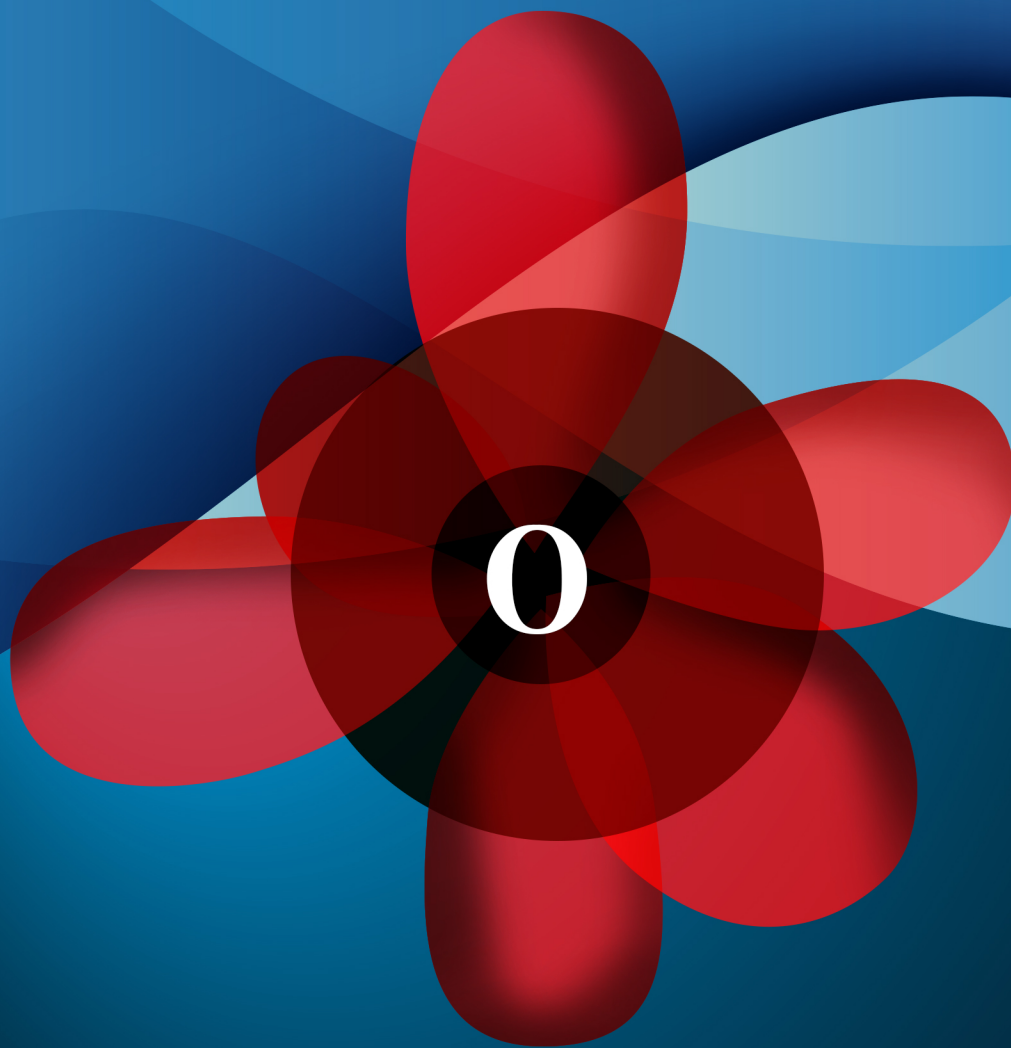


# OXYGEN ATOM TRANSFER REACTIONS



**Editor:**  
**Robert Bakhtchadjian**

**Bentham Books**

**CHEMICAL REACTION MECHANISMS**

*Mechanisms of Oxidation Reactions*

*Volume 1*

**Oxygen Atom Transfer  
Reactions**

Edited by

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## FOREWORD

Oxygen atom transfer reactions have been widely explored in biological systems and chemical synthesis studies. This volume outlines some basic mechanistic understanding and recent achievements in the study of the oxygen atom transfer reactions catalyzed by transition metal-oxo complexes. The influence of the nature of the central metals and the coordinated ligands on mechanisms of oxygen atom transfer reactions are summarized. In the first chapter, the type of oxidation reactions and the general classification of oxygen atom transfer reactions are introduced in detail. It is very useful for readers to be acquainted with the catalytic oxidation reaction via oxygen atom transfer of organometallic complexes. The following chapters of this volume are reviews involving the study of different aspects of oxygen atom transfer reaction mechanisms, such as O<sub>2</sub> activation driven by transition metal complexes and oxygen atom transfer reactions catalyzed by nickel-based organic complexes. These chapters provide readers with some efficient catalytic strategies for the activation of O<sub>2</sub> and the functionalization of C-H bonds and C=C bonds. This volume not only offers the basic knowledge of oxygen atom transfer reactions but also introduces the main development of this field. This book is promising to play an important role in motivating the interests of chemists and biology scientists from all over the world to further develop oxygen atom transfer reactions. The knowledge obtained in this field should also serve other oxidation reactions.

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## SERIES PREFACE

The investigation of the reaction mechanism plays a central role in chemistry. The overall chemical transformation of substances is a complex process that often involves elementary chemical reactions, the sequence of which composes the reaction mechanism. Modern perceptions of the mechanisms of chemical reactions are based on both experimental and theoretical investigations in physics, chemistry, and biology. The study of reactions and their mechanisms requires periodic adjustment, detailing, and permanent perfection in the light of new experimental data and theoretical perceptions. The discovery of new reactions and investigation of their kinetic peculiarities change the perceptions of the existing reaction mechanisms. Sometimes, over a long period, perceptions of how the reaction occurs can be changed so much that only the historical significance of their initial version of the mechanism may remain in science. The introduction of new ideas and new concepts in science and the changes related to the reaction mechanism is a permanent process. However, usually, this information is scattered across various specialized periodicals and scientific reports. It is clear that for a certain period, it becomes necessary to collect and summarize information about the reaction mechanisms in more general editions in the form of book series.

