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Effect of different carboxylic acids on the aromatic hydroxylation with H_2O_2 in the presence of an iron aminopyridine complex

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ABSTRACT

In this contribution, the effect of the structure of the catalytic additive – carboxylic acid – on the catalytic performance of the iron based catalyst [(PDP)Fe(OTf)$_2$], **2** (PDP = *N,N*′-bis(2-pyridylmethyl)-(*S,S*)-2,2′-bipyrrolidine) in the selective aromatic oxidation of alkylbenzenes with H_2O_2 is presented. Eight (linear and branched) carboxylic acids have been tested; in the presence of 2-ethylhexanoic acid, the system [(PDP)Fe(OTf)$_2$]/RCOOH/H_2O_2 has demonstrated the highest substrate conversion and the highest selectivity for oxygen incorporation into the aromatic ring (up to > 99%) at the same time. Low-temperature EPR spectroscopic study of the system [(PDP)Fe(OTf)$_2$]/2-ethylhexanoic acid/H_2O_2 witness the presence of the low-spin perferryl intermediate $\mathbf{2a^{EHA}}$ with small *g*-factor anisotropy ($g_1 = 2.069$, $g_2 = 2.007$, $g_3 = 1.963$), which directly reacts with benzene at −80 °C with the rate constant $k_2 = 0.6\ M^{-1}s^{-1}$, and with toluene with $k_2 > 1\ M^{-1}s^{-1}$, thus giving evidence for its key role in the selective oxygenation of aromatic substrates.

1. Introduction

Chiral bipyrrolidine-derived iron complexes of the PDP family (PDP = N,N′-bis(2-pyridylmethyl)-2,2′-bipyrrolidine) have emerged as very fruitful, active and efficient biomimetic catalysts for the oxidation of olefinic C=C and aliphatic C–H groups with hydrogen peroxide [1–9], as well as for the aerobic asymmetric oxidative C–C coupling of 2-naphthols [10]. At the same time, in aromatic hydroxylation reactions [11–18], Fe(PDP) complexes have not been represented until very recently [19,20].

Encouragingly, in 2018 we have found that iron complex [(PDP*)Fe^{III}(μ-OH)$_2$Fe^{III}(PDP*)](OTf)$_4$, **1** (PDP* = *N,N*′-bis(3,5-dimethyl-4-methoxypyridyl-2-methyl)-(*S,S*)-2,2′-bipyrrolidine, Fig. 1) is capable of mediating the hydroxylation of aromatic substrates (benzene and substituted benzenes) with H_2O_2, with good efficiency (up to 36.5 TN) and high selectivity for oxygen incorporation into the aromatic ring (up to 91%) [19]. Subsequently, a series of iron-PDP complexes, bearing different substituents at the PDP ligands, and different counteranions, have been tested in the oxidation of alkylaromatic compounds with H_2O_2, and the parent complex [(PDP)Fe(OTf)$_2$] (**2**) has been identified as the most efficient catalyst, performing up to 84 catalytic turnovers under the reaction conditions and demonstrating higher aromatic oxygenation selectivity (up to 93%) [20].

So far, acetic acid (AA) has been used as the additive in Fe(PDP)-catalyzed aromatic hydroxylations with H_2O_2 [19,20]. In this work, we present a systematic study of different (linear and branched) carboxylic acids in these reactions, catalyzed by complex **2**, witnessing that 2-ethylhexanoic (EHA) acid has optimal structure, ensuring the highest conversion and aromatic oxidation selectivity. Noticeably, according to the EPR data, the high-valent iron species observed in the presence of AA and EHA are different: the low-spin complex with large *g*-factor anisotropy $\mathbf{2a^{AA}}$ ($g_1 = 2.66$, $g_2 = 2.42$, $g_3 = 1.71$) and the low-spin complex with small *g*-factor anisotropy $\mathbf{2a^{EHA}}$ ($g_1 = 2.069$, $g_2 = 2.007$, $g_3 = 1.963$). The results of evaluation of their reactivity toward arenes at low temperature are reported.

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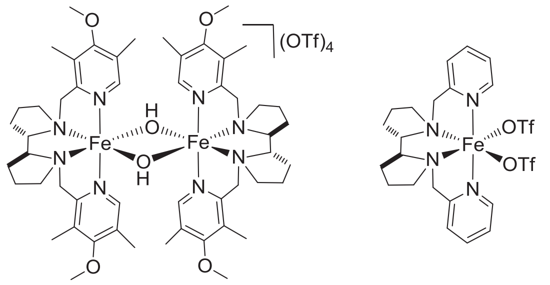


1 **2**

Fig. 1. Structures of complexes **1** and **2** discussed in this work.

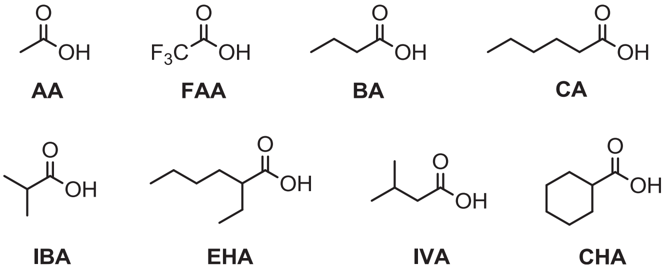


Fig. 2. Structures and abbreviations of carboxylic acids used in this work.

