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Oxidation of Cycloalkanes by Hydrogen Peroxide in a Biomimetic Iron Porphyrin System

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Abstract—The kinetics of cyclohexane and cyclopentane oxidation by hydrogen peroxide catalyzed by iron porphyrins (FeTPP and FeTDCPP) in acetonitrile solutions is studied at room temperature by analyzing product accumulation with the GLC method. The effects of various additives (acetic acid, imidazole, and hydroquinone) on the substrate selectivity of the competitive oxidation of C_6H_{12} and C_5H_{10} are studied. In the FeTDCPP/H_2O_2/O_2/AcOH/CH_3CN system, cyclohexane is oxidized to the corresponding alcohol, ketone, and hydroperoxide. The fraction of the product (hydroperoxide) formed by the radical mechanism is 20–30%. The alcohol and ketone are formed by the molecular pathway in a ratio of (6–7) : 1. Kinetic parameters of cycloalkane oxidation are compared in a biomimetic system with hydrogen peroxide (the shunt system) and the system based on dioxygen with electron and proton donors. The latter system modeled cytochrome P-450. It is shown that active species are the same in both systems. The kinetic scheme of the alkane oxidation process is proposed for the shunt system.

INTRODUCTION

Hydrogen peroxide is a widely used, environmentally friendly oxidant because it contains active oxygen and the side product of oxidation is water. Unfortunately, the use of this oxidant and dioxygen leads to a complex and poorly controllable product composition [1]. However, there are numerous highly selective natural processes based on these two oxidants [2, 3]. The design of chemical analogs of such processes is a topical problem [4, 5]. Current studies in the field of hydrocarbon oxidation catalyzed by synthetic porphyrin complexes of metals are successful [3, 6].

We proposed and studied a biomimetic system for alkane oxidation catalyzed by iron porphyrins (FeP) in acetonitrile solutions. Dioxygen was used in this system as an oxidant, which is activated on an iron porphyrin center in the presence of a reducing agent (zinc powder) and a proton donor (acetic acid) to form complexes capable of attacking C–H bonds [7, 8]. The kinetic study of cyclohexane oxidation in this system showed that the addition of methyl viologen increases the rate of product accumulation by more than an order of magnitude [8]. In the absence of a catalyst in the reaction mixture, hydrogen peroxide is formed. On this basis, we proposed that the role of FeP in the presence of methyl viologen is reduced to the catalysis of H_2O_2 decomposition. In this work, we tested this hypothesis by studying the kinetics and substrate selectivity of the competitive oxidation of cyclopentane and cyclohexane by hydrogen peroxide catalyzed by FeP.

EXPERIMENTAL

The reaction was carried out in an air atmosphere at 20°C with stirring by a magnetic stirrer. Iron(III) tetraphenylporphyrin (FeTPP) and *meso*-tetrakis(2,6-dichlorophenyl)porphyrin (FeTDCPP) chlorides were synthesized using techniques described earlier [7]. These reagents were added to the reaction mixture in the form of benzene solutions (50 μl) with necessary concentrations. Hydrogen peroxide was added to the mixture either in the form of a 30% aqueous solution (100 μl) in 10-μl portions every 5 min (in substrate selectivity studies) or in the form of an 18% solution in methyl *tert*-butyl ether (instantaneously or in portions with intervals) in all other experiments. The volume of the liquid phase of the reaction mixture was 1 ml. The volume of the gas phase was 50 ml. The concentration of cyclopentane was 0.55 mol/l. The concentration of FeTPP was 4×10^{-3} mol/l. The concentrations of other components were varied in the following ranges: [FeTDCPP] = $(1–10) \times 10^{-5}$ mol/l, $[C_6H_{12}] = (23–70) \times 10^{-2}$ mol/l, $[H_2O_2] = (1–100) \times 10^{-3}$ mol/l. Acetonitrile was a solvent. The products of cycloalkane oxidation were analyzed by GLC using a metallic chromatographic column packed with 10% Carbowax-20M on Celite.

The concentrations of cyclohexyl hydroperoxide, cyclohexanol, and cyclohexanone in the reaction mixture during cyclohexane oxidation in the system under study were determined by comparing the results of analyzing GLC samples with triphenylphosphine (TPP) that reduced hydrogen peroxide and without TPP, according to the method described in [9]. The concen-

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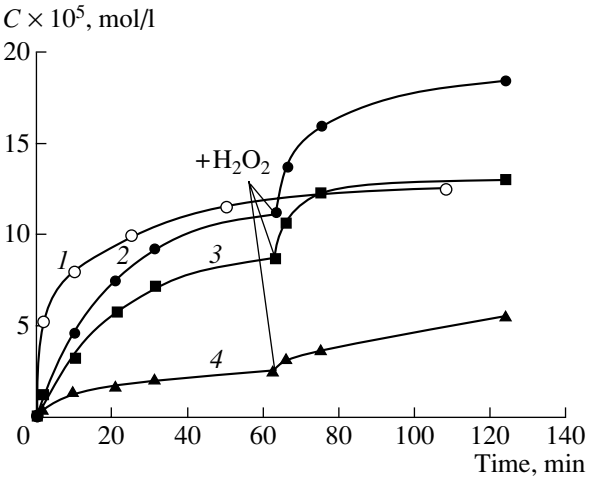

Fig. 1. Kinetic curves of product accumulation in cyclohexane oxidation by hydrogen peroxide (samples without TPP): (*1, 2*) $C = \sum[P] = ([C_6H_{11}OH]_a + [C_6H_{10}O]_a)$, (*3*) $C = [C_6H_{11}OH]_a$, and (*4*) $C = [C_6H_{10}O]_a$. $[H_2O_2]_0 = 0.1$ mol/l. Reaction conditions: [FeTDCPP] = 8.4×10^{-5} mol/l, $[C_6H_{12}]_0 = 6.0 \times 10^{-5}$ mol/l; [AcOH] = 0.1 mol/l. In runs *2–4*, 0.1 mol/l H_2O_2 was added after 63 min.

trations of products were calculated according to the following formulas:

$$[C_6H_{10}O] = [C_6H_{10}O]_{TPP} = [1/(1+b)]\sum[P], \quad (1)$$

$$[C_6H_{11}OOH] = 1.7([C_6H_{10}O]_a - [C_6H_{10}O]_{TPP}) = 1.7[(b-a)/(1+a)(1+b)]\sum[P], \quad (2)$$

$$[C_6H_{11}OH] = [C_6H_{11}OH]_a - 0.7([C_6H_{10}O]_a - [C_6H_{10}O]_{TPP}) = (\sum[P]) - [C_6H_{10}O] - [C_6H_{11}OOH]), \quad (3)$$

where $[C_6H_{10}O]_a$ and $[C_6H_{11}OH]_a$ are the concentrations of ketone and alcohol, respectively, obtained in analyses without TPP; $[C_6H_{10}O]_{TPP}$ and $[C_6H_{11}OH]_{TPP}$ are the concentrations of ketone and alcohol, respectively, obtained in analyses with TPP; $a = [C_6H_{11}OH]_a/[C_6H_{10}O]_a$; $b = [C_6H_{11}OH]_{TPP}/[C_6H_{10}O]_{TPP}$; and $\sum[P] = [C_6H_{11}OH]_a + [C_6H_{10}O]_a = [C_6H_{11}OH]_{TPP} + [C_6H_{10}O]_{TPP}$.

