Published in Advanced Synthesis & Catalysis, 346, issues 2-3, 317 - 332, 2004
which should be used for any reference to this work

Hydrogen Peroxide Oxygenation of Alkanes Including Methane and Ethane Catalyzed by Iron Complexes in Acetonitrile

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Received: September 9, 2003; Accepted: January 17, 2004

Abstract: This paper describes an investigation of the alkane oxidation with hydrogen peroxide in acetonitrile catalyzed by iron(III) perchlorate (**1**), iron(III) chloride (**2**), iron(III) acetate (**3**) and a binuclear iron(III) complex with 1,4,7-triazacyclononane (**4**). The corresponding alkyl hydroperoxides are the main products. Nevertheless in the kinetic study of cyclohexane oxidation, the concentrations of oxygenates (cyclohexanone and cyclohexanol) were measured after reduction of the reaction solution with triphenylphosphine (which converts the cyclohexyl hydroperoxide to the cyclohexanol). Methane and ethane can be also oxidized with TONs up to 30 and 70, respectively. Chloride anions added to the oxidation solution with **1** activate the perchlorate iron derivative in acetonitrile, whereas the water as additive inactivates **2** in the H_2O_2 decomposition process. Pyrazine-2-carboxylic acid (PCA) added to the reaction mixture decreases the oxidation rate if **1** or **2** are used as catalysts, whereas compounds **3** and **4** are active as catalysts only in the presence of small amount of PCA. The investigation of kinetics and selectivities of the oxidations demonstrated that the mechanisms of the reactions are different. Thus, in the oxidations catalyzed by the **1**, **3** + PCA and **4** + PCA systems the main oxidizing species is hydroxyl radical, and the oxidation in the presence of **2** as a catalyst has been assumed to proceed (partially) with the formation of ferryl ion, $(Fe^{IV}{=}O)^{2+}$. In the oxidation catalyzed by the **4** + PCA system (TONs attain 240) hydroxyl radicals were generated in the rate-determining step of monomolecular decomposition of the iron diperoxo adduct containing one PCA molecule. A kinetic model of the process which satisfactorily describes the whole set of experimental data was suggested. The constants of supposed equilibriums and the rate constant for the decomposition of the iron diperoxo adduct with PCA were estimated.

Keywords: alkanes; alkyl hydroperoxides; hydrogen peroxide; iron complexes; methane; oxidation

Introduction

Iron compounds are used as initiators and catalysts in oxidation of various organic compounds with hydrogen peroxide.[1,2] Iron complexes containing various ligands (usually chelating cyclic *N*-bases) play a very important role in living cells as well as in biomimetic oxidations.[3,4] In addition to the well-known Fenton reagent (which uses Fe^{II} in stoichiometric amounts), synthetically useful so-called Gif systems,[5] and "oxygenated Fenton reagents"[6] have been described by Barton and Sawyer groups. Interesting studies on iron-catalyzed alkane oxidations have been carried out in recent decades by the groups of Feringa,[7] Fish,[8] Fontecave,[9] Groves,[10] Lippard,[11] Mansuy,[12] Mascharak,[13] Ménage,[14] Nam,[15] Newcomb,[16] Nishida,[17] Que,[18] Shilov and Shteinman,[19] Sobkowiak,[20] and Stavropoulos.[21] Many papers are devoted to mechanisms of hydrocarbon oxidations catalyzed by iron ions.[22] In a recent publication, Pacześniak and Sobkowiak[20d] demonstrated that "in acetonitrile, in contrast to water, iron(III) is reduced by hydrogen peroxide, according to 2:1 stoichiometry". The authors concluded that "the system is very sensitive towards almost any experimental variables, i.e., solvent, ligand, water content in organic solvent, and the oxidation state of metal ion, which can be rapidly changed at the beginning of the experiment".[20d]

In the present study we have investigated alkane oxidation with hydrogen peroxide in acetonitrile catalyzed by simple iron(III) complexes such as the perchlorate (containing "naked" iron cation) (**1**; see Scheme 1) and those bearing more strongly bound ligands, i.e., chloride (**2**) and acetate (**3**). Finally, we employed as a catalyst a binuclear iron(III) complex with 1,4,7-triazacyclononane (**4**) which can be considered as a structural model of some iron-containing biologically active compounds, and especially enzymes. Some fragments of this work have been published previously as preliminary communications.[23]

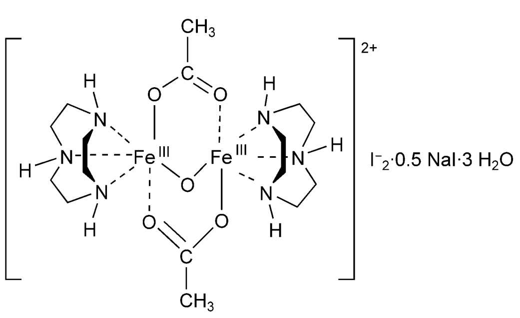
Results and Discussion

We have found that iron(III) salts catalyze the hydrogen peroxide decomposition in acetonitrile. In the presence of alkane, RH, for example, cyclohexane, CyH, in addition to the decomposition of H_2O_2 to afford O_2 and H_2O (catalase activity of the catalyst) one can observe alkane oxygenation with formation of the corresponding alkyl hydroperoxide, ROOH (cyclohexyl hydroperoxide, CyOOH) as the main primary product (oxygenase activity) which further gradually decomposes yielding more stable products, the ketone (aldehyde) and alcohol. Concentrations of the three products were determined by GC using a method proposed by us previously.[1d,24] The reactions were quenched by the addition of solid triphenylphosphine to the reaction solution, and GC analysis gave the concentrations of cyclohexanol and cyclohexanone. A comparison of the alcohol and ketone concentrations (measured by GC) before and after the addition of PPh_3 testified that cyclohexyl hydroperoxide was formed as main product in the initial period. Indeed, the solution untreated with PPh_3 contained alkyl hydroperoxide, CyOOH, which completely or partially decomposed in GC to produce CyOH, Cy=O and other compounds. Added triphenylphosphine quantitatively reduced CyOOH to CyOH. For the precise determination of oxygenate concentrations only data obtained after reduction of the reaction sample with PPh_3 were usually used, taking into account, however, that the original reaction mixture contained the three products, cyclohexyl hydroperoxide (as a predominant product), cyclohexanone, and cyclohexanol.

$Fe(ClO_4)_3$ (**1**)

$FeCl_3$ (**2**)

$Fe(OCOCH_3)_2OH$ (**3**)



(**4**)

Scheme 1.

Oxidation Catalyzed by Iron(III) Perchlorate

First of all we investigated the cyclohexane oxidation with hydrogen peroxide under catalysis by the most “simple” iron salt, i.e., iron(III) perchlorate (**1**) which does not contain any ligands strongly bound to iron. The oxygenation leads to the formation of cyclohexyl hydroperoxide, cyclohexanol and cyclohexanone. The reaction efficiency is not high and turnover numbers (i.e., number of mols of products per one mol of the catalyst, TON) attain only 10 after approximately 3 min. The rate dependency of the oxygenation is first order with respect to the initial hydrogen peroxide (Figure 1). The initial rate of molecular oxygen evolution is also proportional to the initial concentration of H_2O_2.

First order has been found for catalyst **1**, and the initial reaction rate decreases when PCA is added to the reaction solution (Figure 2). The dependence of the initial cyclohexane oxidation rate on the initial cyclohexane concentration (a plateau at $[\text{cyclohexane}]_0 > 0.4\ \text{mol dm}^{-3}$; Figure 3) is in accordance with the assumption concerning competition between cyclohexane and the solvent (acetonitrile) for the interaction with an active oxidizing species (see below).

