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NEW METHOD OF KINETIC MODELING OF ETHYLENE OXIDATION REACTION TO ETHYL ALCOHOL AND ACETALDEHYDE BY HYDROGEN PEROXIDE ON THE PER-FTPhPFe^{3+}OH/Al_2O_3

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Abstract: *The process of biomimetic monooxidation of ethylene into ethyl alcohol and acetaldehyde by hydrogen peroxide on the per-FTPhPFe^{3+}OH/Al_2O_3 bioimitator, which showed high activity and unique resistance to the action of high-active intermediate reaction products was investigated. As a result of studying the kinetic regularities of the selective biomimetic oxidation of ethylene by hydrogen peroxide, a coherent-synchronized nature of the reaction was observed, consisting of two reactions: 1) primary (catalase) and 2) secondary (monooxygenase and peroxidase) reactions. A new approach to the kinetic modeling based on the determinant equation and coherence correlation of catalase-monooxygenase and catalase-peroxidase reactions coherently synchronized with each other was developed. The kinetic model of the process was developed on the basis of the determinant equation, which allows assessing the coherent nature of synchronously flowing reactions both qualitatively and quantitatively. Effective rate constants of catalase, monooxygenase and peroxidase reactions were determined based on this model as well as their effective activation energies were calculated.*

Keywords: *ethylene, ethyl alcohol, acetaldehyde, hydrogen peroxide, biomimetic catalyst, kinetic model, coherent-synchronized reactions.*
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Introduction

The purpose of this work is to determine new characteristics of kinetics of multidisciplinary interrelated chemical reactions occurring in terms of chemical interference [1-4]. One of these interrelated (coherent) synchronous reactions is biomimetic oxidation of ethylene by hydrogen peroxide with subsequent conversion to acetaldehyde [5]:

$$C_2H_4 \xrightarrow{ImtOH,H_2O_2} C_2H_5OH \xrightarrow{ImtOH,H_2O_2} CH_3CHO$$

Ethylene is the most available and cheap raw material from which ethyl alcohol and acetaldehyde are obtained in the presence of a number of metal oxide catalysts (copper oxide, zeolites, mercury salts) and various oxidants: O_2, H_2O_2, N_2O and others [6-8]. However, in the presence of these catalysts, high selectivity was not achieved and the processes were carried out at high temperatures, requiring large energy costs.

The developed heterogeneous biomimetic catalysts based on ironporphyrin complexes applied to solid carriers of acid-base nature, manifested high activity and selectivity in the processes of large number of hydrocarbons oxidation by hydrogen peroxide [9-13].

One of these synthesized heterogenized biomimetic catalysts is perfluorinated iron (III) tetraphenylporphyrin immobilized on alumina (per-FTPhPFe^{3+}OH/Al_2O_3), the use of which in

the process of ethylene oxidation by hydrogen peroxide made it possible to increase the yield and selectivity of target products: the yields of ethyl alcohol and acetaldehyde were 15.4 and 34.6 wt.%, respectively, with high selectivity (99.7%).

Experimental part

According to the results of the experimental investigation of ethylene monooxidation by hydrogen peroxide shown in Fig. 1 as an example of the reaction products yields dependence on the concentration of hydrogen peroxide aqueous solution, along with the reaction of ethylene monooxidation to ethyl alcohol (curve 3), the decomposition reaction of hydrogen peroxide also proceeds in the reaction system with the formation of molecular oxygen (curve 5).

The interrelationship between these reactions and their synchronous flow can also be seen by the nature of the curves, as by the accumulation of secondary reaction products (ethyl alcohol and acetaldehyde), the amount of primary reaction products (water and molecular oxygen) decreases, and kinetic curves 1 and 5 pass through extreme points, i.e. the minimum of kinetic curve 5 (catalase reaction) corresponds to the maximum of kinetic curve 1 (monooxygenase reaction).

In case where, due to kinetic reasons, the synchronization of the monooxygenase reaction (curve 1) with the catalase reaction (curve 5) occurs with some delay, a phase shift (Δ), shown in Fig. 1 by a dotted curve, occurs. On this curve, the maximum is shifted to the right by Δ, which can be characterized as a quantitative value of the phase shift. In other words, the phase shift means the difference between the minimum of catalase (curve 1) and the maximum of monooxygenase (curve 5) reactions, which is observed in some cases of the process, associated with the reaction conditions. So, from the data in Fig. 1, it unambiguously follows that the kinetics of acetaldehyde formation from ethylene is sequential: the observed maximum on the formation curve of C_2H_5OH in the reaction system is 20 wt.% aqueous solution of H_2O_2 taken into the reaction, and the curve of CH_3CHO formation is S-shaped.

