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H_2O_2-oxidation of α-aminoisobutyric and cyclic amino acids catalyzed by iron(III) isoindoline complexes

Dóra Lakk-Bogáth, Miklós Harasztia, Róbert Csonka, Gábor Speier, József Kaizer *

Department of Chemistry, University of Pannonia, H-8200 Veszprém, Hungary

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ABSTRACT

Series of dichloroiron(III) complexes of 1,3-bis(2′-arylimino)isoindoline have been used as catalysts for the oxidative decarboxylation and deamination reaction of acyclic [α-aminoisobutyric acid (AIBH)] and cyclic amino acids [1-aminocyclohexane-1-carboxylic acid (ACHH), 1-aminocyclopentane-1-carboxylic acid (ACPH), 1-aminocyclobutane-1-carboxylic acid (ACBH), 1-aminocyclopropane-1-carboxylic acid (ACCH)] to ethylene or the corresponding carbonyl compounds. We have found that the title complexes are very efficient and selective as catalysts, and linear correlations were observed between the reaction rate and the oxidation potential, $E^{o\prime}_{pa}$ of the iron complexes, and the endocyclic bond angle of the substrates used.

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1. Introduction

Selective catalytic oxidations of organic molecules such as amino acids by hydrogen peroxide and especially dioxygen under mild conditions are among the most important technological processes in synthetic chemistry as well as in chemical industry from an economical and environmental point of view [1–3]. Amino acids are widely used in cosmetics, pharmaceuticals, and foods [4]. In the nature metal-containing proteins are able to perform oxidation reactions at room temperature under atmospheric pressure in spite of the relative inertness of the C—H and N—H bonds in non-activated substrates. The reactivity studies of transition metal complexes are of particular interest for the development of bioinspired catalysts for metal ion-catalyzed oxidations (MCO) of amino acids [5–11]. Biomimetic models of the non-heme iron enzyme 1-aminocyclopropane-1-carboxylic acid oxidase (ACCO) [12–13] have also been extensively studied using copper [14,15] (Scheme 1), and iron [16,17] complexes as catalysts.

During the past decade isoindoline-based ligands became subject of growing interest due to their modular set-up. They are considered pincer type ligands based on the tridentate coordination mode and the aromatic planarity around the metal ions. They are monoanionic, nevertheless complexes of protonated ligands can form as well with suitable metal ions and the proper conditions applied [18]. Furthermore, the meridional configuration is open enough to host other coligands or various substrates. The 1,3-bis(2′-pyridylimino)isoindoline shows affinity towards a great variety of transition metal ions [19–21]. In these complexes, it was possible to control the redox potential of the metal center by varying the aryl substituent on the bis-iminoisoindoline moiety as illustrated in Scheme 1. Recently, a series of iron(II) and iron(III) complexes of 1,3-bis(2′-arylimino)isoindoline with various N-donor aryl groups have been characterized for mimicking highly selective biological reactions that proceed under mild conditions, namely the dioxygenolytic cleavage of catechols [22], superoxide dismutase (SOD) mimic activity [23], oxidative coupling reaction of 2-aminophenols [24], and catalytic oxidation of alcohols and sulfides [25,26].

Since, the direct oxygenation processes require harsh operating conditions because the triplet state of molecular oxygen hampers the reaction with organic compounds in its singlet state, hydrogen peroxide is a suitable oxidant due to the facts of having high oxygenation selectivity and generating environmentally benign water as by-product. In this paper we discuss the reactivity of these complexes as catalysts against various cyclic and acyclic amino acids by the use of hydrogen peroxide as oxidants in context with the ligand modifications and redox chemistry (Scheme 1).

2. Experimental

2.1. Materials and methods

All manipulations were performed under a pure argon atmosphere using standard Schlenk-type techniques unless otherwise stated. Solvents used for the reactions were purified by literature

* Corresponding author. Tel.: +36 88 624 720; fax: +36 88 624 469.
E-mail address: kaizer@almos.vein.hu (J. Kaizer).

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methods [27] and stored under argon. The isoindoline-based ligands HL^1–HL^4, and their complexes $Fe^{III}Cl_2(L^{1-4})$ have been synthesized according to published procedures [22,24,28–31]. All other chemicals were commercial products and were used as received without further purification.

