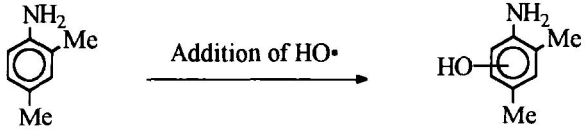
CHAPTER X

HOMOGENEOUS CATALYTIC OXIDATION OF HYDROCARBONS BY PEROXIDES AND OTHER OXYGEN ATOM DONORS

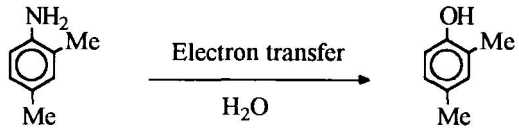
Along with oxidation with molecular oxygen, the reactions of hydrocarbons and other organic compounds with peroxides, first of all with hydrogen peroxide, are of great importance. They may be a basis for creating new technologies for direct selective transformations of alkanes and aromatics into valuable oxygen-containing products. It is noteworthy that despite numerous works of iron-promoted oxidations by hydrogen peroxide there are many questions concerning the mechanisms [1] of such processes. For example, the following scheme of the interaction of Fe(II) with H_2O_2 (well-known Fenton's reagent [2]) to produce hydroxyl radicals is adopted [1]:

$$Fe^{2+} + H_2O_2 \longrightarrow Fe^{3+} + HO^- + HO\bullet$$
$$Fe^{2+} + HO\bullet \longrightarrow Fe^{3+} + HO^-$$
$$H_2O_2 + HO\bullet \longrightarrow H_2O + HOO\bullet$$
$$Fe^{3+} + H_2O_2 \longrightarrow Fe^{2+} + HOO\bullet + H^+$$
$$Fe^{3+} + HOO\bullet \longrightarrow Fe^{2+} + O_2 + H^+$$
$$Fe^{2+} + HOO\bullet \longrightarrow Fe^{3+} + HOO^-$$
$$HOO^- + H^+ \rightleftharpoons H_2O_2$$
$$HOO\bullet + HOO\bullet \longrightarrow H_2O_2 + O_2$$

The interaction of 2,4-dimethylaniline with hydroxyl radicals generated by Fenton's reagent can be expected to produce aminophenols:



However, it has been found recently [2g] that thermal or photochemically enhanced Fenton reactions, in the presence of 2,4-dimethylaniline, yield primarily 2,4-dimethylphenol as an intermediate product, the genesis of which may only be explained by an electron transfer mechanism:



Books [3] and reviews [1, 4] have appeared in recent years on metal-catalyzed oxidations by peroxides. This chapter deals with hydrocarbon oxidations by peroxides. We will also consider briefly oxygenations by other oxygen atom donors.

X.1. OXIDATION BY HYDROGEN PEROXIDE

X.1.A. ALKYL HYDROPEROXIDES AS PRODUCTS

Formation of Alkyl Hydroperoxides in H_2O_2 Oxidations ofAlkanes

One can read in many publications that various metal-catalyzed oxidations of alkanes by hydrogen peroxide afford corresponding alcohols and carbonyl compounds (ketones or aldehydes) which are usually determined by GC analysis. However, it has been demonstrated [5] that H_2O_2 oxidations of alkanes catalyzed by $FeSO_4$ (in $MeCN–H_2O$ in the presence of H_2SO_4), LMnCl [L = tetrakis(2,3,4,5,6-pentafluorophenyl)porphyrinate](in $MeCN–CH_2Cl_2$ in the presence of imidazole), $Pd(OCOCF_3)_2$ (in MeCN), and $^nBu_4NVO_3$-pyrazine-2-carboxylic

acid (in MeCN) give substantial amounts of the corresponding alkyl hydroperoxides (in addition to usually smaller concentrations of alcohols and ketones). The method of alkyl hydroperoxide determination by GC analysis of samples *before* and *after* the reduction with PPh_3 has been used [5]. The oxidation process was monitored by withdrawing aliquots at specific intervals and analyzing them not only without any treatment but also after reduction with triphenylphosphine. One of the merits of this method is the possibility to estimate the concentration of the alkyl hydroperoxide formed from the alkane in the presence of an excess of an oxidant (hydrogen peroxide, alkyl hydroperoxide or metal peroxide). This very simple method was used in studies of hydrogen peroxide oxidations (see below) as well as in oxygenations with molecular oxygen (see, for example, [6]).

Estimation of Alkyl Hydroperoxide Content by GC Analysis of the Reaction Solution Samples Before and After Reduction with PPh_3

If an excess of solid triphenylphosphine is added to a solution of alkane (for example, cyclohexane) 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 triphenylphosphine. After the reduction, the cyclohexanol peak rises markedly while the intensity of the cyclohexanone peak decreases. 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 triphenylphosphine. These results can be explained by the fact that the mixture of products of the reaction under discussion contains cyclohexyl hydroperoxide as the main component.

Indeed, it is known that cyclohexyl hydroperoxide is usually totally decomposed in the chromatograph to produce cyclohexanol and cyclohexanone:

$$c\text{-}C_6H_{11}OOH \longrightarrow c\text{-}C_6H_{11}OH + c\text{-}C_6H_{10}O + \ldots \qquad (X.1)$$

The cyclohexyl hydroperoxide is readily and quantitatively reduced by triphenylphosphine to yield cyclohexanol:

$$c\text{-}C_6H_{11}OOH + PPh_3 \longrightarrow c\text{-}C_6H_{11}OH + OPPh_3 \qquad (X.2)$$

Thus, by comparing the data of chromatographic analysis of the reaction solution before and after reduction with triphenylphosphine, the amounts of cyclohexyl hydroperoxide, cyclohexanol and cyclohexanone present in the solution at a given moment can be estimated.

Generally, the oxidation of cyclohexane can give rise to the formation of cyclohexyl hydroperoxide [real current concentration in the reaction solution is $(C_{prxd})^{reaction}$], cyclohexan*ol* [$(C_{ol})^{reaction}$] and cyclohexan*one* [$(C_{one})^{reaction}$]. Cyclohexyl hydroperoxide decomposes in the injector of the chromatograph to produce additional amounts of cyclohexanol (the increment ΔC_{ol}) and cyclohexanone (ΔC_{one}). The ratio $\omega = \Delta C_{ol}/\Delta C_{one}$ can usually vary in the interval ~ 0.7–1.5 and seems to depend on the solvent, components of the solution and the chromatograph used. In this case:

$$(C_{prxd})^{reaction} = \Delta C_{ol} + \Delta C_{one} = \omega \Delta C_{one} + \Delta C_{one} = (\omega+1)\Delta C_{one} \quad (X.3)$$

The value of the coefficient co can be determined for the chromatograph used and for the solvent in which CyOOH is dissolved. By chromatography either of the solution of pure authentic CyOOH or of the reaction solution in the initial period of the reaction when almost pure CyOOH is present in the solution and concentrations of ketone and alcohol are very low.

If it is assumed that the alkyl hydroperoxide decomposition in the injector gives the two products in approximately equal amounts, (that is $\Delta C_{ol} \approx \Delta C_{one}$), the concentrations are

$$(C_{prxd})^{reaction} = \Delta C_{ol} + \Delta C_{one} \approx 2\,\Delta C_{one}. \quad (X.4)$$

Total concentrations of detectable stable products (cyclohexanol and cyclohexanone) in the chromatogram of the sample unreduced with PPh_3 will be $(C_{ol} + \Delta C_{ol})^{unred}$ and $(C_{one} + \Delta C_{one})^{unred}$, respectively. Triphenylphosphine reduces the alkyl hydroperoxide to yield, quantitatively, cyclohexanol. So the concentrations of *ol* and *one* determined by GC in the sample treated with PPh_3 will be $(C_{ol} + C_{prxd})^{red}$ and $(C_{one})^{red}$, respectively. The real amount of ketone present in the reaction mixture may thus be determined by measuring the concentration $(C_{one})^{red}$ of this product in the reduced sample.

$$(C_{one})^{reaction} = (C_{one})^{red} \quad (X.5)$$

Then, since $(C_{one})^{reaction} = (C_{ol})^{reaction}/\omega$, we can calculate the concentration of the alkyl hydroperoxide present in the reaction solution:

$$(C_{prxd})^{reaction} = (C_{ol})^{red} - (C_{one})^{red}/\omega \qquad (X.6)$$

The second way to determine the real concentrations of the products in the solution is based on measuring values ΔC_{ol} and ΔC_{one}

$$\Delta C_{one} = (C_{one})^{unred} - (C_{one})^{red} \qquad (X.7)$$

$$\Delta C_{ol} = (C_{ol})^{unred} - (C_{ol})^{red} \qquad (X.8)$$

Using equations (X.7), (X.8) and (X.3), it is possible to calculate $(C_{prxd})^{reaction}$ as well as $(C_{one})^{reaction}$ and $(C_{ol})^{reaction}$. If the values determined by the two ways are similar, it testifies that these concentrations are the real concentrations of the products in the solution.

