OXO-ATOM TRANSFER REACTIONS OF TRANSITION METAL COMPLEXES IN CATALYTIC OXIDATION WITH O₂ ON THE LIGHT OF SOME RECENT RESULTS IN MOLYBDENUM-OXO CHEMISTRY∗

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Abstract

The oxo-atom transfer reactions, which are one of the important fields of transition metals coordination chemistry, are widely spread in nature and used in chemical and pharmaceutical industries. This review presents some aspects of the application of oxo-atom transfer reactions in catalytic oxidation. A special attention was paid to the oxidation reactions catalyzed by metal-oxo and peroxo complexes using molecular oxygen as the direct oxidant. The main part of given examples are taken from the literature of Mo-oxo transfer reactions chemistry, including the data obtained at the laboratory of CNRS (France) in Marseilles by H. Arzoumanian and his collaborators during the recent decades. The characteristics of metal-oxygen bonds, as well as their role in oxo-atom transfer reactions, are described. The probable mechanisms of the transfer of oxo and oxo-peroxo moieties in catalytic cycles also have been discussed. It has also been shown that the anchoring of these complexes on solid matrices ameliorates their catalytic properties.

Fig. 4, schemes 9, references 64.

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Introduction

Among the oxidation reactions of organic molecules, the catalytic and photocatalytic processes by transition metal coordination compounds have an essential importance. The vital function of all living organisms is wildly based on the enzymatic processes, particularly, on the oxidation reactions catalyzed by natural organometallic complexes through the mechanism of oxo-atom transfer reactions to the substrates [1-6]. Furthermore, the chemical and pharmaceutical industries have realized a great number of syntheses applying various transition metal complexes, including oxo-complexes [7-9]. The chemical industry permanently requires new technological processes, since only the high yield of products or accessibility of processes are not sufficient conditions, nowadays, the ecological advisability and economy of energy are indispensable conditions for modern industry.

The oxo-atom transfer chemistry of transition metals is a very large domain for investigation [1, 2, 6]. An oxo-atom, bonded to the transition metal, depending on the nature of metal and its oxidation state, as well as its coordination sphere, takes part in a number of processes, such as oxidation, reduction, olation, acid-base reactions, etc. [2, 3, 6, 10]. Among them, the oxidation by oxygen atoms transfer via transition metal complexes is successfully used in both homogeneous and heterogeneous systems for the synthesis of a number of organic compounds [7, 9]. The highly selective transfer of oxygen atom onto the substrate, without formation of by-products, makes these processes very valuable in both industrial and laboratory scales. This review will, particularly, emphasize oxidation processes with dioxygen being the direct oxidant. Here we will attempt to throw some light on the new tendencies in this area, exemplifying the Mo-complex-catalyzed oxidation reactions via an oxo-atom transfer process tested in different oxidation reactions at the laboratory of CNRS (France) in Marseilles during the last decades.

Transition metal oxo-complexes, character of metal-oxo chemical bond

Complex compounds containing transition metal which is bonded to the oxo-atom, are found in minerals and live organisms [8-11]. The oxo-ligand entities are known for nearly all chemical elements of groups 4-8 [6, 12]. From the point of view of the chemical structure, an oxo-atom of transition metal (M) coordination complex can exist in two structures: “terminal-oxo”(1) and “bridging-oxo” or µ-oxo (2):

\[ M = O \quad M \rightarrow O \rightarrow M \]

(1)  (2)

The metallic center of coordination compound can bear one or several “terminal” oxygen atoms giving a large variety of monomeric, dimeric, and oligomeric structures of oxo-ligand complexes (Scheme 1).
Similarly, in metal-peroxo complexes the dioxygen can be bonded to the metal either by a side-on or an end-on structure. In the later case, the oxygen may be bonded to another metal atom, hydrogen or radical giving superoxo and superoxide species [11].

\[
\begin{align*}
\text{MO} & \quad \text{MO} \\
\text{X} & = \text{M; H; R}
\end{align*}
\]

Determination of the nature of the chemical bond in these complexes between a metal and oxygen plays a key role in understanding some of their chemical properties. The character of the bond for a “terminal” oxo-ligand complex in some aspects is analogous to the C=O in organic compounds [13-15]. The metal-oxygen bonds are partially polarized, inducing a donor-acceptor character as shown below:

\[
\begin{align*}
\delta^+ & - \text{O} = \delta^- \\
\text{M} & \quad \text{M}
\end{align*}
\]

Here the oxygen atom (or ion O\(^2^-\)) exhibits nucleophilic properties, for example, it can activate the C-H bond in \(\alpha\) position of a double bond or an aromatic ring [12, 6].

