

On the nature of the active intermediates in iron-catalyzed oxidation of cycloalkanes with hydrogen peroxide and peracids

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ABSTRACT

Iron complexes of the PDP family [$((S,S)\text{-PDP})\text{Fe}^{\text{II}}(\text{OTf})_2$] (1) and [$((S,S)\text{-PDP}^*)\text{Fe}^{\text{III}}(\mu\text{-OH})_2\text{Fe}^{\text{III}}((S,S)\text{-PDP}^*)$] (OTf)₄ (3), (S,S)-PDP = N,N' -bis(2-pyridylmethyl)-(S,S)-2,2'-bipyrridine, (S,S)-PDP* = N,N' -bis(3,5-dimethyl-4-methoxyphenyl)-2-methyl-(S,S)-2,2'-bipyrridine, and of the TPA family [$(\text{TPA})\text{Fe}^{\text{II}}(\text{CH}_3\text{CN})_2$] (ClO_4)₂ (4) and [$(\text{TPA}^*)\text{Fe}^{\text{III}}(\mu\text{-OH})_2\text{Fe}^{\text{III}}(\text{TPA}^*)$] (OTf)₄ (5), TPA = tris(2-pyridylmethyl)amine, TPA* = tris(3,5-dimethyl-4-methoxyphenyl)-2-methylamine, catalyze the selective hydroxylation of alkanes with hydrogen peroxide and peroxycarboxylic acids as terminal oxidants. The nature of the active species of these catalytic systems has been evaluated by combined EPR spectroscopic and catalytic studies. To this end, the catalytic systems Fe complex/oxidant/RCOOH (catalyst: 1, 3, 4, 5; oxidant: H₂O₂, CH₃CO₃H, *m*-chloroperoxybenzoic acid = *m*-CPBA; RCOOH: acetic acid = AA, 2-ethylhexanoic acid = EHA), exhibiting EPR spectra of iron-oxo and/or iron-acylperoxo intermediates, have been systematically studied in the chemoselective oxidation of cyclohexane and regioselective oxidation of adamantane. In the latter case, high yield of oxidation products (up to 67 TN per Fe atom, or 67%) and high regioselectivity (3°/2° up to 41) were observed. Depending on the nature of the catalyst, oxidant and catalytic additive, various iron-oxygen intermediates have been observed in the catalytic systems studied. Iron (V)-oxo intermediates have been suggested to be the major active species of C–H hydroxylation by the systems catalyst/H₂O₂/RCOOH and catalyst/CH₃CO₃H/RCOOH. In contrast to the catalytic systems with H₂O₂ and CH₃CO₃H as oxidants, in the systems relying on *m*-CPBA, the contribution of iron-acylperoxo intermediates into the oxidation may be significant.

1. Introduction

Regio- and stereoselective oxidation of aliphatic C–H groups of complex organic compounds is a challenging task of modern chemistry [1]. Recently, White and coworkers described the hydroxylation catalysts based on non-heme iron complexes of Fe(PDP) family (1^{SbF6} and 2, Fig. 1) that used hydrogen peroxide to selectively oxidize the aliphatic C–H bonds of complex molecules [2]. A highly electrophilic oxidant, most likely Fe(O)(carboxylate), was proposed to be active species of this oxidations [2e]. Intermediates of this type were observed in the catalytic systems based on complexes 3, 5 [3a], 1 [3b], 4 [4a], 6 [4c] and 6' [4d] (Fig. 1).