It is noteworthy that lithium chloride added to the reaction solution dramatically accelerates the dioxygen evolution process (Figure 4). Another remarkable feature of this effect is a bell-shaped dependence on $[LiCl]_{added}$. It is reasonable to assume that in the presence

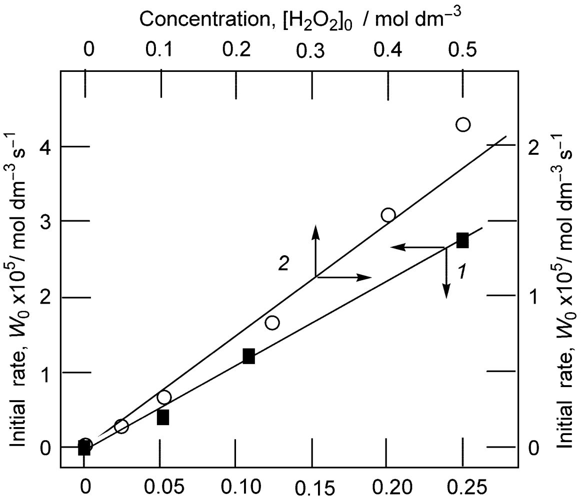


Figure 1. Cyclohexane ($0.46\ \text{mol dm}^{-3}$) oxidation with H_2O_2 catalyzed by $Fe(ClO_4)_3$ ($5 \times 10^{-4}\ \text{mol dm}^{-3}$) in MeCN at 25 °C. Plots of initial rates of oxygenate accumulation (curve *1*) and O_2 evolution (curve *2*) *versus* initial concentration of H_2O_2 are shown.

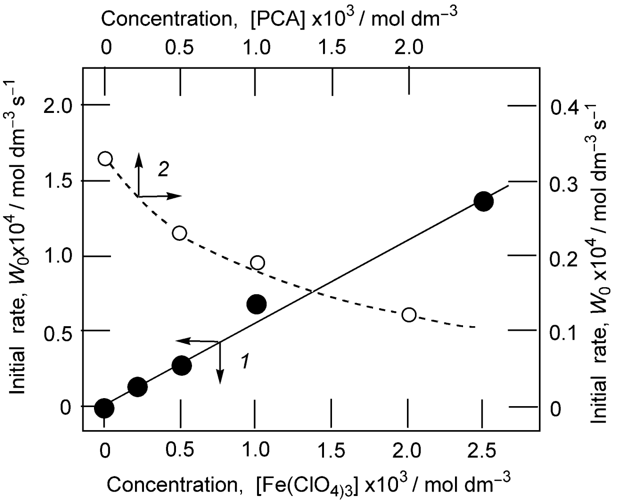


Figure 2. Cyclohexane (0.46 mol dm^{-3}) oxidation with H_2O_2 (0.25 mol dm^{-3}) catalyzed by $Fe(ClO_4)_3$ in MeCN at 25 °C: initial oxygenate formation rate *versus* concentration of $Fe(ClO_4)_3$ (curve *1*) and *versus* concentration of added PCA ($[Fe(ClO_4)_3] = 5 \times 10^{-4}$ mol dm^{-3}) (curve *2*).

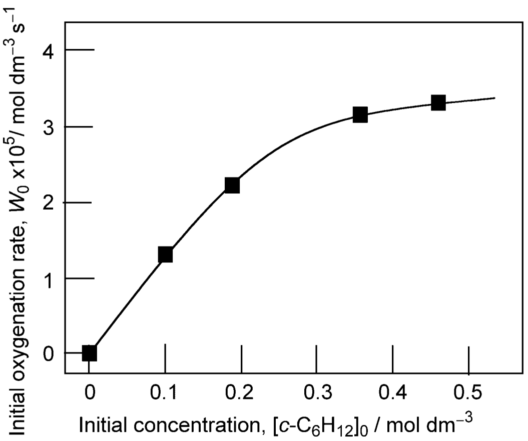


Figure 3. Plot of the cyclohexane oxygenate accumulation initial rate *versus* initial concentration of cyclohexane (in MeCN at 25 °C; $[H_2O_2]_0 = 0.25$ mol dm^{-3}; $[Fe(ClO_4)_3] = 5 \times 10^{-4}$ mol dm^{-3}).

of LiCl iron(III) cations can coordinate chloride anions to afford the same species that are present in the solution of $FeCl_3$ (the oxidation catalyzed by iron chloride will be discussed in the next Section).

We also determined regioselectivity parameters for the oxidations of certain higher branched alkanes. In Table 1 the parameters are summarized for the oxidations catalyzed by the iron complexes studied in the present work as well as, for comparison, by certain other systems for which the mechanism is clear. It can be concluded that the selectivity parameters are similar to those found previously for the systems operating with generation of free hydroxyl radicals (the "H_2O_2-VO_3^--PCA" reagent, "H_2O_2-hν", "H_2O_2-$FeSO_4$").

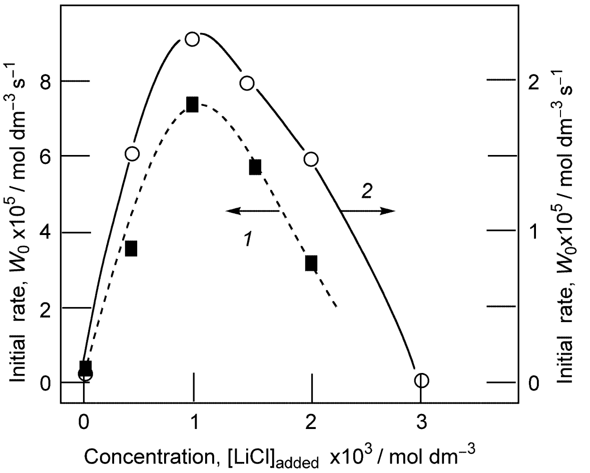


Figure 4. Hydrogen peroxide (0.05 mol dm^{-3}) decomposition catalyzed by $Fe(ClO_4)_3$ (5×10^{-4} mol dm^{-3}) in MeCN at 25 °C: H_2O_2 consumption (curve *1*) and O_2 evolution (curve *2*) *versus* initial concentration of added LiCl.

The data on methane and ethane oxidation with hydrogen peroxide catalyzed by iron perchlorate are summarized in Tables 2 and 3. It can be seen that in the case of ethane the TONs attain 68.

Iron(III) Chloride as a Catalyst

It has been demonstrated by spectrophotometry that no aggregation of $FeCl_3$ species takes place in the acetonitrile solution. Indeed, absorbance with iron ions is proportional to iron concentration in the 2×10^{-5} to 10^{-3} mol dm^{-3} range and thus Beer's law is valid. The rate dependency of the oxygenation is first order with respect to compound **2** as a catalyst at $[FeCl_3] < 2 \times 10^{-3}$ mol dm^{-3} (Figure 5). In contrast to the situation found for the catalysis by compound **1**, in the case of the $FeCl_3$-catalyzed oxidation the reaction is first order for cyclohexane and no plateau was observed (Figure 6). The initial rate dependence is depicted with bell-shape curves for oxygenate accumulation, hydrogen peroxide consumption and O_2 evolution (Figure 7).

The efficient activation energy of the $FeCl_3$-catalyzed oxidation of cyclohexane was estimated to be equal to 14 kcal mol^{-1} (Figure 8). As could be predicted, $LiClO_4$ added to the reaction solution decreased the initial reaction rate only insignificantly (Figure 9).

The oxidation of methane gave methyl hydroperoxide as the main product and a lesser amount of formaldehyde (Figure 10). Benzene is oxidized mainly to phenol. The dependence of the initial oxidation rate on benzene concentration is shown in Figure 11. Propane and isobutane can also be oxidized by the same system to afford mainly the corresponding alkyl hydroperoxides (Table 4). It is noteworthy that, like in the case of compound **1**, oxidation catalyzed by **2** is also depressed

Table 1. Selectivity parameters in the iron-catalyzed oxidations of higher alkanes by H_2O_2.

