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Uspekhi Khimii

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Kinetics and Mechanism of the Decomposition of Organic Hydroperoxides in the Presence of Transition Metal Compounds

I.P.Skibida

The principal features of the homogeneous-catalytic decomposition of hydroperoxides in the presence of variable-valence metal compounds are examined and kinetic and physicochemical evidence for the formation of intermediate catalyst-hydroperoxide complexes and their subsequent decomposition into free radicals and molecular products is presented. Factors influencing the change in the mode of decomposition of the hydroperoxide are analysed and a special section is devoted to the catalysis of the decomposition of hydroperoxides by soluble molybdenum, vanadium, and tungsten compounds and also to the mechanism of the catalytic epoxidation of olefins by bound oxygen.
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I. INTRODUCTION

The theory of liquid-phase oxidation processes of hydrocarbons has been developed in fair detail, to a large extent by Emanuel' and his school[1,2]. The problem of the influence of various additives on the liquid-phase oxidation, the solution of which would permit the inhibition of undesirable oxidation process[3,4] or the acceleration of the oxidation and would make the latter more selective as a result of the employment of homogeneous or heterogeneous catalysts[5,6], has now become of primary importance.

The problems of the mechanism of homogeneous-catalytic oxidation reactions have been analysed fairly recently in a number of reviews[7-9]. The mechanism of one of the principal stages in the oxidation of hydrocarbons —the decomposition reactions of hydroperoxides and chain branching in the presence of homogeneous catalysts— are discussed below. Studies on the mechanism of the homogeneous-catalytic decomposition of hydroperoxides are important not only from the standpoint of the further development of the theory of liquid-phase oxidation but also for the determination of the general characteristics of homogeneous catalysis, since the decomposition of hydroperoxides constitutes a convenient model for a quantitative investigation of the influence of the structures of the hydroperoxide and the catalyst on the rate and mechanism of the process. In view of the extensive data available for the decomposition of peroxide compounds, we shall consider only the most characteristic features of the mechanism of the decomposition of organic hydroperoxides.

II. RADICAL DECOMPOSITION

Modern ideas concerning the mechanism of the catalytic action of transition metal compounds in hydroperoxide decomposition reactions are based on the mechanism proposed by Haber and Weiss[10], according to which the hydroperoxide alternatively behaves as an oxidant and as a reductant in the reaction with the reduced or oxidised form of the metal respectively:

$$ROOH + M^{n+} \rightarrow RO^{\cdot} + OH^{-} + M^{(n+1)+}; \quad (1)$$

$$ROOH + M^{(n+1)+} \rightarrow ROO^{\cdot} + H^{+} + M^{n+}. \quad (2)$$

The alternation of reactions (1) and (2) ensures the constancy of the ratio of the different valence forms of the catalyst in the course of the process and is responsible for the catalytic effect. Depending on the type of the hydroperoxide and the nature of the catalyst, the number of molecules of the hydroperoxide decomposed per catalyst molecule may be up to 1000 and more. This hydroperoxide decomposition mechanism in non-aqueous media has been confirmed in a number of investigations[7,8].

When the compounds of metals which can exist typically in more than two valence states are used as the catalysts, the decomposition of hydroperoxides may involve a more complex mechanism. Thus the decomposition of hydroperoxides in the presence of rhodium compounds can lead to the formation in the system of three valence forms: rhodium(I), rhodium(II), and rhodium(III). It has been suggested that the process is catalysed by the rhodium(II)–rhodium(III),[11] rhodium(I)–rhodium(II),[12] or rhodium(I)–rhodium(III)[13] pairs. However, in the latter case the process does not proceed via the two-electron mechanism proposed by the authors:

$$Rh(I) + 2\,ROOH \rightarrow Rh(III) + 2\,RO^{\cdot} + 2\,OH^{-},$$
$$Rh(III) + 2\,ROOH \rightarrow Rh(I) + 2\,ROO^{\cdot} + 2H^{+},$$

but is accompanied by the formation (at least as an intermediate) of a rhodium(II) species, which may be identified[12] by its ESR spectrum in the decomposition of cumenyl hydroperoxide in the presence of $Rh(I)(PPh_3)_3$.COCl.

The valence forms of the metal do not necessarily change when the hydroperoxide is involved in stages (1) and (2). Metals in the highest valence state can react rapidly with hydroperoxide decomposition products and also with the solvent[1,2,14–16]. Thus it has been suggested[17] that, in the oxidation of aldehydes in an aqueous phase, the cobalt(III) → cobalt(II) transition takes place with participation of benzaldehyde; the reaction of cobalt(III) with C_6H_5COOH is extremely slow, although in a later study[18] the possibility of reducing cobalt(III) by perbenzoic acid was noted. Nickel(III) reacts rapidly with benzaldehyde[18]. The rate of the valence transformation manganese(III) → manganese(II) increases appreciably in the presence of aldehydes[19]. The involvement of aldehydes in the degenerate branching of chains in the catalytic oxidation of alkanes has been postulated[20]. The involvement of alcohols, ketones, and acids in oxidation-reduction reactions with participation of metal ions is also extremely likely. For example, the steady-state concentration of manganese(III) in the catalytic decomposition of t-butyl hydroperoxide falls as the process develops, which may be due to the reduction of manganese(III) by the ROOH decomposition products—methyl alcohol or acetone[19]. It has been shown[21–23] that, in the decomposition of acyl hydroperoxides cobalt(II) is almost wholly converted into the tervalent form. In the decomposition of alkyl hydroperoxides cobalt is also mainly present in the tervalent form, although the rate of the transition cobalt(II) → cobalt(III) is much lower than for acyl peroxides. In the presence of organic acids cobalt is present only in the bivalent form during the reaction. When cobalt(III) is used as the catalyst in the presence of organic acids, the transition cobalt(III) → cobalt(II) takes place rapidly. The oxidation of alcohols, ketones, and acids by cobalt(III) ions has been studied in a number of investigations[24–26].

The ratio of the valence forms of the catalyst is determined by the different reactivities of the oxidised and reduced forms of the metal ion in the reaction with the hydroperoxide or other products[21,27].

The formation of free peroxy-radicals in the decomposition of hydroperoxides in the presence of variable-valence metal compounds has been demonstrated[28–30]. The ESR spectra of free peroxy-radicals have been observed in the decomposition of t-butyl, cumenyl, diphenylethyl, and triphenylmethyl hydroperoxides in the presence of cobalt compounds[31]. The method of inhibitors has been used to identify hydroperoxides and to measure the rates of their radical decomposition[5,31].

