Selective oxidation of ethylbenzene by dioxygen in the presence of complexes of nickel and cobalt with macrocyclic polyethers

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The oxidation of alkylarenes by dioxygen in the presence of complexes of nickel and cobalt with macrocyclic ethers 18-crown-6 and 15-crown-5 was studied. The conditions for selective catalytic oxidation of ethylbenzene to α-phenylethyl hydroperoxide were determined. The kinetics of the accumulation of all oxidation products was studied. The order of the formation of the products at different stages of chain oxidation was determined. The activity of the complexes at the elementary stages of the chain oxidation of ethylbenzene is discussed.

Key words: oxidation, dioxygen, homogeneous catalysis, macrocyclic polyethers, nickel and cobalt complexes, ethylbenzene.

The efficiency of oxidation of alkylarenes by dioxygen to the corresponding hydroperoxides in the presence of metal bisacetylacetonates can be substantially increased by using two-component catalytic systems $M(acac)_2$—L ($M = Ni^{II}$, Co^{II}; L is *N*-methylpyrrolidone-2, HMPA, DMF, or another electron-donating ligand capable of coordinating to the fifth coordination site of the metal).[1–4]

We have previously established[3] that the mechanism of controlling the catalytic activity of $M(acac)_2$ by monodentate ligands changes in the course of oxidation. At the initial stages, the activation of dioxygen by the $M(acac)_2 \cdot L$ complexes and the homolytic decomposition of ROOH under the action of the complexes play the most important role. Later in the process, the selectivity of oxidation increases due to transformation of the complex promoted by the L ligand. This increase in selectivity is achieved by the participation of the transformed form of the complex in chain initiation and by a considerable decrease in the rates of both homolytic and heterolytic decomposition of the hydroperoxides. The mechanism of transformation of the catalyst in the course of oxidation depends on the nature of the metal. In the case of $Ni(acac)_2$, this transformation involves dioxygen. The limiting stage of the process is the regioselective addition of O_2 to the γ-C atom of the $acac^-$ ligand. This addition is controlled by the L ligand and results in the oxidation of the acetylacetonate ion to the acetate ion. It is assumed that for the $Co(acac)_2$—L system the central metal ion rather than the $acac^-$ ligand is oxidized and, most likely, free peroxide radicals $RO_2^{\cdot}$ act as the oxidant.[4]

When the monodentate L ligand is replaced by macrocyclic polyether 18-crown-6 (18C6), the initial oxidation rate (w^0) and selectivity (*S*) increase substantially due to the fact that the activity of the "primary" $M(acac)_2 \cdot 18C6$ complexes in chain initiation is higher than that of $M(acac)_2$ activated by monodentate ligands and their activity in reactions of branching and propagation of the oxidation chain is lower.[5]

As in the presence of monodentate ligands, in the course of oxidation, the $M(acac)_2 \cdot 18C6$ adduct is transformed into a more catalytically active form, and the selectivity of the oxidation increases.

In the present work, the oxidation of ethylbenzene in the presence of Ni^{II} and Co^{II} complexes with macrocyclic polyethers 18-crown-6 and 15-crown-5 ($Ni(NO_3)_2 \cdot 18C6 \cdot 6H_2O$ (**1**), $2NiCl_2 \cdot 15C5 \cdot 6H_2O$ (**2**), $2Co(NO_3)_2 \cdot 18C6 \cdot 6H_2O$ (**3**), and $2Co(NO_3)_2 \cdot 15C5 \cdot 6H_2O$ (**4**)) was studied.

Unlike porphyrin complexes, whose mechanism of action in oxidation by dioxygen has been studied in detail,[6] the mechanism of the oxidation of hydrocarbons in the presence of variable-valence metal complexes with macrocyclic ligands is almost unknown.