In this context, the aim of the creation of this Book Series is to present a certain part of the modern achievements in mechanism investigations in some important fields of chemistry and biology. The mechanisms of various classes of chemical reactions will be the subject of separate volumes of this book series. The first two volumes are devoted to the mechanisms of oxidation reactions.

The first volume is entitled as:

***Mechanisms of Oxidation Reactions: Volume 1. Oxygen Atom Transfer Reactions***

I am grateful to Bentham Science for this opportunity to create and edit this Book Series.

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## PREFACE

Understanding the reaction mechanism is one of the keys to achieving controllable processes in chemistry, biology, and some applied sciences. Obviously, this refers to oxidation processes that are so widespread in nature, including living cells, and in manmade systems, including the chemical industry. Oxidation processes in the chemical industry are mainly catalytic reactions, in general, using metals, their oxides or organometallic compounds as catalysts. In living systems, enzymes, natural complex catalysts, also containing metallic elements, most of which are organometallic complexes of transition metals play a similar role. From the viewpoint of the reaction mechanism, the reactions occurring *via* the transfer of oxygen atoms to the substrate are one of the widespread types of oxidation processes, observed both in manmade chemical and natural biological systems. Currently, the high efficiency and selectivity of enzymatic oxidation under very mild conditions are not yet available in manmade chemical systems. What and how can we learn from Nature? Two very close and, at the same time, different approaches may serve this purpose. They are known as bio-inspiration and biomimicry. In this regard, the present volume, discussing different catalytic strategies, also involves certain achievements obtained both in bio-inspired and biomimetic systems in comparison with the application of traditional organometallic catalysts of transition metal elements in oxidation reactions.

The intended audience of this book may comprise not only researchers in the fields of chemistry, physics, and biology, but also practitioners in the fields of chemical and biological engineering, pharmaceutical industry, medicine, as well as students at different learning levels. For this reason, the first chapter is written mainly for scientists and engineers, as well as other interested specialists, undergraduates, and postgraduates, who are not familiar with the problems of oxidation processes occurring by the mechanism of oxygen atom transfer reactions to substrates. This chapter acquaints the reader with some fundamentals related to the kinetic peculiarities of these reactions, which may be useful for understanding the state-of-the-art in this area of investigation. Present developments in at least two main branches of catalysis are based on achievements in this area of investigation. One of them is catalytic or enzymatic oxidation of organic substrates by the participation of transition metal-oxo compounds in the presence of different oxidants, including dioxygen. The second important area is considered the catalytic or photocatalytic oxidation of water using transition metal-oxo complexes. Both of these branches are of fundamental importance in biology. As a part of the biological evolution of life, Nature carries out these chemical transformations using enzymes, through the reactions of oxo-atom transfer in photochemical formation of oxygen (oxygenic photosynthesis), on the one hand, and its reduction in the respiration processes, on the other hand. In this chapter, the main types of oxidation reactions and the place of oxygen atom transfer reactions in their general classification, from the point of view of the mechanisms, have been discussed. Modern perceptions of the mechanism of oxygen atom transfer reactions in oxidation processes by the participation of transition metal-oxo complexes permit to distinguish at least two main types of reactions. Here, a brief description of these has been presented. The first group of mechanisms involves inner sphere reactions of transition metal-oxo complexes forming an intermediate complex with the substrate with the direct participation of the metallic centers. Then, this intermediate decomposes into an oxygenated product and a reduced form of the initial metal in a complex compound. For the second type of mechanism, named the outer sphere reaction mechanism, it has been considered that the intermediate complex is formed due to the interaction between the oxo-ligand of transition metal complex and the substrate. This chapter addresses the different aspects of the problems of the functionalization of C-H bonds of organic compounds in oxidative catalysis by transition metal-oxo complexes. According to the accepted mechanism, the catalytic cycle involves either the direct transfer of oxygen-atom from the catalyst to the substrate or the

hydrogen atom abstraction from the substrate, hydroxylation of metal-ion and subsequent formation of oxygenated products. To perform this catalytic cycle, the reduced metal-ion returns to its initial state being oxidized by another oxidant in the reaction medium. Thermodynamic and kinetic analyses of the catalytic cycles indicate that the major factors determining the reaction mechanism are the energy required to rupture the C-H bonds in oxo-atom transfer reactions and the energy of metal-oxygen bond in re-oxidation of metal. For a successful catalysis, these two energy values must be comparable. These problems are briefly discussed in this chapter. In the last section of the mentioned chapter, the mechanism of oxo-atom transfer reactions has been discussed in light of the phenomenon of multiple spin-state reactivity. It has been exemplified by the reactions of “bare” transition metal-oxo cations  $(MO)^+$ , where M is a transition metal, with inorganic ( $H_2$ ) and organic ( $CH_4$ ) compounds. A great number of theoretical calculations and experimental results indicate that the relationships between the spin states of transition metal-oxo complexes and their reactivity are common for the majority of oxo-atom transfer reactions in the catalysis. In chemical or biological systems, changes in the spin state in transition metal-oxo complexes and, consequently, changes in the reaction pathways permit to explain some of the unusual kinetic features observed in oxo-atom transfer reactions.

