Homogeneous Dioxoruthenium(VI) Catalysts for the Oxidation of Alcohols

by

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Preface

The experimental work described in this dissertation was carried out in the School of Pure and Applied Chemistry, University of Natal, Durban, from February 1998 to February 2000, under the supervision of Dr. Holger B. Friedrich.

These studies represent original work by the author and have not otherwise been submitted in any form for any degree or diploma to any tertiary institution. Where use has been made of the work of others it is duly acknowledged in the text.

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1st day of March 2000.

Abstract

Compounds of the form $RuO_2(Y\text{-}py)_2Cl_2$ **1** (py = pyridine, Y = H, 4-*t*-Bu, 3-CN, 4-CN, 2-Br, 3-Br, 4-Br, 4-Cl, 4-Me, 4-C(O)C_6H_5, 3-COOH, 4-COOH), RuO_2ZCl_2 **2** (Z = bipyridine, phenanthroline) and $RuO_2(OH)_2(Y\text{-}py)_2$ **3** (py = pyridine, Y = H, 4-CN, 4-*t*-Bu) were prepared and the effects of the various substituents on the properties of the compounds were investigated. The position of the ν(Ru=O) bands of the complexes **1** correlate with the Hammett σ_I (or Taft σ^*) and Pauling-type electronegativity values of the substituents on the pyridine ring. A comparative study of most of these complexes as both stoichiometric and catalytic oxidants for the oxidation of 1-hexanol to hexanal was carried out.

The known dioxoruthenium(VI) compound $[PPh_4][RuO_2(OCOCH_3)Cl_2]$ (**a**) and a range of new compounds $[PPh_4][RuO_2(OCOR)Cl_2]$ (R = CF_3 **b**, C_6H_5 **c**, C_6F_5 **d**, C_5H_{11} **e**) were synthesized and characterized. High synthetic yields were obtained for the fluorinated complexes **b** and **d** relative to their protonated equivalents **a** and **c**, possibly due to the varying charge distributions within such complexes. No clear trend in catalytic activity was noticed on varying the ligand on the ruthenium for the oxidation of 1-hexanol and 2-hexanol to hexanal and 2-hexanone respectively, with a range of co-oxidants. The complexes **c** and **d** were used very successfully in the catalytic oxidations of a variety of alcohols with the co-oxidants tetrabutylammonium periodate and 4-methylmorpholine N-oxide. The novel compounds $[PPh_4][RuO_2(OCOC_6H_5)Cl_2]$ and $[PPh_4][RuO_2(OCOC_6F_5)Cl_2]$ were supported on poly-4-vinylpyridine and used catalytically in oxidizing cyclohexanol to cyclohexanone, using 4-methylmorpholine N-oxide and tetrabutylammonium periodate as co-oxidants.

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None of the research carried out would have been possible without the financial assistance given by the NRF, my loving sister Ritha and brother Manoj.

My family has stood by me and supported me over my entire University career. I am eternally grateful to them. My uncle and aunt (*i.e.* Mr. and Mrs. Kambaran) have always opened their home and heart to me, and were always willing to help me. I will never forget their kindness. Finally, a very special thank you is due to Ms. Asha Ramsarup who gave up so much over the last few years to make my dreams a reality. Your love and support meant the world to me. Thank you.

Dedication

This work is dedicated to my loving late grandparents and

my mum, dad, Ritha, Pradeep, Manoj and Asha.

You all have been the source of my spirit to live and

succeed at every challenge that life has thrown me.

May God Bless You.

List of Abbreviations

14-TMC = 1,4,8,11-tetramethyl-1,4,8,11-tetraazacyclotetradecane

15-TMC = 1,4,8,12-tetramethyl-1,4,8,12-tetraazacyclopentadecane

16-TMC = 1,5,9,13-tetramethyl-1,5,9,13-tetraazacyclohexadecane

bipy = 2,2’-bipyridine

dmp = bis-dimethyl-1,10-phenanthroline

EOP = octaethylporphyrin

H_2Por* = 5,10,15,20-tetrakis[(1S,4R,5R,8S)-1,2,3,4,5,6,7,8-octahydro-1,4:5,8-dimethanoanthracen-9-yl]-porphyrin

H_2salophen = N,N’-bis(salicylidene)-o-phenylenediamine

NMO = 4-methylmorpholine N-oxide

N_4OH = bis[2-(2-pyridyl)ethyl(2-hydroxy-2-2-(2-pyridyl)ethyl]amine

phen = phenanthroline

PVP = poly(4-vinylpyridine)

py = pyridine

TBAP = tetrabutylammonium perruthenate

t-BuOOH = *tertiary*-butyl hydroperoxide

TEMPO = 2,2’,6,6’-tetramethylpiperidine N-oxyl

TMANO = trimethylamine-N-oxide dihydrate

(TMEA)$_2$ = bis(N,N,N’,N’-tetramethyl-1,2-diaminoethane)

TMP = 5,10,15,20-tetramesitylporphyrinato

TPAP = tetrapropylammonium perruthenate

tpy = 2,2’:6’2’’-terpyridine

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Publications

The following work from this thesis has already been presented.

Papers:

1. **"The Effects of substituents (Y) on pyridine in the Ru(VI) Compounds RuO_2Cl_2(Y-pyridine)$_2$ and RuO_2Cl_2Z (Z = bipyridine, phenanthroline)"**, H. B. Friedrich, E. Friedrich, V. Gokul, K. K. Kubeka and N. Rinder, *S. Afr. J. Chem.*, 2000, **54**, 2.

Conference Contributions:

1. **"Ruthenium Oxidants for the Conversion of Alcohols to Aldehydes"**, H. B. Friedrich and V. Gokul, presented at the *1st Conference of the Indo-Pacific Catalysis Society (IPCAT1)*, Cape Town, South Africa, 1998.

2. **"Studies on Oxidations by High-Valent Dioxoruthenium(VI) Complexes"**, V. Gokul and H. B. Friedrich, presented at the *7th International Chemistry Conference in Africa (ICCA)* and the *34th Convention of the South African Chemical Institute (SACI)*, Durban, South Africa, 1998.

