

# The Nature of Active Species in Catalytic Systems Based on Non-Heme Iron Complexes, Hydrogen Peroxide, and Acetic Acid for Selective Olefin Epoxidation

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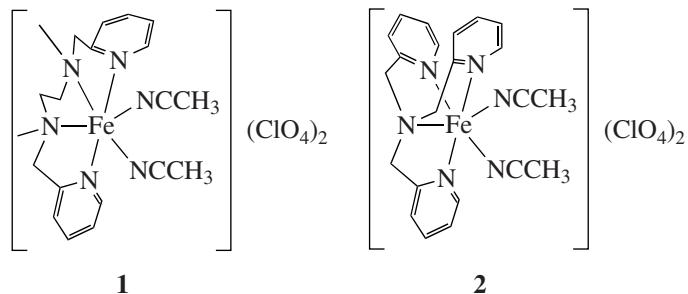
Received October 4, 2006

**Abstract**—The catalytic systems  $[(\text{BPMEN})\text{Fe}^{\text{II}}(\text{CH}_3\text{CN})_2](\text{ClO}_4)_2/\text{H}_2\text{O}_2/\text{CH}_3\text{OOH}$  and  $[(\text{TPA})\text{Fe}^{\text{II}}(\text{CH}_3\text{CN})_2](\text{ClO}_4)_2/\text{H}_2\text{O}_2/\text{CH}_3\text{OOH}$ , where  $\text{BPMEN} = N,N'$ -dimethyl- $N,N'$ -bis(2-pyridylmethyl)-1,2-diaminoethane and  $\text{TPA} = \text{tris}(2\text{-pyridylmethyl})\text{amine}$ , provide selective olefin epoxidation. Proton NMR studies showed that the mononuclear iron(IV) oxo complexes  $[(\text{L})\text{Fe}^{\text{IV}}=\text{O}]^{2+}$ , with  $\text{L} = \text{BPMEN}$  or  $\text{TPA}$ , are present in the cited catalytic systems. These intermediates are the decomposition products of the acylperoxo complexes  $[(\text{L})\text{Fe}^{\text{III}}-\text{O}_3\text{CCH}_3]^{2+}$ . Such a complex was observed by the  $^2\text{H}$  NMR technique at low temperatures. The  $[(\text{L})\text{Fe}^{\text{IV}}=\text{O}]^{2+}$  and  $[(\text{L})\text{Fe}^{\text{V}}=\text{O}]^{3+}$  oxo complexes are possible active species in the studied catalytic systems.

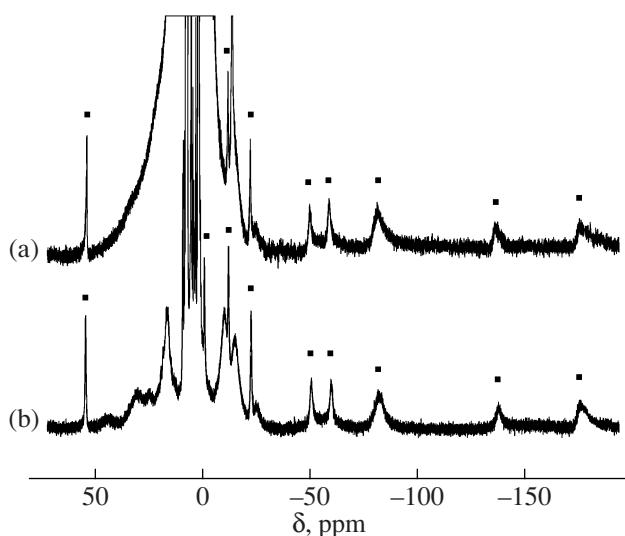
**DOI:** 10.1134/S0023158408030099

Non-heme iron-containing enzymes provide selective oxidation of organic substrates by molecular oxygen and hydrogen peroxide under mild conditions [1–5]. The development of catalytic systems based on non-heme iron complexes and hydrogen peroxide capable of initiating such transformations is an intriguing and promising problem. Among the few systems of this type that were revealed to date, there are dinuclear iron complexes based on bipyridine and phenanthroline and the mononuclear iron complexes with such ligands as  $\text{tris}(2\text{-pyridylmethyl})\text{amine}$  (TPA) and  $N,N'$ -dimethyl- $N,N'$ -bis(2-pyridylmethyl)-1,2-diaminoethane (BPMEN) [6–12] (scheme). The additions of acetic acid markedly enhance the activity and selectivity of the catalytic systems  $[\text{Fe}^{\text{II}}(\text{BPMEN})(\text{CH}_3\text{CN})_2](\text{ClO}_4)_2$  (1)/ $\text{H}_2\text{O}_2$  and  $[\text{Fe}^{\text{II}}(\text{TPA})(\text{CH}_3\text{CN})_2](\text{ClO}_4)_2$  (2)/ $\text{H}_2\text{O}_2$  [9, 11]. Today,

the 1/ $\text{H}_2\text{O}_2/\text{CH}_3\text{COOH}$  system is the only efficient catalytic system that is based on an iron complex and hydrogen peroxide and is suitable for preparatory olefin epoxidation [9]. It is important to find out which active species provide selective olefin oxidation in the catalytic systems 1/ $\text{H}_2\text{O}_2$ , 2/ $\text{H}_2\text{O}_2$ , 1/ $\text{H}_2\text{O}_2/\text{CH}_3\text{COOH}$ , and 2/ $\text{H}_2\text{O}_2/\text{CH}_3\text{COOH}$ . In this work, the summary of the results of our EPR and ( $^1\text{H}$ ,  $^2\text{H}$ ) NMR studies of the unstable iron-oxygen species formed in the cited systems is presented. In the catalytic systems 1/ $\text{H}_2\text{O}_2/\text{CH}_3\text{COOH}$  and 2/ $\text{H}_2\text{O}_2/\text{CH}_3\text{COOH}$ , the mononuclear oxo complexes  $[(\text{L})\text{Fe}^{\text{IV}}=\text{O}]^{2+}$ , with  $\text{L} = \text{BPMEN}$  or  $\text{TPA}$ , and the species that can be either dinuclear complexes of the type  $[(\text{L})\text{Fe}^{\text{III}}-\text{O}-\text{Fe}^{\text{IV}}=\text{O}(\text{L})]^{3+}$  or mononuclear  $[(\text{L})\text{Fe}^{\text{V}}=\text{O}]^{3+}$  complexes are observed.