However, if there is only one channel of the *ol* and *one* formation in the course of the oxidation, i.e., gradual decomposition of the alkyl hydroperoxide to produce both products again in approximately equal amounts, the concentrations of *ol* and *one* in the chromatogram of the untreated sample should be equal. This situation has been noticed in many cases of alkane oxidation. If the concentrations of *ol* and *one,* determined by GC, in the untreated sample are different, it testifies that the real amounts of products are not equal and either the alkyl hydroperoxide decomposes to produce predominantly the alcohol (or, on the contrary, the ketone) or there is an additional channel leading to cyclohexanol or cyclohexanone. This third simplified (without determination of ω) method can give relatively precise values of the real concentrations of the alkyl hydroperoxide (as well as cyclohexanol and cyclohexanone) only if all conditions mentioned above are valid. For example, if the chromatogram of a solution before the reduction exhibits two peaks of approximately equal area for cyclohexanol and cyclohexanone, and after the reduction only cyclohexanol is determined by the GC, these data testify that only cyclohexyl hydroperoxide is present in the solution and its concentration can be determined precisely.

It should be noted, that the approximate equality of alcohol and ketone yields determined in the untreated sample generally by no means can be interpreted as evidence for the presence of the alkyl hydroperoxide in the reaction

solution. The alkyl hydroperoxide may be decomposed in the course of a reaction to produce approximately equal amounts of alcohol and ketone; this equality could, in certain cases, arise through the coincidence of competitive reactions. Only on the basis of the comparison of the chromatograms of the initial and treated with PPh_3 samples, one may testify to the formation of an alkyl hydroperoxide as well as estimate its concentration. In any case, the difference between the chromatogams of the reaction solution samples before and after the reduction with PPh_3 can unambiguously certify the formation of an alkyl hydroperoxide in the course of the reaction. In order to determine the concentrations of all components of the reaction mixture in the oxidation of branched alkanes, it is necessary to measure the ratio ketone:alcohol (coefficient ω) separately for the decomposition of each isomer of the alkyl hydroperoxide formed. Principally, it is possible to do this if the reaction time is short enough and only isomeric hydroperoxides are present in the solution.

In some cases, 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_3, while peaks of the corresponding alcohols grow [7].

X.1.B. METAL-CATALYZED OXIDATIONS WITH H_2O_2

Various metal complexes catalyze efficient oxygenations of organic compounds with hydrogen peroxide (see, e.g., [8]). Tables X.I and X.2 summarize some examples of hydrocarbon oxidations with hydrogen peroxide catalyzed by transition metal complexes.

Mechanisms of metal-catalyzed oxidations by hydrogen peroxide may be different for alkanes and arenes as well as for different metal complexes. For example, for the oxidation of alkanes by the complex $[Ru(dmp)_2(S)_2](PF_6)_2$ (where S = MeCN or H_2O) a mechanism analogous to the "oxygen rebound" radical mechanism, assumed for cytochrome P450 and its models (see Chapter XI), has been proposed (Scheme X.I) [13b].

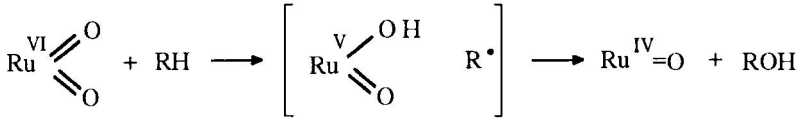


Table X.1. Oxidation of saturated hydrocarbons or fragments with hydrogen peroxide catalyzed by metal complexes.

Substrates	Catalyst	Ref.
Alkanes, arylalkanes	Mn-porphyrin + imidazole	9
Alkanes	Mn-porphyrin + carboxylic acid + heterocyclic base	10a
Adamantane	Mn-porphyrin	10b
Cyclohexane, ethylbenzene	CrO_3, $(^nBu_4N)_2CrO_4$, $(^nBu_4N)_2Cr_2O_7$, $(^nBu_4N)_2Cr_4O_{13}$	11
Cycloalkanes	Iron salts	12
Methane	*cis*-$[Ru(dmp)_2S_2](PF_6)_2$ [a]	13a
Alkanes	*cis*-$[Ru(dmp)_2S_2](PF_6)_2$ [a]	13b
Alkylaromatics	Polyoxometalates	14a
Alkylaromatics	$H_5PV_2Mo_{10}O_{40}$	14b
Alkanes	$[\gamma\text{-}SiW_{10}\{Fe(OH_2)\}_2O_{38}]^{6-}$	14c
Arylalkanes	$PZnMo_2W_9O_{39}^{5-}$	14d
Alkanes	$(Bu_3SnO)_2CrO_2$	14e
Alkanes	$FeSO_4$, $Pd(OCOCF_3)_2$, CrO_3, LMnCl [b] + imidazole	5
Alkanes	V derivative + pyrazine-2-carboxylic acid	5, 7, 15
Cyclohexane	$VO(PA)_2$ [c] encapsulated into NaY zeolite	16a
Cyclohexane	Cu(II) complexes	17
Cyclohexane, ethylbenzene	μ-Oxo diferric complexes	18a
Alkanes	Iron(II) complexes	18b,c
Cyclohexane	Peroxide adduct of Fe(III)	18d
Cyclohexane	Fe-porphyrin	18e
n-Hexane	Zeolite TS-1	19a,b
Cyclohexane	Ti silicate	19c
Toluenes	Ce(III) + Br^-	20a
Toluenes	Co(II) acetate + bromide source	20b
Arylalkanes	Cu(II) nitrate on clay	21
Alkanes	$[L_2Mn_2O_3](PF_6)_2$ (**X-1**) [d] + carboxylic acid	16p,q, 22

[a] dmp = 2,9-dimethyl-1,10-phenanthroline, S = H_2O or MeCN. [b] L = tetrakis(2,3,4,5,6-pentafluorophenyl)porphyrinate. [c] PA = picolinic acid anion. [d] L = 1,4,7-trimethyl-1,4-7-triazacyclononane.

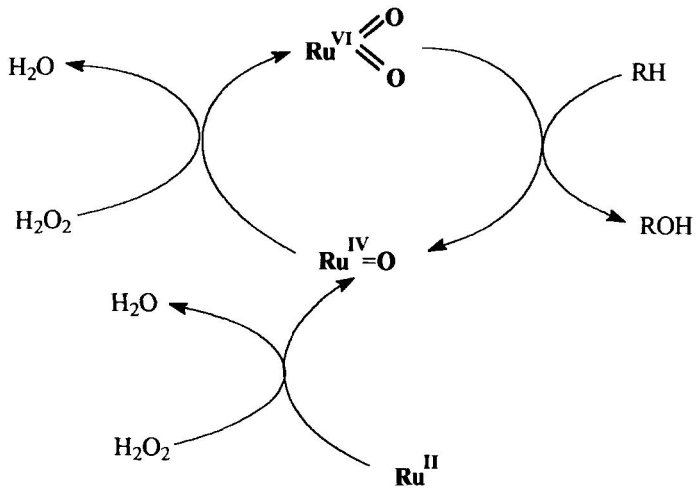
Table X.2. Oxidation of arenes with hydrogen peroxide catalyzed by metal complexes.

