Pergamon

Tetrahedron 58 (2002) 9231–9237

TETRAHEDRON

Hydroperoxidation of methane and other alkanes with H_2O_2 catalyzed by a dinuclear iron complex and an amino acid

Galina V. Nizova,[a] Bernt Krebs,[b] Georg Süss-Fink,[c] Siegfried Schindler,[d] Lars Westerheide,[b] Laura Gonzalez Cuervo[c] and Georgiy B. Shul'pin[a,*]

[a]*Semenov Institute of Chemical Physics, Russian Academy of Sciences, ul. Kosygina 4, Moscow 119991, Russian Federation*
[b]*Anorganisch-chemisches Institut, Universität Münster, D-48149 Münster, Germany*
[c]*Institut de Chimie, Université de Neuchâtel, CH-2007 Neuchâtel, Switzerland*
[d]*Institut für Anorganische-Chemie, Universität Erlangen-Nürnberg, D-91058 Erlangen, Germany*

Received 13 May 2002; revised 4 September 2002; accepted 16 September 2002

Abstract—The compound $[Fe_2(HPTB)(\mu\text{-}OH)(NO_3)_2](NO_3)_2{\cdot}CH_3OH{\cdot}2H_2O$ (**1**) containing a dinuclear iron(III) complex in which HPTB=*N*,*N*,*N*′,*N*′-tetrakis(2-benzimidazolylmethyl)-2-hydroxo-1,3-diaminopropane catalyzes the oxidation of alkanes with hydrogen peroxide in acetonitrile solution at room temperature only if certain amino acids (pyrazine-2-carboxylic, pyrazine-2,3-dicarboxylic or picolinic acid) are added to the reaction mixture. Alkyl hydroperoxides are formed as main reaction products. The turnover numbers attain 140 for cyclohexane, 21 for ethane and four for methane oxidation. The oxidation proceeds non-stereoselectively and bond selectivity parameters are low which testifies the participation of hydroxyl radicals in alkane functionalization.

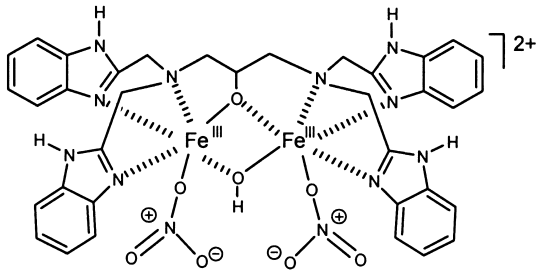
1. Introduction

Oxygen-activating proteins and especially enzymes containing non-heme diiron sites attracted considerable interest in last decades.[1–20] For example, it is known that hemerythrin, which has been isolated from a variety of marine invertebrates, functions in a manner comparable to hemoglobin (Scheme 1). Some of enzymes with diiron sites are capable of activating C–H bonds.[8,16] Methane monooxygenase (MMO) from methane-utilizing bacteria converts methane to methanol in a process that is coupled to the oxidation of biological reducing agent NADH:

$$CH_4 + O_2 + H^+ + NADH = CH_3OH + H_2O + NAD^+$$

In a simplified version, the dioxygen activation and the consecutive methane hydroxylation in the hydroxylase component (MMOH) of this enzyme is shown in Scheme 2. The reaction is assumed to proceed via intermediates **P** and **Q** which are a (μ-peroxo)diiron(III) and a diiron(IV) species, respectively.

Various dinuclear iron complexes have been synthesized as structural models of diiron non-heme enzymes and their properties were studied. In some cases activity of such complexes in saturated and aromatic hydrocarbon oxygenations was reported.[8,16,21–32] Usually polydentate nitrogen-containing ligands have been used in these complexes, and either molecular oxygen or hydrogen peroxide have been employed as oxidant. The efficiency of these systems was rarely high: The turnover numbers (TON, i.e. the number of moles of all products per one mol of a catalyst) did not exceed 2–30 in the oxidations of cyclohexane and other higher alkanes.



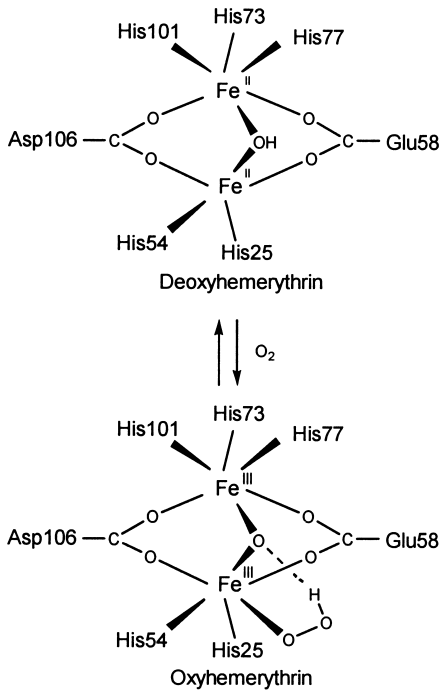
Cation of compound **1**
(catalyst)

This work is devoted to a study of alkane oxidation with hydrogen peroxide catalyzed by the compound $[Fe_2(HPTB)(\mu\text{-}OH)(NO_3)_2](NO_3)_2{\cdot}CH_3OH{\cdot}2H_2O$ (**1**)

