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We studied the mechanism of aldehydes oxidation by the system selenium-containing catalyst–hydrogen peroxide. On the basis of literature data analysis, our experimental results and developed kinetic model of the reaction, we stated that the oxidation of unsaturated aldehydes by Se-containing compounds and hydrogen peroxide occurs through the formation of intermediate active compound of peroxide nature, selenium peracid. Study of the kinetics of reaction with Se-containing catalysts in different oxidation state (0, +4, and +6) showed that the highest reaction rate was observed when selenium oxidation level was +4. It was also found that the nature of solvent significantly affects the reaction rate and solvents can be ranged by their positive effect as follows: formic acid>tertiary alcohols>acetic acid>dioxane>acetone. It was shown that the oxidation reaction in acetic acid occurs even without catalyst but proceeds in several directions that causes low selectivity towards the target products. As a result of kinetic study, we determined that the concentration of hydrogen peroxide had no effect on the reaction rate; however, an increase in water concentration in the reaction mixture (which is introduced into the reaction mixture together with hydrogen peroxide solution) decreases the reaction rate. On the basis of the results of kinetic simulation, we showed that the oxidation of unsaturated and saturated aldehydes occurs through two following ways: it chiefly proceeds through the step of non-catalytic interaction of aldehyde with hydrogen peroxide in the case of saturated aldehydes, whereas this route occurs only to a small extent in the case of unsaturated aldehydes.

**Keywords:** unsaturated aldehydes, oxidation, selenium compounds, hydrogen peroxide, reaction kinetics.

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**Introduction**

Selective synthesis of unsaturated acids is possible via oxidation of unsaturated aldehydes by hydrogen peroxide in the presence of Se<sup>+4</sup> compounds at the temperature of 293–313 K and reagents conversion of 95%. It is a convenient, simple and environmentally friendly method of performing the reaction [1] which uses hydrogen peroxide as an oxidizer, unsaturated acid and water being the products. It is easy to isolate the main product from the reaction mixture by the rectification after reaction completion. Nevertheless, a disadvantage of the use of hydrogen peroxide as an oxidant is its low reactivity without promoter that will induce oxygen transfer; therefore, reaction efficiency is limited by its kinetics [2]. Hydrogen peroxide can be activated under different conditions: nucleophilic, electrophilic,

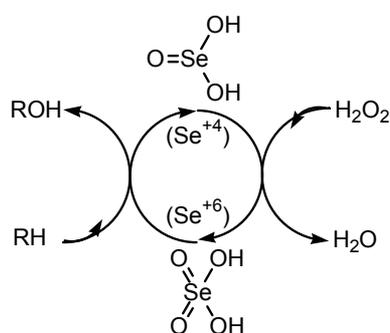
radical activation and activation with organic compounds that give more active and efficient peroxidic species [3]. The use of catalyst that is able to activate hydrogen peroxide might allow overcoming kinetic limitations of the oxidation reaction with H<sub>2</sub>O<sub>2</sub> and will lead to the necessary reaction course with a high reaction rates [4]. Since selenium exhibits few oxidation states, it can take part in numerous reduction-oxidation reactions. SeO<sub>2</sub> has been discovered as a hydrogen peroxide activator in 1970s. However, the use of this type of selenium catalyst resulted in a low reaction yield and difficulties in product separation [5]. Nowadays, different types of selenium compounds are used as catalysts for various oxidation reactions, such as oxidation of olefins, Baeyer-Villiger oxidation, oxidation of sulfides to sulfoxides, oxidation of amines to

hydroxylamines, oxidation of alcohols to aldehydes and ketones, oxidation and oxidative esterification of aldehydes to acids and esters [6].

Although the application of selenium catalyst in oxidation reactions has been widely studied, there are no unambiguous systematic data in literature on the reaction kinetics and the mechanism of  $\text{Se}^{+4}$  compounds participation in the reaction.

Several ways of the catalyst interaction are possible in case of organic compounds oxidation by system selenium compound– $\text{H}_2\text{O}_2$  as follows:

1. Selenic acid ( $\text{H}_2\text{SeO}_4$ ) is formed via interaction between  $\text{H}_2\text{SeO}_3$  and hydrogen peroxide which is present in the catalytic process (Scheme I).



Scheme I

This mechanism of the reaction was proposed in study [7]. The authors believe that selenic acid is an oxidant in the reaction of unsaturated aldehydes to acids, and there is a cyclic change of the oxidation state of Se from +6 to +4 due to the reaction of aldehyde with  $\text{H}_2\text{SeO}_4$  and reoxidation of  $\text{Se}^{+4}$  to  $\text{Se}^{+6}$  via interaction with  $\text{H}_2\text{O}_2$ .

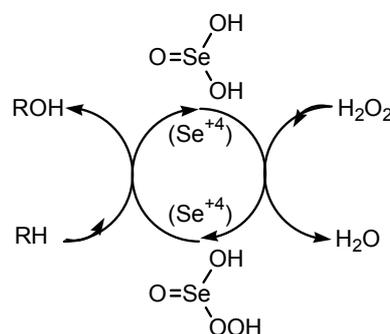
There facts confirming this scheme are as follows:

- selenic acid has a strong oxidizing properties [8] and is much stronger oxidant than selenous acid;
- selenic acid can be synthesized by the reaction of  $\text{H}_2\text{O}_2$  with  $\text{SeO}_2$  or  $\text{H}_2\text{SeO}_3$  and this is one of the methods of selenic acid preparation [9].

2. An aldehyde can be oxidized by peroxide compound of selenium formed via interaction between hydrogen peroxide and  $\text{SeO}_2$  or  $\text{H}_2\text{SeO}_3$  (oxidation state of selenium does not change in the course of this reaction) (Scheme II).

To check these hypotheses, a number of experimental investigations have been performed, and it has been established that neither unsaturated acids nor another reaction products are formed when mixing equivalent amounts of  $\text{SeO}_2$ ,  $\text{H}_2\text{SeO}_3$  and  $\text{H}_2\text{SeO}_4$  solutions with unsaturated aldehydes. In

addition, the reaction mixture turned into tar when aldehydes contacted with  $\text{H}_2\text{SeO}_4$ . And, most importantly, the introduction of  $\text{H}_2\text{SeO}_4$  into the mixture of aldehyde, solvent and hydrogen peroxide leads only to a weak acceleration of the reaction (the reaction rate constant is 7 times less than in the presence of the same molar amount of  $\text{SeO}_2$  or  $\text{H}_2\text{SeO}_3$ ) (Table 1).



