

# Metal-catalyzed hydrocarbon oxygenations in solutions: the dramatic role of additives: a review

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## Abstract

This review describes examples of remarkable acceleration of metal-catalyzed oxidation reactions by certain additives. In some cases, reactions proceed 2 or 10 times more rapidly in comparison with the process in the additive's absence, in other cases, reactions become possible only in the presence of the additive. Varying ligands at the metal center or additives, one can not only dramatically improve yields of oxygenates but also control the selectivity of the reaction. Understanding mechanisms of the additive's action is very important for search of new efficient catalysts and catalytic systems. Additives considered in the review can play roles of the ligands at metal ion or proton or electron transfer reagents and they mimic certain enzymes (the active center or its environment). Often the mechanism of the effect of additives on the reaction rate and the product yield is unknown, and the main aim of the review is to attract investigator's attention in creating new efficient catalytic systems, which contain not only a metal ion but also a necessary "additive".

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## 1. Introduction

Chemical inertness of alkanes (saturated hydrocarbons may be called the "noble gases of organic chemistry") causes great difficulties in their selective activation, especially under mild conditions. Only in the past decades, the vigorous development of metal-complex catalysis allowed the beginning of an essentially new chemistry of saturated hydrocarbons [1,2]. Transformations of hydrocarbons under the action of metal-complex catalysts seem to be a very promising field. Indeed, in contrast to almost all presently employed processes, reactions with metal

complexes occur at relatively low temperatures and can be selective.

The oxidation of hydrocarbons with dioxygen and donors of an oxygen atom such as hydrogen peroxide ( $H_2O_2$ ), alkyl hydroperoxides as well as iodosylbenzene and other compounds, is an important field, since some industrial processes are based on these reactions. They may be a basis for creating new technologies for direct selective transformations of alkanes and aromatics into valuable oxygen-containing products. Examples of such oxidations are known when the reaction either proceeds noticeably less efficiently or does not occur at all if certain additives are not present in the reaction mixture. The additives which often are the potential ligands for metal-ion centers were found in searches oriented to the creation of models for enzyme reaction centers. The aminoacids or heterocyclic

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amines can mimic the protein environment around the enzyme reaction center [3–12]. It is very interesting that in many cases only particular specific molecules can play roles of efficient co-catalysts and even very similar compounds turn out to be much less reactive or completely inactive in the catalysis. In this brief review, we will consider examples of various catalytic reactions when addition of certain compounds in small amounts dramatically enhances the reaction rate and the product yield. These reactions are mainly oxidation of saturated hydrocarbons but the oxidative transformations of other compounds will be also described. It should be noted that mechanisms of the additives' action are not usually known although the authors tentatively proposed mechanistic explanations.

## 2. Estimation of alkyl hydroperoxide content by GC analysis of the reaction solution samples before and after reduction with triphenylphosphine

In 1992, we demonstrated [13,14] that  $\text{H}_2\text{O}_2$  oxidations of alkanes catalyzed by some transition metal complexes give substantial amounts of the corresponding alkyl hydroperoxides in addition to usually smaller concentrations of alcohols and ketones. We used a very simple method which we developed in our earlier works devoted to the alkane oxidations with  $\text{H}_2\text{O}_2$  [1,2,14–16] as well as by air under visible light irradiation [13,17–21]. This method is based on comparison of the chromatograms of the reaction solution made before and after the treatment of the sample with triphenylphosphine ( $\text{PPh}_3$ ). If  $\text{PPh}_3$  is insoluble in the reaction mixture, for example in water solution, other reducing agents, such as  $\text{NaBH}_4$  or  $\text{Na}_2\text{S}_2\text{O}_3$  can be used. One of the merits of this method, which was used later by other authors [22–25], is the possibility to estimate the concentration of the alkyl hydroperoxide formed from the alkane in the presence of an excess of an oxidant ( $\text{H}_2\text{O}_2$ , alkyl hydroperoxide or metal peroxide). It is reasonable to describe this method before discussion of various oxidations that afford mainly alkyl hydroperoxides.

We have found [13–21] that if an excess of solid  $\text{PPh}_3$  is added to a solution of the alkane oxidation products 10–20 min before the GC analysis, the resulting chromatogram differs drastically from that of a sample not subjected to the reduction with  $\text{PPh}_3$ . The

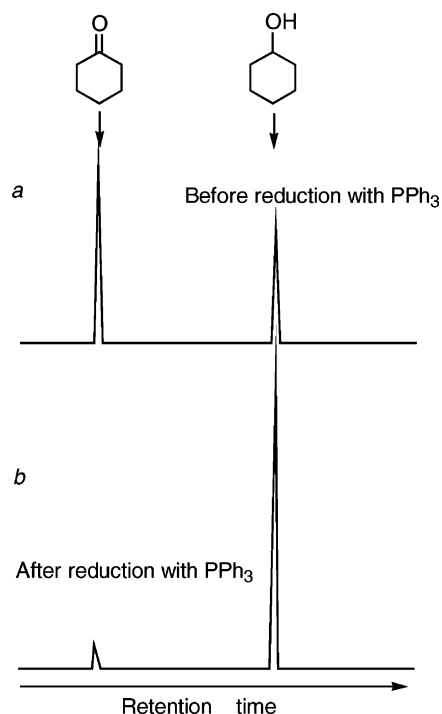
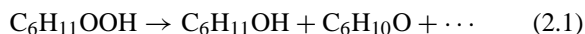
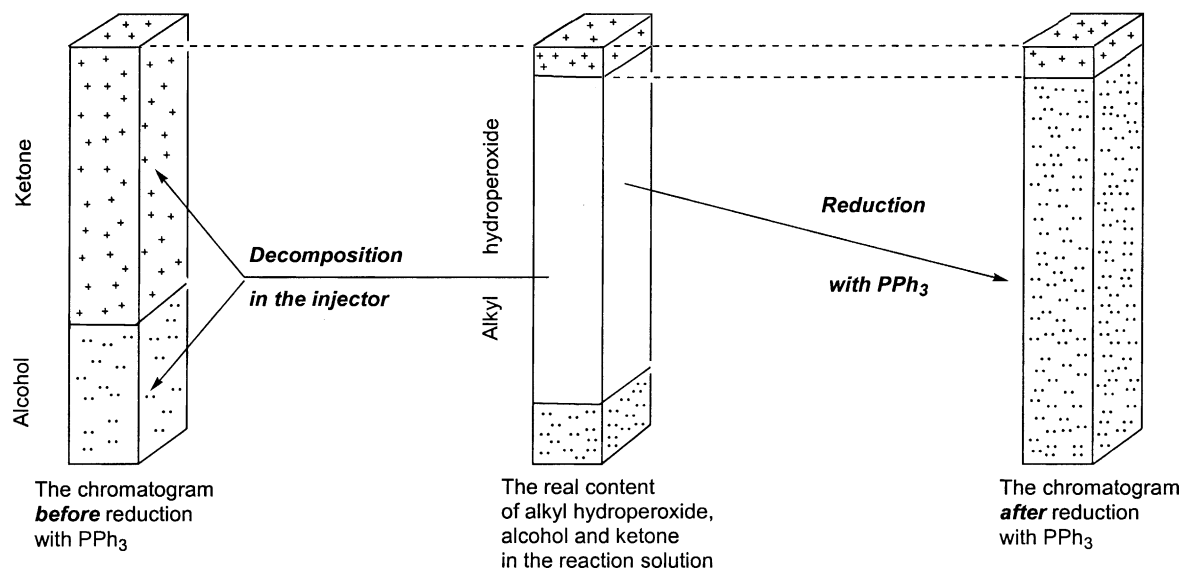


Fig. 1. Typical chromatograms of a reaction mixture obtained in the metal-catalysed  $\text{H}_2\text{O}_2$  oxidation of cyclohexane. After the reduction with  $\text{PPh}_3$ , the cyclohexanol peak rises while the intensity of the cyclohexanone peak decreases which testifies that in reality the reaction mixture contains cyclohexyl hydroperoxide as the main product (the amount of cyclohexanol in chromatogram b corresponds to the sum of cyclohexyl hydroperoxide and cyclohexanol really present in the reaction mixture) and only very small amount of cyclohexanone (its real concentration can be determined from chromatogram b).

example is as shown in Fig. 1. After the reduction, the cyclohexanol peak rises markedly while the intensity of the cyclohexanone peak decreases. Usually the sum of alcohol and ketone concentrations in the reduced sample is approximately equal to the total concentration of products in the solution untreated with  $\text{PPh}_3$  (Scheme 1). These results can be explained by the fact that the mixture of the products of the reaction under consideration contains cyclohexyl hydroperoxide as the main component. Cyclohexyl hydroperoxide can totally decompose in the chromatograph to produce mainly cyclohexanol and cyclohexanone according to the scheme:

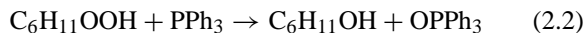




Scheme 1. The GC analysis of the mixture obtained in the alkane oxidation. This method allows to estimate real concentrations of the alkyl hydroperoxide, ketone (aldehyde) and alcohol present in the reaction solution.

The cyclohexanone:cyclohexanol ratio in decomposition of Eq. (2.1) can vary depending on the properties of the particular chromatograph (the material of the injector, columns, the stationary phase, etc.) being roughly around 1:1. Since, a reaction affords not only cyclohexyl hydroperoxide but also certain amounts of cyclohexanone and cyclohexanol, the chromatogram obtained for the “native” reaction solution will give amounts of the ketone and alcohol in accordance with Eq. (2.1) plus amounts of these products really present in the reaction mixture.

Alkyl hydroperoxides are known to be readily and quantitatively reduced by  $\text{PPh}_3$  to yield corresponding alcohols. In the case of cyclohexyl hydroperoxide, the reaction gives cyclohexanol:



After treatment of the reaction solution with  $\text{PPh}_3$ , the GC analysis will give the amount of cyclohexanone which corresponds to the real concentration of this product in the reaction solution. The amount of cyclohexanol will correspond to the sum of real concentrations of cyclohexyl hydroperoxide and cyclohexanol. Thus, by comparing the data of chromatographic analysis of the reaction solution before and after reduction with  $\text{PPh}_3$ , the amounts of cyclo-

hexyl hydroperoxide, really present in the solution at a given moment can be estimated quantitatively. The cyclohexanol:cyclohexanone ratio from the cyclohexyl hydroperoxide decomposition, which is specific for the particular chromatograph, can be determined by injecting a sample of pure alkyl hydroperoxide or analyzing the cyclohexanol:cyclohexanone ratio in the initial period of the reaction when the alkyl hydroperoxide is the sole product. In order to determine the concentrations of all components of the reaction mixture in the oxidation of various alkanes, it is necessary to measure the ketone:alcohol ratio separately for the decomposition of each isomer of the formed alkyl hydroperoxide. Principally, it is possible to do this if the reaction time is short enough and only isomeric hydroperoxides are present in the solution. This method can be used also for the qualitative determination of the alkyl hydroperoxide because the difference between the chromatograms of the reaction solution samples before and after the reduction with  $\text{PPh}_3$  can unambiguously testify the formation of an alkyl hydroperoxide in the course of the reaction.

In some of the cases, the sum of all products determined before the reduction of the reaction sample is noticeably lower than that calculated from the chromatogram obtained for the reduced sample. It can be

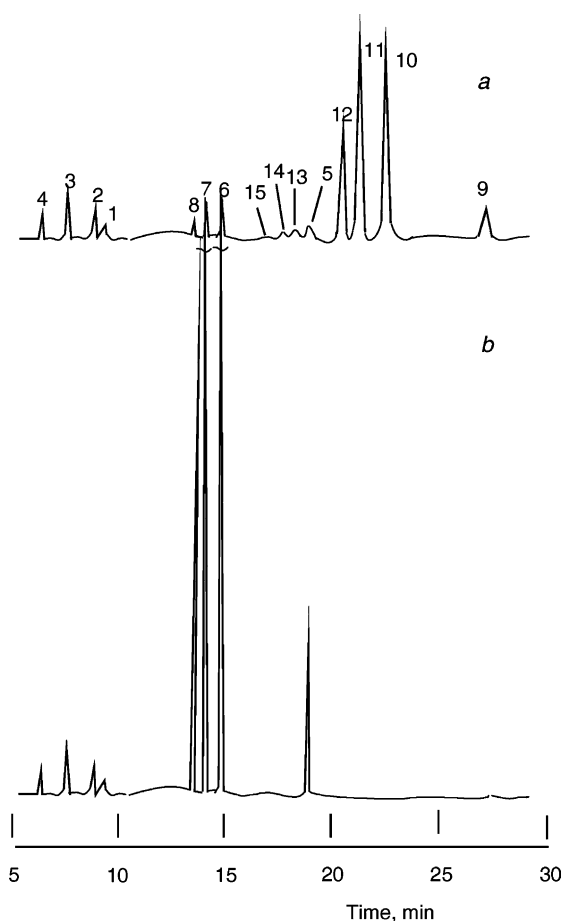


Fig. 2. The GC analysis of the products of *n*-heptane oxidation with the “O<sub>2</sub>–H<sub>2</sub>O<sub>2</sub>–VO<sub>3</sub><sup>–</sup>–PCA” reagent in acetonitrile at 23 °C (3 h) before (a) and after (b) the reduction of the reaction mixture with PPh<sub>3</sub>: peaks are attributed to heptanal (1), 2-, 3-, and 4-isomers of heptanone (2–4, respectively), 1-, 2-, 3-, and 4-isomers of heptanol (5–8, respectively), 1-, 2-, 3-, and 4-isomers of heptyl hydroperoxide (9–12, respectively); peaks 13–15 are from unidentified peroxide products.

due to the partial decomposition of the alkyl hydroperoxide with C–C bond splitting to afford products other than expected ketone and alcohol. More interestingly, using a quartz-lined injector and quartz columns in the GC, it is possible to find peaks due to alkyl hydroperoxides. These peaks disappear completely after the treatment of the solution with PPh<sub>3</sub>, while peaks of the corresponding alcohols grow (Fig. 2) [26]. Since, some (ca. 10–15%) decomposition of alkyl hydroperoxide occurs during the “direct” GC determination,

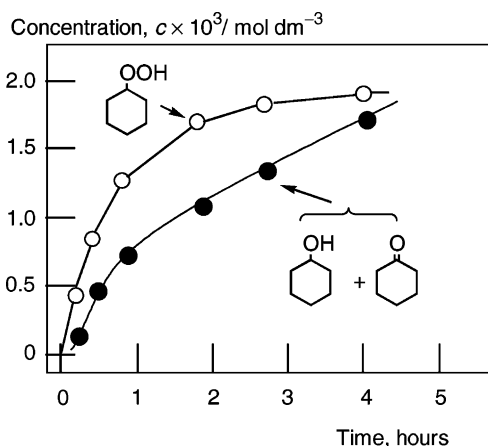


Fig. 3. The kinetics of cyclohexane (0.61 mol dm<sup>–3</sup>) oxygenation by H<sub>2</sub>O<sub>2</sub> (0.42 mol dm<sup>–3</sup>) in acetonitrile at 40 °C catalyzed by Pd(OCOCF<sub>3</sub>)<sub>2</sub> (1.0 × 10<sup>–3</sup> mol dm<sup>–3</sup>).

even in this case, it is more convenient to estimate the real concentrations of all products by comparing chromatograms before and after treatment with PPh<sub>3</sub>. An example of an alkyl hydroperoxide accumulation with time is as shown in Fig. 3 [14].

