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The Role of Peroxide Derivatives of the Elements in the Selective Catalytic Oxidation of Organic Substances

I.V.Spirina, V.P.Maslennikov, and Yu.A.Aleksandrov

Various mechanisms of the selective action of catalysts in the liquid-phase oxidation of organic substances are discussed. It is shown that the high selectivity of the autoxidation of organic substances catalysed by compounds of transition and non-transition elements is due to the interaction of the substrate being oxidised with the peroxide derivative of the element formed via the reaction between oxygen or the hydroperoxide product and the catalyst.
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I. INTRODUCTION

The oxidation of hydrocarbons and other organic substances by molecular oxygen is one of the principal ways of synthesising oxygen-containing chain compounds: aliphatic acids and alcohols, phenols, ketones, epoxides, etc. According to the ideas which have developed, this process is assigned to the class of degenerate-branched chain reactions; it leads to the formation of a large number of intermediates and final products.[1-3] The development of methods for the selective conversion of the petroleum raw material into oxygen-containing compounds under mild conditions is at present one of the most important tasks in chemical science.[4] As a rule, in order to increase the selectivity, the oxidation process is carried out in the presence of catalysts such as the salts of constant- and variable-valence elements, metal complexes, Lewis acids, etc. The study of the detailed mechanisms and kinetics of the above catalytic processes is therefore especially important for the solution of the problem of increasing selectivity.

The autoxidation of hydrocarbons in the presence of various catalysts has been the subject of numerous investigations and has been discussed in detail in a series of reviews and monographs.[2,3,5-11] Various mechanisms have been proposed in the literature for the action of catalysts in the liquid-phase oxidation of hydrocarbons. The increase of process selectivity in the presence of the catalyst is usually explained either by the milder reaction conditions, which is caused by the formation of a complex between oxygen or the hydroperoxide and the catalytic additive, and the subsequent decomposition of this complex with generation of free radicals, or by the appearance of new non-radical stages in the reaction of oxygen or the hydroperoxide activated in a complex with the catalyst.[5-11]

One of the mechanisms of the catalysis of oxidation reactions of organic compounds by derivatives of various elements, which ensures a high selectivity, involves the interaction of the substrate being oxidised with the peroxide derivative of the element formed via the reaction between oxygen or the hydroperoxide product and the catalyst.[12,13]

II. CATALYSIS OF FREE-RADICAL CHAIN OXIDATION REACTIONS OF HYDROCARBONS

The catalytic action of variable-valence metal compounds in chain oxidation reactions of hydrocarbons has been investigated in detail and is widely used.[2,3,5-10] The most important details of the mechanism of these reactions have been reliably demonstrated. Thus it is generally recognised that metal compounds can participate in any stage of a degenerate-branched chain oxidation reaction of a hydrocarbon: initiation, chain propagation, or chain branching.[2,3,6,7,11]

The principal radical formation reaction in the oxidation chain initiation stage in the presence of a catalyst is the activation of oxygen and the interaction of the resulting oxygen-containing metal (M) complex with the hydrocarbon:[3,6,7,11]

$$M^{n+} + O_2 \rightleftharpoons M^{(n+1)+}O_2^{\cdot-};$$
$$M^{(n+1)+}O_2^{\cdot-} + RH \rightarrow M^{n+} + HO_2^{\cdot} + R^{\cdot}.$$

The free-radical chain oxidation of hydrocarbons is catalysed via this mechanism by low-valence complexes of iridium, rhodium, ruthenium, osmium, platinum, etc.[14-16]. The occurrence of this type of initiation has been demonstrated using inhibitors in relation to the oxidation of ethylbenzene in the presence of nickel bis(acetylacetonate)[17] and has been confirmed in a study of the oxidation of cumene catalysed by *o*-phenanthroline complexes of copper.[18]

The commonest method for chain branching in oxidation by compounds of various elements presupposes catalysis of the homolytic decomposition of the primary hydrocarbon oxidation products, namely hydroperoxides.[2]

The catalysis by variable-valence metals is based on one-electron oxidation-reduction reactions between metals ions and the hydroperoxide:[2,3,6,11]

$$ROOH + M^{n+} \rightarrow RO^{\cdot} + M^{(n+1)+} + HO^{-};$$
$$ROOH + M^{(n+1)+} \rightarrow RO_2^{\cdot} + M^{n+} + H^{+}.$$

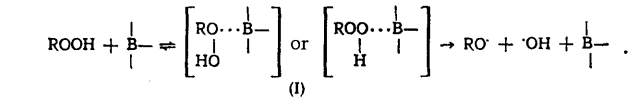
It has been shown[10,19-22] that Lewis acids and compounds of alkali and alkaline earth metals can also induce the radical decomposition of hydroperoxides. The mechanism of the catalytic action of Lewis acids and constant-valence metal salts in the autoxidation reactions of hydrocarbons has been inadequately investigated. The existence of two alternative pathways has been postulated: the homolysis of the hydroperoxide bound in a complex with the catalyst and the bimolecular interaction of this adduct with a second hydroperoxide molecule:[10,19-22]

$$ROOH \cdot Ct \rightarrow RO^{\cdot} + HOCt;$$
$$ROOH \cdot Ct + ROOH \rightarrow RO^{\cdot} + H_2O \cdot Ct + RO_2^{\cdot}.$$

where Ct is a Lewis acid or a constant valence metal ion. Furthermore, radicals may be generated in the interaction of the complex with the substitute being oxidised, for example styrene:[19]

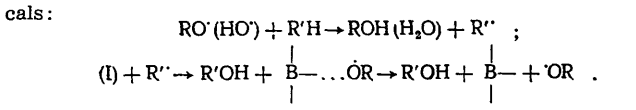
$$ROOH \cdot Ct + H_2C{=}CHC_6H_5 \rightarrow ROCH_2\dot{C}HC_6H_5 + HOCt^{\cdot}.$$

The ability of boron compounds to increase the yield of secondary alcohols in the liquid-phase autoxidation of paraffins has been known for a long time.[23] However, the mechanism of this process has not been treated unambiguously. According to some investigators,[24–26], the complex formation reaction between the catalyst and the hydroperoxide accelerates the reaction of ROOH with formation of free radicals initiating new chains:



(I)

The preferential formation of alcohols in the oxidation of alkanes catalysed by boron compounds takes place, according to Wolf et al.,[27] as a result of the decomposition of the hydroperoxide coordinated to the catalyst induced by solvent radicals:

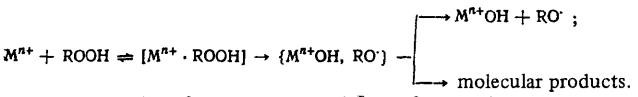


Thus the primary step in the catalytic initiation and branching of oxidation chains is complex formation between the catalyst and oxygen or the hydroperoxide product, which leads to the activation of the oxidant. The catalyst makes it possible to carry out the oxidation at high rates under milder conditions. However, there is no significant increase in the selectivity of the process as a result of its being achieved via a free-radical mechanism.[3] The mixture of oxidised products contains in this case various oxygen-containing substances.