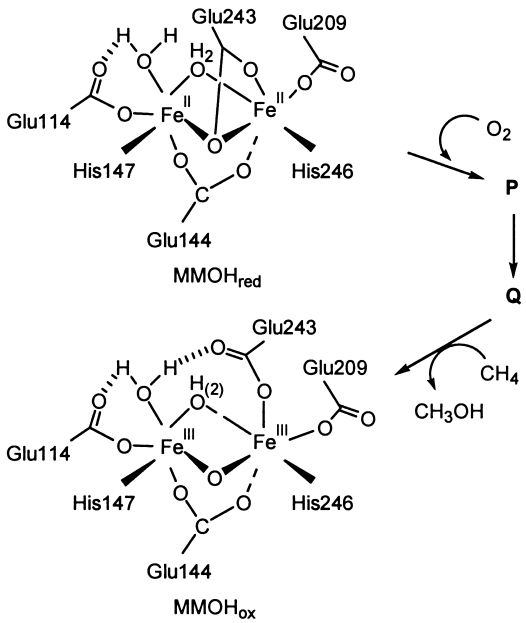
Keywords: alkanes; hydroperoxidation; alkyl hydroperoxides; biomimetics; homogeneous catalysis; hydrogen peroxide; iron complexes; methane; oxidation; oxygenation; picolinic acid; pyrazine-2-carboxylic acid.

* Corresponding author. Tel.: +7-095-939-7317; fax: +7-095-938-2156; e-mail: shulpin@chph.ras.ru (G.B. Shul'pin) http://members.fortunecity.com/shulpin

0040–4020/02/$ - see front matter
PII: S0040-4020(02)01182-1



Scheme 1. Two forms of hemerythrin.



Scheme 2. Diiron sites of the hydroxylase component of methane monooxygenase.

(HPTB=*N*,*N*,*N*′,*N*′-tetrakis(2-benzimidazolylmethyl)-2-hydroxo-1,3-diaminopropane) containing the cationic diiron(III) complex the structure of which is shown above.[33–39]

2. Experimental

Synthesis and properties of compound **1** were published previously in the literature.[33–39]

The oxidations of higher hydrocarbons were carried out in air in thermostated Pyrex cylindrical vessels with vigorous stirring. The total volume of the reaction solution was 0.5–5 mL. Initially, a portion of 35% aqueous solution of hydrogen peroxide ('Fluka') was added to the solution of the catalyst, co-catalyst and substrate in acetonitrile (Fluka, was distilled over P_2O_5 before the reaction).

The oxidations of light alkanes (ethane and methane) were carried out in a Pyrex inlet tube placed in an stainless steel autoclave with intensive stirring (volume of the reaction solution was 1 mL and total volume of autoclave was 100 mL). The autoclave was charged with air (under atmospheric pressure) and then, consecutively, with the reaction solution containing the catalyst and co-catalyst in acetonitrile and the alkane to the appropriate pressure.

The reaction solutions were analyzed by GC (instruments LKhM-80-6, columns 2 m with 5% Carbowax 1500 on 0.25–0.315 mm Inerton AW-HMDS; carrier gas was argon and DANI-86.10, capillary column 50 m×0.25 mm× 0.25 μm, Carbowax 20M; integrator SP-4400; the carrier gas was helium). Usually samples were analyzed twice, i.e. before and after the addition of the excess of solid PPh_3. This very simple method (solid triphenylphosphine is added to the samples 10–15 min before the GC analysis and the chromatogram obtained is compared with the chromatogram prepared for the sample untreated with PPh_3) was proposed and described by us earlier.[16,40–46] Since alkyl hydroperoxides, which are transformed in the GC injector into a mixture of the corresponding ketone and alcohol, are quantitatively reduced with PPh_3 to give the corresponding alcohol, this method allows to calculate the real concentrations not only of the hydroperoxide but of the alcohols and ketones present in the solution at a given moment. It should be noted that total concentration of the oxygenates (cyclohexanol and cyclohexanone in the oxidation of cyclohexane) determined before treatment of the reaction sample with PPh_3 is usually lower than the concentration of the same products after reduction with PPh_3. This difference can be easily understood, if we assume either the partial decomposition of ROOH in the GC to produce ring-opened products (e.g. adipic acid) or/and the appearance of ROOH as a separate peak on the chromatogram (in some cases we were able to detect such peaks). Due to this difference, for precise determination of oxygenate concentrations, we used in many experiments data obtained only after reduction of the reaction sample with PPh_3, remembering, however, that really the reaction mixture consists of cyclohexyl hydroperoxide (as predominant product) and cyclohexanone and cyclohexanol. Authentic samples of all oxygenated products were used to attribute the peaks in chromatograms (comparison of retention times was carried out for different regimes of GC-analysis).

In experiments involving molecular oxygen evolution, the volume of dioxygen evolved was measured using a thermostated burette. The reaction system was connected to a manometric burette with water which was saturated with oxygen prior to use. After certain time intervals, the pressure was equilibrated using a separation funnel by adjusting the water level to the same heights.

