Metal complex catalyzed oxidations with hydroperoxides: Inner-sphere electron transfer

Natalia I. Moiseeva [a], Alexander E. Gekhman [b], Ilya I. Moiseev [b,*]

[a] N.N. Semenov Institute of Chemical Physics, Russian Academy of Science, Moscow, Russia
[b] N.S. Kurnakov Institute of General and Inorganic Chemistry, Russian Academy of Science, Moscow, Russia

Abstract

The reactions involving electron transfer between peroxidic oxidant and a substrate capable of coordination to a metal atom are reviewed. A metal ion can act as a mediator between the coordinated reactants in such a redox reaction. Oxidation of acetylacetonate and related compounds, singlet dioxygen formation and decomposition of H_2O_2 to form ozone are discussed as examples.

Keywords: Vanadium; Molybdenum; Tungsten; Hydrogen peroxide; Peroxo complexes; Trioxo dianion; Singlet dioxygen; Ozone; Metal complex catalysis; Alkene; Perfluoroalkenes; Arenes; Perfluoroarenes; β-Diketonates

1. Introduction

Fenton chemistry is based on reactions involving one-electron transfer reactions between H_2O_2 and a catalyst ion [1–7]. Examples of one-electron exchange between metal coordinated peroxo groups are less common.

Thus, one-electron exchange between two vanadium peroxo complexes $VO(O_2)PIC(H_2O)_2$ (where PIC is picolinic acid anion) was proposed to rationalize a variety of oxidations in CH_3CN and aqueous solutions by this complex [8–11]. The kinetics of both arene hydroxylation by this complex and H_2O_2 decomposition in CH_3CN solution suggested a mechanism involving formation of a dimer consisting of two picolinato complexes $VO(O_2)PIC(H_2O)_2$ and

inner molecular one-electron transfer between two peroxo groups coordinated to two different V^V ions (Eq. (1)):

L = H₂O, N⌒O = picolinic acid anion

(1)
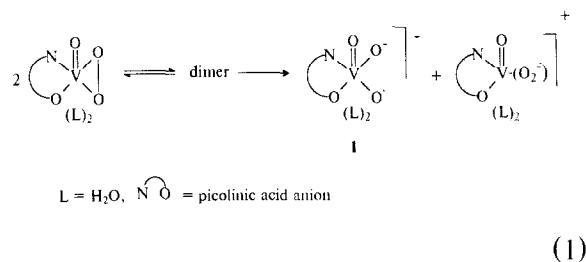
The Modena radical 1 containing anion radical O⁻˙ coordinated to V^V ion and the V^V superoxide complex, $(PIC)VO(O_2)^{+˙}(L)_2$ are assumed to play roles of chain carriers in H_2O_2 decomposition and arene oxidations [8,9]. In contrast to Fenton chemistry, no change in the

* Corresponding author.

oxidation state of the metal atom is presumed in initiation steps described by Eq. (1).

Reactions in which both the peroxo ligand and the substrate under oxidation can be coordinated to a common metal atom will be discussed in this section. In such a reaction, the oxidation state of the central metal ion is not changed in the act of oxidation. The metal ion seemingly plays the role of a mediator contributing to the electron transfer from a coordinated substrate to the coordinated oxidant.

2. Oxidation of 1,3-dicarbonyl compounds by H_2O_2 catalyzed with Mo^{VI} and W^{VI} complexes [12,13]
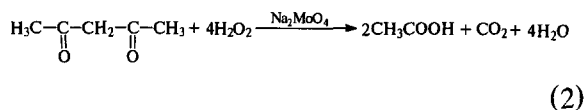
Acetylacetone Hacac and WOF_4 are known to form in CH_3CN solution an octahedral complex $[WOF_3(acac)]$ [14], in which two oxygen atoms of acetylacetonate ligand occupy the *cis* and *trans* position with respect to the multiply bonded oxygen atom. A marked exothermic effect was observed on adding 70% H_2O_2 to this solution. Subsequently, a vigorous CO_2 evolution accompanied the development of the reaction. A ^{19}F-NMR study showed that on the completion of the reaction the spectrum contained only the signals of the $[WOF_5]^-$ and $[W_2O_2F_5(OH)_4]^-$ complexes.

The peroxo complexes of tungsten $[WOF_3(O_2)MeCN]^-$ and $[WOF_2(O_2)(MeCN)_2]^-$ prepared by reaction of WOF_4 with H_2O_2 in MeCN solution are pentagonal bipyramids in which the peroxo group occupies two coordination sites and lies in the equatorial plane of the bipyramids in the *cis* position to the double-bonded oxygen atom [15]. When Hacac was added to a solution of tungsten peroxo complexes, heat emission and CO_2 evolution were observed. Moreover, the signals of the peroxo fluoride complexes disappeared from the ^{19}F-NMR spectrum, being substituted by the signals of the $[WOF_5]^-$ and $[W_2O_2F_5(OH)_4]^-$ complexes [15]. After completion of the reaction of Hacac
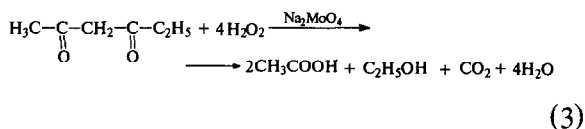
with tungsten peroxo complexes in CD_3CN, the PMR spectrum does not show the Hacac signals but only a singlet at 1.73 ppm (relative to TMS), corresponding to the CH_3 group of acetic acid.
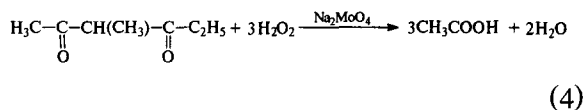
The Hacac molecule underwent oxidation not only in a solution of tungsten(VI) and hydrogen peroxide (or in solutions of peroxo complexes of tungsten(VI)), but also in analogous solutions of Mo^{VI} complexes. Thus, when Hacac was added to an aqueous $SrMoO_6$ solution, rapid heating of the mixture occurred and CO_2 was evolved, along with dioxygen formed by decomposition of the peroxomolybdate. On completion of the reaction, acetic acid, but not Hacac, was detected in the solution by GLC. Hacac also underwent oxidation by 20–30% aqueous H_2O_2 in the presence of Na_2MoO_4. Stoichiometric experiments showed that 2 mol of acetic acid and 1 mol of CO_2 are formed for each H_2O_2 molecule consumed in accordance with Eq. (2):
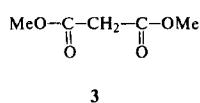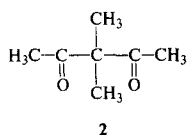
$$H_3C-\underset{O}{\underset{\|}{C}}-CH_2-\underset{O}{\underset{\|}{C}}-CH_3 + 4H_2O_2 \xrightarrow{Na_2MoO_4} 2CH_3COOH + CO_2 + 4H_2O$$

$$(2)$$

Analogous, ethyl acetoacetate was oxidized by H_2O_2 in aqueous Na_2MoO_4 solution according to Eq. (3):

$$H_3C-\underset{O}{\underset{\|}{C}}-CH_2-\underset{O}{\underset{\|}{C}}-C_2H_5 + 4H_2O_2 \xrightarrow{Na_2MoO_4}$$
$$\longrightarrow 2CH_3COOH + C_2H_5OH + CO_2 + 4H_2O$$

$$(3)$$

Methyl acetylacetone also entered into the reaction with H_2O_2 in the presence of MoO_4^{2-}. However, no CO_2 was found among the reaction products of this compound. 3 mol of acetic acid were formed per 1 mol of methyl acetylacetone oxidized, according to Eq. (4):

$$H_3C-\underset{O}{\underset{\|}{C}}-CH(CH_3)-\underset{O}{\underset{\|}{C}}-C_2H_5 + 3H_2O_2 \xrightarrow{Na_2MoO_4} 3CH_3COOH + 2H_2O$$

$$(4)$$

Thus, H_2O_2 reacts with all the 1,3-dicarbonyl compounds bearing at least one H atom at the central C atom by splitting the C–C bond between this C atom and the acetyl groups. Remarkably, no oxidations were observed when 2,2-dimethyl acetylacetone **2** or dimethylmalonate **3** were added to CH_3CN or aqueous solution of H_2O_2/Na_2MoO_4 or H_2O_2/WOF_4.