The following two chapters of the present volume are scientific reviews devoted to the different aspects of some modern problems of the mechanisms in oxygen atom transfer reactions mainly related to the biological systems. Chapter 2 discusses the mechanisms of oxygen atom transfer reactions related to the bio-inspired activation of dioxygen and its subsequent reactions. The mechanisms of enzymatic oxidation are compared with the schemes of catalytic cycles in oxidation by transition metalorganic complexes as synthetic models of enzymes. In general, this chapter, to some extent, summarizes different catalytic strategies (bio-inspired, biomimetic, synthetic models of enzymes, industrial catalysts) in the activation of dioxygen and its further reactions, including oxygen atom transfer reactions from transition metal complexes to substrates. The bio-inspired activation of dioxygen is exhibited in examples of substrate oxidation by some popular enzymes, such as P450s, monooxygenases, and dioxygenases. Here, the catalytic cycle for P450 is based on the heme-Fe(III) complex, which forms the key intermediate  $Fe(IV)=O^+$  and carries out the hydrogen atom abstraction from RH and further transfer of OH to the substrate. This is a classic example of the oxygen rebound mechanism activating the C-H bonds *via* the radical pathway. A number of other examples demonstrate the widespread importance of oxygen rebound mechanisms in biomimetic chemistry. The analogies and differences of the catalytic cycles of monooxygenases and dioxygenases in bio-inspired oxidation of substrates have been discussed using numerous examples. Here, the discussion is also centered on comparable descriptions of the differences in the enzymatic cycles of dioxygenases with respect to the structural and chemical peculiarities of substrates. For example, according to the proposed schemes, when the pyrrole ring of L-tryptophan is cleaved and two oxygen atoms are inserted into the structure, in the case of tryptophan 2,3-dioxygenase (TDO) and indoleamine 2,3 dioxygenase (IDO), the supplier of four electrons to the oxygen atoms is the same substrate, but in schemes for intradiol ring-cleaving dioxygenases and extradiol dioxygenases, the activation of oxygen requires two electrons from external donor(s) other than the substrate. Special attention has been paid to oxidation systems which are of interest to the chemical and pharmaceutical industries. Among them, the cleavage of C=C bond and stereoselective or asymmetric epoxidation of olefins catalyzed by synthetic transition metalorganic complexes is one of the important areas in modern catalysis. The final section of this chapter covers new catalytic strategies for the activation of dioxygen in oxidation reactions. Among the numerous factors influencing the catalytic activity, the structure of the first coordination sphere of the metal-ions and the surrounding hydrogen bond network is crucial for the successful oxidation of substrates. Apparently, hydrogen bonds play a stabilizing role in the generation of

superoxo radicals and promote the cleavage of the O-O bond *via* the formation of metal-oxo moieties. Lewis acids play an analogous role in chemical systems. These perceptions have been demonstrated by the example of vanadium(IV) complexes oxidation schemes. Summarizing the literature data presented in Chapter 2, the authors remark that the creation of efficient industrial catalysts, particularly, in olefin epoxidation, may be achieved using dioxygenase-type enzymes that do not require extra electron suppliers.

Unlike the previous chapter, the third chapter is a review highlighting the peculiarities of oxygen atom transfer reactions from the viewpoint of biomimetic chemistry on the examples of only nickel organometallic complexes. On the occasion of the preparation of this chapter, one of the authors, pr. Sankaralingam, wrote: *In synthetic biomimetic model chemistry, iron and manganese complexes are the most exploited catalysts in the realm of organic transformations reactions. In contrast to a large number of high level and comprehensive reviews reported based on Mn, Fe and Cu oxygen species in various oxidation reactions, relatively less emphasis has been put on nickel oxygen species in oxo-atom transfer reactions. This chapter aims at summarizing the noteworthy attempts in oxo-atom transfer reactions catalyzed by nickel complexes.* In this regard, thorough data are available involving the methods of synthesis, characterization, and revelation of the electronic and geometric structural features of the nickel organometallic complexes, as well as reaction intermediates in the activation of dioxygen and further oxygen atom transfer reactions to substrates. Considerable attention has been paid to the effects of the stereoelectronic properties of the ligand structure on the catalytic efficiency in oxo-atom transfer reactions. Chapter 3 consists of three main paragraphs involving the reactions of oxygen atom transfer and hydrogen atom abstraction catalyzed by nickel organic complexes separately, as well as reactions exhibiting both oxygen atom transfer and hydrogen atom abstraction reactivity jointly. The catalytic role of Ni ions of enzymes, such as glyoxylase I, nickel superoxide dismutase, urease, NiFe hydrogenase, CO dehydrogenase, acetyl-CoA synthase and, methyl-CoM reductase, among others, was the subject of a great number of investigations in biomimetic chemistry. In oxidation processes, involving oxo-atom transfer reactions, as has been shown in this chapter, the active forms of complexes mainly contain Ni(I) and Ni(III), and often Ni(0) and Ni(II) species. In the activation of dioxygen, different nickel oxo, peroxy, superoxy intermediates may be formed, the majority of which are active in oxygen atom transfer or hydrogen abstraction reactions. Of particular interest is the section of Chapter 3 devoted to the discussion of the Ni-complexes exhibiting both the oxygen atom transfer and the hydrogen atom abstraction reactivities. Apparently, these observations are related to the electromeric states of Ni-complexes, (i)  $\text{Ni}^{\text{II}}-\text{O}^\bullet$  and (ii)  $\text{Ni}^{\text{III}}=\text{O}$ , exhibiting different reactivity depending on the nature of substrates (for example, the electrophilicity with PPh<sub>3</sub> or CO and nucleophilicity with ArCHO). This review also emphasizes the importance of the ligand architecture in the reactivity of organometallic oxo, dioxy, peroxy superoxy, and hydroperoxy Ni-organic complexes. Usually, their reactivity in oxo-atom transfer reactions correlates with the stereoelectronic properties of the ligands.

The aim of Chapter 4 is to acquaint the reader with the reactions of oxygen atom transfer in the oxidation of organic compounds with dioxygen or other oxidants that occur under visible light or UV irradiation in heterogeneous catalytic systems. Usually, heterogeneous photocatalytic redox reactions occur in multicomponent systems consisting of at least a substrate, oxidant, catalyst, catalyst support, solvent, often also sensitizer. Visible light or UV irradiation may be absorbed by one or more component(s) of the system, which become electronically excited species. Subsequently, they may enter different physical and chemical interactions, transferring energy or electrons to other components involving the catalyst or nominal catalyst. Often, the photochemically generated intermediates, active oxygen species, act as catalysts, for example metal-oxo moieties in transition metal complexes in oxidative

