Review

Hydrogen peroxide, water oxide and catalysis [1]

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Abstract

Data related to an oxygen atom transfer from hydrogen peroxide or organyl hydroperoxide to unsaturated and saturated hydrocarbons, trisubstituted phosphines, arsines or stibines catalyzed with metal complexes are discussed. A peroxo metal complex with the non-symmetrically coordinated peroxo ligand resembling the anion of water oxide, $H_2O^+–O^-$, is suggested to play the role of transition state fragment of active species in the reactions mentioned. © 1997 Elsevier Science B.V.

Keywords: Hydrogen peroxide; Organic hydroperoxides; Water oxide; Metal complex catalysis; Alkene epoxidation; Oxidation of molecules containing *n*-donor atoms

1. Introduction

Hydrogen peroxide and organyl hydroperoxides belong to the family of the most important commercially used oxidants [1–10].

The field of oxidative catalysis with these oxidants and metal complexes as catalysts ranks among the oldest branches of homogeneous catalysis and originates from Fenton's discovery of the ability of ferrous ion to promote oxidation of organic substrates with hydrogen peroxide [11]. For seventy years or so this branch of homogeneous catalysis was developed mainly as a part of free radical chemistry [12,13] being

impacted by the pioneering work of Haber and Weiss [14] on the mechanism of free radical formation. Recently, the field of catalysis with iron complexes has been impacted by the discovery and development of Gif-systems and related non-aqueous systems [15,16].

Polar (heterolytic) reactions, not involving free radicals as intermediates, constitute another wing of peroxide catalytic chemistry. This class of reactions includes acid–base and transition metal catalyzed reactions and originates in Prileschaev's discovery of alkene epoxidation with organic peracids [17]:
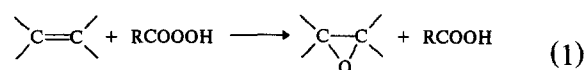
$$\text{C}{=}\text{C} + \text{RCOOOH} \longrightarrow \text{C}{-}\text{C}\underset{O}{} + \text{RCOOH} \tag{1}$$

Until the late 1950s, the field of polar peroxide transformations was occupied with reactions catalyzed by acids and bases. The reactions
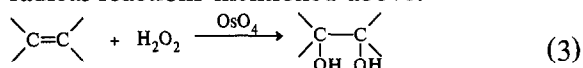
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catalyzed with metal salts were exemplified by the autoxidations involving free radical chain reactions [1,5,12,18]. As an illustration, the epoxidation of alkenes with alkyl hydroperoxides can be mentioned:

$$CH_2=CH-CH_3 + ROOH \longrightarrow CH_2-CHCH_3 + ROH$$
$$\underset{O}{\diagdown\diagup}$$

$$(2)$$
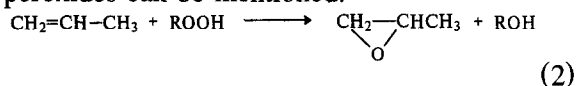
R = t-Bu or CH(CH$_3$)Ph

The first observation concerning the epoxidation catalyzed by V_2O_5 was discussed in 1950 within a scheme involving RO_2^- radical addition across the C=C alkene double bond [19].

At that time, Milas dihydroxylation of alkenes, a polar reaction catalyzed by osmium tetroxide [20–25], (Eq. (3)), looked like an outcast in comparison with the rich family of free-radical reactions mentioned above.

$$\underset{\diagup}{\overset{\diagdown}{C}}=\underset{\diagdown}{\overset{\diagup}{C}} + H_2O_2 \xrightarrow{OsO_4} \underset{OH}{\overset{\diagdown}{\underset{|}{C}}}-\underset{OH}{\overset{\diagup}{\underset{|}{C}}}$$

$$(3)$$

Nowadays the peroxide oxidations catalyzed by transition metal complexes constitute an area of intensive studies. The peculiarities of the oxidations of alkanes, alkenes, arenes, phenols, organic arsines, stibines, amines and sulfides were reviewed in Refs. [1–10,25–28]. The selective epoxidations both in catalytic reactions by alkylhydroperoxides (see Eq. (2)) and in a stoichiometric way by metal peroxocomplexes has been the focus of the recent studies because of their industrial, preparative and basic significance. The molecular structures of reaction intermediates, e.g., complexes with alkyl hydroperoxide monoanion and peroxo dianions as ligands were resolved with X-ray techniques [25,29–35]. The bonding between metal atom and the peroxidic ligands was studied by using calculations on different levels of theory [35,36]. Despite all those intensive studies, the mechanism of catalyst action in the polar reactions mentioned above still remains a matter of discussions [2,5,6,25].

The aim of this paper is to call the reader's attention to the conceivable role of peroxidic

oxidant coordination mode in heterolytic oxidations.

2. Hydrogen peroxide and water oxide

2.1. Oxywater

Traditionally the H_2O_2 molecule is considered as consisting of two HO bars, HO–OH, rotating around the O–O bond. The geometry (see Scheme 1) of the H_2O_2 molecule has been studied by different techniques. Electric dipole moments of H_2O_2 molecules [37,38], X-ray diffraction of crystalline $CO(NH_2)_2 \cdot H_2O_2$ [39], H_2O_2 [40], and $H_2O_2 \cdot 2H_2O$ [41], neutron diffraction of crystalline H_2O_2 [42] far-infrared spectra of H_2O_2 [43,44] and D_2O_2 [45] showed the H_2O_2 molecule to have a skew equilibrium geometry (Scheme 1, c) with an azimutal angle close to 90°.

A similar structure with dihedral angle of 87.5° and F–O–O angle equal to 109.5° was found for difluoroperoxide F_2O_2 [46,47]. O–O distances are indicated as 1.453 Å in H_2O_2 and 1.217 Å in F_2O_2 molecules [46,47].

The transitions between the skew-, cis-, and trans-configurations of H_2O_2 molecules were observed by studying H_2O_2 with IR- and microwave spectra and interpreted as a hindered rotation around the O–O bond. The energy barriers estimated from IR data, microwave spectra, low-temperature calorimetry, quadrupole moments, and Fourier coefficients measurements (see Ref. [48] and references therein) range from 1–10 kcal/mol for the skew → trans transition and twice as much for the skew → cis one. Calculations on different levels of theory [48–50] have been used to study these configuration transitions.
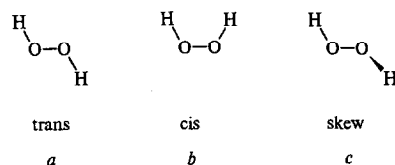
Scheme 1. The geometry of the H_2O_2 molecule.

Two HOMOs of antibonding type π_X^* and π_Y^* are available for proton bonding with a peroxo dianion as can be seen from the primitive electronic formula of the O_2^{2-} unit: $(\sigma_S^b)^2(\sigma_S^*)^2(\sigma_Z^b)^2(\pi_{X,Y}^b)^2(\pi_{X,Y}^*)^4$. If both $(\pi_X^*)^2$ and $(\pi_Y^*)^2$ orthogonal orbitals are used for overlaps with the proton 1s vacant functions, the lowest energy of the system can be tentatively expected for the skew configuration of the H_2O_2 molecule. The transitions between the skew-, cis- and trans-configurations of the H_2O_2 molecule can be described in terms of proton movement over the hypersurface constructed of π_X^* and π_Y^* functions of the O_2^{2-} unit. During the process of this migration both protons can accumulate at the common oxygen atom. This configuration of the H_2O_2 molecule is known as water oxide or oxywater, $H_2O^+-O^-$.

The idea of the oxywater form for the H_2O_2 molecule was forwarded by Linton and Maas (see Ref. [37]) who measured the dipole moment of H_2O_2 and found it to have a surprisingly large value of 2.13 D (modern-day value is 2.26 D [51]). Later on, the observed value of the dipole moment was shown to be in agreement with the skew configuration of the H_2O_2 molecule [37,38]. The first theoretical attempt to investigate the existence of oxywater led to the energy of the oxywater 4.2 eV higher than that of the skew H_2O_2 form [49]. This value was regarded as an upper limit, since the internuclear distances were assumed to be equal to those found for the normal H_2O_2 molecule. Actually, recent calculations showed the transformation of the skew H_2O_2 into oxywater molecule to be accompanied by remarkable changes in bond lengths and angles [52–55]. The reaction (Eq. (4)) seems a sufficiently less endoergic one than was predicted in Ref. [49]:

$$H_2O_2 \longrightarrow \overset{H}{\underset{H}{\diagdown}}O^+ \text{---} O^- \qquad \text{-49.7 kcal/mole} \qquad (4)$$
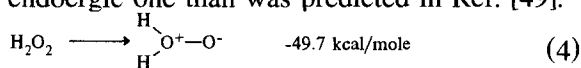
Oxywater is actually the dioxygen ylide form of hydrogen peroxide [56].

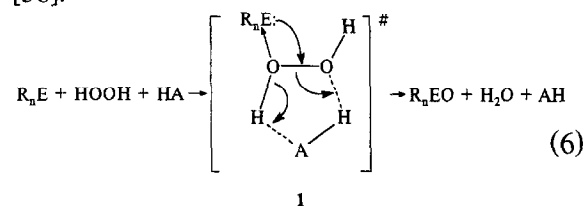H-bonding with a protic solvent, e.g. water, has been found to catalyze H_2O_2 into oxywater

isomerization and stabilize the oxywater molecule [56,57]. A hypothetical dihydrate of water oxide $(H_2O)_2H_2O^+-O^-$ is only 7 kcal/mol higher in energy than the isolated H_2O_2 and two H_2O molecules [53,54].

