ISSN 0036-0244, Russian Journal of Physical Chemistry A, 2010, Vol. 84, No. 11, pp. 1895–1900. © Pleiades Publishing, Ltd., 2010.
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CHEMICAL KINETICS AND CATALYSIS

The Role Played by Acid and Basic Centers in the Activity of Biomimetic Catalysts of the Catalase, Peroxidase, and Monooxidase Reactions

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Received October 16, 2009

Abstract—The acid-basic centers of heterogeneous carriers of catalase, peroxidase, and monooxigenase biomimetics, in particular, iron protoporphyrin deposited on active or neutral aluminum magnesium silicate, were studied. The catalytic activity of biomimetics was stabilized, which allowed us not only to synthesize fairly effective biomimetics but also to clarify certain details of the mechanism of their action and perform a comparative analysis of the functioning of biomimetics and the corresponding enzymes.

DOI: 10.1134/S0036024410110130

INTRODUCTION

Biomimetics simulating certain catalytic functions of peroxidase, monooxidase, and oxidase enzymes are H^+-dependent redox catalytic systems [1, 2]. Catalysts of this type are intermediate between homogeneous and heterogeneous catalysts and the corresponding enzymes. Biomimetic catalysts have a comparatively simple chemical structure. Nevertheless, the mechanism of their action is in many respects similar to the mechanism of the action of the enzyme simulated [3, 4].

Immobilized metal porphyrin (Fe(III) hemin, tetraphenylporphyrin, and perfluorotetraphenylporphyrin redox active centers) biomimetic catalysts deposited on inorganic acid-base matrices (Al_2O_3, SiO_2, $Al_2O_3 \cdot SiO_2$, etc.) play an important role in the mechanism of biomimetic oxidation of various substrates. Very scarce information about the qualitative and quantitative characteristics of the surface acid-base centers of inorganic carriers bearing redox active centers in the adsorbed state makes studies of their physicochemical peculiarities an important task.

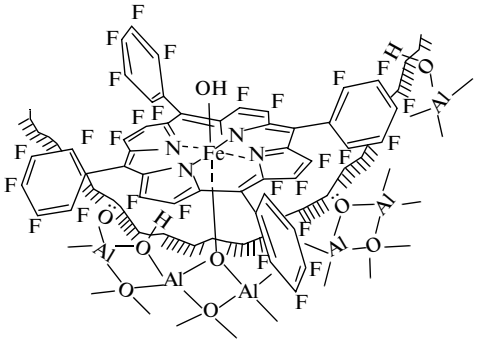
In [5], temperature-programmed desorption was used to perform a first-approximation study of the acid-base centers of heterogeneous carriers of monooxigenase biomimetics, in particular, Fe(III) protoporphyrin (Fe(III)PP) deposited on active or neutral Al_2O_3 and aluminum magnesium silicate. The destruction of the cyclic structure and, as a consequence, catalytic activity loss was related to the oxidative action of hydrogen peroxide intermediates on bridge hydrogen atoms. To stabilize the catalytic activity of biomimetics, the corresponding stabilizers were introduced by impregnation into the catalytic matrix.

It is known that an organic ligand in the fifth coordination position at the Fe(III) ion influences the activity and oxidation of Fe(III)PP present in the active center of enzymes (catalase, peroxidase, and monooxigenase). The selection of modifier-stabilizers (ionol, hydroquinone, *o*-phenylenediamine, diphenylamine, and diphenylguanine) modeling biochemical analogues allowed not only fairly effective biomimetics to be synthesized, but also certain details of the mechanism of functioning of the corresponding enzymes to be clarified [6]. Heterogenized porphyrin biomimetics possess qualities inherent in heterogeneous catalysts. Their modification by heterogeneous catalysis methods, in particular, thermal treatment that influences their catalytic activity, is therefore believed to be quite justified [7].

Studies showed that preliminary thermal treatment performed to influence the stability and activity of biomimetic catalysts was in addition an effective approach to the improvement of the catalytic properties of biomimetics. The general picture of the transfer of two protons to carrier (Al_2O_3) acid-base groups with electron transfer to the Fe(III)PPOH center is seen for the example of Fe(III)PPOH/Al_2O_3 and other inorganic biomimetics within a unified bond redistribution chain. As a result, a substrate experiences redox transformation similar to that occurring during enzymatic catalysis with the obligatory participation of acid-base groups of the protein matrix [3, 4].