Although it has been suggested in the majority of studies that the interaction of the reduced form of the catalyst with the hydroperoxide [reaction (2)] entails the formation of the hydroxide ion and a free alkoxy-radical $RO^{\cdot}$, in some instances, for example in the decomposition of tetralinyl hydroperoxide in the presence of cobalt carboxylates, the composition of the ROOH decomposition products can be explained by simply postulating the formation in this process of an $OH^{\cdot}$ radical and an RO^{-} ion[33–35].

Kinetic studies on the decomposition reactions of hydroperoxides have shown that the overall order of the reaction with respect to the catalyst and the hydroperoxide depends on the solvent and the nature and concentration of the hydroperoxide and the catalyst and can vary from zero to two. Second-order decomposition of hydroperoxide with respect to the catalyst and first-order decomposition with respect to the hydroperoxide have been observed in the decomposition of tetralinyl hydroperoxide in xylene and acetic acid[36–39], in the decomposition of t-butyl hydroperoxide in the presence of cobalt(II) ethylenediaminetetraacetate[40], and in the decomposition of n-decyl hydroperoxide in the presence of cobalt stearate[41].

There have been numerous instances where the order of the reaction with respect to the catalyst proved to be 1 or 1.5;[5,32] in some cases the reaction order varies during the process or depends on the initial concentration of the hydroperoxide or the catalyst. Thus the decomposition of tetralinyl hydroperoxide in the presence of chromium, copper, and cobalt oleates is a first-order reaction with respect to the hydroperoxide, while the order with respect to the catalyst varies from 0.5 to 0.7.[23] The decomposition of cumenyl hydroperoxide in chlorobenzene in the presence of cobalt salts is a first-order reaction with respect to ROOH and the catalyst[42–45]. A linear variation of the rate of decomposition with catalyst concentration was observed in the decomposition of hydroperoxides by cobalt salts in alcohols[46] and by cobalt complexes in chlorobenzene and benzene[47,48]. In the decomposition of t-butyl hydroperoxide in chlorobenzene in the presence of cobalt 2-ethylhexanoate the order of the reaction with respect to the catalyst depends strongly on its concentration. At 20°C the order of the reaction with respect to the catalyst increases from 1 to 1.6 with increase of the salt concentration from 1.3×10^{-5} to 8.4×10^{-5} M and then falls as

the salt concentration rises further. At 0°C the order of the reaction with respect to the catalyst diminishes with increasing salt concentration[36].

In the inhibited decomposition of t-butyl hydroperoxide in acetic and butyric acids and their mixtures with chlorobenzene the order of the reaction with respect to cobalt acetate is close to unity[44,49], while for the non-inhibited reaction it is greater than unity[44]. A reaction order greater than unity has been observed in other investigations[40,43,50-54].

The order of the hydroperoxide decomposition reaction with respect to ROOH also depends on the nature and concentration of the latter. Thus in the decomposition of ethylphenyl hydroperoxide in the presence of copper stearate, the order of the reaction with respect to ROOH was unity[55], while in the decomposition of n-decyl hydroperoxide it was 2, falling to zero with increase of [ROOH].[56,57] In most of the cases investigated the reaction order with respect to ROOH tends to zero with increase of the hydroperoxide concentration[5,47,48,55-58].

Various mechanisms have been proposed for the decomposition of hydroperoxides in the presence of cobalt, copper, and manganese salts[36,49,59-63]. In certain instances the formation of organometallic peroxide compounds decomposing subsequently into free radicals[64]:

$$\mathrm{ROOH} + \mathrm{M}^{n+}\mathrm{X} \rightarrow \mathrm{ROOM}^{n+} + \mathrm{HX}, \quad (3)$$

$$\mathrm{ROOM}^{n+} \rightarrow \mathrm{RO}^{\cdot} + \mathrm{OM}^{(n+1)+} \quad (4)$$

$$\searrow \mathrm{ROO}^{\cdot} + \mathrm{M}^{(n+1)+}, \quad (5)$$

(X represents the anion) or oxidative addition of ROOH to the catalyst:

$$\mathrm{ROOH} + \mathrm{M}^{n+} \rightarrow \mathrm{ROM}^{(n+2)+}\mathrm{OH} \quad (6)$$

with subsequent decomposition of the complex formed were suggested.

The decrease of the order of the hydroperoxide decomposition reaction with respect to ROOH with increasing concentration of the latter was explained in terms of intermediate formation of a complex by the hydroperoxide and the catalyst[5,32]:

$$n\,\mathrm{ROOH} + m\,\mathrm{M}^{n+} \xrightarrow{k_1} n\,\mathrm{ROOH}\cdot m\,\mathrm{M}^{n+}. \quad (7)$$

The resulting complex is unstable and decomposes into the reaction products:

$$n\,\mathrm{ROOH}\cdot m\,\mathrm{M}^{n+} \xrightarrow{k_1} \mathrm{RO}^{\cdot} + \mathrm{OH}^{-} + \mathrm{M}^{(n+1)+} + (n-1)\,\mathrm{ROOH} + m-1)\,M^{n+}. \quad (8)$$

The reduced form of the catalyst also decomposes via the intermediate formation of the complex:

$$n_1\,\mathrm{ROOH} + m_1\,\mathrm{M}^{(n+1)+} \rightleftarrows n_1\,\mathrm{ROOH}\cdot m_1\,\mathrm{M}^{(n+1)+} \rightarrow \mathrm{ROO}^{\cdot} + \mathrm{H}^{+} + \\ + \mathrm{M}^{n+} + (n_1-1)\,\mathrm{ROOH} + (m_1-1)\,\mathrm{M}^{(n+1)+}. \quad (9)$$

The mechanism of reactions (7)–(9) yields a simple expression of the Michaelis–Menten type for the variation of the rate of decomposition with the concentrations of the hydroperoxide and the catalyst[5,32]. For $n = m = n_1 = m_1 = 1$, the equation is

$$W = \frac{Kk_1\,[\mathrm{ROOH}]\,[M^{n+}]}{1 + K\,[\mathrm{ROOH}]} \quad (10)$$

and makes it possible to determine the complex formation constant K and the rate constant k_1 for the decomposition of the complex into free radicals.