catalysis. Two main classes of reactions, namely the photogenerated and catalyzed photolysis, are known in heterogeneous photoredox systems depending on the type of catalyst functionality. Examples of heterogeneous photocatalytic redox reactions, given in this chapter, involving mainly the reactions of organic compounds on  $\text{TiO}_2$  or  $\text{TiO}_2$ -based semiconductor catalysts, demonstrate the predominant role of oxygen atom transfer reactions in the mechanisms of a great number of oxidation or oxidative decomposition processes. Discussing some aspects of the determination of the type of heterogeneous photocatalytic systems, it was concluded that, seemingly, the majority of known heterogeneous photocatalytic reactions on  $\text{TiO}_2$ , in particular, oxidation through oxygen atom transfer mechanisms, are photoassisted (catalyzed photolysis) processes. Among the oxygen atom transfer agents, transition metal-oxo complexes constitute the main class of compounds widespread in living nature and synthetic chemical systems. Some peculiarities of the photoassisted transfer of oxygen atom in oxidation reactions are discussed in this chapter. Using molybdenum metal-oxo complexes as an example, a significant enhancement of the catalytic activity in oxygen atom transfer on the heterogenization of the homogeneous catalyst was observed. Mo-oxo complexes anchored on  $\text{TiO}_2$  with covalent chemical bonds, exhibit improved photocatalytic activity in selective oxidation and oxidative destruction reactions, such as the interaction of  $\text{O}_2$  with DDT (dichlorodiphenyltrichloroethane) or other chlorophenyl substituted alkanes, which may not be oxidized at so mild conditions even other strong oxidants. All the examples of photocatalytic reactions mentioned in this chapter also indicate that oxidation occurring by oxygen atom transfer is one of the effective pathways for the creation of new catalytic systems that are economically advantageous and environmentally benign.

Generally, all chapters of this volume introduce not only some fundamentals and state-of-the-art, but also the main directions of development in investigations leading to the revelation of the reaction mechanisms in oxygen atom transfer reactions. For obvious reasons, a separate volume cannot address most of the problems in this field. However, I hope that this volume will be of interest to a wide range of readers, from researchers to students. On the other hand, the discussion of certain problems will apparently give rise to new problems and new interests. This is one of the main aims of creating such a volume.

I am very grateful to academician Jincai Zhao for the foreword for this volume. I would also like to acknowledge the valuable contributions of all authors preparing this volume during a very difficult time for humanity, caused by Covid-19 in the world.

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## CHAPTER 1

# Introductory Notes on Mechanisms in Oxygen Atom Transfer Reactions of Transition Metal Complexes

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**Abstract:** Investigations of the mechanisms of oxygen atom transfer reactions of transition metal organometallic complexes are mainly related to their abundance in chemical syntheses and biological oxidation processes. They are important stages in the catalytic and enzymatic oxidation cycles of substrates, as well as in the catalytic oxidation of water.

These brief notes on the mechanisms of oxygen atom transfer reactions involve certain fundamentals (geometric and electronic structures, spin states and reactivity of oxo-complexes), as well as some specific peculiarities of the oxo-atom transfer reactions of transition metal complexes (hydrogen atom abstraction and oxygen rebound mechanisms, intra- and intermolecular types of oxo-atom transfer, multistate reactivity). This chapter introduces readers to the categorization and place of oxo-atom transfer reactions in the classification of catalytic oxidation processes in the context of general problems of the mechanisms in this area. The chapter also provides readers with certain data on the activation of dioxygen and the functionalization of C-H bonds in oxidation processes *via* the oxo-atom transfer reactions of transition metal complexes. The role of the two and multiple spin states reactivity in the mechanisms of these reactions has also been discussed.

This chapter is written mainly for non-specialist readers in this area and serves as a general introduction to the next chapters of this collection of works.

**Keywords:** Oxygen atom transfer, Catalytic oxidation of water, Multiple spin state reactivity, Oxo-atom transfer in catalytic oxidation, Transition metal-oxo complexes.

---

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## INTRODUCTION

This chapter of introductory notes on oxygen atom transfer reactions is devoted to the reaction mechanisms of oxidation processes by the participation of transition metal-oxo compounds (transition metal oxides, metalorganic complexes with different ligands, and salts of transition metals). Compared to the next chapters of this volume, it is addressed primarily to readers who are not specialized in this area of investigation. The availability of scientific information to readers unfamiliar with the mechanisms of oxidation reactions requires a preliminary acquaintance with the scientific outlines of general problems. Therefore, this brief chapter, in my opinion, may be useful for researchers, engineers, or students working in neighboring fields, as well as for readers who are first acquainted with the catalytic oxidation reactions by transfer of the oxygen atom of transition metal organometallic complexes.

The revelation of the reaction mechanisms of oxygen atom transfers of transition metals is of pivotal importance for understanding, influencing, and even, controlling the catalytic oxidation of organic or inorganic compounds, including the biological oxidation processes. Oxygen atom transfer reactions are basic stages in the two main domains of oxidation catalysis: (i) oxidative addition of an oxo-atom of transition metals or their complexes with different ligands to organic and inorganic compounds (substrates), and (ii) oxidation of water by the catalysts or enzymes. These catalytic processes are widely used in chemical syntheses on both laboratory and industrial scales and are also basic in understanding the natural biological processes of oxidation occurring through the participation of enzymes. According to the opinion of Gray [1, 2], a pioneer in the area of the electronic structure of metal-oxo complexes, from the point of view of the biological evolution of life on our planet, these two chemical transformations may be considered “top reactions,” since one of them is related to the photochemical oxidation of water forming oxygen, and the other is a reduction of oxygen to water during respiration. To carry out these reactions, nature has created complex “machines,” enzymes, using transition metal elements. Oxo-atom transfer reactions play an essential role in both basic biochemical transformations. In this regard, the great importance of investigations in this area is evident in the biology, chemical synthesis, medicine, chemical and pharmaceutical industries, *etc.*

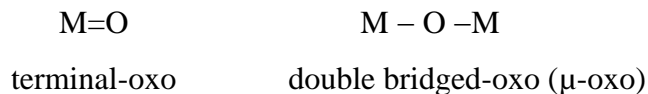
### Transition Metal-oxo Complexes and their Formation

According to the IUPAC nomenclature, the chemical entities containing one (single) oxygen atom doubly bonded ( $=O$ ) to the atom of another chemical element are termed oxo-compounds [3]. If that chemical element is carbon, the oxo-compounds can be aldehydes, ketones, carboxylic acids, and so on. In another

