DOI: 10.1002/ejic.200600895

The Active Intermediates of Non-Heme-Iron-Based Systems for Catalytic Alkene Epoxidation with H_2O_2/CH_3COOH

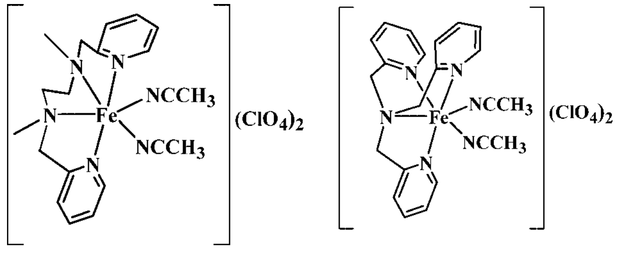
Eduard A. Duban,[a] Konstantin P. Bryliakov,[a] and Evgenii P. Talsi*[a]

Keywords: Oxidoiron(IV) complexes / Acylperoxido complexes / EPR spectroscopy / Paramagnetic NMR spectroscopy / Intermediates / Oxidation

Iron complexes with aminopyridine ligands $[Fe^{II}(BPMEN)(CH_3CN)_2](ClO_4)_2$ (**1**) [BPMEN = *N*,*N′*-dimethyl-*N*,*N′*-bis(2-pyridylmethyl)-1,2-diaminoethane] and $[Fe^{II}(TPA)(CH_3CN)_2](ClO_4)_2$ (**2**) [TPA = tris(2-pyridylmethyl)amine] are rare examples of iron-based catalysts for selective olefin epoxidation with H_2O_2/CH_3COOH combination. Using $^{1,2}H$ NMR and EPR spectroscopy, it was shown that the active species of the catalytic systems **1**/H_2O_2/CH_3COOH and **2**/H_2O_2/CH_3COOH are mononuclear iron(IV)-oxido complexes $[(BPMEN)Fe^{IV}{=}O(S)]^{2+}$ and $[(TPA)Fe^{IV}{=}O(S)]^{2+}$, respectively (S = solvent molecule). These intermediates are formed via decomposition of the corresponding acylperoxido complexes $[(L)Fe^{III}(O_3CCH_3)]^{2+}$ (L = BPMEN or TPA). The acylperoxido complex $[(BPMEN)Fe^{III}(O_3CCD_3)]^{2+}$ was identified in the catalytic system **1**/H_2O_2/CD_3COOD by ^2H NMR spectroscopy. The improved epoxidation activity and selectivity of the catalytic systems **1**/H_2O_2/CH_3COOH and **2**/H_2O_2/CH_3COOH, with respect to **1**/H_2O_2 and **2**/H_2O_2, is caused by the effective formation of intermediates $[(L)Fe^{IV}{=}O(S)]^{2+}$ via decomposition of the acylperoxido complexes $[(L)Fe^{III}(O_3CCH_3)]^{2+}$.

Introduction

Iron complexes with aminopyridine ligands are known to efficiently catalyze selective olefin oxidation using H_2O_2 or CH_3CO_3H as terminal oxidants.[1–13] $[Fe^{II}(BPMEN)(CH_3CN)_2](ClO_4)_2$ (**1**) [BPMEN = *N*,*N′*-dimethyl-*N*,*N′*-bis(2-pyridylmethyl)-1,2-diaminoethane] and $[Fe^{II}(TPA)(CH_3CN)_2](ClO_4)_2$ (**2**) [TPA = tris(2-pyridylmethyl)amine] (Figure 1) represent the catalysts investigated thus far in the most detail.[1–3,10] Interestingly, the epoxidation of olefins by H_2O_2 catalyzed by **1** and **2** was improved by the addition of acetic acid,[2] and the in situ formation of peroxyacetic acid was later inferred in these systems.[4] The iron(IV)-oxido species $[LFe^{IV}{=}O(S)]^{2+}$ (L = BPMEN or TPA, S = solvent molecule) are considered as possible reactive intermediates of the catalytic systems **1**/H_2O_2/CH_3COOH and **2**/H_2O_2/CH_3COOH. This postulate was derived from nearly identical product distribution obtained for olefin oxidations catalyzed by **1** and **2** with CH_3CO_3H and H_2O_2/CH_3OOH as oxidants.[12] However, whereas the $[(TPA)Fe^{IV}{=}O(S)]^{2+}$ intermediate active towards cyclooctene was trapped in the catalytic system **2**/CH_3CO_3H,[14] such type of species have never been detected in **2**/H_2O_2/CH_3COOH and **1**/H_2O_2/CH_3COOH combinations. Thus, the experimental proof is required for the proposed key role of an $Fe^{IV}{=}O$ oxidant in **1**/H_2O_2/CH_3COOH and **2**/H_2O_2/CH_3COOH systems.



1 **2**

Figure 1. Structures of complexes **1** and **2**.

For **1**/H_2O_2 and **2**/H_2O_2 catalytic systems, the nature of active intermediates is even less clear. The low-spin ferric hydroperoxo species $[LFe^{III}(OOH)(S)]^{2+}$ were identified in **1**/H_2O_2[6] and **2**/H_2O_2.[15,16] Later, it was proposed that $[(TPA)Fe^{III}(OOH)(S)]^{2+}$ by itself is a sluggish oxidant but could be a precursor of more reactive species (e.g. $[(TPA)Fe^{IV}{=}O(S)]^{2+}$).[17] However, mononuclear $[LFe^{IV}{=}O(S)]^{2+}$ intermediates have never been detected in **1**/H_2O_2 and **2**/H_2O_2 systems.

