of peroxides in the presence of D is formation of a complex between peroxide and D [reaction (6)]. This stage was detected by means of calorimetry at 298 K [31,32] and also kinetically at the decomposition temperatures of the peroxides[38–43] and the values of K and ΔH of the peroxide–donor complexes were determined (Tables 1 and 2). The degree of charge transfer in the complexes $Si(OOBu\text{-}t)_4 - C_5H_5N$ and $Et_3SnOOBu\text{-}t - C_5H_5N$ is 0.2 and 0.1 respectively.

In order to determine which of the atoms (E or O) is coordinated to D, ^{1}H NMR spectroscopy was used to study the change in chemical shifts of the protons of the Me_3C and Me_3Sn groups in the peroxide $Me_3SnOOBu\text{-}t$ in the presence of D.[45] For comparison the chemical shifts of the protons in TBP were determined in relation to the composition of the solution.[45] Gorbatov et al.[45] were able to maintain from the results obtained that coordination of D occurs on the tin heteroatom. From the nature of the change in the chemical shift in the system peroxide–chloroform (electron acceptor) it may be concluded that the latter forms a complex with both $Me_3SnOOBu\text{-}t$ and TBP, and the coordination occurs on the peroxide bond, more precisely, on the oxygen atom of the peroxide bond that has highest electron density.[46]

At the rate-limiting stage of the decomposition of the complex between peroxides and donors, either displacement of electron density along a system of σ-bonds (olefins, ethers, phosphates) or with transfer of an electron (amines, sulphides, phosphites), which assists homolysis of the peroxide, or the transfer of two electrons in a heterolytic S_N2 process (sulphides, phosphites) occurs:



If the equilibrium constant K is small, the proportion of peroxide decomposing outside the complex with rate constant k_1 may be significant:

$$R_3EOOR' \xrightarrow{k_1} R_3EO^{\cdot} + R'O^{\cdot},$$

if [D] ≫ [organoelemental peroxide], the experimentally determined rate constant for decomposition of organoelemental peroxide (k_{exp}) is calculated from the equation:

$$k_{exp} = \frac{k_1 + k_2K[D]}{1 + K[D]},$$

where k_2 is the decomposition constant for the peroxide–donor complex. The values of k_1, k_2, K, and ΔH for certain complexes are given in Table 2.

If follows from an analysis of these results that the proportion of the peroxides bonded to the complex is small and depends on the nature of the peroxide and the basicity of the ligand. Organosilicon peroxides that have a lower capacity for complex formation mainly decompose outside the complex. Organotin monoperoxides and organosilicon polyperoxides, which have greater acceptor properties relative to D, decompose in the presence of D both in the form of a complex ($k_2 \gg k_1$) and without it.

Table 2. Values of k_1, k_2, and K for peroxide–donor complexes.

Complex	T, K	$k_1 \cdot 10^5$, s^{-1}	$k_2 \cdot 10^5$, s^{-1}	K	$-\Delta H$, kJ mol^{-1}	Refs.
$Et_3SnOOBu\text{-}t.C_6H_{10}$	433	2.8	122	0.02	—	[14]
$Et_3SnOOBu\text{-}t.Ph_2C{=}CH_2$	433	2.8	190	0.025	—	[14]
$Me_3SiOOCMe_2Ph.C_5H_5N$	453	2.5	10.3	0.64	28.0	[14]
$Me_3SiOOCMe_2Ph.Bu_2O$	463	6.6	61.6	0.13	—	[38]
$Et_3SnOOBu\text{-}t.C_5H_5N$	433	2.8	64.0	0.59	12.1	[41]
t-BuOOC(O)Ph.HTP*	383	8.1	58.9	1.14	—	[42]
$[Me(CH_2)_{10}CO]_2$.DMF**	353	13.1	50.6	0.3	—	[42]

* HTP—hexamethyltriamidophosphate;
** DMF—dimethylformamide.

