Synthesis and Catalytic Activity of the Fe(II) and Fe(III) Complexes with a New Polydentate Ligand Containing an Amide Donor

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Abstract—The iron complexes $[Fe^{2+}(tpcaH)(MeCN)_2](ClO_4)_2$ (I) and $[Fe_2O(tpca)_2(H_2O)_2](ClO_4)_2$ (II) based on the new potentially tetradentate ligand bis(2-pyridyl)methyl-2-pyridylcarboxamide (tpcaH) with the amide donor group inside the molecule were synthesized. The composition of the complexes was confirmed by elemental and mass spectrometric analyses and various spectral methods. Compounds I and II exhibited good catalytic activity in the stereospecific oxidation of alkanes by hydrogen peroxide.

INTRODUCTION

The transfer of an oxygen atom from various oxidants and its insertion into a C–H bond catalyzed by transition metal complexes

$$RH + H_2O_2 \longrightarrow ROH + H_2O$$
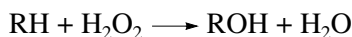
has attracted the attention of researchers [1]. Along with porphyrin complexes [2], non-heme iron complexes [3] are beginning to play an increasingly important role as catalysts in this reaction. Both mono- and binuclear non-heme iron complexes are considered as models of natural oxidoreductases. Since heme [4, 5] and non-heme [6, 7] iron complexes exhibited unusual regioselectivity and stereospecificity in the catalysis of alkane oxidation by peroxides, these complexes can directly transfer an oxygen atom and incorporate it into the C–H bond without the participation of free radicals:

$$[Fe^{3+}] + H_2O_2 \longrightarrow [Fe^{5+}=O] + H_2O,$$

$$RH + [Fe^{5+}=O] \longrightarrow ROH + [Fe^{3+}].$$
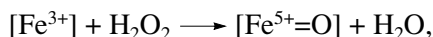
When $H_2^{18}O$ is added to the reaction medium, ^{18}O appears in the alcohol formed. This confirms that the oxygen atom of the ferryl intermediate $Fe^{5+}=O$, which can exchange its oxygen with water, is involved in the transfer process [4, 8]. Only a few types of non-heme iron complexes capable of catalyzing oxygen transfer to alkanes are known to date. These are the complexes with phenanthroline (**phen**) [6, 9], trispicolylamine (**tpa**) [8], and methylated bispicolylethylenediamine (**bpmen**) [7]. A search for new catalysts of these reactions is continued, and new ligands are designed and synthesized. Therefore, polydentate ligands with amide donor groups similar to polypeptide donors in enzymes are of great interest [10]. Similarly to carboxylates, carboxamide donors stabilize higher oxidation states of transition metals and enhance the resistivity of ligands to oxidative degradation. This is especially attractive for the design of catalysts for oxidation reactions.
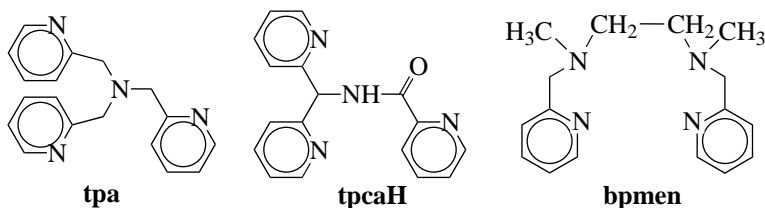
In this work we report the synthesis of the new potentially tetradentate ligand with the amide donor inside the molecule, namely, bis(2-pyridyl)methyl-2-pyridylcarboxamide (**tpcaH**). Fe(II) and Fe(III) complexes with this ligand are synthesized, and their catalytic activity in the oxidation of alkanes by hydrogen peroxide in acetonitrile is studied.

EXPERIMENTAL

Commercially available reagents (Aldrich and Lancaster) were used without additional purification. Domestic solvents were purified using standard procedures. Fe(II) complexes sensitive to oxygen and moisture were synthesized using a box filled with argon and Schlenk apparatus.