The coefficient equal to 1.7 in Eq. (2) and 0.7 in Eq. (3) are the experimental ratios of alcohol and ketone in the decomposition of cyclohexyl hydroperoxide in the chromatographic column (0.7 : 1). This ratio was independent of the presence of other reactants present in the system.

The ratio of cyclopentane and cyclohexane reactivities per one C–H bond was estimated by the method described in detail in [10] from the substrate selectivity parameter (5/6) calculated by the formula

$$(5/6) = 1.2([C_6H_{12}]_0/[C_5H_{10}]_0)([C_5H_8O]_a + [C_5H_9OH]_a)/([C_6H_{10}O]_a + [C_6H_{11}OH]_a), \quad (4)$$

where the subscript 0 refers to the initial concentrations of cyclopentane and cyclohexane.

RESULTS

The substrate selectivity of cycloalkane oxidation in the FeP/H_2O_2/O_2/CH_3CN system. The values of parameters of substrate selectivities in cyclopentane and cyclohexane oxidation by hydrogen peroxide catalyzed by FeTPP and FeTDCPP in an acetonitrile solution with the additives of 2-methylimidazole and/or acetic acid and without them in the presence and in the absence of hydroquinone were calculated by Eq. (4) (Table 1). It can be seen that the addition of hydroquinone to the system without imidazole and AcOH somewhat decreases the value of the substrate selectivity parameter (5/6). This parameter was measured reliably in the case of catalysis by FeTDCPP (cf. $(5/6)_{FeTDCPP}$ = 0.59–0.65 without hydroquinone and $(5/6)_{FeTDCPP}$ = 0.46–0.50 with hydroquinone). In the presence of at least one of the cited additives (imidazole or AcOH), the addition of hydroquinone to the reaction mixture does not affect the value of the (5/6) parameter. For all studied variants (with and without additives), hydroquinone weakly affects the rates of formation and the product ratio of alcohol and ketone (changes smaller than by a factor of 1.5) for each of the cycloalkanes.[1]

Kinetic curves of cyclohexanol and cyclohexanone accumulation in cyclohexane oxidation in the FeTDCPP/H_2O_2/O_2/CH_3CN system obtained by GLC without TPP are shown in Fig. 1. It can be seen that the overall initial rate of oxidation product buildup increases with an increase in the initial concentration of hydrogen peroxide. Changes in the initial concentration of iron porphyrin in the range of [FeTDCPP] = $(1–10) \times 10^{-5}$ mol/l weakly affects the oxidation rate. The initial rate of accumulation of cyclohexane oxidation products $w_0 = d\sum[P]/dt$ in the range of studied concentrations of initial reactants is proportional to $[H_2O_2]_0^{0.5-1}$ and $[FeP]_0^{0-0.5}$.

In the course of reaction, the rate of oxidation product buildup decreases (Fig. 1). The addition of a new portion of hydrogen peroxide (which is 4 times greater than the initial one) 63 min after the reaction begins leads to an increase in the rate of oxidation product buildup (Fig. 1, curves *2–4*). However, the rate of reaction does not reach the value of the initial rate of oxidation product buildup for the same concentration of hydrogen peroxide in the initial mixture (cf. curves *1* and *2* in Fig. 1). The maximal rate u_{max} of C_6H_{12}

[1] The concentrations of products were obtained by GLC without TPP.

accumulation in the studied range of reactant concentrations ($[C_6H_{12}]$ = 0.23–0.70 mol/l, [FeTDCPP] = (1–10) × 10^{-5} mol/l, $[H_2O_2]$ = (1–20) × 10^{-3} mol/l) is lower than $w_{max} < 10^{-6}$ mol l^{-1} s^{-1}. The transition from hydrogen peroxide addition to the reaction mixture in the initial moment to the addition of the same amount of H_2O_2 in the course of the reaction in portions with a small (ten times lower) concentration results in a decrease in the rate of oxidation product buildup. The conversion of cyclohexane is lower than 1%. Both in the case of one-time addition of hydrogen peroxide and when it is added in portions in the course of reaction, iron porphyrin destruction is observed.

Kinetic curves of cyclohexyl hydroperoxide, cyclohexanol, and cyclohexanone accumulation in the FeTDCPP/H_2O_2/O_2/AcOH/CH_3CN system calculated from experimental data using formulas (1)–(3) are shown in Fig. 2. It is seen from this figure that an increase in the concentration of hydrogen peroxide leads to a proportional increase in the rate of accumulation of all three products.

Selectivities to the products of cyclohexane oxidation in the FeTDCPP/H_2O_2/O_2AcOH/CH_3CN system. A relative yield of cyclohexyl hydroperoxide z = [ROOH]/([ROOH] + [ROH] + [R'O]) = 0.20–0.27 is independent of the concentrations of initial reactants in the ranges $[FeTDCPP]_0$ = (1–10) × 10^{-5} mol/l and $[H_2O_2]_0$ = (1–20) × 10^{-2} mol/l. The value of z change very little during the reaction up to the deep destruction of iron porphyrin, which is accompanied by its decoloration. The ratio between the initial rates of alcohol and ketone formation $w_{ROH}/w_{R'O}$ = 6.2–7.0 does not change with a change in $[FeTDCPP]_0$. When H_2O_2 in a high concentration is added to the system in portions (0.250 mol/l, 0.025 mol/l every 2 min), about the same ratio of the yields of cyclohexyl hydroperoxide, alcohol, and ketone (25 : 61 : 11) is observed after 50 min (Table 2) as in the case of one-time addition of hydrogen peroxide. The extent of iron porphyrin destruction reaches 90% by that time. Then, the rate of product accumulation decreases and z increases during the reaction. After one day, cyclohexyl hydroperoxide makes up 85% of the cyclohexane oxidation products. The overall rate of product accumulation in this case is at most 10^{-6} mol l^{-1} s^{-1}.