It should be noted in conclusion of this section that in studies on alkane oxidations, it is necessary to reduce the reaction solution with PPh<sub>3</sub> prior to the GC analysis in order to know the precise values for the product concentrations. Indeed, if we operate with data obtained before the reduction, we could diminish the real concentrations because some amount of the alkyl hydroperoxide can give a separate peak and some decomposition of this alkyl hydroperoxide can occur in the chromatograph to produce various derivatives which will not be included into a sum of all products. For example, C–C bond splitting can occur. On the other hand, a reaction between H<sub>2</sub>O<sub>2</sub> and a hydrocarbon can proceed in the GC at high temperature yielding products which are not really produced in the reaction solution.

### 3. Aminoacids as co-catalysts

#### 3.1. Oxidations by the “O<sub>2</sub>–H<sub>2</sub>O<sub>2</sub>–vanadium derivative–pyrazine-2-carboxylic acid” reagent

In the absence of any additives soluble vanadium complexes do not catalyze alkane oxidation with

$\text{H}_2\text{O}_2$  in acetonitrile solution. However, the situation can be dramatically changed if pyrazine-2-carboxylic acid (PCA) is added. We have described the reagent “ $\text{O}_2\text{-H}_2\text{O}_2\text{-vanadium complex-PCA}$ ” which efficiently oxidizes saturated hydrocarbons in MeCN at temperatures 20–70 °C [14,26–45]. The following soluble vanadium derivative have been used as catalysts: vanadate-anion in the form  ${}^n\text{Bu}_4\text{NVO}_3$ , or  $\text{VOSO}_4$ ,

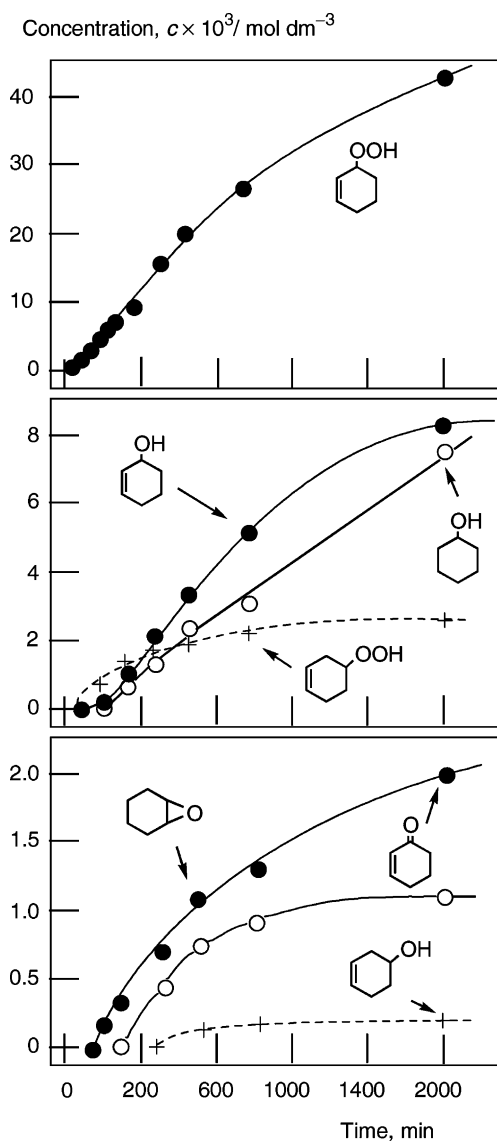
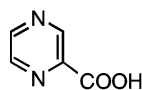
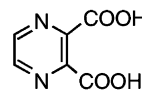


Fig. 4. The kinetics of  $\text{H}_2\text{O}_2$  oxidation of cyclohexene ( $0.47 \text{ mol dm}^{-3}$ ) catalyzed by  $\text{VO}_3^-$  ( $1.0 \times 10^{-4} \text{ mol dm}^{-3}$ ) and PCA ( $4.0 \times 10^{-4} \text{ mol dm}^{-3}$ ) in acetonitrile at 23 °C.

*High activity:*

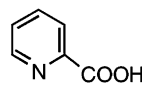


Pyrazine-2-carboxylic acid (PCA)

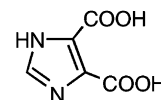


Pyrazine-2,3-dicarboxylic acid

*Moderate activity:*

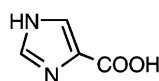


Picolinic acid

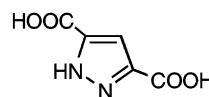


Imidazole-4,5-dicarboxylic acid

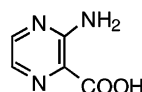
*Low activity:*



Imidazole-4-carboxylic acid

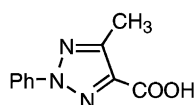


Pyrazole-3,5-dicarboxylic acid



3-Aminopyrazine-2-carboxylic acid

*Very low activity:*



5-Methyl-2-phenyl-1,2,3-triazol-4-carboxylic acid

Scheme 2. Cyclic aminoacids which were tested as co-catalysts in vanadium-catalyzed  $\text{H}_2\text{O}_2$  oxidation of cyclohexane.

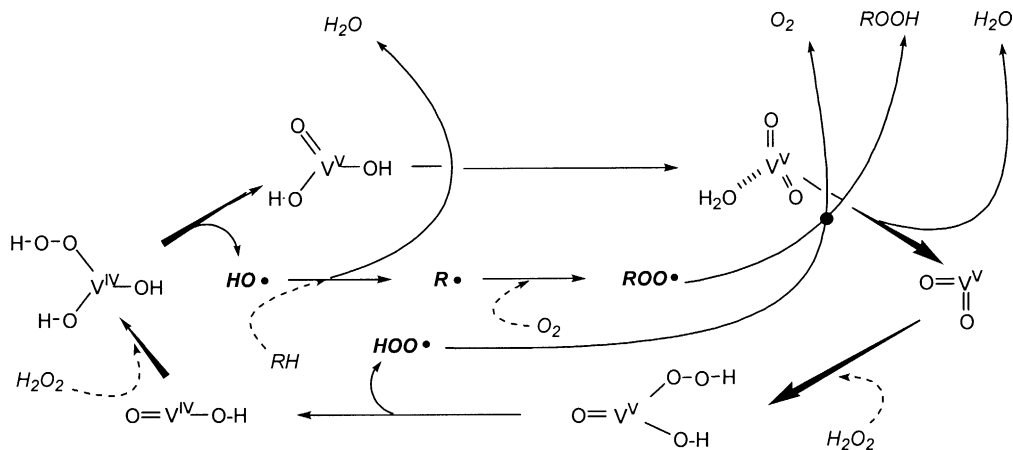
$\text{VCl}_3$ ,  $\text{VO}(\text{acac})_2$ , the first complex salt being the best catalyst. The maximum oxidation rates were attained for the ratios  $[\text{V}]:[\text{PCA}] = 1:4$  to  $1:10$ . As it was shown by the method described in the previous section, at low temperatures in acetonitrile, the predominant product of the alkane oxidation is the corresponding alkyl hydroperoxide, and alcohols and ketones or aldehydes are formed simultaneously in smaller amounts. This alkyl hydroperoxide then slowly decomposes to produce the corresponding ketone and

alcohol. It has been demonstrated that the atmospheric oxygen takes part in this reaction; in the absence of air, the oxygenation reaction does not proceed. The oxidation of *n*-heptane by the reagent under consideration exhibits low selectivity, C(1):C(2):C(3):C(4)  $\approx$  1:6.2:6.2:5.3, where the C(1):C(2):C(3):C(4) parameter is relative (and normalized, i.e. calculated, taking into account the number of hydrogen atoms at each carbon) reactivities of hydrogen atoms at carbons 1–4 of the chain of non-branched alkanes. This parameter is close to that found for the oxidation of *n*-heptane by H<sub>2</sub>O<sub>2</sub> in MeCN under UV irradiation ( $\sim$ 1:7:7:7). Cyclohexene affords a mixture of oxygenates (Fig. 4) [34]. Methane, ethane, propane, *n*-butane and isobutane can be also readily oxidized in acetonitrile by the same reagent. In addition to alkyl hydroperoxides as the primary oxidation products, alcohols, aldehydes or ketones, and carboxylic acids are obtained with high total turnover numbers and H<sub>2</sub>O<sub>2</sub> efficiency.

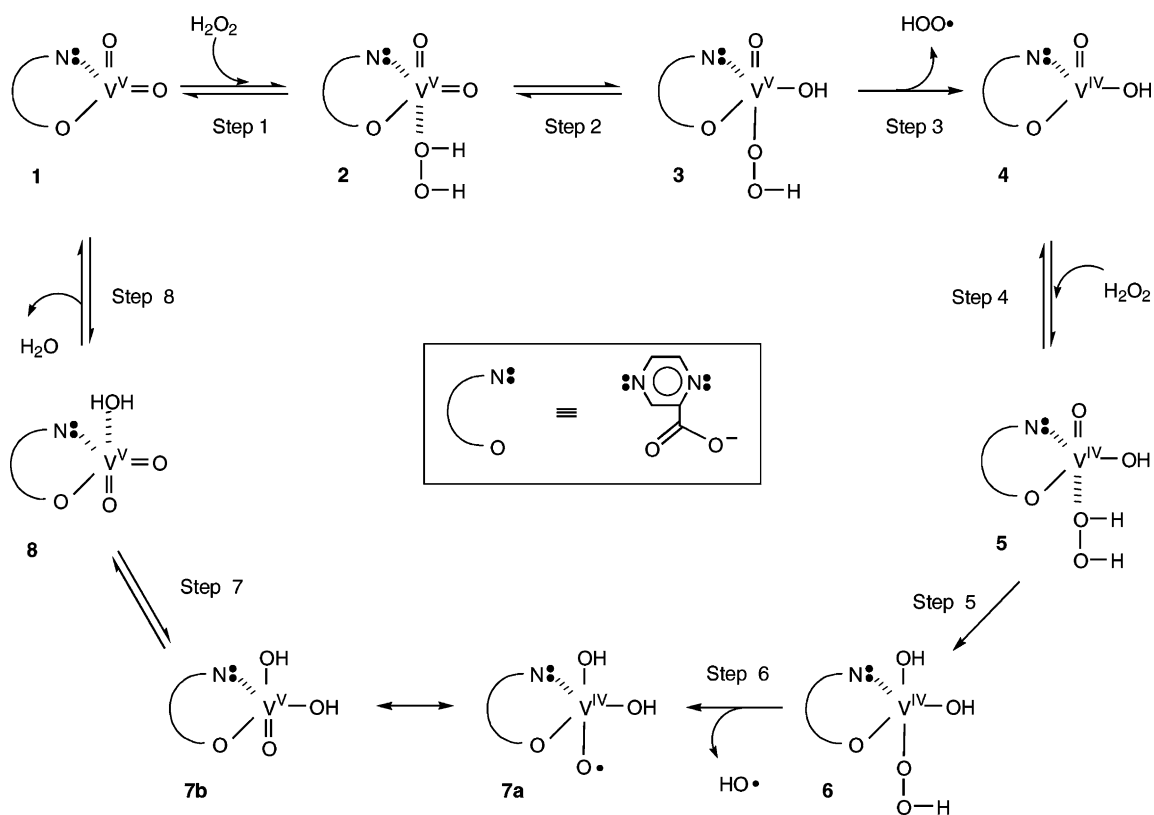
While the oxo complex [V(O)<sub>2</sub>(pca)<sub>2</sub>]<sup>−</sup> (where pca is PCA anion), used as tetrabutylammonium salt, itself catalyses the H<sub>2</sub>O<sub>2</sub> alkane oxidation, if free PCA is added to the reaction mixture, the rate is noticeably higher. It has been demonstrated recently by Iwasama and co-workers that the vanadium complex with picolinic acid, VO(pic)<sub>2</sub>, encapsulated into the NaY zeolite retains solution-like activity in the liquid-phase oxidation of hydrocarbons [46,47]. It is also important to emphasize that although certain aminoacids which are similar to PCA can play the role of co-catalysts, the oxidation rates and final product yields are lower for

picolinic and imidazole-4,5-dicarboxylic acids, while imidazole-4-carboxylic, pyrazole-3,5-dicarboxylic and 5-methyl-2-phenyl-1,2,3-triazole-4-carboxylic acids are almost inactive (Scheme 2).

