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# MACROKINETIC COHERENCE OF GAS-PHASE ETHYLENE MONOOXIDATION REACTION BY HYDROGEN PEROXIDE

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## ABSTRACT

The gas-phase monooxidation of ethylene by hydrogen peroxide on a biomimetic heterogeneous catalyst, perfluorinated iron (III) tetraphenylporphyrin, deposited on alumina (per-FTPhPFe3+OH/Al2O3)was studied under comparatively mild conditions. The biomimetic oxidation of ethylene with hydrogen peroxide was shown to be coherently synchronized with the decomposition of H2O2. Depending on reaction medium conditions, one of two desired products was formed, either ethanol or acetaldehyde. The probable mechanism of ethylene transformation was studied. A kinetic model that fits the experimental data is studied on the basis of the most probable mech-anism of ethylene oxidation by hydrogen peroxide over a biomimetic catalyst (per-FTPhPFe3+OH/Al2O3). Effective rate constants for the catalase and monooxygenase reactions and their effective activation energies are found.

**KEYWORDS:** biomimetic, oxidation, ethylene, kinetic model, hydrogen peroxide, alumina.

## INTRODUCTION

High activity and steadiness of heterogeneous iron porphyrin catalyst – per-FTPhPFe$^{3+}$OH/$Al_2O_3$ to oxidizer in the reactions of alkanes and alkenes monooxidation allowed us to use this biomimetic with high efficiency in the gas-phase monooxidation reaction of ethylene by hydrogen peroxide.Biomimetic catalysts, which are mimetic analogues of hemin-containing enzymes, are known to be $H^+$-dependent redox systems. Metalloporphyrin biomimetic catalysts, which contain inorganic oxides, for instance, $Al_2O_3$, as a matrix, have acid-base centers, which play an important role in the mechanism of formation of reaction products [1].

## MATERIALS AND METHODS

*Materials.*The synthesis of the active center of biomimetic catalyst per-FTPhPFe$^{3+}$ is a multistep process described in [2,3]. The solid matrix for the immobilization of active center was activated or neutral alumina from Aldrich (standard) with spherical particles 1.5mm in diameter and with a specific surface area no less than 500m$^2$/g. Possible impurities (in particular, stabilizers) were removed from hydrogen peroxide (Perhydrol) of kh.ch. (chemically pure) grade by vacuum distillation. Another starting material was ethylene with purity of 99.99%.
*Methods.*The immobilization of per-FTPhPFe$^{3+}$OH on $Al_2O_3$ (1.58mg/g) was performed from its solution in dimethylformamide by impregnating alumina.

The gas-phase monooxidation reaction with the participation of hydrogen peroxide was conducted in a flow quartz reactor with a 3 cm$^3$ reaction zone volume (d=1.8cm); the construction of the reactor enabled $H_2O_2$ to be introduced in undecomposed form [4]. Reaction products were analyzed byChrome-mass spectrometer of thecompany Saturn 2100T Varian and gas-liquid chromatography using a column (length=100cm, d=0.3cm) packed with Paropack Q as the adsorbent. The temperature of the column was 120ºC, and the pressure of carrier gas (helium) was 0.4kgf/cm$^2$.

Experimental studies have demonstrated the possibility of flexible control over ethylene monooxidation by hydrogen peroxide for the production of both ethyl alcohol and acetaldehyde (temperature, 120°C; $H_2O_2$ concentration, 30%; molar ratio, $C_2H_4$:$H_2O_2$ = 1:1.7; rate of supply, $C_2H_4$ 0.22l/h, $H_2O_2$ 1.72ml/h) to obtain the best yield of ethyl alcohol, 15.4wt% (acetaldehyde 12wt%) and, in contrast (temperature, 200°C; concentration

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of a solution of hydrogen peroxide in water, 30%; molar ratio $C_2H_4$:$H_2O_2$ = 1:1.7), an acetaldehyde yield of 34.6wt% (ethanol 4.6wt%). The selectivity of the process under the conditions of maximum ethyl alcohol yield and minimum acetaldehyde yield was virtually 100wt%, recalculated for monooxygenase products. Selectivity in obtaining maximum acetaldehyde yield was somewhat lower (87wt%) due to the production of $CO_2$ as a by-product.