Scheme II

Table 1

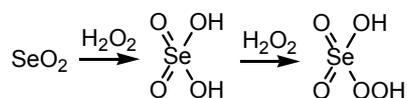
Rate constants of 2-ethylpropenal oxidation in the presence of selenium compounds.  $C_{\text{cat}}=0.03 \text{ mol/dm}^3$ ,  $T=303 \text{ K}$

Catalyst	$k \cdot 10^5, \text{ dm}^3/(\text{mol} \cdot \text{s})$
Se	8.9
$\text{SeO}_2$	10.3
$\text{H}_2\text{SeO}_3$	10.5
$\text{PhSe(O)OH}$	9.9
$\text{H}_2\text{SeO}_4$	1.4
$\text{NaHSeO}_3$	4.3

Thus the second of the proposed schemes is the most probable. It is based on the fact that the role of a catalyst in reactions involving Se compounds consists in the formation of an intermediate active compound of a peroxide nature, which oxidizes an aldehyde like organic peroxides do. The proof of this scheme of oxidation is the possibility of the formation of Se peroxy compounds in the interaction between  $\text{Se}^{+4}$  compounds and  $\text{H}_2\text{O}_2$ , which has been established in our study. Although selenium peracids are not formed individually, we have found that the combination of  $\text{Se}^{+4}$  compounds with  $\text{H}_2\text{O}_2$  leads to the formation of compounds the oxidizing capacity of which exceeds the oxidizing capacity of selenium compounds and  $\text{H}_2\text{O}_2$ . In particular, a mixture of  $\text{H}_2\text{O}_2$  with  $\text{SeO}_2$  or  $\text{H}_2\text{SeO}_3$  is capable of displacing bromine from a solution of potassium bromide. Neither selenium compounds nor hydrogen peroxide

have any such ability. The data on the possibility of the formation of peroxyselenic acid via the interaction of  $\text{H}_2\text{O}_2$  with  $\text{SeO}_2$  are shown elsewhere [8]. Based on these data, it can be concluded that peroxyselenous acid  $\text{O}=\text{Se}(\text{OH})\text{OOH}$  is formed in the mixtures of  $\text{H}_2\text{O}_2$  with selenium (IV) compounds.

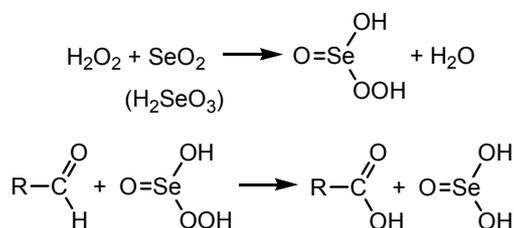
One could also assume that the oxidizing agent of the aldehyde may be peroxyselenic acid ( $\text{H}_2\text{SeO}_5$ ) which could be formed according to the following scheme (Scheme III).



Scheme III

However, it is known that peroxyselenic acid can only be prepared by the interaction of chloroselenic acid with 100%  $\text{H}_2\text{O}_2$  and is unstable in an aqueous medium [8]. These data indicate that the participation of peroxyselenic acid in the oxidation of unsaturated aldehydes by  $\text{H}_2\text{O}_2$  is hardly probable.

The above data [10–12] on the participation of selenium compounds in oxidative processes, as well as numerical data on the formation of inorganic peracids in the interaction of the corresponding oxides with  $\text{H}_2\text{O}_2$  indicate that the oxidation of aldehydes by the system  $\text{SeO}_2\text{--H}_2\text{O}_2$  occurs according to the following scheme (Scheme IV).



Scheme IV

### Experimental

The study of the reaction of unsaturated aldehydes with hydrogen peroxide was carried out in a 50 cm<sup>3</sup> thermostated glass reactor with a magnetic stirrer, a reflux condenser and a thermometer. Solvent and 0.05 mol of aldehyde were placed in the reactor and  $\text{H}_2\text{O}_2$  (in the form of 70–90% water solution) was added at a constant temperature. Then, the solution of the catalyst was added to the mixture. The moment of the catalyst solution addition was assumed as the beginning of the reaction. The samples of the reaction mixture were periodically taken for analysis. The content of  $\text{H}_2\text{O}_2$  was determined by

the iodometric method. The content of unsaturated acid was determined according to the procedure described elsewhere [12].

### Results and discussion

*Kinetics of the reaction of unsaturated aldehydes with hydrogen peroxide*

According to most authors, the reaction of carbonyl compounds with hydrogen peroxide is described by the second order equation [13]. The curves of hydrogen peroxide consumption and unsaturated acid accumulation during the oxidation of one of the aldehydes are shown in Fig. 1.

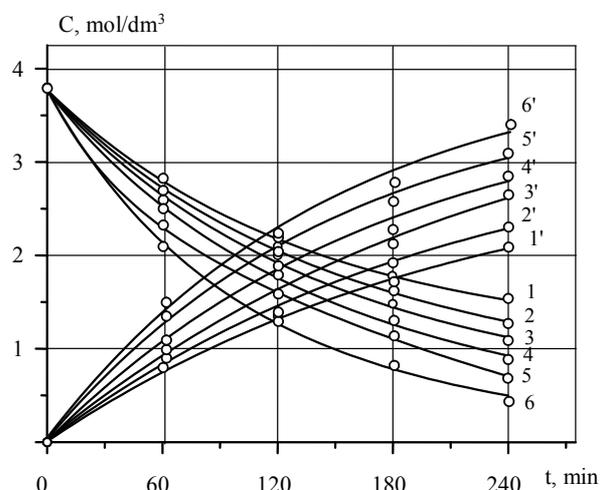


Fig. 1. Kinetic curves of hydrogen peroxide consumption and unsaturated acid accumulation (curves with strokes) during oxidation of 2-propylpropenal in the presence of  $\text{SeO}_2$  (0.03 mol/dm<sup>3</sup>): (1) 283 K; (2) 288 K; (3) 293 K; (4) 298 K; (5) 303 K; (6) 313 K

As can be seen in Fig. 1, the curves of peroxide consumption are well conformed to the acid accumulation curves. This indicates a good selectivity of the reaction and suggests that the kinetics of the reaction is not complicated by some parallel or sequential reactions.