In the system under discussion, the catalytic hydroxyl radical generation is presented in Schemes 3 and 4. It has been shown by the kinetic analysis that the interaction between vanadate anion and PCA (=pcaH) molecule results in the formation of dioxo complex **1** of vanadium(V) bearing only one pca ligand. Complex **1** can coordinate H<sub>2</sub>O<sub>2</sub> molecule and this process is presented by step 1 in Scheme 4. The following transformation is the reduction of vanadium(V) to vanadium(IV) by a H<sub>2</sub>O<sub>2</sub> molecule. This reaction, which is a rate-determining stage, corresponds to a hydrogen atom abstraction by an oxo ligand of V(V) complex which gives hydroperoxyl radical, HOO• and oxo-hydroxy V(IV) derivative **4**. It was assumed that the reduction occurs in two steps: proton transfer from coordinated H<sub>2</sub>O<sub>2</sub> to one of the two oxo ligands with simultaneous formation of a new covalent V–O bond (step 2) and the subsequent homolysis of this V–OOH bond (step 3). The second H<sub>2</sub>O<sub>2</sub> molecule adds to a vacant site of complex **4** forming in step 4 the V(IV) complex **5**. Other proton transfer (step 5) results in the formation of dihydroxy-hydroperoxy V(IV) derivative **6**. Complex **6** decomposes via the homolysis of the O–O bond in the hydroperoxy ligand (step 6), generating a free hydroxyl radical. This reaction seems to be favorable because it leads to an oxygen-centred radical V(IV)–O• (**7a**) which is a mesomeric form of the



Scheme 3. Catalysis by vanadium complex of hydroxyl radical generation and RH oxidation.



Scheme 4. Proposed catalytic cycle which involves proton transfer from the vanadium-coordinated  $\text{H}_2\text{O}_2$  molecule to the oxo ligand with participation of the pca ligand.

stable oxo vanadium(V) complex (**7b**). The formation of a stable species can be “a driving force” for the liberation of hydroxyl radicals. Mesomeric form **7a** can be considered as excited state of species **7b** existing in the ground state.

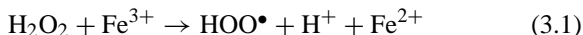
It was proposed that in this process the pca ligand plays the role of “a robot-manipulator’s arm” facilitating the proton transfer within the vanadium complex [37]. The nitrogen atom of the pca ligand can be de-coordinated from vanadium and abstract a proton from the coordinated  $\text{H}_2\text{O}_2$  molecule to form a pyridinium base which, after rotation of “the robot’s arm”, approaches another  $=\text{O}$  ligand of the complex and protonates it to produce  $-\text{OH}$  ligand.

Vanadium(V) derivatives are known to play in some biological systems the role of catalysts for hydroxyl radical generation due to which these compounds are toxic. Possibly, the accelerating role of PCA for the

generation of hydroxyl radicals, which we have found for the “ $\text{O}_2\text{--H}_2\text{O}_2\text{--}n\text{-Bu}_4\text{NVO}_3\text{--PCA}$ ” reagent, is played in living organisms by aminoacids of peptides or free aminoacids of various cell components. Thus, we can conclude that processes which occur under the action of the described reagent mimic some biological reactions and this reagent can be considered as a biomimetic system.

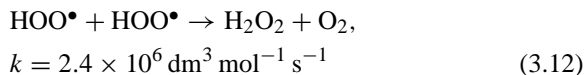
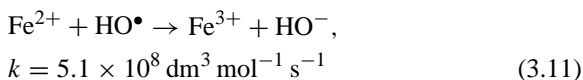
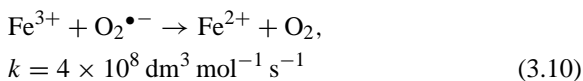
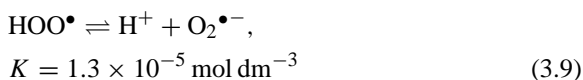
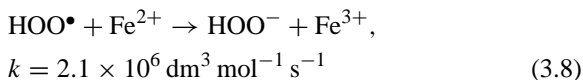
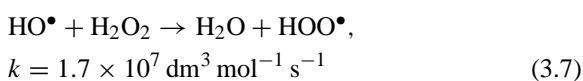
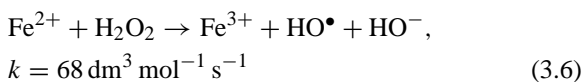
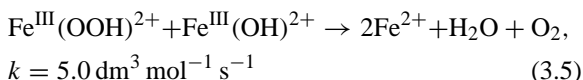
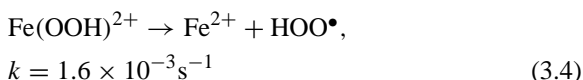
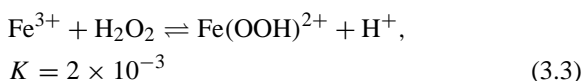
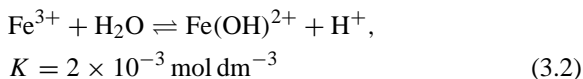
The vanadium-based reagent described previously, apparently has some mechanistic similarities with the “ $\text{Fe(III)--Fe(II)--H}_2\text{O}_2$ ” system, as well as with Fenton’s reagent (i.e. “ $\text{Fe(II)--H}_2\text{O}_2$ ” system). It is interesting to compare the reactive efficiencies of these reagents [37] (for the accelerating effect of various additives in Fe-induced oxidations, see Sections 3.3 and 3.4). The stoichiometric Fenton ( $\text{Fe(II)--H}_2\text{O}_2$ ) system is transformed gradually into the catalytic “ $\text{Fe(III)--Fe(II)--H}_2\text{O}_2$ ” system in the course of the

H<sub>2</sub>O<sub>2</sub> decomposition according to Eq. (3.1):



with the effective rate constant  $k_{3.1} = 2 \times 10^{-4} \text{ dm}^3 \text{ mol}^{-1} \text{ s}^{-1}$  at 25 °C and  $[\text{H}^+] = 1.0 \times 10^{-2} \text{ mol dm}^{-3}$ .

Both Fe-containing systems operate in aqueous solution (see p. 430 of [1], and [48–52]) at room temperature. The modified and complemented chain Haber–Weiss mechanism [51,52] contains stages (3.2)–(3.12):



In this scheme for the decomposition of H<sub>2</sub>O<sub>2</sub> to produce O<sub>2</sub> and H<sub>2</sub>O, reactions (3.4) and (3.5) are the chain initiation steps, reactions (3.6), (3.7) and (3.10) are the chain propagation steps and reactions (3.8), (3.11) and (3.12) are the chain termination steps. Note that in the case of Eq. (3.2) concentration of H<sub>2</sub>O is included into *K*. In general, the catalytic V–PCA-based system has many mechanistic similarities with the catalytic “Fe(III)–Fe(II)–H<sub>2</sub>O<sub>2</sub>” system, in both the cases, in the key step the interaction of H<sub>2</sub>O<sub>2</sub> with a low-valent form of the metal complex affords hydroxyl radicals.

The hydroxyl radical generation by the ‘catalytic’ “O<sub>2</sub>–H<sub>2</sub>O<sub>2</sub>–*n*-Bu<sub>4</sub>NVO<sub>3</sub>–PCA” reagent is less efficient than that by the ‘stoichiometric’ “Fe(II)–H<sub>2</sub>O<sub>2</sub>” system (Fenton’s reagent). Indeed, the rate constant for reaction (3.6) in water at 25 °C (68 dm<sup>3</sup> mol<sup>−1</sup> s<sup>−1</sup>) is higher than the effective rate constant for the cyclohexane oxygenation with the V–PCA-containing reagent (0.44 dm<sup>3</sup> mol<sup>−1</sup> s<sup>−1</sup> at 40 °C). Let us compare, however, the activities of the peroxy complex Fe<sup>III</sup>(OOH)<sup>2+</sup> (Eq. (3.4)) and the analogous vanadium(V) peroxy derivative V(PCA) H<sub>2</sub>O<sub>2</sub> in the monomolecular decomposition reactions to generate active species. The constant for the vanadium complex decomposition is 0.4 s<sup>−1</sup> at 40 °C, whereas, the corresponding value for the iron compound  $k_{3.4} = 1.6 \times 10^{-3} \text{ s}^{-1}$  at 25 °C. Using the value  $E_{3.4} = 22 \text{ kcal mol}^{-1}$ , we can estimate  $k_{3.4} \approx 10^{-2} \text{ s}^{-1}$  at 40 °C. Thus, it can be concluded that the activity of the vanadium complex with PCA in the generation of radicals in acetonitrile solution is more than one order of magnitude higher than that of Fe(III) ion in acidified aqueous solution. It should also be noted that unlike the classical radical-chain oxidation of alkanes with molecular oxygen [1,53,54], the oxygenation with the V–PCA-containing reagent under discussion proceeds at relatively low temperature and gives rise to the formation mainly of alkyl hydroperoxides.

### 3.2. Some other reactions co-catalysed by pyrazine-2-carboxylic acid

Alkanes can be oxidized by H<sub>2</sub>O<sub>2</sub> in acetonitrile using tetra-*n*-butylammonium salts of the vanadium-



Table 1  
Oxidation of hydrocarbons by H<sub>2</sub>O<sub>2</sub> in MeCN catalyzed by the CH<sub>3</sub>ReO<sub>3</sub>–PCA system

Substrate	Products (mmol dm <sup>-3</sup> )				TON <sup>a</sup>	<i>o:p</i> ratio
	Ketone	Alcohol	ROOH			
Cyclohexane	0.55	4.89	7.18		126	
Cyclooctane	3.75	4.87	20.48		291	
<i>n</i> -Heptane	C(1)	C(2)	C(3)	C(4)	134	
Carbonyl derivative	0.21	0.16	0.45	0.20		
Alcohol	0.04	0.85	1.15	0.54		
Alkyl hydro-peroxide	0.54	3.62	3.90	1.71		
Benzene	Phenol (3.04) Quinone (0.60)				31	
Toluene	<i>o</i> -Cresol (9.05) <i>p</i> -Cresol (3.08) Benzaldehyde (0.50) Benzyl alcohol (1.10) Benzoic acid (0.39) Benzyl hydroperoxide (0.80)				149	25:75
Ethylbenzene	<i>o</i> -Ethylphenol (4.96) <i>p</i> -Ethylphenol (2.14) Acetophenone (1.06) 1-Phenylethanol (2.57) 1-Phenylethyl hydroperoxide (5.35)				160	30:70

Real concentrations of all products were calculated from the GC analysis before and after treatment of the reaction samples with PPh<sub>3</sub>.

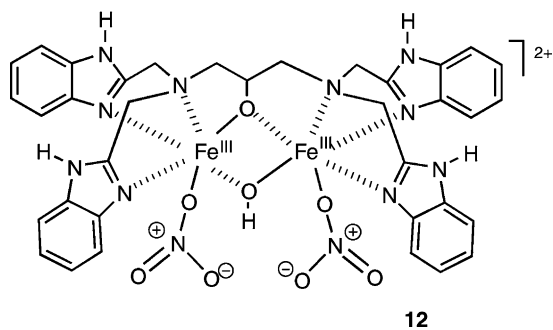
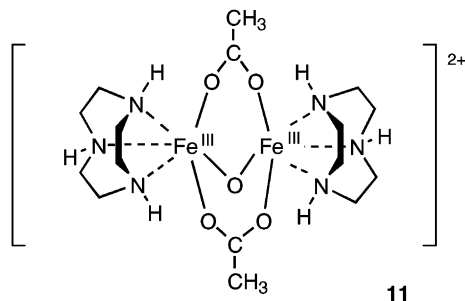
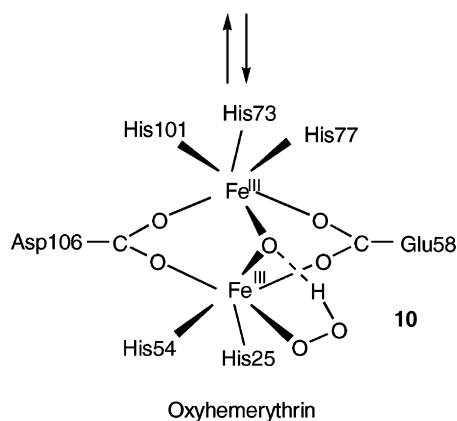
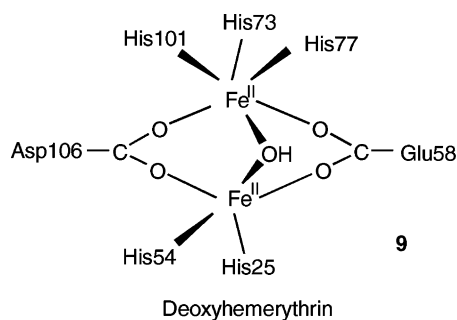
<sup>a</sup> The turnover number of the catalyst, moles of all detected products per 1 mol of CH<sub>3</sub>ReO<sub>3</sub>.

containing polyphosphomolybdate [PMo<sub>11</sub>VO<sub>40</sub>]<sup>4-</sup> as catalyst [55]. The oxidation of alkanes gives rise to the corresponding alkyl hydroperoxides as the main products, which slowly decompose in the course of the reaction to produce the corresponding ketones (aldehydes) and alcohols. It turned out that the total yield of the reaction products in the presence of PCA is almost unchanged (with the PCA:V ratio being 10). However, the initial reaction rate is higher in this case. PCA accelerates the hydrocarbon oxidation catalyzed by CH<sub>3</sub>ReO<sub>3</sub> (Table 1) [56]. Addition of 2,2'-bipyridine to the reaction solution completely inhibits the formation of oxygenated products. Employing a (+)-camphor derived PCA as a potential co-catalyst in the CH<sub>3</sub>ReO<sub>3</sub>-catalyzed oxidation of methyl phenyl sulfide with urea-H<sub>2</sub>O<sub>2</sub> adduct, the corresponding sulfoxide was obtained with an e.e. of 15% [57]. Purine derivatives were selectively oxidized to the corresponding oxides by the catalytic system MeReO<sub>3</sub>–H<sub>2</sub>O<sub>2</sub>, the best yield being obtained in the presence of PCA [58].

