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Effect of the Hydrogen Peroxide Concentration in Stereospecific Oxidation of Alkanes by Models of Non-heme Oxygenases

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Abstract—The biomimetic oxidation of alkanes (cyclohexane, adamantane, *cis*-1,2-dimethylcyclohexane) with hydrogen peroxide catalyzed by Fe(II) complexes containing tetradentate nitrogen ligands (M = $[Fe(bpmen)(MeCN)_2](ClO_4)_2$ (bispicolyl-1,2-dimethylethylenediamine), $[Fe(bpen)(MeCN)_2](ClO_4)_2$ (bispicolylethylenediamine), and $[Fe(tpcaH)(MeCN)_2]_2(ClO_4)_4$ (tripyridylcarboxamide)) is studied. The effects of the hydrogen peroxide concentration on the alcohol/ketone (*A*/*K*) ratio and on the regioselectivity of oxidation (*3*/*2*) are discovered. Rather high stereospecificity (*RC* = 96–99%) persisting at high hydrogen peroxide concentrations is hardly consistent with the participation of the $HO^{\bullet}$ radical, inferred from the rather low regioselectivity and low *A*/*K* ratio observed under these conditions. The molecular mechanism of oxygen transfer from hydrogen peroxide, which was earlier proved reliably for low concentrations of hydrogen peroxide ($[H_2O_2]/[M] \ll 10$), can be applied to high peroxide concentrations ($[H_2O_2]/[M] > 10$) if a new ferryl species containing two equivalents of the oxidant is assumed to be involved in the process. This assumption is confirmed by the direct stereospecific formation of alkyl hydroperoxide from alkane at a high concentration of hydrogen peroxide.

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INTRODUCTION

Recent years have been marked by considerable progress in studying and modeling oxygenases, which are biological catalysts for the enzymatic oxygenation of organic compounds through oxygen atom transfer from the oxidant. In iron-containing monooxygenases, oxygen is activated on a metal center to form a series of metal–oxygen intermediates capable of hydroxylating alkanes and epoxiding olefins [1]. Depending on the structure of the active center, heme and non-heme monooxygenases are distinguished. Heme monooxygenases are represented by the family of cytochrome P450 containing the mononuclear iron–porphyrin complex in the active center. Non-heme oxygenases include mononuclear oxygenases with facial 2-imidazole-1-carboxylate coordination of iron and binuclear 4-Im-2-COO oxygenases, such as methane monooxygenase capable of oxidizing methane to methanol under mild conditions.

Biomimetic models of cytochrome P450 have become perfect and have approached close to biological catalysts in efficiency, whereas success in the simulation of alkane oxidation by non-heme oxygenases is much more modest [1, 2]. Simple heme and non-heme iron complexes act as catalysts in model chemical systems, while hydrogen peroxide can conveniently be used instead of O_2 as the oxidant in the reaction

$$RH + H_2O_2 \longrightarrow ROH + H_2O.$$

Other oxygen-containing oxidants that can replace oxygen in enzymatic systems can also be used.

The biomimetic oxidation of alkanes was observed for the first time in 1983 using the iron tetraphenylporphyrin complex [3]. Evidence for the participation of the ferryl intermediate in alkane oxidation in the presence of this complex was presented somewhat later [4]. As has been shown [4], an important criterion of biomimetic oxidation is the retention of configuration (*RC*) during the oxidation of *cis*- or *trans*-1,2-dimethylcyclohexane (stereospecific oxidation). The involvement of the ferryl intermediate in the attack on alkane can be proved by the observed incorporation of a label into the alcohol formed when oxygen-labeled water is added to the reaction system. This two-electron mechanism was named molecular or oxenoid to be distinguished from standard chain-radical oxidation. The retention of configuration during alkane oxidation with hydrogen peroxide involving the non-heme (bpy, phen) iron complexes was observed first in 1996 [5]. Somewhat later stereospecific oxidation was shown for iron complexes with tris(2-pyridylmethyl)amine (tpa) [6], methylated bispicolylethylenediamine (bpmen) [7], and tripyridylcarboxamide (tpcaH) [8]. In [5, 8], the oxidation reaction was initiated by the introduction of the entire hydrogen peroxide into the system containing a solution of the catalyst and alkane in acetonitrile. To decrease the unproductive decomposition of hydrogen peroxide, the authors [6, 7] developed a method of gradual introduction of peroxide into a catalytic solu-

