

Oxidation of Ethylbenzene with Dioxygen in the Presence of Iron(III) Tris(acetylacetonate)–Based Catalytic Systems:

1. Mechanism of Ethylbenzene Oxidation with Dioxygen Catalyzed by Fe(III)(acac)_3

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Abstract—The catalytic activity of Fe(III)(acac)_3 (Cat) in ethylbenzene oxidation with dioxygen is studied. 1-Phenylethyl hydroperoxide (PEHP), acetophenone (AP), and methyl phenyl carbinol (MPC) are the main products of the process throughout the Cat concentration range examined. Phenol (Ph) is formed in much smaller amounts. The highest PEHP selectivity, $S_{\text{PEHP}} = 65\%$, is observed at an ethylbenzene conversion of $C \approx 2\%$ at low [Cat] values. PEHP and the other main oxidation products (AP and MPC) form by parallel reactions at any Cat concentration. Depending on [Cat], AP and MPC form by parallel or consecutive reactions. When [Cat] is high enough, AP results from MPC oxidation. At the initial stages of the reaction, the MPC selectivity ($S_{\text{MPC}} = 50\%$) exceeds the PEHP selectivity ($S_{\text{PEHP}} = 25\text{--}30\%$). The mechanism of ethylbenzene oxidation catalyzed by Fe(III)(acac)_3 and the role of active complexes in its steps are considered.

Our recent investigations have been devoted to the elaboration of highly efficient catalytic systems based on transition metal complexes for selective hydrocarbon oxidation. On the one hand, such systems should be active in chain initiation; on the other hand, they should not be active in the free-radical decomposition of active intermediates. This problem is of importance in catalytic oxidation of hydrocarbons to hydroperoxides (ROOH). The high rates of ROOH decomposition in the presence of most of the known homogeneous and heterogeneous complexes of transition metals [1] do not allow one to use these compounds as selective catalysts for hydrocarbon oxidation to ROOH.

We found previously that the initial rate of alkyl-arene oxidation with dioxygen catalyzed by nickel(II) or cobalt(II) bis(acetylacetonate) $[\text{M}(\text{L}^1)_2]$, the ROOH selectivity of this process, and RH conversion are higher in the presence of electron-donor monodentate ligands L^2 ($\text{L}^2 = \text{HMFA, DMFA, } N\text{-methylpyrrolidone-2, nontransition metal salts}$) [2, 3]. An increase in selectivity (S_{ROOH}) and conversion (C) is due to the transformation of the complexes $\text{M}(\text{L}^1)_2\text{L}^2$ to more active catalysts of RH oxidation into ROOH in the course of the process [4]. We proposed methods for optimizing $\text{M}(\text{L}^1)_2\text{L}^2$ catalytic systems, including the use of quaternary ammonium salts and macrocyclic polyethers as L^2 ligands [4–9].

As distinct from catalysis by M(II)(acac)_2 ($\text{M} = \text{Ni, Co}$), the mechanism of ethylbenzene oxidation catalyzed by $[\text{Fe(III)(acac)}_3] \approx 10^{-3}$ was not clearly understood [10]. We found that the oxidation rate at $[\text{Fe(III)(acac)}_3] \approx 10^{-3}$ mol/l is considerably higher than

the oxidation rate in the absence of a catalyst. However, the selectivity of the process with respect to 1-phenylethyl hydroperoxide (PEHP) and RH conversion were not high ($S_{\text{PEHP}} \approx 50\%$; $C = 5\text{--}6\%$). Addition of HMFA or DMFA increased the rate of oxidation but had no significant effect on RH conversion or PEHP selectivity. In order to understand why S_{PEHP} is low in the presence of Fe(III)(acac)_3 , it is necessary to elucidate the mechanism of formation of PEHP, acetophenone (AP), and methyl phenyl carbinol (MPC). Furthermore, there is a need to evaluate the role of Fe(III)(acac)_3 in the elementary steps of the oxidation reaction.

EXPERIMENTAL

The catalytic oxidation of ethylbenzene with dioxygen was performed at 120°C and an Fe(III)(acac)_3 concentration of $(0.5\text{--}7.5) \times 10^{-3}$ mol/l.

