Critical phenomena in ethylbenzene oxidation in acetic acid solution at high cobalt(II) concentrations

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Critical phenomena in ethylbenzene oxidation in an acetic acid solution at high cobalt(III) concentrations (from 0.01 to 0.2 mol L^{-1}) were studied at 60—90 °C by the gasometric (O_2 absorption), spectrophotometric (Co^{III} accumulation), and chemiluminescence (relative concentration of radical $RO_2^{\bullet}$) methods. These phenomena are as follows: (1) increase in the oxidation rate above the theoretical limiting rate of radical autooxidation ($k_3{}^2[RH]^2/2k_6$); (2) achievement of a maximum and a sharp decrease in the oxidation rate and concentration of radical $RO_2^{\bullet}$ with the further increase in the Co^{II} concentration (existence of critical concentrations). The oxidation rate increases due to the reaction $RO_2^{\bullet} + Co^{II} + H^+ \longrightarrow ROOH + Co^{III}$, while the inhibition effect is caused by the decay of $RO_2^{\bullet}$ radical involving two cobalt(II) atoms: $RO_2^{\bullet} + 2\,Co^{II} \longrightarrow R'CO + Co^{III} + Co^{II}$ ($k(70\ °C) \approx 300\ L^2\,mol^{-2}\,s^{-1}$). The detailed scheme (through the formation of the complex $RO_2^{\bullet}Co^{II}$) describing the conjugation of these reactions was proposed.

Key words: autooxidation, ethylbenzene, peroxide radical, cobalt(II), complex $RO_2^{\bullet}Co^{II}$, hydroperoxide, chemiluminescence, chain termination, electron transfer reactions, critical concentration.

Oxidation of alkylaromatic hydrocarbons in an acetic acid solution in the presence of cobalt(II) salts and bromides (NaBr, HBr, *etc.*) is an important industrial process. The main features of cobalt-bromide catalysis can also be observed in the absence of bromide. To reveal specific features of elementary steps involving cobalt compounds, we chose the well-studied reaction of ethylbenzene oxidation in an acetic acid solution in the presence of cobalt(II) acetate.

The existence of a limiting rate of radical autooxidation in the liquid-phase oxidation of hydrocarbons was advanced[1] in 1948 on the basis of Semenov's theory for degenerate branching chain reactions. The limiting rate is achieved when the branching rate due to radical decomposition of hydroperoxide, which is formed in the reaction

$$RO_2^{\bullet} + RH \xrightarrow{k_3} ROOH + R^{\bullet},$$

becomes equal to the rate of quadratic termination due to the recombination of peroxide radicals

$$RO_2^{\bullet} + RO_2^{\bullet} \xrightarrow{k_6} R'CO + ROH + O_2.$$

The limiting rate phenomenon has been confirmed experimentally for the first time for the oxidation of tetralin,[2] ethylbenzene,[3] diphenylmethane, and other hydrocarbons[4] in an acetic acid solution containing cobalt(II) acetate.

The kinetics of ethylbenzene oxidation at low cobalt concentrations (10^{-3}—10^{-2} mol L^{-1}) is described[3] by the scheme of radical autooxidation. According to this scheme, the cobalt salt participates in the initiation step during the reaction with hydroperoxide and is not involved in chain propagation and termination (Scheme 1).

Scheme 1

$$RO_2^{\bullet} + RH \xrightarrow{k_3} ROOH + R^{\bullet}$$

$$ROOH + Co^{II} \xrightarrow{k_1} RO^{\bullet} + Co^{III} + OH^-$$

$$ROOH + Co^{III} \xrightarrow{k_1{}^1} RO_2^{\bullet} + Co^{II} + H^+$$

$$RO^{\bullet} + RH \xrightarrow{k_5} ROH + R^{\bullet}$$

$$R^{\bullet} + O_2 \xrightarrow{k_2} RO_2^{\bullet}$$

$$RO_2^{\bullet} + RO_2^{\bullet} \xrightarrow{k_6} R'CO + ROH + O_2$$

Under steady-state conditions of autooxidation ($d[ROOH]/dt = 0$, $d[Co^{III}]/dt = 0$), the concentration of

