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

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Abstract—The formation of cyclohexyl hydroperoxide during cyclohexane oxidation by air oxygen in a biomimetic iron porphyrin system with proton (AcOH) and electron (Zn) donors and with or without an electron carrier (methylviologen (MV)) in an acetonitrile solution is detected by gas-liquid chromatography. The kinetics of $C_6H_{11}OOH$ decomposition in this system catalyzed by iron porphyrins with various substituents in the phenyl rings is studied, and the rate constants of this process are determined. A kinetic scheme of cyclohexane oxidation is proposed. The contribution of the radical pathway to the reaction product formation is quantitatively estimated in the pseudo-steady-state approximation. For all iron porphyrins under investigation (FeTPP, FeTDCPP, and FeTpivPP), the fraction of the products formed via the radical pathway is smaller than 20%.

INTRODUCTION

Monooxygenases catalyze substrate oxidation by molecular oxygen in the presence of a reducing agent via the stoichiometric reaction

$$RH + O_2 + 2H^+ + 2e^- \longrightarrow ROH + H_2O;$$

that is, one oxygen atom is incorporated into the substrate molecule, whereas the other forms water. Monooxygenases containing cytochrome P450 also include iron porphyrin complexes (FeP). An organic reducing agent, which is necessarily present in the system, produces two reducing equivalents required for the monooxygenase cycle. The function of the reducing agent is to transfer an electron to an iron atom incorporated into the enzyme molecule. After reduction, the iron atom becomes capable of activating molecular oxygen for reactions with alkanes [1].

Modeling of the key process of monooxygenase catalysis, molecular oxygen activation on a metal complex in the presence of the electron donor (the reducing agent), is of practical and theoretical interest.

Superoxo and peroxo iron porphyrin complexes, synthesized from O_2 and PFe in the presence of the reducing agent, are relatively stable and inert with respect to alkanes. Only the addition of acetic anhydride into the system allowed us to construct the first complete chemical model of cytochrome P450, which is active with respect to saturated hydrocarbons [2]. Acetic acid present as an admixture in acetic anhydride upon its conventional purification acts as an effector in this system [3, 4].

Our experimental data [3, 5] suggest that cyclohexane oxidation in the $FeP/O_2/Zn/AcOH/CH_3CN$ biomimetic system with and without methylviologen (MV) is not a radical chain process. However, it seems necessary to consider the probability of alkyl radical formation in the course of the hydrocarbon reaction with the active iron porphyrin complexes. In this case, the reactions of free alkyl radicals under aerobic conditions result in the formation of cyclohexyl hydroperoxide, the catalytic decomposition of which in the reaction mixture or in a chromatographic column produces alcohol and ketone by hydrocarbon oxidation as is usually observed in the experiments.

The aim of this study was to determine the contribution of the radical pathway to the formation of the products of cyclohexane oxidation in the $FeP/O_2/Zn/AcOH/CH_3CN$ biomimetic system with and without MV using a specially designed quantitative method of alkyl hydroperoxide analysis in the presence of a catalyst.

EXPERIMENTAL

Cyclohexane oxidation or cyclohexyl hydroperoxide decomposition was carried out under conditions of continuous mixing with a magnetic stirrer in air at 20°C. Fe(III) porphyrin chlorides (tetraphenylporphyrin (FeTPP), *meso*-tetrakis(2,6-dichlorophenyl)porphyrin (FeTDCPP), and α,α,α,α-*meso*-tetrakis(*o*-pivaloylphenyl)porphyrin (FeTpivPP)) synthesized as described in [2] were introduced into the reaction mixture as a benzene solution of a prescribed concentration (50 μl). 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 con-

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centration was 0.1 mol/l, $[C_6H_{12}]$ = 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 or cyclohexyl hydroperoxide decomposition in the $FeP/O_2/Zn/AcOH/CH_3CN$ system (with or without MV) were determined by the comparison of GLC analyses of the samples with and without triphenylphosphine (TPP) acting as a reducing agent for hydroperoxide. At a certain time, two samples were withdrawn from the reaction mixture, one of which was introduced into a vessel with TPP and intensively stirred to reduce hydroperoxide to alcohol, and then both probes were analyzed by gas-liquid chromatography using a metallic chromatographic column packed with 10% Carbowax-20M on Tselit. We found that, under the conditions of this analytical method, cyclohexyl hydroperoxide in an acetonitrile solution decomposes to alcohol and ketone (0.7 : 1) in the chromatographic column virtually independently of the presence of other reagents in the solution analyzed. Taking into account this ratio, we calculated the concentrations of ketone ($C_6H_{10}O$, [R'O]), hydroperoxide $C_6H_{11}OOH$ ([ROOH]), and alcohol $C_6H_{11}OH$ ([ROH]) in the reaction mixture by the equations:

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

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

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

where $[R'O]_a$ and $[ROH]_a$ are the ketone and alcohol concentrations, respectively, obtained by analyzing the sample without TPP, and $[R'O]_{TPP}$ and $[ROH]_{TPP}$ are the ketone and alcohol concentrations, respectively, obtained by analyzing the sample with TPP. The validity of this calculation method was checked with a specially designed glass chromatographic column allowing one to analyze hydroperoxide without its decomposition in the reaction mixture without the catalyst. The comparison of the samples with and without the reducing agent for hydroperoxide used in this study ensures better accuracy in measuring the alcohol, ketone, and hydroperoxide concentrations in the reaction mixture than 10%.

RESULTS AND DISCUSSION

Earlier [3], we suggested a kinetic scheme of oxygen activation on iron porphyrin in the biomimetic system with and without methylviologen. This scheme is a series of the redox reactions in a catalytic cycle similar to the cycle of cytochrome P450. For this study, one should only introduce two overall reactions (active intermediate formation from iron porphyrin and regeneration of the latter) into the kinetic scheme:

$$(Fe(III))^+ \xrightarrow{2e^-, 2H^+, O_2} (FeO)^+ + H_2O, \quad (I)$$

$$(FeO)^+ \xrightarrow{2e^-, 2H^+} (Fe(III))^+ + H_2O. \quad (II)$$

Reactions (I) and (II) are multistep processes with the rate constants equal to the apparent rate constants for the limiting steps. The kinetics of this process corresponds to the steady-state conditions [3].

Most researchers believe that, in the catalytic cycle of cytochrome P450, the high-valence oxo complexes of iron porphyrin (formally, PFe(V)=O or $P^{+\cdot}Fe(IV)$ =O) directly react with the C–H bonds. Unfortunately, none of the available physical methods have detected the hypothetical iron oxo species with double metal-oxygen bonds for this enzyme so far. The $P^{+\cdot}Fe(IV)O$ complexes were identified by the physical and chemical methods for the model system of hydrocarbon oxidation based on iron porphyrin (FeTMPCl) and the active oxygen donor (perbenzoic acid) [6, 7]. The presence of the reducing agent in biomimetic systems shortens the lifetime of active intermediates and makes their identification difficult. In this case, special tests based on studying the kinetic isotopic effect (KIE), substrate selectivity and stereoselectivity are used to investigate the active species [8].

We found earlier [5] that both the kinetic isotopic effect and the abnormally low substrate selectivity during the competitive oxidation of cyclopentane and cyclohexane (a so-called 5/6 parameter) in the $FeP/O_2/Zn/AcOH/CH_3CN$ biomimetic system with and without methylviologen correspond to the electrophilic attack of the active oxygen-containing complexes of iron porphyrins on the C–H bonds. A strong effect of the nature of substituents in the phenyl rings of iron porphyrins on the 5/6 parameter provides further evidence for the fact that a metalloporphyrin is incorporated into the active intermediate.

The active nonradical intermediate $(FeO)^+$ formed in the catalytic cycle of reactions (I) and (II) reacts with saturated hydrocarbons to give radical or molecular products with the probabilities α and $1 - \alpha$, respectively:

$$RH + (FeO)^+ \begin{cases} \xrightarrow{\alpha} R^{\cdot} + {}^{\cdot}OH + (Fe(III))^+ \\ \xrightarrow{1-\alpha} (Fe(IV)\text{–}\overset{H}{\overset{|}{\underset{+}{O}}}\text{–}R) \end{cases} \quad (III)$$

