Selective oxidation of ethylbenzene by dioxygen. The effect of chelate center on catalysis by bicyclic nickel complexes

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The effect of the nature of the chelate center in Ni^{II} complexes on their catalytic activity in the selective oxidation of ethylbenzene by dioxygen to α-phenylethyl hydroperoxide in the presence of nickel bis(acetylacetonate) (chelate center $Ni(O,O)_2$) and nickel bis(enaminoacetonate) (chelate center $Ni(O,NH)_2$) was studied. The efficiency of selective oxidation of ethylbenzene increases substantially in the presence of the chelate with the $Ni(O,NH)_2$ active center as a catalyst, which is mainly due to the transformation of the catalyst into more active species during the oxidation process. The mechanism of transformation of nickel bis(enaminoacetonate) under the action of dioxygen was suggested. The sequence of formation of the reaction products at different stages of the catalytic process was determined. The activity of the nickel complex with the $Ni(O,NH)_2$ chelate center and the products of its transformation in the elementary stages of chain oxidation of ethylbenzene is discussed.

Key words: ethylbenzene, oxidation, homogeneous catalysis, dioxygen, nickel chelates, nickel bis(acetylacetonate), nickel bis(enaminoacetonate).

We have observed previously[1–3] that two-component catalytic systems based on transition metal complexes $M(L^1)_2$ (M = Ni, Co; L^1 is the bis(acetylacetonate) anion) and electron-donor auxiliary ligands L^2 (HMPA, DMF, *N*-methylpyrrolidone-2, quaternary ammonium salts, and crown ethers) possess a high catalytic activity in selective oxidation of alkylarenes by dioxygen to the corresponding hydroperoxides. The $M(L^1)_2L^2$ complexes participate in the stages of chain initiation (activation of O_2) and propagation and in the case of L^2, which is a monodentate ligand, of homolytic decomposition of ROOH as well. During development of the oxidation process, the $M(L^1)_2L^2$ complexes are transformed into more active selective catalytic species. In the case of cobalt(II) bis(acetylacetonate), the catalyst is transformed due to the interaction with peroxide radicals into catalytically active complexes of the $[Co^{III}(L^1)_2L^2(RO_2^-)]$ type.[4] The nickel complexes are transformed into the catalytically active form under the action of O_2. This changes substantially the ligand environment of the complex due to the regioselective addition (controlled by the L^2 ligand) of O_2 to the γ-C atom of the acetylacetonate ligand.[2,5] The insertion of O_2 into the C=C bond of one of the ligands $(acac)^-$ is accompanied by the cleavage of the chelate cycle to form the OAc^- ion, CO, acetaldehyde, and catalytically active species with the binuclear heteroligand structure:[2] $Ni_2(AcO)_3(acac) \cdot L^2$ (A).

Similar changes in the ligand environment of the complexes under the effect of dioxygen were observed in reactions of oxygenation imitating the action of dioxygenases, for example, during the oxygenation of α-diketonates in the coordination sphere of Cu^I (analogs of quercetinase).[6]

In addition to the study of the role of the L^2 exoligand, it was of interest to study the effect of the nature of the chelate unit on the mechanism of catalysis by the nickel complexes in oxidation reactions, including that on the mechanism of oxidative transformation resulting in a change in the catalytic activity of the complex in the developed process. In this connection, we compared the catalytic activities of two bicyclic nickel complexes: nickel bis(acetylacetonate) ($Ni(acac)_2$, chelate unit $Ni(O,O)_2$) and nickel bis(enaminoacetonate) ($Ni(enamac)_2$, chelate unit $Ni(O,NH)_2$).

Experimental

Ethylbenzene (RH) was oxidized at 120 °C in a glass bubbling-type reactor. The oxidation products were analyzed as follows: α-phenylethyl hydroperoxide (PEH), by iodometry; by-products (P) (methylphenylcarbinol (MPC), acetophenone (AP), and phenol (PhOH)), by GLC. The content of ethylbenzene in the oxidate was also determined by GLC.[1]

The overall reaction rates were determined from the rates of accumulation of the sum of oxidation products. It was established by balance experiments that

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$\Delta[RH] = \Sigma[PEH] + [P]$.