3. **"High Valent Ruthenium and Osmium Compounds as Oxidants"**, H. B. Friedrich, V. Gokul, W. A. Herrmann, K. K. Kubheka, N. Singh, presented at the *7th International Chemistry Conference in Africa (ICCA)* and the *34th Convention of the South African Chemical Institute (SACI)*, Durban, South Africa, 1998.

4. **"Ruthenium Oxidants for the Conversion of Alcohols to Aldehydes"**, H. B. Friedrich, V. Gokul, K. K. Kubheka and N. Rinder, *11th International Symposium on Homogenous Catalysis*, St. Andrews, Scotland, 1998.

5. **"Substituent Effects in Ruthenium Oxo Compounds"**, H. B. Friedrich, E. Friedrich, V. Gokul, K. K. Kubheka and N. Rinder, *Inorganic '99*, Stellenbosch, South Africa, 1999.

6. **"The Synthesis of Dioxoruthenium(VI) Salts and Investigations into their use as Catalytic Oxidants"**, V. Gokul and H. B. Friedrich, *Inorganic '99*, Stellenbosch, South Africa, 1999.

7. **"The Effects of Substituents (Y) on Pyridine in the Ru(VI) Compounds RuO_2Cl_2(Y-pyridine)$_2$ and RuO_2Cl_2Z (Z = bipyridine, phenanthroline)"**, H. B. Friedrich, E. Friedrich, V. Gokul, K. K. Kubeka and N. Rinder, *Inorganic Chemistry '99*, Wellington, New Zealand, 1999.

8. **"The Influence of Varying Ligand Systems on the Synthesis and Catalytic Activity of Dioxoruthenium(VI) Salts"**, V. Gokul and H. B. Friedrich, *7th International Conference –The Chemistry of the Platinum Group Metals*, Nottingham, United Kingdom, 1999.

9. **"Ruthenium(VI) Compounds as Catalytic Oxidants"**, H. B. Friedrich, V. Gokul, F. Khan, N. Singh, *Inorganic 2000, 11th Royal Australian Chemical Institute Convention (RACI)*, Canberra, Australia, 2000.

Chapter One

Introduction

1.1. Catalysis

The word catalysis, which was first used by J. J. Berzelius in 1836 to rationalize strange observations in chemical reactivity, is derived from two Greek words, *cata-* meaning down and *lysien-* meaning to split or break [1]. The *catalytic species* or catalyst is defined as "an additive that increases the rate of a chemical process" [2] or "the substance that increases the rate at which a chemical system approaches equilibrium, without being consumed in the process" [1]. However, often, the term "catalyst" is used loosely to describe primary oxidants that are reduced during oxidation reactions, but that are continuously regenerated by co-oxidants (or secondary oxidants), and thus are able to carry out further oxidations. This difference in the description becomes more apparent later in the text.

Catalysis can be divided into two categories [1-5]:
(1) Homogeneous catalysis: where the catalyst is in the same phase (almost always liquid) as the reactants without the existence of a phase boundary;
(2) Heterogeneous catalysis: where a phase boundary separates the catalyst from the reactants (which are usually in a vapour or liquid phase).

Both categories have advantages and disadvantages [1-5]. The activities (relative to metal content) of homogeneous catalysts are higher than those of the sometimes variable heterogeneous catalysts. Homogeneous catalysts are highly selective, allow for reactions to proceed under relatively mild temperatures and pressures, experience no diffusion problems and show low sensitivity towards catalytic poisons. It is often easier to optimize homogeneous catalysts by varying the steric and electronic properties of the catalysts since the mechanistic processes of such reactions can be studied. The disadvantages of homogeneous catalysis though, are the difficulty of separating the catalytic species from the reaction products and the expense involved in regenerating the homogeneous catalyst for re-use.

In contrast, heterogeneous catalysts show variable selectivity, often require harsh reaction conditions, experience diffusion problems, and have a high sensitivity towards catalyst poisons. Varying the steric and electronic nature of heterogeneous catalysts is not possible and it is difficult to study the mechanistic aspects of catalytic reactions. However, heterogeneous catalysts have high stability to temperature and can be easily separated from reaction products, which are distinct advantages over homogeneous catalysis.

The mechanisms of heterogeneous catalytic reactions are difficult to study in comparison to homogeneous reactions, due to the complexity of the catalyst's surface. Since most homogeneous reactions occur in solutions and involve discrete metal complexes, detailed investigations of such systems are possible. The information gained from studying homogeneous reactions can thus aid in the explanation of results obtained for heterogeneous reactions [6].

Presently, as much as 85% of all industrial processes are carried out using heterogeneous catalysts [5,7,8], however, hydroformylation, olefin polymerization, acetaldehyde synthesis, and olefin additions have been dominated industrially by homogeneous catalysts [2-6].

The factors above have contributed to the development of a relatively new field of research that attempts to incorporate the advantages of both homogeneous and heterogeneous catalysis. Catalytically active homogeneous complexes are supported on organic (*eg*. poly-4-vinylpyridine) or inorganic (*eg*. alumina, zeolite) supports to enhance ease of catalyst separation [5,6]. Presently, though, no industrially important "supported homogeneous catalyst" is known, since the "leaching" of the catalyst from the support is a major problem. The "leaching" of metals that comprise such catalysts results in the toxic contamination of reaction products [9], and is accompanied by the possible loss of expensive ligands from such metals [5,6]. Polymers have also been found to experience a certain degree of mechanical weakness, as was observed in the partial degradation of the carbon-carbon backbone in poly-4-vinlypyridine, after oxidative treatment of the polymer by the homogeneous catalyst [9]. The steric crowding of catalysts on the support and the diffusion problems experienced by heterogeneous catalysts, are still negative factors that plague "supported homogeneous catalysis".

1.2. Oxidation Catalysis

The oxidation of primary alcohols to aldehydes (equation i) and secondary alcohols to ketones (equation ii) is of paramount importance in organic chemistry [2,10].

$$RCH_2OH \xrightarrow{\text{oxidant}} RCHO \qquad \text{(i)}$$

$$RCH(OH)R^1 \xrightarrow{\text{oxidant}} RC(O)R^1 \qquad \text{(ii)}$$

Primary alcohol oxidation to aldehydes (equation i) in particular is important since often over-oxidation of the aldehyde occurs in the presence of water, thus resulting in the carboxylic acid (equation iii) [11,12].

$$RCHO \xrightarrow{H_2O} RCOOH \qquad \text{(iii)}$$

Numerous oxidizing agents have been developed to effect the oxidation of primary and secondary alcohols [2,13-15]. However, in many cases the reagents are required in stoichiometric amounts, require high or low temperatures, are extremely aggressive, do not give complete transformations, or have limited substrate ranges. Furthermore, the oxidants used may be toxic or hazardous, thereby making purification of reaction products a demanding task.