Ethylbenzene and the products of its oxidation—MPC, AP, and phenol (Ph)—were analyzed using GLC [2]. PEHP concentration was measured by the iodometric method. The overall rate of the process was determined as the rate of accumulation of the totality of oxidation products. A correlation between RH consumption and product accumulation was established: $\Delta[\text{RH}] = [\text{PEHP}] + [\text{P}] + [\text{Ph}]$, where $\text{P} = \text{AP} + \text{MPC}$.

The overall rate of the reaction (w) and the rates of product accumulation (w_p) were determined with an accuracy of $\pm 5\%$ by a method described in [5]. The catalytic oxidation of RH with dioxygen was carried out in the O_2 –solution two-phase system in a glass bubbler under kinetic control.

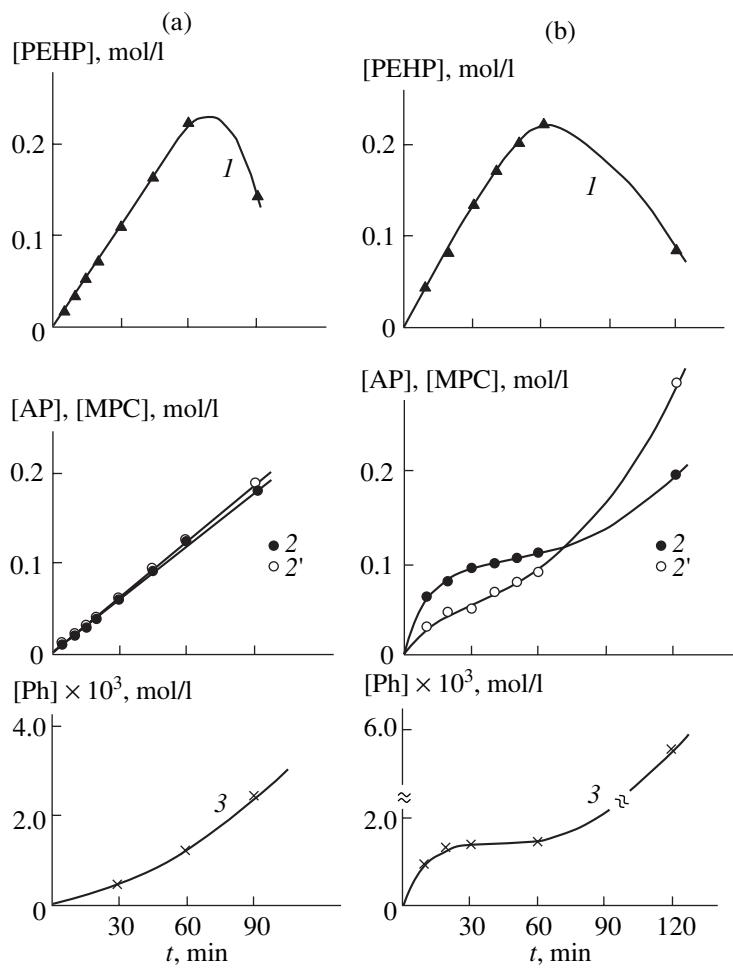


Fig. 1. Kinetics of accumulation of the products of ethylbenzene oxidation by dioxygen catalyzed by Fe(III)(acac)_3 : (1) 1-phenyl-ethyl hydroperoxide (PEHP), (2) methyl phenyl carbinol (MPC), (2') acetophenone (AP), (3) phenol (Ph); [Cat] = (a) 5.0×10^{-3} and (b) 7.5×10^{-3} mol/l; $T = 120^\circ\text{C}$.

The order in which PEHP, AP, and MPC formed was determined from the time dependence of product accumulation rate ratios at $t \rightarrow 0$. The variation of these ratios with time was evaluated by graphic differentiation [9]. PEHP selectivity and RH conversion were calculated using the formulas $S_{\text{PEHP}} = \frac{[\text{PEHP}]}{\Delta[\text{RH}]} \times 100\%$

and $C = \frac{\Delta[\text{RH}]}{[\text{RH}]_0} \times 100\%$, respectively.

RESULTS AND DISCUSSION

Three main products—PEHP, AP, and MPC—result from ethylbenzene oxidation at 120°C in the presence of $(0.5\text{--}7.5) \times 10^{-3}$ mol/l of Fe(III)(acac)_3 . Phenol is accumulated in considerably smaller amounts ([Ph] is lower than [PEHP], [AP], or [MPC] by a factor of 100) (Fig. 1).