$$H_3C-\underset{O}{\overset{\parallel}{C}}-\underset{\underset{CH_3}{|}}{\overset{\overset{CH_3}{|}}{C}}-\underset{O}{\overset{\parallel}{C}}-CH_3$$

2

$$MeO-\underset{O}{\overset{\parallel}{C}}-CH_2-\underset{O}{\overset{\parallel}{C}}-OMe$$
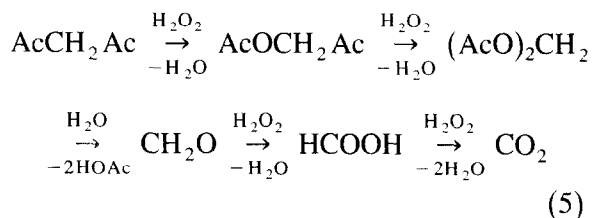
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Both **2** and **3** do not undergo enolization and are incapable of forming complexes with Mo^{VI} and W^{VI} ions.

To rationalize the observed data, it is essential to assume that both participants of the reaction, the peroxy group and 1,3-diketonate, are coordinated to a metal atom. Thus, when a solution of $[WOF_3(acac)]$ containing excess of $[WOF_4MeCN]^-$ and $[W_2O_2F_9]^-$ to ensure the absence of free Hacac, is mixed with a solution of $[WOF_3(O_2)MeCN]^-$ and $[WOF_2(O_2)(MeCN)_2]^-$ not containing free H_2O_2, warming of the mixture and changes in the ^{19}F-NMR spectra were observed, indicating the oxidation of Hacac. When Hacac is oxidized in aqueous peroxymolybdate solutions, the reaction is always preceded by complete dissolution of the Hacac, probably as a result of coordination to a metal ion, since the solubility of Hacac in water is significantly below the concentration used in the experiments. So, any mechanisms involving participation of free 1,3-diketones and H_2O_2 can be excluded from consideration.

The reaction of tris(β-ketoenolato)cobalt(III) complexes with protic acids results in a ligand–metal electron transfer with the formation of a variety of β-ketoenolyl radicals which

were detected by ESR spectroscopy [16]. Free-radical displacement of an H atom in a coordinated 1,3-diketonate has been observed in the reactions of acetylacetonates with *N*-bromosuccinimide [17]. The reactions (Eqs. (2)–(4)) could have been formally assumed to involve the attack on the coordinated 1,3-diketonate of $HO^{\cdot}$ or $HO_2^{\cdot}$ radicals generated under the reaction conditions. However, this mechanism appears quite unlikely, since the reactions proceed smoothly in aqueous ethanol, which reacts effectively with free oxyl radicals. Moreover, such strong free-radical acceptors as stable iminoxyl radicals, *p*-benzoquinone or 2,4,6-tri-tert-butylphenol, did not affect the course of the reaction. No free O or C centered free radicals were detected with ESR in the reaction course.

One might have expected intermediate formation of CH_2O and/or $HCOOH$, if Hacac or coordinated $acac^-$ were oxidized according to Baeyer–Villiger reaction (e.g., see Eq. (5)):

$$AcCH_2Ac \xrightarrow[-H_2O]{H_2O_2} AcOCH_2Ac \xrightarrow[-H_2O]{H_2O_2} (AcO)_2CH_2$$
$$\xrightarrow[-2HOAc]{H_2O} CH_2O \xrightarrow[-H_2O]{H_2O_2} HCOOH \xrightarrow[-2H_2O]{H_2O_2} CO_2$$

$$(5)$$

However, joint oxidation of Hacac and CH_2O or $HCOOH$, showed the acetylacetone to react much more rapidly than the latter. These facts and the absence of $HCOOH$ in the oxidation products of Hacac (GLC data), eliminate the possibility that $AcCH_2Ac$ oxidation can proceed according to the Baeyer–Villiger reaction.

In the oxidation of both acetoacetic ester and Hacac, the volume of CO_2 evolved into the gas phase amounts to 75–80% of that stoichiometrically expected, while 20–25% remains in the reaction mixture according to the GLC data. This fact cannot be explained by the solubility of CO_2 in water and is apparently indicative of a precursor to the observed product formation. This intermediate decomposes under the conditions of the hot injector of the chromatograph.

^{1}H-NMR spectra of Hacac and Na_2MoO_4 in D_2O (Fig. 1) showed that singlet (2.33 ppm) corresponding to the CH_3 groups of the ketone form of Hacac, and singlet (2.28 ppm) evidently belonging to the CH_3 groups of coordinated acac[−] in $[MoO_4(acac)]^{3−}$ grew smaller and a broadened singlet (width of the line at half the height ca. 8 Hz) 1.95 ppm (see Fig. 1b) appeared as H_2O_2 is added. The intensity of this singlet increased, and at a mole ratio H_2O_2:Hacac ≈ 2 it reaches a maximum value

(see Fig. 1d, e). Increasing the molar ratio H_2O_2:Hacac to 4 leads to a 0.1 ppm weak-field shift of the signal; however, the signal belonging to the CH_3 group in AcOH (2.13 ppm) does not appear. Both CO_2 and AcOH were formed only when the reaction solution was heated to 50°C for 20 min.

It is significant that the addition of the first portions of H_2O_2 to a solution containing Na_2MoO_4 and β-diketone leads to an appreciable heat emission. Neither coordination of Ha-
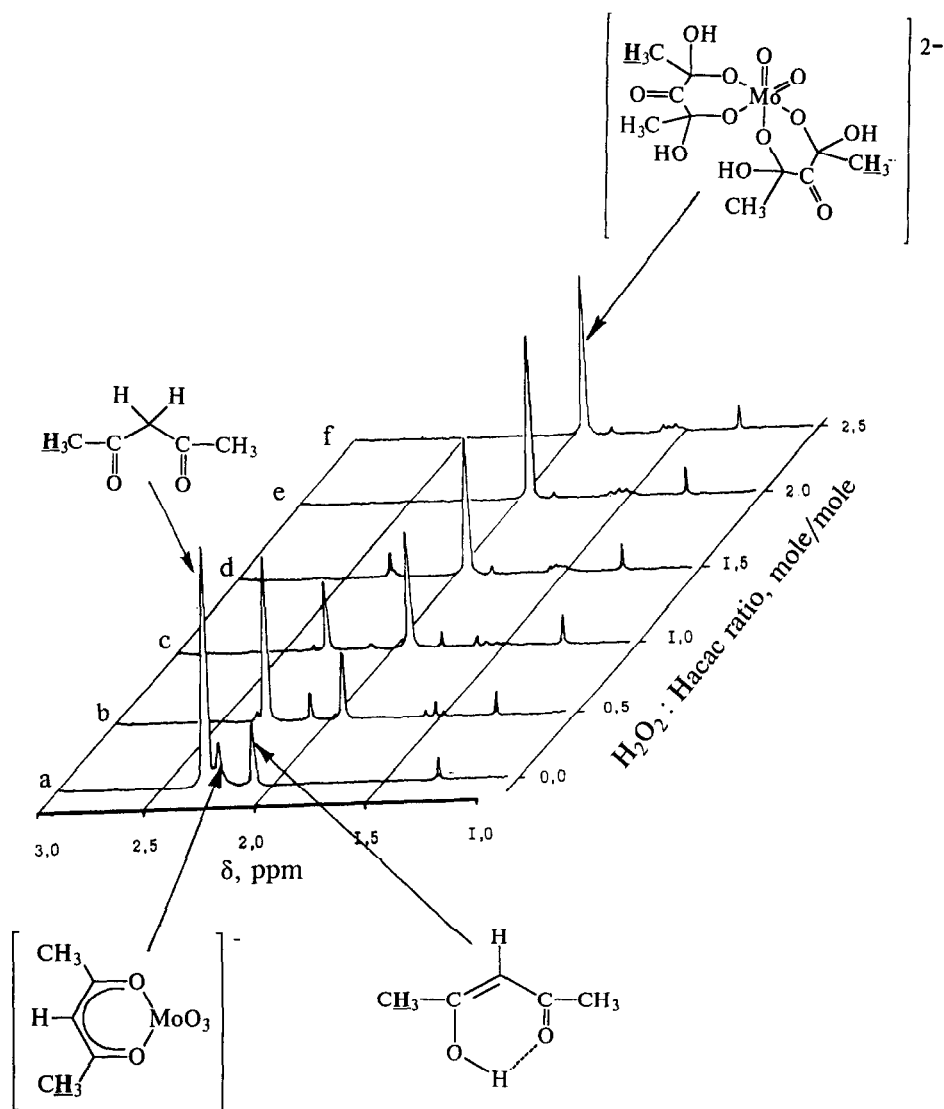