Despite the importance of oxidation of alcohols industrially and the growing environmental concerns regarding the use of hazardous, toxic and expensive oxidants (often in stoichiometric proportions) [2,7,16,17], few viable catalytic oxidants have been developed [7,16,18]. There is thus a need to develop milder, more selective alcohol oxidants, with higher rates of conversion. Recently, a few ruthenium based oxidation systems that come closer to the above criteria have been reported [7,16,18].

The chemistry of ruthenium has been extensively reviewed [18-26]. Together with osmium, ruthenium is unique in the periodic table since it displays oxidation states from +VIII to –II. This implies the use of the entire electron configuration of d^0 to d^{10}, eleven possible configurations in all. The high oxidation states attainable by ruthenium are effectively stabilized by the strongly ($\sigma+\pi$) donating O^{2-} ligands, that make ruthenium-oxo complexes attractive as oxidants [24].

The study that follows will be introduced by a brief examination of the chemistry of ruthenium-oxo complexes. Although the content of the introduction has been limited to the oxidation of alcohols achieved by ruthenium-oxo complexes, the value and importance of other ruthenium oxidants should not be overlooked. Among such oxidants are the recently reported triple catalytic systems. Bäckvall *et al.* [27,28] have investigated the aerobic oxidation of alcohols (mainly benzyl alcohols) by a triple catalytic system involving a ruthenium complex (*eg.* [RuCl(OAc)PPh$_3$]), a quinone (*eg.* Hydroquinone), and a cobalt macrocycle {*eg.* [Co(salophen)(PPh$_3$)]} [H$_2$salophen = N,N'-bis(salicylidene)-o-phenylenediamine]. The ruthenium complex is proposed to dehydrogenate the secondary alcohol and the resulting "RuH$_2$" complex transfers the abstracted hydrogens to the quinone, thereby regenerating the ruthenium complex. The hydroquinone that results from the hydride transfer is reoxidized to the corresponding quinone by oxygen, which is activated by the cobalt macrocycle {(ML^n)}[n = normal] (equation iv, figure 1.2.1). This redox system usually functions at temperatures below 100°C and at ambient pressures. The rate of conversion of the secondary alcohol was also found to be solvent dependant.

$$\text{Secondary Alcohol} \quad + \tfrac{1}{2}\,O_2 \quad \xrightarrow[\text{solvent, }100^{o}\text{C}]{\substack{\text{Cat. Ru Complex}\\ \text{Cat. Quinone}\\ \text{Cat. Co macrocycle}}} \quad \text{Ketone} \quad + \quad H_2O \qquad \text{(iv)}$$

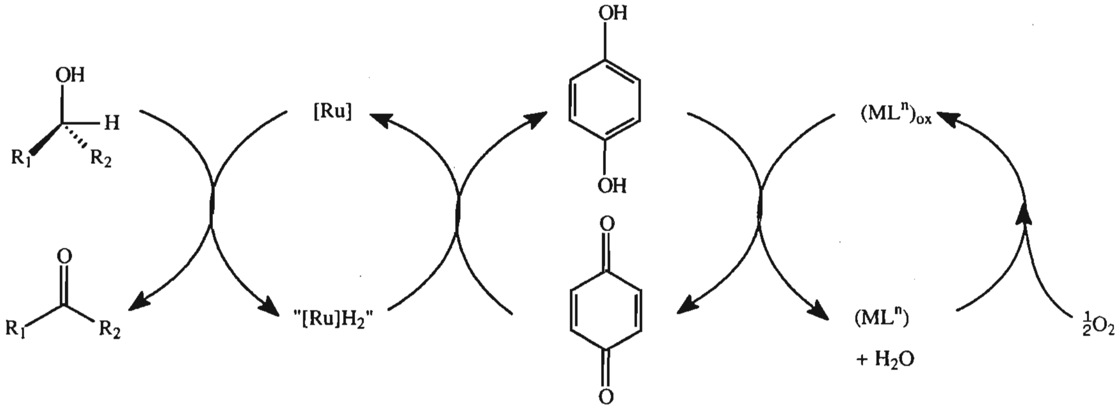

Figure 1.2.1. Aerobic triple catalytic system for the oxidation of alcohols [27,28].

A similar reaction for the aerobic oxidation of primary alcohols to aldehydes involving a Ru(PPh$_3$)$_3$Cl$_2$ / hydroquinone system has been reported [29]. However, the reaction pathway for this system has not been described.

The combination of the catalyst [Ru(PPh$_3$)$_3$Cl$_2$] and various derivatives of TEMPO (TEMPO = 2,2',6,6'-tetramethylpiperidine N-oxyl) have afforded an efficient catalytic system for the aerobic oxidation of primary alcohols to aldehydes and secondary alcohols to ketones, with high selectivity [30,31]. The presence of TEMPO in the reaction was shown to prevent over-oxidation of the aldehyde, 1-octanal, to the carboxylic acid octanoic acid [31].

Further examples of such research can be found in the recent review by Naota *et al.* [26].

1.3. Ruthenium(VIII)

The yellow crystalline RuO_4 (mp. 25.4°C, bp. 40°C) is the only proven fully characterized compound of ruthenium in the (VIII) oxidation state. RuO_4 is highly volatile and can be identified by its distinctive pungent odour [19,21,32]. RuO_4 is an extremely vigorous oxidant that reacts explosively with solvents like ethanol, diethyl ether and benzene, but is stable in unreactive solvents such as chloroform or carbon tetrachloride, in which it is also readily soluble [33]. Light decomposes RuO_4 and when pure, RuO_4 can explode above 180°C to give RuO_2 and O_2 [34].

