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Elementary Stages and Kinetics of Phenoxide Radicals Reactions with Cobalt and Iron Ions

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Abstract—Introduction of cobalt acetylacetonate to the solution containing phenoxide radicals has led todecelerating their termination. Cobalt acetylacetonate reactivity is dual, it has acted as an inhibitor when introduced in a certain concentration to the low-temperature oxidizing mixture.

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Phenoxide radicals are intermediates found in many tissues, biochemical and photochemical systems. The study of phenoxide radicals reactivity is therefore an important field of physical chemistry of radical reactions.

The accelerating or inhibiting effect of the transition metal compounds on the liquid-phase oxidation reactions has been extensively studied [1]. The observed effects are due to organometallic compounds interaction with radicals: peroxide, alkyl oxide, alkyl, etc. The details of the mechanism of such interactions still remains unkown. For instance, the interaction of a radical with a metal chelate can proceed as a reaction with the ligand, or via ligand substitution with the radical in the complex structure, or via electron transfer through medium. The information of these processes is obtained by comparing the structures of the products obtained in the presence or in the absence of the metal compound; the determination of kinetic parameters (in particular, indiction period) can also add to the knowledge of the mechanism. Direct study of the elementary stages is complicated due to small lifetimes and stationary concentrations of the radicals under usual conditions.

In this work we applied the impulse photolysis method to study the kinetics of termination of *o*-methylphenoxide radical in nonpolar medium in the presence and in the absence of cobalt acetylacetonate $Co(acac)_2$. The pulsed photoexcitation in toluene, benzene, and hexane led to the appearance of absorption due to the presence of imtermediates (Fig. 1).

In all solutions, the band at $\lambda = 405$ nm was assigned to the methylphenoxide radical. The introduction of cobalt acetylacetonate to the solutions of *o*-cresol in toluene changed the absorption spectra of the intermediates (Fig. 1). The changes were evidently due to complex formation between phenoxide radical and cobalt acetylacetonate. The complexes formation could occur via the fast reaction (1), Ph symbol standing for methylphenylene.

$$PhO^{\cdot} + Co(acac)_2 \rightarrow PhO^{\cdot} \cdots Co(acac)_2 . \qquad (1)$$

The possibility of similar complex formation between 2,4,6-tri-*tert*-butylphenoxide radical and $Co(acac)_2$ was proved in [1] basing on ESR data.

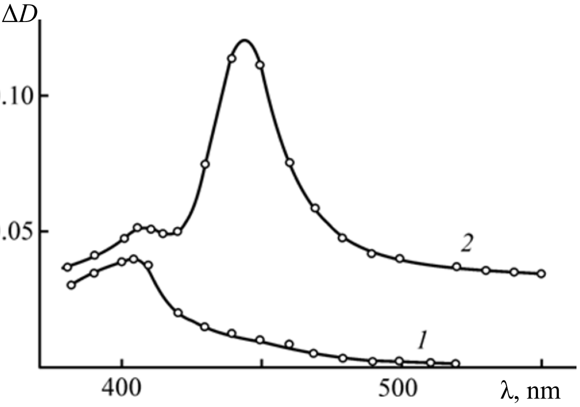

Fig. 1. Absorption spectra of the intermediates at time 3×10^{-5} s in the course of pulse photolysis of the aerated solutions. (*1*) *o*-cresol in toluene (5×10^{-3} mol L^{-1}), (*2*) *o*-cresol (5×10^{-3} mol L^{-1}) and cobalt acetylacetonate (3×10^{-4} mol L^{-1}) in toluene.