## RESULTS AND DISCUSSION

The kinetic regularities obtained as a result of experimental studies [5-7] provide an idea (albeit incomplete) of the mechanism of ethylene monooxidation by hydrogen peroxide.

It can be seen from Fig.1 that the kinetics of acetaldehyde production from ethylene is sequential in character. The observed maximum on the kinetic accumulation curve in the reaction system $C_2H_5OH$ corresponds to a concentration of 20wt% $H_2O_2$ (Fig. 1, curve 3), while the curve of $CH_3CHO$ production has an S shape. The kinetic curve in Fig.1b indicates the sequential character of $CH_3CHO$ production; the yield of $C_2H_5OH$ declines, while the yield of $CH_3CHO$ increases. The kinetic curve of ethyl alcohol yield has a shape with a maximum, while the curve of $CH_3CHO$ production has an S shape.

It also follows from the kinetic data shown in Fig.1b that kinetic curves 1 and 5 (which correspond to the yields of monooxygenase products and molecular oxygen) are coherently synchronized; i.e., the highest $O_2$ yield corresponds to the lowest yield of monooxygenase products, while the lowest yield of molecular oxygen corresponds to the highest yield of monoxide compounds. Both curves (*1* and *5*) in Fig.1 approach one another asymptotically with a negligible phase shift Δ [1].

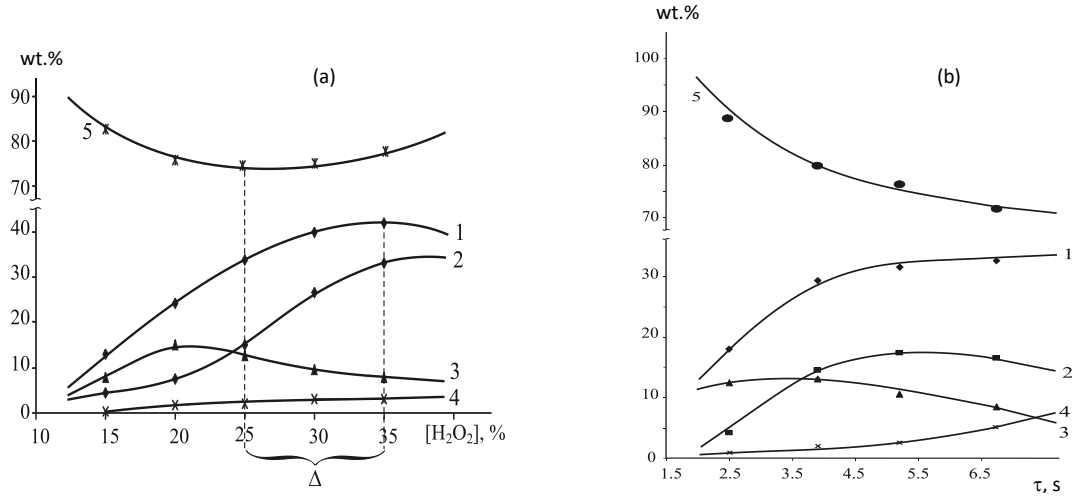


*Figure 1.* ***Product yields of ethylene monooxidation reaction as functions of (a) the concentration of water solution of hydrogen peroxide and (b) contact time τ under the following conditions: T = 140°C, (a) $W_{C_2H_4}$ = 0.22 l/h, (b) $W_{H_2O_2}$ = 1.72 ml/h, $C_{H_2O_2}$ = 25%; (1) $C_2H_4$ conversion, (2) $CH_3CHO$ yield, (3) $C_2H_5OH$ yield, (4) $CO_2$ yield, (5) $O_2$ yield.***

It follows from the experimental kinetic regularities that the transformation of ethylene into monooxygenase products proceeds according to the following scheme:

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

Each of these transformations is a complex reaction and consists of two coherent synchronized reactions: (1) primary (catalase) and (2)-(3) secondary (monooxygenase and peroxidase) reactions:

$H_2O_2 + H_2O_2 = 2H_2O + O_2 + 207.92$ kJ/mol, (1)
(actor) (inductor)

$H_2O_2 + C_2H_4 = C_2H_5OH + 1/2O_2 + 148.08$ kJ/mol, (2)
(actor) (acceptor)

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$H_2O_2 + C_2H_5OH = CH_3CHO + 2H_2O + 315.08$ kJ/mol, (3)
(actor) (acceptor)

The coherence condition is satisfied for synchronous reactions [8]:

$$f^0_{H_2O_2} = f^1_{1,H_2O_2} + f^1_{2,H_2O_2} = f^2_{1,H_2O_2} + f^2_{2,H_2O_2} = f^3_{1,H_2O_2} + f^3_{2,H_2O_2} = ... = const, \quad (4)$$

where $f^0_{H_2O_2}$ is the initial amount of hydrogen peroxide (actor), $f_{1,H_2O_2}$ and $f_{2,H_2O_2}$ are the amount of actor ($H_2O_2$) spent on the production of final products in the primary (catalase) and secondary (monooxygenase) reactions, respectively.

According to the theory of coherent synchronized reactions [1] and the concepts of the mechanisms of monooxygenase reactions, the probable mechanism of ethylene oxidation can be presented as follows:

$$H_2O_2 + per - FTPhPFe(III)OH / Al_2O_3 \Leftrightarrow H_2O + per - FTPhPFe(III)OOH / Al_2O_3 \quad (5)$$

$$H_2O_2 + per - FTPhPFe(III)OOH / Al_2O_3 \xrightarrow{K_2} H_2O + O_2 + per - FTPhPFe(III)OH / Al_2O_3 \quad (6)$$

$$C_2H_4 + per - FTPhPFe(III)OOH / Al_2O_3 \xrightarrow{K_3} C_2H_5OH + per - FTPhPFe = O / Al_2O_3 \xrightarrow{H_2O} per - FTPhPFe(III)OH / Al_2O_3 \quad (7)$$

$$C_2H_5OH + per - FTPhPFe(III)OOH / Al_2O_3 \xrightarrow{K_4} CH_3CHO + H_2O + per - FTPhPFe(III)OH / Al_2O_3 \quad (8)$$

In ethylene monooxidation reaction (7), intermediate per-FTPhPFe$^{3+}$OOH/$Al_2O_3$ reduction takes place via a stage of incomplete single-electron reduction with the production of per-FTPhPFe$^{4+}$=O/$Al_2O_3$, which is instantaneously reduced in a water environment to the initial state of biomimetic catalyst (per-FTPhPFe$^{3+}$OH/$Al_2O_3$) [9].

In our kinetic description of the reactions in the system, it is assumed that the stage of intermediate per-FTPhPFe$^{3+}$OOH/$Al_2O_3$ production proceeds quickly (1) [1]. If we calculate the thermal effect of stages (2) and (3), it can be seen that stage (3) (a peroxidase reaction) is much more exothermic than monooxygenase reaction (2). We may therefore assume that the stage of the production of ethyl alcohol from ethylene is probably limiting. This allows us to use Michaelis-Menten equation in terms of the Lineweaver-Burk coordinates for the kinetic simulation of ethylene oxidation above a biomimetic catalyst:

$$\frac{1}{r} = \frac{1}{r_{max}} + \frac{k_m}{r_{max}} \frac{1}{[C_2H_4]} \quad (9)$$

where $r$ is the $C_2H_4$ transformation rate, $r_{max}$ is the maximum reaction rate, $k_m$ is the Michaelis constant, $k_m = (k_{-1} + k_2 + k_3)/k_1$, where $k_1$, $k_{-1}$ are the rates of production and consumption of per-FTPhPFe$^{3+}$OOH/$Al_2O_3$ intermediate at stage (5), $k_2$ is the catalase reaction rate, and $k_3$ is the rate of the ethylene oxidation reaction.