RuO_4 can be generated from $RuO_2.xH_2O$ or $RuCl_3.nH_2O$ by oxidizing them in aqueous media with sodium hypochlorite (NaOCl) [35,36], sodium metaperiodate ($NaIO_4$) [36,37], sodium bromate ($NaBrO_3$) [38], active chlorine species (Cl_2 or $[Cl]^+$) [39], and recently by ozone (O_3) at neutral pH [40]. $RuO_2.xH_2O$ is favoured as a starting material since it is oxidized quickly and completely to RuO_4 in acid or neutral media, and does not contain the Cl^- ions that can be oxidized to Cl_2 and consequently result in unwanted side reactions [38,41]. These are important considerations in synthetic reactions where high quality products are required.

RuO_4 in alkaline solutions is reduced by hydroxide ions first to the perruthenate ion, $[RuO_4]^-$, (equation v) and then to the ruthenate ion, "$[RuO_4]^{2-}$" {actually *trans*-$[RuO_3(OH)_2]^{2-}$ - see later} (equation vi), at higher hydroxide ion concentrations [42,43].

$$4RuO_4 + 4OH^- \longrightarrow 4RuO_4^- + 2H_2O + O_2 \qquad (v)$$

$$4RuO_4^- + 4OH^- \longrightarrow 4\text{"}RuO_4^{2-}\text{"} + 2H_2O + O_2 \qquad (vi)$$

Consequently, the use of the oxidant NaOCl for the preparation of RuO_4 is not advisable since NaOCl is unstable below pH 8 and has to be stabilized by NaOH in its preparation commercially. This raises the pH of bleach to approximately 11, at which RuO_4 is not stable.

RuO_4 generated *in situ* has been used extensively in organic chemistry both stoichiometrically and catalytically [36,44,45] for the oxidation of saturated hydrocarbons, oxidation of olefins [46,47], hydroxylation of olefins [48,49], oxidation of unsaturated fatty acids [35] and in carbohydrate manipulations [39,50]. RuO_4 has also been used to design and construct new proteins with tailor-made structural and functional properties. The manipulation of the delicate proteins proceeded with chiral retention and without influencing N-protecting groups [51].

RuO_4 has also been investigated with respect to degradation of toxic dioxins, with the aim of purging industrial reactors to prevent build up of polychloro-p-dioxin residues [20,52,53]. The uses of RuO_4 have been restricted commercially due to its high volatility and by the fact that its vapours are irritating to eye tissue and the respiratory tract [54].

1.4. Ruthenium(VII)

The only established ruthenium(VII) ion is the perruthenate ion, $[RuO_4]^-$. The perruthenate ion is stable in aqueous base between pH's 8 and 10.1, with the ruthenate ion found at a pH > 10.1 [42,43,55]. $[RuO_4]^-$ was found to function as a one-electron oxidant in water since the oxidation of cyclobutanol gave an acyclic product, which was further oxidized, again by a one electron donation by a perruthenate anion, to other products. Ruthenate that was generated by the reduction of perruthenate was involved in the synthesis of further oxidation products (Figure 1.4.1) [56]. In oxidation reactions, perruthenate is less efficient than ruthenate and milder than RuO_4. The perruthenate ion oxidizes primary alcohols to carboxylic acids, secondary alcohols to ketones and cleaves double bonds [57].

Although the sodium and potassium compounds of perruthenate exist, their use is restricted to oxidations in aqueous media [1] and consequently to a limited range of organic substrates. Griffith *et al.* [58] attempted the use of an 18-crown-ether to increase the solubility of $K[RuO_4]$ in dichloromethane. Only a limited solubility of the salt was observed, together with an increase in reaction times for stoichiometric oxidations.

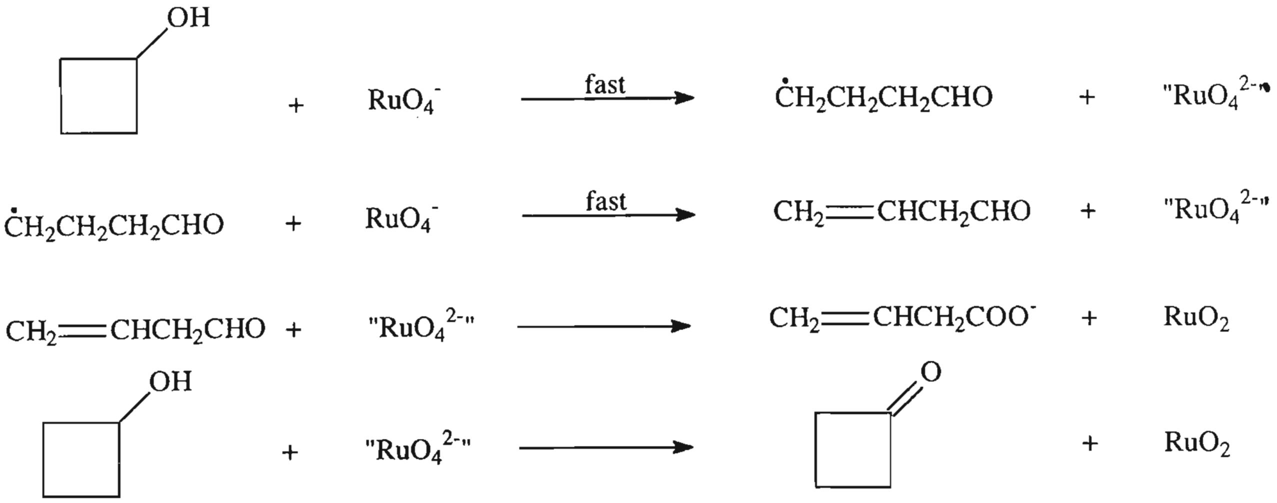

Figure 1.4.1. The range of products from the oxidation of cyclobutanol by $[RuO_4]^-$ [56].

The synthesis of the first organic salts of perruthenate, tetrabutylammonium perruthenate (TBAP) [59] and tetrapropylammonium perruthenate (TPAP) [60] overcame the solubility problems in organic media faced by the inorganic perruthenate complexes. TBAP and TPAP were stabile in air, non-volatile, selectively oxidized primary alcohols to aldehydes and secondary alcohols to ketones, and were rendered catalytic with 4-methylmorpholine N-oxide (NMO) as co-oxidant. The salts $R[RuO_4]$ $\{R = PPh_4, N(PPh_3)_2\}$ have since also been synthesized [61,62], however, the chemistry of TPAP has been most studied due to its ease of synthesis and largely predictable oxidative ability [7,63].

