

Mechanism of Cyclohexane Oxidation by Molecular Oxygen in the Biomimetic Iron Porphyrin System with Proton and Electron Donors: II. A Molecular Pathway

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Abstract—The kinetics of the accumulation of cyclohexyl hydroperoxide, alcohol, and ketone during cyclohexane oxidation in an $O_2/FeP/AcOH/Zn/CH_3CN$ biomimetic system is studied by gas–liquid chromatography. The factors determining the selectivity of the nonradical oxidation pathway, which results in the formation of more than 80% of the products, are considered. A scheme of the molecular pathway of alcohol and ketone formation is proposed, which agrees well with the experimental data. The kinetic parameters for cyclohexane oxidation catalyzed by iron porphyrins with various substituents in the phenyl rings in this system with and without an electron carrier (methylviologen) are calculated.

INTRODUCTION

Monooxygenases containing cytochrome P450 are actively studied enzymatic systems [1] because of their great functional importance. Cytochromes P450 exhibit a unique ability to catalyze the oxidation of hundreds of thousands of low-molecular compounds, including saturated hydrocarbons. These enzymatic systems still ensure the best selectivity of alkane oxidation. Therefore, the biomimetic approach implying the development of their chemical analogs is particularly promising [2].

The mechanism of oxygen atom transfer to the C–H bond by porphyrin complexes in both model and natural systems has been the subject of considerable discussion. Different cases of the molecular mechanism and the hidden-radical abstraction–recombination mechanism are considered. In the model systems, where radical abstraction is also possible, an ordinary radical process involving the intermediate formation of hydroperoxide, whose transformation yields alcohol and ketone as final products is also possible.

We observed [3] the formation of cyclohexyl hydroperoxide, alcohol, and ketone during cyclohexane oxidation in our biomimetic system containing molecular oxygen, iron porphyrin (FeP), acetic acid, zinc powder, acetonitrile, and methylviologen (MV). In this system, hydroperoxide is an intermediate that decomposes in the reaction with iron porphyrin complexes. The kinetic study of cyclohexyl hydroperoxide decomposition [3] allowed us to take into account this reaction in the kinetics of cyclohexane oxidation. Calculations accord-

ing to our kinetic scheme in the pseudo-steady-state approximation, with regard to both the experimental relative yield of hydroperoxide and the apparent rate constants of its decomposition, allowed us to determine for the first time the fraction of the oxidation products formed by the radical pathway. For all iron porphyrins studied, the radical pathway via alkyl radical abstraction in the reaction of high-valence iron porphyrin complexes with cyclohexane yields less than 20% of all oxidation products. As might be expected, the probability of the free radical formation is determined exclusively by the iron porphyrin structure independently of the concentrations of the initial reactants and various additives introduced into the reaction mixture.

Therefore, more than 80% of the products of cyclohexane oxidation catalyzed by iron porphyrins with various substituents in the phenyl rings in the biomimetic system based on molecular oxygen and proton and electron donors are formed via the nonradical pathway.

In this work, we studied the kinetics and selectivity of the nonradical pathway of alcohol and ketone formation during cyclohexane oxidation in the $FeP/O_2/Zn/AcOH/CH_3CN$ biomimetic system with and without MV.

EXPERIMENTAL

Cyclohexane oxidation was carried out under conditions of continuous mixing with a magnetic stirrer in air at 20°C. Fe(III) porphyrin chlorides (tetraphe-

nylporphyrin (FeTPP), *meso*-tetrakis(2,6-dichlorophenyl)porphyrin (FeTDCPP), and $\alpha,\alpha,\alpha,\alpha$ -*meso*-tetrakis(*o*-pivaloylphenyl)porphyrin (FeTpivPP), synthesized as described in [4], were introduced into the reaction mixture as a benzene solution of a prescribed concentration (50 μ l). The volume of the liquid phase of the reaction mixture was 1 ml, and the gas phase volume was 50 ml. The reaction was initiated by the introduction of a zinc powder into the reaction mixture. The CH_3COOH concentration was 0.1 mol/l, $[\text{C}_6\text{H}_{12}] = 0.7$ mol/l, the Zn amount was 30 mg, and CH_3CN was used as a solvent.