The positively charged complex of the active species with a hydrocarbon either decomposes to give alcohol or reacts with some other reactants to give ketone or alcohol, which seems unlikely at first glance. Because this article is devoted to the radical pathway, let us assume for simplicity that the probability β of alcohol formation via the molecular pathway takes into account these two possibilities:

$$(Fe(IV)\text{–}\overset{H}{\overset{|}{\underset{+}{O}}}\text{–}R) \begin{cases} \xrightarrow{\beta} ROH \\ \xrightarrow{1-\beta} R'O \end{cases} \quad (IV)$$

The formation of the R˙ and ˙OH radicals under aerobic conditions in the presence of proton and electron donors results in hydroperoxide formation:

$$RH + {}^{\cdot}OH \longrightarrow R^{\cdot} + H_2O, \quad (V)$$

$$R^{\cdot} + O_2 \longrightarrow RO_2^{\cdot}, \quad (VI)$$

$$RO_2^{\cdot} \xrightarrow{e^-, H^+} ROOH \quad (VII)$$

Hydroperoxide reacts with various intermediate iron porphyrin complexes and decomposes to alcohol and ketone in the reaction mixture:

$$ROOH + (A) \begin{cases} \xrightarrow{\gamma} ROH + (A') \\ \xrightarrow{1-\gamma} R'O + (A''), \end{cases} \quad (VIII)$$

where (A) represents iron porphyrin complexes; γ and $1 - \gamma$ are the probabilities of the processes; and (A') and (A") specifies the products of iron porphyrin complex transformation.

The presence of proton and electron donors in the reaction mixture also favors the reaction:

$$^{\cdot}OH \xrightarrow{e^-, H^+} H_2O \quad (IX)$$

The above scheme of cyclohexane oxidation differs from that developed earlier in [3, 5] because it takes into account the probabilities α of alkyl radical formation during the reaction of a hydrocarbon with a high-valence iron porphyrin complex. The new scheme also includes the steps of hydroperoxide formation and decomposition. To identify hydroperoxide in the presence of the catalyst is a challenge. GLC analyses are usually performed at high temperatures in both an evaporator and a column thermostat. When metallic chromatographic columns are used for the analysis, hydroperoxide decomposes to alcohol and ketone in the course of the experiment even in the absence of the catalyst. We found that reliable results for the glass chromatographic columns may be obtained only in a freshly prepared column. The catalyst is collected in the column during its operation, thus favoring both a decrease in the hydroperoxide peak and the appearance of the peaks of alcohol and ketone in the chromatogram. There are two approaches to solve this problem: either to remove the catalyst, which is rather difficult, or to quantitatively convert hydroperoxide into a stable chemical compound before the analysis. In the latter case, triphenylphosphine that reduces alkyl hydroperoxide to alcohol with a high rate constant is usually employed. An increase in the relative concentration of alcohol upon the addition of TPP into the sample analyzed suggests the presence of alkyl hydroperoxide in the reaction mixture.

No effect of TPP on the ratio of the cyclohexane oxidation products in the $Zn/O_2/AcOH/CH_3CN/MV$ system was found for the relatively high FeTPP concentrations ((2–4) C_6H_{12} mol/l) [3]. However, a further study of this system at lower initial FeP concentrations suggested a slight increase in the relative alcohol yield upon the addition of TPP into the samples analyzed.

Table 1. Effect of TPP on the results of the analysis of the C_6H_{12} oxidation products in the $FeTDCPP/O_2/Zn/MV/AcOH/CH_3CN$ system. $[MV] = 7.5 \times 10^{-3}$ mol/l and $[FeTDCPP] = 4.8 \times 10^{-5}$ mol/l

t, min	$[ROH] \times 10^4$, mol/l		$[R'O] \times 10^4$, mol/l		[ROH]/[R'O]	
	without TPP	+TPP	without TPP	+TPP	without TPP	+TPP
1	3.9	4.3	1.1	0.7	3.6	6.1
2	8.2	9.0	2.2	1.4	3.7	6.4
3	12.0	12.9	3.0	2.1	4.0	6.1
4	16.0	17.1	3.9	2.9	4.1	5.9
10	18.0	19.5	6.0	4.5	3.0	4.3

