Review

SYNTHESIS AND REACTIVITY OF GROUP IIIB ORGANOMETALLIC PEROXIDES

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Organometallic peroxides (OMPs) and their spontaneous reactions have rapidly acquired increasing importance. This is due to the development of new effective methods of synthesis of organic compounds with the use of OMPs, the stabilization of common organometallic compounds (OMCs) against oxidative destruction, the control of OMP oxidation to give useful products, and the use of OMPs as components of systems for initiating polymerization and copolymerization of vinyl monomers and the vulcanization of rubbers, sealants and so on. In the last few years the preparation of mono- and poly-component metal oxide films by OMP technology has become important in electronics and radiotechnique.

The Group IIIB OMPs have been described in numerous reviews and monographs [1–3, 4], which report their isolation and their physico-chemical properties, and the questions of their stability, photostability, and hydrolysis reactions, and interaction with OMCs.

Ten years have passed since the last reviews were published (1977, 1978 [2, 4]). During this time, much new experimental and theoretical material has accumulated: gallium and indium peroxides, which were previously unknown, have been prepared, and the

mechanism of their thermal decompositiion has been studied in detail; the sphere of reactions of Group IIIB OMPs (with solvents, alcohols, esters, aldehydes, rearrangement with α-hydrogen atom migration) has been extended, OMP complexing has been investigated and some earlier works have been rationalized. Considerable advances have been made in investigations of the synthesis of OMPs, and data on complex formation between OMCs and oxygen and hydroperoxides have helped to elucidate the mechanisms of their reactions.

The object of this review is to generalize and systematize the above new data on synthesis and reactivity of Group IIIB OMPs.

I. Preparation of Group IIIB organometallic peroxides.

The two the most general and universal methods for preparing alkylperoxides of non-transition element derivatives are [1-3, 5, 6]:

1) OMC oxidation by molecular oxygen;

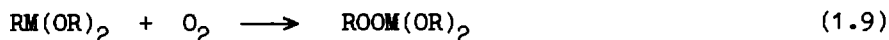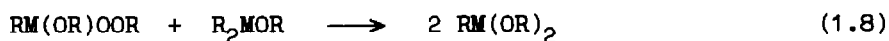2) OMC interaction (homoleptic alkyl compounds, alkoxides, alkyl halides[1]) with organic hydroperoxides.

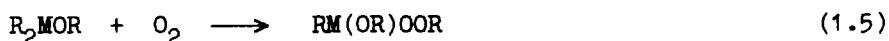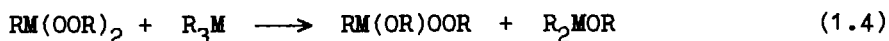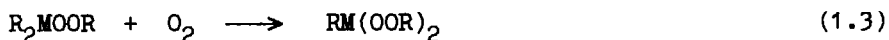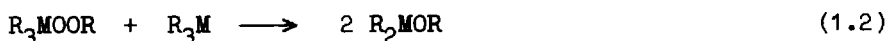The yield of OMP depends upon many factors, as the mechanism of the processes is usually complex, comprising a combination of

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[1] In this review the reactions between alkyl halides and hydroperoxides are not considered, as, in our opinion, this material is a separate study.

primary and secondary reactions, which are very specific to different reaction systems.

I.1. The autooxidation of homoleptic alkyl compounds of Group IIIB metals by molecular oxygen

The literature on the autooxidation of organo-boron and -aluminium compounds is extensive, and was covered in the previous reviews [1, 2]; in the last ten years the number of publications in this field has greatly decreased. On the other hand the investigation of the autooxidation of organo-gallium and -indium compounds has been carried out only recently [7-10], and studies of organogallium compounds are as yet very incomplete [11]. All the results emphasize the extremely high activity of Group IIIB OMCs towards oxygen. The formal scheme of the process is as follows [2]:

$$R_3M + O_2 \longrightarrow R_2MOOR \qquad (1.1)$$

$$R_3MOOR + R_3M \longrightarrow 2 R_2MOR \qquad (1.2)$$

$$R_2MOOR + O_2 \longrightarrow RM(OOR)_2 \qquad (1.3)$$

$$RM(OOR)_2 + R_3M \longrightarrow RM(OR)OOR + R_2MOR \qquad (1.4)$$

$$R_2MOR + O_2 \longrightarrow RM(OR)OOR \qquad (1.5)$$

$$RM(OR)OOR + R_3M \longrightarrow RM(OR)_2 + R_2MOR \qquad (1.6)$$

$$RM(OR)OOR \longrightarrow M(OR)_3 \qquad (1.7)$$

$$RM(OR)OOR + R_2MOR \longrightarrow 2 RM(OR)_2 \qquad (1.8)$$

$$RM(OR)_2 + O_2 \longrightarrow ROOM(OR)_2 \qquad (1.9)$$
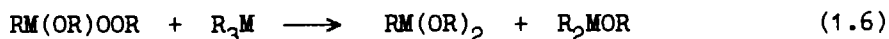
According to the reaction conditions the peroxide content of the products of autooxidation of the homoleptic alkylboron

compounds varies from 0 to 195% [1-3, 12-18] and under certain conditions it is possible to prepare the diperoxide in good yield by reaction (1.3) [1, 2, 14]. In the oxidation of organoaluminium compounds the products contain almost no peroxides [1-3, 19-24] because they are usually transformed through reactions (1.2, 1.4, 1.6-1.8). This is why the organo-boron and -aluminium compound autooxidation reaction is now rarely used for preparing the OMPs.

Unlike organo-boron and -aluminium compounds the oxidation of the second and the third M-C bonds is not typical for trialkyl-gallium, -indium and -thallium compounds [7, 8, 25-30], as is seen from Table 1.1 [7, 11].

The autoxidation of trialkyl-gallium, -indium and -thallium compounds provides an effective method for preparing alkylmonoper-oxides of the corresponding elements. Thus, autoxidation of Me_3Ga and Me_3In gives a quantitative yield of dialkyl monoalkylperoxides at -78 and $-60^{O}C$ respectively (see Table 1.1). At higher tempera-tures the OMP yield decreases because of the increasing contribu-tion of reaction (1.2). For higher trialkyl OMCs the yield of peroxide is less than 100% even at $-78^{O}C$ (Table 1.1), but at this temperature quantitative yields can be obtained when the etherates of the organo-gallium and -indium compounds are used, or 1-2 moles of diethyl ether or dioxan per mole of OMC are present. Amines, tetrahydrofuran, or esters are not effective for this purpose.

The investigation of kinetic and activation parameters of Group IIIB OMP autoxidation has not been mainly carried out in solution, because of high rates of their reaction. This is not due so much to the high reactivity of substrates to oxygen, as to the

Table 1.1

Yield of products on R_3M autooxidation (M = Ga, In, Tl) in moles per mole of initial OMC (P_{O_2} = 300 Torr, C^0_{OMC} = 0.05 - 0.1 mol·l^{-1})

R_2E	$T^O C$	R_2MOOR	R_2MOR	N_{O_2} [a]
Me$_3$Ga (heptane)	-78	0.99	0	1.00
	-21	0.62	0.38	0.84
	0	0.33	0.61	0.65
	20	0.24	0.74	0.60
Et$_3$Ga Bu$^n_3$Ga (heptane)	-78	0.7 - 0.8	0.3 - 0.2	0.6 - 0.9
Me$_3$Ga·OEt$_2$ (heptane)	-78	1.00	0	1.00
	-30	0.84	0.15	0.90
Me$_3$In (toluene)	-60	1.00	0	0.98
	0	0.57	0.43	0.76
	20	0.30	0.68	0.61
Me$_3$In·OEt$_2$ (toluene)	-78	1.00	0	1.00
	-30	0.89	0.10	0.95
Et$_3$Tl (heptane)	-50	1.00	0	1.00

[a] N - moles of oxygen absorbed per mole of OMC.

great difficulties in conducting the experiment in the liquid phase under kinetic controlled conditions.

With organoboron compounds it was shown qualitatively that

the reactivity of Group IIIB OMCs towards oxygen decreases with increasing alkyl radical length and the number of bonds oxidized [31]. The quantitative data in literature on the liquid phase autoxidation of Group IIIB OMCs are very scarce; they are available only for several organo-aluminium, -gallium, and -indium compounds, and they are summarized in Table 1.2.

It has been impossible to determine the kinetic characteristics of autoxidation of Me_3Ga in saturated or aromatic hydrocarbons[2] because of the extremely high initial rates of the process even at $-78^{\circ}C$, and an oxygen pressure of 60 Torr, an initial organometallic compound concentration of 0.06 mol$\cdot l^{-1}$ and a rate of stirring ring of 600 cycles$\cdot min^{-1}$. Under these conditions the reaction is complete in 1.5 min [7, 30].

The above given scheme of reactions (1.1–1.9), as already mentioned, is formal and does not reflect the mechanism of the process.

A variety of evidence conclusively establishes the free radical chain mechanism of the liquid phase oxidation of Group IIIB OMCs. This includes the composition and the yield of products in the autooxidation of organo-boron and -aluminium compounds [12, 13, 18, 19, 23, 24, 33– 35], the ability of systems R_3M (M = B, Al, Ga) + O_2 to initiate radical polymerization [36, 37], the loss of stereospecificity in the reaction of organoboron compounds [38, 39] and the influence of inhibitors [7, 40-43]. The principal characteristics of the process are similar to those for the

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[2] A glass vacuum installation with automatic registration of pressure was used.

<div align="right">Table 1.2</div>

Effective kinetic and activation parameters[a] of autooxidation of Group III B OMC [7, 32]

R$_3$M	1st bond		2nd bond		3d bond	
	k_o [b]	$E^{\neq}$, $\dfrac{kJ}{mol}$	k_o, $\dfrac{1}{mol \cdot s}$	$E^{\neq}$, $\dfrac{kJ}{mol}$	k_o, $\dfrac{1}{mol \cdot s}$	$E^{\neq}$, $\dfrac{kJ}{mol}$
$(C_6H_{13})_3Al$[c]	$2.28 \cdot 10^6$, $1 \cdot mol^{-1} \cdot s^{-1}$	35.0	$7.77 \cdot 10^8$	57.3	–	–
$(C_{12}H_{25})_3Al$[c]	$2.47 \cdot 10^6$, $1 \cdot mol^{-1} \cdot s^{-1}$	38.0	$2.12 \cdot 10^9$	60.8	$2.01 \cdot 10^{10}$	69.8
$(C_{14}H_{29})_3Al$[c]	$3.12 \cdot 10^7$, $1 \cdot mol^{-1} \cdot s^{-1}$	45.6	$7.41 \cdot 10^9$	64.8	–	–
$(C_{16}H_{33})_3Al$[c]	$1.15 \cdot 10^8$, $1 \cdot mol^{-1} \cdot s^{-1}$	50.0	$2.63 \cdot 10^{10}$	69.0	$2.98 \cdot 10^{11}$	79.4
Me$_3$In[d]	$10^{(4.16 \pm 0.26)}$, s^{-1}	29.06 ± 1.02	–	–	–	–
Me$_3$Ga$\cdot$OEt$_2$[c]	$10^{(2.52 \pm 0.24)}$, s^{-1}	22.74 ± 1.00	–	–	–	–
Me$_3$In$\cdot$OEt$_2$[d]	$10^{(6.73 \pm 0.72)}$, s^{-1}	41.34 ± 2.93	–	–	–	–

a) In the expression $k = k_o \cdot e^{-E^{\neq}/RT}$.