In a study of the bond character of the metal-oxo moiety Rappé and Goddard [16-18] had compared the mono-oxo-metal coordination complexes with the dioxo-metal in the reaction of alkene oxidation and proposed the so-called “spectator effect” of an oxo-atom. On the basis of theoretical calculation it had been shown that for mono-oxo-atom complexes the metallic center can be bonded with the oxygen by a triple chemical bond. For example, in OMoCl\(_4\) the metallic atom have 6 valence electrons, four of which form \(\sigma\) Mo-Cl and 2 others form two chemical bonds (\(\sigma\) and \(\pi\)) with the oxygen atom. The lone electronic pair of oxygen overlaps a second empty \(\pi\) –MO (molecular orbital). The qualitative energetic diagram of MO for chemical bonds of the metal-oxygen moiety in the ground state is represented in Scheme 2 [19].
This electronic configuration is characteristic for the metal-oxo complexes when the oxidation state of metal ion is equal to +6 (Cr, Mo and W). Thus, the metal-oxygen chemical bond of a “terminal” mono-oxo complex has a triple bond character (one σ and two π). Then, observing the dioxo-complex \( \text{O}_2\text{MoCl}_2 \), it can be seen that 2 electrons from 6 valence electrons of metal form two σ Mo-Cl bonds and other 4 electrons form two σ and two π bonds with the oxygen atoms. As the two π-MO already were overlapped by two π-bonds of oxygen, the lone electronic pairs of oxygen atoms have not a possibility to overlap a MO indispensable for stabilization of triple chemical bond. From this point of view, in dioxo-atom transition metal complexes the triple character of metal-oxygen stabilized bond cannot takes place.

In Scheme 3 two reactions of Mo-complexes with ethylene are represented, the first one of which is a reaction with the monooxo-ligand and the second with the dioxo-ligand.
The calculations show that for the first reaction the $\Delta G_{300} = +49 \text{ kcal} \cdot \text{mol}^{-1}$, but for the second reaction the $\Delta G_{300} = -21 \text{ kcal} \cdot \text{mol}^{-1}$. The essential differences of reactivity between two complexes may be explained by the second oxo-ligand “spectator effect”. In the second reaction with ethylene the dioxo-complex gradually loses one of the $\pi$-bonds opening a possibility to occupy the empty molecular orbital by the lone electronic pair of oxygen in the developing transition state. In this case the reaction of dioxo-oxo complex becomes thermodynamically and kinetically more feasible, than that for mono-oxo-ligand. Thus the second oxo-ligand (“spectator”) plays an important role in stabilization of intermediates by increasing the bond strength. Obviously, the monooxo-ligand has not this possibility and thus the first reaction is more unfavorable, than the second.

Complexes containing a metal in a high oxidation state ($\geq 4$), depending on its structural specificity and reaction conditions, are able to exhibit oxidative properties toward a great number of organic compounds, including hydrocarbons and oxygenated organic molecules, accompanied by the reduction of metallic centers [1, 2, 6]. On the other hand, an oxo-atom bonded to the transition metal, in other reaction conditions, shows activity also in a great number of reduction-catalyzed processes, such as the conversion of carbonyl containing compounds to alcohols and alkynes to alkenes via hydrogenation [20, 6]. The discussion all of these chemical properties of an oxo-ligand is not the aim of this article. Here we will pay attention only to the application of transition metal-oxo or peroxo complexes in catalytic oxidation reactions.

**Transition metal oxo-complexes in catalytic oxidation reactions**

Transition metal oxo-atom transfer to the organic substrates in many cases can occur in a stoichiometric manner:

$$\text{Ln} M^n=O + S \rightarrow \text{LnM}^{n-2} + SO$$

where $M$ is a transition metal (Mn, W, Mo, V, Fe, Cr, Ru, etc.), $Ln$ is a ligand, $S$ is a substrate.