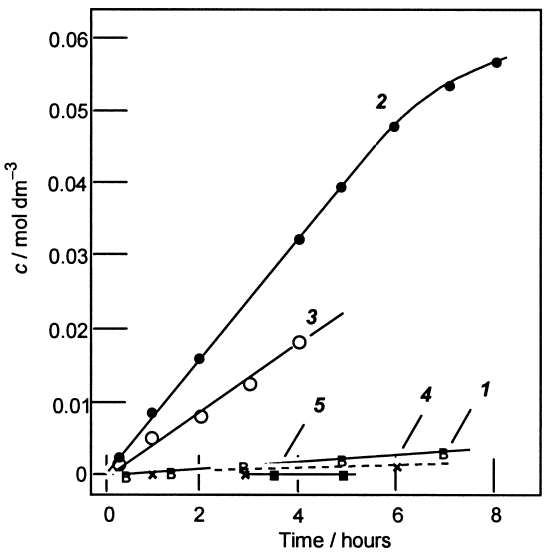


Figure 1. Accumulation of oxygenated products (predominantly cyclohexyl hydroperoxide) in the reaction of cyclohexane (0.46 mol dm^{-3}) with hydrogen peroxide (0.625 mol dm^{-3}) in acetonitrile at 25°C catalyzed by **1** (4×10^{-4} mol dm^{-3}) in the absence of additives (curve 1) and in the presence of amino acids (0.01 mol dm^{-3}): pyrazinic acid (curve 2), pyrazine-2,3-dicarboxylic acid (curve 3), picolinic acid (curve 4) and pyridine-2,6-dicarboxylic acid (curve 5).

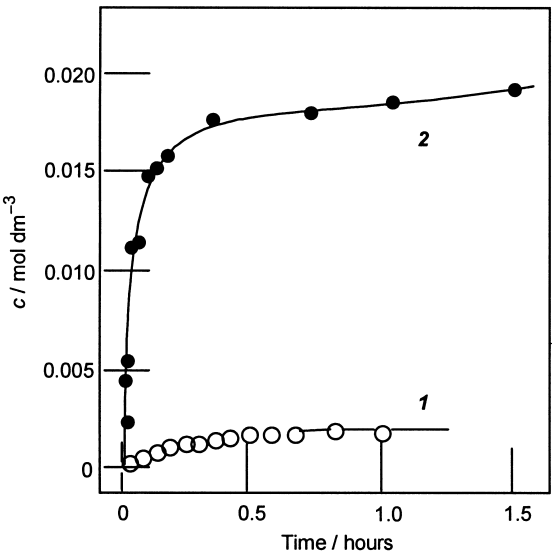


Figure 2. Dioxygen evolution in the reaction of hydrogen peroxide (0.625 mol dm^{-3}) with **1** (4×10^{-4} mol dm^{-3}) in acetonitrile at 25°C in the presence of cyclohexane (0.46 mol dm^{-3}) in the absence of additives (curve 1) and in the presence of pyrazinic acid (0.01 mol dm^{-3}) (curve 2).

3. Results and discussion

Compound **1** is insoluble in dry acetonitrile. If some amount of 35% aqueous hydrogen peroxide is added to the suspension, the complex is dissolved rapidly to produce a homogeneous solution. We have found that when used in relatively low concentration (4×10^{-4} mol dm^{-3}) compound **1** does not catalyze cyclohexane oxidation with H_2O_2 in acetonitrile at room temperature (Fig. 1, curve 1). However, when certain amino acids—pyrazine-2-carboxylic (pyrazinic acid, PCA, compound **2**) or pyrazine-2,3-dicarboxylic acid—are added in concentration of 0.01 mol dm^{-3} efficient cyclohexane oxygenation can be noticed (Fig. 1, curves 2 and 3; Table 1, entries 2–4). For the case of pyrazinic acid, the total concentration of oxygenates attains 0.056 mol dm^{-3} after 8 h which corresponds to TON=140 (Fig. 1, curve 2; Table 1, entry 3). The efficiency of pyrazine-2,3-dicarboxylic acid as co-catalyst is somewhat lower under exactly the same conditions (Fig. 1, curve 3). Picolinic (compound **3**) and pyridine-2,6-dicarboxylic acid are inactive when used in concentration of 0.01 mol dm^{-3} (Fig. 1, curves 4 and 5, respectively).

Pyrazinic acid (PCA)
2

Picolinic acid
3

Co-catalysts

Concentrations of cyclohexanone and cyclohexanol formed in the reaction were measured by GC twice—before and after treatment the samples with triphenylphosphine (see Section 2).[16,40–46] This method showed that cyclohexyl hydroperoxide, $C_6H_{11}OOH$, was the main (ca. 90%) product in the oxidation while cyclohexanone, and cyclohexanol were formed in much lower concentrations. Cyclohexane oxygenation is accompanied by dioxygen evolution which is negligible in the absence of co-catalyst (compare Fig. 2, curves 1 and 2). It is noteworthy that intensive dioxygen evolution occurs only in the initial period of the reaction. This can testify that a catalytically active species is gradually transformed into other species which can

Table 1. Alkane oxidations with H_2O_2 catalyzed by compound **1**

Entry	Substrate	Co-catalyst, L	Time (h)	Yield[a]	TON
1	Cyclohexane	None	4	0.5	–
2	Cyclohexane	Pyrazinic acid (**2**)	4	8	87
3			6	12	140
4	Cyclohexane	Pyrazine-2,3-dicarboxylic acid	4	4	45
5	Cyclohexane	Picolinic acid (**3**)	4	0.4	4
6	Cyclohexane	Pyridine-2,6-dicarboxylic acid	4	0.1	1
7	Methane	Pyrazinic acid (**2**)	6	0.3	4
8	Ethane	Pyrazinic acid (**2**)	6	1.4	21

Reaction conditions. Solvent, acetonitrile; 25°C; [**1**]=4×10^{-4} mol dm^{-3}; [L]=0.01 mol dm^{-3}; $[H_2O_2]_0$=0.6 mol dm^{-3}; [cyclohexane]$_0$=0.46 mol dm^{-3}; methane, 90 bar; ethane, 30 bar.