b) The autoxidation of Me$_3$In, Me$_3$Ga$\cdot$OEt$_2$ and Me$_3$In$\cdot$OEt$_2$ is zeroth order in oxygen.

c) In heptane.

d) In toluene.

oxidation of hydrocarbons in the liquid phase [44]:

initiation: $\longrightarrow$ R· (1.10)

chain growth: R· + O_2 $\longrightarrow$ ROO· (1.11)

ROO· + $>$M–R $\longrightarrow$ ROOM$<$ + R· (1.12)

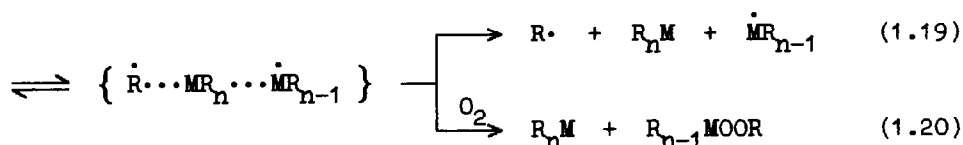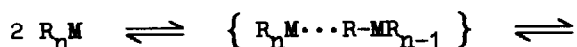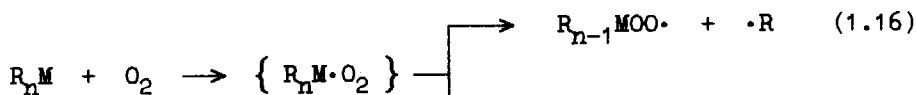chain termination: 2 ROO· $\longrightarrow$ inactive products (1.13)
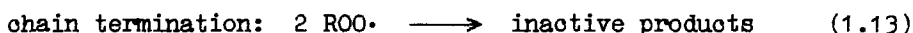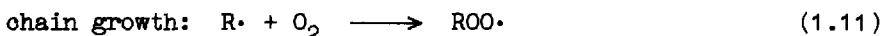
The theory of chainfree radical OMC oxidation is based on bimoleculer homolytic substitution (S_H2) by the alkylperoxyl radical at the metal centre [41]. Such S_H2 reactions [45-47] for RO·, RĊ=O, ROO· radicals of B, Al, Ga, Tl, Zn, Cd etc. have been shown to proceed many orders of magnitude faster than substitution at hydrogen in the solvent. Thus, for the S_H2 reaction of n-butylperoxyl radical at the boron atom in $B(Bu^n)_3$ the rate constant is ~10^7 times higher than that for similar reaction of benzyl hydrogen in toluene [41], with the result that only a small quantity of products come from solvent conversion and radical recombination (see Table I.I).

For OMC + O_2 systems the primary radical generation occurs by spontaneous OMC decomposition into radicals or bimolecularly through the reactions OMC + O_2 and OMC + OMC [2, 5, 48]. This mechanism is distinguished from the primary radical generation reactions in hydrocarbon autoxidation which involve tri- and bi-molecular interaction between oxygen and hydrocarbon [44]:

RH + O_2 $\longrightarrow$ R· + HO_2· (1.14)

2 RH + O_2 $\longrightarrow$ 2 R· + H_2O_2 (1.15)
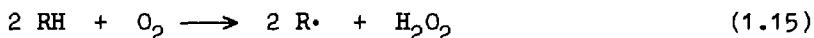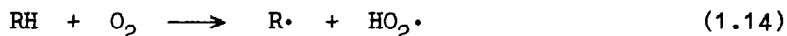
Dissociation reactions are highly improbable because the C-M bond energy is usually lower than the C-C and C-H bond energies in hydrocarbons [49].

At the present time the primary radical generation in OMC autoxidation is believed to occur by the following concurrent reactions [5]:

$$R_n M + O_2 \longrightarrow \{ R_n M \cdot O_2 \}$$

$$\longrightarrow R_{n-1} MOO \cdot + \cdot R \quad (1.16)$$

$$\longrightarrow R_{n-1} MOOR \quad (1.17)$$

$$R_n M \longrightarrow R_{n-1} \cdot + \cdot R \quad (1.18)$$

$$2 R_n M \rightleftharpoons \{ R_n M \cdots R\text{-}MR_{n-1} \} \rightleftharpoons$$

$$\rightleftharpoons \{ \dot{R} \cdots \dot{M}R_n \cdots \dot{M}R_{n-1} \}$$

$$\longrightarrow R\cdot + R_n M + \dot{M}R_{n-1} \quad (1.19)$$

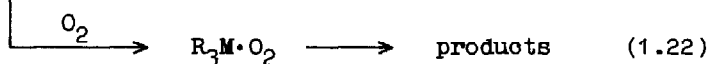$$\xrightarrow{O_2} R_n M + R_{n-1} MOOR \quad (1.20)$$

It is difficult to obtain information on the initiation of the autoxidation of Group IIIB OMCs; this is associated with the difficulty of selecting effective inhibitors [44], which can compete in the reaction with a chain-carrying radical, and are inactive in all the other reaction steps. For example, the rate of the slowest stage of the chain propagation (1.12) for tri-n- and tri-sec-butylboron is extremely high, $k_{1.12} \sim 10^5 - 10^6$ l·mol^{-1}·s^{-1}, however, almost all classical inhibitors of chain reactions extremely rapidly interact with alkyl Group IIIB OMCs. For this reason, right up to the late sixties the autooxidation of Group IIIB OMCs was thought to be non-radical in nature.

Reliable data on the primary initiation stage (1.10) of Group IIIB OMCs are absent from the literature, and there are only 2 publications concerned with this problem for organoboron compounds [45, 46]. The methods are dubious as the appropriate kinetic data on the behaviour of the inhibitors (iodine [42], galvinoxyl [43]) is lacking, but the extremely low rate of the primary initiation $\sim 10^{-7}-10^{-8}$ $1 \cdot mol^{-1} \cdot s^{-1}$ (benzene, 25 C^o, $C^o_{OMC}= 0.008 - 0.021$ $mol \cdot 1^{-1}$, $C_{O_2} = 0.002 - 0.008$ $mol \cdot 1^{-1}$) is beyond doubt.

We attempted to study the initiation of organo-gallium and -indium autoxidation by using various inhibitors (1,3,5-triphenyl-verdazyl, o-quinone, phenothiazine, o-phenylenediamine, galvinoxyl, 2,6-di-t-butyl-4-methoxyphenol). However, these are all weak inhibitors, and their kinetic behaviour was non-classical (above $2 \cdot 10^{-2}$ mol%, phenothiazine retards completely the process without change in concentration; galvinoxyl and 2,6-di-t-butyl-4-methoxyphenol decrease the rate of the process after initial completion of the retardation period; at an initial concentration of more than $1.4 \cdot 10^{-2}$ mol% 1,3,5-triphenylverdazyl promotes the process; and the induction period for 2,6-di-t-butyl-4-methoxyphenol depends nonlinearly upon the initial inhibitor concentration). We consider that the peculiarities observed are the consequence of deactivation of the inhibitor by their direct reaction with the OMC. By changing the concentration of 2,6-di-t-butyl-4-methoxyphenol inhibitor in the course of the process we have found that the Me_3Ga initiation rate in heptane (-78^oC, $P_{O_2} = 300$ Torr, $C^o_{OMC} = 0.15$ $mol \cdot 1^{-1}$) does not exceed $f \cdot 5 \cdot 10^{-7}$ $1 \cdot mol^{-1} \cdot s^{-1}$, where f is the inhibition coefficient.

In some studies [1, 2, 5] the occurrence of radicals in the OMC + O_2 system is associated with the formation of an intermediate complex OMC·O_2 (reaction 1.16). The assumption that this can occur with main-group metals is encouraged by the fact that there are similar complexes for transition element OMCs [50-52] and that many nontransition element OMCs form strong complexes with amines, ethers and some other compounds which, like an oxygen molecule, carry lone electron pairs [53]. The rate retardation effect of the donor additives (ethers, amines and others [1, 2, 7, 30]) on the OMC autooxidation process can be seen as indirect evidence in favour of OMC·O_2 complex formation. That fact may be interpreted as the saturating of the coordination capacity of a metal and an interaction of O_2 molecule only with a non-coordinated OMC molecule:

$$R_3M \quad \underset{\longleftarrow}{\overset{L}{\longrightarrow}} \quad R_3M \cdot L \qquad (1.21)$$

$$\Big\downarrow O_2 \quad R_3M \cdot O_2 \quad \longrightarrow \quad products \qquad (1.22)$$

In the present literature there are data on the formation of non-transition OMC complexes with molecular oxygen only for organo-cadmium, -mercury and -gallium compounds [9, 10, 54-57]. The absence of other examples may be due to their low stability and small equilibrium concentration. To clear up the role of OMC·O_2 complexes in the initiation of autoxidation is experimentally extremely complicated, as the high oxygen activity in the propagation reactions conceals the chemical behaviour of their complexes [58]. Again, the ability to complex with O_2 does

not mean that radical generation in the OMC + O_2 system is necessarily through such a complex. The character of the primary initiation will be due to the competition of the radical initiation reactions (reactions 1.16–1.20), which is depending on the nature of the OMC and the reaction conditions. Thus, in spite of the fact that organo-cadmium and -mercury compounds form a complex with molecular oxygen [54, 55], the chain initiation on their autooxidation proceeds without participation of the OMC·O_2 complex [2, 5].

The most complete model of the primary interaction mechanism of non-transition element OMCs with molecular oxygen, and of the electronic structure of OMC·O_2 complex, its stability and possible paths of transformation have been obtained rather recently in quantum chemical studies of the Me_3M (M = B, Al, Ga) + O_2 system [9, 10, 59–61].

The calculations point to the possible deactivating formation in the initial interaction stage of some labile donor-acceptor complexes $Me_3M·O_2$ (M = B, Al, Ga) distinguished by their multiplicity and the orientation of the O_2 fragment with respect to Me_3M. The existence of these complexes avoids the problem of the change of multiplicity by the system Me_3M-O_2 from 3 to 1 in the course of the transformation which is formally prohibited by selection rules. The enthalpy of reactions of the intermediate complex formation is estimated as $-17...-100$ kJ·mol^{-1}, depending on the nature of the metal, the multiplicity, and the structure. The optimal direction of the approach of the oxygen is along the C_3 symmetry axis of the Me_3M molecule. The results show that the transfer of

electron density from the O_2 fragment onto Me_3M is not more than 0.2 e$^-$. On complexation, the Me_3M core skeleton rearranges from planar (D_{3h}) to pyramidal (C_{3v}). The intermediates are extremely labile and easily transformed into peroxide with an activation barrier of about 25 kJ·mol^{-1} relative to an intermediate. Some selective weakening of the M-C bond is observed in the $Me_3M·O_2$ complex with multiplicity 1, which can be a precondition for its homolysis (radical generation):

$$Me_3M·O_2 \longrightarrow \left\{ Me_2MOO· , \ Me· \right\} \qquad (1.23)$$
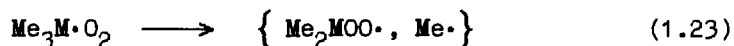
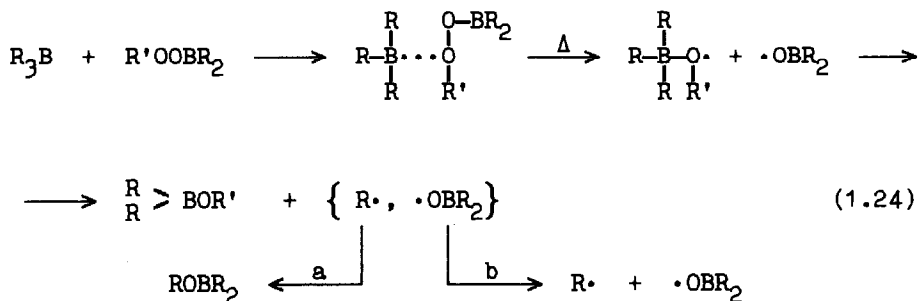Evidence for the formation of an OMC·O_2 complex has been obtained in the $Me_3Ga - O_2$ system by IR-spectroscopy of the solid film which was frozen onto silicon plates [9, 10] at -110 to -70°C. Organogallium compounds are appropriate for such investigation because of the absence of phase transitions and side processes (dialkylmonoperoxide stability) under the experimental conditions.