The initial rates of oxidation (including the initial rates of accumulation of individual products of oxidation, w^0_{PEH} and w^0_P) were determined in the absence of diffusion retardation in the biphase O_2—contact solution system by the method[3] that made it possible to calculate these values with an accuracy to ±5%. The sequence of formation of the products of ethylbenzene oxidation was determined from the time dependence of the ratio of accumulation rates of individual products at $t \to 0$.[7,8] The change in the ratio of rates in time was estimated by the method of graphical differentiation.[7]

Results and Discussion

Based on the published data, we could expect that $Ni(enamac)_2$ exhibits a higher catalytic activity than $Ni(acac)_2$ in the chain radical oxidation of ethylbenzene by dioxygen. It is known that nickel complexes with azacrown ethers have very low redox potentials E^0 for the pair $M^{II} \rightleftharpoons M^{III}$ and possess a high activity with respect to dioxygen and in oxygenation of aromatic compounds.[9] The increase in the N : O ratio from 2 : 4 to 4 : 2 in the coordination sphere of iron chelates favors an increase in the activity of the complexes in the catalytic decomposition of *tert*-butyl hydroperoxide.[10]

It could be expected that $Ni(enamac)_2$ is transformed during oxidation into catalytically active complexes according to the mechanism described in detail for $Ni(acac)_2$,[2] *i.e.*, by the regioselective addition of O_2 to the γ-C atom of the ligand. It is known that the reactivity of the nucleophilic C atom of β-diketonates of various metals and complexes with Schiff's bases is almost independent of the structure of the equatorial ligand (the nature of chelate-forming O and N atoms).[5] At the same time, the reactions of catalytic oxygenation of enamines with insertion of O_2 into the C=C bond conjugated with the NH group followed by the cleavage of the cyclic configuration and formation of carbonyl compounds are described. This, *e.g.*, catalysis by the Cu^I complex with pyridine, is a nonenzymatic model imitating the action of pyrrolase.[11] Cobalt compounds also catalyze similar oxygenation of enamines.[11] It is also known that Co, Cu, and Ni porphyrin complexes in methylene dichloride and Mn phthalocyanine in DMF catalyze dioxygenation of alkyl derivatives of indol, which

