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I. V. Zakharov, V. Ya. Shlyapintokh

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Abstract

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I. V. Zakharov, V. Ya. Shlyapintokh

Chemiluminescence and the Mechanism of the Reaction of the Catalyzed Decomposition of Ethylbenzene Hydroperoxide

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In works (1a–b), the regularities of chemiluminescence discovered by the authors in the oxidation reaction of ethylbenzene catalyzed by a salt of a variable-valence metal—cobalt acetate—were described. In this reaction, chemiluminescence is due to the recombination of peroxide radicals formed as a result of the catalyzed decomposition of hydroperoxide. The decomposition proceeds with first order with respect to hydroperoxide

$$-\frac{d(\mathrm{ROOH})}{dt} = k_{\mathrm{eff}}(\mathrm{ROOH}) \tag{1}$$

and the intensity of chemiluminescence is proportional to the rate of decomposition

$$I \sim \frac{d(\mathrm{ROOH})}{dt}. \tag{2}$$

In accordance with (1) and (2), the luminescence intensity in the course of the reaction decreases according to an exponential law. The values of k_{eff} obtained from the decay curves of the luminescence and from analysis of hydroperoxide consumption (by the iodometric method) coincide. This opens the possibility of using the chemiluminescent method to study the kinetics of the catalyzed decomposition of hydroperoxide. The intensity of chemiluminescence was measured on a high-sensitivity photometric apparatus (1g). The reaction was carried out in a thermostated vessel, which was placed in front of the window of a photomultiplier in a light-tight chamber. The decomposition was carried out in the presence of oxygen (during the experiment, air dried with calcium chloride was bubbled through the solution). The values of the effective rate constants of decomposition under the conditions of ongoing oxidation were determined from the kinetic curves of chemiluminescence by the method described in our work (1b). As can be seen from Fig. 1, k_{eff} depends in a complex manner on the concentration of the catalyst.

Essential for the interpretation of the kinetic mechanism was the study of decomposition at low catalyst concentrations and low temperatures, when the decomposition rate is small. Under these conditions, the kinetics of chemiluminescence at the initial stage of the decomposition process is characterized by a clearly expressed two-stage character (Fig. 2a). In the first stage, over a time $t \leq 5$ sec, the intensity of chemiluminescence rapidly increases from zero to a certain value I_0. In the second stage, a much slower increase in the luminescence intensity occurs up to a certain maximum value, and as a result the luminescence intensity doubles. It follows from this that at the end of the second stage the rate of decomposition of hydroperoxide is twice as high as at the end of the initial stage (relation 2). As can be seen from Fig. 3b, the maximum intensity of chemiluminescence $I_{\max}$ and k_{eff} change with the catalyst concentration according to a law close to quadratic. The initial intensity of chemiluminescence changes according to the same law. Both $I_{\max}$ and I_0 depend linearly on the concentration of hydroperoxide (Fig. 3a). The rate of attaining the maximum intensity of chemiluminescence and, correspondingly, the maximum rate of decomposition is the greater, the higher the concentration of hydroperoxide and catalyst (Fig. 2). The regularities obtained—

···regularities can be described by the following kinetic scheme:

$$\mathrm{ROOH} + \mathrm{CoAc_2} \underset{k_2}{\overset{k_1}{\rightleftarrows}} [\mathrm{ROOH} \cdot \mathrm{CoAc_2}]; \qquad \text{(I)}$$

$$[\mathrm{ROOH} \cdot \mathrm{CoAc_2}] + \mathrm{CoAc_2} \xrightarrow{k_4} \dot{\mathrm{R}}\mathrm{O} + \mathrm{CoAc_2} + \mathrm{CoAc_2OH}; \qquad \text{(II)}$$

$$[\mathrm{ROOH} \cdot \mathrm{CoAc_2}] + \mathrm{CoAc_2OH} \xrightarrow{k_5} \dot{\mathrm{R}}\mathrm{O_2} + 2\mathrm{CoAc_2} + \mathrm{H_2O}. \qquad \text{(III)}$$

