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Selective catalytic oxidation of hydrocarbons. New prospects

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Abstract. Methods for enhancing the catalytic activity of transition metal complexes in hydrocarbon (particularly, alkylarene) oxidation with dioxygen are briefly discussed. Attention is focused on the original method of controlling the catalytic activity of complexes ML^1_n [M = Ni(II), Fe(II,III); L = acac, enamac; $n = 2, 3$] in the alkylarene oxidation to hydroperoxides by introducing additional electron-donating mono- or polydentate modifying ligands L^2. The role played by H-bonds in the mechanisms of homogeneous catalysis is discussed. A strategy of controlling the catalytic activity of Fe(II,III)(acac)$_n \cdot L^2$ complexes ($L^2 = R_4NBr$ or 18-crown-6) by adding H_2O to small concentrations is proposed. The activity of Ni and Fe catalysts in microsteps of chain initiation and propagation in the radical chain process of ethylbenzene oxidation is assessed. The bibliography includes 143 references.

I. Introduction

Oxidation of hydrocarbons with air or molecular oxygen is the simplest way to produce many valuable chemicals, such as alcohols, carbonyl compounds and epoxides.[1] The majority of hydrocarbon oxidation processes carried out on the industrial scale are the auto-oxidation reactions. Theoretical studies of the mechanism of hydrocarbon oxidation were initiated first of all by the demands of the ever-growing polymer industry. The studies carried out under supervision of N N Semenov (gas-phase oxidation reactions)[2] and later by N M Emanuel[3] and R A Sheldon[4] (liquid-phase oxidation reactions of hydrocarbons with molecular oxygen) substantiated the concept of chain reactions of hydrocarbon auto-oxidation and laid the firm basis for the theory of free-radical auto-oxidation.

The progress in industrial processes of hydrocarbon oxidation depends primarily on the ability of scientists to control these processes. One of effective methods of exerting control over the rate and the mechanism of hydrocarbon free-radical auto-oxidation consists of changing the medium in which this oxidation occurs (see Refs 1, 5, 6). The choice of catalyst plays no less important role in controlling liquid-phase oxidation of hydrocarbons. Selective oxidation of hydrocarbons with molecular oxygen most often employs metal complex catalysts. In recent years, the studies in the field of homogeneous catalytic oxidation of hydrocarbons with molecular oxygen were developed in two directions, namely, the free-radical chain oxidation catalyzed by transition metal complexes and the catalysis by metal complexes that mimic enzymes. Low yields of oxidation products in relation to the consumed catalyst caused by the fast catalyst deactivation are the main obstacle to the use of the majority of biomimetic systems on the industrial scale.[1, 7]

In the studies by Emanuel and his school,[8–13] it was established for the first time that transition metal compounds take part as catalysts (Ct) in all elementary steps of hydrocarbon chain oxidation with molecular oxygen, namely, chain initiation ($Ct + O_2$, activation of O_2), branching ($Ct + ROOH$), propagation ($Ct + RO_2^{\bullet}$) and termination (linear termination of chains on catalysts).† Later, this discovery was confirmed and described in several reviews and monographs (see Refs 17–21). However, no complete understanding was reached so far on the mechanism of hydrocarbon oxidation catalyzed by transition-metal complexes. Attention of scientists is focused on the role of transition metal compounds in the steps of generation of free radicals (in chain initiation and hydroperoxide decomposition), while the reaction of a catalyst with peroxide

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† Ethylbenzene oxidation with molecular oxygen, catalyzed by nickel compounds [acetylacetonates (acac) and stearates (St)] was studied in detail by Matienko *et al.*[13–16]

radicals (chain propagation) still remains insufficiently explored.

The most challenging problem is the selective oxidation of hydrocarbons to hydroperoxides, the primary oxidation products. The selectivity (S) of oxidation of alkylarenes with activated C–H bonds (of ehylbenzene or cumene) to hydroperoxides is sufficiently high ($\sim$80%–95%) where the degree of conversion is low ($\sim$1%–2%).[22] In this case, the challenge is synthesizing target products at high rates and in high yields. It should be noted that no efficient catalysts, except for Ni(II)-based catalytic systems proposed by Matienko *et al.*,[13–16] were found so far for the selective oxidation of ethylbenzene to α-phenylethyl hydroperoxide, despite the fact that the ethylbenzene oxidation catalyzed by both homogeneous and heterogeneous catalysts was sufficiently well studied and described in many publications (*e.g.*, see Refs 22–26).

In addition to academic interest, the problem of selective oxidation of alkylarenes to hydroperoxides is economically sound. Hydroperoxides are used as intermediates in the large-scale production of important monomers. For instance, propylene oxide and styrene are synthesized from α-phenylethyl hydroperoxide, and cumyl hydroperoxide is the precursor in the synthesis of phenol and acetone.[1,6]

Oxidation of alkylarenes with dioxygen catalyzed by model systems mimicking biological systems (mono- and dioxygenases) that favour the selective insertion of oxygen atoms into C–H bonds of organic molecules affords alcohols and carbonyl compounds.[27–31] Unfortunately, dioxygenases capable of effecting alkane dioxygenation to hydroperoxides are so far unknown.[28]

The recently discovered molybdenum-containing enzyme, namely, ethylbenzenede hydrogenase (EBDH), catalyzes anaerobic oxidation of ethylbenzene to (S)-1-phenylethanol.[30]

The present review briefly surveys the methods used for enhancing the catalytic activity of transition metal complexes in the processes of alkylarene oxidation with dioxygen.

Attention is focused on a method of modifying the Ni(II) and Fe(II,III) complexes used in the selective oxidation of alkylarenes (ethylbenzene and cumene) with molecular oxygen to afford the corresponding hydroperoxides aimed at increasing their selectivities. This method first proposed by Matienko[32] consists of introducing additional mono- or multidentate modifying ligands into catalytic metal complexes. The mechanism of action of such modifying ligands was elucidated. New efficient catalysts of selective oxidation of ethylbenzene to α-phenylethyl hydroperoxide were developed.[32]

II. Homogeneous catalytic oxidation of alkylarenes with dioxygen

The processes of selective radical chain oxidation of alkylarenes with molecular oxygen catalyzed by systems based on transition metal compounds include first of all the reactions that afford deep oxidation products.[6,33] One of the brightest examples is the oxidation of alkylarenes to carbonyl compounds and carboxylic acids in the presence of so-called MC-catalysts [complexes of Co(II) and Mn(II), HBr, HOAc].[6] For example, cobalt complexes with pyridine catalyze the ethylbenzene solvent-free oxidation to acetophenone with 90% selectivity and 70% conversion.[34] Manganese porphyrin complexes catalyze the ethylbenzene aerobic oxidation in the presence of acetaldehyde to a mixture of 1-phenylethanol (methylphenylcarbinol, MPC) and acetophenone (AP) in the 3 : 14 ratio.[35]

In the presence of acetaldehyde, the $CuCl_2$–18-crown-6 ether system efficiently catalyzes oxidation of ethylbenzene, indane and tetralin with molecular oxygen to afford the corresponding alcohols and ketones (70 °C) with a high TON (TON is the turnover number of a catalyst).[36] It was found that this reaction follows the radical chain mechanism rather than proceeds *via* a transient metal-oxo intermediate. Indan oxidation at room temperature resulted in the corresponding hydroperoxide. The latter was the main reaction product in both the presence and the absence of a crown ether.[37]

Solvent-free oxidation of ethylbenzene with dioxygen at 70–110 °C catalyzed by the FeTPFPP complex [TPFPP is 5,10,15,20-tetrakis(pentafluorophenyl)porphyrin] afforded a mixture of α-phenylethyl hydroperoxide, methylphenylcarbinol and acetophenone (1 : 1 : 1). The oxidation proceeded by the radical chain mechanism, the degree of conversion of ethylbenzene did not exceed 5%.[38]

Aerobic oxidation of ethylbenzene at $T > 60$ °C and atmospheric pressure catalyzed by μ-oxo-bis[iron(or mangenese)tetraphenylporphyrinate] ($[TPPFe]_2O$ or $[TPPMn]_2O$) in the absence of additives afforded methylphenylcarbinol and acetophenone. In this case too, the oxidation followed the radical chain route. In the catalysis with $[TPPFe]_2O$, the ketone : alcohol ratio was 3.76 (ethylbenzene conversion was 8.08%), while for the catalysis with $[TPPMn]_2O$, this ratio was 2.74 (ethylbenzene conversion was 3.73%).[39]

III. Methods for enhancing the activity and selectivity of homogeneous catalysts in oxidation processes

Metal complex catalysis allows one to regulate the relative rates of elementary steps of chain initiation, branching and propagation, thus controlling the rate and the selectivity of the overall process of radical chain oxidation.[22] By changing the ligand environment of the metal atom and adding different activating compounds, it is possible to vary the yields of target products and thus control the reaction selectivity.

The catalyst operation is usually accompanied by its deactivation. It should be mentioned that in its original form, a catalyst often represents only a precursor of a real catalytic species. By introducing additives into the oxidation reaction, it is possible to accelerate the formation of catalytically active species and prevent or hinder the processes that lead to the catalyst deactivation. Understanding of the mechanism of operation, in elementary steps of radical chain oxidation, of active catalytic species formed upon the introduction of additives may apparently lead to the development of new efficient catalytic systems and selective oxidation processes.

In heterogeneous catalysis, the method of modifying a catalyst by different additives that enhance its activity and prevent its deactivation were used rather extensively, whereas in the homogeneous catalysis, the use of various modifiers was not systematic. Studies aimed at investigation of the mechanism of action of additives were scarce. They were basically aimed at studying the effect of added modifying ligands on the catalyst activity in the chain initiation steps, namely, the O_2 activation and the homolytic decom-

position of ROOH.[22,23] Moreover, in the majority of schemes of catalytic radical-chain oxidation of hydrocarbons, the O_2 activation with a transition metal complex was totally ignored.

The effect of modifying ligands, which usually occupy the axial position in a complex, was as a rule studied using model compounds that mimic active sites of enzymes, namely, mono- and dioxygenases. At present, examples of catalytic systems are known that substantially increase the rates of catalyzed reactions and, sometimes, the yields of products upon the addition of modifiers. As a rule, the mechanisms of action of additives were not established, although possible schemes were put forward to explain the action of modifying ligands.[40]

Selective aerobic oxidation of light normal alkanes to alcohols at 100 °C catalyzed by halogen-substituted metalloporphyrins was described.[41–44] The introduction of electron-withdrawing substituents into the porphyrin ligand increased both the stability of iron porphyrin complexes in the oxidative destruction ‡ and their activity.[41,42] Moreover, the presence of additional ligands at the metal atom favoured the increase in the catalyst activity. Oxidation of branched alkanes such as 2-methylbutane, 3-methylpentane, 2,3-dimethylbutane and 1,2,3-trimethylbutane resulted in a mixture of products of the C–C bond secondary cleavage.[42] At present, the radical chain oxidation involving peroxide radicals is assumed to be the most probable mechanism of this reaction. This mechanism differs from that of alkane oxidation mediated by cytochrome P-450 and methane monooxygenase (transfer of an oxygen atom to the substrate, which involves the formation of an active high-valence metal-oxo intermediate).[43–45]

Calculations have confirmed the radical chain mechanism of isobutane autooxidation with dioxygen in the presence of halogen-substituted iron porphyrin complexes.[43–45] It was shown that the key role of electronegative substituents consists of increasing the Fe(III)/Fe(II) reduction potential and accelerating the decomposition of the intermediate (*tert*-butyl hydroperoxide) with a Fe(III) complex.

1. Immobilization of homogeneous catalysts on heterogeneous supports

Several studies[46–53] were devoted to the processes of alkylarene oxidation in the presence of metal complexes immobilized on the surface of a polymer or a mineral carrier (silica gel, zeolite). The advantages of using immobilized catalysts include the enhancement of stability of metal complexes upon their fixation, a possibility of catalyst separation from the oxidation products to be reused and the control over the catalyst activity through its microenvironment exerted by the support. For example, metal complexes fixed in zeolite pores are protected by the inert zeolite cage from deactivation, as a result of which the lifetime of an encapsulated catalyst increases.[47] Moreover, zeolite controls the product formation by exerting the electronic and steric effects on the reaction transition state. Zeolites also control entry of the reactants into pores and the exit of reaction products from the pores.

One limitation to the use of zeolites is the small size of tunnels and pores, not exceeding 10 Å, which makes the inner surface of zeolites poorly accessible for reagents.[49] The formation of mesopore-modified zeolites aimed at making their inner surface more accessible had become the subject of many studies. For this purpose, different methods of chemical treatment of zeolites were used, which made possible achievement of the pore sizes of ~5–50 nm.[47]

Yet another limitation to the use of zeolites in the oxidation of low-polar alkanes is their high hydrophilicity that leads to deactivation of zeolites due to the sorption of polar products and solvents in their pores. The high hydrophilicity of zeolites is the result of a low Si/Al ratio (however, even with a substantially higher Si/Al ratio, the zeolite activity increased insignificantly).[47] A more effective method is design of a hydrophobic environment for the active site, which allows one to solve the problems of catalyst activity and desorption of polar products.

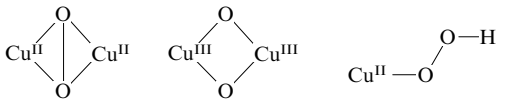
Aerobic oxidation of cyclohexane to adipic acid carried out using Fe–aluminophosphate-31 (ALPO-31) molecular sieves, *i.e.*, zeolites with narrow pores 0.54 nm in diameter, has demonstrated that cyclohexane easily adsorbs in the zeolite micropores.[50] However, the desoption of primary products of cyclohexane oxidation such as cyclohexyl peroxide and cyclohexanone proceeded slowly; hence, they underwent further transformations that led to opening of the cyclohexane ring. Adipic acid formed was sufficiently mobile to diffuse out of the molecular sieve. On the other hand, the use of Fe–ALPO-5 molecular sieves with larger pores afforded cyclohexanol and cyclohexanone (~60%) as the main oxidation products. It follows from the considered example that the localization of a free-radical reaction inside micropores apparently favours the increase in its selectivity.

Immobilization of metal complexes on a support often did not change their activity. Thus in the aerobic ethylbenzene oxidation catalyzed by iron(III) tetrakis(pentafluorophenyl)porphyrin[48] immobilized on silica gel or a polymer surface the same products, namely, α-phenylethyl hydroperoxide, methylphenylcarbinol and acetophenone (1 : 1 : 1), were formed as in the catalysis with homogeneous FeTPFPP. This suggests the same reaction mechanism in both cases. Heterogeneous catalytic oxidation proceeds more slowly than homogeneous; the yields of products depend on the iron porphyrin stability : activity ratio, which is associated with the catalyst loading and the support-based microenvironment.