Fig. 1. Hacac oxidation by hydrogen peroxide in the presence of Na_2MoO_4 in D_2O solution. ^{1}H-NMR spectra. [Hacac]$_o$ = 0.86, [Na_2MoO_4]$_o$ = 0.86 M. According to Ref. [13].

cac (in the absence of H_2O_2) nor that of H_2O_2 (in the absence of Hacac) with the Mo^{VI} complex in a solution of Na_2MoO_4, nor decomposition of H_2O_2, catalyzed with MoO_4^{2-} (at the concentrations of H_2O_2 and Na_2MoO_4 used in the experiments on the oxidation of Hacac) was accompanied by any appreciable heating of the reaction mass. The absence of thermodynamically stable products, CO_2 and AcOH, at this stage of the reaction indicates that the thermal effect is due mainly to the formation of primary oxidation products of Hacac.

In the ^{1}H-NMR spectra (Fig. 1) all the observed intermediate products have chemically equivalent CH_3 groups. If the Hacac were oxidized according to a Baeyer–Villiger mechanism or through a step of epoxidation of the C=C bond of the enol form $acac^-$ ligand, then signals of equal intensity from nonequivalent CH_3 groups would be observed at molar ratios H_2O_2:Hacac < 2. The absence of the inequality of CH_3 groups suggests that at the first stages of reaction (Eq. (2)) only the C^3 atom of the Hacac molecule is involved in the reaction.

All data available suggest the oxidation of $acac^-$ anion to involve two-electron removal or two successive steps each of one electron removal. The removal of electron pair from the HOMO orbital of $acac^-$ anion would convert this ligand into a carbonation (Eq. (6)):

$$\tag{6}$$
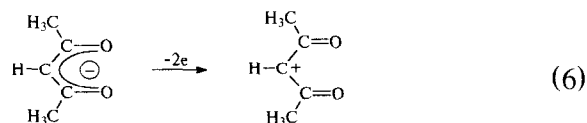
It is apparent that this transformation should be impossible without the nucleophilic assistance of a solvent molecule attacking the C^3 atom when redox reaction (Eq. (6)) occurs. Thus, the reaction between $SrMoO_4$ and Hacac in dry CH_3CN does not take place until at least small amounts of water are added to the solution. After the addition of the water, rapid oxidation of Hacac was observed suggesting the
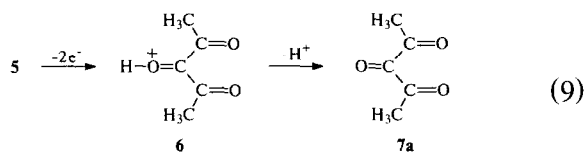
oxidation of coordinated $acac^-$ ligand to proceed according to Eq. (7):

$$\tag{7}$$
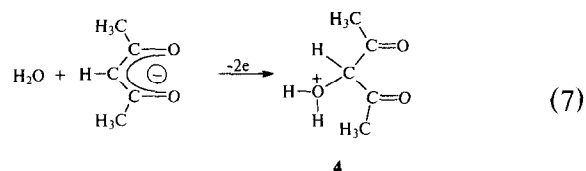
The elusive cation 4 can form 3-hydroxy-2,4-pentadione after deprotonation which after enolization and deprotonation affords anion 5 (Eq. (8)) capable of coordinating to Mo^{VI}:

$$\tag{8}$$
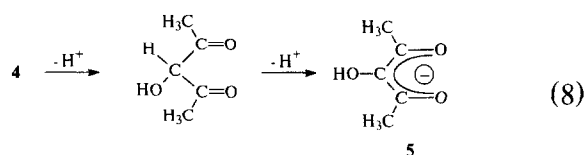
The two electron oxidation of anion 5 should give cation 6 and, after its deprotonation, 2,3,5-pentatrione 7a (Eq. (9)):

$$\tag{9}$$

A detailed study [13] showed the signal at 1.95 ppm in the spectra of the reaction mixture (Fig. 1) to belong to the dihydrate of the triketone 7a, tetrahydroxy-3-pentanone 7b (Eq. (10)):

$$\tag{10}$$
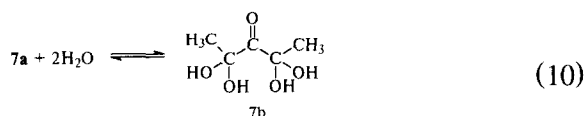
The independently synthesized 7b was found to form a complex with Mo^{VI} which gave AcOH and CO_2 upon treatment with H_2O_2 presumably via a Baeyer–Villiger mechanism.

Coordinated peroxo groups are to accept the electrons which are removed from $acac^-$ anion and related species in Eqs. (6)–(8).

Transfer of an electron from the 1,3-diketo-nate to O_2^{2-} would necessarily lead to the appearance of an electron in the antibon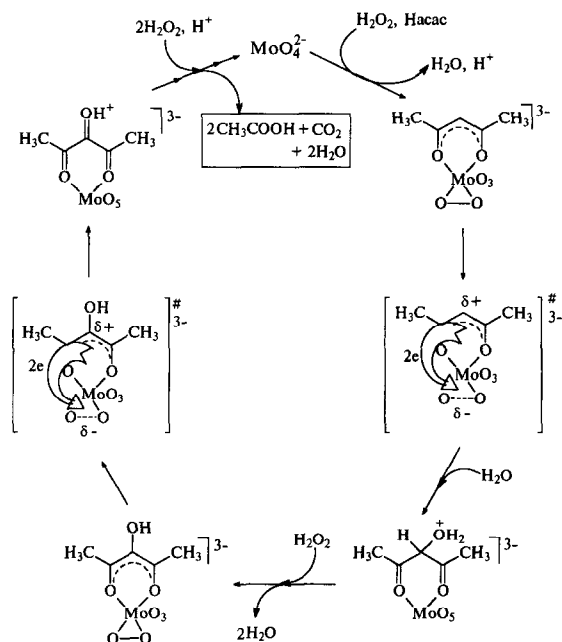ding σ^* orbital of the $O-O^{2-}$ fragment and consequently to decomposition of this fragment. In place of it, double-bonded O^{2-} and a coordinated $O^{-\cdot}$ or $\cdot OH$ radical, arising from protonation of $O^{-\cdot}$, must appear in the metal complex. The lack of any evidence for free radicals taking part in the reaction suggests that it involves two- rather than one-electron transfer between the coordinated ligands (Eq. (11)):

$$(11)$$
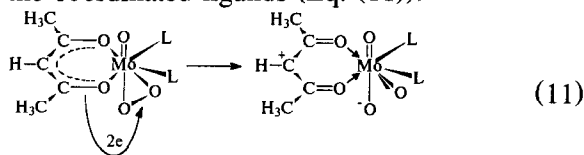
Such a redox reaction can occur as a one-step process or two successive acts with the second one being faster than the first. The whole reaction is depicted in Scheme 1.