Experimental

Ethylbenzene was oxidized in the presence of complexes **1**—**4** at 120 °C with concentrations of the complexes of $1 \cdot 10^{-3}$—$1 \cdot 10^{-4}$ mol L^{-1}. As shown in the previous works,[1–5] this region of small concentrations of $M(acac)_2$ is optimum for studying the effect of doped electron-donating ligands (L) on the selectivity of oxidation. In this case, the main by-products of oxidation, alcohols and ketones, are formed in the reaction of square chain termination and chain propagation when the catalyst (Cat) reacts with the $RO_2^{\cdot}$ radicals (Scheme 1) rather than due to the decomposition of ROOH.

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Scheme 1

$$RO_2^{\bullet} \xrightarrow{Cat} R'C{=}O\ (ROH) + R^{\bullet}$$

Under these conditions, less than 1% alcohol and ketone is formed due to the homolytic decomposition of ROOH.[5]

Ethylbenzene (RH) and the products of its oxidation, methylphenylcarbinol (MPC), acetophenone (AP), and phenol (P), were analyzed by GLC using a known procedure.[1] The concentration of α-phenylethyl hydroperoxide (PEH) was measured iodometrically. The overall reaction rate was determined by the rate of accumulation of all of the oxidation products.

The initial reaction rates w^0 and rates of accumulation of individual products $w^0{}_P$ were determined in the absence of diffuse retardation in the biphase O_2—contact solution system by a method[7] that allows one to calculate these values with an accuracy up to ±5%.

The order of the formation of the oxidation products was determined by the character of the time dependence of the ratio of the rates of product formation at $t \to 0$. It was determined from the experimental plots of $\Delta[P_1]_{ij}/\Delta[P_2]_{ij}$ on t_j, where $\Delta[P_1]_{ij}$ and $\Delta[P_2]_{ij}$ are the increase in the concentrations of the P_1 and P_2 products for $\Delta t = t_j - t_i$ (Fig. 1).

Results and Discussion

In the presence of complexes **1**—**4**, the initial rate and selectivity of the oxidation of ethylbenzene to hydroperoxide are considerably greater than in the noncatalytic process.

Our experiments showed that in the presence of all complexes studied, the initial reaction rate w^0 increases and the selectivity of the oxidation decreases as [Cat] increases (Fig. 2) similarly to that observed previously[2] for the oxidation of ethylbenzene in the presence of $Ni(acac)_2$, $Co(acac)_2$, and $Fe(acac)_3$. These dependences of w and S on the concentration of the catalyst were explained[2,8] by the most complete scheme of catalytic oxidation including the reaction of chain propagation in the interaction of Cat with $RO_2^{\bullet}$.