[a] Yields (%) are based on [cyclohexane]$_0$ or (for the methane and ethane oxidations) on $[H_2O_2]_0$.

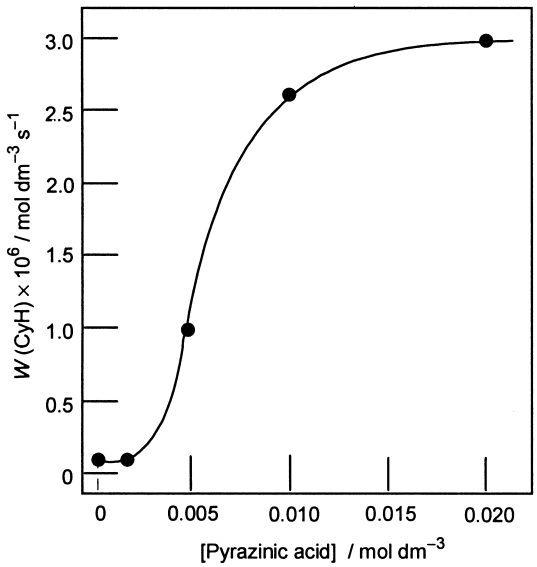


Figure 3. Oxidation rate vs concentrations of pyrazinic acid **2** added in the reaction of hydrogen peroxide (0.625 mol dm^{-3}) with cyclohexane (0.46 mol dm^{-3}) catalyzed by **1** (4×10^{-4} mol dm^{-3}) in acetonitrile at 25°C.

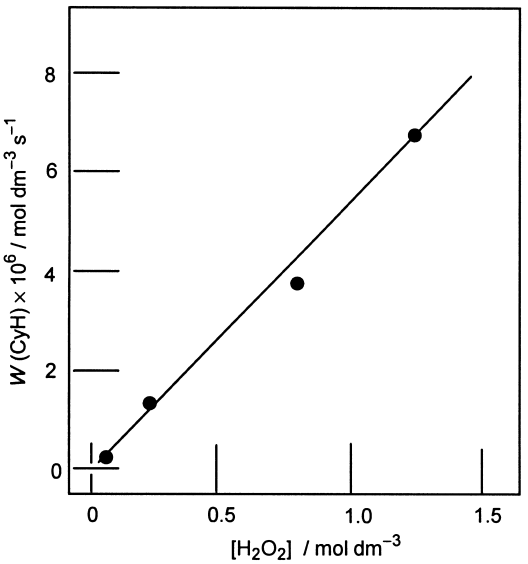


Figure 5. Oxidation rate vs initial concentration of H_2O_2 in its reaction with cyclohexane (0.46 mol dm^{-3}) catalyzed by **1** (4×10^{-4} mol dm^{-3}) and pyrazinic acid **2** (0.01 mol dm^{-3}) in acetonitrile at 25°C.

oxygenate cyclohexane but is less efficient in the non-productive hydrogen peroxide decomposition to O_2 and H_2O.

The reaction requires relatively high concentration of pyrazinic acid as co-catalyst. It is interesting that the dependence of the reaction rate on the pyrazinic acid concentration has an S-like shape (Fig. 3). Surprisingly, we have found that picolinic acid (compound **3**) also accelerates the cyclohexane oxygenation but in this case the co-catalyst should be used in much smaller concentration. Indeed, the curve for the initial rate dependence on the concentration of co-catalyst **3** has a maximum at approximately 4×10^{-4} mol dm^{-3} (Fig. 4). At relatively high concentrations of **3** no oxygenation occurs (see Fig. 1, curve 4; Table 1, entry 5).

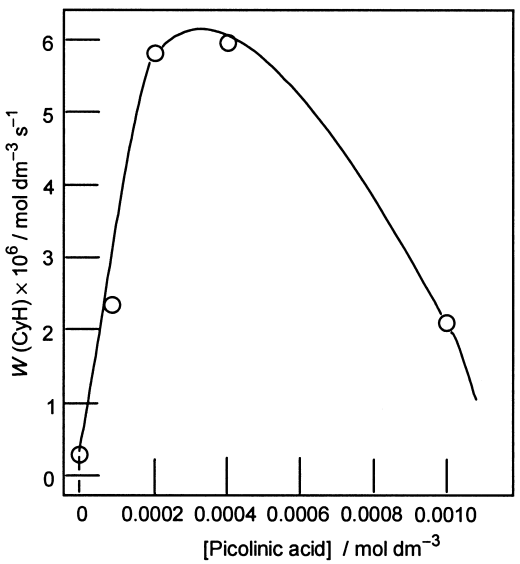


Figure 4. Oxidation rate vs concentrations of picolinic acid **3** added to the reaction of hydrogen peroxide (0.625 mol dm^{-3}) with cyclohexane (0.46 mol dm^{-3}) catalyzed by **1** (4×10^{-4} mol dm^{-3}) in acetonitrile at 25°C.