In the autoxidation of Me_3Ga to dialkylmonoperoxide an intermediate compound is formed which has the same absorption band as a peroxide (545 cm^{-1}); this is formed more rapidly than peroxide, then disappears. From calculation of normal peroxide vibrations and different Me_3Ga configurations, this band at 545 cm^{-1} is assigned not only to Ga-C bond vibrations in peroxide molecule but to the totally symmetrical vibrations of the C_3Ga fragment in the pyramidal intermediate. Thus the C_3Ga fragment changes from planar to pyramidal when the complex is formed with O_2; this agrees well with results of quantum-chemical calculations and shows that such a structural rearrangement is necessary for complexation of the

Me_3M moleoule (M = B, Al, Ga) with dioxygen.

These results [9, 10] oharaoterize the prooess whioh ooours in the solid phase, when the mobility of the moleoules and radioals is hindered. There are no reasons to suppose that the same prooess ooours in the liquid phase. Diffusion, solvation and so on [62] may permit an alternative radioal prooess whioh oannot ooour in the solid film.

In some papers [6, 63-66] the role of a seoondary initiation prooess for the meohanism has been disoussed. The organometallio peroxides are regarded as possible seoondary radioal souroes as in reaotion (1.24) [64-66]:

$$R_3B \ + \ R'OOBR_2 \ \longrightarrow \ \underset{\overset{|}{R}}{\overset{R}{\underset{|}{R}}}B\cdots\underset{\overset{|}{R'}}{\overset{\overset{|}{O-BR_2}}{O}} \ \overset{\Delta}{\longrightarrow} \ \underset{R \ R'}{\overset{R}{R-B-O\cdot}} \ + \ \cdot OBR_2 \ \longrightarrow$$

$$\longrightarrow \ \overset{R}{\underset{R}{}}\!\!> BOR' \ + \ \left\{ R\cdot, \ \cdot OBR_2 \right\} \qquad\qquad (1.24)$$

$$ROBR_2 \ \overset{a}{\longleftarrow} \quad \overset{b}{\longrightarrow} \ R\cdot \ + \ \cdot OBR_2$$

The effioienoy of the seoondary initiation (b) oan be very low due to the rapid reaotion in a "oage" (a) [31] or an intramoleoular peroxide rearrangement [43].

The possibility of seoondary initiation is olosely assooiated with the study of reaotivity of organometallio peroxides under the autoxidation oonditions.

Thus, oonsiderable advanoes have been made in the area of Group IIIB OMC autooxidation. The ohain free-radioal meohanism of
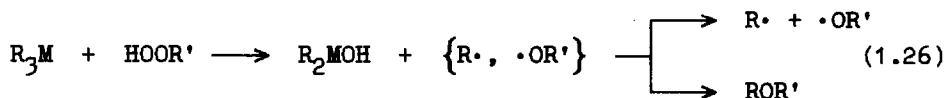
the process has been unequivocally proven in the liquid phase, the principal possibilty of OMC·O$_2$ complex formation in the initial reactions has been shown, and the dependence of the degree of OMC oxidation on the nature of the metal has been found. Yet, most results are of a qualitative and frequently contradictory character and require continuation and extension. Many theoretical questions are still unanswered; the mechanism of primary reactions has not been studied; the stage of radical initiation is unknown; and the role of organometallic peroxides in the course of the process, and of solvatation effects remains vague. Again, the kinetic and activation parameters of the total process and of its elementary stages are largely not calculated

I.2. Interaction of Group IIIB element trialkyl compounds with hydroperoxides

This reaction provides a classic route to individual OMPs. It proceeds at a high rate [1, 3, 6, 67] and two directions compete [2, 6]: nucleophilic substitution at the metal atom to conserve the peroxide bond and to give an OMP:

$$R_3M \; + \; HOOR' \longrightarrow R_2MOOR' \; + \; RH \qquad\qquad (1.25)$$
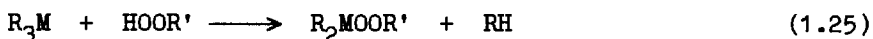
and a free-radical one accompanied by loss of peroxidic oxygen [2, 4, 67-71]:

$$R_3M \; + \; HOOR' \longrightarrow R_2MOH \; + \; \{R\cdot, \; \cdot OR'\} \longrightarrow \begin{array}{l} R\cdot \; + \; \cdot OR' \\[6pt] ROR' \end{array} \qquad (1.26)$$

$$R_3M + HOOR' \longrightarrow R_2MOR' + \{R\cdot, \ \cdot OH\} \longrightarrow \begin{array}{l} \longrightarrow R\cdot + \cdot OH \\ \longrightarrow ROH \end{array} \quad (1.27)$$

$$R_3M + R'O\cdot \longrightarrow R_2MOR' + R\cdot \qquad (1.28)$$

$$R_3M + HO\cdot \longrightarrow R_2MOH + R\cdot \qquad (1.29)$$
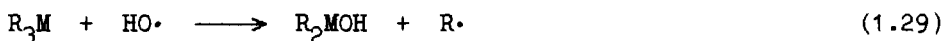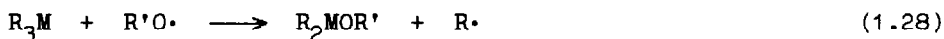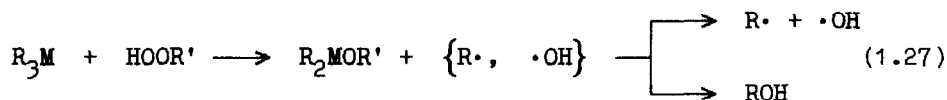
Further a similar interaction of the hydroperoxide with R_2MOH and R_2MOR' occurs.

The splitting of the second and third M-C bonds is not characteristic for Group IIIB OMCs.

The relative contribution of one or the other direction of the reaction depends upon the nature of the metal. With decreasing electronegativity of the metal from B to Tl, i.e. with increasing M-C bond polarity the contribution of the heterolytic conversion rises and that of the homolytic reaction decreases [2, 4, 71]. Thus, for trialkylboranes the contribution of reaction (1.25) does not exceed 5 – 10%, for trialkylaluminium it accounts for 60-80% [4], and from our data for trialkyl-gallium and -indium, as well as -thallium [72], it is the main one. Probably that is due not so much to the decreasing rate of radical reactions as to the considerable increase in the rate of the parallel heterolytic conversions [71].

The radical scheme of reactions (1.26-1.29) for trialkyl-boron and -aluminium compounds was established by a detailed analysis of the products formed by interacting OMC with O-deuterated hydroperoxide [4, 68, 69] and by the CIDNP effect obtained later in the reaction of R_3B with tert-butyl hydroperoxide [70]. This accounts

for the ability of these systems to initiate the low temperature polymerization of vinyl monomers [36, 73-75].

The radicals are formed essentially by reaction (1.26), and the contribution of reaction (1.27) is negligible [68, 69]. The escape of radicals from the radical pairs is close to quantitative.

The effective rate constants of radical formation from R_3B + R'OOH in hydrocarbon solution are given in Table 1.3 [67, 71].
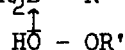
Table 1.3

The general expression of the effective rate constants for radical formation from R_3B + R'OOH (octane, 20-50°C, initial reagent concentrations 0.002 - 0.1 $mol \cdot l^{-1}$) [67]

R_3B	Hydroperoxide	k, $l \cdot mol^{-1} \cdot s^{-1}$ ($E^{\neq}$, $kJ \cdot mol^{-1}$)
$(C_3H_7)_3B$	tert-butyl	$10^{2.2} \cdot \exp\{-8/RT\}$
$(C_5H_{11})_3B$	tert-butyl	$10^{3.7} \cdot \exp\{-17/RT\}$
$(C_5H_{11})_3B$	cumyl	$10^{4.8} \cdot \exp\{-23/RT\}$
$(C_5H_{11})_3B$	1-methylcyclohexyl	$10^{3.9} \cdot \exp\{-17/RT\}$
$(C_5H_{11})_3B$	1,1-diphenylethyl	$10^{3.9} \cdot \exp\{-15/RT\}$
$(C_6H_5)_3B$	tert-butyl	$10^{1.8} \cdot \exp\{-15/RT\}$

The data listed in Table 1.3 show that the radical formation rate in the R_3B + R'OOH system (k = 0.1-25 $l \cdot mol^{-1} \cdot s^{-1}$ at 20-50°C) is considerably smaller than the rate of subsequent S_H2 radical reactions (1.28-1.29), which have at boron k = 10^5-10^6 $l \cdot mol^{-1} \cdot s^{-1}$ [41].

In the last few years it has been established that the radicals are generated in the R_3B + R'OOH system from the intermo-

lecular complex. The similar complexes $R_3B(R_2BOR', R_2BCl) \cdot$peroxide have been identified and their constants of complex formation have been measured [76-78] ($K_{30^\circ C} = 0.4 - 3\ l \cdot mol^{-1}$ [78]). Complexation is by the hydroperoxyl's α-oxygen atom [71, 78]:

$$R_2B - R$$
$$HO - OR'$$

. The small value for the effective activation energy of radical forma-tion from $R_3B + R'OOH$ (8 - 23 $kJ \cdot mol^{-1}$) (Table 1.3) confirms that radicals are formed from a complex between the reagents.

The secondary reactions in the $R_3M + R'OOH$ system are not limited to stages (1.28-1.29). With the increase in the degree of transformation, the reactions of an exchange interaction make a large contribution to [79-82]:

$$R_2MOX + HOOR' \rightleftharpoons R_2MOOR' + HOX, \quad X = H, R' \qquad (1.30)$$
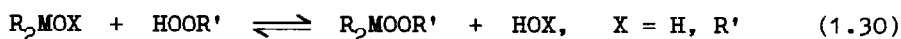
In the interaction between R_3M and hydroperoxides the yield of OMP decreases not only because of the homolytic reactions (1.26- 1.29) but also because of the transformation of the OMP in the course of the process [1-6] through a reaction with the initial OMC or because of OMP decomposition by intramolecular re-arrangement. The contribution of such transformations for organo-aluminium compounds is especially high ~100% [4, 24, 83], with the result that although the contribution of reaction (1.25) is high (60-80%) [4], OMPs have not been found in the final products [24, 83]. For boron trialkyls the role of secondary OMP tranformations is insignificant [63, 67].