Table 1 presents the results of the analysis of the samples with and without TPP for cyclohexane oxidation by air oxygen catalyzed by FeTDCPP in the system with MV. As Table 1 shows, TPP causes both an increase in the alcohol concentration and a decrease in the ketone concentration measured by gas-liquid chromatography. Similar results in the system with and without MV were also obtained for other iron porphyrins studied at the FeP concentrations ranging from 1×10^{-5} to 4×10^{-5} mol/l. The lower the initial iron porphyrin concentration in the reaction mixture, the more pronounced the effect of TPP. At relatively high concentrations $[FeP]_0 > 10^{-4}$ mol/l, the results of the analysis of the samples with and without TPP are within the experimental error. This action of TPP suggests that the samples taken contained cyclohexyl hydroperoxide, which reduced to alcohol in the beginning of the analysis in the presence of TPP or decomposed to alcohol and ketone in the metallic chromatographic column during analysis in the absence of TPP. The presence of hydroperoxide in the reaction mixture was confirmed by the results of the analysis in a specially prepared glass chromatographic column. For quantitative measurements, we compared the samples with and without TPP, because the presence of the catalyst in the samples causes a decrease in the accuracy of measurements in the glass column during its operation. Thus, the sample without TPP contained alcohol and ketone (ROH and R'O) formed during cyclohexane oxidation and alcohol and ketone (0.7 : 1) formed during cyclohexane hydroperoxide decomposition in the metallic column. The sample with TPP contained ROH, R'O, and alcohol formed via hydroperoxide reduction. Using equations (1)–(3), we calculated the alcohol, ketone, and hydroperoxide concentrations in the reaction mixture at the time of sample withdrawal from the alcohol and ketone concentrations in the samples with and without TPP measured by gas-liquid chromatography.

Figure 1 presents the kinetic curves of the accumulation of the cyclohexane oxidation products in the

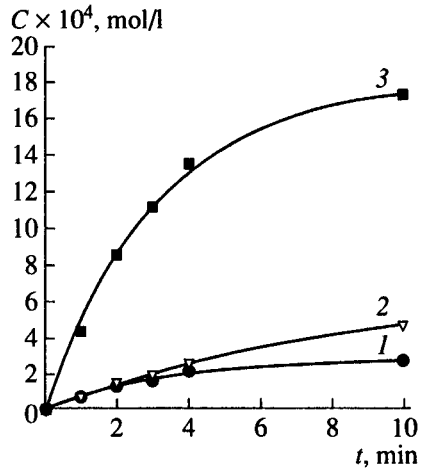

Fig. 1. Kinetic curves of the accumulation of C_6H_{12} oxidation products: (*1*) $C_6H_{11}OOH$, (*2*) $C_6H_{10}O$, and (*3*) $C_6H_{11}OH$. [MV] = 7.5×10^{-3} mol/l and [FeTDCPP] = 4.8×10^{-5} mol/l.

FeTDCPP/Zn/O_2/AcOH/CH_3CN/MV system calculated by equations (1)–(3) and shows that the corresponding hydroperoxide (curve *1*), ketone (curve *2*), and alcohol (curve *3*) are formed in this system. The ratio of the oxidation products [ROH] : [R'O] : [ROOH] changes from 5 : 1 : 1 (for 60 s) to 7 : 2 : 1 (for 600 s). Therefore, the ketone concentration increases as compared to that of alcohol and simultaneously the hydroperoxide concentration decreases as compared to that of each of two other products in the course of the reaction. The kinetic curves of the oxidation catalyzed by iron porphyrins with various substituents in the phenyl rings exhibit the same behavior. The rate of the formation of each product remains unchanged during the first 2–3 min and then dramatically decreases and, after 10–15 min, cyclohexane oxidation virtually completely terminates. We found [6] that the kinetic curves in this case demonstrate the dependence of the oxidation rate on the acetic acid concentration, which is completely consumed in the reaction. The same products of cyclohexane oxidation are formed in the absence of MV, but the rate of their formation is lower by an order of magnitude. The concentrations of ketone and hydroperoxide as compared to that of alcohol are higher than in the system with MV and remain virtually unchanged in the course of the reaction until its termination (in 20–60 min). The presence of substituents in the phenyl rings of iron porphyrin affects both the selectivity and the rate of cyclohexane oxidation in the system with and without MV.