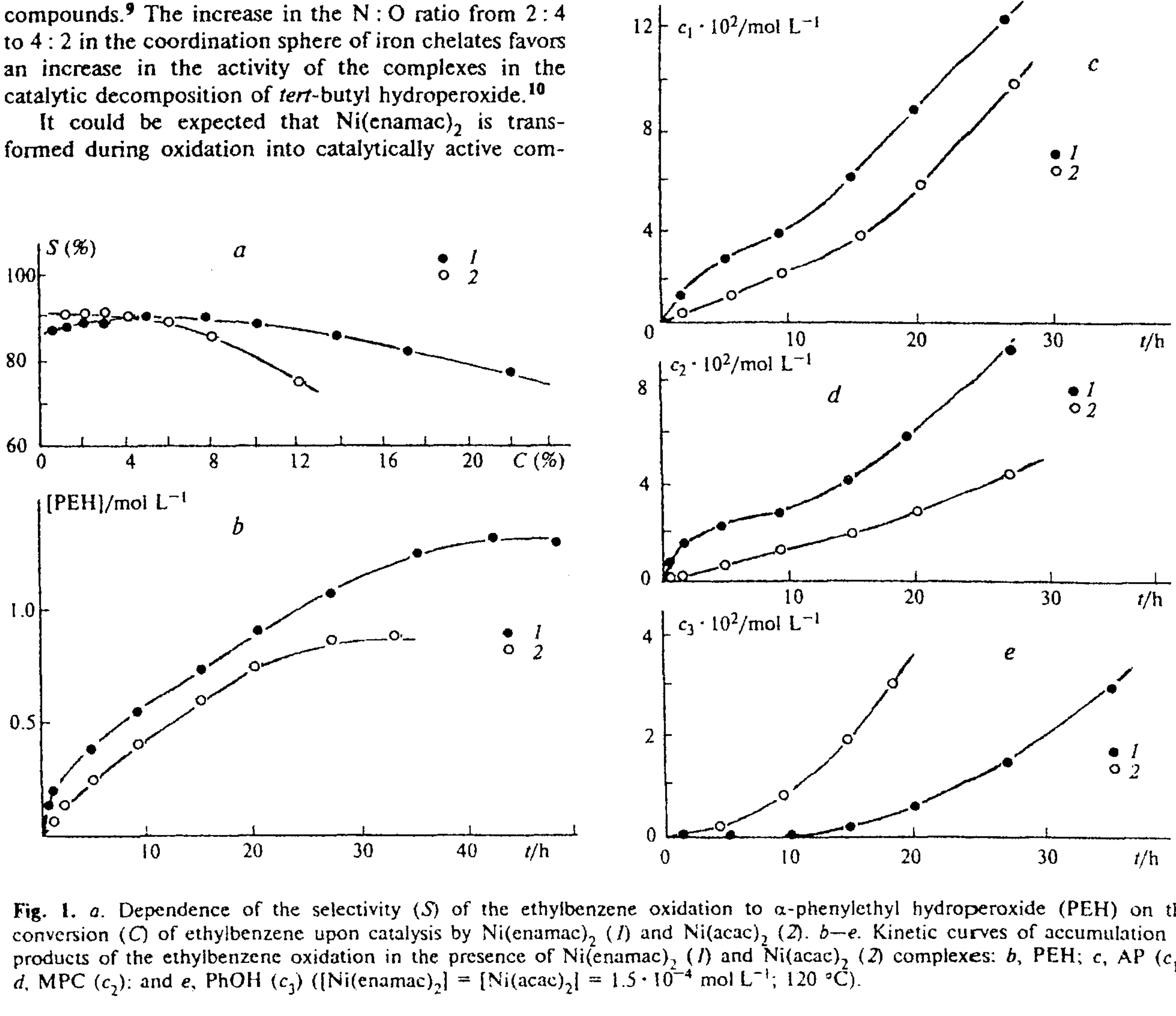

Fig. 1. *a*. Dependence of the selectivity (*S*) of the ethylbenzene oxidation to α-phenylethyl hydroperoxide (PEH) on the conversion (*C*) of ethylbenzene upon catalysis by $Ni(enamac)_2$ (*1*) and $Ni(acac)_2$ (*2*). *b—e*. Kinetic curves of accumulation of products of the ethylbenzene oxidation in the presence of $Ni(enamac)_2$ (*1*) and $Ni(acac)_2$ (*2*) complexes: *b*, PEH; *c*, AP (c_1); *d*, MPC (c_2); and *e*, PhOH (c_3) ($[Ni(enamac)_2] = [Ni(acac)_2] = 1.5 \cdot 10^{-4}$ mol L^{-1}; 120 °C).

can be considered as enamines by analogy with the action of tryptophan-2,3-dioxygenase, through the formation of a ternary complex of the catalyst with O_2 and indol with opening of the indol cycle and formation of the corresponding ketoamides.[12]