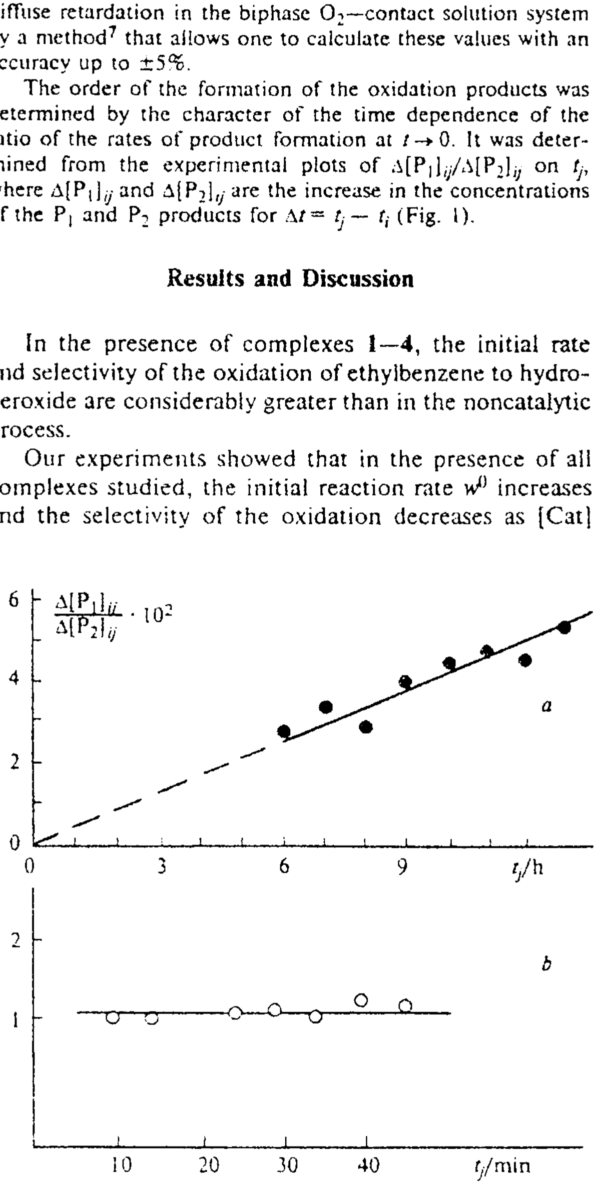


Fig. 1. Dependence of $\Delta[P_1]_{ij}/\Delta[P_2]_{ij}$ on t_j for the oxidation of ethylbenzene in the presence of complexes **1** (*a*) and **2** (*b*): P_2 = PEH; *a*. P_1 = AP, *b*. P_1 = MPC.

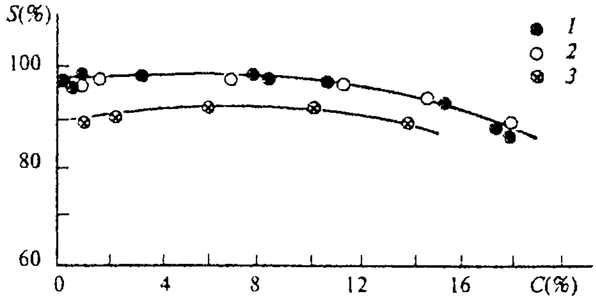


Fig. 2. Dependence of the selectivity of the oxidation of ethylbenzene to PEH on the degree of conversion of ethylbenzene in the presence of complex **1** ($Ni(NO_3)_2 \cdot 18C6 \cdot 6H_2O$) at: [**1**] = $1.0 \cdot 10^{-4}$ (*1*), $1.5 \cdot 10^{-4}$ (*2*), $1.0 \cdot 10^{-3}$ (*3*) mol L^{-1}, and T = 120 °C.

As can be seen in Figs. 2—4, all complexes studied provide rather high selectivity (S = 80—97%) of the oxidation of ethylbenzene to hydroperoxide up to a degree of conversion $C = \Delta[RH]/[RH]_0$ = 10—20%. These values considerably exceed the analogous parameters for noncatalytic oxidation (S = 80% at C = 5—7%). For complexes **1**, **2**, and **4**, the maximum selectivity of the reaction is achieved at the beginning of the process, while when complex **3** is used the selectivity passes through a maximum when the degree of conversion of ethylbenzene is ~20%. In all cases, the appearance of phenol in the reaction products coincides with the beginning of a sharp decrease in the selectivity of the reaction.

The efficiency of complexes **1**—**4** was estimated from the value of the parameter $Y = \bar{S} \cdot C$, where $\bar{S}$ (%) is the average selectivity of the reaction at $S > S_{\lim}$ (the value of 85% was used for $S_{\lim}$. This value is somewhat lower than the maximum value (S_{max} = 90%, see Fig. 4) achieved in the presence of the least active complex (**3**) of the complexes studied); C (%) is the degree of conversion at which $S = S_{\lim}$.

The values of the parameter $Y = \bar{S} \cdot C$ in the oxidation of ethylbenzene in the presence of complexes of nickel and cobalt with crown ethers (the concentration of the catalyst is $1.5 \cdot 10^{-4}$ mol L^{-1}, 120 °C) are presented below.