In 2015, the highly unstable iron-oxygen intermediates 3a^{AA} and 5a^{AA} ($g_1 = 2.07$; $g_2 = 2.01$; $g_3 = 1.96$) were detected by EPR spectroscopy in the catalytic systems [$((S,S)\text{-PDP}^*)_2\text{Fe}^{\text{III}}(\mu\text{-OH})_2$] (OTf)₄(3)/H₂O₂/AA and [$(\text{TPA}^*)_2\text{Fe}^{\text{III}}(\mu\text{-OH})_2$] (OTf)₄(5)/H₂O₂/AA, respectively (AA = acetic acid) (Fig. 1, Table 1, entries 4 and 7). 3a^{AA} and 5a^{AA} directly reacted with electron-rich olefins at –85 °C to afford the

corresponding epoxides [3a]. Superscript AA denotes that acetate anion is incorporated into the structure of the intermediate.

Initially, by analogy with compound I of cytochromes P450, we assumed that 3a^{AA} and 5a^{AA} are the formally oxoiron(V) intermediates with the unpaired electron preferentially localized on the ligand $[(L)\cdot^+\text{Fe}^{\text{IV}} = \text{O}(\text{OC}(\text{O})\text{CH}_3)]^{2+}$ [3a]. However, very recently, Lipscomb, Que et al. have observed similar intermediate 4a^{AA} ($g_1 = 2.07$, $g_2 = 2.01$, $g_3 = 1.95$) in the related catalytic system 4/CH₃CO₃H (Fig. 1, Table 1, entry 6), and interpreted its EPR spectroscopic data in favor of its (L)Fe^V = O structure [4a]. Therefore, we have used here the $[(\text{PDP}^*)\text{Fe}^{\text{V}} = \text{O}(\text{OC}(\text{O})\text{CH}_3)]^{2+}$ formulation for 3a^{AA} and related species, leaving unambiguous discrimination between (L)Fe^V = O and (L)·⁺Fe^{IV} = O isomeric structures to further studies. Very recently, we have reported that 3a^{AA} can directly hydroxylate cyclohexane and cyclooctane at –70 °C, which corroborates its key role in the oxidation of alkanes [3d]. This year, Fan et al. have presented Mössbauer spectroscopic data supporting Fe^V = O structure of the intermediate 6a' ($g_1 = 2.07$, $g_2 = 2.01$, $g_3 = 1.94$) formed in the catalytic system 6'/

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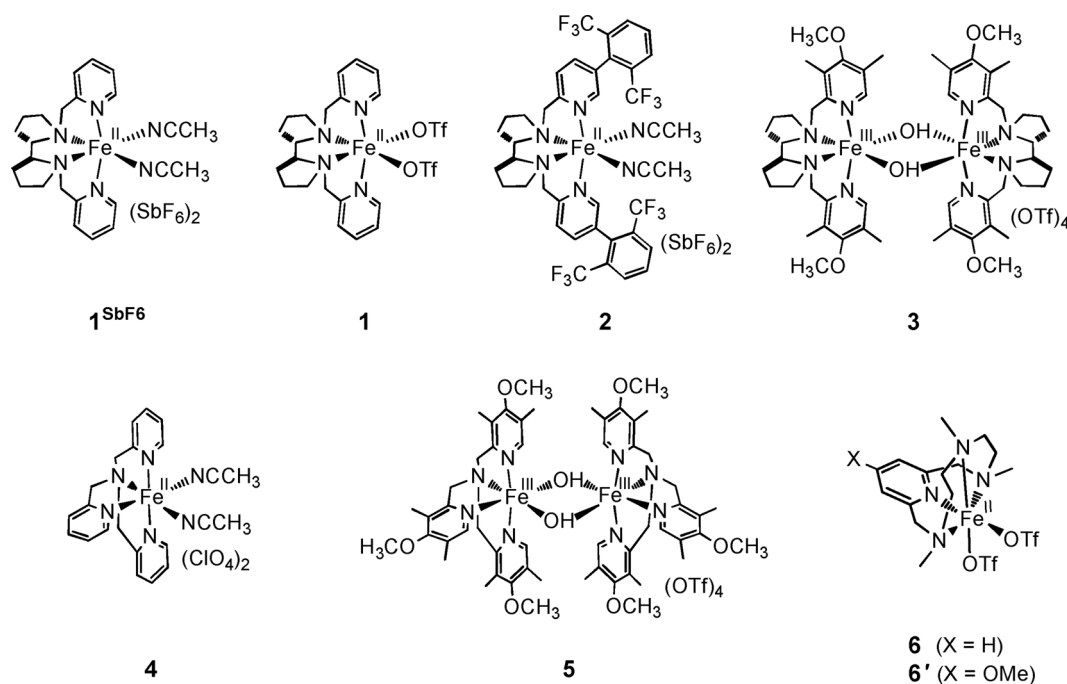