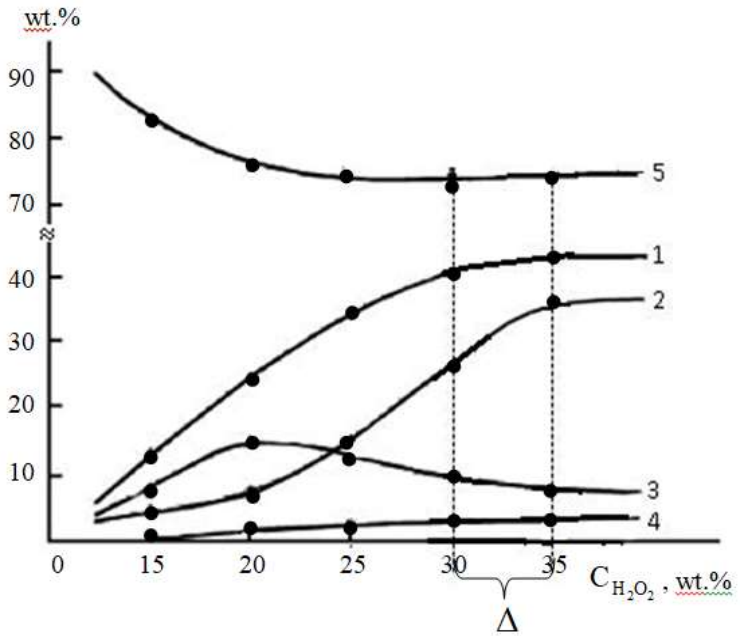
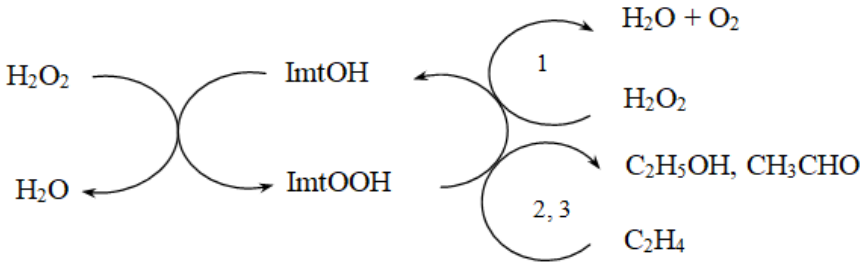


Fig. 1. Dependence of the ethylene monooxidation reaction products yields on the concentration of hydrogen peroxide aqueous solution (t = 140ºC, $V_{C_2H_4}$ = 0.22 l/h, $V_{H_2O_2}$ = 1.72 ml/h). 1 – conversion of C_2H_4; 2 – CH_3CHO; 3 – C_2H_5OH; 4 – CO_2; 5 – O_2.

Thus, a common characteristic feature follows from the experimental data, which make it possible to conclude that curves 1 (catalase reaction) and 5 (monooxygenase reaction) clearly show coherent-synchronized relationship between them: the highest yield of molecular oxygen is in line with the lowest yield of the monooxygenase product. Both curves 1 and 5 (Fig. 1) approach asymptotically with a very small phase shift (Δ).

Results and discussion

The established coherent-synchronized nature and mechanism of the successive stepwise reaction of ethylene oxidation to acetaldehyde associated with the use of hydrogen peroxide as an oxidizing agent can be described by the following scheme [2–4]:



where ImtOH is a per-FTPhPFe^{3+}OH/Al_2O_3 biomimetic catalyst, ImtOOH is an intermediate of bioimitator, per-FTPhPFe^{3+}OOH/Al_2O_3, 1 is a catalase (primary) reaction, 2 and 3 are mono-oxygenase and peroxidase (secondary) reactions. The interrelation between these reactions occurs with the help of the intermediate active complex (ImtOOH), which is formed as a result of the interaction of hydrogen peroxide with a bioimitator.

Each stage of the sequential conversion of ethylene by hydrogen peroxide on a biomimetic catalyst is a complex (conjugate) reaction. Due to the inducing effect of the catalase reaction these complex reactions also consist of two coherent-synchronized occurring reactions: 1 is the reaction of hydrogen peroxide decomposition, 2 is the reaction of ethylene oxidation to ethyl alcohol and 3 is the reaction of ethyl alcohol oxidation to acetaldehyde.