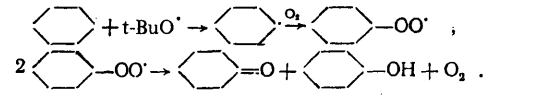
III. MOLECULAR SELECTIVE CATALYTIC OXIDATION REACTIONS OF HYDROCARBONS

1. The Mechanisms of the Selective Catalytic Oxidation of Hydrocarbons with Participation of the Catalyst–Hydroperoxide Complex

In the autoxidation reactions of hydrocarbons, catalysts not only influence the rate of oxidation but also change the ratios of the products formed in the reaction, increasing the process selectivity. Thus the catalytic acceleration of the decomposition of organic hydroperoxides by copper, cobalt, nickel, chromium, molybdenum, and vanadium compounds increases the content of ketones in the reaction mixture.[28–34] In this case the radical decomposition is accompanied also by the molecular decomposition of the hydroperoxides, whose contribution can reach 90%. Both pathways in the catalytic decomposition of hydroperoxides involve the formation of the same catalyst–hydroperoxide complex.[29,32–34] The molecular decomposition is an example of the manifestation of the "cage effect": some of the radicals formed in the solvent cage interact with the metal ions affording molecular products, while others are released into the surrounding space:[3,11,34]

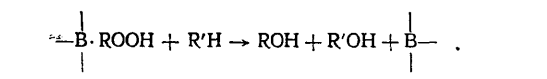


In the study of the decomposition of organic hydroperoxides catalysed by cobalt, chromium, vanadium, boron, molybdenum, titanium, etc. compounds the oxidation of the hydrocarbon used as the solvent has been observed, which leads to an increased content of alcohols or ketones in the reaction mixture.[35–41] According to Sheldon and Van Doorn,[35] up to 50% of cyclohexanol and cyclohexanone in the products of the decomposition of t-butyl hydroperoxide in cyclohexane in the presence of variable valence metal stearates and acetylacetonates is formed as a result of radical processes:



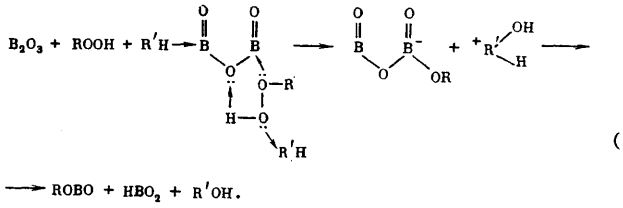
However, it has been shown[36] that the oxidation of nonane and cyclohexane by t-butyl hydroperoxide, catalysed by transition metal compounds and involving the formation of ketones and cyclohexanol, proceeds without the participation of free t-butoxy-radicals.

According to Pek Lak Von et al.,[39] only a small proportion of the radicals (10–15%) formed in the decomposition of the hydroperoxide bound in a complex with borate are released into the surrounding space and ensure the initiation of the oxidation process. The preferential accumulation of alcohols in this instance takes place as a result of the non-radical decomposition of the complex of the hydroperoxide with the catalyst in its bimolecular interaction with the paraffin:



(1)

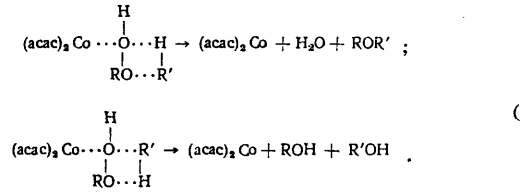
It has been suggested[40] that the catalysis of the oxidation of hydrocarbons by boron trioxide proceeds via an electrophilic substitution mechanism:



(2)

According to Eqns.(1) and (2), the increased yield of alcohols is caused by the formation of two alkanol molecules—one from the hydroperoxide and the other directly from the paraffin.

The participation of hydrocarbons with a labile C–H bond in the decomposition of cumenyl hydroperoxide catalysed by cobalt acetylacetonate has been described.[41] A mechanism has been proposed according to which the hydroperoxide forms a coordinate bond with the catalyst and there is simultaneous activation of the hydrocarbon forming part of the composition of the solvate shell of the adduct. The ternary complexes formed decompose via a non-radical mechanism:



(3)

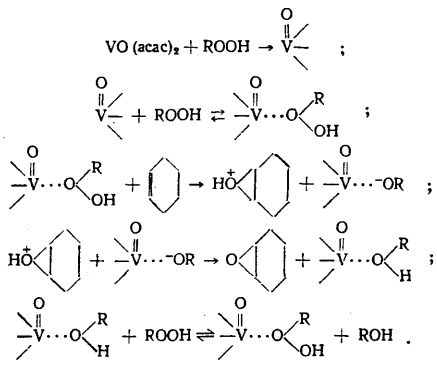
The contribution of molecular decomposition to the overall reaction of the hydroperoxide depends on the nature of the solvent and increases with decrease of the strength of the C–H bonds in the hydrocarbon. Thus cumenyl hydroperoxide reacts to the extent of 40% via the molecular pathway in ethylbenzene.[41] Since methylphenylmethanol was not detected among the reaction products, the authors[41] believe that the process proceeds via the mechanism (3).

Thus the significant increase of the selectivity of the autoxidation of hydrocarbons occurs when, together with the homolytic decomposition of the hydroperoxide bound in a complex with the catalyst, there is a possibility of its reaction via the

molecular mechanism. The molecular pathway in many instances is an example of the "cage effect". Certain catalysts are capable of involving the hydroperoxide in an oxidation reaction via the C–H bonds of the hydrocarbon, which leads to an increased yield of oxygen-containing products. It has been suggested[41] that this process represents molecular interaction of the catalyst–hydroperoxide complex with the solvent.

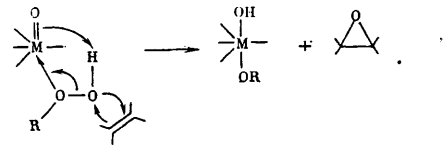
The high selectivity of the catalytic epoxidation of olefins by hydroperoxides is also caused by the molecular character of the process. This is indicated by the lack of influence by oxygen on the rate of epoxidation, the passivity in this reaction of catalysts reacting with hydroperoxides to form free radicals, and the stereospecificity of the catalytic epoxidation. The absence of a single point of view on the mechanism of this process is noteworthy; only the involvement in it of the metal in the highest oxidation state is not open to doubt.[9,42,43,46]

According to some investigators,[9,35,42–48] the catalytically active species in these processes is the complex of the catalyst with a hydroperoxide molecule, with the aid of which oxygen is transferred to the olefin. Thus a mechanism has been proposed for the epoxidation of cyclohexene by t-butyl hydroperoxide in the presence of vanadyl acetylacetonate,[44] according to which the first stage involves the rapid activation of the metal by the hydroperoxide, i.e. the transition of the metal to the highest valence state. This is then followed by the rapid and reversible formation of an active complex of the catalyst with a hydroperoxide molecule. The complex formation reaction induces the heterolysis of the O–O bond with transfer of the hydronium cation to the substrate. The elimination of a proton and its transfer to the alkoxide anion, bound to the complex, lead to the formation of the olefin oxide and the catalyst–alcohol complex. The interaction of this complex with the hydroperoxide entails ligand exchange and the regeneration of the active species:[44]

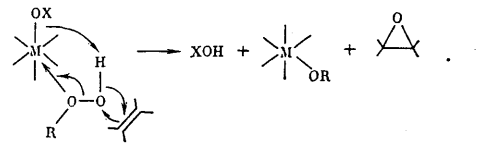


An analogous mechanism has been proposed[35] for the epoxidation of cyclohexene by t-butyl hydroperoxide catalysed by $Mo(CO)_6$. According to Sheldon,[43] catalysts based on tungsten(VI), vanadium(V), and titanium(IV), act in the same way.