tion through a syringe, which improved substantially the yields of products based on peroxide. However, the reaction conditions, especially peroxide concentrations, were different in these two approaches, and it was difficult to compare the results. In the present work, we aimed at verifying the effect of the hydrogen peroxide concentration in the oxidation of alkanes (cyclohexane, adamantane, *cis*-1,2-dimethylcyclohexane) catalyzed by the Fe(II) complexes containing tetradentate nitrogen ligands (M): bispicolyl-1,2-dimethylethylenediamine $[Fe(bpmen)(MeCN)_2](ClO_4)_2$ (**I**), bispicolylethylenediamine $[Fe(bpen)(MeCN)_2](ClO_4)_2$ (**II**), and tripyridylcarboxamide $[Fe(tpcaH)(MeCN)_2]_2(ClO_4)_4$ (**III**). We found the dependence of the alcohol/ketone ratio (*A*/*K*) and regioselectivity (*3*/*2*) on the hydrogen peroxide concentration for all the catalysts under study. The high stereospecificity (*RC* ~ 96–100%) observed at all peroxide concentrations, indicating the molecular mechanism of oxidation, was poorly consistent with the low regioselectivity and low *A*/*K* ratio at a high hydrogen peroxide concentration, which were usually attributed to the involvement of the $HO^{\bullet}$ radical. We concluded that the molecular mechanism of oxygen transfer from hydrogen peroxide, which was reliably proved for low ($[H_2O_2]/[M] \ll 10$) concentrations of hydrogen peroxide [6, 7, 9], can be applied to high ($[H_2O_2]/[M] > 10$) peroxide concentrations under the assumption that a new active intermediate containing two equivalents of the oxidant is involved in the process.

EXPERIMENTAL

Chemicals (Aldrich and Lancaster) were used as received. Solvents manufactured in Russia were purified using standard procedures. The iron(II) complexes sensitive to oxygen and moisture were synthesized in a box filled with argon using Schlenk techniques.

UV–vis absorption spectra were recorded on a Specord M-40 spectrophotometer. Elemental analysis was performed at the Analytical Laboratory of the Institute of Problems of Chemical Physics, Russian Academy of Sciences.

The experimental study of the *catalytic activity* was carried out at 20°C in glass vessels (10 ml) closed with rubber plugs. A solution of alkane and the catalyst in MeCN was placed in the vessel, and the reaction was initiated by the introduction of hydrogen peroxide under vigorous stirring (the volume of the catalytic solution was about 3 ml). Hydrogen peroxide was introduced using two different methods: either the entire H_2O_2 was added at the beginning of the reaction as a 30% aqueous solution, or a solution of H_2O_2 diluted with acetonitriled was slowly syringed through a polyethylene capillary throughout the reaction time. The hydrogen peroxide flow rate was controlled with a special syringe-type pusher (Harvard). After H_2O_2 supply was stopped, the reaction solution was stirred for another 5 min to complete the reaction. The catalyst concentration usually was 0.70 mmol, and the H_2O_2 and alkane concentrations varied for different experiments: catalyst/peroxide/alkane = 1 : (10–420) : (10–1000). The oxidation products were analyzed on a Hewlett Packard 5880A chromatograph with a flame-ionization detector and Carbowax 20M capillary column (length 30 m, diameter 0.32 mm) for cyclohexane oxidation and AT-1 capillary column (length 30 m, diameter 0.25 mm) for the oxidation of adamantane and *cis*-1,2-dimethylcyclohexane. To determine alkyl hydroperoxide, the reaction of hydrocarbon oxidation was carried out as usual. Then the reaction mixture was halved: one portion was used for analysis of the products on a chromatograph (C_1), excess triphenylphosphine was added to the other half, the mixture was stirred for 15 min, and the products were analyzed similarly (C_2). The amount of alkyl hydroperoxide was calculated from an increase in the amount of alcohol in the products after the treatment with triphenylphosphine: $[ROOH] = C_2 - C_1$ according to the reaction