TPAP was found to be tetrahedral like $K[RuO_4]$ from electron spin resonance [61] and infrared / Raman [64] studies. The reaction of TPAP with propan-2-ol was found to be autocatalytic, which is possibly due to the formation of colloidal RuO_2 that may result in $[RuO_4.nRuO_2^-]$ being formed. Mechanistic studies showed TPAP to be an overall three-electron oxidant [65].

TPAP was found to be sterically demanding in oxidation reactions since primary alcohols reacted faster than secondary alcohols [66]. The complex was able to tolerate a range of reactive groups including double bonds, epoxides, halides, cyclopropanes, esters, amides, lactones, amines, peroxides, catechols, protecting groups and pyridines, without racemization. As a result, use of TPAP in tandem / sequential reactions was possible. Turnovers obtained in some catalytic oxidation reactions were very high and have yet to reach limits. Recently, molecular oxygen was used as a stoichiometric oxidant in TPAP catalyzed oxidations of alcohols [66-68]. Markó *et al.*, however, found that TPAP, under such aerobic oxidation conditions, isomerized the alcohol geraniol to geranial and citronellal, instead of giving the desired product geraniol only [68].

Finally, in view of the concerns expressed earlier regarding the problem of separating homogeneous catalysts, Lenz and Ley prepared a polymer supported perruthenate complex [69,70]. An Amberlyst anion exchange resin (containing quarternary ammonium groups) was mixed by ultrasound with an aqueous solution of powdered potassium perruthenate. This "tethered homogeneous catalyst" selectively oxidized primary alcohols to aldehydes (without over-oxidation to the carboxylic acid), secondary alcohols to ketones and was easily separated by filtration.

1.5. Ruthenium(VI)

Ruthenate was incorrectly believed to be the tetrahedral anion "$[RuO_4]^{2-}$" until the crystal structure of the potassium salt was determined. The structural analysis revealed a trigonal bipyramidal ruthenium(VI) moeity, dihydroxoruthenate(VI), with three equatorial oxygens and two apical hydroxyl ions [71] (Figure 1.5.1).

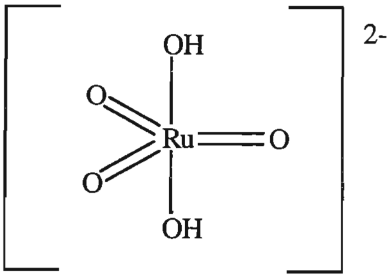

Figure 1.5.1. Structure of the ruthenate anion *trans*-$[RuO_3(OH)_2]^{2-}$ [71].

As mentioned previously, the ruthenate anion exists at pH > 10.1 in aqueous medium [42,43,55]. It can be generated from $RuO_2.nH_2O$ or $RuCl_3.nH_2O$ with $NaIO_4$, $Na_2S_2O_8$, NaOCl [55], and, as shown recently, by ozonolysis [40]. Synthesis by using the oxidants $NaBrO_3$ and $Na_2[B_2(O_2)_2(OH)_4].6H_2O$ was also possible, however, the resulting peroxoborate reagent was unstable and was a poor catalytic oxidant [62].

Sodium ruthenate, when used in stoichiometric oxidations, attacked double bonds when high temperatures and long reaction times prevailed [72,73]. Sodium ruthenate was also investigated with respect to the catalytic oxidation of propan-2-ol with a range of co-oxidants (hexacyanoferrate(III), diperiodatocuprate(III), chloroamine-T and periodate). The role of the co-oxidant was established to be solely to regenerate the ruthenium(VI) ion, except in the case of chloramine-T, in which case the co-oxidant appeared to react directly with the ruthenium(VI) ion (Figure 1.5.2) [74]. The mechanistic observations, however, apply only to the oxidation reaction in aqueous medium and may be different in non-aqueous media.

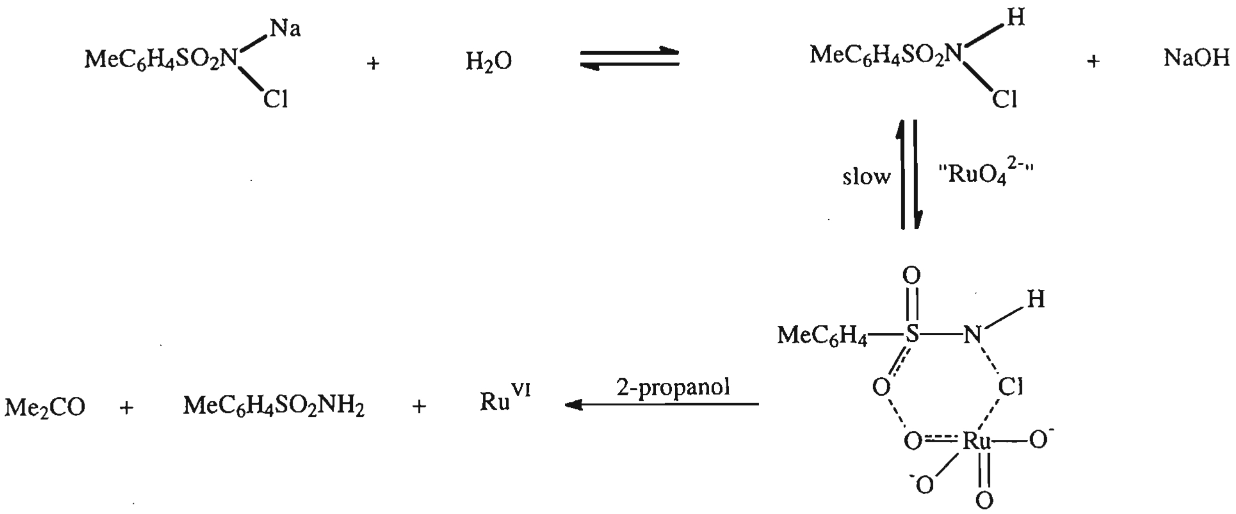

Figure 1.5.2. Proposed mechanism for the activation of ruthenate by chloramine-T prior to the oxidation of 2-propanol [74].