We have found that in contrast to boron and aluminium peroxides, organo-gallium and -indium peroxides can be prepared by

reaction (1.25) in quantitative yield [8]. Thus, the reaction of Me_3Ga, Bu_3^nGa, and Me_3In with tert-butyl hydroperoxide in hydrocarbon solution at $-78^\circ C$ proceeds rapidly to give dialkyl monoperoxides in 100% yield (relative to the amount of the component taken in a deficiency). Substitution of the second and the more so the third alkyl groups in R_3Ga and R_3In is not observed even with a 2- or 3-fold excess of hydroperoxide. A quantitative yield of peroxide is observed under similar conditions when the etherates of trialkyl-gallium and -indium are used, but the rate of the process is decelerated, perhaps because the hydroperoxide cannot attack the coordinatively saturated metal in the etherate. The rate of the process will be determined by the equilibrium concentration of the non-solvated form R_3M, which is not large [53]:

$$R_3M \cdot OEt_2 \; \rightleftharpoons \; R_3M \; + \; OEt_2 \qquad (1.31)$$
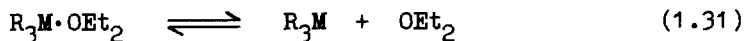
Thus, the interaction of Group IIIB element trialkyl compounds with hydroperoxides is a complicated process which has been studied rather comprehensively and can be used as an effective method for the synthesis of gallium, indium, and thallium peroxides and but not for boron and aluminium peroxides.

I.3. Interaction of Group IIIB metal alkoxides with hydroperoxides

Many OMPs [71, 79-81, 84-90] have been prepared through an exchange reaction of organometallic alkoxides with hydroperoxides:

$$R_{n-1}MOR' \; + \; R''OOH \; \rightleftharpoons \; R_{n-1}MOOR'' \; + \; R'OH \qquad (1.32)$$
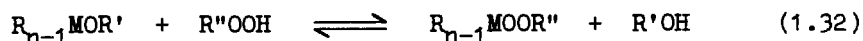
The reaction is reversible, yet in many cases the equilibrium is to the side of OMP formation, and reaction (1.32) provides a well-established route to OMPs of boron [71], aluminium [87], silicon, germanium and tin [88].

The reactivity of organometallic alkoxides with hydroperoxides has been studied comprehensively for organoboron derivatives [79-81, 84]. In [81] equilibrium constants (K), kinetic and activation parameters of the process have been evaluated (see Table 1.4). The boron monoalkoxides have the highest reactivity towards hydroperoxides; the time for equilibrium to be achieved at 10 – $50^{\circ}C$ is 0.2 – 5 s (with initial concentrations 0.002 – 0.1 $mol \cdot l^{-1}$); for dialkoxides, 0.2 – 15 s; for trialkoxides, 15 – 16 s. The equilibrium constants for the exchange reaction of the first alkoxy group vary for boron monoalkoxides within the range of 1 – 60 and above, but for di- and tri-alkoxycompounds they are not large. The further exchange of the second and the more so the third alkoxy-group is not practically realized. The process occurs with negligible heat evolution and has a small effective activation energy.

Our [91, 92] equilibrium constants of reaction (1.32) for some organogallium monoalkoxides (Table 1.5) are similar to those for organoboron compounds. Temperature has little effect on K^{3}, although the effect of the medium may be large, indicating the significant role of solvation.

The side processes (cleavage of the second and third Ga-C bonds and OMP decomposition) are not observed at room temperature.

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[3] see in more detail in Section II.2

Table 1.4

Equilibrium constants (K, 30°C), reaction enthalpy (ΔH) and kinetic parameters (k, $E^{\neq}$, k_0) for the direct exchange reaction (1.32) of R'O-organoborane fragment by R"OO-hydroperoxide fragment (octane, with initial reagent concentrations 0.002 - 0.1 $mol \cdot l^{-1}$) [81].

Alkoxy-boron	Hydroper-oxide	K	ΔH, $\frac{kJ}{mol}$	$k_{30°C}$, $\frac{1}{mol \cdot s}$	$E^{\neq}$, $\frac{kJ}{mol}$	lg k_0
$(C_4H_9O)_3B$	tert-butyl	$4.0 \cdot 10^{-3}$	-8.4	0.5	30.9	5.0
$C_3H_7B(OC_4H_9)_2$	tert-butyl	$1.4 \cdot 10^{-1}$	-16.7	$1.5 \cdot 10^2$	10.5	4.0
$C_5H_{11}B(OC_4H_9)_2$	tert-butyl	$1.3 \cdot 10^{-1}$	-16.7	2.9	28.0	5.3
$C_5H_{11}B(OC_4H_9)_2$	cumyl	$8 \cdot 10^{-2}$	-19.2	2.0	28.0	5.2
$C_5H_{11}B(OC_4H_9)_2$	1,1-diphe-nylethyl	$1.3 \cdot 10^{-1}$	-21.3	5.7	18.4	3.9
$C_5H_{11}B(OC_4H_9)_2$	1-methyl cyclohexyl	$9 \cdot 10^{-2}$	-32.6	7.6	2.5	1.3
$C_6H_5B(OC_4H_9)_2$	tert-butyl	$8 \cdot 10^{-2}$	-25.5	30	0	1.5
$(C_3H_7)_2BOC_4H_9$	tert butyl	>60	–	$>8 \cdot 10^3$	–	–
$(C_3H_7)_2BOC_4H_9$	1,1-diphe-nylethyl	6.2	–	–	–	–
$(C_3H_7)_2BOC_4H_9$	1-methyl cyclohexyl	19	–	–	–	–
$(C_5H_{11})_2BOC_4H_9$	tert-butyl	>60	–	$1.7 \cdot 10^3$	-1.7	2.9
$(C_5H_{11})_2BOC_4H_9$	cumyl	4.0	-36.4	$1 \cdot 10^3$	-15.5	0.33
$(C_5H_{11})_2BOC_4H_9$	1,1-diphe-nylethyl	25	-27.2	$1.4 \cdot 10^3$	-25.1	-1.2
$(C_5H_{11})_2BOC_4H_9$	1-methyl-cyclohexyl	16	-36.0	$\sim 5 \cdot 10^3$	-33.0	-2
$(C_6H_5)_2BOC_4H_9$	tert-butyl	1.1	-27.0	$2.2 \cdot 10^2$	–	–
$(C_6H_5)_2BOC_4H_9$	cumyl	1.0	–	$1.8 \cdot 10^2$	–	–
$(C_6H_5)_2BOC_4H_9$	1-methyl-cyclohexyl	1.8	–	$2.9 \cdot 10^2$	–	–
$(C_6H_5)_2BOSi(C_2H_5)_3$	tert-butyl	$4.5 \cdot 10^{-1}$	-41.8	40	0	1.6

Preliminary coordination of the reagents considerably influences the mechanism of the reaction (1.31), as is shown by small

Table 1.5

Equilibrium constants (K) for the reaction of organogallium
alkoxides with hydroperoxides at room temperature
(initial reagent concentrations 0.09 - 0.05 mol$\cdot$l^{-1})

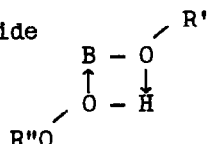| Alkoxide	Hydroperoxide	Solvent	K
Me$_2$GaOMe	MeOOH	CCl$_4$	2.56 $\pm$ 0.41[a]
Me$_2$GaOMe	MeOOH	toluene	0.99 $\pm$ 0.02
Me$_2$GaOBu^n	MeOOH	toluene	2.73 $\pm$ 0.20
Me$_2$GaOBu^t	MeOOH	toluene	102 $\pm$ 12
Me$_2$GaOBu^t	Bu^{t}OOH	heptane	9.21 $\pm$ 0.37
Me$_2$GaOBu^t	Bu^{t}OOH	CCl$_4$	7.42 $\pm$ 1.87
Me$_2$GaOBu^t	Bu^{t}OOH	toluene	2.39 $\pm$ 0.24

[a] temperature 18°C

activation energies (Table 1.4), which in some cases are negative.
Yet, evaluation of the reagent complexation in the reaction (1.32)
is difficult due to high rates of the reverse reaction and the
small concentration of the complexes, which is estimated [81] not
to exceed 10% of the initial reagent concentration.

It was possible to determine the physico-chemical characteri-
stics of the reversible coordination in the tert-butyl hydro-
peroxide - vanadium tetraisopropoxide system [90]. The values of
equilibrium constants (K = 10$^{-1.4}\cdot$exp$\{500/RT\}$, l$\cdot$mol^{-1}) and the
Bu^{t}OOH$\cdot$V(OPr^i)$_4$ complexation rate constants (k = 10$^{5.3}\cdot$exp$\{-3000/RT\}$,
l$\cdot$mol$^{-1}\cdot$s^{-1}) in toluene point to the very rapid complexation stage
proceeding with small energy consumption.

Thermochemical measurements of heat of mixing of boron alkox-
ides with some donors [93-96] has shown that the DA-bond B$\leftarrow$D in

the complex is much weaker than that for trialkylboranes. The electronic structure of the hydroperoxide complex with boron alkoxides involves the simultaneous appearance of the main DA-interaction B←O and the hydrogen bond [84, 85, 97, 98]. The hydrogen bond energy in such system accounts for about 17 $kJ \cdot mol^{-1}$ [84, 98]. The energy of the B←O bond evaluated from the enthalpy of the reaction for $(Me_3O)_3B$ complexation with tert-butyl peroxide ($\Delta H = -13$ $kJ \cdot mol^{-1}$ [84]), together with the planar → pyramidal structural reorganization energy of organoboron fragment (~50 $kJ \cdot mol^{-1}$ [99]), equals ~54 – 75 $kJ \cdot mol^{-1}$ [98].

The B←O coordination seems to be by the α-oxygen in the hydroperoxide

$$\begin{array}{c} \qquad\qquad / \text{R}' \\ \text{B} - \text{O} \\ \uparrow \qquad \downarrow \\ \qquad \text{O} - \overset{\cdot}{\text{H}} \\ / \\ \text{R"O} \end{array}$$

as evidenced by the absence of reaction

products through coordination of the β-oxygen, though in [98] the participation of both hydroperoxide oxygen atoms is supposed in complexation.

Since reaction (1.32) is reversible and boron peroxides are also known [93, 96] to possess a higher complexing ability than alkoxides, the reverse reaction (1.32) is sure also to proceed through reagent coordination. It is quite possible that complexation of alcohols with alkoxides and that of hydroperoxides with OMPs occurs as well as the exchange reactions. The exchange in the $(MeO)_3B$ + MeOH system is shown [100] to occur and at a high rate.

Thus, from the literature data for organo-boron and -gallium compounds the reaction between organometallic alkoxides and hydroperoxides can be generally used to prepare Group IIIB OMPs; yet it

is necessary to take account of the reversible nature of the process and to consider that the value of the equilibrium constant depends substantially upon the nature of the reacting compounds and of the medium.

II. Thermal decomposition of organic peroxides of Group IIIB metals in hydrocarbon solution

The thermal stability of Group IIIB OMPs depends upon many factors: the nature of the metal and its organic environment, the number of peroxide groups, the character of the medium, the presence of impurities and others [1, 2, 4, 16, 31]. Below in Table 2.1 the effective initial kinetic and activation parameters for Group IIIB OMP thermal decomposition in hydrocarbon solution are listed.

As a rule, the thermal stability of peroxides increases with growth of the length of the hydrocarbon radical and of the number of alkoxy groups.

The boron and aluminium peroxides, which do not contain M-C bonds show the highest thermal stability [2, 4]. Such peroxides have been rather well characterized, and the mechanisms and the products of their decomposition have been studied in detail.