The oxidation process becomes catalytic, if an oxygen-donor agent is capable to regenerate the metallic center to its initial oxidation state in reaction media [1-6, 21-25]:

where DO is an oxygen atom-donor molecule. Some “oxo-donor” agents are given below:

$$\text{O}_2, \text{H}_2\text{O}_2, \text{ROOH}, \text{DMSO}, \text{N}_2\text{O}, \text{PhIO}, [\text{ClO}_4]^-. $$

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Among these compounds, the use of O\(_2\), as an oxygen atom-donor agent, would be ideal for catalytic oxidation. Molecular oxygen is the cheapest oxidant agent, but usually, in ordinary conditions, it reacts very slowly with the majority of organic substances. Being a triplet in the ground energetic state, the reactions of molecular oxygen with some organic substances in singlet spin state are forbidden. The O\(_2\) can be used as an oxidant in the complex-catalyzed oxidation [26-34], but often, when the reaction has free radical chain mechanism, the selectivity of final products is moderate [9]. There exist a number of catalyzed-oxidation processes by complexes using dioxygen, which have other mechanism, than oxygen atom transfer, as the known industrial Wacker process (oxidation of ethylene to acetaldehyde using tetrachloropalladium(II) in water, containing also copper(II) chloride, in 120-130°C and 3-4 atm), where the oxidation occurs indirectly by molecular oxygen, but not by oxo-atom direct transfer to the substrate [26]. The overall Wacker process is

\[
\text{C}_2\text{H}_4 + \frac{1}{2}\text{O}_2 \rightarrow \text{CH}_3\text{CHO}
\]

and involves the following stages:

\[
\begin{align*}
[\text{PdCl}_4]^{2-} + \text{C}_2\text{H}_4 + \text{H}_2\text{O} & \rightarrow \text{CH}_3\text{CHO} + \text{Pd} + 2 \text{HCl} + 2 \text{Cl}^{-} \\
\text{Pd} + 2 \text{CuCl}_2 + 2 \text{Cl}^{-} & \rightarrow [\text{PdCl}_4]^{2-} + 2 \text{CuCl} \\
2 \text{CuCl} + \frac{1}{2}\text{O}_2 + 2 \text{HCl} & \rightarrow 2 \text{CuCl}_2 + \text{H}_2\text{O}
\end{align*}
\]

When O\(_2\) is the primary oxidant, several approaches are possible. Some examples are presented below (Scheme 4:5:7).

Many transition metals in their reduced state are known to interact with dioxygen to give a metal-peroxo complex. When this complex is able to transfer only one oxygen atom to a substrate, the completion of the catalytic cycle can be attained by the use of a coreductor in order to reduce the metal to its original state (Scheme 4) [27-29].

![Scheme 4. Catalytic cycle involving a coreductor.](attachment:scheme4.png)

For example, the quantitative epoxidation reactions of olefin catalyzed by Ni(II)-complexes using O\(_2\) as the oxidant, and primary alcohols or aldehydes as coreductors, under “mild conditions”, have been extensively studied and applied [29].

When a transition metal complex cannot directly be peroxidized with dioxygen, the use of a second metal, able to interact with O\(_2\) in a bimetallic catalytic system, was elaborated in a “double jump” dioxygen activation [31, 32]. Indeed, in such system a first metal (M\(_A\)), able to react with O\(_2\), gives a metal peroxo complex (M\(_A\)O\(_2\)), although
unable to transfer any oxygen atom to a substrate, it can, on the other hand, play the role of O-donor to a second metal (M$_B$), which in turn has the capacity to transfer its O-atoms to a substrate (Scheme 5).

![Scheme 5. Catalytic cycle involving transition metals A and B.](image)

For example, RhCl(PPh$_3$)$_3$ is able to interact with O$_2$ to give reversibly a Rh(III)-peroxo complex, but is unable to transfer an oxygen to cyclohexene. Equally, the V(acac)$_3$ cannot be peroxydized directly with dioxygen and, thus cannot be a catalyst for cyclohexene oxidation. On the other hand, a mixture of RhCl(PPh$_3$)$_3$ and V(acac)$_3$ in a bimetallic catalytic system allows the epoxidation of cyclohexene with O$_2$ [31].

For biological activity some enzymes require one or more non-protein molecules called cofactors [1-3]. They are organic molecules (coenzymes) or inorganic ions (Mg$^{2+}$, Cu$^+$, Mn$^{2+}$ or Fe-S clusters). The so-called molybdenum cofactor is one of them. It is a coordination complex containing an organic part called molybdopterin (which does not contain molybdenum) and an oxide of Mo or W. These two parts of cofactor usually are bonded by sulfur (or selenium) atoms, as shown in Scheme 6. Molybdenum containing enzymes are able to catalyze the oxidation reactions of a great number of substrates via an oxo-transfer reaction [33].