The catalytic activity of the $Ni(enamac)_2$ complex was studied in the concentration range $[Ni(enamac)_2] = (0.15-5) \cdot 10^{-3}$ mol L^{-1}. In the presence of $Ni(enamac)_2$, as well as upon catalysis by $Ni(acac)_2$, α-phenylethyl hydroperoxide is the main product of the ethylbenzene oxidation (Fig. 1). By-products of the oxidation (AP, MPC, and PhOH) are formed in considerably lower amounts. In the optimum regime of ethylbenzene oxidation ($[Cat] = 1.5 \cdot 10^{-4}$ mol L^{-1}), the maximum concentration of hydroperoxide ($[PEH]_{max} = 1.4$ mol L^{-1}) is considerably higher than that upon catalysis by $Ni(acac)_2$ ($[PEH]_{max} = 0.9$ mol L^{-1}). The initial rates of oxidation in the presence of $Ni(enamac)_2$ are higher: $w^0_{PEH+\Sigma P}(Ni(O,NH)_2) > w^0_{PEH+\Sigma P}(Ni(O,O)_2)$. Unlike catalysis by nickel acetylacetonate, in the presence of the complex with the $Ni(O,NH)_2$ chelate unit, no formation of phenol (the product of heterolysis of PEH) is observed during first hours of oxidation (Figs. 1 and 2, *b*). In addition, the conversion (*C*) with selectivity (*S*) with respect to PEH not lower than 80% increases considerably as compared to that for the oxidation in the presence of $Ni(acac)_2$: S = 90—80% at C = 22% ($Ni(O,NH)_2$) and at C = 11% ($Ni(O,O)_2$). These data indicate a higher catalytic activity of $Ni(enamac)_2$ in the oxidation of ethylbenzene than that of $Ni(acac)_2$.

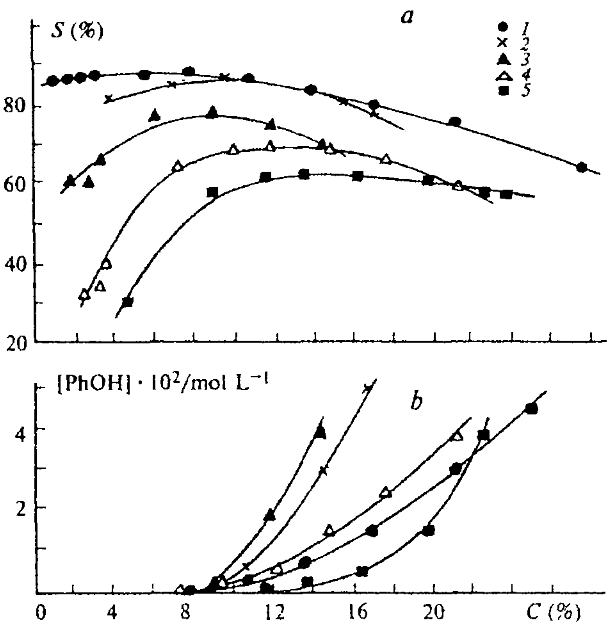

Fig. 2. Dependences of the selectivity (*S*) of the ethylbenzene oxidation in PEH (*a*) and of the phenol concentration (*b*) on the conversion (*C*) of ethylbenzene upon catalysis by $Ni(enamac)_2$: $[Cat] \cdot 10^3$/mol L^{-1} = 0.15 (*1*), 0.28 (*2*), 0.5 (*3*), 1.5 (*4*), and 3.0 (*5*) (120 °C).

The catalytic efficiency of the complex with the $Ni(O,NH)_2$ chelate unit as a selective catalyst of oxidation of ethylbenzene to α-phenylethyl hydroperoxide was estimated by the $\bar{S} \cdot C$ value (Table 1). Here $\bar{S}$ is the averaged selectivity of oxidation with respect to PEH ($S = [PEH]/\Delta[RH]$) at a certain concentration of the catalyst varying from S_0 in the beginning of the reaction to some sufficiently high value of S_{lim} in the developed process, which was conventionally chosen for a series of catalytic reactions compared by efficiency; C is the conversion of hydrocarbon ($C = \Delta[RH]/[RH]_0$) at $S = S_{lim}$. The selectivity values were estimated within the limits: $S_0 < S \geq S_{lim}$ ($S_{max} > 80\%$) and $S_0 < S \leq S_{lim}$ ($S_{max} \leq 80\%$). The value of 80% was chosen as S_{lim}. As can be seen from the data in Table 1, the $Ni(O,NH)_2$ chelate is a more efficient catalyst of selective oxidation of ethylbenzene to PEH than $Ni(O,O)_2$ most likely due to the electron-donating NH groups in the coordination unit of the nickel complex. It follows from Table 1 that the complex with the $Ni(O,NH)_2$ chelate unit, by the efficiency in the oxidation of ethylbenzene to PEH, can be compared to the $Ni(acac)_2$ complexes with the electron-donating ligands Me_4NBr and 18-crown-6 (18C6).