Preliminary processing of the curves of hydrogen peroxide consumption shows that they obey well the second-order equation up to a conversion of 30%. At deeper stages, a decrease in the rate constant with time becomes noticeable. However, one can use the second-order equation for qualitative comparative data. The rate constants of the reaction in the presence of various selenium compounds are given in Table 1.

Table 1 shows that the highest rate is observed for the compounds in which selenium is in the

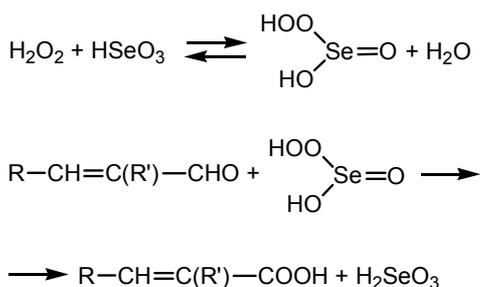
oxidation state +4. Therefore, a further study was conducted in the presence of  $\text{SeO}_2$  and  $\text{H}_2\text{SeO}_3$ . In the presence of elemental selenium, the rate and selectivity (88%) are somewhat lower. Obviously, a decrease in the reaction rate is caused by the complication of the reaction (due to the oxidation reaction of  $\text{Se}^0$  to  $\text{SeO}_2$ ).

Possible solvents for the reaction may be alcohols, ketones, carboxylic acids and dioxane. These compounds provide the dissolution of organic substances and  $\text{H}_2\text{O}_2$  ( $\text{H}_2\text{O}$ ). It has been found out that the nature of solvent significantly affects the rate of  $\text{H}_2\text{O}_2$  consumption. Depending on the solvent type, the reaction rate constant for 2-butylpropenal ( $T=303\text{ K}$ ,  $C_{\text{SeO}_2}=0.03\text{ mol/dm}^3$ ) is equal to  $6.8 \cdot 10^{-6}\text{ dm}^3/(\text{mol}\cdot\text{s})$  in acetone,  $1.35 \cdot 10^{-5}\text{ dm}^3/(\text{mol}\cdot\text{s})$  in benzyl alcohol,  $3.4 \cdot 10^{-5}\text{ dm}^3/(\text{mol}\cdot\text{s})$  in dioxane,  $4.7 \cdot 10^{-5}\text{ dm}^3/(\text{mol}\cdot\text{s})$  in allyl alcohol,  $6.6 \cdot 10^{-5}\text{ dm}^3/(\text{mol}\cdot\text{s})$  in acetic acid,  $8.1 \cdot 10^{-5}\text{ dm}^3/(\text{mol}\cdot\text{s})$  in tert-amyl alcohol,  $8.1 \cdot 10^{-5}\text{ dm}^3/(\text{mol}\cdot\text{s})$  in tert-butanol and  $12.8 \cdot 10^{-5}\text{ dm}^3/(\text{mol}\cdot\text{s})$  in formic acid.

Thus, in terms of the positive effect on the reaction rate, the solvents can be ranged in the following sequence: formic acid > tertiary alcohols > acetic acid > dioxane > acetone.

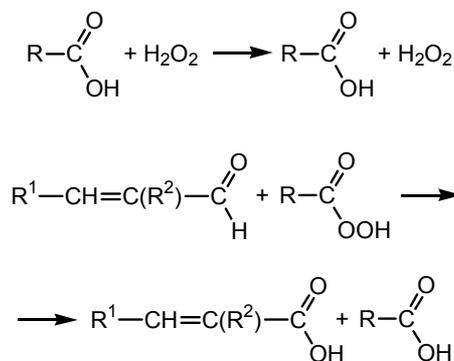
The slowest rate of the reaction is observed in acetone. The reaction rate can be increased by increasing the amount of the catalyst, but this leads to a decrease in the yield of unsaturated acid. In addition, the acetone itself is capable of reacting with  $\text{H}_2\text{O}_2$ , so the reaction may be decelerated because of the binding of a part of hydrogen peroxide to  $\alpha$ -hydroxyperoxyalkanol.

In a carboxylic acid medium, two routes of the formation of unsaturated acid are possible. In case of the first route, the acid acts only as a solvent (Scheme V).



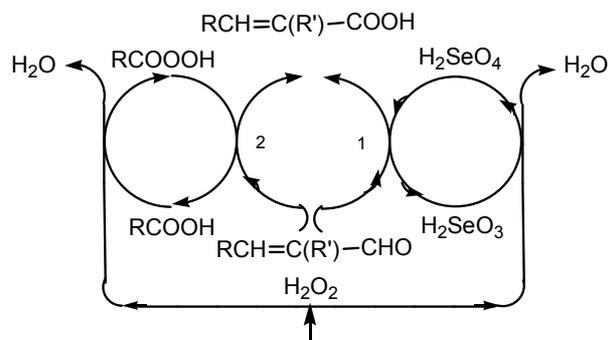
Scheme V

The second way is a transfer of active oxygen through a solvent with intermediate formation of peracids (Scheme VI).



Scheme VI

It should be noted that both paths lead to the formation of unsaturated acid (Scheme VII).



Scheme VII. Formation of products in the oxidation of unsaturated aldehyde with hydrogen peroxide in the presence of  $\text{H}_2\text{SeO}_4$  in a carboxylic acid medium

Therefore, in our case, both mechanisms occur simultaneously, and their ratio depends on the properties of the solvent (i.e. acid). The data that allow estimating the contribution of both mechanisms in the oxidation of unsaturated aldehydes are given in Fig. 2. As can be seen, the reaction in acid media proceeds without a catalyst and the reaction rate depends on the acid strength. So, the acids can be placed by their effect on the reaction rate in the following range: trichloroacetic acid > formic acid > acetic acid.

