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EPR and ^1H NMR spectroscopic characterization of the ferric species formed in the iron picolinate/(pyridine/acetic acid)/HOOH catalytic system for the direct ketonization of methylenic carbons

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Abstract

Using EPR and ^1H NMR spectroscopy, ferric species formed in the iron picolinate/(pyridine/acetic acid)/HOOH catalytic system for the direct ketonization of methylenic carbons were characterized. The initial complex $\text{K}[\text{Fe}^{\text{II}}(\text{PA})_3]$ (PA-pyridine-2-carboxylato) converts into mononuclear hydroxo complex $\text{Fe}^{\text{III}}(\text{PA})_2(\text{OH})\text{Py}$ via interaction with equimolar amount of HOOH in 2:1 Py/AcOH molar mixture. Addition of the great excess of HOOH to the solution of $\text{Fe}^{\text{III}}(\text{PA})_2(\text{OH})\text{Py}$ in 2:1 Py/AcOH at 253 K gives rise to the formation of the unstable high-spin ferric peroxo complex with suggested structure $\text{Fe}^{\text{III}}(\text{PA})_2(\text{OOH})\text{Py}$. This complex is supposed to be reactive intermediate of oxidation.

Keywords: Ferric peroxo complexes; EPR; NMR; Oxidation; Cyclohexane

1. Introduction

Recently a family of new chemical systems which allow the oxidation of saturated hydrocarbons under mild conditions was reported, the so-called Gif systems (see [1–5] and references therein). All of them involve a pyridine–acetic (or other carboxylic acid) solution of the hydrocarbon being oxidized, a Fe-based catalyst and an oxidant.

In spite of extensive work on these systems, many of the mechanistic details remain unclear. Several proposed intermediates have not been observed directly and their structures are quite speculative. One of the most effective systems for the selective ketonization of cyclohexane to cyclohexanone (cyclohexane is transformed with 72% efficiency to give *c*- $\text{C}_6\text{H}_{10}(\text{O})$ 95% and *c*- $\text{C}_6\text{H}_{11}\text{OH}$ (5%)) is $\text{Fe}(\text{PA})_2/\text{HOOH}$ (PA – anion of picolinic acid) in the pyridine/HOAc (molar ratio 2:1) solvent mixture [4].

This background prompted us to undertake a study to characterize reactive intermediates in the $\text{K}[\text{Fe}^{\text{II}}(\text{PA})_3]/\text{HOOH}/\text{Py}/\text{AcOH}$ catalytic system, using EPR and ^1H NMR spectroscopy.

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2. Experimental

Cyclohexane and cyclohexene were purified according to the standard methods. Deuterated pyridine, methanol and acetic acid were commercially available products used as received without additional purification. Hydrogen peroxide 90–95% was titrated with KMnO_4 just before experiments.

The initial complex $\text{K}[\text{Fe}^{\text{II}}(\text{PA})_3]$ was prepared by following procedure performed under argon: 2 mmol of $\text{FeCl}_2 \cdot 4\text{H}_2\text{O}$ was obtained from 2 mmol of iron metal (0.112 g) by dissolving in 35% HCl under argon followed by vacuum evaporation to dryness. The residue was dissolved in ethanol and potassium picolinate (0.967 g, 6 mmol) was added. Potassium chloride was filtered off and the solution was evaporated under vacuum. Recrystallization from ethanol gives $\text{K}[\text{Fe}^{\text{II}}(\text{PA})_3]$ as dark-red microcrystalline powder.

Anal. Calcd for $\text{C}_{18}\text{H}_{12}\text{O}_6\text{N}_2\text{KFe}$: C 46.85, H 2.60, N 9.11. Found C 45.9, H, 3.09, N 9.32.

The reaction with HOOH was carried out by the addition of HOOH to the solutions of $\text{K}[\text{Fe}^{\text{II}}(\text{PA})_3]$ under air, directly in NMR or EPR tubes at appropriate temperatures. The samples for EPR measurements were rapidly frozen in liquid nitrogen at various moments of time after the addition of HOOH.

The ^1H NMR spectra were recorded at 400.13 MHz using pulsed FT-NMR technique, on a Bruker MSL-400 NMR spectrometer. Deuterated solvents were used to prepare the samples for the ^1H NMR studies. The following operating conditions were used for ^1H NMR measurements: sweep width 125 000 Hz; spectrum accumulation frequency 5 Hz; number of scans 1000–3000. The data were accumulated with 16 K data points in the time domain and transformed with optimal exponential multiplication 1–20 Hz. Chemical shifts were calculated in ppm with positive values in the low field direction with respect to internal reference TMS. The error in chemical shift values was ± 0.1 ppm for line widths below 200 Hz and ± 2 ppm for

the line width around 4 kHz. The error associated with the line-widths values, $\Delta\nu_{1/2}$, was ± 20 Hz for $\Delta\nu_{1/2}$ between 100 and 500 Hz.