The appropriate gross reactions have the following form:

Catalase reaction (the reaction of hydrogen peroxide decomposition):

$$H_2O_2 + H_2O_2 = 2H_2O + O_2 + 207.92\,kJ/mol \quad \text{primary} \qquad (I)$$

Actor inductor

Monooxygenase reaction (the reaction of ethylene oxidation to ethyl alcohol):

$$H_2O_2 + C_2H_4 = C_2H_5OH + \tfrac{1}{2}O_2 + 148.08\,kJ/mol \quad \text{secondary} \qquad (II)$$

Actor acceptor

Peroxidase reaction (the reaction of ethyl alcohol oxidation to acetaldehyde):

$$H_2O_2 + C_2H_5OH = CH_3CHO + 2H_2O + 315.08\,kJ/mol \quad \text{secondary} \qquad (III)$$

Actor acceptor

According to the theory of coherent-synchronized reactions [2-4] and ideas about the mechanisms of monooxygenase reactions, a probable scheme of the mechanism of ethylene monooxidation by hydrogen peroxide on the per-FTPhPFe^{3+}OH/Al_2O_3 biomimetic catalyst can be presented in the form of the following elementary stages:

$$H_2O_2 + Im\,tOH \underset{k_1}{\Leftrightarrow} H_2O + Im\,tOOH \quad (IV)$$

$$H_2O_2 + ImtOOH \xrightarrow{k_{-1}\ k_2} H_2O + O_2 + ImtOH \quad (V)$$

$$C_2H_4 + ImtOOH \xrightarrow{k_3} C_2H_5OH + Imt{=}O \xrightarrow{H_2O} ImtOH \quad (VI)$$

$$C_2H_5OH + ImtOOH \xrightarrow{k_4} CH_3CHO + H_2O + ImtOH \quad (VII)$$

In the kinetic description of the reactions taking place in the system, it is commonly assumed that the stage of the intermediate (ImtOOH) formation is fast (IV). The calculated values of thermal effects of catalase, monooxygenase and peroxidase reactions (I)-(III) show that the stage (VII), peroxidase reaction, is much more exothermic than monooxygenase (VI). This gives us the opportunity to assume that the stage of ethyl alcohol formation from ethylene is likely to be limiting, i.e. the rate of the ethylene monooxidation reaction can be taken as the rate of ethylene consumption in step (VI).

Establishing the coherent-synchronized nature of the stepwise reaction of ethylene oxidation by H_2O_2 requires a new approach to kinetic studies that takes into account the chemical interference in the reaction medium. The condition of chemical interference is qualitatively and quantitatively characterized by the determinant equation as follows [1-4]:

$$D = \nu\left(\frac{r_{A_1}}{r_{Acc}} + \frac{r_{A_2}}{r_{Acc}}\right)^{-1} \quad (1)$$

where D is the determinant factor, the value of which within 0 < D < 1 corresponds to the conditions of chemical interference; r_{A_1} and r_{A_2} are the rates of actor consumption (H_2O_2) for the formation of target products in the primary (catalase) and secondary (monooxygenase and peroxidase) reactions; where r_{Acc} is the rate of acceptor consumption (C_2H_4); ν is the stoichiometric coefficient of the actor, which makes it possible to identify the type of interaction between reactions on the quantitative basis (in our case, ν = 1).

It is of interest to conduct a kinetic study of the stepwise reaction of ethylene oxidation by hydrogen peroxide on the biomimetic catalyst using the determinant equation, which makes it possible to calculate separately the rates of all elementary stages (4-6).

$$r_{1,H_2O_2} = k_1[H_2O_2][ImtOH] \quad (2)$$

$$r_{2,H_2O_2} = k_2[H_2O_2][ImtOOH] \quad (3)$$

$$r_{mon.} = k_3[C_2H_4][ImtOOH] \quad (4)$$

$$r_{per.} = k_4[C_2H_5OH][ImtOOH] \quad (5)$$

where r_{1,H_2O_2} is the rate of hydrogen peroxide consumption in the reaction of intermediate formation; r_{2,H_2O_2} is the rate of hydrogen peroxide consumption in the catalase reaction; $r_{mon.}$ is the rate of the monooxygenase reaction (the reaction of hydrogen peroxide consumption in the reaction of ethylene monooxidation; $r_{per.}$ is the rate of the peroxidase reaction of acetaldehyde formation; $[C_2H_5OH]$ is the current concentration of ethanol.

As noted above, the rate of the ethylene monooxidation reaction can be taken as the rate of ethylene consumption in step 6, while neglecting the rate of the peroxidase reaction.