Substrates	Catalyst	Ref.
Benzene	α-Pyrrolidonate-bridged tetranuclear Pt complexes	23a
Arenes	(P–P)Pt(CF_3)X [a]	23b
Benzene	Iron salts	24
Methylnaphthalene	CH_3ReO_3	25a
Arenes	CH_3ReO_3 + pyrazine-2-carboxylic acid	25b
Arenes	CH_3ReO_3	25c
Arenes	$VO(O_2)(PA)(H_2O)_2$ [b]	26a
Phenol	Ti silicalite	27
Phenol	Metallosilicalite xerogels	28
Arenes	Ti silicate molecular sieve	29
Phenol	Fe(II)–1,10-phenanthroline	30
Benzene	Hexagonal silicas	31
Benzene	$[PMo_{11}VO_{40}]^{4-}$	32

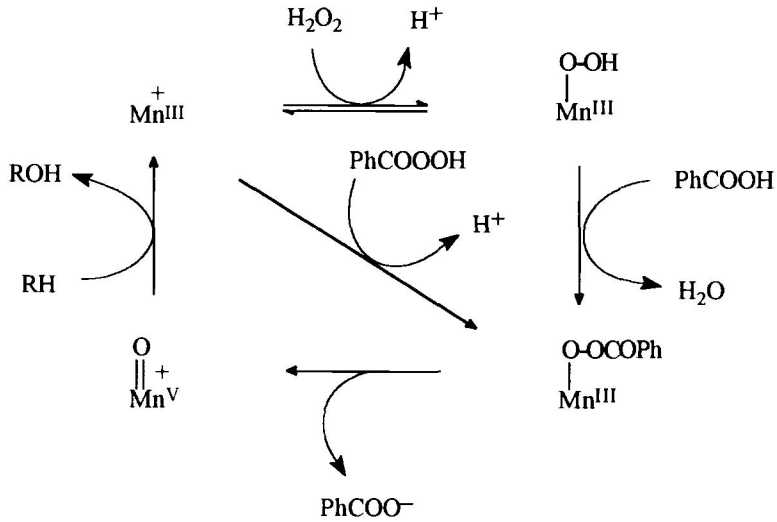
[a] P-P = tetraaryldiphosphine, X = OH, OPh. [b] PA = picolinic acid anion.

Analogously, the oxidation of alkanes catalyzed by manganese(III) tetraarylporphyrins in the presence of carboxylic acids and heterocyclic bases can involve the formation of a Mn(V) derivative and proceed via the oxygen rebound mechanism (Scheme X.2) [10a].

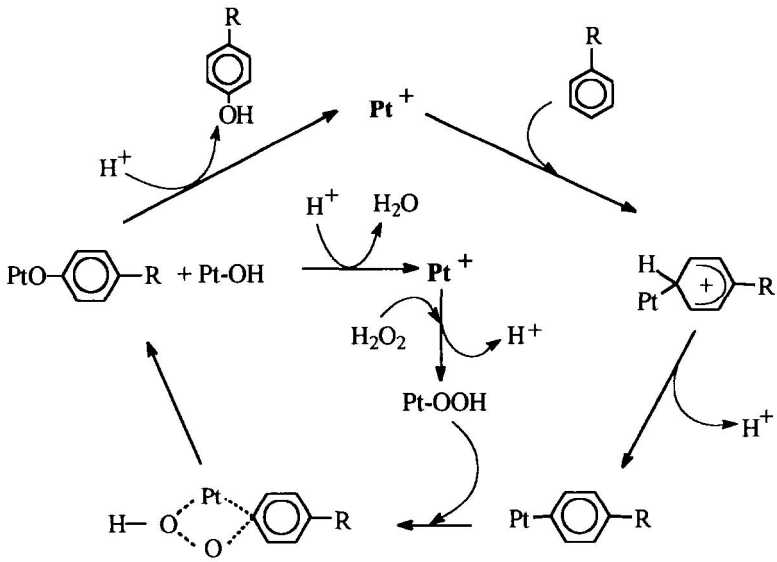
Meanwhile, the mechanism proposed for the hydroxylation of aromatics catalyzed by cationic complexes of platinum(II) involves an electrophilic metalation of the aromatic ring to yield platinum–aryl intermediates followed by oxygen transfer from a platinum-hydroperoxy species (Scheme X.3) [23b]. Finally, the oxidation [26a] of aromatic compounds by hydrogen peroxide catalyzed by the peroxovanadium complex **$VO(O_2)$(Picolinate)$(H_2O)_2$** is proposed to occur via oxygenation of the arene by this complex, which is restored under the action of **H_2O_2**.



Scheme X.1. The mechanism proposed for the H_2O_2 oxidation of alkanes, RH, catalyzed by a Ru complex.



Scheme X.2. The mechanism proposed for the H_2O_2 oxidation of alkanes, RH, catalyzed by Mn(III) porphyrins.



Scheme X.3. The mechanism proposed for the H_2O_2 oxidation of aromatic compounds catalyzed by cationic Pt complexes.

An efficient oxidation of alkanes by the reagent "O_2 – H_2O_2 – vanadium complex – pyrazine-2-carboxylic acid" has been described [15] (the kinetics of the cyclohexane oxidation are shown in Figure X.I). Any soluble vanadium derivative [vanadate-anion in the form $^nBu_4NVO_3$, or $VOSO_4$, VCl_3, $VO(acac)_2$] can be used as a catalyst. The reagent also oxygenates arenes to phenols, alcohols to ketones and hydroperoxidizes the allylic position in olefins. At low temperatures in acetonitrile, the predominant product of alkane oxidation is the corresponding alkyl hydroperoxide (alcohols and ketones or aldehydes are formed simultaneously in smaller amounts). This alkyl hydroperoxide then slowly decomposes to produce the corresponding ketone and alcohol. The amounts of alkyl hydroperoxide, alkanol and alkanone were estimated by comparing the data of chromatographic analysis of the solution before and after reduction with triphenylphosphine (see above), as well as by directly measuring the intensities of peaks corresponding to ROOH [15]. It has been demonstrated that atmospheric

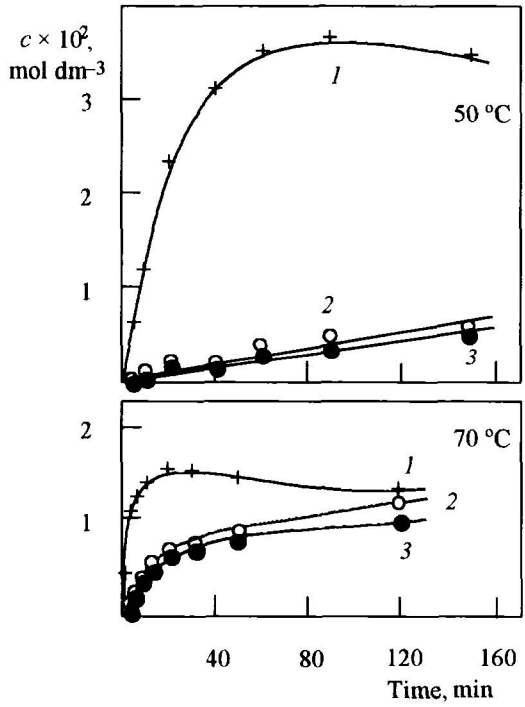


Figure X.1. Kinetic curves of cyclohexyl hydroperoxide (*1*) formation and its decomposition to yield cyclohexanol (*2*) and cyclohexanone (*3*) in the oxidation of cyclohexane (0.46 mol dm^{-3}) by the reagent 'O_2 – H_2O_2 – vanadium complex – pyrazine-2-carboxylic acid' in MeCN at 50 (top) and 70 °C (bottom).