$$ROOH + P(Ph)_3 \longrightarrow ROH + P(Ph)_3{=}O.$$

Experiments in an inert atmosphere were carried out with argon bubbling through the reaction solution. To avoid a decrease in the alkane concentration due to alkane entrainment by the gas flow, argon was saturated with the vapor of the alkane under study in a bubbler placed upstream of the reaction vessel on the pass of the gas. Since about 10% solvent was removed in this case, the volume of the reaction solution was brought to the initial volume by the addition of acetonitrile before analysis.

All reactions were carried out at least three times, and the results obtained were averaged. The catalytic properties of the complexes in cyclohexane oxidation with hydrogen peroxide were estimated in the parameters *TN* (turn-over number of catalyst) and *A*/*K* (alcohol to ketone ratio). Regioselectivity was estimated from the ratio of attacks on the tertiary and secondary bonds of alkanes in adamantane oxidation (parameter *3*/*2*). Stereospecificity was estimated from the degree of retention of configuration during the oxidation of the tertiary C–H bond in *cis*-1,2-dimethylcyclohexane expressed as the percentage ratio of the difference in the amounts of obtained stereomeric alcohols to their sum (parameter *RC*).

Since, at high H_2O_2 concentrations, the further oxidation of the forming alcohol to ketone becomes noticeable, for the estimation of the *A*/*K* parameter, we applied the correction *x* calculated by the approximate formula $x = k_{app}t[ROH]_t/2$, where $[ROH]_t$ is the observed concentration of cyclohexanol at the time point *t* and k_{app} was determined from cyclohexanol oxidation under the conditions identical to the cyclohexane oxidation conditions. The corrected *A*/*K* ratio was thus determined as

$$\frac{A}{K} = \frac{[ROH]_t + x}{[R'O]_t - x}. \quad (1)$$

Table 1. Catalysis of the stereospecific oxidation of alkanes by the Fe(II) complexes

Complex (M)	$[H_2O_2]/[M] \ll 10$				$[H_2O_2]/[M] = 140$			
	A/*K*	*TN*	*3*/*2*	*RC*, %	*A*/*K*	*TN*	*3*/*2*	*RC*, %
$[Fe(bpmen)]^{2+}$	13	4.70	22	100	2.8	37.0	3.8	89
$[Fe(bpen)]^{2+}$	3.7	0.40	11	100	2.0	4.9	7	97
$[Fe(tpcaH)]^{2+}$	3.5	1.0	16	100	2.1	10.0	6.3	96*

* $[M]/[H_2O_2]/[Alkane] = 1 : 420 : 1000$.

The *x* correction is the amount of alcohol $[ROH]_t$ that was oxidized to ketone $[R'O]_t$ during time *t*. With allowance for these approximations, the estimate gives the lower limit for *x* and *A*/*K*.

Synthesis of Complexes

$[Fe(bpmen)(MeCN)_2](ClO_4)_2$ (I). The complex was synthesized according to a modified procedure [7]. The bpmen · 4HCl salt (208 mg, 0.50 mmol) with a saturated aqueous solution of K_2CO_3 and $CHCl_3$ (10 ml) was shaken in a dropping funnel, the chloroform layer was poured off, and the free ligand was extracted by two additional portions of $CHCl_3$. After $CHCl_3$ was distilled off, bpmen (135 mg, 0.5 mmol) was obtained. This amount of the ligand was dissolved in MeCN (10 ml) in an argon-filled box, the solution was mixed with a solution of $Fe(ClO_4)_3 \cdot 6H_2O$ (182 mg, 0.5 mmol) in MeCN (2 ml), and the mixture immediately turned red-brown. A twofold excess of ether was added, and the mixture was left for 1 day in a refrigerator. The next day, dark red crystals that precipitated were filtered off. The yield was 80%. UV–vis (λ_{max}, nm): 330, 370, 490, 531. NGR (mm/cm): $\delta = 0.50$, $\Delta E_Q = 0.25$.