Copper complexes with tri- and tetraazamacrocyclic ligands such as 1,4,7-triazacyclononane, 1,4,7-trimethyl-1,4,7-triazacyclononane, 1,4,7,10-tetraazacyclododecane, 1,4,7,10-tetramethyl-1,4,7,10-tetraazacyclododecane and 1,4,8,11-tetraazacyclotetradecane, both 'neat' complexes and encapsulated into zeolite-Y manifested activity in the regioselective ethylbenzene oxidation with *tert*-butyl hydroperoxide.[51] Acetophenone was the main reaction product, but small amounts of *o*- and *p*-hydroxyacetophenones were formed. Thus, not only the C–H bond of the alkyl chain, but also the C–H bonds of the aromatic ring were activated. The latter is typical of homogeneous 'neat' complexes, but virtually was not observed for encapsulated complexes. The possible reasons for the different activity : selectivity ratios of encapsulated and soluble catalysts consist of the encapsulation of the molecules of the complex and the absence of intermolecular interactions for encapsulated catalysts (as confirmed by the EPR spectroscopic data) and also of the interaction of copper complexes with the zeolite cage and the limited access of ethylbenzene to the

‡ Though observed to increase, the stability of such complexes remained moderate as indicated by the low conversion of alkanes.

catalyst active sites. The different selectivity of homogeneous and encapsulated catalysts is associated with formation of different types of active intermediates (**A**–**C** species) in the reaction of *tert*-butyl hydroperoxide with copper atoms and in their different ratios.



A **B** **C**

Water-soluble catalysts based on metal complexes and containing terminal functionalized poly(ethylene glycols) (PEG) or block-co-polymers of ethylene oxide and propylene oxide with different combinations of ethylene and propylene oxide fragments were described.[52] Such catalysts combined the properties of metals and surfactants. Polymers functionalized with bipyridyl and acetylacetone were used as the ligands in the preparation of the corresponding Co(II) complexes. Under the same conditions (120 °C), the PEG–acacCo complexes§ exhibited the higher activity in ethylbenzene oxidation with dioxygen as compared with their non-polymeric analogue $Co(acac)_2$. Acetophenone was the only oxidation product.

Oxidation of cyclooctane with dioxygen catalyzed by NaX-zeolite-encapsulated cationic metalloporphyrins of Co, Mn, Fe produced the higher cyclooctanone : cyclooctanol ratio as compared with the catalysis with metalloporphyrins immobilized on silicon, polystyrene, or montmorillonite supports and virtually coincided with the ratio obtained in the reaction catalyzed by soluble cationic metalloporphyrines.[53]

2. Modification of metallocomplex catalysts by addition of monodentate axial ligands

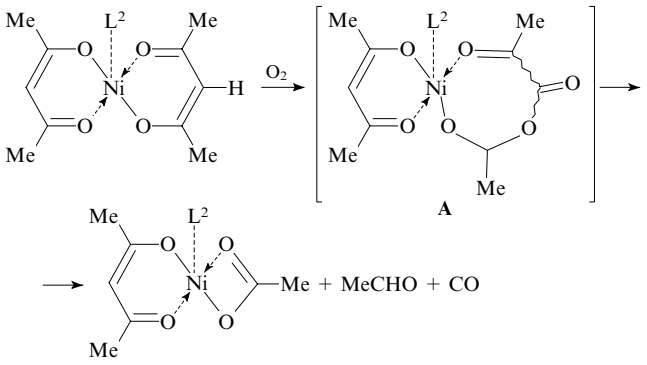
The phenomenon of a substantial increase in the initial rate (w_0), selectivity (S) and conversion (C) of the alkylarene (ethylbenzene and cumene) oxidation to the corresponding hydroperoxides upon addition of electron-donating monodentate ligands L^2 (L^2 is hexamethylphosphorotriamide (HMPA), dimethylformamide (DMF), *N*-metyl-2-pyrrolidone (MP), alkali metal stearate M′St (M′ = Li, Na, K) to metal complexes $M(acac)_2$ [M = Ni(II), Co(II), Fe(II)] was discovered.[54–57]

By the example of ethylbenzene oxidation with dioxygen (120 °C), the mechanism of controlling the catalytic activity of $Ni(acac)_2$ by adding electron-donating monodentate ligands L^2 was elucidated (see Refs 32, 58—60).

The coordination of the ligand L^2 to an NiL^1_2 complex changes the symmetry and the activity of the complex. The catalytic activity of the *in situ* formed $NiL^1_2 \cdot L^2$ complexes containing ligands L^2 in the axial position is higher than that of the original complexes NiL^1_2, which is manifested in the acceleration of free radical formation in the steps of chain initiation (O_2 activation) and homolytic decomposition of α-phenylethyl hydroperoxide (PEH) and also in the increase in the initial rate of ethylbenzene oxidation in the first macro stage.[57, 58] In the latter oxidation stage, the selectivity of ethylbenzene oxidation to PEH was fairly low [$(S_{PEH})_{max} \approx 80\%$]. As this process developed further (to the second macro stage), its selectivity increased [$(S_{PEH})_{max} = 90\%$] and the reaction rate (w) decreased. It was found that in the second macro stage, ligands L^2 control the conversion of $Ni(acac)_2$ complexes to reactive species $Ni(acac)(AcO) \cdot L^2$ thus changing the direction of side product formation, namely, the sequential formation of acetophenone and methylphenylcarbinol as a result of PEH decomposition gives way to their parallel formation by the quadratic radical termination and in the catalyst-mediated step of chain propagation. In the third macro stage of ethylbenzene oxidation, S_{PEH} sharply decreased, which is associated with the heterolytic decomposition of α-phenylethyl hydroperoxide to phenol and acetaldehyde catalyzed by $Ni(OAc)_2$. The latter complex is the final transformation product of the primary complex $Ni(acac)_2 \cdot L^2$ (see Refs 32, 58–60).

It was shown[32] that the selective catalyst $Ni(acac)(AcO) \cdot L^2$ was formed as a result of the ligand L^2-controlled regioselective addition of O_2 to a nucleophilic carbon atom (γ-C) of the acac ligand. The coordination of the electron-donating axial ligand L^2 with the $Ni(acac)_2$ complex stabilized the intermediate zwitter-ion $[L^2(acac)Ni(acac)^+ \cdots O_2^-]$ and increased the probability of regioselective insertion of O_2 to the acetylacetonate ligand activated by coordination with the nickel(II) ion. Further incorporation of O_2 into the chelate acac-ring was accompanied by the proton transfer and the redistribution of bonds in the transition complex **A** leading to the scission of the cyclic system C(O)MeC(O)OCH(Me)O to form a chelate ligand OAc^-, acetaldehyde and CO (in the Criegee rearrangement) (Scheme 1).

Scheme 1



As a result of this process, reactive mono- and polynuclear heteroligand complexes with the general composition $Ni_x(acac)_y(AcO)_z(L^2)_n$ were formed.[32, 58–60]

$$Ni(acac)_2 \cdot L^2 \xrightarrow{O_2} [L^2(acac)Ni(acac)^+ \cdots O_2^-] \longrightarrow$$
$$\longrightarrow L^2(acac)Ni(AcO) + MeCHO + CO,$$

$$2\,Ni(acac)_2 \cdot L^2 \xrightarrow{O_2} Ni_2(AcO)_3(acac)L^2 + 3\,MeCHO + 3\,CO + L^2.$$

L^2 = HMPA, DMF, MP, M′St (M′ = Na, Li, K).

The structure of the complex $Ni_2(OAc)_3(acac)L^2$ (L^2 = MP) was confirmed kinetically and using different physicochemical methods (mass spectrometry, electron and IR spectroscopies) and elemental analysis.[32]

The only known Ni(II)-containing dioxygenase ARD (acireducton dioxygenase), which catalyzes the oxidative decomposition of β-diketones, operates in the analogous

§ In a PEG–acacCo complex, the Co atom is fixed at the end of the polymeric chain by the acac ligand and surrounded by oxygen atoms of the PEG chain. Such a surrounding is labile and does not prevent the activation of molecular oxygen.

way.[61] This applies to the functional enzyme models, namely, Cu(II)- and Fe(II)-containing quercetin 2,3-dioxygenases, which catalyze the decomposition of β-diketones in the enol form to carbonyl compounds with CO evolution.[62, 63]

The transformations of the complex $Ni(enamac)_2$ [$enamac^- = C(O)MeCHC(Me)NH^-$, the chelate group in (O/NH)] occurred in both the presence and the absence of activating ligands (L^2)[59] by analogy with oxygenation reactions that mimic L-triptophan 2,3-dioxygenase.[64, 65]

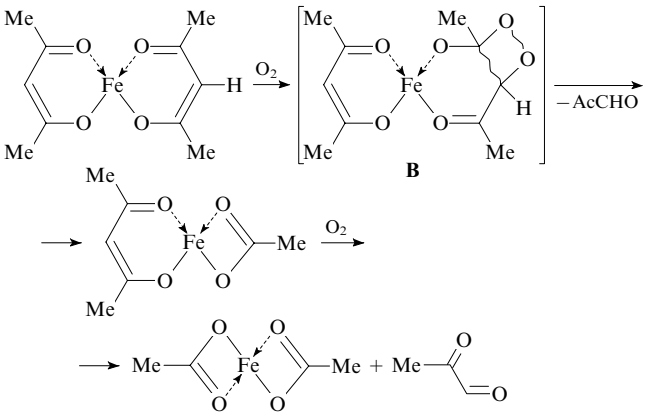
$$Ni(enamac)_2 + O_2 \longrightarrow [(enamac)Ni(enamac)^+\cdots O_2^-] \longrightarrow$$

$$\longrightarrow (enamac)Ni(NHCOMe) \xrightarrow{H_2O} (enamac)Ni(AcO) + NH_3$$

The common kinetic features of ethylbenzene oxidation in the presence of catalytic systems such as $\{Ni(acac)_2 + L^2\}$ (L^2 = HMPA, DMF) and $\{Fe(acac)_3 + L^2\}$ (L^2 = DMF) at 120 °C make it possible to assume that the transformation of *in situ* formed (nascent) $Fe^{II}(acac)_2 \cdot DMF$ complexes into more reactive catalytic species could also be a result of the ligand L^2-controlled regioselective addition of O_2 to the γ-C atom of the acetylacetonate ligand.[66] However, the favourable combination of electronic and steric factors that operate during the inner- and outer-sphere (hydrogen bonding) coordination of a DMF ligand to $Fe(acac)_2$ may promote the acetylacetonate ligand oxygenation by another route realized in the action of Fe(II) acetylacetone dioxygenase (Dke 1).

An illustration of O_2-dependent conversion of 2,4-pentadione catalyzed by Fe(II) acetylacetone dioxygenase is as follows (Scheme 2).

Scheme 2


Me
O
Fe
H
O2
−AcCHO
B
Me
Me
Me

the catalytically active $Ni_x(acac)_y(OAc)_z(L^2)_n$ complex (see Scheme 1) responsible for the oxidation selectivity. The activation proceeds in the following two steps: the first step represents the fast exchange interaction of the primary complex $Ni(acac)_2 \cdot L^2$ with a $Ni(OAc)_2$ complex formed during the ethylbenzene oxidation to afford a heteroligand complex $Ni(acac)(OAc) \cdot L^2$; the second step is the regioselective oxygenation of the latter to form a binuclear $Ni_2(acac)(OAc)_3 \cdot L^2$ complex.

$$Ni(acac)_2 \cdot L^2 + Ni(OAc)_2 + L^2 \longrightarrow 2\,Ni(acac)(OAc) \cdot L^2,$$

$$2\,Ni(acac)(OAc) \cdot L^2 + O_2 \longrightarrow$$

$$\longrightarrow Ni_2(acac)(OAc)_3 \cdot L^2 + MeCHO + CO + L^2.$$

The exchange interaction between $Ni(acac)_2 \cdot L^2$ and $Ni(OAc)_2$ was confirmed by the activation of the $\{Ni(acac)_2 + L^2\}$ catalytic system upon the addition of acetylacetone (acacH). However, in this case the degree of conversion $C_{S=90\%}$ increased to the lesser extent as compared with the addition of $Ni(acac)_2$ to this system, which was attributed to the oxidation of uncoordinated acacH.

The role of the second stage in the catalyst activation, namely, in the formation of a binuclear nickel complex was proved by introducting electron-withdrawing additives. We have found[58] that the simultaneous addition of the $Ni(acac)_2$ complex and a π-acceptor E (tetracyanoethylene or chloranil) into the $\{Ni(acac)_2 + L^2\}$ catalytic system did not increase the degree of conversion $C_{S=90\%}$. The passivation of the catalytic system upon the introduction of tetracyanoethylene or chloranil can be rationalised as follows. These electron acceptors electrophilically attack the γ-C atom of the $acac^-$-ligand stronger than O_2 thus preventing the O_2 addition and the formation of a reactive binuclear heteroligand complex.

3. Modelling the catalytic activity of transition metal complexes by adding quaternary ammonium salts and macrocyclic polyethers as the modifying ligands

Quaternary ammonium salts are well known as cationic surfactants. In aqueous solutions, amphiphilic molecules of these salts are associated into micelles; at higher concentrations, they form liotropic [trimethylcetylammonium bromide (CTAB) is their typical representative] or thermotropic mesophases. Quaternary ammonium salts are used as the phase-transfer catalysts or as ionic liquids (IL) in the synthesis of nanosized catalysts.[69–73]

As was shown earlier, in a catalytic reaction that occurs in a water–organic medium, quaternary ammonium salts (R_4NX) play two different roles, namely, act as phase-transfer catalysts and simultaneously interact with the catalyst thus activating the latter. For example, in the reaction of oxybromination of aromatic compounds, a lipophilic ammonium salt R_4NBr not only transferred H_2O_2 to the organic phase but, being a Lewis acid, formed $R_4NBr(Br_2)_n$ or $R_4NBr(HBr)_n$ adducts thus activating the Br_2 or HBr molecules for the electrophilic attack on the aromatic ring.[73]

In the reactions of catalytic oxidation of styrene to benzaldehyde with hydrogen peroxide in the water–organic solvent system, ammonium salts transfer (due to the formation of hydrogen bonds) H_2O_2 and the catalyst (Ru, Pd) to the organic phase. Moreover, they change the catalyst properties by forming complexes with it, thus affecting its activity (reaction rate and selectivity).[74] Thus, the *p*-xylene oxidation in water–organic media in the presence of $CoBr_2$ and R_4NBr salts involved participation of catalytically active complexes $CoBr_2 \cdot R_4NBr$.[75] Complexes $[Me_4N]NiBr_3$ were synthesized and their physical properties were studied.[76] It is known that the catalytic activity of metal compounds in the presence of CTAB depends on the structure of inverse micelles formed.[77,78]

Quaternary ammonium salts also form complexes with transition metal complexes. For example, it was shown that $M(acac)_2$ (M = Ni, Cu) and salts $Me_4N^+(acac)^-$ form complexes with the composition $[Me_4N][M(acac)_3]$.[79] Spectral methods revealed the octahedral geometry of these complexes.

Selective complexation of crown ethers is among their most attractive properties. Crown ethers are also of interest as the models of enzyme active sites.[70,80] In processes involving crown ethers, the important role is played by intermolecular and intramolecular hydrogen bonds.[80]

The recent years were marked by the increased interest in studying the structure and catalytic activity of nickel complexes (especially nickel complexes with macrocyclic ligands) due to the discovery of nickel-containing enzymes. The latter are the already mentioned Ni(II)-containing dioxygenase ARD;[61] urease with a binuclear nickel complex containing N/O-donor ligands in their active site; redox enzymes [methyl-*S*-coenzyme M-reductase with a factor 430 (F_{430}), *i.e.*, a nickel complex with dodecahydroporphyrin (corphin)]; [NiFe]-hydrogenase with a Ni(III) complex in the active site; superoxide dismutase that contains a catalytic cycle $Ni(II) \leftrightarrow Ni(III)$.[81–85]

To date, the incorporation of transition metals into the cavities of macrocyclic polyethers was confirmed by different physicochemical methods; moreover, the specific structure of resulting complexes is determined not only by the geometric compatibility between the metal atom and the crown-ether cavity, but also by the whole ensemble of electronic and spatial factors induced by the metal atom, the polyether, the other ligands and also the solvent.[86]

The ability of quaternary ammonium salts and crown ethers to form complexes with compounds of transition metals was used in designing new effective catalytic systems for ethylbenzene selective oxidation to α-phenylethyl hydroperoxide.