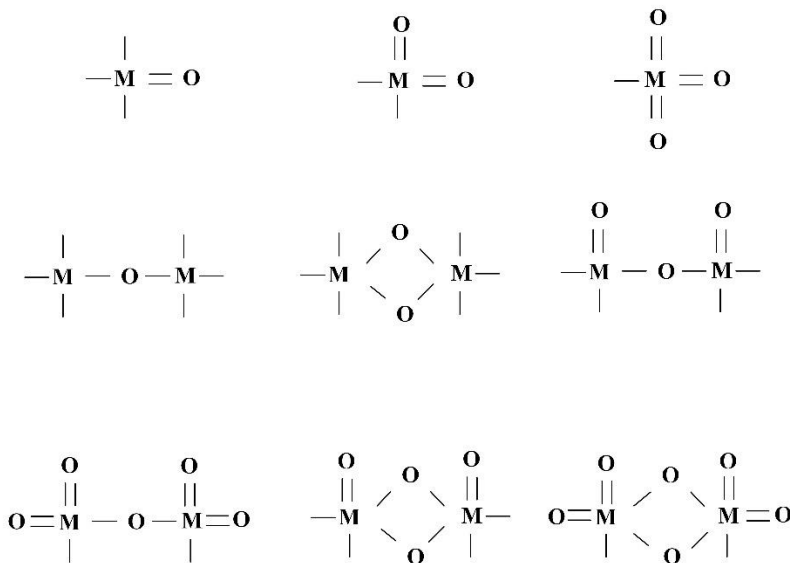


case, if that element is a metal or semimetal (or their ions), the formed chemical entities are metal-oxo ( $M=O$ ) compounds, for example oxo-molybdenum; oxo-tungsten, *etc.* Here, formally,  $O^{2-}$  is a ligand bonded to a metal or metal ion ( $M^{n+}$ ). Compounds of the d- and f-block transition metals of the periodic table containing oxo ligand(s) and various organic and inorganic ligands, constitute a large class of transition metal-oxo coordination complexes [4, 5].

In oxo-complexes of transition metal elements, an oxygen atom can be bonded to one or more metallic centers. If it is bonded to only one metal atom, the compound is named mononuclear and the oxo-atom is named "terminal-oxo". If the complex is binuclear, the oxo-atom is named double bridged-oxo [4].



Depending on the number of oxo-atoms, the compounds are named mono-, di(bi)-, tri-, polyoxometallic or organometallic complexes. Moreover, the fragments of the chemical structures presented below can be moieties in organometallic complexes of different geometries.



## CHAPTER 2

# Bio-Inspired Dioxygen Activation and Catalysis By Redox Metal Complexes

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**Abstract:** In nature, redox enzymes mediated dioxygen activation with oxidations proceeds smoothly and highly selectively under ambient temperature, whereas in the chemical industry, versatile oxidations are commonly performed at elevated temperature, which leads to the occurrence of radical chain process, thus causing low product selectivity and environmental pollution. This chapter will first introduce the strategies of enzymes including P450s, methane monooxygenase, dioxygenases in dioxygen activation and catalysis, thus illustrating how enzymes activate dioxygen and selectively transfer the resulting active oxygen to their substrates. Then, inspired by enzymatic dioxygen activation, the progress in biomimetic dioxygen activation with related catalytic oxidations by synthetic redox metal complexes will be presented, and its current challenges will be discussed as well. Finally, a recent new strategy for dioxygen activation and catalysis, that is, Lewis acid promoted dioxygen activation by redox metal complexes, will be introduced; this new strategy may have more closely biomimicked enzymatic dioxygen activation than those traditional strategies, thus shedding new light on catalyst design for industrial oxidations.

**Keywords:** Bio-inspired O<sub>2</sub> activation, Catalytic oxidation, Enzymatic O<sub>2</sub> activation.

## INTRODUCTION

Oxidation is one of the most significant processes in nature and the chemical industry. In biological cells, versatile redox enzymes can highly efficiently activate dioxygen and transfer the resulting active oxygen to the substrate with high selectivity at ambient temperature. To achieve this target, the co-enzymes, the active sites of proteins combined together with the electron transfer chain, if needed, synergistically catalyze dioxygen activation and oxygen transfer. However, in the chemical industry, most of the oxidations are performed at eleva-

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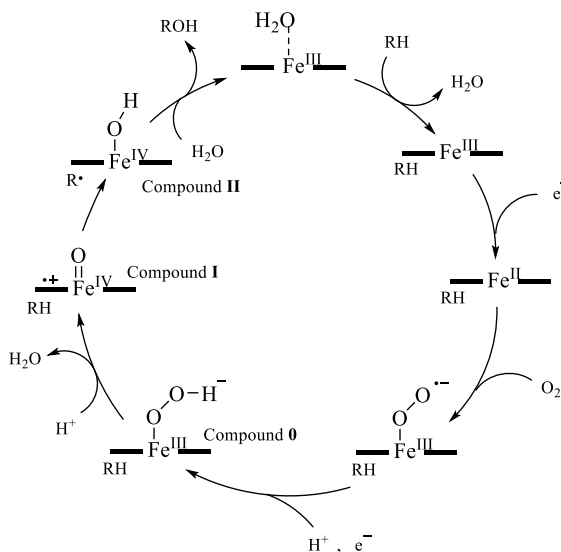
ted temperature for achieving reasonable oxidation efficiency, and radical chain processes are hardly avoided, which leads to the low selectivity of the targeted products with resource loss and environmental pollution. Even more seriously, the stoichiometric oxidants are employed in certain cases. For example, the production of adipic acid, a significant monomer for polyamide-6,6 synthesis, represents one of the most important, but also most polluted oxidations in the industry [1]. Commercially, adipic acid is mainly produced through air oxidation of cyclohexane to cyclohexanol and cyclohexanone (KA oil), followed by nitric acid oxidation. The first process in Dupont's is performed at 155-165 °C and 8-10 atm with Co-Mn catalyst, and the oxidation proceeds through a classic radical chain process [2]. To achieve an 85% selectivity of KA oil, the conversion of cyclohexane needs to be controlled below 5-7%. The next nitric acid oxidation of KA oil can achieve 95% selectivity with 100% conversion by using Cu-V catalyst, however, it suffers severe drawbacks including the use of corrosive nitric acid as the oxidant and the unavoidably leaching of N<sub>2</sub>O to the atmosphere, which contributed a significant content in the global N<sub>2</sub>O emissions. Up to now, industrial oxidations still face serious challenges in dioxygen activation and next selective oxygen transfer to the substrate when compared with those biological oxidations. Currently, the catalytic cycles of dioxygen activation and oxygenation by redox enzymes have been mostly interpreted for some significant oxidation events in nature, and many bio-inspired strategies for dioxygen activation have also been explored for chemical oxidations [3, 4], however, the applications for these biomimetic oxidations in large scale industry is still scarce. This chapter provides a brief summary of the dioxygen activation mechanisms of some popular enzymes with their inspired catalytic oxidations by redox metal complexes.