Very recently we found that H<sub>2</sub>O<sub>2</sub> oxidizes alkanes in acetonitrile at room temperature if dinuclear iron complex with 1,4,7-triazacyclononane (TACN), compound **11** (Scheme 5) [59–61], (which is a model for O<sub>2</sub>-transporting proteins hemerythrins, structures **9** and **10** [62,63]) is used as a catalyst. PCA accelerates the oxidation [64]. Analogous picolinic acid enhances [65] the catalytic activity of complex **12** (see [66–73]) in the alkane oxidation with H<sub>2</sub>O<sub>2</sub>.

### 3.3. The effect of additives and ligands in the oxidations by Fenton's reagent

Bianchi et al. developed a new iron-based catalyst for the oxidation of benzene to phenol in a biphasic system [74]. Full system consists of FeSO<sub>4</sub>·7H<sub>2</sub>O, H<sub>2</sub>O<sub>2</sub> (i.e. Fenton's reagent), CF<sub>3</sub>COOH, H<sub>2</sub>O, organic solvent (acetonitrile, acetone, *n*-octane, etc.), benzene and, finally, heterocyclic aminoacid as co-catalyst. Among various heterocyclic additives (Table 2) 5-carboxy-2-methylpyrazine-*N*-oxide was the most efficient co-catalyst. 1,2-Dihydroxybenzene



Scheme 5. Two forms of hemerythrin as well as dinuclear iron complexes.

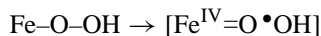
Table 2

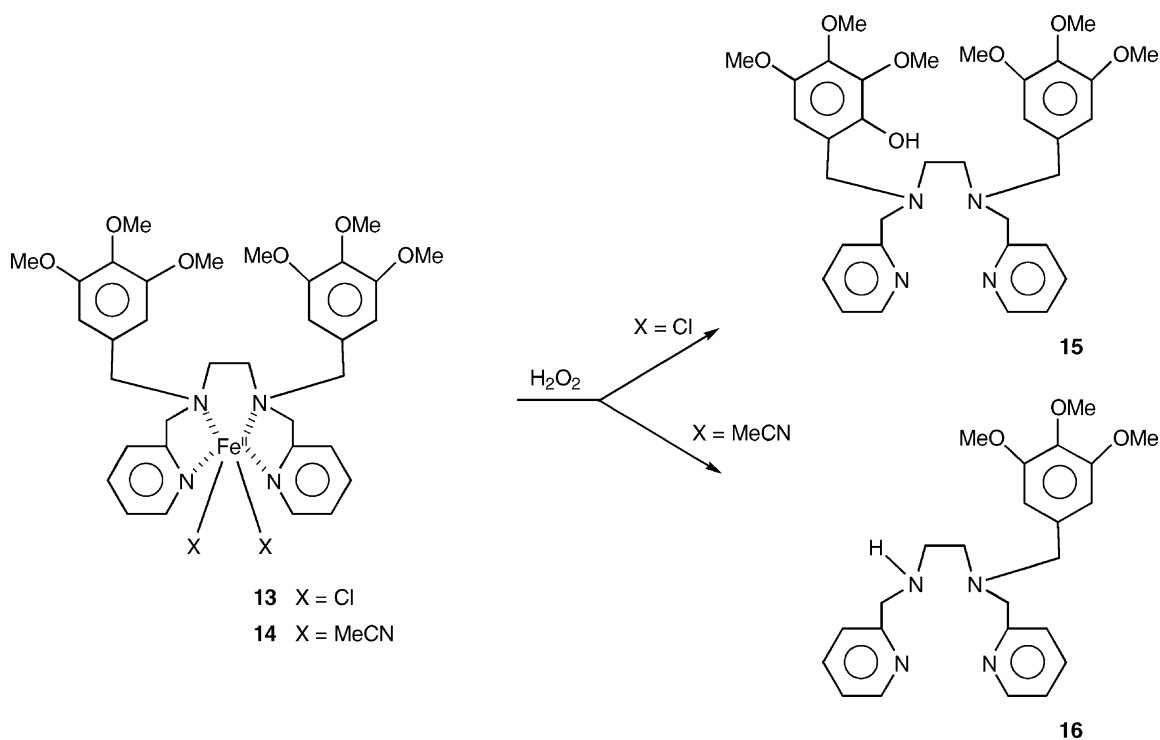
Hydroxylation of benzene by  $\text{H}_2\text{O}_2$  in biphasic system catalyzed by  $\text{FeSO}_4$

Additive	$\text{H}_2\text{O}_2$ conversion (%)	Selectivity (%)	
		$\text{H}_2\text{O}_2$	Benzene
None	77	38	33
Picolinic acid	13		15
Pyridine-2,6-dicarboxylic acid	2		<1
Quinoline-2-carboxylic acid	90		33
PCA	78	70	81
Pyrazine-2,3'-dicarboxylic acid	90	52	78
5-Carboxy-2-methyl-pyrazine- <i>N</i> -oxide	94	78	85

was found to improve the oxidation while 2,2'-bipyridine inactivate the system. It is important that in the reported biphasic system, only a negligible amount (<1%) of biphenyl was detected, whereas, in the classical Fenton oxidation the yield of this product is 8–39%.

It is reasonable to consider, in this section, another publication despite it describes the effect of ligands other than aminoacids on a Fenton-type reagent. In a very recent study, Ménage and co-workers have found [75] that the reactivity of iron complexes as catalysts in  $\text{H}_2\text{O}_2$  oxidations can be tuned by modifying the simple monodentate ligand. Complex **13** (with ligands  $\text{X} = \text{Cl}$ ) behaves as a typical Fenton reagent yielding the hydroxylated polydentate N-ligand **15** (Scheme 6). The oxidation of *cis*-1,2-dimethylcyclohexane catalyzed by **13** gave an equimolecular mixture of *cis*- and *trans*-1,2-dimethylcyclohexanol. Complex **14** ( $\text{X} = \text{MeCN}$ ) functions through metal-based mechanism leading to the formation of compound **16**. The oxidation of *cis*-1,2-dimethylcyclohexane led in this case to the catalytic formation of *cis*- and *trans*-1,2-dimethylcyclohexanol in a 10:1 ratio. The participation of free hydroxyl radicals in the latter case is unlikely. The authors explained the difference between complexes **13** and **14** in the reaction with  $\text{H}_2\text{O}_2$  by the presence of labile sites only in **14**. These sites allow the binding of  $\text{H}_2\text{O}_2$  molecule to the metal center leading to the formation of an iron-peroxo species followed by the homolysis which gives a caged radical pair:





Scheme 6. Two different oxidative pathways in the ligand oxidation depending upon the metal complex structure.

It has been proposed that the complex **13** reacts with  $\text{H}_2\text{O}_2$  through an outer-sphere electron transfer resulting in the formation of the hydroxyl radical.

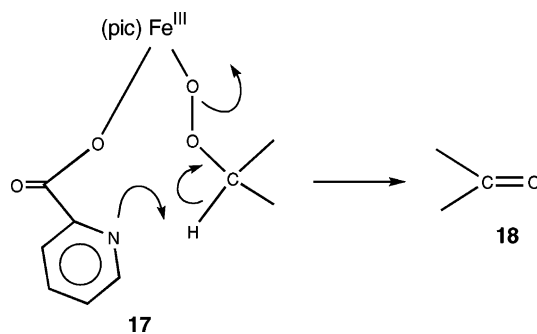
Table 3  
Effect of added carboxylic acids on oxygen and ketone formation from cyclooctane in the Gif oxidation<sup>a</sup>

Additive	O <sub>2</sub> (mmol)	Ketone (mmol)
None	1.70	0.25
Acetic acid	1.67	0.12
Benzoic acid	1.43	0.15
PCA	0.13	0.86
Pyrazine-2,3-dicarboxylic acid	0.45	0.90
Pyridine-2,6-dicarboxylic acid	0.04	0.35
Picolinic acid	0.06	1.28
5-Carboxypyridine- <i>N</i> -oxide	0.22	1.39
Quinaldic acid	2.01	0.00
Quinoline-3-carboxylic acid	1.45	0.26
Isoquinoline-1-carboxylic acid	0.05	1.57
Isoquinoline-3-carboxylic acid	0.13	1.42
Quinoline-8-carboxylic acid	1.68	0.21

<sup>a</sup> Conditions:  $\text{FeCl}_3 \cdot 6\text{H}_2\text{O}$  (1 mmol), additive (4 mmol), cyclooctane (20 mmol),  $\text{H}_2\text{O}_2$  (4 mmol), pyridine (33 ml).

### 3.4. Gif-systems and picolinic acid

Alkane oxidations by so-called Gif-systems (see reviews [76–79] and some of the recent publications [80–83]) occur in pyridine in the presence of a carboxylic acid and are catalyzed by complexes of transition metals (mainly iron). If dioxygen is used as an oxidizing reagent, a reductant must also take part in



Scheme 7. The tentatively proposed mechanism for the accelerating role of picolinic acid in Gif oxidations.

the reaction.  $\text{H}_2\text{O}_2$  was also employed as an oxygen atom donor. It has been found that “the addition of picolinic acid and a number of its congeners increases the rate of oxidation up to 50-fold” [84–86]. It should be, however, emphasized that Gif-systems exhibit very low efficiency in respect to a catalyst: the turnover number (i.e. total number of moles of all products per 1 mol of the catalyst (TON)) attains usually only 2–3. As can be seen from Table 3 [85], the oxygen formation is almost completely suppressed by adding a few equivalents of picolinic acid in the solution. The authors tentatively proposed that the decomposition of intermediate **17** (Scheme 7) yields ketone **18**. However, “the decomposition of **17** would occur via a nine-membered transition state, which is of course a disfavoured process” [85]. Due to this the authors postulated decomposition with the aid of the second iron-picolinate.

#### 4. Nitrogen-containing bases in alkane and olefin oxidations

##### 4.1. The role of bases in biological and biomimetic oxidations

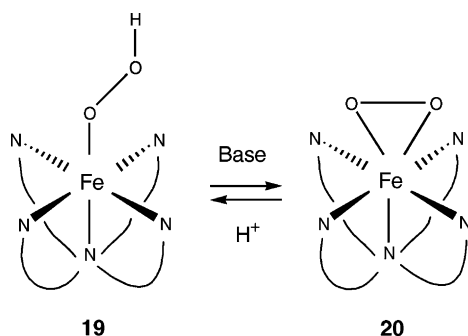
The active centers of certain oxidizing enzymes contain metal ions surrounded with various “ligands” which are often parts of peptide aminoacids (see, e.g. a book [1], reviews [2–6,63,87–89] and some recent publications [90–94]). Protonation and deprotonation of the metal-containing species are essential for hydrocarbon oxidations and often constitute the key steps

of these processes [95,96]. For example, in a modelling system, species **19** (Scheme 8), which is capable of activating the O–O bond to oxidize alkanes, is transformed under the action of a base into species **20** which is unreactive towards such substrates [95].

