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Selective Oxidation of Ethylbenzene by Molecular Oxygen: Effect of Macrocyclic 18-Crown-6 Polyether Additives on Catalysis by Bicyclic Nickel Complexes

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Abstract—The catalytic activity of the two-component catalytic system based on nickel bis(enaminoacetonate) (enamac) and 18-crown-6 (18C6) macrocyclic polyether is studied in ethylbenzene oxidation by molecular oxygen. The {$Ni(enamac)_2$ + 18-crown-6} system is a more active catalyst of ethylbenzene oxidation into α-phenylethyl hydroperoxide compared to $Ni(enamac)_2$ and the {$Ni(acac)_2$ + 18-crown-6} system. The formation of $Ni(enamac)_2$–18-crown-6 complex is confirmed both kinetically and spectroscopically. It is suggested that a rise in the oxidation selectivity is due to $Ni(enamac)_2$ transformation activated by 18-crown-6. The order of oxidation product formation at different oxidation stages is determined. The activity of catalysts in the elementary steps of the chain process is discussed.

INTRODUCTION

Ethylbenzene oxidation is a well-studied process [1–3]. However, the problem of increasing the rate and selectivity of ethylbenzene oxidation into α-phenylethyl hydroperoxide still remains unclear.

Most of the available homogeneous and heterogeneous catalytic systems based on transition metal compounds accelerate and improve the selectivity of ethylbenzene oxidation to α-phenylethyl hydroperoxide (up to 90%) compared to the noncatalytic oxidation only at low conversions (~5%) [2].

Earlier [4–9], we found that the use of two-component systems comprising combinations of compounds $M(L^1)_n$ of variable- or constant-valence metals (M) with electron-donor mono- and multidentate ligands (L^2) markedly improve the efficiency of alkylarene oxidation by molecular oxygen to the corresponding hydroperoxides. The mechanism for the control of the catalytic activity of $M(acac)_2$ (M = Ni, Co) by L^2 ligands changes in the course of oxidation.

At early reaction stages, the coordination of L^2 with $M(L^1)_2$ favors an increase in the redox activity of $M(L^1)_2$; namely, the activity of the $M(L^1)_2 \cdot L^2$ complexes increases during chain generation (O_2 activation), whereas, when monodentate ligands are used, this also occurs during the homolytic decomposition of α-phenylethyl hydroperoxide.

In the course of the process involving L^2 ligands, the $M(L^1)_2$ complexes are transformed into more selective catalytic species. In this case, the rise in selectivity is due to the participation of the transformed catalyst in chain initiation (O_2 activation) and a noticeable retardation of chain and heterolytic decomposition of α-phenylethyl hydroperoxide.

The mechanism of $M(L^1)_2$ transformation promoted by the L^2 ligand depends on the metal ion, and, in the case of cobalt(II) bis(acetylacetonate) (L^1 = acac, chelate node (O, O), the catalyst transforms into the catalytically active complexes $[Co^{III}(L^1)_2 \cdot L^2 \cdot (RO_2^-)]$ via the reaction with the peroxy radicals [6].

The nickel complexes become active under the action of O_2. This is accompanied by a substantial change in the ligand surrounding of the metal ion. The L^2 ligand controls the regioselective addition of O_2 to the nucleophile γ carbon atom of one of the acetylacetonate ligands [5, 10] to give an intermediate zwitter ion $[L^2 \cdot M(L^1)_2]^+O_2^-$. The introduction of O_2 into the chelate cycle followed by the bond rearrangement in the resulting intermediate complex causes the breakdown of the cyclic configuration resulting in CO liberation, the formation of OAc^-, acetaldehyde, and catalytically active species of binuclear structure with complex ligands $Ni_2(acac) \cdot (OAc)_3 \cdot L^2$ [5].

Similar changes in the ligand surrounding of the complexes under the action of molecular oxygen were also observed in oxygenation reactions that imitate the action of dioxygenases, for example, during the oxidative decomposition of α-diketonates activated in the coordination sphere of Cu(I) (quercetinase analogs) [11].

Besides studies of the role of the L^2 external ligand, we also investigated the effect of the nature of the chelate center on the mechanism of catalysis of oxidation by nickel complexes in oxidation reactions, including the mechanism of oxidative transformation resulting in a change in the catalytic activity of the complex in the developed process [8].