Published in Russian in *Izvestiya Akademii Nauk. Seriya Khimicheskaya,* No. 8, pp. 1823—1827, August, 2005.

peroxide radicals and O_2 absorption rate achieve limiting values.

$$[\mathrm{RO_2^{\bullet}}]_{\mathrm{st}} = k_3[\mathrm{RH}]/(2k_6) \qquad (1)$$

$$W_{\mathrm{O_2}}{}^{\mathrm{st}} = k_3{}^2[\mathrm{RH}]^2/(2k_6) \qquad (2)$$

The $k_3{}^2/(2k_6)$ parameter determined from the limiting oxidation rate coincided[3] with its value measured independently for photochemical and initiated oxidation. This quantitatively proved the scheme of catalytic oxidation of ethylbenzene at low cobalt concentrations.

Chemiluminescence accompanying catalytic oxidation of hydrocarbons due to the energy evolved upon peroxide radical recombination was observed[4] for ethylbenzene oxidation. According to earlier published data,[5] the recombination of ethylbenzene peroxide radicals affords acetophenone, methylphenylcarbinol, and O_2. The authors of monograph[6] concluded that carbonyl compounds formed in the excited state upon recombination of radicals $\mathrm{RO_2^{\bullet}}$ are responsible for chemiluminescence in liquid-phase oxidation of hydrocarbons and the chemiluminescence intensity is proportional to the recombination rate

$$Y = k_{\mathrm{f}}[\mathrm{R'CO^*}] = \eta k_6[\mathrm{RO_2^{\bullet}}]^2,$$

where η is the luminescence quantum yield ($\sim 10^{-10}$).

As found[7] for ethylbenzene oxidation with the cobalt-bromide catalyst, the introduction of NaBr into ethylbenzene oxidation catalyzed by cobalt(II) acetate enhances sharply the oxidation rate (apparent rate is tenfold higher than the theoretical limiting rate of radical autooxidation $k_3{}^2[\mathrm{RH}]^2/(2k_6)$) and chemiluminescence intensity. Simultaneously, they begin to depend (quadratic growth) on the cobalt content. It was concluded[7] that the reaction of the peroxide radical $\mathrm{RO_2^{\bullet}}$ with cobalt(II) occurs in the Co—Br system and affords hydroperoxide.

$$\mathrm{RO_2^{\bullet} + Co^{II} \xrightarrow[\mathrm{H^+}]{k_4} ROOH + Co^{III}}$$

Under the conditions when $\mathrm{Co^{III}}$ is reduced by the bromide ion to form radicals $\mathrm{Br^{\bullet}}$ capable of chain propagating for the reaction with hydrocarbon (Scheme 2), this reaction provides the development of an autooxidation route through cobalt(II).

Scheme 2

$$\mathrm{Co^{III} + Br^- \longrightarrow Co^{II} + Br^{\bullet}}$$

$$\mathrm{Br^{\bullet} + RH \longrightarrow H^+ + Br^- + R^{\bullet}}$$

$$\mathrm{Co^{III} + RH \longrightarrow Co^{II} + R^{\bullet} + H^+}$$

In this work, critical phenomena that appear at high cobalt(II) concentrations in an acetic acid solution were studied.

Experimental

The oxidation rate was measured by O_2 absorption in a constant-pressure gasometric system.[6] Chemiluminescence was recorded on a photometric setup[6] using a P25232 Photodetector Package photon counter with a sensitivity region of 280—630 nm. Spectrophotometric measurements were carried out on an SF-4A spectrophotometer in a temperature-controlled cell. The kinetics of $\mathrm{Co^{III}}$ accumulation at high $\mathrm{Co^{II}}$ concentrations was measured from an increase in the absorbance of the solution at 380 nm. Ethylbenzene, acetic acid, $\mathrm{Co(OAc)_2}$ and NaBr (reagent grade) were used.