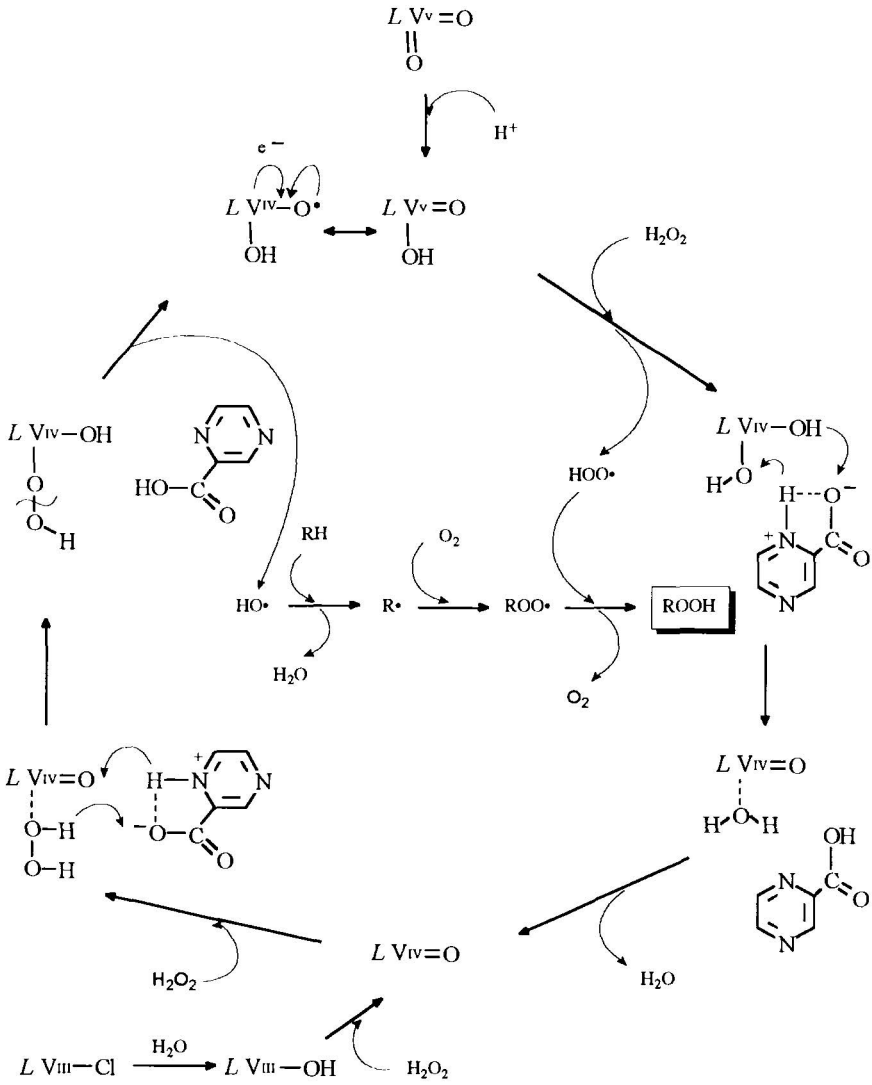
oxygen takes part in this reaction; in the absence of air the oxygenation reaction does not proceed. The cyclohexane oxidation under an $^{18}O_2$ atmosphere unambiguously showed a high degree of ^{18}O incorporation into the oxygenated products. Thus it may be concluded that in alkane oxidation, hydrogen peroxide plays the role of a promoter while atmospheric oxygen is the true oxidant. The oxidation of *n*-heptane by the reagent under consideration exhibits low selectivity, C(1): C(2) : C(3) : C(4) ≈ 1 : 4 : 4 : 4 . This parameter is close to that found for the oxidation of *n*-heptane by H_2O_2 in MeCN under UV irradiation (1.0

: 3.4 : 3.2 : 3.0). It is interesting that the oxidation of higher linear alkanes yields some amounts of C-C bond splitting (lower alcohols, especially methanol). The selectivities of the reactions with branched alkanes (2- and 3-methylhexane, *cis*- and *trans*-decalin) are also very similar to those observed with hydroxylation of the alkanes with hydrogen peroxide under UV irradiation. Methane, ethane, propane, *n*-butane and isobutane can be also readily oxidized in acetonitrile by the same reagent. In addition to the primary oxidation products (alkyl hydroperoxides), alcohols, aldehydes or ketones, and carboxylic acids are obtained with high total turnover numbers (at 75 °C after 4 h: 420 for methane and 2130 for ethane) and H_2O_2 efficiency. Methane can also be oxidized in aqueous solution, giving in this case methanol as the product (after 20 h at 20 °C the turnover number equals 250).

It has been proposed that the crucial step of the oxidation by the reagent "$O_2 - H_2O_2 - VO_3^-$ – pyrazine-2-carboxylic acid" is the very efficient generation of HO• radicals [15]. These radicals abstract a hydrogen atom from the alkane, RH, to generate the alkyl radical, R•. The latter reacts rapidly with an O_2 molecule affording the peroxo radical, ROO•. This radical is then transformed simultaneously into three products: alkyl hydroperoxide, ketone, and alcohol. The relative content of the last two products is increased if the reaction temperature is higher.

The proposed mechanism involves the reduction of V(V) by the first molecule of H_2O_2 to give a V(IV) derivative. The possible role of pyrazine-2-carboxylic acid is its participation (in a zwitter-ionic form) in the proton transfer which gives the hydroperoxy derivative of vanadium (Scheme X.4) [15p,q]. No oxidation occurs in the absence of pyrazine-2-carboxylic acid.

Picolinic acid also accelerates the H_2O_2 oxidations but less efficiently than pyrazine-2-carboxylic acid. It has been demonstrated recently that the vanadium complex with picolinic acid, $VO(PA)_2$, encapsulated into the NaY zeolite retains solution-like activity in the liquid-phase oxidation of hydrocarbons [16a]. It is noteworthy that pyrazine-2-carboxylic acid accelerates the hydrocarbon oxidation catalyzed by CH_3ReO_3 [25b]. Employing a (+)-camphor derived pyrazine-2-carboxylic acid as a potential co-catalyst in the CH_3ReO_3-catalyzed oxidation of methyl phenyl sulfide with urea-H_2O_2 adduct, the corresponding sulfoxide was obtained with an e.e. of 15% [16b].



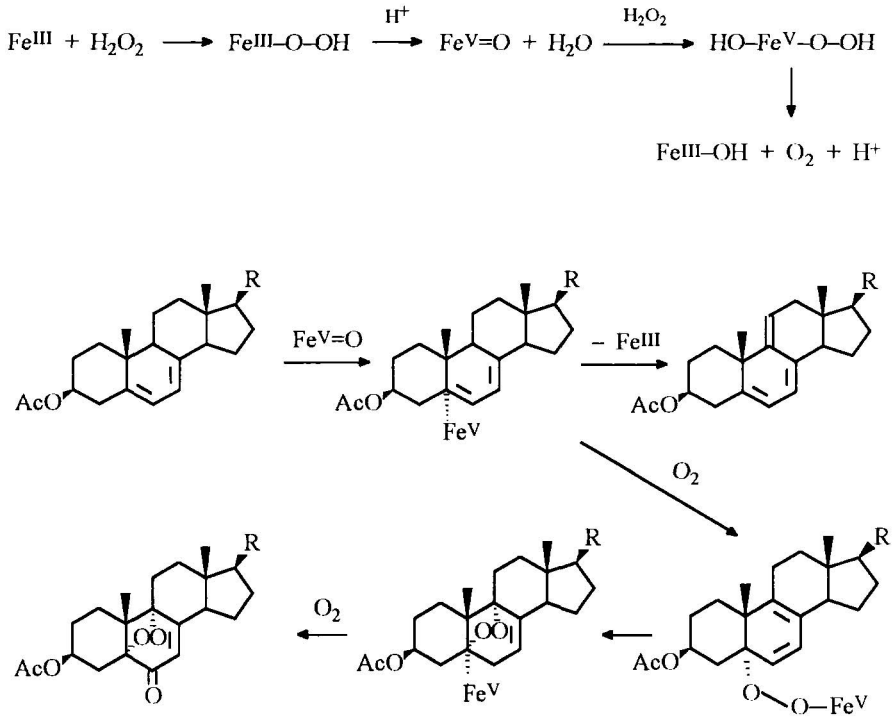
Scheme X.4. The simplified mechanism proposed for the oxidation of alkanes, RH, by the reagent "O_2 – H_2O_2 – vanadium complex – pyrazine-2-carboxylic acid".