In considering in our case that ν = 1, the stoichiometric coefficient of the actor, hydrogen peroxide (gross reaction 1), the rate of the catalase reaction ($r_{cat.}$) or the rate of hydrogen peroxide consumption will be as follows:

$$r_{cat.} = r_{1,H_2O_2} + r_{2,H_2O_2} \quad (6)$$

And the rate of the monooxygenase reaction will be:

$$r_{C_2H_4} = r_{mon.} = k_3[C_2H_4][ImtOOH] \quad (7)$$

And this is equal to the rate of hydrogen peroxide consumption in the reaction of ethylene monooxidation to ethyl alcohol $r_{C_2H_4} = r_{3,H_2O_2}$.

Taking into the account expressions (Eq. 6) and (Eq. 7), the determinant equation (Eq. 1) will be as follows:

$$D = \nu\left(\frac{r_{cat.}}{r_{C_2H_4}} + \frac{r_{mon.}}{r_{C_2H_4}}\right)^{-1} \quad (8)$$

According to the method of stationary concentrations, we know that:

$$\frac{d[ImtOOH]}{d\tau} = k_1[H_2O_2][ImtOH] - k_2[H_2O_2][ImtOOH] - k_3[C_2H_4][ImtOOH] \approx 0 \quad (9)$$

$$r_{3,H_2O_2} = r_{1,H_2O_2} - r_{2,H_2O_2} \quad (10)$$

Substituting (Eq. 6) and (Eq. 7) into equation (Eq. 1), we have:

$$D = \nu\left(\frac{r_{1,H_2O_2} + r_{2,H_2O_2}}{r_{C_2H_4}} + \frac{r_{1,H_2O_2} - r_{2,H_2O_2}}{r_{C_2H_4}}\right)^{-1} \quad (11)$$

Transforming equation (Eq. 11) we have:

$$D = \frac{r_{C_2H_4}}{2r_{1,H_2O_2}} \quad \text{or} \quad r_{1,H_2O_2} = \frac{r_{C_2H_4}}{2D} \quad (12)$$

The expression for the concentration of the intermediate derived by the method of stationary concentrations is:

$$[ImtOOH] = \frac{k_1[H_2O_2][ImtOH]}{k_2[H_2O_2] + k_3[C_2H_4]} \quad (13),$$

Substituting into the equation (Eq. 7) we obtain the kinetic equation for the rate of ethylene consumption in the monooxygenase reaction:

$$r_{C_2H_4} = \frac{k_1 k_3}{k_2}[ImtOH][C_2H_4] \quad (14)$$

Let us express in the equation (Eq. 14) the reaction rate constants and the concentration of the bioimitator through the effective rate constant of the monooxygenase reaction as

$$k_{eff.}^{mon.} = \frac{k_1 k_3}{k_2}[ImtOH] \quad (15)$$

we have: $r_{C_2H_4} = k_{eff.}^{mon.}[C_2H_4]$ (16)

Substituting the equation (Eq. 16) into (Eq. 12), we obtain an equation for the rate of hydrogen peroxide consumption in the reaction of intermediate formation:

$$r_{1,H_2O_2} = \frac{k_{eff.}^{mon.}[C_2H_4]}{2D} \quad (17)$$

Or for the effective rate constant of the monooxygenase reaction we have:

$$k_{eff.}^{mon.} = \frac{2r_{1,H_2O_2}D}{[C_2H_4]} \quad (18)$$

Substituting expressions (Eq. 2) – (Eq. 4) into the determinant equation (Eq. 8), and taking into account that the rate of the catalase reaction is much higher than the rate of the monooxygenase reaction $k_2[H_2O_2] >> k_3[C_2H_4]$, we obtain the following expression for the concentration of the intermediate:

$$[ImtOOH] = \frac{k_1}{k_3}\frac{D[H_2O_2][ImtOH]}{[C_2H_4]} \quad (19)$$

Substituting the concentration of the intermediate, expressed through equation (Eq. 19), into the equation for the rate of hydrogen peroxide consumption in the catalase reaction (Eq. 3) we have:

$$r_{2,H_2O_2} = k_2\frac{k_1}{k_3}\frac{D[H_2O_2][ImtOH]}{[C_2H_4]}[H_2O_2] \quad (20)$$

