Characterization and application of peroxo-diiron(III)-containing intermediates in oxygen atom transfer (OAT) and hydrogen atom transfer (HAT) reactions

PHD THESES

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Abstract

Characterization and application of diiron(III)-containing intermediates in oxygen atom transfer (OAT) and hydrogen atom transfer (HAT) reactions

By Miklós István Szávuly

Nonheme diiron enzymes are involved in many oxidative metabolic pathways in nature. The group of these enzymes including ribonucleotide reductase (RNR R2), soluble methane monooxygenase (sMMO), human deoxyhypusine hydroxylase (hDOHH), cyanobacterial aldehyde deformylating oxygenase (cADO), stearoyl-acyl carrier protein Δ^9 desaturase (Δ^9D), and hemeritine (Hr) are containing reactive peroxo- and oxo intermediates.

In our research peroxo-diiron(III) complexes have been prepared and characterized, which can be considered as structural models of these enzymes.

The aim of our research was to investigate of the reactivity of this metastable peroxo-diiron(III) intermediates in OAT and HAT reactions using cyclic ketones, phenols, benzyl alcohols, organic sulfides and different hydrocarbons as substrates.

INTRODUCTION

Synthetic models of peroxo-diiron(III) intermediates

The primary question about oxidoreductases and their synthetic models is, how to oxygen activation is achieved? Intermediate research can be helpful in understanding this process, which is responsible for providing information to the mechanism of substrate and dioxygen activation **Figure 1**.

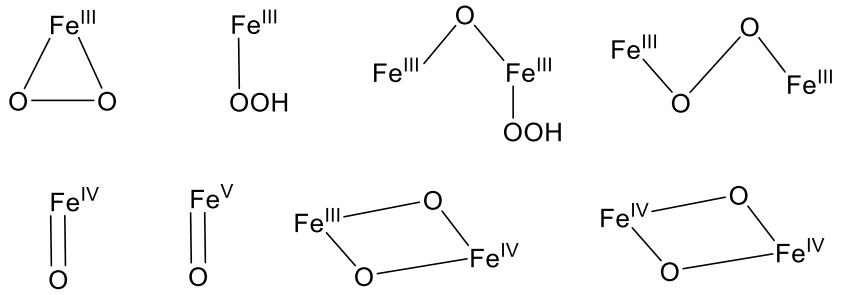

Figure 1. Reactive intermediates of iron containing enzymes

By analyzing literature data we can say that peroxo-diiron(III) complexes reactivity depends on the Fe-Fe distance what is naturally regulated by the corresponding bridge ligand. Generally, protonation of oxo-bridges and alkylation increases the bond distance.

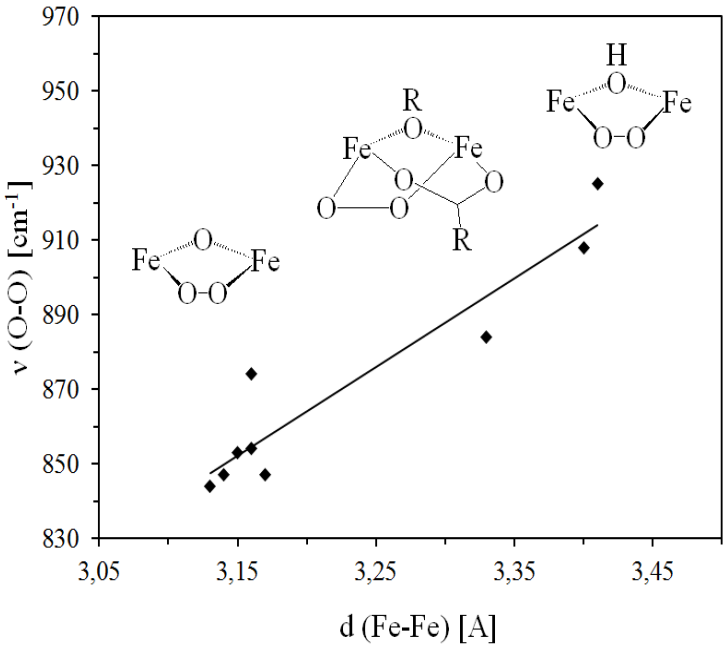

Figure 2. Correlation between the structure (EXAFS) and the spectroscopic characteristics (rRaman) for peroxodiiron(III) intermediates

Various values of Raman *ν*(O–O) vibrations can confirm the differences in bond distances **Figure 2**, furthermore the articles often contain theoretical quantum chemical calculations to support experimental data. Based on this correlation can be estimated the distance between the two irons, which affects both the stability and the reactivity of the intermediate.

APPLIED EXPERIMENTAL TECHNIQUES

Schlenk-technique was used during the preparation of oxygen and moisture sensitive materials. Carbon dioxide and water traces were removed from the argon by potassium hydroxide, phosphorous pentoxide and columns filled with blaugel. The oxygen traces were removed by DEOXO® catalyst.

UV-VIS measurements were performed on Agilent 8453 and Agilent Cary 60 spectrophotometers.

Gas chromatographic measurements were performed on Agilent 7820A and HP / Agilent 5890 gas chromatograph with Super Cowax 10, HP-5 column. GC-MS measurements were performed using Shimadzu QP2010SE, an electron multiplier detector, with a 30 m HP-5MS column.

Cyclic voltammetry measurements were performed with a CHI630B potentiometer.