III. Effect of electron acceptors on the decomposition of peroxides in alkanes and polymerising media

1. Reactions of organoelemental compounds with peroxides

The published data[28–30,47–51] on the reaction of organoelemental compounds with peroxides indicate that the systems organoelemental compound–organic peroxide and organoelemental compound–organoelemental peroxide have potential use as radical sources. The tendency to associate and form complexes is a characteristic feature of organoelemental compounds of lithium, magnesium, cadmium, etc. Therefore in reactions of organoelemental compounds of Groups I and II with peroxides the role of coordination interactions of the organoelemental reagent is displayed particularly clearly. A peroxide-base affects the organoelemental compound in several ways: it decreases the degree of association of the initial compound, increases the polarity of the C–E bond, and probably assists the transfer of an electron from the C–E bond to the peroxide bond.[52] As a result of this a radical pathway is the main one for the reaction of organoelemental compounds of Groups I and II with peroxides and a scheme for the process including coordination and association of the reactants may be represented in the following way:[28]

$$(R_nE)_x + R'OOR'' \rightleftarrows [(R_nE)_y \cdot R'OOR''] \rightleftarrows [(R_n\overset{e}{\overbrace{}}E)_y \cdot R'O\overset{e}{\overbrace{}}OR''] \rightarrow$$
$$\rightarrow \begin{bmatrix} R^{\cdot} & R_{n-1}E^{+} \\ R'O^{\cdot} & R''O^{-} \end{bmatrix} (R_nE)_{y-1} \rightarrow (\overline{R^{\cdot}\ \ OR'})\,(R_nE)_{y-1} + R''OER_{n-1}$$
$$\downarrow \qquad\qquad \downarrow$$
$$(R_nE)_{y-1} + R^{\cdot} + {}^{\cdot}OR' \qquad ROR' + (R_nE)_{y-1}\ .$$

This scheme is based on a single-electron transfer (SET) mechanism, which has been demonstrated by chemically induced polarisation of nuclei. However, the detection of radicals using this method does not provide a basis for the assumption that the whole process is radical since the effect of chemical induced polarisation of nuclei can occur even when the contribution of a radical route is small.

Not all reactions of organoelemental compounds or organoelemental peroxides can be expected to occur by a common mechanism since organoelemental compounds differ according to their degree of association in the initial state, the polarity of the E–C bond, and their ability to coordinate with electron donors. The probability that a SET mechanism will occur should increase as the ionic character of the E–C bond increases.[49]

The suggestion that the reactions of alkyl peroxides with alkyls of Group III elements are radical in character was put forward about 30 years ago.[53,54] The proof of this was subsequently obtained,[55] when it was shown that Et_3B reacts with $EtOOBEt_2$ in benzene in the absence of oxygen to form ethane, ethylene, butene, ethylbenzene, etc. It was also established that this system induces the radical polymerisation of MMA.

Quite recently when R_3Al (R = Alk, Ar) was reacted with t-$BuOOER_3$ (E = C, Si, Ge, Sn) it was possible by means of a spin trap (2-methyl-2-nitrosopropane) to detect the radicals $R^{\cdot}$ and $R_3EO^{\cdot}$,[56,57] the existence of which had previously been postulated.[58–60]

At the present time it is taken as proven that the primary reaction in the interaction of peroxides with organoelemental compounds of Groups I–III is complex formation:[61–63]

$$R_nE + R'OOR'' \rightleftarrows [R_nE \cdot R'OOR'']. \qquad (I)$$

In a number of cases these complexes have been isolated and characterised. For example, the formation of complexes between alkyllithium and organic peroxides was established kinetically.[61] The existence of the complexes n-$Bu_3B.Me_3COOCMe_3$ and n-$Bu_3B.Me_3SiOOCMe_3$ in hexane at –196 °C was demonstrated by electronic emission spectroscopy.[46,64] It was established that the alkylborane is coordinated with the oxygen atom of the Me_3CO residue.

The question then arises as to which mechanism is followed in the conversion of the complex formed and which factors are responsible for it generating radicals? How is the energy that is necessary for the homolysis of the E–C and O–O bonds, and also possibly the C–O bond, redistributed in it?