The second order with respect to the catalyst[41,65] may be due to the two-stage process

$$\mathrm{ROOH} + \mathrm{CoX}_2 \rightleftarrows \mathrm{ROOH}\cdot\mathrm{CoX}_2,$$
$$\mathrm{ROOH}\cdot\mathrm{CoX}_2 + \mathrm{CoX}_2 \rightarrow \mathrm{RO}^{\cdot} + \mathrm{CoX_2OH} + \mathrm{H_2O} + \mathrm{CoX}_2.$$

It has been suggested that the first order with respect to the catalyst in acetic acid[38,65] is due to the involvement of the dimeric form of cobalt acetate in the reaction:

$$2\mathrm{CoAc}_2\cdot\mathrm{AcH} \rightleftarrows (\mathrm{CoAc}_2)_2\cdot\mathrm{AcH} + \mathrm{AcH},$$
$$\mathrm{ROOH} + \mathrm{AcH} \rightleftarrows \mathrm{ROOH}\cdot\mathrm{AcH},$$
$$(\mathrm{CoAc}_2)_2\cdot\mathrm{AcH} + \mathrm{ROOH} \rightarrow \text{radicals}.$$

The second-order with respect to the hydroperoxide in the presence of copper salts may be attributed to the formation of the hydroperoxide–catalyst complexes having the composition $CuX_2.2ROOH$ [56,57] or $2CuX_2.2ROOH$.[66]

The formation of catalyst–hydroperoxide complexes has been confirmed by various physicochemical methods: spectrophotometrically in the decomposition of cumenyl hydroperoxide in the presence of bis-[*N*-(2-hydroxy-3-methoxybenzylidene)aniline] cobalt[47] and of ethylphenyl hydroperoxide in the presence of copper stearate[55], the formation of copper 2-ethylhexanoate complexes with t-butyl hydroperoxide[66] and of bis-(α-thiopicolinanilide)-copper with ethylphenyl hydroperoxide[67] has been demonstrated by ESR, and the formation of complexes of cumenyl hydroperoxide with cobalt and nickel chelates has been demonstrated by NMR.[68,69] In the last case the formation of complexes was inferred from the chemical shifts of the OH protons of the hydroperoxides and it may be regarded as established that (at least for the systems investigated) ROOH does not add as a result of ligand exchange via reactions (3) or (6), as postulated by Waters[64]. The hydroperoxide is coordinated to the central metal ion via the oxygen atom of the hydroxy-group[69].

The equilibrium constants for the formation of the complexes have been calculated by Eqn. (10) for a large number of catalysts and hydroperoxides[70]. It has been shown for the decomposition of cumenyl hydroperoxide in the presence of substituted bis-[*N*-aryl-*N*-(2-hydroxy-3-methoxybenzylidene)amine]cobalt complexes that the introduction of electron-donating substituents into the ligand has only a slight influence on the rate constant for the decomposition of the catalyst–hydroperoxide complex and leads mainly to a change in the equilibrium constant for the formation of the complex[58].

Quantitative evidence for the role of complex formation in the catalytic decomposition of hydroperoxides is provided by the agreement[68] between the equilibrium constants for the formation of cobalt chelates with cumenyl hydroperoxide determined by two independent methods: from the chemical shift of the OH proton of the hydroperoxide in the presence of the catalyst and by a kinetic method from the dependence of the rate of decomposition of ROOH on its concentration using Eqn. (10). This suggested that the formation of the complexes, identified by a physicochemical method, in the catalyst–hydroperoxide system is indeed an intermediate stage in the catalysis.

The decrease of the reaction order with respect to the catalyst with increase of its concentration has been explained in some investigations by the aggregation of the catalyst[38,56,66,71] or by the interaction of one of its valence forms with free radicals[72]. The latter hypothesis can explain the relative decrease of the rate of reaction only in the presence of a chain mechanism of the decomposition of ROOH. The study of the decomposition of cumenyl hydroperoxide in the presence of copper stearate complexes with *o*-phenanthroline (*o*-phen) in benzene and chlorobenzene showed that there is no chain mechanism of the hydroperoxide decomposition reaction and that the decrease of the reaction order with respect to the catalyst from 1 to 0 with increase of [$CuSt_2$.*o*-phen] is not related to the formation of micelles[73].

It has been suggested that deactivation of the catalyst in the process occurs owing to the formation of inactive dinuclear complexes. The process mechanism involves stages in which copper(I) complexes of the hydroperoxide are formed:

$$\text{Cu(II)} \cdot o\text{-phen} \xrightarrow{\text{ROOH}} \text{Cu(I)} \cdot o\text{-phen} \quad ,$$

$$\text{Cu(I)} \cdot o\text{-phen} + \text{ROOH} \rightarrow \text{Cu}^{\delta+}\text{(I)}\ o\text{-phen}\ \overset{\delta-}{\text{ROOH}} \quad .$$

This is followed by the reactions of the complexes $\overset{\delta+}{\text{Cu(I)}}(o\text{-phen})(\overset{\delta-}{\text{ROOH}})$ with the catalyst (catalyst deactivation) and the hydroperoxide (catalytic stage). The mechanism proposed explained quantitatively the kinetic curves for the decomposition of the hydroperoxide and also the variation of the rate of decomposition of ROOH with the concentrations of the catalyst and the hydroperoxide.

III. MOLECULAR DECOMPOSITION

The so called "molecular" mechanism of the decomposition of the hydroperoxide, which leads to the formation of non-radical products, has been observed in the decomposition of many organic hydroperoxides in the presence of various organometallic catalysts.

This decomposition mechanism was postulated initially on the basis of data for the influence of variable-valence metal compounds on the oxidation of hydrocarbons[74]. The increase of the rate of decomposition of the hydroperoxide via the molecular mechanism lowers the rate of formation of free radicals in the system. In certain cases, where the rate of formation of the radicals in the presence of the catalyst is lower than the rate of their formation in the absence of the catalyst, the introduction of organometallic compounds can lead to the appearance of induction periods. The inhibition of the oxidation of hydrocarbons in the presence of nickel, cobalt, platinum, and palladium dithioketonates, which are effective catalysts of the decomposition of hydroperoxides, is treated from precisely this standpoint[75].

This treatment of the inhibiting effect of variable-valence compounds is not unambiguous, since almost all the compounds employed are radical acceptors and may inhibit the oxidation not only owing to the decomposition of ROOH but also owing to the increase of the rate of chain termination[76-78]. Direct evidence for the occurrence of the molecular mechanism in the decomposition of the hydroperoxide in the presence of the catalyst was obtained with the aid of inhibitors[32,56]. It was shown that, in the decomposition of n-decyl hydroperoxide in the presence of copper stearate, the rate of consumption of ROOH is significantly higher than the rate of consumption of the inhibitor, which is equal to the rate of formation of free radicals. An appreciable molecular decomposition of the hydroperoxide was demonstrated in a study of the decomposition of tetralinyl hydroperoxide under the influence of cobalt salts in various solvents[34,35].