LIGANDS AND COMPLEXES USED IN THIS WORK

$[Fe^{II}(PBI)_3](CF_3SO_3)_2 \cdot 2H_2O$ (**1**) complex

$[Fe^{II}(MePBI)_3](CF_3SO_3)_2 \cdot 2H_2O$ (**2**) complex

$[Fe_2(\mu\text{-}O_2)(PBI)_4(CH_3CN)_2]^{2+}$ (**3**) intermediate

$[Fe_2(\mu\text{-}O_2)(MePBI)_4(CH_3CN)_2]^{2+}$ (**4**) intermediate

$[Fe^{II}(TBZ)_3](CF_3SO_3)_2$ (**5**) complex

$[Fe^{III}_2(\mu\text{-}O_2)(TBZ)_2(H_2O)_2]$ **(6)** intermediate

$[Fe^{II}(HL^1)(CH_3CN)_3](ClO_4)_2$ (**7**) complex

$[Fe^{III}_2(\mu\text{-}O)(\mu\text{-}1,2\text{-}O_2)(HL^1)_2(MeCN)_2]^{2+}$ (**8**) intermediate

$[Fe_2(\mu\text{-}O)(HL^3)_2Cl_2]$ (**9**) complex

$[Fe_2(\mu\text{-}O)(HL^5)_2Cl_2]$ (**10**) complex

$[Fe_2(\mu\text{-}O)(HL^7)_2Cl_2]$ (**11**) complex

$[Fe_2(\mu\text{-}OMe)_2(H_2L^4)Cl_4]$ (**12**) complex

$[Fe_2(\mu\text{-}OMe)_2(H_2L^6)Cl_4]$ (**13**) complex

$[Fe_2(\mu\text{-}OMe)_2(H_2L^8)Cl_4]$ (**14**) complex

$Fe^{III}Cl_2(HL^1)$ (**15**) complex

$Fe^{III}Cl_2(HL^2)$ (**16**) complex

$Fe^{III}Cl_2(HL^3)$ (**17**) complex

$Fe^{III}Cl_2(HL^5)$ (**18**) complex

$Fe^{III}Cl_2(HL^7)$ (**19** complex

$[(Fe^{III}Cl_2)_2(HL^6)]$ (**20**) complex

PBI 2-(2-pyridyl)benzimidazole

MePBI 2–(2'–pyridyl)–*N*–methylbenzimidazole

TBZ thiabendazole

HL^1 1,3-bis(2'-pyridyl-imino)isoindoline

HL^2 1,3-bis(2'-thiazolyl-imino)isoindoline

HL^3 1,3-bis(2 '- (4'-methyl-pyridyl)imino)isoindoline

HL^5 1,3-bis(5'-methyl-2'-thiazolylimino)isoindoline

HL^6 O-phenylene-bis[6-oxy-1,3-bis(2'-pyridyl-imino)isoindoline]

HL^7 1,3-bis(2'-benzothiazolyl-imino)isoindoline

H_2L^2 1,4-di-(2'-pyridyl)aminophthalazine

H_2L^4 1,4-di-(4'-methyl-2'-pyridyl)aminophthalazine

H_2L^6 1,4-di-(5'-methyl-2'-thiazolyl)aminophthalazine

H_2L^8 1,4-di-(2'-benzothiazolyl)aminophthalazine

OBJECTIVES

Based on previous knowledge it can be said, that activation of dioxygen in non-heme diiron containing enzymes occurs through reactive, unstable peroxo-diiron(III) intermediates. These particles have a dual role, can act as precursors of intermediates which responsible for oxidation, and may also be involved in oxidation reactions themselves:

- in the case of RNR R2, the role of the peroxo-diiron(III) complex is in the formation of $Fe^{III}O\text{-}Fe^{IV}O$, which is responsible for the formation of tyrosyl radical in the key step of DNA biosynthesis. As a functional model of this system, we intend to examine the role of the peroxo-2 (III) intermediate in the oxidation reaction of phenols, through the development of detailed reaction kinetic measurements.
- in addition to electrophilic enzymatic reactions, nucleophilic processes also can be found (cADO enzyme) in nature, however, we have little knowledge of these. We want

to study the role of peroxo-diiron(III) intermediate as a possible nucleophilic reactant in the oxidation reaction of carbonyl compounds and to propose a reaction mechanism based on detailed kinetic measurements.

- further object is to examine the role of peroxo-diiron(III) intermediates in competitive reactions by electrophilic and nucleophilic substrates.
- in the case of sMMO, the role of the peroxo-diiron(III) complex is in the formation of the catalytically active electrophilic diiron(IV) which is responsible for the hydroxylation of alkanes. To modeling this enzyme we want to design isoindoline and phthalazine type diiron(III) containing complexes. We want to use these complexes in catalytic systems using different bond strength hydrocarbon compounds, benzyl alcohols and organic sulfides as substrates to study HAT and OAT reactions.
- using the results of these functional models, we want to develop another biomimetic systems.