When potassium ruthenate was used catalytically with the persulphate ion for the oxidation of organic substrates, under mild conditions, primary alcohols were converted to carboxylic acids and secondary alcohols to ketones. There did not appear to be any effect on double bonds when the reaction times were short [75]. Subsequent work showed that catalytic oxidations by the reagent *trans*-$[RuO_3(OH)_2]^{2-}$ / $S_2O_8^{2-}$ converted primary alcohols, aldehydes, activated alkyl halides and primary nitro compounds to their corresponding carboxylic acids. Activated secondary alcohols were converted to ketones and the double bond in cinnamic acid was not cleaved [62]. With $[Fe(CN)_6]^{3-}$ as co-oxidant, primary alcohols were oxidized to a mixture of aldehydes and carboxylic acids [55].

The kinetics and mechanism of the oxidation of alcohols by ruthenate have been studied [74,76,77]. The reaction of ruthenate with cyclobutanol yielded cyclobutanone as the only product and thus implied that a two-electron oxidation process was involved (equation vii) [56].


(vii)

Carboxylato dioxoruthenium(VI) complexes of the form $[RuO_2(OCOR)Cl_2]^-$ (R = CH_3, Et, Pr) were synthesized by passing a stream of RuO_4 vapour into a concentrated acetic, propionic or butyric acid solution containing $[PPh_4]Cl$. For the complex where R = CHF_2, RuO_4 in CCl_4 was added to an acetonitrile solution of the acid and $[PPh_4]Cl$ [78,79]. The crystal structure for the acetato anion showed a distorted octahedral structure, with symmetrically bound acetato ligands, and *cis*-dioxo ligands in one plane (Figure 1.5.3).

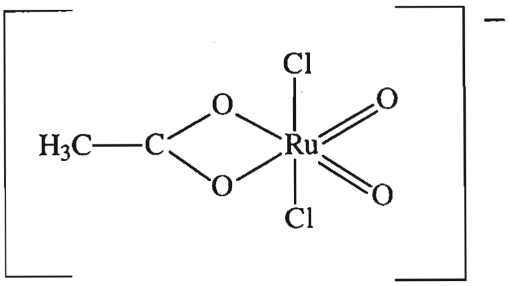

Figure 1.5.3. Structure of $[RuO_2(OCOCH_3)Cl_2]^-$.

The complex $[PPh_4][RuO_2(OCOCH_3)Cl_2]$ proved to be an effective two-electron donor and catalyzed the oxidation of primary alcohols to aldehydes, secondary alcohols to ketones, sulphides to sulphoxides and suphones, and triphenylphosphine to triphenylphosphine oxide, with NMO as co-oxidant. Competing double bond cleavage and oxidation of activated halides was not observed for the oxidations involving the complex, although the co-oxidant NMO oxidized activated halides on its own [80,81]. The yields and turnovers achieved for the individual complexes were approximately the same, for the range of alcohols oxidized with NMO as co-oxidant. Since this type of complex contained a good leaving group (acetate) and a reactive site (*cis*-dioxo), it was seen as a good precursor for the synthesis of other complexes.

The attempted synthesis of the propionic complex, $[PPh_4][RuO_2(OCOPr)Cl_2]$, by passing an O_3-O_2 mixture through a solution of $RuCl_3.nH_2O$ and $[PPh_4]Cl$ in propionic acid failed to give the desired product. However, orange-red crystals of the new compound

$[PPh_4]_2[Ru_2O(\mu\text{–}OCOEt)_2Cl_6]$ were obtained [40]. The crystal structure of the complex showed the first example of a tetravalent ruthenium complex containing both, a bridging oxo ligand and two bridging carboxylate groups. Attempted synthesis of the other carboxylato complexes mentioned above, by ozonolysis, gave undefined products.

Transition metal periodato complexes are rare and methods of preparation are often unsatisfactory. However, salts of the anion *trans*-$[RuO_2(HIO_6)_2]^{6-}$ [82,83] and the compound $[RuO_2(bipy)\{IO_3(OH)_3\}].1.5H_2O$ [84] have been successfully synthesized and fully characterized. For the former, it was established that both the ruthenium(VI) ion and the $[IO_5(OH)]^{4-}$ ligands functioned independently as two electron donors (*ie.* six electrons donated overall). These diamagnetic salts were rendered catalytic with periodate, oxidizing primary alcohols to carboxylic acids, secondary alcohols to ketones, and appeared to resemble reactions of *trans*-$[RuO_3(OH)_2]^{2-}$ at pH >12. The compound $[RuO_2(bipy)\{IO_3(OH)_3\}].1.5H_2O$ is an efficient catalyst for alkene epoxidation under mild conditions, and also oxidizes primary alcohols to aldehydes and secondary alcohols to ketones, using the co-oxidants $NaIO_4$ or Bu_4NIO_4. Stoichiometrically $[RuO_2(bipy)\{IO_3(OH)_3\}].1.5H_2O$ also functions as a six electron oxidant overall.

The first *trans*-dioxoruthenium(VI) porphyrin complex $[Ru(TMP)O_2]$ (TMP = 5,10,15,20-tetramesitylporphyrinato) [85] was capable of stoichiometric and catalytic epoxidations of olefins at ambient temperatures and pressure [86]. Research in this field by Che and his colleagues produced a range of dioxoruthenium(VI) complexes of the type *trans*-$[Ru(L)O_2]^{2+}$
{L = (14-TMC) = 1,4,8,11-tetramethyl-1,4,8,11-tetraazacyclotetradecane [87,88]
= (15-TMC) = 1,4,8,12-tetramethyl-1,4,8,12-tetraazacyclopentadecane
= (16-TMC) = 1,5,9,13-tetramethyl-1,5,9,13-tetraazacyclohexadecane [88,89]
= $(TMEA)_2$ = bis(N,N,N',N'-tetramethyl-1,2-diaminoethane) [88]}.

All the complexes were diamagnetic and were synthesized by the oxidation of *trans*-$[Ru(TMC)Cl_2]^+$ with H_2O_2. The Ru=O bond lengths of *trans*-$[Ru(15\text{-}TMC)O_2]^{2+}$ and *trans*-$[Ru(16\text{-}TMC)O_2]^{2+}$ of 1.718 Å and 1.705 Å respectively, showed that the Ru=O bond distance was insensitive to the ring size of the macrocycle [89]. Furthermore, the macrocyclic ring size was found to have little effect on the reactivity of the complexes.