Alyasov et al.[29] considered that $Alk_3B.t\text{-}BuOOEr_3$ (E = C, Si, Be) complexes do not generate radicals in the absence of radical acceptors (solvent, monomer, halocarbon). In the absence of radical traps, radicals may possibly still be formed but they are destroyed in the solvent cage and the escape of free radicals into the main volume is negligible. Probably a radical acceptor in the reaction system is "built on" to complex (I) in such a way that in the activated state an energetically and sterically favourable structure occurs, in which all three components—peroxide, organoelemental compound, and radical acceptor stabilising the radical particles formed—are "excited". For example, it was proposed[58–60] that in the reaction of Alk_3Al with benzoyl peroxide (BP) in a polymerising medium a complex with monomer (M) is first formed—$Alk_3Al.M$ (this naturally occurs since $[M] \gg [Alk_3Al]$ and $[M] \ll [BP]$). Subsequently BP interacts with the complex formed according to the reaction

$$[Alk_3Al.M] + BP \rightleftarrows [BP.Alk_3Al.M] \rightleftarrows$$
$$Alk_2AlOC(O)Ph + Alk^{\cdot} + PhC(O)OM^{\cdot}.$$

Organoelemental compounds of Group IV (R_4E) as a rule react with peroxides at the decomposition temperatures of the latter. The peroxides constitute the source of primary radicals and tetralkyl derivatives of silicon, germanium, and tin are hydrogen donors.[47,48]

$$R_4E + R'O^{\cdot} \rightarrow R'OH + R_3ER^{\cdot}_{H}.$$

The subsequent fate of the radicals is determined by the nature of E. Organosilicon radicals readily dimerise, germanium-containing radicals both dimerise and undergo disproportionation, while for tin-containing radicals dimerisation is not typical. The main reaction of the latter is cleavage of their Sn–C bond:[48]

$$R_3Sn{-}CH_2CH_2^{\cdot} \rightarrow R_3Sn^{\cdot} + C_2H_4.$$

Thus, organoelemental compounds of Group IV react with peroxides as a rule according to a homolytic mechanism. Firstly, homolysis of the peroxide occurs on the O–O bond, then there is a homolytic S_N2 reaction of the resulting radicals with the organoelemental compound. If the peroxide decomposes by several parallel reactions (homolysis, heterolysis, or intramolecularly), its reaction with Group IV organoelemental compounds is complicated.

It is not possible to determine unequivocally the mechanism for decomposition of a peroxide coordinated with an organoelemental compound in complex (I). It may be either a redox process involving a single-electron transfer of an S_N2 reaction of the radical generated from the peroxide with the organoelemental compound or an intramolecular reaction or a heterolytic S_N2 process. The ratio of radical to non-radical pathways is to date difficult to determine in each individual case.

For example, the formation of radicals may be due to the transfer of an electron

$$[R_nE \cdot R'OOR''] \xrightarrow{e} \begin{bmatrix} R^{\cdot} & {}^{+}ER_{n-1} \\ R'O^{\cdot} & {}^{-}OR'' \end{bmatrix} \begin{cases} \longrightarrow ROR' + R_{n-1}EOR'' \\ \longrightarrow R^{\cdot} + R'O^{\cdot} + R_{n-1}EOR'' \end{cases}$$

However, this complex can be converted via different activated states by two routes—homolytic and heterolytic:

$$[R_nE \cdot R'OOR''] \begin{cases} \longrightarrow \begin{bmatrix} R^{-} & {}^{+}ER_{n-1} \\ R'O^{+} & {}^{-}OR'' \end{bmatrix}^{\neq} \rightarrow ROR' + R''OER_{n-1} \\ \longrightarrow \begin{bmatrix} R^{\cdot} & {}^{+}ER_{n-1} \\ R'O^{\cdot} & {}^{-}OR'' \end{bmatrix}^{\neq} \rightarrow R^{\cdot} + R'O^{\cdot} + R''OER_{n-1} \end{cases}$$

Several other variants of the decomposition of the complex can be proposed (a cryptoradical process, concerted homolytic cleavage, etc.), but it is not possible at the present time to come to any definite conclusion about the mechanism of the reaction.[50]

The system organoelemental compound–peroxide generates free radicals at quite low temperatures and can serve as an effective initiator for the polymerisation of vinyl monomers.[58–60,65–72]

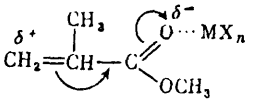
Information about the efficiency of initiation obtained by various methods provides an insight into what proportion of radicals leaves the solvent cage and is of use in radical chain polymerisation. But this method cannot be used to determine the proportion of cryptoradical processes occurring within the solvent cage.