**Scheme.**



**Fig. 1.** (a)  $^1\text{H}$  NMR spectra of the 1 : 2 **1**/ $\text{CH}_3\text{CO}_3\text{H}$  and (b) 1 : 1 **1**/PhIO systems recorded at  $-50^\circ\text{C}$  10 min after mixing the reactants at  $-50^\circ\text{C}$  in a 1 : 1  $\text{CD}_2\text{Cl}_2/\text{CD}_3\text{CN}$  mixture ( $[\mathbf{1}] = 0.05 \text{ mol/l}$ ). Dots indicate the  $^1\text{H}$  NMR signals of complex **3**.

## EXPERIMENTAL

Acetonitrile, acetonitrile- $d_3$ , dichloromethane, dichloromethane- $d_2$ , acetic acid- $d_4$ , 2-picolyl chloride hydrochloride, *N,N'*-dimethyl-1,2-diaminoethane, and cyclohexene (all reagents from Aldrich) were used as received. A 95% hydrogen peroxide was obtained by concentrating a 30% aqueous solution of  $\text{H}_2\text{O}_2$  in *vacuo* at room temperature. Catalytic systems were prepared using 95% hydrogen peroxide diluted tenfold in a 1 : 1 mixture of dichloromethane and acetonitrile. Acetyl hydroperoxide  $\text{CH}_3\text{CO}_3\text{OH}$  ( $\text{CD}_3\text{CO}_3\text{H}$ ) was prepared by mixing equivalent amounts of 95%  $\text{H}_2\text{O}_2$  and  $\text{CH}_3\text{COOH}$  ( $\text{CD}_3\text{COOD}$ ) at room temperature in the presence of  $\text{H}_2\text{SO}_4$  (1 mol %), and the mixture was allowed to stand overnight prior to use. The  $[(\text{TPA})\text{Fe}^{\text{II}}(\text{CH}_3\text{CN})_2](\text{ClO}_4)_2$  and  $[(\text{BPMEN})\text{Fe}^{\text{II}}(\text{CH}_3\text{CN})_2](\text{ClO}_4)_2$  complexes were prepared as described, respectively, in [10] and [13].

To detect the unstable intermediates, to a solution of 0.5 ml of 0.05 M **1** or **2** in a  $\text{CH}_2\text{Cl}_2/\text{CH}_3\text{CN}$  or  $\text{CH}_2\text{Cl}_2/\text{CH}_3\text{CN}/\text{CH}_3\text{COOH}$  mixture placed in a quartz cell (EPR) or glass tube (NMR) with a diameter of 5 mm was added 1.5–2.0 equiv of  $\text{CH}_3\text{CO}_3\text{H}$  or  $\text{H}_2\text{O}_2$  at  $-60$  to  $-50^\circ\text{C}$ . For the kinetic EPR studies, the cells containing unstable intermediates were thermostatted at the corresponding temperature. To stop the reaction, the cell was cooled in liquid nitrogen, whereupon the EPR spectrum of the frozen solution was recorded at  $-196^\circ\text{C}$ . When conducting kinetic ( $^1\text{H}$ ,  $^2\text{H}$ ) NMR measurements, the spectra of intermediates were recorded sequentially at the corresponding temperature. If necessary, a substrate (cyclohexene) was added to the reaction solution.

The EPR spectra were recorded at  $-196^\circ\text{C}$  at a frequency of 9.2–9.3 GHz on a Bruker ER-200 D spectrometer. Measurements were carried out in a quartz Dewar vessel with liquid nitrogen. To determine the concentration of paramagnetic particles ( $S = 1/2$ ), the second integral of the corresponding EPR signal was compared with the reference signal (from a  $\text{CuCl}_2 \cdot 2\text{H}_2\text{O}$  single crystal) at  $-196^\circ\text{C}$ .

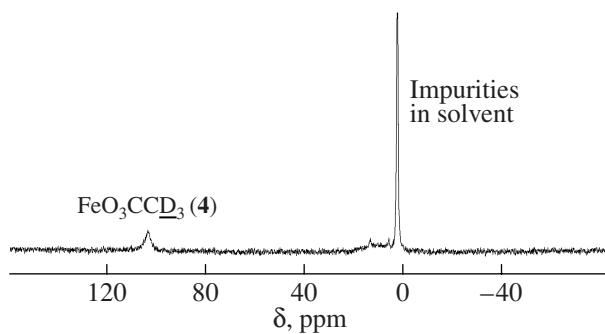
The ( $^1\text{H}$ ,  $^2\text{H}$ ) NMR spectra were recorded on a Bruker Avance 400 spectrometer at 400.13 and 61.425 MHz. The  $^1\text{H}$  parameters were the following: spectral width 125 kHz, accumulation frequency 10 Hz, number of accumulations 5000–10000, and 5- $\mu\text{s}$ -long  $20^\circ$ – $40^\circ$  pulse. The  $^2\text{H}$  NMR parameters: spectral width 125 kHz, accumulation frequency 2.5 Hz, number of accumulations 5000–10000, and 10- $\mu\text{s}$   $45^\circ$  pulse. The  $^1\text{H}$  and  $^2\text{H}$  chemical shifts ( $\delta$ ) were referenced to the residual NMR peaks of a deuterated or protonated solvent ( $\text{CHD}_2\text{CN}$  or  $\text{CDH}_2\text{CN}$ ,  $\delta = 1.96 \text{ ppm}$ ).

The  $^1\text{H}$  NMR spectrum of compound **3** ( $[(\text{BPMEN})\text{Fe}^{\text{IV}}=\text{O}(\text{Sol})]^{2+}$ ) (1 : 1  $\text{CD}_2\text{Cl}_2/\text{CD}_3\text{CN}$ ,  $-50^\circ\text{C}$ ) is characterized by the following values of  $\delta$  (ppm):  $-175.4$  (2H,  $\Delta\vartheta_{1/2} = 1.5 \text{ kHz}$ ,  $\text{CHH-CHH}$ ),  $-136.3$  (2H,  $\Delta\vartheta_{1/2} = 1.1 \text{ kHz}$ ,  $\text{CHH-N}$ ),  $-81.3$  (6H,  $\Delta\vartheta_{1/2} = 2.1 \text{ kHz}$ ,  $\text{CH}_3$ ),  $-58.9$  (2H,  $\Delta\vartheta_{1/2} = 740 \text{ Hz}$ ,  $\text{CHH-CHH}$ ),  $-49.7$  (2H,  $\Delta\vartheta_{1/2} = 730 \text{ Hz}$ ,  $\text{CHH-N}$ ),  $-22.0$  (2H,  $\Delta\vartheta_{1/2} = 240 \text{ Hz}$ , picoline H),  $-11.7$  (2H,  $\Delta\vartheta_{1/2} = 220 \text{ Hz}$ , picoline H),  $-0.81$  (2H,  $\Delta\vartheta_{1/2} = 230 \text{ Hz}$ , picoline H), and  $54$  (2H,  $\Delta\vartheta_{1/2} = 220 \text{ Hz}$ , picoline H).