In this work, we report $^{1,2}H$ NMR and EPR detection and reactivity studies of $[LFe^{IV}{=}O(S)]^{2+}$ and other intermediates formed in the catalytic systems **1**/CH_3CO_3H, **2**/CH_3CO_3H, **1**/H_2O_2/CH_3COOH, **2**/H_2O_2/CH_3COOH, and **1**/H_2O_2.

---

[a] Boreskov Institute of Catalysis, Siberian Branch of the Russian Academy of Sciences,
630090, Novosibirsk, Russian Federation
Fax: +7-383-3308056
E-mail: talsi@catalysis.ru

Results and Discussion

Catalytic Systems 1/CH_3CO_3H and 1/H_2O_2/CH_3COOH

The ^1H NMR spectrum recorded 10 min after onset of the reaction of **1** with 2 equiv. of CH_3CO_3H at –50 °C in a 1:1 CD_2Cl_2/CD_3CN mixture displays broad peaks of Fe^{III}–O–Fe^{III} dimers and additional sharp peaks (marked by points) of the new complex **3** (Figure 2, a). Most of the ^1H NMR peaks of **3** possess negative ^1H NMR chemical shifts, whereas mononuclear high-spin ferrous complex **1** and dinuclear Fe^{III}–O–Fe^{III} species with BPMEN ligands exhibit mainly the ^1H NMR peaks with positive chemical shifts.[6,18] Such unusual negative ^1H NMR chemical shifts were previously observed for X-ray characterized low-spin mononuclear complex $[(N_4Py)Fe^{IV}{=}O]^{2+}$, where N_4Py is the pentadentate ligand *N*,*N′*-bis(2-pyridylmethyl)-*N*-bis(2-pyridyl)methylamine.[19] Thus, complex **3** could be assigned to a mononuclear $Fe^{IV}{=}O$ complex. In agreement with this assumption, complex **3** could also be obtained upon reaction of **1** with 1 equiv. of iodosylbenzene at –50 °C in a 1:1 CD_2Cl_2/CD_3CN mixture (Figure 2, b). The reaction of a ferrous precursor with iodosylbenzene is the commonest method for the generation of $Fe^{IV}{=}O$ species.[14] By analogy with X-ray characterized complex $[(TMC)Fe^{IV}{=}O(CH_3CN)]^{2+}$ (TMS is tetradentate ligand tetramethylcyclam, cyclam = 1,4,8,11-tetraazacyclotetradecene),[20] the following structure could be proposed for **3**: $[(BPMEN)Fe^{IV}{=}O(CH_3CN)]^{2+}$. A molecule of solvent (CH_3CN) occupies the sixth coordination site of **3**.

$[(BPMEN)Fe^{IV}{=}O(CH_3CN)]^{2+}$	**3**
$[(BPMEN)Fe^{III}(O_3CCH_3)]^{2+}$	**4**
$[(BPMEN)Fe^{III}{–}O{–}Fe^{IV}{=}O(BPMEN)(S)]^{3+}$	**5**
$[(TPA)Fe^{IV}{=}O(S)]^{2+}$	**6**
$[(OH)(BPMEN)Fe^{III}{–}O{–}Fe^{III}(BPMEN)(H_2O)](ClO_4)_3$	**7**
$[(BPMEN)Fe^{III}(OOH)]^{2+}$	**8**

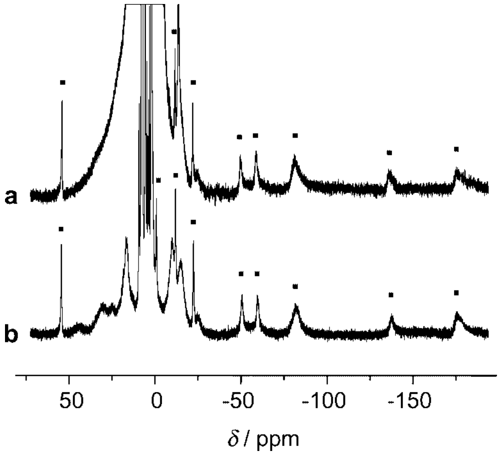


Figure 2. ^1H NMR spectra (–50 °C) of **1**/CH_3CO_3H (a) and **1**/PhIO (b) systems recorded 10 min after mixing the reagents at –50 °C in a 1:1 CD_2Cl_2/CD_3CN mixture ([**1**] = [PhIO] = 0.05 M, [CH_3CO_3H] = 0.1 M). Points denote peaks of **3**.

The number of the ^1H NMR peaks of **3** corresponds to the number of chemically nonequivalent protons of the BPMEN ligand.[21] The intensities of the ^1H NMR peaks of **3** correspond to the conversion of up to 30% of **1** into **3**. Complex **3** is stable in a 1:1 CD_2Cl_2/CD_3CN mixture at –50 °C and decays at higher temperatures (the half-life time $\tau_{1/2}$ is 15 min at –10 °C). After the addition of 5 equiv. of cyclohexene to the solution containing **3** at –50 °C, the latter disappears within several minutes. This decay is accompanied by the rise of the ^1H NMR peaks of the 1,2-epoxycyclohexane. Thus, complex **3** is the key intermediate of epoxidation by the catalytic system **1**/CH_3CO_3H.