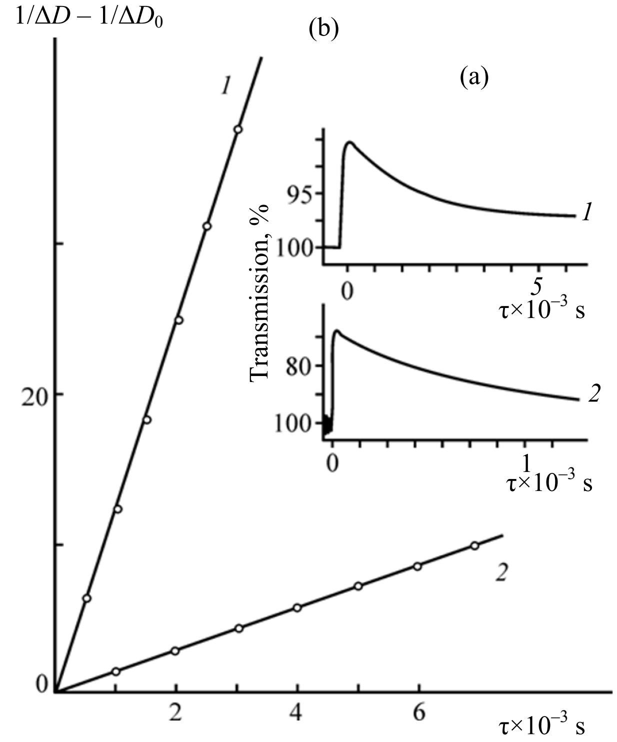

Fig. 2. Oscillograms (a) of the spectral changes at λ = 405 nm due to termination of *o*-methylphenoxide radicals (*1*) and complexes of *o*-methylphenoxide radical with cobalt acetylacetonate (*2*) in toluene; corresponding linear anamorphoses (b).

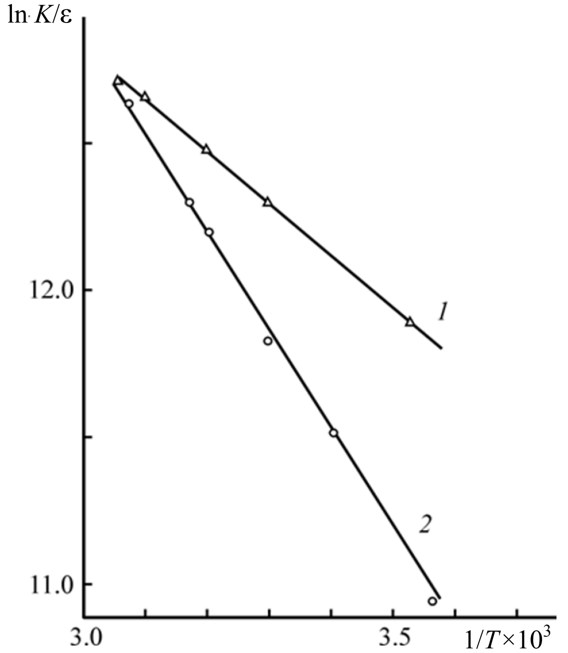

Fig. 3. Arrhenius plots of termination of (*1*) *o*-methylphenoxide radicals in benzene, λ = 405 nm, E_{act} = 3.1 kcal mol^{-1} and (*2*) of *o*-methylphenoxide complex with cobalt acetylacetonate in benzene, λ = 405 nm, E_{act} = 6.5 kcal mol^{-1}.

It was additionally demonstrated that the observed spectral changes were not due to photolysis of the additive itself. In particular, upon impulse photoexcitation of cobalt acetylacetonate solutions in toluene and hexame no signal in the studied spectral range was observed.

Phenoxide radicals with no bulk substituens are terminated according to the second order reaction (2).

$$PhO^{\cdot} + PhO^{\cdot} \rightarrow \text{Products}. \quad (2)$$

The rate constants k_2 were close to the diffusion ones, and the activation energy was about several kcal [2]. The kinetics of phenoxide radicals termination was studied by observing the spectral changes in the absorption maximum (Fig. 2). The corresponding k/ε for the used solvents are given in the table.

Values of K/ε for the three solvents [a]

Solvent	k_2/ε	λ, nm	k_3/ε	λ, nm	k_3/k_2
Toluene	2.5×10^5	405	1.5×10^4	450	0.20
Benzene	1.5×10^5	405	6.0×10^4	445	0.85
Hexane	6.5×10^5	405	8.0×10^4	455	0.05

[a] All values are given for 20°C.