According to this equation, we obtain for all temperatures straight lines that produce a cross section equal to $1/r_{max}$ on the ordinate axis and $1/k_m$ on the abscissa axis (Fig.2).

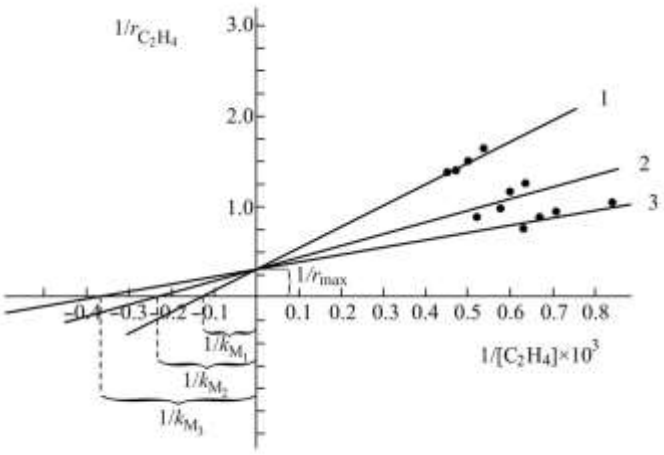

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*Figure 2.* ***Ethylene consumption rate as a function of the concentration in ethylene monooxidation at different temperatures: (1) 140, (2) 160, and (3) 200°C***

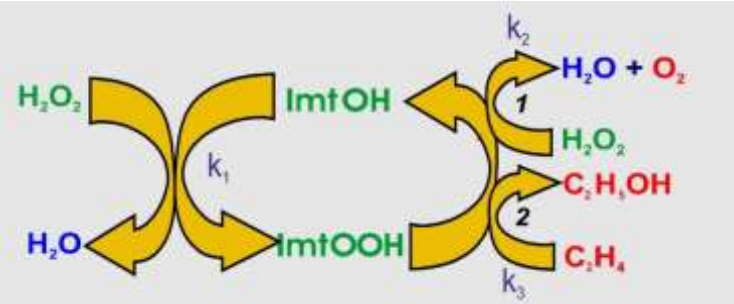
If $k_1 >> k_3$, the quantity $k_m$ is the equilibrium constant for the production of a mimico-substrate complex. Under the condition $k_3 >> k_{-1}$, the quantity $k_m = k_3/k_1$ and the effective reaction rate constant $k_{eff} = 1/k_m$.
The values of $k_m$ found from the plot (Fig.2) allow us to determine the effective reaction rate and effective activation energy (table) for the ethylene oxidation reaction ($E_{eff}$ = 42.0 kJ/mol); this value agrees with the activation energy for enzymatic reactions.

From Eq. (9), we found a common value of *k* for a certain temperature; this value can deviate considerably from the one found in each experiment.

If the Michaelis-Menten equation is used, we thus make a number of assumptions; of course, these assumptions influence the kinetic model's degree of adequacy: (1) an average value is taken in estimating the reaction rates for each temperature, and it cannot be understood from this average value whether the reaction rates in each experiment deviate from one another (the temperature is constant); (2) only one full reaction is described in the case of conjugation.

These disadvantages can be largely avoided if we employ the method of stationary concentrations, which is widely used in chemical kinetics [1]. In this method, we must propose one or a number of hypothetical mechanisms, of which only one fits the experimental data.

The coherent synchronized character of the catalase and monooxygenase reactions is nicely illustrated by the scheme that is essentially a reflection of the mechanism of reactions (5) - (8),




where ImtOH is the biomimetic of per-FTPhPFe$^{3+}$OH/$Al_2O_3$, ImtOOH is the per-FTPhPFe$^{3+}$OOH/$Al_2O_3$ intermediate, 1 is the catalase (primary) reaction, 2 is the monooxygenase (secondary) reaction, $k_1$ is the intermediate production rate, $k_2$ is the catalase reaction rate, and $k_3$ is the monooxygenase reaction rate.

