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Stereospecific Oxidation of Alkanes Catalyzed by Fe_2(μ-Carboxylato) Complexes, which Model Some of the Structural Features of the Active Center of Methane Monooxygenase

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Abstract—Binuclear μ-oxalate iron complexes (**1** and **2**) that model the Fe_2(μ-COO) nucleus of the methane monooxygenase active center catalyze the stereospecific transfer of an oxygen atom from H_2O_2 to C–H bonds in alkanes. Due to the framework nature of the ligand, the binuclear structure of the iron complex is retained in the solution. These data reliably confirm the fact that the catalytic reaction occurs at a binuclear center via a mechanism with the participation of both iron atoms.

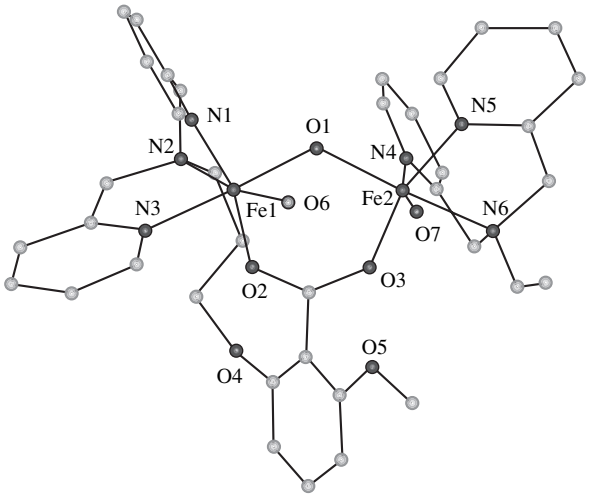
The reaction of stereospecific transfer of an oxygen atom from H_2O_2 to a C–H bond in alkanes catalyzed by nonheme iron complexes [1],

$$RH + H_2O_2 \xrightarrow{[Fe]} ROH + H_2O,$$

models a similar process that is catalyzed by monooxygenase enzymes, specifically by methane monooxygenase (MMO) [2]. Several mono- and binuclear iron complexes have been found that are capable of catalyzing the above transformation [3]. However, their structure is far from the structure of the active center in MMO. Moreover, due to the kinetic lability of simple iron complexes, there is always an equilibrium between mono-, bi-, and polynuclear complexes in a catalytic solution preventing us from obtaining a definite conclusion on the structure of the active component.

Earlier [4], we characterized the structure of the binuclear iron complex $[Fe_2OL^1(X)_2](ClO_4)_2$ (**1**), where L^1 = 2,6-{$(PyCH_2)_2NCH_2CH_2CH_2O$}$_2C_6H_3COO^-$ and X = 1/2$RCOO^-$ or H_2O (see figure). In this work we prepared a similar complex $[Fe_2OL^2(X)_2](ClO_4)_2$ (**2**) with the framework ligand L^2 = 2,6-{$(PyCH_2)_2NCH_2CH_2O$}$_2C_6H_3COO^-$. The relative energies of complexes **1** and **2** were estimated by the method of molecular mechanics using HyperChem5 software and showed that the dimer is more stable than a monomer in the case of complex **1** and the reverse pattern is observed in the case of complex **2**. The results of these calculations are supported by the electrospray ionization mass spectrometry (ESI–MS) of complexes **1** and **2** in an acetonitrile solution: in the case of micromolar concentrations, the dimer peak dominates in the case of complex **1** and the monomer peak dominates in the case of complex **2** under the same conditions of recording the mass spectra of molecular ions. An important element of the structural similarity with the MMO active center in these complexes is the binding of two iron ions by the immobilized carboxylate bridge, and the presence of two labile coordination sites, which are capable of attaching and exchanging mono- and bidentate ligands. These features are important for catalysis.

Complexes **1** and **2** catalyze the stereospecific oxidation of alkanes by hydrogen peroxide mostly to alcohols with practically the same efficiency (see table). This confirms the independence of the work of the binuclear center on its association into a dimer, which agrees with earlier spectral and magnetic data on the independence of the binuclear centers in the dimer from each other [4]. Note that the yield based on reacted



Structure of the binuclear center of complex **1** according to XRD data; labile coordination sites occupied by oxygen donors from carboxylate or water are in the front.