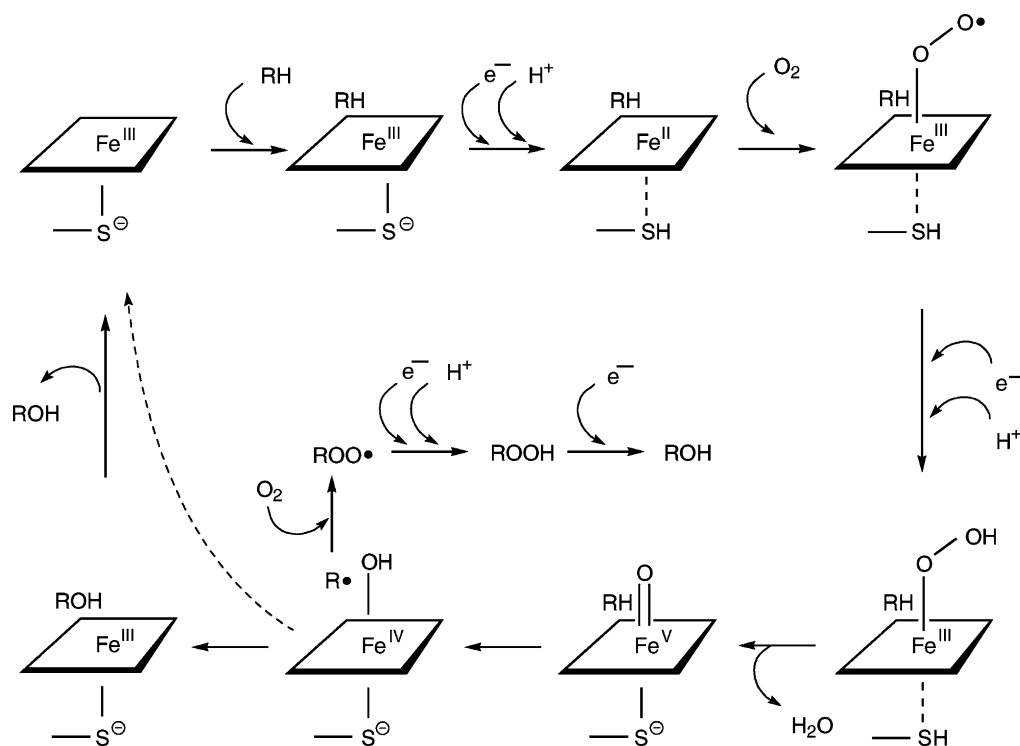
Many oxygenases contain the heme prosthetic group. For example, four coordination sites of the iron-ion involved in the active center of cytochrome P450 are coupled by nitrogen atoms from the porphyrin molecule and the fifth position is occupied by a sulfur atom from the cysteine molecule. The catalytic cycle proposed for alkane oxidation by dioxygen in the presence of cytochrome P450 [1,2,97–100] is as shown in Scheme 9. Some stages involve the protonation or deprotonation of the sulfur residue. It has been recently demonstrated that the thiolate ligand facilitates the O–O bond cleavage by P450 enzymes [101]. In other enzymes, such as catalases and peroxidases, the fifth position is occupied by a nitrogen atom of the histidine molecule. Metal porphyrins were used as catalysts in the simulation of heme monooxygenases. For example, in modeling cytochrome P450 porphyrin complexes of iron(III) as well as of manganese(III), chromium(III), and ruthenium(III) were usually employed as models of active centers of enzymes [1,2]. Important role of protonation and deprotonation with participation of residues surrounding the active center was stated [102–117]. Protonated bases take part in the cleavage of the oxygen–oxygen bond in peroxides [118–121] (see Scheme 9). The reaction of iron porphyrinates with peroxides can proceed [122] either as heterolytic cleavage or homolytically.

##### 4.2. Effect of imidazole in metalloporphyrin-catalyzed reactions

In 1982, Oae et al. reported the ability of imidazole (Im) to accelerate the S-oxygenation of thioethers by  $\text{H}_2\text{O}_2$  catalyzed by iron porphyrinates [123] and in the mid of 1980s, Mansuy et al. [124] and Mansuy and co-workers discovered that in the presence of imidazole or its derivatives manganese-porphyrins catalyze the epoxidation of alkenes and hydroxylation of alkanes by alkyl hydroperoxides and  $\text{H}_2\text{O}_2$  [125–127]. Later, the effect of imidazole and its derivatives on the rate of hydrocarbon oxidation with



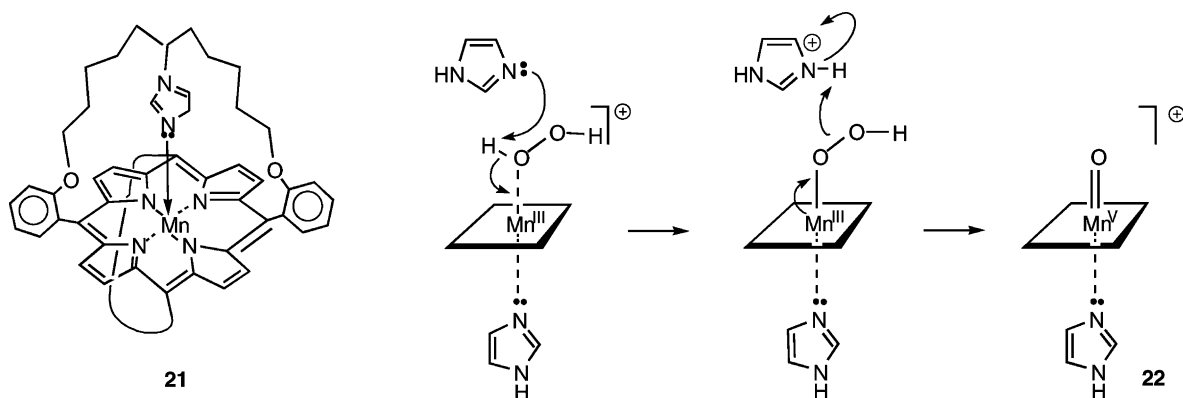
Scheme 8. Transformations of two forms of metal peroxide complex.



Scheme 9. The catalytic cycle proposed for the alkane (RH) oxygenation catalyzed by cytochrome P450.

various oxygen atom donors was studied for the catalysis by Mn-porphyrins [128–133], Fe-porphyrins [134,135] as well as by other manganese [136] and iron [137] complexes. It has been shown [14] that the oxidation of cyclohexane with  $\text{H}_2\text{O}_2$  in  $\text{CH}_3\text{CN}-\text{CH}_2\text{Cl}_2$  in the presence of  $\text{LMnCl}$ , where L

is tetrakis(2,3,4,5,6-pentafluorophenyl)porphyrinate, and imidazole at room temperature gave cyclohexyl hydroperoxide as the main product. The interactions of imidazole and its derivatives with various metalloporphyrins were investigated [138–144]. A comparison of imidazole and thiolate anion coordinated with



Scheme 10. The role of imidazole in metalloporphyrin-catalyzed oxygenations.

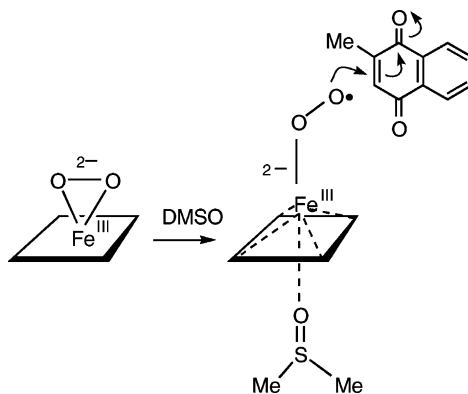
iron porphyrin complexes as models for cytochrome P450 was made [145].

In order to evaluate the mechanistic role of imidazole, compound **21**, which contains an imidazole bound to the metal, was used as a catalyst in epoxidation [146]. It turned out that in the presence of complex **21** (Scheme 10) no epoxidation by  $\text{H}_2\text{O}_2$  occurred. However, the addition of 10 equivalent of imidazole to the reaction mixture led to the formation of the expected epoxide. It was concluded that the role of imidazole as an Mn-ligand only is not sufficient for epoxidation to take place. When similar chiral basket-handle manganese porphyrin which did not contain the imidazole moiety was used, no epoxidation occurred in the presence or absence of imidazole in excess. The authors assumed that imidazole plays two roles in the oxidations: as a Mn-ligand (enriches the metal center and favors an heterolytic cleavage of the O–O bond of  $\text{H}_2\text{O}_2$  molecule) and as a base catalyst (facilitates the removal of a proton from  $\text{H}_2\text{O}_2$  and departure of  $\text{H}_2\text{O}$  to generate a Mn(V)=O species **22**).

Manganese porphyrins have been also reported to catalyze the olefin epoxidations by  $\text{NaIO}_4$  [147] or *m*-chloroperoxybenzoic acid [148] in the presence of 1-methylimidazole. It is interesting that in the alkane oxidation with iodosylbenzene (PhIO) catalyzed by iron porphyrin, addition of excess imidazole to the system results in a decrease in the alcohol yield which is due to the formation of the hexacoordinated complexes  $\text{PorphFeIm}_2$  [149].

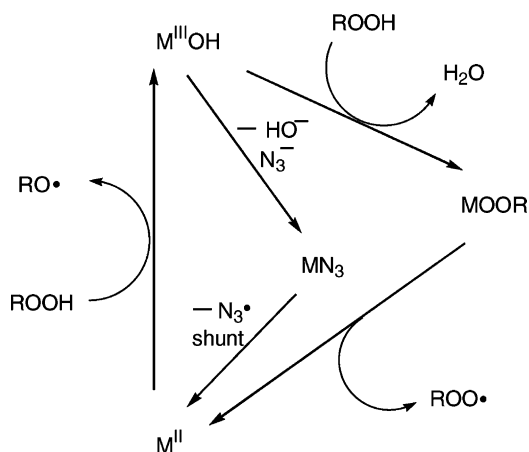
#### 4.3. Effect of some other bases in metalloporphyrin-catalysed oxidations

In the presence of free cysteine or histidine, the efficiency of stereoselective cholesterol oxidation to  $3\beta,5\alpha$ -cholestandiol is markedly higher [150]. Sodium boron hydride and molecular oxygen were used as an oxidation system. The profiles of the rate constant dependencies on aminoacid concentration differed in shape: curves with saturation in the case of histidine and curves with pronounced maximum for cysteine. Addition of DMSO to the stoichiometric epoxidation of menadione with complex  $[\text{Fe}(\text{F}_{20}\text{TPP})\text{O}_2]^-$ , where  $\text{F}_{20}\text{TPP}$  is 5,10,15,20-tetrakis(pentafluorophenyl)porphyrinate, enhances the reactivity of the porphyrin [151]. The



Scheme 11. The enhanced reactivity of complex  $[\text{Fe}(\text{F}_{20}\text{TPP})\text{O}_2]^-$ , where  $\text{F}_{20}\text{TPP}$  is 5,10,15,20-tetrakis(pentafluorophenyl)porphyrinate, in the menadione stoichiometric epoxidation in the presence of DMSO.

authors proposed that coordinated as an axial ligand DMSO pushes the triangularly bound peroxo complex open and makes the peroxo ligand much more nucleophilic (Scheme 11). It has been shown recently [152] that the reactivity of iron porphyrin catalysts in epoxidation and hydroxylation reactions is influenced by the nature of anionic axial ligands. The oxidation of complex  $\text{Fe}(\text{III})(\text{tdcpp})$  (tdcpp is 5,10,15,20-tetrakis(2,6-dichlorophenyl)porphyrinate) with *p*-nitroperoxy benzoic acid or pentafluoroiodosylbenzene at  $-90^\circ\text{C}$  in  $\text{CH}_2\text{Cl}_2$  gave  $\text{O}=\text{Fe}(\text{IV})(\text{tdcpp})$   $\pi$ -cation radical [153]. However, in the presence of a small amount of methanol this reaction produced a new type of high-valent oxoiron porphyrin which is a high spin complex of either an  $\text{O}=\text{Fe}(\text{V})$  porphyrin or  $\bullet\text{O}-\text{Fe}(\text{IV})$  porphyrin. The authors proposed that the ligation of methanol causes the destabilization of iron's d-orbitals. It is interesting that the hydroxylation of aromatic hydrocarbons with  $\text{H}_2\text{O}_2$  catalyzed by manganese  $\beta$ -polynitroporphyrins occurs only in the presence of ammonium mandelate [154]. Finally, the oxidation of light alkanes catalyzed by metal complexes including metalloporphyrins in solution [155–157] is promoted by group 1 metal azides [155]. It has been proposed that a possible reason for high activity of azido complexes of first row metals in the coordination sphere of electron deficient porphyrins is an azide shunt (Scheme 12).



Scheme 12. The accelerating effect of metal azides on the oxidation of light alkanes catalyzed by metal complexes.

#### 4.4. Hydrocarbon oxidations in the presence of heterocyclic amines: another examples

Pyridine is one of the necessary components of Gif-systems, however, it has been demonstrated that this amine can be largely substituted by acetonitrile as the solvent with the use of a small amount 4-*tert*-butylpyridine as the heterocycle base. As a result increased efficiency and greater number of turnovers was attained [158–160].

Sobkowiak and co-workers have found that the cyclohexene oxidation with *tert*-butyl hydroperoxide in pyridine–acetic acid mixture (2:1) catalyzed by manganese(III) complexes gives predominantly 2-cyclohexen-1-one if bipyridine, picolinic acid or PPh<sub>3</sub> oxide is present in the reaction mixture [161]. It is interesting that Schiff-base complexes produce under these conditions (in the absence of added ligands) 2-cyclohexen-1-one, 2-cyclohexen-1-ol and the epoxide in almost equal yields. The oxidation of cyclohexene using the same oxidant in benzene catalyzed by CrO<sub>3</sub> gave the epoxide, 2-cyclohexen-1-ol and 2-cyclohexen-1-one in the ratio of 3:1:40. Pyridine and imidazole were found to have negative effects on the yield of epoxide [162]. It turned out that more generally pyridine-derived additives alter the behavior of this system [163]. Monodentate pyridines and *trans*-chelated bidentate bipyridines retard the decomposition of *tert*-butyl hydroperoxide (with the

Table 4  
Decomposition of various hydroperoxides

Hydroperoxide	Catalyst	Pyridine effect
Ethylbenzene hydroperoxide	Ru(III)	Acceleration
Cyclohexyl hydroperoxide	Mn(III)	Acceleration
Benzyl hydroperoxide	Cu(II), Cu(I)	Acceleration
Cumyl hydroperoxide	Fe(II)	Retardation
Cumyl hydroperoxide	Co(II)	Retardation
<i>tert</i> -Butyl hydroperoxide	Cr(VI)	Retardation
<i>tert</i> -Butyl hydroperoxide	Rh(I)	Inhibition
Cumyl hydroperoxide	Ir(I)	Inhibition

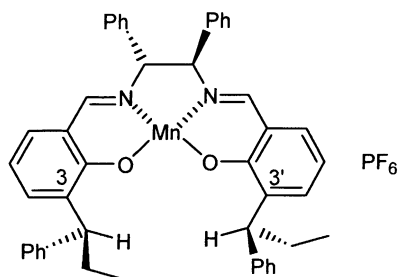
formation of *t*-BuOO• and *t*-BuO• radicals) and arrest the epoxidation reaction shifting the product selectivity towards allylic oxidation. It is worth noting that *cis*-chelated bipyridines accelerate the decomposition of this hydroperoxide. Pyridine effects on hydroperoxide decomposition depends on the catalyst (Table 4) and co-catalyst (Table 5) [163].