So the isomerization of solvated hydrogen peroxide into a cluster containing the oxywater molecule H-bonded to two water molecules requires 28.9 kcal/mol [55]:

$$H_2O_2 \cdot (H_2O)_2 \longrightarrow \qquad \text{-28.9 kcal/mole} \qquad (5)$$
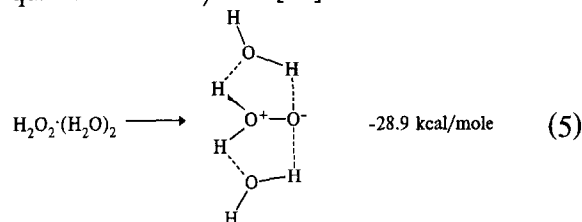
Even this reduced energy difference between hydrogen peroxide and oxywater molecules seems to be too high for liquid phase polar H_2O_2 chemistry.

Calculations using ab initio MO methods showed oxidation of ammonia, dihydrogen sulfide and dimethylsulfide by H_2O_2 to involve a 1,2-hydrogen shift before oxygen transfer to a substrate takes place [56]. One or two molecules of Brønsted acid reduce the calculated barriers (50 kcal/mol in the gas phase) by ca. 10 kcal/mol. An increase in the pK_a of the acid catalyst results in a decrease in the activation energy for the oxygen atom transfer from the H_2O_2 molecule. In those reaction schemes the function of the catalyst HA is to remove a proton from oxygen atom of the oxidant attacking the substrate molecule and to protonate the second oxygen atom of the H_2O_2 molecule [56]:

$$R_nE + HOOH + HA \longrightarrow \left[\begin{matrix} R_nE \cdots & & H \\ O \text{---} O \\ H & & H \\ & A \end{matrix} \right]^{\#} \longrightarrow R_nEO + H_2O + AH$$

$$(6)$$

$$\mathbf{1}$$

where $R_nE = NH_3$, H_2S, R_2S.

The canonical structure **1b** with oxywater as

a constituent fragment of the transition state **1** can contribute to the energy of the state.
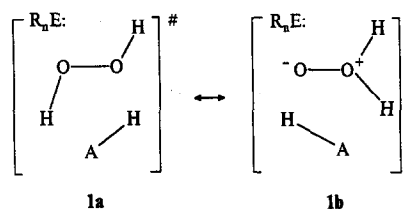
However, the calculations [56] showed the Eq. (6) type reactions and similar processes to have activation barriers ranging from 36 to 48 kcal/mol. The O–O bond energy in H_2O_2, relative to two HO˙ radicals, is 49.2 kcal/mol and $D_o = 43.2$ kcal/mol as was calculated at the same level of theory [56].

## 2.2. Carbonyl oxides, perepoxides and persulfoxides

Oxywater has never been observed and rather seldom been considered in the literature. However, organic chemists are familiar with the derivatives of the oxywater.

It is generally accepted that the photooxygenations of alkenes (Schenck reaction [58], Scheme 2) involves formation of a perepoxide (**2**) [59,60].

The diastereoselectivity and regioselectivity of the photooxygenation of allylic amines and their acyl derivatives is controlled by the step of the perepoxide **2** formation involving an $^1O_2$-alkene charge-transfer intermediate (exciplex) [59].

The perepoxide intermediate has been trapped in the photooxidation of *trans*-cyclooctene in the presence of triphenyl phosphite, P(OPh)$_3$. *Trans*-epoxide and triphenyl phosphate have been found to be main products of the reaction [60]:


$$(7)$$
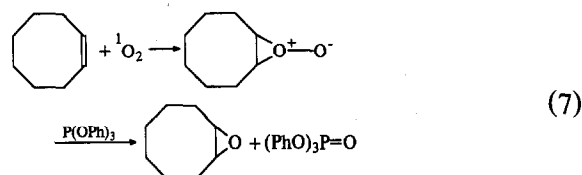
No such trapping was observed in the reaction of the *cis*-alkene. It was suggested that this difference in the reactivities of two alkenes was due to the difference in the geometry of corresponding perepoxides. Because of lack a syn-parallel arranged allylic hydrogen, the rate of rearrangement of the *trans*-alkene perepoxide into the allylic hydroperoxide (Scheme 2, step 'a') is slow enough to be rate limiting and allows the phosphite to trap the perepoxide. In the *cis*-cyclooctene, the transition state for H^+ abstraction is much lower, and the first step (perepoxide formation) is rate determining [60].

Photooxidation of dialkyl sulfides [61] is viewed as involving intermediate persulfoxide formation [62–64]:


$$(8)$$
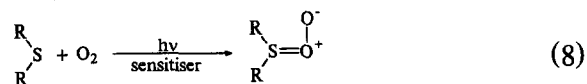
A cyclic sulfide, thietane, has been shown to undergo photooxidation into the corresponding persulfoxide (**3**) as the first intermediate of the reaction resulting in the sulfoxide and traces of sulfone formation [63]:
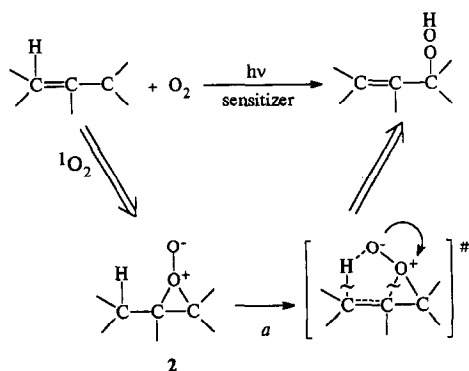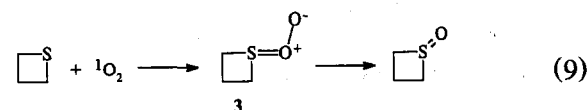

Scheme 2. A mechanistic scheme for the Schenck reaction [58].

$$(9)$$

The persulfoxide **3**, a short-living intermediate, was trapped by reacting with diphenyl sulfide and diphenyl sulfoxide (both scavengers are inert toward $^1O_2$ under reaction conditions, see the following equation).

$$\text{(10)}$$
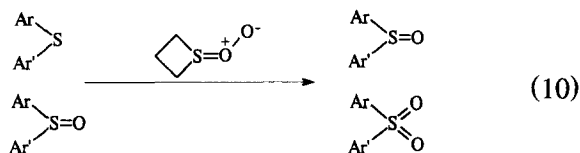
Hammett trapping studies with a series of diaryl sulfoxides and sulfides provided evidence for the presence of two intermediates with ρ values of $+1.05$ and -1.26 or for the biphilicity of a single intermediate [63].

Ozonolysis (ozonation, ozonization) of alkenes (Eq. (11)) is considered to involve at least three steps (Criegee mechanism [65]).

$$\text{(11)}$$
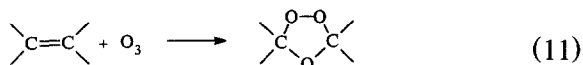
The first step is a cycloaddition between the ozone 1,3-dipole and the alkene molecule leading to a primary ozonide [65,66]:

$$\text{(12)}$$
Primary ozonide
(molozonide)
4
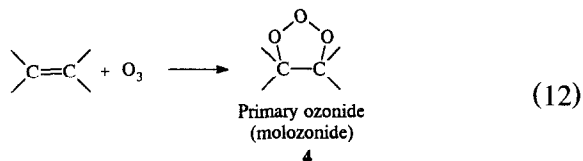
The reaction is known to involve the alkene-ozone charge-transfer complex as an intermediate [67,68].

The unstable molozonide **4** cleaves via cycloreversion to a stable carbonyl compound and an elusive carbonyl oxide **5**:

$$\text{(13)}$$
5
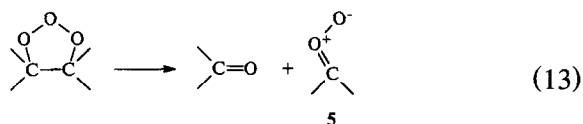
The carbonyl oxide **5** quickly combines with the carbonyl compound in another 1,3-cycloaddition process to produce the observed product of alkene ozonation:

$$\text{(14)}$$
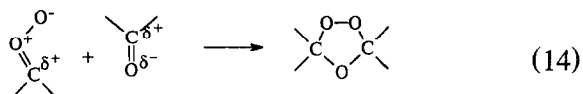
The carbonyl oxides can be readily trapped by carbonyl compounds, alcohols, and a vinylic ether [66].

Ozonolysis of alkynes constitutes another important pathway towards carbonyl oxides [69–71]. However, the most clean and convenient method for carbonyl oxide generation is probably the reaction of diazo compounds with singlet dioxygen [72–74]:

$$R_1R_2C=N^+=N^- + {}^1O_2$$
$$\rightarrow R_1R_2C=O^+-O^- + N_2 \qquad \text{(15)}$$
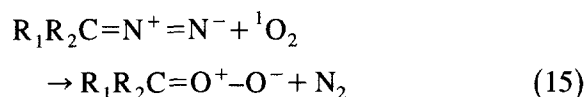
The first direct experimental detection of a carbonyl oxide has been achieved by using time-resolved laser spectroscopy [75]. Matrix isolation [76,77] and laser photolysis [75,78–80] have been used to characterize carbonyl oxides. The spectroscopic characterization of carbonyl oxides, their structure and reactivity are extensively discussed in the literature [81–84].

3. Oxygen atom transfer

The entitled group of the reactions encompasses the oxidations of alkanes, alkenes, halide ion, organic amines, sulfides, arsines, stibines, and phosphines [1–10,23–29,35,85–101]. In these reactions alkanes are transformed into alcohols and ketones. *n*-Donor substrates add one oxygen atom being converted into organic element oxides. Alkene give rise to carbonyl compounds (Wacker-like oxidation by using platinum metal ions as catalysts [25]) or epoxides, glycols, halohydrines and glycol esters in the presence of a d^0 metal compound. The present discussion is focused on some aspects of the possible roles of metal atoms in *n*-donor polar

substrate oxidations and an alkene into epoxide conversion.