The reaction rate increases in the presence of a catalyst. The catalyst makes the highest contribution to the increase of the reaction rate when the reaction is conducted in acetic acid, whereas it makes the least contribution in trichloroacetic acid. We can draw the following conclusions from this fact: since in acetic acid medium the reaction practically does not occur without the catalyst, we can state that the mechanism 1 prevails in this case. The selectivity of

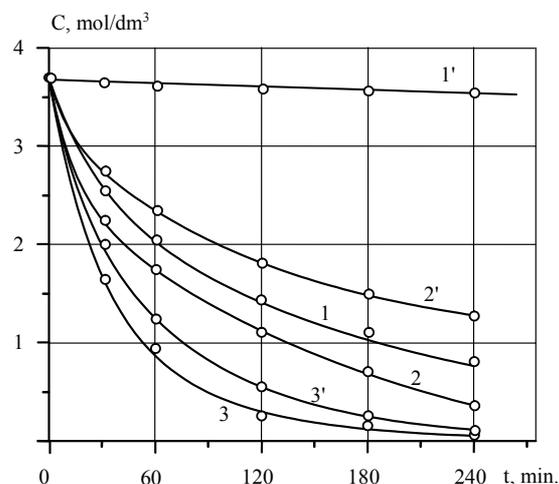


Fig. 2. Curves of hydrogen peroxide consumption during oxidation of 2-butylpropenal in the presence of the catalyst and without it (curves with strokes) in different acids: (1) – acetic acid; (2) – formic acid; (3) – trichloroacetic acid.  $C_{\text{cat}}=0.03 \text{ mol/dm}^3$ .  $T=303 \text{ K}$

the formation of unsaturated acid in acetic acid is 90–92%. In formic acid, mostly, mechanism 2 occurs and the selectivity of unsaturated acid is 84%.

In trichloroacetic acid,  $\text{H}_2\text{O}_2$  consumption curves during oxidation of aldehyde in the presence and absence of the catalyst are very close. This indicates that scheme 2 is dominant in this case. The selectivity of unsaturated acid in this case is 68%. Consequently, the greater the contribution of mechanism 2, the lower is the selectivity of the reaction. These data are in good agreement with the results of the study of the reaction of unsaturated aldehydes with peracids [14].

The obtained data show that from the point of view of studying kinetics the most suitable solvents for the reaction of unsaturated aldehydes with  $\text{H}_2\text{O}_2$  are tertiary alcohols and dioxane, since in other tested solvents the reaction proceeds in several directions and it is impossible to unambiguously interpret the kinetic data.

To build a kinetic model, the following research scheme was used: the reaction orders were determined for reagents, the reaction model was created based on the reaction scheme, the parameters of the model were calculated and the model and experiment were reconciled.

The following conditions for studying the kinetics of the reaction have been chosen: the temperature range of 283–323 K; the range of reagents concentration of 1–6 mol/dm³; the range of the catalyst concentration of 0.005–0.100 mol/dm³; the solvents used were tert-butanol and dioxane. These conditions provide a sufficient reaction rate

and create favorable conditions for monitoring the change in the concentration of reagents.

Since the reaction involves three participants (aldehyde, hydrogen peroxide and catalyst), it was necessary to determine the reaction orders with respect to the reagents. When conducting a series of experiments at constant initial concentrations of hydrogen peroxide and unsaturated aldehyde and at different initial concentrations of the catalyst, linear dependence of the rate constant on the catalyst concentration have been established. This dependence is valid in a wide range of the catalyst concentration (Fig. 3) and indicates that the reaction has a first order with respect to the catalyst concentration. The same dependence of the rate constant on the catalyst concentration is observed for  $\text{H}_2\text{SeO}_3$  and  $\text{PhSe(O)OH}$  in both tert-butanol and dioxane.

To establish the order of the reaction with respect to the aldehyde, a series of experiments were carried out under isothermal conditions at a constant excess concentration of hydrogen peroxide and different initial concentrations of the aldehyde (the concentration of the catalyst in this series was constant). In this and subsequent series of experiments, the kinetics was evaluated via determining the concentration of hydrogen peroxide. The obtained series of curves are shown in Fig. 4. Similar dependences have been obtained for other aldehydes in dioxane.

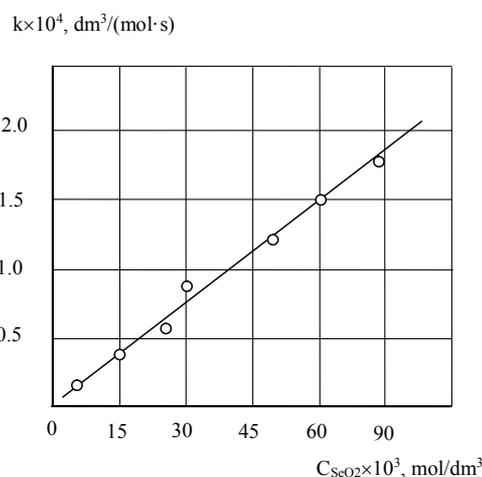


Fig. 3. Dependence of the rate constant of the reaction of 2-propylpropenal with  $\text{H}_2\text{O}_2$  in tert-butanol on the concentration of  $\text{SeO}_2$ .  $T=303 \text{ K}$

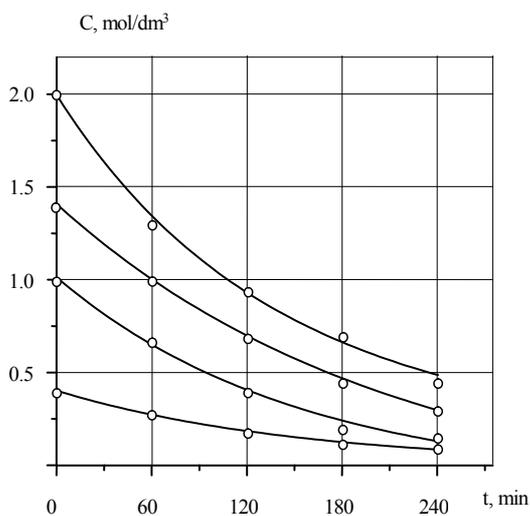


Fig. 4. Curves of the aldehyde consumption at different initial concentrations of 2-propyl-propenal in tert-butanol.  $C_{\text{cat}}=0.03 \text{ mol/dm}^3$ . Initial concentration of  $\text{H}_2\text{O}_2$  is  $6.0 \text{ mol/dm}^3$

Fig. 5 shows the dependence of the initial rates ( $W_0$ ) on aldehyde concentration. The linear dependence of  $W_0$  on the aldehyde concentration (linear regression coefficient is 0.997 for 2-ethylpropenal and 0.998 for 2-butenal) indicates that the reaction exhibits a first order with respect to the aldehyde.

In the next series of experiments, conducted under isothermal conditions with a constant initial concentrations of aldehyde and catalyst and different initial concentrations of hydrogen peroxide, the order of reaction with respect to hydrogen peroxide was established. The obtained data were unexpected as it was found out that the reaction rate practically does not depend on the concentration of peroxide and hence it was concluded that the order of the reaction with respect to hydrogen peroxide is close to zero. This result may be explained by the fact that peroxyseleous acid is an oxidizer in the proposed mechanism and its concentration is constant.