Cyclohexyl hydroperoxide decomposition in the FeTDCPP/H_2O_2/O_2/AcOH/CH_3CN system occurs with a relatively low rate constant. When the concentration of [FeTDCPP] ranges from 1 × 10^{-5} to 10 × 10^{-5} mol/l, a decrease in the concentration of $C_6H_{11}OOH$ is smaller than 10% for 30 min.

Table 1. Substrate selectivity in cycloalkane oxidation ($[C_6H_{12}]_0$ = 0.23 mol/l, $[C_5H_{10}]_0$ = 0.55 mol/l)

FeP	Oxidant	[AcOH], mol/l	[Imidazole], mol/l	[Hydroquinone], mol/l	(5/6)
FeTPP	O_2[a]	0.35	0.05	0	0.45 ± 0.03
	H_2O_2[b, c]	0	0	0	0.49 ± 0.01
		0	0	0.04	0.45 ± 0.03
		0.1	0	0	0.45 ± 0.02
		0	0.05	0	0.47 ± 0.02
		0.1	0.05	0	0.46 ± 0.03
		0.1	0.05	0.04	0.47 ± 0.03
FeTDCPP	O_2[a]	0.35	0.05	0	0.50 ± 0.02
		0.35	0.05	0.04	0.49 ± 0.02
	H_2O_2[b, d]	0	0	0	0.62 ± 0.03
		0	0	0.04	0.48 ± 0.02
		0.1	0.05	0	0.48 ± 0.02
		0.1	0	0	0.50 ± 0.05
		0	0.05	0	0.49 ± 0.02
		0	0.05	0.04	0.48 ± 0.02

Note: [a] Complete biomimetic system: 30 mg Zn, 7.5 × 10^{-3} mol/l methyl viologen; 2 × 10^{-4} mol/l FeP [11].
[b] Shunt biomimetic system; 0.2 mol/l H_2O_2 (aqueous 0.02 mol/l added in portions with 5-min intervals).
[c] 4 × 10^{-3} mol/l FeP.
[d] 10^{-4} mol/l FeP.

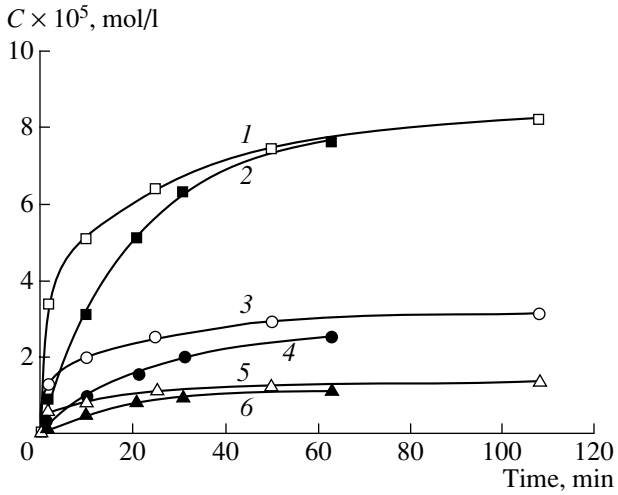

Fig. 2. Kinetic curves of product accumulation in cyclohexane oxidation by hydrogen peroxide (calculated using the results of GLC analysis of the samples with and without TPP): (*1*, *2*) $C_6H_{11}OH$, (*3*, *4*) $C_6H_{11}OOH$, and (*5*, *6*) $C_6H_{10}O$. Reaction conditions: (*1*, *3*, *5*) $[H_2O_2]_0$ = 0.1 mol/l; (*2*, *4*, *6*) $[H_2O_2]_0$ = 0.025 mol/l, [FeTDCPP] = 8.4×10^{-5} mol/l; $[C_6H_{12}]_0 = 6 \times 10^{-5}$ mol/l; and [AcOH] = 0.1 mol/l.

DISCUSSION

Earlier, we found compelling evidence [7, 8] that the FeP/O_2/Zn/AcOH/CH_3CN system models the catalytic cycle of natural monooxygenase, cytochrome P-450 (Fig. 3). This cycle is a sequence of steps for the reductive activation of dioxygen. These steps are well studied except for those where the products of complex HR—Fe^+O_2 protonation are formed via the X—RH intermediate (Fig. 3). The FeP/H_2O_2/O_2/CH_3CN system studied in this work can be called a shunt system by analogy with biological systems for hydrocarbon oxidation because it uses a donor of active oxygen as an oxidant and the catalytic cycle is shortened (see Fig. 3). First of all, we had to check if the same species are formed in the shortened cycle of iron porphyrins (the shunt biomimetic FeP/H_2O_2/O_2/CH_3CN system) as in the complete cycle for the reductive activation of dioxygen (the complete biomimetic FeP/O_2/Zn/AcOH/CH_3CN system).

Table 2. Selectivity of cyclohexane oxidation in the process when hydrogen peroxide* is added in portions to the reaction mixture (0.25 mol/l H_2O_2, 0.025 mol/l portions with 5-min intervals) ($[C_6H_{12}]_0$ = 0.7 mol/l, [AcOH] = 0.1 mol/l, [FeTDCPP] = 6.0×10^{-5} mol/l)

Time, min	$\Sigma[P] \times 10^5$, mol/l	[ROOH], %	[ROH], %	[R'O], %
50	12.5	25	64	11
85	16.1	28	61	11
170	21.2	35	52	13
1500	123.3	85	11	4

* 18% H_2O_2 in methyl *tert*-butyl ether.