EPR spectra (77 K) were recorded at 9.2–9.3 GHz on a Bruker ER-200D spectrometer using quartz 5 mm tubes. Magnetic resonance parameters of EPR spectra were found by automatic iterative search using extended version of EPR spectra simulation program EPR1 described earlier [6]. An individual line was assumed to have a Lorentzian $f(x) = \sigma / [\pi(x^2 + \sigma^2)]$ or Gaussian $f(x) = [1 / (\sigma\sqrt{2\pi})] \exp[-x^2 / 2\sigma^2]$ line shape with the orientation dependent line width parameter σ .

The concentration of paramagnetic centers was measured by EPR by comparing at 77 K second integrals of EPR spectra of the sample of interest and of the reference, acidic solution of $[\text{Fe}(\text{EDTA})\text{H}_2\text{O}]^-$ prepared from appropriate amount of $(\text{NH}_4)\text{Fe}(\text{SO}_4)_2 \cdot 12\text{H}_2\text{O}$ with the excess of $\text{Na}_2\text{H}_2\text{EDTA}$. Measurements were made in quartz dewar with liquid nitrogen. The dual EPR cavity furnished with the spectrometer was used. Periclase crystal (MgO) with impurities of Mn^{2+} and Cr^{3+} which served as a side reference, was placed into the center of the second compartment of the dual cavity. The accuracy of the measurements of the concentrations of ferric mononuclear species was about 30%.

3. Results and discussion

3.1. Characterization of the initial complex $\text{K}[\text{Fe}^{\text{II}}(\text{PA})_3]$ in various solvent systems

The initial complex $\text{K}[\text{Fe}^{\text{II}}(\text{PA})_3]$ prepared as described in Section 2 is high-spin ferrous complex. It is EPR silent and exhibits in the ^1H NMR spectrum (CD_3OD) four paramagnetically shifted resonances with equal integral intensities (at 113 (α), 63.5 (β), 47.1 (β), 24.6 (γ) ppm) from the hydrogen atoms of picolinic ligands (Fig. 1a). The notations α , β , γ refer to proton positions in pyridine ring of picolinic ligands.

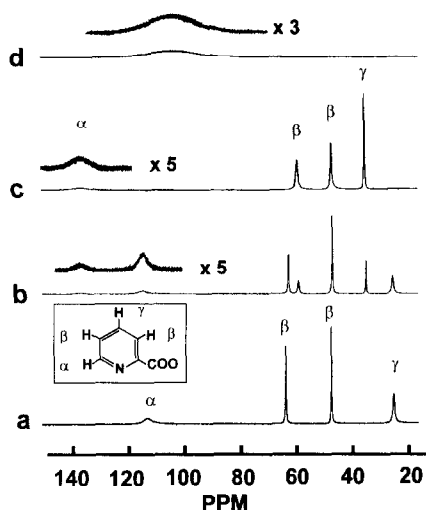


Fig. 1. ^1H NMR spectrum of 0.05 M $\text{K}[\text{Fe}^{\text{II}}(\text{PA})_3]$ (293 K): (a) in CD_3OD ; (b) in 1:1 $\text{CD}_3\text{OD}/\text{C}_5\text{D}_5\text{N}$; (c) in $\text{C}_5\text{D}_5\text{N}$; (d) in 2:1 $\text{C}_5\text{D}_5\text{N}/\text{CD}_3\text{COOD}$ 1 min after addition of 95% HOOH (0.05 M).

No signals of non-coordinated picolinic acid were observed in the ^1H NMR spectrum of $\text{K}[\text{Fe}^{\text{II}}(\text{PA})_3]$ in CD_3OD . Picolinic acid would exhibit resonances near 8 ppm, that was verified by the addition of NaPA into the sample. Picolinic acid is in slow exchange with picolinic ligands of $\text{K}[\text{Fe}^{\text{II}}(\text{PA})_3]$ in the ^1H NMR time scale. Thus, picolinic ligands of $\text{K}[\text{Fe}^{\text{II}}(\text{PA})_3]$ remain intact in CD_3OD . With the increase of the concentration of $\text{C}_5\text{D}_5\text{N}$ in CD_3OD , the intensities of four signals of $\text{K}[\text{Fe}^{\text{II}}(\text{PA})_3]$ diminish, and those of the other four ones grow (at 134 (α), 58.9 (β), 46.9 (β), 34.7 (γ) ppm, Fig. 1b, c). This effect can be explained by the conversion of $\text{K}[\text{Fe}^{\text{II}}(\text{PA})_3]$ into $\text{Fe}^{\text{II}}(\text{PA})_2\text{Py}_2$ (**1**), when CD_3OD is replaced by $\text{C}_5\text{D}_5\text{N}$ as a solvent. We have not detected ^1H NMR signals of the pyridine ligands of complex **1** in non-deuterated pyridine as a solvent, because of their fast exchange between complex and solution. The low field shift (up to several ppm) of the pyridine signals evidences in favor of such exchange. This shift gradually increases with the increase of $\text{K}[\text{Fe}^{\text{II}}(\text{PA})_3]$ concentration in 0.1 M solution of Py in CD_3OD .