In our experiments, we used hydrogen peroxide, which always contained a certain amount of water. Consequently, we proportionally increased the concentration of water when increasing the concentration of hydrogen peroxide in this series of experiments. Considering this fact, the effect of water on the reaction rate should be studied. For this purpose, a series of experiments were carried out under isothermal conditions in which initial

concentrations of aldehyde and hydrogen peroxide were constant and the initial concentration of water was changed. The data on the effect of water content on the reaction of 2-ethylpropenyl with hydrogen peroxide are shown in Fig. 6. When the concentration of water increases, the reaction rate decreases (Fig. 6, curve 1). This indicates the inhibitory effect of water on the reaction rate.

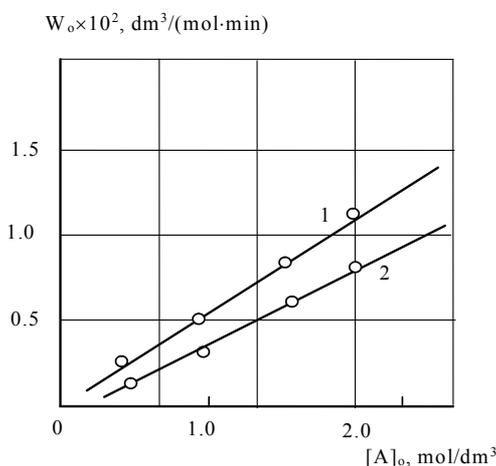


Fig. 5. Dependence of the initial reaction rate on the initial concentration of the aldehyde.  $\text{CH}_2\text{O}_2=5 \text{ mol/L}$ .  $C_{\text{cat}}=0.03 \text{ mol/L}$ . Solvent dioxane.  $T=313 \text{ K}$ . (1) – 2-ethylpropenal; (2) – 2-butenal

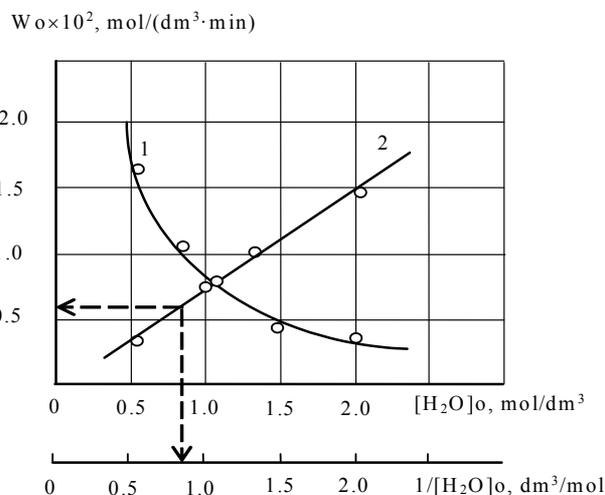


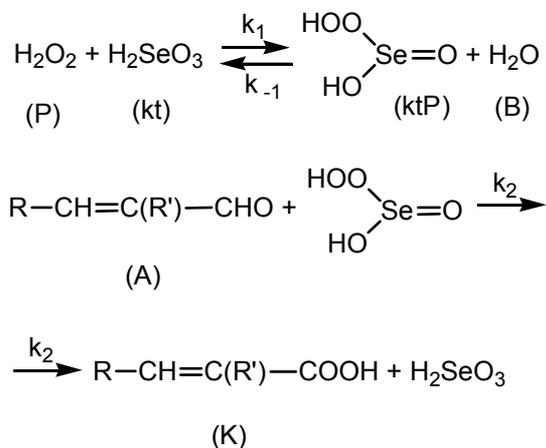
Fig. 6. Dependence of the initial reaction rate on the initial concentration of water during oxidation of 2-ethylpropenal in dioxane and concentration of reagents  $2.5 \text{ mol/dm}^3$ .  $C_{\text{cat}}=0.02 \text{ mol/dm}^3$ .  $T=313 \text{ K}$

The linearization of curve 1 in the coordinates

$W_0$  vs. the inverse water concentration (Fig. 6, curve 2) shows that the order of reaction is equal to  $-1$  with respect to water (the water concentration is in the denominator of the kinetic equation).

*Kinetic model of the reaction of unsaturated aldehydes with hydrogen peroxide*

Reactions of unsaturated aldehydes with hydrogen peroxide may be represented by the scheme (Scheme VIII).



Scheme VIII

In this mechanism, the formation of peroxyseleous acid (ktP) and water (B) is assumed in the first stage of the equilibrium reaction of hydrogen peroxide (P) with a catalyst (kt). The formed peracid then interacts with the aldehyde (A) as an organic peracid. As a result, the final product of the reaction, an unsaturated acid (K), is formed and the catalyst is regenerated.

To derive kinetic equations for the reaction participants, let us introduce the following designations:  $C_{P_0}$  is the concentration of hydrogen peroxide;  $C_A$  is the concentration of aldehyde;  $C_{Kt}$  is the catalyst concentration;  $C_K$  is the concentration of unsaturated acid;  $C_{ktP}$  is the concentration of peroxyseleous acid; and  $C_B$  is the concentration of water.

In accordance with the proposed scheme, the changes in the concentrations of hydrogen peroxide, aldehyde and peroxide form of the catalyst can be expressed as the following system of differential equations and algebraic equations of the material balance for aldehyde and hydrogen peroxide:

$$\frac{dC_P}{dt} = -k_1 C_P C_{kt} + k_{-1} C_{ktP} C_B, \quad (1)$$

$$\frac{dC_A}{dt} = -k_2 C_A C_{ktP}, \quad \frac{dC_A}{dt} = -k_2 C_A C_{ktP}, \quad (2)$$

$$\frac{dC_{ktP}}{dt} = k_1 C_P C_{kt} - k_{-1} C_{ktP} C_B - k_2 C_A C_{ktP}, \quad (3)$$

$$C_{A_0} = C_A + C_K, \quad (4)$$

$$C_{P_0} = C_P + C_B. \quad (5)$$

As stated above, hydrogen peroxide always contains a certain amount of water, therefore, Eqs. (1) and (3) should contain the sum  $(C_{B_0} + C_B)$  instead of  $C_B$ , where  $C_{B_0}$  is the initial concentration of water in the reaction mixture.