It can therefore be suggested that the catalytic action of Fe(III)PPOH/Al_2O_3 and other biomimetics of this series is performed at the molecular level as the interaction of catalytic groups contained in a catalytic domain with a substrate by the synchronous mechanism. These ideas were used in [8] to suggest a design

of a catalytic domain of biomimetics, which can generally be represented as



A catalytic domain on an Al_2O_3 matrix has terminal and bridge Broensted acid centers and, accordingly, Broensted basic centers. Redox active catalytic domain centers are iron porphyrin complexes, whose structure is stabilized and activated by the coordination of the Fe(III)PP axial ion to the matrix support (Al–O:).

EXPERIMENTAL

Catalytically active hemin-containing biomimetics are most often synthesized using aqueous-alcoholic solutions of iron protoporphyrin at pH ≥ 8.5–9.5 to prevent their interaction with each other. Catalase biomimetics were synthesized on five forms of aluminum oxide (α-, β-, acid, basic, and neutral [3, 4]). The most catalase-active carriers were the neutral and basic Al_2O_3 forms. Before adsorption, hemin was dissolved in an aqueous-alcoholic solution (pH 8.5–9.5), where it transformed into hematin. Hematin was then deposited on the surface of Al_2O_3 to produce catalase biomimetic Fe(III)PPOH/Al_2O_3 [7, 9]. Using the same procedure, we were able to deposit iron protoporphyrin on SiO_2. Carriers were subjected to two-stage calcining, at 130°C for 1–2 h and then at 250°C for 5 h. After the adsorption of hemin, the catalyst was subjected to vapor treatment at 200°C for 4 h; water was supplied at a 3.4 ml/h rate.

The results obtained in [8–10] led the authors to conclude that only isolated hemin molecules were active in the decomposition of H_2O_2 on the surface of Al_2O_3, whereas the activity of larger associates was low. The oxidative destruction of PP is primarily related to the appearance of free radicals, mainly $\dot{O}H$, generated in the system as a result of the homolytic decomposition of H_2O_2. For this reason, the use of "traps" for free radicals protects the system from their destructive action.

Hydroquinone was introduced into the catalytic reaction system (Fe(III)PPOH/Al_2O_3 by two methods: (1) it was dissolved in an aqueous solution of H_2O_2 and (2) it was deposited on the surface of the biomimetic. None of the methods increased the activity of the biomimetic. Moreover, the second method decreased its activity [3, 6]. The use of ionol as a stabilizer insignificantly increased activity when it was dissolved in aqueous ethanol, but the results were of little efficiency. The use of diphenylamine and *o*-phenylenediamine as free radical traps decreased the catalytic activity of the biomimetic compared with the control system. Only diphenylguanidine allowed us to obtain a stable increase in the activity of the catalase biomimetic irrespective of the method of its introduction into the reaction medium.

Biomimetics were subjected to thermal treatment with varying the duration and temperature of treatment and the composition of reaction medium. The use of an inert gas (helium) instead of air in calcining biomimetics increased catalase activity up to 600°C. An increase in calcining temperature above 600°C decreased activity, and, at 800°C, catalytic activity completely disappeared.

Organic ligands were varied (tyrosine, aspartic acid, histidine, and imidazole) in the fifth coordination position of the Fe^{3+} ion to synthesize modified catalase biomimetics and test them for catalytic activity. The results showed that only imidazole noticeably increased the activity and stability of biomimetics in the catalase reaction. Hemin immobilized on various acid-base carriers (Al_2O_3, $Al_2O_3 \cdot SiO_2$, SiO_2) exhibited different catalase activities. The best sample was Fe(III)PPOH/Al_2O_3 [3].

The synthesis of active centers of TPhPFe^{3+} and per-FTPhPFe^{3+} biomimetic catalysts is a multistage process [4]. As mentioned, the solid matrix on which these catalysts were adsorbed was activated or neutral alumina in the form of spherical particles 1.5 mm in diameter with a specific surface area no less than 500 m^2/g.