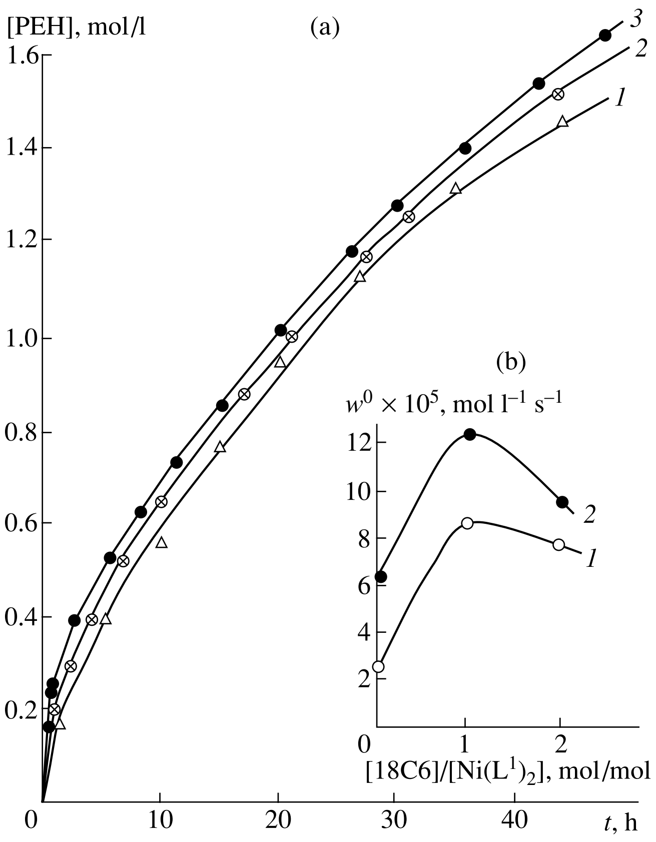

Fig. 1. (a) Kinetic curves of α-phenylethyl hydroperoxide (PEH) accumulation during ethylbenzene oxidation catalyzed by (*1*) $Ni(enamac)_2$ and the $Ni(enamac)_2$ + 18C6 system: $[Ni(enamac)_2] = 1.5 \times 10^{-4}$ mol/l, (*3*) $[18C6] = 1.5 \times 10^{-4}$ and (*2*) 3×10^{-4} mol/l; 120°C. (b) The initial rate of the catalytic ethylbenzene oxidation (w^0) in the presence of the bicyclic complexes of nickel $Ni(L^1)_2$ and 18C6 additives vs. the concentration ratio of [18C6] and $[Ni(L^1)_2]$: (*1*) L^1 = acac and (*2*) L^1 = enamac. $[Ni(L^1)_2] = 1.5 \times 10^{-4}$ mol/l; 120°C.

Recently, the structure and catalytic activity of nickel complexes have aroused increasing interest due to the discovery of nickel-containing enzymes [12–14]. Halcrow and Chistou [13] speculated that the active sites of the enzyme urease are binuclear nickel complexes containing N/O donor ligands, whereas the cofactor of the redox enzyme methyl-S-coenzyme-M of methylreductase involved in methanogen bacteria is the tetra-aza-macrocyclic nickel complex $Ni(I)F_{430}$ of the porphyrinate structure, which is axially coordinated inside the enzyme cavity.

In this work, we studied the effect of the macrocylic polyether 18-crown-6 (18C6) on the mechanism of catalysis of ethylbenzene oxidation by nickel bis(enaminoacetonate) $Ni(enamac)_2$ (chelate node (O, NH) and compared it with the catalytic action of $Ni(acac)_2 \cdot 18C6_n$ complexes (n = 1, 2).

EXPERIMENTAL

Ethylbenzene (RH) oxidation was studied at 120°C in a glass bubbling-type reactor in the presence of $Ni(enamac)_2$ and 18C6 additives. The highest selectivity (S = 90–80%) and conversion (C = 20%) were attained during ethylbenzene oxidation catalyzed by $Ni(enamac)_2$ at $[Ni(enamac)_2] = 1.5 \times 10^{-4}$ mol/l [8]. Taking this into account, the $Ni(enamac)_2$ concentration was set equal to 1.5×10^{-4} mol/l (S = 90–80%, C = 20%) in all the experiments aimed at investigating the effect of the 18C6 additives.

$$\left(S = \frac{[\mathrm{ROOH}]}{\Delta[\mathrm{RH}]} \times 100\%,\ C = \frac{\Delta[\mathrm{RH}]}{[\mathrm{RH}]_0} \times 100\%\right).$$

Analysis of Oxidation Products

α-Phenylethyl hydroperoxide oxidation was analyzed by iodometry, whereas by-products (P), including methyl phenyl carbinol (MPC), acetophenone (AP), and phenol (PhOH), as well as the RH content in the oxidation products, were examined by gas-liquid chromatography.

The overall reaction rate was determined from the rate of accumulation of all oxidation products (it was found in separate experiments that $\Delta[RH] = \Sigma([PEH] + [P])$.

The initial oxidation rates w^0 (including also the initial rates of accumulation of individual oxidation products w^0_{PEH} and w^0_P) were determined under conditions excluding diffusion retardation in an O_2–contact solution two-phase system using a technique allowing the calculation of these parameters accurate to ±5% [7].

The order of the formation of the products (α-phenylethyl hydroperoxide, acetophenone, and methyl phenyl carbinol) was judged based on the time variation in the product ratio at $t \longrightarrow 0$. The kinetics of the reactions was estimated by graphic differentiation [15].

The UV spectra of $Ni(enamac)_2$ in the presence of 18C6 additives were recorded in acetonitrile on a Specord UV–VIS spectrometer.

RESULTS AND DISCUSSION

The introduction of 18C6 in the beginning of ethylbenzene oxidation catalyzed by $Ni(enamac)_2$ causes an increase in the initial oxidation rate, as well as the selectivity and conversion of ethylbenzene oxidation to α-phenylethyl hydroperoxide (Figs. 1, 2). The increase in the oxidation rate is mainly due to a growth in [PEH] (whereas the methyl phenyl carbinol and acetophenone concentrations somewhat decrease).