![Scheme 6. Molybdenum cofactor [3].](image)

Catalytic cycle for enzymatic oxidation represented in Scheme 7 is analogous to the above exemplified catalytic cycles by coreductor.
The most common reaction in this case is the insertion reaction of one oxygen atom into an organic substrate and the reduction of the second oxygen atom to water:

\[
S + O_2 + 2e^- + 2H^+ \xrightarrow{\text{cytochrome P450}} SO + H_2O
\]

In representative example of Cytochrom P450’s, which are enzymes oxidizing a great number of substrates (lipids, steroidal hormones, hydrocarbons), the catalytic cycle is realized between Mo(VI) and Mo(IV) or analogously W(VI) and W(IV)-centers [3,33].

**Application of oxo-molybdenum complexes in catalysis**

Above represented catalytic cycles demonstrate more common cases of the application of oxo-atom transfer reactions in catalysis. Among the oxo-complexes of transition metals the Mo-containing complexes may be considered relatively more investigated, exhibiting many reaction types. One common feature to most metal-oxo species is the high polarity of the M=O ligand which can be assimilated to an electron well, into which electrons can be taken away or added at will [6].

The pentacyano-oxo-molybdate(IV) was the first molybdenum complex, able to react with dioxygen to give the tetracyano oxo-peroxo-molybdate(VI) anion which exhibited an unexpected stoichiometry towards triphenylphosphine [32]:

\[
\begin{align*}
&\left[\text{(CN)}_5\text{Mo}^{\text{IV}}\right]^{-3} + \text{O}_2 + \text{CN}^- \rightarrow \left[\text{(CN)}_4\text{Mo}^{\text{VI}}\text{O}^\cdot\text{O}^\cdot\text{O}^\cdot\text{O}^\cdot\text{O}^{-2}\right]^{-2} \\
&\left[\text{(CN)}_4\text{Mo}^{\text{VI}}\text{O}^\cdot\text{O}^\cdot\text{O}^\cdot\text{O}^\cdot\text{O}^{-2}\right]^{-2} + \text{PPh}_3 \rightarrow \left[\text{(CN)}_4\text{Mo}^{\text{VI}}\cdot\text{O}^\cdot\text{O}^\cdot\text{O}^\cdot\text{O}^\cdot\text{O}^{-2}\right]^{-2} + \text{OPPh}_3
\end{align*}
\]

In fact, in the resulting reaction 1 mol of Mo-complex oxidized 1.5 mol of substrate. It is well known that Mo(VI)-oxo-peroxo species can stoichiometrically oxidize only 1 mol substrate while being reduced to Mo(VI)-dioxo. The rest of substrate (0.5 mol) can be oxidized by reduction of dioxo-Mo(VI) to monooxo-Mo(IV) species and their further
reoxidation. This was known only for species containing electron rich sulfur ligands as dialkyldithianocarbamates, in contrast to CN ligand in this case. The probable explanation is the following. Here, the so-called “proximity effect” takes place which arises when the “neighboring” dioxo-molybdenum unit plays the role of electron supplier for the transfer of oxygen atom to the substrate:

Then, the Mo(V)-µ-oxo dimer undergoes a further disproportionation giving Mo(IV)-oxo and Mo(VI)–dioxo species. The catalytic cycle can be represented as follows:

It is noteworthy that the analogous catalytic cycle was proposed for Ru-porpherinic epoxidation of alkenes using O$_2$ [35].

It may be noted also that the “proximity effect” is a very useful concept for explaining the reactivity in organized assemblies, including supramolecular aggregates, colloidal structures, liquid crystals, nanoparticles mono- and multilayers, etc. [36].

It is known from number of investigations [37-42] that the oxo-atom transfer capacity of complexes increases when CN is replaced by S-bonded ligand. Moreover, it was shown also that the partial or complete elimination of ionic character of complexes correlates with its oxo-transfer ability. The comparative reactivity of oxo-atom transfer from the metallic center to the substrate PPh$_3$ increases in the following order [Mo(VI)O$_2$(CN)$_4$]$^{2-} <$ Mo(VI)O$_2$[dialkyledithiocarbamate]$_2$ < [Mo(VI)O$_2$(SCN)$_4$]$^{2-} <$ Mo(VI)O$_2$(SCN)$_2$[bipyridine ligand]. The kinetic curves represented in Fig.1 confirm these observations.
Fig 1. Kinetic curves of triphenylphosphane oxide formation demonstrating comparative reactivity of oxo-atom transfer from the different dioxo- Mo-complexes to the substrate triphenylphosphine [37].