Entry	Substrate	Catalyst	Selectivity
	2,2,4-Trimethylpentane		**1°:2°:3°**[a]
1		$Fe(ClO_4)_3$	1:5:13
2		$FeCl_3 \cdot 6\,H_2O$	1:7:57
3		$Fe(OAc)_2(OH)$ + PCA	1:5:13
4		**4** + PCA	1:2.5:18
5		n-u$_4$NVO$_3$-PCA[b]	1:4:9
6		hν	1:2:6
7		$FeSO_4$	1:3:6
8		$[LMn^{IV}(O)_3Mn^{IV}L](PF_6)_2$-$MeCO_2H$[c]	1:5:50
	Methylcyclohexane		**1°:2°:3°**[a]
9		$Fe(ClO_4)_3$	1:7:43
10		**4** + PCA	1:8.5:34
11		n-Bu$_4$NVO$_3$-PCA[b]	1:6:18
12		$[LMn^{IV}(O)_3Mn^{IV}L](PF_6)_2$-$MeCO_2H$[c]	1:26:200
	3-Methylhexane		**1°:2°:3°**[a]
13		$Fe(ClO_4)_3$	1:4:30
14		**4** + PCA	1:8:61
15		n-Bu$_4$NVO$_3$-PCA[b]	1:6:22
16		hν	1:4:12
17		$[LMn^{IV}(O)_3Mn^{IV}L](PF_6)_2$-$MeCO_2H$[c]	1:22:200
	cis-Decalin		***trans/cis***[d]
18		$FeCl_3 \cdot 6\,H_2O$	1
19		$Fe(OAc)_2(OH)$ + PCA	3
20		**4** + PCA	9
21		n-Bu$_4$NVO$_3$-PCA[b]	2
22		hν	1.3
23		$FeSO_4$	3.5
24		$[LMn^{IV}(O)_3Mn^{IV}L](PF_6)_2$-$MeCO_2H$[c]	0.12
	trans-Decalin		***trans/cis***[d]
25		$FeCl_3 \cdot 6\,H_2O$	1
26		$Fe(OAc)_2(OH)$ + PCA	4.5
27		**4** + PCA	3
28		n-Bu$_4$NVO$_3$-PCA[b]	2.4
29		hν	1.3
30		$FeSO_4$	9
31		$[LMn^{IV}(O)_3Mn^{IV}L](PF_6)_2$-$MeCO_2H$[c]	33

[a] Parameter 1°:2°:3° are normalized (i.e., calculated taking into account the number of hydrogen atoms at each position) relative reactivities of hydrogen atoms at primary, secondary and tertiary carbons, respectively. The parameters were calculated based on concentrations of isomeric alcohols formed in the reaction and were measured after the reduction of the reaction solution with PPh_3.

[b] PCA is pyrazine-2-carboxylic acid; for this system, which oxidizes with the formation of hydroxyl radicals, see Refs.[1b, d,24b, c,f, g,25]

[c] L is 1,4,7-trimethyl-1,4,7-triazacyclononane; for this system, which operates without involvement of free radicals, see Refs.[1d,24f, g,26]

[d] This parameter is the *trans*/*cis* ratio of isomers of *tert*-alcohols formed in the oxidation of *cis*- or *trans*-decalins.

by the addition of PCA and for **2** this effect is even more strongly pronounced (Figure 12).

Comparison of $Fe(ClO_4)_3$ and $FeCl_3$ as Generators of Oxidizing Species. On the Mechanism of the Oxidation

On the one hand neither hydrogen peroxide nor iron salts induce the alkane oxidation under mild conditions. On the other hand saturated hydrocarbons are not known to form strong complexes with iron ions. Therefore the observed alkane oxidation induced by iron-catalyzed hydrogen peroxide decomposition is due to an oxidizing action of an intermediate species generated in the course of H_2O_2 decomposition.

It is known[27] that catalytic decomposition of hydrogen peroxide with iron ions in aqueous solution occurs as an ion-radical-chain process, and the oxidation state of

Table 2. Methane oxidation with H_2O_2 catalyzed by iron complexes.[a]

Entry	Catalyst [mol dm^{-3}]	Time [h]	Product concentration, × 10^3 (mol dm^{-3})			TON	Yield [%]
			CH_3OOH	CH_3OH	HCHO		
	$Fe(ClO_4)_3$ (1×10^{-3})						
1		1	5.6	2.3	2.2		
2		3[b]	3.5	2.4	2.4	7	1.4
	$Fe(OAc)_2(OH)$ (1×10^{-3}) + PCA (5×10^{-3})						
3		2	0.0	9.6	1.0		
4		4	0.0	19.3	1.1		
5		6	0.0	24.0	4.2		
6		7	0.0	25.0	5.6	31	5.1
	$Fe(OAc)_2(OH)$ (1×10^{-4}) + PCA (3.5×10^{-4})						
7		6[c]	8.0	0.0	2.5	10	1.8

[a] Conditions: methane, 90 bar; H_2O_2, 0.6 mol dm^{-3}; 25 °C; solvent acetonitrile. Turnover number (TON) equals the number of moles of all products per mole of a catalyst. Yields of all products are based on H_2O_2 introduced into the reaction.

[b] In the analogous reaction in the absence of methane, formaldehyde (formed from acetonitrile) was detected (1.3×10^{-3} mol dm^{-3}).

[c] In the absence of methane formaldehyde (0.8×10^{-3} mol dm^{-3}) was detected.

Table 3. Ethane oxidation with H_2O_2 catalyzed by iron complexes.[a]

Entry	Catalyst [mol dm^{-3}]	Time [h]	Product concentration, × 10^3 (mol dm^{-3})			TON	Yield [%]
			CH_3CH_2OOH	CH_3CH_2OH	CH_3CHO		
1	$Fe(ClO_4)_3$ (5×10^{-4})	3[b]	30.0	1.0	3.2	68	5.7
2	$Fe(OAc)_2(OH)$ (1×10^{-3}) + PCA (5×10^{-3})	2[c]	0.4	7.8	3.3	12	1.9
3	$Fe(OAc)_2(OH)$ (1×10^{-4}) + PCA (3.5×10^{-4})	4	2.5	4.0	1.8	8	1.4

[a] Conditions: ethane, 27 bar; H_2O_2, 0.6 mol dm^{-3}; 25 °C; solvent acetonitrile. Turnover number (TON) equals the number of moles of all products per mole of a catalyst. Yields of all products are based on H_2O_2 introduced into the reaction.

[b] Acetic acid was not detected.

[c] In the absence of ethane acetaldehyde and ethanol were not detected after 3 h.

Table 4. Oxidation of light alkanes with H_2O_2 catalyzed by $FeCl_3$.[a]

Entry	Alkane	Products (concentration × 10^3, mol dm^{-3})	TON	Yield [%]
1	Propane[a]	$CH_3CH(OOH)CH_3$ (5.5), CH_3CH_2CHO (1.0), $CH_3CH_2CH_2OOH$ (1.4), CH_3COCH_3 (1.1), $CH_3CH_2CO_2H$ (0.3)	17	1.6
2	Isobutane[b]	$(CH_3)_3COOH$ (0.24), $(CH_3)_3COH$ (5.0), $(CH_3)_2CCHO$ (5.0), $(CH_3)_2CCO_2H$ (0.25)	21	1.7

[a] Conditions: propane, 7 bar; H_2O_2, 0.05 mol dm^{-3}; $FeCl_3$, 5×10^{-4} mol dm^{-3}; solvent acetonitrile; 25 °C; 1 h. Turnover number (TON) equals the number of moles of all products per mole of a catalyst. Yield of all products is based on H_2O_2 introduced into the reaction.

[b] Conditions: isobutane, 5 bar; H_2O_2, 0.05 mol dm^{-3}; $FeCl_3$, 5×10^{-4} mol dm^{-3}; solvent acetonitrile; 25 °C; 1 h.

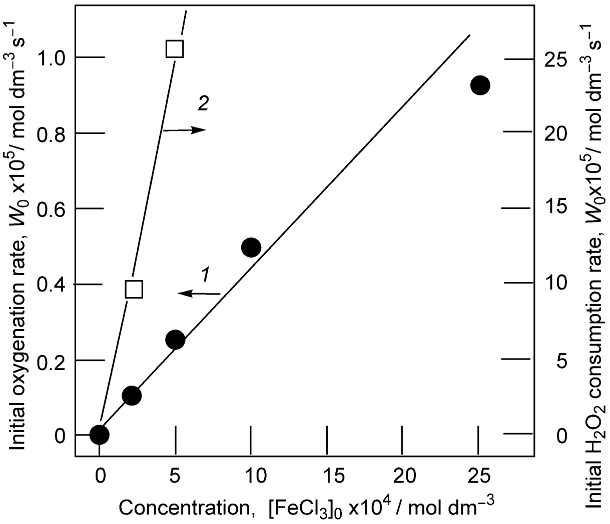


Figure 5. Cyclohexane oxidation with H_2O_2 catalyzed by $FeCl_3$: plot of dependence of the oxygenate accumulation initial rate (curve *1*) and the H_2O_2 consumption initial rate (curve *2*) on initial $FeCl_3 \cdot 6\,H_2O$ concentration (at $[\text{cyclohexane}]_0 = 0.46$ mol dm^{-3} and $[H_2O_2]_0 = 0.05$ mol dm^{-3}) at 25 °C.