2. Reactions of Lewis acids with peroxides

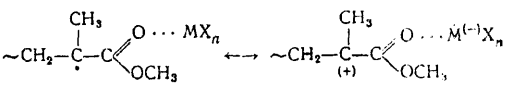
Polymerisation of acrylic monomers that is initiated by organoelemental compounds is accelerated by the addition of Lewis acids [$ZnCl_2$, $SnCl_4$, $SbCl_3$, $SbCl_5$, $TiCl_4$, R_nSiCl_{4-n} (n = 1–4), R_3SnCl, R_2SnCl_2 (R = Me, Et, n-Pr, n-Bu)] or compounds such as PCl_3 and SO_2Cl_2. Lewis acids have an effect on the fundamental stages of polymerisation and in particular on initiation and chain propagation. In the presence of Lewis acids as well as PCl_3 and SO_2Cl_2 the rate of polymerisation of acrylic monomers increases, the energy of activation of the process being reduced.[15,73–76]

Definite ideas about the mechanisms that are responsible for the change in rate and the initiation constants in radical polymerisation in the presence of the system organic(organoelemental) peroxide–Lewis acid can be put forward by studying the nature of the interaction between Lewis acids and monomers and peroxides.

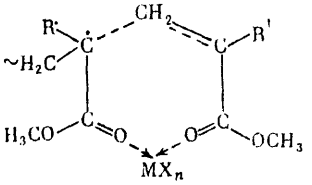
According to published results[77–80] Lewis acids (MX_n) form complexes with acrylic monomers. The composition and structure of double complexes, for example, between MMA and acids such as $AlCl_3$, $AlBr_3$, $ZnCl_2$, $AlEt_3Cl$, $SnCl_4$, were studied by IR,[79,80] UV,[78] and NMR [81,82] spectroscopy. It was shown that complexes are formed as a result of an interaction between the complexing agent and the carbonyl group of the monomer. The strength of these complexes is such that it can be determined from the magnitude of the shift of the IR absorption bands due to stretching vibrations of the carbonyl group or from the displacement of the band due to a $\pi-\pi^*$ transition in the UV region.[78] It follows from UV spectroscopic data[78] that the formation of a complex between MMA and $ZnCl_2$, for example, leads to an increase in conjugation energy in the monomer.



It was shown by EPR [80] that a complex is formed between polymethyl methacrylate (PMMA) radicals and Lewis acids, which leads to a change in properties of these radicals. Zubov et al.[80] represent the state of the radical bonded in a complex as a resonance hybrid of two structures—radical and polar:



A Lewis acid bonded in a complex with the monomer or growing radical does not act as an inert substituent but as a "complementary particle involved in the formation of an intermediate complex at the growth stage".[4]



3. Formation of triple complexes in polymerising media

In the triple system monomer–Lewis acid–organic(organoelemental) peroxide several reactions for complex formation can take place. If the monomer is MMA and the Lewis acid is $SnCl_4$, these reactions may be represented in the following manner:[34]