In contrast to catalysis by $Ni(enamac)_2$, the maximum selectivity to α-phenylethyl hydroperoxide is observed at the very beginning of oxidation rather than in the developed process, after which the S value slowly decreases. The maximum selectivity S = 94–80% and the conversion of oxidation in α-phenylethyl hydroperoxide C = 24% were attained at the ratio $[Ni(enamac)_2]/[18C6]$ = 1 : 1 (Fig. 2). The induction period of formation of phenol, which is the product of α-phenylethyl hydroperoxide heterolytic decomposition, increases in the presence of 18C6 additives (Fig. 2). We observed a similar pattern of increase in the rate w_0, selectivity, and conversion of oxidation to α-phenylethyl hydroperoxide, as well as the retardation of phenol accumulation upon addition of 18C6 when ethylbenzene oxidation was catalyzed by nickel bis(acetylacetonate [7]).

We also found [7] that the process with the initial rates, which are an order of magnitude lower, is self-accelerated in the presence of only 18C6 without nickel complexes and that the selectivity of the process to α-phenylethyl hydroperoxide equal to 85% at the beginning of the reaction dramatically decreases as the ethylbenzene conversion increases. In this case, phenol is formed from the very beginning of the reaction.

By analogy with [7, 8, 15], the efficiency of the selective catalysis of ethylbenzene oxidation to α-phenylethyl hydroperoxide in the presence of $Ni(enamac)_2$ and 18C6 additives was estimated by the parameter $\bar{S}C$ (Table 1). Here, $\bar{S}$ is the averaged selectivity to α-phenylethyl hydroperoxide at certain concentrations [18C6] that varies from S_0 at the reaction beginning to a certain rather high $S_{\lim}$ value in the developed process, arbitrarily chosen for a given series of catalytic reactions that are comparable in their efficiency, and C is the hydrocarbon conversion at $S = S_{\lim}$. As was done earlier, we set $S_{\lim}$ equal to 80%. The selectivity was assessed at the boundaries $S_0 > S \geq S_{\lim}$. Table 1 shows that the $Ni(enamac)_2$–18C6 mixture (1 : 1) is a more efficient catalyst for selective ethylbenzene oxidation in α-phenylethyl hydroperoxide compared to $Ni(enamac)_2$ and is characterized by an $\bar{S}C$ parameter similar to that of the $Ni(acac)_2$–18C6 complex of composition 1 : 1.

Figure 1 shows that the initial rate of ethylbenzene oxidation w^0 catalyzed by $Ni(O, NH)_2$ increases in the presence of 18C6 and reaches its maximum value at $[18C6] : [Ni(enamac)_2]$ = 1 : 1. Similar oxidation acceleration is also observed during catalysis by the $Ni(O,O)_2$ complex (Fig. 1).

By analogy with the effect of 18C6 on ethylbenzene oxidation catalyzed by $Ni(acac)_2$ [7] and $Co(acac)_2$ [6], the observed increase in the values of w^0 and $\bar{S}C$ during ethylbenzene oxidation catalyzed by $Ni(enamac)_2$ in the presence of 18C6 additives may be attributed to the formation of complexes between $Ni(enamac)_2$ and 18C6 of composition 1 : 1 and 1 : 2 that are more active in oxidation. Crown ethers and other macrocyclic ligands favor oxygen coordination by metal complexes [16, 17]. For example, the complexes of cobalt carboxylates with monoalkyl-substituted dibenzo-18C6 forms the adducts with O_2 of the composition 1 : 2. The presence of bulky alkyl substituents in the macrocyclic rings favors the formation of adducts with O_2 [18].

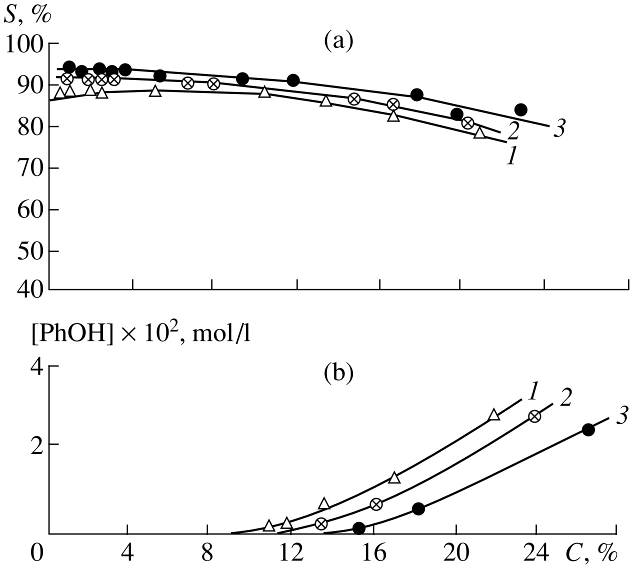

Fig. 2. (a) Selectivity (S) of ethylbenzene oxidation to α-phenylethyl hydroperoxide and (b) phenol concentration in ethylbenzene oxidation catalyzed by (*1*) $Ni(enamac)_2$ and (*2*, *3*) the catalytic system $\{Ni(enamac)_2 + 18C6\}$ vs. ethylbenzene conversion (C) at [18C6] = (*3*) 1.5×10^{-4} and (*2*) 3.0×10^{-4} mol/l. $[Ni(enamac)_2] = 1.5 \times 10^{-4}$ mol/l; 120°C.