Reactions leading to luminescence:

$$\dot{\mathrm{R}}\mathrm{O} + \mathrm{RH} \rightarrow \mathrm{ROH} + \dot{\mathrm{R}}; \qquad \dot{\mathrm{R}}\mathrm{O_2} + \mathrm{RH} \xrightarrow{k_3} \mathrm{ROOH} + \dot{\mathrm{R}}; \qquad \dot{\mathrm{R}} + \mathrm{O_2} \rightarrow \dot{\mathrm{R}}\mathrm{O_2};$$

$$\dot{\mathrm{R}}\mathrm{O_2} + \dot{\mathrm{R}}\mathrm{O_2} \xrightarrow{k_6} \mathrm{M}^* + \mathrm{O_2}; \qquad \mathrm{M}^* \xrightarrow{k_7} \mathrm{M} + h\nu; \qquad \mathrm{M}^* \xrightarrow{k_8} \mathrm{M},$$

where $\mathrm{CoAc_2OH}$ is the oxidized form of the catalyst, and $\dot{\mathrm{R}}$, $\dot{\mathrm{R}}\mathrm{O}$, and $\dot{\mathrm{R}}\mathrm{O_2}$ are, respectively, hydrocarbon, alkoxyl, and peroxy radicals; M^* and M are excited and unexcited molecules. Chemiluminescence is due to recombination of peroxy radicals. From the scheme we have that the concentration of the complex (at a low rate of decomposition) is

$$[\mathrm{ROOH}\cdot\mathrm{CoAc_2}] = \frac{k_1}{k_2}(\mathrm{ROOH})(\mathrm{CoAc_2}) \tag{3}$$

and the rate of hydroperoxide decomposition and the luminescence intensity in the steady state are as follows:

$$-\frac{d(\mathrm{ROOH})}{dt} = 2k_4\frac{k_1}{k_2}(\mathrm{ROOH})(\mathrm{CoAc_2})^2 = k_{\mathrm{eff}}(\mathrm{ROOH}), \tag{4}$$

$$I = \frac{k_7}{k_7+k_8}\,2k_4\frac{k_1}{k_2}(\mathrm{ROOH})(\mathrm{CoAc_2})^2. \tag{5}$$

The rate of decomposition and the luminescence intensity at the end of the first stage are

$$-\frac{d(\mathrm{ROOH})}{dt} = k_4\frac{k_1}{k_2}(\mathrm{ROOH})(\mathrm{CoAc_2})^2, \tag{6}$$

$$I_0 = \frac{k_7}{k_7+k_8}\,k_4\frac{k_1}{k_2}(\mathrm{ROOH})(\mathrm{CoAc_2})^2. \tag{7}$$

Fig. 1. Dependence of the effective decomposition constant on catalyst concentration (1). $t^\circ = 70^\circ$C; (RH) = 20% (by volume); $(\mathrm{ROOH})_0 = 2.2\cdot10^{-3}$; linear anamorphosis of the dependence in the coordinates

$$\frac{(\mathrm{CoAc_2})^2}{k_{\mathrm{eff}}} \div (\mathrm{CoAc_2}) \tag{2}$$

Fig. 2. *a*—kinetics of chemiluminescence at the initial stage of the decomposition process, $t^\circ = 50^\circ$C.
1—$(\mathrm{CoAc_2}) = 4\cdot10^{-3}$, $(\mathrm{ROOH})_0 = 6.8\cdot10^{-3}$;
2—$(\mathrm{CoAc_2}) = 4\cdot10^{-3}$, $(\mathrm{ROOH})_0 = 2.9\cdot10^{-3}$;
3—$(\mathrm{CoAc_2}) = 16\cdot10^{-3}$, $(\mathrm{ROOH})_0 = 6.8\cdot10^{-3}$.
b—dependence of the rate constant for establishment on catalyst concentration, $t^\circ = 50^\circ$C, $(\mathrm{ROOH})_0 = 6.8\cdot10^{-3}$.

Expressions (4)—(7) explain the observed dependences of the decomposition rate and the luminescence intensity on the concentrations of hydroperoxide and catalyst.