## RESULTS AND DISCUSSION

### Catalytic Systems **1**/ $\text{CH}_3\text{CO}_3\text{H}$ and **1**/ $\text{H}_2\text{O}_2/\text{CH}_3\text{COOH}$

The  $^1\text{H}$  NMR spectrum recorded 10 min after the beginning of the reaction between **1** and 2 equiv of  $\text{CH}_3\text{CO}_3\text{H}$  in a 1 : 1  $\text{CD}_2\text{Cl}_2/\text{CD}_3\text{CN}$  mixture at  $-50^\circ\text{C}$  displays broad signals from the  $\text{Fe}(\text{III})-\text{O}-\text{Fe}(\text{III})$  dimers and narrower signals (indicated by dots in Fig. 1a) from the mononuclear iron(IV) oxo complex  $[(\text{BPMEN})\text{Fe}^{\text{IV}}=\text{O}(\text{Sol})]^{2+}$  (**3**), where Sol is the solvent molecule. Complex **3** can also be prepared by reacting **1** with 1 equiv of iodobenzene in a 1 : 1  $\text{CD}_2\text{Cl}_2/\text{CD}_3\text{CN}$  mixture at  $-50^\circ\text{C}$  (Fig. 1b). The  $^1\text{H}$  NMR signals of paramagnetic complex **3** are observed mainly in the upfield region of the spectrum, which is typical of the low-spin ( $S = 1$ ) mononuclear  $[\text{LFe}(\text{IV})=\text{O}]^{2+}$  complexes [14]. The number of  $^1\text{H}$  signals from **3** corresponds to the number of chemically nonequivalent protons in BPMEN. The signal intensities show that 30% of the starting complexes **1** turn to **3**. In a 1 : 1  $\text{CD}_2\text{Cl}_2/\text{CD}_3\text{CN}$  mixture, **3** is stable at  $-50^\circ\text{C}$  and decomposes at higher temperatures (half-life at  $-10^\circ\text{C}$  equals 15 min). After adding 5 equiv of cyclohexene to a solution containing **3**, the NMR signals from **3** disappear within few minutes at  $-50^\circ\text{C}$  and signals corresponding to 1,2-epoxycyclohexane appear instead. Therefore, complex **3** may be a key intermediate of the



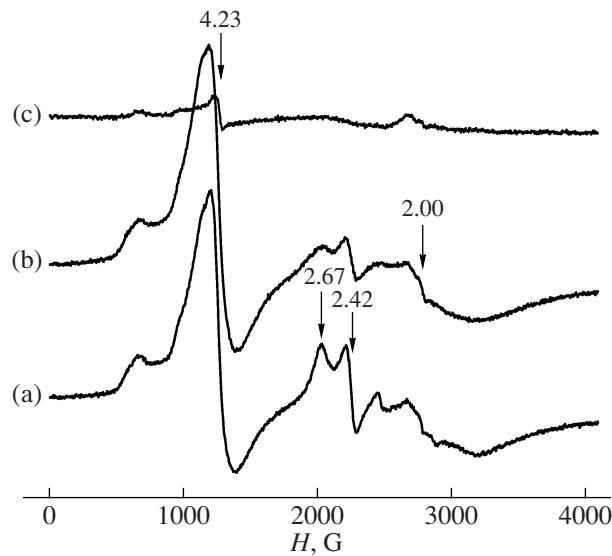
**Fig. 2.**  $^2\text{H}$  NMR spectra of the **1**/ $\text{CD}_3\text{CO}_3\text{H}$  system recorded at  $-50^\circ\text{C}$  10 min after mixing the reactants at  $-50^\circ\text{C}$  in a 1 : 1  $\text{CH}_2\text{Cl}_2/\text{CH}_3\text{CN}$  mixture ( $[\mathbf{1}] = 0.05 \text{ mol/l}$ ,  $[\text{CD}_3\text{CO}_3\text{H}] = 0.075 \text{ mol/l}$ ).

olefin epoxidation reaction in the catalytic system **1**/ $\text{CH}_3\text{CO}_3\text{H}$ .

Complex **3** is also detected by  $^1\text{H}$  NMR after the addition of  $\text{H}_2\text{O}_2$  to the **1**/ $\text{CH}_3\text{COOH}$  system ( $[\mathbf{1}] = [\text{H}_2\text{O}_2] = [\text{CH}_3\text{COOH}] = 0.05 \text{ mol/l}$ , 1 : 1  $\text{CD}_2\text{Cl}_2/\text{CD}_3\text{CN}$ ,  $-50^\circ\text{C}$ ). In this case, the concentration of the formed compound **3** is close to its concentration in the **1**/ $\text{CH}_3\text{CO}_3\text{H}$  system ( $[\mathbf{1}] = [\text{CH}_3\text{CO}_3\text{H}] = 0.05 \text{ mol/l}$ , 1 : 1  $\text{CD}_2\text{Cl}_2/\text{CD}_3\text{CN}$ ,  $-50^\circ\text{C}$ ). Consequently, **3** may be the active particle in the processes of cyclohexene epoxidation not only in the **1**/ $\text{CH}_3\text{CO}_3\text{H}$  system but also in the **1**/ $\text{H}_2\text{O}_2/\text{CH}_3\text{COOH}$  system.

It is obvious that the acylperoxo complex  $[(\text{BPMEN})\text{Fe}^{\text{III}}(\text{O}_3\text{CCH}_3)]^{2+}$  (**4**) is the precursor of oxo complex **3**. We attempted to detect **4** by the  $^2\text{H}$  NMR technique using the deuterated peracetic acid  $\text{CD}_3\text{CO}_3\text{H}$ . The spectrum recorded 10 min after the addition of 1.5 equiv of  $\text{CD}_3\text{CO}_3\text{H}$  to a solution of **1** in a 1 : 1  $\text{CH}_2\text{Cl}_2/\text{CH}_3\text{CN}$  mixture at  $-50^\circ\text{C}$  exhibits a signal at 102.7 ppm ( $\Delta\nu_{1/2} = 230 \text{ Hz}$ , Fig. 2). The same signal is observed upon the addition of 1 equiv of  $\text{H}_2\text{O}_2$  to the sample containing **1** and 1 equiv of  $\text{CD}_3\text{COOD}$  in a 1 : 1  $\text{CH}_2\text{Cl}_2/\text{CH}_3\text{CN}$  mixture at  $-50^\circ\text{C}$  ( $[\mathbf{1}] = 0.05 \text{ mol/l}$ ). This signal disappeared upon heating the sample (at  $-30^\circ\text{C}$ ,  $\tau_{1/2} = 10 \text{ min}$ ).