Ethylbenzene oxidation in the presence of Fe(III)(acac)_3 depends strongly on the initial concentration of the catalyst.

1. At $[\text{Cat}] = (0.5\text{--}5.0) \times 10^{-3}$ mol/l, MPC and AP accumulate at a rate of $w_p = w_{\text{max}}$ starting at the very beginning of the reaction (the autoacceleration period is $\tau \approx 3\text{--}5$ min). At $[\text{Cat}] = 5.0 \times 10^{-3}$, 3.0×10^{-3} , and 0.5×10^{-3} mol/l, the maximum rate of PEHP accumulation is attained at $\tau \approx 5$, $\tau \leq 10$, and $\tau \leq 20$ min, respectively. The rates w_{AP} and w_{MPC} remain invariable after the [PEHP] maximum is reached ($w_p = w_{\text{max}} = \text{const}$); $w_{\text{AP}} \geq w_{\text{MPC}}$ (at $[\text{Cat}] = 3.0 \times 10^{-3}$ and 5.0×10^{-3} mol/l, $w_{\text{AP}} = w_{\text{MPC}}$). The PEHP selectivity is constant up to the conversion corresponding to $[\text{PEHP}] = [\text{PEHP}]_{\text{max}}$ (Fig. 2). $S_{\text{PEHP}} = 65\text{--}45\%$ at $C = 1.5\text{--}6.0\%$ (Fig. 2). The rate of phenol accumulation grows with increasing ethylbenzene conversion. Typical product accumulation curves are presented in Fig. 1.

2. The experimental data obtained at Fe(III)(acac)_3 concentrations slightly exceeding 5.0×10^{-3} mol/l, specifically, 6.0×10^{-3} and 7.5×10^{-3} mol/l, indicate a

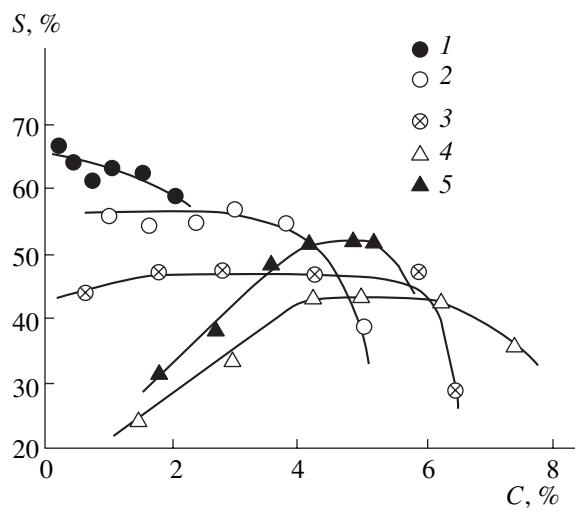


Fig. 2. PEHP selectivity of ethylbenzene oxidation (S) versus ethylbenzene conversion (C) at various initial concentrations of Fe(III)(acac)_3 ($\times 10^3$ mol/l): (1) 0.5, (2) 3.0, (3) 5.0, (4) 6.0, and (5) 7.5; $T = 120^\circ\text{C}$.

change in the mechanism of catalysis. The initial formation rate is the highest for all oxidation products, including phenol. The initial rate of MPC accumulation ($w_{0, \text{MPC}}$) is twice as high as that of AP accumulation ($w_{0, \text{AP}}$) ($[\text{MPC}]/[\text{AP}] \approx 2$ up to $t = 30$ min). At the early stages of ethylbenzene oxidation, MPC is the main product of the reaction: $S_{\text{MPC}} = \frac{[\text{MPC}]}{\Delta[\text{RH}]} \approx 50\%$; $S_{(\text{MPC} + \text{PEHP})} \approx 75\%$ (Fig. 1b). The dependence of S_{PEHP} on C has a well-defined extremum (Fig. 2a). $S_{\text{max, PEHP}}$ is 45 and 55% at $[\text{Cat}] = 6.0 \times 10^{-3}$ and 7.5×10^{-3} mol/l, respectively. The growth of S_{PEHP} is accompanied by a considerable decrease in the rates of PEHP, MPC, AP, and Ph accumulation. This phenomenon can be explained by the transformation of the iron complex into new catalytically active complexes. The observed changes in S and w during oxidation are similar to those detected in ethylbenzene oxidation in the presence of $\text{M}(\text{L}^1)_2$ ($\text{M} = \text{Ni}, \text{Co}$) and $\text{Ni}(\text{Co})$ -based composite catalysts. The rates of MPC, AP, and Ph accumulation begin to grow once the PEHP concentration has passed through a maximum (Fig. 1b).