Hydrogen peroxide of kh. ch. (chemically pure) grade was purified from possible impurities (in particular, from stabilizers) by distillation in a vacuum. The active centers of the TPhPFe^{3+} and per-FTPhPFe^{3+} catalysts were deposited on the surface of Al_2O_3 following known procedures [4]. The TPhPFe^{3+}OH/Al_2O_3 biomimetic catalyst was synthesized by the adsorption of TPhPFe^{3+} from a solution in benzene on Al_2O_3. The adsorption of per-FTPhPFe^{3+} on Al_2O_3 was performed from a solution in dimethylformamide by impregnating the matrix.

An experimental study of gas-phase catalase, peroxidase, and monooxidase reactions with the participation of hydrogen peroxide was performed in a flow quartz reactor with a 3 cm^3 reaction zone volume (d = 1.8 cm). Its design ensured the introduction of H_2O_2 in the undecomposed form [3, 4].

Catalase activity. The synthesized biomimetic catalysts were subjected to liquid-phase testing for catalase activity in a statistical system. Tests showed that the synthesized biomimetics had high catalase activity; TPhPFe^{3+}OH/Al_2O_3 and per-FTPhPFe^{3+}OH/Al_2O_3 in addition showed high stability to the action of the oxi-

dizer and its intermediate and to heating. The perfluorinated biomimetic was in addition tested for stability to high concentrations of H_2O_2. During a long time, it stably exhibited high catalase activity in a 30% aqueous solution of H_2O_2 and thereby demonstrated unique stability to the action of high-activity oxidizer intermediates.

RESULTS AND DISCUSSION

In terms of heterogeneous catalysis, the peroxidase reaction can be defined as oxidative dehydration. Currently, oxidative dehydration, in particular, with the participation of oxidizers other than O_2, such as hydrogen peroxide, attracts much interest. As is known, ethanol is a classic peroxidase substrate, and the development of chemical basics for a model peroxidase reaction is therefore of certain interest for practical applications, for petroleum chemical synthesis and heterogeneous biomimetic catalysis. On the one hand, ethanol is a nonspecific substrate for catalases. At the same time, the catalase reaction is an inducing (primary) reaction in coherently synchronous oxidation.

A comparison of the peroxidase activities of three biomimetics showed that $TPhPFe^{3+}OH/Al_2O_3$ had the highest and $PPFe^{3+}OH/Al_2O_3$ the lowest activity. The noticeable difference in activity is likely related for the hemin biomimetic to the oxidation of adsorbed hemin at the bridge C–H bond by both the oxidizer and its intermediates. This process becomes more intense as the contact time increases, which decreases the total number of active centers. At the same time, $TPhPFe^{3+}OH/Al_2O_3$ exhibits not only high activity but also considerable stability to oxidation. This is mainly explained as a result of the replacement of bridge hydrogen atoms in the porphyrin ring by phenyl radicals, which stabilizes bridges between pyrrole fragments. In addition, this observation allows us to assert that pyrrole hydrogen atoms do not undergo oxidation, at least under the conditions of our experiments. The presence of phenyl radicals in the porphyrin ring on the whole decreases its π-electronic density, which in turn increases the acidity of the central transition metal atom (Fe^{3+}) and increases its monooxidase and peroxidase activity.

As concerns the perfluorinated form of Fe^{3+} tetraphenylporphyrin, as is shown in [11], it undoubtedly has an almost absolute stability to the action of hydrogen peroxide and its intermediates. Unfortunately, fluorine increases the aromatic character of the porphyrin ring in this compound, which slightly decreases the acidity of the Fe^{3+} ion and its comparative monooxigenase and peroxidase activity.

The experimental data on the coherent-synchronous oxidation of ethanol to acetaldehyde depending on temperature are shown in Fig. 1. A comparison of the peroxidase activities of three biomimetic catalysts