The formation of cyclohexyl hydroperoxide in substantial amounts suggests that cyclohexane oxidation in the biomimetic system studied occurs, at least in part, via the radical pathway.

Using our kinetic scheme of hydrocarbon oxidation in the pseudo-steady-state approximation (assuming that the concentrations of all intermediates, except for [ROOH], are stationary), we calculated the rates of the radical reactions (hydroperoxide accumulation (P_1) and its decomposition to alcohol (P_2) and ketone (P_3)):

$$\frac{d[P_1]}{dt} = \frac{d[ROOH]_{rad}}{dt} = k_6[R^\cdot][O_2] - k_8[ROOH][(A)], \quad (4)$$

$$\frac{d[P_2]}{dt} = \frac{d[ROH]_{rad}}{dt} = \gamma k_8[ROOH][(A)], \quad (5)$$

$$\frac{d[P_3]}{dt} = \frac{d[R'O]_{rad}}{dt} = (1-\gamma)k_8[ROOH][(A)]. \quad (6)$$

Moreover, in accordance with the above scheme, alcohol and ketone are formed via the nonradical pathway with the rates

$$\frac{d[P_4]}{dt} = \frac{d[ROH]_{mol}}{dt} = \beta k_4[FeORH] = (1-\alpha)\beta k_3[RH][(FeO)^+], \quad (7)$$

$$\frac{d[P_5]}{dt} = \frac{d[R'O]_{mol}}{dt} = (1-\beta)k_4[FeORH] = (1-\alpha)(1-\beta)k_3[RH][(FeO)^+]. \quad (8)$$

Taking into account the formulas for the steady-state concentrations of the intermediates and the fact that the concentration of the active iron porphyrin complexes (A), which catalyze hydroperoxide decomposition, is proportional to that of the initial iron porphyrin in accordance with the balance equations, we arrive at:

$$\frac{d[ROOH]_{rad}}{dt} = \alpha'(k_1/k_2)k_3[RH][FeP]_0 - k_8^{app}[ROOH][FeP]_0, \quad (9)$$

$$\frac{d[ROH]_{rad}}{dt} = \gamma k_8^{app}[ROOH][FeP]_0, \quad (10)$$

$$\frac{d[R'O]_{app}}{dt} = (1-\gamma)k_8^{app}[ROOH][FeP]_0, \quad (11)$$

$$\frac{d[ROH]_{mol}}{dt} = (1-\alpha)\beta(k_1k_3/k_2)[RH][FeP]_0, \quad (12)$$

$$\frac{d[R'O]_{mol}}{dt} = (1-\alpha)(1-\beta)(k_1k_3/k_2)[RH][FeP]_0, \quad (13)$$

where $k_8^{app} = k_8[(A)]/[FeP]_0$,

$$\alpha' = \frac{2k_5[RH] + k_9}{k_5[RH] + k_9}\alpha, \quad (14)$$

where k_1, k_2, and k_9 are the apparent rate constants of the corresponding reactions.

Note that $\alpha' = \alpha$ if $k_9 \gg 2k_5[RH]$.

The overall rate w of the accumulation of the oxidation products P_i is expressed as follows:

$$w = \frac{d\sum_{i=1}^{5}[P_i]}{dt} = \frac{d[ROOH]_{rad}}{dt} + \frac{d[ROH]_{rad}}{dt} + \frac{d[ROH]_{mol}}{dt} + \frac{d[R'O]_{rad}}{dt} + \frac{d[R'O]_{mol}}{dt} = (1 - \alpha + \alpha')(k_1/k_2)k_3[RH][FeP]_0. \quad (15)$$

Because the oxidation rate remains unchanged on the greatest portion of the kinetic curve, we assume that w = const. Integrating equation (9) and taking into account equation (15), we derive an expression for the hydroperoxide concentration at time t:

$$[ROOH]_t = \frac{\alpha'' w}{k_8^{app}[FeP]_0}\{1 - \exp(-k_8^{app}[FeP]_0 t)\}, \quad (16)$$

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

As follows from both the α'' definition and equation (14) for the α' parameter, $\alpha'' = \alpha' = \alpha$ if $k_9 \gg 2k_5[RH]$.