In the spectrum of the high-spin complex  $(\text{TPP})\text{Fe}^{\text{III}}-\text{OOCD}_2\text{CD}_3$  (TPP is a dianion of tetra-*para*-tolylporphine), the chemical shifts of the  $\text{CD}_2$  and  $\text{CD}_3$  groups are, respectively, 180 and 4 ppm [15]. This allows the signal at 102.7 ppm to be assigned to the  $\text{OOCCD}_3$  or  $\text{O}_3\text{CCD}_3$  ligand entering the high-spin  $\text{Fe}^{\text{III}}$  complex. To make sure that the signal at 102.7 ppm comes not from  $\text{OOCCD}_3$ , the deuterated acetic acid  $\text{CD}_3\text{COOD}$  was added to the solution of **1** in a 1 : 1  $\text{CH}_2\text{Cl}_2/\text{CH}_3\text{CN}$  mixture at  $-50^\circ\text{C}$  ( $[\mathbf{1}] = 0.05 \text{ mol/l}$ ). In this case, no  $^2\text{H}$  signal was observed near 100 ppm. Consequently, the signal at 102.7 is due to the  $\text{O}_3\text{CCD}_3$  group in the high-spin acylperoxo complex **4**. The maximal concentration of **4** does not exceed 10% of the starting concentration of **1**.

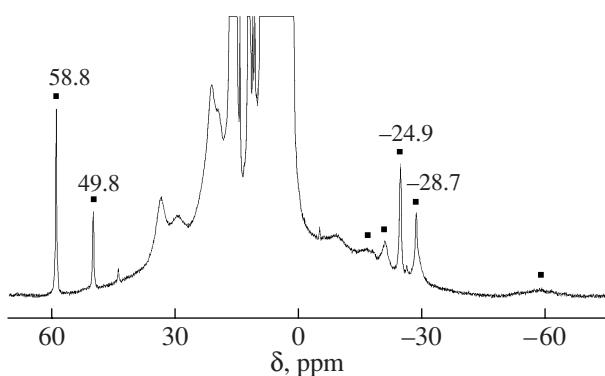


**Fig. 3.** (a) EPR spectra recorded at  $-196^\circ\text{C}$  (a) 1 and (b) 10 min after the beginning of the reaction between **1** and  $\text{CH}_3\text{CO}_3\text{H}$  at  $-60^\circ\text{C}$  in a 2 : 1  $\text{CH}_2\text{Cl}_2/\text{CH}_3\text{CN}$  mixture. Spectrum (c) is recorded after heating sample b to room temperature.  $[\mathbf{1}] = 0.05 \text{ mol/l}$  and  $[\text{CH}_3\text{CO}_3\text{H}] = 0.1 \text{ mol/l}$ .

According to [1, 5], the  $g$  factor of the high-spin mononuclear complex **4** equals 4.23. The EPR spectra recorded at different instants of time after the beginning of the reaction of **1** with 2 equiv of  $\text{CH}_3\text{O}_3\text{H}$  in a 2 : 1  $\text{CH}_2\text{Cl}_2/\text{CH}_3\text{CN}$  mixture at  $-60^\circ\text{C}$  show a signal with  $g = 4.23$  ( $\Delta H = 260 \text{ G}$ ), an axially anisotropic signal with  $g_1 = g_2 = 2.42$ ,  $g_3 = 2.67$ , and a very broad signal near  $g = 2$  ( $\Delta H = 1.2 \text{ kG}$ ; Figs. 3a, 3b). The signal with  $g = 4.23$  ( $\Delta H = 260 \text{ G}$ ) disappears upon heating to room temperature, and a new weaker and narrower signal ( $\Delta H = 70 \text{ G}$ ) appears with the same  $g$  factor. The latter belongs to the stable high-spin  $\text{Fe}(\text{III})$  complexes. The broad signal near  $g = 2$  also disappears upon heating to room temperature (Fig. 3c).

The signal with  $g = 4.23$  ( $\Delta H = 260 \text{ G}$ ) cannot be unambiguously assigned to acylperoxo complex **4**, because other species, e.g., high-spin iron(III) hydroxo complex  $[(\text{BPMEN})\text{Fe}^{\text{III}}(\text{OH})]^{2+}$ , can also display a signal in this spectral region. For this reason, the contribution from **4** to the signal with  $g = 4.23$  ( $\Delta H = 260 \text{ G}$ ) cannot be determined reliably. The origin of the broad signal near  $g = 2$  also remains to be clarified.

The axial signal ( $g_1 = g_2 = 2.42$ ,  $g_3 = 2.67$ ) is due to the unstable complex **5** ( $\tau_{1/2} = 10 \text{ min}$  at  $-60^\circ\text{C}$ ). The same signal, along with the rhombic spectra of low-spin hydroperoxo complexes  $[(\text{BPMEN})\text{Fe}^{\text{III}}(\text{OOH})\text{Sol}]^{2+}$ , was observed in the catalytic system **1**/ $\text{H}_2\text{O}_2$  (see below). The principal values of the  $g$  tensor of **5** (2.42, 2.42, 2.67) differ from those of the low-spin hydroxo complex  $[(\text{BPMEN})\text{Fe}^{\text{III}}(\text{OH})\text{Sol}]^2$  ( $g = 1.91$ , 2.19, 2.39) and low-spin hydroperoxo complex  $[(\text{BPMEN})\text{Fe}^{\text{III}}(\text{OOH})(\text{H}_2\text{O})]^{2+}$  ( $g = 1.970$ , 2.128, 2.195) [16]. The iron complexes resulting from the photooxi-



**Fig. 4.**  $^1\text{H}$  NMR spectrum of the  $2/\text{H}_2\text{O}_2/\text{CH}_3\text{COOH}$  system recorded at  $-50^\circ\text{C}$  10 min after the addition of  $\text{H}_2\text{O}_2$  at  $-50^\circ\text{C}$  to a solution containing  $2/\text{CH}_3\text{COOH}$  in a  $1:1$   $\text{CD}_2\text{Cl}_2/\text{CD}_3\text{CN}$  mixture ( $[2] = [\text{CH}_3\text{COOH}] = 0.05 \text{ mol/l}$ ,  $[\text{H}_2\text{O}_2] = 0.1 \text{ mol/l}$ ). Dots indicate the signals of **6**.

