IS-T 1763

Organic Transformations Catalyzed by Methylrhenium Trioxide

by

Zhu, Zuolin

PHD Thesis submitted to Iowa State University

Ames Laboratory, U.S. DOE
Iowa State University
Ames, Iowa 50011

Date Transmitted: October 6, 1995

PREPARED FOR THE U.S. DEPARTMENT OF ENERGY
UNDER CONTRACT NO. W-7405-Eng-82.

DISCLAIMER

GENERAL INTRODUCTION

Introduction

Methylrhenium trioxide (MTO), CH_3ReO_3, was first prepared in 1979. An improved route to MTO was devised from dirhenium heptoxide and tetramethyltin in the presence of hexafluoroglutaric anhydride reported by Herrmann in 1992.

MTO forms stable or unstable adducts with electron-rich ligands, such as amines (quinuclidine, 1,4-diazabicyclo[2,2,2]-octane, pyridine, aniline, 2,2'-bipyridine), alkynes, olefins, 1,2-diols, catechols, hydrogen peroxide, water, thiophenols, 1,2-dithiols, triphenylphosphine, 2-aminophenols, 2-aminothiophenols, 8-hydroxyquinoline and halides (Cl^-, Br^-, I^-). After coordination, different further reactions will occur for different reagents. Unstable adducts give secondary reaction products, such as the interaction between MTO and olefins that leads to olefin metathesis, and the interaction between MTO and water that results in oxo-exchange of MTO. There are two kinds of stable adducts. One of them reacts with additional substrates, such as the adducts formed from MTO and hydrogen peroxide. That reaction yields two peroxo complexes which catalytically oxidize almost all oxidizable substrates to their corresponding products (sulfides to sulfoxides, olefin to epoxides, tertiary phosphines to tertiary phosphine oxides, etc.). MTO is an attractive catalyst for these oxidations because hydrogen peroxide is considered to be an environmentally "green" oxidant. Another kind of stable adducts are inert, toward further reactions, such as the adducts formed from MTO and catechols, MTO and 2,2'-bipyridine, etc.

Organic transformations catalyzed by methylrhenium trioxide

Zuolin Zhu

Major Professor: James H. Espenson

Iowa State University

Several organic transformations were found to be catalyzed by methylrhenium trioxide, CH_3ReO_3 (MTO): decomposition of ethyl diazoacetate (EDA) to 2-butenedioic acid diethyl esters; cycloadditions of EDA with imines (to aziridines), with olefins (to cyclopropanes), and with aldehydes or ketones (to epoxides). In the presence of MTO, the reactions of EDA with alcohols, phenols, thiols or amines yield, respectively, the corresponding α-alkoxy, α-phenoxy, α-thio ethyl acetate or ethyl glycine esters. These reactions occur under mild conditions and give satisfactory to high product yields.