The highest concentration of PEHP in the process catalyzed by Fe(III)(acac)_3 is equal to 0.22–0.24 mol/l (Fig. 1); that is, it is considerably lower than the $[\text{PEHP}]_{\text{max}}$ value observed in the presence of nickel or cobalt bis(acetylacetone) (0.9–1.0 mol/l) [2–9].

The table presents the maximum rates of ethylbenzene oxidation w_{max} at various initial concentrations of Fe(III)(acac)_3 . The observed rates are 10–100 times higher than the maximum rate of oxidation without a catalyst.

As in the case of ethylbenzene oxidation catalyzed by nickel and cobalt complexes [10], the maximum PEHP selectivity of the process increases as $[\text{Cat}]$ is reduced. However, this increase is insignificant, from $S = 45\text{--}55\%$ to $S = 65\%$ (Fig. 2). Analysis of the complete scheme of radical chain hydrocarbon oxidation catalyzed by transition metal compounds, which involves the reaction of Cat with RO_2^\cdot (chain propagation) along with catalytic radical decomposition of ROOH , leads to the following conclusions. $[\text{ROOH}]_{\text{max}}$ must gradually increase and the rate of the reaction must fall with decreasing $[\text{Cat}]$ [11]. We did observe these trends in the process catalyzed by nickel and cobalt complexes [10]. We also observed a reduction in the rate of ethylbenzene oxidation as $[\text{Fe(III)(acac)}_3]$ decreased. However, the dependence of $[\text{PEHP}]_{\text{max}}$ on $[\text{Fe(III)(acac)}_3]$ shows an extremum (Fig. 3), suggesting that the mechanism of catalysis is more complicated in this case.

Estimation of the ratio of the $(\text{AP} + \text{MPC})$ and PEHP accumulation rates demonstrated that $w_{\text{P}}/w_{\text{PEHP}}$ is constant and nonzero at $t \rightarrow 0$ throughout the Fe(III)(acac)_3 concentration range examined. Thus, AP and MPC do not form from PEHP and result from paral-

Rates of accumulation of ethylbenzene oxidation products ($\text{mol l}^{-1} \text{s}^{-1}$)* and the rates of chain initiation (w_i) and chain propagation (w_p) calculated for various initial concentrations of Fe(III)(acac)_3

$[\text{Fe(III)(acac)}_3] \times 10^3$, mol/l	$w_{\text{PEHP}} \times 10^5$	$w_{\text{AP} + \text{MPC}} \times 10^5$	$w_{\text{PEHP} + \text{P} + \text{Ph}} \times 10^5$	$w_i \times 10^6$	$w_p \times 10^5$	$(w_i/w_p) \times 100\%$
–	0.15	0.07	0.22	–	–	–
0.5	1.75	1.11	3.13	0.23	1.09	2.1
3.0	4.44	3.27	7.86	1.56	3.2	4.8
5.0	6.58	7.13	13.7	3.32	6.8	4.9
6.0	8.27	12.8	21.2	–	–	–
7.5	7.86	20.8	24.6	–	–	–

* $w = w_{\text{max}}$ ($[\text{Cat}] = (0.5\text{--}5.0) \times 10^{-3}$ mol/l), $w = w_0 = w_{\text{max}}$ ($[\text{Cat}] = 6.0 \times 10^{-3}$ and 7.5×10^{-3} mol/l).