Results and Discussion

The reaction of $\mathrm{RO_2^{\bullet}}$ with $\mathrm{Co^{II}}$ affording ROOH is the key step in the cobalt-bromide catalysis mechanism and can occur without bromide ions (Scheme 3)

Scheme 3

$$\mathrm{RO_2^{\bullet} + RH \xrightarrow{k_3} ROOH + R^{\bullet}} \qquad (3)$$

$$\mathrm{RO_2^{\bullet} + Co^{II} \xrightarrow[\mathrm{H^+}]{k_4} ROOH + Co^{III}} \qquad (4)$$

$$\mathrm{ROOH + Co^{II} \xrightarrow{k_1} RO^{\bullet} + Co^{III} + OH^-} \qquad (5)$$

$$\mathrm{ROOH + Co^{III} \xrightarrow{k_1'} RO_2^{\bullet} + Co^{II} + H^+} \qquad (6)$$

$$\mathrm{RO^{\bullet} + RH \xrightarrow{k_5} ROH + R^{\bullet}} \qquad (7)$$

$$\mathrm{R^{\bullet} + O_2 \xrightarrow{k_2} RO_2^{\bullet}} \qquad (8)$$

$$\mathrm{RO_2^{\bullet} + RO_2^{\bullet} \xrightarrow{k_6} R'CO + ROH + O_2} \qquad (9)$$

It is clear that the introduction of reaction (4) into the oxidation scheme does not change (due to reversibility of reactions (4) and (6)) Eqs (1) and (2) for the $\mathrm{RO_2^{\bullet}}$ concentration and O_2 absorption rate under the steady-state autooxidation conditions.

We found an important feature of oxidation at high cobalt(II) concentrations, indicating that the latter is involved in chain propagation. As can be seen from the data in Fig. 1, the higher the initial cobalt(II) concentration, the longer the time of achieving the limiting autooxidation rate, which is independent of the cobalt concentration ($W_{\mathrm{O_2}}{}^{\mathrm{st}} = k_3{}^2[\mathrm{RH}]^2/(2k_6)$). The initial oxidation rate W_0 is higher than W_{st}, and its value increases with an increase in the cobalt(II) concentration.

Hydroperoxide ROOH decomposes more rapidly with an increase in the cobalt(II) concentration. According to published data,[8] in ethylbenzene oxidation the time of half-accumulation of hydroxide at 70 °C and $[\mathrm{Co(OAc)_2}] > 4 \cdot 10^{-2}$ mol L^{-1} is shorter than 10 s and the steady-state ROOH concentration is lower than

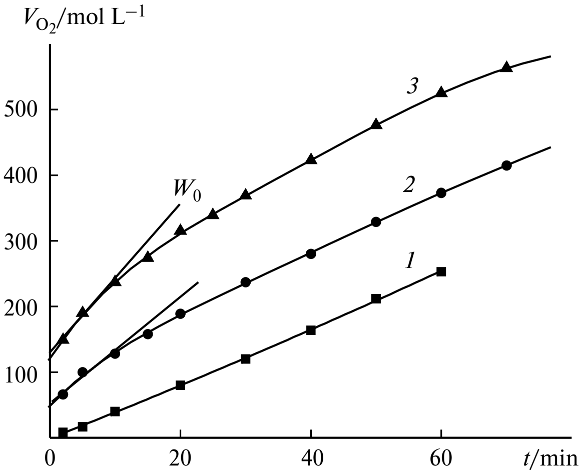


Fig. 1. Kinetic curves of O_2 absorption during ethylbenzene oxidation (1.5 mol L^{-1}) at high cobalt concentrations and 90 °C: [Co] = $15 \cdot 10^{-3}$ (*1*), $3 \cdot 10^{-2}$ (*2*), and $6 \cdot 10^{-2}$ mol L^{-1} (*3*).

10^{-5} mol L^{-1}. Therefore, at high cobalt(II) concentrations (>$4 \cdot 10^{-2}$ mol L^{-1}), the system becomes stationary with respect to ROOH almost instantly. At the same time, for the cobalt(II) concentrations ~0.1 mol L^{-1} and oxidation rate 10^{-7}—10^{-6} mol L^{-1} s^{-1}, a considerable time (10^3—10^4 s) is needed to accumulate the cobalt(III) steady-state concentration (several percentage of [Co^{II}][9]).

Thus, at low cobalt(II) concentrations (10^{-4}—10^{-2} mol L^{-1}) the establishment of steady-state conditions is limited by the rate of ROOH accumulation, while for high cobalt concentrations the cobalt(III) accumulation rate is determining.