It can be seen from this scheme that the catalase reaction is the primary reaction, and the monooxygenase reaction is the secondary reaction.

We thus derive the following kinetic equation based on the proposed scheme for the coherent synchronized oxidation of ethylene by hydrogen peroxide on a biomimetic [5]:

$$r_{C_2H_4} = k_3[C_2H_4][\mathrm{Im}\,tOOH] \quad (10)$$

$$\frac{d[\mathrm{Im\,tOOH}]}{dt} = k_1[H_2O_2][\mathrm{Im\,tOH}] - k_2[H_2O_2][\mathrm{Im\,tOOH}] - k_3[C_2H_4][\mathrm{Im\,tOOH}] \approx 0, \quad (11)$$

this yields

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$$[\text{Im tOOH}] = \frac{k_1[H_2O_2][\text{Im tOH}]}{k_2[H_2O_2] + k_3[C_2H_4]} \quad (12)$$

Substituting expression (11) into Eq. (9), we obtain

$$r_{C_2H_4} = k_1 k_3 [\text{Im tOH}] \frac{[H_2O_2][C_2H_4]}{k_2[H_2O_2] + k_3[C_2H_4]} \quad (13)$$

The rate of the catalase reaction, as a rule, considerably exceeds that of the monooxygenase reaction; it may therefore be assumed that$k_2$ $[H_2O_2]$ >> $k_3$ $[C_2H_4]$.

We then obtain

$$r_{C_2H_4} = k_{eff}[C_2H_4] \text{ or } k_{eff} = \frac{r_{C_2H_4}}{[C_2H_4]} \quad (14)$$

where $k_{eff} = \frac{k_1 k_3}{k_2}[\text{Im } tOH]$

We calculated the values of$k_{eff}$ (table) based on Eq. (14) and the experimental data for each particular experiment at different temperatures. It can be seen from the table that the values of $k_{eff}$ for each temperature differ by an allowable deviation from an average of about 10%. Using the average value of $k_{eff}$ determined for each temperature, the Arrhenius equation was used to determine $E_{eff}$ = 59.0 kJ/mol (see table). This value also agrees with the activation energy values for enzymatic reactions.

Note that the method of stationary concentrations has certain disadvantages: (1) the difference between the rates of accumulation and consumption of a highly active intermediate substance is equal to zero; (2) the coherent synchronous character of the primary and secondary reactions is not taken into account.

In this relation, the obtained kinetic information is incomplete: on the one hand, there is no kinetic estimate of the coherence between synchronous reactions (catalase and monooxygenase); on the other hand, the production of molecular oxygen is completely ignored.

***Table.Effective rate constants of ethylene monooxidation by hydrogen peroxide on per-FTPhPFe$^{3+}$OH/$Al_2O_3$ biomimetic ( I - according to Michaelis-Menten equation; II – using the method of stationary concentrations; III – using the determinant equation. $E_{eff}$ in kJ/mol***

| T, K | $k_{eff} \times 10^7$ $sm^3/s/mol$ | $k_1$, $g/(mol\ s)$ | $k_{eff}$, $s^{-1}$ | $k_1$, $g/(mol\ s)$ | $k_{eff}^{cat} \times 10^4$ $s^{-1}$ | $k_{eff}^{mon}$ $s^{-1}$ | $k_1'$ $s^{-1}$ |
|---|---|---|---|---|---|---|---|
| | I, $E_{eff}$ = 42.0 | | II, $E_{eff}$ = 59.0 | | III, $E_{eff}^{cat}$ = 46.0, $E_{eff}^{mon}$ = 58.2 | | |
| 413 | 4.5 | 0.4 | 0.09 | 45.4 | 0.33 | 0.09 | 19.2 |
| 433 | 8.1 | 0.8 | 0.14 | 65.7 | 0.55 | 0.14 | 31.4 |
| 473 | 13.0 | 1.2 | 0.20 | 92.2 | 0.88 | 0.20 | 48.2 |

It follows from the proposed probabilistic mechanism (see the scheme above) of biomimetic ethylene oxidation by hydrogen peroxide that the monooxygenase reaction (the oxidation of ethylene into ethyl alcohol) takes place in conjugation with the catalase reaction (the decomposition of hydrogen peroxide).