Absorption spectra in the UV and visible regions were recorded on a Specord M-40 spectrophotometer. IR spectra were recorded on Specord 75-IR and Specord M-82 spectrometers in KBr cells or in liquid paraffin. Mössbauer spectra were recorded on a standard installation at 85 K using the ^{57}Co-Rh source, and isomeric shifts are presented relatively to metallic iron. ^{1}H NMR spectra were recorded on Varian-300 and Tesla spectrometers with working frequencies of 300 and 200 MHz, respectively. Elemental analysis was carried out at the Analytical Laboratory of the Institute of Chemical Problems, Russian Academy of Sciences. Mass spectrometric measurements with electrospray ionization (ESI–MS) were carried out on a unique model of a high-resolution time-of-flight mass spectrometer at the laboratory headed by Professor A.F. Dodonov at the Institute of Energy Problems of Chemical Physics, Russian Academy of Sciences.

The procedure of alkane oxidation is analogous to that described previously [11]. The catalytic activity of complexes was studied in the oxidation of cyclohexane, adamantane, and dimethylcyclohexane (DMCH) by hydrogen peroxide at 25°C. Experiments were carried out in an open glass vessel with a magnetic stirrer. The vessel was filled with a 0.7–1.4 mmol/l solution (1−2 ml) of the iron complex, hydrocarbon, and a solution of H_2O_2. The catalyst : H_2O_2 : alkane ratio was 1 : 420 : 1000.

Reaction products were analyzed by GLC on a Hewlett-Packard 5880A chromatograph equipped with a flame-ionization detector and an AT-1 branded capillary column.

RESULTS

Synthesis of Ligands

Dipyridylmethylamine. Zinc powder (5 g) was added for 30 min to a solution containing dipyridylketoxime (3.5 g) and ammonium acetate (2.2 g) in ethanol (60 ml) 35 ml of water and 50 ml of 23% aqueous solution of ammonia. Then the mixture was heated with a reflux condenser for 4.5 h along with weak boiling. After the end of the reaction, the reaction mixture was brought to pH 10 with a concentrated solution of NaOH and extracted five times with 15 ml of CH_2Cl_2. The combined extracts were washed with a saturated solution of NaCl and dried with anhydrous potash. After the solvent was distilled off on a rotary evaporator, dipyridylmethylamine was obtained with a 90% yield (2.9 g) as colorless oil, which was used without purification [12]. ^{1}H NMR spectrum (CDCl$_3$), δ, ppm: 8.54 d (2H py), 7.63–7.57 m (2H, py), 7.37 d (2H, py), 7.14–7.10 m (2H, py), 5.31 s (1H, CH), 2.39 br.s (2H, NH$_2$).^{1}

Bis(2-pyridyl)methyl-2-pyridylcarboxamide (tpcaH). A solution of dipyridylmethylamine (0.8 g, 4.0 mmol)

in THF (8 ml) was added in drops to a stirred mixture of picolyl chloride (0.57 g, 4.0 mmol) and Et$_3$N (1 ml) in THF (15 ml) cooled to 0°C. After addition, the mixture was stirred for 20 min at the same temperature and for 30 min at 50°C, cooled again to 0°, and filtered. After solvent evaporation, the crude product crystallized as a yellowish mixture. The product was purified by treatment with a concentrated alkali solution (pH 11) and recrystallization. The pure ligand was obtained with an 82% yield (0.95 g) as a white powder with m.p. 145–146°C (from ethanol) and the following spectral IR characteristics (ν, cm^{-1}): 609, 753, 1000, 1433, 1462, 1477, 1504, 1571, 1589, 1669, 3030, 3070, 3350. ^{1}H NMR (CDCl$_3$), δ, ppm: 10.03 d (1H, CH), 8.67 d (1H, pyCO), 8.59 d (2H, py), 8.17 d (1H, pyCO), 7.85–7.79 m (1H, pyCO), 7.67–7.60 m (2H, py), 7.51 d (2H, py), 7.45–7.41 m (1H, pyCO), 7.17–7.13 m (2H, py), 6.44 d (1H, NH). ESI–MS, m/z (%): 291.16 (92), 313.15 (6), 329.12 (2). Calculated, m/z: LH$^+$ 291.12, LNa$^+$ 313.11, and LK$^+$ 329.08. Elemental analysis data:

For $C_{17}H_{14}N_4O$ anal. calcd. (%): C, 70.33; H, 4.86; N, 19.30.