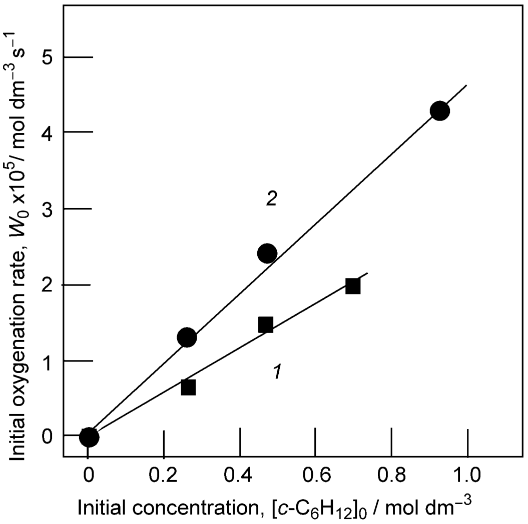


Figure 6. Plot of the cyclohexane oxygenate accumulation ($[FeCl_3] = 5 \times 10^{-4}$ mol dm^{-3}) initial rate *versus* initial concentration of cyclohexane at 25 °C (curve *1*: at $[H_2O_2]_0 = 0.02$ mol dm^{-3}; curve *2*: at $[H_2O_2]_0 = 0.05$ mol dm^{-3}).

iron ions alternates ($Fe^{3+} \rightleftharpoons Fe^{2+}$). The oxidation of Fe^{2+} ion with H_2O_2 leads to the formation of hydroxyl radical. The present study demonstrates that an oxidizing species generated in the H_2O_2-$Fe(ClO_4)_3$-CH_3CN system is the hydroxyl radical and we propose that the mechanism of $HO^{\bullet}$ formation includes the same stages as in aqueous solution:

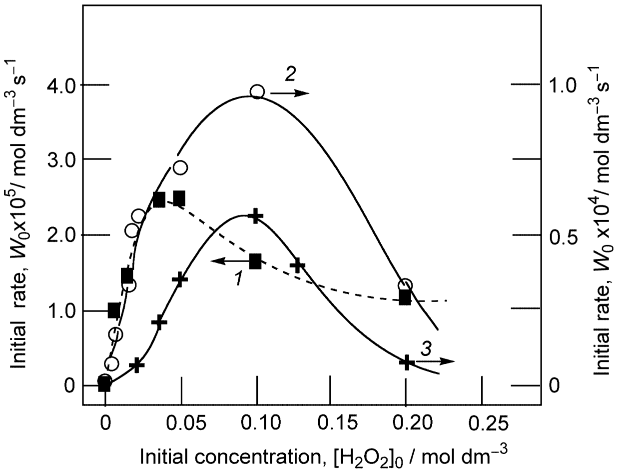


Figure 7. Decomposition of H_2O_2 catalyzed by $FeCl_3 \cdot 6\,H_2O$ (5×10^{-4} mol dm^{-3}) in MeCN at 25 °C. Plots of initial rates of the cyclohexane oxygenates accumulation (curve *1*) as well as (in the absence of cyclohexane) of H_2O_2 consumption (curve *2*), and O_2 evolution (curve *3*) *versus* initial H_2O_2 concentration are shown.

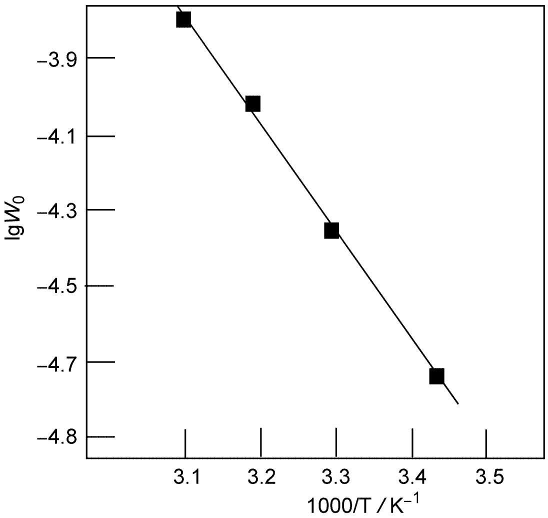


Figure 8. The Arrhenius plot for the cyclohexane (0.23 mol dm^{-3}) oxygenation by H_2O_2 (0.02 mol dm^{-3}) in MeCN catalyzed by $FeCl_3$ (5×10^{-4} mol dm^{-3}) which corresponds the activation energy $E_a = 14$ kcal mol^{-1}.

$$Fe^{3+} + H_2O_2 \rightleftharpoons Fe(H_2O_2)^{3+} \qquad (A)$$

$$Fe(H_2O_2)^{3+} \longrightarrow Fe^{2+} + H^+ + HO_2^{\bullet} \qquad (B)$$

$$Fe^{3+} + HO_2^{\bullet} \longrightarrow Fe^{2+} + H^+ + O_2 \qquad (C)$$

$$Fe^{2+} + H_2O_2 \longrightarrow Fe^{3+} + HO^- + HO^{\bullet} \qquad (D)$$

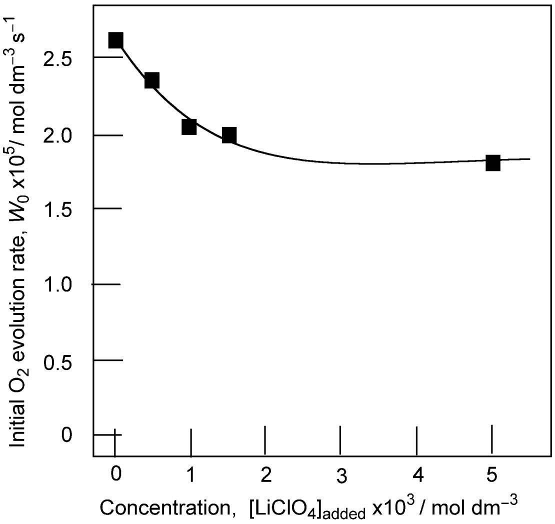


Figure 9. Hydrogen peroxide decomposition catalyzed by $FeCl_3$ (5×10^{-4} mol dm^{-3}): plot of O_2 evolution initial rate *versus* concentration of added $LiClO_4$ (in acetonitrile, 25 °C, $[H_2O_2]_0 = 0.05$ mol dm^{-3}).

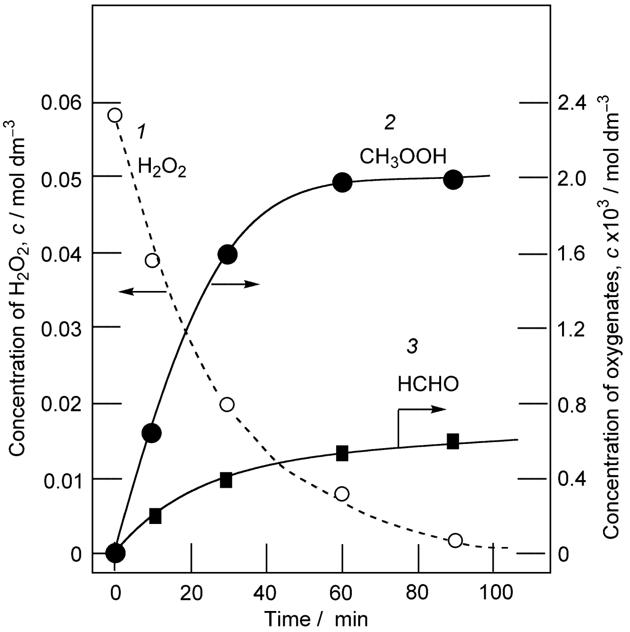


Figure 10. Oxidation of methane (55 bar) by H_2O_2 (initial concentration 0.06 mol dm^{-3}) in MeCN in the presence of artificial air (1 bar) catalyzed by $FeCl_3$ (5×10^{-4} mol dm^{-3}) at 40 °C. Curves for H_2O_2 consumption (*1*), accumulation of methyl hydroperoxide (*2*) and formaldehyde (*3*) are shown. Concentrations of methanol were measured by GC before and after the reduction of the reaction mixture with PPh_3.