The same complex **3** was observed by ^1H NMR upon addition of H_2O_2 into the **1**/CH_3COOH system ([**1**] = [H_2O_2] = [CH_3COOH] = 0.05 M, 1:1 CD_2Cl_2/CD_3CN mixture, –50 °C). The concentration of **3** was close to that for the **1**/CH_3O_3H system ([**1**] = [CH_3CO_3H] = 0.05 M, 1:1 CD_2Cl_2/CD_3CN mixture, –50 °C). Thus, mononuclear ironoxido complex $[(BPMEN)Fe^{IV}{=}O(S)]^{2+}$ (**3**) is the active species of cyclohexene epoxidation by the catalytic systems **1**/CH_3CO_3H and **1**/H_2O_2/CH_3COOH.

Apparently, it is the ferric acylperoxido complex $[(BPMEN)Fe^{III}(O_3CCH_3)]^{2+}$ (**4**) that is the precursor of **3**. We have undertaken the search for **4** by ^2H NMR using deuterated peroxo acetic acid (CD_3CO_3H). The ^2H NMR spectrum recorded 10 min after the addition of 1.5 equiv. of CD_3CO_3H to **1** in a 1:1 CH_2Cl_2/CH_3CN mixture at –50 °C exhibits a broad peak at δ = 102.7 ppm (the half height width $\Delta\nu_{1/2}$ = 230 Hz) (Figure 3). The same peak was observed after the addition of 1 equiv. of H_2O_2 to the sample containing **1** and 1 equiv. of CD_3COOD in a 1:1 CH_2Cl_2/CH_3CN mixture at –50 °C ([**1**] = 0.05 M). This peak disappeared upon warming ($\tau_{1/2}$ = 10 min at –30 °C). For the high-spin complex (TPP)Fe^{III}–O–O–CD_2–CD_3 (TPP = dianion of tetra-*p*-tolylporphyrin), a CD_2 peak was observed at δ = 180 ppm, and a CD_3- peak at 4 ppm.[22] On the basis of these data, the resonance at δ = 102.7 ppm could be assigned to the $OOCCD_3$ or O_3CCD_3 moiety bound to high-spin Fe^{III}. To rule out the assignment of the observed peak to the $OOCCD_3$ moiety, CD_3COOD was added to the solution containing **1** at –50 °C. In this case, no ^2H NMR peaks near 100 ppm were observed. Thus, the ^2H NMR resonance at δ = 102.7 ppm belongs to the O_3CCD_3 moiety of the high-spin ferric acylperoxido complex **4**. The maximum

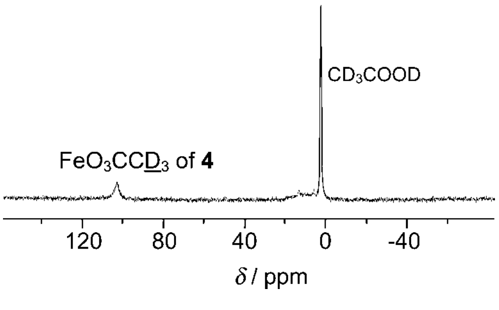


Figure 3. The ^2H NMR spectrum (–50 °C) of the system **1**/CD_3CO_3D recorded 10 min after mixing the reagents at –50 °C in a 1:1 CH_2Cl_2/CH_3CN mixture ([**1**] = 0.05 M, [CD_3CO_3H] = 0.075 M).

concentration of **4** was about 10% of the initial concentration of **1**.

The high-spin mononuclear ferric complex **4** should display an EPR signal at $g = 4.23$.[23,24] EPR spectra recorded in various moments of time after onset of the reaction of **1** with 2 equiv. of CH_3CO_3H at –60 °C in a 2:1 CH_2Cl_2/CH_3CN mixture show: (1) a signal at $g = 4.23$ (peak-to-peak width $\Delta H = 260$ G), (2) an axially anisotropic signal ($g_1 = g_2 = 2.42$, $g_3 = 2.67$), and (3) a very broad signal at $g \approx 2$ ($\Delta H = 1200$ G) (Figure 4, a and b). The signal at $g = 4.23$ ($\Delta H = 260$ G) was gone upon warming to room temperature, and another weaker and sharper signal ($\Delta H = 70$ G) with the same g-factor was observed. The latter signal persists after storing at room temperature for hours and thus belongs to a stable mononuclear high-spin ferric species. The broad signal near $g = 2$ disappeared upon warming (Figure 4, c).

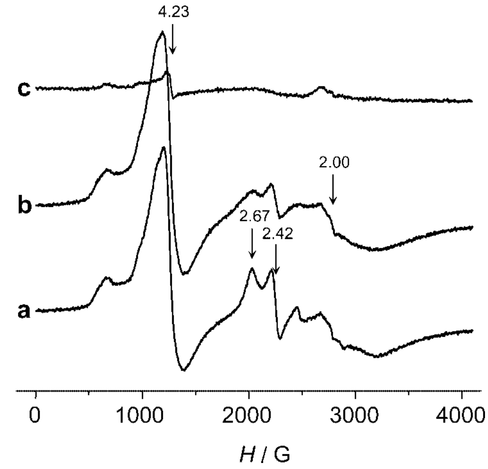


Figure 4. X-band EPR spectra (–196 °C) recorded 1 min (a) and 10 min (b) after mixing **1** and CH_3CO_3H at –60 °C in a 2:1 CH_2Cl_2/CH_3CN mixture. Sample (b) after warming to room temperature (c). ([**1**] = 0.05 M, [CH_3CO_3H] = 0.1 M).