## **Dioxygen Activation and Catalytic Oxygenation by Cytochrome P450, Methane Monooxygenases With Their Synthetic Models**

### ***1) P450 Mechanism***

The cytochrome P450 enzymes represent a superfamily of hemoproteins, which are responsible for the metabolism of xenobiotics and the biosynthesis of critical signaling molecules used for control of development and homeostasis [5, 6]. The active site of the P450 enzymes consists of a heme-iron with a fifth proximal Cys ligand, and the sixth coordination site of the iron center is the site for dioxygen activation with related oxygenation reaction. A simplified mechanism for P450 mediated substrate hydroxylation is illustrated in Scheme 1. The catalytic cycle starts from the substrate RH binding to the resting state of P450, that is a heme-iron(III) complex, which triggers the change of the spin state of the iron(III) from LS to HS. Next, the electron transfer from NAD(P)H to the iron(III) reduces it to iron(II). Dioxygen activation by the resulting iron(II) generates an iron(III)-OO<sup>-</sup>

superoxo radical species. Further electron and proton transfer to this iron(III)-OO<sup>•</sup> species yields an iron(III)-OOH<sup>-</sup> species, which is called the compound 0. Then, the proton assisted hetero-cleavage of the peroxide leads to the formation of the iron(IV)=O<sup>+</sup> cation radical intermediate, which is called the compound I, an formal iron(V)=O species. This iron(IV)=O<sup>+</sup> functions as the key active species for coming substrate oxidations. After the hydrogen atom abstraction from the substrate RH by the iron(IV)=O<sup>+</sup>, it generates a substrate radical, R<sup>•</sup>, with the iron(IV)-OH species, which is called compound II. Next, the iron(IV)-OH transfers the OH group to R<sup>•</sup> to give the resting state of the catalytic cycle, the heme-iron(III) complex, with the oxygenation product ROH. This oxygenation mechanism by compound I is called as oxygen rebound mechanism, which was coined by Groves [7]. We may see from Scheme 1, and will further discuss it in the future, that the electron transfer from NAD(P)H plays a key role in triggering dioxygen activation through reducing the iron(III) to the corresponding iron(II). The hydrogen bond network around the active site also play a crucial role in stabilizing the resulting iron(III)-OO<sup>•</sup> superoxo radical species after dioxygen activation, and in driving the next O-O bond cleavage in the iron(III)-OOH species to generate the compound I, which is responsible for substrate oxidation. In addition, you may also see that P450 enzymes are monooxygenases, which transfer one oxygen atom from dioxygen to their substrates to generate the oxygenation product with another oxygen atom from dioxygen released into the surrounding water.



**Scheme (1).** A simplified catalytic cycle for P450 mediated substrate hydroxylation reaction.

## Highlights of Oxygen Atom Transfer Reactions Catalysed by Nickel Complexes

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**Abstract:** Oxygen atom transfer (OAT) reactions catalyzed by metal complexes have been a subject of intensive research over the century, owing to the prevalent involvement of OAT in organic transformations mediated by several biologically important enzymes such as methane monooxygenases, cytochrome P450, etc as well as in synthetic chemical reactions. In biomimetic model chemistry, iron and manganese complexes are the most exploited catalysts in the realm of oxygen atom transfer reactions and many of these metal complexes produce very short-lived reactive metal-oxygen intermediates during the catalytic reactions. Characterization of such reactive intermediates of numerous heme and non-heme iron and manganese complexes and comparing them with their natural enzyme analogous have emerged as a promising approach toward understanding several intricate enzymatic mechanisms. Considerable research advancements in the studies of OAT reactions involving late transition metal complexes such as cobalt, nickel, and copper have also been recognized in the past few years. In this account, various reports have been published, demonstrating catalytic oxidation of organic substrates by the active nickel-oxygen species generated either *via* heterolysis or homolysis of O-O bond of oxidant bound nickel complexes. This book chapter aims at a comprehensive summary of noteworthy attempts contributed towards nickel catalyzed OAT reactions and various implicated or well-characterized nickel-oxygen active intermediates. The effect of stereoelectronic properties of ligand architecture on catalytic efficiency and various characterization techniques used to identify the catalytically active nickel-oxygen species are also discussed.

**Keywords:** Oxo atom transfer reaction catalyzed by nickel complexes, Hydrogen atom abstraction reaction catalyzed by nickel complexes.