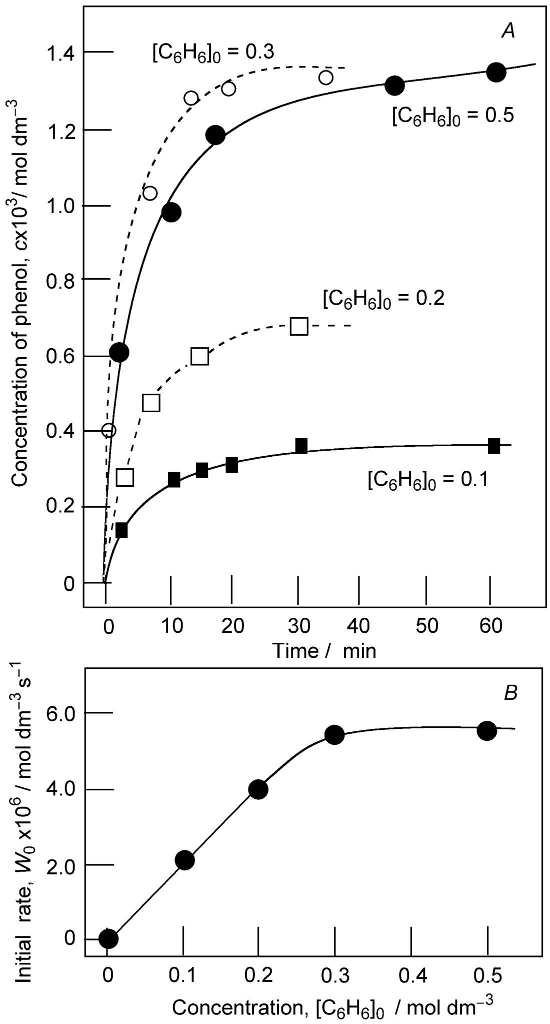


Figure 11. Reaction of benzene with H_2O_2 (0.04 mol dm^{-3}) catalyzed by $FeCl_3$ (5×10^{-4} mol dm^{-3}) in MeCN at 25 °C. Graph *A*: accumulation of phenol with time at various initial concentrations of benzene (mol dm^{-3}). Graph *B*: plot of phenol accumulation initial rate measured from data of graph *A versus* initial concentration of benzene.

In the presence of a substantial concentration of cyclohexane when all hydroxyl radicals are accepted by the alkane ($[CyH] > 0.46$ mol dm^{-3}) the cyclohexyl hydroperoxide formation rate corresponds to the rate of active species initiation by the H_2O_2-$Fe(ClO_4)_3$-CH_3CN system. In accordance with this proposal the CyOOH formation rate should be proportional to the concentrations of both H_2O_2 and $Fe(ClO_4)_3$. Our experimental data (see Figures 1 and 2) support this proposal. The effective bimolecular rate constant of the initiation reaction with iron(III) perchlorate in acetonitrile was calculated using the rate of ROOH formation at 25 °C and it equals to 0.24 dm^3 mol^{-1} s^{-1}.

Radical HO$^•$ can react both with alkane, RH, and solvent, CH_3CN, *via* routes (1) and (2):

$$HO^{\bullet} + RH \xrightarrow{k_1} R^{\bullet} + H_2O \qquad (1)$$

$$HO^{\bullet} + CH_3CN \xrightarrow{k_2} \text{products} \qquad (2)$$

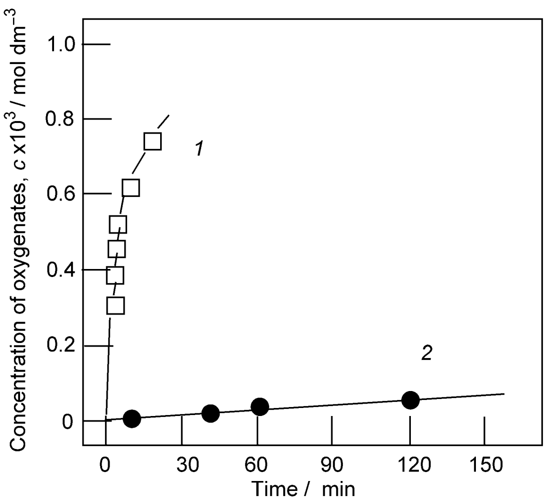


Figure 12. Accumulation of oxygenates in cyclohexane (0.23 mol dm^{-3}) oxidation with H_2O_2 (0.05 mol dm^{-3}) catalyzed by $FeCl_3$ (5×10^{-4} mol dm^{-3}) in MeCN at 25 °C in the absence (curve *1*) and in the presence of PCA (5×10^{-4} mol dm^{-3}; curve *2*).

The observed alkane oxidation rate should depend on the RH concentration as depicted by Eq. (3):

$$-\frac{d[RH]}{dt} = \frac{d[ROOH]}{dt} = \frac{W_i}{1 + \dfrac{k_2[CH_3CN]}{k_1[RH]}} \qquad (3)$$

where W_i is the rate of the hydroxyl radical generation in this system. The alkane (cyclohexane) oxidation rate approaches W_i when $[RH]_0$ grows. It follows from Eq. (3) that a two-fold decrease of the oxidation rate in comparison with the maximum possible rate can be realized at the alkane (cyclohexane) concentration determined from the condition

$$\frac{k_2[CH_3CN]}{k_1[RH]} = 1 \qquad (4)$$

independently of the rate and mechanism of hydroxyl radical formation.

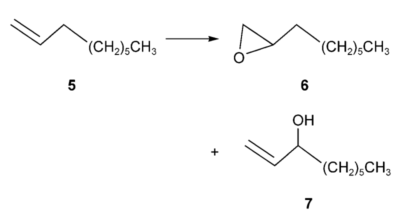
We have demonstrated in our kinetic experiments that the dependence modes of the ROOH formation rate on the cyclohexane concentration are different for cases of $Fe(ClO_4)_3$ and $FeCl_3$ as catalysts (compare Figure 3 and Figure 6). We found a curve with a plateau in the first case whereas only linear dependency can be noted for the second catalyst in the same concentration interval. This difference means that the ratios between rate constants for the CH_3CN and RH oxidations are different for the cases of $Fe(ClO_4)_3$ and $FeCl_3$, and consequently that oxidizing species are different for the two catalysts. The rate constant ratio found for $Fe(ClO_4)_3$ is close to those calculated on the basis of radiation-chemical measurements[25] (in more detail such a discussion will be given below in the Section devoted to the catalysis by complex **4**). The same ratio is noticeably higher for $FeCl_3$.

When chloride ions (LiCl) were added to the iron(III) perchlorate solution the complex dependence of the reaction rate was noticed (see Figure 4). At the $[LiCl]_0/[Fe(ClO_4)_3]_0 = 3$ the rates of oxidations and oxygen evolution are practically equal to the rates of processes catalyzed by $FeCl_3$. This influence of the LiCl additive is due to different reactivities in the initiation of "naked" Fe^{3+} ion and its chloride complexes (formed in equilibrium $Fe^{3+} + n\ Cl^- \rightleftharpoons FeCl_n^{(3-n)+}$). Data presented in Figure 4 show that complexes containing one and two Cl^- ions in the iron coordination sphere exhibit the highest activity. When the number of iron-bound chloride ions grows (to 3 and 4) the catalyst activity decreases. Consequently, adding Cl^- ions to the reaction solution not only changes the process selectivity (replacing $HO^\bullet$ by $Fe^{IV}=O$ as oxidizing species, see below) but also increases the oxidation rate.

In the case of $FeCl_3$ a complex mode for the rate dependence on hydrogen peroxide concentration can be due to the addition of water (present in 30% aqueous H_2O_2) to the reaction solution. The water additive does not practically affect the catalytic activity of iron perchlorate, however it does decrease the corresponding activity of iron chloride.

Selectivity parameters obtained in the oxidation of branched alkanes (see Table 1) also support the conclusion about different active species operating in the studied systems. The selectivity obtained in $Fe(ClO_4)_3$-catalyzed oxidation is close to that determined in hydroxyl radical-induced oxidations. The corresponding parameters for $FeCl_3$-catalyzed oxidations are higher.

We have also found striking differences in selectivity of the dec-1-ene (compound **5**) oxidation according to Scheme 2 by the two systems. The data obtained are summarized in Table 5. It can be clearly seen that if $Fe(ClO_4)_3$ is used as a catalyst the main product of the dec-1-ene oxidation is (after reduction of the reaction mixture with PPh_3) the corresponding allyl alcohol **6**, which is formed by the hydroperoxidation of allylic C–H bonds. On the contrary, catalysis with $FeCl_3$ gave predominantly the corresponding epoxide **7**.



Scheme 2.