It is tempting to assign the observed signal at $g = 4.23$ (Figure 4, a and b) to acylperoxido complex **4**. However, another high-spin ferric species (e.g., high-spin hydroxido complex $[(BPMEN)Fe^{III}(OH)]^{2+}$) could have an EPR signal in the same range. At present, it is difficult to determine the contribution of **4** to the observed signal at $g = 4.23$. The origin of a very broad signal near $g = 2$ (Figure 4, a and b) is also unclear.

The axial spectrum ($g_1 = g_2 = 2.42$, $g_3 = 2.67$) (Figure 4, a and b) belongs to the very unstable complex **5** ($\tau_{1/2}$ = 10 min at –60 °C). The same signal could be observed in the catalytic system **1**/H_2O_2 along with the rhombic spectra of the low-spin ferric hydroperoxido complexes $[(BPMEN)Fe^{III}(OOH)S]^{2+}$ (see below).

EPR spectra of the low-spin ferric complexes (heme and non-heme) show a rhombic pattern ($g_x \neq g_y \neq g_z$) with g-values in the range ca. 1–4 (one of the g-values is less than $g_e = 2.0024$)[10,23–26] These spectra differ markedly from that of **5** ($g_1 = g_2 = 2.42$, $g_3 = 2.67$). The EPR spectra of high-spin ferric complexes with TPA- and BPMEN-type ligands display an EPR signal at $g_{eff} = 4.23$.[10,23–26] Therefore, complex **5** is not the low-spin, nor the high-spin ferric complex. EPR spectra of binuclear $Fe^{III}Fe^{II}$ moieties reported for some enzymes (methane monooxygenase, ribonucleotide reductase, Rieske-type dioxygenase, etc) and model compounds exhibit resonances in the range g_1 = 1.93–2.01, g_2 = 1.85–1.92, g_3 = 1.64–1.80,[24,25] and again are very different from that of **5**. Complexes with $Fe^{III}–O–Fe^{III}$, $Fe^{IV}=O$, and $Fe^{IV}–O–Fe^{IV}$ fragments are EPR silent.[13,14,24,27] Thus, it is reasonable to assume that **5** is a binuclear $Fe^{III}Fe^{IV}$ complex. Recently, Wieghardt et al. have identified iron species formed upon photooxidation of *trans*-$[(cyclam)Fe(N_3)_2]ClO_4$ in acetonitrile solution by Mössbauer and EPR spectroscopy. The major photolysis product in liquid solution at room temperature was nitrido-bridged binuclear (Fe^{III}, Fe^{IV}) complex with localized antiferromagnetically coupled Fe^{III} ($S = 3/2$) and low-spin Fe^{IV} ($S = 1$) units, the total spin being $S = 1/2$.[28] The EPR spectrum of this (μ-nitrido) diiron complex (g-values of 2.04, 2.06, and 2.20) resembles that of complex **5**. Both the spectra display almost axial symmetry and for both spectra all the g-values are larger than g_e. Thus, complex **5** can be tentatively assigned to a mixed-valence $Fe^{III}Fe^{IV}$ complex. The formation of $Fe^{III}–O–Fe^{III}$ binuclear complexes is highly characteristic for the catalytic systems studied.[18,29] Therefore, the existence of binuclear intermediates $[(BPMEN)Fe^{III}–O–Fe^{IV}=O(BPMEN)(S)]^{3+}$ (**5**) along with mononuclear species $[(BPMEN)Fe^{IV}=O(S)]^{2+}$(**3**) seems to be rather probable. The attempts to obtain additional spectroscopic evidences in favor of the proposed structure of **5** were unsuccessful due to the low concentration of **5** with respect to the concentrations of the other iron species present in the sample.

Intermediate **5** ($\tau_{1/2}$ = 10 min at –60 °C) is far less stable than **3** ($\tau_{1/2}$ = 15 min at –10 °C). As was mentioned, in the presence of cyclohexene, the decay of **3** at –50 °C is accompanied by the rise of concentration of the 1,2-epoxycyclohexane. Thus, despite the fact that intermediate **5** could also react with cycloxehene (see below), intermediate **3** is the active species of cyclohexene epoxidation by the catalytic systems **1**/CH_3CO_3H and **1**/H_2O_2/CH_3COOH.