Cyclohexene can be epoxidized by H<sub>2</sub>O<sub>2</sub> if insoluble polynuclear manganese(III)–Schiff base complexes are used as catalysts and imidazole plays the role of co-catalyst [164]. It has been recently shown that the addition of 1–10 mol% of 3-cyanopyridine increases the efficiency of the alkene epoxidation with H<sub>2</sub>O<sub>2</sub> catalyzed by methyltrioxorhenium [165]. Meunier and co-workers [166,167] showed that the alkene epoxidations with sodium hypochlorite catalyzed by metal porphyrins are strongly accelerated if small amounts of pyridines are added. Pyridines can be replaced by 4'-imidazolylacetophenone [168,169]. A large improvement of asymmetric yield was observed by adding 2-methylimidazole to the epoxidation of (*E*)-1-phenylpropene by PhIO catalyzed by complex

Table 5  
Initial rates of the *tert*-butyl hydroperoxide decomposition catalysed by CrO<sub>3</sub> in the presence of some additives (CH<sub>2</sub>Cl<sub>2</sub>, 22 °C)

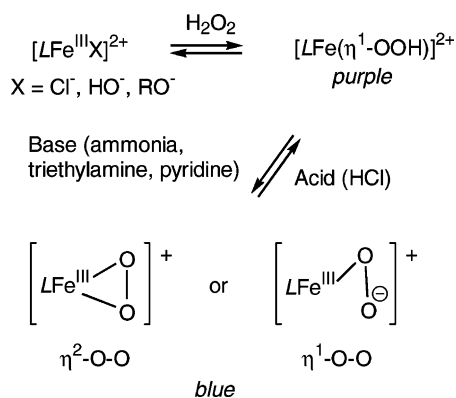
Additive (mol%)	Relative initial rate
<i>cis</i> -1,2-Bis(2-pyridyl)ethylene (1%)	0.12
2,6-Lutidine (2%)	0.38
3,5-Lutidine (2%)	0.50
3-Picoline (2%)	0.58
Pyridine (2%)	0.65
None	1.00
Pyridine (1%)	1.05
2,2'-Bipyridine (1%)	72.0
1,10-Phenanthroline (1%)	73.0

**23** [170,171]. The authors assumed that the change in asymmetric induction is due to the conformational change of the skeleton of (salen)manganese(III) complexes and of C-3 and C-3' substituents accompanied by coordination of a donor ligand.



In the  $\text{H}_2\text{O}_2$  oxidation of alkanes, including methane and ethane, in acetonitrile catalyzed by  $\text{OsCl}_3$ , the yield of products is significantly enhanced if a nitrogen-containing heterocycle is added [172]. The alcohol:ketone ratio for the products depends on the nature of the heterocycle: it was found to be 5.4 for 2,5-dichloropyridine and only 0.2 for pyridine. Moreover, whereas, the oxidation of *cis*-decalin occurs without retention of the configuration (the *trans*:*cis* ratio of the products being more than unity), in the presence of pyridine the reaction becomes more stereoselective, the *trans*:*cis* ratio decreasing with increasing pyridine concentration. The  $\text{H}_2\text{O}_2$  oxidation of ethane and other alkanes catalyzed by  $\text{H}_2\text{CrO}_4$  [173] is accelerated but insignificantly (ca. 15%) if pyridine is added to the reaction solution. Alkylhydroperoxides or iodosylbenzene oxidize saturated hydrocarbons if a manganous salt is used as catalyst and in the presence of 2,2'-bipyridine as co-catalyst [174]. Finally, addition of 1,4,7-trimethyl-1,4,7-triazacyclononane to the reaction solution accelerates the alkane hydroperoxidation with  $\text{H}_2\text{O}_2$  (in acetonitrile at  $70^\circ\text{C}$ ) catalyzed by  $\text{Ni}(\text{ClO}_4)_2$ . The analysis of bond selectivities in the oxidation of normal heptane [C(1):C(2):C(3):C(4) = 1.0:6.3:7.2:6.1] and 3-methylhexane ( $1^\circ:2^\circ:3^\circ = 1:5:50$ ) testifies that the process proceeds with participation of hydroxyl radicals [175]. The  $\text{H}_2\text{O}_2$  oxidation catalyzed by  $\text{PtCl}_6^{2-}$  at  $70^\circ\text{C}$  ( $1^\circ:2^\circ:3^\circ = 1:7:180$ ) and  $\text{Cu}(\text{ClO}_4)_2$  at  $38^\circ\text{C}$  ( $1^\circ:2^\circ:3^\circ = 1:13:330$ ) proceeds in acetonitrile more selectively in the absence of any additive [175].

The high values of the NIH and Me-NIH shifts were observed [176] in the monooxygenation of



Scheme 13. The reversible deprotonation of purple Fe(III)–hydroperoxide complex ions to give transient blue species, iron(III)–peroxide complex: L = *N*-ethyl-*N,N,N'*-tris(2-pyridylmethyl)ethane-1,2-diamine (ettpen) or *N*-benzyl-*N,N,N'*-tris(2-pyridylmethyl)ethane-1,2-diamine (bztpen).

aromatic compounds catalyzed by the “non-heme iron complex–hydroquinone– $\text{O}_2$ ” system. It is interesting that added pyridine greatly affected not only the NIH shift but the selectivity (the aromatic ring:side chain ratio). The authors proposed  $\text{LFe}(\text{V})=\text{O}$  as an active species. Pyridine acts as a deprotonating reagent, and the lower NIH value in pyridine in comparison with that in acetonitrile may be due to the enhanced de-deuteration before migration. Heterocyclic N-bases probably play the role of proton transfer reagent in many of the oxidation reactions as discussed previously. In some cases, however, a base can deprotonate a reactive species which leads to its inactivation. An example has been demonstrated in Scheme 8. An analogous mutual transformation of protonated and deprotonated forms of iron(III)–hydroperoxide complex is as shown in Scheme 13 [177].

Table 6  
Oxidation of toluene by oxygen in the presence of acetylacetone or phenanthroline<sup>a</sup>

Products	Phenanthroline	Acetylacetone
Benzyl alcohol	0.15	0
Benzaldehyde	0.85	0
Benzoic acid	1.11	0
Benzyl benzoate	2.77	0
Bitolyls	0.06	5.0

<sup>a</sup> Reaction at  $120\text{--}200^\circ\text{C}$  in neat toluene.



Table 7  
Oxidation of toluene

Additive	Turnover frequency (h <sup>-1</sup> )	Isomer distribution (%)					
		2,2'	2,3'	2,4'	3,3'	3,4'	4,4'
Acetylacetone	20	1	58	26	8	6	2
Phenanthroline	1.4	0.3	15	7	18	38	21
2,2'-Bipyridine	1.9	2	54	17	13	12	2

The nature of added chelating ligands plays a very important role in the oxidation of alkylbenzenes catalyzed by palladium salts. Thus, palladium acetate in the presence of acetylacetone transforms under oxygen atmosphere toluene exclusively into isomeric bitolyls. However, when phenanthroline is added instead of acetylacetone only side-chain oxidation occurs while activation of the ring carbons is minimal (<1%) (Table 6) [178]. It is interesting that methyl benzoate under these conditions gives exclusively dimers even if phenanthroline is used as co-catalyst. Variation of added ligands dramatically changes not only the aromatic ring:side chain ratio and the product yield but also the distribution of dimer isomers. For example, in the oxidation of methyl benzoate, ligands with strong *trans* influence (phen, bipy) direct the oxidative coupling away from 2,2'-isomers (*N* = 2, 3, or 4) (Table 7) [179].

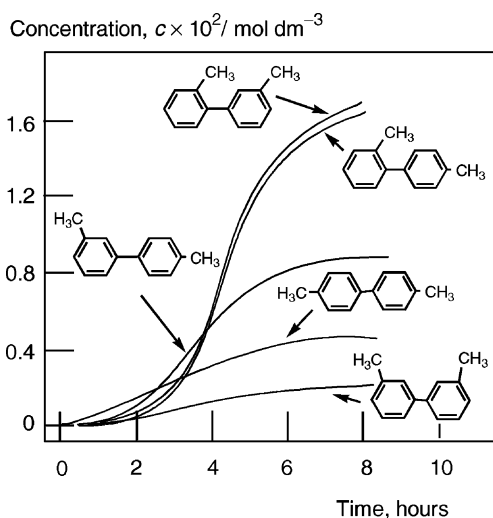


Fig. 5. Formation of bitolyl isomers in the reaction of H<sub>2</sub>PtCl<sub>6</sub> with toluene in CF<sub>3</sub>COOH–H<sub>2</sub>O (4.5:1) at 90 °C.

The stoichiometric reaction between H<sub>2</sub>PtCl<sub>6</sub> and toluene in CF<sub>3</sub>COOH–H<sub>2</sub>O which gives isolable intermediate  $\sigma$ -tolylplatinum(IV) complexes [180–182] can be a close model of the Pd-catalyzed coupling. It is worthy noting that in the reaction with PtCl<sub>6</sub><sup>2-</sup>, it was observed that, together with the ‘expected’ 3,3'-, 4,4'-, and 3,4'-bitolyl isomers, a large amount of the ‘surprising’ 2,3'- and 2,4'-bitolyls is formed after a long induction period (Fig. 5). The products of *ortho*-substitution relative to the methyl group are apparently formed on interaction of *meta*- and *para*-platinated toluenes with free toluene present in the solution.

#### 4.5. “Heterocyclic base plus acid” as an electron transfer agent

Alkanes and olefins can be oxygenated by oxygen if manganese [183–186] or iron [187–189] complexes (including porphyrinates) are used as catalysts and zinc powder as reducing agent. Acetic acid provided protons in the oxidation of zinc metal. One of the interesting features of these reactions is that they require either alkylviologen dication (i.e. N-alkylated 4,4'-bipyridine) [185–187] or a nitrogen base (1-methylimidazol [183], pyridine [183,188,189] or 2,2'-bipyridine [188]). It is clear that the nitrogen-containing heterocycle in the presence of acetic acid exists in the equilibrium with its protonated form. The protonated N-base will play the role (in addition, possibly, to other functions, for example the proton transfer) of an electron transfer agent like methylviologen. One can assume that a protonated (by acetic acid) pyridine is a species which takes part in the Gif oxidations as an electron mediator. We have found recently [190] that gold complexes catalyze alkane oxidation with atmospheric oxygen in acetonitrile in the presence of Zn–CH<sub>3</sub>COOH reducing couple and either methylviologen or pyridine (or 2,2'-bipyridine) as well as with H<sub>2</sub>O<sub>2</sub>. Vanadium complexes catalyze the hydroxylation of benzene and cyclohexane in acetonitrile by air in the presence of such reductants as Zn–CH<sub>3</sub>COOH and ascorbic acid [191]. The reaction proceeds efficiently only if all of the following additives are present: pyridine, PCA, acetic acid. It is interesting that irradiation ( $\lambda > 310$  nm) of an air-saturated solution of an alkylbenzene (or even cyclohexane) in acetonitrile

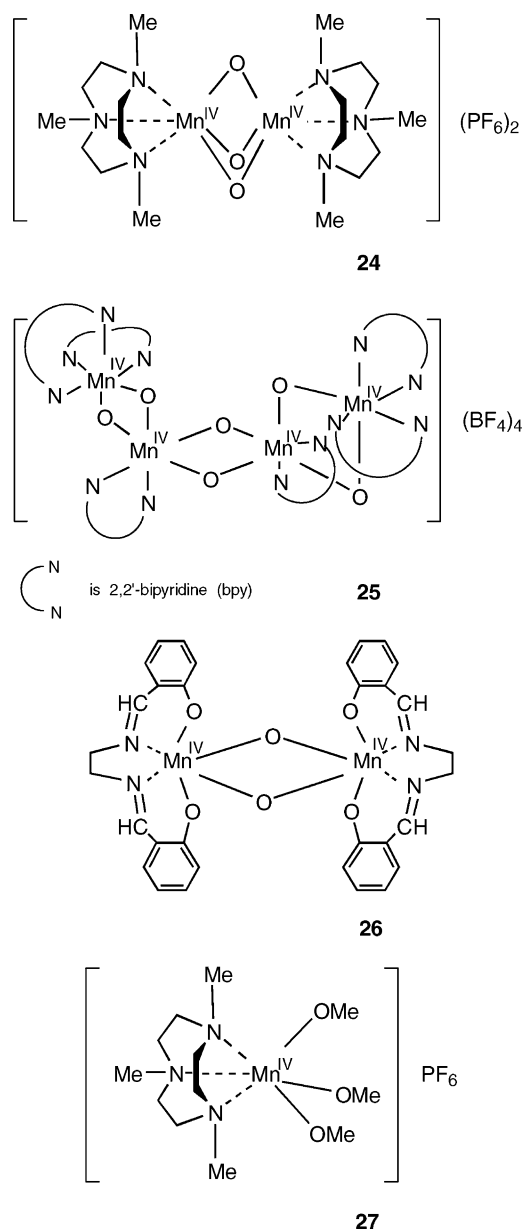
[192] or acetic acid [193] in the presence of catalytic amounts of *o*-phenanthroline or 2,2'-bipyridine and sulfuric acid gives oxygenated products (benzaldehyde from toluene). Some analogous systems do not need either a catalyst or an electron transfer reagent. Thus, cyclohexene can be epoxidized by the “O<sub>2</sub>-Zn-benzoic anhydride-Br<sup>-</sup>” system which does not need the presence of a metal-complex catalyst [194]. Additionally, alkane oxidation with the “O<sub>2</sub>-Zn-CF<sub>3</sub>COOH-vanadium complex” system described by Yamanaka et al. occurs in the absence of a N-base [195].