The tendency of Mo and W atoms to form 'oxometal' groups, $M=O$, must favor such a conversion. According to the mechanistic

scheme under discussion, the metal atom is assumed to play the role of a mediator transferring the electrons from the coordinated ligand under oxidation to the coordinated oxidant, peroxo group by using its vacant d-orbitals.

Oxidation of the acetylacetonato ligand was also observed in the $TiO(acac)_2/H_2O_2$ system in $CDCl_3$ solution at 25°C [18]. Hence, titanium(IV), a metal ion with d^0 configuration, can serve as electron transfer mediator like molybdenum(VI) and tungsten(VI) metal ions.

3. Singlet dioxygen formation

Hydrogen peroxide decomposition to form triplet dioxygen and water is a thermodynamically favorable process ($\Delta G_{298}^0 = -56$ kcal/mol, $\Delta H_{298}^0 = -47$ kcal/mol) and is catalyzed by a number of metals. H_2O_2 decomposition to form singlet dioxygen although being thermodynamically less favored ($\Delta H_{298}^0 = -24$ kcal/mol) could proceed also.

Hydrogen peroxide is quite stable for a long time if protected against light in the absence of any catalysts in neutral aqueous solution. The hydrogen peroxide molecule is both a weak one-electron reductant and one-electron oxidant. Decomposition into H_2O and $^3O_2$ is observed in basic Py solution as a consequence of an initiation reaction of the type described by Eq. (12) [19]:

$$HO_2^- + HOOH \rightarrow O_2^{-\cdot} + H_2O + HO\cdot \qquad (12)$$
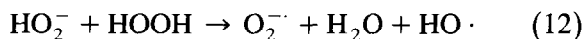
Hypochlorite ion is known to oxidize H_2O_2 in alkaline solution giving rise to singlet dioxygen formation [20,21]. According to mechanistic studies [21–23], the reaction involves the intermediacy of a chlorohydroperoxy anion as the active species as shown in Eqs. (13)–(15):

$$HOO^- + Cl-OH \rightarrow HOO-Cl + HO^- \qquad (13)$$

$$HO^- + HOO-Cl \rightarrow {}^-OO-Cl + H_2O \qquad (14)$$

$$(15)$$

Scheme 1. Mechanism of H_2O_2 oxidation of acetylacetone catalyzed with Mo^{VI} complexes. According to Ref. [13].

The intramolecular redox reaction (Eq. (15)),

involving heterolysis $Cl–O_2^-$ bond, is responsible for singlet dioxygen generation.

Carboxylic peracids undergo two-electron dismutation in alkaline solution yielding singlet dioxygen as is exemplified by the decomposition of diisoperoxyphtalic acid (Eq. (16)) [24]:

$$(16)$$
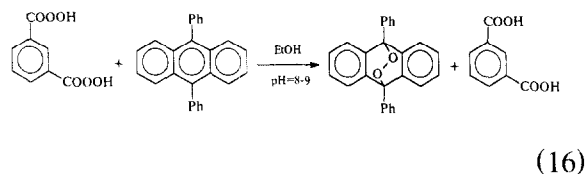
The oxygen–oxygen bond in percarboxylic group, $RCOO^{\delta-}{}^{-\delta+}OH$, seems to be polar enough to enable the disproportionation of two percarboxylic acid depicted by Eq. (17):
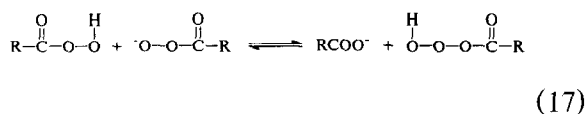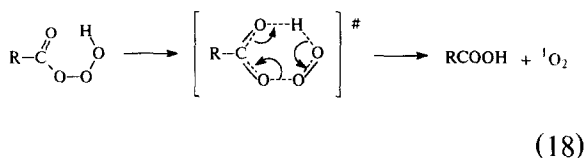

$$(17)$$

The idea of trioxide derivatives formation via nucleophilic metathesis of polar peroxo compounds (see Eq. (17)), has been discussed in the literature with peroxycarboximic acids as an example [25].

Subsequent decomposition of the intermediate monoacyl hydrotrioxide is expected to give rise to singlet dioxygen (Eq. (18)):

$$(18)$$

Thus, benzoic acid and singlet dioxygen (96%) were reported to be main decomposition products of benzoyl hydrotrioxide prepared from benzaldehyde and ozone [26].

Singlet dioxygen formation under metal complex catalysis was first observed when 9,10-di-

phenylanthracene and some other scavengers of singlet dioxygen were oxidized with $tBuOOH/Mo^{VI}$ systems (e.g., see Eq. (19)) [27].

$$(19)$$
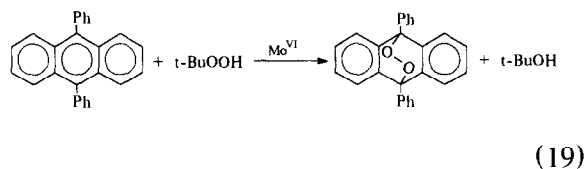
9,10-Endoperoxide formation (Eqs. (16) and (19)) is a typical reaction indicating intermediate $^1O_2$ involvement [21].

Another example of singlet dioxygen transfer from a peroxide compound to an organic substrate was observed with the $V^V/H_2O_2/AcOH$ system [28–32]. So, 9,10-anthracene endoperoxide intermediate formation was detected with NMR and GC–MS in the case of anthracene reaction with H_2O_2 in acetic acid solution containing V^V compounds at room temperature [31]. 9,10-Dimethylanthracene was converted into 9,10-dimethyl-9,10-epidioxy anthracene with ca. 70–90% yield under the same conditions of oxidation [32] (Eq. (20))

$$(20)$$
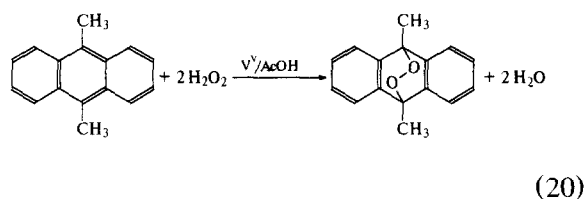
According to kinetic data, H_2O_2 decomposition catalyzed by V^V compounds in AcOH solution involves triperoxo complex $V(O_2)_3^{2-}$ formation as a key intermediate [29–31]. In the slow step, this complex is believed to form a complex with a singlet dioxygen molecule as a ligand (see Scheme 2, step **A**).

Coordinated singlet dioxygen is captured by an anthracene molecule to form intermediate 9,10-dihydro-9,10-epidioxyanthracene (see Scheme 2, step **B**). The subsequent oxidation of
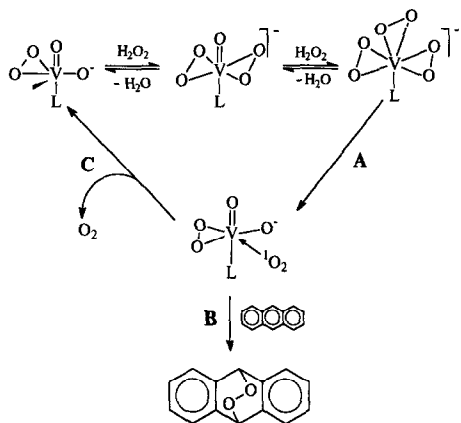
Scheme 2. Mechanism of H_2O_2 decomposition and singlet dioxygen to anthracene transfer. According to Refs. [28–31].

this short-living intermediate with hydrogen peroxide affords anthraquinone (Eq. (21)):

$$(21)$$
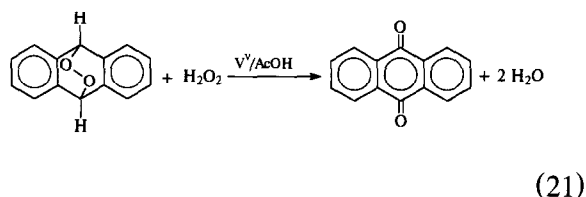
No oxygen evolution is observed in AcOH solution containing anthracene until all aromatic substrate is exhausted, suggesting step **B** (Scheme 2) to be faster than step **C** responsible for dioxygen evolution. The rate of $^1O_2$ quenching with an AcOH molecule in solution is ca. 10^2 times greater than that of anthracene oxidation with the $V^V/AcOH/H_2O_2$ system [31,33].