The equilibrium in the first stage of the reaction is established quickly. The catalyst loaded into the mixture is distributed between two forms, (kt) and (ktP), and the material balance for the catalyst is expressed by the following equation:

$$C_{kto} = C_{kt} + C_{ktP}. \quad (6)$$

The condition of the stationary process in terms of the catalyst should be taken into account:

$$\frac{dC_{kt}}{dt} = 0.$$

Taking into account Eq. (6), we can express the unknown concentrations of  $C_{kt}$ ,  $C_{ktP}$  and  $C_B$  through the initial one:

$$C_{ktP} = \frac{k_1 C_P C_{kto}}{k_{-1} (C_B + C_{B_0}) + k_2 C_A + k_1 C_P}. \quad (7)$$

Let us substitute the Eq. (7) into Eqs. (1) and (2) and derive the differential equations for the consumption of peroxide and aldehyde:

$$\frac{dC_P}{dt} = \frac{dC_A}{dt} = \frac{k_1 k_2 C_P C_{kto}}{k_{-1} (C_B + C_{B_0}) + k_2 C_A + k_1 C_P}. \quad (8)$$

Further, let us divide the numerator and denominator of this equation by  $k_{-1}$  as follows:

$$\frac{dC_P}{dt} = \frac{dC_A}{dt} = \frac{k_1 / k_{-1} k_2 C_P C_{kto} C_A}{(C_B + C_{B_0}) + k_2 / k_{-1} C_A + k_1 / k_{-1} C_P}$$

and designate  $W = -\frac{dC_P}{dt}$  is the invariant reaction rate and  $K = k_1/k_{-1}$  is the equilibrium constant of the first stage.

The condition of the stationary reaction is fulfilled if the first reaction proceeds quickly, therefore  $k_2 \ll k_{-1}$  and the term  $k_2/k_{-1} C_A$  can be neglected. Then the rate equation is expressed as follows:

$$W = \frac{k_2 K C_{kto} C_A}{C_B + C_{Bo} + K C_P}. \quad (9)$$

The analysis of this equation for the case of dependence of the initial reaction rate  $W_0$  on the initial concentrations of reagents gives the following results.

1) when changing the initial concentration of aldehyde and at  $C_B \approx 0$ ,  $C_{Bo} = \text{const}$  and  $C_{Po} = \text{const}$ , we have

$$W = \frac{k_2 K C_{kto} C_{Po}}{C_{Bo} + K C_{Po}} C_{Ao} = k'_{ef} \cdot C_{Ao}. \quad (10)$$

Therefore, the first order with respect to the aldehyde should be observed, this was also established experimentally (Fig. 5).

2) when the initial concentration of hydrogen peroxide  $C_{Po}$  changes (at  $C_B \approx 0$ , and  $C_{Ao} = \text{const}$ ), the initial concentration of water  $C_{Bo}$  also changes. If we have hydrogen peroxide with constant water content, its content can be expressed through the concentration of hydrogen peroxide in the following way:

$$C_{Bo} = \beta \cdot C_{Po}.$$

Then Eq. (9) can be written in the following form:

$$W_0 = k_2 K C_{kto} C_{Ao} C_{Po} / (\beta \cdot C_{Po} + K C_{Po}) = k''. \quad (11)$$

Therefore, in this case, we must observe a zero order of the reaction with respect to peroxide; this is also consistent with the experimental results.

3) when changing the initial concentration of water  $C_{Bo}$  at constant concentration of hydrogen peroxide and aldehyde ( $C_B \approx 0$ ,  $C_{Ao} = \text{const}$  and  $C_{Po} = \text{const}$ ), we obtain:

$$W_0 = \frac{k_2 K C_{kto} C_{Po} C_{Ao}}{K C_{Po} + C_{Bo}}. \quad (12)$$

Therefore, an inverse ratio between the initial reaction rate and the concentration of water should be observed. This was also confirmed experimentally (Fig. 6).

The obtained rate equation is also consistent with the experimentally found first order of reaction with respect to the catalyst.

Therefore, we can conclude that the reaction rate equation derived from the proposed scheme is fully consistent with the experimental data. This can be considered as a confirmation of the proposed mechanism of the reaction.

*Calculation of the kinetic parameters of the reaction between unsaturated aldehydes and hydrogen peroxide*

The basis for the calculation of the kinetic parameters of the reaction between unsaturated aldehydes and hydrogen peroxide in the presence of selenium compounds is the following equation:

$$W = \frac{k_2 K C_{kto} C_{Po} C_{Ao}}{C_B + C_{Bo} + K C_P}.$$

If we integrate this equation and consider the fact that  $C_A = (C_{Ao} - C_{Po} + C_P)$  and  $C_B = (C_{Po} - C_P)$ , then we get:

$$(1 - K) \ln \frac{C_P + C_{Ao} + C_{Po}}{C_{Ao}} + \frac{C_{Po} + C_{Bo}}{C_{Ao} - C_{Po}} \times \times \ln \frac{C_{Ao} C_P}{C_{Po} (C_P + C_{Ao} + C_{Po})} = k_2 K C_{kto} t. \quad (13)$$

After transformation of the obtained equation to the form which is convenient for calculating the constants  $k_2$  and  $K$ , we obtain:

$$\frac{1}{t} \frac{C_{Po} + C_{Bo}}{C_{Ao} - C_{Po}} \ln \frac{C_{Ao} C_P}{C_{Po} (C_P + C_{Ao} + C_{Po})} = = k_2 K C_{kto} + \frac{K - 1}{t} \ln \frac{C_P + C_{Ao} + C_{Po}}{C_{Ao}}. \quad (14)$$

If we follow the reaction kinetics by determining the change in the concentration of hydrogen peroxide and obtain the corresponding kinetic curve, then we can easily calculate both unknown constants  $k_2$  and  $K$  from this equation by the least squares method.

The values of  $K$  calculated in this way are close to 1 in the investigated temperature range. Thus, the following values of  $K$  were obtained: 0.795, 0.887, 0.953 and 0.970 for the oxidation of 2-butylypropanal

at 283, 293, 303 and 313 K, respectively (experiments were carried out in tert-butanol at the  $\text{SeO}_2$  concentration of  $0.03 \text{ mol/dm}^3$ ).