3.1. General considerations

According to the calculations [55,56], the more the peroxide fragment in the reactant cluster (e.g. $H_2O_2 \cdot H_2O_2$ or, generally, $H_2O_2 \cdot HA$) resembles water oxide, the lower is the estimated activation barrier for the reaction. This is illustrated by the comparison of two pathways for H_2S oxidation with H_2O_2 (Scheme 3).

Less activation energy is required for the rearrangement of the Cluster **A** (Scheme 3) containing the oxywater molecule stabilized with the substrate molecule (H_2S) and the acid catalyst (H_2O_2), than for that of the cluster **B** of the same composition, but containing slightly distorted H_2O_2 molecules instead of the $H_2O^+-O^-$ structure. In the transition state **C** the oxywater

molecule is seemingly prepared for the S_{N2} substitution reaction, at H-bonded oxygen atoms, with the H_2S molecule as the entering substrate and H_2O as a leaving group.

However, transformation of the H_2O_2 molecule into the $H_2O^+-O^-$ structure is always an energetically unfavorable process. The energy consumed at this stage makes all mechanisms involving oxywater, as a persistent fragment of the transition state, too costly energetically [56]. A sufficient part of this expenditure of energy could perhaps be attributable to the repulsion between geminal H-atoms of oxywater. Taking into account this assumption, one can expect the transition states including, as a key fragment, a derivative of oxywater in which both H-atoms are substituted for a transition metal ion, to be energetically more favorable than those with oxywater.

Such a metal derivative can be expected to
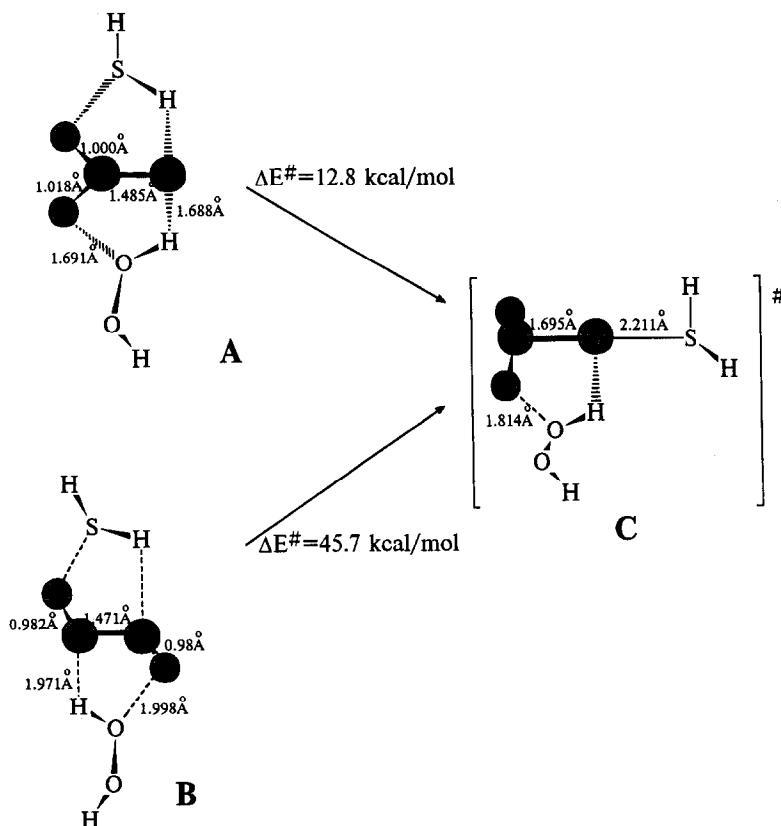
Scheme 3. Role of preliminary H-atom transfer for the oxidations of H_2S by H_2O_2 dimer (adapted from Ref. [56]).

emerge in oxidations with H_2O_2 catalyzed by d^0-metal complexes. d^0-Metal ions are known to form symmetrical peroxo complexes in which both metal–oxygen distances are almost equal [30–34,102]. The metal atom is bound to the O_2^{2-} entity because of σ-, π- and possibly δ-donation ability of the latter. The side-on coordination is preferable though a few examples of end-on coordination are known [32,34]. Attempts to detect the equilibrium (Eq. (16)) for the Mo-complex by using ^{17}O NMR measurements have failed [88,102].

$$M \overset{O}{\underset{O}{\triangleleft}} \; = \; \left[M^+ \overset{O}{\diagdown}_{O^-} \; \longleftrightarrow \; M \overset{O^+}{\diagdown}_{O^-} \right] \qquad (16)$$
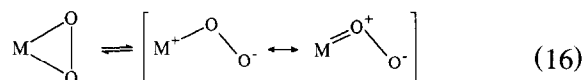
The failure does not mean, however, that such an end-on configuration can not be achieved in the transition state of the oxidation of a substrate with the metal peroxo complex:

$$\left[M \overset{+}{\overset{O}{=}} \diagdown_{O}\text{·········Sub} \right]^{\#}$$
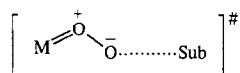
A ^{51}V NMR study showed an oxodiperoxo-vanadium anion $[VO(O_2^{2-})_2 \cdot (OH_2)]^-$ to undergo protonation in aqueous acidic (pH = 0.3–1) solution forming a peroxo complex containing coordinated hydroperoxo ligand $[VO(O_2^{2-})(OOH) \cdot (OH_2)]$ with V–O and V···OH distances being different [102]. Ab initio calculations suggested the hydroperoxo group to be coordinated unsymmetrically with protonated oxygen atoms more distanced from vanadium atom [103]:
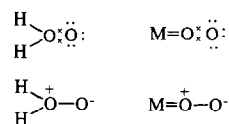
$$\left[M^+ \overset{O}{\diagdown}_{O^-} \longleftrightarrow M \overset{O^+}{\diagdown}_{O^-} \right] + H^+ \longrightarrow M^+ \overset{O}{\diagdown}_{OH} \quad (17)$$
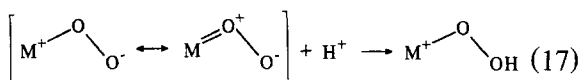
Highly bent $(M\text{-}\overset{O}{\underset{}{}})$, bent $(M\text{-}O\overset{O}{\diagup})$ and linear M–O–O along with side-on conformations have been observed for Fe–O_2 complexes [104,105].

Significantly non-equivalent metal oxygen distances were detected in the metal η^2-coordi-

nated O_2^{2-} unit of tetraperoxides of chromium(V) and molybdenum(VI) of formula $M(O_2)_4^{n-}$ (M = Cr, n = 3; M = Mo, n = 2) with D_{2d} symmetry [106]. So, one may expect a continuum from the two extremes of a triangular to a linear end-on coordinated peroxo complex in transition states for the oxidations under consideration. It is an easy matter to see that, within the approach under discussion, the schemes elaborated [54,56] for the reactions involving the hypothetical oxywater molecule as an oxidant or a fragment of the transition state can be used as model structures. The following vectors for the oxidation reactions involving peroxo complexes can be deduced from the calculations mentioned above.

(1) The oxygen–oxygen bond is sufficiently elongated in the oxywater structure in comparison with that in hydrogen peroxide (1.517 Å in H_2O^+–O^- structure instead of 1.468 Å in the starting H_2O_2 molecule according to the MP2/3-21G* level of theory [53]). No such changes were found by calculations [107] for methylene carbonyl oxide. Seemingly, the elongation of the oxygen–oxygen bond in the $M=O^+$–O^- structure can be expected to be a function of the nature of the M atom. Its ability to form a multiple bond with the coordinated oxygen atom may play an important role. The more pronounced this tendency, the more stable the 'leaving group' (H_2O in the case of oxywater, M=O group in the case of molybdenum or vanadium catalysts); correspondingly, the structure $M=O^+$–O^- is better prepared for an oxygen atom transfer reaction. In the hypothesis [53,54] that oxywater is a hydrate of a singlet (^1D) oxygen atom, the complex containing oxywater dianion, $M=O^+$–O^-, should be considered as a 'solvate' of the singlet oxygen atom where the role of solvating agent belongs to the metal oxide group M=O:

$$\overset{H}{\underset{H}{>}}O\text{:}\overset{\cdot\cdot}{\underset{\cdot\cdot}{O}}\text{:} \qquad M=O\text{:}\overset{\cdot\cdot}{\underset{\cdot\cdot}{O}}\text{:}$$

$$\overset{H}{\underset{H}{>}}\overset{+}{O}\text{—}O^- \qquad M=\overset{+}{O}\text{—}O^-$$

The stronger the metal oxygen bonding, M=O, the less grounds there are to expect the group to be a good solvating agent for the O(^{1}D) atom. Typical catalysts like titanium(IV), molybdenum(VI), and vanadium(V) ions are known to form multiple bonds with an oxygen ligand by using the vacancies in the metal-atom valence shell. Hence, the oxywater derivatives of those metals can be expected to reveal a tendency toward oxygen atom transfer to a better solvating agent like organic sulfides, arsines, and stibines or alkenes, etc.