THESES

1. **Preparation of RNR R2 functional enzyme models; Investigation of the $[Fe_2(\mu\text{-}O_2)(PBI)_4(CH_3CN)_2]^{2+}$ and $[Fe_2(\mu\text{-}O_2)(MePBI)_4(CH_3CN)_2]^{2+}$ intermediates in HAT reaction**

The $[Fe_2(\mu\text{-}O_2)(PBI)_4(CH_3CN)_2]^{2+}$ (**3**) and $[Fe_2(\mu\text{-}O_2)(MePBI)_4(CH_3CN)_2]^{2+}$ (**4**) complexes were/have been investigated in oxidation reactions of 2,6-di-tertbutylphenol, and 1,4-hydroquinones as a structural and functional model of RNR-R2 enzyme **Figure 3**.

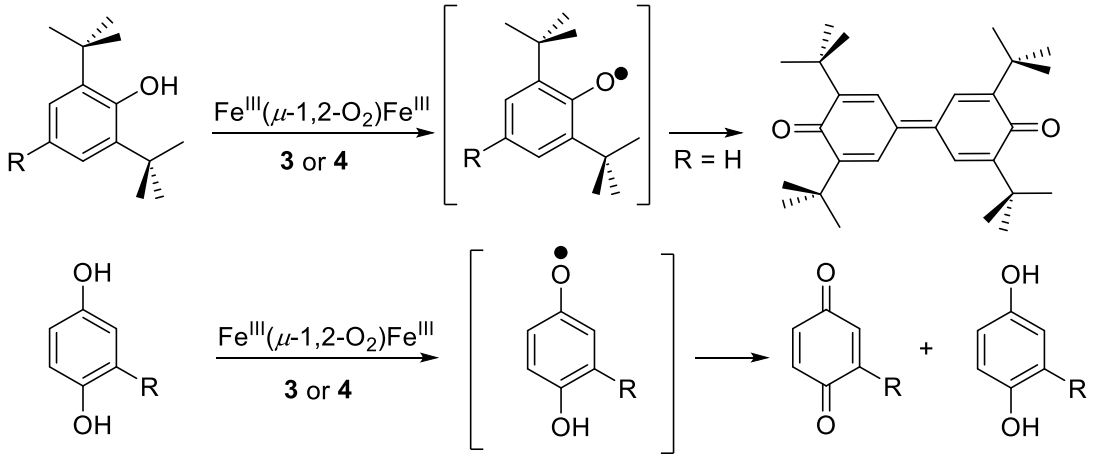

Figure 3 (μ-1,2-peroxo)diiron(III)-mediated oxidation of phenols and hydroquinones

1.1. Based on the kinetic results for both substrates the half-order dependence for **3** and **4** was found. That suggests the electrophilic oxoiron(IV) species formed from the $Fe^{III}(\mu\text{-}1,2\text{-}O_2)Fe^{III}$ intermediate by homolytic cleavage of the O-O bond. In the case of 2,6-di-tert-butylphenol, the reaction kinetic parameters for complexes **3** and **4** at 20˚C are: k_{ox} = 20.2 × 10^{-5} $M^{-1/2}$ s^{-1}, $\Delta H^{\#}$ = 43 kJ mol^{-1}, $\Delta S^{\#}$ = -171 J mol^{-1} K^{-1}, and k_{ox} = 5.75 × 10^{-5} $M^{-1/2}$ s^{-1}, $\Delta H^{\#}$ = 64 kJ mol^{-1}, $\Delta S^{\#}$ = -108 J mol^{-1} K^{-1}. For 2-chloro-1.4-hydroquinone, complexes **3** and **4** at 5˚C are: k_{ox} = 0.38 $M^{-1/2}$ s^{-1}, $\Delta H^{\#}$ = 36 kJ mol^{-1}, $\Delta S^{\#}$ = -121 J mol^{-1} K^{-1}, and k_{ox} = 0.06 $M^{-1/2}$ s^{-1}, $\Delta H^{\#}$ = 51 kJ mol^{-1}, $\Delta S^{\#}$ = -83 J mol^{-1} K^{-1}. The different reactivity between **3** and **4** can be explained by the introduction of the methyl-substituent on the NH group of the benzimidazole which increases the electron density on the iron center, and decreases its electrophilic character.

1.2. The *Hammett ρ* values for 2,6-DTBPh (ρ = −0.67 and −0.71 for **3** and **4**) where the electron-releasing substituents accelerated the rate significantly, suggesting the electrophilic character of the key oxidant. A linear correlation between logk_{ox} and O–H bond dissociation energy (BDE) for **3** and **4**, suggesting that the HAT mechanism is implemented through H-atom abstraction in both cases. Further evidence for the H-atom abstraction mechanism is the kinetic isotope effect (KIE) value of 1.78 (**3**) for 2,6-DTBPh and 2.9 (**3**) and 2.3 (**4**) for H2Q-Cl.

1.3. Based on these results we can say that the $Fe^{III}(\mu\text{-}1,2\text{-}O_2)Fe^{III}$ intermediate can be generated quickly from the precursor iron(II) complex with H_2O_2. From this intermediate by homolytic cleavage of the O-O bond formed the reactive electrophilic Fe^{IV}=O species. The proposed reaction mechanisms are in **Figure 4**.