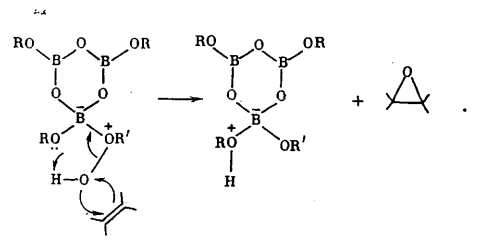
From the parallel variation of the electron-accepting properties of the catalytic additive and the rate constants for the epoxidation reaction, it has been suggested[27,35,47,48] that the function of the catalyst is to withdraw electron density from the oxygen atoms of the peroxide bridge, i.e. the catalyst acts in this instance as a Lewis acid. Two probable mechanisms have been proposed for the reaction of the catalyst–hydroperoxide complex with the olefin.[35] For compounds containing the M=O fragment, the process proceeds via a cyclic transition state:



The second mechanism has been proposed for compounds containing the M–OX (X = H, R) group, which acts as a proton acceptor:[35]



The epoxidation of olefins by alkyl hydroperoxides in the presence of metaborates has been explained analogously:[27,47–49]



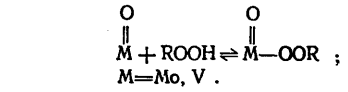
Consequently the molecular conversion of the hydroperoxide coordinated to the catalyst in the reaction with the saturated or unsaturated compound to form oxygen-containing products can be the cause of the high selectivity of the catalytic autoxidation of hydrocarbons and the epoxidation of olefins. The formation of complexes of the hydroperoxide with the compounds of transition and non-transition elements used as catalytic additives has been demonstrated by kinetic and physicochemical methods.[3,11,22,26,32] However, the numerous experimental data obtained do not conflict with the hypothesis that peroxide derivatives of the elements participate in selective catalytic processes.

2. The Involvement of Peroxide Derivatives of the Elements in Selective Catalytic Processes

(a) *The formation of intermediate alkyl peroxide derivatives of the elements in the liquid-phase catalytic oxidation of hydrocarbons.*

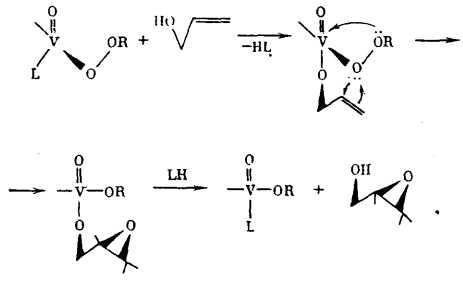
According to Mimoun[12] and Spirina et al.,[13] organoelemental peroxides play an active role in the hydroperoxide epoxidation of olefins and their conversion into ketones, catalysed by added compounds of non-transition and transition elements.

Thus in the middle 1970s, it was suggested[50,51] that, in the epoxidation of olefins in the presence of molybdenum and vanadium compounds, the accumulation of the peroxides of these elements may be a result of the reactions of the corresponding molybdenyl and vanadyl derivatives with the alkyl hydroperoxide:



The higher reactivity of allyl alcohols compared with olefins and their high *syn*-selectivity indicate the participation of the peroxides of transition elements in the catalytic epoxidation of unsaturated compounds.[42,52–55] In this case one of the

ligands in the organo-metallic peroxides is substituted by the allyloxy-fragment and the epoxidation takes place intramolecularly, the disposition of the reacting fragments favouring the formation of the *syn*-epoxyalcohol:



(4)

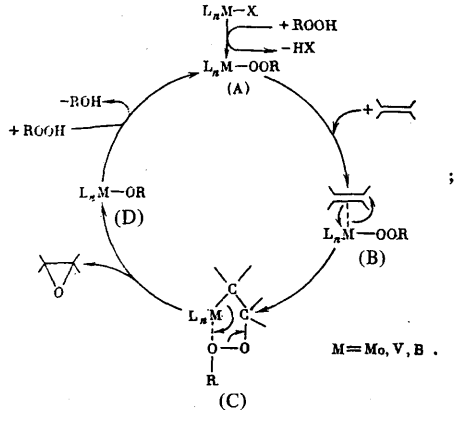
The high stereoselectivity of the epoxidation of aryl-alcohols by t-butyl hydroperoxide in the presence of tri(t-butoxy)aluminium is caused also by the participation of organoelemental peroxides in this process, whose mechanism is assumed to be analogous to Scheme (4).[56]

From the results obtained in a number of studies,[57–60] the catalytic cycle illustrated in Scheme I has been proposed to explain the epoxidation of olefins and allyl alcohols by hydroperoxides, catalysed by molybdenum, vanadium, and boron compounds.[12] It is suggested that the active species in the reaction are the organometallic peroxides (A). The process involves the formation of a complex of the unsaturated compound with the peroxide of the given element (B), which is accompanied by the peroxymetallation of the substrate. This reaction proceeds via the formation of a five-membered peroxometallocyclic intermediate (C), which decomposes to the epoxy-compound and the alkoxy-derivative of the metal (D). The interaction of the alkyl hydroperoxide with compound (D) leads to the regeneration of the initial organoelemental peroxide (A).

However, the occurrence of the stage involving the formation of compound (B) in catalysis by boron compounds is in our view extremely unlikely, since, according to Nesmeyanov and Sokolik,[61] the addition of an alkene to an organoboron compound is possible only at the boron–carbon bond at temperatures in excess of 100 °C. The olefin is not inserted in the boron–oxygen bond.

The possibility of the formation of intermediate peroxide derivatives of vanadium and cobalt in catalytic liquid-phase oxidation reactions of hydrocarbons has been postulated[62,63] from kinetic data obtained in the study of the reactions of t-butyl and cumenyl hydroperoxides in the presence of cobalt and vanadium acetylacetonates.

Scheme I



According to Makin et al.,[64] the interaction of borates with hydroperoxides leads to the establishment of the equilibrium

$$ROOH + B(OR')_3 \rightleftharpoons B(OOR)(OR')_2 + R'OH \quad (5)$$

Direct proof of the formation of alkyl peroxide derivatives of boron, vanadium, molybdenum, and tungsten in the reactions of alkyl peroxides with the derivatives of these elements and their participation in selective oxidation reactions has been obtained.[65–72]

The study of the interaction of a mixture of t-butyl hydroperoxide with the organoborane $R_mB(OR')_{3-m}$, where $m = 0 - 2$, R = C_3H_7, C_5H_{11}, or C_6H_5, and R' = C_4H_9 [65–88] or with derivatives of quadrivalent or quinquevalent vanadium [$V(OC_4H_9)_4$ and $VO(OC_4H_9\text{-}t)_3$][69,70] by IR and ^1H NMR spectroscopy demonstrated that the alkoxy-group is exchanged for the alkylperoxy-fragment in the system. It is preceded by complex formation between the reactants. Depending on the nature of the organo-elemental compound, the process takes place during a fraction of a second or over a period of several minutes. The yield of the alkyl peroxide derivative of the element for the equimolar reactant ratio at 20 °C is between 10 and 90%.[65–70] Organoelemental peroxide derivatives of boron, aluminium, silicon, vanadium(V), and cobalt(III) have been obtained by a reaction analogous to reaction (5).[13,69,73–75]

The study of the oxidation of alkanes by t-butyl hydroperoxide catalysed by boron, aluminium, silicon, titanium, vanadium, and palladium compounds[13,69,76–80] demonstrated that at 50–160 °C paraffins are converted into oxygen-containing products—aliphatic alcohols and ketones, in nearly quantitative yields (Table 1).

Table 1. The yields of the products of the oxidation of paraffins by the system t-butyl hydroperoxide–derivative of the element (in moles per mole of the peroxide which has reacted).