$[Fe(bpen)(MeCN)_2](ClO_4)_2$ (II). Complex **II** was synthesized similarly to compound **I** from bpen (0.5 mmol) and $Fe(ClO_4)_3 \cdot 6H_2O$ (0.5 mmol). The yield was 55%. UV-Vis (λ_{max}, nm): 370, 512, 550. NMR (δ, ppm): 26.1, 23.5, 17.8, 13.4, 13.3, 12.0, 8.7, 8.5.

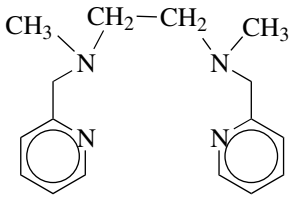
For $C_{18}H_{24}N_6O_8Cl_2Fe$ anal. calcd. (%): C, 37.33; H, 4.18; Cl, 12.24; N, 14.51; Fe, 9.64.

Found (%): C, 37.71; H, 4.49; Cl, 12.20; N, 14.62; Fe, 9.30.

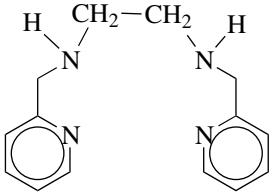
$[Fe(tpcaH)(MeCN)_2](ClO_4)_2$ (III). The synthesis was carried out according to described procedures [8].

RESULTS AND DISCUSSION

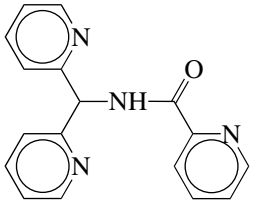
To study the catalytic activity in stereospecific alkane oxidation, we chose the Fe(II) complexes, each containing four coordination sites at the iron atom occupied by the tetradentate pyridine ligand, and the remaining two sites contain readily exchangeable acetonitrile molecules. The presence of two labile cis ligands at the iron atom is an important condition for catalysis of stereospecific alkane oxidation [9]. As follows from the structures of the ligands, their electron-releasing properties decrease in the series bpmen > bpen > tpcaH, which makes it possible to estimate the effect of the electronic nature of the ligands on the catalytic activity of these single-type complexes.



bpmen



bpen



tpcaH

We studied the main characteristics of the stereospecific oxidation of alkanes with hydrogen peroxide catalyzed by the iron complexes: the degree of retention of configuration (*RC*) for the oxidation of the tertiary C–H bond in *cis*-1,2-dimethylcyclohexane (DMCH), the alcohol/ketone ratio (*A*/*K*), regioselectivity of attack to the tertiary and secondary C–H bonds of adamantane (*3*/*2*), and their dependences of the hydrogen peroxide concentration and the nature of the ligands. The results obtained are presented in Table 1 and in Figs. 1–3.

Firstly, note that the high degree of retention of configuration at the asymmetric carbon atom of DMCH (close to 100%) was observed for all iron complexes studied and at all concentrations of hydrogen peroxide (Table 1). Then, as follows from the data in Table 1, the *A*/*K* ratio and regioselectivity *3*/*2* decrease with an increase in the H_2O_2 concentration.