The cyclohexane oxygenation reaction is of a first order with respect to both hydrogen peroxide and alkane concentration since the initial rate of the reaction is proportional to $[H_2O_2]_0$ and $[\text{cyclohexane}]_0$, respectively (see Figs. 5 and 6, respectively).

Finally, we investigated the oxidation of light alkanes by the system under discussion. Ethane was transformed mainly to ethyl hydroperoxide as well as to a minor amount of acetaldehyde (Fig. 7). Acetic acid in a very small concentration was detected (1×10^{-4} mol dm^{-3}) after 6 h. After this time, the concentrations of ethyl hydroperoxide and acetaldehyde were measured to be 6.8×10^{-3} and 1.4×10^{-3} mol dm^{-3}. Thus total TON attains for ethane 21. Methane (pressure 90 bar) was oxidized with hydrogen peroxide (0.6 mol dm^{-3}) in acetonitrile at 25°C in the

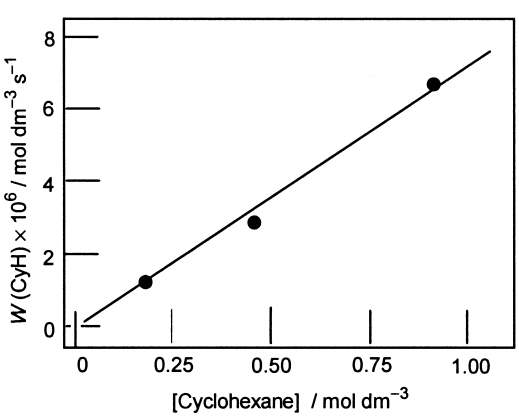


Figure 6. Oxidation rate vs initial concentration of cyclohexane in its reaction with H_2O_2 (0.625 mol dm^{-3}) catalyzed by **1** (4×10^{-4} mol dm^{-3}) and pyrazinic acid **2** (0.01 mol dm^{-3}) in acetonitrile at 25°C.

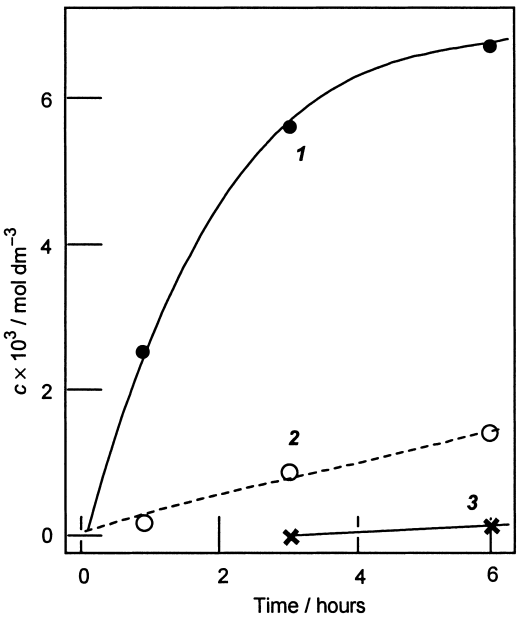


Figure 7. Accumulation of oxygenated products in the reaction of ethane (pressure 30 bar) with hydrogen peroxide (0.6 mol dm^{-3}) in acetonitrile at 25°C catalyzed by **1** (4×10^{-4} mol dm^{-3}) in the presence of pyrazinic acid **2** (0.01 mol dm^{-3}). Curves are shown for ethyl hydroperoxide (curve 1), acetaldehyde (curve 2) and acetic acid (curve 3).

presence of **1** (4×10^{-4} mol dm^{-3}) and **2** (0.01 mol dm^{-3}) to produce after 6 h methyl hydroperoxide (1.2×10^{-3} mol dm^{-3}) and formaldehyde (4×10^{-4} mol dm^{-3}) with TON=4.

In order to get a mechanistic understanding of the reaction with saturated hydrocarbons, we also studied the oxidation of higher branched and cyclic alkanes with hydrogen peroxide. The selectivity parameters thus obtained are summarized in Table 2. For comparison, the corresponding parameters measured for oxidations by certain other systems are also given. It can be seen that all selectivity parameters are close to that obtained for the systems known to oxidize alkanes via formation of hydroxyl radicals. These systems ('O_2–H_2O_2–$h\nu$', 'O_2–H_2O_2–$FeSO_4$' and H_2O_2–VO_3^-–pyrazinic acid) are characterized with relatively low selectivity parameters 1:2:3:4 and 1°:2°:3° (approximately 1:5:5:5 for *n*-heptane, 1:5:15 for 3-methylhexane and methylcyclohexane and 1:3:7 for isooctane). The oxidation with the 'H_2O_2–compound **1**–pyrazinic acid' system proceeds non-stereoselectively (the *t*/*c* parameter was found to be 3.5 and 5.1 for *cis* and *trans*-decalin, respectively) which is typical for systems operating via hydroxyl radicals. In contrast, the 'H_2O_2–$LMn^{IV}(O)_3Mn^{IV}L^{2+}$–acetic acid' system (where L=1,4,7-trimethyl-1,4,7-triazacyclononane),[16,51–55] which does not apparently involve free hydroxyl radicals, exhibits stereoselectivity (*t*/*c*=0.12 and 33 for the oxidation of *cis* and *trans*-decalin, respectively) and noticeably higher 1:2:3:4 and 1°:2°:3° parameters.