It is interesting that oxidations of alkanes by Gif systems (see Chapter IX, as well as certain recent publications [33]) can afford in pyridine-acetic acid mixture, not only products of ketonization but also carboxylic acids (PA = picolinate):

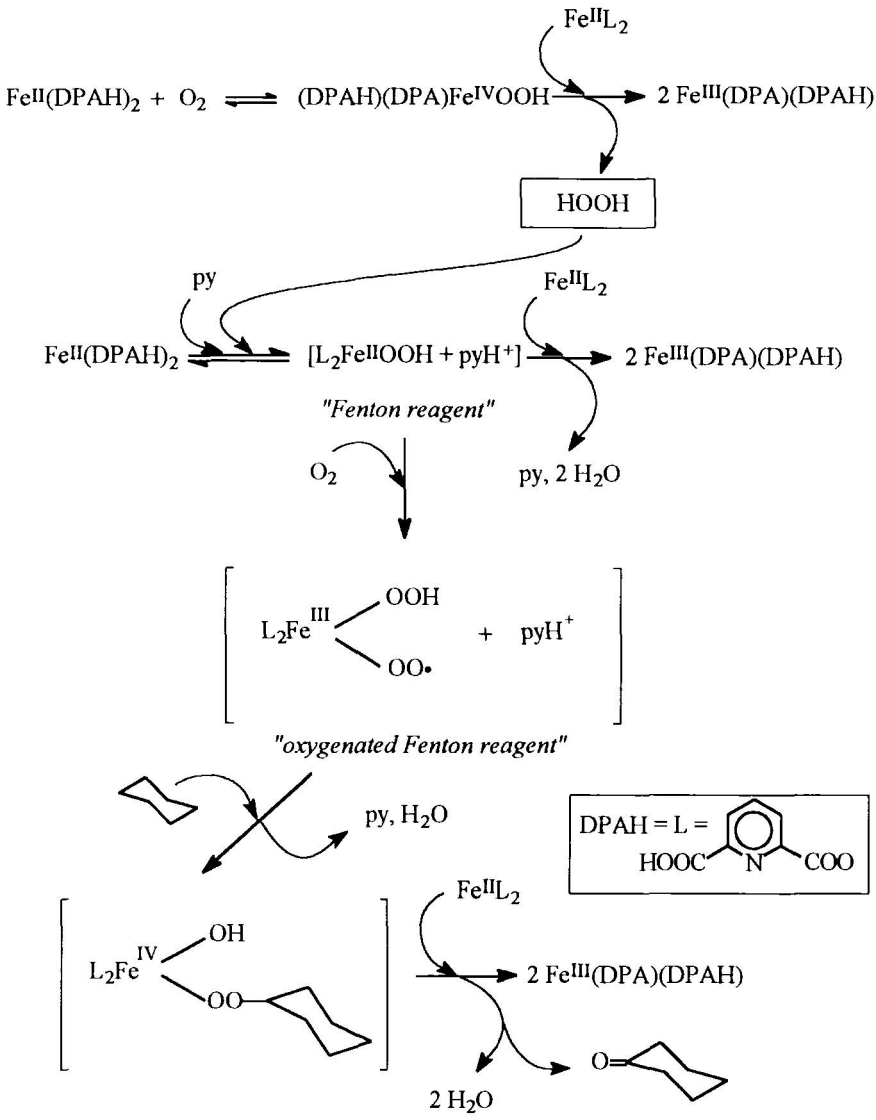
$$RH + Fe(PA)_3 + P(OMe)_3 + CO + H_2O_2 \longrightarrow RCOOH \quad [34a]$$

$$RH + Fe(CO)_5 + H_2O_2 \longrightarrow RCOOH \quad [34b]$$

and products of dehydrogenation and peroxidation (Scheme X.5) [35].



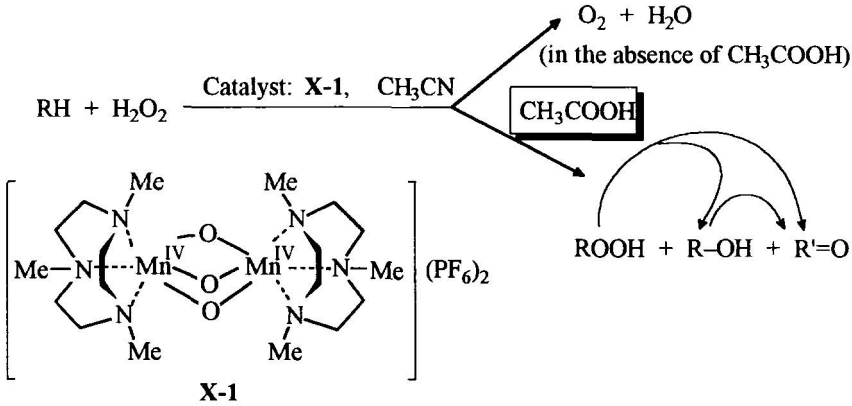
Scheme X.5. The mechanism proposed for the peroxidation of ergosterol acetate by H_2O_2–$FeCl_3$ in pyridine.



Scheme X.6. The mechanism proposed for the ketonization of alkanes, RH, catalyzed by iron complexes ("oxygenated Fenton chemistry").

Sawyer *et al.* have developed "oxygenated Fenton chemistry": the iron-, cobalt- and copper-induced activation of hydrogen peroxide (along with dioxygen) for the oxidation of organic substances, especially alkanes [36]. The main feature of these reactions is the predominant formation of ketones from cycloalkanes. The ketonization is carried out in a pyridine-acetic acid solution and so is relevant to the oxidation by Gif-type systems. For example, it has been found that the combination of $Fe(DPAH)_2$ ($DPAH_2$ = 2,6-dicarboxypyridine) and dioxygen in a pyridine-acetic acid (2:1) mixture results in rapid autoxidation to produce hydrogen peroxide and the complex Fe(DPA)(DPAH). The hydrogen peroxide thus formed reacts with an excess of the starting iron(II) compound to yield "a Fenton reagent", $[(DPAH)_2–FeOOH + pyH^+]$. This species adds dioxygen and then attacks a cyclohexane molecule to produce cyclohexanone as shown in Scheme X.6. It should be noted, however, that according to the results obtained by Ingold *et al.* [37a] and Walling [37b], "oxygenated Fenton chemistry" in organic solvents (and by implication in water) involves simple *free-radical-mediated* chemistry. It is not radical-free as Sawyer has suggested [37a].

Recently, a highly efficient alkane oxidation has been described [15p,q, 22] for the system consisting of hydrogen peroxide, the manganese(IV) salt $[L_2Mn_2O_3](PF_6)_2$ (X-1) (L = 1,4,7-trimethyl-1,4-7-triazacyclononane) as the catalyst, and a carboxylic acid as an obligatory component of the reaction mixture (Scheme X.7).



Scheme X.7. Different routes of the alkane oxidation by H_2O_2 catalyzed by complex **X-1** in the absence and presence of acetic acid.

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 if acetonitrile (or nitromethane) is used as a solvent. Turnover numbers of 3300 have been attained and the yield of oxygenated products is 46% based on the alkane. The oxidation initially affords the corresponding alkyl hydroperoxide as the predominant product, however this compound decomposes later to produce the corresponding ketones and alcohols (see Figure X.2 [15p,q]).

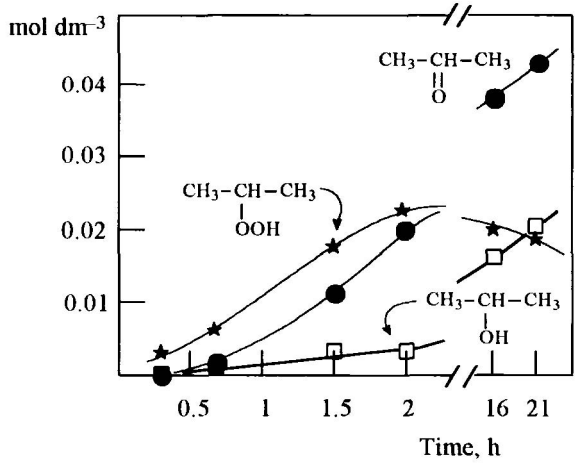


Figure X.2. Kinetic curves of the formation of 2-propyl hydroperoxide, 2-propanol, and acetone from the oxidation of propane (1 bar) by the system "H_2O_2 (0.5 mol dm^{-3}) – complex **X-1** (1.0×10^{-4} mol dm^{-3}) – acetic acid (0.25 mol dm^{-3})" in MeCN at 0 °C.