Catalytic Systems 2/CH_3CO_3H and 2/H_2O_2/CH_3COOH

By analogy with BPMEN-based systems, it is natural to assume that the active species of **2**/CH_3CO_3H and **2**/H_2O_2/CH_3COOH systems is the oxidoiron(IV) complex $[(TPA)Fe^{IV}=O(S)]^{2+}$ (**6**). In full agreement with this assumption, peaks of **6** (marked by points) were observed in the ^1H NMR spectra of **2**/H_2O_2/CH_3COOH and **2**/CH_3CO_3H in 1:1 CD_2Cl_2/CD_3CN at –50 °C (Figure 5). The remaining paramagnetically shifted signals belong to binuclear $Fe^{III}–O–Fe^{III}$ species.[29] Complex **6** is unstable ($\tau_{1/2}$ = 10 min at –10 °C). The most characteristic and easily assignable peaks of **6** belong to β,β′-protons of the picolinic rings [1:1 $CDCl_3/CD_2Cl_2$, –50 °C, δ = 58.8 (2 H), 49.8 (1 H), –24.9 (2 H), and –28.7 (1 H)]. The ratio between the four observed peaks (2:1:2:1) corresponds to two equivalent and one unique picolinic rings of a coordinated TPA ligand. The observed pattern of β,β′-protons of **6** resembles that for X-ray characterized complex $[(N_4Py)Fe^{IV}{=}O]^{2+}$ [δ = 44.4 (2 H), 30.05 (2 H), –11.2 (2 H), –17.8 (2 H)].[19] The assignment of the other signals of **6** is more complicated and is still not completed, as in the case of $[(N_4Py)Fe^{IV}{=}O]^{2+}$. Complex **6** is stable at –50 °C and rapidly (within several minutes) disappears at this temperature in the presence of 5 equiv. of cyclohexene. The decay of **6** was accompanied by the rise of the ^{1}H NMR peaks of 1,2-epoxycyclohexane. Fresh portions of CH_3CO_3H or H_2O_2/CH_3COOH restore the concentration of **6**. Apparently, it is the oxidoiron intermediate $[(TPA)Fe^{IV}{=}O(S)]^{2+}$ (**6**) that is the active species of the catalytic systems **2**/H_2O_2/CH_3COOH and **2**/CH_3CO_3H. An intermediate similar to intermediate **5** in the BPMEN-based system was not detected in the TPA-based analogue.

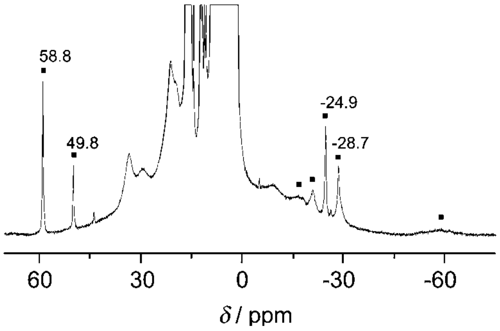


Figure 5. The ^{1}H NMR spectrum (–50 °C) of the **2**/H_2O_2/CH_3COOH system recorded 10 min after addition of H_2O_2 to **2**/CH_3OOH in a 1:1 CD_2Cl_2/CD_3CN mixture at –50 °C ([**2**] = [CH_3COOH] = 0.05 м, [H_2O_2] = 0.1 м). Points denote peaks of **6**.

Catalytic System 1/H_2O_2

The ^{1}H NMR spectrum of **1** in CD_3CN at high temperature corresponds to a paramagnetic high-spin ferrous complex. Complex **1** decreases its spin state with decreasing temperature and displays the ^{1}H NMR spectrum characteristic of diamagnetic low-spin ferrous species at –40 °C.[8,30] The addition of 2 equiv. of H_2O_2 to the 0.03 м solution of **1** in CD_3CN at 20 °C gives rise to immediate conversion of the major part of **1** into a new complex with a ^{1}H NMR spectrum very similar to that reported for binuclear complex $[(OH)(BPMEN)Fe^{III}–O–Fe^{III}(BPMEN)(H_2O)](ClO_4)_3$ (**7**).[18] Thus, the predominant iron-containing species in the **1**/H_2O_2 system is μ-oxo diferric complex **7**. To identify unstable intermediates, the reaction between **1** and H_2O_2 was studied at low temperatures.

Figure 6 shows the EPR spectrum recorded 1 min after onset of the reaction between **1** and 1.5 equiv. of H_2O_2 in a 2:1 CH_2Cl_2/CH_3CN mixture at –60 °C. It is seen that besides the characteristic signals of the low-spin ferric hydroperoxo intermediates $[(BPMEN)Fe^{III}(OOH)(CH_3CN)]^{2+}$ (**8**-CH_3CN) (g_1 = 2.218, g_2 = 2.178, g_3 = 1.967) and $[(BPMEN)Fe^{III}(OOH)(H_2O)]^{2+}$ (**8**-H_2O) (g_1 = 2.195, g_2 = 2.128, g_3 = 1.970),[6] the axially symmetric signal of complex **5** (g_1 = g_2 = 2.42 and g_3 = 2.67) is observed. In the presence of 8 equiv. of cyclohexene, the decay of **5** at –60 °C increases at least by a factor of 5, whereas the rate of **8**-CH_3CN and **8**-H_2O decomposition remains unchanged (Figure 7 and Figure 8). These data are in agreement with

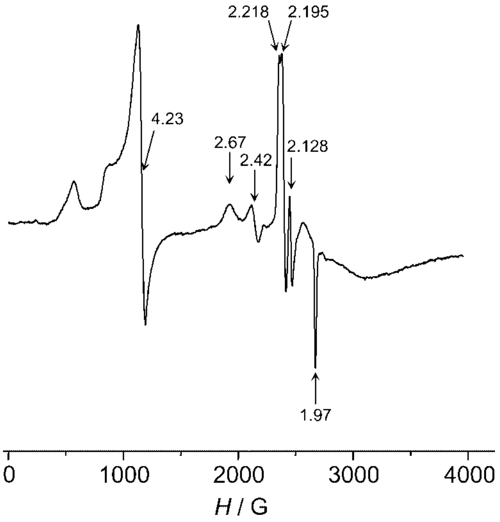


Figure 6. X-band EPR spectrum (–196 °C) recorded 1 min after mixing **1** and 1.5 equiv. of H_2O_2 at –60 °C in a 2:1 CH_2Cl_2/CH_3CN mixture. ([**1**] = 0.05 м).