It should be emphasized that active free radical species in the $V^V/AcOH/H_2O_2$ system are absent. In this respect, the system is different from those based on OCl^-/H_2O_2 reagents which produces various free radicals capable of inducing autoxidative reactions [21].

A systematic study of H_2O_2 decomposition in alkaline aqueous solution showed that many mineral oxides, hydroxides or oxoanions, including vanadate and molybdate salts, can cat-

alyze the reaction described by the Eq. (22) [34]:

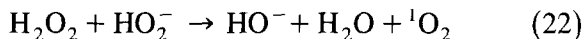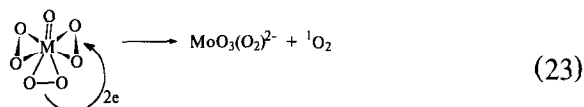$$H_2O_2 + HO_2^- \rightarrow HO^- + H_2O + {}^1O_2 \qquad (22)$$

The most thoroughly studied catalyst is the molybdate ion MoO_4^{2-} [34–39]. The kinetic study showed that oxotriperoxomolybdate $MoO(O_2)_3^{2-}$ is the main precursor of singlet dioxygen (see Eq. (23)) [39]:

$$(23)$$

A study of the bleaching of phenolphthalein by H_2O_2 catalyzed by Mo^{VI} in high pH solution suggests $Mo(O_2)_4^{2-}$ and $W(O_2)_4^{2-}$ to be the active species. In the range of $(0.5–5) \times 10^{-3}$ M of K_2MoO_4 and Na_2MoO_4, oxidation with singlet dioxygen was found to contribute to the reaction hand in hand with the direct oxidation by peroxo complexes. No influence of free radical scavenger, N-tert-butyl-α-phenylnitrone, on reaction kinetics was observed [38].

Another candidate for catalytic singlet dioxygen formation is Cr^{VI} [40]. However, the participation of singlet dioxygen in Cr^{VI} oxidations has not been firmly established, despite extensive studies [41].

Like acetylacetone oxidation (see Section 2), the dismutation of two peroxo groups to form singlet dioxygen (see Scheme 2, step **A**, and Eq. (23)) is an example of an inner-sphere redox process in which the oxidation state of the central atom seems to remain unchanged in all stages of the reaction. Simultaneous inner-sphere transfer of two electrons or two fast one-electron consecutive transfers between reacting peroxo groups are the critical requirements for singlet dioxygen formation. Vacant metal orbitals can be used to mediate such a redox process between coordinated reactants. So, the data available can be considered as suggesting that vacant d-levels of a catalyst, V^V and Mo^{VI} ions with d^0 non-bonding electron configuration, can be used for electron transfer in the

redox reactions between coordinated ligands, e.g., two peroxo groups, peroxo group and acac⁻ anion, peroxo group and trioxo dianion (see Section 4).

There is evidence implying that such a mediator mechanism can be possible in the cases when d-orbitals of the central atom are partially filled. Thus, Mn^{III} porphyrin-like complexes have been found to catalyze oxidation of naphthalene into naphthaquinone via an intermediate endoperoxide pathway [42,43]. Oxidation of naphthalene and its derivatives into the corresponding 1,4-naphthaquinones and 1-naphthols by AcOOH catalyzed with PMnCl (P = 3,5-octanitrophthalocyanine) in CH_3CN at 20°C has been shown to proceed via a thermally unstable intermediate(s) formation. On the base of chemical reactions of the intermediates, 1,4-endoperoxide and 2,3-epoxy-1,2,3,4-tetrahydronaphthalene-1,4-endoperoxide were proposed to be involved into the oxidation.

Oxygenation of rubrene and 9,10-diphenylanthracene with H_2O_2 induced by $Fe^{II}(CH_3CN)_4(ClO_4)_2$ in dry CH_3CN gives rise to the corresponding 9,10-endoperoxides with yields ranging from 70 to 85% [44]. No evidence for free radical oxidation was found, iron(II) complexes do not undergo oxidation into iron(III) compounds under the conditions of the dioxygenations [44].

A free singlet dioxygen molecule is a rather unstable species in solution, undergoing quenching by interaction with solvent molecules. Metal complexes with $^1O_2$ molecule as a ligand can be expected to be more stable. In this context, oxidations in the $V^V/H_2O_2/AcOH$ system seems to be of interest.

3.1. Oxidation reactions with the $V^V/H_2O_2/AcOH$ system

Anthracene and 2-ethylanthracene are selectively converted into the corresponding anthraquinones (the yields are close to 100%) by reacting with the $V^V/H_2O_2/AcOH$ system.

No anthrone (**8**), bianthrone or anthracene
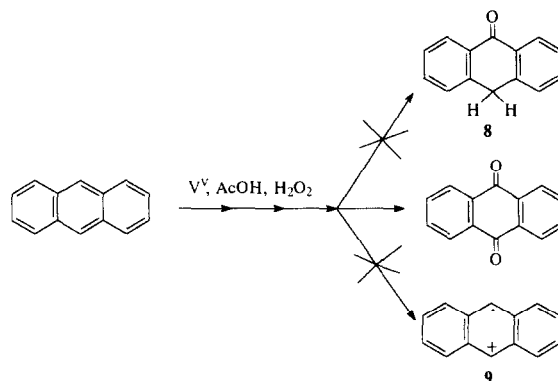
Scheme 3. Selective oxidation of anthracene into anthraquinone in $V^V/AcOH/H_2O_2$ system. According to Refs. [28–31].

cation radical (**9**) were detected under the conditions of anthracene oxidation with the $V^V/H_2O_2/AcOH$ system consistent with the reaction not involving one-electron transfer from the substrate molecule toward the active oxidant species (see Scheme 3).

Both H_2O_2 decomposition and anthracene oxidation were not affected by the presence of such traditional inhibitors of free-radical reactions as p-benzoquinone and tris(tert-butyl)phenol suggesting the reactions to proceed via polar ways [29–31].

The selective oxidation of anthracene into 9,10-anthraquinone was rationalized within a scheme involving intermediate formation of 9,10-dihydro-9,10-epidioxy anthracene trapping singlet dioxygen molecule from vanadium(V)/$^1O_2$ donor (see Scheme 2, step **B**) and consequent transformations of the primary endoperoxide to give finally anthraquinone (Eq. (21)) [33].

A different pathway for aromatic substrate into quinone oxidation was forwarded in [45]. A series of Re^{VII} compounds, Re_2O_7, CH_3ReO_3, $EtReO_3$, η^5-$C_5H_5ReO_3$, and η^5-$C_5H_4MeReO_3$, have been shown to catalyze oxidation reactions of different substrates with hydrogen peroxide [45,46]. The oxidation of 2,3-dimethylnaphthalene in acetic acid with 85% aqueous H_2O_2 yielded 2,3-dimethyl-1,4-naphthoquinone [45]. The highest activity (75% for 4 h at ca. 20°C) has been revealed by CH_3ReO_3 (catalyst con-
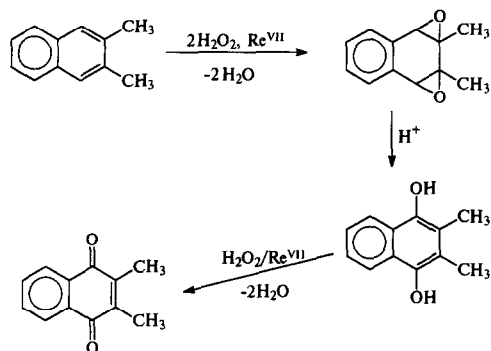
Scheme 4. Hypothetical mechanism of 2,3-dimethylnaphthalene oxidation in acetic acid solution by H_2O_2 catalyzed with MTO [45].

centration 0.1 M, starting substrate concentration 5 M). The reaction has been rationalized as involving epoxidation of naphthalene derivative by analogy with [47,48] as shown by Scheme 4.