In certain cases, radical formation can substantially be accelerated, for instance, during hydroperoxide decomposition catalyzed by metal complexes with macrocyclic polyethers [19] or in chain initiation during autooxidation involving the adducts of the metal macrocyclic complexes with O_2 [20]. For example, cobalt and nickel porphyrinate or cyclam complexes react with molecular oxygen and initiate acylperoxy radical formation in the course of aldehyde autooxidation, and the radicals thus generated (or metal complexes with acylperoxy radicals) act as epoxidizing agents in the cooxidation of olefins and aldehydes by molecular oxygen [20].

Table 1. $\bar{S}C$ in ethylbenzene oxidation catalyzed by nickel complexes. $[Cat] = 1.5 \times 10^{-4}$ mol/l, 120°C

Cat	$\bar{S}C \times 10^{-2}$, %
$Ni(enamac)_2$	15.9
$Ni(enamac)_2 \cdot 18C6$	21.2
$Ni(acac)_2$	9.6
$Ni(acac)_2 \cdot 18C6$	20.6

Earlier [15], we hypothesized that the acceleration of ethylbenzene oxidation catalyzed by nickel and cobalt chloride and nitrate complexes with 15-crown-5 and 18C6, compared to noncatalytic oxidation, is due to the participation of these complexes in chain initiation (O_2 activation) and propagation [15]. A significant (by more than an order of magnitude) increase in the rate of chain initiation is observed during ethylbenzene oxidation catalyzed by $Ni(acac)_2$ in the presence of 18C6 additives [7].

The incorporation of the transition metal cations inside macrocyclic polyethers has been confirmed by different physicochemical methods [21]. X-ray diffraction data suggest that small transition metal atoms usually coordinate with all atoms of a crown ether (and, therefore, are considered as incorporated into it) and are either located inside its cavity (the $CoCl_2$–15-crown-5 complex) or above its plain (the $CoCl_2$–18C6 complex) [22].

In this case, the particular structure of the complex is determined not only by the geometric coincidence of the metal ion and the crown-ether cavity but also by all the electron and spatial factors created by the metal atom, polyether, other ligands, and the solvent.

Nickel complexes with crown ethers have been less studied than Co, Mn, and Cu complexes.

For example, the formation of strong bonds Ni–18C6, Ni–15-crown-5, and Ni–12-crown-4 on mixing $NiCl_2$ (or $NiCl_2 \cdot 6H_2O$) solutions with crown ethers was verified using the FAB/MS method [23].

The extraction of Ni^{2+} ions by the crown ether dicyclohexane–18C6 (L) from aqueous solutions of $NiCl_2$ via the reaction

$$Ni^{2+}(6H_2O) + L + 2Cl^- \longrightarrow NiLCl_2 + 6H_2O$$

was described in [24].

Dibenzo–18C6, which is covalently bound to the porphyrinate ring has virtually no effect on the activity of Mn(III) tetraarylporphyrinates (PPh) during epoxidation. At the same time, the activity of Mn(III) tetraarylprophyrinate substantially increases in the presence of dibenzo-18C6 additives, which are obviously coordinated inside the sphere of the Mn complex [25].

We confirmed the formation of complexes between $Ni(acac)_2$ and 18C6 both kinetically and spectrometrically when analyzing the UV absorption spectra of the mixtures of $Ni(acac)_2$ and 18C6 solutions [7]. Spectral analysis indicates that 18C6 coordinates with the metal ion and the acetylacetonate ligand is preserved in the internal coordination sphere of the complex.

The formation of complexes between $Ni(enamac)_2$ and 18C6 may be judged from the comparison of the UV spectra of the $Ni(enamac)_2$ solutions and the $Ni(enamac)_2$–18C6 mixture. The addition of 18C6 to an acetonitrile solution of $Ni(enamac)_2$ results in an increase in the intensity of the absorption band of the eneminoacetonate ion in the nickel complex and a hypsochromic shift of its maximum from 295 to 290 nm, as well as in a decrease in the absorption of weak bands at λ = 265 and 348 nm compared to the $Ni(enamac)_2$ spectrum (Fig. 3, spectra *1*, *2*).

After a day, the optical density of the $(enamac)^-$ absorption band increases and its maximum shifts to λ = 285 nm, the absorption band with λ = 265 nm disappears completely, and the absorption intensity at λ = 348 nm decreases (spectrum *3*).

Changes in the $Ni(enamac)_2$ spectrum in the presence of 18C6 suggest that 18C6 is incorporated into the coordination sphere of the metal ion, apparently, while preserving the enaminoacetonate ligand in the internal coordination sphere of the complex. The removal of the enamicoacetonate ion should have caused a noticeable increase in the absorption intensity at λ = 290 nm corresponding to the absorption band maximum of the free ligand, because the spectra of free enaminoacetone (enamacH) (Fig. 3, spectra *4*, *5*) were obtained at the concentrations of enamacH, which are 500–1000 times lower than those of $Ni(enamac)_2$. Moreover, the spectrum of the mixture lacks the absorption bands on the free ligand at λ = 255 and 265 nm but contains the $Ni(enamac)_2$ absorption band at λ = 348 nm.

Similar changes in the absorption spectrum of $Cu(acac)_2$ were observed in the presence of manganese naphthenate, which is axially coordinated with $Cu(acac)_2$ to form the Cu–O–Mg bond [26].