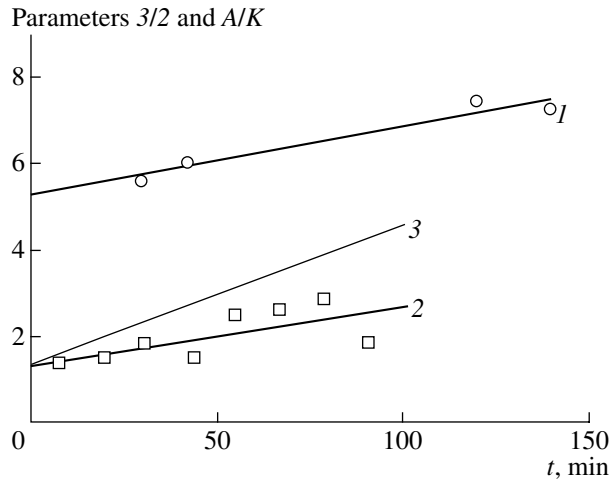


Fig. 1. Time dependence of (*1*) *3/2* during adamantane oxidation and (*2*, *3*) *A*/*K* during cyclohexane oxidation for complex **III** at $[H_2O_2]/[M] = 420$ and (*3*) calculation by Eq. (1).

The changes in the *3/2* (*1*) and *A*/*K* (*2*) parameters in time are shown in Fig. 1 for cyclohexane and adamantane oxidation with complex **III**. Both plots are close to linear. Although, as shown previously [8], most of the ketone is formed in parallel with alcohol, the subsequent oxidation of the alcohol to ketone also occurs. A corrected dependence for *A*/*K* (*3*) was obtained after we carried out experiments on cyclohexanol oxidation under these conditions and applied the correction (see Experimental). The increase of both parameters with time is most likely caused by the fast decrease in $[H_2O_2]$ during the reaction due to the bimolecular nonproductive decomposition of peroxide: $2H_2O_2 \longrightarrow H_2O + O_2$. Since a decrease in the peroxide concentration in time should be taken into account, the results presented in Table 1 and in Figs. 2 and 3 were obtained by the extrapolation of the experimental values to the time $t = 0$ and, in addition, the reaction time was shortened to 0.5 h. The data on the H_2O_2 concentration effect on the regioselectivity and *A*/*K* ratio for catalysis by complex **III** in the $[H_2O_2]/[M]$ and $[M]/[H_2O_2]$ coordinates are presented in Figs. 2 and 3. It can be seen that, when the H_2O_2 concentration changes in wide ranges, both parameters change smoothly with a change in $[H_2O_2]$, apparently tending to some limit at $[H_2O_2] \longrightarrow 0$ or ∞. This dependence of the regioselectivity and alcohol/ketone ratio on the hydrogen peroxide concentration suggests that at least two different intermediates are involved in the reaction with alkanes, and their ratio depends on $[H_2O_2]$. The decrease in the regioselectivity at high H_2O_2 concentrations and the *A*/*K* ratio equal to ~2–3 (right part of Table 1) are usually attributed to the attack of the $HO^{\bullet}$ or $RO^{\bullet}$ radicals to the C–H bond [2, 10]. However, in our case, this conclusion is contradicted by the high stereospecificity (~100%, Table 1) found under these conditions and the retention of the dependence of the oxidation parameters on the nature of the ligands. In our opinion, stereospecificity of the reaction is an unambiguous indication that the process occurs in the coordination sphere of the metal complex [2, 5], because, for free radical processes of alkane oxidation catalyzed by metal complexes, any noticeable retention of configuration for oxidation at the asymmetric carbon atom was never observed [11].