It was shown that for relatively low concentrations ($\sim 1.5 \times 10^{-4}$ mol litre^{-1}) of nickel catalysts $Ni(acac)_2$ and $Ni(enamac)_2$ the selectivity of ethylbenzene oxidation to α-phenylethyl hydroperoxide is sufficiently high $(S_{PEH})_{max} = 90\%$. This can be rationalized by analyzing the proposed[3,8] scheme of catalytic oxidation of hydrocarbons in the presence of transition metal compounds (in this process, hydroperoxides, the primary products of hydrocarbon oxidation, are involved).

Scheme 3

$$M^{n+} + O_2 \longrightarrow M^{n+}...O_2 \xrightarrow{RH} M^{(n+1)+} + R^{\bullet} + HO_2^{\bullet}, \quad (1)$$

$$ROOH \longrightarrow RO^{\bullet} + {}^{\bullet}OH, \quad (1')$$

$$RH + O_2 \longrightarrow R^{\bullet} + HO_2^{\bullet}, \quad (1'')$$

$$R^{\bullet} + O_2 \longrightarrow RO_2^{\bullet} \xrightarrow{RH} ROOH + R^{\bullet}, \quad (2)$$

$$RO_2^{\bullet} + M \longrightarrow \text{products} + (R')^{\bullet}, \quad (2')$$

$$RH + (R')^{\bullet} \longrightarrow R^{\bullet} + R'H, \quad (2'')$$

$$ROOH + M^{n+} \longrightarrow M^{(n+1)+} + OH^- + RO^{\bullet} \xrightarrow{RH} \quad (3)$$

$$\longrightarrow ROH + R^{\bullet} + M^{(n+1)+},$$

$$ROOH + RO_2^{\bullet} \longrightarrow \text{products} + (R')^{\bullet}, \quad (4)$$

$$ROOH + M^{(n+1)+} \longrightarrow M^{n+} + RO_2^{\bullet} + H^+, \quad (4')$$

$$2\,RO_2^{\bullet} \longrightarrow \text{products}, \quad (5)$$

$$RO_2^{\bullet} + M \longrightarrow \text{products}. \quad (5')$$

According to Scheme 3, the catalyst is involved in reactions of chain initiation (1) and propagation (2′) and also in reactions of homolytic decomposition of ROOH (3) and chain termination (5′). The experimental data agree well with a scheme that includes reactions of chain initiation (1′, 2, 2″), ROOH chain decomposition (4), quadratic chain termination (5) and also reactions of the catalyst with ROOH (3) and radicals $RO_2^{\bullet}$ (2′). The involvement of the catalyst in the chain propagation (2′) makes it possible to explain the dependence of the maximum reaction rate on the catalyst concentration. Under these conditions, as the concentration [M] decreases, the reaction rate should decrease while the $[ROOH]_{max}$ concentration should increase.[3,8]

$$[ROOH]_{max} = \frac{k_2 k_{2''}[RH]^2}{k_4(k_{2'}[M] + k_{2''}[RH])},$$

$$w_{max} = k_2^2[RH]^2\sqrt{\frac{k_3[M]}{2k_4k_5(k_2[RH] + k_{2'}[M])}}.$$

Indeed, as the catalyst concentration decreased from 5×10^{-3} to 1.5×10^{-4} mol litre^{-1}, both deceleration of ethylbenzene oxidation and increase in $[ROOH]_{max}$ were observed; the $(S_{PEH})_{max}$ value also increased. The pathway of side product formation was also observed to change. Under these conditions, acetophenone and methylphenylcarbinol were formed in parallel with PEH ($w_{AP(MPC)}/w_{PEH} \neq 0$ at $t \to 0$) rather than as a result of PEH decomposition. Moreover, $w_{AP}/w_{MPC} \neq 0$ at $t \to 0$, which points to the parallel formation of AP and MPC.[32,59]

Introduction of electron-donating monodentate ligands L^2 (L^2 = HMPA, MP) into ethylbenzene oxidation mixture catalyzed by nickel complexes in small concentrations ($[Ct]_0 \leqslant 1.5\times10^{-4}$ mol litre^{-1}) proved ineffective and the quantities $(S_{PEH})_{max}$ and $C_{S=90\%}$ virtually remained unchanged.[32,55,58]

Taking into account the known ability of crown ethers and R_4NX to catalyze the electrophilic addition to the γ-C atom of the acetylacetonate ligand[70,87,88] and of quaternary ammonium salts to form complexes with acetylacetone in hydrocarbon media with strong hydrogen bonds $R_4N^+(X\cdots HOCMe{=}CHCOMe)^-$ (see ¶) where acetylacetone is completely enolysed,[88] we assumed that in the presence of a crown ether (18C6) or R_4NX the conversion of ethybenzene in the oxidation reaction catalyzed by the $Ni(acac)_2$ complex ($[Ni(acac)_2]_0 \approx 1.5\times10^{-4}$ mol litre^{-1}) may increase with retention of $(S_{PEH})_{max}$ at the level of no lower than 90%.

The favourable combination of electronic and steric factors as well as the formation of H-bonds upon the coordination of 18C6 and R_4NX to the $Ni(acac)_2$ complex not only favour the formation of active n-nuclear heteroligand complexes, but also hinder the transformation of the active catalyst into inactive species.

¶ In this context, the R_4NX controlled regioselective addition of an O_2 molecule to the γ-C atom of the acetylacetonate ligand in an $M(acac)_n\cdot R_4NX$ complex seems quite probable.

Our assumption was totally confirmed. Indeed, in the presence 18C6 the conversion of ethylbenzene to PEH upon oxidation catalyzed by $Ni(acac)_2$ and $Ni(enamac)_2$ complexes considerably increased: from 4% – 6% for $Ni(acac)_2$ to 12% for $Ni(acac)_2\cdot(18C6)_n$ (n = 1, 2) and from 12% for $Ni(enamac)_2$ to 16% for $Ni(enamac)_2\cdot18C6$; moreover, S_{PEH} exceeded 90%. Furthermore, the addition of 18C6 substantially increased the initial rate (w_0) of ethylbenzene oxidation (Table 1) and the maximum selectivity of its oxidation to PEH [$(S_{PEH})_{max}$] increased from 90% to 98% – 99%.[32,89,90]

Table 1. Dependence of initial rates of ethylbenzene oxidation in the presence of Ni complexes on the 18C6 concentration.

Catalyst	$w_0\times10^5$ (in mol litre^{-1} s^{-1}) at $[18C6]\times10^4$ (in mol litre^{-1})				
	0	0.8	1.5	3.0	6.0
$Ni(acac)_2$	2.36	5.38	8.61	8.15	4.44
$Ni(enamac)_2$	6.25	–	12.64	9.65	–

Note. The reaction temperature was 120 °C, $[ML_2] = 1.5\times10^{-4}$ mol litre^{-1}.

The introduction of Me_4NBr also increased the values of C (up to 19%), $(S_{PEH})_{max}$ (up to 95%) and w_0 in the reaction of ethylbenzene oxidation catalyzed by $Ni(acac)_2$.[32,91,92] However, in the case of 18C6, the maximum selectivity was observed in the very beginning of the reaction ($C \leqslant 1\%$), while for Me_4NBr this was observed only at deeper degrees of ethylbenzene conversion (C = 2% – 3%).

At the same time, in the ethylbenzene oxidation catalyzed by $Ni(acac)_2$ the addition of 18C6 or Me_4NBr led to a substantial inhibition of the PEH heterolysis to afford phenol [the latter reaction is responsible for the $(S_{PEH})_{max}$ reduction in the fully developed process]. Moreover, the induction period of PhOH formation in the presence of Me_4NBr additives considerably exceeded that in the case of 18C6 (see Refs 89 – 92).

The effect of R_4NX on the activity of the $Ni(acac)_2$ catalyst in the ethylbenzene oxidation to PEH depends on the structure of radical R in the ammonium cation. Thus upon the substitution of an n-$C_{16}H_{33}$ radical for one of methyl radicals in Me_4NBr, $(S_{PEH})_{max}$ decreased from 95% to 80% – 82%;[91,92] however, the initial reaction rate $(w_{PEH})_0$ substantially increased (Table 2). When the

Table 2. Initial rates of ethylbenzene oxidation to PEH and accumulation of side products (acetophenone and methylphenylcarbinol) as a function of the catalyst type.

Catalyst	$[R_4NBr]\times10^3$ /mol litre^{-1}	$(w_{PEH})_0\times10^5$ /mol litre^{-1} s^{-1}	$(w_{AP+MPC})_0\times10^6$ /mol litre^{-1} s^{-1}
$Ni(acac)_2$	–	2.1	2.7
$\{Ni(acac)_2 +$	0.5	2.7	2.2
$+ Me_4NBr\}$	1.0	2.9	1.8
	2.0	2.3	2.6
$\{Ni(acac)_2 +$	1.0	6.1	27.0
$+ CTAB\}$			

Note. $[Ni(acac)_2] = 1.5\times10^{-4}$ mol litre^{-1}, temperature is 120 °C.

$\{Ni(acac)_2 + Me_3(n\text{-}C_{16}H_{33})NBr\}$ system was used, the initial PEH accumulation rate $(w_{PEH})_0$ was higher as compared with the catalysis with the $\{Ni(acac)_2 + Me_4NBr\}$ system; however, the initial buildup rates of side products (AP and MPC) were also considerably higher. [When Me_4NBr was replaced by $Me_3(n\text{-}C_{16}H_{33})NBr$, the phenol formation and a decrease in the selectivity S_{PEH} were observed at lower ethylbenzene conversions.]

The analysis of the sequence of formation of ethylbenzene oxidation products catalyzed by the systems $\{NiL_2^1 + 18C6\}$ (L = acac, enamac) and $\{Ni(acac)_2 + R_4NBr\}$ has shown that in the course of this reaction, PEH, AP and MPC are formed in parallel ($w_{AP}/w_{PEH} \neq 0$, $w_{MPC}/w_{PEH} \neq 0$, $w_{AP}/w_{MPC} \neq 0$ at $t \to 0$).

The catalysis of ethylbenzene oxidation with the $\{Ni(acac)_2 + Me_3(n\text{-}C_{16}H_{33})NBr\}$ system is not apparently associated with the formation of a microphase such as inverse micelles, because the micellar effect of cetyltrimethylammonium bromide manifested at $T < 100$ °C [77] is as a rule insignificant at $T \geqslant 120$ °C. Furthermore, the system is inactive in the reaction of ROOH decomposition.

To assess the catalytic activity of nickel complexes $\{NiL_2^1 + L^2\}$ in ethylbenzene oxidation to α-phenyl ethylhydroperoxide, a parameter $\tilde{S} \cdot C$ ($\tilde{S}$ is the averaged selectivity of ethylbenzene oxidation to PEH) was chosen, which changes during the oxidation from S_0 (in the beginning of reaction) to a certain value S_{lim} (S_{lim} is an arbitrary value chosen as a standard); C is the degree of hydrocarbon conversion at $S = S_{lim}$).[32, 59] For S_{lim}, a value $(S_{PEH})_{max} = 80\%$ in the reaction of non-catalytic ethylbenzene oxidation was chosen. As regards the parameter $\tilde{S} \cdot C$, the system $\{Ni(acac)_2 + Me_4NBr\}$ proved to be the most active in the ethylbenzene oxidation to PEH.[32, 92]

Complex	$Ni(acac)_2$	$\{Ni(acac)_2 + 18C6\}$	$\{Ni(acac)_2 + Me_4NBr\}$
$(\tilde{S} \cdot C) \times 10^{-2}$ (%%)	9.6	20.6	24.3

In the presence of 18C6 or R_4NBr alone, without nickel complexes, the process of ethylbenzene oxidation to PEH was also autocatalytic; however, its initial rates were considerably lower than with NiL_2^1 complexes. The increase in w_0 and $\tilde{S} \cdot C$ on going from NiL_2^1 complexes to $\{NiL_2^1 + L^2\}$ systems points to the formation of active complexes of NiL_2^1 with L^2 with the following composition: 1 : 1 (for L^1 = acac$^-$; $L^2 = R_4NBr$) [90–93] and 1 : 1 or 1 : 2 (for L^1 = acac$^-$, enamac$^-$; L^2 = 18C6), and also of their transformation products. The stability of mono- and polynuclear heteroligand complexes $Ni_x(L^1)_y(L^1_{ox})_z(L^2)_n$ ($L^1_{ox} = AcO^-$, L^2 = 18C6, R_4NBr) formed upon oxidation could be due to the formation of both inter- and intra-molecular hydrogen bonds. In this case, the formation of supramolecular structures is highly probable.[94–96]

The formation of $NiL_2^1 \cdot L^2$ (L^2 = 18C6, R_4NBr) complexes was confirmed by UV spectra. The coordination of ligand L^2 with the metal ion proceeds without displacement of the ligand L^1 from the inner coordination sphere of the complex.[89–91] When complexes are formed with NiL_2^1, the ligand L^2 usually occupies the axial position [the fifth coordination place at the nickel(II) ion]; however, the outer-sphere coordination of L^2 with L^1 anion (H-bonding) is also probable.