Thus, the initial complex exists in CD_3OD in

the form of $\text{K}[\text{Fe}^{\text{II}}(\text{PA})_3]$ and in $\text{C}_5\text{D}_5\text{N}$ in the form of $\text{Fe}^{\text{II}}(\text{PA})_2\text{Py}_2$ (**1**).

We have also studied the variations of the ^1H NMR spectrum of complex **1** with the increase of the concentration of CD_3COOD in $\text{C}_5\text{D}_5\text{N}$. It was found that up to $[\text{CD}_3\text{COOD}]/[\text{C}_5\text{D}_5\text{N}] = 1$, the ^1H NMR spectrum of complex **1** does not change. When $[\text{CD}_3\text{COOD}]/[\text{C}_5\text{D}_5\text{N}]$ exceeded 1, the growth of the CD_3COOD concentration was accompanied by the decrease of the resonances of complex **1** and the increase of those of $\text{K}[\text{Fe}^{\text{II}}(\text{PA})_3]$. Probably, the protonation of Py makes it less competitive in coordination ability with respect to picolinic acid.

According to Ref. [5], the catalytic system $\text{Fe}(\text{PA})_2/\text{HOOH}$ is the most effective in 2:1 Py/AcOH solvent system. In this solvent system, the initial complex $\text{K}[\text{Fe}^{\text{II}}(\text{PA})_3]$ is presented in the form of $\text{Fe}^{\text{II}}(\text{PA})_2\text{Py}_2$.

3.2. Formation of ferric hydroxo complex $\text{Fe}^{\text{III}}(\text{PA})_2(\text{OH}) \cdot \text{Py}$ (**2**)

Immediately after the addition of equimolar amount of 95% HOOH to the 0.05 M solution of complex **1** in 2:1 $\text{C}_5\text{D}_5\text{N}/\text{CD}_3\text{COOD}$, the ^1H NMR resonances of complex **1** disappeared and a new very broad signal at ca. 110 ppm (8 kHz) was observed (Fig. 1d). In the course of this reaction, the red-brown solution of the initial complex became pale brown. EPR spectrum (77 K) of the same sample exhibits the intense anisotropic signal near $g = 4$ and weak transition at $g = 9$, typical for simple mononuclear ferric chelate high-spin complexes (Fig. 2) [7]. The signal near $g = 4$ can be well described by the theoretical spectrum with rhombic anisotropy ($g_1 = 4.43$; $g_2 = 4.23$; $g_3 = 3.83$; $\sigma_1 = 43$ G; $\sigma_2 = 35$ G; $\sigma_3 = 145$ G) and Lorentzian shape of the individual line. The quantitative EPR measurements show that all the initial ferrous complex **1** converts into stable mononuclear ferric complex **2** upon interaction with equimolar amount of HOOH .

We have independently prepared the binuclear μ -hydroxo complex $[\text{Fe}(\text{PA})_2\text{OH}]_2$, as de-

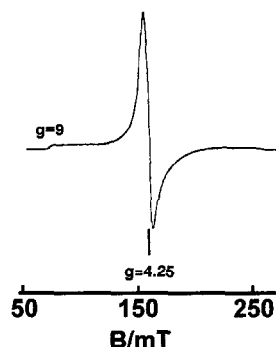


Fig. 2. EPR spectrum (77 K) of 0.05 M $K[Fe^{II}(PA)_3]$ in 2:1 C_5D_5N/CD_3COOD 1 min after addition of 95% $HOOH$ (0.05 M).

scribed in Ref. [8]. This binuclear complex dissociated into mononuclear species upon dissolving in various solvents, as was evidenced by EPR. The EPR spectrum of these species in 2:1 $Py/AcOH$ was very similar to that of complex 2. It is natural to suppose that complex 2 is a hydroxo ferric complex of the type $Fe^{III}(PA)_2(OH) \cdot Py$.