The contribution of the molecular decomposition of the hydroperoxide depends significantly on the nature of the catalyst and the hydroperoxide[79]. Thus in the presence of cobalt stearate t-butyl hydroperoxide decomposes at 50°C in chlorobenzene only into free radicals; the rates of decomposition of tetralinyl[35] and cumenyl[79] hydroperoxides into free radicals under the same conditions are 1.2 and 36% of the overall rate of decomposition of ROOH respectively; the contributions of the radical pathways to the decomposition of α-phenylethyl hydroperoxide in the presence of tin 2,2'-thiobis-[4-methyl-6-(α-methylbenzyl)-phenoxide] and 2,2'-thiobis-(6-t-butyl-4-methylphenoxide) are 0.1 and 3.5% respectively[80]. When the metal in the catalyst is changed, the relative contributions of the molecular and radical mechanisms of the decomposition of ROOH also change. In the presence of $CoSt_2$, n-decyl hydroperoxide decomposes only via the radical pathway[41], while in the presence of $CuSt_2$ the contribution of the molecular decomposition is 20–50% [56,57] of the overall rate of decomposition of ROOH. The contribution of the radical decomposition of t-butyl hydroperoxide is 100% in the presence of $CoSt_2$ [81] and 4–10% in the presence of manganese stearate[19].

The study of the dependence of the rates of decomposition of hydroperoxides and of the consumption of the inhibitor on the catalyst and hydroperoxide concentrations established that in all cases the molecular decomposition of the hydroperoxide proceeds, like the radical decomposition, via a stage involving the formation of catalyst–hydroperoxide complexes. Determination of the thermodynamic characteristics and compositions of these complexes from the rates of the molecular and radical decompositions of ROOH showed that, in the decomposition of cumenyl, n-decyl, tetralinyl, and α-phenylethyl hydroperoxides in the presence of copper, cobalt, and nickel compounds, both mechanisms of the decomposition of the hydroperoxides involve the formation of the same complexes[79,82-84].

Kinetic data for the variation of the rates of decomposition of hydroperoxides with their concentrations and with that of the catalyst made possible in many instances the calculation of the individual rate constants for the decomposition of the catalyst–hydroperoxide complexes into free radicals (k_r) and the molecular products (k). It was found that the k_r are as a rule associated with very low pre-exponential factors[70]. The relative contributions of the molecular and radical mechanisms of the decomposition of the hydroperoxide depend markedly on the viscosity of the medium—with increase of η, the contribution of the molecular decomposition of ROOH increases, but the overall rate remains unchanged. The variation of the ratio k_r/k is described by the Stokes–Einstein formula, which leads to the conclusion that the role of diffusion processes in the mechanism of the catalytic decomposition of ROOH is important[79].

The kinetic data obtained suggested a mechanism for the molecular decomposition of the hydroperoxide in which the "cage effect" of the solvent plays an important role[19,79,82-86]. The radicals formed in the decomposition of the complex MX_2.ROOH can either recombine in the solvent cage (molecular decomposition of the hydroperoxide) or can diffuse from the cage (radical decomposition):

$$MX_2 + ROH \rightleftarrows MX_2 \cdot ROH \rightarrow [MX_2OH,\ RO]$$

$$RO^{\cdot} + MX_2OH \qquad MX_2 + H_2O + R'COR'' \quad .$$

It has been suggested[34] for the decomposition of tetralinyl hydroperoxide in the presence of cobalt salts that ROOH decomposes when the complex MX_2.ROOH reacts with the hydrocarbon as follows:

$$[MX_2 \cdot ROOH] + R'H \rightarrow [MX_2^{\cdot} \ \ldots\ R''] + \text{product.} \qquad (11)$$

The relative contributions of the molecular and radical mechanisms of the decomposition of ROOH are then determined by the ratio of the rates of recombination of the radicals R'' within the cage and by the number of

radicals released from the cage when the complex $MX_2 \ldots R''$ reacts with a second R'H molecule:

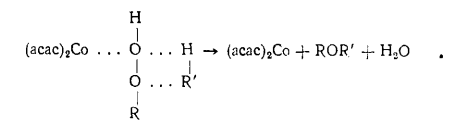
$$[\dot{M}X_2 \ \ldots \ R'']+R'H \rightarrow 2R''+MX_2+\text{product}. \qquad (12)$$

In this mechanism of the decomposition of the hydroperoxide an increase of the rate of consumption of ROOH [stage (11)] and of the contribution of the radical ROOH decomposition mechanism [stage (12)] was to be expected with decrease of the C–H bond strength in the hydrocarbon solvent.

This mechanism of the molecular decomposition of the hydroperoxide does not hold in the decomposition of cumenyl hydroperoxide (CHP) in the presence of cobalt acetylacetonate [$Co(acac)_2$].[86] In this case the rate of decomposition of CHP is almost independent of the solvent and the contribution of the molecular decomposition of ROOH increases in the sequence benzene < ethylbenzene < tetralin, i.e. with decrease of the C–H bond strength in the hydrocarbon. This suggested a more complex role of the solvent in the ROOH decomposition mechanism. As in inert solvents, in the presence of hydrocarbons the consumption of hydroperoxides is determined by the stage

$$Co(acac)_2 \cdot ROOH \rightarrow [\overset{\delta+}{Co}(acac)_2; \ \overset{\delta-}{ROOH}].$$

The $[\overset{\delta-}{Co(acac)_2}, \ \overset{\delta+}{ROOH}]$ species formed reacts further with RH to form non-radical products, most probably ethers. Such interaction can proceed via a stage involving the formation of ternary complexes:



This pathway, involving a bimolecular interaction of the hydroperoxide with the hydrocarbon, is a characteristic feature of the catalytic decomposition of the hydroperoxide and is due to the activation of ROOH when it is bound in a complex with the catalyst (probably as a result of partial electron transfer). In the absence of a catalyst the hydroperoxide interacts with the hydrocarbon to form only free radicals as the reaction products[1].

IV. INDUCED CHAIN DECOMPOSITION

The decomposition of the hydroperoxide induced by free radicals (chain decomposition of the hydroperoxide) is largely characteristic of the non-catalytic decomposition, which is probably associated to a considerable extent with the marked increase of the rate of formation of the radicals and the corresponding decrease of chain length in the presence of the catalyst.

The hypothesis of an appreciable contribution of the decomposition of the hydroperoxide induced by free radicals was put forward for the first time in a study of the kinetics of the oxidation of n-decane in the presence of manganese(II) stearate[87]. Direct methods using inhibitors of free-radical processes demonstrated the occurrence of the chain pathway in the decomposition of t-butyl and cumenyl hydroperoxides in the presence of cobalt acetate in a chlorobenzene–acetic acid mixture[88], of cumenyl hydroperoxide in benzene in the presence of substituted *N*-aryl-*N*-(2-hydroxy-3-methoxybenzylidene)aminocobalt complexes[89], and of tetralinyl hydroperoxide in the presence of cobalt acetate in tetralin[38].