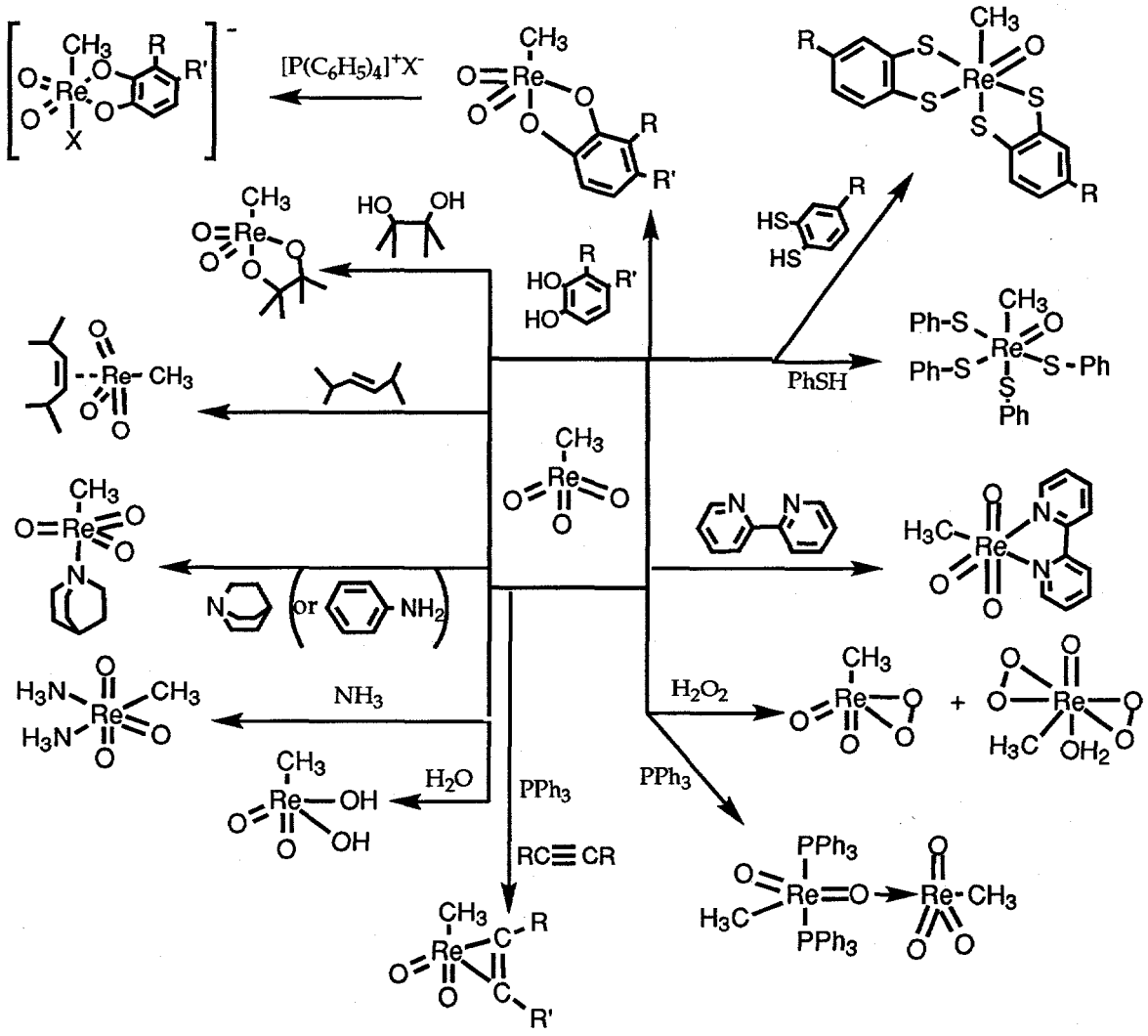
The other reactions catalyzed by MTO are dehydration of alcohols to ethers and olefins; direct amination of aromatic alcohols, and the disproportionation of alcohols to alkanes and carbonyl compounds.

MTO activates H_2O_2 through the formation of two active species (mono-peroxo-Re(VII) **A**, and bisperoxo-Re(VII), **B**). These two peroxo species oxidize alkynes to the corresponding 1,2-dicarbonyl compounds or carboxylic acids, and anilines to nitroso benzenes or *N*-oxides in high yields. Tertiary phosphines are oxidized by molecular oxygen to the corresponding phosphine oxides in the presence of MTO. Similarly, oxygen transfer from sulfoxides, epoxides, *N*-oxides, triphenylarsine oxide and triphenylstibine oxide to triphenylphosphine is also catalyzed by MTO. The reactions of MTO and epoxides yield bis(alkoxy)rhenium(VII) complexes.

TABLE OF CONTENTS

These versatile catalytic and noncatalytic reactions of MTO have triggered a massive area of research waiting exploration. In order to provide a detailed understanding of MTO, and to extend this scheme (**Scheme I**) which is far from complete now, more questions need to be answered about this complex. What kind of compounds can coordinate with MTO, are these kinds of complexes stable or not, what kind of further reactions can occur?

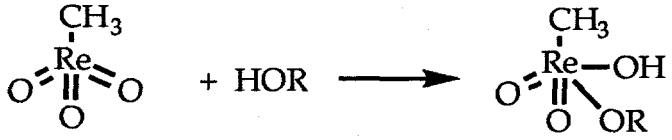
Scheme I



Since the discovery of diazo chemicals in 1858 by Peter Griess, the synthetic uses of organic diazo compounds through thermal and photochemical processes have found important applications in organic chemistry. Due to the complicated thermal or photochemical reactions of diazo chemicals, catalytic methods are need to supplant those processes for efficient cyclopropanation, dipolar addition and insertion.

Methylrhenium trioxide can catalyze the decomposition of diazo chemicals with and without substrates to yield olefins through dimerization; cyclopropanes, aziridines and epoxides by cycloaddition; and α-alkoxy esters, α-thio esters and glycine esters through insertion. Besides diazo compounds, organic azides also have some reactions catalyzed by MTO as described in Chapter I.

