Hydrocarbon Oxygenations with Peroxides Catalyzed by Metal Compounds

Georgiy B. Shul'pin*

Semenov Institute of Chemical Physics, Russian Academy of Sciences, Ulitsa Kosygina, dom 4, Moscow 119991, Russia

Abstract: Recent works devoted to the oxygenations of saturated, aromatic as well as olefinic hydrocarbons are surveyed, and the emphasis is made on the author's own publications. Both soluble metal complexes and solid metal compounds catalyze oxidative transformations of hydrocarbons. Hydrogen peroxide, alkyl peroxides, and peroxy acids were used in these reactions as oxidants. The catalytic systems often include obligatory co-catalysts, for example, nitrogen-containing bases or acids (inorganic, carboxylic or amino acids).

Keywords: Alkanes, olefins, aromatics, epoxidation, metal-complex catalysis, alkyl hydroperoxides.

1. INTRODUCTION

Saturated hydrocarbons (alkanes: propane, cyclohexane, *n*-heptane etc.) may be called the "noble gases of organic chemistry" due to their chemical inertness. Methane – the least reactive organic compound – can be compared with helium. During last decades, many reactions of hydrocarbons with various metal compounds occurring under mild conditions have been described (see reviews [1a–f]). Such processes with participation of metal complexes are carried out at relatively low temperatures and can be selective. The oxidations of hydrocarbons with donors of an oxygen atom such as hydrogen peroxide, alkyl hydroperoxides and peroxy acids constitute an important field of contemporary catalytic chemistry, and some industrial processes can be based on these reactions. It is interesting that even water can play the role of an oxidizing reagent for the hydrocarbon functionalization [1g]. In this review, we briefly discuss oxidations of alkanes and aromatics with peroxides in solutions under mild conditions catalyzed by soluble and solid derivatives of various metals.

2. SOLVENTS

Since alkanes (and also aromatics) are inert compounds, the solvents which can be easily oxidized should not be used in the reactions with these hydrocarbons. For example, alcohols or ketones are often not appropriate for reactions with saturated and aromatic hydrocarbons because a solvent and not a substrate is oxidized in this case. Liquids containing C–H bonds deactivated by electron-withdrawing substituents can be, however, used as appropriate solvents; these are acetic acid, acetonitrile, nitromethane, methylene chloride. Water is a very attractive green solvent but it may be efficiently employed only in the case of lower alkanes (methane and ethane) or in biphasic systems. Strong organic acids are known to enhance sufficiently the electrophilicity of metalating species. For example, trifluoroacetic acid was used as a solvent in the introduction of the platinum(IV)-containing substituent from H_2PtCl_6 into aromatic rings [2] and has been found to be a convenient solvent for the oxidative carbonylation of various alkanes including methane [3].

3. SUBSTRATES AND PRODUCTS. THE ANALYSIS OF FORMED ALKYL HYDROPEROXIDES

Reactions of alkanes and aromatics with peroxides are usually carried out in air and afford oxygenates, that are the products of insertion of oxygen atoms into C–H bonds. In many cases, if the reaction conditions are relatively mild, alkyl hydroperoxides are formed at least in the initial period. After long time, the alkyl hydroperoxides can gradually decompose to produce the corresponding ketones (aldehydes) and alcohols. Unfortunately, usually chemists analyzing the products by GC method inject the samples into the chromatograph without any pre-treatment. Such an analysis does not give the reliable information on the real composition of the reaction solution at the given moment. Indeed, usually alkyl hydroperoxides extensively decompose in the injector and columns of the chromatograph to produce mainly the corresponding ketones (aldehydes) and alcohols. In addition, various carboxylic acids can be formed from alkyl hydroperoxides *via* C–C bond cleavage at high temperature of the injector. Moreover, introducing into the chromatograph "native" reaction solution can lead to the further oxidation of the hydrocarbon by unreduced peroxy oxidant (for example, by *meta*-chloroperbenzoic acid, *m*-CPBA) in the hot injector. It is evident that the investigator will be able to measure only amounts of the ketones (aldehydes) and alcohols and will get the information which is far from the real composition of the reaction mixture. Meantime, if we know that alkyl hydroperoxides are formed as initial products of the oxygenation we can propose a reaction mechanism which is different from a scheme assumed for the direct "alkane hydroxylation" to the alcohol.

To demonstrate the formation of alkyl hydroperoxide in alkane oxidation with peroxides or/and molecular oxygen and to estimate its concentration in the course of the reaction we used a simple method developed by us earlier (see, for example, [1b, 4]). If an excess of solid PPh_3 is added to the sample of the reaction solution *ca.* 10 min before the GC analysis, the alkyl hydroperoxide present is completely reduced to the corresponding alcohol. As a result, the chromatogram differs from that of a sample not subjected to the reduction (the alcohol peak rises, while the intensity of the ketone peak decreases). The examples are shown in Fig. (**1**). Comparing the intensities of peaks attributed to the alcohol and ketone before and after the reduction, it is possible to estimate the real concentrations of the ketone, alcohol, and alkyl hydroperoxide present in the reaction solution. If the oxidation is carried out in water solution, other water-soluble reducing reagents can be used or acetonitrile can be added to the sample prior the reduction with PPh_3. This method can be employed also for the qualitative estimation of the alkyl hydroperoxide presence since the difference between the chromatograms of the reaction solution samples before and after the reduction with PPh_3 can unambiguously indicate the formation of an alkyl hydroperoxide in the course of the reaction. If a peak of the ketone present in the chromatogram before the reduction completely disappears after the treatment, it indicates that only pure alkyl hydroperoxide is formed in the reaction (see Fig. (**1A**)). It should be noted that in kinetic studies of alkane oxidations, it is necessary to reduce (quench) the reaction solution with triphenylphosphine prior the GC analysis in order to measure 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. Finally, the advantage of our method is the possibility to measure alkyl hydroperoxides in the presence of hydrogen peroxide and other peroxides. In recent years,