### INTRODUCTION

In nature, enzymes are the most complicated yet fundamental molecules. Apprehending the intricate catalytic processes involved in enzymatic reactions

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has remained a challenge until the emergence of biomimetic chemistry by bioinorganic chemists. Biomimetic chemistry involves the design, synthesis, and reactivity studies of model systems of biological molecules and it has become an effective approach to comprehend complicated enzymatic reactions [1 - 10]. Rigorous research on various model complexes of non-heme and heme enzymes has paved the way for reinforcement of our understanding of the detailed mechanism and the process of dioxygen activation in various enzymes [11 - 22]. Iron is one of the main protagonists in the field of oxo atom transfer reactions and cytochrome P450 (CYP 450) is the most celebrated and studied enzyme in this area. Identification of the involvement of a high-valent iron(IV)-oxo porphyrin cation radical species (Compound I) generated *via* putative heterolytic cleavage of O-O bond in the catalytic cycle of CYP 450s has attracted great research interest among biomimetic chemists [23]. Intensive research efforts to examine the chemical and physical properties of compound I to compare this intermediate with other such enzymatic analogous have always been a matter of interest. Organic transformation reactions especially oxidation reactions such as epoxidation, sulfoxidation, hydroxylations, carbonylation, *etc.* have fascinated a lot of researchers because of their biological and industrial importance. Epoxides are useful intermediates in the production of polyurethane, polyamides, polyesters, resins, and in bioinspired oxidation to produce drug metabolites. Sulfur-containing compounds are well known for their antimicrobial activity and hydroxylated compounds are widely used in petrochemical industry [24]. The first synthetic iron(III) porphyrin complex catalyst for olefin epoxidation and alkane hydroxylation was reported in 1979 by Groves *et al.* [25] and, iron porphyrin chemistry has been a subject of study since then. Various metalloporphyrins models of CYP450s capable of catalyzing the oxidation of hydrocarbons, alcohols, sulfides, and olefins have been reported over the past three decades [26]. Rahimi and co-workers demonstrated a CYP450 model reaction by a Cu(II) meso-tetraphenyl porphyrin in the oxidation of benzyl alcohols to corresponding carbonyl compounds [27]. Nam *et al.* reported the reaction pathways of O-O bond cleavage in hydrogen peroxide and *tert*-alkyl hydroperoxides using iron(III) porphyrin complexes. On the one hand, electron rich porphyrins and hydroperoxide having electron-releasing substituents tend to favor the homolytic cleavage of O-O bond. On the other hand, heterolytic O-O bond cleavage is facilitated by electron-deficient porphyrins and electron-withdrawing group substituted hydroperoxide. Moreover, analysis of the products obtained after iron porphyrin catalyzed the epoxidation reaction of olefins in the presence of hydrogen peroxide or alkyl hydroperoxide can be used to distinguish the mode of O-O bond cleavage. The heterolytic cleavage results showed the formation of stereospecific epoxide with high yields, whereas homolytic cleavage afforded less stereospecific epoxide in lower yield [28]. Very recently, Nam *et al.* reported the

remarkable reactivities of Mn(III)-iodosylarene porphyrins in C-H bond activation and oxygen atom transfer reactions. Interestingly, unlike the iron-oxo porphyrins, the reactivities of these complexes are found to be independent of the electronic nature of the porphyrin ligands [29].

Despite being a trace element, nature prefers nickel center as an active site in a few enzymes such as glyoxylase I, nickel superoxide dismutase, urease, NiFe hydrogenase, CO dehydrogenase, acetyl-CoA synthase, and methyl-CoM reductase [30]. After the discovery of the first-ever nickel-containing metalloenzyme urease, many researchers have been interested to uncover the involvement of nickel in biologically important molecules. Flexibility in its coordination and redox chemistry draws a lot of research interest towards nickel. The presence of nickel center in a few biologically available enzymes such as Ni-superoxide dismutase and quercetin 2,4-dioxygenase that are involved in oxidation reactions has gained considerable research interest in the area of nickel mediated oxidation chemistry [31]. However, when compared to iron and manganese, reports on oxidation reactions involving nickel chemistry are sparse. A number of comprehensive and high-level reviews and book chapters have been published over the years notably concerning the use of iron, manganese, and copper complexes as bioinspired catalysts for the variety of oxidation reactions in biomimetic chemistry [32 - 65]. However, less emphasis has been put on the oxo transfer reactions using nickel complexes but related approaches are developing fast [1]. So we took an opportunity and advantage to summarize the nickel-mediated oxidation chemistry.

### **Oxygen Atom Transfer Reactions**

Oxygen atom transfer reactions such as sulfoxidation, phosphine oxidation, and epoxidation reactions are very important and the resulting products are very useful in many industrial processes. Long ago in 1969, Otsuka *et al.* demonstrated the oxygenation of alkyl isocyanides and triphenyl phosphines by a Ni(II)-peroxo complex derived from the oxygenation of zero-valent nickel isocyanide complex,  $\text{Ni}(\text{RCN})_4$  (R=*tert*-butyl or cyclohexyl). After that, a few articles on CO fixation by a series of nickel complexes such as  $\text{Ni}(\text{NO}_2)_2(\text{PMe}_3)_2$  (**1**),  $\text{Ni}(\text{NO}_2)_2(\text{PEt}_3)_2$  (**2**),  $\text{Ni}(\text{NO}_2)_2(\text{DPPE})$  (**3**) (where,  $\text{PMe}_3$ , trimethylphosphine,  $\text{PEt}_3$ , trimethylphosphine, and DPPE,  $\text{Ph}_2\text{PCH}_2\text{CH}_2\text{PPh}_2$ ) have been reported. During the reaction of these complexes with CO to form  $\text{CO}_2$ , a pentacoordinated intermediate is likely to be involved. The source of oxygen atom was found to be  $\text{NO}_2$  ligand as evident from the  $^{18}\text{O}$ -labeling experiment. Enhanced reactivity of **1** compared to **2** also supported the notion of involvement of a pentacoordinated intermediate,  $\text{Ni}(\text{CO})(\text{NO}_2)_2(\text{PR}_3)_2$  owing to the ability of more basic  $\text{PMe}_3$  to stabilize pentacoordinate monocarbonyl complex [66]. In 2004, Riordan *et al.* identified a