Although many efforts have been applied to the catalytic direct ether synthesis with transition-metal complexes, there has been no success until the appearance of MTO. Alcohols, one structural analog of water, coordinate with MTO by a similar pathway to water.



This interaction results in formation of ethers, olefins through dehydration of alcohols, or products from alcohol amination or alcohol disproportionation. The first example of the catalytic direct ether preparation using this transition metal complex as catalyst is shown in Chapter II.

The transfer of an oxygen atom is one of the fundamental processes in chemistry, such as olefin formation by epoxide deoxygenation. Oxygen transfer is

still an interesting area of research in organic synthesis and biochemical studies. Deoxygenation of epoxides, *N*-oxides, sulfoxides and triphenylarsine oxide is catalyzed by MTO as described in Chapter III.

Selective oxidation by molecular oxygen is a desirable method for both organic and industrial preparations. The first report of MTO being reactive in catalytic oxidation with molecular oxygen is given in Chapter III.

From the reported studies, it seems to be true that catalytic oxidation with hydrogen peroxide as oxidant occurs for almost all chemicals that have nucleophilic centers. But many compounds remain untouched so far including alkynes and anilines. Investigations of these oxidations are presented in Chapters IV and V.

Chapter VI describes the interaction between MTO and epoxides which offers a synthetic method for bis (alkoxy) rhenium (VII) complexes.

Dissertation organization

The dissertation consists of six chapters. Chapter I corresponds to a manuscript in preparation. Chapters II, IV and VI are three manuscripts submitted. Chapter III is in press in *J. Mol. Catal.*, and Chapter V has been published in *J. Org. Chem.* Each section is self-contained with its own equations, tables, figures and references. Following the last manuscript is the general conclusion. All the work in this dissertation was performed by myself.

GENERAL SUMMARY

Methylrhenium trioxide, CH_3ReO_3 (MTO), catalyzes the decomposition of ethyl diazoacetate to yield diethyl 2-butenedioic acid esters or azine depend on the ratio of MTO and diazo chemicals used. In the presence of substrates which contain double bonds, such as olefins, imines or organic carbonyl compounds, cyclopropanes, aziridines or epoxides were formed by cycloaddition. These reactions may occur through a [2+3] process. Catalytic reactions between ethyl diazoacetate and alcohols, phenols, thiols, thiophenols or amines yield α-alkoxy ethyl acetates, α-thio ethyl acetates or ethyl glycine esters. Organic azides was converted azo compounds mediated by MTO. In the presence of triphenylphosphine, MTO catalyzed the reactions between organic azides and aromatic aldehydes that yielded organic imines in high yields.

The interaction between MTO and alcohols gives dehydration products, such as ether or olefins, depending on the alcohols used. The electron-donor groups of aromatic alcohols cause the disproportionation of alcohols to occur, leading to carbonyl compounds and alkanes. The amination of alcohols with amines was also catalyzed by MTO. Besides these reactions, oxygen transfer occurs from epoxides, sulfoxides, tertiary amine *N*-oxides and some metal oxides to triphenyl phosphine in the presence of catalytic amount of MTO.

Several oxidations with molecular oxygen and hydrogen peroxide were found to be catalyzed by MTO. With molecular oxygen, tertiary phosphines were converted to corresponding oxides; using hydrogen peroxide, anilines were

converted to nitroso benzene and tertiary aromatic amines were transferred to *N*-oxides. The fact that electron withdrawing groups decrease this reaction rate constants suggest peroxo group of A and B is electrophilic under these conditions.

Coordination of epoxides with MTO yields corresponding bis(alkoxy)rhenium (VII) complexes which are water sensitive and react with triphenyl phosphine to form triphenyl phosphine oxide, olefins and MTO.

ACKNOWLEDGMENTS

I would like to thank Professor James Espenson for his guidance and encouragement during my graduate career. I am also thankful to the members of my research group for their friendship and for sharing with me their own ideas and useful discussions. I am pleased to acknowledge informative discussion with Professor Glen A. Russell.

I would like to acknowledge my wife Meng for her support and love which give me direction, hope, encouragement and help.

I would like to thank Methylrhenium trioxide which, by using its amazing character, have make me enjoy research and allowed me to obtain a Ph.D. degree.

The work was supported by the U. S. Department of Energy, Office of Basic Energy Science, Division of Chemical Sciences under contract W-7405-Eng-82. The United States government has assigned the DOE Report number IS-T 1763 to this thesis.