(2) The negative charged atom in the canonical formula of oxywater $H_2O^+-O^-$ and an enhanced gas-phase proton affinity of oxywater (-167.5 kcal/mol for H_2O_2 and -217.1 kcal/mol for $H_2O^+-O^-$ [55]) suggest that oxywater is a stronger nucleophyle than hydrogen peroxide. A peroxidic oxidant acts as an electrophilic reagent because of its σ_{oo}^* orbital. However, in the transition state of the reaction a back donation involving a vacant asymmetric orbital of the substrate and filled p-orbital of the transferring oxygen atom should be expected. The back donation can contribute to a binding energy between the reagents and thus lower the activation barrier [25,56].

Both slightly positive and slightly negative Hammett ρ values were observed for a variety of peroxidic oxidations including reactions involving substituted carbonyl oxides and perepoxides [104,107–109]. The Hammett ρ values are not always consistent with the Adam probe [110] with thianthrene 5-oxide for the nucleophilicity and electrophilicity of the reagents:

$$(18)$$
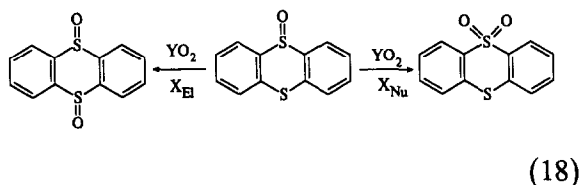
where YO_2 is a peroxidic oxidant, X_i is its nucleophilicity or electrophilicity measure, $X_{Nu} + X_{El} = 1$.

This suggests that the initial attack of the peroxidic oxidant can be governed substantially by the charge borne by the distal oxygen atom and the back donation developed as the reagent approaches.

(3) The computed (QCISD/6-31G*) LUMO's levels of H_2O_2, $H_2O^+-O^-$ and $H_3O_2^+$ are 0.214, 0.161 and -0.118 au, respectively. The HOMO's levels in this row are -0.477, -0.434 and -0.846 au, respectively [55]. These data suggest that the oxywater molecule and hydroperoxonium ion are better electrophilic reagents than hydrogen peroxide. The resulting changes in HOMO and LUMO levels of oxywater make them better mixable with the corresponding levels of a substrate.

Weakening of the O–O bond and appreciable admixture of O–O σ^* antibonding character to the low lying virtual molecular orbitals in a stable molybdenum peroxo complex was determined with SCF-MS-Xα MO-calculations [106]. Analogously, a combination of σ^* orbital of oxywater dianion with corresponding vacant orbitals of the metal atom can be expected to enhance the electrophilicity of the coordinated oxidant.

In this context, oxidation involving an oxygen atom transfer can be considered as S_{N2}-substitution of a leaving group (water molecule, M=O group, etc.) for another base at the oxygen atom to be transferred. The reaction becomes possible if the entering base is a better nucleophyle than the H_2O molecule or M=O group leaving the coordination sphere of the O atom. Back donation from the lone pair of the transferred oxygen atom to an empty orbital of the substrate being oxidized and enhanced electrophilicity of the oxidant moiety are considered to be important vectors for the reactions under consideration.

3.2. Alkene epoxidation

Complexes with an alkyl hydroperoxide molecule coordinated to a metal atom [1–8], i.e. a complex with an alkylperoxo anion [86], and complexes with a peroxo dianion, O_2^{2-}, as a ligand were considered to be active interme-
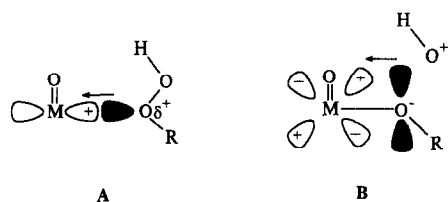
diates in epoxidation reactions [1–9,25, 29,35,86,96–99,111].

The catalyst, a compound of Mo^{VI}, W^{VI}, V^V, or Ti^{IV}, was largely viewed as a Lewis acid, the principal function of which is to withdraw electrons from the O–O bond of a coordinated peroxo or alkyl peroxo ligand [2] (See Scheme 4, **A**).
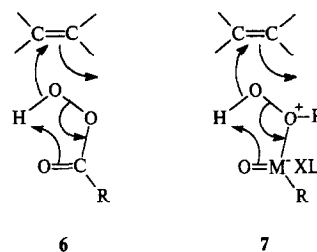
Hyperconjugation involving vacant p- or d-orbitals of the metal center and the O–O σ-bond can be added (structure **B**, Scheme 4) to the donor–acceptor interaction described by structure **A** (Scheme 4). The tendency of a metal atom to use its vacant d,p-orbitals for π-bonding with a coordinated oxygen atom is well known for the metals of IV–VI groups.

Both **A** and **B** (Scheme 4) interactions should facilitate the transfer of the HO^+ cation or, after its deprotonation, an oxygen atom to an alkene molecule. If this were the case, a similarity between metal catalyzed epoxidation reactions and electrophilic additions across the C=C double bond could have been expected.

Actually, in an apparent agreement with the electrophilic mechanism, the rates of epoxidation increase as the alkenes become more substituted with alkyl or other electron-donating groups [2,111]. However, the observed increase of the reactivity of olefins toward the $TBHP/Mo(CO)_6$ system or peracetic acid is less pronounced than those determined for the hydration or bromination of alkenes in polar solvents [112]. Hence, the data available [2,111] do not show a strong similarity between metal catalyzed epoxidation and typical ionic alkene

Scheme 5. A comparison of transition states proposed for alkene epoxidations: **7** – noncatalytic epoxidation by percarboxylic acid, **8** – epoxidation by alkylhydroperoxide catalyzed with a metal complex X is a monoanion; L – neutral ligand. See for reviews Refs. [1–4].

reactions in polar solvents. No evidence for a large charge separation was observed for epoxidation reactions by $ROOH/MX_n$ systems (MX_n is a complex of VI–IV group metals) or the corresponding peroxo complex.

A simulating mechanism that one proposed for the Prileschaev reaction transition state was discussed in the literature [1–3] (see Scheme 5).

It is tacitly assumed that the driving force for the oxygen atom transfer in the Prileschaev reaction (TS **6**) is conjugation:

Often, the protocol for the epoxidation with a percarboxylic acid calls for use of a base and/or buffer solution to avoid glycol formation. In such a reaction the anion of the percarboxylic acid can be expected to be an epoxidizing agent. The canonical structure **8** of a percarboxylic anion

suggests an analogy between the water oxide and this epoxidizing agent. The transition state for epoxidation with the non-protonated peracid

Scheme 4. Orbital overlap for the metal atom complex with monodentately coordinated alkyl hydroperoxide. A – σ-donor–acceptor interaction, B – $P_{d,p}$-hyperconjugation. The shading refers to occupancy of the orbitals, and the +, – signs to the symmetry.
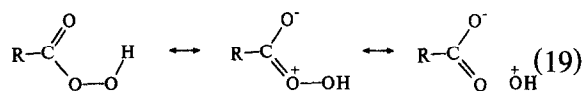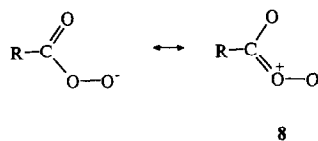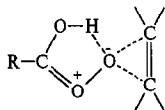
molecule can involve a canonical structure resembling the oxywater derivative:

A back donation from the negatively charged O atom to antibonding alkene orbital was suggested to be a stabilizing factor reducing the activation barrier [113]. As an example, a scheme of orbital overlaps for ethylene oxidation by the oxywater molecule is shown in Scheme 6.

The catalyst, e.g. a Mo^{VI} or W^{VI} compound, is known to coordinate alkanediol monoanions as ligands under the conditions for industrial alkenes epoxidation with alkylhydroperoxides [1,2]. As far as diolate monoanion is a stronger base than the alkylhydroperoxide, the epoxidizing agent in the Arco/Halcon process should be actually a salt of the starting alkylhydroperoxide. Epoxidation of this sort, being modeled by the reaction of ethylene with trihydroxytitanium hydroperoxide, has been studied by the nonlocal density functional method [114]. A η^2 structure, determined for a vanadium alkylhydroperoxide complex with X-ray technique [86,96–99,115], was not found for the titanium complex under study. However, the titanium–oxygen bond Ti-OOH was found to be elongated and the tita-
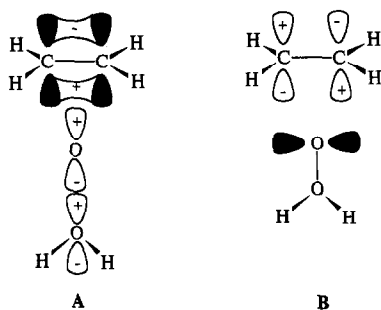
Scheme 6. Orbital overlaps for hypothetical ethylene oxidation with oxywater molecule. A – acceptor interaction involving vacant σ^* orbital of oxywater and filled π-orbital of ethylene. B – back donation involving a lone pair of distal oxygen atom of oxywater and empty, π^*-orbital of ethylene.
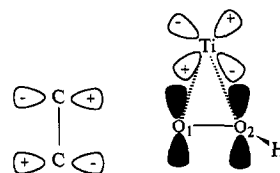
Scheme 7. Ethylene π^*-orbital overlap with the π^* orbital of coordinated hydroperoxide anion [114].

nium–distal oxygen distance to be shortened in the transition state. In other words, the Ti–atom undergoes a 1,2-shift as the oxygen atom initially coordinated to the Ti-atom is inserted into the C=C double bond. Hence, in the transition state the bonding between the hydroperoxide anion HOO$^-$ and the Ti atom ion can be described in terms of resonance involving titanium oxywater derivative structure **11** besides the canonical structures **10** and **9**:
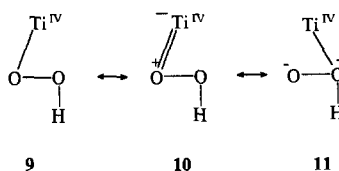
The ethylene molecule approaches the HOO bond of the (HO)$_3$TiOOH complex in the spiro fashion with the alkene molecule nearly antiperiplanar to the O–O bond, in a symmetrical conformation depicted by Scheme 7.