Paraffin	c_{hp}, M	Element-containing additive	c_a, M	t, °C	Yield: alkanols	Yield: alkanones	Refs.
Dodecane	0.10	$(C_4H_9O)_3B$	0.10	150	0.48	—	[76]
Octane	0.10	$(C_3H_3F_4O)_3B$	0.10	130	0.98	—	[80]
Pentane	0.10	$(t\text{-}C_4H_9O)_3Al$	0.01	50	—	0.49	[77]
Nonane	0.10	$(C_4H_9O)_4Si$	0.10	160	0.84	—	[80]
Nonane	0.10	$(C_4H_9O)_4Si$	0.05	140	0.42	0.11	[80]
Octane	0.10	$(C_4H_9O)_4Ti$	0.005	60	0.02	0.29	[79]
Octane	0.12	$(t\text{-}C_4H_9O)_3VO$	0.02	50	—	0.30	[69, 78]
Octane	0.10	$(CF_3COO)_2Pd$	0.01	60	—	0.40	[79]

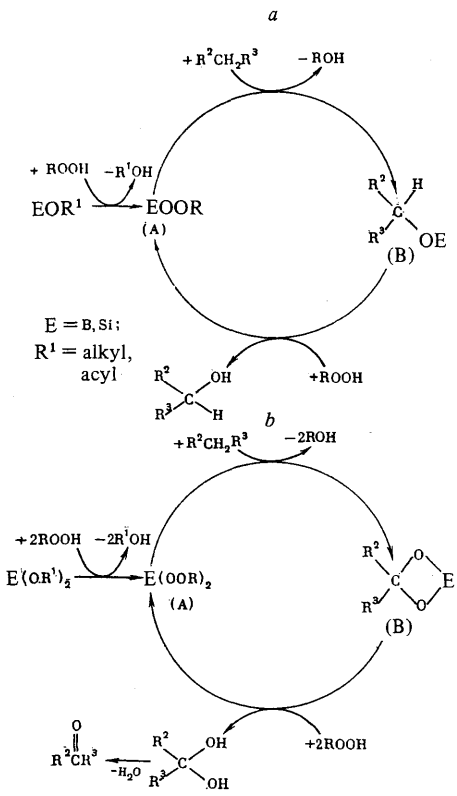
Notation: c_{hp} is the concentration of t-butyl hydroperoxide and c_a the concentration of the additive.

The oxidation of hydrocarbons by alkyl hydroperoxides in the presence of catalysts—alkoxy– or acyloxy-derivatives of the elements—can be achieved in the catalytic cycles illustrated in Scheme II. The boron and silicon compounds in cycle *a* catalyse mainly the conversion of paraffins into secondary alcohols. Cycle *b* operates in the catalysis of the oxidation of hydrocarbons by derivatives of aluminium, titanium, vanadium, and palladium, which leads to aliphatic ketones. The oxidising agents in this process are the organoelemental peroxide (A), which interacts with the C–H bonds of the substrate to form organoelemental compounds containing a fragment of the hydrocarbon oxidised (B), and the alcohol corresponding to the hydroperoxide. The element-containing derivative (B) gives rise to the oxidation product (the alcohol or ketone)

under the influence of the excess hydroperoxide and the initial organoelemental peroxide is regenerated. The operation of Scheme II has been confirmed also by the fact that the products of the oxidation of paraffins by the alkyl hydroperoxides–organoelemental compound system (with the equimolar reactant ratio) contain no free alcohols or ketones, with the hydrocarbon skeleton corresponding to the initial alkane.[79,80]

These compounds are formed either when an excess of the hydroperoxide is used or as a result of the hydrolysis of the reaction mixture.

Scheme II



E = Al, Ti, V, Pd; R¹ = alkyl, acyl.

In order to confirm the participation of organoelemental peroxides in catalytic oxidation processes, a detailed study has been made[13,69,76–80] of one of the stages in the catalytic autoxidation of hydrocarbons—the thermal decomposition of a series of alkyl peroxide derivatives of boron, aluminium, silicon, vanadium, and palladium in solutions in paraffin. It was found that the peroxides of these elements interact with hydrocarbons to produce in the hydrolysed reaction mixture high yields of the oxidation products identical with the oxygen-containing compounds obtained in the hydroperoxide oxidation of alkanes catalysed by non-peroxide derivatives of the elements (Tables 1 and 2).

The character and structure of the peroxide derivative and also its state in solution determine the composition of the hydrocarbon reaction products. Thus boron and silicon monoperoxides oxidise paraffins with a high selectivity to organoelemental compounds, which affords secondary aliphatic alcohols after hydrolysis.[80,81] The introduction into the molecule of the peroxide of the given element of one or two additional alkylperoxy-groups leads to the accumulation of aliphatic ketones together with alcohols in the hydrolysed reaction mixture.[76,79–81] The oxidation of alkanes by aluminium, vanadium, or palladium peroxide leads to the preferential formation, under mild conditions, of element-oxyderivatives, which hydrolyse to the isomeric ketone.[77–80]

Table 2. The yields of the products of the oxidation of paraffins by element peroxides (in moles per mole of the peroxide which has reacted, after the hydrolysis of the reaction mass).

Paraffin	Peroxide*	c_0 **	t, °C	Yield		Refs.
				s-alkyl-alcohols	alka-nones	
Dodecane	$(C_4H_9O)_2BOOR$	0.10	150	0.48	—	[79]
Octane	$(C_3H_3F_4O)_2BOOR$	0.10	130	0.98	—	[80]
Nonane	$C_4H_9B(OOR)_2$	0.05	140	1.66	0.15	[81]
Octane	$(C_2H_5O)_2AlOOR$	0.02	70	—	0.01	[77]
Octane	$(t\text{-}C_4H_9O)_2AlOOR$	0.04	70	—	0.15	[77]
Nonane	$(C_4H_9O)_3SiOOR$	0.08	160	0.84	—	[80]
Nonane	$(C_4H_9O)_2Si(OOR)_2$	0.05	140	0.83	0.22	[80]
Octane	$(t\text{-}C_4H_9O)_2V(O)OOR$	0.03	20	—	0.42	[69]
Octane	$CF_3C(O)OPdOOR$	0.002	80	—	0.50	[79]

*R = t-C_4H_9.
**Initial peroxide concentration.

The peroxides of elements are capable of more than the oxidation of saturated hydrocarbons at the C–H bond. They interact with alkenes to form olefin oxides and methyl ketones,[12,71,72,82–87] they oxidise ethers to acetals[88] and alcohols to aldehydes and ketones;[56,75] they hydroxylate aromatic and unsaturated compounds[80,89,90] and they lead to the ring expansion in cyclic acetals, converting them into diol monoethers[91] (Table 3).

Table 3. The yields of the products of the oxidation of organic substances by element peroxides (in moles per mole of the peroxide which has reacted, after the hydrolysis of the reaction mass).

Peroxide*	Substrate oxidised	t, °C	Product	Yield	Refs.
$(C_4H_9O)_2BOOR$	Dibutyl ether	90	Acetals of butyraldehyde	0.56	[88]
$(C_4H_9O)_2BOOR$	Anisole	90	*o*- and *p*-methoxyphenols	0.99	[90]
$(C_4H_9O)_2BOOR$	Butyl phenyl ether	90	*o*- and *p*-butoxyphenols	0.97	[88]
$(C_4H_9O)_2BOOR$	Toluene	90	*o*- and *p*-cresols	0.80	[90]
$(C_4H_9O)_2BOOR$	Mesitylene	90	Mesitol	0.85	[90]
$(C_4H_9O)_2BOOR$	Oct-1-ene	120	1,2-Epoxyoctane	0.97	[82]
$(C_3H_3F_4O)_2BOOR$	Mesitylene	80	Mesitol	0.99	[90]
$(C_4H_9O)_2SiOOR$	Mesitylene	150	Mesitol	0.06	[80]
$(C_4H_9O)_2SiOOR$	Oct-1-ene	150	1,2-Epoxyoctane and s-octenyl alcohols	0.08 0.46	[80]
$CF_3C(O)OPdOOR$	Oct-1-ene	20	Hexyl methyl ketone	0.90	[84–86]
$(PPh_3)_2Pt(CH_3)OOR$	Oct-1-ene	80	Hexyl methyl ketone	0.80	[87]
$(CH_3)_2GaOOR$	Hex-1-ene	120	1,2-Epoxyhexane	0.80	[83]

*R = t-C_4H_9.