2. Experimental section

Iron complexes **1** and **2** were prepared as described [21,22]. Catalytic oxidations were conducted as follows: aromatic substrate (0.10 mmol), followed by carboxylic acid (10 equiv., 1.0 mmol), was added to the solution of iron complex **2** (1.24 μmol) in CH_3CN (0.40 mL), and the solution was thermostated at 0 °C. The solution of H_2O_2 (4 equiv., 0.40 mmol) in CH_3CN (total volume 0.10 mL) was injected to the reaction mixture by a syringe pump over 30 min upon stirring. The reaction mixture was stirred for 2.5 h at 0 °C and then analyzed by GC/MS.

Detailed experimental data can be found in the Supplementary data.

3. Results and discussion

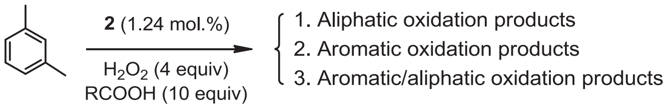
3.1. *Effect of the structure of carboxylic acid on the catalytic performance of complex* **2**

First of all, different carboxylic acids (Fig. 2) were tested as additives in the oxidation of *m*-xylene by the catalyst systems **2**/RCOOH/H_2O_2 under the same optimized conditions [19,20]. The results are collected in Table 1. For alkylbenzenes, the reaction mixtures contained the products of aromatic oxidation (containing oxygen at the aromatic ring), aliphatic oxidation (containing oxygen at alkyl side chain) and aromatic/aliphatic oxidation (containing oxygen both at the aromatic ring and at alkyl side chain). In agreement with the previously used approach [19,20], the aromatic oxidation selectivity was calculated as {amount of aromatic oxidation products + amount of aromatic/aliphatic oxidation products}/overall amount of oxidation products. Minor unidentified products, if any, were not taken into calculation, owing to the impossibility of their identification and reliable quantification. The mass balance was typically better than 95%.

With trifluoroacetic acid, the yield of oxidized products dropped substantially (Table 1, entry 1). As a general trend, the use of branched acids (entries 6–8) led to higher yields of oxidized products, compared with linear acids (entries 2–4); at the same time, the selectivity for aromatic oxidation was higher with branched acids, in some cases exceeding 99% (entries 2–8). Gratifyingly, 2-ethylhexanoic acid, previously established as probably one of the most effective additives in Fe and Mn catalyzed asymmetric epoxidation reactions [5–7,9,23–26], ensured the highest yield of oxygenated products and the highest aromatic oxidation selectivity at the same time (entry 8). Without added carboxylic acid, inferior substrate conversion and aromatic oxidation selectivity was obtained (entry 9 of Table 1).

Next, the oxidation of different substrates by system **2**/EHA/H_2O_2 was studied (Table 2). In most cases, the aromatic oxidation selectivity was higher than 95% (entries 2, 3, 5–9). For several substrates, aromatic oxidation selectivity of up to 99% was achieved (entries 2, 5, 6, 7). Interestingly, the oxidation of *m*-xylene occurred with preferential formation of 2,6-dimethylhydroquinone (entry 7 of Table 2; entry 7 of Table S2). For all substrates, system **2**/EHA/H_2O_2 demonstrated higher aromatic oxidation selectivities than

Table 1
Catalytic oxidation of *m*-xylene with H_2O_2 in the presence of complexes **2**.[a]



Entry	Carboxylic acid	Conversion (%)	Aliphatic oxidation[b]	Aromatic oxidation[b]	Aromatic/aliphatic[b]	Selectivity for aromatic oxidation (%)[c]	TN[d]
1	FAA	1.6	0.5	0.6	0.2	62	1.9
2	AA	67.0	0.8	32.0	17.4	98	96.8
3	CA	17.5	0.6	6.2	6.8	96	25.6
4	BA	46.4	0.4	20.5	14.3	99	67.4
5	CHA	31	0.2	13.4	9.1	99	40.3
6	IBA	75.1	0.3	31.7	24.3	99	109.9
7	IVA	83.3	–	26.8	35.1	>99	120.8
8	EHA	98.3	–	51.6	26.2	>99	151.9
9	–[e]	8.0	4.3	3.1	2.2	55	17.5

[a] Conditions: 0 °C; *m*-xylene (0.10 mmol), H_2O_2 (0.40 mmol), RCOOH (1.0 mmol), catalyst (1.24 μmol), CH_3CN (0.40 mL), syringe-pump addition of H_2O_2 during 30 min, followed by 2.5 h stirring.

[b] Yields, moles of products/mole of Fe. Detailed compositions of the reaction mixtures are provided in Table S1, Supplementary data.

[c] Calculated as 100%•{"aromatic oxidation products" + "aromatic/aliphatic oxidation products"}/overall amount of identified oxidation products.

[d] TN defined as {moles of single oxidation products/mole of Fe}+2{moles of double oxidation products/mole of Fe}. Ketones and aldehydes were considered as double oxidation products.

[e] Carboxylic acid was not added; 3 mmol of exogenous H_2O was present in the reaction mixture from the beginning of the reaction.