For example, the formation of 18C6 complexes with metal β-diketonates without removal of the β-diketonate ligand was observed for the β-diketonate complexes of An(III) and Ln(III) actinide and lanthanide ions ($M(A)_2^+$ or $M(A)_3$) [27]: 18C6 enters the internal coordination sphere of the complexes as a multidentate ligand, and its three oxygen atoms coordinate with the metal ion in the cation complex $[M(A)_2 \cdot 18C6]^+$ or as a monodentate ligand in the neutral complex $[M(A)_3 \cdot 18C6]$. The formation of these complexes is related to the synergistic extraction of An(III) and Ln(III) ions from the aqueous solutions into dichloroethane containing β-diketone and 18C6.

Table 2 gives the accumulation rates w_{PEH} and w_{AP+MPC} at the early stage of oxidation (w_0 up to 1 h) and in the developed process (w from 5 to 15 h) when the process rate remains unchanged.

Within the framework of the radical-chain mechanism, we estimated the activity of the $Ni(enamac)_2 \cdot 18C6_n$ complexes in the elementary oxidation steps by the method developed earlier to estimate the catalytic activity of $Ni(enamac)_2$, $Ni(acac)_2$, the $Ni(acac)_2 \cdot 18C6$ complexes, and the complexes of nickel and cobalt salts with crown ethers using a simplified scheme that assumes quadratic chain termination and the absence of homolytic decomposition of α-phenylethyl hydroperoxide [7, 8, 15].

Apparently, for catalysis by $Ni(enamac)_2 \cdot 18C6_n$ complexes, we can also assume that the homolytic decomposition of α-phenylethyl hydroperoxide may be ignored (compared to its formation) because of the high selectivity (94–90%) of RH oxidation to α-phenylethyl hydroperoxide in the course of reaction examined. Furthermore, the estimate of the ratio of the rates of accumulation of by-products and α-phenylethyl hydroperoxide showed that $w_P/w_{PEH} \neq 0$ at $t \longrightarrow 0$ both at the early stages of the reaction and in the developed process (5–15 h), thus indicating the parallel formation of by-products and α-phenylethyl hydroperoxide. Earlier [8], we found that $w^0 \sim [\mathrm{Cat}]^{1/2}$ and $w_i^0 \sim [\mathrm{Cat}]$ for the catalysis by $\mathrm{Ni(enamac)_2}$ ($[\mathrm{Cat}] \leq 3 \times 10^{-4}$ mol/l). It was believed that these conditions are also fulfilled for catalysis by $\mathrm{Ni(enamac)_2 \cdot 18C6}$ complexes and that the linear radical termination on the catalyst may be neglected.

Then, we arrive at the following equation for the rate of the quadratic chain termination (w_{term}):

$$w_{\mathrm{term}} = k_6[\mathrm{RO}_2^{\bullet}]^2 = k_6\left\{\frac{w_{\mathrm{PEH}}}{k_2[\mathrm{RH}]}\right\}^2, \qquad (1)$$

where w_{PEH} is the rate of α-phenylethyl hydroperoxide accumulation at the beginning of the reaction (w_{PEH}^0) or in the developed process (w_{PEH}).

In our calculations, we used the following rate constants at 120°C: $k_2 = 19.2$ l mol^{-1} s^{-1}, $k_6 = 1.9 \times 10^7$ l mol^{-1} s^{-1} [28], and $[\mathrm{RH}]_0 = 8.2$ mol/l (we took into account RH consumption in the developed process).

Using data of Table 2 and Eq. (1), one can calculate the w_{term} both at the beginning of the reaction and in the developed process.

We found that the w_{term} value coincides with the rate of acetophenone and methyl phenyl carbinol formation ($w_{\mathrm{AP+MPC}}^0$) at $[\mathrm{Ni(O, NH)_2}] : [\mathrm{18C6}] = 1 : 1$ at the beginning of the reaction, that is, the only reaction of acetophenone and methyl phenyl carbinol formation is the quadratic chain termination. A similar result was obtained earlier for catalysis by $\mathrm{Ni(O, O)_2 \cdot 18C6}$ complexes [7].

The w_{term} values calculated in the steady-state approximation for $\mathrm{RO}_2^{\bullet}$ radicals and equal to the initiation rates may be considered as parameters characterizing the molecular oxygen activation.

By analogy with catalysis by $\mathrm{Ni(O, NH)_2}$ and the results of [7, 8, 15], a slight difference between the values of w_{term} and $w_{\mathrm{AP+MPC}}^0$ for the $\mathrm{Ni(O, NH)_2 \cdot 18C6}$ complex (1 : 2) may be explained by the additional formation of acetophenone and methyl phenyl carbinol during chain propagation (I) (w_{pr}) assuming the absence of the linear termination of the $\mathrm{RO}_2^{\bullet}$ radicals on the catalyst molecules:

$$\mathrm{RO}_2^{\bullet} \xrightarrow{\mathrm{Cat}} \mathrm{R'C{=}O(ROH)} + \mathrm{R}^{\bullet}, \qquad (I)$$