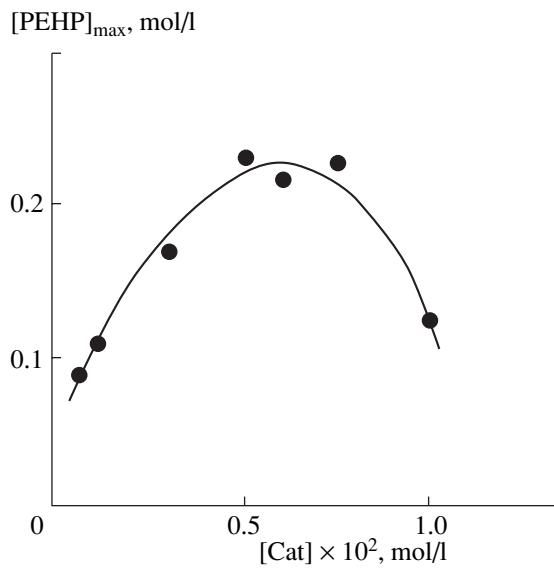


Fig. 3. The highest PEHP concentration attained in ethylbenzene oxidation catalyzed by $\text{Fe(III)}(\text{acac})_3$ as a function of the initial concentration of the catalyst.

lel reactions. At $[\text{Cat}] = 6.0 \times 10^{-3}$ and 7.5×10^{-3} mol/l, $w_{\text{AP}}/w_{\text{MPC}} \rightarrow 0$ at $t \rightarrow 0$; in other words, AP results from MPC oxidation. Note that, at $[\text{Cat}] \leq 5 \times 10^{-3}$ mol/l, AP and MPC result from parallel reactions ($w_{\text{AP}}/w_{\text{MPC}} \neq 0$ at $t \rightarrow 0$).

At $\text{Fe(III)}(\text{acac})_3$ concentrations of $(0.5-5.0) \times 10^{-3}$ mol/l, it was possible to evaluate the role of the catalyst in the chain initiation and propagation steps of the radical chain ethylbenzene oxidation using the method described in our earlier publications [5-7, 9]. We found that AP and MPC form simultaneously with PEHP until $[\text{PEHP}]_{\text{max}}$ is attained; therefore, ROOH decomposition can be neglected. This inference is supported by the fact that $\text{Fe(III)}(\text{acac})_3$ is inactive in the decomposition of cumyl hydroperoxide (in a nonpolar medium) [12] and of PEHP (in chlorobenzene in contact with flowing O_2) [13].

It is likely that AP and MPC result from simultaneous reactions of chain propagation (I) and chain termination (II)



The relationship $w \sim [\text{Cat}]^{1/2}$ (where $w = w_{\text{PEHP}} + w_{(\text{AP} + \text{MPC})}$) is valid at $[\text{Cat}] \leq 5.0 \times 10^{-3}$ mol/l, suggesting that linear chain termination involving the catalyst can be ignored. The relationship $w \sim [\text{Cat}]^{1/2}$ also points to the radical chain mechanism of the reaction under the above conditions (at $[\text{Cat}] > 5.0 \times 10^{-3}$ mol/l, the order of the reaction with respect to the catalyst is above 1/2). Assuming that bimolecular recombination of the RO_2^\cdot radicals takes place and the rate of the homolytic

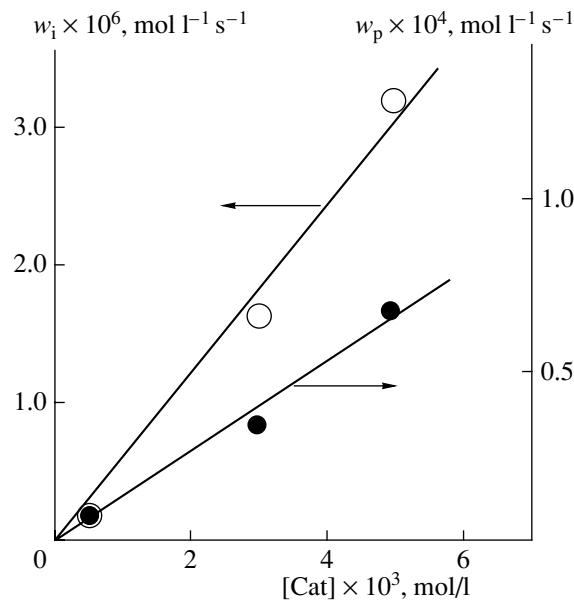


Fig. 4. Rates of chain initiation (w_i) and chain propagation $\text{Cat} + \text{RO}_2^\cdot \longrightarrow (w_p)$ as a function of $[\text{Cat}]$ in ethylbenzene oxidation with dioxygen catalyzed by $\text{Fe(III)}(\text{acac})_3$ at 120°C.

decomposition of PEHP is equal to zero, we obtain the following equation for the rate of quadratic chain termination:

$$w_t = k_6 [\text{RO}_2^\cdot]^2 = k_6 \left\{ \frac{w_{\text{PEHP}}}{k_2 [\text{RH}]} \right\}^2, \quad (1)$$

where w_{PEHP} is the rate of PEHP accumulation.