$$MMA + SnCl_4 \rightleftarrows [MMA - SnCl_4], \quad (8)$$

$$[MMA - SnCl_4] + MMA \rightleftarrows [MMA_2 - SnCl_4], \quad (9)$$

$$MMA + P \rightleftarrows [MMA - P], \quad (10)$$

$$P + SnCl_4 \rightleftarrows [PSnCl_4], \quad (11)$$

$$P + [MMA - SnCl_4] \rightleftarrows [P - SnCl_4 - MMA], \quad (12)$$

$$MMA + P - SnCl_4] \rightleftarrows [P - SnCl_4 - MMA]. \quad (13)$$

A molecule of organoelemental peroxide has two coordination sites—donor (O–O) and acceptor (E). According to our studies[36] complexes of different chlorides of silicon and tin having the structure R_nECl_{4-n} (E = Si, Sn, R = Alk, n = 1–4) with organoelemental peroxides have the composition 1 : 1 or 1 : 2. ^1H NMR studies on the formation of a complex between $Me_3SnOOCMe_3$ and pyridine,[45] $CHCl_3$,[83] Bu_2SnCl_2, and $SiCl_4$ [84] and the results obtained on the dependence of the change in chemical shift of the protons from the Me_3Sn and Me_3C groups on the mole fraction of the second component showed that pyridine acts as an electron donor towards the peroxide and it coordinates with the tin atom. On the other hand the tin and silicon halides, like chloroform, act as

electron acceptors and they coordinate with the peroxide bond (probably with the oxygen atom of the Me_3CO residue, which has a higher electron density).[46]

The equilibrium constants for formation of complexes between $Me_3SiOOCMe_2Ph$ and Me_3SiCl and Me_2SiCl_2 were found to be equal to 5.6 ± 0.9 and 8.3 ± 1.1 at 443 and 423 K respectively.[84]

The coordinating capacity of Lewis acids such as $SnCl_4$ or $SiCl_4$ is usually not exhausted by the addition of a single molecule of peroxide or monomer. Hence the logical conclusion is that in the presence of electron donors the process of complex formation, as depicted by equations (8), (10), and (11), can go further and result in the formation of a triple complex in which a double complex acts as an electron pair acceptor [equations (9), (12), (13)].

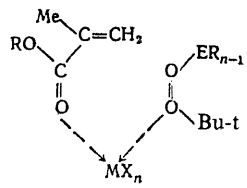
Three-component $nV\pi$-complexes that contain two monomers and a Lewis acid have been detected experimentally by IR, UV, and NMR spectroscopy.[81,82,85–88] Triple $nV\pi$-complexes of MMA–$ZnCl_2$–styrene, AN–$ZnCl_2$–styrene, methacrylonitrile-(MAN)–$ZnCl_2$–1-hexene, and MAN–$ZnCl_2$–styrene have been detected by UV spectroscopy from an analysis of the charge-transfer band in the long wavelength region of the spectrum.[85–87] Equilibrium constants and enthalpies of complex formation were calculated for some complexes. For example, the equilibrium constants for formation of an MMA–$SnCl_4$–styrene complex is equal to 0.24 and 0.67 at 298 and 233 K respectively.[86] The limiting shifts of protons in individual $nV\pi$-complexes were determined from ^{1}H NMR spectroscopic data.[82] From a quantitative analysis of the shifts and their correlation with the values calculated according to the Hückel method and the ionisation potentials of the molecules it was possible to determine the structure and possible conformations of triple complexes.

Using the known literature data on double and triple complexes that occur in the presence of Lewis acids,[4,78–88] we have developed a scheme for "including" the Lewis acid in the initiation stage of radical polymerisation involving an organoelemental peroxide.[15,34] According to this scheme double complexes are first formed. The addition of the third component to the double complex creates an energetically and sterically favourable situation for the formation of an activated complex in the initiation of radical polymerisation.

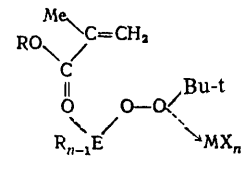
The triple systems MMA–$SnCl_4$–TBP, MMA–$SnCl_4$–$Me_3SiOOBu$-t, MMA–PCl_3–TBP, MMA–PCl_3–TBP, MMA–PCl_3–$Me_3SiOOBu$-t, and BMA–PCl_3–$Me_3SiOOBu$-t were studied using ^{1}H NMR spectroscopy in nonane in the temperature range 228–283 H by following the variation in the difference between the chemical shifts of the *cis*- and *trans*-olefinic protons of MMA or BMA (internal chemical shift ν).[34,89] The magnitude of ν depends on the structure of the monomer molecule and the distribution of electron density in it and is therefore sensitive to complex formation. Other factors (the presence of an inert solvent, temperature, concentration) have only a slight effect on it. The study of triple complexes was preceded by a study of double ones: olefin–peroxide, peroxide–Lewis acid, olefin–Lewis acid (Table 3).[34,89]