The data described above make it possible to explain fairly reliably the decrease of the rate of reaction observed in the autoxidation of alkanes in the presence of boron-containing

additives, with simultaneous increase of the yield of secondary alcohols.[23] The alkyl hydroperoxide accumulated in the autoxidation of the paraffin reacts with the catalyst to form an organoboron peroxide. The probability of chain branching in the oxidation process then diminishes, because the homolytic decomposition of the boron peroxide proceeds at higher temperatures than the decomposition of the corresponding alkyl hydroperoxide. The molecular reaction of the organoboron peroxide with the initial alkane is accompanied by the formation of secondary alcohols, which increases the selectivity of the oxidation reaction.

(b) *The mechanisms of the oxidation of organic compounds at the C–H bond by alkyl peroxides and peroxo-complexes of the elements.*

In the study of the interaction of organoelemental peroxides (Table 2) with organic compounds it has been observed that the oxidation of the substrate is accompanied by the disappearance of peroxide oxygen.[13,69,76–81] Analysis of the composition of the products of the decomposition of the element peroxides in various organic solvents and also the character of their accumulation show that the element peroxides react via two parallel pathways in solutions in organic compounds:

1) via the oxidation of the solvent:

$$EOOR + HR' \rightarrow EOR' + ROH;$$

2) homolytically with dissociation of the peroxide bond:

$$EOOR \rightarrow EO^{\cdot} + \dot{O}R.$$

The interaction of an organoelemental peroxide with the hydrocarbon used as the solvent was observed for the first time in the thermal decomposition of t-butylperoxytriethylstannane in n-dodecane.[92]

The kinetic parameters of the oxidation of organic substances by organoelemental peroxides and of the homolytic decomposition of peroxide compounds have been determined.[80–82,88,90] The activation energy for the homolytic cleavage of the peroxide bond is significantly higher (by 10 to 20 kcal mol^{-1}) than the activation energy for the interaction of element-containing peroxides with organic compounds. The decrease of the yield of the oxidation products with increase of the process temperature is consistent with this finding.[13]

It has been demonstrated by a thermochemical method that the reaction of organoelemental peroxides in solutions in ethers and in unsaturated and aromatic compounds proceeds via the preliminary formation of a complex of the peroxide with a solvent molecule. The constants for the complex formation reactions of t-butylperoxydi(butoxy)borane with organic substances, calculated by the method of Becker et al.,[93] range from 0.16 to 0.35 litre mol^{-1} (at 20 °C).[80,94] The 1:1 complex formed then decomposes as a result of the oxidation of the organic substrate or homolytically, generating two hydroxy-radicals.[13,80,88,90]

As stated above, organoelemental peroxides interact with the organic substances being oxidised to form element alkoxide derivatives of the substrate. When the reactions proceed via a free-radical mechanism, these compounds can accumulate only on decomposition of the organoelemental peroxide compound induced by solvent radicals R'•:

$$EOOR + R'^{\cdot} \rightarrow EOR' + RO^{\cdot}.$$

However, the reaction rate constant is independent of the initial peroxide concentration and remains unchanged when inhibitors of free-radical reactions (galvinoxyl, ionol) are introduced into the system.[80,82,88,90] Furthermore, as the process temperature is reduced, the yield of oxidation products increases. Consequently, hydroxy-derivatives of the elements, containing the substrate radical, appear in reactions involving the oxidation of organic compounds by organoelemental peroxides in the absence of the induced decomposition of alkyl peroxide derivatives of the elements. They are formed via the molecular mechanism (6) or the cryptoradical mechanism (7):

$$EOOR + HR' \rightarrow \left[\begin{array}{c} EO\text{—}OR \\ \vdots \quad \vdots \\ R'\text{—}H \end{array}\right] \rightarrow EOR' + ROH \quad ; \qquad (6)$$

$$EOOR + HR' \rightarrow \{EO^{\cdot} + R'^{\cdot} + ROH\} \begin{cases} \rightarrow EOR' + ROH \quad ; \\ \rightarrow EO^{\cdot} + R'^{\cdot} + ROH \quad . \end{cases} \qquad (7)$$

The rate of release of radicals from the solvent cage is then correlated with the variation of the viscosity of the medium.[10] The study of the influence of the viscosity of the medium on the interaction of t-butylperoxydi(butoxy)borane with a series of hydrocarbons ranging from hexane to hexadecane at 150 °C[80] revealed that a change in solvent viscosity from 0.168 to 0.532 cP does not affect the kinetic parameters and the yield of the products of this reaction (Table 4). The data in Table 4 support the molecular mechanism, but they can also arise from a cryptoradical process when the cage effect is manifested in this reaction to an inadequate extent.

Table 4. The influence of the viscosity of the medium η on the oxidation of alkanes by t-butylperoxydi(butoxy)borane at 150 °C and an initial peroxide concentration of 0.10 M.[80]

Hydrocarbon	η_{150}, cP	$10^5 k_{eff}$, s^{-1}	W, mol mol^{-1}	$10^7 k_{ox}$, litre $mol^{-1} s^{-1}$
Octane	1.168	3.0	0.48	3.0
Decane	0.249	3.1	0.46	3.3
Dodecane	0.339	3.2	0.48	3.1
Tridecane	0.380	3.1	0.45	3.3
Hexadecane	0.532	3.3	0.47	3.2

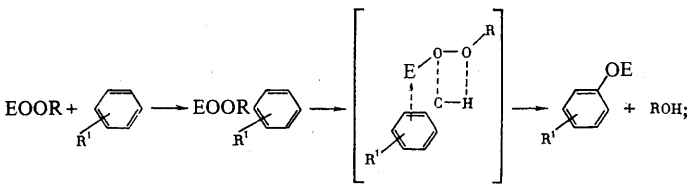
Notation: W is the yield of s-alkyl alcohols, k_{eff} the effective rate constant for the disappearance of the peroxide oxygen, and k_{ox} the rate constant for the oxidation of alkanes.

In the study of the oxidation of mesitylene by t-butylperoxydi-(1,1,3-trihydrotetrafluoropropoxy)borane in magnetic fields with an induction of 0.05–0.4 T, it was observed that the yield of mesitol diminishes by 5–15% compared with the yield in the Earth's magnetic field.[95] This effect can be explained as follows. The peroxide investigated reacts via two parallel pathways in solutions in organic substances: via the oxidation of the substrate and homolytically with formation of two hydroxy-radicals. The magnetic field acts on the liquid-phase radical reactions at the stage involving the recombination of two radicals in the cage. The rate of transition of the radical pairs from the singlet to the triplet state and the fraction of these states and ultimately also the yield of the product of the recombination within the cage depend on the induction of the magnetic field. In the oxidation of mesitylene by an organoboron peroxide, which proceeds via a cryptoradical or molecular mechanism, the yield of mesitol is independent of the induction of the magnetic field. On the other hand, the rate of the parallel process in which radicals are released from the cage (via the triplet state) varies with the induction, which leads to the observed magnetic effect.

Thus the results obtained in the study of the influence of the viscosity of the medium and of the magnetic field on the oxidation of organic substances by element peroxides indicate

the molecular character of the interaction of organoelemental peroxides with organic substrates.