Let us consider the regularities of the initial oxidation step (d[ROOH]/dt = 0, d[Co^{III}]/dt > 0) at high cobalt(II) concentrations when reaction (6), *viz.*, reduction of the formed cobalt(III) with hydroperoxide, can be neglected and, hence, cobalt(III) is simply accumulated in the system. Then, from the steady-state conditions with respect to the concentrations of R$^•$, RO$^•$, RO$_2^•$, and ROOH, we have that the concentration of peroxide radicals would not change compared to that under the steady-state conditions and the initial rate of O_2 absorption and the rate of cobalt(III) accumulation would increase with an increase in the cobalt(II) concentration.

$$[RO_2^{\bullet}]_0 = k_3[RH]/(2k_6) \tag{10}$$

$$W_{O_2}{}^0 = 1.5k_3{}^2[RH]^2/(2k_6) + k_3k_4[RH][Co^{II}]/(2k_6) \tag{11}$$

$$W_{Co^{III}}{}^0 = k_3{}^2[RH]^2/(2k_6) + k_3k_4[RH][Co^{II}]/k_6 \tag{12}$$

The results of spectrophotometric measurements of the rate of cobalt(III) accumulation (Fig. 2) agree with Eq. (12): the rate of cobalt(III) accumulation increases indeed with an increase in the initial cobalt(II) concentration in solution. This confirms that reaction (4) occurs between RO$_2^•$ and Co^{II} and affords ROOH and Co^{III}.

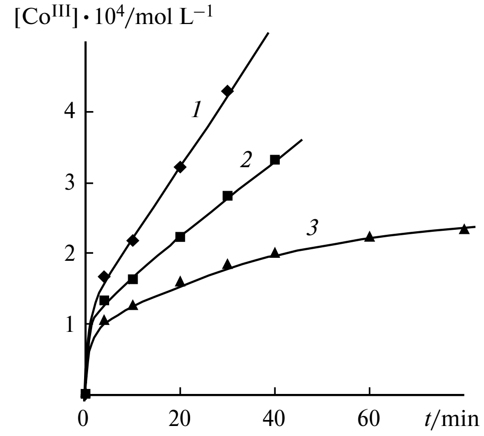


Fig. 2. Kinetics of Co^{III} accumulation in oxidation of ethylbenzene (1.2 mol L^{-1}) at high cobalt(II) concentrations and 60 °C; [ROOH]$_0$ = 10^{-4} mol L^{-1}; [Co] = 0.096 (*1*), 0.064 (*2*), and 0.041 mol L^{-1} (*3*). The initial jump of [Co^{III}] is related to ROOH decomposition *via* reaction (3).

However, in experiments on measurements of the accumulation rate of cobalt(III) with the further increase in the cobalt(II) concentration, we faced the existence of the critical catalyst concentration. When approaching to this value, the accumulation rate of cobalt(III), whose maximum (Co^{II}, 0.1 mol L^{-1}) several times exceeds the limiting rate of radical autooxidation $W_{O_2}{}^{st} = k_3{}^2[RH]^2/(2k_6)$, decreases sharply almost to zero (Fig. 3).

Spectrophotometric measurements of the cobalt(III) accumulation rate at 70 °C enabled us to measure the critical concentrations ([Co]$_{cr}$) at different ethylbenzene concentrations.

[RH] (vol.%)	4	5	6	8	10	12	14	16	18
[Co]$_{cr}$ • 10^2 /mol L^{-1}	7.5	8.4	9.5	11	12.4	14	15.5	17	19

According to the these data (Fig. 4), the squared critical concentration of cobalt is proportional to the ethyl-

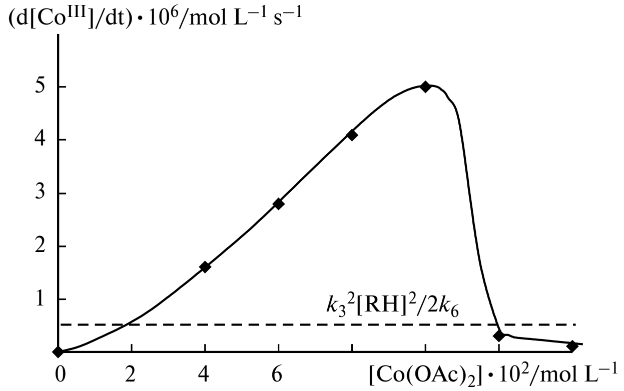


Fig. 3. Initial rate of cobalt(III) accumulation *vs.* cobalt(II) concentration during oxidation of ethylbenzene (0.82 mol L^{-1}) at 70 °C according to the data of spectrophotometric measurements at 380 nm (0.4D = 10^{-3} mol L^{-1} Co^{III}).