$$w_{\mathrm{pr}} = w_{\mathrm{AP+MPC}} - w_{\mathrm{term}}.$$

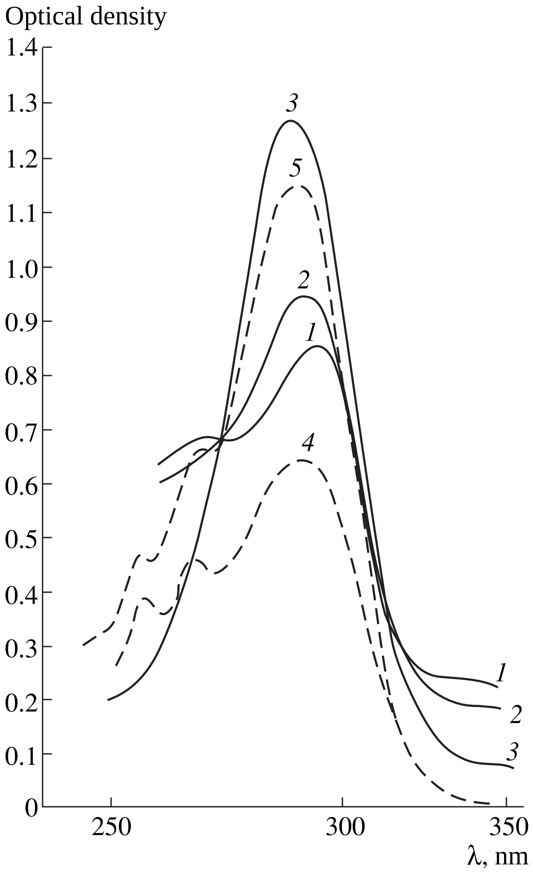

Fig. 3. Electron absorption spectra of solutions in $\mathrm{CH_3CN}$: (*1*) $\mathrm{Ni(enamac)_2}$; (*2*, *3*) $\{\mathrm{Ni(enamac)_2} + \mathrm{18C6}\}$; (*4*, *5*) enamacH at concentrations, mol/l: $[\mathrm{Ni(enamac)_2}] = 0.5 \times 10^{-4}$, $[\mathrm{18C6}] = 1.0 \times 10^{-4}$, (*4*) $[\mathrm{enamacH}] = 0.5 \times 10^{-7}$, and (*5*) 1.0×10^{-7}; 20°C; (*3*) one day after the solution preparation.

Table 2 shows that the coordination of 18C6 with $\mathrm{Ni(O, NH)_2}$ causes a nearly fivefold increase in the rate of chain initiation (the molecular oxygen activation) and a decrease in the rate of chain propagation (to zero in the case of a 1 : 1 complex).

This probably explains the increase in the selectivity of ethylbenzene oxidation to α-phenylethyl hydroperoxide at an early oxidation stage (Fig. 2a) compared to catalysis by $\mathrm{Ni(O, NH)_2}$ without 18C6 additives. $\mathrm{Ni(O, NH)_2 \cdot 18C6}$ complexes are twice as active as $\mathrm{Ni(O, O)_2 \cdot 18C6}_n$ complexes in chain initiation. However, the crown effect is less pronounced in the case of catalysis by $\mathrm{Ni(O, NH)_2}$: in the presence of 18C6 additives, the values of w^0 and w_i^0 increase two and five times, respectively, whereas, during catalysis by $\mathrm{Ni(O, O)_2}$, they increase by a factor of 4 and 18.3, respectively. The retardation of chain propagation in the presence of 18C6 was also observed earlier for the catalysis of ethylbenzene oxidation by $\mathrm{Ni(O, O)_2}$ ($\mathrm{Ni(acac)_2}$) complexes, which may be due to steric hindrances for the

Table 2. Rate of accumulation of the products of ethylbenzene oxidation at the beginning of the reaction (w^0) and in the course of oxidation (w) at t = 5–15 h and the calculated rates of chain initiation (w_i) and propagation (w_{pr}) during catalysis by the complexes $Ni(L^1)_2$ (L^1 = enamac, acac) and $Ni(L^1)_2 \cdot L^2_n$ (L^2 = 18C6, n = 1, 2); 120°C

NiL^1_2	$[18C6] \times 10^4$, mol/l ($[Ni(L^1)_2]/[18C6]$)	$w^0_{PEH} \times 10^5$, mol l^{-1} s^{-1}	$w^0_{AP+MPC} \times 10^6$, mol l^{-1} s^{-1}	$w_{PEH} \times 10^5$, mol l^{-1} s^{-1}	$w_{AP+MPC} \times 10^6$, mol l^{-1} s^{-1}	$w^0_i \times 10^6$, mol l^{-1} s^{-1}	$w^0_{pr} \times 10^6$, mol l^{-1} s^{-1}	$w_i \times 10^7$, mol l^{-1} s^{-1}	$w_{pr} \times 10^7$, mol l^{-1} s^{-1}
$Ni(enamac)_2^*$	–	5.5	7.5	1.1	0.9	2.4	5.1	1.1	8.4
	1.5(1 : 1)	11.77	9.44	1.0	1.5	10.49	–	0.8	14.2
	3.0(1 : 2)	8.88	7.72	1.0	1.6	6.04	1.18	0.8	15.2
Without catalyst	–	–	–	1.0	6.3	–	–	–	–
$Ni(acac)_2^*$	–	2.1	2.6	1.1	1.1	0.3	2.1	–	–
	1.5(1 : 1)	8.12	4.9	1.6	1.3	5.1	–	–	–
	3.0(1 : 2)	7.7	4.5	1.4	2.0	4.5	–	–	–

* $[Ni(L^1)_2] = 1.5 \times 10^{-4}$ mol/l.

coordination of $RO_2^\bullet$ radicals by nickel complexes with 18C6 [7].