Found (%): C, 70.38; H, 5.14; N, 19.23.

Synthesis of Iron Complexes

[Fe(tpcaH)(MeCN)$_2$](ClO$_4$)$_2$ (I). A solution of Fe(ClO$_4$)$_2$ · 6H$_2$O (0.36 g, 1 mmol) in MeCN (5 ml) was poured into a stirred solution of **tpcaH** (0.29 g, 1 mmol) in MeCN (10 ml). The solution turned yellow for several minutes. After a short period, an equal volume of diethyl ether was added, and the solution was allowed to stay overnight at –30°C. The next day, amber crystals of compound I (0.50 g, 80%) precipitated. They were filtered and characterized by several methods. UV–VIS (MeCN), λ$_{max}$, nm (ε): 356(1500), 425 (650). IR (ν, cm^{-1}): 1635, 1601, 1534, 1470, 1440, 1376, 1162, 1049, 1012, and 760. Mössbauer spectrum, mm/s: δ = 1.18, ΔE_Q = 2.05. ESI–MS, m/z (%, fragment of the complex): 173.08 (8, [X]$^{2+}$), 182.09 (11, [X(H$_2$O)]$^{2+}$), 193.60 (32, [X(MeCN)$^{2+}$), 634.22 (49, [XL]$^+$), where X = FeL. Elemental analysis data:

For $C_{21}H_{20}N_6O_9Cl_2Fe$ anal. calcd. (%): C, 40.21; H, 3.21; N, 13.40; Cl, 11.31; Fe, 8.90.

Found (%): C, 39.85; H, 3.70; N, 13.23; Cl, 11.50; Fe, 8.0.

[Fe$_2$O(tpca)$_2$(H$_2$O)$_2$](ClO$_4$)$_2$ (II). 1. A solution of Fe(ClO$_4$)$_3$ · 10H$_2$O (0.27 g, 0.5 mmol) in MeOH (5 ml) was poured together with a stirred solution of **tpcaH** (0.15 g, 0.5 mmol) into methanol (10 ml). The dark red solution formed was stirred for 1 h, and then the methanol was evaporated until dry. After the residue was recrystallized from MeCN, complex **II** was obtained with a 32% yield (75 mg) as a greenish-brown finely crystalline powder. UV–VIS (MeCN, λ$_{max}$, nm (ε): 600 sh (5000), 825 (950). IR (ν, cm^{-1}): 3420, 1620, 1590, 1480, 1435, 1355, 1290, 1200, 1045, 825, 765,

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^{1} Notation used hereinafter: d is for doublet, s is for singlet, m is for multiplet, and sh is for shoulder.
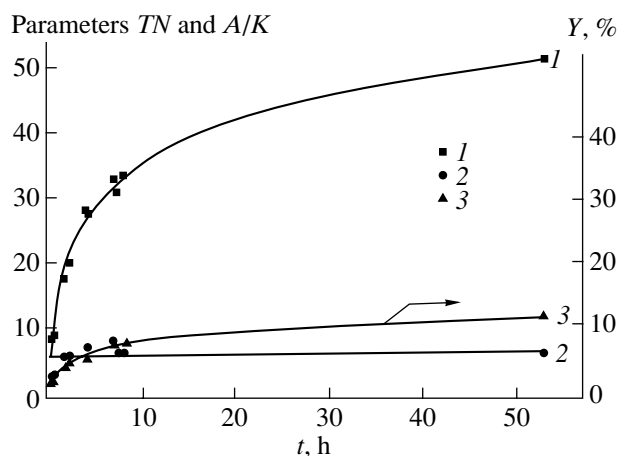
Fig. 1. Oxidation of cyclohexane by hydrogen peroxide in acetonitrile catalyzed by complex **I**: (*1*) turnover number (*TN*); (*2*) alcohol to ketone ratio (*A/K*); and (*3*) yield of products (per taken peroxide) (*Y*).