On the basis of the results described above we can propose the following mechanism of alkane oxidation by the H_2O_2–compound **1**–pyrazinic acid system which is similar to the mechanism operating in H_2O_2–Fe^{III} systems.[16] The first step of the process is the reduction of one Fe^{III} ions with a hydrogen peroxide molecule to produce hydroperoxy radicals and Fe^{II}:

$$Fe^{III}–Fe^{III} + H_2O_2 = Fe^{III}–Fe^{II} + H^+ + HOO^{\cdot}$$

$$Fe^{III}–Fe^{II} + H_2O_2 = Fe^{II}–Fe^{II} + H^+ + HOO^{\cdot}.$$

Subsequent reactions proceed partly via stages operative in Fenton's reagent and give rise to the formation of both molecular oxygen and hydroxyl radicals:

$$Fe^{III}–Fe^{III} + HOO^{\cdot} = Fe^{III}–Fe^{II} + H^+ + O_2$$

$$HOO^{\cdot} + HOO^{\cdot} = H_2O_2 + O_2$$

$$Fe^{III}–Fe^{II} + H_2O_2 = Fe^{III}–Fe^{III} + HO^- + HO^{\cdot}$$

$$Fe^{II}–Fe^{II} + H_2O_2 = Fe^{III}–Fe^{II} + HO^- + HO^{\cdot}$$

Table 2. Selectivities of alkane oxidations by various systems in MeCN

Entry	System	Hydrocarbon oxidized/the selectivity parameter[a]							
		n-Heptane (1:2:3:4)	3-Methyl-hexane (1°:2°:3°)	2,4,4-Tri-methylpentane (1°:2°:3°)	Methyl-cyclohexane (1°:2°:3°)	*cis*-Decalin (*t*/*c*)	*trans*-Decalin (*t*/*c*)	Toluene	
								Me/Ri	*o*/*m*/*p*
1	H_2O_2–**1**–**2**	1:5.6:5.9:4.9	1:5.0:14	1:3.5:7.8	1:5.9:13	3.5	5.1	0.5	38:33:29
2	O_2–H_2O_2–$h\nu$	1:7:6:7	1:4:12	1:2:6		1.3	2.7		
3	O_2–H_2O_2–$FeSO_4$	1:5:5:4.5		1:3:6		3.4	8.8		
4	H_2O_2–VO_3^-–**2**[b]	1:6.2:6.3:5.3	1:5.7:22	1:4:9	1:6:18	2.1	2.4	0.5	50:23:27
5	H_2O_2-$Fe(ClO_4)_3$		1:4:30	1:5:45	1:7:43			1.1	60:26:14
6	H_2O_2–$Fe(ClO_4)_3$–**2**		1:5:45	1:5:45	1:8:30			0.35	67:18:15
7	H_2O_2–Mn(IV)–CH_3COOH[c]	1:46:35:34	1:22:200	1:5:55	1:26:200	0.12	33	2.0	38:18:44

The concentrations of alcohols formed in the reaction were measured after reduction with PPh_3.

[a] Parameter 1:2:3:4 is normalized (i.e. calculated taking into account the number of hydrogen atoms at each position) relative reactivities of hydrogen atoms in positions 1, 2, 3, and 4 of *n*-heptane chain, respectively. Parameter 1°:2°:3° is normalized relative reactivities of hydrogen atoms at primary, secondary and tertiary carbons, respectively. Parameter *t*/*c* is the *trans*/*cis* ratio of isomers of *tert*-alcohols formed in the oxidation of *cis* or *trans*-decalin. Parameter Me/Ri is non-normalized relative reactivities of the methyl hydrogens and aromatic hydrogens. Parameter *o*/*m*/*p*is the non-normalized ratio of concentrations of *ortho*, *meta*, and *para*-cresols formed in the reaction.

[b] For this system, see Refs. 8,16,41,45,47–50.

[c] Mn(IV) is complex $LMn^{IV}(O)_3Mn^{IV}L^{2+}$, where L=1,4,7-trimethyl-1,4,7-triazacyclononane. The oxidation at 20°C. For this system, see Refs. 16, 51–55.

The interaction of Fe^{II} with H_2O_2 possibly begins from the formation of a hydroperoxy derivative similar to that proposed for the hemerythrin oxidized form (see Scheme 1). Apparently, certain amino acids added to the reaction mixture play a very important role in this stage, because addition of these amino acids dramatically enhances the oxidation efficiency. We can assume that an amino acid facilitates the proton transfer between the coordinated H_2O_2 molecule and ligands at iron centers to produce the Fe–OOH fragment (see a discussion of such type processes in vanadium-PCA-catalyzed oxidations[48–50]). Furthermore, hydroxyl radical attacks an alkane molecule and the alkyl radical thus formed adds rapidly an oxygen molecule affording corresponding alkyl peroxy radical:

$$RH + HO^{\cdot} = R^{\cdot} + H_2O$$

$$R^{\cdot} + O_2 = ROO^{\cdot}$$

This radical can be reduced by one of the two iron(II) centers in the dinuclear complex and, after addition of a proton, a molecule of the alkyl hydroperoxide is formed:

$$ROO^{\cdot} + Fe^{II}–Fe^{II} = ROO^{-} + Fe^{III}–Fe^{II}$$

$$ROO^{-} + H^{+} = ROOH$$

We realize that the scheme described above is a very simplified sequence of reactions which operate in our system. One can assume that in addition or instead of hydroxyl radicals, metal-containing oxygen-centered radicals are species which abstract hydrogen atoms from alkanes to produce corresponding alkyl radicals. In any case, nevertheless, activation of inert C–H bonds in alkanes proceeds with low selectivity via attack of strong oxygen-centered radicals. Such a mechanism is postulated for the alkane oxidations by MMO and, thus the system described in the present paper can be considered as a structural and functional model of MMO.