*Address correspondence to this author at the Semenov Institute of Chemical Physics, Russian Academy of Sciences, Ulitsa Kosygina, dom 4, Moscow 119991, Russia; E-mail: gbsh@mail.ru and shulpin@chph.ras.ru
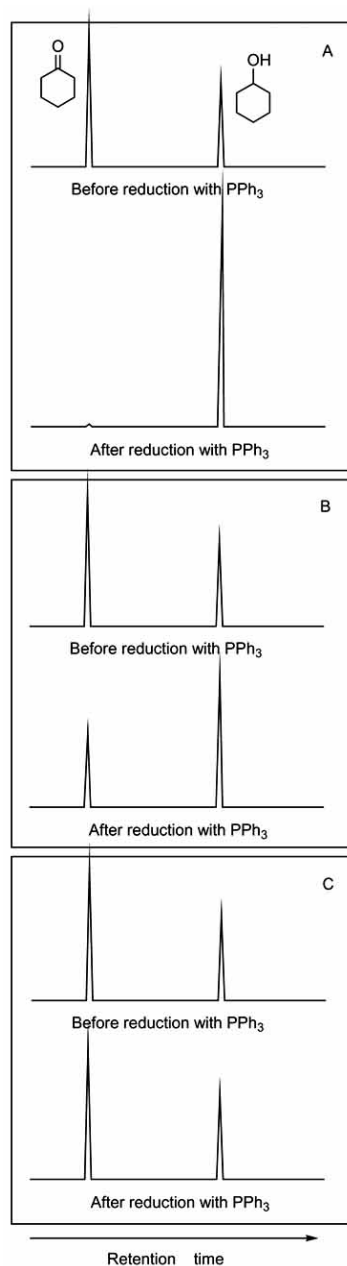
Fig. (1). Chromatograms of a sample containing cyclohexane oxygenates before and after reduction with triphenylphosphine are shown. A comparison of the bottom and top chromatograms indicates that in the case A almost pure cyclohexyl hydroperoxide is formed (which is reduced to the cyclohexanol). Case B corresponds to the situation when cyclohexanol, cyclohexanone and cyclohexyl hydroperoxide are present in the reaction mixture in comparable concentrations (*ca.* 1:1:1). In case C, the reaction mixture does not contain cyclohexyl hydroperoxide at all.

our method was employed by other chemists for the analysis of reaction products in various oxidations of C–H compounds by molecular oxygen, hydrogen peroxide and other peroxides [5].

Aromatic hydrocarbons are oxidized by peroxides to give phenols which can be further transformed by the same system into quinones. As phenols are much more reactive than starting aromatics, the oxygenation of benzene and its analogues often leads to the formation of quinones which (especially if a large excess of the oxidant is used) will be converted into the products of more deep

oxidation such as carboxylic acids. It is necessary to use a high substrate/oxidant ratio in order to obtain mainly the phenol.

4. CO-CATALYSTS

In many cases metal-catalyzed oxidations with peroxides proceed only in the presence of small amounts of specific additives, such as chelating organic compounds or acids [3a]. We will discuss here only three examples of such co-catalysis taken from the author's works. The first two systems are based on vanadium derivatives and the third one contains a manganese complex.

4.1. Oxidations by the 'H₂O₂ – vanadium derivative – pyrazine-2-carboxylic acid' and 'H₂O₂ – NaVO₃ – H₂SO₄' Reagents

We have discovered that the vanadate anion (as well as any other vanadium derivative) efficiently catalyzes the oxidation of organic compounds including alkanes and aromatics in acetonitrile, if pyrazine-2-carboxylic acid (PCA ≡ pcaH) is present as a co-catalyst in the solution in low concentrations [4c,e, 6]. On the basis of a kinetic study of the alkane oxidation, we proposed a mechanism with two crucial steps: decomposition of a transient peroxovanadium(V) complex to produce a peroxyl radical and a V(IV) derivative ("V^V–OOH" → "V^{IV}" + HOO$^•$) and further interaction of this V(IV) complex with another hydrogen peroxide molecule to afford hydroxyl radical ("V^{IV}" + H$_2$O$_2$ → "V^V" + HO$^-$ + HO$^•$) which attacks the hydrocarbon.

The first reaction is a rate-limiting step. We assumed that PCA coordinated to the vanadium center in the form of the pca ligand facilitates the proton transfer between the oxo or hydroxy ligands of the vanadium complex on the one hand and molecules of hydrogen peroxide or water on the other hand, for example: "O=V···O₂H₂" → "HO–V–OOH". We called this principle a "robot's arm mechanism" (Fig. (**2**)) and assumed that it may have analogies in enzyme catalysis (vanadium and other metals are known to promote hydroxyl radical formation in living organisms). Bell and co-workers [7a] studied the mechanism of hydrocarbon oxidation by our reagent using density functional theory (DFT) and found, in accord with our proposal, that the generation of HOO$^•$ radicals cannot occur *via* cleavage of a V–OOH bond in the complex formed directly from the precursors because the activation barrier for this process is too high. Instead, peroxyl radicals are formed *via* a sequence of additional steps and di- and tri-peroxo complexes are involved into this transformation. Besides, the conversion of the precursors requires hydrogen transfer from H$_2$O$_2$ to a vanadyl group, and the calculations by Bell and co-workers showed "that direct transfer has a higher barrier than pca-assisted indirect transfer. Indirect transfer occurs by migration of hydrogen from coordinated H$_2$O$_2$ to the oxygen of a pca ligand connected to the vanadium atom" [7a]. We have studied the oxidation by the reagent under discussion of isopropanol and cyclohexane [7b], and this investigation led to the conclusion that the crucial step of the process is the monomolecular decomposition of a diperoxovanadium(V) complex containing the pca ligand to afford the peroxyl radical, HOO$^•$, and a V(IV) derivative. It was assumed that the rate-limiting step in the overall process may not be this (rapid) decomposition itself, but (prior to this step) the slow hydrogen transfer from a coordinated H$_2$O$_2$ molecule to the oxygen atom of a pca ligand at the vanadium center. The V(IV) derivative reacts with a new hydrogen peroxide molecule to generate the hydroxyl radical, active in the oxidation of isopropanol: HO$^•$ + Me₂CH(OH) → H$_2$O + Me₂C$^•$(OH). The reaction with an alkane, RH, in acetonitrile proceeds analogously, and in this case the hydroxyl radical abstracts a hydrogen atom from the alkane: HO$^•$ + RH → H$_2$O + R$^•$. These conclusions were in a good agreement with the results obtained by Bell and co-workers [7a].