The increase in the rate of hydroperoxide decomposition during the stage of establishment of the regime is associated with accumulation in the system of trivalent cobalt

Fig. 3 and Fig. 4

Figure 1: Fig. 3 and Fig. 4

$$\frac{d(\mathrm{CoAc_2OH})}{dt} = k_4\frac{k_1}{k_2}(\mathrm{ROOH})(\mathrm{CoAc_2})^2 - k_5\frac{k_1}{k_2}(\mathrm{ROOH})(\mathrm{CoAc_2})(\mathrm{CoAc_2OH}). \tag{8}$$

The rate of decomposition doubles when the rate of consumption of trivalent cobalt becomes equal to the rate of its formation. It follows from (8) that the con-

constant of the establishment rate

$$k_{\mathrm{est}} = k_5\frac{k_1}{k_2}(\mathrm{ROOH})(\mathrm{CoAc_2}). \tag{9}$$

Relation (9) explains the observed dependence of the rate of establishment of the decomposition regime on the concentrations of hydroperoxide and catalyst.

The concentration of the trivalent cobalt salt in the established regime (see (8)) is

$$(\mathrm{CoAc_2OH}) = \frac{k_4}{k_5}(\mathrm{CoAc_2}). \tag{10}$$

The ratio $\frac{k_4}{k_5}$ can be calculated by comparing the decomposition rate constant k_{eff} (4) with the establishment rate constant (10). Thus, for $t^\circ = 50^\circ$C (according to the data of Figs. 2 and 3), the value of $\frac{k_4}{k_5}$ is 0.015, i.e., the concentration of the tri-

Fig. 3. *a*—dependence of the maximum (1) and initial (2) luminescence intensities on the concentration of hydroperoxide, $t^\circ = 50^\circ$C, $(\mathrm{CoAc_2}) = 4 \cdot 10^{-3}$; *b*—dependence of the maximum luminescence intensity $\sqrt{I_{\max}}$ and the effective decomposition constant $\sqrt{k_{\mathrm{eff}}}$ on the catalyst concentration, $t^\circ = 50^\circ$, $(\mathrm{ROOH})_0 = 6.8 \cdot 10^{-3}$

Fig. 4. Effect of oxygen removal on the intensity of chemiluminescence. *a*—$t^\circ = 50^\circ$C, [RH] = 20%, $[\mathrm{CoAc_2}] = 6 \cdot 10^{-3}$, $[\mathrm{ROOH}]_0 = 6.8 \cdot 10^{-3}$, $k_{\mathrm{eff}} = 0.5 \cdot 10^{-3}$ s^{-1}, $I_2/I_1 = 0.25$; *b*—$t^\circ = 50^\circ$C, [RH] = 40%, $[\mathrm{CoAc_2}] = 6 \cdot 10^{-3}$, $[\mathrm{ROOH}]_0 = 13.6 \cdot 10^{-3}$, $k_{\mathrm{eff}} = 0.58 \cdot 10^{-3}$ s^{-1}, $I_2/I_1 = 0.16$

valent salt amounts to only 1.5% relative to the divalent salt, and in accordance with this, the characteristic green coloration of trivalent cobalt is not observed in the experiment.

Thus the scheme describes the principal regularities of the kinetics and chemiluminescence. The scheme is valid in the region of low catalyst concentrations. As the catalyst concentration is increased, terms accounting for the reactions of interaction of the complex with the catalyst must be introduced into the expression for the concentration of the complex. In addition, with increasing catalyst concentration, the fraction of hydroperoxide bound into the complex increases:

$$(\mathrm{ROOH})_0 = (\mathrm{ROOH}) + [\mathrm{ROOH} \cdot \mathrm{CoAc_2}]. \tag{11}$$

Taking these factors into account and under the condition $(\mathrm{CoAc_2}) \gg (\mathrm{ROOH})_0$,

$$[\mathrm{ROOH} \cdot \mathrm{CoAc_2}] = \frac{k_1(\mathrm{ROOH})_0(\mathrm{CoAc_2})}{k_2 + (k_1 + 2k_4)(\mathrm{CoAc_2})}. \tag{12}$$

The effective decomposition rate constant is

$$k_{\text{eff}} = \frac{2k_1k_4(\mathrm{CoAc_2})^2}{k_2 + (k_1 + 2k_4)(\mathrm{CoAc_2})}$$

or

$$\frac{(\mathrm{CoAc_2})^2}{k_{\text{eff}}} = \frac{k_2}{2k_1k_4} + \frac{k_1 + 2k_4}{2k_1k_4}(\mathrm{CoAc_2}).$$

As is seen from Fig. 1, the dependence of k_{eff} on the catalyst concentration becomes linear in the coordinates $\frac{(\mathrm{CoAc_2})^2}{k_{\text{eff}}} \div (\mathrm{CoAc_2})$. This means that the kinetic scheme obtained as a result of studying the kinetics of chemiluminescence during the establishment stage describes the kinetics of the steady-state decomposition process over the entire investigated range of catalyst concentrations.