The concentrations of cyclohexyl hydroperoxide, cyclohexanol, and cyclohexanone in the reaction mixture during cyclohexane oxidation in the $\text{FeP}/\text{O}_2/\text{Zn}/\text{AcOH}/\text{CH}_3\text{CN}$ system (with or without MV) were determined by the comparison of the results of sample analysis with and without triphenylphosphine (TPP) acting as a reducing agent for hydroperoxide [3]. The concentrations of ketone $\text{C}_6\text{H}_{10}\text{O}$ ($[\text{R}'\text{O}]$), hydroperoxide $\text{C}_6\text{H}_{11}\text{OOH}$ ($[\text{ROOH}]$), and alcohol $\text{C}_6\text{H}_{11}\text{OH}$ ($[\text{ROH}]$) in the reaction mixture were calculated by the equations

$$[\text{R}'\text{O}] = [\text{R}'\text{O}]_{\text{TPP}}, \quad (1)$$

$$[\text{ROOH}] = 1.7([\text{R}'\text{O}]_a - [\text{R}'\text{O}]_{\text{TPP}}), \quad (2)$$

$$[\text{ROH}] = [\text{ROH}]_a - 0.7([\text{R}'\text{O}]_a - [\text{R}'\text{O}]_{\text{TPP}}), \quad (3)$$

where $[\text{R}'\text{O}]_a$ and $[\text{ROH}]_a$ are the ketone and alcohol concentrations, respectively, obtained by analyzing the sample without TPP, and $[\text{R}'\text{O}]_{\text{TPP}}$ and $[\text{ROH}]_{\text{TPP}}$ are the ketone and alcohol concentrations, respectively, obtained by analyzing the sample with TPP.

RESULTS AND DISCUSSION

In our previous paper [3], we showed that cyclohexane oxidation by air oxygen in the $\text{O}_2/\text{FeP}/\text{AcOH}/\text{Zn}/\text{CH}_3\text{CN}$ biomimetic system with and without MV occurs mainly via the molecular pathway of alcohol and ketone formation (for all FeP studied). To elucidate the mechanism of this nonradical process, we studied the effect of various factors on its selectivity.

To eliminate both the contribution of FeP destruction and the consecutive oxidation of alcohol to ketone, we studied the selectivity of cyclohexane oxidation at a short reaction time ($t' = 120$ and 480 s for the systems with and without MV, respectively). On the kinetic curve segment limited by this time t' , the reaction products are formed at a virtually constant rate. Therefore, the selectivity parameters x , y , and z , calculated from the oxidation product concentrations at time t' by the equations given below, are also the relative yields of the oxidation products and the relative rates of their accumulation:

$$x = [\text{ROH}]/\Sigma P = d[\text{ROH}]/d\Sigma P,$$

$$y = [\text{R}'\text{O}]/\Sigma P = d[\text{R}'\text{O}]/d\Sigma P,$$

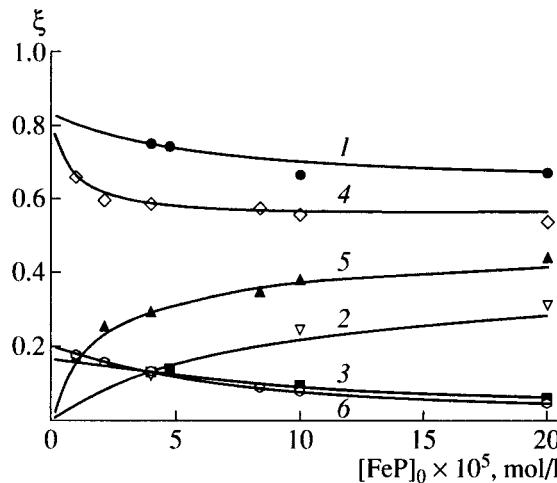


Fig. 1. Selectivity of the formation of the C_6H_{12} oxidation products ($\xi = \frac{[\text{P}]}{\Sigma P}$) as a function of $[\text{FeTDCPP}]_0$: (1, 4) $[\text{ROH}]$, (2, 5) $[\text{R}'\text{O}]$, and (3, 6) $[\text{ROOH}]$ at (1–3) $[\text{MV}] = 7.5 \times 10^{-3}$ mol/l and (4–6) $[\text{MV}] = 0$. The curves and the points correspond to the calculation and the experiment, respectively.

$$z = [\text{ROOH}]/\Sigma P = d[\text{ROOH}]/d\Sigma P,$$

where $\Sigma P = [\text{ROH}] + [\text{R}'\text{O}] + [\text{ROOH}]$.