dation of the *trans*-[(cyclam)Fe( $\text{N}_3$ ) $_2$ ] $\text{ClO}_4$  (cyclam = 1,4,8,11-tetraazacyclotetradecene) complex in acetonitrile were identified in [17] using Mössbauer and EPR spectroscopy. The main photolysis product of this compound in a room-temperature liquid solution was a dinuclear  $\mu$ -nitrido complex containing the antiferromagnetically coupled Fe(III) ( $S = 3/2$ ) and Fe(IV) ( $S = 1$ ) atoms with the total spin  $S = 1/2$ . In outline, the EPR spectrum of this complex ( $g_1 = 2.04$ ,  $g_2 = 2.06$ ,  $g_3 = 2.20$ ) resembles the spectrum of **5**. For both complexes, the spectrum anisotropy is close to axial. In both cases, all  $g$  factors exceed  $g_e = 2.0023$ . Therefore, compound **5** can be regarded as a mixed dinuclear Fe<sub>2</sub>(III,IV) complex. In 2007, Prof. Que et al. reported the first observation of a mononuclear iron(V) oxo complex  $[\text{Fe}^{\text{V}}=\text{O}]^{3+}$  containing a tetraamide ligand [18]. The EPR spectrum of this complex is characterized by  $g_1 = 1.74$ ,  $g_2 = 1.97$ , and  $g_3 = 1.99$ . This result allows the alternative structure to be suggested for intermediate **5**; namely,  $[(\text{BPMEN})\text{Fe}^{\text{V}}=\text{O}(\text{Sol})]^{3+}$ . Intermediate **5** ( $\tau_{1/2} = 10 \text{ min}$  at  $-60^\circ\text{C}$ ) is much less stable than **3** ( $\tau_{1/2} = 15 \text{ min}$  at  $-10^\circ\text{C}$ ). Both these species can be regarded as active epoxidation intermediates, because the self-decay rates of **3** and **5** increased in the presence of cyclohexene.

#### Catalytic Systems $2/\text{CH}_3\text{CO}_3\text{H}$ and $2/\text{H}_2\text{O}_2/\text{CH}_3\text{COOH}$

In analogy with the BPMEN-based catalytic systems, it would appear reasonable to assume that the active species in the catalytic systems  $2/\text{CH}_3\text{CO}_3\text{H}$  and  $2/\text{H}_2\text{O}_2/\text{CH}_3\text{COOH}$  are either the mononuclear iron(IV) oxo complex  $[(\text{TPA})\text{Fe}^{\text{IV}}=\text{O}(\text{Sol})]^{2+}$  (**6**) or the iron(V) complex  $[(\text{TPA})\text{Fe}^{\text{V}}=\text{O}(\text{Sol})]^{3+}$ . In compliance with this assumption, the signals from **6** (indicated by dots in Fig. 4) were observed in the  $^1\text{H}$  NMR spectra of these systems in a  $1:1$   $\text{CD}_2\text{Cl}_2/\text{CD}_3\text{CN}$  mixture at  $-50^\circ\text{C}$ . The other paramagnetically shifted signals belong to

the dinuclear Fe<sup>III</sup>-O-Fe<sup>III</sup> complexes. Complex **6** is unstable ( $\tau_{1/2} = 10 \text{ min}$  at  $-10^\circ\text{C}$ ). The most characteristic and easy-to-interpret signals belong to  $\beta, \beta'$  protons of picoline rings (in a  $1:1$   $\text{CDCl}_3/\text{CD}_2\text{Cl}_2$  mixture, the shifts  $\delta$  are 58.8 (2H), 49.8 (1H), -24.9 (2H), and -28.7 (1H) ppm). The ratio between the four observed signals (2 : 1 : 2 : 1) is consistent with the assumption that two of the three picoline rings in the TPA ligand are equivalent. Analogous signals belonging to  $\beta, \beta'$  protons of picoline rings were observed in the spectrum of the X-ray characterized  $[(\text{N}_4\text{Py})\text{Fe}^{\text{IV}}=\text{O}]^{2+}$  complex, where  $\text{N}_4\text{Py} = N,N'$ -bis(2-pyridylmethyl)- $N$ -(2-pyridyl)methylamine [14]. The spectrum showed signals at  $\delta = 44.4$  (2H), 30.05 (2H), -11.2 (2H), and -17.8 (2H) ppm. The other signals of **6** and  $[(\text{N}_4\text{Py})\text{Fe}^{\text{IV}}=\text{O}]^{2+}$  remain to be assigned. Complex **6** is stable at  $-50^\circ\text{C}$  and rapidly (within few minutes) disappears upon the addition of 5 equiv of cyclohexene at this temperature. It disappears simultaneously with an increase in the intensity of the  $^1\text{H}$  signals in the NMR spectrum of 1,2-epoxycyclohexane. The addition of new portions of  $\text{CH}_3\text{CO}_3\text{H}$  or  $\text{H}_2\text{O}_2/\text{CH}_3\text{COOH}$  regains the concentration of **6**. Therefore, the iron(IV) oxo complex  $[(\text{TPA})\text{Fe}^{\text{IV}}=\text{O}(\text{Sol})]^{2+}$  may play the role of an active particle in the processes of olefin epoxidation in the catalytic systems  $2/\text{CH}_3\text{CO}_3\text{H}$  and  $2/\text{H}_2\text{O}_2/\text{CH}_3\text{COOH}$ . No intermediates that could be referred to the  $[(\text{TPA})\text{Fe}^{\text{V}}=\text{O}(\text{Sol})]^{3+}$  species were found in the catalytic systems  $2/\text{CH}_3\text{CO}_3\text{H}$  and  $2/\text{H}_2\text{O}_2/\text{CH}_3\text{COOH}$ .

#### Catalytic System $1/\text{H}_2\text{O}_2$

The starting complex **1** in a  $\text{CH}_3\text{CN}$  solution is air-stable. It is known that cyclohexene is oxidized by the catalytic system **1**/ $\text{H}_2\text{O}_2$  mainly to 1,2-epoxycyclohexane (~70% selectivity,  $[1] = 0.03 \text{ mol/l}$ ,  $[\text{H}_2\text{O}_2] = [\text{C}_6\text{H}_{10}] = 1 \text{ mol/l}$ ,  $20^\circ\text{C}$ ,  $\text{CH}_3\text{CN}$ ). The  $^1\text{H}$  NMR spectrum of **1** in  $\text{CD}_3\text{CN}$  at  $20^\circ\text{C}$  corresponds to the spectrum of a high-spin paramagnetic iron(II) complex. As follows from [19, 20], complex **1** turns into the low-spin state with lowering temperature and its spectrum at  $-40^\circ\text{C}$  is typical of the diamagnetic low-spin iron complexes.