In the proposed catalysis scheme, decomposition proceeds in reactions in which salts of divalent and trivalent cobalt participate alternately. In the interaction of the hydroperoxide with the divalent salt, the radical $\dot{\mathrm{R}}\mathrm{O}$ (II) is formed; with the trivalent salt, the radical $\mathrm{R}\dot{\mathrm{O}}_2$ (III) is formed. The rates of both processes are equal. Since the radicals $\mathrm{R}\dot{\mathrm{O}}$ have high reactivity, in the presence of oxygen they are completely converted by reactions (IV) and (VI) into peroxy radicals.

Table 1

T, °C	$\left(\frac{\text{l}}{\text{mol}\cdot\text{sec}}\right)^{1/2}\cdot 10^4$	$\frac{k_3}{\sqrt{k_6}}$*, $\left(\frac{k_3}{\sqrt{k_6}}\right)\cdot 10^4$ (2)
90	14.2	16.8
70	7.3	8.3
50	3.6	4.0

* Average value from several experiments.

Therefore, a doubling of the luminescence intensity occurs in the second stage of establishment of the decomposition regime. If, in the steady-state regime, oxygen is removed from the system (by bubbling hydrogen purified from oxygen), then the luminescence intensity drops sharply to a certain level, and it decreases by more than a factor of two (Fig. 4). This result can be explained if one takes into account that, in the absence of oxygen, conversion of radicals $\dot{\text{RO}}$ into $\dot{\text{RO}}_2$ is impossible, and that part of the $\dot{\text{RO}}_2$ radicals is consumed in reaction with the hydrocarbon and hydrocarbon radicals. The radicals $\dot{\text{RO}}$ and $\dot{\text{RO}}_2$ are formed at equal rates, equal to $\frac{k_{\text{eff}}(\text{ROOH})}{2}$. If the scheme is supplemented by the reactions $\text{RO}_2 + \text{R} \xrightarrow{k_9}$ termination, $\text{R} + \text{R} \xrightarrow{k_{10}}$ termination, proceeding in the absence of oxygen, then one can obtain an expression relating the kinetic parameter $k_3/\sqrt{k_6}$ to the rates of recombination of peroxy radicals in the presence (w_1) and in the absence (w_2) of oxygen (assuming that $k_9 = \sqrt{k_6 \cdot k_{10}}$).

$$\frac{k_3}{\sqrt{k_6}} = \frac{w_1 + w_2 - 2\sqrt{w_1 w_2}}{2\sqrt{w_2}\,(\text{RH})}. \tag{13}$$

In deriving this dependence, the liberation of oxygen in the recombination reaction of peroxy radicals was taken into account. The values of w_2 were determined from measurements of the luminescence intensity (Fig. 4). As is seen from the data in Table 1, the values of $\frac{k_3}{\sqrt{k_6}}$ calculated from relation (13) are close to the literature values.

This confirms the correctness of the concepts developed both regarding the mechanism of the catalyzed decomposition of ethylbenzene hydroperoxide and regarding the nature of the chemiluminescence in this reaction.

Institute of Chemical Physics
Academy of Sciences of the USSR

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REFERENCES CITED

1. I. V. Zakharov, V. Ya. Shlyapintokh, a) *Kinetics and Catalysis*, **4**, no. 2 (1963); b) *Kinetics and Catalysis*, **4**, no. 4 (1963); c) Proc. Moscow Institute of Physics and Technology, no. 9 (1962); d) *Kinetics and Catalysis*, **2**, 165 (1961).

2. Z. G. Kozlova, V. F. Tsepalov, V. Ya. Shlyapintokh, *Transactions on Chemistry and Chemical Technology*, Gorky, no. 1, 95 (1961).

Note: Figure translations are in progress. See original paper for figures.