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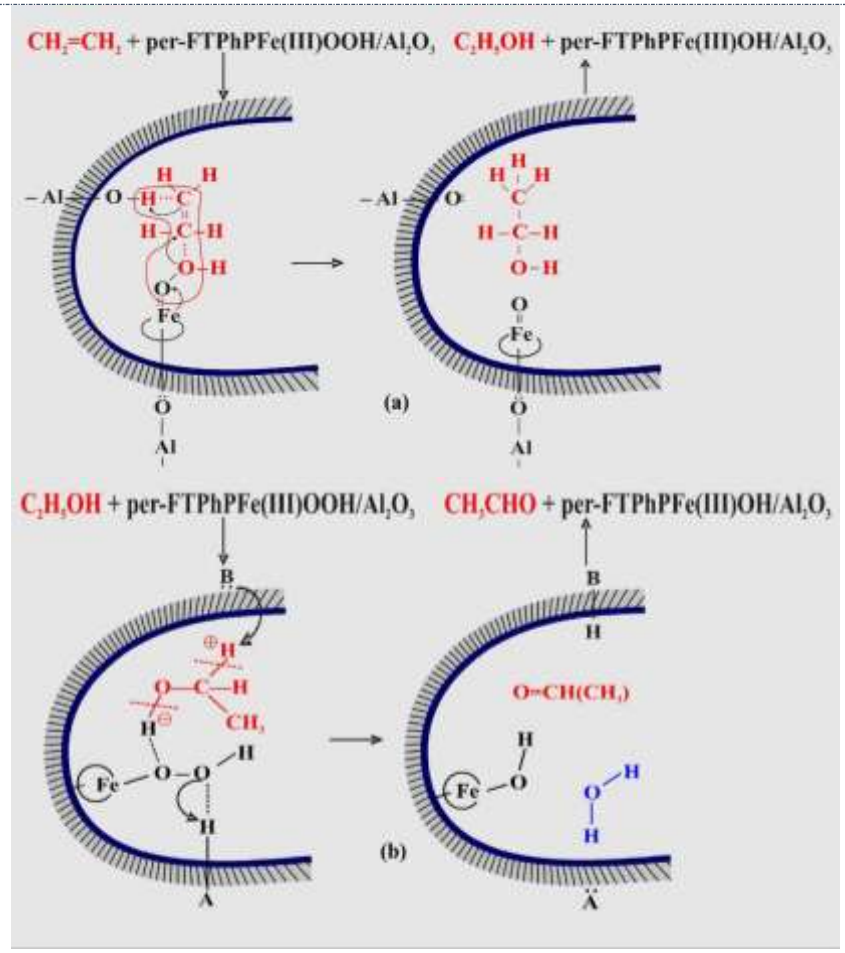


***Figure 3. Mechanisms of biomimetic ethylene oxidation with hydrogen peroxide into (a) ethanol and (b) acetaldehyde***

It is known [1] that a necessary condition for achieving chemical conjugation in this system is its quantitative characteristic, determined by the equation:

$$D = \nu\left(r_{A_1}/r_{Acc} + r_{A_2}/r_{Acc}\right)^{-1} \qquad (15)$$

where $r_{A_1}$ and $r_{A_2}$ are the rates of actor ($H_2O_2$) consumption for the production of final products in the primary (catalase) and secondary (monooxygenase) reactions, respectively; $r_{Acc}$ is the rate of acceptor ($C_2H_4$) consumption; and ν is the stoichiometric coefficient of the actor (in our case, ν = 1).