Using equations (9)–(11) and (14)–(16), one can easily derive the equations for the relative yields of the products of the radical pathway of cyclohexane oxidation z, x_{rad}, and y_{rad} for hydroperoxide and its decomposition products, alcohol and ketone, respectively, at time t:

$$\begin{cases} x_{rad} = \dfrac{d[ROH]_{rad}}{d\sum_{i=1}^{5}[P_i]} = \alpha''\gamma\left\{1 + \dfrac{\exp(-k_8^{app}[FeP]_0 t) - 1}{k_8^{app}[FeP]_0 t}\right\} \\ y_{rad} = \dfrac{d[R'O]_{rad}}{d\sum_{i=1}^{5}[P_i]} = \alpha''(1 - \gamma)\left\{1 + \dfrac{\exp(-k_8^{app}[FeP]_0 t) - 1}{k_8^{app}[FeP]_0 t}\right\} \\ z = \dfrac{d[ROOH]_{rad}}{d\sum_{i=1}^{5}[P_i]} = \dfrac{\alpha''\{1 - \exp(-k_8^{app}[FeP]_0 t)\}}{k_8^{app}[FeP]_0 t}. \end{cases} \quad (17)$$

In accordance with equations (17), the relative fraction of the oxidation products formed via the radical pathway ($P_{rad,i}$) may be represented by the following equation:

$$\frac{\sum_{i=1}^{3}[P_{rad,i}]}{\sum_{i=1}^{5}[P_i]} = z + x_{rad} + y_{rad} = z\frac{k_8^{app}[FeP]_0 t}{1 - \exp(-k_8^{app}[FeP]_0 t)} = \alpha''. \quad (18)$$

Thus, the relative fraction of the hydrocarbon oxidation products formed via the radical pathway is α''. As noted above, $\alpha'' = \alpha' = \alpha$ if $k_9 \gg 2k_5[RH]$; that is, the fraction of the oxidation products formed via the radical pathway is equal to the probability of alkyl radical formation via reaction (III). If this ratio is not true, the α'' value is higher than the α value, which is quite natural because, in this case, the reaction between $^{\cdot}OH$ radicals and a hydrocarbon contributes to hydroperoxide formation.

According to equation (18), the k_8^{app} value may be calculated from the current hydroperoxide concentration z (in arbitrary units), corresponding to reaction time t and the initial iron porphyrin concentration $[FeP]_0$, using the experimental apparent rate constants for hydroperoxide decomposition (k_8^{app}). To obtain the z values, we studied the kinetics of the accumulation of the cyclohexane oxidation products over a wide concentration range of iron porphyrins with various substituents in phenyl rings (1×10^{-5}–4×10^{-4} mol/l) in the biomimetic system with and without MV. To determine the k_8^{app} values, we investigated here the kinetics of cyclohexyl hydroperoxide decomposition under the same experimental conditions.

Cyclohexane hydroperoxide decomposes to alcohol and ketone in the system studied. Figure 2 presents the kinetic curves of hydroperoxide decomposition and alcohol and ketone accumulation in the reaction mixture calculated by equations (1)–(3). The initial rate of

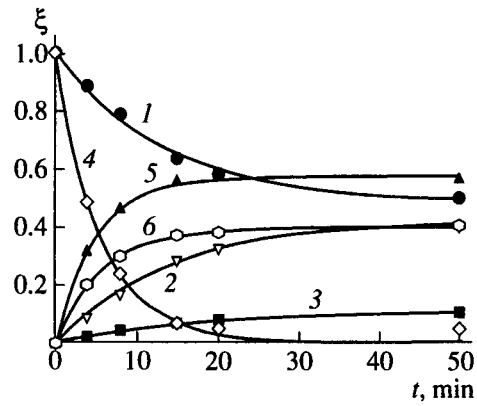

Fig. 2. Variations in the relative concentrations of (*1*, *4*) hydroperoxide and (*2*, *3*, *5*, *6*) the products of its decomposition catalyzed by FeTDCPP: (*1*, *4*) $C_6H_{11}OOH$, (*2*, *5*) $C_6H_{11}OH$, and (*4*, *6*) $C_6H_{10}O$. $\xi = \frac{[P_i]_t}{[C_6H_{11}OOH]_0}$, where $[P_i]_t$ is the substrate or product concentration at time *t*. [MV] = 0, [FeTDCPP] = 1×10^{-5} mol/l and (*4*–*6*) [FeTDCPP] = 6×10^{-5} mol/l.