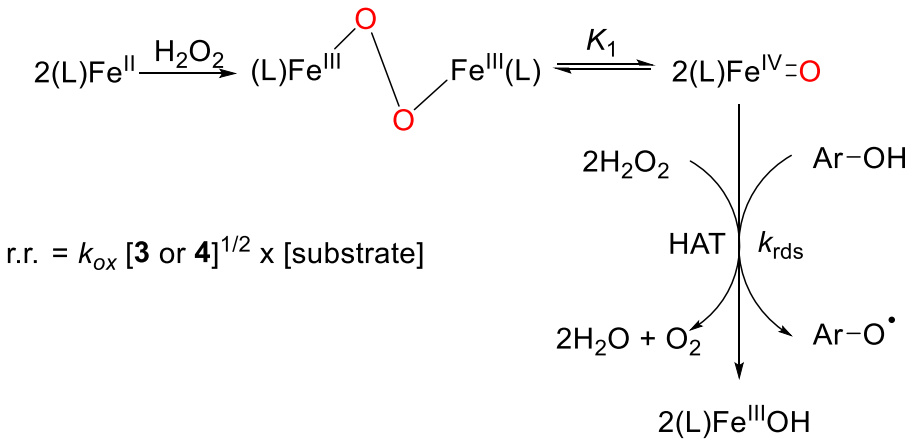

Figure 4 The proposed reaction mechanism for the catalase reaction, oxidations reactions of 2,6-DTBPh and 1,4-hydroquinone by $Fe_2(\mu\text{-}O_2)(PBI)_4(CH_3CN)_2]^{2+}$ (**3**) and $[Fe_2(\mu\text{-}O_2)(MePBI)_4(CH_3CN)_2]^{2+}$ (**4**) complexes.

1.4. Upon formation, the peroxo-diiron(III) complexes **3** and **4** decompose to form dioxygen and regenerate the precursor Fe(II) complexes **Figure 5**.

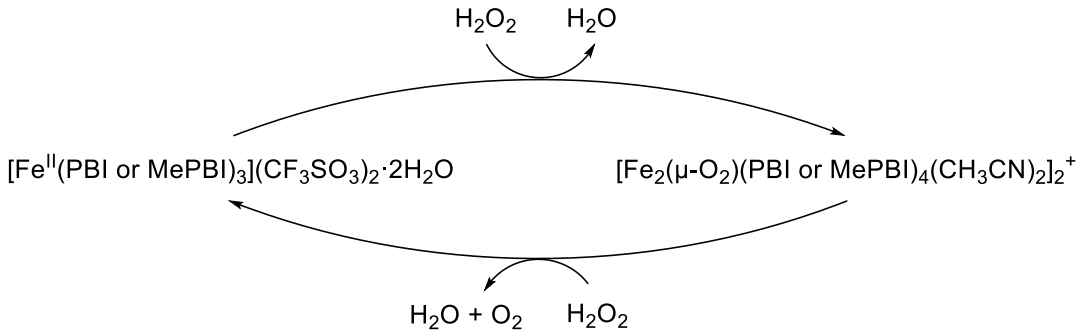

Figure 5 Catalase activity of $Fe_2(\mu\text{-}O_2)(PBI)_4(CH_3CN)_2]^{2+}$ (**3**) and $[Fe_2(\mu\text{-}O_2)(MePBI)_4(CH_3CN)_2]^{2+}$ (**4**) complexes

1.5. Based on the detailed kinetic measurements we determined the reaction rate constants. The estimated initial rates (under same conditions) were $V_0 = 2.95 \times 10^{-5}$ M s^{-1} (TOF = 0.65 min^{-1}), and $V_0 = 5.10 \times 10^{-5}$ M s^{-1} (TOF = 1.43 min^{-1}), respectively to the compound **3** and **4**. Based on the observed initial rates, compound **4** was more reactive than **3**. Furthermore, there is direct kinetic, and computational evidence that the in situ formed peroxo-diiron(III) complexes catalyze the dismutation of H_2O_2 into O_2 suggesting, catalase-like activities

2. Characterization and investigation of $[Fe_2(\mu\text{-}O_2)(PBI)_4(CH_3CN)_2]^{2+}$, $[Fe_2(\mu\text{-}O_2)(MePBI)4(CH_3CN)_2]^{2+}$ and $[Fe_2(\mu\text{-}O_2)(TBZ)_4(CH_3CN)_2]^{2+}$ intermediates as a possible nucleophilic reactant in the oxidation reaction of carbonyl compounds (Baeyer-Villiger reaction)

2.1. The new $[Fe^{II}(TBZ)_3](CF_3SO_3)_2$ (**5**) complex was prepared by the reaction of TBZ and Fe^{II}, and the molecular structure was characterized by UV-VIS spectroscopy, resonance Raman, and X-ray diffraction. $[Fe_2(\mu\text{-}O_2)(TBZ)_4(CH_3CN)_2]^{2+}$ (**6**) intermediate was generated from the **5** with H_2O_2, has a characteristic absorption band in UV-VIS range (λ_{max} = 705 nm (ε = 1200 M^{-1} cm^{-1}). The rate constant k = 6.54 $M^{-1}s^{-1}$ was determined from the formation kinetics. The resonance Raman spectrum of **6** obtained with λ_{exc} = 785 nm exhibits features at 877 and 463 cm^{-1}, which can be assigned to a ν(O─O) and ν(Fe─O) stretching modes, respectively.

2.2. The $[Fe_2(\mu\text{-}O_2)(PBI)_4(CH_3CN)_2]^{2+}$ (**3**), $[Fe_2(\mu\text{-}O_2)(MePBI)4(CH_3CN)_2]^{2+}$ (**4**) and $[Fe_2(\mu\text{-}O_2)(TBZ)_4(CH_3CN)_2]^{2+}$ (**6**) intermediates were generated ***in situ*** with different oxidants (such as PhIO, *m*-CPBA, H_2O_2).