The selectivity parameters of cyclohexane oxidation for all iron porphyrins studied change with the initial FeP concentration. An increase in the $[\text{FeP}]_0$ value corresponds to a decrease in the x and z parameters and an increase in the y parameter. For FeTDCPP (Fig. 1), the introduction of MV into the reaction mixture causes an increase in the relative alcohol yield (curves 2 and 5) and a decrease in the relative ketone yield (curves 1 and 4), but has virtually no effect on the relative hydroperoxide yield (curves 3 and 6) at the FeP concentrations ranging from 1×10^{-5} to 2×10^{-4} mol/l.

The experimental data shown in Fig. 1 illustrate how the relative hydroperoxide yield changes with the $[\text{FeP}]_0$ value. This is due to the occurrence of cyclohexyl hydroperoxide decomposition, which accelerates with an increase in the initial FeP concentration and results in a decrease in the ROOH concentration in the reaction mixture. A study of the catalytic decomposition of cyclohexyl hydroperoxide in the presence of iron porphyrins with various substituents in the phenyl rings and proton and electron donors (acetic acid and zinc powder) [3] allowed us to take into account the contribution of this reaction into the kinetics of cyclohexane oxidation. We also showed that the relative yields of the products of the radical pathway of cyclohexane oxidation at time t (via the intermediate formation of cyclohexyl hydroperoxide) can be calculated by the equations

$$\left\{ \begin{array}{l} x_{\text{rad}} = \frac{d[\text{ROH}]_{\text{rad}}}{d \sum_{i=1}^5 [\text{P}_i]} = \alpha'' \gamma \left\{ 1 + \frac{\exp(-k_{\text{app}}[\text{FeP}]_0 t) - 1}{k_{\text{app}}[\text{FeP}]_0 t} \right\} \\ y_{\text{rad}} = \frac{d[\text{R}'\text{O}]_{\text{rad}}}{d \sum_{i=1}^5 [\text{P}_i]} = \alpha'' (1 - \gamma) \left\{ 1 + \frac{\exp(-k_{\text{app}}[\text{FeP}]_0 t) - 1}{k_{\text{app}}[\text{FeP}]_0 t} \right\} \\ z = \frac{d[\text{ROOH}]_{\text{rad}}}{d \sum_{i=1}^5 [\text{P}_i]} = \frac{\alpha'' \{ 1 - \exp(-k_{\text{app}}[\text{FeP}]_0 t) \}}{k_{\text{app}}[\text{FeP}]_0 t}, \end{array} \right. \quad (4)$$

where k_{app} is the apparent rate constant for cyclohexyl hydroperoxide decomposition; γ is the probability of alcohol formation during cyclohexyl hydroperoxide decomposition by iron porphyrin complexes; P_i represent the products of the radical ($\text{P}_{\text{rad},i}$) and molecular ($\text{P}_{\text{mol},i}$) pathways of cyclohexane oxidation, and α'' is the fraction of the products of cyclohexane oxidation formed via the radical pathway:

$$\alpha'' = \frac{\sum_{i=1}^3 [\text{P}_{\text{rad},i}]}{\sum_{i=1}^5 [\text{P}_i]} = z \frac{k_8^{\text{app}}[\text{FeP}]_0 t}{1 - \exp(-k_8^{\text{app}}[\text{FeP}]_0 t)}.$$

The experimental relative fractions of alcohol (x) and ketone (y) at time t (Fig. 1) are equal to

$$x = x_{\text{rad}} + x_{\text{mol}}, \quad y = y_{\text{rad}} + y_{\text{mol}}. \quad (5)$$