It has been considered for a long time that the ferryl iron complex $Fe^{V}=O$ is the only iron–oxygen intermediate capable of hydroxylating nonactivated C–H bonds in iron-containing monooxygenases and their models. However, recent studies provided convincing experimental evidence that many other metal–oxygen inter-

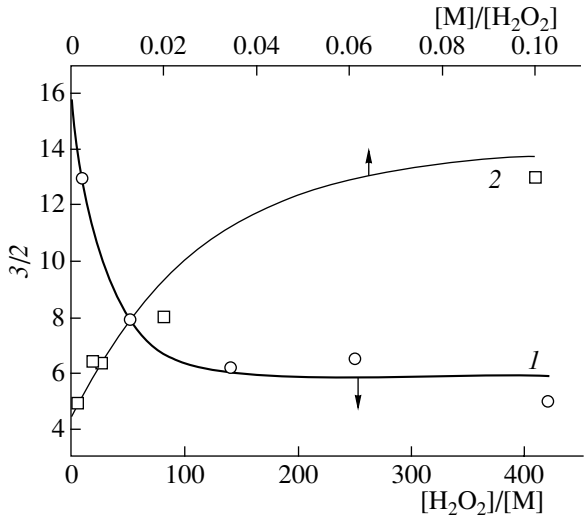


Fig. 2. Bond regioselectivity *3/2* versus (*1*) $[H_2O_2]/[M]$ and (*2*) $[M]/[H_2O_2]$ for complex **III**.

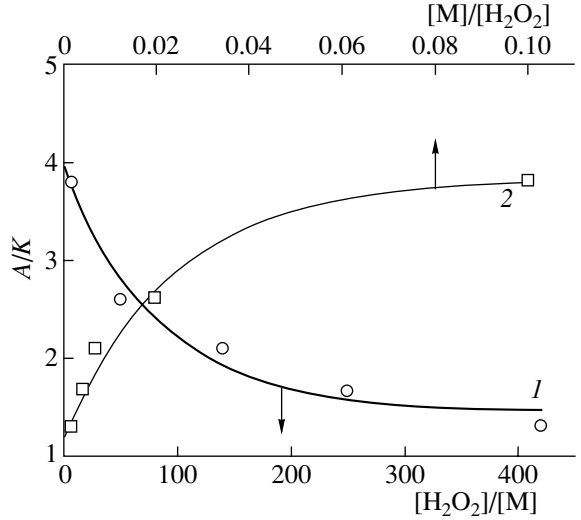


Fig. 3. *A*/*K* ratio versus (*1*) $[H_2O_2]/[M]$ and (*2*) $[M]/[H_2O_2]$ for complex **III**.

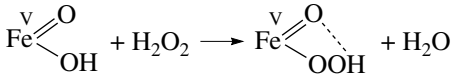
mediates can be active oxidants and the mechanism of O atom transfer is much more complicated than was proposed earlier [12, 13].

Our results indicate the involvement of at least two types of ferryl (or, more widely, metal–oxygen) intermediates depending on the H_2O_2 concentration. The possibility of participation of two different ferryl intermediates, depending on the oxidant concentration, for benzene oxidation on the FeZSM-5 zeolite follows from theoretical calculations [14].

Let us consider the problem about intermediates in the systems under study. There are numerous proofs, including spectral observations [9], that the Fe=O(OH) ferryl complex (F1) is an active intermediate at low H_2O_2 concentrations in acetonitrile. The intermediate involved in alkane oxidation at high H_2O_2 concentrations (let us call it F2) is much more active and, hence, less selective than F1. Judging from the *3/2* regioselectivity value, F2 can be as active as the $HO^{\bullet}$ radical.

The estimates of the *3/2* and *A/K* parameters for intermediates F1 and F2 found from the data in Figs. 2 and 3 by the extrapolation to $[H_2O_2] = 0$ and ∞ are given in Table 2. These values give the lower limit of the parameters for F1 and the upper limit for F2 for catalysis by complex **III**.