The complex *trans*-$[Ru(14\text{-}TMC)O_2]^{2+}$ was found to be inert to oxidation of alkanes, but showed preferential attack on activated C-H bonds when compared to the complex *trans*-$[Ru(TMP)O_2]$ [86,90]. The shorter, stronger Ru=O bond in *trans*-$[Ru(14\text{-}TMC)O_2]^{2+}$ favoured hydride abstraction, which was evident from the observed conversion of toluene to benzaldehyde and benzyl alcohol, without attack on the aromatic ring.

The complex *cis*-$[Ru(Y)O_2]^{2+}$(Y = N,N,N',N'-3,6-hexamethyl-3,6-diazaoctane-1,8-diamine) [91] functioned as either a 1, 2, 3 or 4 electron donor in stoichiometric oxidations. Primary alcohols were oxidized to aldehydes, secondary alcohols to ketones, alkenes to a mixture of epoxides and carbonyl products, and aromatic hydrocarbons to their corresponding aldehydes or ketones. The complex *cis*-$[Ru(Y)O_2]^{2+}$ was compared to *trans*-$[Ru(14\text{-}TMC)O_2]^{2+}$, since a study suggested that *cis*-dioxoruthenium(VI) complexes were more reactive than their *trans*-counterparts [92]. Both complexes contained a chelating tetradentate tertiary amine ligand, however, the longer Ru=O bond length and higher E° value of *cis*-$[Ru(Y)O_2]^{2+}$ suggested that it would be the better oxidant. The difference in reactivity between these complexes was shown by the observation that *cis*-$[Ru(Y)O_2]^{2+}$ was able to oxidize alkenes and aromatic hydrocarbons, but under the same conditions *trans*-$[Ru(14\text{-}TMC)O_2]^{2+}$ could not.

Novel dioxoruthenium(VI) porphyrin cation radicals have been prepared by the stoichiometric oxidation of $[Ru(TMP)O_2]$ and $[Ru(EOP)O_2]$ (EOP = octaethylporphyrin) with phenoxathiin hexachloroantimonate. Stoichiometric oxidations of PPh_3 gave two moles $Ph_3P{=}O$ as product [93], but further research on $[Ru(TMP)O_2]$ proved that it was a poor oxidant of *iso*-propanol [94].

Irradiation of the complex {*trans*-$[Ru(L)O_2]Y_2$} (Y = PF_6, ClO_4; L = meso-1,2,6,10,11-pentamethyl-2,6,10-triazo[11]2,6-pyridinophane) in the presence of an organic substrate yielded the corresponding oxidized organic products. Propan-2-ol was oxidized to acetone, cyclohexene was oxidized to a mixture of products, and norbonene was oxidized to its corresponding epoxide, all in low yield [95].

Griffith *et al.* synthesized the green complex, $[Y][RuO_2Cl_3]$ (Y = PPh_4, $AsPh_4$), by reacting Y^+ with ruthenate and HCl at 0°C [58]. Later, Perrier and Kochi (by a different method) [96] synthesized and fully characterized the phosphonium and ammonium salts of $[RuO_2Cl_3]^-$ and $[RuO_2Cl_4]^{2-}$, the former converting to the six co-ordinate complex in dichloromethane (equation viii).

$$RuO_2Cl_3^- \quad + \quad Cl^- \quad \longrightarrow \quad RuO_2Cl_4^{2-} \qquad \text{(viii)}$$

The crystal structure of the dark red ammonium salt of $[RuO_2Cl_4]^{2-}$ showed an octahedral structure which had a ν_{asym} *trans*-(Ru=O) infra-red peak at 830 cm^{-1}. Similar salts, *trans*-$R_2[RuO_2X_4]$ {X = Cl, Br; R = $Me_2NH(CH_2)_2NHMe_2$, $Me_2N(C_2H_4)_2NMe_2$} have been prepared and were found to be viable oxidants of alcohols [97]. The crystal structure of the emerald green, co-ordinatively unsaturated *cis*-$[(PPh_3)_2N][RuO_2Cl_3]$ salt showed a trigonal bipyramidal structure, with the *cis*-dioxo peaks showing a strong single infra-red peak at 882 cm^{-1}. The crystal structure of $[PPh_4][RuO_2Cl_3]$ appeared to be disordered between trigonal bipyramidal and square-pyramidal conformations. The square-pyramidal component of $[RuO_2Cl_3]^-$ was assigned a *trans*-dioxo infrared peak at 891 cm^{-1}, and the trigonal bipyramidal component the *cis*-dioxo infrared peak at 878 cm^{-1}. Griffith *et al.* reported that $[PPh_4][RuO_2Cl_3]$ functioned as a mild oxidant in dichloromethane, converting primary alcohols to aldehydes and secondary alcohols to ketones in good yield, without competing double bond cleavage (except in large electron rich complexes like cholesterol) [58]. However, Perrier and Kochi found that $[PPh_4][RuO_2Cl_3]$ did in fact oxidize cyclohexene to a mixture of products. Furthermore, $[PPh_4][RuO_2Cl_3]$ was found to oxidize triphenylphosphine to triphenylphosphine oxide and 2,6-di-*tert*-butylphenol to 2,6-di-*tert*-butyl-p-benzoquinone [96].

Reaction of RuO_4 in CCl_4 with "ice cold solutions" of HX and CsX (X = Br, ½ C_2O_4) in water gave the salts $Cs_2[RuO_2X_4]$ [98]. Complexes of the form $[RuO_2(R)_2Cl_2]$ (R = py [= pyridine], 4-*t*-Bu-py, 4-Cl-py) and *trans*-$[RuO_2(py)_2Br_2]$ have also been synthesized [98-100] by treating an aqueous solution of *trans*-$[RuO_3(OH)_2]^{2-}$ and the appropriate substituted pyridine, with HX (X = Cl, Br). The complex $[RuO_2(bipy)Cl_2]$ (bipy = 2,2'-bipyridine) was prepared by a similar method.