The occurrence of the chain pathway in the hydroperoxide decomposition reaction depends strongly on the nature of the catalyst. Thus, according to data obtained by the method of inhibitors using ionol as the inhibitor[72], in the presence of iron-phthalocyanine t-butyl hydroperoxide decomposes via the chain mechanism, while in the presence of cobalt salts there is no chain decomposition of the hydroperoxide.

This influence of the nature of the catalyst on the mode of decomposition of the hydroperoxide may be one of the manifestations of the dual function of the catalyst discovered in 1959 by Emanuel' and coworkers[90], which consists in the ability of the catalyst not only to generate free radicals but also to participate in the chain termination reaction. It was shown in later studies that metal compounds can interact with both peroxy-[77,91] and alkoxy-radicals[92,93] formed in the decomposition of hydroperoxides. In hydrocarbon media, where there is a possibility of chain transfer to the solvent, the interaction of metal compounds with free alkyl radicals may play an important role[94].

Unfortunately in the presence of the catalyst the use of inhibitors greatly alters the properties of the catalyst itself, for example as a result of complex-formation effects. The inhibition of the catalytic decomposition of the hydroperoxide by the addition of the inhibitor can be caused in this case not only by the suppression of the chain decomposition of the hydroperoxide but also by the "poisoning" of the catalyst. Furthermore, there is a possibility of oxidation-reduction reactions between one of the forms of the catalyst and the inhibitor, which leads to a change in the relative amounts of the different valence forms of the catalyst, and hence in the measured rate of decomposition of ROOH. For this reason, the available information in the literature concerning the occurrence of the induced decomposition of ROOH in the presence of the catalyst is frequently contradictory. Thus Skibida et al.[35] showed, in contrast to Kamiya et al.[38], that tetralinyl hydroperoxide does not undergo chain decomposition in benzene in the presence of $CoSt_2$. One cannot rule out the possibility that the ionol employed by Kamiya et al.[38] as the inhibitor interacted with the catalyst in the highest valence state, which has in fact been demonstrated, for example by Gernet et al.[95]

The occurrence of the chain decomposition of ROOH is determined to a large extent by the nature of the alkyl radical and the hydroperoxide. t-Butyl and cumenyl hydroperoxides decompose in the presence of cobalt salts via the chain mechanism, which is apparently not characteristic of the decomposition of triphenylmethyl and diphenylethyl hydroperoxides[30,43,88].

In certain cases conclusions concerning the occurrence of the induced decomposition of the hydroperoxide are reached on the basis of a comparison of the rates of the overall decomposition of hydroperoxides having different structures. The rate of decomposition of the primary n-butyl hydroperoxide in chlorobenzene in the presence of cobalt 2-ethylhexanoate is lower than the rate of decomposition of t-butyl hydroperoxide under the same conditions, which suggested a greater contribution of the chain decomposition of the tertiary hydroperoxide. This hypothesis is consistent with the change in the reactivity of the free radicals: the rate of recombination increases on passing from the t-butyl to the n-butyl-peroxy-radical; consequently the probability of chain propagation diminishes. However, the above influence of the nature of the hydroperoxide on the rate of its decomposition can be caused also by the influence of the structure of the radical

on the rate of the primary decomposition of the hydroperoxide into free radicals. Furthermore, there is also a possibility of a change in the mechanism of the radical decomposition of ROOH. As stated above, the primary step in the hydroperoxide decomposition reaction may lead to the formation of a free hydroxy-radical and an alkoxide anion and not a hydroxide ion and an RO· radical[33,35,36]. The chain decomposition of ROOH can then be induced by the OH· radical[33,36,96]. It has been suggested[97] that the decomposition products of t-butyl hydroperoxide are formed when free peroxy-radicals react with the hydroperoxide–catalyst complex.

The available factual data suggest that the chain decomposition of the hydroperoxide in the presence of the catalyst is mainly characteristic of tertiary hydroperoxides in aprotic media.

V. THE INFLUENCE OF SOLVENTS ON THE CATALYTIC DECOMPOSITION OF HYDROPEROXIDES

As in the thermal decomposition of hydroperoxides, the rate of their decomposition in the presence of catalysts is largely determined by the nature of the solvent. A study of the decomposition of cumenyl hydroperoxide in different solvents catalysed by cobalt abietate[43] showed that the rate of decomposition and the effective activation energy greatly depend on the solvent. The above solvents can be arranged in the sequence nonane < toluene < chlorobenzene < benzene in terms of the rate of decomposition. The activation energies fall in the same sequence from 21 kcal mole^{-1} for nonane to 13 kcal mole^{-1} for benzene.

The rate of decomposition of the hydroperoxide varies even more in the presence of oxygen-containing compounds. The addition of dimethylphenylmethanol to give a concentration comparable to that of t-butyl hydroperoxide reduces the rate of decomposition of the latter by a factor of four in the presence of cobalt abietate[98]. The rate of decomposition of cumenyl hydroperoxide in the presence of dimethylphenylmethanol (25% relative to the hydroperoxide employed) decreases almost by a factor of two, while α-tetralinone strongly inhibits the decomposition of tetralinyl hydroperoxide[36]. In the decomposition of cumenyl hydroperoxide by cobalt salts in alcoholic solutions a deviation was observed from the equation for first-order kinetics with respect to the hydroperoxide[46]. Acetophenone and dimethylphenylmethanol inhibit the decomposition of the hydroperoxide in the presence of copper stearate[55].

Organic acids as a rule strongly inhibit the decomposition of hydroperoxides in the presence of homogeneous catalysts; low-molecular-weight acids exhibit the strongest influence[38,99,100]. The rate of decomposition of tetralinyl hydroperoxide in a mixed solvent consisting of benzene and an organic acid falls in proportion to the square of the concentration of the acid[38,99]. A detailed study of the decomposition of cumenyl hydroperoxide catalysed by cobalt carboxylates in chlorobenzene, organic acids, and their mixtures has been carried out[31]. With increase of the concentration of acid in the solution, the rate constant for the decomposition of the hydroperoxide falls. The hydroperoxide decomposition rate constant in the presence of cobalt(II) oenanthate decreases by a factor of 90 on passing from a solvent containing 6% of butyric acid to pure butyric acid. The apparent activation energy rises from 12 kcal mole^{-1} in chlorobenzene to 22 kcal mole^{-1} in the presence of butyric acid, but depends only slightly on the amount of added acid.