Our studies showed (Table 1) that the values of parameters of substrate selectivity for the shunt system $(5/6)_{FeTPP}$ = 0.48–0.50 and $(5/6)_{FeTDCPP}$ = 0.59–0.65 differ (in the latter case for certain) from the values corresponding to the complete system [10]: $(5/6)_{FeTPP}$ = 0.42–0.48 and $(5/6)_{FeTDCPP}$ = 0.48–0.52. The addition of AcOH or imidazole to the shunt system leads to a decrease in the (5/6) parameter to the values corresponding to the complete system (Table 1). In this case, hydroquinone has virtually no effect on the value of the substrate selectivity. In the absence of the above additives, hydroquinone (see Table 1) decreases the (5/6) parameter to the value of the substrate selectivity in the complete system (within the experimental accuracy). It is generally agreed [11] that the parameter of substrate selectivity determined from the ratio of the rate constants of active intermediate interaction with the C–H bond in the competitive oxidation of cyclohexane and cyclopentane is a measure of the partial charge of the carbon atom in the transition state. For hydrogen atom abstraction by a radical or a radical ion, the value of this parameter ranges from 0.7–1.2 independently of the reactant charge. For the electrophilic attack of the positively charged reactant, the (5/6) parameter is lower than or equal to 0.5 and this value changed with a change in the reactant charge. Analysis of our data shows that, in the absence of additives in the shunt system, the $(5/6)_{FeTDCPP}$ value is well above 0.5 and close to the value that is characteristic of hydrogen abstraction by $^{\bullet}OH$ (1–0.7) [11, 12]. In all other cases, the value of (5/6) is close to that observed in the case of the attack by a positively charged reactant. A change in the (5/6) value when substituents are introduced into the phenyl rings of a porphyrin (cf. $(5/6)_{FeTPP}$ and $(5/6)_{FeTDCPP}$) points to the fact that, in the shunt system with hydroquinone, imidazole, and acetic acid additives, iron porphyrin complexes are immediate reactants that attack alkanes.

The structure of iron porphyrin complexes in biomimetic systems like those discussed in this paper and in natural biosystems has not yet been definitively established [3]. Without going into details, we denote iron porphyrin complexes, which attack alkanes in our biomimetic systems, by $(PFeO)^+$.

It is likely that in the shunt system without additives there are two different active species, the $(PFeO)^+$ complexes and hydroxyl radicals. The values of the (5/6) parameter and the way hydroquinone affects it show that the main reactant is $^{\bullet}OH$ in the catalysis by FeTDCPP and the $(PFeO)^+$ complex in the catalysis by FeTPP.

Indeed, when metal complexes react with H_2O_2, several active species can be generated depending on the

reaction conditions: hydroxyl radicals and metal oxo complexes. In the case of the homolytic dissociation of the O–O bond in hydrogen peroxide coordinated to metal porphyrin, PM(IV)=O (M is metal) and $OH^{\bullet}$ radicals are formed. In the case of heterolytic dissociation, water and PM(V)=O or $P^{+\bullet}$ M(IV) =O are formed. Therefore, the first step in the shunt system is the reaction

$$(PFe(III))^{+} + H_2O_2 \xrightarrow{\delta} (PFeO)^{+} + H_2O, \qquad (I)$$
$$\xrightarrow{1-\delta} (PFe(IV)OH)^{+} + {}^{\bullet}OH,$$

where δ and $1 - \delta$ are the probabilities of heterolytic and homolytic dissociation of the O–O bonds in hydrogen peroxide.

The probability of heterolytic dissociation of H_2O_2 in metal porphyrin biomimetic systems is a widely debated question. Traylor *et al.* [13] concluded that the O–O bond in hydrogen peroxide coordinated to iron porphyrin in proton solvents only dissociates heterolytically to form PFe(V)O, which then reacts with either olefins or a peroxide. Interaction with peroxides (H_2O_2 or ROOH) produces radical intermediates ($OH^{\bullet}$, $HO_2^{\bullet}$, $RO^{\bullet}$, and $RO_2^{\bullet}$). By increasing the electronegativity of FeP (by introducing substituents in the porphyrin ring), Traylor *et al.* [13] forced dominant interactions of active species with the olefin and thus increased the yield of epoxide based on the peroxide to 60–100%. Others assume that homolysis is the main pathway in, for instance, the MnTDCPP–H_2O_2 system [6, 14]. The addition of imidazole to the system changes the kinetics and oxidation product composition [14]. The high activity of this system is explained by a dual function of imidazole: it serves as a nucleophilic axial ligand, which favors the heterolytic dissociation of the O–O bond with the formation of PMn(V)O complexes, and as an electrophilic acid catalyst of this decomposition [14].

In accordance with the above speculation, it is necessary to add the following step to the kinetic scheme of the process in the shunt system:

$$(PFeO)^{+} + H_2O_2 \xrightarrow{\gamma} (PFe(III))^{+} + O_2 + H_2O, \qquad (II)$$
$$\xrightarrow{1-\gamma} (PFe(III))^{+} + {}^{\bullet}OH + HO_2^{\bullet}.$$

In this step, hydrogen peroxide heterolytically decomposes into oxygen and water with probability γ. Note that the sequence of steps (I) and (II) (with probabilities δ and γ, respectively) model the catalytic cycle of catalase.

The $(PFeO)^{+}$ complexes formed in the shunt system by the heterolysis of hydrogen peroxide (I) are the immediate reactants that attack the C–H bond. As we showed earlier for the complete system [9], the free radical $R^{\bullet}$ is formed with probability α and the iron porphyrin complex with a hydrocarbon is formed with probability $(1 - \alpha)$:

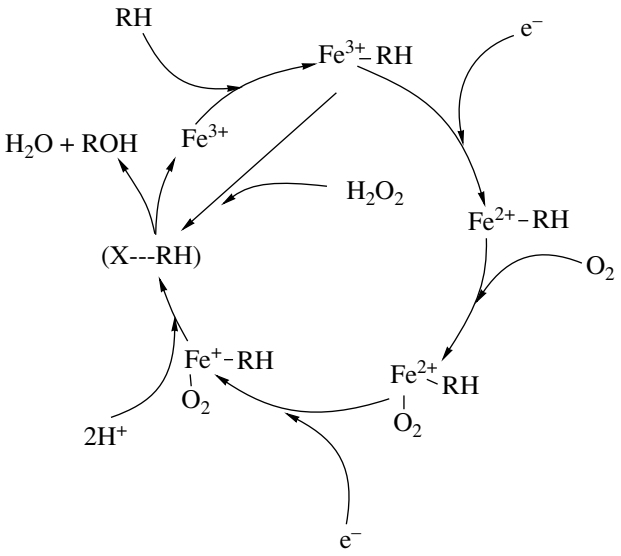

Fig. 3. Catalytic cycle of cytochrome P-450.

$$(PFeO)^{+} + RH \xrightarrow{\alpha} (PFe(III))^{+} + {}^{\bullet}OH + R^{\bullet}, \qquad (III)$$
$$\xrightarrow{1-\alpha} (PFe{-}{-}{-}O{-}{-}{-}HR)^{+}.$$

Earlier, we proposed a scheme for the formation of oxidation products from the $(PFe{-}{-}{-}O{-}{-}{-}HR)^{+}$ complex in the complete system, which agrees well with experimental observations [15]. Based on the fact that the species are identical, we assume the analogous scheme for the formation of an alcohol and ketone via a nonradical pathway in the shunt system:

$$(PFe{-}{-}{-}O{-}{-}{-}HR)^{+} \longrightarrow ROH + (PFe(III))^{+}, \qquad (IV)$$

$$(PFe{-}{-}{-}O{-}{-}{-}HR)^{+} + O_2 \longrightarrow R'O + HO_2^{\bullet} + H^{+} + (PFe(II)). \qquad (V)$$

In the presence of oxygen, iron(II) porphyrin formed in step (V) produces the $(PFe(II)O_2)$ complex with a high rate constant. Then, this complex decomposes into a peroxo radical and iron(III) porphyrinate in the absence of a reducing agent.