Upon the addition of 3–4 equiv of  $\text{H}_2\text{O}_2$  to a solution of 0.03 M **1** in  $\text{CD}_3\text{CN}$  at  $20^\circ\text{C}$ , **1** completely turns to high-spin antiferromagnetically coupled dimeric  $\mu$ -oxo complex **7**. The  $^1\text{H}$  NMR spectrum of **7** is similar to the spectrum of the dimeric  $\mu$ -oxo complex  $[(\text{OH})(\text{BPMEN})\text{Fe}^{\text{III}}-\text{O}-\text{Fe}^{\text{III}}(\text{BPMEN})(\text{H}_2\text{O})](\text{ClO}_4)_3$  [21]. Therefore, the major part of iron in the catalytic system **1**/ $\text{H}_2\text{O}_2$  occurs in the form of this complex.

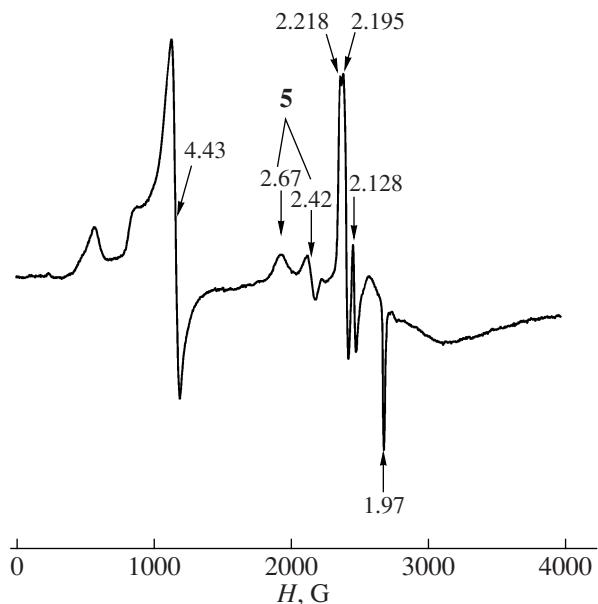
To observe very unstable hydroperoxy intermediates  $[\text{Fe}^{\text{III}}(\text{BPMEN})(\text{OOH})\text{Sol}](\text{ClO}_4)_2$  (**8**), we used a  $2:1$   $\text{CH}_2\text{Cl}_2/\text{CH}_3\text{CN}$  mixture as a solvent instead of  $\text{CH}_3\text{CN}$ . The addition of  $\text{CH}_2\text{Cl}_2$  allowed one to reduce the temperature of the reaction solution to  $-70^\circ\text{C}$  without solid-phase transition and, simultaneously, improve the quality of EPR spectra of frozen solutions at  $-196^\circ\text{C}$ .

(narrower signals). The latter effect is caused by the vitrification of the frozen solution.

The EPR spectrum recorded 1 min after the beginning of the reaction between **1** and 1.5 equiv of  $\text{H}_2\text{O}_2$  in a 2 : 1  $\text{CH}_2\text{Cl}_2/\text{CH}_3\text{CN}$  mixture at  $-60^\circ\text{C}$  exhibits an axially anisotropic signal from **5** ( $g_1 = 2.67$ ,  $g_2 = g_3 = 2.42$ ) and signals characteristic of the low-spin iron(III) hydroperoxo complexes  $[(\text{BPMEN})\text{Fe}^{\text{III}}(\text{OOH})(\text{CH}_3\text{CN})]^{2+}$  (**8-CH<sub>3</sub>CN**) ( $g_1 = 2.218$ ,  $g_2 = 2.178$ ,  $g_3 = 1.967$ ) and  $[(\text{BPMEN})\text{Fe}^{\text{III}}(\text{OOH})(\text{H}_2\text{O})]^{2+}$  (**8-H<sub>2</sub>O**) ( $g_1 = 2.195$ ,  $g_2 = 2.128$ ,  $g_3 = 1.970$ ) [16] (Fig. 5). In the presence of 10 equiv of cyclohexene, the decay rate of **5** increased no less than five times at  $-60^\circ\text{C}$ , whereas it did not change for complexes **8-CH<sub>3</sub>CN** and **8-H<sub>2</sub>O**. The activity of complex **5** toward cyclohexene correlates with the assumption that this complex contains active grouping  $\text{Fe}^{\text{IV}}=\text{O}$  or  $\text{Fe}^{\text{V}}=\text{O}$ . The concentrations of intermediates **5** and **8** did not exceed 5% of the concentration of the starting complex **1**.

It is well known that the dinuclear complexes containing oxo bridge  $\text{Fe}_2^{\text{III}}(\mu\text{-O})$  are the thermodynamically most stable and most widespread iron(III)-based structures. It is thus natural that **1** would react with  $\text{H}_2\text{O}_2$  to give mononuclear hydroperoxo complexes **8** only at the initial step of reaction, whereupon oxo-bridged dimeric species would dominate the solution, and the ligand  $\text{OOH}$  would enter into the coordination sphere of the dimeric species in the form of the complexes of the  $\text{HOO}-\text{Fe}^{\text{III}}-\text{O}-\text{Fe}^{\text{III}}$  type. In this case, the heterolytic decomposition of  $\text{OOH}$  can be accompanied by the formation of mixed-valence complexes.

Complex **3** or **5** is the key intermediate of the catalytic system **1**/H<sub>2</sub>O<sub>2</sub>/CH<sub>3</sub>COOH. In the **1**/H<sub>2</sub>O<sub>2</sub> system, only one intermediate was observed, whose decomposition rate increased in the presence of cyclohexene. It was complex **5**. The formation of different intermediates in the **1**/H<sub>2</sub>O<sub>2</sub>/CH<sub>3</sub>COOH and **1**/H<sub>2</sub>O<sub>2</sub> systems correlates with the fact that their activity and selectivity in the reaction of olefin epoxidation are different. However, whereas the key role of mononuclear intermediates of the Fe<sup>IV</sup>=O or Fe<sup>V</sup>=O type seems to be quite possible, the participation of dinuclear mixed-valence intermediates in the olefin epoxidation by the catalytic system **1**/H<sub>2</sub>O<sub>2</sub> is not justified as yet. The literature data on the reactivity of dinuclear and mononuclear iron complexes are rather contradictory. It was recently shown [22] that, under identical conditions, the dinuclear iron  $\mu$ -oxo complexes with the BPMEN ligand are less active in the olefin oxidation with hydrogen peroxide than mononuclear complex **1**. At the same time, the iron(III)  $\mu$ -oxo complexes containing ethylene-bridged TPA ligands, exhibit higher activity and selectivity, as compared to their mononuclear analogs [23]. Thus, the nature of active species in the catalytic systems **1**/H<sub>2</sub>O<sub>2</sub>/CH<sub>3</sub>COOH and **1**/H<sub>2</sub>O<sub>2</sub> calls for further investigation.