The inhibiting effect of acetic and 2-ethyloenanthic acids on the rate of decomposition of t-butyl hydroperoxide catalysed by cobalt salts has been demonstrated[100]. The decrease of the catalytic activity of nickel stearate in the decomposition of α-phenylethyl hydroperoxide in the presence of acetic acid has also been established[101]. Aliphatic alcohols, ketones, and acids greatly reduce the rate of decomposition of n-decyl hydroperoxide in the presence of copper stearate[102].

The above data show that such influence of the solvent can be due to several causes.

1. Since in the majority of the studies quoted the influence of the solvent on the overall rate of decomposition of the hydroperoxide was considered, the observed influence of hydrocarbon solvents is possibly associated with a change in the contribution of the induced decomposition of the hydroperoxide owing to the change in the reactivity of the radicals caused by the involvement of the solvent in the chain transfer reaction.
2. Many solvents, particularly alcohols, ketones, and acids, can alter the relative amounts of the different valence forms of the catalyst as a result of reaction with the highest valence form of the metal. This effect also leads to an alteration of the rate of decomposition of the hydroperoxide.
3. Finally, the possible formation of complexes by the metal with the solvent may be a significant factor influencing the efficiency of the catalyst. Below we shall consider in somewhat greater detail the role of the formation of complexes of the catalyst and the solvent in the mechanism of the homogeneous-catalytic decomposition of hydroperoxides.

The decrease of the induction period in the oxidation of cyclohexanone catalysed by manganese stearate following the addition of benzoic acid and the acceleration of the oxidation in the presence of butyric acid have been attributed[103] to the formation of a complex of the acid and the catalyst, as a result of which the latter is activated.

The influence of acids on catalytic oxidation processes depends on the structure of the catalyst employed, particularly on the metal ion. For example, the addition of caprylic acid activates cobalt stearate but passivates manganese caprylate in the oxidation of cyclohexane[104]. It has been suggested that the hydroperoxide decomposes via the following mechanism in the coordination sphere of the metal:

$$M[X_5, ROOH]^{n+} \rightarrow M[X_5, (OH^-)]^{(n-1)+} + RO^{\cdot}.$$

In the presence of acids there is a possibility of the simultaneous coordination of hydroperoxide and acid molecules to the metal ion:

$$M[X_5, ROOH, R'COOH]^{n+} \rightarrow M[X_4, (R'COO), (H_2O)]^{(n-1)+} + RO^{\cdot}.$$

Depending on the relative rates of these reactions, the presence of the acid in the coordination sphere of the metal can either inhibit or accelerate the decomposition of the hydroperoxide and can lead to a corresponding retardation or acceleration of the oxidation reaction.

There are many fewer examples of the suppression of the catalytic activity of homogeneous catalysts by the addition of compounds capable of forming complexes with organometallic compounds. The decrease of the rate of oxidation of cyclohexane in the presence of cobalt stearate has been attributed[105] to the formation in the system of polar substances such as cyclohexanol or water, which

block the catalyst molecules and reduce the rate of initiation thereby. The deviation from the bimolecular kinetics of the decomposition of α-phenylethyl hydroperoxide in chlorobenzene in the presence of copper stearate as oxidation proceeds may be caused by the formation of complexes of the decomposition products (acetophenone and methylphenylmethanol) and the catalyst. The occurrence of such complex formation has been confirmed qualitatively by a spectrophotometric method. The formation of cobalt(II) and cobalt(III) complexes with α-tetralinone has been postulated to account for the retardation of the decomposition of tetralinyl hydroperoxide in the presence of cobalt 2-ethylhexanoate when α-tetralinone is introduced into the solution[36].

In the oxidation of *o*-xylene in acetic acid in the presence of cobalt acetate the reaction product (*o*-phthalic acid) forms chelate complexes with cobalt(II) and cobalt(III) ions, which alters the oxidation-reduction potential of the system: there is a considerable increase of the stability and hence of the concentration of cobalt(III) in solution. Terephthalic acid, formed in the oxidation of *p*-xylene, also binds cobalt ions into catalytically inactive complexes[103]. A change in the activity of the catalyst as a result of the formation of complexes with acetic and 2-ethylhexanoic acids has been observed in a study of their influence on the decomposition of t-butyl hydroperoxide in the presence of cobalt carboxylates[100]. The changes in the absorption spectrum of cobalt 2-ethylhexanoate in the presence of acids demonstrate qualitatively the formation of complexes of the acid with the cobalt salt. The formation of dinuclear acid–catalyst complexes is possible.

Polar solvents can form complexes with cobalt stearate[34,39]. The rate of decomposition of the hydroperoxide is determined then by the competition between the complex-formation reactions of the catalyst with the hydroperoxide, its decomposition products, and the solvent[39]. A quantitative confirmation of the role of the formation of complexes by copper salts with alcohols, ketones, and acids in the passivation of the catalyst of the decomposition of hydroperoxides was obtained in a study of the decomposition of n-decyl hydroperoxide in the presence of copper stearate in oxygen-containing solvents[102]. Using the method of inhibitors, it was established that there is no chain decomposition of n-decyl hydroperoxide. Alcohols, ketones, and acids inhibit to an equal extent both the decomposition of the hydroperoxide and the formation of free radicals. The relative contributions of the hydroperoxide decomposition pathways do not change in the presence of the compounds used. Furthermore it was shown that under the experimental conditions copper stearate does not oxidise decanol, decanone, and higher carboxylic acids.

Kinetic data for the dependence of the rate of decomposition of n-decyl hydroperoxide on the concentration of alcohols, ketones, or acids and the hydroperoxide established that the observed inhibition of the decomposition of ROOH by the addition of oxygen-containing solvents (S) can be accounted for if it is supposed that, together with the complexes $CuSt_2.2ROOH$, ROOH.S, and $CuSt_2.S$, mixed-ligand complexes $CuSt_2.2ROOH.S$ are produced in the system. The hydroperoxide in such a complex decomposes at rates several orders of magnitude lower than the rate of decomposition of the hydroperoxide in the complex $CuSt_2.2ROOH$. The stabilisation of the hydroperoxide in the complex $CuSt_2.2ROOH.S$ may be due to the fact that in this case the solvent is incorporated in the inner, rather than outer, coordination sphere of the metal. This entails the decomposition of the hydrogen bond between two ROOH molecules bound in a complex with copper stearate and the rate of decomposition of the hydroperoxide falls.