The internal chemical shift of MMA or BMA increases when $SnCl_4$ or PCl_3 is added. When the third component—an organic or organoelemental peroxide—is introduced, ν decreases. The observed chemical shift in the triple system is an average of the shifts from all the resonance forms. The values of the chemical shifts of the free monomer (MMA or BMA) and that bonded in a complex as well as the equilibrium constants for formation of double complexes served as the initial data for the calculation of the parameters of triple complexes. As a result, the formation constants of the triple complexes were obtained (Table 3).

On the basis of the strength of donor–acceptor bonds in double complexes, the most likely structure of the triple complex is that of (A), in which the relatively strong bond of monomer with Lewis acid is preserved.



(A)



(B)

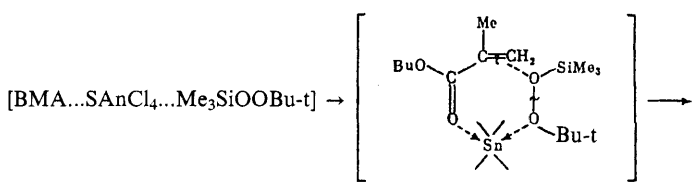
On the other hand, since we found that the formation of a complex between peroxide and monomer was possible,[34,89] structure B, in which the donor properties of the peroxide are strengthened by the supply of electron density from the monomer, cannot be completely ruled out. This type of complex (B) is probable for the system MMA(BMA)–peroxide–PCl_3.

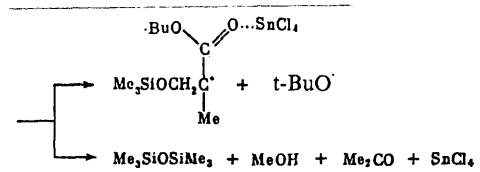
Table 3. Parameters of complex formation in double and triple systems at 253 K.

System	K*	$-\Delta H$, kJ mol^{-1}	Refs.
MMA–PCl_3	0.17±0.02	7.5±0.5	[89]
$Me_3SiOOBu$-t–PCl_3	7±3	26±9	[89]
$Me_3SiOOBu$-t–MMA	0.23±0.02	23±4	[89]
TBP–MMA	0.1±0.04	6.0±0.3	[34]
MMA–$SnCl_4$	15±2	—	[90]
MMA_2–$SnCl_4$	3±0.3	—	[90]
MMA–PCl_3–$Me_3SiOOBu$-t	34 3	29±4	[89]
MMA–$SnCl_4$–TBP	2.7—8.7	8±4	[34]

*Solution with concentration 1 mol litre^{-1} chosen as the standard state.

We believe that in a triple complex the peroxide is activated and decomposes by both a homolytic and a heterolytic mechanism at a higher rate. For example, in the triple system BMA–$SnCl_4$–$Me_3SiOOBu$-t the scheme for "including" the peroxide and $SnCl_4$ in the initiation of polymerisation of BMA may be represented in the following manner:





When the concentration of Lewis acid is increased, the rate of the parallel reaction of non-radical decomposition of the peroxide also rises. This can be assessed from the quantitative yield of $Me_3SiOSiMe_3$ that is obtained twenty four hours after mixing stoichiometric quantities of $Me_3SiOOBu$-t and $SnCl_4$ in nonane at 298 K.[15] This apparently causes the decrease in the rate of polymerisation of BMA at relatively high concentrations of $SnCl_4$.

Thus these reactions relate to the slowest and most energy-consuming stage of radical polymerisation—the initiation stage. The main role of electron donors and acceptors as catalytic components is to form complexes with the initiator, which results in activation of the latter.