Detailed comparative kinetic and spectroscopic studies of the oxidations of hydrocarbons and isopropanol using n-Bu₄NVO₃ and oxovanadium(V) triethanolaminate (vanadatrane) as catalysts has
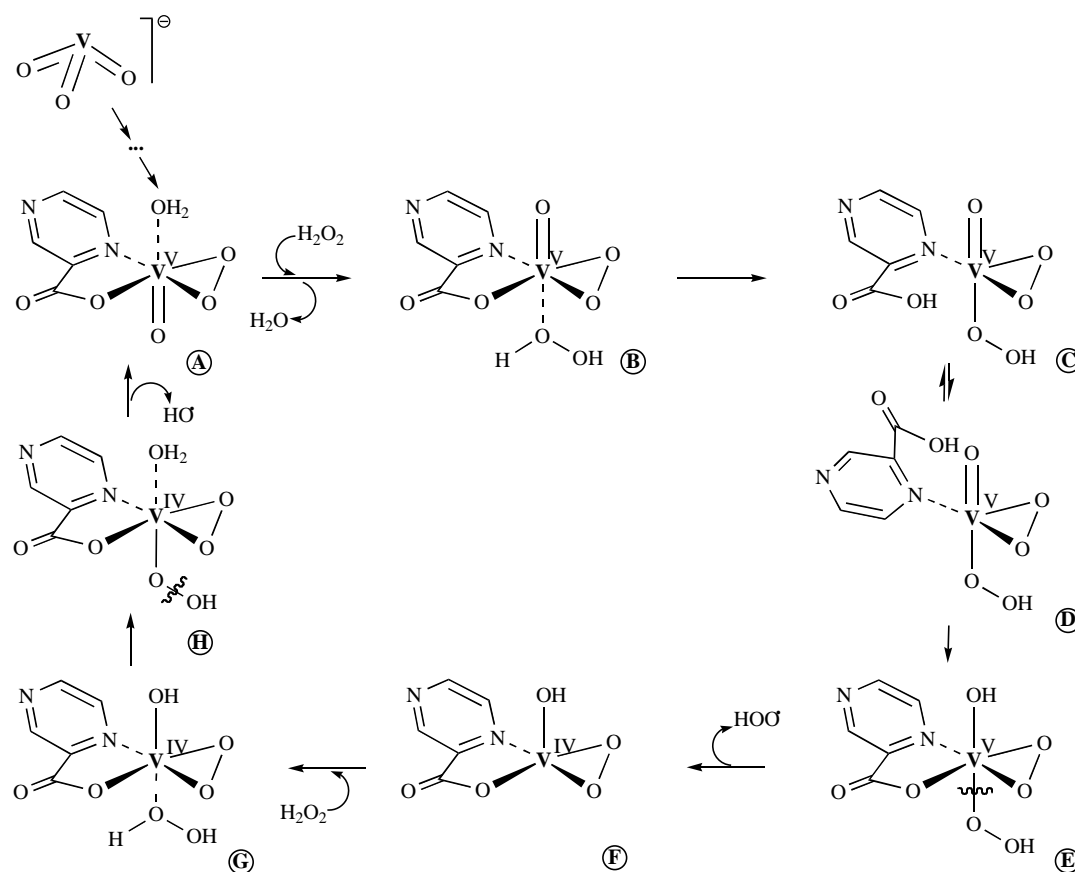
Fig. (2). A simplified catalytic cycle proposed for the radical generation by the 'vanadate/PCA/H_2O_2' reagent [6,7]. The pyrazinecarboxylate ligand assists in proton transfer from the coordinated H_2O_2 molecule (in structure **B**) to the oxo ligand (to form the hydroperoxy derivative **E**) *via* formation of intermediate species (rotamers) **C** and **D**. Analogously, the transformation of the V(IV) derivative **G**, containing the coordinated H_2O_2 molecule, into the hydroperoxy species **H** (with proton transfer to the hydroxyl ligand) is assisted by the pca ligand. We say that pca-ligand plays the role of an arm in the "robot's arm mechanism".

been carried out very recently.[1] The ^{51}V NMR data showed that the catalytic cycles for the two catalyst precursors involve the same intermediate species, and it has been unexpectedly found that both catalytic systems activate C–H bonds *via* a common reaction mechanism. It has been stated on the bases of the DFT calculations [1] that proton transfer from the coordinated hydrogen peroxide molecule to the oxo- or peroxo ligand is one of the crucial steps in the overall mechanism of the radical generation. As the oxidation reaction occurs in the presence of water, taking into account that the H_2O is a strongly polar molecule, it can be assumed that the water is directly involved into proton transfers being the member of the corresponding transition states (TSs). Indeed, such TSs bear a six-membered metal-containing cycle and, therefore, are more stable ones (by 6.6–7.5 kcal/mol). A simplified scheme of the catalytic cycle with participation of "water-assisted mechanism" is shown in Fig. (**3**). In this alternative cycle, the rate-accelerating role of PCA can be the stabilization of certain intermediate species and lowering the TSs by the coordination with the pca ligands.

Methane can be oxidized by the 'H_2O_2 – KVO$_3$ – PCA' if water is used as a solvent instead of acetonitrile [7c]. However, under used conditions (50–90 °C, 4 h) PCA is partly or completely de-structed and this co-catalyst should be used in large excess over vanadate to attain relatively high (up to 80) turnover numbers (TONs). Perchloric acid (0.1 M) in combination with KVO$_3$ (10^{-3}

M) and H_2O_2 (0.2 M) turned out to be a good catalytic system to oxygenate methane with TON = 150 after 24 h at 50 °C [7c]. We have found very recently [2] that addition of a mineral (e.g. sulfuric) or carboxylic (e.g. oxalic) acid to NaVO$_3$ solution in acetonitrile allows us to very efficiently oxidize alkanes at 50 °C exclusively to the corresponding alkyl hydroperoxides. Thus, hydroperoxidation of cyclohexane with the 'H_2O_2 – NaVO$_3$ – H_2SO_4' reagent gives the sole product (cyclohexyl hydroperoxide) with TON = 1700, and yield based on cyclohexane is 38%. The reaction occurs also in water, although less efficiently.

4.2. Oxidations by the 'H_2O_2 – [Mn$_2$L$_2$O$_3$]$^{2+}$ (L = 1,4,7-trimethyl-1,4,7-triazacyclononane) –Carboxylic Acid' System

The third oxidizing system invented by us consists of the binu-clear manganese(IV) complex **1** containing 1,4,7-trimethyl-1,4,7-triazacyclononane and a carboxylic acid as an obligatory co-catalyst [8]. Hydrogen peroxide or *tert*-butyl hydroperoxide (TBHP) were used as oxidants. The '**1**/carboxylic acid/H_2O_2' combination in acetonitrile solution very efficiently oxidizes inert alkanes to afford primarily the corresponding alkyl hydroperoxides which are trans-formed further into the more stable ketones (aldehydes) and alco-hols. It turned out that the system oxidizes not only alkanes but also epoxidizes olefins, transforms alcohols into ketones (aldehydes), and sulfides into sulfoxides. Oxalic, acetic, trifluoroacetic and other acids were used as co-catalysts.