In the equation (Eq. 21), we express the rate constants and the bioimitator concentration through the effective rate constant of the catalase reaction:

$$k_{eff.}^{cat.} = \frac{k_2 \cdot k_1}{k_3}[ImtOH] \quad (21)$$

We obtain an equation for the rate of hydrogen peroxide consumption in the catalase reaction:

$$r_{2,H_2O_2} = k_{eff.}^{cat.}\frac{D[H_2O_2]^2}{[C_2H_4]} \quad (22)$$

$$k_{eff.}^{cat.} = \frac{r_{2,H_2O_2}[C_2H_4]}{D[H_2O_2]^2} \quad (23)$$

As can be seen from the equations (Eq. 18) and (Eq. 23), the effective rate constants of the catalase and monooxygenase reactions depend, in addition to other reaction parameters, on the value of the determinant factor D, which is a fundamental result confirming the coherent-synchronized nature of these reactions.

Considering the sequential nature of ethylene transformation into ethyl alcohol, and then the ethyl alcohol into acetaldehyde, we can develop the kinetic equation for the ethylene oxidation reaction with due regard for the rate of hydrogen peroxide consumption in the peroxidase reaction ($r_{4,H_2O_2} = r_{per.}$) into the determinant equation (Eq. 1), where we have:

$$D = \nu\left(\frac{r_{2,H_2O_2} + r_{3,H_2O_2} + r_{4,H_2O_2}}{r_{C_2H_4}}\right)^{-1} \quad (24)$$

For $\nu = 1$, the determinant equation will be as following:

$$D = \frac{r_{C_2H_4}}{r_{2,H_2O_2} + r_{3,H_2O_2} + r_{4,H_2O_2}} \quad (25)$$

Based on the method of stationary concentrations [14] from the equations (Eq. 2) – (Eq. 5) we have:

$$r_{1,H_2O_2} = r_{2,H_2O_2} + r_{3,H_2O_2} + r_{4,H_2O_2} \approx 0 \quad (26)$$

Substituting the expressions for the rates of hydrogen peroxide consumption for all four reactions (Eq. 2) - (Eq. 5) into equation (Eq. 26), we have:

$$k_1[H_2O_2][ImtOH] = k_2[H_2O_2][ImtOOH] + k_3[C_2H_4][ImtOOH] + k_4[C_2H_5OH][ImtOOH] \quad (27)$$

Expressing the rate of hydrogen peroxide consumption in the peroxidase reaction through reaction rate constants, we obtain:

$$r_{4,H_2O_2} = r_{CH_3CHO}^{form.} = r_{1,H_2O_2} - r_{2,H_2O_2} - r_{3,H_2O_2} = k_1[H_2O_2][ImtOH] - k_2[H_2O_2][ImtOOH] - k_3[C_2H_4][ImtOOH] \quad (28)$$

Substituting (Eq. 28) into the determinant equation (Eq. 25) for the concentration of the ImtOOH intermediate, we obtain the following expression:

$$[ImtOOH] = \frac{Dk_1[H_2O_2][ImtOH]}{k_3[C_2H_4]} \quad (29)$$

Substituting (Eq. 29) into equation (Eq. 23) for the rate of the peroxidase reaction (Eq. 30), i.e. the rate of acetaldehyde formation, we get:

$$r_{CH_3CHO}^{form.} = \frac{k_1k_4D[ImtOH]}{k_3}\frac{[H_2O_2][C_2H_5OH]}{[C_2H_4]} \quad (30),$$

Where $k_{eff.}^{per.} = \frac{k_1 k_4 [ImtOH]}{k_3}$ (31)

Then the rate of the peroxidase reaction of acetaldehyde formation will take the following form:

$$r_{CH_3CHO}^{form.} = k_{eff.}^{per.} \frac{[H_2O_2][C_2H_5OH]D}{[C_2H_4]} \quad (32)$$

From where the effective rate constant of the peroxidase reaction can be represented as the following expression:

$$k_{eff.}^{per.} = r_{CH_3CHO}^{form.} \frac{[C_2H_4]}{[H_2O_2][C_2H_5OH]D} \quad (33)$$

As can be seen from the equation (Eq. 34), the effective rate constant of the peroxidase reaction also depends on the determinant factor (D) and takes into account the coherent-synchronized nature of the reactions occurring in the system.

Using the values of the effective rate constants of catalase, monooxygenase and peroxidase reactions calculated from experimental data from equations (Eq. 18), (Eq. 23) and (Eq. 33) and the values of the determinant, we can calculate the effective activation energies of these reactions, given in Table 1.