hydroperoxide decomposition is proportional to the initial FeP and ROOH concentrations and obeys the equation:

$$w_0' = \frac{d[ROOH]}{dt} = k_{app}[ROOH]_0[FeP]_0. \quad (19)$$

In the course of the reaction, iron porphyrin destruction is observed, which is accompanied by a decrease in w'. However, a substantial portion of the kinetic curves corresponds to iron porphyrin destruction of less than 5%. For this portion, the kinetics of hydroperoxide decomposition follows the law:

$$\ln\frac{[ROOH]_t}{[ROOH]_0} = -k_{app}[FeP]_0 t. \quad (20)$$

The kinetic parameters of this process were calculated from the experimental results obtained for the reaction time corresponding to the iron porphyrin destruction of less than 5% (120 and 480 s for the systems with and without MV, respectively). Table 2 presents the rate constants for the catalytic decomposition of cyclohexyl hydroperoxide by iron porphyrin with various substituents in the phenyl rings calculated by equation (20). The highest reaction rate constants were obtained for FeTPP and FeTDCPP in the presence of MV. The selectivity to alcohol (γ = [ROH]/([ROH] + [R'O])) depends on the iron porphyrin nature and its concentration. Table 2 also lists the γ values at $[FeP]_0 = 4 \times 10^{-5}$ mol/l for iron porphyrins with various substituents in the phenyl rings. For all iron porphyrins studied (with and without MV), the selectivity to alcohol γ ranges from 0.5 to 0.9. In the system with MV (7.5×10^{-2} mol/l), the γ value remains virtually unchanged when varying the initial iron porphyrin concentrations. In the absence of MV, an increase in $[FeP]_0$ is accompanied by a decrease in the γ value. For example, the γ (for t = 480 s) dependence on $[FeTDCPP]_0$ in the absence of MV can formally be described by the equation:

$$\gamma = 0.5 + 0.38\exp(-175t[FeP]_0). \quad (21)$$

The mechanism of cyclohexyl hydroperoxide decomposition in the presence of iron porphyrin and proton and electron donors will be considered elsewhere. Note only that the apparent kinetics suggests the molecular mechanism of this process.

Let us assume that the apparent rate constants for cyclohexyl hydroperoxide decomposition in the absence of cyclohexane k_{app} (Table 2) are identical to those for step (VIII) of cyclohexane oxidation k_8^{app}. Moreover, to calculate the α'' values by equation (18), one should know the relative current concentration of cyclohexane hydroperoxide at a certain time t of cyclohexane oxidation. We took t = 120 s for the system with MV and t = 480 s for the system without MV. Our choice was governed by the following facts: (1) a noticeable amount of cyclohexane oxidation products is accumulated during this time interval, which improves the accuracy of measurements; (2) the reaction rate remains unchanged at these times on the kinetic curves of the accumulation of the cyclohexane oxidation products; and (3) in the experiments on cyclohexane hydroperoxide decomposition, these times correspond to the iron porphyrin destruction of less than 5%.

For each iron porphyrin, the α'' values calculated from the experimental z values for the reaction times chosen and the corresponding values of $k_8^{app} = k_{app}$ remain unchanged within the experimental error over a wide $[FeP]_0$ range (10^{-5}–10^{-4} mol/l). This confirms the validity of our assumption that $k_8^{app} = k_{app}$. Table 3 presents the average α'' values calculated from the experimental data for different initial iron porphyrin concentrations. As Table 3 shows, the fraction of the oxidation products formed via the radical pathway is less than 20% of the overall product yield. The introduction of MV into the reaction mixture does not change the α'' value within the experimental error. The fact that meth-

Table 2. Apparent rate constants and selectivity of $C_6H_{11}OOH$ decomposition catalyzed by iron porphyrins (FeP)

Parameter	FeTDCPP		FeTPP	FeTpivPP
$[MV] \times 10^3$, mol/l	7.5	0	7.5	7.5
k_{app}, l mol^{-1} s^{-1}	120	50	120	67
γ*	0.80	0.80	0.80	0.83