Table 5. Dec-1-ene (**5**) oxidation by hydrogen peroxide catalyzed by iron(III) salts.[a]

Entry	Reaction time [min]	1,2-Epoxydecane (**6**) concentration [$\times 10^3$ mol dm^{-3}]	3-Hydroxydec-1-ene (**7**) concentration [$\times 10^3$ mol dm^{-3}]	Product **6**/**7** ratio
Catalyst $Fe(ClO_4)_3$				
1	0.5	0.13	0.33	0.39
2	1.0	0.20	0.70	0.29
Catalyst $FeCl_3$				
3	0.5	1.04	0.22	4.72
4	1.0	2.10	0.40	5.25

[a] Product concentrations were measured after reduction of the reaction solution with triphenylphosphine. Reaction conditions: dec-1-ene, 0.4 mol dm^{-3}; catalyst, 5×10^{-4} mol dm^{-3}; hydrogen peroxide, 0.25 mol dm^{-3} (entries 1 and 2), 0.05 mol dm^{-3} (entries 3 and 4); 25 °C.

For the two systems based on $Fe(ClO_4)_3$ and $FeCl_3$ the modes of dependency of the initial rate on the initial hydrogen peroxide concentration are distinct (compare Figure 1, curve *1* and Figure 7, curve *1*). We assume that this situation is a result of a competition between chloride anion, hydrogen peroxide and water for the site at coordination sphere of iron ion. The composition of this sphere affects the reactivity of a formed species. Changes of the hydrogen peroxide concentration in the system lead simultaneously to the corresponding changes of water content because we use 30% or 35% aqueous solutions of H_2O_2. In the case of $FeCl_3$ a complex mode for the rate dependence on hydrogen peroxide concentration can be due to the addition of water to the reaction solution. The water additive does not practically affect the catalytic activity of iron perchlorate, however it does decrease the corresponding activity of iron chloride. Complexes containing in the coordination sphere both H_2O and Cl^- exhibit less reactivity in comparison with complexes which do not contain water molecule. It can be thus concluded that Cl^- additive activates the perchlorate iron derivative in acetonitrile whereas the water additive inactivates chloride complexes in the H_2O_2 decomposition process.

As was mentioned above all the data obtained testify that in the case of $Fe(ClO_4)_3$ as a catalyst the properties of the oxidizing species are close to those of hydroxyl radical. In these experiments the chloride anion was absent and concentrations of hydrogen peroxide and water were 0.25 and 1.0 mol dm^{-3}, respectively. When $FeCl_3$ was used as a catalyst ($[H_2O_2]_0 = 0.05$ mol dm^{-3} and $[H_2O] = 0.2$ mol dm^{-3}) the experimental data showed that the oxidation was induced by a more selective and less reactive species. One can assume that this species is the ion of iron(IV), for example, in the form of ferryl ion, $Fe^{IV} = O$.

Different oxidizing species can be generated *via* several routes. It is probable that the ratio of one-electron, Eq. (5), and two-electron, Eq. (6), channels of the H_2O_2 oxidation of complex $Fe^{2+}(L_i)_j$ (where L_i are various ligands, for example, Cl^-, H_2O_2, H_2O, and j is number of these ligands in the iron ion coordination sphere) in accordance with Eqs. (5) and (6) depends on the composition of this coordination sphere. If so, the less water there is in the coordination sphere of the chloride complex the higher is the yield of species $Fe(L_i)O^{2+}$, which is confirmed by our experimental data. In the reaction with a perchlorate complex containing water, the one-electron channel, Eq. (5), is a predominant route.

$$\mathrm{Fe}^{2+}(L_i)_j \longrightarrow \mathrm{Fe}^{3+}(L_i)_j + \mathrm{HO}^- + \mathrm{HO}^{\bullet} \tag{5}$$

$$\mathrm{Fe}^{2+}(L_i)_j \longrightarrow \mathrm{Fe}(L_i)_j\mathrm{O}^{2+} + \mathrm{H_2O} \tag{6}$$

An alternative route of the formation of various oxidizing species can be the following. The first stage of the oxidation of $Fe^{2+}(L_i)_j$ species proceeds as the transfer of two electrons. However, in the absence of the chloride ion and a substantial amount of water the following transformation occurs:

$$\mathrm{Fe}(L_i)_j\mathrm{O}^{2+} + \mathrm{H_2O} \longrightarrow \mathrm{Fe}^{3+}(L_i)_j + \mathrm{HO}^- + \mathrm{HO}^{\bullet} \tag{7}$$

The rate constant of reaction (7) governs the life time of $Fe(L_i)_jO^{2+}$ species and consequently the probability of alkane oxidation either by this species or by hydroxyl radical. In this process the increase of water content will lead to a decrease in the selectivity.

Iron(III) Acetate as a Catalyst

We obtained some preliminary results on the catalysis by iron(III) acetate existing in the form of $Fe(OAc)_2(OH)$ (**3**). Surprisingly, it turned out that compound **3** catalyzes the alkane oxidation only if PCA is added as a co-catalyst (Figure 13). The initial reaction rate and the final yield of products grow with increases of the PCA concentration. Selectivity parameters of branched alkane oxidations under catalysis by $Fe(OAc)_2(OH)$-PCA system are low (see Table 1) and we can conclude that the reaction proceeds with participation of hydroxyl radicals. This system oxidizes also methane (TONs were up to 31; see Table 2, entry 6) and ethane (see Table 3, entries 2 and 3).

Oxidation Catalyzed by a Binuclear Iron(III) Complex Containing 1,4,7-Triazacyclononane

Finally, we studied the catalytic action of the binuclear iron(III) complex **4** containing the 1,4,7-triazacyclononane ligand.[28] Complex **4** turned out to be almost inactive as a catalyst in the cyclohexane oxidation with H_2O_2 at room temperature. However, the addition of a comparatively small amount of PCA to the reaction solution caused intense alkane oxidation (Figure 14). The primary reaction product was cyclohexyl hydroperoxide, which decomposed during the reaction to produce the corresponding cyclohexanone and cyclohexanol. Total TON attained was 240 after 24 h. In kinetic measurements we determined only the concentrations of the ketone and the alcohol after the reduction with triphenylphosphine.

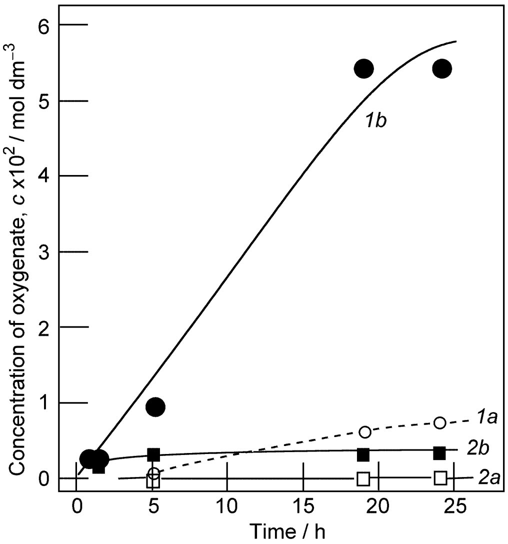


Figure 14. Cyclohexane (0.46 mol dm^{-3}) oxidation by H_2O_2 (0.59 mol dm^{-3}) catalyzed by **4** (2.5×10^{-4} mol dm^3) in the absence (curves *a*) and in the presence of PCA (25×10^{-4} mol dm^{-3}; curves *b*) in MeCN at 25 °C. Accumulation of cyclohexanol (curves *1*) and cyclohexanone (curves *2*) (concentrations were measured after the reduction with PPh_3) are shown.

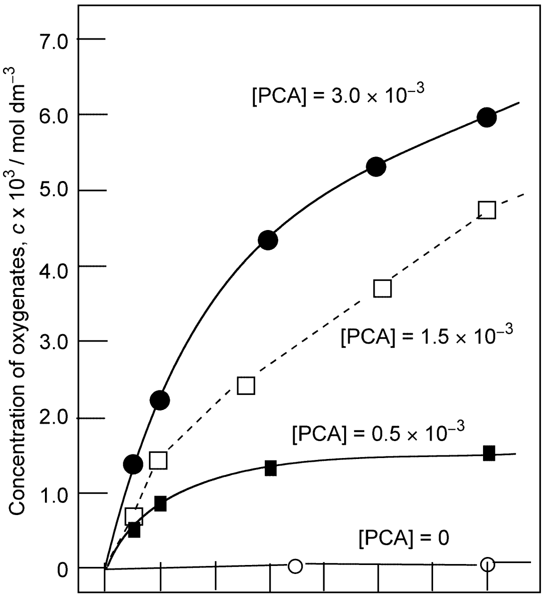


Figure 13. Cyclohexane (0.46 mol dm^{-3}) oxidation by H_2O_2 (0.1 mol dm^{-3}) catalyzed by $Fe(OAc)_2(OH)$ (5×10^{-4} mol dm^{-3}) in MeCN at 25 °C. Kinetic curves for accumulation of the oxygenates at various concentrations of added PCA (in mol dm^{-3}) are shown.