Table 1. Values of the effective kinetic parameters of the reaction found on the basis of the kinetic model using the determinant equation

T, [K]	D	$k_{eff.}^{cat.} \times 10^4$ [s^{-1}]	$k_{eff.}^{mon.}$ [s^{-1}]	$k_{eff.}^{per.}$ [s^{-1}]	$E_{eff}^{cat.}$, [kJ/mol]	$E_{eff}^{mon.}$, [kJ/mol]	$E_{eff.}^{per.}$, [kJ/mol]
413	0.20	0.33	0.09	62.37	19.5	37.2	25.6
433	0.25	0.55	0.14	121.47			
473	0.29	0.88	0.20	188.56			

The obtained values of the effective activation energies of three reactions occurring in the system (catalase, monooxygenase and peroxidase) allowed us to reach the following significant factor: $E_{eff.}^{mon.} > E_{eff}^{per.} > E_{eff.}^{cat.}$

When comparing the effective activation energies of the three reactions occurring in the system (catalase, monooxygenase and peroxidase), we conclude that the rate of the monooxygenase reaction is lower than the rates of the catalase and peroxidase reactions, which confirms the aforementioned about the rates of these reactions.

It should also be noted that the $E_{eff}^{per.}$ (25.06 kJ/mol) of the elementary peroxidase stage of ethylene oxidation to ethyl alcohol and then to acetaldehyde corresponds to the $E_{eff}^{per.}$ (24.78 kJ/mol) of the peroxidase oxidation of ethyl alcohol to acetaldehyde [14].

An analysis of the numerical values of k_{eff} (Table 1) makes it possible to compare the rate constants of the elementary stages of the ethylene biomimetic oxidation reaction (k_2, k_3 and k_4), from which the following consequences can be deduced:

1) $k_2 >> k_3$, then $k_{eff} \approx k_2$
2) $k_3 >> k_2$, then $k_{eff} \approx k_3$
3) $k_4 >> k_3$, then $k_{eff} \approx k_4$

4) $k_2 > k_3$ or $k_3 > k_2$, analysis becomes more complex
5) $k_2 \approx k_3$ – these reactions are equalized.

Knowing the effective rate constants of the reactions occurring in the system (catalase, monooxygenase and peroxidase), it is possible to compare the rate constants of elementary reactions. With the ratio of effective rate constants of catalase and monooxygenase reactions, we have the following ratio of constants (k_2 and k_3):

$$\frac{k_{eff}^{cat.}}{k_{eff}^{mon.}} = \left(\frac{k_2}{k_3}\right)^2 \quad (34)$$

Through the substitution of the values of the identified effective rate constants of the catalase and monooxygenase reactions into equation (Eq. 34), we observe that the rate constant of the catalase reaction exceeds the rate constant of the monooxygenase reaction by approximately $2 \cdot 10^2$ times, which confirms our earlier assumptions about the rates of these reactions.

With the ratio of the effective rate constants of the peroxidase and monooxygenase reactions, we have the following ratio of the rate constants (k_4 and k_3):

$$\frac{k_{eff}^{per.}}{k_{eff}^{mon}} = \frac{k_4}{k_3} \quad (35)$$

With the ratio of the effective rate constants of the catalase and peroxidase reactions, we have the following ratio of the rate constants (k_2 and k_4):

$$\frac{k_{eff}^{cat.}}{k_{eff}^{per.}} = \frac{k_2}{k_4} \quad (36)$$

When substituting the numerical values of the effective rate constants of the catalase, monooxygenase, and peroxidase reactions into equations (Eq. 33), (Eq. 34) and (Eq. 35) and entering the obtained data in Table 2, we have:

Table 2. Ratio of rate constants of reactions occurring in the system.

T,[K]	k_2/k_3	k_2/k_4	k_4/k_3
413	191.5	221	168.7
433	198.2	141	282.4
473	209.8	122	365.0

As can be seen from the Table 2, the rate constant of the catalase reaction exceeds the rate constants of the monooxygenase and peroxidase reactions, while the rate constant of the peroxidase reaction exceeds the rate constant of the monooxygenase reaction, which confirms our assumptions about the rates of these reactions.