The molecular mechanism of this process has also been confirmed by data for the oxidation of aromatic compounds by element peroxides. In the study of the hydroxylation of toluene and mesitylene by organoelemental peroxides at 90 °C [80,90,95] no products of the interaction of the radicals EO· and RO· with the CH_3 groups of the aromatic compounds were detected in the reaction mixtures. The mechanism of the action of element-containing peroxides in the reaction with aromatic derivatives is analogous to the mechanism of the hydroxylation of the latter by organic hydroperoxide (or hydrogen peroxide)–Lewis acid systems, i.e. an electrophilic substitution reaction obtains in the given instance:[13,90,95]



E = B, Si; R = t-C_4H_9; R' = CH_3, OCH_3, OC_4H_9.

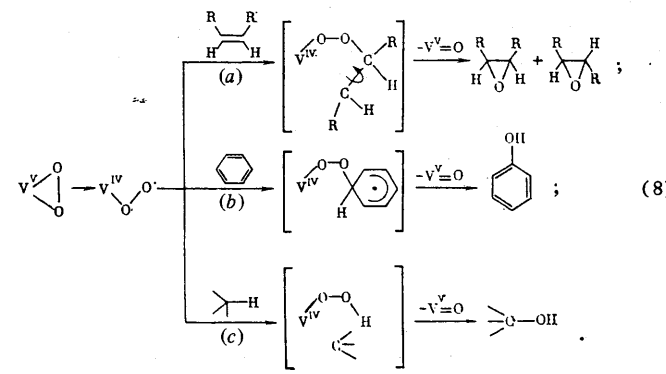
Consequently, in many cases the active oxidising agents in the catalytic autoxidation of organic substances are organoelemental peroxides formed as a result of exchange between the intermediate in the oxidation of hydrocarbons (a hydroperoxide) and the catalytic additive. Alkyl peroxide derivatives of the elements oxidise organic compounds with formation of products whose composition is identical to that obtained using peroxide forms of these elements as the catalyst.[13,76–82,90] The high selectivity of the catalytic oxidation is caused by the interaction of the element peroxides with organic compounds via a molecular mechanism.

The compounds of certain transition elements, used as catalysts of the autoxidation of hydrocarbons, are capable of binding molecular oxygen with formation of peroxo-complexes of the metals.[5,12,96] The peroxide character of the oxygen coordinated to the metal is indicated by IR spectroscopic data for these compounds[5,96] and also by the finding that the peroxo-complexes can be obtained both by the reaction of hydrogen peroxide with derivatives of elements containing the M=O bond[12,97–99] and as a result of the direct interaction of molecular O_2 with the metal complex.[5,12] Furthermore, hydrogen peroxide was evolved in the hydrolysis by strong acids of the adducts of molecular oxygen and palladium and platinum complexes.[12]

Like the alkyl peroxide derivatives of the elements, the peroxo-complexes of metals participate in the catalytic oxidation of saturated hydrocarbons[5,6,11,16–18,99–101] and arenes.[4,99,101] The mechanism of the interaction of the oxygen complex of the metal with the hydrocarbon depends on the nature of the metal complex and the substrate being oxidised; it can be of the free-radical, cryptoradical, or molecular type. The involvement of the peroxo-complexes of metals in the radical-chain oxidation of hydrocarbons, described above (Section II), does not lead to a significant increase of the process selectivity.

The covalent and anionic oxoperoxo-complexes of vanadium(V) of the type $VO(O_2)(O–N)L_IL_2$ or $[VO(O_2)(Pic)_2]^-A^+L$ (where O – N = pyridine-2-carboxylate, Pic = picoline-2-carboxylate, L_1, L_2 = H_2O, MeOH, or hexamethylphosphoramide, and A^+ = H^+ or PPh_4^+) in aprotic media under mild conditions, epoxidise olefins and hydroxylate aromatic hydrocarbons to form phenols and hydroxylate alkanes to form alcohols and ketones in yields up to 50, 60, and 25% respectively.[99] The peroxo-complexes of vanadium(V) differ sharply in their reactivities from the analogous molybdenum(VI) compounds.[57,58,86] The vanadium complexes are active only in aprotic solvents, epoxidise olefins non-stereospecifically, and behave as hydroxylating agents. From experimental data, the authors[99] suggested that peroxovanadium(V) complexes are homolytically converted into the reactive V^{IV}–O–O· species in aprotic media. This distinguishes them from the peroxo-complexes of rhodium and molybdenum, investigated elsewhere,[57–60] which interact with olefins via the 1,3-dipolar addition of the fragment $M^+–O–O^-$.

A cryptoradical mechanism has been suggested[99] for the reaction of peroxovanadium(V) complexes with hydrocarbons:



(8)

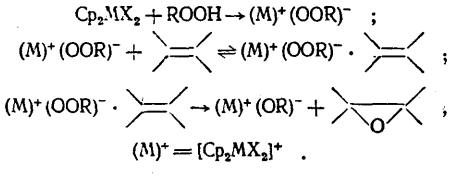
The peroxochromium complex $Ph_3POCrO(O_2)_2$ in the mixed alkane–methylene chloride–t-butyl alcohol solvent oxidises saturated hydrocarbons to alcohols and carbonyl compounds at room temperature. It has been suggested that the mechanism of this reaction is described by an equation analogous to that for pathway (*c*) in Scheme (8).[101] A characteristic feature of the mechanism proposed[99,101] is the combination of the stages involving the reduction of the metal in the peroxo-complex to $M^{(n-1)+}OO^·$ and the formation of a new radical species as a result of the interaction of this radical with the olefin or arene [see formula (8), pathways (*a*) and (*b*). In its interaction with the paraffin, $M^{(n-1)+}OO^·$ is converted into the metal hydroperoxide $M^{(n-1)+}OOH$ and an alkyl radical [see formula (8), pathway (*c*)]. These intermediate compounds are then oxidised to vanadium(V) or chromium(VI) derivatives and oxygen-containing organic products.

The one-electron oxidation-reduction reactions with participation of the transition metal ion and the hydroperoxide in the catalytic oxidation of hydrocarbons are well known. Furthermore, it has been shown[70] that derivatives of quadrivalent vanadium and t-butyl hydroperoxide, taken in 1:1 proportions, react with one another at room temperature to form vanadium(V) compounds. The re-reduction of the latter to vanadium(IV) derivatives under these conditions takes place to an extent not greater than 5%. Consequently, in the oxidation of organic substances by peroxo-complexes of vanadium and chromium, the occurrence of oxidation-reduction reactions of the type $M^{n+} \rightarrow M^{(n-1)+} \rightarrow M^{n+}$ is unlikely.

In our view the oxidation of hydrocarbons by peroxo-complexes of vanadium and chromium with formation of olefin oxides as well as alcohols and phenols probably proceeds without the participation of radicals.

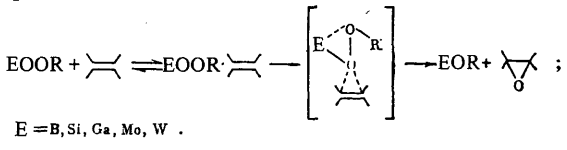
Thus the high selectivity of the catalytic liquid-phase oxidation of organic substances is due to the interaction via a molecular mechanism of the peroxide derivatives of the elements with the C–H bonds of the substrate being oxidised.