The equilibrium constants for the formation of the complexes $CuSt_2.S$, ROOH.S, and $CuSt_2.2ROOH.S$ were calculated from the kinetic data for the decomposition of the hydroperoxide. At the same time the equilibrium constants for the formation of $CuSt_2.S$ complexes were determined spectrophotometrically from the change in the optical density of $CuSt_2$ solutions in the presence of S.[106] The agreement between the equilibrium constants for the formation of the $CuSt_2.S$ complexes found by the two independent methods made it possible to establish the following mechanism for the decomposition of n-decyl hydroperoxide in the presence of copper stearate and oxygen-containing compounds:

$$CuSt_2 + 2\,ROOH \rightleftarrows CuSt_2 \cdot 2\,ROOH \rightarrow \text{decomposition of ROOH},$$
$$CuSt_2 + S \rightleftarrows CuSt_2 \cdot S,$$
$$ROOH + S \rightleftarrows ROOH \cdot S,$$
$$CuSt_2 \cdot 2\,ROOH + S \rightleftarrows CuSt_2 \cdot 2ROOH \cdot S.$$

VI. DECOMPOSITION OF HYDROPEROXIDES IN THE PRESENCE OF GROUP V–VI METAL COMPOUNDS AND CATALYTIC EPOXIDATION OF OLEFINS BY HYDROPEROXIDES

There has been a recent increase of interest in the study of the mechanism of the catalytic decomposition of hydroperoxides in the presence of Group V–VI metal compounds in connection with the problem of the catalytic epoxidation of olefins by bound oxygen (hydroperoxides, hydrogen peroxide, and peracids) in the presence of molybdenum, vanadium, tungsten, and chromium compounds[107]. The interaction of olefins with hydroperoxides in the presence of these compounds takes place with a high degree of selectivity. Group IB, VII, and VIII transition metals are as a rule relatively inactive in the epoxidation; metals with a constant valence do not catalyse the epoxidation of olefins by hydroperoxides[108,109].

The absence of an appreciable catalytic effect in the epoxidation of olefins in the presence of cobalt, nickel, copper, and manganese compounds, which are typical catalysts of the radical (homolytic) decomposition of hydroperoxide, led to the hypothesis that, in the presence of molybdenum, vanadium, and tungsten compounds, the heterolytic pathway predominates in the decomposition of hydroperoxides[110].

The experimental studies on the decomposition pathways for cumenyl and cyclohexyl hydroperoxides in the presence of vanadium, vanadyl, molybdenyl, and chromium acetylacetonates and stearates showed that the hydroperoxides decompose (as in the presence of transition metals) via two pathways: molecular and free-radical[111]. Depending on the type of catalyst and temperature, the contribution of the radical decomposition may vary from 1 to 100% relative to the overall rate of decomposition of the hydroperoxide[111]. Thus in the decomposition of cumenyl hydroperoxide in the presence of chromium stearate the yield of radicals increases from 1 to 100% as the temperature is raised from 70° to 120°C; cyclohexyl hydroperoxide decomposes in the presence of chromium, vanadyl, and molybdenyl acetylacetonates at 120–130°C with a 3–12% yield of radicals[111].

The study of the kinetics of the decomposition of hydroperoxides in the presence of such catalysts led to the hypothesis that, in contrast to cobalt, copper, and nickel compounds, the molecular decomposition is not in this case a manifestation of the "cage" effect.

The principal decomposition products are acetophenone, dimethylphenylmethanol, α-methylstyrene, and carbon dioxide for cumenyl hydroperoxide and cyclohexanone and cyclohexanol for cyclohexyl hydroperoxide[111]. Phenol, a typical product of the heterolytic decomposition of cumenyl hydroperoxide, is absent from the reaction products, which throws doubt on a significant contribution of the heterolytic hydroperoxide decomposition reaction.

In many studies dealing with the epoxidation of olefins by hydroperoxides it was noted that the epoxidation process is preceded by the interaction of the catalyst with the hydroperoxide, which converts the catalyst into an active valence form. This hypothesis is supported in the first place by the finding that the catalytic epoxidation is always preceded by an induction period, during which the catalyst is altered, in many cases with a change in the colour of the solution. Preliminary incubation of hydroperoxide solutions with the catalyst as a rule eliminates the induction period.

The study of the catalysis of the decomposition of t-butyl hydroperoxide and hydrogen peroxide by vanadium compounds established that a red complex is formed in the initial stage of the process[110-115] when vanadyl chelate complexes are used as the initial forms of the catalyst: vanadyl bis(acetylacetonate) [$VO(acac)_2$]; vanadyl bis-(hexafluoroacetylacetonate) [$VO(hfac)_2$]; vanadyl bis(dipivaloylmethide) [$VO(dpm)_2$]; vanadyl chloride. The $V(acac)_3$ and $V(t\text{-}C_3H_7O)_3$ catalysts do not form a red complex. The stability of the complex depends on the nature of the catalyst employed. It has been suggested[112] that the red colour of the solution is due to the formation of the vanadium(IV)...ROOH complex the decomposition of which involves the transition of vanadium(IV) → vanadium(V).

The stoichiometry of the decomposition of H_2O_2 in aqueous solutions in the presence of $VOCl_2$ corresponds to the equation[113]

$$2\,VO^{2+} + H_2O_2 \rightarrow 2\,VO^{+} + 2\,H^{+} + O_2.$$

The formation of the complex $O{=}V{-}OOH^{+}$ in the first stage via the reaction

$$VO^{2+} + H_2O_2 \rightleftarrows O{=}V{-}OOH^{+} + H^{+},$$

with subsequent decomposition of the peroxo-complex via the mechanism

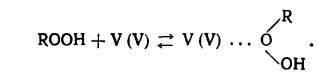
$$O{=}V{-}OOH^{+} \rightarrow VO_2^{+} + OH^{\cdot},$$

$$VO_2^{+} + H_2O_2 \rightarrow VO_3^{+} + H_2O,$$

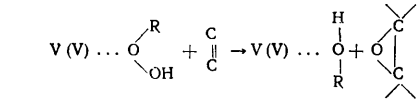
has been postulated.

The VO_3^{+} species can form complexes with free hydroxy-radicals, which ultimately leads to the reduction of vanadium(IV) in the system. The possibility of the interaction of VO_2^{+} with H_2O_2 to form VO_3^{+} has been demonstrated[114]. The disappearance of paramagnetism from the $ROOH{-}VO(acac)_2$ system suggests that vanadium is in the +5 state in the red complex[111].