2.3. After their characterization, reactivities were investigated in *Baeyer-Villiger* reaction, using various cycloketone derivatives as substrates. We found that the nucleophilic peroxo-diiron(III) species is able to oxidize the cyclohexanone derivatives to the corresponding ε-caprolactones, including its nucleophile attack on the carbonyl group, which is a synthetic model of the cADO enzyme. The low activation enthalpies and the large negative activation entropies ($\Delta H^{\neq}$ = 12 kJ mol^{-1} and $\Delta S^{\neq}$ = -187 J mol^{-1} K^{-} at 15°C) are typical associative processes. The k_{ox} values (0.4 M^{-1} s^{-1}; 0.08 M^{-1} s^{-1}; 1.6 M^{-1} s^{-1}) for the complexes **3** ($1/H_2O_2$), **4** and **6** vary in the order: $[Fe^{III}_2(\mu\text{-}O_2)(TBZ)_2(CH_3CN)_2]^{2+}$ (**6**) > $[Fe^{III}_2(\mu\text{-}O_2)(PBI)_2(CH_3CN)_2]^{2+}$ (**3**) ($1/H_2O_2$) > $[Fe^{III}_2(\mu\text{-}O_2)(MePBI)_2(CH_3CN)_2]^{2+}$ (**4**). These results are in good agreement with the Baeyer-Villiger oxidations, where the nucleophilic attack of the eroxo-diiron(III) on the electrophilic carbonyl not involved in the rate-determining step, here is a Criegge-like rearrangement. Based on reaction kinetic measurements, we proposed a reaction mechanism **Figure 6**.

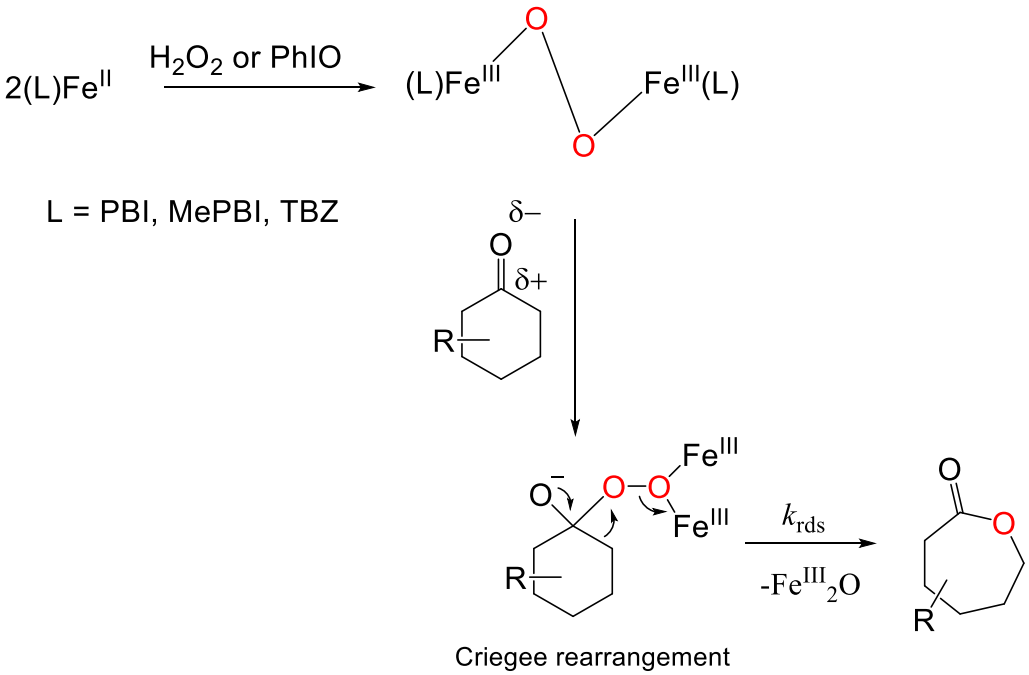

Figure 6 The proposed reaction mechanism for *Baeyer-Villiger* reaction by **3** ($1/H_2O_2$)**,** **3** (1/PhIO), **4** or **6** complexes

3. Ambiphilic reactivity of a $[Fe^{III}_2(\mu\text{-}O)(\mu\text{-}1,2\text{-}O_2)(HL^1)_2(MeCN)_2]^{2+}$ (8) intermediate

The $[Fe^{III}_2(\mu\text{-}O)(\mu\text{-}1,2\text{-}O_2)(HL^1)_2(MeCN)_2]^{2+}$ (**8**) intermediate was generated ***in situ*** with H_2O_2 from the $[Fe^{II}(HL^1)(CH_3CN)_3](ClO_4)_2$ (**7**) complex. The reactivity was investigated in oxidation reactions using cyclohexane and different C-H bond strength hydrocarbons as substrates.

3.1. We have proved by detailed kinetic studies (k_2 = 0.4 $M^{-1}s^{-1}$, $\Delta H^{\ddagger}$ = 22 kJ mol^{-1} $\Delta S^{\ddagger}$ = -172 J mol^{-1} K^{-1}) that the nucleophilic peroxo-diiron(III) intermediate attacks the electrophilic carbonyl group of the substrate. These reaction have been documented well for mononuclear peroxo-iron(III) complexes, our observations are the first example of this type of reactivity of the peroxo-diiron(III) complex, so this complex can be described as a functional model of the cADO enzyme.