The interaction between the HOMO of the C$_2$H$_4$ molecule and the LUMO of the TiOOH fragment was found to dominate in the transition state. Hence, the epoxidizing complex acts as an electrophilic species. The LUMO of the TiOOH fragment is a combination of σ^* O–O with the $d_{x^2-y^2}$ orbital of Ti atom. The interaction between the HOMO of TiOOH and the LUMO of C$_2$H$_4$, the π^*(OO bond) back donation to π^*(C$_2$H$_4$), contribute to the stabilization of the spiro conformation of the transition state (see Scheme 7).

The chemistry of the platinum group elements is characterized by π-complex formation and subsequent insertion reactions [116,117].

An insertion of an alkene molecule into a metal–oxygen bond of a peroxo complex (see Eq. (20)) was proposed to rationalize alkene epoxidation by peroxo compounds [25,96–99].

$$(20)$$
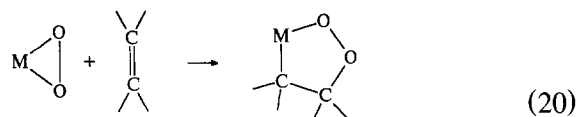
M=V, Mo

The scheme is appropriate in the case of d^8 metal complexes (Pt^{II}, Pd^{II}, Rh^I [25]). However, it seems to be doubtful if such a soft base as an alkene molecule is capable of substitution of an oxygen or nitrogen centered ligand at such a hard acid as molybdenum(VI), vanadium(V) or titanium(IV) ions. No alkene π-complexes of these ions were isolated or detected with any physical technique in the presence of alcohols, amines, or in aqueous solutions.

A free radical mechanism assuming inner sphere transformation of a V^V peroxo complex into V^{IV} complex containing superoxide anion O_2^- (see Eq. (21)) was proposed at an early stage of the epoxidation study [115]:

$$(21)$$
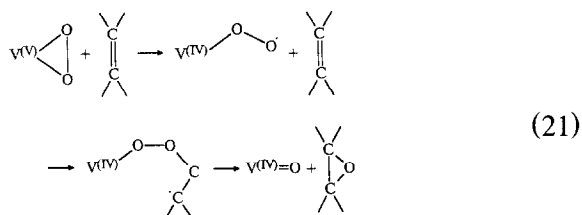
There is no strong evidence supporting the involvement of free radicals in the epoxidation reactions under consideration.

Substantial diradical character has been claimed for the related organic compounds, e.g. dioxiranes, $R_1R_1C\!\!\stackrel{O}{\underset{O}{<}}$ [118], and carbonyl oxides [107]. The carbonyl oxides are known to exhibit nucleophilic activity in their reactions. The electrophilic properties of these short-living intermediates were attributed to the diradical form $XYC^{\cdot}\!-\!O\!-\!O^{\cdot}$ [107]. The energy gap between the more stable zwitterionic state $XYC_{\underset{\cdots}{}}^{\delta+}O_{\underset{\cdots}{}}^{\delta+}O^-$

and the diradical state increases with the decrease of Hammett's sigma (σ_t) constant of the substituent group Y or X in XYCOO molecule. All the data support the concept that the reactivity of carbonyl oxides and related structures (e.g. gem.-dialkylperoxonium ions, $R^1R^2CO^+OH$) [108] can be tunable to some extent through choice of the substituents X and Y. Carbonyl oxides become zwitterions in polar solutions. The polar solvents capable of stabilizing zwitterionic structure contribute to increase the diradical-polar structure gap [107]. A quantum-chemical calculation by means of CASSCF and MRDCI ab initio approximations showed formaldehyde and acetaldehyde carbonyl oxides in the lowest singlet states can lose an $O(^1D)$ atom in rather endothermic reactions (37.7 and 35.5 kcal/mol) correspondingly [119]. In contrast to that, the dissociation channel for triplet states of the carbonyl oxides with $O(^3P)$ splitting are rather strong exothermic reactions (-38.9 and -39.7 kcal/mol) correspondingly [119]. It is not surprising that aliphatic carbonyl oxides are rather bad epoxidizing agents towards electrophilic alkenes.

These experimental and theoretical findings suggest that the reactivity of inorganic analogies of carbonyl oxides, namely, metal complexes with end-on coordinated peroxo dianion, $M=O^+\!-\!O^-$, can be varied over a wide range by changing ligands at the metal center and the nature of the solvent.

The negative charge borne by the distal oxygen atom in a carbonyl oxide $XYC=O^+\!-\!O^-$ is rather low, ranging from 0.20 to 0.30 [107]. Interestingly, no or little epoxide is formed by reacting ozone with alkenes confirming that intermediate carbonyl oxides are not capable of epoxidizing electrophilic alkenes. Only a trace, if any, of cyclohexene oxide was formed by reacting carbonyl oxide (from 1,2,3-trioxolane of *trans*-di-*tert*-butylethylene) in neat cyclohexene at 60°C [120]. However, the carbonyl oxide under study was capable of epoxidizing the strongly electrophilic tetracyanoethylene (TCNE) [120]. Ozonolysis of alkenes in the

presence of TCNE produces the epoxide of TCNE [121]. Analogously, strongly electrophilic fluoroalkenes, e.g. trifluoroethylene, tetrafluoroethylene, give rise to the corresponding epoxides by reacting with ozone [122–124]. The electron withdrawing groups (EWG) are favorable vectors for stabilizing the zwitterionic state of a carbonyl oxide [107]. Alternatively, EWG substitution at the C=C double bond is a factor enhancing the electrophilicity of an unsaturated substrate. As a result, the epoxidation takes place:
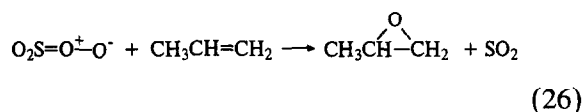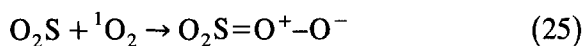
$$R_FCF{=}CF_2 + {}^-O{-}O^+{=}C{\overset{F}{\underset{R'_F}{\big\langle}}} \longrightarrow R_FC\underset{O}{\overset{}{F{-}}}CF_2 + R'_FCF{=}O$$

(22)
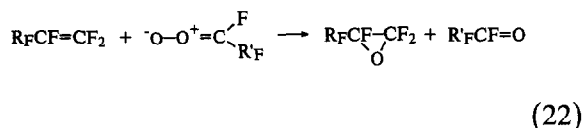
Carbonyl oxide (from benzyl azide and $^1O_2$) coordinated with Pd^{II} complex has been shown to epoxidize alkenes [74].

Persulfone formed from $(CH_3)_2SO$ and $^1O_2$ was not effective in epoxidation of α-methylstyrene [125]. On the other hand, photochemical oxidation of propylene in the presence of sulfur dioxide gives rise to 1,2-epoxypropane [126]:

$$CH_3CH{=}CH_2 + O_2 + SO_2 \xrightarrow{\ h\nu\ } CH_3C\underset{O}{\overset{}{H{-}}}CH_2 + [C_3H_6SO_3]_n$$

(23)
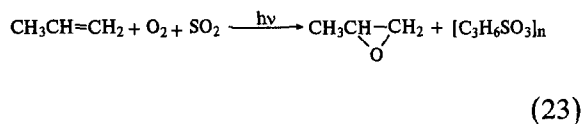
A probable candidate for the epoxidation agent can be a short-living peroxide of formula $O_2S^+{-}O{-}O^-$ (Eqs. (24)–(26)):

$$O_2 \overset{h\nu}{\to} {}^1O_2$$

(24)

$$O_2S + {}^1O_2 \to O_2S{=}O^+{-}O^-$$

(25)

$$O_2S{=}O^{\pm}O^- + CH_3CH{=}CH_2 \longrightarrow CH_3C\underset{}{\overset{O}{H{-}}}CH_2 + SO_2$$

(26)

The expected high electrophilicity of the sulfur trioxide peroxide, $O_2S^+{-}O{-}O^-$, a good leaving group, SO_3, and seemingly a high capability of the distal oxygen atom for back donation are factors exerting control over the epoxidation reaction (Eq. (26)).

3.3. Oxidation of n-donors

The group of reactions under discussion was the most intensively studied with Mo^{VI}, V^V, W^{VI} compounds [6,87,88,111] and methylrhenium trioxide (MTO) [89–92,127] which was originally used as a catalyst for hydrogen peroxide oxidation of alkenes, alkynes, and ketones [128,129].

Picolinic vanadium(V) complex containing anion radical O^- as a ligand has been shown to be an active species in organic sulfur compound oxidation by the picolinate vanadium oxodiperoxo complex $VO(O_2)O_2CNC_5H_4(H_2O)_2$ in chloroform solution [86,88]. Free radical and polar pathways can seemingly compete in the reactions of vanadium peroxo compounds. The analogous molybdenum and tungsten peroxo complexes and MO_5HMPT ($M = Mo$, W) complexes oxidize the organic sulfide p-$ClC_6H_4SCH_3$ predominantly over the sulfoxide $C_6H_5SOCH_3$ in the competitive experiments exhibiting the electrophilic oxidative properties of the peroxo complexes. A negative Hammett ρ constant of -1.6 was observed in the oxidation reactions of p-$XC_6H_4SCH_3$ with complex $[PMo_4O_8(O_2)_8]_3$–$[Py^+{-}(CH_2)_{15}CH_3]_3$ supporting this conclusion [130].