The boron and aluminium dialkylmonoperoxides are the least stable among the known Group IIIB peroxides, and in spite of the considerable interest in them as regards their behaviour in the course of autooxidation processes, they have not been thoroughly

Table 2.1

Effective (initial) kinetic and activation parameters for
thermal decomposition of Group IIIB OMPs in hydrocarbons

Peroxide	Solvent	C_{O-O}^o, $mol \cdot l^{-1}$	k_o, s^{-1}	$E^{\neq}$, $kJ \cdot mol^{-1}$	Reference
1	2	3	4	5	6
Et_2BOOEt	heptane	0.1	$7.5 \cdot 10^4$	50.2	101
$Bu_2^nBOOBu^n$	isooctane	–	$6.0 \cdot 10^3$	46.4	43
$Pr^n(Bu^nO)BOOCu$	nonane	0.09	$3.5 \cdot 10^9$	104.5	102
$Bu^n(Bu^nO)BOOCu$	toluene	0.08	$1.7 \cdot 10^9$	104.5	102
$(Bu^nO)_2BOOBu^n$	nonane	0.11	$1.4 \cdot 10^5$	71.1	103
$(Bu^nO)_2BOOBu^s$	nonane	0.1	$4.9 \cdot 10^9$	109.1	104
$(Bu^nO)_2BOOBu^t$	nonane	0.1	$1.7 \cdot 10^9$	109.5	105
$(Bu^nO)_2BOOCu$	nonane	0.1	$3.5 \cdot 10^7$	90.7	103
$(EtO)_2BOOBu^t$	nonane	0.1	$9.0 \cdot 10^{10}$	131.7	106
$(MeO)_2BOOBu^t$	nonane	0.1	$1.4 \cdot 10^4$, $1 \cdot mol^{-1} \cdot s^{-1}$	122.5	107
$Bu^nOB(OOBu^t)_2$	nonane	0.1	$2.5 \cdot 10^{10}$	119.6	102
$Pr^nOB(OOBu^t)_2$	nonane	0.05	$5.5 \cdot 10^9$	121.2	106
$B(OOBu^t)_3$	nonane	0.1	$8.9 \cdot 10^5$	76.9	108
$(EtO)_2AlOOBu^t$	ethyl benzene	–	$3.6 \cdot 10^6$	58.5	109
$(EtO)_2AlOOBu^t$	styrene	–	$5.4 \cdot 10^{10}$	83.6	109
$(EtO)_2AlOOBu^t$	octane	0.02–0.06	–	94.5	110
$(Bu^tO)_2AlOOBu^t$	octane	0.02–0.06	–	83.6	110
$Et_2GaOOEt$	toluene	0.078	$10^{(16.2\pm1.0)}$	137.0 ± 7.0	111
$Bu_2^nGaOOBu^n$	heptane	0.084	$10^{(16.2\pm0.5)}$	134.9 ± 3.5	111
$Bu_2^nGaOOBu^n$	toluene	0.080	$10^{(15.4\pm1.6)}$	130.0 ± 10.9	111

Table 2.1 (continued)

1	2	3	4	5	6
$Ga(OOBu^t)_3$	nonane	0.26	$1.7 \cdot 10^{13}$	101.2	112
$Ga(OOBu^t)_3$	isopropyl benzene	0.15	$2.4 \cdot 10^{13}$	81.2	112
$Me_2InOOMe$	toluene	0.081	$10^{(6.5 \pm 0.6)}$	65.0 ± 4.1	a)
$Me_2InOOBu^t$	heptane	0.048	$10^{(11.3 \pm 0.3)}$	106.5 ± 2.3	a)
$Et_2TlOOEt$	octane	–	$7.9 \cdot 10^6$	72.7	11
$Ph_2TlOOBu^t$	toluene	0.1	$2.0 \cdot 10^{14}$	145.1	113
$Ph_2TlOOCu$	toluene	0.1	$3.2 \cdot 10^{17}$	169.3	113

a) Our data

investigated. The corresponding gallium, indium and thallium peroxides are considerably more stable [11, 111-115].

In the last few years we have studied thoroughly the properties of some gallium dialkylmonoperoxides in hydrocarbon solution [111, 115]. Due to the stability of the second M-C bond, the organogallium peroxides are convenient models for the study of the phenomenological regularities and reaction mechanisms of Group IIIB OMPs which proceed without M-C bond participation.

The autoacceleration of the process is a characteristic feature of the decomposition of dialkylgallium peroxides [113]. The kinetic and activation parameters of the thermal decomposition of $Me_2GaOOMe$ and $Me_2GaOOBu^t$ in hydrocarbon solution which are calculated by a complete equation of the autocatalysis* [116,

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* The rate of the process is satisfactorily expressed by a complete autocatalysis equation up to the peroxide transformation ~90%.

p.346] are given in Table 2.2 [111].

Table 2.2

The general expresstion of effective rate constants for thermal decomposition of organogallium peroxides

OMP	Effective rate constants[a]
Me$_2$GaOOMe (heptane) c^o = 0.087 mol·l^{-1}	$k_1 = 10^{(12.7\pm2.0)} \cdot \exp\left\{-(124.3\pm14.7)^{b}/RT\right\}$, s^{-1} $k_2 = 10^{(9.7\pm1.0)} \cdot \exp\left\{-(83.6\pm7.3)/RT\right\}$, l·mol^{-1}·s^{-1}
Me$_2$GaOOBu^t (heptane) c^o = 0.087 mol·l^{-1}	$k_1 = 10^{(10.6\pm0.6)} \cdot \exp\left\{-(109.1\pm4.6)/RT\right\}$, s^{-1} $k_2 = 10^{(8.1\pm1.5)} \cdot \exp\left\{-(83.4\pm11.1)/RT\right\}$, l·mol^{-1}·s^{-1}
Me$_2$GaOOBu^t (toluene) c^o = 0.088 mol·l^{-1}	$k_1 = 10^{(9.8\pm0.8)} \cdot \exp\left\{-(103.0\pm5.6)/RT\right\}$, s^{-1} $k_2 = 10^{(8.2\pm1.0)} \cdot \exp\left\{-(82.7\pm7.4)/RT\right\}$, l·mol^{-1}·s^{-1}

[a] k_1 – rate constant in the initial stage of the process,
   k_2 – rate constant in the catalytic stage of the process;
[b] kJ·mol^{-1}

For Et$_2$GaOOEt and Bu$_2^n$GaOOBu^n peroxides, autoacceleration of the process is also observed, but the indefinite induction periods do not allow carrying out the correct mathematical treatment of the kinetic curves for autocatalysis; for them the initial kinetic parameters are listed in Table 2.1.

The stability of dialkyl-gallium and -indium monoperoxides decreases with an increase in the length of the hydrocarbon radical on the metal; the absence of hydrogen on the α-carbon atom (relative to the peroxide bond) increases their stability. Organo-

indium peroxides are less stable than gallium peroxides.

The mechanism of thermal decomposition of Group IIIB OMPs was earlier supposed to be rather simple and to include, mainly, the homolysis of peroxide bond and intra- and inter-molecular 1,2-re-arrangement. However, recent investigations of gallium, indium, aluminium, and boron OMPs have shown that the process is much more complicated. It is determined by competition between the main primary reactions (spontaneous homolytic decomposition, rearrangement, interaction with a solvent) and the reactivity of the product in the secondary reactions.

For organo-boron and -aluminium peroxides the primary reactions determine the direction of the process, and the composition and yield of the products. Secondary reactions are not significant and if they appear, it is only in the final phase of transformation. For dialkyl-gallium, -indium, -thallium peroxides the secondary reactions make a major contribution and are involved in practically all the known reactions for organic and organometallic peroxides [114]: catalysis by alkoxides, reactions with alcohols, aldehydes, ketones, induced decomposition, complexation etc. Their importance can be judged by the following: without the secondary reactions the decomposition of dimethyl(methylperoxy)gallium in toluene at 110°C should be 90% complete in 8.3 hours, but in practice it takes only 55 min.

The main primary and secondary reactions of the thermal decomposition of Group IIIB OMPs in hydrocarbons will be considered in the Section below.

II. 1. Primary reactions of Group IIIB OMP
thermal decomposition

The spontaneous homolysis of the peroxide bond occurs with practically all Group IIIB OMPs:

$$>MOOR \longrightarrow >MO\cdot + \cdot OR \qquad (2.1)$$

For dialkyl-gallium, -indium, -thallium monoperoxides which do not contain a hydrogen atom on the α-carbon atom (relative to the O-O bond), the homolysis of the peroxide bond is the only primary reaction; for boron and aluminium peroxides such as $(RO)_n M(OOR)_m$ [2, 4] reaction (2.1) is the main one, but competes with the interaction with the solvent [4, 106, 110] and decreases with lowering the temperature. The activation energy for the homolysis of the O-O bond does not depend strongly upon the nature of the metal and is 120–134 $kJ\cdot mol^{-1}$ [71, 106] for boron peroxides, 103–137 $kJ\cdot mol^{-1}$ [111] for gallium and indium peroxides and 145–165 $kJ\cdot mol^{-1}$ [113] for thallium peroxides.

The contribution of reaction (2.1) for the decomposition of boron and aluminium peroxides containing an M-C bond, is negligible and the intramolecular rearrangement is dominant. For gallium, indium and thallium peroxides with hydrogen on the α-carbon atom, the contribution of reaction (2.1) decreases in favour of isomerization to non-peroxidic products by migration of the α-hydrogen atom.

Homolysis of the O-O bond has a rather high activation energy and reaction (2.1) takes place only in the absence of easier
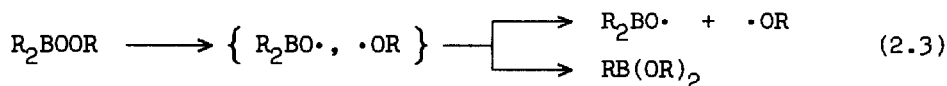
alternatives, for example, rearrangements.

The intramolecular rearrangement into isomeric oxy-derivatives is the main reaction for boron and aluminium peroxides containing one or two M-C bonds:

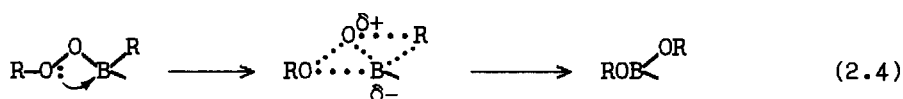$$R-\underset{|}{M}-OOR \longrightarrow -M(OR)_2 \qquad (2.2)$$
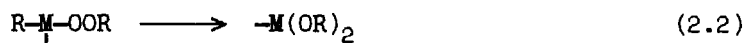
Boron and especially aluminium peroxides R_2MOOR tend to transform through reaction (2.2). Thus, [21] diethyl(ethylperoxy)aluminium even in very dilute solutions at $-75^{\circ}C$ decomposes completely into the diethoxide during 10 min. The half-life of dimethyl(methylperoxy)boron [16] in the vapor state at room temperature is 60 days.