The study of the dependences of the initial oxidation rate w^0 and selectivity S_{max} on the catalyst concentration [Cat] shows that w^0 increases (Table 2) and S_{max} decreases as [Cat] increases (Fig. 2, *a*) similarly to that observed by us previously in the ethylbenzene oxidation in the presence of Ni^{II}, Co^{II}, and Fe^{III} acetylacetonates and cobalt complexes with cyclic polyethers.[4,7,13] These dependences of the rate and selectivity of oxidation on the catalyst concentration are explained[7,8,13] by the full scheme of chain radical oxidation catalyzed by compounds of metals with variable valence, which includes necessarily the elementary stage of chain propagation (the interaction of the catalyst with $RO_2^{\cdot}$ radicals):

$$RO_2^{\cdot} \xrightarrow{Cat} R'C{=}O(ROH) + R^{\cdot}. \qquad (1)$$

The extreme character of the dependence of S on C in the whole range of catalyst concentrations is a specific feature of the ethylbenzene oxidation in the presence of $Ni(enamac)_2$, and it is most pronounced when

Table 1. $\bar{S} \cdot C$ value in reactions of ethylbenzene in the presence of nickel complexes at 120 °C

Catalyst, chelate unit	$[Cat] \cdot 10^4$ /mol L^{-1}	$\bar{S} \cdot C \cdot 10^2$ (%)
$Ni(O,NH)_2$	1.5	15.9
	2.8	13.3
	5.0	6.1
$Ni(O,O)_2$	0.5	9.8
	1.5	9.6
$Ni(acac)_2 \cdot 18C6$	1.5	20.6
$Ni(acac)_2 \cdot Me_4NBr$	1.5	23.0

[Cat] increases. For low concentrations of $Ni(acac)_2$ ($\sim 5 \cdot 10^{-5}$—$1 \cdot 10^{-3}$ mol L^{-1}), $S = S_{max}$ in the beginning of the reaction, and the extreme character of the dependence of S on C is observed only at [Cat] $\geq 1 \cdot 10^{-2}$ mol L^{-1}. The increase in selectivity of formation of PEH during the ethylbenzene oxidation catalyzed by the complex with the $Ni(O,NH)_2$ chelate unit is accompanied by a decrease in the oxidation rate; characteristic inflections appear in the kinetic curves of accumulation of AP and MPC at the stages corresponding to $S = S_{max}$. Similar changes in S and w values during the ethylbenzene oxidation have been observed by us previously for composite catalysts based on $Ni(acac)_2$, $Co(acac)_2$, $Fe(acac)_3$, and electron-donor activating ligands and complexes of cobalt salts with cyclic polyether 18C6, which is related to oxidative transformations of the starting complexes during the oxidation of ethylbenzene.[1-4,7] For the reaction involving the $Ni(acac)_2 \cdot L$ catalysts, the nature of active intermediate species was established. The regularities of changes in the S and w values during the ethylbenzene oxidation in the presence of the complex with the $Ni(O,NH)_2$ chelate unit agree with the previous assumption about the possible oxidative transformation of the catalyst into more active selective intermediate complexes, which can occur, in this case, in the absence of additives of activating axial ligands.