2.2. Determination of products

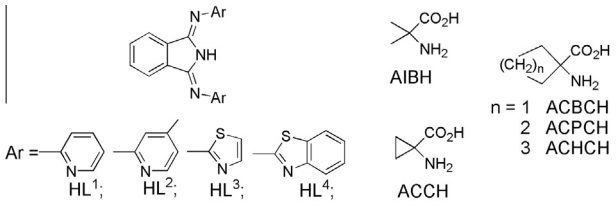
Reactivity assays were performed as follows [16,17]: the respective amino acid (ACCH, ACBH, ACPH, ACHH, AIBH) was dissolved in 10 mL of DMF/H_2O mixture (3/1 V/V) in a 20 mL sealable tube. With MeCN (10 μL) as inner standard, NH_4OH and the catalyst were then added to the mixture. Hydrogen peroxide was added through the septum with a syringe and the evolved ethylene, cyclobutanone, cyclopentanone, cyclohexanone or acetone was measured by removing 0.25 mL from the headspace with a gastight syringe and the sample was injected into a gas chromatograph. The concentration of the corresponding product in the headspace is linearly proportional to the concentration of the product in the reaction mixture [16]. GC analyses were performed on a Hewlett Packard 5890 gas chromatograph equipped with a flame ionization detector and a 30 m Supelcowax column.

3. Results and discussion

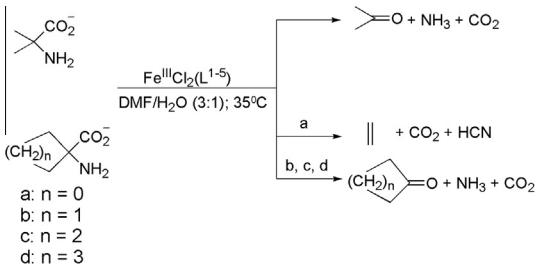
3.1. Catalysis

We have found that complexes $[Fe^{III}Cl_2(L^{1-4})]$ selectively and highly efficiently catalyze the oxidative decarboxylation and deamination of α-aminoisobutyric acid into acetone with H_2O_2 in alkaline DMF/water solution (see Scheme 2).

The evolved acetone was monitored by gas chromatography following our previously reported procedure [16]. The optimum conditions used for the amino acid oxidation by this catalytic system were: catalyst, oxidant, base and substrate in a molar ratio of 1:5000:5000:50,000, respectively. The influence of reaction parameters such as H_2O/DMF ratio, time of the reaction on the catalytic behavior were investigated using complexes $[Fe^{III}Cl_2(L^1)]$. First, we varied the DMF/H_2O from 1:3 to 1:1 and 3:1 (Table 1, entries 1, 2, and 5). The turnovers (yield) (TON = mol of product per mol of catalyst) during these conditions above were found to be 370 (7%), 1048 (21%) and 3528 (71%) after 0.5 h at 35 °C, respectively (Table 1). In the absence of base induction period, and much lower yield has been observed (Table 1, entry 3). The stability of the active species was probed as well using the complex $[Fe^{III}Cl_2(L^1)]$ by varying reaction times from 1800 s to 2700 s (Table 1, entries 4–6). Increasing reaction time from 900 s to 1800 s increased the TON from 3264 to 3647. The general increase in product yields indicate appreciable stability of the active species. The ligand framework also influenced the catalytic activities of these complexes. TONs = 3339–3915, and yields = 67–78% have been found for the complexes $[Fe^{III}Cl_2(L^{2-4})]$ (Table 1, entries 7–15). The TOF (Turnover frequency) values vary in the order: $[Fe^{III}Cl_2(L^2)] > [Fe^{III}Cl_2(L^3)] > [Fe^{III}Cl_2(L^1)] > [Fe^{III}Cl_2(L^4)]$. Furthermore, the rates are dependent on the oxidation potential, $E^{\circ\prime}_{pa}$ of the iron center



Scheme 1. Structure of the isoindoline-based ligands and substrates used.



Scheme 2. Reactions catalyzed by $[Fe^{III}Cl_2(L^{1-4})]$.