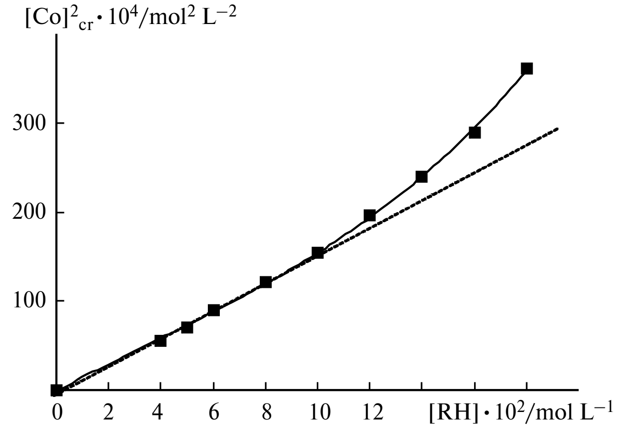


Fig. 4. Squared critical cobalt(II) concentration *vs.* ethylbenzene concentration at 70 °C according to the data of spectrophotometric measurements of the cobalt(III) accumulation rate.

benzene concentration in a region of ethylbenzene concentrations to ~8 vol.%. The $[Co]_{cr}$ value at [RH] = 10 vol.% and 70 °C is 0.12 mol L^{-1}.

The proportionality between $[Co]_{cr}^2$ and [RH] observed at low ethylbenzene concentrations can be explained with allowance for participation of two cobalt(II) atoms in the step resulting in chain termination.

$$RO_2^{\bullet} + 2\,Co^{II} \xrightarrow{k_7} \mathbf{A} + Co^{III} + Co^{II} + OH^- \qquad (13)$$

A is ketone

Reaction (4) was proposed[10] to proceed *via* two steps through the intermediate formation of a complex with the partial electron transfer. The addition of a proton from solvated acetic acid molecules (proton assistance) affords hydroperoxide.

$$RO_2^{\bullet} + Co^{II} \underset{k_{4d}}{\overset{k_{4a}}{\rightleftharpoons}} RO_2^{\bullet}Co^{II} \qquad (14)$$

$$RO_2^{\bullet}Co^{II} \xrightarrow[H^+]{k_{4r}} ROOH + Co^{III} \qquad (15)$$

k_a, k_d, and k_r are the activation, deactivation, and reaction rate constants, respectively

The observed effect of inhibition by cobalt(II) can be explained by the reaction between the $RO_2^{\bullet}Co^{II}$ complex and a cobalt(II) species. This interaction allows the electron transfer in the complex to the peroxide radical to occur and RO_2^- that formed to decompose with formation of ketone ($RO_2^{\bullet} \xrightarrow{e} RO_2^- \longrightarrow$ **A** + OH$^-$).

$$RO_2^{\bullet}Co^{II} + Co^{II} \xrightarrow{k_{4b}} \mathbf{A} + Co^{III} + Co^{II} + OH^- \qquad (16)$$

k_b is the binuclear interaction constant

The sum of Eqs (14) and (16) gives the formal trimolecular reaction (13).

However, the concentration of the intermediate complex $RO_2^{\bullet}Co^{II}$ decreases due to reaction (16), which impedes the kinetic regularities. From the steady-state condition with respect to the $RO_2^{\bullet}Co^{II}$ complex, we have

$$[RO_2^{\bullet}Co^{II}] = k_{4a}[RO_2^{\bullet}][Co^{II}]/(k_{4d} + k_{4r} + k_{4b}[Co^{II}]), \quad (17)$$

The steady-state conditions with respect to all intermediates (steady-state oxidation regime) give

$$k_3[RO_2^{\bullet}][RH] - k_{4b}[RO_2^{\bullet}Co^{II}][Co^{II}] - 2k_6[RO_2^{\bullet}]^2 = 0.$$

The latter equality implies that the peroxide radicals formed in reaction (3), which leads to branching, disappear due to both quadratic recombination and linear decay involving the cobalt(II) complex.