The complex synthesized by the following reaction [39]

\[
[\text{SCN}_4\text{Mo}^{VII}\text{O}_2]^{2-} + \text{Ph}_3\text{N} \rightarrow \text{Ph}_3\text{ON}^{\text{O}}\text{O}^{\text{O}}\text{Mo}^{VII}\text{O}_2 + 2\text{SCN}^{-}
\]

exhibits an exceptional oxidative reactivity towards alcohols, some olefins, aryl alkanes and their derivatives. Some reactions of Mo(VI)O(SCN)$_2$(4,4′-di-tert-butyl-2,2′-bipyridine) complex with different substrates are given below:

1. Phosphines

\[
\text{PPh}_3 + \text{DMSO} \rightarrow \text{PPh}_3\text{O} + \text{DMS}
\]

The reaction occurs stoichiometrically with complex and becomes catalytic in addition of DMSO [40].
2. Alcohols

\[ R\text{CHOH} + \text{DMSO} \rightarrow R\text{C}=\text{O} + \text{DMS} \]

\( R, R' = \text{H, Alkyl, Aryl} \)

The reaction may be used for oxidation both primary and secondary alcohols. Example: diphenylcarbinol quantitatively (94%) reacts with complex giving acetophenone at 80°C, in benzene, during 1h. In the same conditions benzyl alcohol is oxidized to benzaldehyde. In the presence of DMSO the reaction is catalytic [40].

3. Aryl alkanes

Example: the oxidation of tetraline by this complex at 80°C for 3h gives \( \alpha \)-tetralol and \( \alpha \)-tetralone, at 100°C or under UV-irradiation. The yield of \( \alpha \)-tetralone becomes quantitative and the reaction occurs catalytically in the presence of DMSO [40].

4. Olefins

Example: styrene stoichiometrically reacts with complex, gives 30% epoxide at 80°C after 8h, the reaction becomes catalytic under UV-irradiation or in addition of Ph\(_2\)SO [40].

The investigations in this field show that catalytically active dioxo-molybdenum(VI) dithiocyanatobipyridinic complex exists in two forms: as “terminal” (1) and as “bridging”-oxo or µ-oxo (2) entries. The conformational equilibrium of µ-oxo-dimers (2) can be clearly observed by \(^1\text{H}\) NMR spectroscopy [43].
Each form of these complexes is active in a number of reactions with the above mentioned and other organic molecules. However, one major problem limits the wide application of these complexes as catalyst, when the direct oxidant is O$_2$. Indeed, the oxo-atom transfer to substrate in solution results, more or less rapidly, to the formation of a reduced oligomeric $\mu^2$-peroxo-Mo(V) entry which is inert for reoxidation and, therefore, stops the catalytic reaction. The Mo(V)-complex was isolated and identified spectrophotometrically, as well as by X-ray crystallographic analysis [44]. The formation of the Mo(V)-oxo species can be schematized in the following manner:

The optimization of catalytic behaviors in these systems can be reached only by prevention of the dimer-Mo(V) formation. One approach would be to use ligands with a high steric requirement to avoid dimerization, and another to isolate the metallic centers on a solid matrix.
As shown in [45-51], the second way to resolve the problem brought satisfactorily solutions. In this context, the syntheses of organometallic complexes anchored on the solid matrix have a special importance for studies of oxo-atom transfer reactions.

**Application of anchored Mo-complexes in catalytic reactions**

The immobilization of active sites of organometallic complexes on a solid matrix by chemical bonds was reported in a number of works [45-48]. The different modifications of silica are well known as solid phase matrix for grafted or anchored organometallic catalysts [49-51]. Titania (TiO$_2$) also was used as a support material for synthesis of organometallic complexes anchored with the surface hydroxyl groups, composing new photosensitive materials [52-55]. Molybdenum oxo–peroxo-complexes, linked on mesoporous silica via acetamid groups, exhibit catalytic activity in epoxidation reactions [56, 57].

The dioxo-molybdenum(VI)-dichloro[4,4’-dicarboxylato-2,2’-bipyridine] complex covalently anchored on a TiO$_2$ (Fig. 2) has been synthesized and characterized by $^{13}$C and $^{15}$N solid state NMR spectroscopies [58-59].