Fig. 1. Iron complexes with aminopyridine ligands.

Table 1

EPR parameters for $S = 1/2$ iron-oxygen species formed in the catalytic systems based on aminopyridine iron complexes.

Entry	Compound	g_1	g_2	g_3	Ref
1	1x	2.66	2.42	1.71	5a
2	4x	2.71	2.42	1.53	5b,c
3	$[(S,S)\text{-PDP}^*]\text{Fe}^{\text{V}} = \text{O}(\text{OC}(\text{O})\text{R})^{2+}$ (1a ^{EHA}) ^a	2.070	2.007	1.963	3b
4	$[(S,S)\text{-PDP}^*]\text{Fe}^{\text{V}} = \text{O}(\text{OC}(\text{O})\text{CH}_3)^{2+}$ (3a ^{AA})	2.071	2.008	1.960	3a
5	$[(S,S)\text{-PDP}^*]\text{Fe}^{\text{V}} = \text{O}(\text{OC}(\text{O})\text{R})^{2+}$ (3a ^{EHA}) ^a	2.070	2.008	1.958	3b
6	$[(\text{TPA})\text{Fe}^{\text{V}} = \text{O}(\text{OC}(\text{O})\text{CH}_3)^{2+}$ (4a ^{AA}) ^b	2.07	2.01	1.96	4a
7	$[(\text{TPA}^*)\text{Fe}^{\text{V}} = \text{O}(\text{OC}(\text{O})\text{CH}_3)^{2+}$ (5a ^{AA})	2.076	2.011	1.964	3a
8	$[(\text{TPA}^*)\text{Fe}^{\text{IV}} = \text{O}(\cdot\text{OC}(\text{O})\text{R})^{2+}$ (5a ^{1EHA}) ^b	2.071	2.004	1.963	3d
9	$[(\text{TPA}^*)\text{Fe}^{\text{V}} = \text{O}(\text{OC}(\text{O})\text{R})^{2+}$ (5a ^{2EHA}) ^a	2.076	2.011	1.964	3d
10	$[(S,S)\text{-PDP}^*]\text{Fe}^{\text{III}}(\kappa^2\text{-OOC}(\text{O})\text{CH}_3)^{2+}$ (3c)	2.52	2.41	1.80	3c
11	$[(S,S)\text{-PDP}^*]\text{Fe}^{\text{III}}(\kappa^2\text{-OOC}(\text{O})\text{C}_6\text{H}_4\text{Cl})^{2+}$ (3c') ^c	2.52	2.41	1.80	3c
12	$[(\text{TPA}^*)\text{Fe}^{\text{III}}(\kappa^2\text{-OOC}(\text{O})\text{CH}_3)^{2+}$ (5c)	2.58	2.38	1.72	4b

^a RCOOH = 2-ethylhexanoic acid.

^b Observed in the system 4/CH₃CO₃H.

^c ClC₆H₄C(O)OOH = *m*-CPBA (3-Cl-peroxybenzoic acid).

cyclohexyl percarboxylic acid (Fig. 1) [4d].