Table 1
Calculated yield and TON values for AIBH, ACCH, ACBH, ACPH and ACHH oxidation with $Fe^{III}Cl_2(L^{1-4})$ in DMF/water (3/1 V/V) at 35 °C. $[S]_0 = 3.6 \times 10^{-2}$ M, $[Fe^{III}Cl_2(L^{1-4})]_0 = 7.2 \times 10^{-6}$ M, $[H_2O_2]_0 = 3.6 \times 10^{-2}$ M, $[NH_4OH]_0 = 3.6 \times 10^{-2}$ M.

Entry	Substrate	Catalyst	t (s)	TON [TOF (1/h)]	Yield (%)
1	AIBH[a]	$Fe^{III}Cl_2(L^1)$	1800	370	7
2	AIBH[b]	$Fe^{III}Cl_2(L^1)$	1800	1048	21
3	AIBH[c]	$Fe^{III}Cl_2(L^1)$	1800	1950	39
4	AIBH	$Fe^{III}Cl_2(L^1)$	900	3264	65
5	AIBH	$Fe^{III}Cl_2(L^1)$	1800	3528 [7056]	71
6	AIBH	$Fe^{III}Cl_2(L^1)$	2700	3647	73
7	AIBH	$Fe^{III}Cl_2(L^2)$	900	3398	68
8	AIBH	$Fe^{III}Cl_2(L^2)$	1800	3914 [7828]	78
9	AIBH	$Fe^{III}Cl_2(L^2)$	2700	3915	78
10	AIBH	$Fe^{III}Cl_2(L^3)$	900	3419	68
11	AIBH	$Fe^{III}Cl_2(L^3)$	1800	3647 [7294]	73
12	AIBH	$Fe^{III}Cl_2(L^3)$	2700	3529	71
13	AIBH	$Fe^{III}Cl_2(L^4)$	900	3264	65
14	AIBH	$Fe^{III}Cl_2(L^4)$	1800	3339 [6678]	67
15	AIBH	$Fe^{III}Cl_2(L^4)$	2700	3342	67
16	ACCH	$Fe^{III}Cl_2(L^1)$	900	30	0.6
17	ACCH	$Fe^{III}Cl_2(L^1)$	1800	218	4
18	ACCH	$Fe^{III}Cl_2(L^1)$	2700	545 [726]	10
19	ACBH	$Fe^{III}Cl_2(L^1)$	900	116	2.5
20	ACBH	$Fe^{III}Cl_2(L^1)$	1800	372	7
21	ACBH	$Fe^{III}Cl_2(L^1)$	2700	720 [960]	14
22	ACPH	$Fe^{III}Cl_2(L^1)$	900	880	17
23	ACPH	$Fe^{III}Cl_2(L^1)$	1800	1372	28
24	ACPH	$Fe^{III}Cl_2(L^1)$	2700	1527 [2036]	31
25	ACHH	$Fe^{III}Cl_2(L^1)$	900	1572	31
26	ACHH	$Fe^{III}Cl_2(L^1)$	1800	1602	32
27	ACHH	$Fe^{III}Cl_2(L^1)$	2700	1671 [2228]	33

[a] In DMF/water (1/3 V/V).
[b] In DMF/water (1/1 V/V).
[c] Absence of base.

in the precursor complexes. To elucidate the electronic effect of the different ligands, the redox properties of the precursor complexes have been investigated by cyclic voltammetry (CV) experiments in DMF. Quasi-reversible, one electron transitions were observed for $Fe^{III}Cl_2(L^3)$ and $Fe^{III}Cl_2(L^4)$ ($E^{\circ\prime}_{pa}$ and $E^{\circ\prime}_{pc}$), whereas $Fe^{III}Cl_2(L^1)$ and $Fe^{III}Cl_2(L^2)$ showed irreversible waves ($E^{\circ\prime}_{pa}$) [24]. In the case of $Fe^{III}Cl_2(L^2)$ the anodic peak ($E^{\circ\prime}_{pa}$) shifted by 164 mV compared to that of $Fe^{III}Cl_2(L^1)$ as a result of methyl substitution on the pyridyl arms [24]. Summarily, the redox properties of the iron(III) isoindoline complexes are very sensitive to the modification of the isoindoline arms, and the introduction of electron-releasing arms on the bis-iminoisoindoline moiety slightly increases the catalytic activity. More importantly, a nice correlation was found between the TOF and the oxidation potential, $E^{\circ\prime}_{pa}$ of the iron center in the precursor complexes (Fig. 1) [24].