The x_{rad} and y_{rad} values for the chosen reaction time may be calculated from the kinetic parameters γ , α'' , and k_{app} [3] by equation (4) (see the table). Then, from the difference between the experimental relative alco-

hol and ketone fractions and the calculated relative fractions of the radical pathway products, one can easily calculate the relative fractions of alcohol and ketone formed via the nonradical pathway:

$$\begin{aligned} x_{\text{mol}} &= x - x_{\text{rad}} = x \\ &- \alpha'' \gamma \left\{ 1 + \frac{\exp(-k_{\text{app}}[\text{FeP}]_0 t) - 1}{k_{\text{app}}[\text{FeP}]_0 t} \right\}, \\ y_{\text{mol}} &= y - y_{\text{rad}} = y \\ &- \alpha'' (1 - \gamma) \left\{ 1 + \frac{\exp(-k_{\text{app}}[\text{FeP}]_0 t) - 1}{k_{\text{app}}[\text{FeP}]_0 t} \right\}. \end{aligned} \quad (6)$$

Figure 2 presents the plots of the selectivity of the molecular pathway of cyclohexane oxidation $y_{\text{mol}}/x_{\text{mol}}$ as a function of $[\text{FeP}]_0$ for iron porphyrins with various substituents in phenyl rings calculated from the experimental data of Fig. 1 by equation (6). As Fig. 2 shows, an increase in the initial iron porphyrin concentration causes an increase in the relative ketone yield in the

Kinetic parameters of C_6H_{12} oxidation catalyzed by iron porphyrins

Parameter	Parameter values			
$[\text{MV}] \times 10^3, \text{ mol/l}$	7.5			0
FeP	FeTPP	FeTpivPP	FeTDCPP	FeTDCPP
$k_{\text{app}}, 1 \text{ mol}^{-1} \text{ s}^{-1}*$	120**	67**	120**	50**
γ^*	0.80***	0.83***	0.80***	0.80***
α^*	0.13	0.12	0.17	0.20
β	0.55	0.67	0.57	0.57
$(k_3 + k_4^{\text{app}})/k_6^{\text{app}}, \text{ mol/l}$	5.4	4.6	8.2	1.2

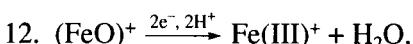
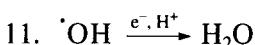
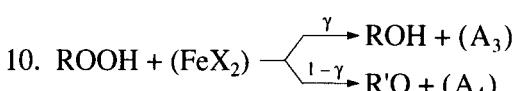
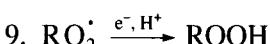
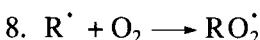
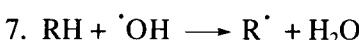
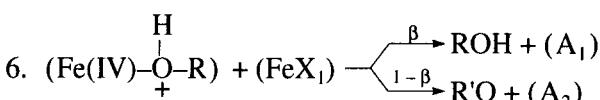
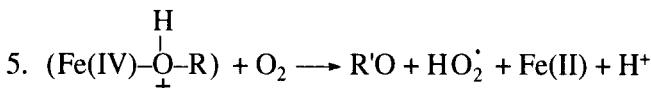
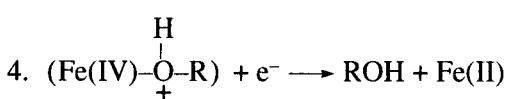
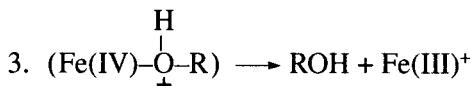
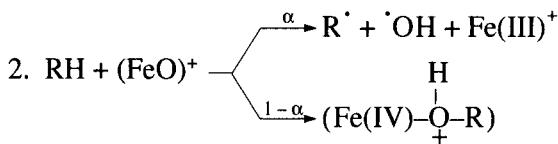
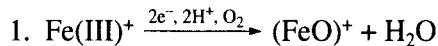
* Data of [3].

** Apparent rate constants for the catalytic decomposition of cyclohexyl hydroperoxide decomposition.

*** The probability of alcohol formation via cyclohexyl hydroperoxide decomposition by iron porphyrin complexes at $[\text{FeP}]_0 = 4 \times 10^{-5} \text{ mol/l}$.

products of the molecular pathway of cyclohexane oxidation.

Based on our previous data [3, 5, 6] and the experimental results obtained in this work, we propose a scheme for the formation of the cyclohexane oxidation products¹.



(FeX_1) and (FeX_2) are the iron porphyrin complexes, and (A_1) , (A_2) , (A_3) , and (A_4) are the products of iron porphyrin complex transformation.