Regio and bond selectivities of the reaction are high: C(1) : C(2) : C(3) : C(4) ≈ 1 : 40 : 35 : 35 and 1° : 2° : 3° is 1 : (15–40) : (180–300). The reaction with *cis-* or *trans-* isomers of decalin gives (after treatment with PPh_3) alcohols hydroxylated in the tertiary position with a *cisltrans* ratio of ~2 in the case of *cis*-decalin, and of ~30 in the case of *trans-decalin* (i.e., in the latter case the reaction is stereospecific). The authors [15p,q, 22] believe that the alkane oxidation by the system under consideration begins with hydrogen atom abstraction from the alkane by an oxygen-centered radical or radical-like species.

The active oxidant is probably a manganese complex, possibly an oxomanganese species, and the reaction occurs in a cage or via an "oxygen-rebound mechanism", both these routes would afford products with retention of stereochemistry. Further, alkyl radicals (R•) that escape from the solvent cage react with dioxygen to generate ROO• and subsequently ROOH with some loss of stereochemistry. An alternative route, abstraction of the alkane H atom by a species Mn–OO• to produce R• and Mn–OOH, followed by the interaction of the two latter particles to give ROOH with retention of configuration cannot be excluded.

X.2. OXYGENATIONS BY ALKYL HYDROPEROXIDES

The oxidation of saturated hydrocarbons by alkyl hydroperoxides catalyzed by various metal complexes yields alcohols, carbonyl compounds (ketones and aldehydes) and peroxides. Examples of recent works devoted to these reactions are given in Table X.3. Usually *tert*-butyl hydroperoxide is employed for these oxidations. Other hydroperoxides, e.g., cumyl hydroperoxide [38a, 42a], have been also reported to oxygenate alkanes.

Scheme X.8 illustrates the proposed [53] mode of alkane oxidation with both peroxo and oxo groups bound to chromium(VI). This scheme also shows a possible way to regenerate an active Cr(VI) species starting from Cr(IV).

It has been shown [54] that the complex $VO(acac)_2$ under the action of alkyl hydroperoxide, ROOH, is initially transformed into the alkylperoxo complex $VO(acac)_2OOR$ and the alkoxo complex $VO(acac)_2OR$, which further decomposes to yield $VO(OR)_3$ and two other vanadium(V) species (an alkylperoxo complex X-2 and an alkoxo complex X-3). Complex X-2 does not react directly with cyclohexane, but produces a free radical:

$$V^{V}O(OOR) \rightleftharpoons V^{IV}O + ROO\bullet$$

The peroxo radical thus formed initiates the oxidation of cyclohexane.

The complex $[Fe(PMA)]^{2+}$ also efficiently catalyzes the oxidation of alkanes with *tert-butyl* hydroperoxide in acetonitrile at room temperature [55]. The mechanism proposed by the authors for this reaction involves the formation of free alkyl radicals and their subsequent reaction with O_2 (Scheme X.9). The

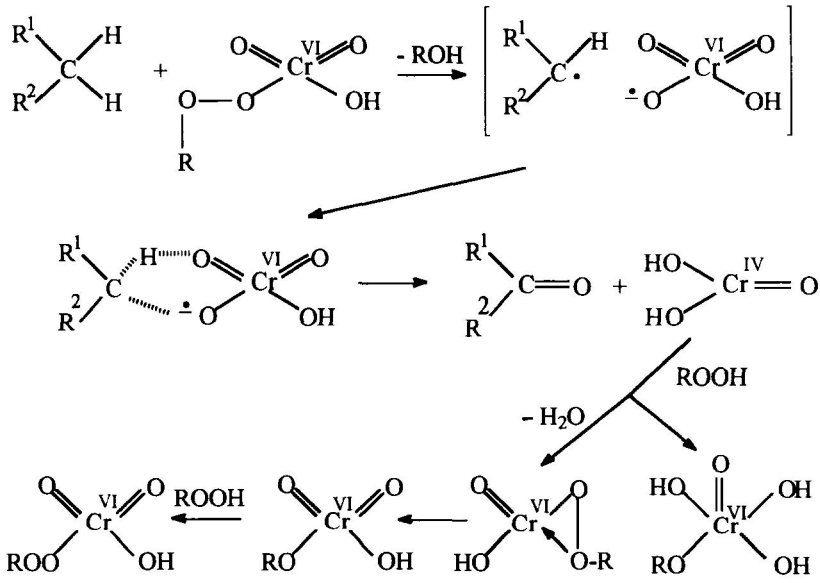
CyOO• radical may be involved in a Russell-type termination which produces cyclohexanol and cyclohexanone in equal amounts, along with molecular oxygen:

$$2\ R_2CHOO\bullet \rightleftharpoons R_2CHOOOOHCR_2 \longrightarrow R_2CHOH + R_2C{=}O + O_2$$

Table X.3. Hydrocarbon oxidation with *tert*-butyl hydroperoxide catalyzed by metal complexes.

Substrates	Catalyst	Ref.
Alkanes	$RuCl_2(PPh_3)_3$	38a
Cyclohexane	$[RuLO_2(CF_3CO_2)]ClO_4$ [a]	38b
Alkanes	$K_5[Ru(H_2O)PW_{11}O_{39}]$	39a
Cyclohexane, adamantane	Transition-metal-containing heteropolycomplexes	39b
Benzylic C-H	CrO_3	40
Cyclohexane	Co(III) complexes	41a
Nitriles	$VO(OAc)_2$	41b
Cyclohexane	Fe(TPA) [b] complexes	42
Cyclohexane	Fe biomimetic complexes	43
Alkanes, arylalkanes	Gif conditions	44
Cyclohexane	Binuclear Fe and Mn oxo-bridged complexes	45
Cyclohexane	Fe(III) and Cu(II) complexes	46a
Δ^5-Steroids	Cu(II) and Cu(I) salts and Cu metal	46b
Cyclooctane	Cu and Co complexes of tetraazacyclotetradecane bearing highly fluorinated tails	46c
Cyclooctane, adamantane	Mn carboxylates	47a
Alkanes	$[Mn_3O_4(dipy)_4(OH_2)_2](ClO_4)_4$	47b
Cyclohexane etc.	$[Mn(bipy)_3](BF_4)_2$	47c
Alkanes	Mn clusters	47d
Ethane	$Mn_4O_2(O_2CPh)_7(bipy)_2$	47e
Alkanes, arylalkanes	Polynuclear Mn Schiff base complexes	48
Cyclohexane	Binuclear Mn and Fe complexes	49
Cycloalkanes	Mn^{2+}-exchanged clay catalyst	50
Benzylic C-H	VAPO-5	51
Cyclooctane	Ru colloids	52

[a] L = *N*,*N*',*N*''-trimethyl-1,4,7-triazacyclononane. [b] TPA = tris(2-pyridylmethyl)amine.