The possibility of outer-sphere coordination of R_4NX with Ni(II) and Fe(III) β-diketonates was demonstrated by the example of complex $Fe(acac)_3$. The UV spectrum of tris(acetylacetonato)iron(III) had an absorption band at $\nu = 37 \times 10^3$ cm^{-1} ($CHCl_3$), caused by the $\pi - \pi^*$-transition in the conjugated chelate acac-ring.[91, 92] In the presence of salts Me_4NBr, $Me_3(n\text{-}C_{16}H_{33})NBr$, Et_4NBr, Et_3PhNCl, Bu_4NI and Bu_4NBr, a decrease in the maximum absorption in this band and its bathochromic shift to $\nu = 36 \times 10^3$ cm^{-1} ($\Delta\lambda \approx 10$ nm) were observed. Such changes in the UV spectra reflect the effect of R_4NX on the conjugation in the acac-ligand in the outer-sphere coordination of R_4NX. A change in the conjugation in the chelate ring of the acetylacetonate complex could be due to the involvement of oxygen atoms of the acac-ligand in the formation of covalent bonds with the nitrogen atom or hydrogen bonds with CH groups of alkyl substituents.[91, 92]

For ethylbenzene oxidation catalyzed by $Fe(acac)_3$ complexes, the reaction rate also decreased and the value $(S_{PEH})_{max}$ increased with a decrease in the catalyst concentration; however, the increase in S_{max} was less pronounced (from 42% – 46% to 65%) than in the case of nickel complexes. The curve that reflected the dependence of $[ROOH]_{max}$ on $[Fe(acac)_3]$ passed through a maximum, which points to a more complicated mechanism of catalysis.[66, 92, 97] Complexes $Fe^{III}(acac)_3$ and $Fe^{II}(acac)_2$ formed during the ethylbenzene oxidation exhibited no activity in the reaction of PEH decomposition.[66, 92, 97]

We have found that oxidation of ethylbenzene in the presence of $Fe^{III}(acac)_3$ $\{[Fe(acac)_3] = (0.5 - 5) \times 10^{-3}$ mol litre^{-1}, 80 or 120 °C$\}$ in addition to α-phenylethyl hydroperoxide results in acetophenone and methylphenylcarbinol as the main products. The latter are formed in parallel with PEH. Both in the beginning of reaction and in stages of deeper oxidation, the ratios $w_P/w_{PEH} \neq 0$ (P = AP and MPC) did not change with $t \to 0$.[66, 92, 97]

In studying the effect of electron-donating modifying ligands (DMF, HMPA and R_4NBr) on the parameters w, S_{PEH}, C and $\tilde{S} \cdot C$ of ethylbenzene oxidation in the presence of $Fe(acac)_3$ (5×10^{-3} mol litre^{-1}, 80 °C), it was found that with the addition of DMF, the magnitude of $(S_{PEH})_{max}$ did not differ from that in the $Fe(acac)_3$-mediated process in the absence of additives; in the presence of a monodentate ligand HMPA, the value of $(S_{PEH})_{max}$ increased from 42% to ~57% and the conversion increased from 5% to 15% (these are the maximum effects reached upon the addition of electron-donating monodentate modifying ligands to $Fe(acac)_3$);[66, 92] in the presence of $Me_3(n\text{-}C_{16}H_{33})NBr$, the magnitude of $(S_{PEH})_{max}$ increased even to 65% (see Ref. 99); moreover, in the initial stages of ethylbenzene oxidation, S_{PEH} sharply decreased (Fig. 2), which was associated with the transformation of Fe(III) complexes to Fe(II) complexes† (the auto-acceleration period). As the degree of conversion increased from 2% to 6%, S_{PEH} was observed to increase (curves *2* and *3* in Fig. 2), which was accompanied by a considerable deceleration of the formation of AP and MPC, while $[ROOH]_{max}$ more than doubled. The simultaneous addition of CTAB and H_2O to $Fe(acac)_3$ led to a still larger increase in S_{PEH} (to 78%). Thus, the addition of CTAB to the $Fe(acac)_3$ catalyst of ethylbenzene oxidation substantially inhibit the PEH heterolysis to phenol, a product responsible for the decrease in S_{PEH}.

† In the reaction of ethylbenzene oxidation catalyzed by the complexes $(Fe(acac)_2)_n(R_4NBr)_m$ formed, an increase in $(w_{PEH})_0$ and a decrease in $(w_P)_0$ were observed.

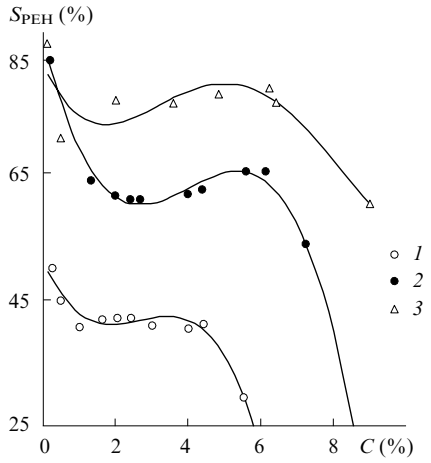


Figure 2. Dependences of S_{PEH} on C in reactions of ethylbenzene oxidation in the presence of $Fe(acac)_3$ (*1*), $\{Fe(acac)_3 + CTAB\}$ (*2*) and $\{Fe(acac)_3 + CTAB + H_2O\}$ (*3*).
$[Fe(acac)_3]_0 = 5 \times 10^{-3}$ mol litre^{-1}, $[R_4NBr] = 0.5 \times 10^{-3}$ mol litre^{-1}, $[H_2O] = 3.7 \times 10^{-3}$ mol litre^{-1}, 80 °C.

We studied the effect of the addition of different ammonium salts on the activity of the catalyst $Fe(acac)_3$. On going from $Fe(acac)_3$ to the $\{Fe(acac)_3 + R_4NBr\}$ systems, the parameter $\tilde{S} \cdot C$ was found to increase 2.6-, 2.36- and 1.4-fold for $Me_3(n\text{-}C_{16}H_{33})NBr$, Et_4NBr and Me_4NBr, respectively $\{[Fe(acac)_3] = 5 \times 10^{-3}$ mol litre^{-1}, $[R_4NBr] = 0.5 \times 10^{-3}$ mol litre$^{-1}\}$. In this case, the value S_{lim} was taken equal to $(S_{PEH})_{max} = 40\%$ in the reaction of ethylbenzene oxidation in the presence of $Fe(acac)_3$ (5×10^{-3} mol litre^{-1}, 80 °C).

Catalyst	$(\tilde{S} \cdot C) \times 10^{-2}$ (%%)
$Fe(acac)_3$	2.1
$\{Fe(acac)_3 + CTAB\}$	5.46
$\{Fe(acac)_3 + Et_4NBr\}$	4.97
$\{Fe(acac)_3 + Me_4NBr\}$	2.9

Considering these data, it is evident that the largest effect is achieved upon the addition of CTAB.‡

The synergistic increase in parameters $\tilde{S} \cdot C$ and w_0, which was observed in reactions of ethylbenzene oxidation in the presence of the complex $Fe(acac)_3$ and R_4NBr additives, together with the revealed kinetic relationships point to the formation of catalytically active complexes with the composition $(Fe(acac)_2)_n(R_4NBr)_m$ [93] as well as of other active species formed as a result of transformations of these complexes during the ethylbenzene oxidation.

Due to the favourable combination of electronic and steric factors that manifest themselves in the inner- and outer-sphere (formation of H-bonds) coordination of CTAB with $Fe(acac)_2$, the mechanism of oxidative decomposition of the acetylacetonate ligand is akin to that of 2,4-pentadione oxidation catalyzed by Fe(II)-containing acetylacetone dioxygenase (see Scheme 2). In this case, the probability of formation of stable Fe(acac)(OAc) complexes is sufficiently high. Obviously, the outersphere coordination of CTAB may bring about steric hindrance to the regioselective oxidation of the acac-ligand and to the transformation of the transient complex Fe(acac)(OAc) to the final dioxygenation product, namely, the complex $Fe(OAc)_2$.

Complexes $Fe^{II}_x(acac)_y(OAc)_z(DMF)_n$ formed in the course of ethylbenzene oxidation in the presence of a $\{Fe(acac)_3 + DMF\}$ system appeared to be instable, although DMF like CTAB formed H-bonds with the acac-anion.[66] If HMPA was used in place of DMF as the axial ligand, a stable complex, $Fe^{II}(acac)_2 \cdot HMPA$, was formed, which did not undergo changes during the ethylbenzene oxidation.

The catalysis of ethylbenzene oxidation by a $\{Fe(acac)_3 + CTAB\}$ system $\{[Fe(acac)_3] = 5 \times 10^{-3}$ mol litre^{-1}, 80 °C$\}$ in the presence of cetyltrimethylammonium bromide in low concentrations (0.5×10^{-3} mol litre^{-1}), an order of magnitude lower than the $[Fe(acac)_3]$ concentrations, was not apparently associated with the formation of a microphase in the form of spherical micelles.[77,78] The system $\{Fe(acac)_3 + CTAB\}$, like $\{Ni(acac)_2 + CTAB\}$, proved to be inactive in the PEH decomposition; AP and MPC are formed in parallel with PEH and with one another ($w_{AP}/w_{PEH} \neq 0$, $w_{MPC}/w_{PEH} \neq 0$ and $w_{AP}/w_{MPC} \neq 0$ at $t \to 0$). A similar mechanism of the formation of PEH, AP and MPC was observed when salts Me_4NBr or Et_4NBr unable to form micelles were added. The increase in the CTAB concentration (5×10^{-3} mol litre^{-1}) led to the sharp decrease in w_{PEH} and $[ROOH]_{max}$. Apparently, this was due to the acceleration of PEH decomposition as a result of incorporation of PEH molecules into surfactant (CTAB) micelles formed as inverse micelles, the probability of their formation increasing with the increase in the CTAB concentration.[77,78]

Thus, we have revealed an interesting fact that the addition of small amounts of R_4NBr [R_4NBr concentration is smaller that that of $Fe(acac)_3$ by an order of magnitude] results in an increase in the catalyst activity. In this case, active mono- and polynuclear heteroligand complexes $(Fe^{II}(acac)_2)_n(R_4NBr)_m$and $Fe^{II}_x(acac)_y(OAc)_z(R_4NBr)_n$ can be formed.

4. Three-component catalytic systems $\{Ni(acac)_2 + L^2 + PhOH\}$

The system $\{Ni(acac)_2 + L^2 + PhOH\}$ (L^2 = MP, M′St, where M′ = Na, Li) is one of the most efficient catalytic systems of ethylbenzene selective oxidation with molecular oxygen to afford α-phenylethyl hydroperoxide.[98] The use of this ternary system results in a considerable increase in $\tilde{S} \cdot C$, C (for $S_{PEH} \approx 85\% - 90\%$) and $[ROOH]_{max}$ as compared with their values obtained in a binary system $\{Ni(acac)_2 + L^2\}$.

The synergistic effect [93] of the increase in parameter $\tilde{S} \cdot C$ in the catalysis with the $\{Ni(acac)_2 + MP + PhOH\}$ system points to the unusual catalytic activity of the ternary complexes $ML^1_2(L^2)_n(PhOH)_m$ formed. The dependence of parameter $\tilde{S} \cdot C$ on the MP concentration at $[PhOH] = [Ni(acac)_2] = 3 \times 10^{-3}$ mol litre^{-1} demonstrated a maximum $[(\tilde{S} \cdot C)_{max} \approx 17.5 \times 10^2$ %%] at $[MP] = 7 \times 10^{-2}$ mol litre^{-1}, which corresponded to the formation of the complex $Ni(acac)_2 \cdot MP \cdot PhOH$ with the 1 : 1 : 1 composition Ref. 98). It is characteristic that the found value $(\tilde{S} \cdot C)_{max}$ exceeds $\tilde{S} \cdot C$ (11.9×10^2 %%) for complexes $Ni(acac)_2 \cdot MP$ and also for coordinatively saturated com-

‡ As was shown above, the addition of CTAB to $Ni(acac)_2$ complexes that catalyze the ethylbenzene oxidation to α-phenylethyl hydroperoxide led to the decrease in $(S_{PEH})_{max}$ from 90% to 80% – 82%, whereas addition of Me_4NBr increased $(S_{PEH})_{max}$ to 94%.[92]

plexes $Ni(acac)_2 \cdot 2\,MP$. The dependence of parameter $\tilde{S} \cdot C$ on the $Ni(acac)_2$ concentration at the constant values $[PhOH] = 3 \times 10^{-3}$ mol litre^{-1} and $[MP] = 7 \times 10^{-2}$ mol litre^{-1} also has an extremum, namely, the parameter $\tilde{S} \cdot C$ (17.47×10^2 %%) has a maximum at $[Ni(acac)_2] = 3 \times 10^{-3}$ mol litre^{-1}. The dependence $\tilde{S} \cdot C$ *vs.* [PhOH] at fixed concentrations of $Ni(acac)_2$ (3×10^{-3} mol litre^{-1}) and MP (7×10^{-2} mol litre^{-1}) has two maxima, namely, $(\tilde{S} \cdot C)_{max} = 17.5$ %% and 18.12×10^2 %% for $[PhOH] = 3 \times 10^{-3}$ and 4.6×10^{-4} mol litre^{-1}, respectively.

$[PhOH] \times 10^3$ /mol litre^{-1}	$(\tilde{S} \cdot C) \times 10^{-2}$ (%%)
0	11.9
0.2	11.9
0.46	18.12
1.0	16.2
1.6	15.9
3.0	17.47
5.0	11.89

The analysis of kinetic relationships for ethylbenzene oxidation catalyzed by two $\{Ni(acac)_2 + MP + PhOH\}$ systems differing in the phenol concentration {for $[Ni(acac)_2] = 3 \times 10^{-3}$ mol litre^{-1}, $[MP] = 7 \times 10^{-2}$ mol litre^{-1} and $[PhOH] = 3 \times 10^{-3}$ (catalytic system *A*) or 4.6×10^{-4} mol litre^{-1} (catalytic system *B*)} suggests that during the oxidation, one and the same catalytically active complexes with the composition 1 : 1 : 1 were formed.[93,98] Slight differences observed in the kinetics of PEH and PhOH accumulation in the initial stages of this reaction catalyzed by systems *A* and *B* were caused by the different initial conditions of the formation of ternary complexes $Ni(acac)_2 \cdot L^2 \cdot PhOH$. In the reaction catalyzed by system *B*, the phenol concentration was observed to rapidly increase to $[PhOH] = (3-5) \times 10^{-3}$ mol litre^{-1} (at $t = 0-5$ h), which corresponded to the formation of the complex $Ni(acac)_2 \cdot L^2 \cdot PhOH$ (Fig. 3). The increase in the phenol formation rate as a result of PEH heterolysis in the initial stages of the reaction catalyzed by system *B* can be explained by the strengthening of phenol acidic properties as a result of its outer-sphere coordination with the nickel complex $Ni(acac)_2 \cdot MP$.[99]

This assumption was confirmed as follows. The ethylbenzene oxidation catalyzed by coordinated saturated complexes $Ni(II)(acac)_2 \cdot 2\,MP$ occurs with phenol accumulation (rather than its consumption) with maximum initial rate $(w_{PhOH})_0 = (w_{PhOH})_{max}$ upon addition of phenol ($[PhOH] = 3.0 \times 10^{-3}$ mol litre^{-1}). Analogous results were obtained for the ethylbenzene oxidation mediated by a binary system $\{Ni(acac)_2 + PhOH\}$ with $[Ni(acac)_2] = 3.0 \times 10^{-3}$ mol litre^{-1} and $[PhOH] = 4.6 \times 10^{-4}$ mol litre^{-1} (see Ref. 98).

Unusual results were obtained in our studies on the ethylbenzene oxidation catalyzed by a ternary system $\{Ni(acac)_2 + NaSt + PhOH\}$ (120 °C, $[Ni(acac)_2] = [NaSt] = [PhOH] = 3.0 \times 10^{-3}$ mol litre^{-1}).§ The observed values of *C* [$C > 35\%$ at $(S_{PEH})_{max} = 85\%-87\%$], $[ROOH]_{max}$ (1.6–1.8 mol litre^{-1}) and $\tilde{S} \cdot C$ ($\sim 30.1 \times 10^2$ %%) far exceeded those obtained with other ternary catalytic systems $\{Ni(acac)_2 + L^2 + PhOH\}$ and the majority of active binary systems.[98]

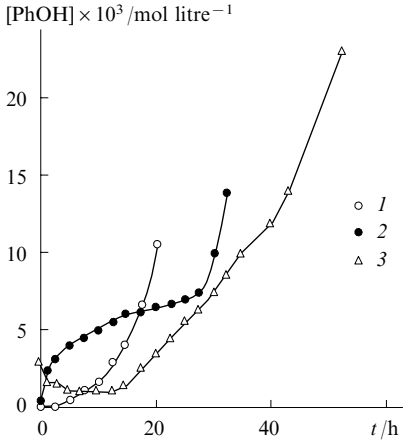


Figure 3. Kinetics of phenol accumulation in the reaction of ethylbenzene oxidation catalyzed by a binary system $\{Ni(acac)_2 + MP\}$ (*1*) and two ternary systems $\{Ni(acac)_2 + MP + PhOH\}$ with $[PhOH] = 4.6 \times 10^{-4}$ mol litre^{-1} (*2*) and 3×10^{-3} mol litre^{-1} (*3*). $[Ni(II)(acac)_2] = 3 \times 10^{-3}$ mol litre^{-1}, $[MP] = 7 \times 10^{-2}$ mol litre^{-1}, 120 °C.