Acknowledgements

We thank the Russian Basic Research Foundation (grant No. 98-03-32015a) and the Swiss National Science Foundation (grant No. 20-64832.01) for support. The authors are indebted to Dr Yuriy N. Kozlov for useful discussions.

References

1. Kurtz, Jr. D. M. *Chem. Rev.* **1990**, *90*, 585–606.
2. Vincent, J. B.; Oliver-Lilley, G. L.; Averill, B. A. *Chem. Rev.* **1990**, *90*, 1447–1467.
3. Wilkins, R. G. *Chem. Soc. Rev.* **1992**, *21*, 172–178.
4. Feig, A. L.; Lippard, S. *J. Chem. Rev.* **1994**, *94*, 759–805.
5. Sychev, A. Ya.; Isak, V. G. *Russ. Chem. Rev.* **1995**, *64*, 1105–1129.
6. Que, Jr. L.; Dong, Y. *Acc. Chem. Rev.* **1996**, *29*, 190–196.
7. Wallar, B. J.; Lipscomb, J. D. *Chem. Rev.* **1996**, *96*, 2626–2657.
8. Shilov, A. E.; Shul'pin, G. B. *Chem. Rev.* **1997**, *97*, 2879–2932.
9. Siegbahn, P. E. M.; Crabtree, R. H. *J. Am. Chem. Soc.* **1997**, *119*, 3103–3113.
10. Yoshizawa, K.; Ohta, T.; Yamabe, T.; Hoffmann, R. *J. Am. Chem. Soc.* **1997**, *119*, 12311–12321.
11. van der Beuken, E. K.; Feringa, B. L. *Tetrahedron* **1998**, *54*, 12985–13011.
12. Fontecave, M.; Ménage, S.; Duboc-Toia, C. *Coord. Chem. Rev.* **1998**, *178–180*, 1555–1572.
13. Willems, J.-P.; Valentine, A. M.; Gurbiel, R.; Lippard, S. J.; Hoffman, B. M. *J. Am. Chem. Soc.* **1998**, *120*, 9410–9416.
14. Deeth, R. J.; Dalton, H. *JBIC* **1998**, *3*, 302–306, and subsequent papers in this issue.
15. Valentine, A. M.; Stahl, S. S.; Lippard, S. J. *J. Am. Chem. Soc.* **1999**, *121*, 3876–3887.
16. Shilov, A. E.; Shul'pin, G. B. Oxidation in Living Cells and its Chemical Models. *Activation and Catalytic Reactions of Saturated Hydrocarbons in the Presence of Metal Complexes*; Kluwer Academic: Dordrecht, 2000; Chapter XI, pp 466–522.
17. Costas, M.; Chen, K.; Que, Jr. L. *Coord. Chem. Rev.* **2000**, *200–202*, 517–544.
18. Solomon, E. I.; Brunold, T. C.; Davis, M. I.; Kemsley, J. N.; Lee, S.-K.; Lehnert, N.; Neese, F.; Skulan, A. J.; Yang, Y.-S.; Zhou, J. *Chem. Rev.* **2000**, *100*, 235–349.
19. Solomon, E. I. *Inorg. Chem.* **2001**, *40*, 3656–3669.
20. Lee, D.; Lippard, S. J. *Inorg. Chem.* **2002**, *41*, 827–837.
21. Nishida, Y.; Yamada, K. *J. Chem. Soc., Dalton Trans.* **1990**, 3639–3641.
22. Kitajima, N.; Ito, M.; Fukui, H.; Moro-oka, Y. *J. Chem. Soc., Chem. Commun.* **1991**, 102–104.
23. Fish, R. H.; Konings, M. S.; Oberhausen, K. J.; Fong, R. H.; Yu, W. M.; Christou, G.; Vincent, J. B.; Coggin, D. K.; Buchanan, R. M. *Inorg. Chem.* **1991**, *30*, 3002–3006.
24. Belova, V. S.; Gimanova, I. M.; Stepanova, M. L.; Khenkin, A. M.; Shilov, A. E. *Doklady Akad. Nauk SSSR* **1991**, *316*, 653–657.
25. Kulikova, V. S.; Gritsenko, O. N.; Shteinman, A. A. *Mendeleev Commun.* **1996**, 119–120.
26. Ménage, S.; Galey, J.-B.; Hussler, G.; Seité, M.; Fontecave, M. *Angew. Chem., Int. Ed. Engl.* **1996**, *35*, 2353–2355.
27. Ito, S.; Okuno, T.; Itoh, H.; Ohba, S.; Matsushima, H.; Tokii, T.; Nishida, Y. *Z. Naturforsch.* **1997**, *52b*, 719–727.
28. Knops-Gerrits, P. P.; Dick, S.; Weiss, A.; Genet, M.; Rouxhet, P.; Li, X. Y.; Jacobs, P. A. In *Third World Congress on Oxidation Catalysis*; Grasselli, R. K., Oyama, S. T., Gaffney, A. M., Lyons, J. E., Eds.; Elsevier: Amsterdam, 1997; pp 1061–1070.
29. Duboc-Toia, C.; Ménage, S.; Lambeaux, C.; Fontecave, M. *Tetrahedron Lett.* **1997**, *38*, 3727–3730.
30. Ménage, S.; Galey, J.-B.; Dumats, J.; Hussler, G.; Seité, M.; Luneau, I. G.; Chottard, G.; Fontecave, M. *J. Am. Chem. Soc.* **1998**, *120*, 13370–13382.
31. Nishino, S.; Hosomi, H.; Ohba, S.; Matsushima, H.; Tokii, T.; Nishida, Y. *J. Chem. Soc., Dalton Trans.* **1999**, 1509–1513.
32. Roelfes, G.; Lubben, M.; Hage, R.; Que, Jr. L.; Feringa, B. L. *Chem. Eur. J.* **2000**, *6*, 2152–2159.
33. Nishida, Y.; Takeuchi, M.; Shimo, H.; Kida, S. *Inorg. Chim. Acta* **1984**, *96*, 115–119.
34. Brennan, B.; Chen, Q.; Juarez-Garcia, C.; True, A.; O'Connor, C.; Que, Jr. L. *Inorg. Chem.* **1991**, *30*, 1937–1943.
35. Tzou, J.-R.; Chang, S.-C.; Norman, R. E. *J. Inorg. Biochem.* **1993**, *51*, 480.
36. Feig, A. L.; Bautista, M. T.; Lippard, S. *Inorg. Chem.* **1996**, *35*, 6892–6898.