3.2. Complex $[Fe^{III}_2(\mu\text{-}O)(\mu\text{-}1,2\text{-}O_2)(HL^1)_2(MeCN)_2]^{2+}$ (**8**) is also involved in the oxidation of hydrocarbon substrates, but in contrast to its reaction with cyclohexanone, neither the nature of the hydrocarbon nor its concentration affects the decay rate of **8**. Nevertheless, concentrations of oxidized products are observed and increasing (cyclohexanol or 1,2-epoxy octane or benzaldehyde) during the oxidation reactions. Based on these results above can be proposed two different oxidants with a nucleophilic and an electrophilic character, respectively. We have proved the ambiphilic reactivity of **8** by ^{18}O-labeling experiments. The complex **8** and the oxo-intermediate **8a** are found to carry out nucleophilic and electrophilic transformations, therefore we have conducted competitive oxidations of cyclohexanone (nucleophilic pathway) and 1-octene or toluene (electrophilic pathway) **Figure 7**.

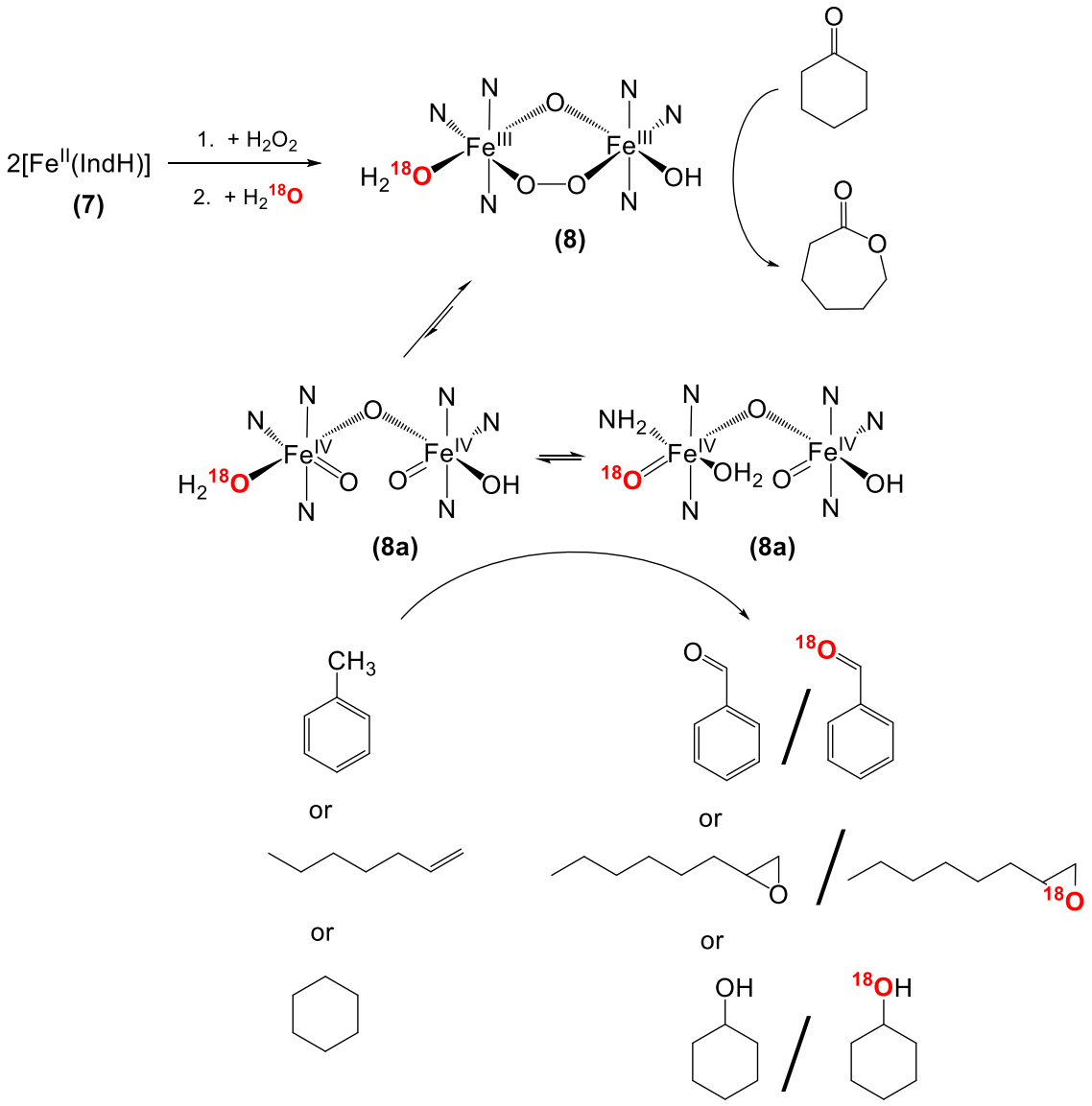

Figure 7 The proposed overall mechanism for substrate oxidation by $[Fe^{III}_2(\mu\text{-}O)(\mu\text{-}1,2\text{-}O_2)(HL^1)_2(MeCN)_2]^{2+}$ (**8**)

4. Catalytic oxidation of alcohols and sulfides with hydrogen peroxide using isoindoline and phthalazine-based diiron complexes