The actual nature of the active species in this process has not been established. The virtual independence of the rate of expoxidation of the olefin of the hydroperoxide concentration observed in a kinetic study of the systems allyl alcohol–α-phenylethyl hydroperoxide–vanadium tris-(acetylacetonate)[116], propene–α-phenylethyl hydroperoxide–molybdenum resinate[117], and many others[110,118,119] led to the hypothesis that catalyst–hydroperoxide complexes are formed reversibly:



In this complex there is a possibility of partial polarisation (heterolysis) of the O–O bond[110], which facilitates the subsequent interaction of the hydroperoxide with the olefin:



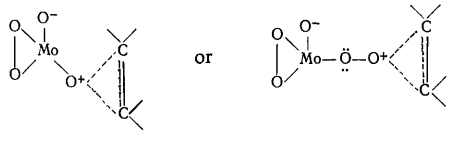
The formation of complexes of t-butyl hydroperoxide with molybdenyl bis(cyclohexanediolate)[120] and molybdenyl bis(acetylacetonate)[121] was observed by NMR from the broadening and partial shift of the signal due to the OH protons of the hydroperoxide in the presence of molybdenum compounds. The existence of two peroxy-species in equilibrium was postulated in this instance[120]:

$$Mo\,(VI)\,ROOH \rightleftarrows Mo\,(V)\,RO_2^{\cdot} + H^{+}. \qquad (13)$$

The formation of the $RO_2^{\cdot}$ radical in the interaction between molybdenum(V) and ROOH has been noted[122].

It has been suggested[123] that molybdenyl peroxo-complexes capable of stoichiometric epoxidation of olefins are formed in the course of the catalytic epoxidation reaction. The capacity of these peroxo-complexes for epoxidation was demonstrated in the epoxidation of olefins[124] and allyl alcohol[125] by the peroxo-complexes $O{=}Mo(O_2)_2L_1L_2$, where L_1 and L_2 are hexamethylphosphoramide and water. Later similar peroxo-complexes [$O{=}Mo(O_2)_2$ and in small amounts $Mo(O_2)_2Cl_2$] were isolated in reactions of organic peroxides with $MoCl_5$ in ethyl alcohol[126].

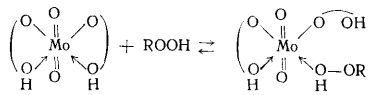
It has been shown with the aid of "labelled" oxygen (^{18}O) that the O=Mo oxo-group is not involved in the epoxidation and that the process proceeds via the formation of intermediate complexes of the type[127]



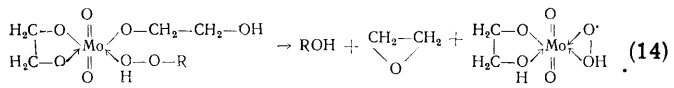
The possibility of the formation of complexes by peroxomolybdenum compounds with an olefin was confirmed[126] by the observation of a change in the colour of $O{=}MoO_4$ from yellow to green in the presence of the olefin. The formation of a complex with allyl alcohol has been demonstrated kinetically for $MoO(O_2)_2L_1L_2$.[125]

Although a peroxomolybdenum(VI) compound has been isolated in the interaction of molybdenum compounds with a hydroperoxide in the absence of an olefin and its capacity for epoxidation has been demonstrated (in stoichiometric proportions of 1 : 1), the mechanism of epoxidation via a successive alternation of stages involving the formation of the peroxo-complex and its reaction with the olefin cannot be regarded as proved. In catalysis by molybdenyl chelate complexes molybdenum bis(diolate) was identified as the main product derived from the catalyst in the presence of an olefin and a hydroperoxide[128,129]. The structure of the diol in the chelate complex corresponds to that of the initial olefin. It has been suggested that such diols can form complexes with hydroperoxides,

probably with dissociation of one of the coordinate bonds between the diol and the molybdenum(VI) ion[120]:

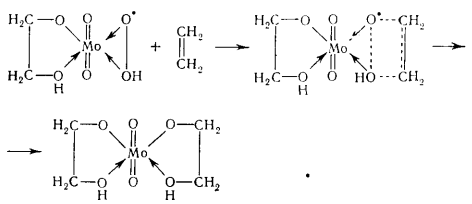


The hydroperoxide in the complex thus formed is activated and can react with the diol in the coordination sphere of the metal to form an oxide (from the diol) and alcohol:



(14)

The initial diolate is reduced and a cyclic catalytic complex is formed via the mechanism



In most investigations of the catalytic epoxidation of olefins the inhibition of the reaction by alcohols was noted. As a rule this effect is attributed to a competitive inhibition mechanism, i.e. the formation of the stable complexes Cat.ROH, which prevent the formation of catalyst–hydroperoxide complexes in the system. Although this mechanism of the inhibition of the epoxidation process by alcohols is extremely probable, it may not be the only one possible.

It has been shown[120] that the introduction of an alcohol into a molybdenum(VI)–ROOH system increases the concentration of the Mo(V).$RO_2^{\cdot}$ species and it has been suggested that the inhibition by alcohols is caused by the acceleration of reaction (13) and the consequent decrease of the concentration of the Mo(VI).ROOH complexes and of the rate of reaction (14). This hypothesis is consistent with the absence of an effect by the alcohol on the kinetics of the formation of the primary red complex in catalysis by vanadyl acetylacetonate and with the increased stability of this complex, if it is supposed that the red complex formed by organic peroxides is analogous to $O{=}VOOH^{+}$. Together with molybdenum(VI) compounds, zero-valent molybdenum carbonyls can serve as active epoxidation catalysts[129–133].

In the absence of an olefin, the hydroperoxide decomposes on $Mo(CO)_6$ via an oxidation-reduction mechanism with a change in the valence of molybdenum. The introduction of phenols into the system leads to the formation of π complexes of the phenol and $Mo(CO)_6$. The decomposition of the hydroperoxide then proceeds without a change in the valence of molybdenum via a synchronous mechanism and involves a reaction between the phenol in the complex and two hydroperoxide molecules[134].

The study of the infrared spectra of molybdenum hexacarbonyl in the presence of an olefin and a hydroperoxide showed that the valence state of molybdenum does not change in the epoxidation reaction[130–133]. The kinetic epoxidation curves nevertheless show a distinct induction period, which suggests the necessity for an $Mo(CO)_6$ dissociation stage. An NMR study of the $Mo(CO)_6$–α-phenylethyl hydroperoxide system in dichloroethane demonstrated the formation of the outer-sphere complexes $Mo(CO)_6$.ROOH with subsequent displacement of CO and the incorporation of the hydroperoxide in the inner coordination sphere:

$$Mo(CO)_6 + ROOH \rightarrow Mo(CO)_6 \cdot ROOH \xrightarrow{-CO} Mo(CO)_5 \cdot ROOH.$$

It is suggested that the epoxidation proceeds via a stage involving the formation of the mixed-ligand complexes $Mo(CO)_{6-1-n}.(olefin)_n.ROOH$.

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Institute of Chemical Physics,
USSR Academy of Sciences,
Moscow