Complex				
1	$Ni(acac)_2 \cdot 18C6$ [5]	**2**	**3**	**4**
1675.0	1780.0	2024.0	1247.0	1292.0

It can be seen that the efficiency of the complexes of Ni with crown ethers depends on the nature of the ligand. In all cases, the efficiency of the Ni complexes

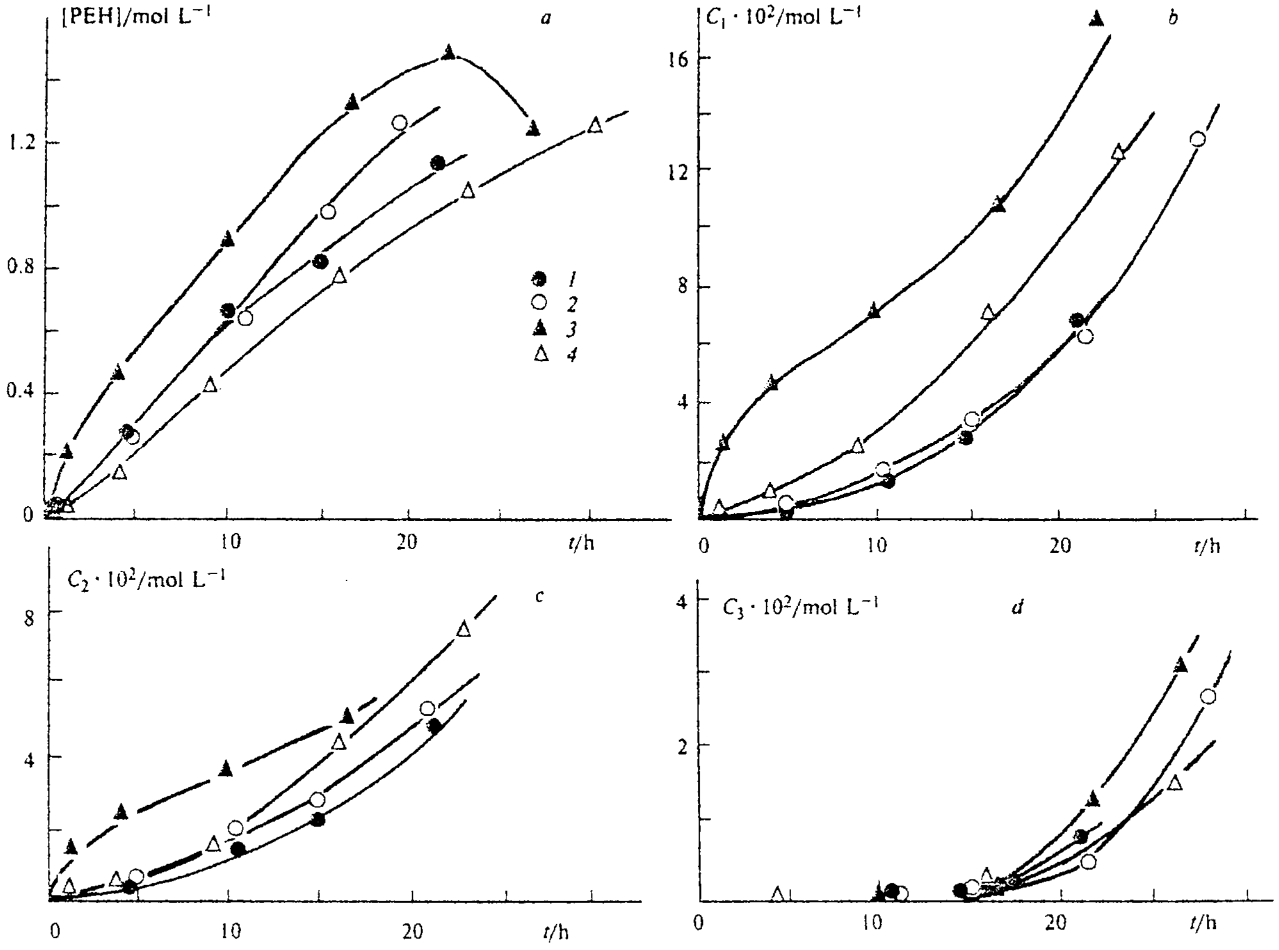


Fig. 3. Kinetic curves of the accumulation of PEH (*a*), AP (*b*), MPC (*c*), and P (*d*) in the oxidation of ethylbenzene in the presence of complexes **1** (*1*), **2** (*2*), **3** (*3*), and **4** (*4*), [**1**] = [**2**] = [**3**] = [**4**] = $1.5 \cdot 10^{-4}$ mol L^{-1}, 120 °C. C_1, C_2, and C_3 are the concentrations of acetophenone, methylphenylcarbinol, and phenol, respectively.