The expression for the concentration of peroxide radicals in the steady-state oxidation regime also follows from the above equality

$$[RO_2^{\bullet}]_{st} = k_3[RH]/(2k_6) - k_{4a}k_{4b}[Co^{II}]^2/\{2k_6(k_{4d} + k_{4r} + k_{4b}[Co^{II}])\}. \quad (18)$$

For the rate of O_2 absorption in the steady-state oxidation regime, we have

$$W_{O_2}^{st} = k_3^2[RH]^2/(2k_6) - k_{4a}k_{4b}k_3[RH][Co^{II}]^2/\{2k_6(k_{4d} + k_{4r} + k_{4b}[Co^{II}])\}. \quad (19)$$

In the region of comparatively low cobalt(II) concentrations, the kinetic regularities of inhibition obey formally trimolecular reaction (13), where $k_7 = k_{4a}k_{4b}/(k_{4d} + k_{4r})$. The rate constant k_7 was estimated from the proportionality region (see Fig. 4) between $[RH]_{cr}$ and $[Co^{II}]_{cr}^2$ at 70 °C: $k_7 \approx 300$ L^2 mol^{-2} s^{-1}.

In the initial step of oxidation at high cobalt(II) concentrations (d[ROOH]/dt = 0, d[Co^{III}]/dt > 0), the expression for the concentration of peroxide radicals remains unchanged ($[RO_2^{\bullet}]_0 = [RO_2^{\bullet}]_{st}$), and the equations for the cobalt(III) accumulation and O_2 absorption rates, respectively, look as follows:

$$W_{Co^{III}}^0 = [RO_2^{\bullet}]_{st}\{k_3[RH] + 2k_{4r}k_{4a}[Co^{II}]/(k_{4d} + k_{4r} + k_{4b}[Co^{II}]) + k_{4b}k_{4a}[Co^{II}]^2/(k_{4d} + k_{4r} + k_{4b}[Co^{II}])\}, \quad (20)$$

$$W_{O_2}^0 = [RO_2^{\bullet}]_{st}\{1.5k_3[RH] + k_{4r}k_{4a}[Co^{II}]/(k_{4d} + k_{4r} + k_{4b}[Co^{II}]) + 0.5k_{4b}k_{4a}[Co^{II}]^2/(k_{4d} + k_{4r} + k_{4b}[Co^{II}])\}. \quad (21)$$

According to the presented formulas, these plots (see Figs 3 and 5) reach a maximum with an increase in [Co^{II}], and then the rate decreases rather sharply. Note that the rate in the maximum is by several times higher than the theoretical limiting autooxidation rate $k_3^2[RH]^2/(2k_6)$. This difference is due, first of all, to the value of the k_4 rate constant of reaction (4) (according to published data,[7] at 90 °C k_4/k_3 = 39, at 70 °C k_4/k_3 = 35, k_4 = 190 L mol^{-1} s^{-1}). In the detailed oxidation scheme, $k_4 = k_{4r}k_{4a}/(k_{4d} + k_{4r})$.

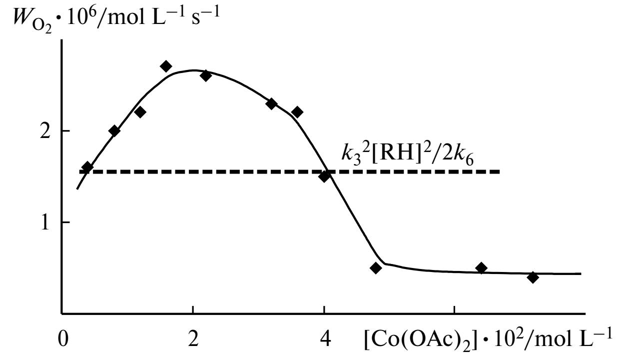


Fig. 5. Initial oxidation rate *vs.* cobalt(II) concentration during oxidation of ethylbenzene (0.82 mol L^{-1}) at 90 °C.