620. Mössbauer spectrum, mm/s: $\delta = 0.32$, $\Delta E_Q = 1.36$. Elemental analysis data:

For $C_{34}H_{30}N_8O_{13}Cl_2Fe_2$ anal. calcd. (%): C, 42.80; H, 3.62; N, 11.87; Cl, 7.28; Fe, 11.22.

Found (%): C, 43.38; H, 3.21; N, 11.91; Cl, 7.53; Fe, 11.87.

2. 20 mol/l H_2O_2 (0.2 ml) was slowly added in drops to a stirred solution of complex **I** (32 mg, 0.06 mmol) in MeCN in an argon atmosphere. The solution changed its color from orange to dark red. The mixture was allowed to stay for a day in a slow argon flow. The precipitate was separated from the solution, washed with diethyl ether, and dried. Complex **II** (12 mg) was obtained as a light brown powder, whose spectral characteristics coincided with those described above.

Study of Catalytic Activity

Complexes **I** and **II** oxidize alkanes (cyclohexane, adamantane, and dimethylcyclohexane) to alcohols and ketones. No other product was found. The results of the experiments are presented in Fig. 1 and in the table. Figure 1 shows the development of the process in time for the oxidation of cyclohexane with hydrogen peroxide catalyzed by complex **I**. The development of the process is described by the following parameters: *TN* (turnover number), *A/K* (alcohol to ketone ratio), and *Y* (yield per peroxide taken, in %). The rate of product accumulation becomes slower as peroxide is consumed, and after 30–50 h hydrogen peroxide is not found in a solution. An argon atmosphere has no effect on the experimental results. Similar results were obtained for complex **II**. Our results are compared in the table with the published data for the catalysts that can oxidize alkanes regioselectivity and stereospecifically. The regioselectivity was estimated from the ratio of products of the attack on the tertiary and secondary bonds of alkanes in adamantane oxidation (parameter 3/2). The stereospecificity was estimated by the degree of retention of the configuration upon the oxidation of the tertiary CH bond in *cis*-, *trans*-1,2-, or 1,4-dimethylcyclohexanes. It was expressed as a fraction of stereomeric alcohols to their total amount (parameter *RC*).

DISCUSSION

Synthesis of Ligand and Iron Complexes

As we described in the experimental section, the ligand was synthesized by the three-stage synthesis

Catalytic oxidation of alkanes by hydrogen peroxide catalyzed by the iron complexes

Initial complex	Time*, h	Cyclohexane			Adamantane	DMCH	References
		TN	*A/K*	*Y*, %	3/2	*RC*, %	
$[Fe_2O(phenNO_2)_4(H_2O)_2](ClO_4)_4$	48	14	2.5	10	3 (5, phen)	72	[6]
$[Fe^{2+}(tpa)(MeCN)_2](ClO_4)_2$	0.25	3	5	32**	17	100	[8]
$[Fe^{2+}(bpmen)(MeCN)_2](ClO_4)_2$	0.50	6	8	70**	15	96	[7]
$[Fe^{2+}(tpcaH)(MeCN)_2](ClO_4)_2$ (**I**)	53	50	7	12	6	96	This work
$[Fe_2O(tpca)_2(H_2O)_2](ClO_4)_2$ (**II**)	28	43	7	10	6	97	This work

Note: *TN* is the turnover number, *A/K* is the alcohol to ketone ratio, *Y* is the yield of products (per taken peroxide), and 3/2 is the ratio of products of the attack to the tertiary and secondary bonds of alkanes in adamantane oxidation.
  * Time for the complete consumption of hydrogen peroxide.
  ** Under conditions of the slow introduction of H_2O_2.