Table 1. Rates of accumulation of the products of the oxidation of ethylbenzene (mol L^{-1} s^{-1}) at the beginning of the reaction (w^0) and in the course of oxidation (w) for t = 5—15 h and calculated rates of chain initiation (w^0_i) and propagation (w^0_{pr}). [Cat] = $1.5 \cdot 10^{-4}$ mol L^{-1}, 120 °C

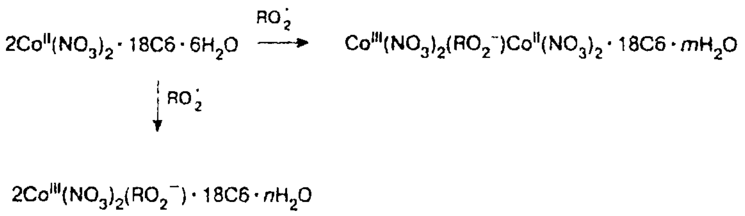
Cat	$w^0_{PEH} \cdot 10^6$	$w^0_{AP+MPC} \cdot 10^6$	$w_{PEH} \cdot 10^6$	$w_{AP+MPC} \cdot 10^6$	$w^0_i \cdot 10^7$	$w^0_{pr} \cdot 10^7$
1	11.3	0.4	18.2	1.3	1.0	3.0
2	6.5	0.4	20.1	1.7	0.3	3.7
4	9.0	2.3	14.3	2.9	0.6	22.4
3	64.5	13.9	18.7	2.1	32.0	107.0
—	1.5	0.7	10.0	6.3	—	—

exceeds that of the Co complexes, which is independent of the nature of the ligand.

The data on the rates of accumulation of hydroperoxide (w_{PEH}) and the sum of acetophenone and methylphenylcarbinol (w_{AP+MPC}) are presented in Table 1. The sum of the rates of accumulation of PEH, AP, and MPC was taken as the overall reaction rate w.

Unlike complexes **1**, **2**, and **4**, in the presence of which the maximum selectivity of oxidation is achieved at the very beginning of the reaction and the process itself develops autocatalytically (see Table 1 and Fig. 3), in the case of complex **3**, the selectivity of oxidation increases in the course of the process. In the presence of this complex, the rate of accumulation of the products is

Scheme 2



$$2Co^{II}(NO_3)_2\cdot 18C6\cdot 6H_2O \xrightarrow{RO_2^{\cdot}} Co^{III}(NO_3)_2(RO_2^{-})Co^{II}(NO_3)_2\cdot 18C6\cdot mH_2O$$

$$2Co^{II}(NO_3)_2\cdot 18C6\cdot 6H_2O \xrightarrow{RO_2^{\cdot}} 2Co^{III}(NO_3)_2(RO_2^{-})\cdot 18C6\cdot nH_2O$$

maximum at the early stages of the reaction and passes through a minimum as the degree of oxidation increases (see Table 1). The kinetic curves have characteristic inflections apparently caused by the formation of complexes providing higher selectivity of the oxidation of ethylbenzene to PEH.[1–5]

Probably, these complexes are Co^{III} compounds. The formation of Co^{III} complexes due to the oxidation products is improbable, because it has been previously shown[9,10] that in this case mainly the ligand is oxidized. The $Co^{II} \rightarrow Co^{III}$ transition under the action of peroxide radicals seems to be the most probable, similarly to that in the case of cobalt complexes with Schiff's bases and cobalt bisacetylacetonate[8,11] (Scheme 2).