Oxidation of organic sulfides by hydrogen peroxide catalyzed by methyl rhenium trioxide was studied in CH_3CN/H_2O at pH 1 and 25°C [90]. Two peroxo complexes are in equilibrium with the starting MTO under the conditions of the oxidation reactions (see Scheme 8).
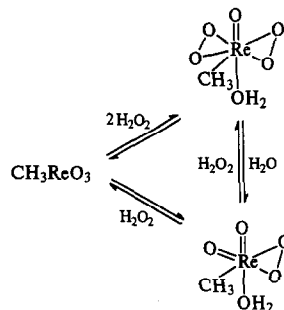

Scheme 8. Equilibrium reactions between MTO and peroxo complexes [89–92].

Both mono- and diperoxo complexes are active in the oxidation reactions, the former being studied in greater detail [90]. The kinetic study showed the peroxo complex to undergo a nucleophilic attack by organic sulfide. The Hammett ρ constant for this step was found to be equal to -0.98 for a series of p-substituted phenyl methyl sulfides [90]. Notice, that the ρ constants observed both in Ref. [130] and Ref. [90] are below the lower limit found for electrophilic reactions. Thus, the ρ value of -2.4 was observed for Friedel–Crafts ethylation of aromatics, -12.1 was found for Br_2 bromination in AcOH solution, -10 for Cl_2 chlorination and -9 for Friedel–Crafts acetylation [131]. So, rather low positive charge is developed at the sulfur atom in the transition state of the oxidation reaction. Similarly, Hammett $\rho = -0.63$ has been shown for triarylphosphine oxidation by H_2O_2 catalyzed with MTO [89] evidencing little change in charge to develop in the transition state of the phosphine oxidation. The comparison of second order rate constants for triphenylphosphine $(7.3 \times 10^5 \ 1 \ mol^{-1} \ s^{-1})$, triphenylstibine $(5.3 \times 10^5 \ 1 \ mol^{-1} \ s^{-1})$ and triphenylarsine $(3.7 \times 10^5 \ 1 \ mol^{-1} \ s^{-1})$ shows low sensibility of the reaction (see Eq. (27)) toward the nature of the element (E) undergoing the oxidant attack:

$$+ \ EAr_3 \longrightarrow \qquad\qquad + \ O=EAr_3 \qquad (27)$$
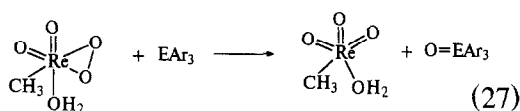
where E=P, Sb, and As.

It is to be noticed that the nucleophilic constants (n_{CH_3J}) of Et_3As (7.1) and Et_3P (8.7) differ sufficiently [132]. The n_{CH_3J} value for $(CH_3)_2S$ is equal to 5.3. However, the rate of methylphenylsulfide oxidation [90] is rather close to that observed for arsine and stibine triphenyl derivatives. On the other hand, even smaller difference in n_{CH_3J} values for chloride ion (4.4) and bromide ion (5.8) is accompanied with much more remarkable changes in the
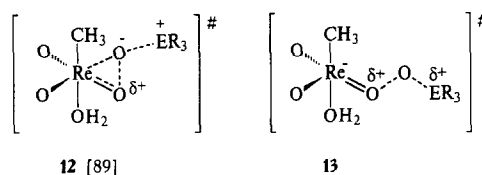
Scheme 9. The transition state structures for the triorganyl element, ER_3, oxidation reactions (E = As, Sb, P).

reactivities of the two ions toward methylrhenium monoperoxo complex: 0.06 1 $mol^{-1} \ s^{-1}$ for Cl^- and 350 1 $mol^{-1} \ s^{-1}$ for Br^- [91]. A rationale for these observations can be that the back donation of the lone pair of O atom of the peroxo ligand in the oxidation reaction contributes to the energy of the transition state much more in the case of the bromide ion than in that of the chloride ion. This interaction plays seemingly a sufficient role in the case of oxidation of sulfur, stibine, phosphorus, and arsine organyls as far as the oxidizing elements have vacant and comparatively low disposed d-levels. In all polar reactions under discussion, the peroxo group acts as both an electrophilic and nucleophilic center. Being electronically the same but sterically very different, $(p\text{-tolyl})_3P$ and $(o\text{-tolyl})_3P$ have a small difference in rates [90]. This rather low sensitivity of the organic phosphine oxidation towards steric requirements, in concert with a small Hammett ρ slope, suggests that an early transition state is involved, with little E=O bond formation [90]. The data was rationalized within a scheme involving a transition state structure 12 (see Scheme 9).

The important vector for the reaction is presumably Re–O multiple bond formation in the transition state 12. It is easily seen that a small and quite feasible distortion of the 'symmetrical' structure 12 can give rise to the structure 13 with a coordinated oxywater dianion as a constituent fragment of the transition state.
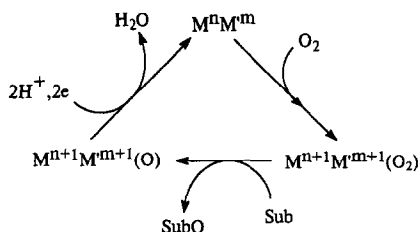
3.4. Activation of dioxygen

Oxygen active multimetal sites have been found in many biological systems responsible

for dioxygen reduction processes [133–141]. The commonly accepted scheme speculates that copper(I)–copper(I), iron(II)–iron(II), or copper(I)–iron(II) sites are involved in a redox cycle in which the dimetal center is sequentially oxidized by forming an adduct with dioxygen, which is a peroxo complex. The peroxo complex oxidizes a substrate and forms an oxide ($M^{n+1}M^{m+1}O$) which is reduced with an appropriate electron donor [133–139,141] (Scheme 10).

Each side of the triangle of Scheme 10 can consist of several elementary steps. Thus, according to kinetic studies of the diiron sites of methane monooxygenase, the reaction of O_2 with the reduced form of MMO, MMO_{red}, first results in an intermediate P, which then converts into another intermediate Q. The last intermediate contains two iron atoms in an oxidized form assumingly above IV and is supposed to be responsible for the methane into methanol conversion [142–146]. Different types of oxygen coordination to dimetal sites bridged by carboxylate groups and/or amino ligands including cis- and trans-μ-1,2-peroxo- and μ-η^2, η^2-peroxo complexes have been found [133–141,145–154] (Scheme 11).

The μ-η^1, η^1-mode of peroxo group coordination has been established with X-ray technique for dioxygen adducts of diiron complexes modeling non-heme metalloproteins [146–149]. Both μ-η^1, η^1- [150] and μ-η^2, η^2-coordinations [151–154] have been found for dicopper peroxo complexes.

The peroxo complexes are thermally unstable

Scheme 10. A hypothetical scheme for dioxygen activation with dimetal center. M and M' can be equal metal atoms, e.g. dicopper, diiron sites, or different metal atoms, e.g. copper/iron sites.
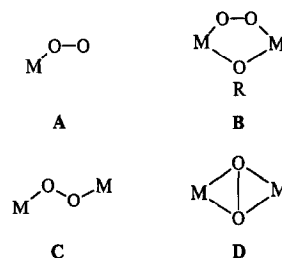
Scheme 11. Peroxide-metal binding modes: (A) end-on monomer; (B) end-on cis-μ-1,2 dimer with a second O bridge; (C) end-on trans-μ-1,2 dimer, (D) side-on μ-η^2, η^2 dimer. Adapted from Ref. [148].

compounds undergoing decomposition in the temperature range 223–270 K. When $[(LCu)_2\,\mu$-η^2, $\eta^2O_2](CF_3SO_3)_2$ (14) (L = 1,4,7-triisopropyl-1,4,7-triazocyclononane) was warmed above $-70°C$ without application of vacuum in CH_2Cl_2 solution, the hydroxo-bridged compound $(LCu)_2(OH)_2](CF_3SO_3)_2$ was formed in 85% yield [155]. Decomposition of the peroxo complex perdeuterated at the isopropyl substituent gave rise to an OD bridged product demonstrating that the H/D atoms of the bridging hydroxo groups originated from the isopropyl groups of the triazocyclononane ligand. Moreover, quantitative radical coupling of 2,4-di-tert-butylphenol was effected by reaction with complex 14 at $-78°C$:

(28)
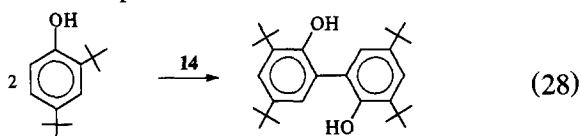
The μ-η^2, η^2-peroxo dicopper complex $\{Cu[HB(3,5-Me_2pz)_3]\}_2(O_2)$ has been found to be inert toward PPh_3 and CO but oxidize cyclohexene to 2-cyclohexene-1-ol and similar products under aerobic conditions with oxygen atoms of non-coordinated O_2 being incorporated into the substrate [156]. Under anaerobic conditions, phenols and catechol underwent oxidative coupling. Under an O_2 atmosphere, oxygenation occurred giving rise to benzoquinones from phenols. The examples cited above suggest that the μ-η^2, η^2-coordinated peroxo ligand is fa-

vorably disposed towards one-electron oxidations.