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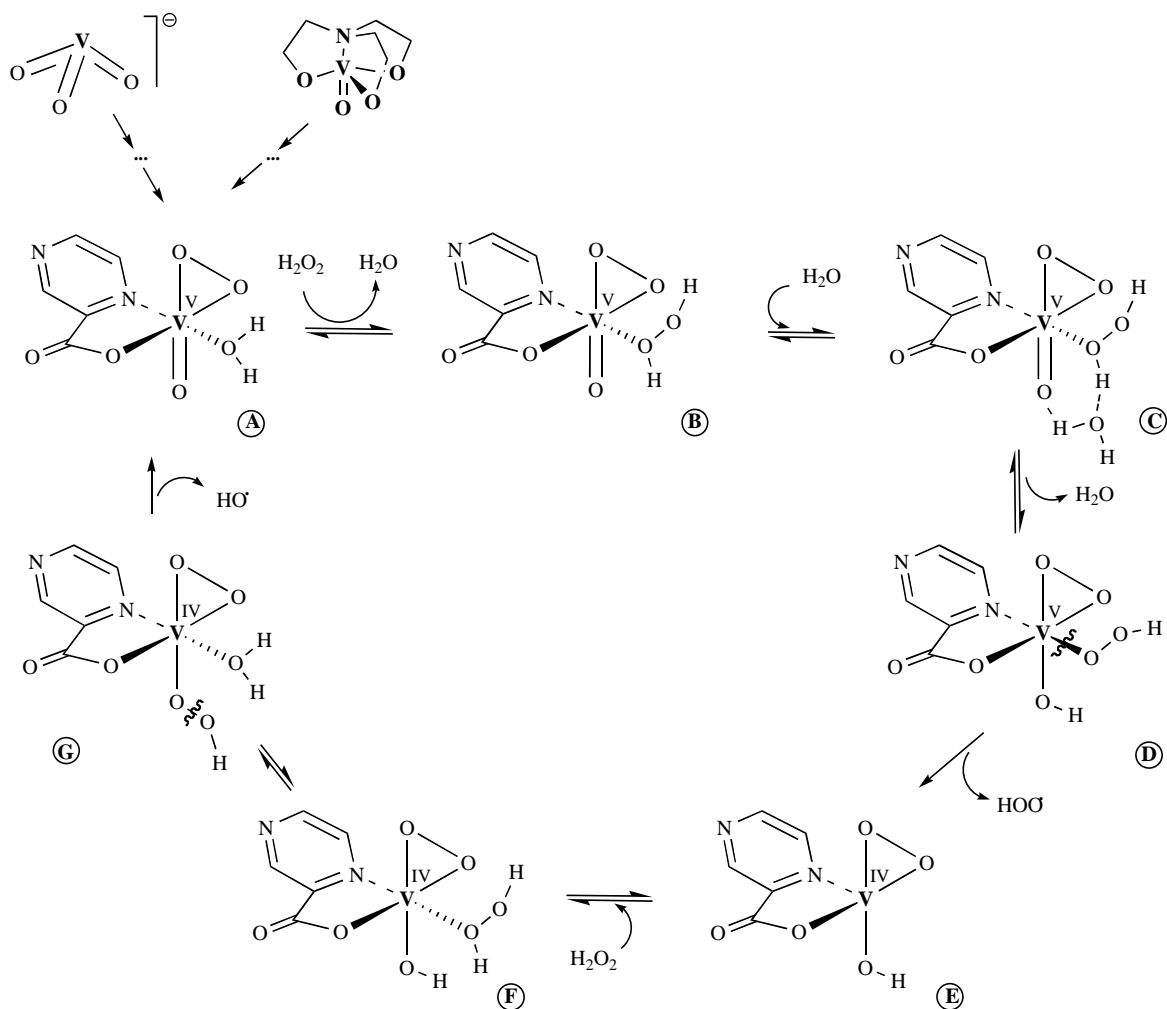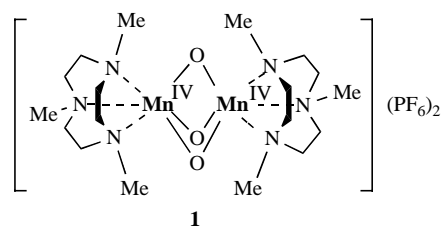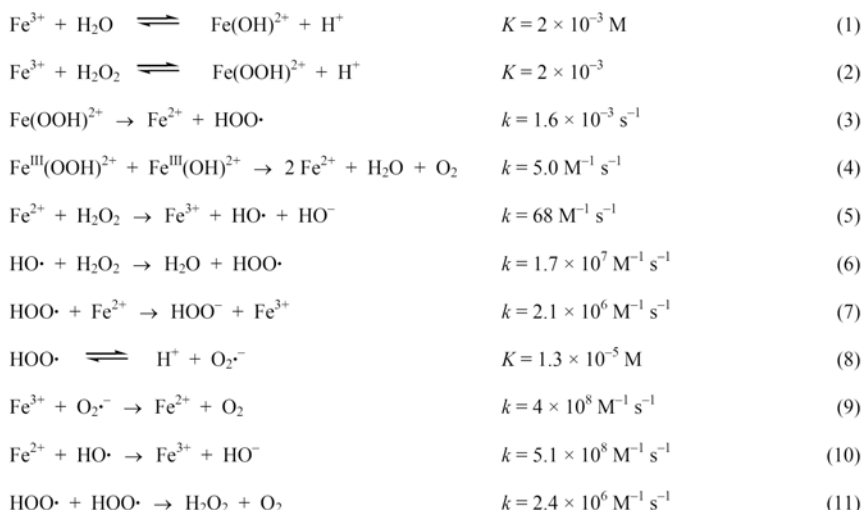
Fig. (3). A simplified catalytic cycle proposed for the radical generation by the 'vanadate (vanadatrane)/PCA/H$_2$O$_2$' reagent involving the steps of 'water-assisted mechanism' (see footnote [1]). Water molecules assist proton transfer from the coordinated H$_2$O$_2$ molecule in structure **B** to the oxo ligand *via* the transition state **C**. In the analogous step **F→G**, water molecules can assist proton transfer from the coordinated H$_2$O$_2$ molecule to the hydroxy ligand. Proton transfer can occur also from the coordinated H$_2$O$_2$ molecule to the peroxo ligand with the formation of two hydroperoxo ligands. The last scheme explains why di- or tri-peroxo species are the most active in the radical generation as it has been shown in Refs. [7a,b].

It is interesting that certain amino acids also accelerate the H$_2$O$_2$ oxidation of cyclohexane [8i]. The efficiency of the co-catalyst dramatically depends on the nature and structure of the amino acid. Pyrazine-2,3-dicarboxylic acid (2,3-PDCA) has been found to be the most efficient co-catalyst among the tested amino acids, whereas picolinic acid is almost inactive in this oxidation. The highest rate has been attained when 2,3-PDCA was used in combination with trifluoroacetic acid. The reaction with olefins in the presence of oxalic acid gave rise to the products of dihydroxylation in addition to the corresponding epoxides. Alkanes, olefins, and alcohols were oxidized also in the absence of acetonitrile. A relevant soluble polymer-bound Mn(IV) complex with *N*-alkylated 1,4,7-triazacyclononane was used as a catalyst in the H$_2$O$_2$ oxygenation of alkanes [8l]. The detailed kinetic study of the dye Rhodamine 6G degradation (decoloration) and competitive epoxidation and α-hydroperoxidation of cyclohexene by H$_2$O$_2$ has been recently carried out [8s]. Both soluble [LMn(O)$_3$MnL](PF$_6$)$_2$ (**1**) and insoluble [LMn(O)$_3$MnL]$_2$[SiW$_{12}$O$_{40}$] (**1b**) catalysts were used in combination with oxalic acid. It has been concluded that both oxidation processes occur with the formation of transient species **D** (which exhibits the properties of a relatively weak radical and is able to

abstract the hydrogen atom from C–H bonds of hydrocarbons) and **E** (which is responsible for the cyclohexene epoxidation). Species **D** is probably an oxygen-centered radical containing also manganese ions. Species **E** is apparently an oxo derivative of high-valent manganese. Catalyst **1** generates predominantly species **E**. When heterogenized catalyst **1b** (see [8t]) is used species **D** prevail.