In our calculations, we used the following values of the rate constants and $[\text{RH}]$ (120°C): $k_2 = 19.21 \text{ mol}^{-1} \text{ s}^{-1}$, $k_6 = 1.9 \times 10^7 \text{ mol}^{-1} \text{ s}^{-1}$, and $[\text{RH}]_0 = 8.2 \text{ mol/l}$ [11]. Under quasi-steady-state conditions with respect to RO_2^\cdot radicals, w_t calculated for $[\text{Cat}] = (0.5-5.0) \times 10^{-3}$ mol/l is equal to the rate of chain initiation (w_i) (table). As in the case of catalysis by $\text{Ni}(\text{L}^1)_2$ [6, 10], the relationship $w_i \sim [\text{Cat}]$ is true (Fig. 4). In the absence of linear chain termination (involving RO_2^\cdot and the catalyst), the rate of AP and MPC formation in reaction (I) may be estimated as

$$w_p = w_{(\text{AP} + \text{MPC})} - w_t, \quad (2)$$

where $w_{(\text{AP} + \text{MPC})}$ is the observed rate of AP and MPC accumulation. The method suggested for estimating w_t and w_p is substantiated by the linear dependences of w_p and w_i on $[\text{Cat}]$ ($[\text{Cat}] = (0.5-5.0) \times 10^{-3}$ mol/l) (Fig. 4).

As is seen from the table, the rate of chain initiation is much higher in the presence of $(0.5-5.0) \times 10^{-3}$ mol/l of $\text{Fe(III)}(\text{acac})_3$ than in the noncatalytic reaction ($w_i \approx 10^{-9} \text{ mol l}^{-1} \text{ s}^{-1}$ [6]).

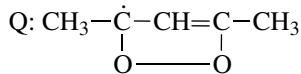
The ratio $w_i/w_p = 2\text{--}5\%$ means that the iron complexes are more active in chain propagation (Cat + $\text{RO}_2^\cdot \longrightarrow$) than in chain initiation. Furthermore, this value indicates that the reaction Cat + RO_2^\cdot plays a greater role in ethylbenzene oxidation catalyzed by the iron(III) complex than in the same reaction catalyzed by Ni(II) or Co(II) complexes. In the latter case, w_i/w_p ranges from 11 to 50%, depending on the nature of the metal ion and its ligand environment, or $w_p = 0$, as in the case of Ni(II) (L^1)₂ complexes with 18K6 [5, 7].

Chain initiation in ethylbenzene oxidation by dioxygen in the presence of Fe(III)(acac)_3 can be represented by the following reaction [14]:



Electron transfer between RH and Fe(III)(acac)_3 is quite possible for alkylarenes with relatively weak C–H bonds. Reaction (III) and the interaction of the resulting Fe(II) complex with dioxygen appear to be responsible for chain initiation in the reaction catalyzed by Fe(III)(acac)_3 at relatively low [Cat] concentrations at 120°C.

The change in the mechanism of catalysis at $[\text{Fe(III)(acac)}_3]_0 > 5.0 \times 10^{-3} \text{ mol/l}$ may be due to the variation of the reactivity of iron complexes because of the transformation of the original iron tris(acetylacetone) into a new catalytically active form (perhaps, $\text{Fe(II)(acac)}_2\text{Q}$). The Q radical, which can result from the oxidation of the $(\text{acac})^-$ ligand by the Fe(III) ion, is stable and inactive as an initiator of radical chain reactions [15, 16]. The relative $\text{Fe(II)(acac)}_2\text{Q}$ content appears to grow with increasing [Cat] under our experimental conditions:



At [Cat] concentrations of $(0.5\text{--}5.0) \times 10^{-3} \text{ mol/l}$, the above transformation can apparently be neglected.