4.1. We have developed new, efficient and cheap catalytic systems by isoindoline and phthalazine type diiron(III) complexes, which can be considered as a functional model of sMMO. The $Fe_2(\mu\text{-}O)(HL^3)_2Cl_2]$ (**9**), $[Fe_2(\mu\text{-}O)(HL^5)_2Cl_2]$ (**10**), $[Fe_2(\mu\text{-}O)(HL^7)_2Cl_2]$ (**11**), $[Fe_2(\mu\text{-}OMe)_2(H_2L^4)Cl_4]$ (**12**), $[Fe_2(\mu\text{-}OMe)_2(H_2L^6)Cl_4]$ (**13**) and $[Fe_2(\mu\text{-}OMe)_2(H_2L^8)Cl_4]$ (**14**) complexes have been characterized, and used as catalysts for the oxidation of *para*-substituted phenyl methyl sulfides, benzyl alcohols and investigated their catalase activity. The molecular

structures of $[Fe_2(\mu\text{-}O)(HL^5)_2Cl_2]$ (**10**) and $[Fe_2(\mu\text{-}OMe)_2(H_2L^6)Cl_4]$ (**13**) complexes were determined by X-ray diffraction.

4.2. We considered that the investigated complexes are capable of catalytic decomposition of H_2O_2. Based this results the examined systems can be considered as functional models of two-core catalase enzymes.

4.3. Based on the obtained reaction kinetic results (*Hammett* ρ = -0.9 reaction constant, logk_{obs} values as a function of E_{ox} the slope value -1.7), the oxidation reaction of thioanisoles with diiron(III) complexes has been involved via direct oxygen transfer mechanism.

4.4. Based on the obtained reaction kinetic results (*Hammett* ρ = -0.8 reaction constant, *KIE* = 9.03), in the oxidation reaction of benzyl alcohols with diiron(III) complexes were indicated the formation of an electrophilic metal-based oxidant, as a key oxidant.

4.5. Based on the results it can be said that both isoindoline and phthalazine type complexes are useful as catalysts in OAT and HAT reactions and the oxidative reactivity may be explained by the formation of $Fe^{III}(\mu\text{-}O)(\mu\text{-}1,2\text{-}O_2)Fe^{III}$, which is responsible for the formation of the key oxidant.

5. Catalytic oxidation of 2-aminophenol by iron(III) isoindoline complexes

5.1. Series of new dichloroiron(III) complexes of 1,3-bis(2'-arylimino)isoindoline, including a new structurally characterized ligand 1,3-bis(5'-methyl-2'-thiazolylimino)isoindoline (HL^5) and its complex ($Fe^{III}Cl_2(L^5)$, have been used as catalysts for the oxidative coupling of 2-aminophenol (OAP) to 2-aminophenoxazine-3-one (APX) **Figure 8**.

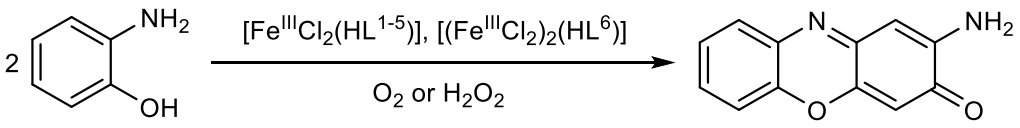

Figure 8 Oxidation reaction of 2-aminophenol in the presence of iron(III) catalysts

5.2. Based on reaction kinetic results the dichloroiron(III) complexes of 1,3-bis(2'-arylimino)isoindoline, including a new structurally characterized ligand 1,3-bis(5'-methyl-2'-

thiazolylimino)isoindoline and its complex, are efficient catalysts for the 2-aminophenol oxidation, which means that the investigated systems serve as functional models for phenoxazinone synthase enzymes. Depending on the oxidant used, two different mechanisms can be proposed, namely a metal-based oxidation for dioxygen (***Route 1*** **in Figure 9**), and a radical process, including zero-order dependence on the concentration of the substrate, for H_2O_2 (***Route 2*** **in Figure 9**).

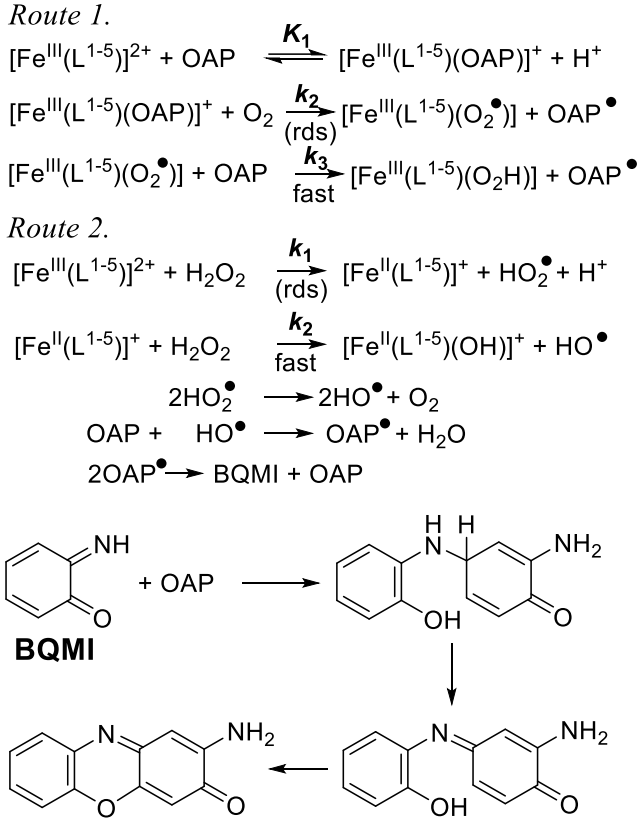

Figure 9 The proposed reaction mechanisms for the oxidation of 2-aminophenol metal-based oxidation for dioxygen (*Route 1.*), and a radical process, including zero-order dependence on the concentration of the substrate, for H_2O_2 (*Route2.*)