Slow decomposition of methylrhenium diperoxide $CH_3ReO(\eta^2O_2)_2H_2O$ in aqueous solution yielding dioxygen and methylrhenium trioxide was observed in [49] (see Eq. (24)):

$$CH_3ReO_3 + O_2 \qquad (24)$$
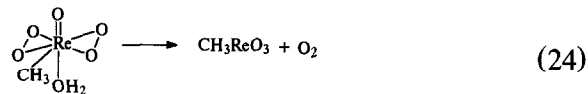
In view of this fact, the transfer of $^1O_2$ molecule from rhenium diperoxo complex to naphthalene substrate seems to be possible.

Another redox reaction involving coordinated singlet dioxygen as the oxidant could be the

oxidation of alkenes in the $V^V/H_2O_2/AcOH$ system.

Vanadium oxide and vanadic acid are capable of forming catalysts for the synthesis of glycols by reaction of olefins with H_2O_2 in both aqueous solution and organic non-aqueous solvents [50–61]. Sodium vanadate is used, under neutral and basic conditions, for selective epoxidation of olefins with hydrogen peroxide [4]. Bromination and hydroxybromination of olefins with H_2O_2 and KBr, catalyzed by NH_4VO_3 in a two phase H_2O/CH_2Cl_2 or $CHCl_3$ systems mimicking the hydrophilic and hydrophobic parts of vanadium dependent bromoperoxidase was described [62,63].

So, the data available suggest that the reaction of olefins with H_2O_2 catalyzed by vanadium(V) compounds is sensitive towards solution composition and pH values.

By analogy with Refs. [50–63], the $V^V/H_2O_2/AcOH$ system could was expected to yield glycols or their esters. However, experiments with hexene-1, 3-methylpentene-1, 4-methylpentene-1, cyclohexene, styrene, and trans-1,2-diphenylethylene showed (see Table 1), all the alkenes but cyclohexene to undergo $> C=C <$ double bond cleavage forming corresponding aldehydes (Eq. (25)) [32]:

$$R^1HC=CR^2H + 2H_2O_2 \rightarrow R^1CHO + R^2CHO \qquad (25)$$
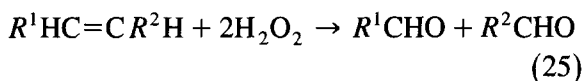
Table 1
Oxidation of olefins by H_2O_2 catalyzed with V^V compounds in AcOH solution [32]

No.	Substrate (M)	$[H_2O_2]_0$ (M)	$[VO(acac)_2] \times 10^2$ (M)	Conversion of Substrate %	Yield of RCHO, %	$[H_2O_2]$ [a] $\times 10^2$, M (time of reaction, hours)
1	3-Methylpetntene-1 (0,092)	0.5	1.02	< 5	1.7	0.4 (1.7)
2	4-Methylpentene-1 (0.10)	0.5	0.88	< 5	2.1	0.5 (1.8)
3	Hexene-1 (0.10)	0.5	1.00	< 5	1.3	0.5 (1.8)
4	Hexene-1 (0.10)	1.0	0.95	6.4	2.9	0.8 (1.8)
5	Cyclohexene (0.10)	1.0	1.01	< 5	< 0.1	0.4 (2.4)
6	Trans-1.2-diphenylethylene (0.10)	0.97	1.09	72	51	0.6 (2.0)
7	Trans-1,2-diphenylehtylene (0.089)	0.5	0.92	48	38	0.8 (1.8)
8	Styrene (0,10)	1.0	1.06	65	40	0.4 (1.8)
9	Styrene (0.10)	0.5	1.20	41	29	0.4 (1.8)

[a] H_2O_2 concentration after the reaction is accomplished

In no case were epoxides, glycols or their esters detected with GC–MS among the products, contrary to the expectation based on literature data mentioned above. Epoxides and vicinal diols are known to undergo oxidative cleavage by reacting with vanadium(V)/TBHP complex in organic solvents (Eq. (26)) [56–59]:

$$\underset{\underset{OH\ OH}{|\ \ |}}{\overset{\diagup}{\underset{\diagdown}{C}}} {-} \overset{\diagup}{\underset{\diagdown}{C}} + 2ROOH \xrightarrow{V^V} 2 \overset{\diagdown}{\underset{\diagup}{C}}{=}O + 2ROH \qquad (26)$$

No benzaldehyde was found among the products of styrene oxide oxidation in $V^V/H_2O_2/AcOH$ system [32]. Moreover, the styrene oxide and ethylene glycol were found to remain rather stable, undergoing oxidation reactions very slowly under the conditions of the oxidation experiments with the $H_2O_2/AcOH/V^V$ system. These facts suggest that neither epoxides nor glycols are intermediates in the reactions under discussion.

Neither epoxycyclohexane nor the corresponding glycol or its ester were found among the products of cyclohexene oxidation with H_2O_2 in acetic acid solution containing V^V. No adipic dialdehyde formation was observed at the same time [32]. Rather low conversions of this alkene were observed. The main direction of the reaction was allylic oxidation yielding cyclohexene-3-ol and cyclohexene-3-on analogous to the oxidations catalyzed with V_2O_5 in acetone solution (Eq. (27)) [64–66]:

$$\bigcirc\!\!\!| + H_2O_2 \xrightarrow{V_2O_5} \overset{OH}{\bigcirc\!\!\!|} + \overset{O}{\bigcirc\!\!\!|} \qquad (27)$$

Acyclic aliphatic alkenes, e.g. hexene-1, 3-methylpentene-1, and 4-methylpentene-1, were oxidatively cleaved into the corresponding aldehydes according to Eq. (25). However, the reactivity revealed by these alkenes towards the $V^V/H_2O_2/AcOH$ system under study was rather low in contrast to the oxidations in organic solvents or aqueous solutions resulting in epoxy derivatives or corresponding glycol for-

mation [50–63]. Unlike aliphatic alkenes, both styrene and trans-1,2-diphenylethylene were found to undergo $>C{=}C<$ bond oxidative cleavage smoothly under very mild conditions. At 20°C, the conversions are in the region of 50–70% in 2 h or so (see Table 1). The enhanced reactivity of aromatic substituted alkenes in comparison with alkyl substituted ones suggests that the active oxidant is an electrophilic agent.

Both the oxidation of anthracenes and oxidative splitting of $>C{=}C<$ bonds in alkyl and aryl substituted alkenes can be rationalized assuming a mechanistic scheme involving intermediate formation of vanadium(V) complex containing a singlet dioxygen molecule as a ligand and interaction of this complex with a substrate resulting in corresponding endoperoxide (Eq. (21)) or dioxetane formation (Eq. (28)):

$$\underset{H}{\overset{R_1}{\diagdown}}C{=}C\underset{R_2}{\overset{H}{\diagup}} + V^V[^1O_2] \longrightarrow \underset{H}{\overset{R_1}{\diagdown}}\underset{\underset{O-O}{|\ \ |}}{C}{-}C\underset{R_2}{\overset{H}{\diagup}} + V^V \qquad (28)$$

The decomposition of intermediately formed dioxetane can give rise to the observed products (Eq. (29)) [67]:

$$\underset{H}{\overset{R_1}{\diagdown}}\underset{\underset{O-O}{|\ \ |}}{C}{-}C\underset{R_2}{\overset{H}{\diagup}} \longrightarrow \underset{O}{\overset{R_1C{-}H}{||}} + \underset{O}{\overset{R_2C{-}H}{||}} \qquad (29)$$

The lack of any 'normal' products, e.g., epoxy compounds, glycols, etc., implies the absence of species responsible for their formation in the $H_2O_2/AcOH/V^V$ system. Correspondingly, it is not surprising that alkene reactivities in this system differ so markedly from the observed ones for 'normal' epoxidating catalysts and systems, e.g., V^V complexes in aqueous solution and organic solvents [56–63].