## 5. Acceleration of oxidations with proton donors

### 5.1. H<sub>2</sub>O<sub>2</sub>-Mn(IV) complex-carboxylic acid system

Manganese-containing enzymes as well as synthetic manganese-containing complexes are known to catalyze very efficiently decomposition of H<sub>2</sub>O<sub>2</sub> (catalase activity; see books [196–198] and recent papers [199–202]). Adding the bases [203–205], particularly imidazole [206,207] accelerate significantly the H<sub>2</sub>O<sub>2</sub> decomposition catalyzed by manganese (as well as by μ-oxo-bridged diiron [208]) complexes. The photosynthetic water oxidation enzyme contains a polynuclear manganese core in the oxygen-evolving center (OEC) (see books [209–212], reviews [213–220] and recent papers [220–227]). It is worthy noting that 4-methylimidazole (which is a model compound of histidine residue in biological systems [228]) remarkably increases the electrocatalytic activity of water-oxidation model systems [213,229]. 4-Methylimidazole plays the role of a mediator for the charge hopping between the catalysts. Another electron acceptor, methylviologen (MV<sup>2+</sup>) was employed in the photochemical Ru-Mn-based systems mimicking OEC and whole photosystem II (see, for example [230]). Many complexes of manganese have been used as models of enzymatic processes. It has been reported that high-valent manganese complexes catalyze various oxidation reactions [231–242] and active in stoichiometric oxidations [243,244].

Recently, we discovered [245–248] that the catalytic activity of the manganese(IV) salt [LMn(μ-O)<sub>2</sub>MnL]-(PF<sub>6</sub>)<sub>2</sub> (L = 1,4,7-trimethyl-1,4,7-triazacyclononane, TMTACN) (complex **24**, Scheme 14) in the oxidation



Scheme 14. Manganese-containing catalysts of alkane oxidations with H<sub>2</sub>O<sub>2</sub> or *t*-BuOOH.

of saturated hydrocarbons with H<sub>2</sub>O<sub>2</sub> (in acetonitrile at room temperature) increases dramatically if small amount of a carboxylic acid is added to the reaction solution. The reaction yielding in the beginning predominantly alkyl hydroperoxides is accompanied by oxygen evolution from H<sub>2</sub>O<sub>2</sub>. In the absence of a

Table 8  
Oxidation of *n*-hexane with H<sub>2</sub>O<sub>2</sub> in acetonitrile catalyzed by complex **24** in the presence of co-catalysts<sup>a</sup>

Additive	Hexanones (mol dm <sup>-3</sup> )	Hexanols (mol dm <sup>-3</sup> )	TON <sup>b</sup>
Acetic acid	0.240	0.03	1350
Propionic acid	0.134	0.02	770
Trifluoroacetic acid	0.056	0.013	345
Formic acid	0	0	0
Acetic anhydride	0.065	0.016	405
Methanesulfonic acid	0.007	0.001	40

<sup>a</sup> Reaction conditions: hexane (0.4 mol dm<sup>-3</sup>), complex **24** (0.2 × 10<sup>-3</sup> mol dm<sup>-3</sup>), additive (1.0 mol dm<sup>-3</sup>), *n*-hexane (0.4 mol dm<sup>-3</sup>), H<sub>2</sub>O<sub>2</sub> (1.0 mol dm<sup>-3</sup>), 20 °C, 1 h. The concentrations of the products in the reaction solution before reduction with PPh<sub>3</sub> are given.

<sup>b</sup> The turnover number of the catalyst (the sum of moles of all products per mole of catalyst).

carboxylic acid compound **24** in acetonitrile solution at 25 °C does not catalyze either the alkane hydroperoxidation (oxygenase activity) or the decomposition of H<sub>2</sub>O<sub>2</sub> to molecular oxygen and water (catalase activity). Surprisingly, in the presence of a carboxylic acid (in low concentration, 0.05–0.5 mol dm<sup>-3</sup>), the very efficient oxidation of the alkane occurs; acetic acid being the most convenient co-catalyst in this reaction, although other carboxylic acids such as propionic or trifluoroacetic acids can be used (Table 8) [245].

The hydroxylation of some alkanes containing tertiary C–H bonds proceeds stereoselectively, thus, the oxidation of the two decalin isomers gives (after treatment with PPh<sub>3</sub>) alcohols hydroxylated in the tertiary positions, the *cis:trans* ratio being ~2 in the case of the oxidation of *cis*-decalin, and the *trans:cis* ratio being ~30 in the case of the oxidation of *trans*-decalin, i.e. in the latter case the reaction is stereospecific. Alkyl hydroperoxides in the course of the reaction are transformed gradually into the corresponding carbonyl compounds and alcohols. Higher and light (methane, ethane, propane, normal butane and isobutane) alkanes can be easily oxidized by this system at room temperature, at 0 °C and even at –22 °C. Turnover numbers of 3300 have been attained and the yield of oxygenated products is 46% based on the alkane. The site selectivity of the *n*-heptane oxidation is C(1):C(2):C(3):C(4) = 1.0:45.6:35.3:34.7 which is noticeably higher than that for the oxidation by the reagent “O<sub>2</sub>–H<sub>2</sub>O<sub>2</sub>–vanadium complex–PCA”. The

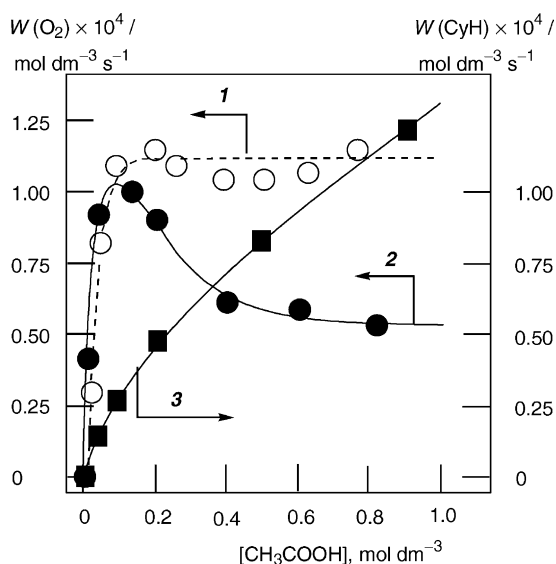


Fig. 6. Decomposition of H<sub>2</sub>O<sub>2</sub> (0.25 mol dm<sup>-3</sup>) in MeCN at 25 °C catalyzed by complex **24** (5 × 10<sup>-5</sup> mol dm<sup>-3</sup>): the dependence of the O<sub>2</sub> evolution rate on [CH<sub>3</sub>CO<sub>2</sub>H] in the absence (curve 1) and in the presence of cyclohexane (0.46 mol dm<sup>-3</sup>) (curve 2), as well as the analogous dependence for the initial rate of the cyclohexanol and cyclohexanone (after PPh<sub>3</sub> reduction) accumulation (curve 3) are shown.

“H<sub>2</sub>O<sub>2</sub>–compound **24**–MeCO<sub>2</sub>H” system oxidizes very efficiently secondary alcohols to the corresponding ketones in acetonitrile solution as well as epoxidizes olefins and oxygenizes sulfides. We have found that under the same conditions dinuclear Mn(IV) derivatives **25** and **26** as well as mononuclear complex **27** are almost inactive in the alkane oxygenation. Complexes **24**–**26** exhibits moderate catalytic activity in the alkane oxidation with *tert*-butyl hydroperoxide, in the case of complex **24** the reaction being also accelerated by acetic acid added in small concentration. The oxidations with *tert*-butyl hydroperoxide proceed non-stereoselectively and seem to occur via a different mechanism [247].

It is worthy noting that the oxygen evolution in the “H<sub>2</sub>O<sub>2</sub>–complex **24**–MeCO<sub>2</sub>H” system proceeds even at very low concentration of added acetic acid and in the presence of cyclohexane in the reaction mixture, the initial rate of this process attains a maximum at [CH<sub>3</sub>COOH] ≈ 0.1 mol dm<sup>-3</sup>. The initial rate of the formation of oxygenates grows monotonously with increase in the acetic acid concentration, and at

$[\text{CH}_3\text{COOH}] > 0.3 \text{ mol dm}^{-3}$ , the yield of the oxygenated products is higher than that of the molecular oxygen evolved (Fig. 6) [249].

Addition of a very small amount ( $10 \times 10^{-5} \text{ mol dm}^{-3}$ , i.e. two equivalents of  $n\text{-Bu}_4\text{NOH}$  relative to complex **24**) to the reaction solution containing acetic acid ( $0.05 \text{ mol dm}^{-3}$ ) gives rise to the growth of the  $\text{O}_2$  evolution rate and, simultaneously to the almost complete inhibition of the hydrocarbon oxygenation (Fig. 7, curve 1g). Addition of four equivalents of the base leads to further enhancement in the catalase activity at the expense of the alkane oxidation: after 20 min, the concentration of oxygenates (Fig. 7, curve 2h) is 85 times less than that in the experiment in the absence of  $n\text{-Bu}_4\text{NOH}$  (Fig. 7, curve 2f). The rate dependencies for both the oxygen evolution and the alkane oxygenation are second order for  $\text{H}_2\text{O}_2$  at its relatively low concentration.

It can be proposed on the basis of the results described previously that in the first step of the process acetic acid protonates one of the oxygen bridges between two manganese(IV) centers, resulting in the formation of a vacant site at one Mn(IV) (Scheme 15). The complex then adds one  $\text{H}_2\text{O}_2$  molecule, acetate anion being the proton acceptor (step 2). The hydroperoxy derivative **29** eliminates hydroperoxyl radical to afford catalytically active Mn(III) and Mn(IV) species **30**. Steps 4 and 5 lead to the formation of dihydroperoxy complex of Mn(III) and Mn(IV), **32**. Acetate anion and acetic acid (both in low concentrations) catalyze the formation and decomposition of complex **32** yielding  $\text{H}_2\text{O}$  and  $\text{O}_2$  (catalase pathway) and derivative **37**. If acetic acid is present in higher concentration, the protonation of  $-\text{OOH}$  ligand in **32** can occur and dinuclear Mn(V)=O derivative **34** is formed. Oxo derivatives of Mn(V) have been shown previously to take part in oxidation processes and have been characterized in some of the cases by spectroscopy and even isolated [250–258]. It should be noted that Mn(V)=O intermediates (also dimers) were proposed to take part in photosynthetic water oxidation [213,259,260]. The high-valent oxomanganese species abstracts a hydrogen atom from the alkane, RH (step 9) to produce an alkyl radical,  $\text{R}^\bullet$ , and Mn(IV)–hydroxy–Mn(IV)–hydroperoxy derivative **36**. Finally the alkyl radical  $\text{R}^\bullet$  and hydroperoxy ligand  $\text{HOO}^\bullet$  combine in the solvent cage to give