The comparatively high concentrations of phenol at the initial stage of ethylbenzene oxidation at $[\text{Fe(III)(acac)}_3] > 5.0 \times 10^{-3} \text{ mol/l}$ (Fig. 1b) can be explained by PEHP heterolysis catalyzed by $\text{Q}(\text{L}^1)_2\text{Fe(II)} \cdot \text{PhOH}$. It was shown previously that the coordination of phenol to $\text{Ni}(\text{acac})_2$ is favorable for heterolytic decomposition of PEHP with the formation of phenol [17, 18].

The presence of an extremum in the dependence of S_{PEHP} on C (Fig. 2a) appears to be due to the transformation of the $\text{Q}(\text{L}^1)_2\text{Fe(II)}$ complexes by a mechanism analogous to the mechanism of the oxidative conversion of nickel complexes. This conversion is a result of the regioselective addition of O_2 to the nucleophilic $\gamma\text{-C}$ atom of the $(\text{acac})^-$ ligand [19, 20]. The resulting $\text{Fe}_x(\text{acac})_y(\text{OAc})_z\text{Q}_n$ species are likely to be inactive in

the heterolytic decomposition of PEHP and in the reaction with the RO_2^\cdot radicals (Figs. 1b, 2).

The ligand environment of Fe(III) has a profound effect on the catalytic mechanism of ethylbenzene oxidation. In ethylbenzene oxidation (70°–110°C) catalyzed by $[\text{Fe(III)TPFPP}]Cl$ (where TPFPP is 5,10,15,20-tetrakis(pentafluorophenyl)porphyrin), PEHP, MPC, and AP are also the main oxidation products and $S_{\text{PEHP}} \sim 50\%$ [21]. A radical chain mechanism was proposed for the last process [22]. According to this mechanism, chain initiation is due to the catalytic decomposition of PEHP; AP and MPC result from quadratic chain termination and linear chain termination involving the catalyst. As this takes place, the catalyst is rapidly deactivated, and the process is terminated at a low RH conversion.

Thus, the PEHP selectivity of ethylbenzene oxidation with dioxygen in the presence of Fe(III)(acac)_3 varies only slightly over a wide range of Cat concentrations ($[\text{Cat}] = (0.5\text{--}7.5) \times 10^{-3} \text{ mol/l}$), being equal to 45–65%.

We established that the relatively low efficiency of Fe(III)(acac)_3 (as a selective catalyst for ethylbenzene oxidation to PEHP) as compared to the efficiency of previously studied Ni(II) and Co(II) complexes is due to the simultaneous formation of PEHP, MPC, and AP throughout the Cat concentration range examined.

The mechanism of catalysis was found to change at a certain initial [Cat] value.

At $[\text{Cat}] \leq 5.0 \times 10^{-3} \text{ mol/l}$, AP and MPC are also formed by parallel reactions. The kinetics of ethylbenzene oxidation is consistent with a radical chain mechanism including the bimolecular recombination of RO_2^\cdot radicals. The estimated ratio between the rates of chain initiation and chain propagation (Cat + RO_2^\cdot ($w_i/w_p = 2\text{--}5\%$)), suggests that AP and MPC form mainly in the chain propagation step (conceivably, through the homolytic decomposition of the intermediate complex $[\text{Fe(III)}-\text{OOR}]$ [23, 24]). Furthermore, this ratio points to an essential contribution from the chain propagation reaction to the overall rate of the process.

At $[\text{Cat}] > 5.0 \times 10^{-3} \text{ mol/l}$, MPC and AP form in another order: the ketone results from the oxidation of the alcohol. At the initial stages of the reaction, MPC is the main oxidation product ($S_{\text{MPC}} \approx 50\%$; $S_{\text{PEHP}} \approx 25\text{--}30\%$). An extremum is observed in the dependence of S_{PEHP} on C ($S_{\text{PEHP},\text{max}} \approx 45\text{--}55\%$). The maximum rate of the phenol formation is observed starting at the reaction onset. The kinetic changes in ethylbenzene oxidation under the conditions examined appear to be due to the oxidative transformation of Fe(III)(acac)_3 , which shows up in the range of high Cat concentrations and results in essential structural changes in the coordination sphere of iron.

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