(c) *The mechanisms of the interaction of peroxide derivatives of the elements with olefins.* According to Aleksandrov et al.,[71,72] t-butyl hydroperoxide epoxidises olefins at a high rate and with a quantitative yield in the presence of compounds of the type Cp_2MX_2 (where Cp = cyclopentadiene, M = Mo or W, and X = Cl, Br, or I). The epoxidising agent in this process is the metal peroxide formed on oxidation of the initial molybdenum or tungsten compound. The process is described by the scheme:



Alkyl peroxide derivatives of molybdenum of the type $[Cp_2.MoX_2]^+ (OOR)^-.ROOH$ have been synthesised by the reaction of biscylopentadienylmolybdenum halides with t-butyl hydroperoxide and their high reactivity in the epoxidation of cyclohexene has been demonstrated.[71]

As stated above (Table 3), the alkyl peroxide derivatives of boron, silicon, and gallium interact with alkenes to form olefin oxides. The alkyl peroxide derivative of the element reacts with the olefin bimolecularly and the epoxidation takes place as a result of the interaction of the electrohpilic peroxide oxygen atom with the π electrons of the double bond in the alkene.[13] The reaction is preceded by the formation of a complex between the reactants:[80,94]

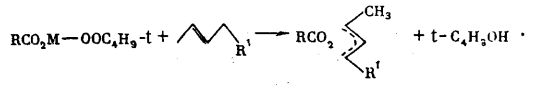


E = B, Si, Ga, Mo, W .

The possibility of the formation of transition states of this type has been confirmed by quantum-chemical calculations.[102,103]

The reactivity of the peroxides of different elements in the epoxidation reaction is determined by the electrophilic character of the peroxide oxygen atoms, which is in its turn related to the acid properties of the heteroatom of the organoelemental compound. The heteroatom, which has an occupied *p* or *d* orbital, interacts with the unshared electron pairs of the peroxide oxygen atoms, which renders the latter more electrophilic and hence more reactive in relation to olefins. There is no information about the electrophilicity of organoelemental peroxides in the literature, but one can postulate that it is correlated with the variation of the acidity of the full oxides of these elements. According to Sheldon and Van Doorn[35] and Tanabe,[104] the properties of the oxides of the elements as Lewis acids weaken in the sequence $MoO_3 \gg Ga_2O_3 > V_2O_5 > B_2O_3 > SnO_2 \gg SiO_2$. The above data for the reactivities of molybdenum, gallium, and boron peroxides in the epoxidation of olefins are consistent with this series. Among the oxides of the elements enumerated, the weakest Lewis acid is SiO_2. Consequently silicon peroxide should not epoxidise olefins effectively. Indeed, on interaction with oct-1-ene, t-butylperoxytributoxysilane forms not more than 0.1 of a mole of octene α-oxide per mole of the peroxide which has reacted, while t-butyl-peroxydibutoxyborane epoxidises oct-1-ene quantitatively under analogous conditions (Table 3).[80]

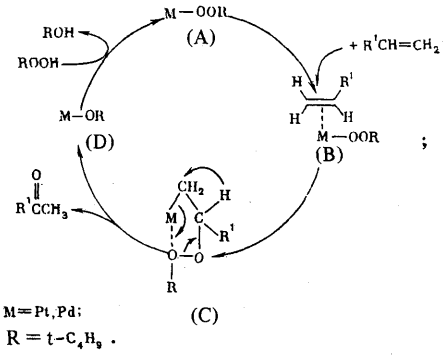
The peroxide derivatives of Group VIIIB elements, whose electrophilic character is weak, convert α-olefins into methyl ketones (Table 3). Thus palladium(II) and platinum(II) t-butylperoxycarboxylates oxidise α-olefins to the corresponding methyl ketones at 20 °C in dry benzene over a period shorter than 10 min (the olefin : peroxide ratio is 50) in 90% yield.[84–86] Aldehydes or other ketones are not formed. β-Olefins are oxidised very slowly or not at all, forming a stable π-allyl complex on substitution of the t-butylperoxy-group at the metal by the olefin:



Platinum(II) t-butyl peroxides of the type *trans*-$(PR_3)Pt(R^1)-OOC_4H_9$-t (where $R_1 = CH_3$, CF_3, or an arene) are also effective in the oxidation of oct-1-ene to 2-octanone (80 °C, 16 h, yield of ketone 80%).[87]

The mechanism of the conversion of α-olefins into ketones by organic peroxide derivatives of palladium and platinum can be represented, according to the authors,[84–87] by a cycle analogous to the catalytic cycle in the hydroperoxide epoxidation of unsaturated compounds in the presence of molybdenum and vanadium derivatives[12] (Scheme III).

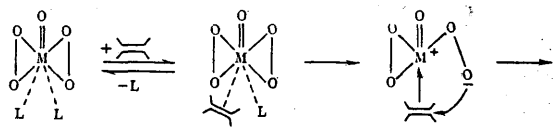
Scheme III

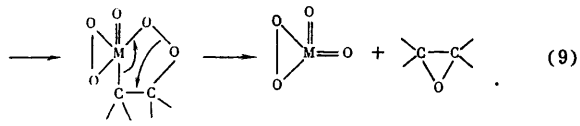


M = Pt, Pd; R = t-C_4H_9 .

The key stage in this mechanism is the peroxymetallation process, which is preceded by the coordination of the olefin to the metal (B). The intermediate five-membered adduct (C) formed decomposes with cleavage of the O–O bond, which is followed by the β-hydride transfer with formation of methyl ketone and the t-butoxy-derivative of the metal (D). In the presence of an excess of the hydroperoxide, the t-butoxy group is substituted by the t-butylperoxy-group and the initial metal peroxide is regenerated.

The peroxymetallation process in the epoxidation of olefins and their conversion into ketones by metal peroxo-complexes has been justified in detail.[12,58–60,105–108] The peroxo-complexes of molybdenum and tungsten of the type $L_2MoO(O_2)_3$ (where L are organic ligands with very pronounced electron-donating properties) epoxidise olefins in organic solvents with a high selectivity (the yield of the epoxide can reach 50–90% relative to active oxygen).[58] The reaction takes place in two stages: the reversible coordination of the olefin to the metal is followed by the irreversible transfer of oxygen to the olefin. It is assumed[12] that the oxygen transfer takes place via a cyclic mechanism involving the 1,3-dipolar addition of the peroxo-complex to the olefin with formation of a five-membered metallocyclic compound, which is converted into the epoxide and the dioxo-complex of the metal:

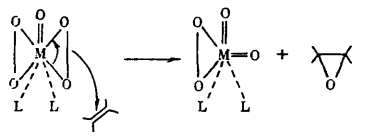




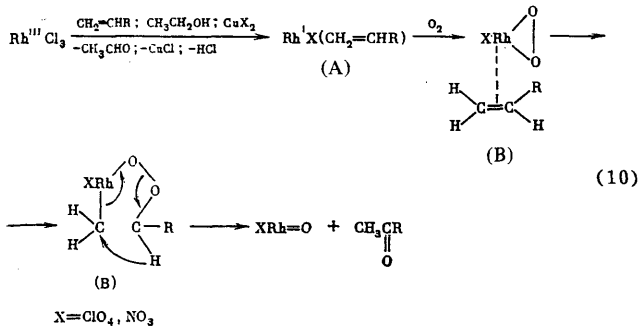
(9)

The exchange of the ligand for the olefin in complexes of this type has been confirmed by analysis of the NMR spectra.[107] Kinetic measurements[105] have shown that the rate of the process is determined by the stage in which the olefin is coordinated to the metal. The results of experiments using the [^{18}O]-labelled peroxomolybdenum complex have shown[106] that exclusively peroxo-oxygen, and not oxo-oxygen atoms as suggested previously,[43] are transferred to the olefin.