Based on the results obtained by us and other authors, we can suggest the following mechanism of transformation of $Ni(enamac)_2$ during the ethylbenzene oxidation. In the $Ni(enamac)_2...O_2$ adduct, the O_2 molecule is added regioselectively to the γ-C atom of the $(enamac)^-$ ligand, then O_2 is inserted into the C=C bond conjugated with the NH group followed by the cleavage of the cyclic configuration by analogy to the catalytic oxidation of enamines[11] resulting in the formation of active heteroligand complexes:

$$Ni(COMeCHMeCNH)_2 + O_2 \rightleftharpoons Ni(COMeCHMeCNH)_2...O_2$$

$$Ni(COMeCHMeCNH)_2...O_2 \longrightarrow$$

$$\longrightarrow \underset{\mathbf{Q}}{Ni(COMeCHMeCNH)(NHCOMe)} + MeCHO + CO$$

$$\Big\downarrow H_2O$$

$$\underset{\mathbf{P}}{Ni(COMeCHMeCNH)(MeCOO)} + NH_3$$

The **Q** complex, the product of its hydrolysis **P**, or related binuclear complexes of the **A** type (see above) can be an active selective catalyst. Then these complexes can be further oxidized to $Ni(AcO)_2$, whose formation in the catalytic process is responsible for the decrease in the selectivity of oxidation to PEH, since $Ni(AcO)_2$ catalyzes heterolysis of PEH (see Fig. 2).

The values of oxidation rates in the initial period (w^0, up to 1 h of oxidation) and in the developed process (w, from 5 to 15 h of oxidation when the process rate remains unchanged until the sharp decrease in selectivity) are presented in Table 2. We can estimate the participation of the $Ni(enamac)_2$ complex in the elementary stages of oxidation within a certain range of catalyst concentrations by the method suggested previously for the estimation of the activity of $Ni(acac)_2$ and its complexes with axial ligands.[3,7] The high selectivity of the reaction with respect to PEH ($S \approx 90\%$ in the initial region and $S = 80$—90% in the developed reaction) as well as the parallel formation of PEH and by-products AP and MPC make it possible to neglect the rate of catalytic decomposition of hydroperoxide as compared to the rate of its formation. The parallel character of formation of the products is indicated by the unchanged w_P/w_{PEH} ratio during the whole process ($w_P/w_{PEH} \neq 0$ at $t \to 0$), except for the case where [Cat] = $1.5 \cdot 10^{-3}$ mol L^{-1}.* In addition, in the range of catalyst concentrations $\leq 3 \cdot 10^{-4}$ mol L^{-1}, the process rate is $w^0 \sim [Cat]^{1/2}$, due to which the linear radical termination on the catalyst most likely cannot be taken into account. Then in the framework of the chain radical mechanism we obtain the following expression for the rate of square chain termination (w_{term}):

$$w_{term} = k_6[RO_2^{\cdot}]^2 = k_6\left(\frac{w_{PEH}}{k_2[RH]}\right)^2, \qquad (2)$$

where w_{PEH} is the rate of accumulation of PEH in the beginning of the process ($w^0{}_{PEH}$) or in the developed process (w_{PEH}).

In the range of catalyst concentration [Cat] > $3 \cdot 10^{-4}$ mol L^{-1}, the reaction order with respect to [Cat] is lower than 0.5, and in this case, the linear termination of radicals on the catalyst should be taken into account.

The following values of rate constants at 120 °C were used in the calculations: $k_2 = 19.2$ L mol^{-1} s^{-1}, $k_6 = 1.9 \cdot 10^7$ L mol^{-1} s^{-1}, as well as $[RH]_0 = 8.2$ mol L^{-1}.[8]

The $w^0{}_{term}$ values calculated at $[Ni(O,NH)_2] = 1.5$ and $2.8 \cdot 10^{-4}$ mol L^{-1} under quasi-stationary conditions with respect to $RO_2^{\cdot}$ radicals equal to the rates of chain initiation (w_i) can be considered as a measure of the degree of activation of dioxygen (see Table 2). For catalysis by both $Ni(acac)_2$ (see Fig. 3) and $Ni(acac)_2 \cdot L$ complexes, $w^0{}_i \sim [Cat]$.[3,7]

As follows from the data in Table 2, the $w^0{}_{AP+MPC}$ rates determined experimentally exceed the calculated values of w_{term}. This implies that along with the square chain termination, there is another route of formation of AP and MPC, independent of the decomposition of PEH. By analogy with our previous works,[3,7] without linear termination of $RO_2^{\cdot}$ on catalyst molecules, the