The above scheme differs from that proposed in [3] in that it takes into account steps 3–6, which are the reactions of the positively charged intermediate hydrocarbon-active iron porphyrin intermediate complex $(\text{Fe(IV)}-\text{O}-\text{RH})^+$. Step 3 is $(\text{Fe(IV)}-\text{O}-\text{RH})^+$ decomposition. Step 4 is $(\text{Fe(IV)}-\text{O}-\text{RH})^+$ reduction by zinc powder or MV^+ cation radicals. Step 5 is the reaction of $(\text{Fe(IV)}-\text{O}-\text{RH})^+$ with oxygen. Step 6 is the reaction of $(\text{Fe(IV)}-\text{O}-\text{RH})^+$ with some iron porphyrin complexes, whose concentration is proportional to $[\text{FeP}]_0$. Step 6 is introduced into the kinetic scheme of cyclohexane ox-

¹ For simplicity, we consider here only one variant of the kinetic scheme that fits the experimental data.

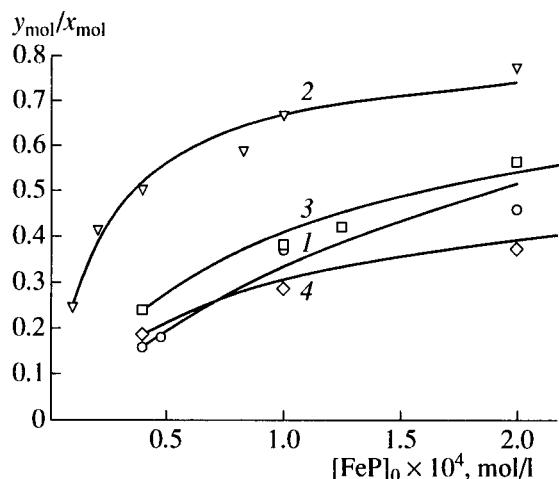


Fig. 2. Selectivity of alcohol and ketone formation via the nonradical pathway of C_6H_{12} oxidation ($y_{\text{mol}}/x_{\text{mol}}$) as a function of $[\text{FeP}]_0$: for (1, 2) FeTDCPP , (3) FeTPP , and (4) FeTpivPP ; (1, 3, 4) $[\text{MV}] = 7.5 \times 10^{-3} \text{ mol/l}$ and (2) $[\text{MV}] = 0$.

dation to explain the effect of the initial iron porphyrin concentration on the process selectivity. By calculating the above scheme in the pseudo-steady-state approximation (assuming that the concentrations of all intermediates, except for $[\text{ROOH}]$, are stationary) and taking into account that $[(\text{FeX}_1)]$ and $[(\text{FeX}_2)]$ are proportional to the initial iron porphyrin concentration, we arrive at the following expression for the overall rate of oxidation product accumulation w :

$$w = \frac{d \sum_{i=1}^5 P_i}{dt} = \frac{d[\text{ROOH}]_{\text{rad}}}{dt} + \frac{d[\text{ROH}]_{\text{rad}}}{dt} + \frac{d[\text{R}'\text{O}]_{\text{rad}}}{dt} + \frac{d[\text{ROH}]_{\text{mol}}}{dt} + \frac{d[\text{R}'\text{O}]_{\text{mol}}}{dt} = (1 - \alpha + \alpha')(k_1/k_{12})k_2[\text{RH}][\text{FeP}]_0, \quad (7)$$

where $\alpha' = \frac{2k_7[\text{RH}] + k_{11}}{k_7[\text{RH}] + k_{11}}\alpha$, k_1 , k_{11} , and k_{12} are the apparent rate constants for the corresponding reactions.

In accordance with the above scheme, the fraction of the cyclohexane oxidation products formed via the radical pathway α'' is related to the probability of alkyl radical abstraction α as follows:

$$\alpha'' = \frac{\alpha'}{1 - \alpha + \alpha'}.$$

The inequality $k_{11} \gg 2k_7[\text{RH}]$ is true under our experimental conditions [3] and, hence, $\alpha' = \alpha = \alpha''$.