The formation of radicals $^{\bullet}OH$ and $HO_2^{\bullet}$ may lead to FeP destruction

$$(PFe(III))^{+} + {}^{\bullet}OH(HO_2^{\bullet}) \longrightarrow H_2O(H_2O_2) + P_1 \qquad (VI)$$

and to the radical oxidation of alkanes to form hydroperoxide in the following reactions:

$$RH + {}^{\bullet}OH(HO_2^{\bullet}) \longrightarrow R^{\bullet} + H_2O(H_2O_2), \qquad (VII)$$

$$R^{\bullet} + O_2 \longrightarrow RO_2^{\bullet}, \quad \text{(VIII)}$$

$$RO_2^{\bullet} + AH \longrightarrow ROOH + A^{\bullet}, \quad \text{(IX)}$$

where P_1 is the product of iron porphyrin destruction and AH is a hydrogen-atom donor.

AH can be hydrogen peroxide or a substrate:

$$RO_2^{\bullet} + H_2O_2 \longrightarrow ROOH + HO_2^{\bullet}, \quad \text{(IX')}$$

$$RO_2^{\bullet} + RH \longrightarrow ROOH + R^{\bullet}. \quad \text{(IX")}$$

Furthermore, it is necessary to consider the formation of alcohol and ketone via a radical pathway, for instance, in reactions

$$RO_2^{\bullet} + RO_2^{\bullet} \longrightarrow R'O + ROH + O_2, \quad \text{(X)}$$

$$FeP + RO_2^{\bullet} \xrightarrow{\varepsilon} P_2 + ROH, \quad \xrightarrow{1-\varepsilon} P_3 + R'O, \quad \text{(XI)}$$

where FeP is iron porphyrin in the oxidized and reduced forms, P_2 and P_3 are iron porphyrin products, and ε is the probability of alcohol formation in reaction (XI).

According to the above scheme and taking into account the values of substrate selectivity parameters, we assume that hydrogen peroxide homolysis in reactions (I) and (II) is the most probable in the shunt system containing FeTDCPP without additives. The addition of a radical trap (hydroquinone, IH) leads to a decrease in the steady-state concentration of hydroxyl radicals due to the high rate constant of the reaction

$$IH + {}^{\bullet}OH \longrightarrow H_2O + I^{\bullet}. \quad \text{(XII)}$$

As a result of this reaction, the balance of active species shifts toward the $(PFeO)^+$ complexes and the value of (5/6) becomes close to the value in the complete system. The same events probably happen in the case of catalysis by FeTPP, although apparent changes in the (5/6) parameter are within the experimental error. Thus, in the absence of imidazole and acetic acid in the shunt system, the hydrocarbon reacts with both iron porphyrin complexes and free radicals.

The addition of acetic acid or imidazole to the shunt system possibly increases the probability of hydrogen peroxide heterolysis in reactions (I) and (II) to values close to unity. In this case, hydroquinone should not affect the value of the (5/6) parameter in agreement with the experiment. To remind, the effect of imidazole on the probability of hydrogen peroxide heterolysis with metal porphyrins has been already studied by other researchers, who came to the same conclusions [14]. Therefore, we gave special attention to the shunt system with acetic acid, which has not been studied before.

In the $FeTDCPP/H_2O_2/O_2/AcOH/CH_3CN$ system, cyclohexane forms mainly alcohol (over 60%) and small amounts of ketone and cyclohexyl hydroperoxide (Fig. 2). The rate constants of reactions (IX') and (IX") can be calculated by a semiempirical method according to the parabolic model of the transition state using reference data [16]:

$$k = A\exp(-E/RT),$$

$$E = E_e - 0.5(hN_A\nu_i - RT),$$

$$E_e = f(\Delta H_e),$$

$$\Delta H_e = D_i - D_f + 0.5(hN_A\nu_i - \nu_f),$$

where E_e is the activation energy that takes into account the zero-point vibrational energy of the attacked bond in a bimolecular reaction; h is the Planck constant; N_A is the Avogadro constant; ΔH_e is the enthalpy of the reaction in the gas phase under standard conditions that take into account the difference in the zero-point vibrations of interacting bonds in a bimolecular reaction; D_i and D_f is the dissociation energy of the bonds being broken (i) and formed (f); ν_i and ν_f are the frequencies of stretching vibrations of these bonds; and $f(\Delta H_e)$ is the function, which can be found in [16]. For reaction (IX'), we obtain the following values using reference data (see Tables 1.1 and 1.2 in *Handbook of Antioxidants* [16]) and the above equations:

$$\Delta H_e = \Delta H = 3.5 \text{ kJ/mol},$$

$$E_e = 44.87 \text{ kJ/mol},$$

$$k_{9'} = 10^8\exp(-25.0/RT) \text{ l mol}^{-1} \text{ s}^{-1}.$$

For reaction (IX"), we obtain the following value using Table 2.6 from *Handbook of Antioxidants* [16]:

$$k_{9''} = 10^9\exp(-64.2/RT) \text{ l mol}^{-1} \text{ s}^{-1}.$$

Using these data, we estimate the ratio of the rate constants of reactions (IX') and (IX") for the studied range of the concentrations of substrate and hydrogen peroxide at 20°C: $w_{9'}/w_{9''} = 10^3$–10^5. This ratio suggests that reaction (IX') is the main pathway to cyclohexyl hydroperoxide.