In the initial investigations [31, 118] reaction (2.2) was supposed to occur by a radical cage reaction ("cage effect"):

$$R_2BOOR \longrightarrow \left\{ R_2BO\cdot, \ \cdot OR \right\} \longrightarrow \begin{array}{l} R_2BO\cdot \ + \ \cdot OR \\ RB(OR)_2 \end{array} \qquad (2.3)$$

Subsequent results [43] have shown that reaction (2.2) is not homolytic, and has a low enthalpy of activation (44, 57, 67 $kJ \cdot mol^{-1}$ for $Bu_2^{n}BOOBu^{n}$, $Bu^{n}B(OOBu^{n})_2$ and $Bu^{s}B(OOBu^{s})_2$, respectively) and high negative entropy of activation ($-43.I$, -39.5, $-34.I$ e.u., respectively). The small values of the activation enthalpy are in agreement with the synchronous intramolecular rearrangement process. The very low activation entropy is due to the formation of a cyclic activated complex:

$$R-O{\overset{\curvearrowleft}{\underset{\cdots}{}}}B{\overset{R}{\diagdown}} \longrightarrow RO{\overset{\cdots}{\cdots}}\underset{\delta-}{B}{\overset{O^{\delta+}\cdots R}{\diagup}} \longrightarrow ROB{\overset{OR}{\diagup}} \qquad (2.4)$$

Quantum-chemical analysis of the mechanism of reaction (2.2) [119] suggests that the 1,2-rearrangement of dialkyl(alkylperoxy)-boranes involves a concerted (synchronous) transformation with a rather unsymmetrical transition state of the bicyclobutane type. The authors [119] believe that two organoboron peroxide conformers can exist: (A) one of the open type, and (B) a cyclic one with an intramolecular coordination bond B←O, separated by a low energy barrier ($\sim$40 kJ·mol^{-1}), and the reaction (2.2) proceeds through following route:

$$\text{>B - O} \diagup^{\text{O - C}} \longrightarrow \text{>B} \diagup^{\text{O}}_{\text{O}}{\diagdown}^{\text{C}} \longrightarrow \begin{array}{c}\text{Transition}\\\text{State}\end{array} \longrightarrow \text{RB(OR)}_2$$

$$\text{(A)} \qquad\qquad\qquad \text{(B)} \qquad\qquad\qquad\qquad\qquad (2.5)$$
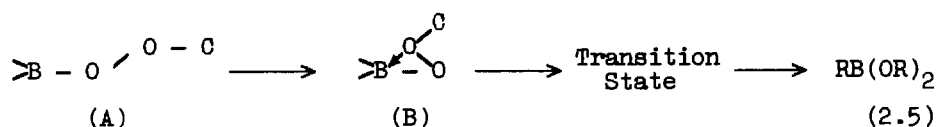
The structure of the conformer (B) is geometrically close to the transition state of the rearrangement and is characterized by a weak steric screening of the O-O bond. This may account for the small activation energy of reaction (2.2) (about 60 kJ·mol^{-1}) and for the high reactivity of dialkyl(alkylperoxy)boranes.

Intramolecular rearrangement is also characteristic for boron and aluminium peroxides such as R(RO)MOOR [22, 102] and occurs alongside the homolysis of the peroxide bond ($\sim$20%).

For some organoboron peroxides, heterolytic rearrangement in the fragment which does not contain a metal atom [38] is also observed:

$$\text{(HO)}_2\text{BOOCH(Me)Ph} \longrightarrow \text{(HO)}_2\text{BOCH(OPh)Me} \qquad (2.6)$$
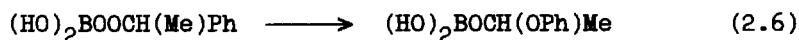
Another type of rearrangement, earlier unknown for Group IIIB

OMPs, is observed for gallium [111], indium [26], thallium peroxides [11] and involves the peroxide isomerization to a non-peroxide product through migration of a hydrogen atom from an α-carbon atom:

$$R_2MOOCH-R' \longrightarrow R_2MOH + R'CHO \qquad (2.7)$$
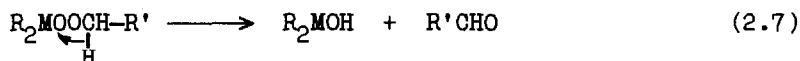
Decomposition of peroxides $Me_2GaOOMe$, $Et_2GaOOEt$, $Bu_2^nGaOOBu^n$, $Me_2InOOMe^5$, $Et_2TlOOEt$ through the reaction (2.7) is ca. 30%.

The aldehyde which is formed in reaction (2.7) may undergo further transformations depending on its reactivity relative to OMPs (the contribution of aldehyde condensation reaction on the metal oxides, in our opinion, is not large). Thus, formaldehyde formed on decomposition of OMPs containing the methyl group is extremely active in secondary reactions and it is absent from the products[6]. Aldehydes with a larger hydrocarbon radical formed from $Et_2GaOOEt$, $Bu_2^nGaOOBu^n$, $Et_2TlOOEt$ are more stable and are found in the products of the OMP thermal decomposition.

The OMP rearrangement through migration of an α-hydrogen atom is already known for Group IV [120, 121] and II [122, 123] OMPs. Reaction (2.7) is believed not to differ fundamentally from the 1,2-rearrangement of peroxides discussed above [120, 124] and occurs intramolecularly through a concerted mechanism in the 4-membered cyclic complex. It is characteristic not only for peroxides

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[5] Our data.

[6] We found a small amount of formaldehyde from the decomposition of $Me_2GaOOMe$ in heptane at 75 - 85% transformation of peroxide.

containing a hydrogen atom at the carbon atom in α-position relative to peroxide bond (A), but also at the metal (B) [124]:

$$R_{n-1}M - \underset{H}{\overset{O}{|}} + \underset{C}{\overset{O}{\|}} \qquad R_{n-2}\underset{H}{\overset{M}{\|}} \cdots \underset{O}{\overset{O}{\|}} - C \qquad (2.8)$$

(A)   (B)
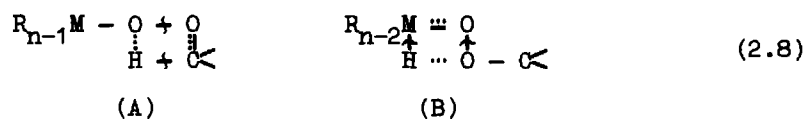
At the present time there are no established examples of the rearrangement (B) for Group IIIB OMPs.

For zinc and cadmium peroxides, which do not contain the hydrogen atom at carbon in α-position relative to the peroxide bond or at the metal atom, the similar rearrangement is realized intermolecularly at a large degree of association of peroxides:

$$\xrightarrow{} MO + CH_2O + CH_3MOC(CH_3)_3 + (CH_3)_3COH \qquad (2.9)$$
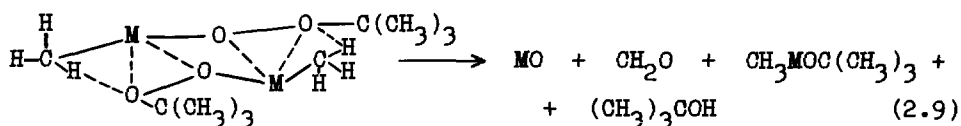
The interaction of an OMP with a solvent has been first found with $Et_3SnOOBu^t$ in n-dodecane [125]. Further it has been shown [4, 106, 126-134] that also the organic compounds of boron, aluminium and those of silicon and vanadium containing alkoxy fragments on the metal, as well as dialkylgallium monoperoxides, under mild conditions, interact with organic compounds to form oxygen-containing products in a high yield. Group IIIB metal peroxides are capable of oxidizing C-H bond in alkanes [132], and interacting with alkenes to form olefin oxides [129], oxidizing ethers to acetals [130], and hydroxylating aromatic compounds [131].

Oxidation of the substrate occurs by a molecular mechanism,

and induced decomposition of the peroxide by the solvent radicals is absent. The low activation enthalpies (45–80 kJ·mol^{-1}) for the interaction of the OMP with organic substrates and large negative $\Delta S^{\neq}$ values (40 – 50 e.u.) point to the realization of reaction through a cyclic transition state [127]:

$$\text{>MOOR} + \text{SH} \longrightarrow \left[\begin{array}{c} \text{>M} - \text{O} - \text{O} - \text{R} \\ \vdots \quad\quad \vdots \\ \text{S} - \text{H} \end{array} \right] \longrightarrow \text{>MOS} + \text{ROH} \quad (2.10)$$
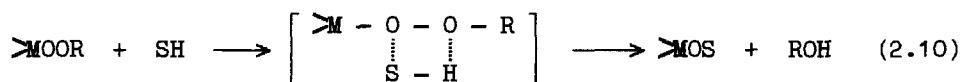
(HS – solvent)

Investigations of the influence of the viscosity of the medium and of the magnetic field on the yield of the oxidation products of the solvent indicate the absence of an alternative latent radical mechanism [128].

The activation energy of the interaction of OMPs with organic compounds is substantially lower (by 40 – 80 kJ·mol^{-1}) than the activation energy for homolysis of a peroxide bond; this is in accord with the decrease in the yield of oxidation product with increase in the temperature [127].

Boron monoperoxides oxidize paraffins (SH) with high selectivity to >BOS to form, after hydrolysis, secondary alkanols [106, 126, 127, 133]. The oxidation of alkanes by organoaluminium peroxides gives principally metaloxyderivatives which are hydrolyzed to isomeric ketones [89, 110]. The yield of ketones when paraffins are oxidized by tert-butylperoxydi(tert-butyloxy)aluminium depends upon the association of the peroxides in solution and increases with increase of the dimer fraction [110]:

$$[(Bu^tO)_2AlOOBu^t]_2 + R'CH_2R'' \longrightarrow \quad\text{[cyclic structure]}\quad \longrightarrow R'-\underset{\underset{-Al-}{\overset{\overset{-Al-}{|}}{\underset{O}{|}}}{C}-R'' + 2 Bu^tOH \quad (2.11)$$
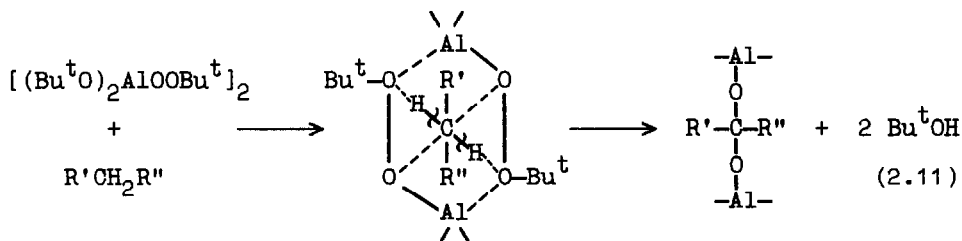
The introduction of the second peroxy group into the OMP molecule is responsible for a successive accumulation of the secondary alcohols and isomeric ketones in the reaction mixture [127]

$$-M(OOR)_2 + R'CH_2R'' \xrightarrow[-ROH]{} ROOMOCH \overset{R'}{\underset{R''}{<}} \xrightarrow[-ROH]{} -M \overset{O}{\underset{O}{<}} > C \overset{R'}{\underset{R''}{<}} \xrightarrow{2H_2O}$$

$$\longrightarrow -M(OH)_2 + \overset{R'}{\underset{R''}{>}} C \overset{OH}{\underset{OH}{<}} \xrightarrow{H_2O} \overset{R'}{\underset{R''}{>}} C = O \quad (2.12)$$
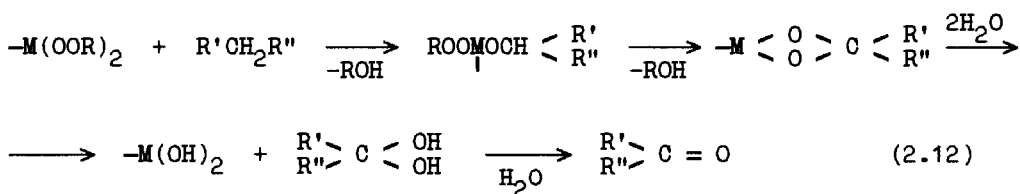
$M = B, Al, R = Bu^t$

OMP transformations in solution in ethers, and in unsaturated and aromatic compounds proceeds through a preliminary peroxide coordination with a substrate molecule [130, 131].