## Mechanisms of Some Heterogeneous Photocatalytic Reactions of Oxidation Occurring *via* Oxygen Atom Transfer

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**Abstract:** Insights into the mechanisms of oxygen atom transfer in the photooxidation of organic compounds for heterogeneous photocatalytic systems have been presented. These reactions have a wide variety of practical applications in chemistry, biology, and applied sciences. The role of the oxygen atom transfer mechanism in homogeneous photocatalysis has been investigated for nearly a century. Relatively little attention has been paid to the disclosure of oxygen atom transfer reactions in heterogeneous photocatalytic systems. This chapter discusses some problems related to the catalytic oxygen atom transfer in the oxidation of organic compounds, mainly with dioxygen, under UV irradiation or visible light, in heterogeneous reaction systems. Various active oxygen species, including oxygen atom transfer agents, as reaction intermediates can be generated in these systems. Depending on the nature of the active oxygen species, including metal-oxo compounds, the photoassisted catalytic oxygen atom transfer can occur mainly by the primary photoexcitation of either the catalyst or its photosensitive solid support, in rare cases, also the catalyst/support complex. The peculiarities of the mechanism of photo-driven oxygen atom transfer were mainly exemplified by the reactions occurring in heterogeneous catalytic systems containing transition metal oxides, their metalorganic complexes, and other photosensitive solid materials, including heterogenized homogeneous photocatalysts on the different supports, such as the transition metal-oxo complexes on the semiconductor materials. Special attention has been paid to the chemistry of TiO<sub>2</sub> and TiO<sub>2</sub>-based semiconductor photocatalysis from the point of view of the reaction mechanisms, including oxygen atom transfer reactions.

**Keywords:** Oxygen atom transfer, Heterogeneous photocatalytic reactions, Reaction mechanism.

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## INTRODUCTION

Photo-driven catalytic reactions are divided into two main branches: homogeneous and heterogeneous photocatalysis [1, 2], although each of them can often be expressed as a bimodal reaction sequence when the key reaction intermediates are transferred from one phase to another [3]. Both heterogeneous and homogeneous photochemical oxidation of organic compounds with dioxygen or other oxidants, more often called photoredox reactions, as a rule, are complex, multistage, and sometimes even multiphase processes occurring *via* the formation and further reactions of different intermediates [4].

The mechanism of photoredox reactions is principally different from the mechanism of thermal reactions, although sometimes the reaction intermediates can be the same in both cases. In a photochemical system that absorbs light energy, one or more components are transferred into excited states, and their further interactions lead to the formation of reaction intermediates and/or products. In this regard, photoredox systems can produce such intermediates (by relaxation of the energetically excited intermediates from a higher energy state to a lower energy state), which may not be generated during thermal oxidation due to energy inaccessibility [5].

Homogeneous photochemical reactions of the oxidation of organic substances, particularly, with dioxygen, in the absence of metal ions or organometallic complexes, are usually radical and chain, often autocatalytic processes. In the presence of metal ions in homogeneous reaction media, the predominant mechanisms of photochemical oxidation are similar to those of reactions with the Fenton reagents, known as photo-Fenton reactions [6]. In the case of the participation of transition metal ions or their organometallic complexes catalyzing oxidation reactions under UV irradiation or visible light, the transfer of electrons or atoms depends mainly on the nature of the central metal ions and their coordination environment [7]. Oxygen atom transfer occurs either by direct insertion of the oxygen atom into the substrate or by the so-called oxygen rebound (radical) mechanisms, *via* the primary abstraction of hydrogen atom from the substrate. The transfer of oxygen atoms can occur either as a stepwise or as a concerted reaction [7].

In heterogeneous photocatalysis, the light energy is absorbed by the solid phase photosensitive component(s) of the chemical system that transforms it into the chemical bond energy. If this transformation takes place on the surface of the catalyst, the photocatalytic process is named “direct”, and, if it occurs through the absorption of light energy by the substrate or substrate-catalyst complex, as well as by another reaction component capable of transferring it to the catalyst or

substrate, it is named “indirect” [8]. The majority of the heterogeneous photocatalysts are semiconductors ( $\text{TiO}_2$ ,  $\text{CuO}$ ,  $\text{ZnO}$ ,  $\text{NiO}$ ), dyes, organic or inorganic polymeric materials [2, 4, 9]. Among them, the exceptional usefulness of the photocatalytic application of “bare” and surface modified  $\text{TiO}_2$  has been revealed in a large number of investigations in recent decades. Taking into consideration the wide application and practical importance of  $\text{TiO}_2$  and  $\text{TiO}_2$ -based photocatalysts in wastewater treatment (AOP technologies), elimination of certain atmospheric pollutants, disinfection of surfaces, *etc* [6, 9, 10], this chapter is mainly devoted to the problems of the mechanism of oxidation in these and analogous systems. Here, we will discuss mainly the problems of “direct” photocatalytic reactions [8].

Investigations of the oxygen atom transfer in heterogeneous photocatalytic reactions are related to the determination or estimation of certain kinetic parameters (rate constant, quantum yield, turnover number, photonic efficiency), the accurate measurement of which is often complicated caused by the complexity of the multiphase and multicomponent photochemical systems. In this regard, it will be shown that the existing data often provide limited possibilities to make summarizing conclusions about the prevalence of one or other mechanisms in oxidation *via* oxygen atom transfer reactions.

Special attention will be paid to heterogeneous photocatalytic systems, where the transfer of oxygen atoms to substrates occurs from transition metal-oxo complexes anchored on the surfaces of semiconductors or supported by non-photosensitive materials. The revealing of the mechanisms of oxo-atom transfer from transition metalorganic complexes may serve as a functional model for enzymatic oxidation, as well as a key to the creation of new photocatalytic redox systems, corresponding to the requirements of “green” and sustainable chemistry.

### **Photocatalytic Oxidation Reactions Occurring *via* Oxygen Atom Transfer**

Heterogeneous photocatalytic oxidation reactions of organic compounds on the surfaces of metals, metal oxides, organometallic complexes, and other photosensitive solid substances occur through the formation of intermediates of different nature (radicals, ions, excited species, metastable compounds, *etc.*) and, therefore, in general, they have different reaction mechanisms. For example, according to the more or less generally accepted mechanisms for the oxidation of alcohols to aldehydes with dioxygen on the noble metals, usually, the main intermediates are alkoxy species adsorbed on the surface of the catalyst, the dehydrogenation of which leads to the formation of aldehydes (Scheme 1) [11].

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