According to the concept of O atom transfer, alcohol should be the single product of the reaction with alkanes. In fact, in the case of the iron porphyrin complexes, *A/K* can be ≥30 [1]. Lower *A/K* values were usually explained by the oxidation of the primarily formed alcohol [2]. In our case, the rather low *A/K* value could also be related to the subsequent oxidation. However, our data, including the estimation of the subsequent oxidation, show that alcohol and ketone are formed in parallel. Under the assumption that F1 forms only alcohol, one can conclude that F2 should include two oxidation equivalents and, therefore, its interaction with alkane can afford both alcohol and ketone. It cannot be excluded that F2 gives only ketone and that the formation of alcohol is associated with the presence of F1 as well under all conditions. Based on these considerations, one can reasonably assume that F2 can be formed by the interaction of F1 with H_2O_2. The simplest structure for F2 is the iron oxo-hydroperoxo complex (ferryl-peroxide intermediate) in which ferryl is additionally stabilized by a hydrogen bond with hydroperoxide to form the H-bonded metallocycle like that in oxyhemerythrin [15, 16].



F1 **F2**

The possibility for this intermediate to exist is the recent observation and characterization of the $Fe^{IV}(OH)(OO$*t*-Bu) intermediate by different spectral methods [17]. The theoretical calculations show that the catalase decomposition of hydrogen peroxide occurs through the interaction of the ferryl intermediate with hydroperoxide [18]. We believe that F2 can be a real intermediate in this reaction. Interestingly, a similar complex of another oxidant (iodosobenzene) with Met=O (Met is metal) was postulated for oxygen transfer catalyzed by metal porphyrin complexes [19]

$$PhIO + Met{=}O \longrightarrow PhIO{-}Met{=}O.$$

It is pertinent to assume that the reaction of F2, like the reaction of F1 [9], begins with the abstraction of a hydrogen atom from the alkane molecule to form a short-lived radical intermediate. However, this intermediate, unlike the similar intermediate in the case of F1 [9], allows two ways of the recombination of the R radical, specifically, recombination with an HO group to form alcohol or recombination with an HOO group to form an alkyl hydroperoxide. In fact, no alkyl hydroperoxide can be found among the reaction products at rather low H_2O_2 concentrations (syringe method), while at $[H_2O_2]/[M] = 420$, ROOH is accumulated simultaneously with the accumulation of alcohol and ketone (Fig. 4). Experiments in argon (Table 3) show that most of the alkyl hydroperoxide originates from H_2O_2 and only the most stable tertiary alkyl radicals (as in the case of adamantane) make a noticeable contribution of ROOH in the reaction with O_2 (Table 3). In the case of cyclohexane, when the catalytic solution was thoroughly purged with argon before the beginning of the reaction and during the whole reaction course (see Experimental), the ratio of the products, including ROOH, was the same within the experimental error as

Table 2. Parameters *3/2* and *A/K* for intermediates **F1** and **F2** determined by extrapolation to $[H_2O_2] = 0$ or ∞

Parameter	**F1**	**F2**
3/2	16	3
A/K	4	1

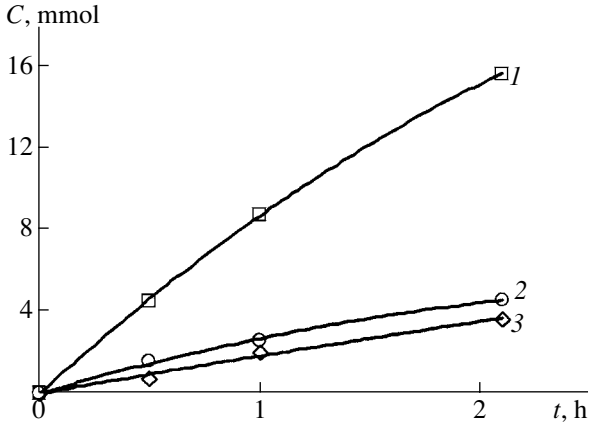


Fig. 4. Kinetics of the accumulation of (*1*) alcohol, (*2*) ketone, and (*3*) alkyl hydroperoxide for cyclohexane oxidation in the presence of complex **III** at $[H_2O_2]/[M] = 420$.