Epoxidation of olefins by organometallic peroxides proceeds through a concerted (synchronous) mechanism with an unsymmetric low-polarity transition state which involves interaction of electrophilic peroxidic oxygen with the π-electrons of the alkene double bond [59, 127, 135], preceded by coordination of the reagents [126, 136]:

$$\overset{>}{\underset{+}{MOOR}} \longrightarrow \text{>MOOR·} \rightleftharpoons \longrightarrow \left[R-\overset{O}{\underset{O}{\cdots}}>M< \right] \longrightarrow \overset{>MOR}{\underset{+}{}} \quad (2.13)$$
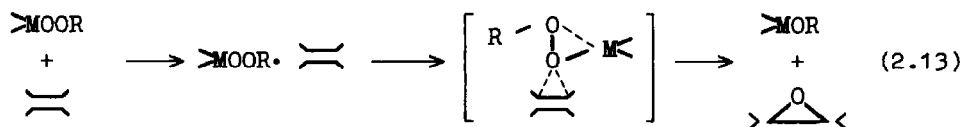
A quantitative yield of epoxide is characteristic for organoboron peroxides [129, 132]. The decomposition of organogallium peroxides in olefinic media gives 85% olefin oxide [134]. For comparison, on decomposition of Group IVB OMPs in olefins, epoxide is usually absent [137] or does not exceed 8% [126]. Such a difference can be due to a weaker complexation with olefins of Group IVB OMPs; the strength of the complex may be insufficient for complete cleavage of the M-O bond in the coordinated peroxide and only cleavage of a weakened peroxide bond in the complex occurs:

$$\left[R_3MOOR' \cdot \rightleftharpoons \right] \longrightarrow R'O \cdot + \left[\rightleftharpoons \cdot R_3\dot{M}O \right] \tag{2.14}$$
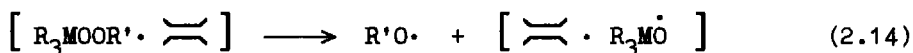
In aromatic solvents the reaction of organometallic peroxides involves hydroxylation of the benzene ring, which was established for organoboron peroxides [127, 130, 131]. The interaction proceeds by an electrophilic substitution mechanism, in which an OMP molecule rather than a free MO^+ cation seems to be the electrophile:


$$\tag{2.15}$$
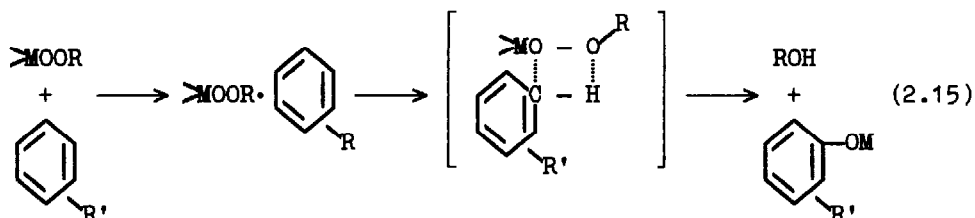
The contribution of reaction (2.15) increases with decrease in temperature, and can be quantitative [128]. The homolysis of a peroxide bond remains the second direction of the process.

II.2. Secondary reactions for thermal decomposition of Group IIIB OMPs

Earlier, in accordance with the results of research on boron and aluminium peroxides, the role of secondary reactions in the thermal decomposition of Group IIIB OMPs was considered to be insignificant [1, 2, 4]. However, as was mentioned above, in the last decade the study of the reactivity of gallium and indium peroxides has shown that these reactions can be important. The reactions of Group IIIB OMPs with various classes of compounds formed in the course of primary reactions will be considered.

The interaction with aldehydes has been studied in the case of the $Me_2GaOOMe$ and butyraldehyde in hydrocarbon solution [138, [139]. IR-spectroscopy showed [139] that the reagents interact reversibly as organic peroxides [117, 140]:

$$R_2GaOOR + R'C(O)H \rightleftharpoons R_2GaOC(R')HOOR \qquad (2.16)$$
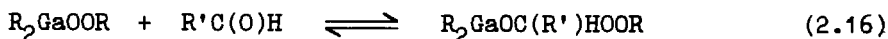
The equilibrium constant (K) for the $Me_2GaOOMe - PrC(O)H$ system in tridecane is of the form:

$$\ln K = (-5.73 \pm 1.37) + (2.82 \pm 0.44)\cdot\frac{1}{T^oK}\cdot10^3 \qquad (2.17)$$

Thermodynamic reaction parameters are as follows:

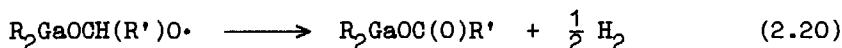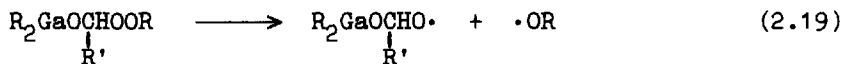$\Delta H_{298} = -23.4 \pm 3.7 \ kJ\cdot mol^{-1}$, $\Delta S_{298} = -47.6 \pm 11.4 \ J\cdot deg^{-1}$,
$\Delta G_{298} = -9.3 \pm 7.0 \ kJ\cdot mol^{-1}$.

The product is a less stable α–metalloxyalkyl peroxide, and

the effective rate constant of its thermodecomposition in heptane is given by the equation:

$$k = (2.0 \pm 0.7) \cdot 10^{13} \cdot \exp \left\{ -(116.5 \pm 10.0)^{7}/RT \right\}, \; s^{-1} \qquad (2.18)$$

The following scheme for α-galliumoxyperoxide decomposition is proposed to account for the presence of carboxylates[a] and of hydrogen in the decomposition products:

$$\underset{\underset{R'}{|}}{R_2GaOCHOOR} \longrightarrow \underset{\underset{R'}{|}}{R_2GaOCHO\cdot} + \cdot OR \qquad (2.19)$$

$$R_2GaOCH(R')O\cdot \longrightarrow R_2GaOC(O)R' + \tfrac{1}{2} H_2 \qquad (2.20)$$

$$RO\cdot \xrightarrow{\;SH\;} ROH \qquad (2.21)$$

This scheme is consistent with the decomposition mechanism of organic α-alkoxyalkyl peroxides.

The contribution of the direction of gallium peroxide decomposition through migration of an α-carbonic hydrogen atom (reactions 2.7, 2.16, 2.19-2.21) decreases with increase in the chain length of R.

Information on the reaction with aldehydes for other Group IIIB OMPs is absent. Information on the interaction of Group I, II, and IVB OMPs with aldehydes is indirect and scanty.

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[7] In kJ·mol^{-1}

[a] In some cases organogallium carboxylate tends to be transformed by a solvolysis reaction as is observed with Me$_2$GaOOMe thermal decomposition in hydrocarbons: Me$_2$GaOC(O)H + MeOH $\longrightarrow$

$\longrightarrow$ Me$_2$GaOC(O)H + HC(O)OMe

<u>Interaction with ketones.</u> Although $Me_2GaOOBu^t$ cannot give carboxylates through reactions (2.16, 2.19-2.20) because of the absence of an α-carbonic hydrogen atom, IR spectroscopy shows the formation of a carboxylate intermediate product ($\sim$0.08 mol per mol of OMP) [115]. We suppose that the interaction of OMPs with ketones[9] to form an α-metalloxyalkylperoxide follows the pattern of the reaction with aldehydes:

$$Me_2GaOOBu^t \ + \ Me_2C{=}O \ \longrightarrow \ Me_2GaO{-}CMe_2{-}OOBu^t \ \longrightarrow$$

$$\longrightarrow \ Me_2GaO{-}CMe_2{-}O\cdot \ + \ \cdot OBu^t \qquad\qquad (2.22)$$

$$Me_2GaO{-}CMe_2{-}O\cdot \ \longrightarrow \ Me_2GaOC(O)Me \ + \ Me\cdot \qquad (2.23)$$
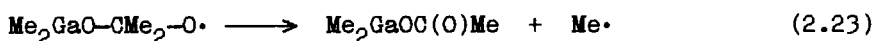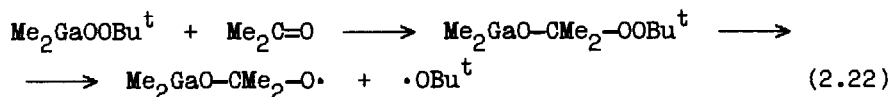
Similar reactions are known for potassium alkyl peroxides [141] and alkyl peroxides [117, 140].

<u>Catalytic decomposition of Group IIIB OMPs on metal alkyloxides.</u> The RMO product of the decomposition of Group IIIB OMPs has a catalytic effect on the thermal decomposition of organic gallium [115] and thallium [113] peroxides. It is supposed [142, 143] that RMO can be formed by the thermal decomposition:

$$R_2MOH \ \xrightarrow{\ >60^\circ C\ } \ RH \ + \ (RMO)_n \qquad\qquad (2.24)$$

IR spectroscopy shows that the product of reaction (2.24) is different from the catalytically active decomposition product, and

[9] The acetone is formed by fragmention of $Bu^tO\cdot$ radicals, which are obtained by the primary homolysis of the O-O bond.

is itself catalytically inert.

The oxide prepared by reaction (2.24) is mainly trimeric, like the initial hydroxide [144, 145], and this may be why it cannot interact with the peroxide. The authors [113] suppose that the catalytically active form of the oxide is monomeric, formed not by reaction (2.24), which also takes place in the course of OMP decomposition, but in a different way:

$$R_2MOOR \longrightarrow RO\cdot + R_2MO\cdot$$
$$\qquad \qquad \qquad \qquad \longrightarrow RMO + R\cdot \qquad (2.25)$$

The existence of compounds containing a double bond to the metal atom, as was shown for silaethylene and silanones [144, 145], is rather problematical. The monomer is supposed to be stabilized [113] by the resonance $R\overset{..}{T}i\overset{..}{-O} \rightleftharpoons R\overset{+}{T}i-O^-$.