1H NMR spectrum of mononuclear ferric complex formed by dissociation of $[Fe(PA)_2OH]_2$ in 1:1 $CDCl_3/CD_3OD$ exhibits the resonances at 208 ppm (30 kHz) (α), 126 ppm (4.5 kHz) (β), 114 ppm (4.4 kHz) (β) and -1.4 ppm (1.0 kHz) (γ). Based on these data, the observed broad resonance in the 1H NMR spectrum of complex 2 (Fig. 1d) can be attributed to β -protons of picolinic ligands. The resonance of α -proton is too broad to be observed at the accessible concentration of the sample and that of γ -proton is masked by the intensive broad resonance of H_2O . The chemical shift ($\delta \sim 110$ ppm) of β -protons of complex 2 is characteristic for mononuclear high-spin ferric complexes [9,10].

Thus, immediately after the addition of an equimolar amount of $HOOH$, the initial complex $Fe^{II}(PA)_2Py_2$ (1) converts into the stable mononuclear ferric complex $Fe^{III}(PA)_2(OH)Py$ (2) in the $Py/AcOH$ solvent system. This conclusion differs from that in Ref. [4], where the formation of binuclear μ -oxo bridged ferric complex $(PA)_2Fe^{III}OFe^{III}(PA)_2$ is supposed.

3.3. Formation of high-spin ferric peroxo complex $Fe(PA)_2(OOH) \cdot Py$ (3)

Recently we have found low-spin ferric peroxo complexes $[Fe(bpy)_2(OOH)Py]^{2+}$ and $[Fe(phen)_2(OOH)Py]^{2+}$ in $Py/AcOH$ solvent system [11]. It was tempting to detect peroxo complexes in the $Fe^{II}(PA)_2Py_2/HOOH$ catalytic system. However, only formation of the high-spin ferric peroxo species is to be expected for picolinic system. In contrast to the low-spin ferric peroxo complexes, EPR spectra of the high-spin peroxo species are not so characteristic [12,13]. Nevertheless, EPR data evidence in favor of the formation of the ferric peroxo complex in the reaction of $Fe^{II}(PA)_2Py_2$ (1) with the great excess of $HOOH$. EPR spectra (77 K) of the samples frozen in 30 s after the addition of various portions of $HOOH$ to the 0.003 M solution of $K[Fe^{II}(PA)_3]$ in 2:1 $Py/AcOH$ at 253 K are shown in Fig. 3. It is seen that the EPR signal of complex 2 decreases, and that of another complex 3 ($g_1 = 4.31$; $g_2 = 4.27$; $g_3 = 3.81$; $\sigma_1 = 51$ G; $\sigma_2 = 32$ G; $\sigma_3 = 200$ G) grows with the increase of the $HOOH$ concentration. The solution of complex 3 is colorless. Note, that the addition of great amounts of H_2O instead of $HOOH$ does not essentially change the EPR spectrum of complex 2. Probably, with the increase of $HOOH$

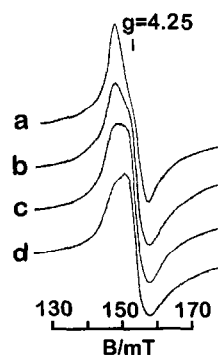


Fig. 3. EPR spectra (77 K) of 0.003 M $K[Fe^{II}(PA)_3]$ in 2:1 C_5H_5N/CH_3COOH 30 s after addition of $HOOH$ of various concentrations at 253 K: (a) 0.03 M; (b) 1 M; (c) 4 M; (d) 7 M.

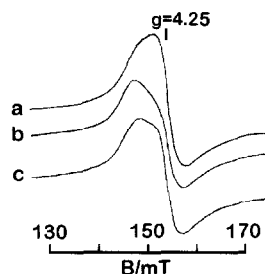


Fig. 4. EPR spectra (77 K) of 0.003 M $K[Fe^{II}(PA)_3]$ in 2:1 C_5H_5N/CH_3COOH after various treatments: (a) the sample frozen in 30 sec after addition of $HOOH$ (7 M) at 263 K; (b) the frozen sample (a) warmed during 2 min up to 273 K and frozen again in liquid nitrogen; (c) the sample (b) stored 24 h at 293 K.

concentration, hydroxo complex **2** ($Fe(PA)_2(OH)Py$) converts into peroxy complex **3** of the type $Fe(PA)_2(OOH)Py$. In agreement with the peroxidic structure, complex **3** is unstable. Its EPR spectrum rapidly changes with a characteristic time of 1–2 min at 273 K (Fig. 4a, b). The observed fast transformation of the EPR spectrum of complex **3** is probably a result of two processes: first, the decomposition of the peroxy moiety, and second, the replacement of picolinic ligands by more strong coordinating ligands, products of pyridine oxidation. The latter effect will be discussed below. The EPR spectrum obtained by keeping the sample in Fig. 4b during a day at 293, is shown in Fig. 4c.