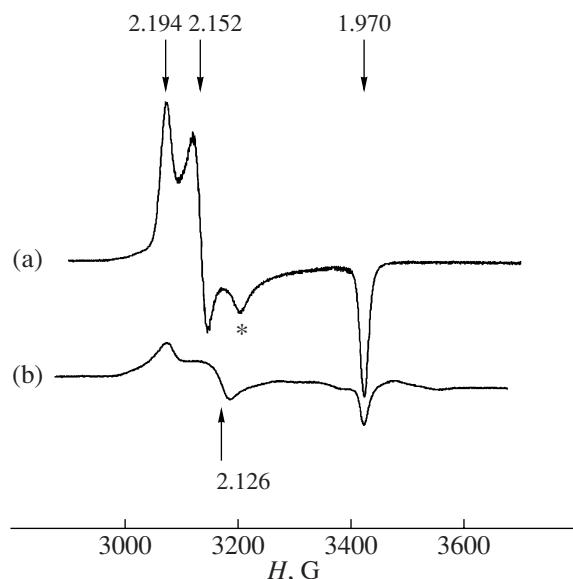


**Fig. 5.** EPR spectrum recorded at  $-196^{\circ}\text{C}$  1 min after the beginning of the reaction between **1** and 1.5 equiv of  $\text{H}_2\text{O}_2$  at  $-60^{\circ}\text{C}$  in a 2 : 1  $\text{CH}_2\text{Cl}_2/\text{CH}_3\text{CN}$  mixture.  $[\mathbf{1}] = 0.05 \text{ mol/L}$ .

### Catalytic System 2/ $H_2O_2$

The EPR spectrum ( $-196^{\circ}\text{C}$ ) of a solution frozen 1 min after the addition of 1.5 equiv of hydrogen peroxide to the solution of **2** in a 1 : 1 (v/v)  $\text{CH}_3\text{CN}/\text{CH}_2\text{Cl}_2$  mixture at  $-50^{\circ}\text{C}$  (Fig. 6a) shows intense signals (arrows) with  $g_1 = 2.194$ ,  $g_2 = 2.152$ ,  $g_3 = 1.970$  and a weak signal with  $g = 2.12$  (asterisk). The first spectrum belongs to the hydroperoxo complex  $[(\text{TPA})\text{Fe}^{\text{III}}(\text{OOH})(\text{CH}_3\text{CN})]^{2+}$  (**9-CH<sub>3</sub>CN**), in which the sixth coordination site of the iron atom is occupied by the  $\text{CH}_3\text{CN}$  molecule. The second signal ( $g = 2.12$ ) refers to the hydroperoxo complex  $[(\text{TPA})\text{Fe}^{\text{III}}(\text{OOH})(\text{H}_2\text{O})]^{2+}$  (**9-H<sub>2</sub>O**) generating a signal with  $g_1 = 2.19$ ,  $g_2 = 2.12$ , and  $g_3 = 1.97$ . Indeed, signals with  $g_1 = 2.194$ ,  $g_2 = 2.126$ , and  $g_3 = 1.972$  are seen in the spectrum of adduct **9**-MeOH prepared by adding MeOH to the solution of **2** in a  $\text{CH}_3\text{CN}/\text{CH}_2\text{Cl}_2$  mixture at  $-45^{\circ}\text{C}$  (Fig. 6b). Obviously, the EPR parameters of complexes **2**-MeOH and **2**-H<sub>2</sub>O must be nearly the same, because the MeOH and H<sub>2</sub>O molecules both are coordinated to the central iron atom via the oxygen atom. The preparation of complex **9-H<sub>2</sub>O** was hampered by the poor solubility of H<sub>2</sub>O in  $\text{CH}_3\text{CN}$  at low temperatures and by the fast decomposition of **9-H<sub>2</sub>O**.

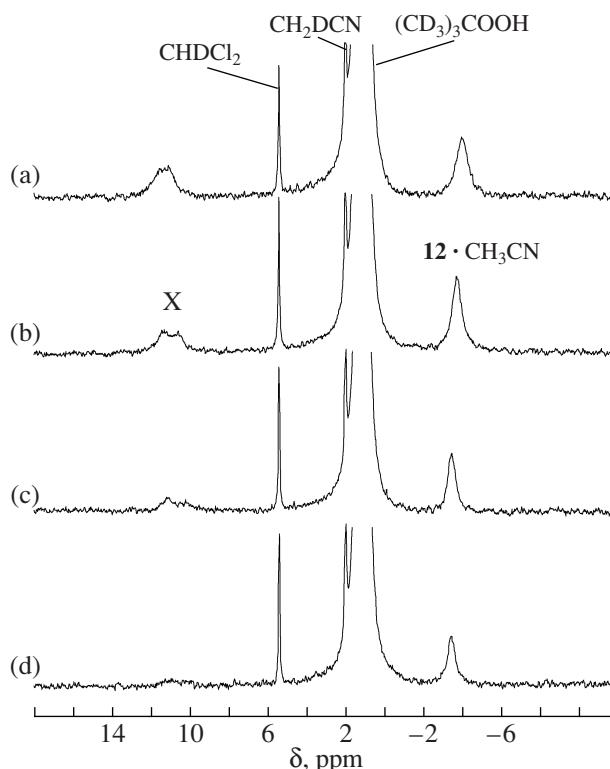
As in the cases of **8**-CH<sub>3</sub>CN and **8**-H<sub>2</sub>O, the decay rate of **9**-CH<sub>3</sub>CN and **9**-H<sub>2</sub>O at -40°C does not change in the presence of cyclohexene [24]. This gives evidence that **9**-CH<sub>3</sub>CN and **9**-H<sub>2</sub>O can react with cyclohexane, if at all, indirectly through the formation of more active species, e.g., oxo complex **6**. However, complex **6** was not detected in the **2**/H<sub>2</sub>O<sub>2</sub> system. One can assume that the role of active species in this system