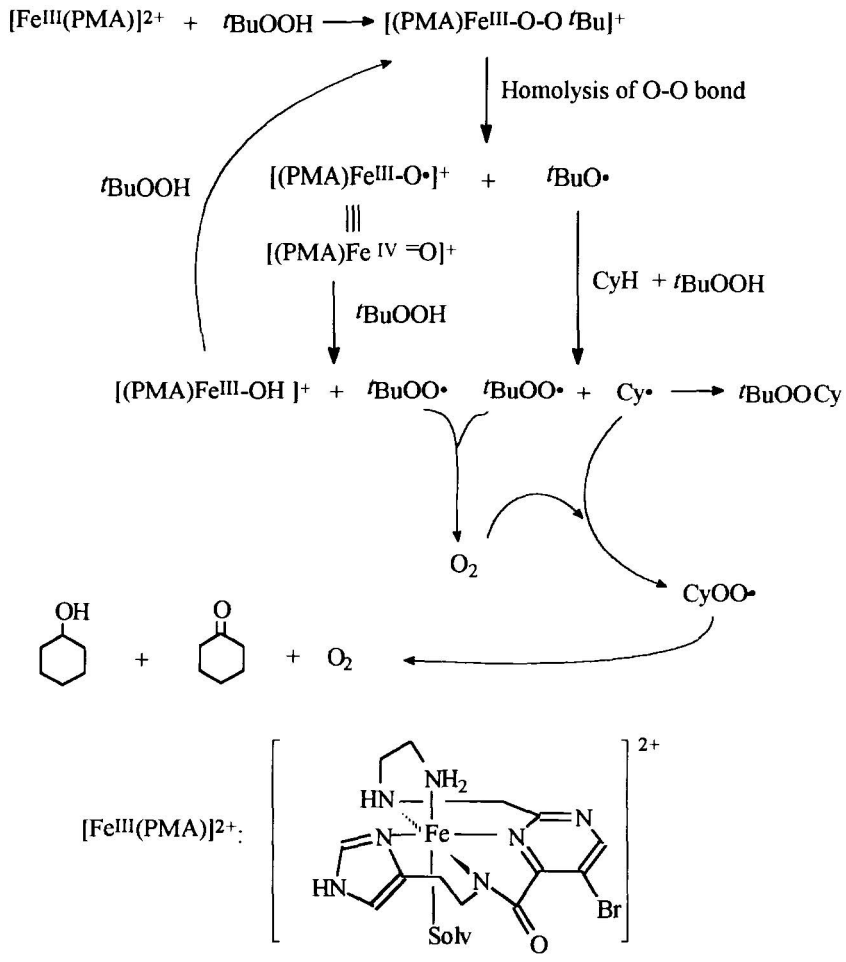
Scheme X.8. The alkane oxidation by alkyl hydroperoxide catalyzed by chromium oxo complexes.

In conclusion, it is useful to cite the papers by Meunier [56]:

> "...many hydroxylation reactions with alkyl hydroperoxides in the presence of transition-metal complexes are not due to a metal-centered active species, but to a free-radical process initiated by RO•"

and by Ingold *et al.* [37a]:

> "We urge all investigators who would like to claim that *tert*-butyl hydroperoxide-derived high-valent metal-oxo species are the effective oxidizing agents in their systems to check that the mechanistic probe hydroperoxides we have described yield the same results as *tert*-butyl hydroperoxide before they draw any mechanistic conclusions".



Scheme X.9. The alkane oxidation by alkyl hydroperoxide catalyzed by the iron complex $[Fe(PMA)]^{2+}$.

The formation of free radicals in alkane oxidations by ^{t}BuOOH, for example, via a route:

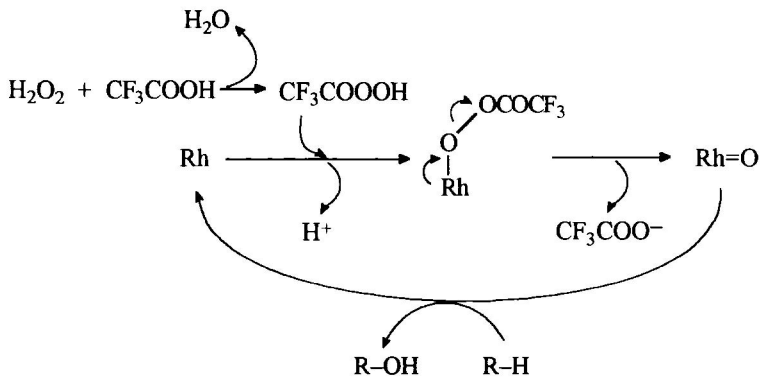
$$Fe(II) + {}^{t}BuOOH \longrightarrow Fe(III) + {}^{t}BuO\bullet + HO^{-}$$

which are responsible for the free radical initiation process, has also been proposed in the papers by Minisci [44] (for the "Gif catalysis") and Fish [43] (for the oxidations in the presence of "biomimetic methane monooxygenase enzyme complexes").

X.3. OXYGENATIONS BY PEROXYACIDS

Soluble derivatives of various metals catalyze the alkane oxidation by peroxyacids (or by H_2O_2 in strong acids as solvents). Examples of these reactions are summarized in Table X.4.

The mechanism proposed for the rhodium-catalyzed oxidation of alkanes with H_2O_2 in trifluoroacetic acid is demonstrated in Scheme X.10 [56], The rhodium oxo derivative is assumed to be a key intermediate in this process.



Scheme X.10. Rhodium-catalyzed oxidation of an alkane by H_2O_2 in CF_3COOH.

X.4. OXIDATIONS BY OTHER OXYGEN ATOM DONORS

Some oxygen-containing oxidizing reagents, A=O, can functionalize hydrocarbons in the presence of transition metal complexes (see, for example, [62]). Usually the oxygen atom transfer from an oxidizing reagent to a metal-complex catalyst, M, gives rise to the formation of a high-valent oxo complex.

Table X.4. Hydrocarbon oxidation by peroxyacids catalyzed by metal complexes.

Substrates	Oxidant	Catalyst	Ref.
Alkanes	H_2O_2–CF_3COOH	$[Rh_3O(OAc)_6(H_2O)_3]OAc$ $Rh_2(OAc)_4$, $RhCl_3$, $Rh(acac)_3$, $RhCl(PPh_3)_3$, $Pd(OAc)_2$, $RuCl_3$, H_2PtCl_6, $FeCl_3$	56
Alkanes	Peroxyacetic acid	Ru derivatives	57
Adamantane, cyclooctane, ethylbenzene	*m*-Chloroperoxybenzoic acid	Ru complexes	58
Alkanes	H_2O_2–CF_3COOH	Vanadium derivatives	59
Cyclohexane, methylcyclo-hexane, adamantane	*m*-Chloroperoxybenzoic acid	Fe μ-oxo-di-μ-acetate complex	60
Cyclohexane	Peroxy acids	Binuclear Mn and Fe complexes	49
Alkanes	Peroxyacetic acid, *m*-chloroperoxybenzoic acid	$[L_2Mn_2O_3](PF_6)_2$ (**X-1**) [a] + carboxylic acid	16p,q, 22
Alkanes	H_2O_2–CF_3COOH	Cu complexes	61

[a] L = 1,4,7-trimethyl-1,4-7-triazacyclononane.

This complex then is capable of oxidizing the alkane, RH, for example, via the "oxygen rebound" radical mechanism:

$$A{=}O + M \longrightarrow A + M{=}O$$

$$M{=}O + RH \longrightarrow [M{-}OH\ \ R\bullet] \longrightarrow M + ROH$$

Table X.5. Oxidation of hydrocarbons with iodosylbenzene catalyzed by metal complexes.

Catalyst	Substrate	Ref.
Manganese porphyrins as insoluble zinc phosphonates	Alkanes	63a
Metalloporphyrins; soluble and on imidazole propyl gel	Cyclohexane	63b–d
Iron porphyrin	α-Alkylbenzyl alcohols (to form C–H and C–C bond cleavage products)	64a
Iron porphyrins	Alkanes	64b
Iron porphyrins	Cyclohexane	64c
Iron porphyrin	Cyclohexane	64d
Manganese porphyrin	Cyclohexane	65a
$[Mn_2L_2(\mu\text{-}OAc)_2]^{2+}$ (L: *N,N′*-dimethyl-*N,N′*-bis(2-pyridilmethyl)ethane-1,2-diamine	Cyclohexane, adamantane 2,3-dimethylbutane	65b
Mn-Salen complex	Benzylic C–H bond	66a
Chiral Mn-Salen complexes	*Meso*-Pyrrolidine derivatives	66b
Chiral Mn-Salen complexes	Benzylic C–H bond	66c
Chiral Mn-Salen complexes	Alkanes	66d
Racemic Mn-Salen complexes	Benzylic C–H bond	66e
Ru(III) diphosphino complexes	Adamantane, hexane	67a
$P_2W_{17}O_{61}(M^{n+}Br)^{(n-11)}$ (M^{n+} = Mn^{3+}, Fe^{3+}, Co^{2+}, Ni^{2+}, Cu^{2+})	Cyclohexane, heptane, adamantane	67b
CrO_3, $VOCl_2$	Cyclohexane, ethylbenzene	67c

Table X.6. Oxidation of hydrocarbons with monopersulfate (HSO_5^-) catalyzed by metal complexes.