IV. Use of organoelemental peroxides for the initiation of radical polymerisation and vulcanisation

The increased production of polymeric materials and the improvement of their quality are due to the development of new, highly effective initiating compositions that can affect the physico-mechanical and performance characteristics of polymeric materials. The compositions organoelemental(organic) peroxide–electron donor or organoelemental(organic) peroxide–electron acceptor are promising initiating systems. The use of organoelemental peroxides for the initiation of polymerisation or vulcanisation as well as for promoting adhesion in the system polymer–substrate has been covered in sufficient detail in two reviews.[91,92] Here we shall only dwell on certain aspects of the use of organoelemental peroxides that have recently undergone development.

MCl_n–t-BuOOH systems, where M = Al, Sn, Ge, In, P, have a high initiating capacity. MMA, styrene, vinyl chloride, and other monomers are polymerised in their presence over a wide range of temperature at high rates and with high degrees of conversion.[93–103] Polymeric materials that are obtained using Lewis acid–peroxide systems have improved physicomechanical properties, are readily processed to sheet products and fibres, can be vulcanised, and in a number of cases have a stereoregular structure.

A large amount of data has been obtained on the initiating activity of boron alkyl–organoelemental peroxide systems, which is dependent on the nature of the boronalkyl substituent, the structure of the peroxide reagent, and the monomer.[30,104–108] The initiating activity of peroxides changes according to the series:

$$Ph_4SbOOBu\text{-t} > Et_3SnOOBu\text{-t} > Et_3GeOOBu\text{-t} > > Me_3SiOOBu\text{-t} \gg TBP.$$

The high rates for generating free radicals in reactions of alkyls of elements with organoelemental peroxides are due, in our opinion, to their ability to form complexes with each other and with monomer. Energetically and sterically favourable conditions are created in a complex for decomposition of the peroxide to radicals and for reaction of the resulting radicals with the monomer.

In the initiation of polymerisation by polyfunctional peroxides such as $R_{4-n}Si(OOCMe_3)_n$, where n = 2–4, R = Me, CH_2 = CH, it is possible to obtain macroperoxysilanes.[109,110] This opens up the possibility for synthesising block copolymers of different monomers during radical polymerisation. For example, macroinitiators obtained by polymerisation of BMA and styrene up to a degree of conversion of 20% were used to initiate the secondary polymerisation of BMA and the synthesis of block copolymers.[110] The high degree of polymerisation initiated by macroperoxysilanes is characterised by the absence of the gel effect, and the addition of Lewis acids (such as $SnCl_4$) activates the decomposition of macromolecular initiators in the same way as their low-molecular analogues.

In the formation of block copolymers the initiation of polymerisation of a second monomer is possible. In particular, active polystyrene containing from 6 to 9 peroxide groups per macromolecule was used as a macroinitiator for the polymerisation of BMA.[110] Samples of polystyrene with peroxide groups in the macromolecule were prepared as a 10% solution in BMA. The block copolymer obtained (97–98%) was separated from the homopolymer by selective extraction and analysed by IR spectroscopy. It transpired that the block copolymer was enriched with BMA units. The main feature of this method for obtaining block copolymers is the virtual absence of homopolymer of the monomer being polymerised.[110]

Thus, by using multifunctional peroxysilanes it is possible to obtain block copolymers without significant inclusion of homopolymer during radical polymerisation. This method can also be applied to other monomers that are capable of radical polymerisation.

It is known that the properties of polymeric composite materials can be improved by chemical modification of the surface of the filler with compounds that act simultaneously as initiator and binder. Silicon polyperoxides are such compounds. Several methods for obtaining peroxidised fillers have been reported.[111–114] We have developed a method for obtaining modified granular fillers (Aerosil, TiO_2, Al_2O_3) by treating them with organosilicon polyperoxides in a volatile organic solvent.[115]

The grafting of an initiator to the surface of a filler results in an increase in the rate of thermal decomposition of the peroxide attached to the surface compared to the decomposition of a similar compound in the liquid phase. The reason for this lies in the specific orientation of the molecule of peroxide in the surface layer and the coordination interaction of peroxide oxygen with the surface groups or atoms, resulting in a weakening of the peroxide bond. It has been shown by chemical and electron-microscope methods that grafting of silicon peroxides to the surface of Aerosil, TiO_2, or Al_2O_3 creates on the surface of the filler chemically bonded reaction sites that can initiate the polymerisation of monomers and chemically graft the polymer matrix to the filler.[116] Homolytic decomposition of the peroxide attached to the surface of the filler results in the formation of two radicals, one of which is chemically bonded to the surface and initiates the formation of the graft polymer and the other is freed into space and either undergoes further decomposition or initiates a homopolymerisation reaction.