The binuclear complex **4** induced catalytic decomposition of hydrogen peroxide dissolved in acetonitrile. The reaction was accompanied by molecular oxygen evolution (catalase activity) and the oxidation of alkane with the formation of the corresponding alkyl hydroperoxide (oxidase activity). The data on the selectivity of the oxidation of several branched hydrocarbons are summarized in Table 1, which also contains the selectivity parameters of other systems capable of oxidizing alkanes *via* various mechanisms. The values presented in Table 1 show that the principle species that induces the alkane oxidation under catalysis by the "**4** + PCA" system is the hydroxyl radical possessing low selectivity. It is necessary to note, however, that the selectivity parameters for the "**4** + PCA" system are somewhat higher than for other systems, whose oxidation action doubtless involves hydroxyl radicals. This leads us to suggest that the "**4** + PCA" system generates not only low-selective hydroxyl radicals but also, in another channel, other species that more selectively interact with alkanes, for instance, ferryl species. Nevertheless, the reaction involving hydroxyl radicals predominates. This conclusion is also substantiated by our estimates of the oxidizing species reactivity in the "**4** + PCA" system.

These estimates were obtained in two series of experiments. In the first one, we studied the dependence of the initial rate of cyclohexane oxidation determined as rate W_0 of the cyclohexyl hydroperoxide, CyOOH, formation on the initial cyclohexane concentration under UV ($\lambda \geq 253$ nm) irradiation of its solution in acetonitrile in the presence of hydrogen peroxide (Figure 15A, curve *1*). It is known that the photolysis of H_2O_2 is accompanied by its decomposition to generate hydroxyl radicals:

$$H_2O_2 + h\nu \longrightarrow 2\,HO^{\bullet} \tag{8}$$

As neither acetonitrile nor cyclohexane absorb in the specified spectral region, it is reasonable to assume that the cyclohexane oxidation observed in the photochemical experiments is induced by hydroxyl radicals and occurs in accordance with Eqs. (9) and (10):

$$HO^{\bullet} + CyH \xrightarrow{k_9} Cy^{\bullet} + H_2O \tag{9}$$

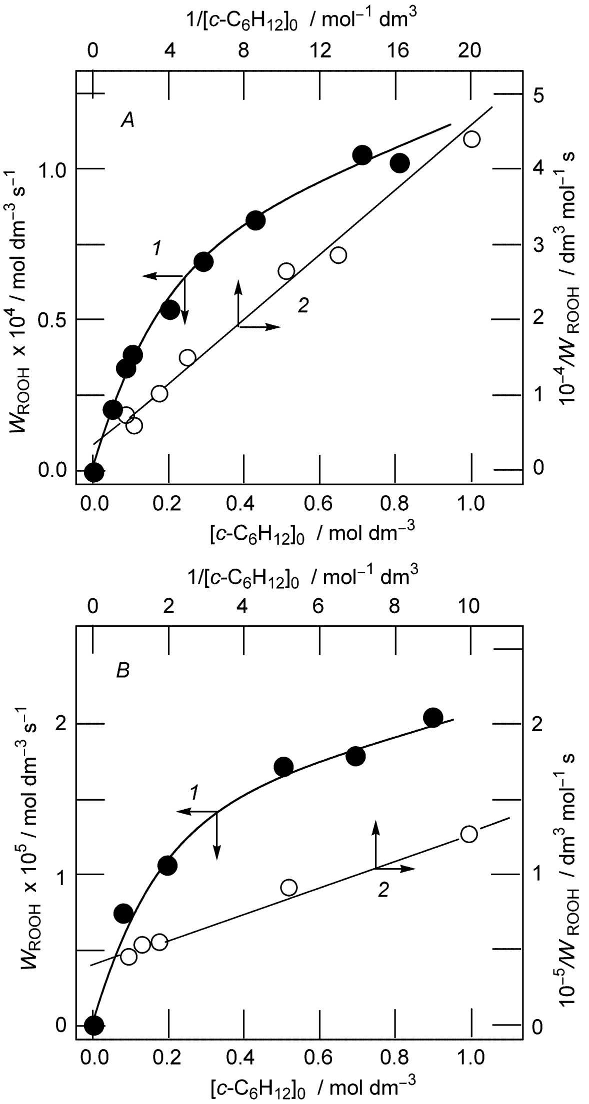


Figure 15. Cyclohexane oxidation by H_2O_2 (0.59 mol dm^{-3}) induced by UV irradiation (graph *A*) and catalyzed by the "**4** (2.5×10^{-4} mol dm^{-3}) + PCA (25×10^{-4} mol dm^{-3})" system (graph *B*) in MeCN at 25 °C. Dependence of the initial oxidation rate, W_{ROOH}, on the initial cyclohexane concentration (curve *1*) as well as its linear anamorphosis (curve *2*) are shown for both cases.

$$HO^{\bullet} + CH_3CN \xrightarrow{k_{10}} \text{products} \tag{10}$$

Taking these transformations into account, the conclusion can be drawn that an increase in the CyH concentration should cause an increase in the rate of its oxidation whose limiting value corresponds to rate W_8 of hydroxyl radical formation in reaction (8). An analysis of kinetic scheme (8) to (10) leads to Eq. (11) for the initial stationary rate of CyOOH formation:

$$-d[CyH]/dt = d(CyOOH]/dt = W_8/\{1 + k_{10}[CH_3CN]/k_9[CyH]\} \tag{11}$$

where k_9 and k_{10} are the rate constants for reactions (9) and (10), respectively. An analysis of the experimental dependence of W_0 on $[CyH]_0$ taking into account Eq. (11) (Figure 15A, straight line *2*) gives the ratio $k_{10}/k_9 = 0.013$.

The second series of experiments were carried out to study the dependence of CyOOH initial rate formation W_0 on $[CyH]_0$ when hydrogen peroxide decomposition was catalyzed by complex **4** (Figure 15B, curve *1*). We assume that hydroxyl radicals are formed in the rate-determining step of this reaction at a rate equal to the rate of cyclohexane oxidation. This assumption leads us to an equation identical to (11). The ratio between the rate constants obtained in these experiments, $k_{10}/k_9 = 0.011$ (Figure 15B, straight line *2*), is very close to that measured in the photochemical experiments (0.013) and to the value determined from radiation-chemical measurements ($k_{10}/k_9 = 0.012$). It follows that the cyclohexane oxidation during the hydrogen peroxide decomposition catalyzed by complex **4** is doubtless induced by hydroxyl radicals. Note that the classic chain mechanism of induced cyclohexane oxidation at rates equal to those observed experimentally is impossible at room temperature because of the low reactivity of cyclohexyl peroxyl radicals and, therefore, a low parameter of hydrocarbon oxidizability by the chain mechanism (see the Electronic Supplement to Ref.[25]).

It is important to note that molecular oxygen evolution is observed even at a high cyclohexane concentration, when all hydroxyl radicals are certainly accepted by the hydrocarbon. This is evidence that hydroxyl radicals do not participate in the hydrogen peroxide decomposition to afford molecular oxygen and water. We must therefore consider two parallel hydroperoxide decomposition processes: those with and without the participation of hydroxyl radicals.

We studied the kinetics of cyclohexyl hydroperoxide formation and molecular oxygen evolution to elucidate the details of the reaction mechanism. First, it was established that both the rate of CyOOH formation and the rate of O_2 evolution were directly proportional to the complex **4**'s initial concentration if PCA was present in a more than five-fold excess with respect to [**4**]. This led us to suggest that the rate-limiting steps of these processes occurred with the participation of non-aggregated initial catalyst molecules.

The dependence of the CyOOH formation initial rate on [**4**] is shown in Figure 16. Its mode indicates the catalytic activity of adducts containing only one PCA molecule. Adducts containing more than one or no PCA molecules do not exhibit catalytic activity. Accordingly, the following transformations should be taken into account in considering the reaction mechanism:

$$\mathbf{4} + \text{PCA} \xrightleftharpoons{K_{12}} \mathbf{4}\cdot\text{PCA} \qquad (12)$$

$$\mathbf{4}\cdot\text{PCA} + \text{PCA} \xrightleftharpoons{K_{13}} \mathbf{4}\cdot 2\text{PCA} \qquad (13)$$

The catalytic activity of the whole system should be attributed to the formation of the **4** · PCA adduct. The CyOOH formation initial rate depended on the initial concentration of hydrogen peroxide in a complex way (Figure 17). Initially, the process was close to second order in hydrogen peroxide, and, at $[H_2O_2]_0 > 1\ \text{mol dm}^{-3}$, the reaction rate ceased to depend on hydrogen peroxide concentration. Such a character of the dependence was evidence of an iron diperoxo complex's participation at the stage of hydroxyl radical generation.