Finally, the oxidation of other cyclic amino acids like 1-aminocyclohexane-1-carboxylic acid (ACHH), 1-aminocyclopentane-1-carboxylic acid (ACPH), 1-aminocyclobutane-1-carboxylic acid (ACBH), and 1-aminocyclopropane-1-carboxylic acid (ACCH) by H_2O_2 in DMF/H_2O (3:1 V/V) at 35 °C was examined using

Table 2
Kinetic data for the oxidation of AIBH catalyzed by $Fe^{III}Cl_2(L^{1-4})$ with H_2O_2 in DMF/water (3/1 V/V) at 35 °C.

N_O	Catalyst	$[S]_0$ (10^{-2} M)[b]	$[Fe]_0$ (10^{-6} M)	$[H_2O_2]_0$ (10^{-2} M)	V (10^{-5} M s^{-1})
1	$Fe^{III}Cl_2(L^1)$	3.6	3.6	3.6	1.69
2	$Fe^{III}Cl_2(L^1)$[a]	3.6	3.6	3.6	1.11
3	$Fe^{III}Cl_2(L^1)$	3.6	5.4	3.6	2.20
4	$Fe^{III}Cl_2(L^1)$	3.6	7.2	3.6	3.04
5	$Fe^{III}Cl_2(L^1)$	3.6	10.8	3.6	4.42
6	$Fe^{III}Cl_2(L^1)$	0.225	7.2	3.6	0.50
7	$Fe^{III}Cl_2(L^1)$	0.36	7.2	3.6	0.68
8	$Fe^{III}Cl_2(L^1)$	0.45	7.2	3.6	0.81
9	$Fe^{III}Cl_2(L^1)$	0.6	7.2	3.6	0.94
10	$Fe^{III}Cl_2(L^1)$	0.9	7.2	3.6	1.22
11	$Fe^{III}Cl_2(L^1)$	1.4	7.2	3.6	1.88
12	$Fe^{III}Cl_2(L^1)$	1.8	7.2	3.6	2.15
13	$Fe^{III}Cl_2(L^1)$	2.2	7.2	3.6	2.53
14	$Fe^{III}Cl_2(L^1)$	2.6	7.2	3.6	2.72
15	$Fe^{III}Cl_2(L^1)$	3	7.2	3.6	2.88
16	$Fe^{III}Cl_2(L^1)$	3.6	7.2	3.6	3.04
17	$Fe^{III}Cl_2(L^1)$	3.6	7.2	0.9	0.82
18	$Fe^{III}Cl_2(L^1)$	3.6	7.2	1.8	1.50
19	$Fe^{III}Cl_2(L^1)$	3.6	7.2	3.6	3.04
20	$Fe^{III}Cl_2(L^2)$	3.6	7.2	0.9	1.07
21	$Fe^{III}Cl_2(L^2)$	3.6	7.2	1.8	1.94
22	$Fe^{III}Cl_2(L^2)$	3.6	7.2	3.6	3.42
23	$Fe^{III}Cl_2(L^3)$	3.6	7.2	0.9	0.72
24	$Fe^{III}Cl_2(L^3)$	3.6	7.2	1.8	1.38
25	$Fe^{III}Cl_2(L^3)$	3.6	7.2	3.6	2.84
26	$Fe^{III}Cl_2(L^4)$	3.6	7.2	0.9	0.53
27	$Fe^{III}Cl_2(L^4)$	3.6	7.2	1.8	0.91
28	$Fe^{III}Cl_2(L^4)$	3.6	7.2	3.6	1.98

[a] In DMF/D_2O (3/1 V/V) SIE (Solvent isotopic effect) = 1.52.
[b] In $[NH_4OH]_0 = 3.6 \times 10^{-2}$ M.