The termination of phenoxide radical complexes with cobalt acetylacetonate followed the second order kinetics as well

$$2PhO^{\cdot} + Co(acac)_2 \rightarrow \text{Products}. \quad (3)$$

Assuming that at the time zero the concentration of phenoxide radicals (irradiation of the solution without cobalt additive) was equal to the concentration of complexes (irradiation in the presence of cobalt acetylacetonate), the following equation would hold.

$$\frac{\Delta D^{PhO}}{\Delta D^{compl}} = \frac{\varepsilon^{PhO}}{\varepsilon^{coml}}.$$

Leading to the rate constants ratio written as follows.

$$\frac{k_3}{k_2} = \frac{\varepsilon^{PhO}\Delta D^{compl}}{\varepsilon^{compl}\Delta D^{PhO}}.$$

The values of k_3/k_2 are given in the table; it was found that $k_3 < k_2$. Thus, introductin of cobalt

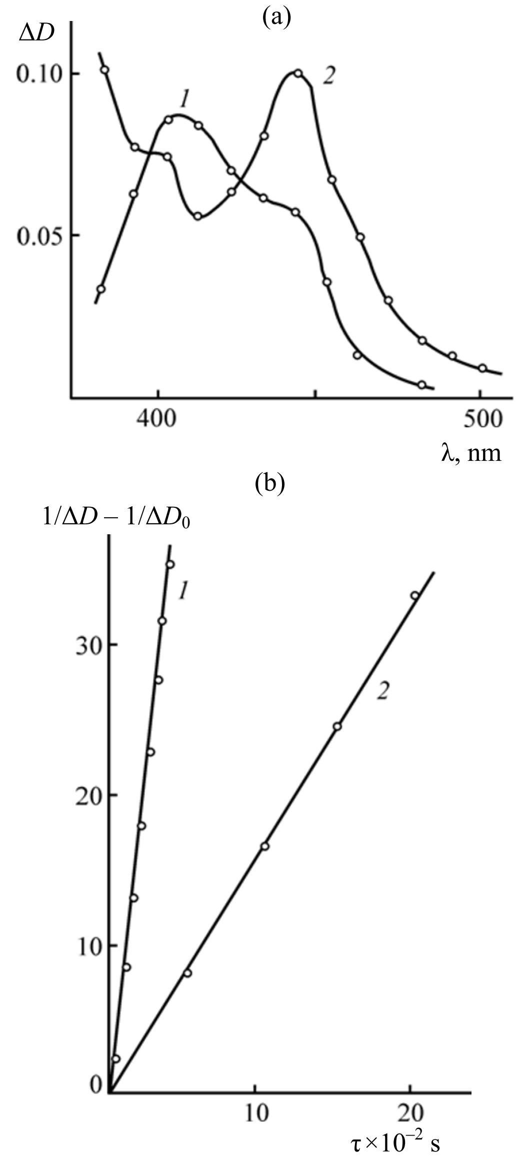

Fig. 4. (a) Absorption spectra of the intermediates at time 3×10^{-5} s in the course of pulse photolysis of the aerated solutions: (*1*) *o*-cresol (5×10^{-3} mol L^{-1}), (*2*) *o*-cresol (5×10^{-3} mol L^{-1}) and iron acetylacetonate (3×10^{-4} mol L^{-1}); and (b) the corresponding linear anamorphoses of spectral changes at $\lambda = 400$ nm (b).

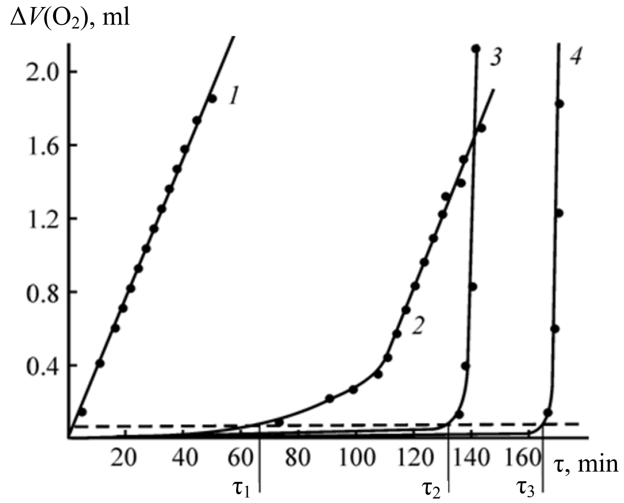

Fig. 5. Kinetics of oxygen absorption in the course of liquid-phase oxidation of isopropylbenzene in the presence of azobisisobutyronitrile (3×10^{-3} mol L^{-1}) at 60°C. (*1*) no additives, (*2*) in the presence of *o*-cresol (10^{-4} mol L^{-1}), (*3*) in the presence of Co(acac)$_2$ (10^{-3} mol L^{-1}), (*4*) in the presence of Co(acac)$_2$, (10^{-3} mol L^{-1}) and *o*-cresol (10^{-4} mol L^{-1}).