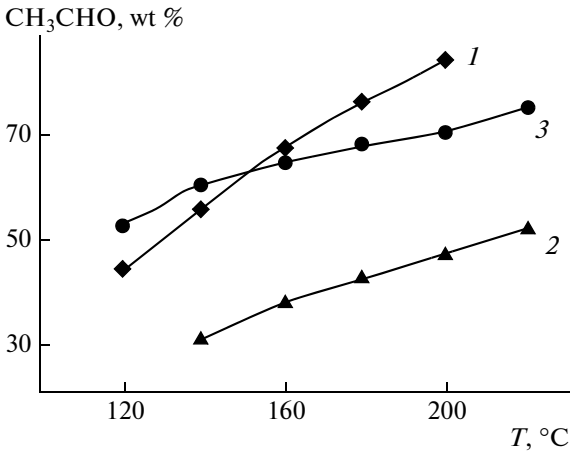


Fig. 1. Temperature dependences of the yields of CH_3CHO on (*1*) $TPhPFe^{3+}OH/Al_2O_3$, (*2*) $PPFe^{3+}OH/Al_2O_3$, and (*3*) per-$FTPhPFe^{3+}OH/Al_2O_3$ biomimetics.

showed that an increase in temperature to 230°C increased the yield of acetaldehyde in all cases and that the $TPhPFe^{3+}OH/Al_2O_3$ biomimetic had the highest peroxidase activity (the yield of acetaldehyde was 93.5 wt %). A comparatively low activity of $PPFe^{3+}OH/Al_2O_3$ can also be explained by the oxidation of methyl propionic acid fragments present in protoporphyrin (hemin) under gas-phase oxidation conditions, which decreases the activity of the biomimetic. The formation of side products and acetic acid was not observed [10].

The experimental data on the consumption of hydrogen peroxide in each synchronized C_2H_5OH oxidation reaction and the decomposition of H_2O_2 depending on the contact time are shown in Fig. 2. We see that the total consumption of H_2O_2 in both reactions equals its initial amount. It follows that, under all conditions, we have [3, 4]

$$f_0 = f_1 + f_2 = \text{const}, \quad (1)$$

where f_0 is the initial amount of H_2O_2 and f_1 and f_2 are the amounts of H_2O_2 consumed in the catalase and peroxidase reactions.

The fulfillment of the condition of coherence of chemical interference as a result of interaction of two synchronous reactions decreases the rate of the catalase reaction (the decomposition of H_2O_2) and increases the rate of the other (peroxidase) reaction synchronized with the first one, and vice versa. The dependences obtained are evidence that both reactions (catalase and peroxidase) not only occur synchronously but are also coherent.

The dependences of the yields of catalase and peroxidase reaction products on the contact time at various temperatures on the $TPhPFe^{3+}OH/Al_2O_3$ biomimetic catalyst are shown in Fig. 3. The kinetic curves of the yield of acetaldehyde, as a rule, pass a maximum at $\tau = 2.0$ s at 120–160°C. They then decrease as τ

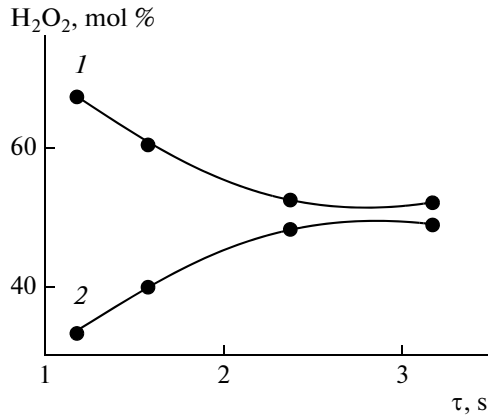


Fig. 2. Consumption of H_2O_2 in (*1*) primary and (*2*) secondary reactions on $TPhPFe^{3+}OH/Al_2O_3$ at 180°C, $[CH_2O_2]$ = 20 wt %, and $C_2H_5OH : H_2O_2 = 1 : 2$.