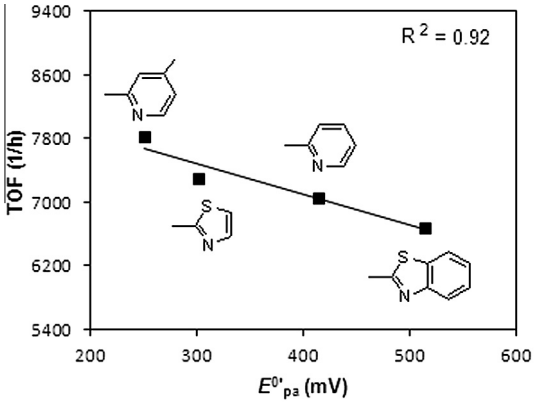


Fig. 1. The calculated TOF (t = 1800 s) values as a function of $E^{o\prime}_{pa}$ [24] of the corresponding $Fe^{III}Cl_2(L^{1-4})$ complexes for the oxidation of AIBH in DMF/water (3/1) at 35 °C. $[AIBH]_0 = 3.6 \times 10^{-2}$ M, $[catalyst]_0 = 7.2 \times 10^{-6}$ M, $[H_2O_2]_0 = 3.6 \times 10^{-2}$ M, $[NH_4OH]_0 = 3.6 \times 10^{-2}$ M.

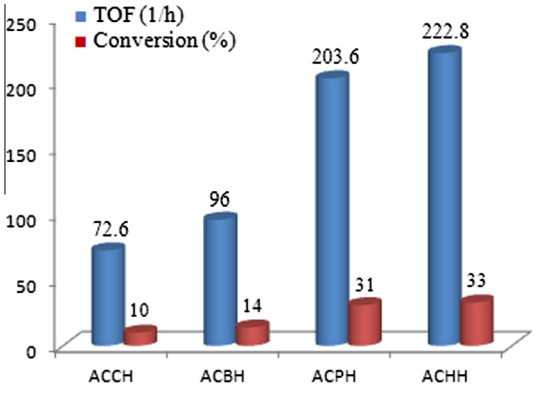


Fig. 2. Calculated conversion and TOF (10×) values (t = 2700 s) for amino acid oxidations with $Fe^{III}Cl_2(L^1)$ in DMF/water (3:1) at 35 °C. $[S]_0 = 3.6 \times 10^{-2}$ M, $[Fe^{III}Cl_2(L^1)]_0 = 7.2 \times 10^{-6}$ M, $[H_2O_2]_0 = 3.6 \times 10^{-2}$ M, $[NH_4OH]_0 = 3.6 \times 10^{-2}$ M.

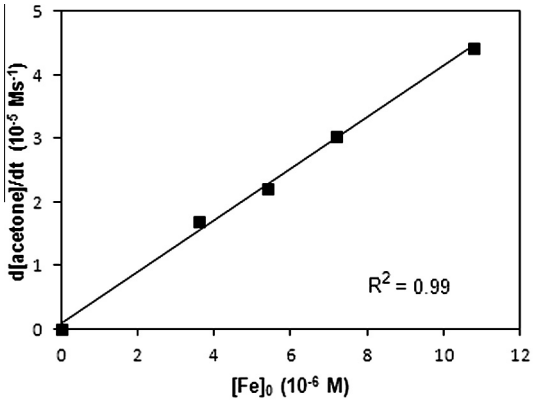


Fig. 3. Dependence of the initial rates on the catalyst concentrations for the oxidation of AIBH with H_2O_2 catalyzed by $Fe^{III}Cl_2(L^1)$ in DMF/water (3/1) at 35 °C. $[AIBH]_0 = 3.6 \times 10^{-2}$ M, $[H_2O_2]_0 = 3.6 \times 10^{-2}$ M, $[NH_4OH]_0 = 3.6 \times 10^{-2}$ M.

$[Fe^{III}Cl_2(L^1)]$ as a catalyst, and the results are summarized in Table 1 (entries 16–27), and Fig. 2. The relative reactivity of substrates shows the following order: ACCH > ACPH > ACBH > ACCH in the case of cyclic amino acids. All reactions were selective, only the corresponding carbonyl compound such as cyclohexanone, cyclopentanone, cyclobutanone or ethylene was formed as main product.