The analysis of Eq. (14) shows that the expression  $(K-1)/t \approx 0$  is valid for  $K \approx 1$ . Then, the kinetic equation simply transforms into a second order equation:

$$\frac{C_{\text{Po}} + C_{\text{Bo}}}{C_{\text{Ao}} - C_{\text{Po}}} \ln \frac{C_{\text{Ao}} C_{\text{P}}}{C_{\text{Po}} (C_{\text{P}} + C_{\text{Ao}} + C_{\text{Po}})} = k_2 K C_{\text{kto}} t. \quad (15)$$

The plot of the left-hand side of Eq. (15), Z vs. time is shown in Fig. 7 for the oxidation of 2-propylpropenal in tert-butanol at 298 K. A straight

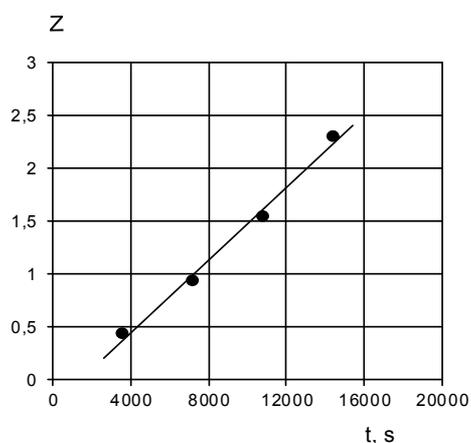


Fig. 7. Linearized curves of hydrogen peroxide consumption (Fig. 1, curve 4) for the oxidation of 2-propylpropenal.  $C_{\text{SeO}_2} = 0.03 \text{ mol/dm}^3$

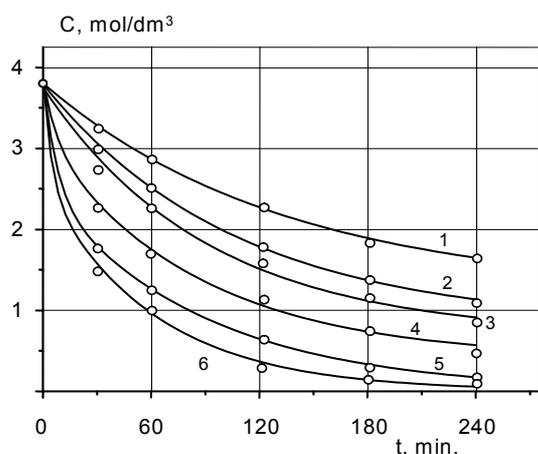


Fig. 8. Kinetic curves of  $\text{H}_2\text{O}_2$  consumption for the oxidation of 2-ethyl-2-hexenal (1), propionic aldehyde (2), 2-butenal (3), 2-methylpropenal (4), benzaldehyde (5) and cinnamic aldehyde (6). Solvent – tBuOH.  $T = 303 \text{ K}$

line in these coordinates confirms the accuracy of the made assumptions. The values of constant  $k_2$  at different temperatures are given in Table 2.

Table 2  
The values of constant  $k_2$  at different temperatures for the oxidation of unsaturated aldehydes in tert-butanol.  $C_{\text{cat}} = 0.03 \text{ mol/dm}^3$

Aldehyde	$k_2 \cdot 10^5, \text{ dm}^3/(\text{mol} \cdot \text{s})$			
	283 K	293 K	303 K	313 K
Propenal	$3.2 \pm 0.1$	$4.7 \pm 0.2$	$9.0 \pm 0.3$	$13.5 \pm 0.4$
2-Methylpropenal	$2.9 \pm 0.1$	$5.5 \pm 0.3$	$10.5 \pm 0.2$	$16.1 \pm 0.3$
2-Ethylpropenal	$3.3 \pm 0.1$	$5.8 \pm 0.2$	$10.5 \pm 0.2$	$10.5 \pm 0.4$
2-Propylpropenal	$2.3 \pm 0.1$	$4.4 \pm 0.3$	$8.3 \pm 0.2$	$11.8 \pm 0.3$
2-Buthylpropenal	$3.3 \pm 0.1$	$4.7 \pm 0.3$	$8.8 \pm 0.3$	$13.5 \pm 0.3$
2-Amylpropenal	$2.8 \pm 0.1$	$4.8 \pm 0.2$	$9.2 \pm 0.2$	$14.2 \pm 0.4$

Table 2 shows that the values of the rate constants, and, consequently, the reaction rate, slightly depend on the structure of alkyl substituent in  $\alpha$ -position towards the carbonyl group of the unsaturated aldehyde.

Table 3 shows the activation parameters of the reaction between unsaturated aldehydes and hydrogen peroxide. It is noteworthy that the activation energies of the reactions are much lower than those of the reaction of unsaturated aldehydes with peracids.

Table 3  
The values of activation parameters of the reaction of unsaturated aldehydes with hydrogen peroxide (according to data from Table 2)

Aldehyde	$E_{\text{act}}, \text{ kJ/mol}$	$k_0, \text{ dm}^3/\text{mol} \cdot \text{s}$	$\Delta H^\ddagger, \text{ kJ/mol}$	$\Delta S^\ddagger, \text{ J/mol}$
Propenal	$35.9 \pm 2$	$1.71 \cdot 10^2$	33.5	-221.0
2-Methylpropenal	$42.7 \pm 2$	$2.28 \cdot 10^3$	40.2	-189.4
2-Ethylpropenal	$38.1 \pm 2$	$3.56 \cdot 10^2$	35.6	-204.0
2-Propylpropenal	$41.1 \pm 3$	$1.09 \cdot 10^3$	38.6	-191.9
2-Buthylpropenal	$41.8 \pm 2$	$1.42 \cdot 10^3$	39.3	-192.0
2-Amylpropenal	$40.2 \pm 2$	$0.92 \cdot 10^3$	37.7	-197.7

The kinetic curves of hydrogen peroxide consumption in the catalytic oxidation of aldehydes of different structure in tert-butanol are shown in Fig. 8. The calculated rate constants are summarized in Table 4.

The data of Table 4 and Fig. 8 show that in terms of the rate of the reaction with  $\text{H}_2\text{O}_2$  in the presence of selenium catalyst, aldehydes can be arranged in the following sequence: cinnamic aldehyde > benzaldehyde > 2-alkylpropenal > 2-butenal > 2-,3-alkyl propenals > saturated

aldehydes.

Thus, as opposite to the oxidation of aldehydes by organic peroxy acids [14], the oxidation of saturated aldehydes by  $H_2O_2$  proceeds much more slowly than that of unsaturated ones [15].