The participation of complexes **1**—**4** in the elementary stages of the oxidation was evaluated by a method suggested previously[5] for the estimation of the activity of $Ni(acac)_2$ complexes with 18C6. Neglecting the rate of the homolytic decomposition of hydroperoxide compared to the rate of its formation, the following equation for chain termination can be obtained:*

$$w_{term} = k_6[RO_2^{\cdot}]^2 = k_6\left(\frac{w_{PEH}}{k_2[RH]}\right)^2, \qquad (1)$$

where $w_{PEH} = w^0_{PEH}$.

The values of w^0_{term} obtained under quasi-steady-state conditions with respect to $RO_2^{\cdot}$ radicals, which were equal to the rates of chain initiation, can be considered to be a measure of the degree of activation of dioxygen in the presence of the complexes studied.

As can be seen in Table 1, the calculated w^0_{term} values are lower than the experimental w^0_{AP+MPC} values. This divergence is associated with an additional formation of AP and MPC in the reactions of the catalyst with the $RO_2^{\cdot}$ radicals, most likely at the stage of chain propagation.

It is likely that in the presence of complexes **1**—**4**, as in the case of $Ni(acac)_2\cdot 18C6$,[5] the linear termination of the $RO_2^{\cdot}$ radicals on the complex can be neglected because the rate of the oxidation $w^0 \sim [Cat]^{1/2}$. In addition, the initiation rate in the oxidation reactions catalyzed by transition metal complexes is proportional to the concentration of the catalyst, $w_i \sim [Cat]$, as was observed for complexes **1**—**4**, as well as for $Ni(acac)_2$ and $Ni(acac)_2\cdot L$.[1]

Therefore, the rate of chain propagation w^0_{pr} can be estimated from the difference between the experimentally determined initial rate of accumulation of the sum of AP and MPC and the rate of chain termination calculated by Eq. (1).[5]

$$w_{pr} = w_{AP+MPC} - w_{term}, \qquad (2)$$

where $w_{pr} = w^0_{pr}$, $w_{AP+MPC} = w^0_{AP+MPC}$.

The proportional dependence of w^0_{pr} on [Cat] ([Cat] = $(1-10)\cdot 10^{-4}$ mol L^{-1}) favors the participation of complexes **1**—**4** at the stage of chain propagation at the beginning of the reaction.

The fact that the initial selectivity of the oxidation of ethylbenzene is lowest in the presence of complex **3** (see above) is likely caused by a high rate of chain termination. In the presence of complexes **1**—**4**, the rate of chain initiation is considerably higher than that of the noncatalytic reaction. The greatest degree of activation of O_2 is achieved in the presence of the binuclear Co^{II} complex with 18C6. A comparison of the rates of chain initiation and propagation indicates that in the presence

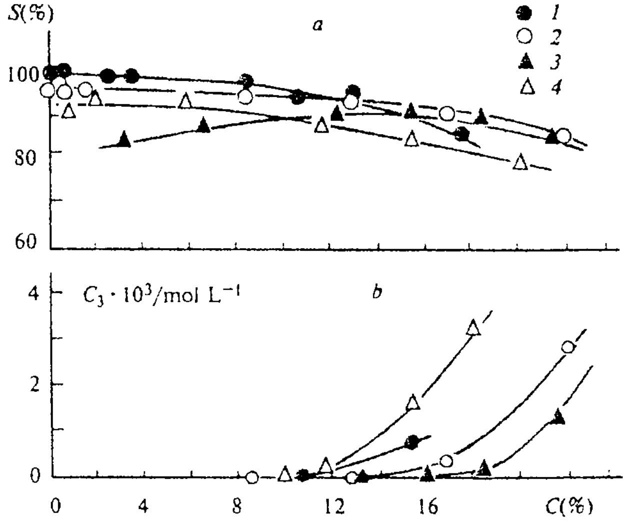


Fig. 4. Dependences of the selectivity of the oxidation of ethylbenzene to PEH (*a*) and the concentration of phenol (*b*) on the degree of conversion of ethylbenzene in the presence of complexes **1** (*1*), **2** (*2*), **3** (*3*), and **4** (*4*). [1] = [2] = [3] = [4] = $1.5\cdot 10^{-4}$ mol L^{-1}, 120 °C.