Catalyst	Substrate	Ref.
Mn porphyrins	Ethylbenzene	68a
Metalloporphyrins	4-(1-Hydroxy-1-methylethyl)benzoic acid	68b
Mn porphyrins	Alkanes	68c
Mn, Fe porphyrins	2-Methylnaphthalene	68d
$SiRu(H_2O)W_{11}O_{39}^{5-}$	Adamantane, cyclohexane	69a
Ru complexes	Ethylbenzene	69b

Examples of hydrocarbon oxidations by some oxygen atom donors which are catalyzed by metal complexes are given in Tables X.5, X.6, and X.7.

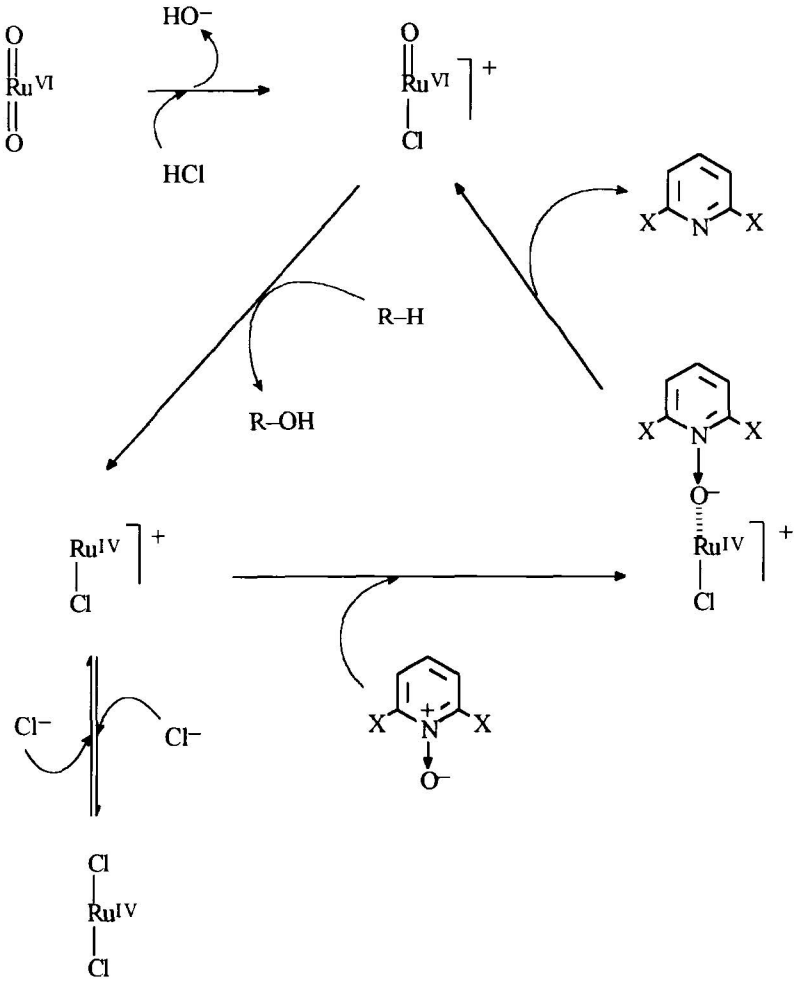
Highly efficient oxygenation reactions have been described by Higuchi, Hirobe and Nagano [74]. Alkanes and other C-H compounds can be oxidized by aromatic jV-oxides (usually by 2,6-dichloropyridine *N*-oxide) under catalysis with ruthenium porphyrin complexes in the presence of strong mineral acids. The oxidation of adamantane under mild conditions gives a turnover number of up to 120000. The reaction occurs via the mechanism depicted in Scheme X.11 [74b] and allows for the hydroxylation of steroids with retention of configuration at the asymmetric center, giving novel steroids (Scheme X.I2) [74d].

It is important to note that alkane oxidation reactions by various oxygen atom donors in cases when a metal-complex catalyst is a metalloporphyrin (or even any other complex) can be considered to be a model for biological hydrocarbon oxidation. The next chapter will be fully devoted to the oxidations of alkanes and arenes in living cells and modeling these processes using metal complexes.

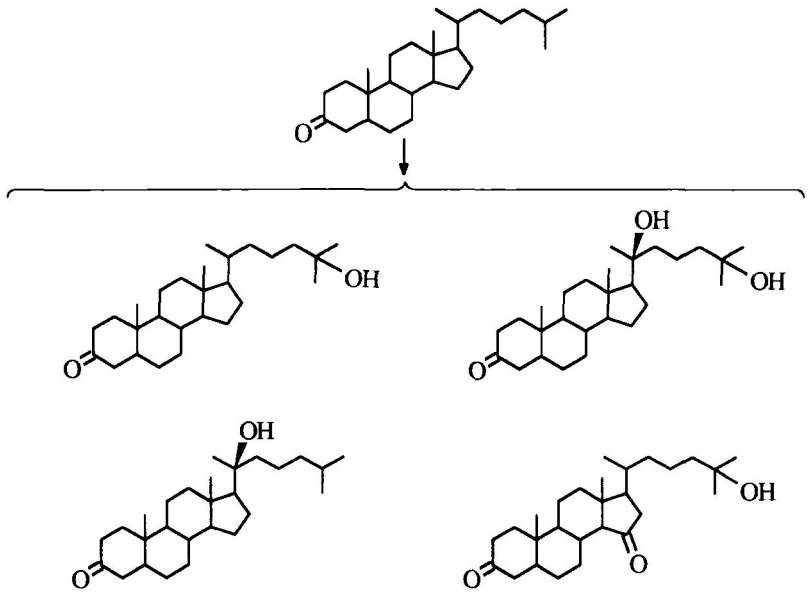
Table X.7. Oxidation of hydrocarbons with various oxygen atom donors catalyzed by metal complexes.

Oxygen atom donor	Catalyst	Substrate	Ref.
Sodium percarbonate ($Na_2CO_3 \cdot 1.5H_2O_2$)	$(n\text{-}Bu_3SnO)_2CrO_2$	Benzylic methylene groups	70a
Magnesium monoperoxyphthalate	Mn porphyrins	Alkanes	70b
Magnesium monoperoxyphthalate	Fe porphyrin	1,2-Dimethoxyarenes	70c
$NaIO_4$	$SiRu(H_2O)W_{11}O_{39}^{5-}$	Adamantane, cyclohexane	71a
$LiClO_4$	Ru(II) complexes	Adamantane, decane, cyclohexane	71b
$HClO_4$	Polyphenylferrosiloxane	1,4-Dimethylcyclohexane	71c
Hypochlorite	$RuCl_3$	Substituted xylenes	72a
$KBrO_3$	Ce salts	Alkyl benzenes	72b
Me_3NO	L_2Cu [a]	Aromatics	73
2,6-Dichloropyridine *N*-oxide	Ru porphyrins	C–H Compounds	74
2,6-Dichloropyridine *N*-oxide	Ru pentafluoro phenylporphyrin	Alkanes	75
(Ad=Ad + $^1O_2$) [b]	metalloporphyrins	Adamantane, cyclohexane	76a
XeO_3	CrO_3; Mn, Fe porphyrins	Benzene, alkylbenzenes	76b
Ozone	Fe porphyrins	Ethylbenzene	76c

[a] L: 2-(*N*-amido)-4-nitrophenolate. [b] Ad=Ad: adamantalydeneadamantane; $^1O_2$: singlet oxygen.



Scheme X.11. The mechanism proposed for the hydroxylation of alkanes, RH, by aromatic *N*-oxides under catalysis with ruthenium porphyrin complexes in the presence of strong mineral acids.



Scheme X.12. The hydroxylation of 5α-cholestan-3-one by 2,6-dichloropyridine *N*-oxide catalyzed with ruthenium porphyrin.

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