Besides the intermediates of the type **3a**^{AA}–**5a**^{AA} with $g_{\text{max}} \approx 2.07$, $\Delta g \sim 0.1$, the catalytic systems based on complexes **1**, **3**–**5** display EPR spectra of intermediates **1x**, **4x**, **3c**, **5c** ($g_{\text{max}} \approx 2.7$, $\Delta g \sim 1$, Table 1, entries 1, 2, 10, 12). The intermediates **3c**, **5c** are most likely Fe^{III}–OOAc species [3,4][3c,4b]. Previously, we have assigned intermediates **1x** and **4x** to (L)Fe^V = O species [5]. Later, Que et al. have assumed that **1x** and **4x** are Fe^{III}–OOAc intermediates [4]. However, at least in the case of **1x**, the latter assumption can be ruled out, because **1x** is also observed in the catalytic system 1/H₂O₂, containing no additives of acetic acid [5a].

Summarizing the results of the earlier studies, one can conclude that, depending on the nature of the catalyst, oxidant and catalytic additive, various iron-oxygen intermediates can be observed in the catalytic systems based on aminopyridine iron complexes **1**, **3**–**5**: (1) the intermediates with small *g*-factor anisotropy ($g_1 = 2.07$, $g_2 = 2.01$, $g_3 = 1.96$), assigned to the oxoiron species of the type [(L)Fe^V = O

(OC(O)R)]²⁺ [3,4][3a,b,4a], (2) the intermediates **1x** and **4x** with large *g*-factor anisotropy ($g_1 \approx 2.7$, $g_2 \approx 2.4$, $g_3 \approx 1.5$ – 1.7) with so far debatable structure [4,5][4a,5], (3) the ferric acylperoxy intermediates ($g_1 = 2.52$, $g_2 = 2.41$, $g_3 = 1.80$), [(L)Fe^{III}(OOC(O)R²)]²⁺ (R² = CH₃, 3-Cl-C₆H₄) [3,4][3c,4b]. It is very interesting to compare catalytic systems exhibiting various iron-oxygen intermediates in the selective oxidations of alkanes.

In this work, catalytic systems **cat**/H₂O₂/AA, **cat**/H₂O₂/EHA, **cat**/CH₃CO₃H/AA, **cat**/CH₃CO₃H/EHA, **cat**/*m*-CPBA/AA and **cat**/*m*-CPBA/EHA (**cat** = **1**, **3**–**5**, AA = acetic acid, EHA = 2-ethylhexanoic acid) have been examined in the selective oxidation of various alkanes, with the aim to correlate catalytic properties of the systems studied with the nature of the observed intermediates.

2. Experimental

Chemicals and solvents used in this study were purchased and used without purification. Commercially available peracetic acid (Acros Organics) contained 35 wt.% CH₃CO₃H in dilute acetic acid. For the EPR experiments, concentrated H₂O₂ ($\approx 95\%$) was obtained by distillation of commercial 30% H₂O₂ from the phosphate buffer, followed by the concentration of distillate at room temperature under reduced pressure. *Caution: Concentrated hydrogen peroxide is potentially explosive and should be handled with care!* The exact oxidant concentrations in the prepared solutions were determined by iodometric titration under argon. Iron complexes [(S,S)-PDP]Fe^{II}(OTf)₂ (**1**) [6], [(S,S)-PDP*]Fe^{III}(μ-OH)₂Fe^{III}((S,S)-PDP*)](OTf)₄ (**3**) [3a], [(TPA)Fe^{II}(CH₃CN)₂](ClO₄)₂ (**4**) [7], and [(TPA*)Fe^{III}(μ-OH)₂Fe^{III}(TPA*)](OTf)₄ (**5**) [3a] were prepared as described.

For detailed experimental procedures, see Supplementary data.

3. Results and discussion

3.1. Catalytic systems exhibiting iron-oxygen intermediates with small and large *g*-factor anisotropy

3.1.1. Catalytic systems **1,3**/H₂O₂/RCOOH in the chemoselective oxidation of cyclohexane

At -70 ... -80 °C, catalytic systems **1**/H₂O₂/AA and **1**/H₂O₂/EHA

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