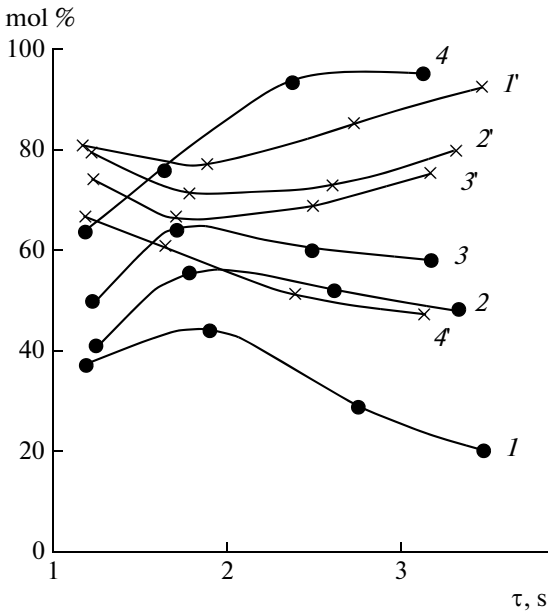


Fig. 3. Contact time dependences of the yields of reaction products ((*1–4*) CH_3CHO and (*1'–4'*) O_2) on the $TPhPFe^{3+}OH/Al_2O_3$ biomimetic at (*1*, *1'*) 120, (*2*, *2'*) 140, (*3*, *3'*) 160, and (*4*, *4'*) 180°C.

increases, most sharply at 120°C. This character of synchronous kinetic curves is likely related to different temperature dependences of the catalytic activities of $TPhPFe^{3+}OH/Al_2O_3$ in two synchronous reactions: catalase activity increases at contact time τ = 2.0 s as the temperature grows, whereas peroxidase activity synchronously decreases. The observed pattern is well seen at 180°C. The curve of the accumulation of acetaldehyde over the range of contact times studied does not contain extrema but decreases consistently. Conversely, the curve of the catalase reaction goes upward. At higher temperatures, the yields of acetaldehyde and O_2 are stabilized. The high rate of the decomposition of H_2O_2 at these temperatures sharply decreases its concentration, which influences the rates of both synchronized reactions.

As is known [3, 4], in the reaction systems studied, the catalase, monooxigenase, and peroxidase reactions have a common intermediate, which is a hydrogen peroxide fragment, OOH, activated and bound with a biomimetic. A bifurcation occurs in the reaction medium with the participation of this high-activity intermediate. This bifurcation is responsible for chemical interference observed in the system, that is, for mutual strengthening and weakening of the reactions

$$H_2O_2 + PPOH/Al_2O_3 \xrightarrow{-H_2O} PPOOH/Al_2O_3 \begin{cases} \xrightarrow[(1)]{H_2O_2} H_2O + O_2 + PPOH/Al_2O_3 \\ \xrightarrow[(2)]{C_2H_5OH} CH_3CHO + H_2O + PPOH/Al_2O_3, \end{cases}$$

where (1) and (2) are the catalase (primary) and peroxidase (secondary) reactions.

The kinetic conditions under which chemical interference is observed are quantitatively described by the determinant equation [3, 4]

$$D = \nu(f_1/f + f_2/f)^{-1}, \quad (2)$$

where f is the amount of ethanol consumed; f_1 and f_2 are the amounts of H_2O_2 consumed in the catalase and peroxidase reactions, respectively; and ν is the stoichiometric coefficient of hydrogen peroxide (actor); in our case, ν = 1. The experimental determinant value calculated using this equation for the optimum regime of the biomimetic oxidation of ethanol to acetaldehyde on $TPhPFe^{3+}OH/Al_2O_3$ (180°C, $[H_2O_2]$ = 20 wt % in aqueous solution, molar ratio $C_2H_5OH : H_2O_2 = 1 : 2$, τ = 1.6–3.2 s) is D = 0.30–0.50. According to the determinant scale of chemical interference [3, 4], this value is in the range of chemical conjugation, when the primary H_2O_2 decomposition reaction induces the secondary C_2H_5OH oxidation reaction (peroxidase reaction).

It follows that both synchronous reactions, because of the fulfillment of coherence (f_0 = const) and induction (D = 0.30–0.50) conditions, are in the state of interaction and form a chemical interference picture in the form of synchronized and mutually related kinetic curves of the catalase and peroxidase reactions.

The biomimetic catalysts under consideration contain alumina with terminal and bridge Broensted acid

and basic centers as a heterogeneous acid-base carrier. These centers play an important role in the catalytic transformation of ethanol. As mentioned, redox active centers $PPFe^{3+}OH$, $TPhPFe^{3+}OH$, and per-$TPhPFe^{3+}OH$ have structures stabilized by the coordination of the basic center of the carrier (Al–O:) with the functional groups of substituted iron porphyrin catalysts, especially in the axial position with respect to the central iron ion.

The mechanism of the peroxidase action of biomimetics suggested above can be represented in the form of elementary reactions quite corresponding to modern views on the mechanism of functioning of their biomimetic analogues in the TsPS theory [12].