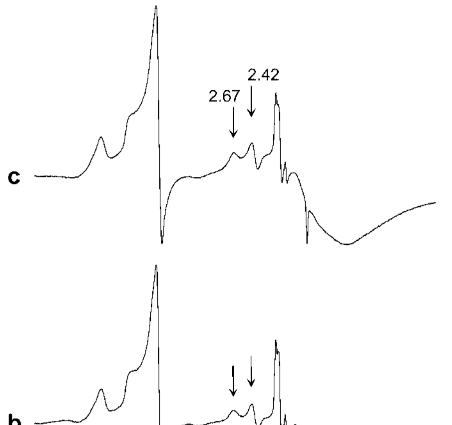


Figure 7. EPR spectra recorded 2 min (a), 5 min (b), and 7 min (c) after onset of reaction of **1** with 1.5 equiv. of H_2O_2 in a 2:1 CH_2Cl_2/CH_3CN mixture at –60 °C.([**1**] = 0.05 м). Arrows denote signals of **5**.

our assumption that **5** contains the active $Fe^{IV}=O$ moiety. The concentration of intermediates **5** and **8** does not exceed 5% of the concentration of **1**.

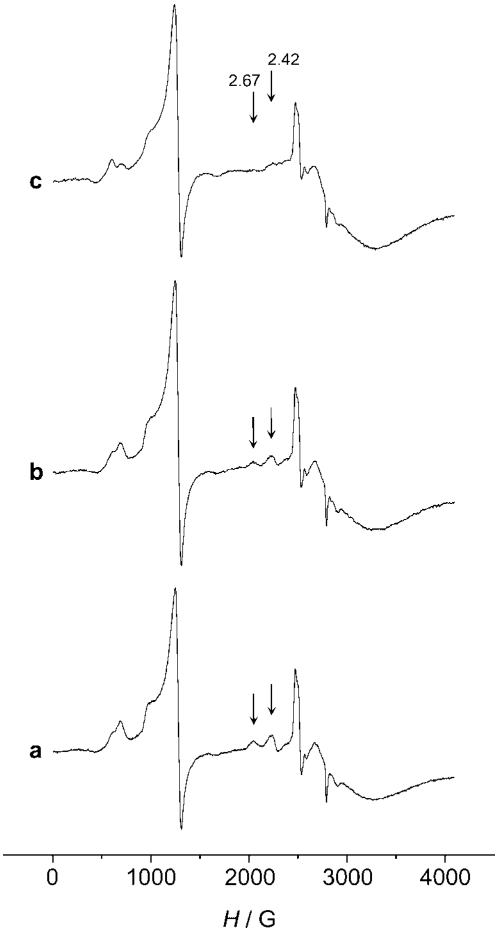


Figure 8. EPR spectra recorded 2 min (a), 3 min (b), and 6 min (c) after onset of reaction of **1** with 1.5 equiv. of H_2O_2 in a 2:1 CH_2Cl_2/CH_3CN mixture containing cyclohexene at –60 °C ([**1**] = 0.05 M, [C_6H_{10}] = 0.4 M). Arrows denote signals of **5**.

In contrast to the **1**/CH_3CO_3H and **1**/H_2O_2/CH_3COOH catalytic systems, the mononuclear iron(IV) oxido intermediate **3** was not detected in the catalytic system **1**/H_2O_2. The only observable intermediate sensitive to the presence of substrate is complex **5** with the proposed structure $[(BPMEN)Fe^{III}–O–Fe^{IV}=O(BPMEN)(S)]^{3+}$. Thus, different intermediates operate in the catalytic systems **1**/H_2O_2 and **1**/H_2O_2/CH_3COOH. This result agrees with differing activities and selectivities of the catalytic systems **1**/H_2O_2 and **1**/H_2O_2/CH_3COOH in epoxidation of olefins.[2,4,12] However, the actual role of intermediate **5** in epoxidation with **1**/H_2O_2 is far from being established. Very recently, it has been shown that binuclear iron(III)-BPMEN complexes are less active in epoxidation with H_2O_2 than mononuclear complex **1** under the same conditions.[31] This result argues against the involvement of a binuclear intermediate in the **1**/H_2O_2 system. On the other hand, the diiron complex with dinucleating, covalently linked TPA derivatives confirms the high reactivity of oxo-bridged diiron(III) species in olefin epoxidation.[32] Further studies are needed to elucidate the active species of the **1**/H_2O_2 and **2**/H_2O_2 catalytic systems.

Fortunately, for the most active and selective epoxidizing systems **1**/H_2O_2/CH_3COOH and **2**/H_2O_2/CH_3COOH, the situation is more definite. On the basis of the results of our study, the active species of these catalytic systems are mononuclear Fe^{IV} species $[(L)Fe^{IV}=O(S)]^{2+}$. The improved epoxidation activity and selectivity of the catalytic systems **1**/H_2O_2/CH_3COOH and **2**/H_2O_2/CH_3COOH, with respect to **1**/H_2O_2 and **2**/H_2O_2, is caused by the effective formation of intermediates $[(L)Fe^{IV}=O(S)]^{2+}$ via decomposition of the acylperoxido complexes $[(L)Fe^{III}(O_3CCH_3)]^{2+}$.