3.2. Kinetic studies

The kinetic runs of the oxidation of amino acids with hydrogen peroxide in the presence of complexes $Fe^{III}Cl_2(L^{1-4})$ were conducted in DMF/H_2O (3:1) at 35 °C under pseudo first-order conditions. The progress of the reaction was followed gas chromatographically by measuring the evolved products from the headspace gas. Detailed kinetic studies on the oxidation of AIBH

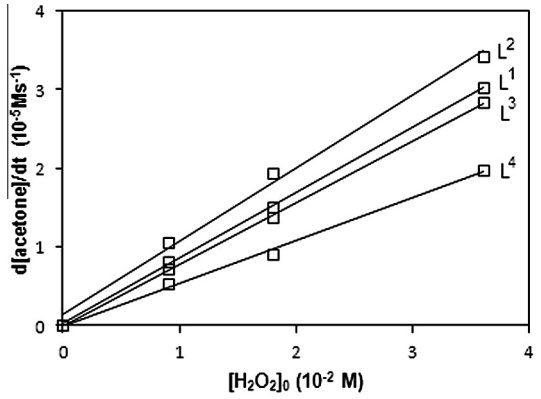


Fig. 4. Dependence of the initial rates on the H_2O_2 concentrations for the oxidation of AIBH with H_2O_2 catalyzed by $Fe^{III}Cl_2(L^{1-4})$ in DMF/water (3/1) at 35 °C. $[AIBH]_0 = 3.6 \times 10^{-2}$ M, $[catalyst]_0 = 7.2 \times 10^{-6}$ M, $[NH_4OH]_0 = 3.6 \times 10^{-2}$ M. (L^1) $R^2 = 0.9994$, (L^2) $R^2 = 0.9921$, (L^3) $R^2 = 0.9997$, (L^4) $R^2 = 0.9971$.

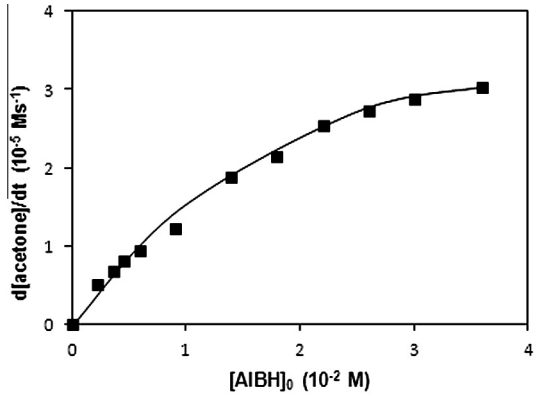


Fig. 5. Dependence of the initial rates on the substrate concentrations for the oxidation of AIBH with H_2O_2 catalyzed by $Fe^{III}Cl_2(L^1)$ in DMF/water (3/1) at 35 °C. $[Fe^{III}Cl_2(L^1)]_0 = 7.2 \times 10^{-6}$ M, $[H_2O_2]_0 = 3.6 \times 10^{-2}$ M, $[NH_4OH]_0 = 3.6 \times 10^{-2}$ M.

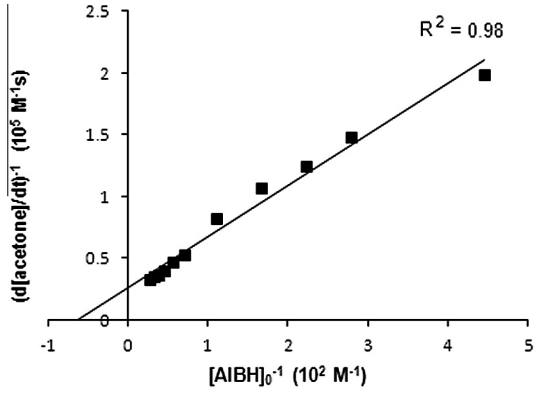


Fig. 6. *Lineweaver–Burk* plot for the oxidation of AIBH with H_2O_2 catalyzed by $Fe^{III}Cl_2(L^1)$ in DMF/water (3/1) at 35 °C. $[Fe^{III}Cl_2(L^1)]_0 = 7.2 \times 10^{-6}$ M, $[H_2O_2]_0 = 3.6 \times 10^{-2}$ M, $[NH_4OH]_0 = 3.6 \times 10^{-2}$ M, DMF/water (3/1), $T = 35$ °C.