Recently, two types of ferric peroxy complexes were detected in the reaction of $[Fe^{III}(EDTA)]^-$ with $HOOH$ [14]. Addition of $HOOH$ to a nearly neutral solution (pH 7.6) of $[Fe^{III}(EDTA)]^-$ resulted in the appearance of a new signal ($g_1 = 4.39$; $g_2 = 4.15$; $g_3 = 3.90$). The addition of $HOOH$ to an alkaline solution (pH 11.2) led to a different species $g_1 = 5.08$; $g_2 = 3.81$; $g_3 = 3.37$. The nearly neutral solution was colorless, whereas the alkaline solution was purple [14]. The authors suppose the end-on coordination of peroxy moiety ($FeOOH$) for colorless peroxy complex and side-on ($(Fe \begin{smallmatrix} \diagup \\ \diagdown \end{smallmatrix} O_2)$) for purple one. The g -factors of complex **3** are more close to those of the end-on

$[Fe(EDTA)OOH]^{2-}$ peroxy complex. Thus, we suppose that the colorless complex **3** is the peroxy complex of the type $Fe(PA)_2(OOH)Py$. The peroxy complex **3** may be the reactive intermediate of cyclohexane oxidation. Recently we have found that peroxy complexes $[Fe(bpy)_2(OOH)Py]^{2+}$ and $[Fe(phen)_2(OOH)Py]^{2+}$ are active towards cyclohexane [11].

3.4. EPR monitoring of the ferric species in the course of the reaction of complex **1** with $HOOH$ in $Py/AcOH$

Complex **2**, formed in the reaction of complex **1** with an equimolar amount of $HOOH$ in $Py/AcOH$, is stable. Its EPR spectrum does not change during a day at 293 K. When the ratio $[HOOH]/[complex\ 1]$, further denoted by α , is greater than unit, the EPR spectrum of complex **2** changes with time (Fig. 5). Heating of the sample ($\alpha = 20$, Fig. 5c) during 2 min at 353 K gives rise to the reduction of ca. 90% of ferric complex into the initial ferrous complex **1** with the characteristic 1H NMR spectrum. A similar reduction was observed for the samples with $\alpha = 3–30$. When α exceeds 300, the initially formed complexes **2** and **3** convert with time into complex or complexes, further denoted by number **4**, which cannot be converted back into complex **1** (Fig. 4c). The EPR spectrum of **4** differs from those of complexes **2** and **3**. Forma-

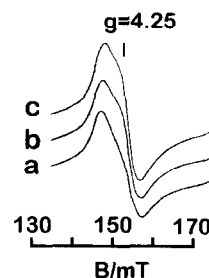


Fig. 5. EPR spectra (77 K) of 0.003 M $K[Fe^{II}(PA)_3]$ in 2:1 C_5H_5N/CH_3COOH at various lengths of time after addition of $HOOH$ (0.06 M): (a) 2 min; (b) 10 min; (c) 30 min.

tion of **4** may be the reason of fast catalyst deactivation. According to Ref. [5], catalyst turnover numbers for oxidation of cyclohexane with catalytic system $\text{Fe}(\text{PA})_2/\text{HOOH}$ was 6. We have supposed that **4** are ferric complexes with strong coordinating molecules, products of pyridine oxidation. The addition of 2,3- and 4-hydroxy pyridines and 2,2'-bipyridine (Aldrich) to the solution of complex **2** does not give an EPR spectrum similar to that of complexes **4**. Probably, complexes **4** are ferric complexes with hydroxy-substituted bipyridines. Further studies are necessary to support this assumption.

3.5. The effect of cyclohexane and cyclohexene on the kinetics of complex **2** transformation

We suppose that the observed changes of the EPR spectrum of complex **2** with time, $\alpha = 20$ (Fig. 5) occur because of the formation of the new ferric complexes containing products of pyridine oxidation as ligands. It was found that the rate of these changes dramatically decreases (at least by a factor of five) when C_6H_{12} or C_6H_{10} ($[\text{C}_6\text{H}_{12}] = [\text{C}_6\text{H}_{10}] = 0.5 \text{ M}$) were preliminary added to the initial solution. Probably, fast reaction of C_6H_{12} and C_6H_{10} with oxidizing intermediates prevents the oxidation of pyridine and thus the formation of the new ferric complexes.

Acknowledgements

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