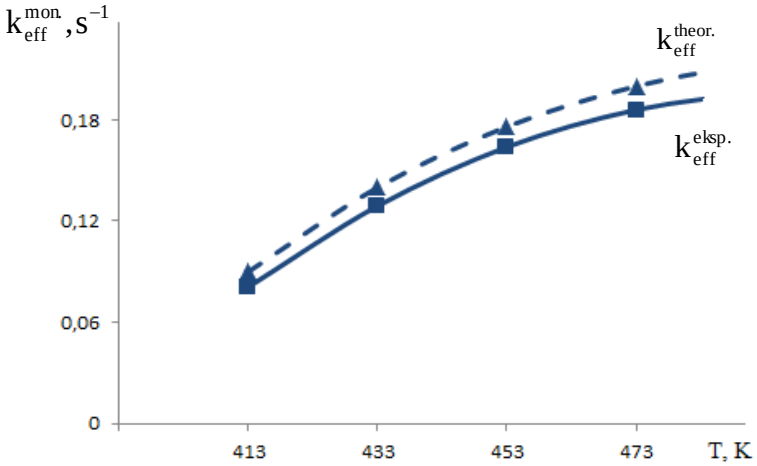


Fig. 2. Dependence of the effective rate constant of monooxygenase reaction on temperature

As can be seen from Fig. 2, increased error values correspond to high process temperatures, which, apparently, are associated with the formation of by-products in very small amounts that are not taken into account in the proposed model.

Conclusion

As a result of our kinetic study of the ethylene biomimetic monooxidation reaction by hydrogen peroxide to ethyl alcohol and acetaldehyde on the per-FTPhPFe^{3+}OH/Al_2O_3 bioimitator, we come to the following conclusion: the kinetic model, developed on the basis of the determinant equation and the coherence ratio of coherent-synchronized catalase, monooxygenase and peroxidase reactions, is characterised by highly adequate description of experimental data.

Thus, a new approach to kinetic modeling has been developed on the basis of the determinant equation and the coherence relation of coherent-synchronized catalase-monooxygenase and catalase-peroxidase reactions, which can be further applied to other complex processes of hydrocarbon oxidation of coherent-synchronized nature. Kinetic modeling was also carried out with the aim of further application of the chosen model in the optimization and design of this process.

References

1. Nagiyev T.M. Chemical conjugation Moscow: Nauka Publ., 1989, 216 p. (In Russian).
2. Nagiyev T.M. Interaction of synchronous reactions in chemistry and biology. Baku: Elm, 2001, 404 p. (In Russian)
3. Nagiyev T.M. Conjugate reactions in the context of modern ideas. Baku, 2020. 205 p.
4. Nagiev T.M. Coherent Synchronized Oxidation Reactions by Hydrogen Peroxide. Amsterdam: Elsevier, 2007. 325 p.
5. Nasirova U.V., Gasanova L.M., Nagiev T.M. Monooxidation of ethylene by hydrogen peroxide on biomimetic per-FTPhPFe^{3+}OH/Al_2O_3. *Russian Journal of Physical Chemistry A*, 2010, vol. 84, no. 6, pp. 941-945.
6. Matveev K.I., Zhizhina Ye.Q., Shitova N.B., Kuznetsova L.M. Kinetics of ethylene oxidation to acetaldehyde by phosphomolybdenum vanadium heteropolyacids in the presence of an aqua complex. *Kinetika i kataliz*, 1977, vol. 18, no.2, pp. 380-386. (In Russian).
7. Minachev Kh.M., Rodin N.Ya., Isakov Ya.I. Catalyst for the oxidation of olefins to aldehydes and ketones. A.S. 680533 (USSR). *Inventions Bulletin*. 1980, no. 31.

8. Rizkalla N., Bays B.S. Method of molecular oxidation of ethylene. Patent N 2335498C2, Rossiya, 2008.
9. Nagiyev T.M. Simulation modeling of enzymatic catalysis *Zhurnal fizicheskoy khimii*, 1996, vol. 70, no. 6, pp. 967-976. (In Russian).
10. T.M.Nagiev. New Approaches to Simulation of Enzymatic Reactions: Mimetic Catalysis. *Journal of Chemistry: Education Research and Practice*. 2019, vol. 3, no 2.
11. Stephenson N.A., Bell A.T. Effects of porphyrin composition on the activity and selectivity of the iron (III) porphyrin catalysts for the epoxidation of cyclooctene by hydrogen peroxide. *Journal of Molecular Catalysis A: Chemical*. Elsevier, July 2007, vol. 272, no. 1-2, pp. 108-117.
12. Nagiyev T.M., Gasanova L.M., Zulfuqarova S.Z., Mustafayeva Ch.A. Ustoychiviy k okisleniyu i naqrevu monooksigenazniy imitator – perftortetrafenilporfirin Fe (III), immobilizovanniy na okside aluminiya. *Zhurnal fizicheskoy khimii*, 1996, vol. 70, no. 11, pp. 2063-2068. (In Russian).
13. Nasirova U.V., Gasanova L.M., Nagieva I.T., et al. Coherent Synchronized Monooxidation of Low Alkenes on Heterogeneous Ironporphyrin Biomimic per-FTPhPFe^{3+}OH/Al_2O_3. Catalysis for a Sustainable World, EuropaCat IX, Salamanca (Spain), 30th August - 4th September 2009, p. 313.
14. Nasirova U.V., Nagiyeva I.T., Gasanova L.M., Nagiyev T.M. Kineticheskoye issledovaniye reaktsii monooksidirovaniya etilena nad biomimeticheskim katalizatorom – per-FTPhPFe^{3+}OH/Al_2O_3 metodom statsionarnix kontsentratsiy. *Chemical Problems.* 2011, no. 1, pp. 131-133.