The analogy observed in the reactions of ethylbenzene oxidation in the presence of $\{Ni(acac)_2 + L^2 + PhOH\}$ (L^2 = NaSt and MP) systems allowed us to assume that both reactions follow the same mechanism of selective catalysis. It is the ternary complexes $Ni(acac)_2 \cdot L^2 \cdot PhOH$ formed during the oxidation that are responsible for the catalysis. The parallel formation of α-phenylethyl hydroperoxide, acetophenone and MPC was observed ($w_{AP}/w_{PEH} \neq 0$, $w_{MPC}/w_{PEH} \neq 0$ and $w_{AP}/w_{MPC} \neq 0$ at $t \to 0$ throughout the reaction of ethylbenzene oxidation). A more considerable increase in the selectivity (S_{PEH}) in the catalysis by $Ni(acac)_2 \cdot L^2 \cdot PhOH$ (L^2 = NaSt, MP) complexes as compared with non-catalytic oxidation was associated with the change in the route of acetophenone and methylphenylcarbinol formation (AP and MPC form in parallel with PEH rather than as a result of its decomposition as observed in the non-catalytic ethylbenzene oxidation) and with the inhibition of the PEH heterolytic decomposition.

The advantage of these ternary systems is the long-term activity of the *in situ* formed complexes $Ni(acac)_2 \cdot L^2 \cdot PhOH$; the $acac^-$-ligand does not undergo transformations is the course of ethylbenzene oxidation. Apparently, the introduction of phenol together with the $\{Ni(acac)_2 + L^2\}$ catalyst in the reaction system in the initial stage of ethylbenzene oxidation is one of the most efficient methods of designing catalytic systems for the ethylbenzene selective oxidation to α-phenylethyl hydroxyperoxide. The high efficiency of three-component systems $\{Ni(acac)_2 + MSt + PhOH\}$ (M = Na, Li) in the reaction of selective oxidation of ethylbenzene to α-phenylethyl hydroxyperoxide was associated with the formation of extremely stable heteroligand complexes $Ni(acac)_2 \cdot MSt \cdot PhOH$, which resulted in the considerable increase in the degree of conversion of ethylbenzene to PEH and in the yield of α-phenylethyl hydroperoxide.[98]

§ These results by Matienko and Masolova are protected by the Russian Federation patent (2004).

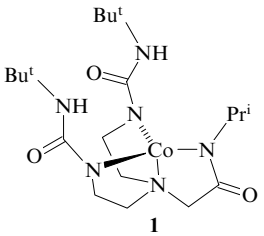
IV. The role of hydrogen bonds in homogeneous catalysis

As a rule, in the quest for axial modifying ligands L^2 that control the activity and selectivity of homogeneous metal complex catalysts, attention of scientists is focused on their steric and electronic properties. The interactions of ligands L^2 with L^1 taking place in the outer coordination sphere are less studied; the same applies to the role of hydrogen bonds, which are usually difficult to control.[100, 101]

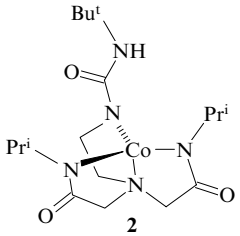
Secondary interactions (hydrogen bonding, proton transfer) play an important role in the dioxygen activation and its binding to the active sites of metalloenzymes.[102] For example, respiration becomes impossible when the fragments responsible for the formation of H-bonds with the $Fe-O_2$ metal site are removed from the haemoglobin active site.[103] Moreover, the O_2-affinity of haemoglobin active sites is in a definite relationship with the network of H-bonds surrounding the Fe ion. Yet another example demonstrating the important role of H-bonds that form the second coordination sphere around metal ions of many proteins is the dysfunction of cytochrome P450 observed upon the cleavage of its H-bonds formed with the $Fe-O_2$ fragment.[104]

In designing catalytic systems that mimic the enzymatic activity, special attention should be paid to the formation of H-bonds in the second coordination sphere of a metal ion.

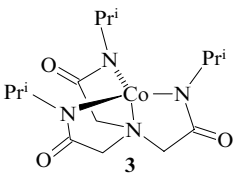
The involvement of H-bonds in binding dioxygen to cobalt complexes and also in the O_2 activation was studied.[105] Cobalt(II) complexes, namely, potassium {bis[(*N′*-*tert*-butylureido)-*N*-ethyl](*N′*-isopropylcarbamoylmethyl)aminato-cobaltate(II)} (**1**) and potassium {[(*N′*-*tert*-butylureido)-*N*-ethyl]bis(*N′*-isopropylcarbamoylmethyl)aminato-cobaltate(II)} (**2**) with multiple H-donating ligands, readily bind and activate molecular oxygen to form a $[Co^{III}-OH]$ complex. Complexes $[Co^{III}-OH]$ containing the larger number of intramolecular hydrogen bonds are more stable. Complex potassium {tris(*N′*-isopropylcarbamoylmethyl)aminato-cobaltate(II)} (**3**) that forms no intramolecular H-bonds, does not react with molecular oxygen. Co(II) complexes with a rigid H-bonded framework are incapable of forming intermolecular H-bonds.



1

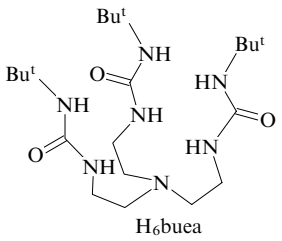


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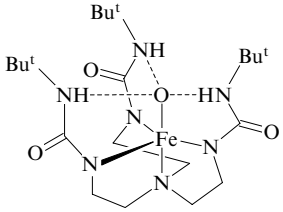


3

Mononuclear non-haem iron proteins are involved in various biological processes. The $Fe-OH$ fragment was assumed to be the active site of many catalytic cycles of enzymes.[106] The synthesis of mononuclear complexes containing a $Fe-OH$ fragment is a difficult problem due to the trend of these complexes towards the formation of multinuclear complexes containing hydroxo- and oxo-bridges. Special models were developed to synthesize stable mononuclear $[Fe-OH]$ complexes.[107–109] Thus it was proposed to use a bulky deprotonated ligand H_6buea in the synthesis of this complexes.[109] This ligand can form intramolecular hydrogen bonds NH···O (complex **4**) with the oxygen atom of the $Fe-OH$ fragment, thus protecting it from further attacks.



H_6buea



4

The synthesis of mononuclear complexes $[Fe^{II}L_2(OH)]^+BF_4^-$ and $[Fe^{III}L_2(OH)]^+BF_4^-$ [L is 1,1-bis(*N*-methylimidazol-2-yl)-3-(methylthio)propan-1-ol] stabilized by intermolecular H-bonds was reported.[106]

Acceleration of chemical reactions due to the favourable reactant orientation provided by hydrogen bonds or hydrophobic interactions is typical of enzymatic catalysis.[110] The formation of urethanes in the coordination sphere of $Fe^{III}(acac)_3$ (Ref. 111) can be considered as an example of a catalytic process sensitive to the orientation of reactants in the outer coordination sphere of a metal complex. The role of the catalyst in this process consists of developing beneficial conditions for the formation of a co-planar complex of the reactants that would provide the optimal mutual orientation of an isocyanide and an alcohol; this lowers of the activation energy.

Transition metal β-diketonates are involved in various substitution reactions. Methine protons of chelate rings in β-diketonate complexes can be substituted by different electrophiles (E) (formally, these reactions are analogous to the Michael addition reactions).[112, 113] This is a metal-controlled process of the $C-C$ bond formation.[114] The complex $Ni(acac)_2$ is the most efficient catalyst of such reactions. The rate-determining step of these reactions is the formation of a resonance-stabilized zwitter-ion $[(M^{II}L^1_n)^+E^-]$ in which the proton transfer precedes the formation of reaction products.[113, 114] The appearance of new absorption bands in electron absorption spectra of $\{Ni(acac)_2 + L^2 + E\}$ mixtures, that can be ascribed to the charge transfer from electron-donating ligands of complexes $L^2Ni(acac)_2$ to π-acceptors E (E is tetracyanethylene or chloranil) supports the formation of a charge-transfer complex $L^2Ni(acac)_2 \cdot E$.[32, 58] The outer-sphere reaction of the electrophile addition to γ-C in an acetylacetonate ligand follows the formation of the charge-transfer complex.

As was mentioned above, in complexes $ML^1_2 \cdot L^2$, the axially coordinated electron-donating ligand L^2 controls the formation of primary active complexes and the subsequent reactions of β-diketonate ligands in the outer coordination sphere of these complexes. The coordination of an electron-donating extra-ligand L^2 with an $M^{II}L^1_2$ complex favourable for stabilization of the transient zwitter-ion $L^2[L^1M(L^1)^+O_2^-]$ enhances the probability of regioselective O_2 addition to the methine $C-H$ bond of an acetylacetonate ligand activated by its coordination with metal ions. The outer-sphere reaction of O_2 incorporation into the chelate ring depends on the nature of the metal and the modifying ligand L^2. Thus for nickel complexes, the reac-

tion of acac-ligand oxygenation follows a mechanism analogous to those of Ni(II)-containing dioxygenase ARD[61] or Cu- and Fe-containing quercetin 2,3-dioxygenases.[62,63] However, the oxygenation of an enamac-ligand proceeds by a mechanism similar to that of L-tryptophan 2,3-dioxygenase[64,65] (see Scheme 1). In the effect of iron(II) acetylacetonate complexes, one can find an analogy with the action of Fe(II) acetylacetone dioxygenase.[67]

In recent years, attention was focused on the interaction of enzyme molecules with water molecules, which is of critical importance for the enzymatic activity.[115,116] Water molecules present in a protein active site may play not only the structuring role (as a nucleophile and proton donor) but also serve as a reagent in biochemical processes.

Thus the first stage in the O—O bond cleavage in an iron-coordinated H_2O_2 molecule (in horseradish peroxidase) is the proton transfer to the histidine residue (His42), which is made easier when a water molecule is present in the peroxidase active site.[117] As was demonstrated by *ab initio* calculations, in the absence of a water molecule, the energy barrier of this reaction is much higher (20 kcal mol^{-1}) as compared with its value found experimentally (1.5 ± 0.7 kcal mol^{-1}).

The role of hydrogen bonds in the mechanism of action of haem oxygenase (HO), metal-free enzyme, in which water acts as a ligand was studied.[118] It was shown that in the absence of H bonds, water axially coordinated with haem Fe has a weak effect on the nearest amino-acid environment of the haem. With the formation of a system of H bonds involving both free and coordinated water molecules, the situation fundamentally changes. The effect of hydroperoxides on the haem oxygenase-mediated haem (iron protoporphyrin IX) decomposition to biliverdin, iron and CO was studied.[119] Haem oxygenase uses haem as the substrate and the co-factor. Apparently, in the first stage, *meso*-hydroxylation occurs, which is followed by its conversion into verdohem and, ultimately, the opening of the verdohem ring (under the action of ROOH or O_2) to form biliverdin.

To get insight into the true mechanism of certain organic reactions catalyzed by transition metals, it is necessary to take into account the presence of water.[120] Thus water is a nucleophile in the palladium-catalyzed oxidative carbohydroxylation of allene-substituted conjugated dienes.[121] This is an example of palladium-mediated diene oxidation accompanied by the formation of a new C—C bond. The reaction proceeds *via* a (π-allyl)palladium intermediate, which is attacked by the water molecule on the allylic carbon atom. Insofar as the changes in the water concentration exerted different effects on the intra- and extradiol oxygenation of 3,5-di(*tert*-butyl)catechol with dioxygen in aqueous tetrahydrofuran catalyzed by $FeCl_2$ or $FeCl_3$, it was assumed that different intermediates were formed in these reactions. The extradiol oxygenation proceeded selectively only with Fe^{2+} salts, in contrast to Fe^{3+} salts (a model of catechol 2,3-dioxygenase).[122]

The Michael addition of 1,3-dicarbonyl compounds to nitroalkenes catalyzed by complexes NiL_2Br_2 [L is (*R*,*R*)-*N*,*N*′-dibenzylcyclohexane-1,2-diamine] was described.[123] It was shown that a monodiamine complex $NiLBr_2$ catalyzes these reactions in the presence of water.

At present, only few examples are known where small concentrations of water ($\sim 10^{-3}$ mol litre^{-1}) affect the hydrocarbon oxidation with dioxygen catalyzed by transition metal complexes. The role of water as a ligand in the oxidation reactions catalyzed by metal complexes is also little studied (see Refs 110, 118 and 124). Only few examples of the effect of small amounts of water on the hydrocarbon oxidation catalyzed by metal compounds in the presence of onium salts are known. Thus in the presence of trace amounts of water (1×10^{-3} mol litre^{-1}), the inhibition of tetralin oxidation catalyzed by anionic V(V) complexes [decavanadates, $H_nV_{10}O_{28}^{(6-n)-}$] and cationic surfactants [R_4NX = (n-C_6H_{13})$_4$NCl, Me(n-C_8H_{17})$_3$NCl] in the 1 : 1 ratio was observed.[125] The reactive catalytic species $[R_4N]^+_{6-n}[H_nV_{10}O_{28}]^{(6-n)-}$ formed *in situ* represented ion pairs and could exist only in the presence of water molecules. The oxidation depended on the concentration of ion pairs. Apparently, this was due to the changes in the structure of inverse micelles.[126]

The effect of small concentrations of H_2O on the homolysis of hydroperoxides catalyzed by onium salts (including quaternary ammonium salts) was studied in more detail. For example, the catalytic effect of H_2O on the hydrocarbon oxidation in the presence of onium salts (QX) was considered.[127] Presumably, water molecules accelerated the ROOH decomposition due to the formation of H bonds involving H_2O, QX and ROOH molecules. This conclusion was confirmed by quantum chemical calculations.[127]

Studying the effect of small amounts of water on the catalytic oxidation of hydrocarbons is also important in view of the fact that these processes always produce certain amount of water. [It should be noted that the addition of low concentrations of water ($\sim 10^{-3}$ mol litre^{-1}) to hydrocarbon solvents did not disturb the homogeneity of the medium.[126]]

1. The effect of small water concentrations on ethylbenzene oxidation with dioxygen catalyzed by the $\{Fe^{III}(acac)_3 + R_4NBr\}$ system

The role of H-bonds in the mechanism of formation of catalytically active complexes was studied in our works by the example of the iron complex-mediated ethylbenzene oxidation with molecular oxygen in the presence of small amounts of water.[128,129]

It was assumed that this have a positive effect on the conversion rate of iron complexes $\{Fe(acac)_3 + L^2\}$ (L^2 = R_4NBr, 18C6) and also, probably, on the parameters S_{PEH} and C in this reaction. The outer-sphere coordination of H_2O molecules can stabilize a transient zwitter-ion $L^2[L^1M(L^1)^+O_2^-]$. In this case, one should expect an increase in the probability of regioselective addition of an O_2 molecule to the γ-C atom of the acac-ligand.