We observed for this system a relatively low rate of cyclohexyl hydroperoxide decomposition. Therefore, the products of this reaction do not contribute noticeably to the overall amount of alcohol and ketone, and cyclohexyl hydroperoxide is one of the end products in oxidation. This is not surprising if we consider the high stability of cyclohexyl hydroperoxide compared to other hydroperoxides. Cyclohexyl hydroperoxide virtually does not dissociate at 70°C in a benzene solution for 270 h. Slow dissociation begins at 150°C [17]. Rapid dissociation occurs under the reductive conditions. For instance reduction by TPP [18] or hydrogen in the presence of platinum oxide [17] leads to the selective formation of alcohol with a very high yield.

Note that even in the case when hydrogen peroxide homolysis does not occur in steps (I) and (II), the $^{\bullet}OH$ radicals are formed in step (III) with probability α according to the kinetic scheme adopted here. However, the parameter of substrate selectivity shows that the main reactants attacking the hydrocarbon in the FeTDCPP/H_2O_2/O_2/AcOH/CH_3CN system are the $(PFeO)^+$ complexes, and radicals do not participate in the formation of oxidation products. Therefore, step (VII) does not contribute noticeably to the process kinetics.

The presence of both hydrogen peroxide and acetic acid in the system suggests that acetic peracid can take part in the formation of active species. However, the absence of the induction period on the kinetic curves of cyclohexane oxidation (Figs. 1 and 2) conflicts with this assumption. Furthermore, the shunt system with added imidazole (without AcOH) did not show any considerable difference from the system with AcOH (with and without imidazole) in the rate or selectivity (including the substrate selectivity, see Table 1) of cycloalkane oxidation. It is likely that the participation of acetic peracid in the formation of active species can be neglected. The main, and probably the only, step for the formation of iron porphyrin complexes is the heterolytic dissociation of hydrogen peroxide via reaction (I).

The radical pathway in this system has the probability α and is due to the formation of radicals $R^{\bullet}$ in reaction (III). The concentration ratio of the products in the radical pathway (with the subscript r) is determined by the ratio of the rates of steps (IX'), (X), and (XI):

$$\begin{aligned}(d[ROOH]/dt)&: (d[ROH]_r/dt): (d[R'O]_r/dt)\\ &= (k_{9'}[HOOH]): (k_{10}[RO_2^{\bullet}]\\ &+ \varepsilon k_{11}[PFe]): (k_{10}[RO_2^{\bullet}] + (1-\varepsilon)k_{11}[PFe]).\end{aligned} \quad (5)$$

It follows from Eq. (5) that the ratio of products formed via the radical pathway should change with a change in the ratio of initial reactants. However, our experiments showed that the ratio of all three products of cyclohexane oxidation remains constant both over a wide range of the initial concentrations of reactants and in the course of reaction (the concentrations of iron porphyrin and hydrogen peroxide decrease with different rates). Because the problem of a radical mechanism is very important for similar systems, we consider it in more detail.

For simplicity, let us first consider the case when reaction (XI) does not contribute to the process kinetics and the products of the radical pathway are only formed in reactions (IX') and (X). Using the method of steady-state concentrations, we obtain

$$\begin{aligned}w_p &= \alpha k_3[RH][(PFeO)^+]\\ &= k_{9'}[H_2O_2][RO_2^{\bullet}] + 2k_{10}[RO_2^{\bullet}]^2,\end{aligned} \quad (6)$$

where w_p is the rate of $RO_2^{\bullet}$ formation.

Let us analyze Eq. (6). If the inequality $k_{9'}[H_2O_2] \gg 2k_{10}[RO_2^{\bullet}]$ is fulfilled, we arrive at the following expressions for the steady-state concentration of $RO_2^{\bullet}$ radicals and the rates of hydroperoxide and ketone accumulation in the radical pathway:

$$\begin{aligned}[RO_2^{\bullet}] &= w_p/k_{9'}[H_2O_2],\\ d[ROOH]/dt &= k_{9'}[RO_2^{\bullet}][H_2O_2] = w_p,\\ d([R'O]_r)/dt &= k_{10}[RO_2^{\bullet}]^2 = k_{10}(w_p/k_{9'}[H_2O_2])^2.\end{aligned} \quad (7)$$

For this case, the ratio of the concentrations of ketone and hydroperoxide is determined by the expression

$$d([R'O]_r)/d[ROOH] = k_{10}w_p/(k_{9'}^2[H_2O_2]^2). \quad (8)$$

If the inequality $2k_{10}[RO_2^{\bullet}] \gg k_{9'}[H_2O_2]$ is fulfilled, we obtain the following expressions:

$$\begin{aligned}[RO_2^{\bullet}] &= (w_p/2k_{10})^{1/2},\\ d[ROOH]/dt &= k_{9'}[H_2O_2](w_p/2k_{10})^{1/2},\\ d([R'O]_r)/dt &= w_p/2,\end{aligned} \quad (9)$$

$$d([R'O]_r)/d[ROOH] = (k_{10}w_p/2k_{9'}^2[H_2O_2]^2)^{1/2}. \quad (10)$$

It follows from Eqs. (8) and (10) that the ratio of the hydroperoxide and ketone concentrations remains constant with a change in the concentration of hydrogen peroxide if the following rate law is correct for w_p:

$$w_p = k_{eff}[H_2O_2]^2. \quad (11)$$

Equation (11) is fulfilled when the steady-state concentration of active $(PFeO)^+$ complexes is proportional to $[H_2O_2]^2$, which is implausible. Moreover, according to Eq. (11), Eq. (7) transforms into

$$d[ROOH]/dt = k_{eff}[H_2O_2]^2 \quad (12)$$

and Eq. (9) transforms into

$$d[ROOH]/dt = k_{9'}(k_{eff}/2k_{10})^{1/2}[H_2O_2]^{3/2}. \quad (13)$$

Equations (12) and (13) were obtained for the two limits of the ratio of rates of steps (IX') and (X). Obviously, in the transient region, the order of the rate of hydroperoxide accumulation with respect to H_2O_2 should be between 1.5 and 2. This conflicts with experimental data. The above analysis suggests that step (X) does not contribute to the process kinetics and it can be excluded from consideration.