НОВЫЙ МЕТОД КИНЕТИЧЕСКОГО МОДЕЛИРОВАНИЯ РЕАКЦИИ ОКИСЛЕНИЯ ЭТИЛЕНА В ЭТИЛОВЫЙ СПИРТ И АЦЕТАЛЬДЕГИД ПЕРОКСИДОМ ВОДОРОДА НА БИОИМИТАТОРЕ per-FTPhPFe^{3+}OH/Al_2O_3

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Аннотация: Исследован процесс биомиметического монооксидирования этилена пероксидом водорода в этиловый спирт и ацетальдегид на биоимитаторе per-FTPhPFe^{3+}OH/Al_2O_3, который проявил высокую активность и уникальную устойчивость к действию высокоактивных промежуточных продуктов реакции. В результате изучения кинетических закономерностей селективного биомиметического окисления этилена пероксидом водорода установлен когерентно-синхронизированный характер протекания реакции, состоящей из двух: 1) первичной (каталазной) и 2) вторичной (монооксигеназной и пероксидазной) реакций. Разработан новый подход к кинетическому моделированию на основе уравнения детерминанты и соотношения когерентности когерентно-синхронизированных между собой каталазной-монооксигеназной и каталазной-пероксидазной реакций. На основе уравнения детерминанты, которая позволяет качественно и количественно оценить когерентный характер синхронно протекающих реакций, составлена кинетическая модель процесса, на основе которой выведены эффективные константы скоростей каталазной, монооксигеназной и пероксидазной реакций, а также рассчитаны их эффективные энергии активации.

Ключевые слова: этилен, этиловый спирт, ацетальдегид, пероксид водорода, биомиметический катализатор, кинетическая модель, когерентно-синхронизированные реакции.

BİOİMİTATOR PER-FTPhPFe^{3+}OH/Al_2O_3 ÜZƏRİNDƏ ETİLENİN HİDROGEN PEROKSİDLƏ ETİL SPİRTİ VƏ ASETALDEHİDƏ OKSİDLƏŞMƏSİ REAKSİYASININ YENİ ÜSULLA MODELLƏŞDİRİLMƏSİ

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Xülasə: Yüksək aktivlik və aktiv aralıq maddələr təsirinə yüksək davamlılıq göstərən bioimitator per-FTPhPFe^{3+}OH/Al_2O_3 üzərində etilenin hidrogen peroksidlə etil spirti və asetaldehidə monooksidləşməsi prosesinin tədqiqi aparılmışdır. Etilenin hidrogen peroksidlə selektiv biomimetik oksidləşməsinin kinetik qanunauyğunluqlarının öyrənilməsi nəticəsində reaksiyanın iki reaksiyadan: 1) ilkin (katalaz) və 2) ikinci (monooksigenaz və peroksidaz) reaksiyalardan ibarət koherent-sinxronlaşmış xarakteri müəyyən edilmişdir. Katalaz-monooksigenaz və katalaz-peroksidaz koherent-sinxronlaşmış reaksiyaların koherentlik nisbəti və determinant tənliyi əsasında kinetik modelləşdirilməsinin yeni metodu işlənib hazırlanmışdır. Sinxron gedən reaksiyaların koherentlik xüsusiyyətini kəmiyyət və keyfiyyətcə təyin edən determinant tənliyi əsasında kinetik model tərtib edilmiş və bu modelə əsasən katalaz, monooksigenaz və peroksidaz reaksiyaların effektiv sürət sabitləri və effektiv aktivləşmə enerjiləri təyin edilmişdir.

Açar sözlər: etilen, etil spirti, asetaldehid, hidrogen peroksid, biomimetik katalizator, kinetik model, koherent-sinxronlaşmış reaksiyalar.