$[Fe(tpa)(MeCN)_2]^{2+}$ $[Fe(tpcaH)(MeCN)_2]^{2+}$ $[Fe(bpmen)(MeCN)_2]^{2+}$
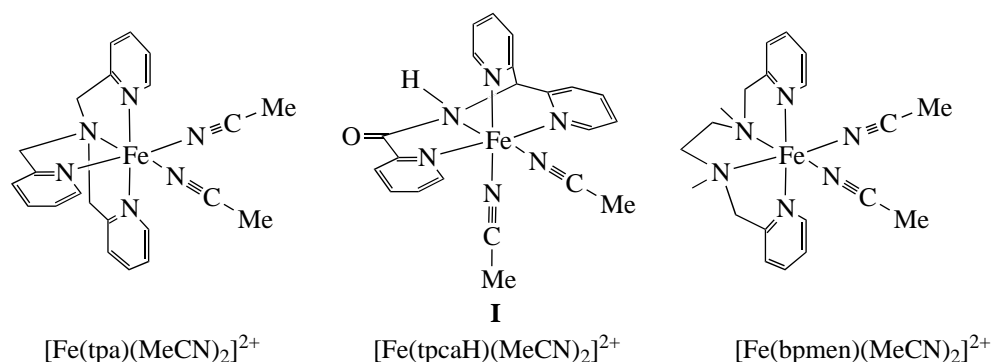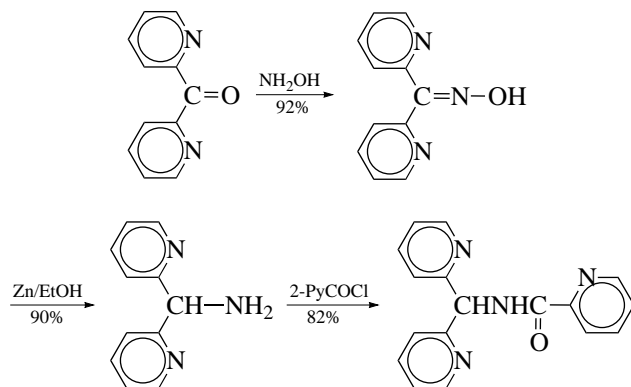
Fig. 2. Assumed structure of complex **I** and X-ray structures of the corresponding complexes with **tpa** and **bpmen**.

from dipyridyl ketone with a 65% yield as is illustrated by the scheme:

Scheme

The new potentially tetradentate ligand **tpcaH** contains three pyridine donors and resembles the well-known tetradentate **tpa** ligand with the only distinction that the carboxamide group acts as a fourth donor instead of aliphatic amine. The presence of this group results in the situation that the ligand can be involved in complex formation with a transition metal ion as either a neutral molecule or an anion (in deprotonated form).

We prepared two iron complexes based on this ligand: mononuclear octahedral Fe(II) complex $[Fe(tpcaH)(MeCN)_2](ClO_4)_2$ (**I**) and binuclear μ-oxo-Fe(III) complex $[Fe_2O(tpca)_2(H_2O)_2](ClO_4)_2$ (**II**). The compositions of the complexes were confirmed by elemental and mass spectrometric analyses and UV–VIS, IR, and Mössbauer spectra. In the mononuclear complex, the ligand exists in neutral form, while in the binuclear complex it is deprotonated probably due to an increase in the acidity of the carboxamide group coordinated to Fe(III). These are first iron complexes containing the ligand with a single carboxamide group [13, 14].

The IR spectrum of the free ligand exhibits the characteristic bands of the carboxamide group: a narrow intense band at 3350 cm^{-1} (ν(NH)) and intense bands at 1670 cm^{-1} (ν(CO), 1st amide band) and 1504 cm^{-1}

(δ(NH), 2nd amide band). When complex **I** is formed, the band at 3350 cm^{-1} weakens considerably and broadens. When complex **II** is formed, this band completely disappears. The first amide band is shifted toward low frequencies during complex formation, and the shift Δ = 35 cm^{-1} for both complexes agrees with the values found for other metal complexes with carboxamide ligands [15]. The second amide band is shifted toward higher frequencies by 80 cm^{-1} for complex **II**, which is characteristic of complexes with deprotonated carboxamide [15]. The IR spectrum of complex **II** contains a broad asymmetric band ν(Fe–O–Fe) = 830 cm^{-1}, which is a characteristic of binuclear μ-oxo iron complexes.