It is well known that the stability of zwitter-ions increases in the presence of polar solvents.[113] The formation of hydrogen bonds of an H_2O molecule with a zwitter-ion can also favour the intramolecular proton transfer in the zwitter-ion, followed by conversion of the latter to the final products (see Scheme 2).[113,114]

Insignificant amounts of water (about several millimoles) increased the yield of γ-C-alkylation products of the acac ion in an R_4N(acac) salt in reactions carried out in an aprotic solvent (see, *e.g.*, Ref. 130). The catalytic activity of crown ethers (particularly, 18C6) in the reactions of electrophilic addition to the γ-C atom of an acetylacetonate ligand in complexes M(acac)$_n$ carried out in THF was observed to increase upon addition of small amounts of water.[130]

The positive effect of the introduction of small amounts of water ($\sim 10^{-3}$ mol litre^{-1}) into the catalytic system

$\{Fe^{III}(acac)_3 + CTAB\}$ on the selectivity of ethylbenene oxidation to PEH was revealed for the first time in our studies.[128] It was found that the addition of small amounts of water leads to a non-additive (synergistic) increase in the selectivity $(S_{PEH})_{max}$, the degree of conversion C and the parameter $\tilde{S}\cdot C$ as compared with their values in reactions of ethylbenzene oxidation catalyzed by $Fe(acac)_3$ and $\{Fe^{III}(acac)_3 + CTAB\}$ in the absence of water (see Fig. 2).

The effect of water in small concentrations on the parameters of $\{Fe^{III}(acac)_3 + R_4NBr\}$-mediated ethylbenzene oxidation substantially depends on the structure of radical R in the cation of R_4NBr. Thus the introduction of $\sim 10^{-3}$ mol litre^{-1} of water to catalytic systems $\{Fe(acac)_3 + Me_4NBr\}$ and $\{Fe(acac)_3 + Et_4NBr\}$ led to a decrease in parameters $(S_{PEH})_{max}$ and $\tilde{S}\cdot C$. In this case (as for the catalysis with the $\{Fe^{III}(acac)_3 + CTAB + H_2O\}$ system), the S_{PEH} *vs.* C dependence had a maximum.

Catalytic system [a]	$(S_{PEH})_{max}$ (%)	$(\tilde{S}\cdot C)\times 10^{-2}$ (%%)
$\{Fe(acac)_3 + Me_4NBr\}$	64	2.9
$\{Fe(acac)_3 + Me_4NBr + H_2O\}$	43	1.14
$\{Fe(acac)_3 + Et_4NBr\}$	48	4.97
$\{Fe(acac)_3 + Et_4NBr + H_2O\}$	43	3.43
$\{Fe(acac)_3 + CTAB\}$	65	5.46
$\{Fe(acac)_3 + CTAB + H_2O\}$	77.5	6.91

[a] $[Fe(acac)_3] = 5\times 10^{-3}$ mol litre^{-1}, $[R_4NBr] = 5\times 10^{-4}$ mol litre^{-1}.

The decrease in parameters $(S_{PEH})_{max}$ and $\tilde{S}\cdot C$ was explained by the high conversion rates of intermediates $Fe^{II}_x(acac)_y(OAc)_z(R_4NBr)_m(H_2O)_n$ to the final oxygenation products of $(Fe^{II}(acac)_2)_x(R_4NBr)_m(H_2O)_n$ complexes (R = Me, Et).

The increase in parameters $(S_{PEH})_{max}$, C and $\tilde{S}\cdot C$ observed in the ethylbenzene oxidation catalyzed by the $\{Fe^{III}(acac)_3 + CTAB + H_2O\}$ system was apparently associated with the increased steady-state concentration of selective heteroligand intermediates $Fe^{II}_x(acac)_y(OAc)_z(CTAB)_n(H_2O)_m$. The outer-sphere coordination of CTAB can give rise to steric hindrance for the coordination of H_2O molecules capable of accelerating the active complex decomposition. Moreover, a part of H_2O molecules can bind to the hydrophilic cation $Me_3(n\text{-}C_{16}H_{33})N^+$,which also leads to a decrease in the rate of conversion of active intermediate complexes such as $Fe^{II}_x(acac)_y(OAc)_z(CTAB)_n(H_2O)_m$ into the final oxygenation products (see Scheme 2).

In the reaction of ethylbenzene oxidation in the presence of a $\{Fe(acac)_3 + (5\times 10^{-4}$ mol litre$^{-1})$ CTAB + $(3.7\times 10^{-3}$ mol litre$^{-1})$ $H_2O\}$ system, no phenol was produced in the first 50 h after the reaction started. This can be explained by substantial reduction of the activity of catalytic complexes formed with respect to the PEH heterolysis and also by deceleration of formation of the complex $Fe(OAc)_2$ capable of accelerating the PEH heterolysis.[128]

The ethylbenzene oxidation reactions under study follow the autocatalytic mechanism at 80 °C. After the autoacceleration period associated with the transition of Fe^{III} ion to Fe^{II}, the reaction passed to the steady-state mode where $w = w_{max} = w_{lim}(w_0)$. The main oxidation products, namely, PEH, AP and MPC, were formed with an autoacceleration period that increased with the addition of water. Under these conditions, the changes in the ethylbenzene oxidation rate were associated with the changes in the accumulation rates of PEH and/or AP and MPC.[128] The increase in w_0 observed in the catalysis by complexes $(Fe(acac)_2)_n(Me_4NBr)_m$ in the presence of 3.7×10^{-3} mol litre^{-1} H_2O as compared with the catalysis by complexes $Fe(acac)_2$ and $(Fe(acac)_2)_n(Me_4NBr)_m$ in the absence of H_2O and only slight deceleration of ethylbenzene oxidation catalyzed by complexes $(Fe(acac)_2)_n(Et_4NBr)_m$ in the presence of H_2O as compared with its catalysis by complexes $(Fe(acac)_2)_n(Et_4NBr)_m$ are extraordinary facts[92, 128] when compared with the well-known observations of a considerable decrease in the hydrocarbon oxidation rate in the presence of water due to the solvation of reactive radicals $RO_2^{\bullet}$ by water molecules[5] and also due to the catalyst deactivation with water formed in the course of the radical-chain oxidation of hydrocarbons with dioxygen in a non-polar medium.[6]

When ethylbenzene was catalyzed by the $\{Fe^{III}(acac)_3 + CTAB + H_2O\}$ system, a substantial decrease in the reaction rate w_0 (2-fold, Table 3) was observed.

Table 3. Initial rates of ethylbenzene oxidation (w_0) and calculated rates of chain initiation $[(w_i)_0]$ and propagation $[(w_{pr})_0]$ (in mol litre^{-1} s^{-1}), parameter $[(w_i)_0/(w_{pr})_0]\times 100\%$ at the catalysis by $Fe(acac)_3$ and also by systems $\{Fe(acac)_3 + L^2\}$ and $\{Fe(acac)_3 + L^2 + L^3\}$.

L^2	L^3	$w_0\times 10^6$	$(w_i)_0\times 10^7$	$(w_{pr})_0\times 10^6$	$[(w_i)_0/(w_{pr})_0]\times 100\%$
–	–	6.30	0.79	3.32	2.38
CTAB	–	7.65	1.63	3.14	5.19
CTAB	H_2O	4.85	1.21	0.98	12.24
18C6	–	2.63	0.24	0.93	2.58
18C6	H_2O	6.94	0.15	5.58	0.27

Note. $[Fe(acac)_3] = 5\times 10^{-3}$ mol litre^{-1}, $[L^3] = [H_2O] = 3.7\times 10^{-3}$ mol litre^{-1}, 80 °C.

It was found that the addition of water $(3.7\times 10^{-3}$ mol litre$^{-1})$ to catalytic systems $\{Fe^{III}(acac)_3 + R_4NBr\}$ [$R_4NBr = Me_3(n\text{-}C_{16}H_{33})NBr$, Me_4NBr, Et_4NBr] did not change the mechanism of formation of the ethylbenzene main oxidation products. As in the absence of H_2O, throughout the reaction, three main products, namely, PEH, AP and MPC were formed in parallel ($w_P/w_{PEH} \neq 0$ and $w_{AP}/w_{MPC} \neq 0$ at $t \to 0$).[128] These results differ from the known facts of acceleration of PEH decomposition when ethylbenzene oxidation was catalyzed by CTAB or catalytic systems based on CTAB and transition metal complexes as a result of PEH incorporation into the CTAB micelles.[77, 78]

2. The effect of small concentrations of water on ethylbenzene oxidation with dioxygen catalyzed by the $\{Fe^{III}(acac)_3 + 18C6\}$ system

In the reaction of ethylbenzene oxidation with dioxygen in the presence of a catalytic system $\{Fe(acac)_3 + 18C6\}$ $\{[Fe(acac)_3] = 5\times 10^{-3}$ mol litre^{-1}, $[18C6] = 5\times 10^{-3}$ or 5×10^{-4} mol litre$^{-1}\}$ at 80 °C, the S_{PEH} *vs.* C dependence had a maximum (Fig. 4). For the same degrees of ethylbenzene conversion in the oxidation reactions, the values $(S_{PEH})_{max}$ corresponding to the catalysis by the $\{Fe(acac)_3 + 18C6\}$ system (70% for $[18C6]_0 = 5\times 10^{-4}$ mol litre^{-1} and 75.7% for $[18C6]_0 = 5\times 10^{-3}$ mol litre^{-1}) exceeded $(S_{PEH})_{max}$ (65%) observed in the catalysis by CTAB and far exceeded S_{PEH} (40%) corresponding to the catalysis by the complex $Fe(acac)_3$ in

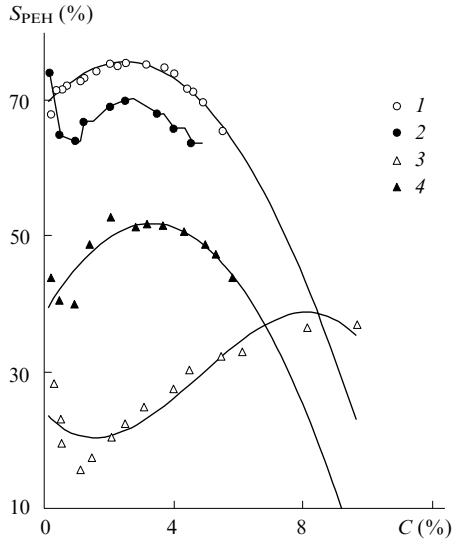


Figure 4. Dependence S_{PEH} *vs.* C in reactions of ethylbenzene oxidation catalyzed by $\{Fe(acac)_3 + 18C6\}$ systems without (curves *1*, *2*) and with addition of water (curves *3*, *4*).
(*1*, *3*) $[18C6] = 5 \times 10^{-3}$ mol litre^{-1}; (*2*, *4*) $[18C6] = 5 \times 10^{-4}$ mol litre^{-1}. $[Fe(acac)_3] = 5 \times 10^{-3}$ mol litre^{-1}, $[H_2O] = 3.7 \times 10^{-3}$ mol litre^{-1}, 80 °C.

the absence of 18C6 [$w = w_{max} = w_{lim}(w_0)$]. With the increase in S_{PEH} from 40% [catalysis by the complex $Fe(acac)_3$] to 70% – 75.7% [catalysis by the $\{Fe(acac)_3 + 18C6\}$ system], the conversion increased two-fold, namely, from 4% to 8% (or 10%).[90, 129]

The addition of 18C6 to the catalyst $Fe(acac)_3$ changed the composition of the oxidation products. A substantial increase in $[PEH]_{max}$ ($\sim$1.6- or 1.7-fold for $[18C6] = 5 \times 10^{-4}$ or 5×10^{-3} mol litre^{-1}, respectively) and a considerable decrease in the AP and MPC concentrations (4.5-fold) were observed. Moreover, the addition of 18C6 resulted in substantial inhibition of the PEH heterolysis to phenol and also in the increase in parameter $\tilde{S} \cdot C$ (2.5- and 2.8-fold for $[18C6] = 5 \times 10^{-4}$ and 5×10^{-3} mol litre^{-1}, respectively) as compared with the value $\tilde{S} \cdot C$ observed in the catalysis by the complex $Fe(acac)_3$.[90, 129]

Below, the parameter $\tilde{S} \cdot C$ in the ethylbenzene oxidation catalyzed by complexes $Fe(acac)_3$, $\{Fe(acac)_3 + 18C6\}$ and $\{Fe(acac)_3 + 18C6 + H_2O\}$ is shown for $[Fe(acac)_3] = 5 \times 10^{-3}$ mol litre^{-1}, $[18C6] = 5 \times 10^{-3}$ and 5×10^{-4} mol litre^{-1} (in parentheses), $[H_2O] = 3.7 \times 10^{-3}$ mol litre^{-1}.

Catalyst	$(\tilde{S} \cdot C) \times 10^{-2}$ (%%)
$Fe(acac)_3$	2.1
$\{Fe(acac)_3 + 18C6\}$	5.89 (5.3)
$\{Fe(acac)_3 + 18C6 + H_2O\}$	2.86 (3.33)

The synergistic effect of the increase in parameters S_{PEH} and $\tilde{S} \cdot C$, observed in ethylbenzene oxidation catalyzed by $\{Fe(acac)_3 + 18C6\}$ systems[90] suggests that catalytically active complexes $(Fe(acac)_2)_p(18C6)_q$ and their transformation products were formed during the oxidation. For example, Fe(II) and Fe(III) halides are known to form complexes with crown ethers with different compositions (1 : 1, 1 : 2, 2 : 1) and structures, depending on the nature of the crown ether and solvent.[86]

Due to the favourable combination of electronic and steric factors that operate at the inner- and outer-sphere coordination (hydrogen bonds) of 18C6 with $Fe(acac)_2$, stable active polynuclear heteroligand complexes with the composition $Fe^{II}_x(acac)_y(OAc)_z(18C6)_n$ are formed with the high probability, which in turn favours the increase in parameters $(S_{PEH})_{max}$ and C.

$$\{Fe(acac)_3 + 18C6\} \longrightarrow [Fe^{II}(acac)_2]_p \cdot (18C6)_q \xrightarrow{O_2} \longrightarrow Fe^{II}_x(acac)_y(OAc)_z(18C6)_n.$$

With the addition of water (3.7×10^{-3} mol litre^{-1}), the efficiency of catalytic systems $\{Fe(acac)_3 + 18C6\}$ specified by parameters $(S_{PEH})_{max}$ and $\tilde{S} \cdot C$ decreased; however, the conversion increased from 4% to $\sim$6.5% (for $[18C6] = 5 \times 10^{-4}$ mol litre^{-1}) or 9% (for $[18C6] = 5 \times 10^{-3}$ mol litre^{-1}).[129]

An analogous decrease in parameters $(S_{PEH})_{max}$ and $\tilde{S} \cdot C$ was also observed for the ethylbenzene oxidation with dioxygen catalyzed by $\{Fe(acac)_3 + R_4NBr\}$ (R = Me, Et) systems in the presence of small portions of water.[128]

Coordination of water with complexes $[Fe^{III,II}(acac)_n]_p \cdot (18C6)_q$ to form complexes $[Fe^{II}(acac)_2]_x(18C6)_y(H_2O)_m$ and the transformation of the latter during the ethylbenzene oxidation into active $Fe^{II}_x(acac)_y(OAc)_z(18C6)_n(H_2O)_m$ species may explain the observed trends in variations of parameters S_{PEH}, C and $\tilde{S} \cdot C$ in the presence of small H_2O concentrations (see Figs 4, 5). Apparently, coordination of water molecules to Fe atoms does not lead to 18C6 displacement by iron complexes to the second coordination sphere,[131] because no decrease in the activity of the $\{Fe(acac)_3 + 18C6\}$ system with respect to oxidation was observed. It is also well-known that water molecules can form molecular complexes with crown ethers through the formation of hydrogen bonds (insertion complexes);[132] however, the enthalpy of their formation is low ($\sim$2 – 3 kcal mol^{-1}).[133]

Apparently, the outer-sphere coordination of water molecules with the complex $[Fe^{II}(acac)_2]_p(18C6)_q$ favours the conversion of the latter into active species such as $Fe^{II}_x(acac)_y(OAc)_z(18C6)_n(H_2O)_m$ capable of catalyzing ethylbenzene oxidation to PEH, as evidenced by the increase in the initial rates of ethylbenzene oxidation (see Table 3) and the increase in S_{PEH} in the course of reaction (see Fig. 4).

