

CITY UNIVERSITY OF HONG KONG

香港城市大學

Stoichiometric and Catalytic Oxidation of  
Organic Substrates by Manganese(V) and  
Osmium(VI) Nitrido Complexes

錳和銱含氮配合物化學計量及催化氧化  
有機化合物之研究

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## ***Abstract***

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This thesis is divided into three parts. Part I reports the catalytic oxidation of alkenes and alcohols by a manganese nitrido complex  $(\text{Ph}_4\text{P})_2[\text{Mn}^{\text{V}}(\text{N})(\text{CN})_4]$ . Part II describes the Lewis-acid activated catalytic oxidation of alkanes and aromatic hydrocarbons by an osmium nitrido complex  $[\text{Os}^{\text{VI}}(\text{N})(\text{quin})_2\text{Cl}]$  (Hquin = quinaldic acid). Part III is concerned with C-H bond activation by some manganese(V) imido species, which are generated by reacting a (salen)manganese(V) nitrido complex  $[\text{Mn}^{\text{V}}(\text{N})(\text{salen})]$  (salen = *N,N'*-ethylenebis(salicylideneaminato) dianion) with various Lewis acids.

In part I, it was found that the oxidation of alkenes and alcohols can be catalyzed by  $(\text{Ph}_4\text{P})_2[\text{Mn}^{\text{V}}(\text{N})(\text{CN})_4]$  effectively at room temperature using  $\text{H}_2\text{O}_2$  as the terminal oxidant. The reaction rate can be greatly increased by the presence of one equivalent of acetic acid. The nature of the active intermediate has been investigated using various mechanistic probes. When MPPH was used as a terminal oxidant in the oxidation of cyclooctene and cyclohexanol, high yields of MPPOH (>90%), cyclooctene oxide (90%) and cyclohexanol (75%) could be detected. In the oxidation of *cis*-stilbene using  $\text{H}_2\text{O}_2$ , high yield of *cis*-stilbene oxide (95%) could be obtained and only a small amount of *trans*-stilbene oxide (3%) could be detected. In the oxidation of cyclobutanol, 100% yield of cyclobutanone was generated while no ring-opening product was produced. These results indicate that ROOH undergoes heterolytic cleavage when it interacts with the manganese center. It is proposed that the manganese catalyst acts as a Lewis acid to facilitate the heterolytic O-O bond cleavage of ROOH. According to the results of computational study by using the DFT method, the accelerating effect of acetic acid is due to the stabilization of the Mn-(HOOH)

intermediate by hydrogen bonding.

In Part II, it was found that the oxidation of various alkanes and aromatic hydrocarbons with  $\text{H}_2\text{O}_2$  can be catalyzed by  $[\text{Os}^{\text{VI}}(\text{N})(\text{quin})_2\text{Cl}]$  effectively at room temperature in the presence of a Lewis acid. The KIE value for the competitive oxidation of cyclohexane and  $d_{12}$ -cyclohexane by  $[\text{Os}^{\text{VI}}(\text{N})(\text{quin})_2\text{Cl}]/\text{FeCl}_3/\text{H}_2\text{O}_2$  is 3.1. For the oxidation of aromatic hydrocarbons, the oxidation of aromatic ring occurs preferentially than the oxidation of side-chain. The major products are the corresponding phenols and benzoquinones. Products arising from the NIH shift of the aromatic ring substituents could also be detected. For  $[\text{Os}^{\text{VI}}(\text{N})(\text{quin})_2\text{Cl}]/\text{FeCl}_3/\text{H}_2\text{O}_2$ , the KIE value for the competitive oxidation of benzene and  $d_6$ -benzene is 0.94. The use of MPPH as the terminal oxidant for the oxidation of *p*-xylene results in the formation of high yields of MPPOH and ring oxidized products. This result suggests that ROOH undergoes a heterolytic O-O bond cleavage when it interacts with the osmium center.

In Part III, it was found that some (salen)manganese(V) imido species generated from the reaction of the corresponding manganese(V) nitrido species with various Lewis acids are able to abstract H-atoms from hydrocarbons with weak C-H bonds. The products resulting from the C-H bond activation of various hydrocarbons have been analyzed, and mechanistic studies have been carried out.

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## ***Objectives***

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This research work is divided into three parts. In part I, the catalytic oxidation of alkenes and alcohols by a manganese(V) nitrido complex  $(\text{Ph}_4\text{P})_2[\text{Mn}^{\text{V}}(\text{N})(\text{CN})_4]$  has been studied. In part II, the effects of Lewis acids on the activation of an osmium(VI) nitrido complex  $[\text{Os}^{\text{VI}}(\text{N})(\text{quin})_2\text{Cl}]$ , towards the catalytic oxidation of alkanes and aromatic hydrocarbons will be discussed. Part III describes the C-H bond activation of hydrocarbons by some manganese(V) imido species, which are generated by the reaction of a (salen)manganese nitrido complex  $[\text{Mn}^{\text{V}}(\text{N})(\text{salen})]$  with Lewis acids.

The objectives of the study in part I are as follows:

- (1) to study the epoxidation of alkenes and the oxidation of alcohols by using  $(\text{Ph}_4\text{P})_2[\text{Mn}^{\text{V}}(\text{N})(\text{CN})_4]$  as a catalyst.
- (2) to study the mechanisms of catalytic alkene and alcohol oxidations by this system.

The objectives of the study in part II are as follows:

- (1) to investigate the effects of Lewis acids on the catalytic oxidation of alkanes and aromatic hydrocarbons by  $[\text{Os}^{\text{VI}}(\text{N})(\text{quin})_2\text{Cl}]$ .
- (2) to study the mechanisms of the catalytic oxidation of alkanes and aromatic hydrocarbons by this system.

The objectives of the study in part III are as follows:

- (1) to analyze the products generated by the C-H bond activation of hydrocarbons by some (salen)manganese(V) imido species.
- (2) to study the mechanism of the C-H bond activation of hydrocarbons by these manganese imido species.