Structure, Reactivity, and Selectivity of Metal-Peroxo Complexes Versus Dioxiranes

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Dioxiranes, MTO/H$_2$O$_2$, and MTO/UHP are becoming increasingly important as efficient and selective oxidants in organic chemistry and numerous publications have appeared on each of them. Here we present a comprehensive review, comparing the chemistry of these reagents with particular emphasis on the oxidation of π bonds, heteroatoms, and σ bonds. We will discuss structural aspects and on this basis, will outline the reactivity and selectivity of these oxidants, along with the mechanistic aspects of the oxygen-transfer process.

**Keywords:** Peroxo complexes, Dioxiranes, Oxygen transfer, Reactivity, Chemoselectivity, Regioselectivity, Diastereoselectivity, Enantioselectivity

1 Introduction .............................................................. 238
2 Structural Aspects .................................................... 242
3 Reaction Types and Reactivity ....................................... 243
  3.1 Oxidation of π Bonds (Olefins, Alkynes, Arenes) ............ 244
  3.2 Oxidation of Heteroatoms (S, N) ............................... 248
  3.3 Oxidation of σ Bonds (C—H, Si—H) ........................... 256
  3.4 Other Oxidation Types ........................................... 260
4 Mechanistic Considerations .......................................... 261
  4.1 π-Bond Oxidations ............................................... 262
  4.2 Heteroatom Oxidations ......................................... 263
  4.3 σ-Bond Oxidations ............................................. 264
5 Selectivities ........................................................... 265
  5.1 Chemoselectivity ................................................. 265
  5.2 Regioselectivity .................................................. 270
  5.3 Diastereoselectivity ............................................. 274
  5.4 Enantioselectivity ............................................... 277
6 Conclusions ........................................................... 279
7 References ............................................................. 281

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List of Abbreviations

1,2 A 1,2-allylic strain
1,3 A 1,3-allylic strain
config. configuration
convn conversion
Cp* pentamethylcyclopentadienyl
Dec decyl
DMD dimethyldioxirane
Hept heptyl
mal malonyl
MTO methyltrioxorhenium
NaY Na-exchanged Y-zeolite with faujasite (FAU) structure
Np naphthyl
O oxidant
pic picolinyl
quin quinoline
SOSO thianthrene 5,10-dioxide
SSO thianthrene 5-oxide
SSO₂ thianthrene 5,5-dioxide
t time
T temperature
TFA trifluoroacetone
TFD methyl(trifluoromethyl)dioxirane
TON turnover number
UHP urea-hydrogen-peroxide adduct

1 Introduction

Oxygen-transfer reactions are of increasing interest to both organic and inorganic chemists and have been the subject of an intensifying partnership [1]. Due to structural similarities between ‘organic’ and ‘organometallic’ oxidants, the study of common reactions and mechanisms, and also their differences, is essential for a better understanding of this burgeoning research field, the goal being the development of new and more efficient oxygen-transferring reagents. Of particular relevance for oxyfunctionalization reactions are those reagents which allow mild reaction conditions and lead to the desired product in both high yield and selectivity. Catalytic reaction conditions are desirable, but should not be enforced at the price of selectivity.

A wide range of both organic and organometallic oxygen-transferring agents has been studied to date with respect to their reactivity and selectivity in oxyfunctionalizations. Different types of metal-based oxidants have been scrutinised, i.e., oxo, superoxo, peroxy, peroxo, perhydrate complexes (Fig. 1), and numerous reports have appeared on oxygen-transfer reactions with such oxidants. We will limit our review to the reactivity and selectivity of rhenium peroxo complexes derived from methyltrioxorhenium (MTO) and $\text{H}_2\text{O}_2$, but