The coherent synchronization of hydroxylation and hydrogen peroxide decomposition with the use of biomimetic catalysts allows these reactions to be performed under the conditions of mutual strengthening and weakening (chemical interference) and the rates of these reactions to be controlled under comparatively mild conditions. This technology nontraditional for chemical experiments was used to hydroxylate propane into isopropanol with hydrogen peroxide in the presence of the per-$FTPhPFe^{3+}OH/Al_2O_3$ catalyst.

The multistage synthesis of the active center of biomimetic catalyst is most complex. At the initial stage, Fe(III)tetrapentafluorophenylporphyrin was synthesized. At the final stage, the active mass of iron (III) perfluorotetraphenylporphyrin was immobilized from a solution in dimethylformamide (DMFA) on an acid-base carrier (Al_2O_3).

In cytochrome R-450, the active catalytic center is iron(III) protoporphyrin complex. Its analogue is the per-$FTPhPFe^{3+}OH/Al_2O_3$ synthesized biomimetic. Of course, the latter is a mimetic model of the corresponding enzyme. If the carrier and conditions are selected most properly, good results can be obtained under the conditions more harsh than in living systems. For instance, it was shown in [3, 4] that gas-phase monooxigenase mimetics immobilized on various carriers possess certain advantages characteristic of usual heterogeneous catalysts.

The dependences of the yields of isopropanol (i-C_3H_7OH) and molecular oxygen (O_2) in the oxidation of propane (C_3H_8) on contact time τ are shown in Fig. 4. At short τ times ($\tau < 0.6$ s), the hydroxylating activity of the biomimetic remains low. Conversely, catalase activity predominates, as follows from the yield of O_2. The yield of i-C_3H_7OH and, accordingly, conversion of C_3H_8 increase at longer τ. Starting with $\tau = 1.1$ s, it becomes clear that the kinetic curves of the catalase and monooxigenase reactions are synchronized. Changes in the yield of O_2 in the catalase reaction show that the almost complete catalytic decomposition of H_2O_2 in the catalase reaction increases the yield of i-C_3H_7OH, which is maximum at $\tau = 1.1$ s [13]. An increase in τ above 1.1 s preserves the coherent synchronized character of product yield curves for

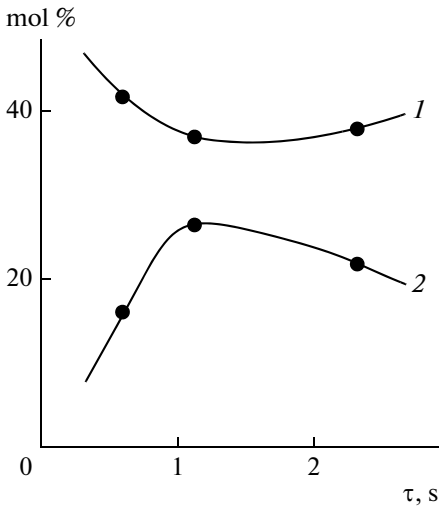


Fig. 4. Contact time dependences of reaction product yields ((*1*) O_2 and (*2*) i-C_3H_7OH) at 40°C, $[H_2O_2]$ = 20 wt %, and $C_3H_8 : H_2O_2 = 1 : 2$.

both the catalase and monooxigenase reactions. It follows that, over the whole range of contact time variations, complete consumption of hydrogen peroxide is observed. According to the kinetics of the catalase and hydroxylation reactions, hydrogen peroxide consumption is properly distributed between these two processes.

The dependences of the yields of i-C_3H_7OH and O_2 on the concentration of H_2O_2 in aqueous solution are shown in Fig. 5. Before it was supplied into the reaction zone, the solution was transformed into a gas. A low yield of i-C_3H_7OH (20.8 mol %) and a high yield of O_2 (42.9 mol %) correspond to a 15% concentration of hydrogen peroxide. As the concentration of H_2O_2 increases, the coherent dependence between the synchronous reactions, catalase and monooxigenase, becomes obvious. At a 20 wt % concentration of hydrogen peroxide, the yield of i-C_3H_7OH reaches a maximum (39.3 mol %), and the yield of O_2 is minimum (40 mol %). A subsequent insignificant decrease in the yield of i-C_3H_7OH at a 25 wt % concentration of hydrogen peroxide (~38 mol %) is accompanied by a smooth increase in the yield of O_2 in the catalase reaction (42.5 mol %) [13]. It follows from the data presented in Fig. 5 that the optimum concentration of hydrogen peroxide for gas-phase heterogeneous catalytic hydroxylation of propanol is 20 wt %. In addition, the conclusion can be drawn that, on the whole, a strong increase in the concentration of hydrogen peroxide decreases the yield of the monooxigenase reaction product (i-C_3H_7OH) and favors the catalase reaction.

