Formation of low-spin peroxoiron(III) complexes in Gif-type catalytic systems

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New low-spin peroxoiron(III) complexes active towards cyclohexene and cyclohexane have been observed in the reaction of $[Fe_2O(bpy)_4{\cdot}2H_2O](NO_3)_4$ and $[Fe_2O(Phen)_4{\cdot}2H_2O](NO_3)_4$ with HOOH in a Py/AcOH solvent system.

Detection and reactivity studies of the alkylperoxo $[LFe^{III}(OOR)]$ and peroxo $[LFe^{III}(OOH)]$ iron(III) species are very important for the elucidation of their role in oxygenations catalysed by enzymes and model systems. Such species were observed in reactions of HOOH and ROOH with various iron complexes. These are iron complexes with natural and synthetic porphyrins,[1–5] bleomycin and related models,[6,7] cyclidens[8] and Fe(6TLA), 6TLA = tris[(6-methyl-2-pyridyl)-methyl]amine.[9] Most of the detected intermediates are low-spin ferric complexes. High-spin alkylperoxo iron(III) complexes were also observed.[9,10] Because of the instability of the peroxo and alkylperoxo-iron(III) intermediates, the reactivity data are very restricted. Only for the bleomycin system is it shown that the low-spin peroxoiron(III) complex, so-called 'activated bleomycin', abstracts a hydrogen atom from the substrate molecule (DNA).[11] Recently, low-spin alkylperoxo-iron(III) intermediate was observed during oxidation of alcohols by *tert*-butyl and cumene hydroperoxides catalysed by the dinuclear μ-oxo bridged complex $[Fe(bpy)_2{\cdot}2H_2O]_2O$.[12] Resonance Raman spectra strongly suggest the presence of an iron-bound alkylperoxo moiety in this intermediate with supposed structure $Fe(bpy)_2(OOBu^t)(ROH)$.[12]

We have observed for the first time transient low-spin ferric peroxo complexes in the so-called Gif-type catalytic systems $[Fe_2O(bpy)_4{\cdot}2H_2O](NO_3)_4$ **1a**/HOOH and $[Fe_2O(phen)_4{\cdot}2H_2O](NO_3)_4$ **1b**/HOOH in Py/AcOH mixture as a solvent. Gif catalytic systems allow oxidation of saturated hydrocarbons under mild conditions.[13–15]

The EPR spectra of the catalytic systems **1a** and **1b** show rhombic signals of the low-spin ferric complexes **2a** and **2b**, respectively (Figure 1 and Table 1).[†] The intensities of the EPR signals of complexes **2a** and **2b** achieved as much as 0.1 spin per iron atom.[‡]

Note that complexes **2a**, **2b** were not observed in pyridine or acetic acid alone, but only in the pyridine/acetic acid solvent system. The *g*-values of complexes **2a** (2.14, 2.11, 1.97) and **2b** (2.13, 2.12, 1.97) resemble those for the alkylperoxo complex $Fe(bpy)_2(OOBu^t)(ROH)$[12] (Table 1). The typical *g*-values for stable low-spin ferric complexes with *O*,*N*-donor ligands are in the range $g_1 = 2.4–2.6$, $g_2 = 2.14–2.2$, $g_3 = 1.85–1.95$.[18,19] The observed extremely small *g*-anisotropy is a highly characteristic property of peroxoiron(III) complexes of the end-on, or monodentate, kind.[8] Most likely, complexes **2a**, **2b** are peroxo complexes $Fe(bpy)_2(OOH)Py$ **2a** and $Fe(phen)_2(OOH)Py$ **2b**. We have studied the reactivity of complexes **2a** and **2b** towards cyclohexane and cyclohexene at 273 K. In the absence of substrate, the concentrations of complexes **2a** and **2b** in the catalytic systems investigated[†] reach a maximum during 10 min at 273 K and then decrease with characteristic time $\tau_{1/2}$ = 25 min. Addition of cyclohexane gives rise to an immediate drop of the concentrations of complexes **2a** and **2b**. This drop was proportional to the concentration of C_6H_{12} (two-fold drop was observed at $[C_6H_{12}]$ = 1 M). Concentration of complexes **2a** and **2b** then diminished with characteristic time $\tau_{1/2}$ = 15 min. A similar picture was observed for cyclohexene as substrate. Most probably, the observed immediate decrease of the concentrations of complexes **2a** and **2b** is caused by their reaction with substrate. The concentrations of complexes **2a** and **2b** are determined by the competition between their rate of formation and decay. The reaction with substrate opens up a new channel for the decay of the complexes **2a** and **2b** and thus decreases their concentrations. The characteristic time of this reaction is less than 30 s at 273 K.[§] Thus, complexes **2a** and **2b** are active towards cyclohexene and cyclohexane and can be reactive intermediates of oxidation. The catalytic systems investigated oxidize cyclohexane into cyclohexanone and cyclohexanol in a 2:1 ratio, and cyclohexene into the products of allylic oxidation (mainly cyclohexenone).[¶]