1

Our '**1**/carboxylic acid/H$_2$O$_2$' system has been used by other authors [9a] for the *cis*-hydroxylation and epoxidation of olefins. Manganese complexes containing triazacyclononane ligands have been shown to catalyze oxidation of alkanes and olefins with peroxyacetic acid and *m*-CPBA [8a,k, 9b,c].

$$Fe^{3+} + H_2O \rightleftharpoons Fe(OH)^{2+} + H^+ \qquad K = 2 \times 10^{-3}\ M \qquad (1)$$

$$Fe^{3+} + H_2O_2 \rightleftharpoons Fe(OOH)^{2+} + H^+ \qquad K = 2 \times 10^{-3} \qquad (2)$$

$$Fe(OOH)^{2+} \rightarrow Fe^{2+} + HOO\cdot \qquad k = 1.6 \times 10^{-3}\ s^{-1} \qquad (3)$$

$$Fe^{III}(OOH)^{2+} + Fe^{III}(OH)^{2+} \rightarrow 2\,Fe^{2+} + H_2O + O_2 \qquad k = 5.0\ M^{-1}\ s^{-1} \qquad (4)$$

$$Fe^{2+} + H_2O_2 \rightarrow Fe^{3+} + HO\cdot + HO^- \qquad k = 68\ M^{-1}\ s^{-1} \qquad (5)$$

$$HO\cdot + H_2O_2 \rightarrow H_2O + HOO\cdot \qquad k = 1.7 \times 10^7\ M^{-1}\ s^{-1} \qquad (6)$$

$$HOO\cdot + Fe^{2+} \rightarrow HOO^- + Fe^{3+} \qquad k = 2.1 \times 10^6\ M^{-1}\ s^{-1} \qquad (7)$$

$$HOO\cdot \rightleftharpoons H^+ + O_2\cdot^- \qquad K = 1.3 \times 10^{-5}\ M \qquad (8)$$

$$Fe^{3+} + O_2\cdot^- \rightarrow Fe^{2+} + O_2 \qquad k = 4 \times 10^8\ M^{-1}\ s^{-1} \qquad (9)$$

$$Fe^{2+} + HO\cdot \rightarrow Fe^{3+} + HO^- \qquad k = 5.1 \times 10^8\ M^{-1}\ s^{-1} \qquad (10)$$

$$HOO\cdot + HOO\cdot \rightarrow H_2O_2 + O_2 \qquad k = 2.4 \times 10^6\ M^{-1}\ s^{-1} \qquad (11)$$

Schemes

5. EXAMPLES OF OXIDATIONS BY VARIOUS PEROXIDES

In this chapter we will very briefly consider selected works on hydrocarbon oxidations catalyzed by transition metal complexes. It should be noted that only a few examples of catalysis by derivatives of non-transition metals have been reported. Thus, bismuth compounds, $BiCl_3$, $NaBiO_3$, catalyze oxidation of weak C–H bonds with TBHP [10]. Solid aluminum oxide has been demonstrated to catalyze olefin epoxidation with hydrogen peroxide in ethyl acetate [11a,b]. Soluble aluminum nitrate catalyzes the olefin epoxidation with H_2O_2 in ethyl acetate [11c]. Aluminum trichloride catalyzes Baeyer-Villiger oxidation of ketones with H_2O_2 in ethanol [11d]. We have recently discovered [3] that solid aluminum-containing materials, montmorillonite $\{M_{x/n}{}^{n+} \cdot aH_2O(Al_{4-x}Mg_x)^{oct}(Si_8)^{tet}O_{20}(OH)_4\}$ and molecular sieves UOP Type 4A $\{Na_{12}[(AlO_2)_{12}(SiO_2)_{12}] \cdot xH_2O\}$ as well as aluminum oxide, Al_2O_3, catalyze the hydrogen peroxide oxygenation of alkanes and aromatics in acetonitrile; the reactions are accelerated by addition of a strong acid (trifluoroacetic acid). Aluminum nitrate, $Al(NO_3)_3$, homogeneously catalyzes alkane oxygenation with H_2O_2 in acetonitrile [11e]. Strong acids (e.g., CF_3COOH) also accelerate the reaction. It has been proposed on the basis of kinetic and selectivity studies that in the case of all aluminum-catalysts the alkane oxygenation occurs *via* the formation of hydroxyl radicals as key intermediate species.

Hydrogen peroxide is a cheap and ecologically friendly oxidant, and thousands of papers have been devoted to its usage in catalysis. Metal-catalyzed reactions proceed usually in homogeneous solutions in acetonitrile or acetic acid or in biphasic systems either in the absence of any solvent or when substrates are dissolved in methylene chloride. Tables **1** and **2** summarize selected examples of hydrocarbon oxidations with hydrogen peroxide catalyzed by soluble and solid metal compounds, respectively. Alkyl hydroperoxides, mainly TBHP (Table **3**), and peroxy acids (Table **4**) are also widely employed in hydrocarbon oxygenations. The advantage of these reagents in comparison with aqueous H_2O_2 is their higher solubility in organic liquids containing dissolved hydrophobic hydrocarbons.