Table 3. Effect of argon purging on the yield of the oxidation products (mmol/l) in 0.5 h at $[H_2O_2]/[M] = 420$

Cyclohexane			Adamantane			*cis*-1,2-DMCH	
products	air	argon	products	air	argon	products	argon
ol	4.5	4.7	1-ol	1.7	1.4	*trans*-ol	0.03
one	2.5	2.4	2-ol	0.6	0.6	*cis*-ol	2.1
ROOH	0.8	0.6	2-one	0.4	0.4	RC_{ROH}, %	97
$\Sigma_{products}$	7.8	7.7	1-ROOH	0.7	0.5	*trans*-ROOH	0.2
$R^{\cdot} + O_2$	0.1		2-ROOH	0.3	0.2	*cis*-ROOH	1.4
			$\Sigma_{products}$	3.7	3.1	RC_{ROOH}, %	75
			$R^{\cdot} + O_2$	0.6			

that for experiments in air. Experiments with less volatile adamantane made it possible to use a more vigorous argon current but the result was virtually the same. Some decrease in the adamantan-1-ol amount in argon indicates, probably, that ~20% of this alcohol could be formed in air involving O_2. In the reaction of *cis*-1,2-dimethylcyclohexane with H_2O_2 when molecular oxygen is thoroughly excluded, the alkyl hydroperoxide that formed retains the configuration of the initial hydrocarbon; i.e., the reaction is stereospecific similarly to the formation of alcohol in this system, namely, the intramolecular recombination of $R^{\cdot}$ with $^{\cdot}OOH$ occurs in the coordination sphere of the complex. Thus, this result supports the assumption that the ferryl-peroxide intermediate is involved at high H_2O_2 concentrations. In fact, the formation of alkyl hydroperoxide due to the chain-radical process always gives racemized ROOH [11]. Therefore, the degree of retention of configuration allows one to judge about the contribution of both processes.

There are two important sequences from these results. Earlier [2] the mechanism of alkane oxidation by hydroperoxides (radical or molecular) was concluded mainly from the estimation of the A/K ratio and regioselectivity, assuming that $A/K \approx 1–2$ and $3/2 \approx 1–2$ are characteristic of radical reactions involving $HO^{\cdot}$, which is not always true, as shown in this paper. It cannot be ruled out that the reactions of O atom transfer can be among the reactions of alkane oxidation with peroxides, which are catalyzed by the iron complexes and have earlier been assigned to radical reactions according to this property. Only additional investigations of the stereospecificity of oxidation and study of the reaction at low H_2O_2 concentrations would provide valid conclusions about the mechanism. Since the assumed intermediate F2 is comparable in activity with the $HO^{\cdot}$ radical, it can react with the CH bond of methane. Therefore, it is of interest to perform further studies in this direction.

Thus, the study of the effect of the hydrogen peroxide concentration during catalysis of alkane oxidation by three single-type complexes containing tetradentate ligands has demonstrated the following. Common regularities are observed for all the catalysts with a change in the H_2O_2 concentration in rather wide ranges from $[H_2O_2]/[M] \ll 10$ to $[H_2O_2]/[M] = 420$, regardless of the nature of the ligands. On the one hand, with a change in the hydrogen peroxide concentration, the A/K and $3/2$ parameters, characterizing the nature of the active oxidant, decrease monotonically and ROOH appears in the products at high H_2O_2 concentrations. On the other hand, stereospecificity of alkane oxidation close to 100% is retained in the whole interval of $[H_2O_2]$ changing. The latter indicates, evidently, that the mechanisms and intermediates are similar in the whole studied interval of $[H_2O_2]$. The high stereospecificity of alkane oxidation is characteristic of processes in the coordination sphere of the metal complex involving the ferryl intermediate.

The change in the parameters characterizing the nature of the active oxidant observed upon changing the H_2O_2 concentration was interpreted as the involvement in the process of at least two ferryl intermediates with different values of these parameters. The stereospecific formation of alkyl hydroperoxide only at high H_2O_2 concentrations and even in argon proves that the second ferryl intermediate with the $LFe^{V}=O(OOH)$ structure and capable of hydroperoxiding alkanes without O_2 acts at these concentrations.

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