* The values are given for $[FeP]_0 = 4 \times 10^{-5}$ mol/l

Table 3. Kinetic parameter α'' for C_6H_{12} oxidation catalyzed by iron porphyrins

Parameter	FeTPP	FeTpivPP	FeTDCPP	FeTDCPP
$[MV] \times 10^3$, mol/l	7.5	7.5	7.5	0
α''	0.13	0.12	0.17	0.20

Table 4. Distribution of the products of the radical ($P_{rad,i}$) and molecular ($P_{mol,i}$) pathways* of C_6H_{12} oxidation in the FeTDCPP/O_2/Zn/MV/AcOH/CH_3CN system at reaction time t. [FeP] = 1×10^{-4} mol/l, t = 120 s for [MV] = 7.5×10^{-3} mol/l and t = 480 s for [MV] = 0

FeP	[MV] × 10^3, mol/l	$(ROOH)_{rad}$	$(ROH)_{rad}$	$(R'O)_{rad}$	$(ROH)_{mol}$	$(R'O)_{mol}$
FeTPP	7.5	7	5	1	65	22
FeTpivPP	7.5	8	4	1	68	19
FeTDCPP	7.5	9	6	2	60	23
FeTDCPP	0	7	7	6	48	32

* Represented in the form $\frac{[P_i]}{\sum_{i=1}^{5}[P_i]} \times 100\%$.

ylviologen affects neither the α" value nor the 5/6 parameter of the substrate selectivity during the competitive oxidation of cyclopentane and cyclohexane [5] suggests that the inequality $k_9 \gg 2k_5[RH]$ is true for the system studied (with and without MV). Therefore, α" = α in this biomimetic system; that is, the reaction of hydroxyl radicals with a hydrocarbon has slight effect on the reaction kinetics, which is natural in the presence of a large number of electrons and protons in the reaction mixture. The radical pathway is governed exclusively by alkyl radical formation via reaction (III) and makes a minor contribution to the formation of the cyclohexane oxidation products.

The concentrations (in %) of the products of the radical pathway of cyclohexane oxidation ($z \times 100\%$, $x_{rad} \times 100\%$, and $y_{rad} \times 100\%$) at the time t may be calculated from the γ, α", and k_8^{app} values by equations (17) assuming that $k_8^{app} = k_{app}$ (Tables 2 and 3). Then, from the experimental concentrations of alcohol and ketone in the reaction mixture at time t,

$$x \times 100\% = \frac{[ROH]_{rad} + [ROH]_{mol}}{\sum_{i=1}^{5}[P_i]} \times 100\%,$$

and

$$y \times 100\% = \frac{[R'O]_{rad} + [R'O]_{mol}}{\sum_{i=1}^{5}[P_i]} \times 100\%,$$

one can calculate the concentrations of alcohol and ketone formed via the nonradical pathway at time t,

$$x_{mol} \times 100\% = \frac{[ROH]_{mol}}{\sum_{i=1}^{5}[P_i]} \times 100\% = (x - x_{rad}) \times 100\%,$$
$$y_{mol} \times 100\% = \frac{[R'O]_{mol}}{\sum_{i=1}^{5}[P_i]} \times 100\% = (y - y_{rad}) \times 100\%. \quad (22)$$

Table 4 lists the composition of the cyclohexane oxidation products in the biomimetic system at the time t (120 and 480 s for the systems with and without MV, respectively) calculated by equations (17) and (22) for iron porphyrins with various substituents in the phenyl rings. Table 4 shows that both alcohol and ketone are mainly formed via the molecular pathway (for all iron porphyrins studied with and without MV). As noted above, alcohol in this case is directly formed during the decomposition of the active intermediate complex with a hydrocarbon. At the same time, ketone is formed in the reaction of this complex with other components of the reaction mixture, which implies a relatively long lifetime of this complex. The mechanism of the formation of cyclohexane oxidation products via the molecular pathway will be considered in our next publication.

CONCLUSION

Our present and earlier findings [3, 5] suggest that iron porphyrin complexes formed by the reductive activation of oxygen in the presence of a proton donor are virtually the only active species that react with the C–H bonds of cyclohexane. The radical pathway of reaction product formation is governed by alkyl radical formation and comprises less than 20%. Therefore, this system is a good model for the mechanism of hydrocarbon oxidation by natural monooxygenases.

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