Taking into account the formation of mono- and diperoxo complexes and assuming that the rate-determining step of hydroxyl radical formation is monomolecular decomposition of the diperoxo complex containing one PCA molecule as a ligand, reactions (12) and (13) should be augmented by the following steps:

$$\mathbf{4}\cdot\text{PCA} + H_2O_2 \xrightleftharpoons{K_{14}} \mathbf{4}\cdot\text{PCA}\cdot H_2O_2 \qquad (14)$$

$$\mathbf{4}\cdot\text{PCA}\cdot H_2O_2 + H_2O_2 \xrightleftharpoons{K_{15}} \mathbf{4}\cdot\text{PCA}\cdot 2\,H_2O_2 \qquad (15)$$

$$\mathbf{4}\cdot\text{PCA}\cdot 2\,H_2O_2 \xrightarrow{k_{16}} \mathbf{4}\cdot\text{PCA} + H_2O + HOO^{\bullet} + HO^{\bullet} \qquad (16)$$

If we assume that the concentrations of the **4** · PCA, **4** · 2 PCA, **4** · PCA · H_2O_2 and **4** · PCA · 2 H_2O_2 intermediate complexes are quasi-equilibrium, then, at a high CyH concentration when all hydroxyl radicals formed in reaction (16) interact with cyclohexane and at $[\text{PCA}]_0/[\mathbf{4}]_0 \geq 5$, the suggested kinetic scheme can be used to obtain the equation for the stationary rate of CyOOH formation:

$$-\frac{d[RH]}{dt} = \frac{d[ROOH]}{dt} = \frac{k_{16}K_{12}K_{14}K_{15}[H_2O_2]_0^2[\text{PCA}]_0[\mathbf{4}]_0}{1 + K_{12}[\text{PCA}]_0 + K_{12}K_{13}[\text{PCA}]_0^2 + K_{12}K_{14}[\text{PCA}]_0[H_2O_2]_0 + K_{12}K_{14}K_{15}[\text{PCA}]_0[H_2O_2]_0^2} \qquad (17)$$

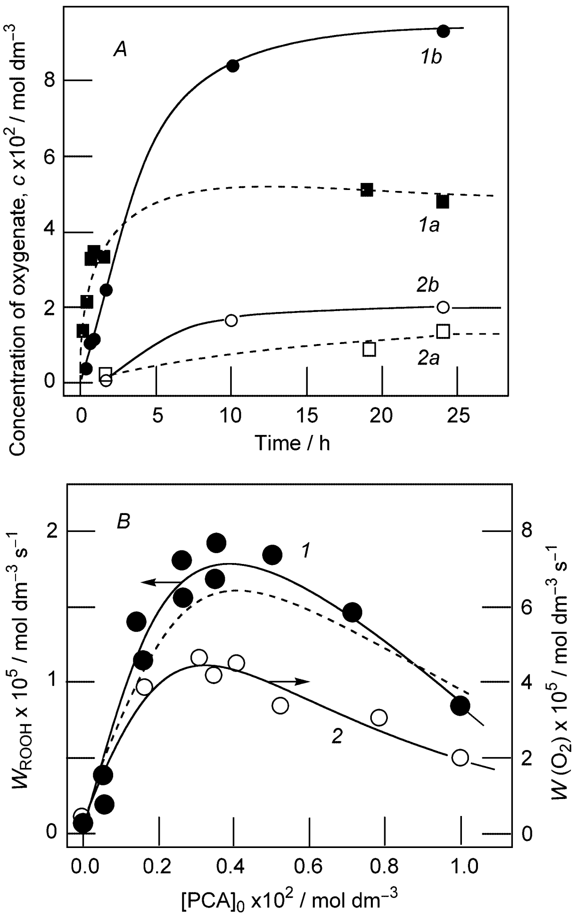


Figure 16. Cyclohexane (0.46 mol dm^{-3}) oxidation by H_2O_2 (0.59 mol dm^{-3}) catalyzed by the "**4** (2.5×10^{-4} mol dm^{-3}) + PCA" system in MeCN at 25 °C. Graph *A*: accumulation of cyclohexanol (curves *1*) and cyclohexanone (curves *2*) (concentrations were measured after the reduction with PPh_3) at different concentrations (in mol dm^{-3}) of added PCA: 25×10^{-4} (curves *a*) and 75×10^{-4} (curves *b*). Graph *B*: dependence of the initial cyclohexane oxidation rate, W_{ROOH}, (curve *1*) and of simultaneous O_2 evolution (curve *2*) on the concentration of added PCA. The simulated curve for W_{ROOH}

Eq. (17) satisfactorily describes the experimental data shown in Figures 16 and 17 at the following constant parameters: $k_{16} = 0.13\ \text{s}^{-1}$, $K_{12} = 16\ \text{dm}^3\ \text{mol}^{-1}$, $K_{13} = 6250\ \text{dm}^3\ \text{mol}^{-1}$, $K_{14} = 12.5\ \text{dm}^3\ \text{mol}^{-1}$ and $K_{15} = 10\ \text{dm}^3\ \text{mol}^{-1}$ (compare the experimental and simulated curves in Figures 16 and 17). The mode of the dependence of the molecular oxygen evolution rate on [PCA] is identical to that of the dependence of d[CyOOH]/d*t* on [PCA]. It follows that the same intermediate complex participates in the rate-limiting steps of both processes, namely, the diperoxo derivative of compound **4** containing one PCA molecule, **4** · PCA · 2 H_2O_2. The dioxy-

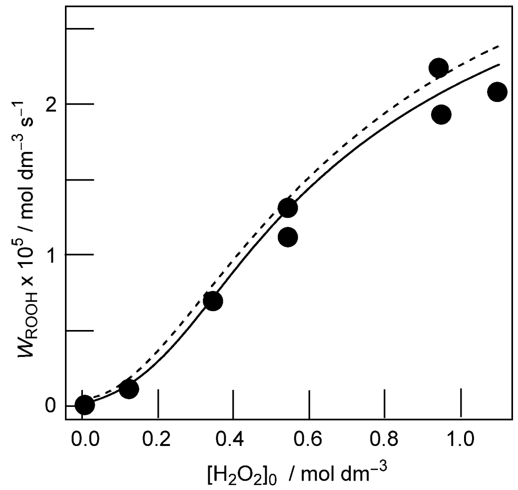


Figure 17. Cyclohexane (0.46 mol dm^{-3}) oxidation by H_2O_2 catalyzed by the "**4** (2.5×10^{-4} mol dm^{-3}) + PCA (25×10^{-4} mol dm^{-3})" system in MeCN at 25 °C. Dependence of the initial cyclohexane oxidation rate, W_{ROOH}, on the initial concentration of hydrogen peroxide is shown. The simulated curve for W_{ROOH} is dashed.

gen evolution can occur in the decomposition of this derivative:

$$\mathbf{4}\cdot PCA\cdot 2\,H_2O_2 \longrightarrow 2\,H_2O + O_2 + \mathbf{4} \tag{18}$$

This process is similar to the decomposition of hydrogen peroxide by enzyme catalase. The competition of reactions (16) and (18) is likely to be caused by the binuclear structure of compound **4**.

Conclusion

Our study shows that ligand environment of iron ions plays a very important role from the point of view of the reaction mechanism. For example, addition of chloride anions to the "naked" iron(III) cation switches the reaction mechanism from that occurring with formation of hydroxyl radicals to another mechanism which operates predominantly with participation of ferryl species. It is interesting that, in contrast to iron chloride case, the oxidation catalyzed by a dinuclear complex containing chelating N_3-ligands proceeds *via* hydroxyl radicals.

Experimental Section

Synthesis and properties of compound **4** were published previously in the literature.[28a]

The oxidations of higher hydrocarbons were carried out in air in thermostatted 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, 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 method was proposed by us earlier.[1d,24] 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 us to calculate the real concentrations not only of the hydroperoxide but of the alcohols and ketones present in the solution at a given moment. 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 thermostatted 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.

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 Prof. Karl Wieghardt for useful discussions.

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