6. MECHANISTIC CONSIDERATION
6.1. Formation of Active Radicals

The interaction of hydrogen peroxide with metal ions leads to the H_2O_2 decomposition to afford molecular oxygen and water. An

Table 1. Oxidations of Hydrocarbons with Hydrogen Peroxide Catalyzed Homogeneously by Soluble Metal Compounds

Hydrocarbon	Catalyst	Solvent	Ref.
Alkanes	Polynuclear Fe complexes	Acetonitrile	[12a–d]
Alkanes	Fe salts and complexes	Acetonitrile	[12e]
Alkanes	$FeCl_3$+dipy	Acetonitrile	[12f]
Alkanes	Fe complexes with PCA	Acetonitrile	[12g]
Alkanes	Non-heme Fe complexes	Acetonitrile	[12h–j]
Alkanes	Fe complex	Acetonitrile	[12k]
Ethylbenzene	Fe phenol-oxazoline	Acetonitrile	[12l]
Adamantane	Gif-type system	Pyridine	[12m]
Naphthalene	Mn or Fe porphyrin	MeOH, MeCN	[12n]
Aromatics	$RuCl_3$	Acetic acid	[12o]
Alkanes	Os complexes	Acetonitrile	[12p–r]
Cyclohexane	Cu(II) complexes	Acetonitrile	[12s,t]
Alkanes	Mn Schiff base complex	Acetonitrile	[12u]
Alkanes	Mn complexes	MeCN–CH_2Cl_2	[12v]
Ethane	Chromic acid	Acetonitrile	[12w]
Toluene	Vanadium oxo complexes	Acetonitrile	[12x]
Benzene	V complexes	Acetonitrile	[12y]
Aromatics	$H_4PMo_{11}VO_{40}$	Acetic acid	[12z,12aa]
Cycloalkanes	Tungstophosphates	Acetonitrile	[12ab,ac]
Cycloalkanes	Re complexes	Acetonitrile	[12ad]
Alkanes	$MeReO_3$	Ionic liquids	[12ae]
Adamantane	$MeReO_3$	Ethanol	[12af]
Alkylaromatics	Metal complexes	Water	[12ag]
Alkylaromatics	Metal complexes	Water	[12ah]
Methane	Fe phthalocyanine	Water	[12ai]
Alkanes	Ni and Pt complexes	Acetonitrile	[12aj]
Alkanes	Au(III), Au(I) complexes	Acetonitrile	[12ak]
Cyclohexane	Fe complexes	Acetonitrile	[12al-an]
Hydrocarbons	V salycylhydroximate	Acetonitrile	[12ao]
Hydrocarbons	Au derivatives		[12ap]
Benzene	$Rh_6(CO)_{16}$	Acetonitrile	[12aq]

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Table 2. Oxidations of Hydrocarbons with Hydrogen Peroxide Catalyzed by Solid and Supported Metal Compounds

Hydrocarbon	Catalyst	Solvent	Ref.
Adamantane	Iso or heteropolyacids/SiO_2	Butyronitrile	[13a]
Alkanes	V-POM/MCM-41	CH_2ClCH_2Cl	[13b]
Benzene	$[(CH_3)_4N]_4PMo_{11}VO_{40}$	Water	[13c]
Alkanes	V complexes/silica	Acetonitrile	[13d]
Ethylbenzene	V-MCM-41	Acetonitrile	[13e]
Alkanes	Vanadosilicate		[13f]
Benzene	Cu over Al-PILC	Acetonitrile	[13g]
Cyclohexane	Cu(II) in Y zeolite	None	[13h]
Benzene	Supported Cu complexes	Acetonitrile	[13i]
Benzene	Fe(III)/Al_2O_3	Acetonitrile	[13j]
Cycloalkanes	Supported $MeReO_3$	*t*-BuOH	[13k]
Tocopherols	Supported $MeReO_3$		[13l]
Linear alkanes	Titanosilicalite TS-1	None	[13m–o]
Benzene	Mn nodule	Acetic acid	[13p]
Benzene	Carbon nanotubes	Water	[13q]
Alkanes	Cu and Fe(salen)Cl+POM	Acetonitrile	[13r]
p-ClC_6H_4Me	V or Cu/polymer	Acetonitrile	[13s]
Cyclohexane	Cu complex/fiberglass		[13t]

Table 3. Metal-Catalyzed Oxidations of Hydrocarbons with Alkyl Hydroperoxides

Hydrocarbon	Catalyst	Solvent	Ref.
R-cyclopropane	CrO_3	CH_2Cl_2	[14a]
Cyclohexane	Fe salen complex	Acetonitrile	[14b]
Cyclohexane	Fe(III) complexes	Acetonitrile	[14c]
Alkylarenes	$FeCl_3$	Pyridine	[14d]
Alkanes	Fe complex/SiO_2	Water	[14e]
Alkanes	Fe(II) complex	Acetonitrile	[14f]
Cyclohexane	$RuCl_3$	Ionic liquid	[14g]
Steroids	Osmiumporphyrin	Benzene	[14h]
Cyclohexene	Cu complexes	Acetonitrile	[14i,j]
Alkanes	Cu/Co complex	Acetonitrile	[14k]
Alkylarenes	Cu-tea complex	Acetonitrile	[14l]
Ethylbenzene	CoSBA-15	Acetonitrile	[14m]
Alkanes	Co complex	Acetonitrile	[14n]
Toluene	M/zeolite	None	[14o]
Cyclohexane	Jacobsen's Mn catalyst	Acetonitrile	[14p]
Ethylbenzene	Zr-K-OMS-2	Acetonitrile	[14q]
Cyclohexane	V_2O_5/SiO_2	None	[14r]
Cyclohexene	Vanadyl/Al_2O_3	Acetonitrile	[14s]
Alkanes	Vanadate anion	Acetonitrile	[14t]
Alkylarenes	Ti(IV)		[14u]
Alkylarenes	Ti(IV)/silica		[14v]
Toluene	Ti(IV)/zeolite		[14w]

example – the reaction of Fe(III) ions with H_2O_2 in water solution (see [6k (Supplement), 16]) – is shown below. In equation (1) concentration of H_2O is included into *K*. This chain process consists of steps of the initiation [reactions (3) and (4) which generate Fe^{2+} ions], propagation [reactions (5), (6), and (9)] and termination [reactions (7), (10), and (11)].

The key step, especially interesting for the hydrocarbon activation, in (Schemes **1-11**) is reaction (5) which generates active hydroxyl radicals. The stoichiometric interaction between Fe(II) and hydrogen peroxide is known as Fenton's reaction. It is necessary, however, to note that the interaction of Fenton reagent with alkanes and aromatics affords the oxygenates only with low yields and unselectively. Many other metal ions as well as iron complexes with certain ligands catalyze hydrocarbon oxidations *via* mechanism with participation of hydroxyl radicals (1)–(11) much more efficiently (see Figs. (**2**) and (**3**) and Tables **1** and **2**). Hydroxyl radicals attack alkane molecules, RH, abstracting hydrogen atoms: HO• + RH → H_2O + R•. Alkyl radicals thus formed rapidly react with molecular oxygen present in the solution: R• + O_2 → ROO•. Peroxy radicals can be converted into the alkyl hydroperoxides *via*, for example, the following route: ROO• + $M^{(n-1)+}$ → ROO^- + M^{n+}; ROO^- + H^+ → ROOH. Analogously, the interaction of TBHP with a metal ion gives rise to the formation of the radical *tert*-BuO• which can attack the alkane: *tert*-BuO• + RH → *tert*-BuOH + R• (see an example in [8r]). In the reactions with participation of peroxyacetic acid, MeC(=O)OOH, species MeC(=O)O• attack substrates in the radical route of the process. Alkyl hydroperoxides formed in the reactions with transient generation of strong radicals can be detected by GC (see Section 2), at least in the initial period of the oxidation because in some cases these compounds decompose in the course of the process to produce the corresponding more stable alcohols and ketones (aldehydes). Many metal-catalyzed reactions between hydrocarbons and peroxides are known that do not involve strong free radicals as intermediates. For example, peroxide oxidants are believed to convert certain catalyst precursors into high-valent oxo derivatives of transition metals. The radical and non-radical reactive intermediates in the iron(III) porphyrin-catalyzed reactions have been discussed in a recent paper [17].