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Oxidation of alkanes by hydrogen peroxide in catalysis by iron complexes

Complex	Cyclohexane			Adamantane	1,2-*cis*-DMCH
	TN	A/K	*Y*, %	$C_{3/2}$	*RC*, %
1, X_2 = $PhCOO^-$	8	2.6	9 (3.8)	4.0	93
1, X = H_2O*	3	4.0	52	4.0	94
2, X_2 = $PhCOO^-$	13	3.3	(6.1)	4.0	94

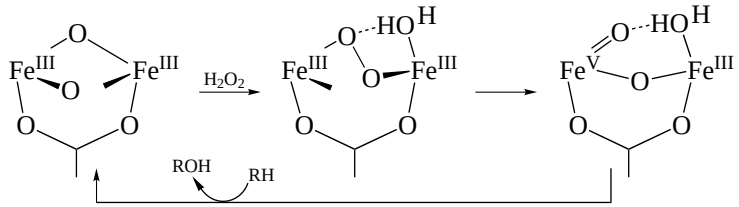
Note: [Fe] = 0.7 mM; the total volume of the reaction mixture, 1–2 ml; [Fe]/[H_2O_2]/[RH] = 1/420/1000 for cyclohexane and 1,2-*cis*-dimethylcyclohexane oxidation and 1/420/10 for adamantane oxidation; 25°C; 4 h. TN is the turnover number; A/K is the alcohol-to-ketone ratio; *Y* is the yield based on reacted H_2O (H_2O_2 taken); $C_{3/2}$ is the selectivity of the attack on the tertiary and secondary CH bond in adamantane; retained configuration RC = (cis – trans)/(cis + trans) × 100%.

* Slow addition of H_2O_2 to the reaction mixture (2.5 h).

hydrogen peroxide *Y* is not high due to the side bimolecular reaction of its decomposition. This reaction is retarded when the concentration of hydrogen peroxide is decreased due to the slow addition of H_2O_2 into the reactor. This makes it possible to increase the yield up to 50% or more. An alcohol/ketone ratio equal to 3 and the apparent stereospecificity of *cis*-dimethylcyclohexane (DMCH) oxidation point to the molecular mechanism of oxygen atom transfer [1, 2, 4]. The relative activity decreases in the series of labile ligands: H_2O, PhCOO, and MeCOO. This is due to an increase in the strength of ligand binding with iron ions because the reaction probably begins with the addition of hydrogen peroxide to the vacancy in the coordination sphere of iron (see scheme).

The results of earlier experiments did not lead to a conclusion on whether mononuclear or binuclear complexes are active in the catalysis of oxygen atom transfer, and a mechanism involving the mononuclear center was commonly proposed [3, 5]. According to ESI-MS data, the binuclear center in complexes **1** and **2** with denucleating framework ligands is intact up to micromolar concentrations in an acetonitrile solution because of the strong binding of iron ions by the framework ligand that models a polypeptide framework of an enzyme. Therefore, in our case, we may assume that μ-carboxylate-bridged binuclear centers similar to those in MMO are catalytically active.

In agreement with available data [2, 3], we propose the following mechanism for oxygen atom transfer from hydrogen peroxide to a C–H bond catalyzed by complexes **1** and **2** (see scheme). It involves the peroxy and ferryl intermediates on the binuclear center:



The participation of the ferryl intermediate is supported by the appearance of the ^{18}O label in the alcohol formed (13% $R^{18}OH$) when $H_2{}^{18}O$ is added to the catalytic solution. It was shown [3, 6] that, in contract to the peroxide intermediate, the ferryl intermediate is capable of exchanging the bound oxygen atom with the oxygen atom from water.

In conclusion, taking into account data presented in [7] that show complex **1** is also capable of catalyzing methane oxidation (although with a low turnover number), we propose that these model complexes are an important step forward in creating the structural–functional MMO model.

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