If X-ray diffraction data are unavailable, it is invalid to categorically assert the structure of complexes **I** and **II**. Nevertheless, based on the results obtained, we can assume that complex **I** is similar to the mononuclear ferro complexes with analogous tetradentate **tpa** and **bpmen** ligands, which were structurally characterized in [7, 8] (Fig. 2). This assumption is justified by the following data.

1. Elemental analysis indicates that one **tpcaH** molecule and two acetonitrile molecules fall on one iron atom. The mass spectrometric data confirm this composition of complex **I** and also indicate that the complex is mononuclear in a solution of acetonitrile.

2. Mössbauer spectra and UV–VIS spectra point to the octahedral structure of the complex ion and the IR spectra show involvement of the carboxamide group in the coordination of the ligand to the iron atom. Together with data on the composition, this information confirms the tetradentate character of **tpcaH** with coordination via the nitrogen atom of the carboxamide group in complex **I**. Molecular modeling shows the coordination of **tpcaH** to iron by the carbonyl group is impossible in the case of a mononuclear complex for steric reasons.

3. The mononuclear octahedral complex containing one tetradentate and two monodentate ligands can exist in two configurations with *cis* or *trans* arrangements of monodentate ligands. The observation of stereospecific alkane oxidation suggests that complex **I** has a *cis*

configuration because, according to the data in [8], this configuration is important for the catalysis of this reaction. The transition from the mononuclear Fe(II) complex to the binuclear μ-oxo-Fe(III) complex due to oxidation does not change the configuration of the coordination environment of the iron, except for the replacement of one acetonitrile molecule at each iron ion by the bridging oxygen atom.

On the other hand, complex **I** in the crystalline state probably has a different structure. The carboxamide group can coordinate to a metal atom via either a nitrogen or an oxygen atom. Coordination via nitrogen leads to breaking in the conjugation of a nitrogen free pair with the carbonyl group, which is indicated by an increase in ν(CO). In contrast, coordination via oxygen leads to a decrease in ν(CO). Thus, according to IR spectra (a decrease in ν(CO) by 35 cm^{-1}), the carboxamide group in the crystalline complex is coordinated via the oxygen atom in our case. As we pointed out above, coordination via oxygen is impossible for mononuclear complexes. Thus, complex **I** in the solid state should have a structure different than in a solution. Possibly, this a dimeric structure formed by the binding of two mononuclear complexes via their ligands. This makes it possible to realize coordination via carbonyl-group oxygen.

Note that, unlike the mononuclear Fe(II) complexes with **tpa** and **bpmen** ligands, **I** is a high-spin complex as follows from its great isomeric shift in the Mössbauer spectrum ($\delta = 1.18$ ppm).

### Oxidation of Alkanes by Hydrogen Peroxide Catalyzed by Complexes *I* and *II*

The evidence for the transformation of the [Fe(**tpa**)(MeCN)$_2$](ClO$_4$)$_2$ complex into the binuclear μ-oxo iron complex at the initial moment of the reaction with hydrogen peroxide have previously been presented [8]. Our data, namely similarity in catalysis by complexes **I** and **II** (see table), agree with this conclusion. We also showed that complex **II** can be obtained by the oxidation of complex **I** with hydrogen peroxide. The alcohol-to-ketone ratio increases at the initial moment when the reaction is catalyzed by complex **I** (Fig. 1) probably due to the formation of complex **II** during the reaction, and then this ratio remains unchanged in the course of the reaction. Both complexes demonstrate good catalytic activity in alkane oxidation by hydrogen peroxide. At the same time, neither our data nor the data in [8] can conclude what iron(III) complex, mono- or binuclear, is responsible for the catalysis because the equilibrium between the binuclear and mononuclear forms always exists in a solution regardless of the initial state: Fe(III)–O–Fe(III) + $H_2O \longrightarrow$ 2Fe(III)–OH.