6.2. Selectivity Parameters

Selectivity parameters measured for an oxygenation of certain alkanes help us to make a decision on the process mechanism. Regio-selectivity parameters C(1) : C(2) : C(3) : C(4) are relative normalized (*i.e.*, calculated taking into account the number of hydrogen atoms at each carbon) reactivities of hydrogen atoms at carbons 1, 2, 3 and 4, of the chain of linear alkanes (hexane, heptane, and octane). Bond-selectivity parameters 1° : 2° : 3° are relative normalized reactivities of hydrogen atoms at primary, secondary and tertiary carbons of branched alkanes. Parameters for certain systems are summarized in Table **5**. It can be seen that hydroxyl radicals generated by light irradiation of H_2O_2 (entry 1) or by Fenton reagent (entry 2) oxygenate alkanes with low selectivity: C(1) : C(2) : C(3) : C(4) ≈ 1 : 8 : 8 : 8. Bond-selectivity parameters are also low: 1° : 2° : 3° are approximately 1 : 2 : 10. The low values of the selectivity parameters for the oxidations by the '*n*-Bu_4NVO_3–PCA–H_2O_2' reagent (entry 3), the 'Ni(ClO_4)$_4$–TMTACN–H_2O_2' combination (entry 4), and the catalysis by (2,3-η-1,4-diphenylbut-2-en-1,4-dione)undecacarbonyl triangulotriosmium (entry 5) led us to the conclusion that the three reactions occur with the formation of hydroxyl radicals. It is evident that oxidations catalyzed by

Table 4. Metal-Catalyzed Oxidations of Hydrocarbons with Peroxy Acids

Hydrocarbon	Catalyst	Solvent	Ref.
Alkanes, olefins	Non-heme Mn complex	Acetonitrile	[15a]
Alkanes	Fe complexes	Acetonitrile	[15b]
Adamantane	Ru complexes	Chloroform	[15c]
Cyclohexane	Ru complexes	Acetonitrile	[15d]
Alkanes	Ni complexes	Acetonitrile	[15e]
Alkanes	V complexes	Acetonitrile	[15f]
Alkanes	Ir and Pd complexes	Acetonitrile	[15g]

Table 5. Selectivity Parameters in Oxidation of Linear and Branched Alkanes by Certain Oxidizing Systems [a]

Entry	System	C(1) : C(2) : C(3) : C(4)			1º : 2º : 3º			
		n-Hexane	*n*-Heptane	*n*-Octane	2,2,4-TMP	MCH	2-MH	3-MH
1	hv–H$_2$O$_2$ (MeCN, 20 ºC)	1 : 10 : 7	1 : 7 : 6 : 7	1 : 10.2 : 6.8 : 6.3	1 : 2 : 6	1 : 2 : 6	1 : 6 : 20	1 : 4 : 12
2	FeSO$_4$–H$_2$O$_2$ (MeCN, 20 ºC)		1 : 5 : 5 : 4.5		1 : 3 : 6			
3	*n*-Bu$_4$NVO$_3$–PCA–H$_2$O$_2$ (MeCN, 40 ºC) [b]	1 : 6.9 : 7.0	1 : 5.7 : 7.2 : 5.0	1 : 6.7 : 7.5 : 5.3	1 : 1.5 : 10		1 : 9 : 37	1 : 14 : 64
4	Ni(ClO$_4$)$_4$–TMTACN–H$_2$O$_2$ (MeCN, 70 ºC) [c]		1 : 6.3 : 7.2 : 6.1		1 : 2.3 : 4.5	1 : 7 : 15		1 : 5.3 : 55
5	**2**–H$_2$O$_2$ (MeCN, 60 ºC) [d]	1 : 6.2 : 7.1	1 : 5.5 : 5.0 : 4.6		1 : 5 : 8.5	1 : 4 : 10		1 : 6 : 19
6	*m*-CPBA (MeCN, 25 ºC)	1 : 36 : 36.5				1 : 20 : 520		1 : 89 : 750
7	H$_2$O$_2$ in CF$_3$COOH	1 : 364 : 363			1 : 52 : 0			
8	NaAuCl$_4$–H$_2$O$_2$ (MeCN, 75 ºC) [e]		1 : 35 : 25 : 23		1 : 10 : 240	1 : 116 : 255		1 : 13 : 100
9	**1**–MeCO$_2$H–H$_2$O$_2$ (MeCN, 25 ºC) [f]		1 : 46 : 35 : 34	1 : 29 : 25 : 24	1 : 5 : 55	1 : 26 : 200	1 : 19 : 204	1 : 22 : 200
10	**1**–oxalic acid–TBHP (MeCN, 50 ºC) [f]		1 : 14 : 13 : 12	1 : 17 : 12 : 15	1 : 0.4 : 32	1 : 0.3 : 0.6		
11	**3**–oxalic acid–H$_2$O$_2$ (MeCN, 25 ºC) [g]	1 : 71 : 78	1 : 91 : 99 : 68	1 : 94 : 99 : 51	1 : 5.3 : 17			
12	**3**–oxalic acid–TBHP (MeCN, 50 ºC) [g]		1 : 76 : 32 : 23	1 : 25 : 18 : 12				
13	H$_2$O$_2$/TS-1 [h]	1 : 80 : 156	1 : 80 : 193 : 100	1 : 80 : 62 : 59	no products	no products	no products	no products
14	H$_2$O$_2$/TS-1/NaOH/MeCN [h]	1 : 6.3 : 5.9	1 : 7.7 : 8.4 : 7.6	1 : 6.5 : 6.6 : 6.2	1 : 5.7 : 21	1 : 4 : 25	1 : 7 : 20	1 : 7 : 20

[a] Abbreviations: 2,2,4-TMP, 2,2,4-trimethylpentane (isooctane); MCH is methylcyclohexane; 2- and 3-MH are 2- and 3-methylhexanes.
[b] For this system, which is believed to oxidize substrates *via* formation of hydroxyl radicals, see [4c, 6].
[c] TMTACN is 1,4,7-trimethyl-1,4,7-triazacyclononane. For this system, see [12aj].
[d] **2** is complex (2,3-η-1,4-diphenylbut-2-en-1,4-dione)undecacarbonyl triangulotriosmium. For this system, see [12q].
[e] For this system, see [12ak].
[f] **1** is complex [Mn$_2$L$_2$(μ-O)$_2$]$^{2+}$ where L is 1,4,7-trimethyl-1,4,7-triazacyclononane. For these systems, see [8].
[g] **3** is complex [Mn$_2$(*R*-L^{Me2R})$_2$(μ-O)$_2$]$^{3+}$ where *R*-L^{Me2R} is (*R*)-1-(2-hydroxypropyl)-4,7-dimethyl-1,4,7-triazacyclononane. For these systems, see [8q].
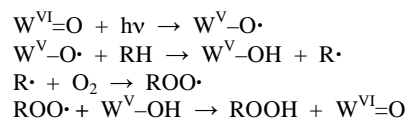[h] For these systems, see [13m–o].