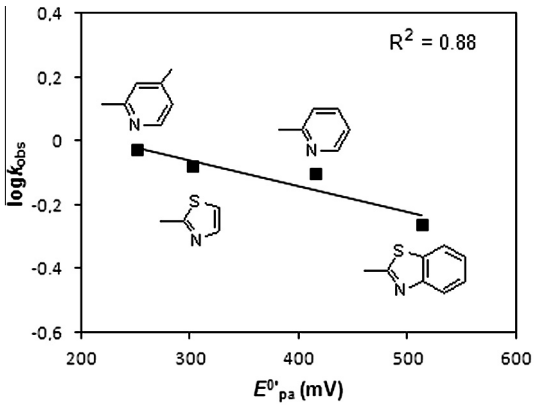


Fig. 7. The reaction rate values as a function of $E^{o\prime}_{pa}$ [24] of the corresponding $Fe^{III}Cl_2(L^{1-4})$ complexes for the oxidation of AIBH with H_2O_2 in DMF/water (3/1) at 35 °C. $[AIBH]_0 = 3.6 \times 10^{-2}$ M, $[catalyst]_0 = 7.2 \times 10^{-6}$ M, $[H_2O_2]_0 = 3.6 \times 10^{-2}$ M, $[NH_4OH]_0 = 3.6 \times 10^{-2}$ M.

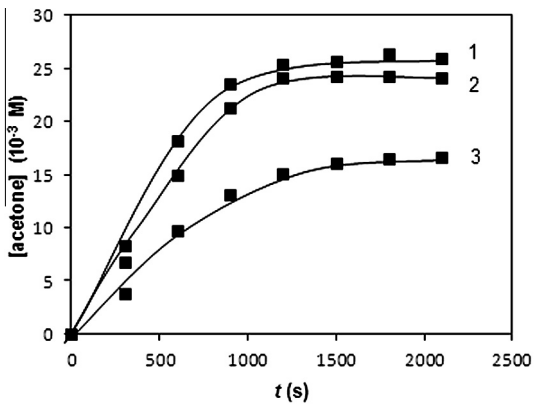


Fig. 8. Formation of acetone vs. time in the oxidation reaction of AIBH with $Fe^{III}Cl_2(L^1)$ in DMF/water (3/1) (1), in DMF/water (3/1) in the presence of 2,4,6-tri-*tert*-butyl-phenol $[2,4,6\text{-}t\text{BuPhOH}]_0 = 3.6 \times 10^{-3}$ M (2) and in DMF/D_2O (3/1) (3) at 35 °C. $[AIBH]_0 = 3.6 \times 10^{-2}$ M, $[Fe^{III}Cl_2(L^1)]_0 = 7.2 \times 10^{-6}$ M, $[H_2O_2]_0 = 3.6 \times 10^{-2}$ M, $[NH_4OH]_0 = 3.6 \times 10^{-2}$ M.

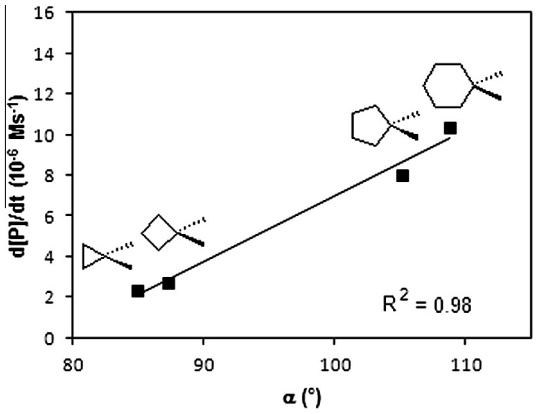
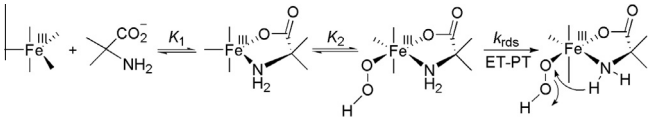