$$H_2O_2 + \mathrm{Im\,tOH} \xrightarrow{K_1} \mathrm{Im\,tOOH} + H_2O \longrightarrow \begin{cases} \xrightarrow[\text{actor}]{K_2,\ H_2O_2} \mathrm{Im\,tOH} + H_2O + O_2 \\ \xrightarrow[\text{acceptor}]{K_3,\ C_2H_4} C_2H_5OH + \mathrm{Im\,tO} \xrightarrow{H_2O} \mathrm{Im\,tOH} \end{cases}$$

The rates of both reactions (primary catalase and secondary monooxygenase) can thus be calculated:

$$r_{1,H_2O_2} = k_1[H_2O_2][\mathrm{Im}\,tOH] \qquad (16)$$

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$$r_{2,H_2O_2} = k_2[H_2O_2][\mathrm{Im}\,tOOH] \quad (17)$$

$$r_{3,H_2O_2} = k_3[C_2H_4][\mathrm{Im}\,tOOH] \quad (18)$$

Since v = 1 (stoichiometric coefficient of the actor, full reaction (1)), we obtain

$$r_{3,H_2O_2} = r_{C_2H_4} = k_3[C_2H_4][\mathrm{Im}\,tOOH] \quad (19)$$

The determinant equation in this case takes the form:

$$D = \nu\left(r_{2,H_2O_2}/r_{C_2H_4} + r_{3,H_2O_2}/r_{C_2H_4}\right)^{-1} \quad (20)$$

Using the method of stationary concentrations, we find that:

$$r_{H_2O_2} = r_{1,H_2O_2} - r_{2,H_2O_2} - r_{3,H_2O_2} \approx 0 \quad (21)$$

Expression (21) yields: $r_{3,H_2O_2} = r_{1,H_2O_2} - r_{2,H_2O_2}$

Substituting Eq. (21) into Eq. (20), we obtain:

$$D = \nu\left(r_{2,H_2O_2}/r_{C_2H_4} + r_{1,H_2O_2} - r_{2,H_2O_2}/r_{C_2H_4}\right)^{-1} \quad (22)$$

Transforming Eq. (22), we have

$$D = r_{C_2H_4}/r_{1,H_2O_2} \text{ or } r_{1,H_2O_2} = r_{C_2H_4}/D \quad (23)$$

Substituting Eq. (14) into (23), we obtain:

$$r_{1,H_2O_2} = \frac{k_{eff}^{mon}[C_2H_4]}{D}, \quad (24)$$

where $k_{eff}^{mon} = \frac{k_1 k_3}{k_2}[\mathrm{Im}\,tOH]$

this yields the following form for the efficiency of the monooxygenase reaction,

$$k_{eff}^{mon} = \frac{r_{1,H_2O_2} D}{[C_2H_4]} \quad (25)$$

Substituting expressions (16)-(18) into the determinant equation, we obtain the following equation in terms of the two constants:

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$$D = \left( \frac{k_1[H_2O_2][\text{Im } tOH]}{k_3[C_2H_4][\text{Im } tOOH]} \right)^{-1} \quad (26)$$

The intermediate concentration is

$$[\text{Im } tOOH] = \frac{k_1}{k_3} \frac{D[H_2O_2][\text{Im } tOH]}{[C_2H_4]} \quad (27)$$

Expressing the concentration of ImtOOH in the equation of the hydrogen peroxide consumption rate in catalase reaction (17) using Eq. (27), we obtain the equation

$$r_{2,H_2O_2} = k_2 \frac{k_1}{k_3} \frac{D[H_2O_2][\text{Im } tOH]}{[C_2H_4]}[H_2O_2] \quad (28)$$

$$\text{where } k_{eff}^{cat} = \frac{k_2 \cdot k_1}{k_3}[\text{Im } tOH]$$

The equation for determining the rate of the catalase reaction and, correspondingly, the effective rate constant of the catalase reaction is written as

$$r_{2,H_2O_2} = k_{eff}^{cat} \frac{D[H_2O_2]^2}{[C_2H_4]} \text{ and } k_{eff}^{cat} = \frac{r_{2,H_2O_2}[C_2H_4]}{D[H_2O_2]^2} \quad (29)$$