![Image of dioxo-molybdenum(VI)-dichloro[4,4’-dicarboxylato-2,2’-bipyridine] complex anchored on a TiO$_2$](image)

**Fig. 2.** The dioxo-molybdenum(VI)-dichloro[4,4’-dicarboxylato-2,2’-bipyridine] complex anchored on a TiO$_2$ (a), photo sensitization of anchored complex under visible light or UV-irradiation (b).

Recently the synthetic route of this new complex was simplified using a nearly one-pot process: transesterification of the trimethylsilylated titania with the carboxylic ligand giving trimethylsilanol (eliminated as hexamethyldisiloxane and water), then the complexation was done by treating the anchored complex with a THF solution containing the calculated amount of MoO$_3$Cl$_2$ [(60):]
One of the characteristic properties of the great importance of this material is its photo sensibility under visible light or UV-irradiation. TiO$_2$ has a number of crystal modifications, however, among them the anatase and rutile structures are most common. As a semiconductor the anatase (n-type) has a band gap equal to 3.23 eV (384 nm) and the rutile (p-type of semiconductor) 3.02 eV (411 nm) [61].

In spite of the absence of experimental measurements, the changes in the electronic and chemical properties of anchored complex may be qualitatively interpreted in the frame of the Wolkenstein theory [62]. When a molecule is chemisorbed on the semiconductor surface, the Fermi level changes its energetic position within the band gap, and the redistribution of electron density takes place in this system, therefore, the chemical properties of anchored complex can be changed. It might be suggested that in this system the electron transfer to molybdenum-oxo bond via TiO$_2$ solid matrix takes place. Titanium dioxide is known as a photosensitive material and the charge transfer from TiO$_2$ to the chemisorbed molecule may be more effective under visible or ultraviolet irradiation ($\lambda < 380-400$ nm). Scheme 8 represents the energetic diagram for titanium dioxide photo sensitization in a redox system.
Scheme 8. Energetic diagram for titanium dioxide photo sensitization in a redox system [61].

The probable mechanism of the photo sensitization of dioxo-molybdenum(VI)-dithiocyanato[4,4’-dicarboxilato-2,2-bipyridyne] complex anchored on the surface of TiO$_2$ has been discussed also in [63].

The reactivity of dioxo-molybdenum(VI)-dihalo[4,4’-dicarboxilato-2,2-bipyridyne] complexes anchored on the surface of TiO$_2$ were tested in oxidation processes of organic compounds of different classes, such as triphenylphosphine, tetraline, ethylbenzene and very recently in oxidative destruction of 1-chloro-4-ethylbenzene using molecular oxygen as the direct oxidant [58-60, 64]. All these reactions are heterogeneous processes as TiO$_2$ is not soluble in ordinary organic or inorganic solvents. Reactions were carried out under visible light or UV-irradiation. In all experimental studies a special protocol was chosen in order to observe the role of the complex in various processes. The oxidation of substrates by the anchored complex was carried out in the conditions excluding the presence of molecular oxygen in reaction media, using inert gases (argon, helium) or N$_2$. After the definite period of time, the O$_2$ was allowed through the reaction mixture in the dark, with the aims of regeneration of the initial Mo(VI) complex. This procedure was repeated periodically until completion of experiment. Fig. 3 and 4 represent the curves of the time profiles of main products of two reactions: oxidation of ethylbenzene onto acetophenone (under visible light irradiation) [60] and oxidative destruction of 1-chloro-4-ethyl benzene onto chlorobenzene (under UV-irradiation) [64]. In all represented cases after the definite periods, reactions become catalytic and the quantity of final product calculated for 1 mol of complex increases during the reaction, which is a direct evidence of catalytic character of these reactions. For oxidative destruction of 1-chloro-4-ethyl benzene the catalytic cycle is as follows (Scheme 9):
Scheme 9. Proposed catalytic cycle of the oxidative decomposition of 1-chloro-4-ethylbenzene by dioxo-Mo(VI)-complex anchored on the TiO$_2$[64].

The advantage of anchored complexes in catalytic processes is obvious. The metallic active centers are isolated via an organic ligand covalently bonded on the surface. The formation of Mo(V) species or its oligomers were not observed. In [64] the absence of Mo(V) species after the reaction had been controlled experimentally by EPR method. On the other hand, the anchored complexes are photo chemically sensible catalysts in oxo-atom transfer processes.