As can be seen from formulas (20) and (21), the critical condition is the zero concentration of peroxide radicals

$$k_3[RH]_{cr} = k_{4a}k_{4b}[Co^{II}]_{cr}^2/(k_{4d} + k_{4r} + k_{4b}[Co^{II}]_{cr}). \quad (22)$$

The square root from the chemiluminescence intensity (proportional to the concentration of radicals $RO_2^\bullet$, Fig. 6) decreases with an increase in the cobalt(II) concentration according to the expression for $[RO_2^\bullet]_{st}$. At 90 °C and ethylbenzene concentration 0.82 mol L^{-1}, the estimated critical cobalt concentration is ~0.13 mol L^{-1}, which is close to the experimentally measured oxidation rate (see Fig. 5).

Thus, the measurement of the intensity of chemiluminescence accompanying ethylbenzene oxidation in the presence of cobalt(II) confirms the conclusions on the inhibition mechanism of cobalt(II) (see Fig. 6).

Thus, cobalt(II) is involved in the step of ROOH radical decomposition (see reaction (5)) and also in the propagation step (formation of ROOH *via* reaction (4) between $RO_2^\bullet$ and Co^{II}) and chain termination (decay of the $RO_2^\bullet$ radical *via* reaction (13) involving two Co^{II} atoms).

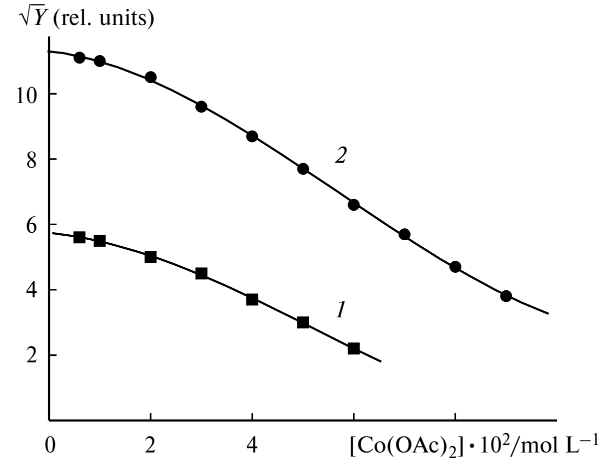
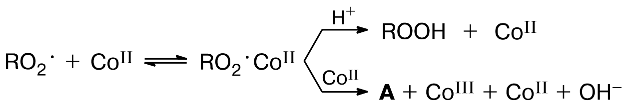


Fig. 6. Square root from the chemiluminescence intensity (relative concentration of peroxide radicals) *vs.* cobalt(II) concentration in ethylbenzene oxidation at 90 °C and for ethylbenzene concentrations of 5 (*1*) and 10% (*2*).

Trimolecular reaction (13) makes it possible to explain the critical phenomena observed in ethylbenzene oxidation. The mechanism of this reaction can be attributed to the electron transfer between free cobalt(II) and cobalt(II) in the composition of the $RO_2^\bullet Co^{II}$ complex.

It can be assumed that these reactions are conjugated: the formation of ROOH in reaction (4) between Co^{II} and $RO_2^\bullet$ and decay of the $RO_2^\bullet$ radical involving two Co^{II} atoms *via* reaction (13) proceed through the formation of the same $RO_2^\bullet Co^{II}$ complex (Scheme 4).

Scheme 4



Under the cobalt-bromide catalysis conditions ($Co^{III} + Br^- \longrightarrow Co^{II} + Br^\bullet$, $Br^\bullet + RH \longrightarrow H^+ + Br^- + R^\bullet$), reaction (4) is transformed from the propagation reaction, which changes the ratio between concentrations of Co^{II} and Co^{III}, into the propagation reaction leading to branching and providing the development of an efficient channel of hydrocarbon autooxidation through cobalt(II). In this case, termination reaction (13) is transformed into the chain propagation reaction and favors an increase in the carbonyl selectivity of oxidation due to the formation of a carbonyl product.

The authors thank V. A. Adamyan for help in the work and valuable remarks.

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Received July 2, 2004;
in revised form June 22, 2005