4. Ozone formation

Combinations of O atoms with dioxygen molecules constitutes the basis for many processes of ozone formation like photolysis of O_2

and NO_2, electrolysis, electrical discharge, ionizing radiation and UHF [68]. Another high energy source for ozone formation can be recombination of certain peroxy radicals [69]. Chemical ways to ozone not involving high energy species are rather rare yielding normally only small quantities of ozone. Thus, small detectable amounts of ozone were reported to occur upon the action of H_2O_2 on selenic acid, an acid on potassium peroxydisulfate, fluorine on aqueous KOH, dioxygen on thin Al-films [70]. Ozone is evolved through the action of strong mineral acids on peroxides [71]. Recently evidence for ozone formation was obtained by reacting iron(III) porphyrin/NO_2^- adduct with dioxygen and an alkene [70].

A peculiarity of the V^V-catalyzed decomposition of H_2O_2 in a CF_3COOH solution is that this reaction yields a substantial amount of ozone (no less than 10–15% (v/v) of the total gaseous products), i.e., the amount of H_2O_2, which decomposes according to Eq. (30) to give ozone (ca. 15%) is comparable with its amount, which decomposes to give dioxygen (Eq. (31)) (ca. 85%) [29,30,72].

$$3H_2O_2 \xrightarrow{V^V/H_2O_2/CF_3COOH} 3H_2O + O_3 \qquad (30)$$

$$2H_2O_2 \xrightarrow{V^V/H_2O_2/CF_3COOH} 2H_2O + O_2 \qquad (31)$$
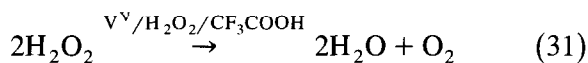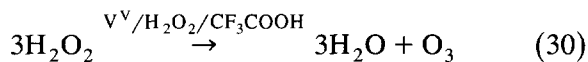
Eq. (30) is the first example of catalytic H_2O_2 in O_3 transformation.

The formation of ozone has also been observed in the decomposition of H_2O_2 in acetic acid solutions containing V^V [72]. However, under those conditions, the yield of ozone was no more than 1% (v/v) of the total gaseous products in the $V^V/H_2O_2/AcOH$ system.

It may seem that the comparison of the yields of ozone in the decomposition of H_2O_2 in acetic and trifluoroacetic acid solutions in the presence of 10^{-5}–10^{-3} M V^V supports the hypothesis that O_3 is formed with the participation of HO^+ ion. For example, the increase in the yield of O_3 on going from CH_3COOH to

Table 2
The formation of ozone in the $H_2O_2/V^V/RCOOH$ system (10°C, [V] = 10^{-3} M) [72]

No.	RCOOH	Compound added (M)	Yield of O_3 (%)
1	CH_3COOH	–	ca. 1
2	CH_3COOH	$HClO_3$	ca. 0
3	CH_3COOH	H_2SO_4	ca. 0
4	CF_3COOH	–	ca. 15
5	CF_3COOH	CF_3COONa	ca. 15

CF_3COOH could have been explained by the fact that CF_3COOH is a strong acid (unlike CH_3COOH) and can protonate H_2O_2 or the peroxide group coordinated to vanadium to give free or coordinated HO^+ ion or similar species. In this case, ozone would actually result from the reaction of these species with H_2O_2 or with the oxygen evolved. In contrast to this suggestion, the presence of 2 M H_2SO_4 or 0.7 M $HClO_4$ in acetic acid completely suppresses the evolution of O_3 (Table 2), and this rules out the possibility of the HO^+ involvement into the formation of O_3. In the presence of 0.2–2 M CF_3COONa in trifluoroacetic acid solution, the yield of O_3 was not considerably changed. These data imply that the formation of ozone is not associated with protonation of H_2O_2 or vanadium complexes or with the participation of type HO^+ species.

A thermodynamically favorable disproportionation of RO_2^- to yield $^1O_2$ and R_2O_2 is known [26,73,74]. In the case of HO_2^-, i.e., when $R = H$, the reaction can be depicted by Eq. (32):

$$2HO_2 \cdot \rightarrow H_2O_2 + {}^1O_2 \qquad (32)$$
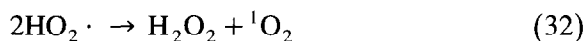
$$\Delta G_{298}^0 \approx -11 \text{ kcal mol}^{-1}$$

Disproportionation of $HO_2 \cdot$ radicals with the formation of ozone is even more thermodynamically favorable (see Eq. (33)):

$$2HO_2 \cdot \rightarrow H_2O + O_3 \qquad (33)$$

$$\Delta G_{298}^0 \approx -23 \text{ kcal mol}^{-1}$$

So, ozone can arise in catalytic systems for the decomposition of hydroperoxides that are able to generate free radicals. For example,

evolution of large quantities of ozone was reported in a patent [75] in which a system consisting of an aqueous solution of a Fe^{II} salt, an ammonium or alkali metal salt of heptamolybdenic acid, and concentrated H_2O_2 is described. The absence of any experimental details (concentrations of the starting compounds, the yield of O_3, the reaction temperature, etc.) makes a comparison of this system with the $V^V/H_2O_2/CF_3COOH$ system impossible.

A small amount of ozone (0.4–0.8%) has been produced [76] in the decomposition of peroxyacetic acid initiated by Co^{II} compounds. The formation of ozone in this catalytic system may be due to the disproportionation depicted by square termination reaction (Eq. (33)).

In principle, this mechanism could occur in the V^V system under consideration being seemingly supported by the existence of a $V^V(O_2^-)$ complex radical in the solutions [28–30]. However, the absence of V^{IV} signals in the ESR spectra recorded during decomposition of H_2O_2 in CF_3COOH solution casts some doubt on the free-radical mechanism of the formation of ozone in the $H_2O_2/V^V/CF_3COOH$ system.

Though the occurrence of reaction (Eq. (33)) under the conditions of the catalysis by vanadium complexes cannot be ruled out completely, all of the facts and considerations outlined suggest that the polar pathways can be responsible for the formation of ozone during the decomposition of H_2O_2 in CF_3COOH solution containing V^V complexes.

A possible intermediate for ozone formation reaction could be a complex with trioxo dianion, O_3^{2-}. Dihydrogen trioxide H_2O_3 and its derivatives like $(RO)_3PO_3$, HO_3SiR_3 are well known [26,77–80]. The kinetic and ^{19}F-NMR study of H_2O_2 into ozone transformation showed the reaction depicted by Eq. (30) to involve perfluoroperacetic acid, CF_3COOOH, and a vanadium(V) peroxo complex [29,30]. For instance, the reaction does not take place in the absence of CF_3COOOH or if its coordination to V^V center is retarded, e.g., as a consequence of F^- ion presence in the reaction solution. These

facts imply the trioxide dianion to form by reacting the perfluoroperacetic acid with peroxo ligand (Eq. (34)):

$$(34)$$
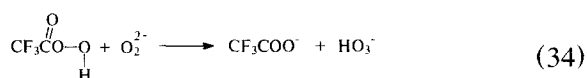
Like reaction described by Eq. (17), this reaction can be considered as nucleophilic substitution at an OH group of the CF_3COOOH molecule with O_2^{2-} dianion as a nucleophile and perfluoro acetate ion CF_3COO^- as a leaving group. The stabilization of this leaving group with V^V metal ion can contribute to the energetics of the inner-sphere analogue of Eq. (34) which represents oxidation of peroxo ligand into trioxo ligand with perfluoroperacetate anion coordinated to V^V and is schematically depicted by Eq. (35):

$$(35)$$
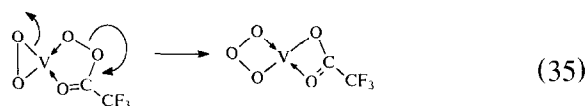
Coordinated trioxo dianions, O_3^{2-}, should lose two electrons to afford free ozone O_3. It is most likely that the coordinated peroxo group, O_2^{2-}, would act as the acceptor of the electrons (Eq. (36)):

$$(36)$$
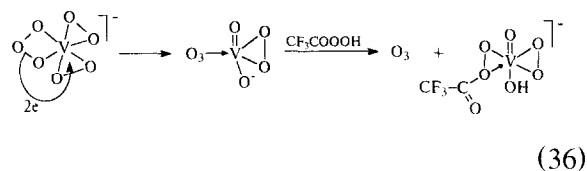
Hypothetical mechanistic considerations concerning the catalytic conversion of H_2O_2 into ozone are represented by Scheme 5.