acetylacetonate slowed down the phenoxide radicals termination. The activation energies of the termination of phenoxide radicals and the complexes in benzene equaled 3.1 and 6.5 kcal mol^{-1} (Fig. 3).

The decrease in the rate constant of radicals termination and the increase in the respective activation energy showed that cobalt acetylacetonate addition led to an effect similar to that of a bulky substituent introduction to phenyloxide radical. Cobalt acetylacetonate likely forms the charge transfer complex with methylphenoxide radical as revealed by the appearance of a new absorption band at λ_{max} of 440–450 nm. Phenoxide radical, having the 7π-electron system, is a π-donor compound; cobalt acetylacetonate, having an unoccupied *3d*-orbital, is an electron acceptor. Thus, a relatively weak bond in the complex could be formed via overlapping of phenoxide radical π-orbital and *3d*-orbital of cobalt.

Similar spectral and kinetic changes pointing at the complex formation were observed in the course of impulse photolysis of *o*-cresol solution in toluene in the presence of iron(II) acetylacetonate. The corresponding spectral data are shown in Fig. 4. Cobalt acetylacetonate is widely used as a catalyst in the process of liquid-phase hydrocarbons oxidation. The catalysis mechanism involves the interaction of hydroperoxides with acetylacetonate with the free radicals formation. However, the deceleration of the termination of short-lived phenoxide radicals in the presence of cobalt acetylacetonate that we have found in this study and the stabilization of peroxide radicals show that cobalt acetylacetonate may play the ole of an inhibitor. Thus, cobalt acetylacetonate reactivity is dual, and it should act as inhibitor when added to the low-temperature oxidizing mixture at a certain concentration.

The dual reactivity of the transition metals compounds is well known, by using such compounds the chain oxidation reaction can be controlled just by the change of the additive concentration. As an example, we studied the oxidation of isopropylbenzene at 60°C in the presence of azobisisobutyronitrile, *o*-cresol, and cobalt(II) acetylacetonate (Fig. 5). With *o*-cresol, oxidation of isopropylbenzene is an oxidation chain reaction in the presence of weak inhibitor (τ_1 is the induction period). Cobalt(II) acetylacetonate (10^{-3} mol L^{-1}) indeed acted as a strong inhibitor, the induction period being of τ_2, but after the inhibitor consumption the reaction preceeded with a rate higher than that of the non-inhibited oxidation (Fig. 5, curves *1*, *3*). The consumption of $Co(acac)_2$ was accompanied with the solution color change from dark-red to green due to the formation of Co(III).

The acceleration of the chain reaction was due to the radical decomposition of hydroperoxides in the presence of cobalt compounds.

In the presence of both *o*-cresol and the chelate, isopropylbenzene oxidation was even more inhibited during the induction period, and proceeded beyond the induction period with the rate equal to that in the presence of only cobalt acetylacetonate. However, the induction period in the case of the mixed additive was shorter than the sum of the induction periods in the cases of individual additives: $\tau_3 < \tau_1 + \tau_2$. That could be explained by the formation of the intermediate complex between *o*-methylphenoxide radical and the chelate, with stability of the complex being higher than that of the initial radical.

The termination of such complexes led to unreactive products.

The stoichiometric coefficient of the chain termination by cresols was close to 2. At the sufficiently high concentration of $Co(acac)_2$, 10^{-3} mol L^{-1}, the complex formation could be the main pathway of phenoxide radicals termination. Thus, the stoichiometric coefficient of the chain termination should be approximately halved, in line with the experimental observations.

Thus, liquid-phase oxidation of hydrocarbons in the presence of a typical inhibitor, *o*-cresol, and the additive with dual reactivity, cobalt chelate, was a complicated process. The complex formation between phenoxide radical and the chelate influenced the induction period of the process.

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