Therefore, the reaction of the $\cdot\text{OH}$ radicals with a hydrocarbon does not contribute significantly to the oxidation product formation, and the fraction of the radical pathway products α'' is equal to the probability of alkyl radical abstraction α . The introduction of steps

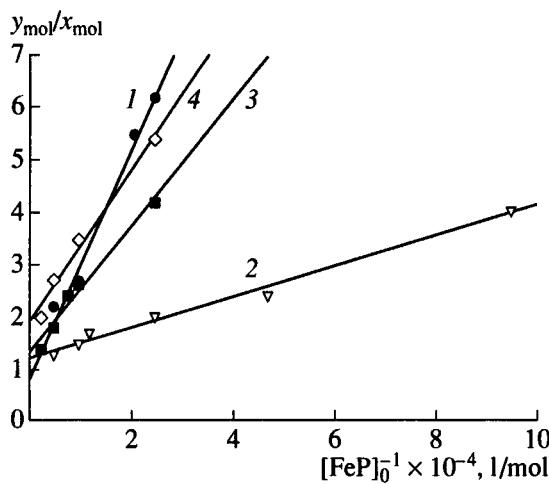


Fig. 3. Selectivity of the nonradical pathway of C_6H_{12} oxidation to alcohol and ketone as a function of $[FeP]_0$ in the coordinates of Eq. (10): (1, 2) for FeTDCPP, (3) FeTPP, and (4) FeTpiVPP; (1, 3, 4) $[MV] = 7.5 \times 10^{-3}$ mol/l and (2) $[MV] = 0$.

3–6 into the kinetic scheme has no effect on the radical pathway of cyclohexane oxidation, which was discussed in detail in [3].

Let us consider alcohol and ketone formation via the nonradical pathway. Under the pseudo-steady-state reaction conditions and assuming that w is constant, we derived the equations for the relative yields of alcohol and ketone formed via the nonradical pathway:

$$x_{\text{mol}} = \frac{d[\text{ROH}]_{\text{mol}}}{d \sum_{i=1}^5 P_i} = (1 - \alpha) \frac{k_3 + k_4^{\text{app}} + \beta k_6^{\text{app}} [FeP]_0}{k_3 + k_4^{\text{app}} + k_5[\text{O}_2] + k_6^{\text{app}} [FeP]_0},$$

$$y_{\text{mol}} = \frac{d[\text{R}'\text{O}]_{\text{mol}}}{d \sum_{i=1}^5 P_i} = (1 - \alpha) \frac{k_5[\text{O}_2] + (1 - \beta) k_6^{\text{app}} [FeP]_0}{k_3 + k_4^{\text{app}} + k_5[\text{O}_2] + k_6^{\text{app}} [FeP]_0}.$$
(8)

The $x_{\text{mol}}/y_{\text{mol}}$ ratio may be represented by the equation

$$\frac{x_{\text{mol}}}{y_{\text{mol}}} = \frac{k_3 + k_4^{\text{app}} + \beta k_6^{\text{app}} [FeP]_0}{k_5[\text{O}_2] + (1 - \beta) k_6^{\text{app}} [FeP]_0},$$
(9)

that is, the selectivity of alcohol and ketone formation via the molecular pathway is determined by the ratio of the rate constants of the reactions of the intermediate $(\text{Fe(IV)}-\text{O}-\text{RH})^+$ complex. The $k_6^{\text{app}} [FeP]_0$ value deter-

mines a change in the selectivity with the initial iron porphyrin concentration.

Obviously, in the system with a reducing agent, the relative contribution of step 5 to the oxidation product formation is insignificant and, hence, the inequality $k_5[\text{O}_2] \ll (1 - \beta) k_6^{\text{app}} [FeP]_0$ is true. Then, equation (9) can be rearranged in the $(x_{\text{mol}}/y_{\text{mol}})$, $([FeP]_0)^{-1}$ coordinates to the form:

$$\frac{x_{\text{mol}}}{y_{\text{mol}}} = \frac{\beta}{1 - \beta} + \frac{k_3 + k_4^{\text{app}}}{(1 - \beta) k_6^{\text{app}}} \frac{1}{[FeP]_0}. \quad (10)$$