Fig. 3. Time evolution profiles of acetophenone ([acetophenone] mol / [MoO$_2$] mol) 100 (%) in ethylbenzene oxidation [60].
Fig. 4. Time evolution profiles of products in oxidative decomposition of 1-chloro-4-ethylbenzene. $\alpha = \frac{[\text{final product}]}{[\text{dioxo-Mo-complex}]} \times 100 (%)$, ClC$_6$H$_5$ (●), ClC$_6$H$_5$C(O)CH$_3$(□), ClC$_6$H$_4$CH(OH)CH$_3$(▲). 1; 3; 5; 7: periods under UV-irradiation and argon, 2; 4; 6: periods of O$_2$ flow in the dark [64].

At least two aspects of the future possible perfection of these systems can be previewed. The first is the use of various porous and modified structures of TiO$_2$ (including the doping in structure, regulation of photocatalytic properties) and the second is the choice of a ligand sterically facilitating the efficiency of oxo-atom transfer.

**Conclusion**

In this review we have represented a number of examples of transition metal-catalyzed oxidation processes occurring by an oxo-atom transfer reaction mechanism. These examples show the existence of certain peculiarities and “common effects” exhibited in oxidation reactions. Evidently, the specificity of oxo-transfer reactions first of all is related to the nature of transition metal-oxygen bond. The influence of the “effect of spectator” to the reactivity of the “actor” moiety may be observed nearly in all transition metal oxo-transfer-catalyzed reactions. Sometimes, the concept of “proximity effect” between two “neighboring” dioxo-molybdenum moieties are useful to understand some specific peculiarities of the oxo-transfer process.

However, the most important aspect for catalytic activity of these complexes remains the capacity to transfer oxygen atom to a substrate, and the ability of transition metal center to combine with dioxygen forming metal-oxo or metal-oxo-peroxo entities.

The application of dioxo-Mo complexes, anchored on the solid matrix, shows catalytic activity in different oxidation processes in the presence of molecular oxygen. The heterogenization of homogeneous catalysts by immobilization of complexes on a solid matrix brings also some major advantages, one of which is the facility of the separation of reaction products, and the other is the possibility of varying either material or its chemical and photochemical properties, prompting catalytic activity of the anchored complexes in a desired direction.
The investigation of the detailed mechanism of above represented catalytic cycles have a great importance not only for synthetic chemistry, including industrial processes, but also for the modeling and understanding of enzymatic reactions which are extensively spread in nature. The perspective for development in this field is related with the rational design and synthesis, either heterobimetallic or heteropolymetallic complexes anchored on a solid matrix by a sterically amended and specific organic ligand.

High selectivity, mild conditions of reaction, use of dioxygen in a number of oxo transfer reactions indicate the possibility to create processes at the nanoscale level which are analogous and comparable by their parameters with the enzymatic transformations.

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РЕАКЦИИ ПЕРЕНОСА ОКСО-АТОМА КОМПЛЕКСОВ ПЕРЕХОДНЫХ МЕТАЛЛОВ В ОКИСЛИТЕЛЬНЫХ КАТАЛИТИЧЕСКИХ ПРОЦЕССАХ С $O_2$ В СВЕТЕ ПОСЛЕДНИХ РЕЗУЛЬТАТОВ В ХИМИИ ОКСО-МОЛИБДЕНОВЫХ СОЕДИНЕНИЙ

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Реакции переноса оксо-атома комплексов переходных металлов в окислительных катализитических процессах широко распространены в живой природе и применяются в химической и фармацевтической промышленности. В этой работе представлены некоторые особенности применения реакций переноса оксо-атома в тех окислительных катализитических системах, в которых в качестве окислителя используется молекулярный кислород. Большая часть представленных литературных данных относится оксо-молибденовым комплексным соединениям, включая данные полученные Г. Арзуманяном и его сотрудниками в лаборатории CNRS (Франция) в Марселе. Описаны некоторые особенности природы химической связи металл-кислород, которые играют важную роль в реакциях переноса оксо-атома. Обсуждена роль оксо- и оксо-пероксо-металлических центров в различных координационных окружениях в механизме катализитического цикла окисления. Показано, что закрепление этих комплексов на поверхности твердого тела улучшает катализитические свойства системы в реакциях с различными субстратами.

REFERENCES