37. Suzuki, M.; Furutachi, H.; Ōkawa, H. *Coord. Chem. Rev.* **2000**, *200–202*, 105–129.
38. Satcher, Jr. J. H.; Droege, M. W.; Olmstead, M. M.; Balch, A. L. *Inorg. Chem.* **2001**, *40*, 1454–1458.
39. Westerheide, L.; Müller, F. K.; Than, R.; Krebs, B.; Dietrich, J.; Schindler, S. *Inorg. Chem.* **2001**, *40*, 1951–1961.
40. Shul'pin, G. B.; Druzhinina, A. N. *React. Kinet. Catal. Lett.* **1992**, *47*, 207–211.
41. Shul'pin, G. B.; Nizova, G. V. *React. Kinet. Catal. Lett.* **1992**, *48*, 333–338.
42. Shul'pin, G. B.; Druzhinina, A. N.; Shul'pina, L. S. *Petrol. Chem.* **1993**, *33*, 321–325.
43. Shul'pin, G. B.; Bochkova, M. M.; Nizova, G. V. *J. Chem. Soc., Perkin Trans. 2* **1995**, 1465–1469.
44. Shul'pin, G. B.; Nizova, G. V.; Kozlov, Yu. N. *New J. Chem.* **1996**, *20*, 1243–1256.
45. Shul'pin, G. B.; Guerreiro, M. C.; Schuchardt, U. *Tetrahedron* **1996**, *52*, 13051–13062.
46. Shul'pin, G. B. *Alkane oxidation: estimation of alkyl hydroperoxide content by GC analysis of the reaction solution samples before and after reduction with triphenylphosphine, The Chemistry Preprint Server, Article CPS: orgchem/0106001* **2001**; pp 1–6. (http://preprint.chemweb.com/orgchem/0106001).
47. Shul'pin, G. B.; Attanasio, D.; Suber, L. *J. Catal.* **1993**, *142*, 147–152.
48. Shul'pin, G. B.; Ishii, Y.; Sakaguchi, S.; Iwahama, T. *Russ. Chem. Bull.* **1999**, *48*, 887–890.
49. Kozlov, Yu. N.; Nizova, G. V.; Shul'pin, G. B. *Russ. J. Phys. Chem.* **2001**, *75*, 770–774.
50. Shul'pin, G. B.; Kozlov, Yu. N.; Nizova, G. V.; Süss-Fink, G.; Stanislas, S.; Kitaygorodskiy, A.; Kulikova, V. S. *J. Chem. Soc., Perkin Trans. 2* **2001**, 1351–1371.
51. Shul'pin, G. B.; Lindsay Smith, J. R. *Russ. Chem. Bull.* **1998**, *47*, 2379–2386.
52. Shul'pin, G. B.; Süss-Fink, G.; Lindsay Smith, J. R. *Tetrahedron* **1999**, *55*, 5345–5358.
53. Shul'pin, G. B.; Süss-Fink, G.; Shul'pina, L. S. *J. Mol. Catal., A: Chem.* **2001**, *170*, 17–34.
54. Lindsay Smith, J. R.; Shul'pin, G. B. *Tetrahedron Lett.* **1998**, *39*, 4909–4912.
55. Shul'pin, G. B.; Nizova, G. V.; Kozlov, Yu. N.; Pechenkina, I. G. *New J. Chem.* **2002**, *26*, 1238–1245.