Figure 3 presents the plots of the ratios of the relative yields of alcohol and ketone formed via the nonradical pathway as a function of the concentrations of the iron porphyrins with various substituents in the phenyl rings calculated from the experimental data in the coordinates of equation (10). The experimental data fit equation (10). Therefore, under our experimental conditions, ketone is mainly formed in step (6) of the reaction of two metal porphyrin complexes and during hydroperoxide decomposition. Both the β value and the ratio of the reaction rate constants $(k_3 + k_4^{\text{app}})/k_6^{\text{app}}$ (see the table) can be calculated from the intercept on the ordinate axis and the slope of the curve (Fig. 3). Both the β value and the ratio of the rate constants for alcohol and ketone formation via the nonradical pathway are determined by the nature of the substituents in the phenyl rings of the iron porphyrin. In this case, the β value is independent of the presence of MV in the reaction mixture, and the rate constant ratio shifts towards the predominant formation of alcohol upon MV introduction into the reaction mixture, that is, $\{(k_3 + k_4^{\text{app}})/k_6^{\text{app}}\}_{\text{MV} = 0.075 \text{ mol/l}} > \{(k_3 + k_4^{\text{app}})/k_6^{\text{app}}\}_{\text{MV} = 0}$. This seems natural because the introduction of the electron carrier (MV) into the system causes an increase in the apparent rate constant for $(\text{Fe(IV)}-\text{O}-\text{RH})^+$ reduction via step 4. The fact that MV does not affect the β parameter suggests that the species involved in the above kinetic scheme as the (FeX_1) complexes are of the same type. For example, the PFeO_2 complexes can act with the same probability as a reducing agent $\text{PFe(III)}\text{O}_2^-$ and as an oxidant $\text{PFe(II)}\text{O}_2$ with respect to the ether with the positive charge on the oxygen atom $(\text{Fe(IV)}-\text{O}-\text{RH})^+$. Then the β parameter is the probability of alcohol formation in the reaction of $(\text{Fe(IV)}-\text{O}-\text{RH})^+$ with these complexes. On the contrary, different species act as the (FeX_2) complexes. For example, PFe(II) reduces hydroperoxide to alcohol, whereas PFeO_2 causes hydroperoxide decomposition to alcohol and ketone. This manifests itself in the experimental dependence of γ on $[FeP]$ or $[MV]$.

Using equations (4), (5), and (8) and the inequalities $k_5[\text{O}_2] \ll (1 - \beta) k_6^{\text{app}} [FeP]_0$ and $k_{11} \gg 2k_7[\text{RH}] (\alpha = \alpha'')$,

one can easily determine how the x , y , and z values vary with $[FeP]_0$ at a certain reaction time t :

$$\begin{aligned}
 x &= x_{\text{mol}} + x_{\text{rad}} = (1 - \alpha) \frac{(k_3 + k_4^{\text{app}})/k_6^{\text{app}} + \beta[FeP]_0}{(k_3 + k_4^{\text{app}})/k_6^{\text{app}} + [FeP]_0} \\
 &\quad + \alpha\gamma \left\{ 1 + \frac{\exp(-k_{\text{app}}[FeP]_0 t) - 1}{k_{\text{app}}[FeP]_0 t} \right\}, \\
 y &= y_{\text{mol}} + y_{\text{rad}} \\
 &= (1 - \alpha) \frac{(1 - \beta)[FeP]_0}{(k_3 + k_4^{\text{app}})/k_6^{\text{app}} + [FeP]_0} \\
 &\quad + \alpha(1 - \gamma) \left\{ 1 + \frac{\exp(-k_{\text{app}}[FeP]_0 t) - 1}{k_{\text{app}}[FeP]_0 t} \right\}, \\
 z &= \frac{\alpha \{ 1 - \exp(-k_{\text{app}}[FeP]_0 t) \}}{k_{\text{app}}[FeP]_0 t}.
 \end{aligned} \tag{11}$$

Equations (11) show that the product composition (in %) in the course of the reaction is determined exclusively by the radical oxidation pathway at an insignificant level of iron porphyrin destruction.