Experimental Section

Acetonitrile, [D$_3$]acetonitrile, dichloromethane, [D$_2$]dichloromethane, [D$_4$]acetic acid, 2-picolyl chloride hydrochloride, and *N*,*N'*-dimethyl-1,2-ethanediamine were purchased from Aldrich and used without additional purification. Hydrogen peroxide (95 %) was obtained by concentration of commercial 30% H_2O_2 under reduced pressure. The concentrated H_2O_2 diluted ten times by a 1:1 CH_2Cl_2/CH_3CN mixture was used for the preparation of samples. CH_3CO_3H (or CD_3CO_3D) was prepared by mixing equivalent amounts of 95% H_2O_2 and CH_3CO_3H (or CD_3COOD) in the presence of 1% H_2SO_4, and stirring the mixture overnight. $[(TPA)Fe^{II}(CH_3CN)_2](ClO_4)_2$ and $[(BPMEN)Fe^{II}(CH_3CN)_2](ClO_4)_2$ were synthesized following a method previously described[3,24] and satisfactorily characterized by ^1H NMR spectroscopy. To start the reaction, 1.5–2 equiv. of CH_3CO_3H or H_2O_2 was added to 0.5 mL of a 0.05 M solution of **1** or **2** in CH_2Cl_2/CH_3CN or CH_2Cl_2/CH_3CN/CH_3COOH mixtures at –60 to –50 °C directly in quartz EPR or glass NMR tubes (d = 5 mm). For kinetic EPR studies, solutions containing unstable intermediates were placed in a thermostat at an appropriate temperature directly in an EPR tube. To stop the reaction, the tube was immersed in liquid nitrogen, followed by registration of the EPR spectrum at –196 °C. For kinetic NMR studies, ^1H or ^2H NMR spectra of intermediates were recorded at selected temperatures. If necessary, the appropriate amounts of cyclohexene were added to the reaction solutions. For evaluation of the concentration of **3** by ^1H NMR, the integral intensity of the N–CH_3 peak of **3** was compared with the integral intensity of the residual peak of CD_2HCN in CD_3CN. The concentration of residual CD_2HCN in CD_3CN was preliminarily determined by ^1H NMR spectroscopy. For this goal the specified amount of $CHCl_3$ was added to CD_3CN. For evaluation of the concentration of **4**, the integral intensity of its CD_3CO_3 peak was compared with that of CD_3COOD.

EPR spectra (–196 °C) were recorded at 9.2–9.3 GHz with a Bruker ER-200D spectrometer. Measurements were made in a quartz Dewar vessel filled with liquid nitrogen. EPR signals near g = 2 were quantified by double integration with copper(II) chloride as a standard at –196 °C. $^{1,2}H$ NMR spectra were recorded at 400.13 and 61.425 MHz in 5-mm glass sample tubes, on a Bruker Avance 400 MHz NMR spectrometer. The following operating conditions were used for ^1H NMR measurements: spectral width 125 kHz, spectrum accumulation frequency 10 Hz; number of scans 5000–10000; 45° pulse at 5 µs. The ^1H and ^2H chemical shifts were referenced to the residual peak of the solvent (C*H*D$_2$CN, and C*D*H$_2$CN, δ = 1.96 ppm). The typical operating conditions used for ^2H NMR measurements were as follows: sweep width 125 kHz; spectrum accumulation frequency 2.5 Hz; number of transients 5000–10000; 45° pulse at 10 µs.

Acknowledgments

We acknowledge the financial support from the Russian Foundation of Basic Research, grant 06–03–32214.

---

[1] K. Chen, L. Que Jr, *Chem. Commun.* **1999**, 1375–1376.

[2] M. C. White, A. G. Doyle, E. N. Jacobsen, *J. Am. Chem. Soc.* **2001**, *123*, 7194–7195.

[3] M. Costas, A. K. Tipton, K. Chen, D.-H. Jo, L. Que Jr, *J. Am. Chem. Soc.* **2001**, *123*, 6722–6723.

[4] M. Fujita, L. Que Jr, *Adv. Synth. Catal.* **2004**, *346*, 190–194.

[5] G. Dubois, A. Murphy, T. D. P. Stack, *Org. Lett.* **2003**, *5*, 2469–2472.

[6] E. A. Duban, K. P. Bryliakov, E. P. Talsi, *Mendeleev Commun.* **2005**, 12–13.

[7] J. Y. Ryu, J. Kim, M. Costas, K. Chen, W. Nam, L. Que Jr, *Chem. Commun.* **2002**, 1288–1289.

[8] K. Chen, M. Costas, J. Kim, A. K. Tipton, L. Que Jr, *J. Am. Chem. Soc.* **2002**, *124*, 3026–3035.

[9] M. Fujita, M. Costas, L. Que Jr, *J. Am. Chem. Soc.* **2003**, *125*, 9912–9913.

[10] M. Costas, M. P. Mehn, M. P. Jensen, L. Que Jr, *Chem. Rev.* **2004**, *104*, 939–986.

[11] S. V. Kryatov, E. V. Rybak-Akimova, S. Schindler, *Chem. Rev.* **2005**, *105*, 2175–2226.