**Fig. 6.** EPR spectra ( $-196^{\circ}\text{C}$ ) of complexes **9**– $\text{CH}_3\text{CN}$  and **9**– $\text{MeOH}$  prepared by the reaction of  $[(\text{TPA})(\text{II})\text{Fe}(\text{CH}_3\text{CN})_2](\text{ClO}_4)_2$  with 4 equiv of  $\text{H}_2\text{O}_2$  at  $-50^{\circ}\text{C}$ : in a (a) 1 : 1  $\text{CH}_3\text{CN}/\text{CH}_2\text{Cl}_2$  mixture and (b) 2 : 2 : 1  $\text{CH}_3\text{CN}/\text{CH}_2\text{Cl}_2/\text{MeOH}$  mixture. The signal with an asterisk belongs to **9**– $\text{H}_2\text{O}$  adduct.

is played by the dinuclear complexes of the type  $[(\text{TPA})\text{Fe}^{\text{III}}\text{—O—Fe}^{\text{IV}}=\text{O}(\text{TPA})]^{3+}$  (**10**) or by the mononuclear complexes  $[(\text{TPA})\text{Fe}^{\text{V}}=\text{O}(\text{Sol})]^{3+}$ . The hydroperoxy complexes  $[(\text{TPA})\text{Fe}^{\text{III}}\text{—O—Fe}^{\text{III}}\text{—OOH}(\text{TPA})]^{3+}$  (**11**) are the possible precursors of **10**. However, complexes **10** and **11** were as yet not observed in the catalytic system **2**/ $\text{H}_2\text{O}_2$ .

Indirect evidence in favor of the formation of **11** is provided by the experiments in which the deuterated *tert*-butyl hydroperoxide  $(\text{CD}_3)_3\text{COOD}$  was used instead of hydrogen peroxide. After the addition of  $(\text{CD}_3)_3\text{COOD}$  to a solution of **2** at  $-52^{\circ}\text{C}$ , two weak signals appear at  $\delta = -4.2$  and  $11.5$  ppm in the  $^2\text{H}$  NMR spectrum, along with the strong signals from  $\text{Bu}'\text{OOH}\text{-d}_9$  and  $\text{Bu}'\text{OH}\text{-d}_9$  at  $1.08$  ppm (Fig. 7a). The intensity of the signal at  $\delta = -4.2$  ppm correlates with the intensity of the EPR signal from **12**– $\text{CH}_3\text{CN}$  ( $[(\text{TPA})\text{Fe}^{\text{III}}(\text{OOBu}'\text{-d}_9)(\text{CH}_3\text{CN})]^{2+}$ ) ( $g = 2.158, 2.117, 1.970$ ). Consequently, the signal at  $-4.2$  ppm belongs to the alkylperoxy group in **12**– $\text{CH}_3\text{CN}$  [24]. The alkylperoxy group in the low-spin alkylperoxy complex  $[\text{Fe}(\text{bpy})_2(\text{OOBu}'\text{-d}_9)\text{CH}_3\text{CN}](\text{NO}_3)_2$  generates a signal with a chemical shift of  $-3.7$  ppm in the  $^2\text{H}$  NMR spectrum [25], thereby confirming the above assignment. The signal at  $\delta = 11.5$  ppm is due to the alkylperoxy group of a new hitherto unidentified particle. With increasing temperature, it splits into two peaks with close intensities (Fig. 7), evidencing the possible existence of two isomeric forms of this new alkylperoxy complex. At  $-35^{\circ}\text{C}$ , the signals at  $\delta = -4.2$  and  $11.5$  ppm disappear gradually, the second faster than the first (Figs. 7c, 7d).



**Fig. 7.**  $^2\text{H}$  NMR spectra recorded after adding 20 equiv of  $(\text{CD}_3)_3\text{COOD}$  to a solution of **2** in a 1 : 1  $\text{CH}_3\text{CN}/\text{CH}_2\text{Cl}_2$  mixture ( $[\text{2}] = 0.01$  mol/l) at temperatures ( $^{\circ}\text{C}$ ) (a)  $-52$ , (b)  $-45$ , and (c)  $-35$ . Spectrum (d) corresponds to sample (c) after holding it at  $-35^{\circ}\text{C}$  for 25 min. The signal marked by X belongs presumably to the dinuclear alkylperoxy complex  $[(\text{CD}_3)_3\text{COO—Fe}^{\text{III}}(\text{TPA})\text{—O—Fe}^{\text{III}}(\text{TPA})]^{3+}$ .

In principle, the signal at  $11.5$  ppm can be assigned to the alkylperoxy group in a mononuclear high-spin iron(III) alkylperoxy complex or a dinuclear high-spin antiferromagnetically coupled iron(III) complex. The  $g$  factor of the EPR signal from the mononuclear complex should be equal to 4.23. However, such a signal was not observed for **2** interacting with  $(\text{CD}_3)_3\text{COOD}$ . It is thus most probable that the signal at  $11.5$  ppm comes from the alkylperoxy complex of the type  $[(\text{TPA})(\text{OOBu}')\text{Fe}(\text{III})\text{—O—Fe}(\text{III})(\text{TPA})(\text{H}_2\text{O})](\text{ClO}_4)_3$ —an analog of the presumed hydroperoxy complex **11**.

As distinct from the **1**/ $\text{H}_2\text{O}_2/\text{CH}_3\text{COOH}$  and **2**/ $\text{H}_2\text{O}_2/\text{CH}_3\text{COOH}$  systems, one failed to detect the mononuclear complexes  $[(\text{L})\text{Fe}^{\text{IV}}=\text{O}(\text{Sol})]^{2+}$  in the catalytic systems **1**/ $\text{H}_2\text{O}_2$  and **2**/ $\text{H}_2\text{O}_2$ . Consequently, the concentration of the  $[(\text{L})\text{Fe}^{\text{IV}}=\text{O}(\text{Sol})]^{2+}$  particles appearing in the **1**/ $\text{H}_2\text{O}_2$  and **2**/ $\text{H}_2\text{O}_2$  systems, if at all, should be much lower than in the **1**/ $\text{H}_2\text{O}_2/\text{CH}_3\text{COOH}$  and **2**/ $\text{H}_2\text{O}_2/\text{CH}_3\text{COOH}$  systems. The  $[(\text{L})\text{Fe}^{\text{IV}}=\text{O}(\text{Sol})]^{2+}$  or  $[(\text{L})\text{Fe}^{\text{V}}=\text{O}(\text{Sol})]^{3+}$  complexes may be the key intermediates in the catalytic systems of interest. To decide between these two structures, further study is required.

## ACKNOWLEDGMENTS

This work was supported by the Russian Foundation for Basic Research, project no. 06-03-32214.

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