If the effective rate constants of the catalase and monooxygenase reactions are known, the effective activation energies for the coherent synchronized catalase and monooxygenase reactions can be determined: $E_{eff}^{cat}$ = 46.0 and $E_{eff}^{mon}$ = 58.2 kJ/mol, respectively. These values of the activation energies are within the ranges typical of enzymatic reactions (see table). The calculated average values of $k_{eff}$ in the investigated temperature range deviate from the values calculated for each experiment by no more than 30 and 10%, respectively.

An analysis of the values of $k_{eff}$ gives a reliable idea of the ratio of the rate constants of the catalase and monooxygenase reactions ($k_2$ and $k_3$):

$$\frac{\kappa_{eff}^{cat}}{\kappa_{eff}^{mon}} = \left( \frac{\kappa_2}{\kappa_3} \right)^2 \text{ or } \frac{\kappa_2}{\kappa_3} = \sqrt{\frac{\kappa_{eff}^{cat}}{\kappa_{эeff}^{mon}}} \quad , \quad (30)$$

This ratio demonstrates that the rate constant of the catalase reaction exceeds the constant rate of the monooxygenase reaction by a factor of approximately 2 x $10^2$, verifying the known data on the rates of these reactions [1].

By comparing the kinetic parameters obtained using the three different methods, we conclude that in kinetic descriptions of complex chemical reactions (including coherent synchronized reactions) the determinant equation yields a more complete description than other methods. Thus, for example, the method of stationary concentrations uses certain assumptions, while the determinant equation is free from them, which is the main advantage of this equation. Moreover, the determinant equation allows us to reveal interaction (coherence) between the synchronous chemical reactions and to quantitatively estimate this interaction.

## CONCLUSION

Our kinetic model constructed on the basis of the determinant equation and coherence ratio of coherent synchronized catalase and monooxygenase reactions adequately describes the experimental data. The synchronous reactions (catalase and monooxygenase) consistently interact (i.e., are coherent) with each other, as is demonstrated by the determinant values (D = 0.1-0.4). As a result, chemical interference is observed in the studied catalytic system [1]: the primary reaction amplifies the secondary reaction; and the latter, in turn, slows down the primary reaction; and vice versa.

## REFERENCES

[1] T. M. Nagiev. Coherent Synchronized Oxidation Reactions by Hydrogen Peroxide (Elsevier, Amsterdam, 2007).
[2] E.Tsuchida, K.Honda, and H.Sato, Biopolimers 13 (10), 2147 (1974).
[3] T. G. Traylor, Pure Appl. Chem. 63 (2), 266 (1991).
[4] T. M. Nagiev. Chemical Conjugation. Nauka, Moscow. 1989. [in Russian].
[5] L. M. Gasanova, Ch. A. Mustafaeva, I. T. Nagieva, et al., inProceedings of the 14th International Congress on Catalysis, July 13-18, 2008 (COEX Convention Center, Seoul, Korea, 2008).
[6] U. V. Nasirova, L. M. Gasanova, I. T. Nagieva, et al., in Catalysis or a Sustainable World, Proceedings of the EuropaCat IX, Salamanca, Spain, Aug. 30-Sept. 4, 2009, p. 313.
[7] U. V. Nasirova, L. M. Gasanova, I. T. Nagieva, et al., in Proceedings of the 16th European Symposium on Organic Chemistry ESOC 2009, Prague, Czech Republic, July 12-16, 2009, p. 2.055.
[8] U. V. Nasirova, L. M. Gasanova, and T. M. Nagiev, Russ. J. Phys. Chem. A**84,** 941 (2010).
[9] T. M. Nagiev, *Interaction of Synchronous Reactions in Chemistry and Biology* (Elm, Baku, 2001) [in Russian].