[12] R. Mas-Ballesté, M. Fujita, C. Hemmila, L. Que Jr, *J. Mol. Catal. A: Chem.* **2006**, *251*, 45–50.

[13] M. R. Bukowski, P. Comba, A. Lienske, C. Limberg, C. L. de Laorden, R. Mas-Ballesté, M. Merz, L. Que Jr, *Angew. Chem. Int. Ed.* **2006**, *45*, 3446–3449.

[14] M. H. Lim, J.-U. Rohde, A. Stubna, M. R. Bukowski, M. Costas, R. Y. N. Ho, E. Münck, W. Nam, L. Que Jr, *Proc. Natl. Acad. Sci.* **2003**, *100*, 3665–3670.

[15] C. Kim, K. Chen, J. Kim, L. Que Jr, *J. Am. Chem. Soc.* **1997**, *119*, 5964–5965.

[16] M. V. Lobanova, K. P. Bryliakov, E. A. Duban, E. P. Talsi, *Mendeleev Commun.* **2003**, 175–177.

[17] M. J. Park, J. Lee, Y. Suh, J. Kim, W. Nam, *J. Am. Chem. Soc.* **2006**, *128*, 2630–2634.

[18] S. Taktak, S. V. Kryatov, E. V. Rybak-Akimova, *Inorg. Chem.* **2004**, *43*, 7196–7209.

[19] E. J. Klinker, J. Kajzer, W. W. Brennessel, N. L. Woodroom, C. J. Cramer, L. Que Jr, *Angew. Chem. Int. Ed.* **2005**, *44*, 3690–3694.

[20] J.-U. Rohde, J.-H. In, M. H. Lim, W. W. Brennessel, M. R. Bukowski, A. Stubna, E. Münck, W. Nam, L. Que Jr, *Science* **2003**, *229*, 1037–1039.

[21] ^{1}H NMR spectrum of **3** (1:1 CD_2Cl_2/CD_3CN mixture, –50 °C, δ values, ppm): –175.4 (s, 2 H, $\Delta\vartheta_{1/2}$ = 1500 Hz, CH*H*–CH*H*), –136.3 (s, 2 H, $\Delta\vartheta_{1/2}$ = 1100 Hz, CH*H*–N), –81.3 (s, 6 H, $\Delta\vartheta_{1/2}$ = 2100 Hz, CH_3), –58.9 (s, 2 H, $\Delta\vartheta_{1/2}$ = 740 Hz, C*H*H–C*H*H),–49.7 (s, 2 H, $\Delta\vartheta_{1/2}$ = 730 Hz, C*H*H–N), –22.0 (s, 2 H, $\Delta\vartheta_{1/2}$ = 240 Hz, picolinic H), –11.7 (s, 2 H, $\Delta\vartheta_{1/2}$ = 220 Hz, picolinic H), –0.81 (s, 2 H, $\Delta\vartheta_{1/2}$ = 230 Hz, picolinic H), 54 (s, 2 H, $\Delta\vartheta_{1/2}$ = 220 Hz, picolinic H).

[22] R. D. Arasasingham, A. L. Balch, C. R. Cornman, L. Latos-Grazynski, *J. Am. Chem. Soc.* **1989**, *111*, 4357–4363.

[23] M. Fontecave, S. Ménage, C. Duboc-Toia, *Coord. Chem. Rev.* **1998**, *178–180*, 1555–1572.

[24] E. I. Solomon, T. C. Brunold, M. I. Davis, J. N. Kemsley, S.-K. Lee, N. Lehnert, F. Neese, A. J. Skulan, Y.-S. Yang, J. Zhou, *Chem. Rev.* **2000**, *100*, 235–349.

[25] E. Y. Tshuva, S. J. Lippard, *Chem. Rev.* **2004**, *104*, 987–1012.

[26] L. Duelund, R. Hazell, C. J. McKenzie, L. P. Nielsen, H. Toftlund, *J. Chem. Soc., Dalton Trans.* **2001**, 152–156.

[27] A. Ghosh, F. Tiago de Oliveira, T. Yano, T. Nishioka, E. S. Beach, I. Kinoshita, E. Münck, A. D. Ryabov, C. P. Horwitz, T. J. Collins, *J. Am. Chem. Soc.* **2005**, *127*, 2505–2513.

[28] K. Meyer, E. Bill, B. Mienert, T. Weyhermüller, K. Wieghardt, *J. Am. Chem. Soc.* **1999**, *121*, 4859–4876.

[29] Y. Dong, H. Fujii, M. P. Hendrich, R. A. Leising, G. Pan, C. R. Randall, E. C. Wilkinson, Y. Zang, L. Que Jr, B. G. Fox, K. Kauffmann, E. Münck, *J. Am. Chem. Soc.* **1995**, *117*, 2778–2792.

[30] K. P. Bryliakov, E. A. Duban, E. P. Talsi, *Eur. J. Inorg. Chem.* **2005**, 72–76.

[31] S. Taktak, S. V. Kryatov, T. E. Haas, E. V. Rybak-Akimova, *J. Mol. Catal. A* **2006**, *259*, 24–34.

[32] M. Kodera, M. Itoh, K. Kano, T. Funabiki, M. Reglier, *Angew. Chem. Int. Ed.* **2005**, *44*, 7104–7106.

Received: September 25, 2006