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* Recall that in the case of noncatalyzed oxidation of ethylbenzene, the ratios of rates of accumulation of by-products to the rates of accumulation of phenylethyl hydroperoxide tend to zero at $t \to 0$.[7]

Table 2. Rates of accumulation of the products of ethylbenzene oxidation in the beginning of reaction (w^0) and in developed reaction (w) at t = 5—10 h and calculated rates of chain initiation (w_i) and propagation (w_{pr}) at 120 °C

Catalyst, chelate unit	$[Cat] \cdot 10^4$ /mol L^{-1}	$w^0_{PEH} \cdot 10^5$	$w^0_{AP+MPC} \cdot 10^6$	$w_{PEH} \cdot 10^5$	$w_{AP+MPC} \cdot 10^6$ $(w_{AP+MPC+PhOH}) \cdot 10^6$	$w^0_i \cdot 10^6$	$w^0_{pr} \cdot 10^6$	$w_i \cdot 10^7$	$w_{pr} \cdot 10^7$
$Ni(O,NH)_2$	1.5	5.5	7.5	1.1	0.9	2.4	5.1	1.1	8.4
	2.8	7.1	1.6	1.4	1.4	3.9	11.6	1.9	12.4
$Ni(O,O)_2$	0.5	1.1	2.2	1.0	(2.8)	0.09	2.1	—	—
	1.5	2.1	2.6	1.1	(2.5)	0.33	2.3	—	—
	3.0	3.2	6.6	0.7	(4.1)	0.77	5.8	—	—
Without catalyst	—	—	—	1.0	6.3	—	—	—	—

* The w^0, w, w_i, and w_{pr} values are given in mol L^{-1} s^{-1}.

difference between the w^0_{AP+MPC} and w^0_{term} values can be explained by an additional formation of AP and MPC at the stage of chain propagation (1):

$$w^0_{pr} = w^0_{AP+MPC} - w_{term}. \qquad (3)$$

The direct proportional dependence of w^0_{pr} on [Cat], an increase in S_{max}, and a decrease in w^0 with the decrease in [Cat] favor the participation of the complex at the stage of chain propagation. .

It follows from the data in Table 2 that as for catalysis by $Ni(acac)_2$, in the ethylbenzene oxidation in the presence of $Ni(enamac)_2$, the increase in the initial oxidation rate is mainly related to the participation of the catalyst at the stage of chain propagation. The w^0_{pr} is twice as large as that in catalysis by $Ni(acac)_2$. At the same time, the rate of chain initiation w^0_i is almost an order of magnitude higher than w^0_i in the $Ni(acac)_2$-catalyzed oxidation reaction. The w^0_i/w^0_{pr} ratio increases considerably as compared to that for catalysis by $Ni(acac)_2$, being 0.47 for $[Ni(O,NH)_2] = 1.5 \cdot 10^{-4}$ mol L^{-1} and 0.33 for $[Ni(O,NH)_2] = 2.8 \cdot 10^{-4}$ mol L^{-1}, which are much higher than the corresponding values for $Ni(acac)_2$: 0.14 ($[Ni(O,O)_2] = 1.5 \cdot 10^{-4}$ mol L^{-1}) and 0.13 ($[Ni(O,O)_2] = 3 \cdot 10^{-4}$ mol L^{-1}).