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* In the calculation k_2 = 19.2 L mol^{-1} s^{-1}, k_6 = $1.9\cdot 10^7$ L mol^{-1} s^{-1}, and $[RH]_0$ = 8.2 mol L^{-1} were used.

Table 2. Change in the ratio of the rates of accumulation of products at the beginning of the reaction (w^0) and later in the process (w) for $t \to 0$. The concentration of complexes is $1.5 \cdot 10^{-4}$ mol L^{-1}, 120 °C

Complex	$\frac{w^0_{AP}}{w^0_{PEH}}$	$\frac{w^0_{MPC}}{w^0_{PEH}}$	$\frac{w_{MPC}}{w^0_{AP}}$	$\frac{w_{AP}}{w_{PEH}}$	$\frac{w_{MPC}}{w_{PEH}}$	$\frac{w_{MPC}}{w_{AP}}$
1	Const	Const	Const	→0	→0	Const
2	Const	Const	Const	Const	Const	Const
3	Const	Const	Const	Const	Const	Const
4	Const	Const	Const	→0	→0	Const
Ligand 18C6*	—	—	—	→0	→0	Const
—	—	—	—	→0	→0	→0
Ni(acac)$_2$ · 18C6	Const	Const	Const	→0	Const	Const

* The concentration of 18C6 in the solution was equal to $1 \cdot 10^{-3}$ mol L^{-1}.

of both Ni and Co complexes, the increase in the rate of the process occurs mainly through an increase in the rate of chain propagation. When 18C6 is used as the ligand, the initiation rate is equal to 30% of the rate of chain propagation for any metal. In the case of 15C5, for Ni complexes, this value is equal to 8.1%, and for Co complexes, it is equal to 2.7%. All of the complexes studied are less active in the reaction of dioxygen activation and enhance the activity of peroxide radicals considerably more strongly than the nickel bisacetylacetonate complexes with 18C6 studied previously.[5]

The data characterizing the tendency for the ratio of the rates of accumulation of different products of the oxidation of ethylbenzene to change for the reaction time $t \to 0$ (see Experimental) are presented in Table 2.

As can be seen in Table 2, at the initial stage of the process, all three products analyzed (PEH, AP, and MPC) are formed in parallel. Differences in the mechanism of action of different complexes appear later in the process. In the presence of **2** and **3**, PEH, AP, and MPC are formed independently of each other as previously. The absence of chain and heterolytic decomposition of PEH when the reaction rate is constant makes it possible to estimate the change in w_i and w_{pr} in the later process and the contribution of their values to the overall reaction rate. As the calculations by Eqs. (1) and (2) show (w_{PEH} and w_{AP+MPC} are the rates of accumulation of the products in the later reaction up to the sharp decrease in the selectivity), for complex **2**, the w_i and w_{pr} values are equal to $3.1 \cdot 10^{-7}$ and $1.4 \cdot 10^{-6}$ mol L^{-1} s^{-1}, and for complex **3**, they are equal to $2.7 \cdot 10^{-7}$ and $1.8 \cdot 10^{-6}$ mol L^{-1} s^{-1}, respectively. It can be seen that in the case of **2**, the increase in the oxidation rate as the process develops is mainly caused by an increase in the rate of chain propagation (*cf.* Table 1). The role of the initiation rate (the w_i/w_{pr} ratio increases to 22.1%) also increases. In the presence of complex **3**, the increase in S and decrease in the oxidation rate are related to the decrease in w_i and w_{pr}, and the w_i/w_{pr} ratio decreases insignificantly from 30% at the initial stage of the reaction to 15%.

In the case of complexes **1** and **4**, the chain decomposition of hydroperoxide makes a noticeable contribution to the formation of AP and MPC, which can be seen in the subsequent formation of these products and PEH ($w_P/w_{PEH} \to 0$ at $t \to 0$, P = AP, MPC).

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