The decrease in parameter $(S_{PEH})_{max}$ can apparently be explained by the decrease in the steady-state concentration of reactive intermediates $Fe^{II}_x(acac)_y(OAc)_z(18C6)_n(H_2O)_m$ in the course of oxidation and the acceleration of their transformation into the final product, catalyst $Fe(OAc)_2$.

In the presence of water in small concentrations, the ratio of main products of ethylbenzene oxidation changed. In the beginning of this reaction ($C \leqslant 1.0\%$) catalyzed by the $\{Fe(acac)_3 + 18C6 + H_2O\}$ system, acetophenone rather than PEH was the main product ([AP] > [PEH] and [AP] $\gg$ [MPC]). The selectivity of ethylbenzene oxidation to acetophenone $[(S_{AP})_0]$ increased from 24 (without added H_2O) to $\sim$70% (with added H_2O), where $(S_{PEH})_0 \approx 25\%$, and the [AP] : [MPC] ratio increased from 1.2 (in the absence of added H_2O) to 6.5 (in the presence of H_2O).

Introduction of small portions of water (3.7×10^{-3} mol litre^{-1}) to the $\{Fe(acac)_3 + 18C6\}$ systems did not affect the mechanism of formation of the main

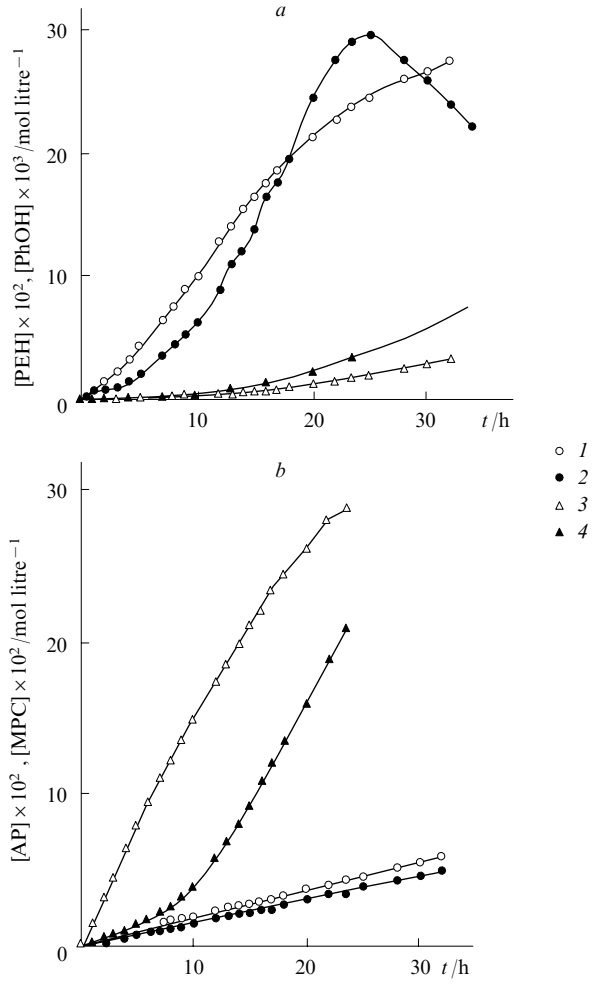


Figure 5. Kinetics of PEH (*a*, curves *1*, *2*), PhOH (*a*, curves *3*, *4*), AP (*b*, curves *1*, *3*) and MPC (*b*, curves *2*, *4*) accumulation in reactions of ethylbenzene oxidation catalyzed by systems {$Fe(acac)_3$ + 18C6} (curves *1*, *3*) and {$Fe(acac)_3$ + 18C6 + H_2O} (curves *2*, *4*). [$Fe(acac)_3$] = [18C6] = 5×10^{-3} mol litre^{-1}; [H_2O] = 3.7×10^{-3} mol litre^{-1}; 80 °C.

oxidation products. Throughout the reaction period, three main products, PEH, AP and MPC were formed in parallel ($w_P/w_{PEH} \neq 0$ and $w_{AP}/w_{MPC} \neq 0$ at $t \to 0$).

V. Assessing the catalytic activity of Ni and Fe catalysts in microsteps of radical-chain ethylbenzene oxidation with dioxygen

An original method was developed for assessing the catalytic activity of metal complexes in the microsteps of chain initiation [(1), see Scheme 3] and propagation (2′) with the use of a simplified scheme. Taking into account that complexes ML_n^1 {M = Ni(II) ([Ct] = $(0.5-1.5) \times 10^{-4}$ mol litre^{-1}) and Fe(II,III) ([Ct] = $(0.5-5) \times 10^{-3}$ mol litre^{-1})} are inactive in the PEH homolysis, the rate of homolytic decomposition of hydroperoxide can be equated to zero.[32,89–92] With the assumption relationships $w_0 \sim [Ct]^{1/2}$ and $(w_i)_0 \sim [Ct]$ established for the radical chain ethylbenzene oxidation catalyzed by complexes ML_2^1 are also fulfilled for the catalysis by complexes ML_2^1 containing activating ligands, then it is possible to ignore the linear radical termination in the catalyst and take into account only quadratic termination.

In this case, the rate of quadratic chain termination can be calculated using equation

$$w_{term} = k_5[RO_2^{\bullet}]^2 = k_5\left(\frac{w_{PEH}}{k_2[RH]}\right)^2, \quad (1)$$

where w_{PEH} is the rate of PEH accumulation, k_5 is the rate constant for quadratic chain termination, k_2 is the rate constant for chain propagation (2).

The w_{term} values determined using formula (1) for quasi-steady state conditions with respect to $RO_2^{\bullet}$ radicals and designated as w_i are the measure of the metal activity with respect to molecular O_2. The deviation between values w_{AP+MPC} and w_{term} in the absence of linear termination of chains on the catalyst was attributed to the additional formation of an alcohol and a ketone in the step of chain propagation. The rate of the chain propagation step

$$w_{pr} = w_{AP+MPC} - w_{term}. \quad (2)$$

The involvement of nickel and iron complexes in the chain propagation step is testified by the direct proportional dependence w_{pr} *vs.* [Ct].

The involvement of transition metal complexes in the chain propagation step of ethylbenzene oxidation was considered exclusively in our studies[32,89–92,128,129] and in theoretical publications.[8,23]

At the same time, studying the reactivity of peroxide complexes [LM−OOR] (M = Co, Fe), pre-synthesized by the reactions of Co and Fe compounds with ROOH or radicals $RO_2^{\bullet}$ (Refs 134–136) confirmed their involvement in the hydrocarbon oxidation.

The schemes of radical chain oxidation of hydrocarbons that involve the transient formation of peroxide complexes [LM−OOR][134–137] followed by their homolytic decomposition {[LM−OOR] → $R_2'C{=}O$(or ROH) + R$^{\bullet}$} allow one to explain the parallel formation of an alcohol and a ketone during the ethylbenzene oxidation in the presence of complexes ML_n^1 and $ML_n^1 \cdot L^2$ [M = Ni(II), Fe(II,III); L^1 = enamac$^-$, acac$^-$; n = 2, 3; L^2 = DMF, HMPA, R_4NBr, 18C6].

It was shown[22,23] that in the non-catalytic reactions of ethylbenzene oxidation at elevated temperatures (active sites are formed by both the reaction of RH with O_2 and the chain decomposition of PEH), the selectivity (S_{PEH}) is determined to a considerable extent by the factor (β) of PEH instability

$$\beta = \frac{(w_{PEH})_d}{(w_{PEH})_{form}},$$

where $(w_{PEH})_d$ is the overall rate of PEH decomposition [thermal (molecular) and chain], $(w_{PEH})_{form}$ is the rate of PEH formation. In the course of ethylbenzene non-catalytic oxidation, β increases due to the increase in the rate of PEH chain decomposition, which results in lower S_{PEH} in the fully developed process. In contrast to this, in the ethylbenzene oxidation catalyzed by nickel(II) complexes, namely, NiL_2^1 (L^1 = acac, enamac), $NiL_2^1 \cdot (18C6)_n$ (n = 1, 2) and $Ni(acac)_2 \cdot R_4NBr$, the quantity β was close to zero both in the beginning and in the fully developed process. Moreover, the route of the AP and MPC formation changed from successive (*via* PEH decomposition) to parallel.

1. Catalysis by nickel ions

According to calculations, the high activity of primary complexes $NiL^1_2 \cdot (18C6)_n$ (L^1 = acac, $n = 1, 2$; L^1 = enamac, $n = 1$) as the catalysts of ethylbenzene oxidation to α-phenylethyl hydroperoxide was attributed to the multiple increase in the initiation rate $(w_i)_0$ (5-fold for L^1 = enamac and 20-fold for L^1 = acac) as compared with the catalysis by complexes NiL^1_2 and also to the substantial decrease in the rate of chain propagation $(w_{pr})_0$ [Eqns (1) and (2)].

The experimentally determined rates of acetophenone and methylphenylcarbinol formation $(w_{AP+MPC})_0$ in ethylbenzene oxidation catalyzed by complexes $NiL^1_2 \cdot (18C6)_n$ coincided with the rates of chain termination $(w_{term})_0$ calculated using Eqn (1), which conforms to the proposed model. In the initial stage of the process, $(w_{pr})_0 = 0$. This may be associated with the fact that coordination of radicals $RO_2^{\bullet}$ with such complexes is sterically hindered by crown ethers; hence, the only reaction of AP and MPC formation is the quadratic chain termination.

Complexes $Ni(enamac)_2 \cdot 18C6$ proved to be twice as active as complexes $Ni(acac)_2 \cdot (18C6)_n$ ($n = 1, 2$) in the step of free-radical initiation $[(w_i)_0]$, although the 'crown-ether' effect [the increase in w_0 and $(w_i)_0$ under the action of 18C6] was weaker for the catalysis by the complex $Ni(enamac)_2 \cdot 18C6$. This can be explained by the weaker acceptor properties of the complex $Ni(enamac)_2$ as compared with the complex $Ni(acac)_2$, which is explained by the covalent nature of Ni—NH bonds and the smaller effective charge on the Ni atom and, hence, the weaker coordination ability of the complex $Ni(enamac)_2$.

The conditions $w_0 \sim [Ct]^{1/2}$ and $w_i \sim [Ct]$ that allow one to assess the rates of chain propagation and initiation in the fully developed process were fulfilled when both $Ni_xL^1_y(L^1_{ox})_z$ and $Ni_xL^1_y(L_{ox}1)_z(18C6)_n$ complexes (L^1 = enamac) were used as the catalysts. According to calculations, the role of chain propagation reactions in the developed process of ethylbenzene oxidation increases. The catalytic species $Ni_xL^1_y(L^1_{ox})_z$ and $Ni_xL^1_y(L^1_{ox})_z(18C6)_n$ formed in the course of reaction were less active in the oxygen activation (w_i) but more active in the chain propagation (w_{pr}) as compared with the primary complexes NiL^1_2 and $NiL^1_2 \cdot (18C6)_n$.

In ethylbenzene oxidation catalyzed by complexes NiL^1_2 (L^1 = acac, enamac), in contrast to the catalysis by complexes $NiL^1_2 \cdot 18C6$, the increase in the initial oxidation rate was largely associated with the catalyst involvement in the chain propagation step. In this case, in the initial stage of the $Ni(enamac)_2$-catalyzed oxidation, the chain propagation rate $(w_{pr})_0$ is twice higher and the rate of chain initiation $(w_i)_0$ is nearly an order of magnitude higher than the corresponding rates observed in the catalysis by the complex $Ni(acac)_2$. Thus, the presence of electron-donating NH groups in the chelate node of the nickel complex favours the increase in the role of a step of molecular oxygen activation in the multistep catalytic process, which is in agreement with the literature data.[32, 59]

The higher activity of complex $Ni(acac)_2 \cdot Me_4NBr$ as compared with the complex $Ni(acac)_2$ is associated with an increase in $(w_i)_0$ and a decrease in $(w_{pr})_0$ (Fig. 6).

The minimum value of $(w_{pr})_0$ was observed for $[Me_4NBr] = 1 \times 10^{-3}$ mol litre^{-1}, which corresponded to the formation of a complex with the 1 : 1 composition. Obviously, for the Me_4NBr coordination (both inner- and outer-sphere) with a Ni ion of the complex $Ni(acac)_2$, steric hindrance to the coordination of radicals $RO_2^{\bullet}$ with metal ions may arise, which leads to a decrease in $(w_{pr})_0$. With an increase in the Me_4NBr concentration ($[Me_4NBr] > 1 \times 10^{-3}$ mol litre^{-1}), the probability that the chelate acac ring opens to vacate the coordination sites at the Ni atom increases; hence, the probability of Ni coordination with $RO_2^{\bullet}$ also increases, being accompanied by an increase in $(w_{pr})_0$.

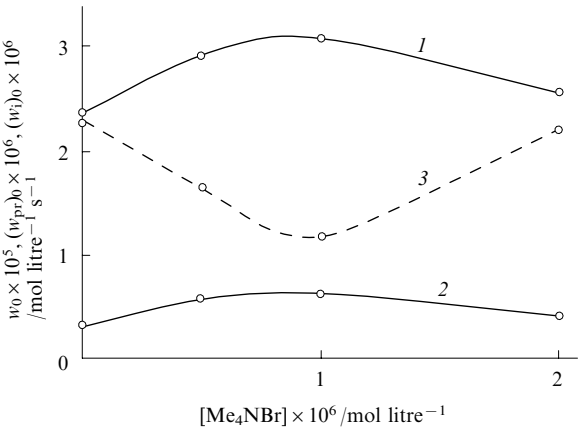


Figure 6. Initial rate of ethylbenzene oxidation (w_0, curve *1*) catalyzed by a $\{Ni(acac)_2 + Me_4NBr\}$ system and calculated initial rates of chain initiation [$(w_i)_0$, curve *2*] and propagation [$(w_{pr})_0$, curve *3*] as a function of Me_4NBr concentration.
$[Ni(acac)_2] = 1.5 \times 10^{-4}$ mol litre^{-1}, 120 °C.