The experimental data on the consumption of hydrogen peroxide in synchronized reactions are shown in Fig. 6. In reality, the curves shown in Fig. 6 are similar to those in Fig. 5, with the difference that

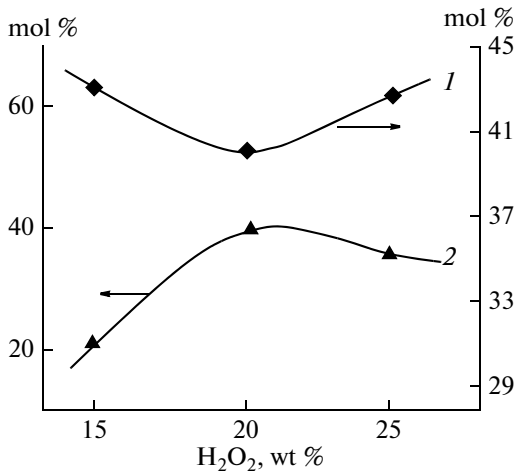


Fig. 5. Dependences of reaction product yields ((*1*) O_2 and (*2*) *i*-C_3H_7OH) on the concentration of H_2O_2 in aqueous solution in the reaction zone, 240°C, $C_3H_8 : H_2O_2 = 1 : 2$, $V_{C_2H_8} = 0.3$ l/h, $V_{H_2O_2} = 4.24$ ml/h, $\tau = 1.2$ s.

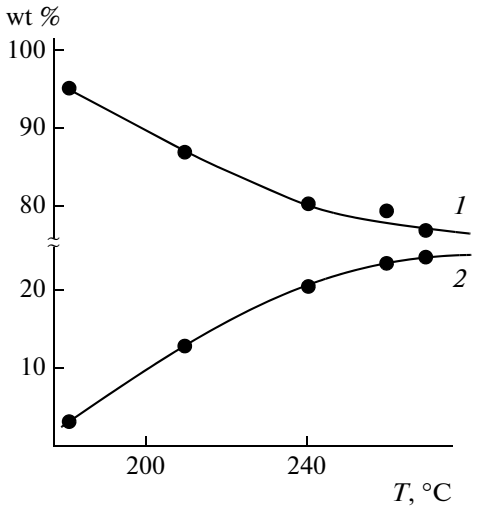


Fig. 6. Temperature dependences of H_2O_2 consumption in the (*1*) catalase and (*2*) hydroxylation reactions.

the total consumption of H_2O_2 in Fig. 6 equals its initial amount. An important conclusion follows that, under each particular condition, the sum of the yields of final products of synchronous reactions should correspond to a constant H_2O_2 (actor) consumption value. In our case (H_2O_2 is fully consumed in the two reactions), Eq. (1) is valid.

To summarize, the condition of coherence of chemical interference is satisfied. The rate of one reaction (catalase) decreases, whereas the rate of the other reaction coherently synchronized with the first one (hydroxylation) increases, and vice versa. The necessary condition for the existence of chemical interference in this reaction system is its quantitative characteristics determined by determinant equation (2). The experimental determinant value obtained using (2) for the optimum regime of hydroxylation (240°C, molar ratio $C_3H_8 : H_2O_2 = 1 : 2$, concentration of aqueous solution of $H_2O_2 = 20$ wt %, $V = 0.3$ l/h, $V = 4.24$ ml/h, $\tau = 1.2$ s) is $D \approx 0.4$. According to the determinant scale of chemical interference [3, 4], this value is in the region of chemical conjugation, where the primary reaction (the decomposition of H_2O_2) induces secondary hydroxylation of C_3H_8.

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