A catalytic effect of alkylmetal oxides (RMO) on OMP thermal decomposition, analogous to that of carbonyl compounds [113] is rather convincing:

$$R_2MOOR + RMO \longrightarrow \begin{bmatrix} R_2M - OOR \\ \vdots \qquad \vdots \\ O = MR \end{bmatrix} \longrightarrow R_2MO-MR-OOR \longrightarrow$$

$$\longrightarrow R_2MO-MR-O\cdot + \cdot OR \qquad (2.26)$$

In the authors' opinion [113], the RMO is regenerated by decomposition of metaloxyl radicals or of the corresponding hydroxide:

$$R_2MO-MR-O\cdot \begin{cases} \longrightarrow R_2MO\cdot + RMO \\ \xrightarrow{SH} R_2MO-MR-OH \longrightarrow R_2MOH + RMO \end{cases} \qquad (2.27)$$

$$RO\cdot, \quad R_2MO\cdot \xrightarrow{\ SH\ } R_2MOH, \quad ROH \tag{2.28}$$

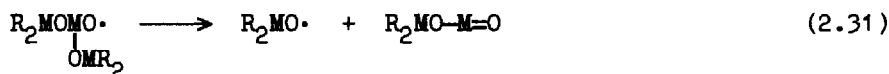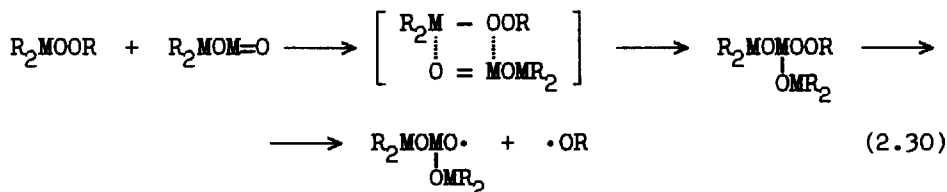Not denying this, we suppose that $R_2MO\cdot$ is more likely to undergo cleavage of a rather weak M–C bond (for Ga–C < 250 kJ·mol^{-1}) to lose a R· radical and to form a double –M=O bond. That is similar to the mechanism of stabilization of an α-oxyradical by the loss of hydrogen on the decomposition of organic and organometallic α-oxyperoxides:

$$R_2MO{-}MR{-}O\cdot \longrightarrow R_2MO{-}M{=}O + R\cdot \tag{2.29}$$
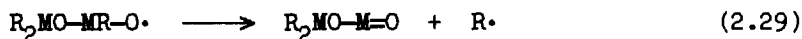
The compound $R_2MO{-}M{=}O$ can be regarded as a dimer of RMO with an active –M=O group, but it is quite probably more stable than the monomer because of π-bond delocalization. The existence of a highly-reactive compound RM=O and its possible isolation in a catalytically active form is speculative.
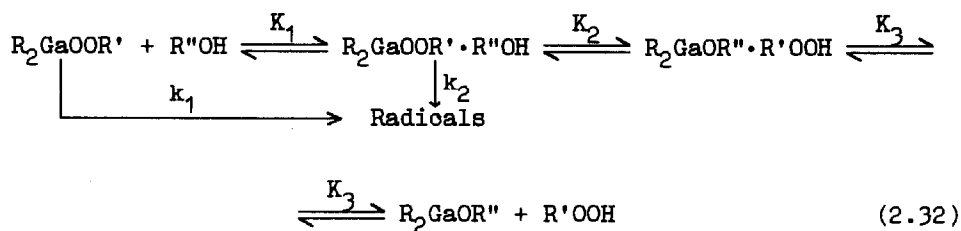
The catalytic mechanism of $R_2MOM{=}O$ is similar to that listed above (reactions 2.26–2.28):

$$R_2MOOR + R_2MOM{=}O \longrightarrow \left[\begin{array}{c} R_2M - OOR \\ \vdots \quad\ \vdots \\ O = MOMR_2 \end{array} \right] \longrightarrow R_2MOMOOR \longrightarrow$$
$$\qquad\qquad\qquad\qquad\qquad\qquad\qquad\qquad\qquad\overset{|}{O}MR_2$$

$$\longrightarrow R_2MOMO\cdot + \cdot OR \tag{2.30}$$
$$\qquad\qquad\overset{|}{O}MR_2$$

$$R_2MOMO\cdot \longrightarrow R_2MO\cdot + R_2MO{-}M{=}O \tag{2.31}$$
$$\overset{|}{O}MR_2$$

Reaction with alcohols. Alcohols as well as the other decomposition products [126, 113] were observed not to affect the rate of the thermal decomposition of boron, aluminium and thallium peroxides.

With the $Me_2GaOOMe$ – MeOH system in hydrocarbons we have found [115, 146] that the addition of alcohol accelerates the decomposition of the organogallium peroxide. Yet, with an initial alcohol concentration > 1 mol per mol of OMP, the process is slower and in alcohol solvent the decomposition is very slow.

The accelerating influence of the alcohol on the decomposition of an organogallium peroxide is similar to the effect of alcohols and other electron donors (ethers, amines, olefins, phosphines) on the thermal decomposition of organic peroxides [147–149] and Group IVB OMPs [150–152]. It is due to the primary coordination of reagents[10] which weakens a peroxide bond leading to an increase in the fraction of the reaction which involves radicals. However, unlike the other electron donors, the complexation of gallium peroxides is reversible [91, 92]. With organoboron compounds it was shown that the reverse reaction also involves coordination of the reagents [79]. Thus, the mechanism of thermal decomposition of gallium peroxide in the presence of alcohol is represented as follows [146]:

$$R_2GaOOR' + R''OH \underset{}{\overset{K_1}{\rightleftharpoons}} R_2GaOOR' \cdot R''OH \underset{}{\overset{K_2}{\rightleftharpoons}} R_2GaOR'' \cdot R'OOH \underset{}{\overset{K_3}{\rightleftharpoons}}$$

$$R_2GaOOR' + R''OH \xrightarrow{k_1} \text{Radicals} \xleftarrow{k_2}$$

$$\underset{}{\overset{K_3}{\rightleftharpoons}} R_2GaOR'' + R'OOH \qquad (2.32)$$

[10] The energetic parameters of complexation of gallium peroxides with electron donors are small and agree well with literature data for boron peroxides and silicon subgroup elements [92].

Reaction (2.32) in the absence of OMP decomposition proceeds very rapidly. The effective rate constant of reaction of $Me_2GaOOMe$ with methanol in toluene is described by a kinetic equation for the second order reaction:

$$k_{ef.} = 10^{(2.14\pm0.08)} \cdot \exp\left\{-(6220\pm447)/RT\right\}, \; 1\cdot mol^{-1}\cdot s^{-1} \quad (2.33)$$

The equilibrium is reached during ~10 s at room temperature. The effective equilibrium constants ($K_{ef.}$) of reaction (2.32) in different solvents are listed in Table 2.3.

Table 2.3

The effective equilibrium constant values of reaction (2.32)
($K_{ef.} = [R_2GaOR''] \cdot [R'OOH]/[R_2GaOOR'] \cdot [R''OH] = K_1 \cdot K_2 \cdot K_3$)
at a room temperature

Me_2GaOOR'	R''OH	Solvent	$K_{ef.}$
$Me_2GaOOMe$	MeOH	CCl_4	0.39 ± 0.07
$Me_2GaOOMe$	MeOH	toluene	1.01 ± 0.02
$Me_2GaOOMe$	Bu^nOH	toluene	0.33 ± 0.03
$Me_2GaOOMe$	Bu^tOH	toluene	$(0.98 \pm 0.13)\cdot10^{-2}$
$Me_2GaOOBu^t$	Bu^tOH	CCl_4	0.13 ± 0.03
$Me_2GaOOBu^t$	Bu^tOH	heptane	0.11 ± 0.01
$Me_2GaOOBu^t$	Bu^tOH	toluene	0.43 ± 0.04

$K_{ef.}$ is ≤ 1. The extension and especially branching of the group R'' of the alkoxide fragment shifts the equilibrium towards the initial components and reaction (2.32) becomes practically

insignificant. The maximum value of $K_{ef.}$ is observed at R' = R". The solvent strongly affects $K_{ef.}$. The general expression for $K_{ef.}$ for the $Me_2GaOOMe$ - MeOH system in toluene is given by the equation:

$$\ln K_{ef.} = -\frac{(0.756 \pm 0.028)\cdot 10^3}{T} + (2.630 \pm 0.092) \qquad (2.34)$$

$$\Delta H = 6.32 \pm 0.23 \ kJ\cdot mol^{-1}$$

The subsequent retardation of the process with the increase of the initial alcohol concentration (> 1 mol per 1 mol of OMP) cannot be due only to the exchange reactions (2.32), as with increase in the initial R"OH concentration, the equilibrium concentration of the OMP·ROH complex responsible for OMP decomposition and the OMP decomposition rate should increase and in the limit approach a maximum. The effect observed can be explained within the scope of non-specific solvation theory [147], when with the increase in concentration of an electron donor, i.e. with the increase in dielectric medium permeability, an initial state of the reacting system (OMP·electron donor complex) is solvated more than the transition state; this results in the decrease in the radical decomposition rate constant for the OMP·electron donor complex (k_2).

The hydroperoxide, produced in the reaction (2.32), can play a role in the thermal decomposition mechanism of organogallium peroxides. The methyl hydroperoxide formed from $Me_2GaOOMe$ undergoes induced decomposition by radicals derived from the gallium peroxide [147].

The interaction of gallium peroxide with alcohol is not limi-

ted to the reaction (2.32). Above $100^{\circ}C$ the cleavage of the second Ga-C bond is observed as a result of the reactions (2.32) and (2.35) [154]:

$$R_2GaOR + ROH \longrightarrow RGa(OR)_2 + RH \qquad (2.35)$$
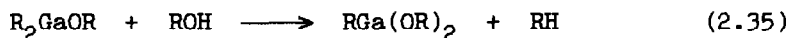
However, the contribution of reaction (2.35) in the thermal decomposition of organogallium peroxides in hydrocarbon media is negligible.

Thus, alcohols in the secondary reactions of thermal OMP decomposition can play a significant role by, firstly, acting as electron donors which can promote radical OMP decomposition and, secondly, by displacing hydroperoxides which again can induce decomposition. With large alcohol concentrations the non-specific solvation of reagents and the cleavage of the second M-C bond in the OMP are of increased importance.

Reaction with esters. We have found [155] that organogallium peroxides react with esters in hydrocarbon solution by reversible exchange of alkylperoxy and alkoxy groups [92]:

$$Me_2GaOOR' + CH_3C(O)OR'' \rightleftharpoons Me_2GaOR'' + CH_3C(O)OOR' \qquad (2.36)$$
$$(R' = Me, Bu^t; \quad R'' = Me, Et)$$
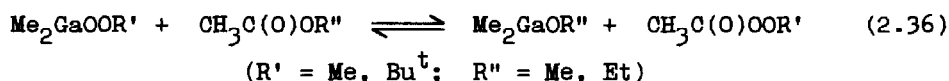
The equilibrium constant of reaction (2.36) in heptane at room temperature is small $(ca.10^{-3})$.

Reaction (2.36) is considered to proceed through complexation of reagents similar to the reaction with alcohols (2.32). The accelerating influence of ethyl acetate (in the case of an initial ester concentration to 5 mols per mol of OMP) on the $Me_2GaOOMe$

thermal decomposition rate confirms this; it can be also due to weakening a peroxide bond in the OMP·electron donor complex. In the presence of ethyl acetate we have found a substantial increase of the radical formation rate[11]. With the further increase of the initial ester concentration (> 5 mols per mol OMP) as with alcohols a decrease of the $Me_2GaOOMe$ thermal decomposition rate is observed. The reactions with alcohols and with esters show a similar trend in media with a similar dielectric permeability[12]. The explanation of this effect has been considered above.

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Thus, the thermal decomposition of Group IIIB OMPs is a rather complicated process which as the latest data show, is not limited only to primary reactions but includes a whole system of secondary reactions. The contribution of particular reactions to the mechanism of the process is to a large extent determined by the nature of the metal. Thus, for boron and aluminium peroxides the primary reactions are the main ones, but for organo-gallium, -indium, -thallium peroxides the role of the secondary reactions is significant. Considerable advances have been made in the study of secondary reactions, and new information about the mechanism of the primary reactions has been obtained.

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[11] By accumulation of bibenzyl in the toluene solution.

[12] The dielectric permeability of methanol is 32.63, and ethyl acetate is 6.00 at room temperature [156].

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