Hydrogen peroxide is decomposed vigorously with diffusion controlled rate at 5–20°C in the presence of ca. 10^{-3} M vanadium(V) compounds in CF_3COOH solution. Many difficult to oxidize substrates undergo fast oxidation under mild conditions with this system.
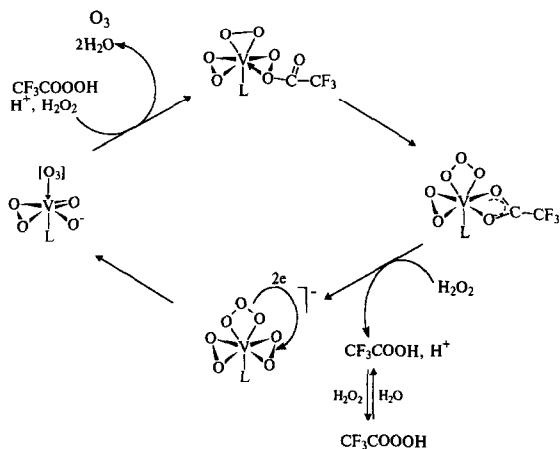
Scheme 5. Mechanism of H_2O_2 decomposition to form ozone. According to Refs. [29,30].

4.1. Oxidation reactions in $V^V / H_2O_2 / CF_3COOH$ system

The $H_2O_2/CF_3COOH/V^V$ catalytic system showed a great activity in a variety of oxidations. Alkanes, electronegatively substituted arenes and perfluoroalkenes were found to react with hydroperoxides in CF_3COOH solution in the presence of V^V complexes under mild conditions (see Scheme 6).

So, cyclohexane was oxidized by the $H_2O_2/CF_3COOH/V^V$ system to give cyclohexanol and its ester as main products (Eq. (37)). The limiting conversion of cyclohexane reaches 85–98% at the ratio $[H_2O_2]_o/[C_6H_{12}]_o = 6$–7, though in the solution of HOAc maxi-

mal conversion of cyclohexane was equal to 8–10% when this ratio was equal to 5 [28–30].


$$\text{(37)}$$
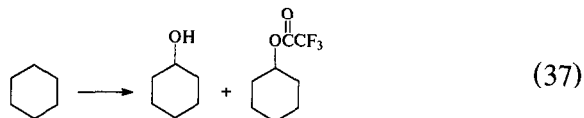
The oxidation reactions of perfluoroalkenes (perfluorooctenes-1 and -2, and perfluorocyclohexene) were found to give rise to the fluoroanhydrides of the corresponding perfluorocarboxylic acids smoothly with 45–100% yield [29,30] (Eq. (38)):

$$R_F^1\text{–CF=CF–}R_F^2 + 2H_2O_2$$

$$\rightarrow R_F^1\text{–CF=O} + \text{O=CF–}R_F^2 + 2H_2O \quad (38)$$
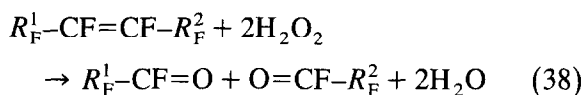
Oxalic acid or its fluoroanhydride (about 10–30%) were found among the reaction products of hexafluorobenzene and benzene oxidations [29,30].

The rates of the individual oxidation reactions were commensurable approaching the rate of H_2O_2 decomposition and controlled by the diffusion of the reagents.

There are five oxidizing species potentially capable of the observed reactions: $^1O_2$, $^3O_2$, O_3, coordinated superoxide anion $V^V(O_2^-)$, and peroxo complexes of type $V^V(O_2)_n$. However, $^1O_2$, $^3O_2$ and coordinated superoxide anion $V^V(O_2^-)$ were shown to be inactive in the reactions under consideration. A detailed study, including comparison of oxidation reactions un-
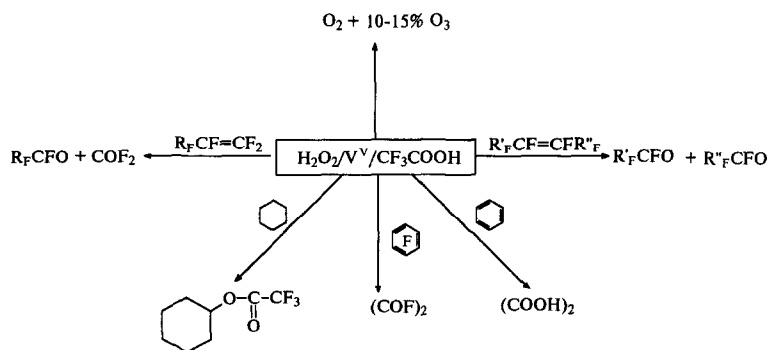
Scheme 6. Oxidation reactions in $V^V/H_2O_2/CF_3COOH$ system. According to Refs. [29,30].

der discussion and ozonization reactions of the same substrates, showed that the only oxidants responsible for the catalytic oxidations observed are vanadium complexes of type **10–13** [29,30].

10

11

12

13
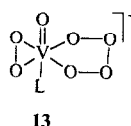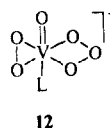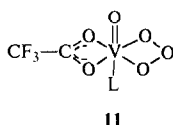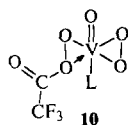
A detailed analysis led to the conclusion that complex **12** is responsible for ozone formation and perfluorooctene-1 oxidation. Complex **10** oxidizes cyclohexane and complex **11** reacts with aromatic compounds, complex **13** reacts with perfluorocyclohexene and internal perfluoroalkenes. The rates of interconvertions **10** → **11** → **12** → **13** are smaller than those for the reactions of the intermediates with corresponding substrates. All the complexes under discussion are capable of dioxygen evolution and their concentrations obeys the steady-state requirements.

5. Concluding remarks

Hydrogen peroxide and organic peroxides have been widely used in organic synthesis since the discovery of Fenton chemistry. Being enlarged tremendously, the approach based on the oxidation with peroxides encompasses different reactions catalyzed by metal complexes like epoxidations reactions after Halcon/ARCO processes, Milas dihydroxylation, Baeyer–Villiger oxidation and many other reactions of practical interest.

The diversity of reaction pathways in an H_2O_2/metal complex/solvent system may be attributed to the different modes of peroxide molecule coordination as well as the variety of peroxide intermediates. Intermediate complexes containing such ligands as dioxo dianion O_2^{2-}, a singlet dioxygen molecule, trioxo dianion O_3^{2-}, or ozone molecule should be taken into consideration in parallel with free oxyl or peroxyl radicals.

A metal atom is able to stabilize a leaving group in reactions involving one oxygen atom transfer from peroxidic oxidant to a substrate molecule. Mixing of HOMO's substrate and LUMO's oxidant orbitals with vacant d-orbitals of central metal atom is believed to be a vector for reactions involving inner-sphere electron transfer. In such a redox reaction, the metal atom serves as an electron mediator and its oxidation state is not changed in the reaction.

Acknowledgements

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