PUBLICATIONS, PRESENTATIONS AND POSTERS RELATED TO THE DISSERTATION

Publications

(1) Functional models of nonheme diiron enzymes: kinetic and computational evidence for the formation of oxoiron(IV) species from peroxo-diiron(III) complexes, and their reactivity towards phenols and H_2O_2
M. I. Szávuly, M. Surducan, E. Nagy, M. Surányi, G. Speier, R. Silaghi-Dumitrescu and J. Kaizer
Dalton Transactions, 2016, **45**, 14709-14718

(2) Divastartalmú oxidoreduktázok szerkezeti és funkcionális modelljei
M. I. Szávuly, D. Lakk-Bogáth, R. Csonka, R. Turcas, G. Speier, J. Kaizer
Magyar Kémikusok Lapja, 2016

(3) 1,3-Bis(5′-methyl-4′-phenyl-2′-thiazolylimino)isoindoline
R. Csonka, M. I. Szávuly, M. Giorgi, G. Speier, J. Kaizer
Molbank 2016, M882

(4) Oxidation of 2-aminophenol by iron(III) isoindoline complexes
M. Szávuly, R. Csonka, G. Speier, R. Barabás, M. Giorgi, J. Kaizer
*J. Mol. Cat. 2014, **392**,120-126*

(5) Catalytic oxidation of alcohols and sulfides with hydrogen peroxide using isoindoline and phthalazine-based diiron complexes
M. Szávuly, Sz. D. Szilvió, R. Csonka, D. Klesitz, G. Speier, M. Giorgi, J. Kaizer
*J. Mol. Cat. 2014, **393**,317-324*

Further scientific publications:

(1) Nemhem-típusú oxidáz és oxigenáz enzimek szintetikus modelljei: szerkezet, reaktivitás, katalízis
D. Lakk-Bogáth, M. I. Szávuly, G. Speier, J. Kaizer
*Magyar Kémikusok Lapja, **LXXI. évf., 4. szám**, 2016. április*

(6) Functional ribonucleotide reductase enzyme models
M. I. Szávuly, J. Kaizer, G. Speier
J. Biol. Inorg. Chem. (2014) 19 (Suppl 2): S857–S857

Presentations and posters presented at international conferences

1. Fenoxazinon szintetáz modellek előállítása és vizsgálata

   M. I. Szávuly, J. Kaizer

   XIX. Nemzetközi vegyészkonferencia, Nagybánya, 2013. november 21-24. (előadás)

2. Functional Ribonucleotid reductase enzyme models

   M. I. Szávuly, J. Kaizer, G. Speier

   International Conference on Hydrogen Atom Transfer, Róma, Olaszország, 2014. június 22-26. (poszter)

3. Funkcionális ribonukleotid reduktáz és metán monooxigenáz enzimmodellek

   M. I. Szávuly, E. Nagy, J. Kaizer, G. Speier

   XX. Nemzetközi vegyészkonferencia, Kolozsvár, 2014. november 6-9. (előadás)

4. Characterizations and applications of the biomimetic non-heme iron-containing complexes

   M. I Szávuly, J. Kaizer, G. Speier

19th European Symposium on Organic Chemistry, Lisszabon, Portugália, 2015. július 12-16. (poszter)

5. Szerkezeti és funkcionális deoxihipuszine hidroxiláz enzimmodellek
   M. I. Szávuly, J. Kaizer, G. Speier
   XXI. Nemzetközi vegyészkonferencia, Csíksomlyó, 2015. szeptember 23-27. (előadás)
6. Structural and functional ribonucleotide reductase and methane monooxygenase enzyme models
   M. I. Szávuly, J. Kaizer
   4th CARISMA Meeting - Catalityc Routines for Small Molecule Activation, Ljubljana, Szlovénia, 2016. március 21-23. (poszter)

Presentations and posters at Hungarian conferences:

1. Nem-hem divasat tartalmazó funkcionális enzimmodellek
   M. I. Szávuly, E. Nagy, J. Kaizer, G. Speier
   48. Komplexkémiai Kollokvium, Siófok, 2014. május 28-30. (előadás)
2. (μ-oxo)(μ-1,2-peroxo)divas(III) intermedier reaktivitása CH, OH aktiválással és oxigén transzferrel járó reakciókban
   M. I. Szávuly, J. Kaizer, G. Speier
   49. Komplexkémiai Kollokvium, Siófok, 2015. május 26-28. (előadás)
3. Peroxo-divas(III) intermedierek reaktivitásának vizsgálata OAT és HAT reakciókban
   M. I. Szávuly, J. Kaizer, G. Speier
   50. Komplexkémiai Kollokvium, Balatonvilágos, 2016. május 30 – június 1. (előadás)