A mechanism of the epoxidation of olefins by peroxo-complexes of metals, involving a three-membered transition state, has been proposed[106] as an alternative to Scheme (9):



It has been observed[59] that, in the presence of copper perchlorate or nitrate, rhodium complexes in alcoholic solutions at room temperature catalyse the selective conversion of olefins containing the double bond at the end of the carbon chain into methyl ketones on treatment with molecular oxygen. The active species in the reaction, whose mechanism is illustrated in Scheme (10), are olefinic cationic complexes of rhodium (A), capable of activating molecular oxygen with formation of the peroxide complex (B). This compound is converted into the peroxometallocycle (C), which decomposes to the ketone and a rhodium compound containing the Rh=O bond after the migration of the proton to the neighbouring carbon atom:

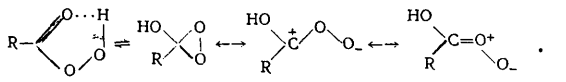


(10)

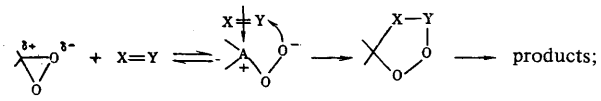
To demonstrate the validity of this mechanism, Igersheim and Mimoun[60] synthesised the peroxorhodium complexes $[Rh(As(Ph_3)_4O_2]^+A^-$, where $A^- = ClO_4^-$ or PF_6^-, and investigated their interaction with unsaturated compounds. It was found that these complexes react with α-olefins at room temperature in methylene chloride in an atmosphere of argon with formation of methyl ketone, whose yield reached 85%. When the [^{18}O]-labelled peroxorhodium complex is used, methyl ketones containing the labelled oxygen atom in the carbonyl group are formed.[60]

The mechanism represented by Eqns.(9) and (10) requires the coordination of the substrate and an oxygen molecule to one metallic centre. The necessity for the coordination of the olefin is confirmed by the fact that the peroxorhodium complex $\{RhO_2[Ph_2P(CH_2)_2PPh_2]_2\}ClO_4$, containing two phosphine ligands and not having a free coordination site, is inactive in the reactions with α-olefins.[107] It has been shown[109,110] that the rhodium complex $RhCl(C_8H_{14})_2$ with two unsaturated ligands absorbs one mole of oxygen with formation of the peroxo-complex. The coordinated oxygen of the latter oxidises quantitatively the coordinated cyclo-octa-1,5-diene to a ketone at 150 °C in cyclohexene. Furthermore, it has been observed[108,111,112] that oxygen adducts of the type $(Ph_3P)_2MO_2$, where M = Ni, Pd, or Pt, in solutions in methylene chloride readily combine with electrophilic olefins. This results in the formation of stable peroxometallocycles in a high yield. It has been demonstrated by NMR and IR spectroscopy that these products are analogous to those formed in accordance with Scheme (10).[61,105,107]

It has been suggested that dioxirans are reactive intermediates in the oxidative reactions of olefins on treatment with oxygen, ozone, and hydroperoxides with participation of catalysts (compounds of different elements and also peroxyacids).[112] The formation of dioxiran, present in the form of a stable zwitterion in the case of peroxyacids, has been confirmed by indirect data:[112]



The transfer of oxygen to organic substrates takes place in two stages. A charge-transfer complex between the nucleophilic substrate (for example, the olefin) and the electrophilic carbon atom of the dioxiran or the metal of the peroxo-complex is formed initially in the slow reversible stage. In the second stage, the coordinated substrate adds to the nucleophilic terminal oxygen atom and a cyclic peroxide is formed and then decomposes to the corresponding products:



A = carbon, metal.

Thus the catalytic reactions involving the oxidation of unsaturated compounds by oxygen and hydroperoxides take place via a non-radical mechanism and with a high selectivity. The peroxide derivatives of the elements—alkyl peroxides and peroxo-complexes—play an active role in these reactions. The interaction of the peroxide derivative of the element with the olefin takes place via intermolecular nucleophilic attack by the peroxide oxygen atom, coordinated to the organoelemental compound of the alkene. There is no unanimous view concerning the structures of the transition states in this process. The nature and yield of the products of the oxidation of the unsaturated compound and also the activity of the peroxide derivative of the element in its reaction with the olefin are determined by the electron-accepting properties of the heteroatom in the organoelemental compound.

IV. CONCLUSION

An increase in the selectivity of the liquid-phase oxidation of organic compounds by molecular oxygen can be achieved by employing compounds of different elements as catalysts. The multiplicity of the catalytic system is responsible for the absence of a single mechanism of the catalytic oxidation of hydrocarbons. However, it has been established firmly that the selectivity of the oxidation of organic compounds increases when the process proceeds without the participation of free radicals and the obligatory activation of the oxidant. The oxidant is in many cases activated as a result of the formation of peroxides of different types, which accumulate in the reaction mixture as a consequence of the addition of oxygen to the metal complex or the exchange between the primary

oxidation product (hydroperoxide) and the ligands of the catalytic additive. The peroxo-complex or the alkyl peroxide derivative of the element interact with the organic substance by a molecular mechanism, effecting with a high selectivity the direct transfer of oxygen to the hydrocarbon.

The activation of the substrate as a consequence of its coordination to the catalyst in selective catalytic oxidation reactions of organic substances has been reliably demonstrated for unsaturated and aromatic hydrocarbons. However, the necessity for the activation of the C–H bonds of alkanes in their selective oxidation needs experimental confirmation. According to Shilov and Shteinman,[113,114] in homogeneous systems alkanes can be activated by their oxidative addition to a transition metal complex.

Since the discovery of the activation of alkanes in aqueous solutions of platinum(II) complexes by Shilov and co-workers,[115] numerous examples of the activation of the C–H bonds of paraffins by iridium, rhodium, ruthenium, and rhenium compounds[116–119] and also by complexes of the type of the Ziegler–Natta catalyst[120] have been discovered. However, hitherto such activation has not been observed in autoxidation processes. On the contrary, there exist data which permit the claim that the activation of the alkane via its oxidative addition to the transition metal complex is not an essential condition for the selective conversion of the substrate into an oxygen-containing product.

Thus it is known that iridium compounds of the type $IrX.(CO)PPh_3$, where X = Cl or Br, activate the O_2 molecule with formation of the peroxocomplex and catalyse the autoxidation of ethylbenzene to acetophenone and of *p*-xylene to *p*-toluic aldehyde.[4] It has been shown recently that the iridium complex η^5-$C_5(CH_3)_5[P(CH_3)_3]Ir(H_2)$ activates alkanes and arenes with formation of hydridoaryl and hydridoalkyl derivatives of iridium.[119] However, treatment of the compounds obtained with oxygen or hydrogen peroxide leads only to the reductive elimination of the unchanged hydrocarbon molecule:

$$\eta^5\text{-}C_5(CH_3)_5[P(CH_3)_3]Ir\begin{matrix}R\\H\end{matrix} \xrightarrow{O_2 \text{ or } H_2O_2} [\eta^5\text{-}C_5(CH_3)_5[P(CH_3)_3]Ir] + RH;$$

$$R{=}CH_3,\ CH_2C(CH_3)_3,\ C_6H_{11},\ C_6H_5\ .$$

Furthermore, in the selective oxidation of hydrocarbons by the alkyl peroxide derivatives of non-transition elements (boron, aluminium, silicon, etc.), it is difficult to imagine that the alkanes are activated as a result of oxidative addition.

Consequently, the decisive factor in this process is the activation of the oxidant. The high selectivity of the oxidation of organic substances with participation of peroxide derivatives of the elements is caused, from our point of view, by the special state of the peroxide bond in the alkyl peroxide or peroxo-complex molecule "activated" by the heteroelement. Thus the activation of the O–O bond can lead to the formation of the oxiran ring, which facilitates the electrophilic attack by the peroxide oxygen on the nucleophilic organic substrate[112] or promotes the molecular interaction of the peroxide with the C–H bonds of the substance oxidised, which proceeds in a cyclic activated state.[113]

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