NaAuCl$_4$ and complexes **1** and **3** (entries 8–12) occur with noticeably higher selectivity and do not involve free hydroxyl radicals.

Hydrogen peroxide in the absence of a solvent oxidizes predominantly methylene groups of linear alkanes if titanosilicalite TS-1 is used as a catalyst (Table **5**, entry 13) [13m,n]. Branched alkanes are not oxidized at all. On the basis of these results we can assume that the oxidation occurs in narrow channels of the TS-1, and an oxidizing fragment is probably a weak radical-like species, for example, Ti–O•, Ti–OO•, or HOO•. Alkyl hydroperoxides have not been detected in these oxidations. It is noteworthy, that in the presence of NaOH and MeCN [13o], alkyl hydroperoxides are the main products, methyl groups of linear alkanes are also intensively oxidized, and parameters of regio- and bond-selectivity are much lower (Table **5**, compare entries 13 and 14). For example, for the oxidation of *n*-octane and 3-methylhexane we measured parameters C(1) : C(2) : C(3) : C(4) = 1 : 6.5 : 6.6 : 6.2 and 1° : 2° : 3° = 1 : 7 : 20, respectively (Table **5**, entry 14). The 'H$_2$O$_2$/TS-1/NaOH/MeCN' system oxidizes also branched alkanes. It can be seen from the data summarized in Table **5** that selectivity parameters for the 'H$_2$O$_2$/TS-1/NaOH/MeCN' system are close to the corresponding values determined for the systems that are believed to operate *via* the formation of hydroxyl radical or similar very reactive species. All these data indicate that the formation of the alkyl hydroperoxides proceeds with generation of hydroxyl radicals or similar species such as acyloxy radicals. Possibly, the interaction between H$_2$O$_2$, HO$^-$ and MeCN gives rise to the formation of peroxycarboximidic acid which under the action of the TS-1 surfaces is decomposed to generate hydroxyl radicals. Mesoporous titanium-silicate Ti-MMM-2 has been found [4] to catalyze alkane oxidation

and olefin epoxidation by H$_2$O$_2$ in acetonitrile solution at 60 °C. The oxidation of C–H bonds is assumed to proceed *via* hydroxyl radical attack on the alkane C–H bond whereas the titanium peroxo species are involved into the epoxidation of double bonds.

6.3. The Classification of Oxidizing Species

Taking into account the selectivity parameters we can make conclusions on the nature of oxidizing species that operate in the alkane oxygenation. Assuming that reaction mechanisms involve the hydrogen atom abstraction or the oxygen atom insertion into C–H bond we can divide oxidizing species into three groups. We place into the first group very reactive radicals, such as HO•, RO•, RC(=O)O•. Radicals Cl• (photochemically generated from FeCl$_3$ or other metal chlorides) are also very reactive in the interactions with alkanes [4b,d, 18]. The hydroperoxidation of alkanes in the presence of Mo or W carbonyls and polyoxometalates proceeds *via* the following mechanism [19a]:

$$W^{VI}=O + hv \rightarrow W^V–O•$$
$$W^V–O• + RH \rightarrow W^V–OH + R•$$
$$R• + O_2 \rightarrow ROO•$$
$$ROO• + W^V–OH \rightarrow ROOH + W^{VI}=O$$

Radicals W^V–O• exhibit high reactivity in the interaction with the alkane. Analogous radical-like species are believed to be active

[4] Bonon, A. J.; Mandelli, D.; Kholdeeva, O. A.; Barmatova, M. V.; Kozlov, Y. N.; Shul'pin, G. B., manuscript in preparation. See also a preliminary communication: Mandelli, D.; Kholdeeva, O. A.; Bonon, A. J.; Barmatova, M. V.; Shul'pin, G. B. *Abstracts of 14 International Congress on Catalysis*, Seoul, S. Korea, 2008, PIII-53-154 (PICC08-0307).

in the alkane photooxygenation by polyvanadate in trifluoroacetic acid [19b], polychromates in acetonitrile [19c] as well as heteropolymetalates [4b]. Selectivity parameters for the oxygenation of linear alkanes with involvement of all radicals mentioned above are very low, usually $C(1) : C(2) : C(3) : C(4) \approx 1 : (4 \div 10) : (4 \div 10) : (4 \div 10)$. Radical-like species formed in a photocatalyzed reaction from quinone are a bit less reactive and attack *n*-hexane with selectivity parameter $C(1) : C(2) : C(3) = 1 : 13 : 14$ [19d].

Species of medium activity constitute the second group. In these cases the selectivity is higher: $C(1) : C(2) : C(3) : C(4) \approx 1 : (20 \div 40) : (20 \div 40) : (20 \div 40)$. Photoexcited anthraquinone attacks *n*-hexane with the selectivity parameter $C(1) : C(2) : C(3) = 1 : 70 : 50$ [19d]. Irradiation of an alkane solution in acetonitrile in air using pyrazine-2-carboxylic acid as a catalyst gave rise to the oxygenates with the selectivity parameter $C(1) : C(2) : C(3) = 1 : 35 : 32$ [20a]. Oxo derivatives of some transition metals, which are formed particularly in the interaction between metalloporphyrins and hydrogen peroxide or iodosyl benzene are examples of such species. The reactivity of radicals Br• (generated by the photolysis of $FeBr_3$) is sufficiently lower [20b] than that of radicals Cl• [18].

Finally, very weak oxidizing species with parameters $C(1) : C(2) : C(3) : C(4) \approx 1 : (60 \div 200) : (60 \div 200) : (60 \div 200)$ can be placed into the third group. The representatives of these group are very weak radicals (HOO•) and peroxy acids which react with alkanes *via* the concerted oxygen insertion mechanism. Some reactions with participation of the species of the three groups are demonstrated in Table **5**.

7. PERSPECTIVES

Surely, further development of hydrocarbon oxygenations catalyzed by soluble, solid, and supported metal compounds will allow us to find new systems for one-pot direct transformations of alkanes and arenes into valuable alkyl hydroperoxides, ketones, aldehydes, alcohols, and carboxylic acids with relatively high yield and selectivity.

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