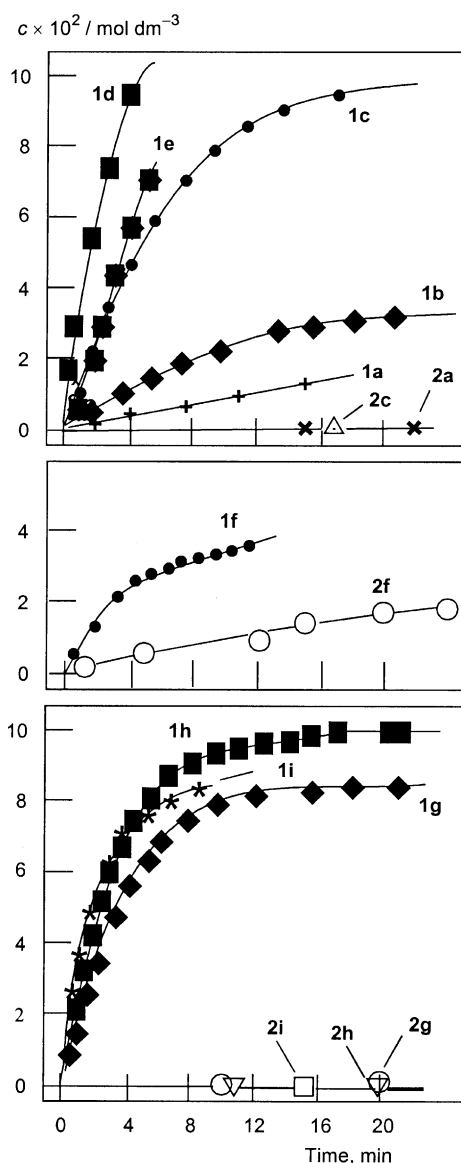
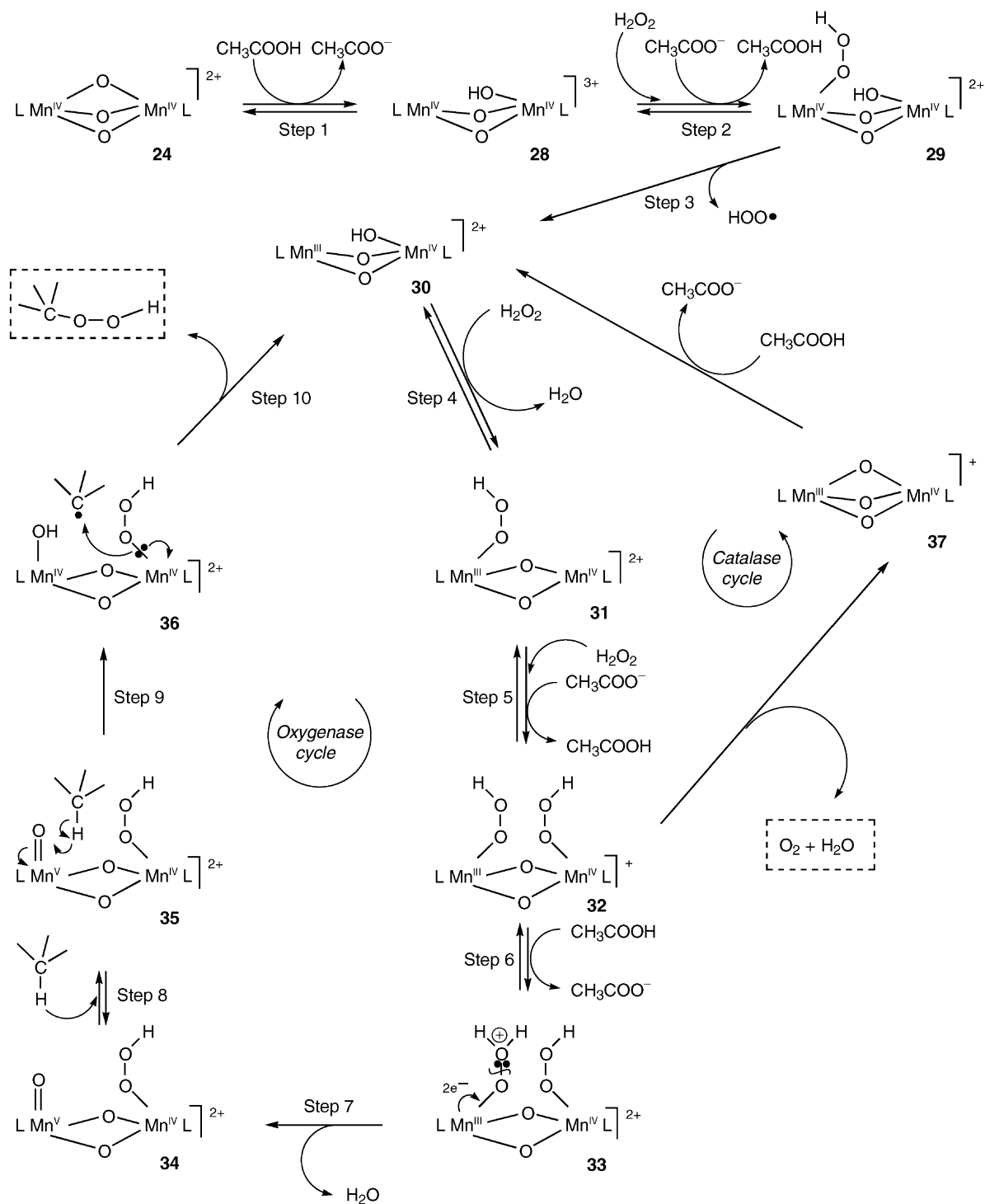
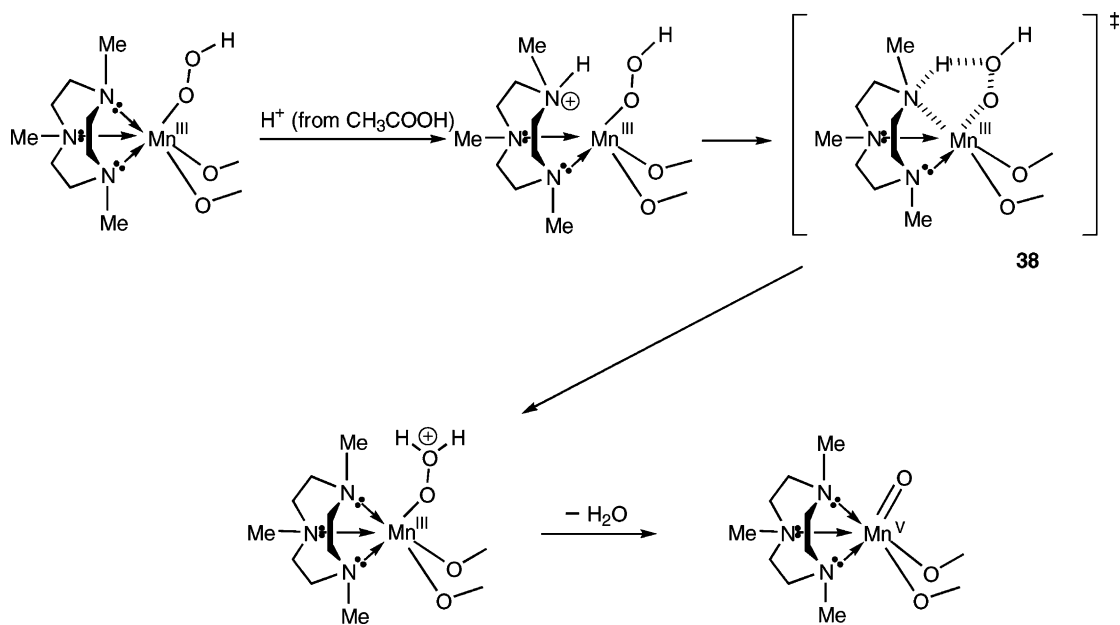


Fig. 7. Decomposition of  $\text{H}_2\text{O}_2$  ( $0.25 \text{ mol dm}^{-3}$ ) in MeCN at  $25^\circ\text{C}$  in the presence of cyclohexane ( $0.46 \text{ mol dm}^{-3}$ ) and  $\text{CH}_3\text{COOH}$  ( $0.05 \text{ mol dm}^{-3}$ ) catalyzed by complex **24** ( $5 \times 10^{-5} \text{ mol dm}^{-3}$ ). The kinetic curves are presented for (1) the  $\text{O}_2$  evolution and (2) for the sum cyclohexanol and cyclohexanone (after  $\text{PPh}_3$  reduction) accumulation (curves a) in the absence of any additive, in the presence of  $n\text{-Bu}_4\text{NOH}$  at various concentrations: (b)  $10 \times 10^{-5}$ , (c)  $40 \times 10^{-5}$ , (d)  $58 \times 10^{-5} \text{ mol dm}^{-3}$ , (e) of TMTCAN ( $10 \times 10^{-5} \text{ mol dm}^{-3}$ ), (f) of acetic acid ( $[\text{CH}_3\text{CO}_2\text{H}] = 0.05 \text{ mol dm}^{-3}$ ) as well as simultaneously of acetic acid ( $[\text{CH}_3\text{CO}_2\text{H}] = 0.05 \text{ mol dm}^{-3}$ ) and of  $n\text{-Bu}_4\text{NOH}$  at various concentrations: (g)  $10 \times 10^{-5}$ , (h)  $20 \times 10^{-5} \text{ mol dm}^{-3}$ , or (i) of TMTCAN ( $10 \times 10^{-5} \text{ mol dm}^{-3}$ ).

Scheme 15. The mechanism proposed for the alkane hydroperoxidation and  $H_2O_2$  decomposition catalyzed by complex **24**.



Scheme 16. Possible TMTACN ligand assistance in the proton transfer between  $\text{CH}_3\text{COOH}$  and the OOH ligand.

the reaction product, alkyl hydroperoxide, ROOH. This process is similar with the main recombination step between  $\text{R}^\bullet$  and  $\text{HO}^\bullet$  to produce ROH in the “oxygen-rebound mechanism” (p. 483 of [1]). Previously, we suggested such a possibility for the light-induced iron-catalyzed alkane oxidations with molecular oxygen (p. 414 of [1]), [18,261]. The alkyl radicals can partially leave the solvent cages and react with molecular oxygen ( $\text{R}^\bullet + \text{O}_2 \rightarrow \text{ROO}^\bullet$ ). The recombination reaction within the solvent cage with partially leaving of the alkyl radicals to the solution explains the partial retention of configuration in the hydroperoxidation of alkanes having tertiary C–H bonds.

It is likely that the TMTACN ligand plays a crucial role in the formation of a catalytically active species, since manganese complexes bearing other similar ligands (e.g. bipyridine, salen, porphyrinate) are almost inactive under the same conditions. We can tentatively assume that the ligand containing tertiary nitrogen atoms assists in the proton transfer stages, for example from the carboxylic acid to the oxygen of the peroxy ligand at the manganese center (Scheme 16). Such a transformation can proceed via a five-membered transition state **38**.

### 5.2. Effect of Na oxalate/oxalic acid buffer in Mn(II)-catalyzed epoxidation

De Vos et al. reported that a catalytic amount of an oxalate/oxalic acid buffer strongly enhances the catalytic activity of the system “ $\text{MnSO}_4\text{--TMTACN--H}_2\text{O}_2$ ” in epoxidation reactions [262]. Trifluoroacetic acid and especially acetic acid turned out to be very poor co-catalysts (the product yields were 15 and <1%, respectively). Addition of fumaric acid, oxalic acid and sodium oxalate gave 57, 94 and 70%, respectively. However, the best results (>99%) were obtained when  $\text{H}_2\text{C}_2\text{O}_4$  (1.5  $\mu\text{mol}$ ) and  $\text{Na}_2\text{C}_2\text{O}_4$  (1.5  $\mu\text{mol}$ ) were added to 0.666 mmol of 1-hexene and 1  $\mu\text{mol}$   $\text{MnSO}_4\text{--TMTACN}$ . The mechanism of the reaction has not been discussed.

### 5.3. Co-catalytic effect of lipophilic carboxylic acids and heterocyclic bases

Italian group found synergistic effect of lipophilic carboxylic acids and heterocyclic axial ligands in hydrocarbon oxygenations by  $\text{H}_2\text{O}_2$  catalysed by manganese porphyrins [263–267]. Thus, oxidation of alkanes is strongly accelerated by addition of small

amounts of lipophilic carboxylic acids and heterocyclic bases. According to the authors' proposal, the reaction proceeds via a Mn(V)=O species which is formed from Mn(III) in the presence of a carboxylic acid.

#### 5.4. Oxidation with heteroaromatic *N*-oxides catalyzed by Ru porphyrins

Higuchi and co-workers [268,269,272], Higuchi et al. [270], Higuchi [271] developed highly efficient oxygenation reactions which used ruthenium porphyrin complexes as catalysts. Alkanes and other C–H compounds can be oxidized by aromatic *N*-oxides (usually by 2,6-dichloropyridine-*N*-oxide) in the presence of strong mineral acids. The authors assumed that HCl plays two different roles: (i) converts the dioxo derivatives of ruthenium porphyrins into the complexes coordinated with the Cl ligand; and (ii) accelerates the deoxygenation of *N*-oxide by the ruthenium porphyrin. It should be noted that more recently Groves et al. [273] and Che and co-workers [274] demonstrated that alkanes can be oxygenated with 2,6-dichloropyridine-*N*-oxide in the absence of strong acids if carbonyl (5,10,15,20-tetrapentafluorophenylporphyrinato)ruthenium(II) or Ru(VI)(Porph)(O)<sub>2</sub>, where Porph = 5,10,15,20-tetrakis[(1*S*,4*R*,5*R*,8*S*)-1,2,3,4,5,6,7,8-octahydro-1,4:5,8-dimethanoanthracen-9-yl]porphyrin are used as catalysts.

#### 5.5. Some other systems

Very recently, Hage and co-workers [275] demonstrated that in catalytic oxidation of primary and secondary alcohols with H<sub>2</sub>O<sub>2</sub> catalyzed by a μ-oxo diiron(III) complex a remarkable increase in reaction rate can be achieved by addition of one equivalent of CF<sub>3</sub>SO<sub>3</sub>H. This effect was attributed to accelerated formation of the active mononuclear catalyst. Clarke and Cole-Hamilton found that addition of molecular sieves to the olefin epoxidation system containing Mo-catalyst increased both the rate and yield of the reaction [276]. It was proposed that the catalyst binds to the sieves and the acidity of the support is important, since, no activity was observed when the sieves were replaced with silica. Finally, platinum complexes derived from the bidiazine ligand family have been reported by Periana et al. [277] to catalyze oxidation

of methane by sulfuric acid to a methanol derivative at >70% one-pass yield based on methane. Remarkably, dichloro(η-2-[2,2'-bipyrimidyl])platinum(II) turned out to be very stable in concentrated sulfuric acid at relatively high temperature and was among the most effective catalysts for methane conversion.

## 6. Concluding remarks

One of the most important questions of chemistry is 'why' certain reactions do occur while many other chemical processes, which look quite nice on paper, are unknown in reality? The answer (quite ironical of course) might be: 'all reactions' which we can imagine could be realized in flasks, chemical reactors or in living cells; we need only to find proper catalysts and proper 'additives' as co-catalysts. However, the only problem is how can we learn 'what' catalysts and 'what' additives.

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