Let us consider the formation of alcohol and ketone or one of them via reaction (XI). According to the proposed scheme, we obtain

$$d[ROH]_r/d[ROOH] = \varepsilon k_{11}[PFe]/k_{9'}[H_2O_2],$$

$$d[R'O]_r/d[ROOH] = (1-\varepsilon)k_{11}[PFe]/k_{9'}[H_2O_2], \quad (14)$$

$$d([ROH]_r + [R'O]_r)/d[ROOH] = k_{11}[PFe]/k_{9'}[H_2O_2].$$

According to Eq. (14), the yield of these products relative to the yield of hydroperoxide should change with a change in the ratio of initial reactant concentrations. This fact contradicts experimental findings. Therefore, reaction (XI) does not contribute to the process kinetics and can be neglected. However, the interaction of $RO_2^{\cdot}$ with any iron porphyrin complex to form hydroperoxide is not ruled out. This reaction will not affect the process kinetics under steady-state conditions and its parameters will be taken into account in the effective rate constant of reaction (IX).

Thus, cyclohexyl hydroperoxide is the only product of the radical pathway, and its relative yield measures the contribution of this pathway to the formation of cyclohexane oxidation products. The alcohol and ketone in this shunt system are only formed via the molecular pathway. Therefore, it is easy to derive the expression for the rate of product accumulation via the molecular (w_m) and radical (w_r) pathways under steady-state conditions:

$$\begin{aligned} w_m &= d([ROH] + [R'O])/dt \\ &= (1-\alpha)k_3[RH](PFeO)^+, \\ w_r &= d[ROOH]/dt = k_9[RO_2^{\cdot}][AH] \\ &= \alpha k_3[RH][(PFeO)^+]. \end{aligned} \quad (15)$$

The overall oxidation rate is described by the equation

$$\begin{aligned} w &= w_m + w_r = d([ROH] + [R'O] + [ROOH])/dt \\ &= k_3[RH][(PFeO)^+]. \end{aligned} \quad (16)$$

The calculation of the proposed kinetic scheme gives the following expression for the concentrations of active complexes:

$$\begin{aligned} &\delta k_1[(PFe(III))^+][H_2O_2] \\ &= k_2[H_2O_2][(PFeO)^+] + k_3[RH][(PFeO)^+]. \end{aligned} \quad (17)$$

Let us analyze this equation. If the inequality

$$k_2[H_2O_2] \gg k_3[RH] \quad (18)$$

is fulfilled, then we obtain the expression for the concentration of active species for conditions when the unproductive interaction with hydrogen peroxide is the main reaction for active species consumption:

$$[(PFeO)^+] = \delta(k_1/k_2)[(PFe(III))^+]. \quad (19)$$

Taking into account the material balance condition

$$[FeP]_0 = [(PFeO)^+] + [(PFe(III))^+],$$

we obtain

$$\begin{aligned} [(PFe(III))^+] &= (k_2/(\delta k_1 + k_2))[FeP]_0, \\ [(PFeO)^+] &= (\delta k_1/(\delta k_1 + k_2))[FeP]_0. \end{aligned} \quad (20)$$

Then, the rate of product accumulation is

$$\begin{aligned} w &= k_3[RH][(PFeO)^+] \\ &= (\delta k_1 k_3/(\delta k_1 + k_2))[RH][FeP]_0. \end{aligned} \quad (21)$$

Equation (21) does not agree with the experimental dependence of the rate of cyclohexane oxidation on the concentration of hydrogen peroxide (see Figs. 1 and 2). Therefore, inequality (18) is not fulfilled under the conditions of our experiments. This conclusion is supported by the results of our experiments when we added small concentrations of hydrogen peroxide in portions in the course of the reaction. The expected increase in the yield of cyclohexane oxidation products was not observed.

When the inequality

$$k_3[RH] \gg k_2[H_2O_2] \quad (22)$$

is fulfilled and the main reaction of active species consumption is interaction with the hydrocarbon, we obtain the following expression for the steady-state concentration of active species:

$$[(PFeO)^+] = \delta(k_1/k_3)[(PFe(III))^+][H_2O_2]/[RH]. \quad (23)$$

Taking into account the material balance equations we obtain

$$\begin{aligned} &[(PFe(III))^+] \\ &= (k_3[RH]/(\delta k_1[H_2O_2] + k_3[RH]))[FeP]_0, \quad (24) \\ &[(PFeO)^+] = (\delta k_1[H_2O_2]/(\delta k_1[H_2O_2] + k_3[RH]))[FeP]_0. \end{aligned}$$

Then, the rate of product accumulation in cyclohexane oxidation is

$$\begin{aligned} w &= k_3[RH][(PFeO)^+] \\ &= (\delta k_1 k_3[RH][H_2O_2]/(\delta k_1[H_2O_2] + k_3[RH]))[FeP]_0. \end{aligned} \quad (25)$$

Unlike Eq. (21), Eq. (25) is capable of explaining the experimental dependence of the rate of product accumulation in cyclohexane oxidation on $[H_2O_2]$ (the rate order with respect to the peroxide is 0.5–1). However, in our experiments, we observed the weak dependence of the rate on the initial concentration of iron porphyrin (the rate order with respect to iron porphyrin is 0–0.5). This contradicts Eqs. (21) and (25). Therefore, in addition to step (III), some other reaction where active species are consumed for interaction with iron porphyrin or its products should contribute noticeably to the process kinetics. For instance,

$$(PFeO)^+ + (PFe(III))^+ \longrightarrow (PFe(III))^+ + P_2 \quad (XIII)$$

or

$$(PFeO)^+ + (PFeO)^+ \longrightarrow 2(PFe(III))^+ + O_2, \quad \text{(XIV)}$$

where P_2 is the product of iron porphyrin destruction.

As mentioned above, the use of hydrogen peroxide as an oxidant usually results in complex and poorly controllable processes of hydrocarbon oxidation [1]. Under the conditions of our experiments, the scatter of experimental data was substantial, especially for the reaction rates. This prevented us from discriminating between steps (XIII) and (XIV) where active species were consumed. For simplicity, let us consider the case when the inequality

$$k_{13}[(PFe(III))^+] \gg k_2[H_2O_2] + k_3[RH] + k_{14}[(PFeO)^+] \quad (26)$$

is fulfilled and the main reaction where active species are consumed is the reaction with the initial form of iron porphyrin. In this case, we obtain the expression for the concentration of active species:

$$[(PFeO)^+] + \delta(k_1/k_{13})[H_2O_2] \quad (27)$$

and for the rate of product accumulation in cyclohexane oxidation

$$w = \delta k_1 k_3/k_{13}[RH][H_2O_2]. \quad (28)$$

This equation agrees well with experimental dependences of the rate on the concentrations of initial reactants. Therefore, a considerable portion of active species should be consumed in the shunt system by the reaction with FeP and its products. A decrease in the rate of product accumulation (without changing the proportion between them) in the course of the reaction reflects the proportionality between the rate and the concentration of hydrogen peroxide (Fig. 2) and the weak dependence on the concentration of FeP, which is decomposed in the course of the reaction. The addition of hydrogen peroxide to the reaction mixture after the rate decreased by more than an order of magnitude led to an increase in the reaction rate (Fig. 1, curve *2*) to a value which is somewhat lower than the estimated one because of FeP destruction. An increase in the concentration of hydrogen peroxide leads to an increase in the destruction of FeP (the color of the solution disappears). When the extent of FeP destruction is high, the fraction of cyclohexyl hydroperoxide in the oxidation products starts to increase (Table 2). It is likely that the products of FeP destruction are incapable of catalyzing the molecular pathway of cyclohexane oxidation, but they do catalyze the radical pathway of cyclohexane oxidation to cyclohexyl hydroperoxide. Because the radical oxidation of cyclohexane catalyzed by FeP destruction products depends on many factors, its rate may change depending on the reaction conditions. This explains a relatively great scatter of experimental values of z = [ROOH]/([ROOH] + [ROH] + [R'O]) = 0.20–0.27 in the shunt system, which probably reflects the small contribution of radical oxidation catalyzed by FeP destruction products in some cases.

It follows from Eqs. (15) and (16) that the relative steady-state yield of cyclohexyl hydroperoxide is

$$z = [ROOH]/([ROOH] + [ROH] + [R'O]) = w_r/w = \alpha. \quad (29)$$

Note that only one condition should be met to make Eq. (29) valid: the contribution of step (VII) to the process kinetics should be negligible, because we used this condition when deriving Eqs. (15) and (16).

According to Eq. (29), the fraction of hydroperoxide is $z = \alpha$. This value should not depend on the concentrations of initial reactants, and this is observed in the experiments. The probability of cyclohexyl radical formation in the reaction of cyclohexane with active complexes formed in the catalytic cycle of FeTDCPP in the shunt system is $\alpha = z = 0.20$–0.27. This coincides within the experimental accuracy with the values of this probability obtained earlier for the biomimetic system with methyl viologen ($\alpha = 0.17 \pm 0.02$) and without it ($\alpha = 0.20 \pm 0.02$) [9]. This is further evidence for the fact that active iron porphyrin complexes in these systems are identical.

The scheme of product formation via the molecular pathway (steps (IV) and (V)) adopted for the shunt system differs somewhat from the scheme of the molecular pathway for the formation of alcohol and ketone in the complete system. The shunt system lacks the reactions of the $(PFe\text{---}O\text{---}HR)^+$ complex with the reducing agent and with the intermediate iron porphyrin species in the catalytic cycle. The interaction with the intermediate forms of iron porphyrin species is reflected in the complete system as an increase in the relative yield of ketone when the initial concentration of FeP increases [15]. For the shunt system, the effect of the FeP concentration on the oxidation product ratio is not observed as expected from the proposed kinetic scheme:

$$[ROH]/[R'O] = (d[ROH]/dt)/(d[R'O]/dt) = k_4/k_5[O_2]. \quad (30)$$

According to Eq. (30), the ratio of alcohol and ketone formed via the molecular pathway is only determined by the ratio of the constants of steps (IV) and (V) and the concentration of dioxygen. Because all experiments were carried out in an air atmosphere, it is clear why the ratio $w_{ROH}/w_{R'O}$ is constant (6.2–7.0) in the shunt $FeTDCPP/H_2O_2/O_2/AcOH/CH_3CN$ system.

The fraction of oxidation products formed via the radical pathway in the complete system equals α. The fraction of cyclohexyl hydroperoxide is smaller than α because the rate of its decomposition is high under reductive conditions. The addition of an electron-transfer agent (methyl viologen) to the reaction mixture led to an increase in the rate of cycloalkane oxidation product buildup in the complete system by more than an order of magnitude [8]. In the absence of iron porphy-

rin, we found hydrogen peroxide (10^{-2} mol/l), which is formed by the interaction of methyl viologen radical cation with dioxygen. Based on these results, we concluded that, in the complete system with methyl viologen, active species are largely formed by the reaction of iron porphyrin with H_2O_2, which determines the rate of the process. Therefore, when methyl viologen is added to the complete system, an increase in the oxidation rate can be achieved if the rate of iron porphyrin interaction with hydrogen peroxide is much higher than the rate of its reduction. However, the results of this work showed that the oxidation rate in the shunt system ($< 10^{-6}$ mol l^{-1} s^{-1} when H_2O_2 is added in small portions during the reaction and when it is added as a single portion) is comparable with the oxidation rate in the complete system without methyl viologen and an order of magnitude lower than the value corresponding to the complete system with methyl viologen. The low oxidation rate at the concentrations of hydrogen peroxide that are much higher than the maximal $[H_2O_2]$ value achievable in the complete system with methyl viologen points to the fact that the high rate of the process cannot be achieved due to the catalysis of H_2O_2 dissociation by the initial FeP form. Thus, the mechanism of oxygen activation proposed earlier for the complete system with the electron-transfer agent (methyl viologen) was not confirmed in the studies of the shunt system.

Note that the shunt system under study and the complete biomimetic system proposed earlier are good functional models of monooxygenases, as the rates of alkane oxidation under mild conditions are close to the rates of those observed in enzymatic systems. In the shunt system without AcOH or imidazole additives, the reaction of hydroxyl radicals with cyclohexane (step (VII)) contributes noticeably to the process kinetics. In catalysis by FeTDCPP, a substantial portion of products is formed via the radical pathway. In the presence of acetic acid, the radical pathway of product formation is due to the formation of alkyl radicals and constitutes 20% in the complete system and 20–30% in the shunt system. The active species in these biomimetic systems are iron porphyrin complexes, as is the case in natural heme monooxygenases. Comparison of kinetic parameters showed that cyclohexane in these systems is oxidized at rates of the same order of magnitude, whereas the selectivity is higher in the shunt system. We failed to obtain a high yield of oxidation products in the shunt system because the rate of iron porphyrin destruction is high. Moreover, the complete system is the best model from the standpoint of reaction mechanism. This system models the key process of the monooxygenase cycle—the activation of dioxygen in the presence of electron and proton donors. The addition of an electron-transfer agent (methyl viologen) to the shunt system leads to an increase in the selectivity of alcohol formation and an increase in the oxidation rate by more than an order of magnitude. However, the results of this work show that the mechanism of oxygen activation in this system remains unclear and calls for further study.

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