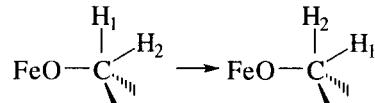
All the parameters of equations (11) can be calculated from the parameters of the radical pathway α , γ , and k_{app} [3] and the parameters of molecular pathway β and $(k_3 + k_4^{\text{app}})/k_6^{\text{app}}$ (see the table). Figure 1 presents the curves (1–3) calculated from the parameters of cyclohexane oxidation and cyclohexyl hydroperoxide decomposition (see the table) in the $O_2/FeTDCPP/AcOH/Zn/CH_3CN/MV$ system (for $t = 120$ s).

$$\begin{aligned}
 x &= 0.136 - 0.944 \{ 1 - \exp(-0.144[FeP]_0) \} [FeP]_0^{-1} \\
 &\quad + (6.8 + 0.473[FeP]_0)(8.2 + [FeP]_0)^{-1}, \\
 y &= 0.034 - 0.236 \{ 1 - \exp(-0.144[FeP]_0) \} [FeP]_0^{-1} \\
 &\quad + 0.357[FeP]_0(8.2 + [FeP]_0)^{-1}, \\
 z &= 1.18 \{ 1 - \exp(-0.144[FeP]_0) \} [FeP]_0^{-1}
 \end{aligned}$$

Figure 1 shows that the calculated curves fit the experimental points. The curves illustrating how the selectivity parameters x , y , and z change with the initial FeTDCPP concentration in the absence of MV calculated in a similar way (for $t = 480$ s taking into account the empirical expression for the selectivity of alcohol and ketone formation from cyclohexyl hydroperoxide under these experimental conditions $\gamma = 0.5 + 0.38\exp\{-175t[FeP]_0\}$ [3]) also agree well with the experimental results (Fig. 1, curves 4–6). Note that the kinetic parameters used for calculations are either averaged or extrapolated for the experiments performed over a wide range of conditions (with or without MV, $t = 120$ or 480 s, and cyclohexane or cyclohexyl hydro-

peroxide used as a substrate). In this case, the coincidence between the experimental and calculated curves over a wide range of the initial iron porphyrin concentrations provides perfect support for the validity of our speculation.

As noted earlier [3], reactions 4–6 require a noticeable lifetime of the $(Fe(\text{IV})-\text{O}-\text{RH})^+$ complex sufficient for the reaction with other reaction mixture components, which seems unlikely. However, the introduction of these reactions was necessary to explain the effect of different factors on the process selectivity. Our earlier findings [7] strongly suggest that the most likely mechanism of alcohol formation in the natural systems and some of their chemical models is the addition of the oxygen atom to the C–H bond via the formation of an intermediate complex with the five-coordinated carbon, whose lifetime is sufficient for its isomerization via the replacement of the hydrogen atoms.



In stereochemical processes, this reaction results in racemate formation [7].

Note that the theoretical calculation suggests the possibility for the existence of triply protonated methane CH_7^{3+} , that is, seven-coordinated carbon [8]. The appropriate choice of ligands ($L = (\text{C}_6\text{H}_5)_3\text{PAu}$ allowed Scherbaum *et al.* [9, 10] to obtain stable complexes of five- and six-coordinated carbon: $\{[(\text{C}_6\text{H}_5)_3\text{PAu}]_5\text{C}\}^+$ and $\{[(\text{C}_6\text{H}_5)_3\text{PAu}]_6\text{C}\}^{2+}$.

Apparently, the intermediate complex with five-coordinated carbon in a polar media forms a relatively stable $(Fe(\text{IV})-\text{O}-\text{RH})^+$ complex, the ether with a positive charge on the oxygen atom, whose further transformations result in the parallel formation of alcohol and ketone.

CONCLUSION

Our present findings and earlier results [3, 5, 6] suggest that alcohol and ketone are formed simultaneously from cyclohexane in the $FeP/O_2/\text{AcOH}/Zn/\text{CH}_3\text{CN}$ system with and without MV, mainly via the molecular mechanism (the nonradical pathway of reaction product formation constitutes more than 80% for all iron porphyrins studied). In this case, the first step of hydrocarbon oxidation is nonradical: the substrate is involved in the oxidation by high-valence iron porphyrin complexes formed by the mechanism of the reductive activation of oxygen in the presence of proton donors. The system studied is a good model of natural monooxygenases that can be used to investigate the process mechanism. The main distinction of the model system from the enzymatic one is the formation of a noticeable amount of ketone. In view of our findings, this is quite natural. The hydrophobic surrounding of the active

center of the enzyme facilitates alcohol molecule formation, thus reducing the lifetime of the intermediate complex. Moreover, the structures of both the enzyme and its active center rule out the reactions of the intermediate complex with other iron porphyrin intermediates. In accordance with the above scheme, it is these reactions of the intermediate complex that result in ketone formation in the biomimetic system.

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