The polymerisation of styrene on the surface of a filler modified with silicon polyperoxide can be used to obtain a composite in which up to 30% of the polymer is grafted to the surface of the filler.[15] The formation of a grafted product takes place not only when the peroxide is initially attached to the surface but also when silicon polyperoxide is introduced in a pure state into the system of filler–monomer.[115] This indicates that silicon polyperoxide dissolved in monomer can be grafted on to the surface during polymerisation and achieves a polymer graft to approximately the same extent as in the case of the initial attachment of this peroxide to the surface of the filler.

The highest rate of graft polymerisation and the maximum yield of graft polymer are attained when vinyltri(t-butylperoxy)silane is used as the modifier. Grafting to the filler occurs via the peroxide groups, while grafting to the polymer is via the peroxide and vinyl residues.[115]

A study of the properties of polystyrene samples filled with Aerosil or Al_2O_3 the surface of which was modified with organosilicon peroxides showed that the composite polystyrene had improved impact strength and good rigidity.[115]

It was recommended that organoelemental peroxides should be used to cure rubbers, primarily organosilicon rubbers.[117–120]

A promising method for modifying synthetic materials is the introduction of peroxidate groups into an oligomer chain. When the oligomeric peroxides are heated, macroradicals are generated and they recombine to form three-dimensional structures without the additional introduction of a vulcanising agent.[121]

We have synthesised previously unreported peroxyoligoorganosilazanes that can be used to cross-link organosilicon compounds.[122]

Heat-cured compounds have been widely used in various branches of the Soviet economy, but dicumyl peroxide (DCP) is mainly used as a curing initiator, and has a number of operating problems connected with its use. The process takes place in two stages, and at the second stage a toxic volatile product—acetophenone, which has an unpleasant acrid smell—is liberated. Organosilicon peroxides such as $RSi(OOBu\text{-}t)_3$, where R = Me, CH_2 = CH, are free from such disadvantages.

A comparative study of the characteristics of vulcanisation of methylvinylphenylsiloxane oligomers in the presence of DCP and $RSi(OOBu\text{-}t)_3$ organosilicon peroxides showed that curing with the silicon peroxides starts 10–20 °C below that with DCP, and the products formed by decomposition of the organosilicon peroxides are considerably less toxic than acetophenone.

Moreover, the products formed in the presence of $RSi(OOBu\text{-}t)_3$ have higher strength and elasticity. This establishes a promising future for the chemical activation of peroxides aimed at reducing the vulcanisation temperature.

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Thus, at the present time it can be taken as reliably established that electron-donor and electron-acceptor compounds (activators) catalyse the decomposition reactions of organic and organoelemental peroxides, including those that decompose to radicals during radical polymerisation of olefinic monomers. The effect of the activators is due to the specific interaction of the components making up activator–peroxide–monomer systems and the formation of mixed double and triple complexes with a fractional contribution differing according to the nature of the activator, peroxide, and monomer.

Electron donors form a complex with peroxide by interaction of *p* (or π) electrons with vacant *d* orbitals in the heteroatom of peroxide. Complex formation weakens the peroxide bond. The rate constant for decomposition of a donor–peroxide complex has a value which is several orders higher than the decomposition constant of pure peroxide in an inert medium.

In the system monomer–peroxide–Lewis acid, together with double complexes of monomer–Lewis acid, monomer–peroxide, and peroxide–Lewis acid, labile triple complexes of monomer–Lewis acid–peroxide are formed, in which both the monomer and peroxide have a coordinate bond with the metal atom at the same time.

From the results obtained it is possible to account for the behaviour of organic and organoelemental peroxides in actual polymerising systems and to predict the main pathways for conversion of initiators in them. The latter is useful for resolving specific problems in developing required initiating systems for the preparation of polymeric materials with given properties.

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