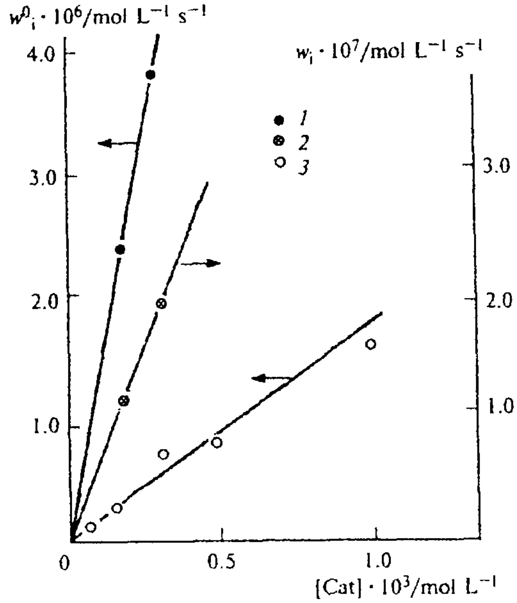

Fig. 3. Dependences of the rates of chain initiation w^0_i on the catalyst concentration in the beginning of the reaction (*1*, *3*) and in the developed reaction (w_i, 5—15 h) of ethylbenzene oxidation (*2*): *1* and *2*, $Ni(enamac)_2$; *3*, $Ni(acac)_2$ (120 °C).

As can be seen from the calculation presented, the presence of donating NH groups in the chelate unit of the complex favors a substantial increase in the role of activation of dioxygen in the mechanism of catalysis by the nickel complex.

As in the beginning of the reaction, at [Cat] = 1.5 and $2.8 \cdot 10^{-4}$ mol L^{-1} in the developed process, the reaction rate $w \sim [Cat]^{1/2}$. Neglecting the rate of PEH decomposition as compared to the rate of its formation, we can use Eq. (2) for the estimation of changes in w_i and w_{pr} in the developed reaction as compared to the initial period and the contribution of these values to the overall rate of the process.

As can be seen from the data in Table 2, during catalysis by the transformed form of the catalyst, the overall reaction rate decreases by 6 times, which is related to a decrease in the w_i and w_{pr} values. The w_i/w_{pr} ratio is 0.13 and 0.15, respectively, *i.e.*, the contribution of the reaction of chain propagation to the overall rate increases as compared to the initial stage. As in the beginning of the reaction, $w_i \sim [Cat]$ (see Fig. 3) and $w_{pr} \sim [Cat]$.

The results obtained indicate that the mechanism of selective catalysis of the ethylbenzene oxidation by the transformed form of the complex with the $Ni(O,NH)_2$ chelate unit (at $[Ni(O,NH)_2] = 1.5$ and $2.8 \cdot 10^{-4}$ mol L^{-1}) is the retardation of PEH decomposition (homolytic and heterolytic) and chain propagation (the interaction of Cat with $RO_2^{\cdot}$ radicals). The complexes formed during ethylbenzene oxidation (probably due to the oxidation of $Ni(O,NH)_2$ by dioxygen) are active in the reaction of generation of free radicals (activation of O_2), since in this case, $w_i \approx 10^{-7}$ mol L^{-1} s^{-1}, which is much higher than the rate of initiation during noncatalytic oxidation of ethylbenzene ($w_i \approx 10^{-9}$ mol L^{-1} s^{-1}).[4]

In the region of concentrations of the complex with the $Ni(O,NH)_2$ chelate unit higher than $1.5 \cdot 10^{-3}$ mol L^{-1}, the decomposition of REH in the developed oxidation process should be taken into account, since under these conditions, AP appears mainly during the chain decomposition of PEH, which is indicated by the successive formation of these products ($w_{AP}/w_{PEH} \rightarrow 0$ at $t \rightarrow 0$). However, unlike noncatalyzed oxidation, MPC and PEH are formed in parallel ($w_{MPC}/w_{PEH} \neq 0$ at $t \rightarrow 0$), and the independent character of formation of AP and MPC is retained ($w_{MPC}/w_{AP} \neq 0$ at $t \rightarrow 0$). The latter most likely explains the higher values of selectivity under these conditions as compared to those in the noncatalyzed oxidation reaction.

In the case of $Ni(acac)_2$-catalyzed oxidation of ethylbenzene, the oxidation rate in the developed process (5—15 h) is independent of [Cat], which can be explained by the complex formation of $Ni(acac)_2$ with the product of PEH heterolysis, phenol[1] (the equilibrium constant of complex formation $K = 3.03 \cdot 10^4$ L mol^{-1},[14] and [PhOH] exceeds $[Ni(acac)_2]$ more than by 2 orders of magnitude).

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