Analysis of the results presented in Fig. 1 and in the table shows that the average alcohol-to-ketone ratio is equal to 7 for both catalysts and is much higher than the

value characteristic of radical chain oxidation, which is ~1. A high stereospecificity of oxidation is also observed. These observations along with the absence of the influence of air oxygen on the process indicate that free radical reactions do not play an important role in oxidation involving these catalysts.

The comparison of the catalytic properties of the synthesized complexes with the previously studied catalytic systems capable of stereospecific hydroxylating alkanes show (see table) that the new catalysts exhibit a good catalytic activity at a moderate hydroxylation rate. It is of interest that, according to [8], only the low-spin Fe(II) complexes with **tpa** result in the stereospecific hydroxylation of alkanes. Our data show that the low-spin nature of the initial Fe(II) complexes is not a necessary condition for stereospecific hydroxylation, although it perhaps decreases the hydroxylation rate, as is seen from the data in the table. An increase in the yield of the oxidation products calculated per H_2O_2 in the systems with **tpa** and **bpmen** results from the slow introduction of hydrogen peroxide into the catalytic solution to decrease the bimolecular decomposition of hydrogen peroxide through its disproportionation with O_2 evolution catalyzed by the iron complexes: $2H_2O_2 \longrightarrow 2H_2O + O_2$.

Our data agree with the mechanism proposed in [8] for the transformation of H_2O_2 on the mononuclear catalytic site

$$LFe^{5+}\!\!\bigg\langle\!\!\begin{array}{c}O\\OH\end{array} \xrightarrow{RH} LFe^{3+}OH + ROH.$$
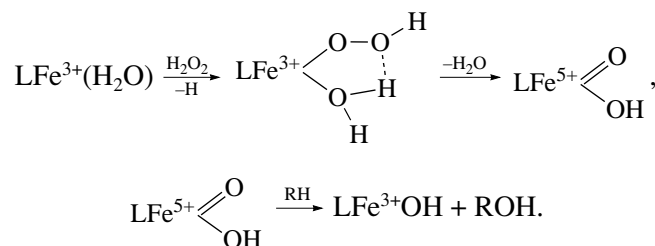
The formation of peroxide intermediates in similar systems has previously been observed by spectral methods [7, 16]. The stereospecific hydroxylation of alkanes and the absence of the influence of O_2 exclude the involvement of hydroxyl radicals, which could be formed due to the homolytic decomposition of the peroxide intermediate: Fe–O–OH $\longrightarrow$ Fe^{4+}=O + HO$^{\bullet}$. The heterolysis of the O–O bond in the peroxide intermediate is enhanced by the protonation of the terminal O atom of the peroxo group. This protonation is intramolecular and occurs due to the binding with the adjacent water molecule. The acidity of water increases due to its coordination with the Fe^{3+} ion. The subsequent heterolysis of the O–O bond is facilitated by the elimination of a water molecule to form the ferryl intermediate. The intramolecular hydrogen bond between the water molecule and ferryl oxygen results in the formation of a stable five-membered ring and probably stabilizes ferryl in the non-heme environment. The involvement of the ferryl intermediate was proved in [8] by the inclusion of

^{18}O from $H_2^{18}O$ in the alcohol, and the degree of inclusion of the label increases with an increase in the strength of the attacked bond due to the competition between the exchange with water and alkane hydroxylation.

CONCLUSION

Thus, in this work we proposed new catalysts for stereospecific alkane oxidation. Catalytic systems of this type capable of stereospecific hydroxylating alkanes and including the peroxide and ferryl intermediates in the non-heme environment are presently rare and can be considered as precursors of functional models of the binuclear active site of methane monooxygenase [1].

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