The higher values of w^0 and w^0_i for catalysis by $Ni(enamac)_2$ might be expected. For example, nickel complexes with azacrown ethers are characterized by very low redox potentials for the $Ni(II) \Leftrightarrow Ni(III)$ pair [29–31].

Nickel dioxopenta-aza-macrocyclic complexes are very active with respect to O_2 and in the oxygenation of aromatic compounds [16, 30].

The activation of molecular oxygen was confirmed for the nickel complexes with tetrahydrozalene (the chelate node $Ni(O, NH)_2$) [31].

A less pronounced crown effect observed for ethylbenzene oxidation catalyzed by $Ni(enamac)_2$ complexes with 18C6 compared to $Ni(acac)_2 \cdot 18C6$ complexes (an increase in the values of w^0 and w^0_i under the action of 18C6 additives) can be explained by a decrease in the acceptor properties of $Ni(enamac)_2$ with respect to 18C6 coordination due to both the covalent character of the Ni–NH bonds and a decrease in the effective charge of the metal ion [32].

A similar order of decrease in the acceptor properties of the complex with respect to the axial coordination of the electron-donor ligand on changing the chelate node was also suggested for copper complexes [33]:

$$Cu(O,O)_2 > Cu(O,N)_2 > Cu(N_4).$$

In the course of ethylbenzene oxidation catalyzed by the $\{Ni(enamac)_2 + 18C6\}$ system, we observed a dramatic decrease in the reaction rate w compared to the early stage of the process w^0 (Table 2) and the constancy of the reaction rate during 5–15 h, while the high selectivity (S = 97–90%) remained unchanged (until the beginning of phenol formation in the system). Similar changes in the values of w and S during oxidation were reported earlier for catalysis by the $\{Ni(acac)_2 + 18C6\}$ system and associated with the transformation of $Ni(acac)_2 \cdot 18C6_n$ complexes into new catalytically active species of a possible structure $Ni_x(acac)_y \cdot (OAc)_z \cdot L^2_n$ (**B**).

Earlier [8], we hypothesized that $Ni(enamac)_2$ transformation in the course of ethylbenzene oxidation into more catalytically active species occurred even without an activating ligand and suggested that its mechanism implies the regioselective addition of O_2 to the γ carbon atom of the ligand.

On the basis of our previous results and literature data, we proposed the following mechanism of $Ni(enamac)_2$ transformation during ethylbenzene oxidation. The O_2 molecule is regioselectively added to the γ carbon atom of one of the ligands in the $O_2 \cdot Ni(enamac)_2$ adduct, and O_2 is incorporated into the heterocyclic ring of the intermediate zwitter ion $Ni(enamac)_2^+ \cdots O_2^-$ formed, followed by the decomposition of the resulting heterocyclic configuration by analogy with the catalytic oxidation of alkylinedols [34, 35] and the formation of active heteroligand complexes via the scheme

$$\mathrm{Ni(COMeCHMeCNH)_2 + O_2 \longrightarrow L\cdot Ni(CoMeCHMeCNH)^{+}\cdots O_2^{-}}$$

$$\mathrm{L\cdot Ni(COMeCHMeCNH)^{+}\cdots O_2^{-} \longrightarrow \underset{\mathbf{Q}_1}{L\cdot Ni(NHCOMe)} + MeCHO + CO}$$

$$\begin{tikzcd} \mathbf{Q}_1 \arrow[d, "\mathrm{H_2O}"] \\ \mathrm{L\cdot Ni(MeCOO) + NH_3}, \\ \mathbf{Q}_2 \end{tikzcd}$$

where L=$(\mathrm{COMeCHMeCNH})^{-}$.

The coordination of 18C6 with $\mathrm{Ni(enamac)_2}$ can favor such a complex transformation [36].

The active and selective catalysts in this case may be the $\mathrm{Q_1 \cdot 18C6}_n$ complex, its hydrolysis product $\mathrm{Q_2 \cdot 18C6}_n$ ($n = 1, 2$), or complexes of type **B** based on them.

Apparently, a decrease in the selectivity of ethylbenzene oxidation in α-phenylethyl hydroperoxide at $C \approx 16$–18% corresponding to a noticeable increase in the rate of phenol accumulation (Fig. 2) may be attributed to the complete oxidation of active heteroligand to homoligand complexes $\mathrm{Ni(NHCOMe)_2}$ or $\mathrm{Ni(MeCOO)_2}$ responsible for α-phenylethyl hydroperoxide heterolytic decomposition [5].

The absence of chain and heterolytic decomposition of α-phenylethyl hydroperoxide allows one to estimate the change in w_{i} and w_{pr} in the developed process occurring at a constant rate (5–15 h) by Eq. (1) and compare them with the values of w_{i} and w_{pr} determined earlier in the absence of 18C6 additives. As with catalysis by $\mathrm{Ni(enamac)_2}$, we also assume in this case (i.e., in the presence of 18C6) that Eq. (1) can be applied to calculate the parameters w_{i} and w_{pr}, namely, that $w \sim [\mathrm{Cat}]^{1/2}$ and $w_{\mathrm{i}} \sim [\mathrm{Cat}]$. Table 2 shows that, as in the absence of 18C6, the value of w_{i} is lower than at the beginning of the reaction, but its decrease in w_{i} is more pronounced (by a factor of ~100).