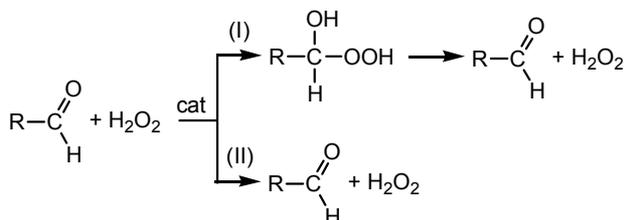
Table 4

**The rate constants of the reaction of aldehydes of different structure with hydrogen peroxide in the presence of 0.03 mol/dm<sup>3</sup> of  $H_2SeO_3$ . Solvent – tBuOH. T=303 K**

Aldehyde	$k_2 \cdot 10^5, \text{dm}^3/\text{mol} \cdot \text{s}$
2-Ethyl-2-hexenal	3.91±0.2
Propionic aldehyde	4.03±0.3
2-Butenal	4.52±0.2
2-methylpropenal	10.50±0.2
Benzaldehyde	23.50±0.5
Cinnamic aldehyde	42.13±0.6

If we take into account that in both cases the oxidizing agent of the aldehyde is peracid, then this may seem strange. However, the reason for this is, obviously, that the interaction between saturated aldehydes and  $H_2O_2$  is complicated by the reaction of the aldehyde hydration [13] ( $H_2O_2$  always contains an admixture of water and water is also formed in the reaction) resulting in the formation of hydroperoxyalkanols and other peroxides in the reaction mixture. In this case, the carbonyl group is blocked and the course of the reaction of peracid with it is hindered.

Oxidation of aldehydes by  $H_2O_2$  can take place in two ways (Scheme IX).



Scheme IX

Moreover, the direction (I) is much slower, since the intermediate peroxides of aldehydes decompose further to form acids at higher temperatures. Therefore, the overall reaction rate is determined by the ratio between two routes of the reaction. Direction (I) plays a significant role for saturated aldehydes, so the reaction is slower. For unsaturated ones, on the contrary, the hydration of the aldehyde and the non-catalytic interaction with  $H_2O_2$  occurs to a small extent, only the pathway (II)

takes place, and  $\alpha$  and  $\beta$ -alkyl propenals occupy an intermediate position.

These conclusions are consistent with the data given in the beginning of this work, concerning the effect of the aldehyde structure on the ability of the aldehyde to be hydrated, and to form peroxides when reacting with  $H_2O_2$ .

The oxidation of unsaturated aldehydes by  $H_2O_2$  in the presence of a catalyst is essentially the only effective way to prepare the corresponding unsaturated acids in terms of rate, selectivity, simplicity of reaction conduction, the acids isolation simplicity and environmental considerations.

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### МЕХАНІЗМ І КІНЕТИКА РЕАКЦІЇ НЕНАСИЧЕНИХ АЛЬДЕГІДІВ З ГІДРОГЕН ПЕРОКСИДОМ У ПРИСУТНОСТІ СПОЛУК СЕЛЕНУ

**З.Г. Піх, Р.В. Небесний, А.З. Піх, В.В. Івасів, Т.В. Харандюк**

Досліджено механізм окислення альдегідів системою селенвмісний каталізатор–гідроген пероксид. На підставі аналізу літератури, результатів виконаних експериментів і запропонованої кінетичної моделі реакції було доведено, що окислення ненасичених альдегідів Se-вмісними сполуками і гідроген пероксидом відбувається за рахунок утворення проміжної активної сполуки пероксидної природи – селенової перкислоти. Вивчення кінетики реакції з Se-вмісними каталізаторами при різних ступенях окиснення (0, +4, +6) показало, що найвища швидкість реакції спостерігалася при ступені окиснення Селену +4. Також було встановлено, що природа розчинника істотно впливає на швидкість реакції і за її позитивним впливом розчинники можуть бути розміщені в ряд: метанова кислота > третинні спирти > етанова кислота > діоксан > ацетон. Показано, що реакція окиснення в середовищі етанової кислоти відбувається навіть без каталізатора, але протікає в декількох напрямках, що зумовлює низьку селективність цільових продуктів. В результаті кінетичних досліджень також встановлено, що концентрація гідроген пероксиду не впливає на швидкість реакції, проте підвищення концентрації води в реакційній суміші (яка надходить з розчином гідроген пероксиду) знижує швидкість реакції. На підставі розрахунків параметрів кінетичної моделі доведено, що окислення ненасичених і насичених альдегідів відбувається двома шляхами: для насичених альдегідів він переважно протікає через стадію некаталітичної взаємодії альдегіду з гідроген пероксидом, тоді як для ненасичених альдегідів такий механізм окиснення відбувається незначною мірою.

**Ключові слова:** ненасичені альдегіди, окиснення, сполуки Селену, гідроген пероксиду, кінетика реакції.

### MECHANISM AND KINETICS OF THE REACTION OF UNSATURATED ALDEHYDES WITH HYDROGEN PEROXIDE IN THE PRESENCE OF SELENIUM COMPOUNDS

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We studied the mechanism of aldehydes oxidation by the system selenium-containing catalyst–hydrogen peroxide. On the basis of literature data analysis, our experimental results and developed kinetic model of the reaction, we stated that the oxidation of unsaturated aldehydes by Se-containing compounds and hydrogen peroxide occurs through the formation of intermediate active compound of peroxide nature, selenium peracid. Study of the kinetics of reaction with Se-containing catalysts in different oxidation state (0, +4, and +6) showed that the highest reaction rate was observed when selenium oxidation level was +4. It was also found that the nature of solvent significantly affects the reaction rate and solvents can be ranged by their positive effect as follows: formic acid > tertiary alcohols > acetic acid > dioxane > acetone. It was shown that the oxidation reaction in acetic acid occurs even without catalyst but proceeds in several directions that causes low selectivity towards the target products. As a result of kinetic study, we determined that the concentration of hydrogen peroxide had no effect on the reaction rate; however, an increase in water concentration in the reaction mixture (which is introduced into the reaction mixture together with hydrogen peroxide solution) decreases the reaction rate. On the basis of the results of kinetic simulation, we showed that the oxidation of unsaturated and saturated aldehydes occurs through two following ways: it chiefly proceeds through the step of non-catalytic interaction of aldehyde with hydrogen peroxide in the case of saturated aldehydes, whereas this route occurs only to a small extent in the case of unsaturated aldehydes.

**Keywords:** unsaturated aldehydes; oxidation; selenium compounds; hydrogen peroxide; reaction kinetics.

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