Fig. 9. Correlation between endocyclic bond angle (α) [15] and the reaction rate (dP/dt) for the oxidation of cyclic amino acids with H_2O_2 catalyzed by $Fe^{III}Cl_2(L^1)$ in DMF/water (3/1) at 35 °C. $[S]_0 = 3.6 \times 10^{-2}$ M, $[Fe^{III}Cl_2(L^1)]_0 = 7.2 \times 10^{-6}$ M, $[H_2O_2]_0 = 3.6 \times 10^{-2}$ M, $[NH_4OH]_0 = 3.6 \times 10^{-2}$ M.

were carried out by the method of initial rates by monitoring the evolved acetone as a function of time. The observed initial rates are compiled in Table 2. In order to determine the rate dependence on the various reactants, oxygenation runs were performed at different catalyst (Fig. 3), oxidant (H_2O_2) (Fig. 4), and at different substrate concentrations (AIBH) (Fig. 5) under pseudo first order conditions. The partial order in H_2O_2 (1st) and the complex $Fe^{III}Cl_2(L^1)$ (also 1st) was determined. The variation of AIBH concentration revealed saturation behavior with $V_{max} = 3.92 \times 10^{-5}$ M s^{-1}, $K_M = 1.63 \times 10^{-3}$ M, and $k_{cat} = 2.4$ s^{-1} (Fig. 6). The low



Scheme 3. Proposed reaction mechanisms for the oxidation of amino acids.

K_M value indicates a strong binding of substrate with the catalyst. The estimated value of the catalytic efficiency (k_{cat}/K_M) is 1469 M^{-1} s^{-1}. The reaction rates follow the order: [$Fe^{III}Cl_2(L^2)$] > [$Fe^{III}Cl_2(L^3)$] > [$Fe^{III}Cl_2(L^1)$] > [$Fe^{III}Cl_2(L^4)$], and a nice correlation was observed between the reaction rate (k_{obs}) and the oxidation potential, $E^{\circ\prime}_{pa}$ of the iron center in the precursor complexes $Fe^{III}Cl_2(L^{1-4})$ (Fig. 7) [24], which results are consistent with our results above (see TOFs) (Table 1, Fig. 1).

Comparison of the reaction rates measured in both DMF/H_2O (3:1 V/V) and DMF/D_2O (3:1 V/V), a noticeable (although not very large) H/D kinetic isotope effect, SIE = 1.52 was observed for $Fe^{III}Cl_2(L^1)$, demonstrating that proton transfer and/or disruption of hydrogen bonding is involved in the rate-determining step (Fig. 8). Furthermore, when 2,4,6-tri-*tert*-butylphenol is present in the catalytic system only a slight inhibition can be observed, suggesting iron-based catalysis instead of hydroxyl radical involvement.

The relative reactivity of cyclic amino acid derivatives shows the following order: ACHH > ACPH > ACBH > ACCH, and correlates very well with their endocyclic bond angles of the used substrates (Fig. 9). It can be explained thermodynamically by a product-driven processes (formation of the more stable product is favored).

Based on kinetic measurements, intramolecular kinetic isotopic effect, and product analysis a mechanism has been suggested for the [$Fe^{III}Cl_2(L^{1-4})$]-catalyzed model system (Scheme 3), including ternary complex formation between catalyst, substrate and H_2O_2 in a pre-equilibrium processes (K_1 and K_2), and a concomitant intramolecular H atom transfer in a slow rate-determining step via an ET–PT (electron transfer–proton transfer) mechanism.

4. Conclusion

We have shown that iron(III) isoindoline complexes can selectively and efficiently carry out the oxidation of AIBH to acetone furthermore oxidize various cyclic amino acids to ethylene or the corresponding carbonyl compounds. As a result of kinetic measurements and the kinetic isotopic effect the oxidation can be explained by the formation Fe(AIB)(O_2H)(L^{1-4}) and the concomitant, intramolecular H atom transfer via an ET–PT mechanism. We have proved that the ligand framework influences the catalytic activities, and linear correlation was found between the reaction rate and the oxidation potential, $E^{\circ\prime}_{pa}$ of the iron complexes, and the endocyclic bond angle of the substrates used.

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