According to broken-symmetry SCF-X α-scattered wave calculations, the charge on the $\mu\text{-}\eta^2$, η^2-coordinated O_2^{2-} ligand is less negative than on the 1,2-μ-peroxo group. The $\sigma^*(O\text{–}O)$ level of $\mu\text{-}\eta^2$, η^2-coordinated peroxo group is reduced in such a way that the back donation from Cu d-filled orbitals can be sufficient [157,158]. These data may account for the electrophilic behavior of a peroxide ligand bound in a $\mu\text{-}\eta^2$, η^2 fashion. A study of the chemical behavior of dicopper complexes (15, 16, 17) with different modes of peroxo group coordination has indicated a number of distinctions in the reactivity patterns of μ-1,2-coordinated peroxo groups in comparison with those of a $\mu\text{-}\eta^2$, η^2-coordinated one [159], manifesting the influence of the coordination fashion on the ligand reactivity.
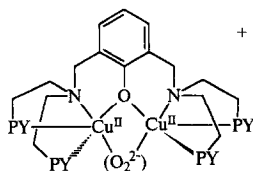
15
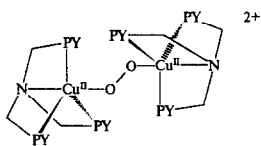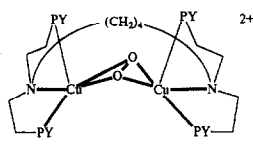
16   **17**

PY = 2-Pyridyl

Reactions of complexes 15 and 16 with PPh_3 readily resulted in the stoichiometric displacement of the bound O_2 ligand producing Cu^I–PPh_3 complexes. With complex 17, slow but complete oxygen atom transfer occurred, giving rise to Ph_3PO. Protonation reactions are particu-
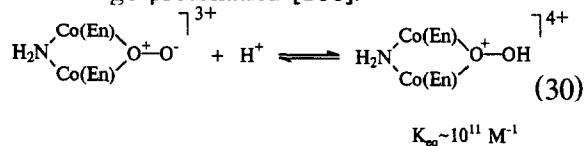
larly striking as addition of HBF_4 or HPF_6 to 15 and 16 gave near-stoichiometric yields of H_2O_2, whereas 17 was relatively insensitive to H^+. Even phenols reacted with 15 and 16 mainly as proton donors. By contrast, one-electron oxidation of 2,4-di-*tert*-butylphenol to 3,3′,5,5′-tetra-*tert*-butyl-2,2′-dihydroxybiphenyl occurred when the former reacted with complex 17. The peroxo-bridged copper(II) complex 15 with a terminal 'non-symmetrically' μ-1,2-coordinated peroxo ligand and μ-*trans*-1,2-peroxo-bridged complex 16 have basic or nucleophilic peroxo groups. By contrast, the complex 17 exhibits electrophilic properties of the $\mu\text{-}\eta^2$, η^2-peroxo group. The reactions of all three complexes with a carbocation Ph_3C^+ were rationalized within a scheme involving an intermediate formation in which both Cu atoms are bound to a common oxygen atom of peroxo ligand [159]:
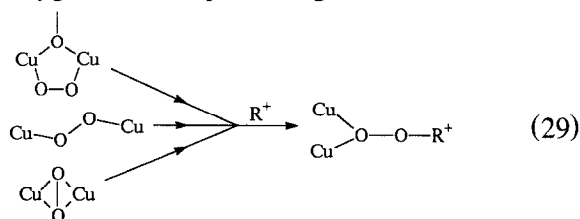
$$(29)$$

One can presume that μ-1,2-peroxo groups are protonated or alkylated first and then rearranged to a μ-1,1-OOR structure (R = H^+ or carbocation). Another possibility is a rearrangement of a complex with a bridging μ-peroxo group into complex with a bridging oxywater dianion which undergoes subsequent alkylation or protonation to form a μ-1,1-OOR structure. The last type of HOO^- coordination is known for Co^{III} peroxo complexes [160]. The molecular structure of the μ-amido-μ-hydroperoxobis[bis(ethylene-diamine)cobalt(III)]$^{4+}$ ion was resolved by X-ray technique [160]. The hypotheses for 1,2-μ into 1,1-μ-peroxo ligand isomerization were discussed with the examples of diiron and dicobalt intermediates [161–165]. Formation of 1,1-μ-peroxo complex in the case of porphyrinato complexes [163,164] can require rather severe steric congestion [165] but

seems quite possible in the case of the dicopper(II) complexes discussed above. Like other oxywater derivatives, the 1,1-μ-coordinated peroxo ligand should be more strongly basic than the μ-η^2, η^2-coordinated one. Thus, the 1,1-μ-coordinated peroxo ligand was found to undergo protonation [160]:

$$\left[\begin{array}{c} \text{Co(En)} \\ H_2N \\ \text{Co(En)} \end{array} O\overset{\pm}{-}O^{-}\right]^{3+} + H^{+} \rightleftharpoons \left[\begin{array}{c} \text{Co(En)} \\ H_2N \\ \text{Co(En)} \end{array} O\overset{+}{-}OH\right]^{4+} \quad (30)$$

$$K_{eq} \sim 10^{11} \text{ M}^{-1}$$

The rate constant of dicobalt(III) μ-amido-μ-1,2-*trans*-peroxo complex isomerization into a complex with the 1,1-μ-coordinated peroxo ligand (see Eq. (31)) [160] in aqueous perchlorate solution is extremely small ($\sim 10^{-12}$ s^{-1}) and the equilibrium depicted by Eq. (31) is shifted to the left.

$$\left[\begin{array}{c} \text{Co(En)} \\ H_2N \\ \text{Co(En)} \end{array} \begin{array}{c} O \\ | \\ O \end{array}\right]^{3+} \rightleftharpoons \left[\begin{array}{c} \text{Co(En)} \\ H_2N \\ \text{Co(En)} \end{array} O\overset{\pm}{-}O^{-}\right]^{3+} \quad (31)$$
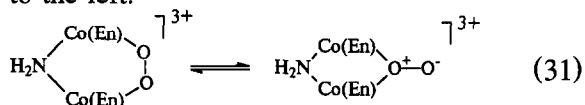
However, both the rate and equilibrium constants of 1,2- into 1,1-μ-peroxo group isomerization can be influenced by the nature of the metal atom, its charge and ligand surrounding. In this context, one might expect the isomerization of copper(II) complexes to proceed more easily than that of cobalt(III) complexes as far as coming within a shorter distance of less charged centers could require less energy consumption.

Dinuclear Cu^I complexes of macrocyclic ligands **18–20** react with dioxygen to form the corresponding copper(II) peroxo complexes [166–174].


18   19   20
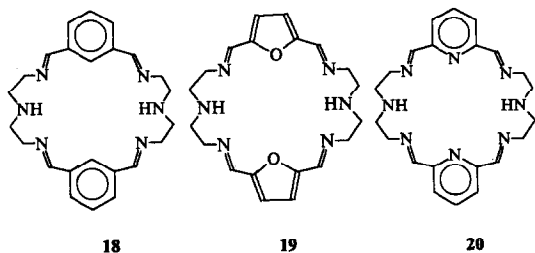
The oxygenation of the dinuclear copper(I) complex of ligand **18** results in a rapid hydroxylation of one of the benzene rings of the macrocycle [166,167]:

(32)
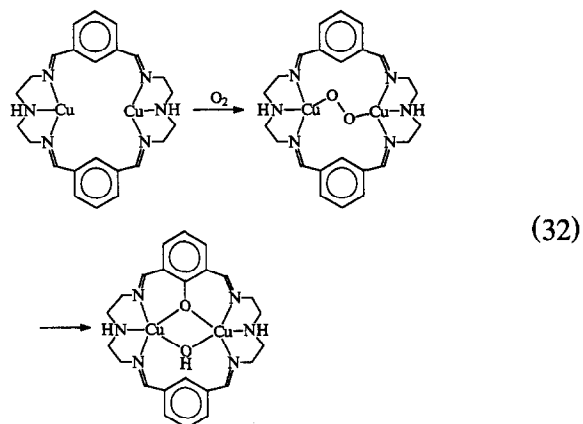
Oxidation with $^{18}O_2$ labeled dioxygen showed the incorporation of one atom of ^{18}O into the aromatic ring of the cyclic ligand **18**. Only one of the arene rings underwent the hydroxylation. All these data can be rationalized within a scheme assuming 1,2-μ- into 1,1-μ-peroxo ligand isomerization:

(33)
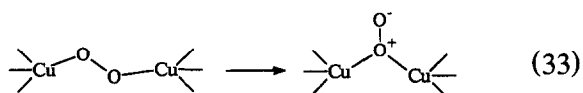
The insertion of one oxygen atom into the aromatic C–H bond of the macrocyclic ligand can be considered as a transfer of the oxygen atom from the coordinated oxywater dianion to the organic substrate:

(34)
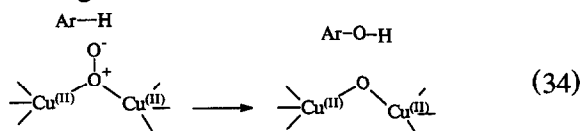
If the resulting copper(II) oxide is reduced by an appropriate reagent to the copper(I) complex, the hydroxylation can become a catalytic. Thus, Cu^I complexes of ligand **19** and **20** with furane and pyridine bridging groups do not undergo hydroxylation because of the lack of an appro-

priate C–H aromatic bond [166,167]. However, the copper(I/II) complexes with these ligands act as catalysts in the oxidation of phenols and catechols as far as complexed Cu^{II} oxide can be reduced by the substrate under oxidation and thus the catalyst can be regenerated.