Going from $Ni(acac)_2 \cdot Me_3(n\text{-}C_{16}H_{33})NBr$ to the complex $Ni(acac)_2 \cdot Me_4NBr$, *i.e.*, the displacement of one Me in the Me_4N^+ cation by an $n\text{-}C_{16}H_{33}$ radical, leads to a decrease in $(S_{PEH})_0$. The activity of complexes $Ni(acac)_2 \cdot CTAB$ in chain initiation and propagation increased 4.6-fold and 20.5-fold, respectively, as compared with the complex $Ni(acac)_2 \cdot Me_4NBr$; $(w_{PEH})_0$ only doubled and $(w_{AP+MPC})_0$ increased 15.4-fold.[32, 91]

2. Catalysis by iron complexes

Chain initiation in the ethylbenzene oxidation with molecular oxygen in the presence of complexes $Fe(acac)_3$ or $\{Fe(acac)_3 + L^2\}$ can be described by the following scheme:

$$Fe^{III}(acac)_3 + RH \longrightarrow Fe^{II}(acac)_2 \cdots Hacac + R^{\bullet}$$

or

$$(Fe^{III}(acac)_3)_m \cdot L^2_n + RH \longrightarrow (Fe^{II}(acac)_2)_x(L^2)_y \cdots Hacac + R^{\bullet}.$$

The subsequent reaction of the Fe(II) complexes formed with dioxygen leads to chain initiation $[(w_i)_0]$ in a region where $w = w_{max} = w_{lim}(w_0)$, *i.e.*, after the end on the induction period associated with the Fe(III) conversion to Fe(II) and to the transition into the steady-state reaction mode.

The rate of chain initiation in the ethylbenzene oxidation in the presence of complexes $\{Fe(acac)_3 + L^2\}$ (L^2 = R_4NBr, HMPA, DMF) is higher than in the presence of $Fe(acac)_3$ and much higher than in the non-catalytic oxidation of ethylbenzene [$(w_i)_0 \approx 10^{-9}$ mol litre^{-1} s^{-1}].

For the ethylbenzene oxidation catalyzed by complexes $\{Fe(acac)_3 + CTAB\}$, $(S_{PEH})_0$ depends on the catalyst activity in the chain initiation and propagation steps. Thus, the increase in $(S_{PEH})_0$ from 45% to ~65% was associated with the twofold increase in $(w_i)_0$ [this was accompanied by an insignificant decrease in $(w_{pr})_0$ (see Table 3)]. The rate of

PEH accumulation in the presence of {Fe(acac)$_3$ + CTAB} in place of Fe(acac)$_3$ increased 1.5-fold and the rate of AP and MPC formation decreased. Similar results were also obtained in the presence of {Fe(acac)$_3$ + Me$_4$NBr}. However, when {Fe(acac)$_3$ + Et$_4$NBr} served as the catalyst of ethylbenzene oxidation, $(S_{PEH})_0$ was observed to decrease because the increase in $(w_{AP+MPC})_0$ much exceeded the gain in $(w_{PEH})_0$.

The increase in $(S_{PEH})_0$ from 40% – 50% to 65% – 70% in the initial stages of ethylbenzene oxidation catalyzed by complexes $(Fe^{II}(acac)_2)_p(18C6)_q$ was largely associated with the deceleration of AP and MPC formation in the microstep of chain propagation. Apparently, due to the steric factors that arise at the inner- or outer-sphere coordination of 18C6 with Fe^{II}(acac)$_2$, the probabilities of coordination of oxygen $[(w_i)_0]$ and/or radicals $RO_2^{\bullet}$ $[(w_{pr})_0]$ with the metal ions to form the primary catalyst complexes with an O_2 molecule and/or a radical $RO_2^{\bullet}$, followed by the formation of active species of the superoxide or peroxide types, decreased.

The ratio $[(w_i)_0/(w_{pr})_0]\cdot 100\% \approx 2\% - 5\%$ means that iron complexes {Fe(acac)$_3$ + L^2} are more active in the chain propagation step than in the step of chain initiation. The products AP and MPC were largely formed in the chain propagation step probably due to the homolytic decomposition of the transient complex [L^{2}FeL$^1_2$ – OOR].[135–138]

Complexes Fe^{II}(acac)$_2$·HMPA formed in the initial stages of ethylbenzene oxidation in the presence of the {Fe^{III}(acac)$_3$ + HMPA} catalytic system remain unchanged during the reaction.[66] The dependences of the reaction rate w, of calculated values w_{pr} and w_i, and also of the parameter $\tilde{S}\cdot C$ on the HMPA concentration for the ethylbenzene oxidation with dioxygen (80 °C) under steady-state conditions had extrema. The maximum values of these parameters were reached for the same HMPA concentration [$\sim(2.5-5.0)\times 10^{-2}$ mol litre^{-1}]. Apparently, this concentration corresponds to the formation of active complexes Fe^{II}(acac)$_2$·HMPA with the 1 : 1 composition and argues for the proposed method of assessing the values w_i and w_{pr}.

Coordination of HMPA with Fe^{II}(acac)$_2$ results in a decrease in the effective activation energies (E_{act}) of microsteps of chain initiation and propagation by 48.15 and 15.9 kJ mol^{-1}, respectively, as compared with E_{act} values obtained in the catalysis by complexes Fe^{II}(acac)$_2$ in the absence of HMPA. The gain in the activation energy of chain initiation observed at the HMPA coordination was equal to the energy consumed in the addition of this extra-ligand to metal acetylacetonates ($\sim$41.87 kJ mol^{-1}).[138] As the temperature decreased from 120 to 80 °C, the difference in E_{act} between the reactions of chain initiation (54.55 kJ mol^{-1}) and propagation (73.81 kJ mol^{-1}) in the presence of HMPA can, apparently, explain the increase in the selectivity of ethylbenzene oxidation to PEH from 46% (at 120 °C) to 57% (at 80 °C).

The higher catalytic activity of complexes Fe(acac)$_2$·DMF as compared with Fe(acac)$_2$·HMPA in the steps of chain initiation and propagation in ethylbenzene oxidation is apparently associated with the π-donating properties of DMF and its trend to H-bonding.[139] It is quite probable that the coordination of a π-donating ligand (DMF) with Ni(acac)$_2$ favours the formation of primary complexes of Fe(acac)$_2$·DMF with oxygen[140,141] of the superoxide type, namely, [DMF·Fe(acac)$_2$·$O_2^{-\bullet}$], and also the increase in their activity in the step of radical formation. Schemes of radical chain oxidation of hydrocarbons that include the transient formation of peroxo complexes [LM – OOR] in the chain propagation step attribute the increase in ethylbenzene oxidation rate and selectivity with respect to MPC $[(S_{MPC})_0 \approx 58\%]$ to the presence of a catalytic complex Fe(acac)$_2$·DMF. The additional coordination of Fe with a DMF ligand favours the stabilization of oxo-species [DMF·Fe^{III} – O$^{\bullet}$] formed in the homolytic decomposition of peroxo complexes [DMF·Fe – OOR] at the O – O bond

$$[L^2Fe^{II}-O^{\bullet}-{}^{\bullet}OR] \longrightarrow [L^2Fe^{II}-O^{\bullet}] + [{}^{\bullet}OR] \longrightarrow$$

$$\longrightarrow R'R''C{=}O(\text{or ROH}) + R^{\bullet},$$

and the probability of escape of radicals RO$^{\bullet}$ from the solvent cage (the inner-cage 'latent-radical' mechanism).

Above, it was also assumed that the mechanism of ethylbenzene oxidation catalyzed by complexes {Fe(acac)$_3$ + R$_4$NBr} or {Fe(acac)$_3$ + 18C6} remains unchanged upon the introduction of small portions of water (3.7×10^{-3} mol litre^{-1}). In this case too, the conditions $w_0 \sim [Ct]^{1/2}$ and $(w_i)_0 \sim [Ct]$ are fulfilled, which allows one to assess the activity of complexes $(Fe^{II}(acac)_2)_x(R_4NBr)_y\cdot(H_2O)_n$ and $(Fe^{II}(acac)_2)_x(18C6)_y(H_2O)_n$ in microsteps of chain initiation and propagation.

In the reaction of ethylbenzene oxidation catalyzed by complexes $(Fe^{II}(acac)_2)_x(CTAB)_y(H_2O)_n$ (see Table 3), the deceleration of reaction in initial oxidation stages was associated with a considerable (3.2-fold) decrease in the chain propagation rate $(w_{pr})_0$. On the other hand, $(w_i)_0$ decreased only $\sim$1.3-fold; hence, the ratio $(w_i)_0/(w_{pr})_0$ increased by a factor of 2.35. This enhanced the selectivity $(S_{PEH})_0$ in the initial reaction stages. The decrease in the chain propagation rate $(w_{pr})_0$ can be explained by the steric hindrance posed by a CTAB ligand to the coordination of radicals $RO_2^{\bullet}$ with the central metal ion.

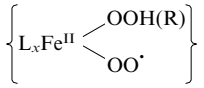
In contrast to the ethylbenzene oxidation catalyzed by complexes $(Fe^{II}(acac)_2)_x(CTAB)_y(H_2O)_n$, for its catalysis by complexes $(Fe^{II}(acac)_2)_x(R_4NBr)_y(H_2O)_n$ (R = Me, Et), the $(w_i)_0/(w_{pr})_0$ ratio decreased by a factor of $\sim$1.4 (R = Et) or $\sim$1.22 (R = Me) as compared with this ratio calculated for the reaction catalyzed by complexes $(Fe^{II}(acac)_2)_x(R_4NBr)_y$ without addition of H_2O.

As follows from the data shown in Table 3, the reaction of chain propagation is the main source of AP and MPC at the ethylbenzene oxidation catalyzed by complexes $(Fe^{II}(acac)_2)_x(L^2)_y(H_2O)_n$ (L^2 = R$_4$NBr, 18C6). The contribution of quadratic chain termination is insignificant. An analogous result was obtained for the catalysis of ethylbenzene oxidation by complexes $(Fe^{II}(acac)_2)_m(R_4NBr)_n$, $(Fe^{II}(acac)_2)_p(18C6)_q$ or $Fe^{II,III}(acac)_n$.

Introduction of water into the reaction of ethylbenzene oxidation catalyzed by complexes {Fe(acac)$_3$ + 18C6} causes a substantial (10-fold) decrease in the $(w_i)_0/(w_{pr})_0$ ratio largely due to the increase in $(w_{pr})_0$. When the {Fe(acac)$_3$ + 18C6 + H$_2$O} system was used as the catalyst, the lowest selectivity of ethylbenzene oxidation to PEH was observed in the initial stages $[(S_{PEH})_0 \approx 25\%]$, where the highest selectivity corresponded to the ethylbenzene oxidation to acetophenone $[(S_{AP})_0 = 70\%]$. The [AP]/[MPC] ratio

increased from ~1.2 (for the catalysis with the {Fe(acac)$_3$ + 18C6}system) to 6.5 (for the catalysis with the {Fe(acac)$_3$ + 18C6 + H_2O}system).¶

The selectivity of radical-chain oxidation of ethylbenzene to acetophenone in the presence of {Fe^{III}(acac)$_3$ + 18C6 + H_2O}) was sufficiently high but lower than in the catalysis by systems mimicking the effect of monooxygenases, for example, the Sawyer system, *i.e.*, {[$Fe^{II}(Mn^{III})$] + L_x + HOOH(HOOR) + Solv} [L_x = bipy, py; Solv are polar solvents (MeCN, py + AcOH)].[142, 143] In the ethylbenzene oxidation with dioxygen (24 °C) catalyzed by the Sawyer system, the selectivity with respect to acetophenone reached 100% for conversion of 0.4%. Presumably, this reaction was catalyzed with species **A** with the hypothetical structure



A

capable of oxygenating ethylbenzene to afford acetophenone. Species **A** were formed upon the addition of an O_2 molecule to the peroxo complexes {L_xFe^{II}OOH(R) + pyH^+} that appeared in the initial stage as a result of nucleophilic addition of HOOH(or HOOR) to L_xFe^{II}.

VI. Conclusion

A problem of the reduction of activity of homogeneous metal complex catalysts in the course of hydrocarbon oxidation with dioxygen is one of central problems of catalysis, because operation of a catalyst is always accompanied by processes of its deactivation. In connection with this, the increase in the stability of catalysts by their modification becomes the central problem. Recently, the idea of immobilizing metal complexes on the surface of a polymer or a mineral support (silica gel, zeolite) has attracted keen attention. Thus heterogenized metal complexes may in certain cases surpass non-immobilized homogeneous metal complexes in activity and selectivity not only due to the protection of a metal complex against deactivation but also as the result of longer lifetimes of active catalytic forms. In supported systems, a support can serve as a matrix that orients both the catalyst and the substrate in a certain way thus increasing the degree of catalyst involvement in the reaction. However, these methods of activation of homogeneous metal complex catalysts have several limitations associated with structural peculiarities of heterogeneous supports.

Yet another way of retention the activity of a homogeneous metal complex catalyst is the introduction of modifying ligands. (As a rule, the mechanisms of action of the modifying ligands are not proved, although different explanations of mechanisms were proposed.)

In the oxidation of alkylarenes with molecular oxygen, different homogeneous metal complex catalysts were used. The majority of them catalyze the alkylarene oxidation to deep oxidation products. Selective oxidation of alkylarenes to the corresponding hydroperoxides, the primary products of alkylarene oxidation, is among the most difficult problems of catalysis, because the majority of the known catalysts decompose hydroperoxides.

The development of efficient catalysts of hydrocarbon oxidation to hydroperoxides attracts keen interest in the context of using hydroperoxides in large-scale production of monomers. We proposed a method of modifying homogeneous catalysts, namely, complexes of transition metals ML_n^1 [M = Ni: L^1 = acac, enamac; M = Fe(II,III): L^1 = acac], with electron-donating ligands-modifiers L^2 (L^2 = DMF, HMPA, R_4NX, 18C6), aimed at enhancing the selectivity of liquid-phase oxidation of alkylarenes (ethylbenzene and cumene) to the corresponding hydroperoxides.

Based on the established (for Ni complexes) and hypothetical (for Fe complexes) mechanisms of formation of catalytically active species and their operation, efficient catalytic systems {$ML_n^1 + L^2$} (L^2 are crown ethers or quaternary ammonium salts) of ethylbenzene oxidation to α-phenylethyl hydroperoxide were modelled. Selectivity $(S_{PEH})_{max}$, conversion, and yield of PEH in ethylbenzene oxidation catalyzed by these systems were substantially higher than those observed with conventional catalysts of ethylbenzene oxidation to PEH.[23–26]

The high activity of systems {$ML_n^1 + L^2$} (L^2 are crown ethers or quaternary ammonium salts) is associated with the fact that during the ethylbenzene oxidation, the active primary $(M^{II}L_2^1)_x(L^2)_y$ complexes and heteroligand $M_x^{II}L_y^1(L_{ox}^1)_z(L^2)_n$ complexes are formed to be involved in the oxidation process. The stability of heteroligand complexes, the intermediate products of oxygenation of primary complexes $(M^{II}L_2^1)_x(L^2)_y$, can be associated with the formation of inter- and intramolecular H-bonds.

Studying the effect of addition of small amounts of water to catalytic systems {$ML_n^1 + L^2$} confirmed the important role of H-bonds in the formation of catalytic species. It was found that the introduction of small portions of water to catalytic systems based on iron complexes leads to the higher catalytic activity of these systems.

¶ Ethylbenzene oxidation with dioxygen (70 °C, CH_2Cl_2, MeCHO), catalyzed by Cu(II) complexes with 18C6, namely, $(CuCl_2)_4(18C6)_2(H_2O)$, afforded acetone as the main product (the acetophenone yield exceeded that of methylphenylcarbinol by a factor of 6.5).[36] Similar results were obtained for oxidation of other hydrocarbons, for example, indane, cyclohexane, tetralin.

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