As with catalysis by $\mathrm{Ni(enamac)_2}$ without 18C6, the $w_{\mathrm{pr}}/w_{\mathrm{i}}$ ratio increases in the developed reaction.

The high selectivity in the developed process of ethylbenzene oxidation catalyzed by the $\{\mathrm{Ni(enamac)_2} + 18\mathrm{C}6\}$ system compared to noncatalyzed oxidation ($S_{\mathrm{noncat}} \leqslant 80\%$) may mainly be due to both the retardation of the chain and heterolytic pathway of α-phenylethyl hydroperoxide decomposition and the change in the mechanism of product formation on catalysis by complexes formed via $\mathrm{Ni(enamac)_2 \cdot 18C6}_n$ transformation. The products α-phenylethyl hydroperoxide, acetophenone, and methyl phenyl carbinol are formed in parallel steps $\left(\dfrac{w_{\mathrm{P}}}{w_{\mathrm{PEH}}} \neq 0 \text{ and } \dfrac{w_{\mathrm{AP}}}{w_{\mathrm{MPC}}} \neq 0 \text{ at } t \longrightarrow 0\right)$. In noncatalyzed ethylbenzene oxidation, the products (acetophenone and methyl phenyl carbinol) are mainly formed during the chain decomposition of α-phenylethyl hydroperoxide, whereas acetophenone is also produced by methyl phenyl carbinol oxidation $\left(\dfrac{w_{\mathrm{P}}}{w_{\mathrm{PEH}}} \longrightarrow 0 \text{ and } \dfrac{w_{\mathrm{AP}}}{w_{\mathrm{MPC}}} \longrightarrow 0 \text{ at } t \longrightarrow 0\right)$ [28].

At the same time, complexes formed during oxidation are active in free-radical generation ($\mathrm{O_2}$ activation) because $w_{\mathrm{i}} \approx 10^{-7}$ mol $\mathrm{l^{-1}}$ $\mathrm{s^{-1}}$, which is much higher than the initiation rate during noncatalytic ethylbenzene oxidation ($w_{\mathrm{i}} \approx 10^{-9}$ mol $\mathrm{l^{-1}}$ $\mathrm{s^{-1}}$) [7].

During ethylbenzene oxidation catalyzed by the $\{\mathrm{Ni(acac)_2} + 18\mathrm{C}6\}$ system, the oxidation products (methyl phenyl carbinol and α-phenylethyl hydroperoxide), as well as acetophenone and methyl phenyl carbinol, are formed in parallel, whereas ketone is formed during α-phenylethyl hydroperoxide decomposition $\left(\dfrac{w_{\mathrm{AP}}}{w_{\mathrm{PEH}}} \longrightarrow 0 \text{ at } t \longrightarrow 0\right)$. The latter fact is obviously related to the more dramatic decrease in the S value in the course of the process (5–15 h) in contrast to ethylbenzene oxidation catalyzed by $\mathrm{Ni(enamac)_2 \cdot 18C6}_n$.

In the presence of known homogeneous and heterogeneous catalysts [2, 26], the selective catalysis at the early stages of ethylbenzene oxidation to α-phenylethyl hydroperoxide was explained by a noticeable retardation of the radical decomposition of α-phenylethyl hydroperoxide and the activation of molecular oxygen (and RH in the case of the heterogeneous catalyst [2]).

Therefore, the modification of $\mathrm{Ni(O, NH)_2}$ with the crown ether 18C6 at the early oxidation stages may be associated with the formation of $\mathrm{Ni(O, NH)_2 \cdot 18C6}_n$ complexes ($n = 1, 2$), which are more active catalysts of ethylbenzene oxidation in α-phenylethyl hydroperoxide than $\mathrm{Ni(O, NH)_2}$ (and $\mathrm{Ni(O, O)_2 \cdot 18C6}_n$ complexes).

Within the framework of the radical-chain mechanism, the coordination of $18\mathrm{C}6_n$ with $\mathrm{Ni(O, NH)_2}$ results in a substantial acceleration of chain initiation ($\mathrm{O_2}$ activation) and, at the same time, in a retardation of both chain propagation during the reaction of the catalyst with $\mathrm{RO_2^{\bullet}}$ and α-phenylethyl hydroperoxide decomposition (homolytic and heterolytic). In this case, $Ni(O, NH)_2 \cdot 18C6_n$ complexes are more active than $Ni(O, O)_2 \cdot 18C6_n$ ones during chain initiation despite the more pronounced crown effect (increase in the w_i^0 value because of 18C6 additives) in the latter case.

In the developed process, 18C6 promotes the formation of new catalytically active species. An increase in the selectivity in α-phenylethyl hydroperoxide under these conditions compared to the noncatalyzed reaction is due to both the participation of the transformed catalyst form in chain initiation and the retardation of the chain and heterolytic decompositions of hydroperoxide.

Higher $\bar{S}C$ values attained upon addition of 18C6 to the system catalyzed by $Ni(O, NH)_2$ may be attributed to the higher stability of the transformed catalyst form to the complete oxidation to compounds that are inactive in selective catalysis.

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