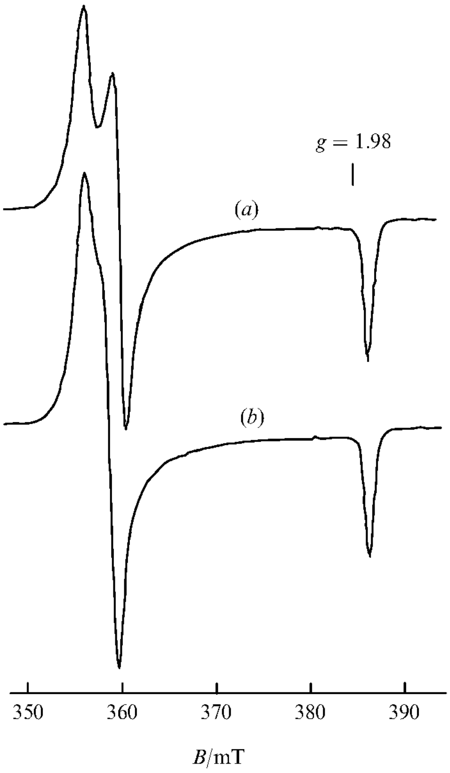

Figure 1 X-band EPR spectra of complexes **2a** (*a*) and **2b** (*b*) at 77 K in 3:1 pyridine/AcOH volume mixture. Spectrometer settings: microwave power 20 mW, modulation frequency 100 kHz, modulation amplitude 5 G.

[†] *General experimental details.* Complexes **1a** and **1b** were prepared as described in refs. 16 and 17, respectively. To start the reaction, 0.02 ml of 90% HOOH was added to 0.1 ml of 0.02 M solution of complexes **1a** or **1b** in a 3:1 Py/AcOH volume mixture, directly in the EPR tubes at 273 K. Within minutes after the onset of the reaction, the samples were frozen in liquid nitrogen and their EPR spectra were recorded at 77 K using a Bruker-ER-200D spectrometer.

[‡] The EPR signal was quantified by double integration with copper chloride as a standard at 77 K.

[§] 30 s is the time of mixing the reaction solution just after the addition of the substrate.

[¶] GS-MS (LKB-209) spectrometer.

Table 1 EPR spectral data for low-spin ferric peroxo and alkylperoxo complexes.

Complex	Solvent	g_1	g_2	g_3	Ref.
Fe(TPP)(OH)OOH	DMF/H_2O	2.27	2.16	1.96	3
Fe(BLM)OOH	H_2O	2.25	2.17	1.94	6
Fe(bpy)$_2$(OOBu^t)(ROH)	MeCN/ROH	2.18	2.12	1.98	12
Fe(bpy)$_2$(OOH)Py **2a**	Py/AcOH	2.14	2.11	1.97	this work
Fe(phen)$_2$(OOH)Py **2b**	Py/AcOH	2.13	2.12	1.97	this work
Fe(bpy)$_2$(OOBu^t)Py **3a**	Py/AcOH	2.19	2.12	1.97	this work
Fe(phen)$_2$(OOBu^t)Py **3b**	Py/AcOH	2.165	2.12	1.96	this work
Fe(phen)$_2$(OOBu^t)MeOH	MeCN/MeOH	2.16	2.10	1.97	this work

We have attempted to obtain alkylperoxo complexes in the Py/AcOH solvent system using Bu^{t}OOH instead of HOOH as an oxidant. At high concentrations of Bu^{t}OOH (up to 3 M) we observed an intense signal of Bu^{t}OO$^\cdot$ radicals ($g_{||} = 2.03$, $g_\perp = 2.008$) and weak rhombic signals of complexes **3a** and **3b** for catalytic systems starting with **1a** and **1b**, respectively. The g-values of complexes **3a** and **3b** are very close to those of Fe(bpy)$_2$(OOBu^t)(ROH) (see Table 1).

Most probably, complexes **3a**, **3b** are alkylperoxo species Fe(bpy)$_2$(OOBu^t)Py **3a** and Fe(phen)$_2$(OOBu^t)Py **3b**. We have also observed an intense rhombic EPR signal during interaction of [Fe$_2$O(phen)$_4$·2H$_2$O](NO$_3$)$_4$ with Bu^{t}OOH in a 1:1 MeCN/MeOH solvent system (Table 1). This signal can be attributed to the alkylperoxo complex Fe(phen)$_2$(OOBu^t)MeOH.

Thus, low-spin ferric peroxo and alkylperoxo species usually observed for iron complexes with macrocyclic ligands can be readily detected in the appropriate solvent systems for iron complexes with simple bidentate ligands. The role of these species in non-Fenton catalytic oxidations should be elucidated.

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