A similar hydroxylation of a non-cyclic ligand has been observed [175]. The hydroxylation of tridentate ligand at benzylic position was observed by oxidizing copper(I) N,N-bis[2-(2-pyridyl)ethyl-2-phenylethylamine (Py$_2$Phe) complex in CH_2Cl_2 solution:

$$(35)$$

21
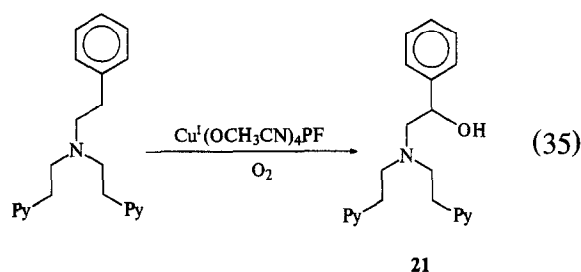
A Cu^{II} complex with the hydroxylated ligand **21** was obtained. Labeling experiments ($^{18}O_2$) showed that the oxygen atom of the OH group comes from molecular oxygen. The stoichiometry O_2:Cu was determined to be 1:2, the yield of hydroxylation based on the Cu^I ion was 50% [175], in agreement with the expectation according to Eqs. (33) and (34). Numerous examples of related reactions have been reviewed [162].

A work by Lippard, Newcomb and co-workers has shown that free carbon radicals are not involved in the MMO action [176]. Moreover, a particulate form of MMO hydroxylates with perfect retention of configuration [177]. The oxygen rebound mechanism for hydroxylation by high valent metal complexes [178] is under critical discussion now [179,180]. The hydroxylation mechanism with five-coordinated carbon atom and ferryl groups was forwarded as an alternative scheme [180]:


$$(36)$$
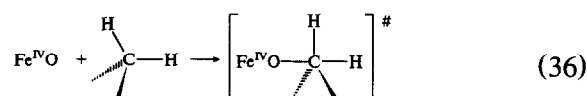
In the context of the approach under discussion, a scheme involving O_2 coordination by dinuclear Fe^{II}–Fe^{II}-center and an isomerization of the Fe^{III}–Fe^{III} peroxo complex into corresponding complex with oxywater anion can be speculatively proposed. The latter is assumed to react with a hydrocarbon undergoing monooxidation (see Eq. (37)).

$$(37)$$
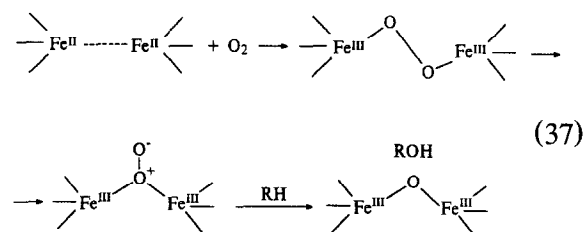
3.5. Decomposition of peroxynitrite

Peroxynitrite, $OONO^-$, and peroxynitrous acid, HO–ONO, are important biological oxidants produced in vivo via recombination of superoxide anion O_2^- with NO [181,182]. Peroxynitrite produced by irradiation of alkali metal nitrates, e.g. KNO_3, is stable for months in the solid solution placed in a closed bottle [181]. No decomposition of $OONO^-$ ions was observed when a sample of the solid solution was dissolved in water at pH 12 in 1 h. However, upon the acidification to pH $\leq$ 7 the acid ONOOH (pK_a 6.75) disappeared in a few seconds at room temperature [181]. In neutral aqueous solution with HCO_3^- or CO_2 absent, peroxonitrous acid isomerizes according to:

$$HOONO \rightarrow NO_3^- + H^+ \qquad (38)$$
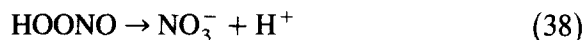
Peroxonitrous acid and its anion are known to be very strong oxidants, stronger than H_2O_2, being capable of oxidizing I^- and Br^- ions, aromatic compounds, arsenite, hydrazine, formaldehyde and thiocompounds [181–183]. The products are consistent with the involvement of free radicals, including $HO^\cdot$, as intermediates

[181]. The presence of free radicals was supported by the observation that methyl acrylate was polymerized in solution containing $HOONO_2$ [184]. The yield of $HO^\cdot$ from HOONO was found to be 40% [181]. However, the homolysis of HO–ONO at ordinary temperatures was considered to be too slow to be involved in oxidations by peroxonitrite and its acid [185]. The isomerization of HOONO into nitrate (see Eq. (38)) was another reaction considered as one involving free radical intermediates [181,185].

The observed Arrhenius pre-exponential factor for Eq. (38) is equal to 6.2×10^{12} s^{-1} [185]. This value corresponds to a small positive change in activation entropy ($+3$ eu) and seems to be too small for homolytic dissociation in the gas phase. A reasonable explanation for this reduction of $\Delta S^{\#}$ could have been a cage effect [185]. If the geminate radical pair is formed in a solvent cage and the diffusive barrier is high enough, recombination of $HO^\cdot$ and $^\cdot NO_2$ to reform HOONO can compete with the pair separation and thus reduce the observed efficiency for the disappearance of HOONO.

Another mechanistic scheme for peroxonitrous acid disappearance assumes formation of a reactive form of this substrate. It is suggested that normal peroxonitrous acid converted into an active or excited form, HOONO*, in an equilibrium reaction:

$$HOONO \rightleftarrows HOONO^* \qquad (39)$$
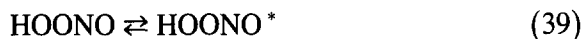
The nature of the active intermediate HOONO* was not refined.

To choose between free radical and molecular mechanisms of HOONO decomposition the influence of solution viscosity on the rate of the reaction was studied [185]. If the free radical mechanism were correct, the cage return would be expected to be of importance. Therefore, in the media of higher viscosity, the radical pair in a cage will live longer. As a consequence, the rate of the rearrangement of peroxonitrous acid to give nitrate must be lower in the solvents of higher viscosity [185,186].

To test the importance of a free radical route, a study of the disappearance of HOONO at pH 5 and 7 in aqueous solution containing dioxane or up to 30% of the poly(ethylene glycol) (PEG) polymers, PEG 3350 and PEG 8000, was undertaken [185].

The experiments [185] showed that the viscosity of the solution has little or no effect on the rate of disappearance of HOONO. Thus, this study casts serious doubt on the free radical mechanism for peroxynitrous acid decomposition.

All the available data can be rationalized within a scheme involving isomerization of HOONO into a nitrosoderivative of oxywater:

$$\text{(40)}$$

22
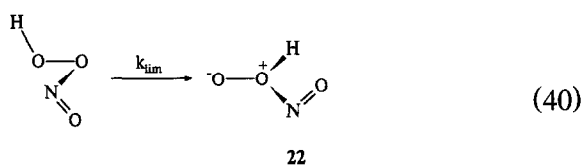
Thus, the excited form of HOONO is assumed to be a derivative of oxywater in which one of the protons is substituted for a nitroso group. The intermediate **22** can be responsible for many HOONO oxidations including aromatic compound hydroxylation, oxidation of sulfhydryl groups and thioethers, iodine and bromine ions. A weak interaction between the O-atom of the nitrosyl group and H-atom in **22** can contribute to this intermediate stabilization and lower the activation barrier for its formation.

The transformation of **22** into nitrate can be thought of as a molecular rearrangement involving a 1,2-oxygen atom shift:

$$\text{(41)}$$
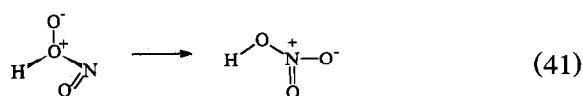
Another possible pathway is intermolecular

oxygen atom transfer between excited and normal HOONO molecules:

$$(42)$$
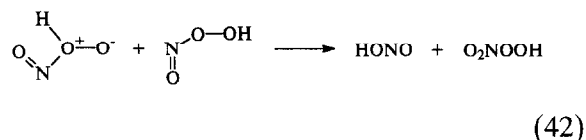
Many oxidations in the system considered as containing peroxonitrous acid can be assumingly attributed to the coexistence and joint action of HOONO and $HOONO_2$ oxidants.

The disappearance of peroxynitrous acid obeys the first-order kinetics suggesting the isomerization of the acid into oxywater derivative **22** (Eq. (40)) to be the rate-limiting s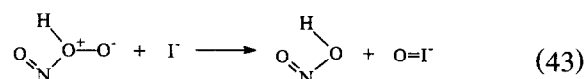tep. However, the oxidation of more easily oxidized substrates can follow a kinetic equation of higher order in substrate concentration. Thus, the oxidation of iodine ions with HOONO is first-order in the concentrations of both reagents [181,187]. So, a possible mechanism can involve an attack on iodine ion by the intermediate **22** in a slow step:

$$(43)$$

4. Concluding remarks

The data available suggest a peroxidic oxidant to act like a biphilic reagent in reactions resulting in one oxygen atom transfer from the oxidant to a substrate molecule. Both electron acceptor and back donation ability of the oxidant species seem to contribute to the energetics of the reaction transition state. In this context, the concept of the asymmetrical coordination of the oxidant entity in a metal complex can be used effectively to rationalize the body of the data available. With such a mode of coordination, the peroxidic distal oxygen atom, bearing an effective negative charge, plays the role of the nucleophilic agent attacking the substrate molecule. At the same time, interaction between

empty d-orbitals of the metal atom and σ^* orbital of the oxidant molecule is expected to enhance the electrophilicity of the latter. A reaction involving one oxygen atom transfer from peroxidic oxidant to a substrate molecule is considered as a nucleophilic substitution at a singlet oxygen (^1D) atom. Within the scheme under discussion, the leaving group is a rather strong oxometallyl group, M=O, in the reaction.

The diversity to reaction channels 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-}, in the form of peroxo group [26–28] or water oxide dianion ($M=O^+-O^-$), a singlet dioxygen molecule, trioxo dianion O_3^{2-}, or ozone molecule [28,188] should be taken into consideration in parallel with free oxyl or peroxyl radicals.

Acknowledgements

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