A range of other dioxoruthenium(VI) complexes have been reported [98-100]: *trans*-$[RuO_2(Y)_4]$ {Y = NH_3, nicotinic acid, 2-COOH-py, 3,4-$(COOH)_2$-py}, *trans*-$[RuO_2(py)_4][L]_2$ {L = BF_4, PF_6}, *trans*-$[RuO_2(2\text{-}COOH\text{-}py)_2]$, *trans*-$[RuO_2Cl_3(L)]^-$ {L = py, 4-*t*-Bu-py, 3-CH_3-py, 3,4-$(CH_3)_2$-py}, *trans*-$[Ru_2O_6(L)_4]$ {L = py, 4-*t*-Bu-py, nicotinic acid, *iso*-nicotinic acid, 2-COOH-py, ½ (2,2'-bipy)}. These complexes function as overall four electron stoichiometric oxidants (except *trans*-$[Ru_2O_6(L)_4]$ which functions as an eight electron oxidant), converting primary alcohols to aldehydes, secondary alcohols to ketones, and function catalytically with the co-oxidant NMO, without attacking double bonds. The more soluble species effected the above mentioned oxidations in good yield, using oxygen as co-oxidant [100]. Some of these complexes are discussed further in Chapter Two.

A range of orange crystalline complexes of the form $[RuO_2(py)_2(O_2CR)_2]$ (R = CH_3, CH_3CH_2, $CH_3CH_2CH_2$, $(CH_3)_2CH$, C_6H_5) [101,102] were obtained from the reaction of a mixture of the appropriate carboxylic acid and pyridine with barium ruthenate in CH_3CN at 0°C. All the complexes showed *trans*- arrangements of the dioxoruthenium(VI) moiety, pyridine ligands and acetato groups (Figure 1.5.4).

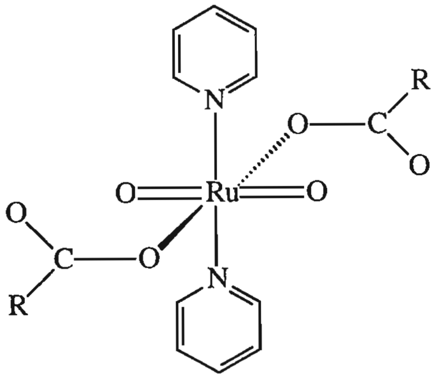

Figure 1.5.4. Structure of $[RuO_2(py)_2(O_2CR)_2]$[101,102].

The Ru=O bond length (1.726 Å) in the complexes was relatively longer than those found for other dioxoruthenium(VI) complexes [91]. Thus, these complexes were capable of oxygen transfer reactions including oxidation of triphenylphosphine to triphenylphosphine oxide, oxidation of olefins to a range of products, oxidation of allylic C-H bonds, oxidation of aromatic C-H bonds, and oxidation of hydrocarbons and ethers. Clear from the above is that these oxidants lacked stereospecificity and selectivity in oxidation reactions.

Dovetoglou *et al.* prepared *trans*-$[RuO_2(tpy)(H_2O)]^{2+}$ (tpy = 2,2':6',2''-terpyridine) with a Ru=O bond length of 1.661 Å. The complex behaved like a *cis*-directed four-electron transfer oxidation agent in reactions, with the transfer of two oxygen atoms to a single reductant [103,104].

Che and co-workers have studied complexes of the form *trans*-$[RuO_2(bipy)_2]$ [105] and *cis*-$[RuO_2(6,6'\text{-}Cl_2\text{-}bipy)_2]$ (6,6'-Cl_2-bipy = 6,6'-dichloro-2,2'-bipyridine) [106]. Both complexes are diamagnetic with the *trans*-complex having ν_{asym}(Ru=O) at approximately 850 cm^{-1}, and the *cis*-complex showing two infra-red bands for ν(Ru=O) at 840 cm^{-1} and 790 cm^{-1}. The *trans*-complex was stable "in the dark and cold", but decomposed when exposed to UV-light at room temperature. The *cis*-complex oxidized chloride to chlorine in high yield from 1M HCl, and oxidized inactivated C-H and C=C bonds in low yields.

Recently, Che *et al.* used $[Ru(Por^*)O_2]$ {H_2Por^* = 5,10,15,20-tetrakis[(1S,4R,5R,8S)-1,2,3,4,5,6,7,8-octahydro-1,4:5,8-dimethanoanthracen-9-yl]-porphyrin} in stoichiometric and catalytic enantioselective hydroxylations of benzylic C-H bonds. The products of the hydride abstraction reactions were enantio-enriched aryl alcohols [107].

Gross and Ini [108] synthesized a novel chiral porphyrin *trans*-dioxoruthenium(VI) catalyst for the epoxidation of styrene. The investigation showed that aromatic solvents and the use of N-oxide based primary oxidants favoured the optimal oxidation of styrene. Kinetic studies of such alkene oxidations, by a range of *trans*-dioxoruthenium(VI) complexes with tetradentate ligands, have been carried out [109].

The complex $[RuO_2(dmp)][PF_6]_2$ (dmp = bis-dimethyl-1,10-phenanthroline) [110] appeared to be a catalyst precursor for the oxidation of alkenes by oxygen, since an induction period of twenty-four hours was required before the active oxidation catalyst was produced. Low conversions for the epoxidation of norbonene were achieved, with the epoxidation of cyclohexene giving a mixture of products.

A mono-oxo complex, $[RuO(CH_2SiMe_3)_4]$, has also been synthesized [111]. The complex was an orange, volatile (bp. 20°C, 1 atm.) oil that was soluble in non-polar solvents and that was sensitive to air and water. This complex is significant in being one of very few organometallic ruthenium(VI) oxo compounds.

The complexes $[RuO_2L_2\{SCH_2CHRC(O)O\}]$ (L = py, ½ bipy; R = H, NHCHO, NHCOMe) were synthesized by Shapley *et al.* as models for the *iso*-penicillin N-synthethase (a metalloenzyme) active site [112]. The starting materials used in the syntheses were $[RuO_2(OH)_2(py)_2]$ (discussed in Chapter Two) and $[RuO_2(bipy)Cl_2]$. The final products showed the characteristic dioxoruthenium(VI) infra-red peaks in the region of 800-833 cm^{-1}.

1.6. Ruthenium(V)

Relatively few ruthenium(V) compounds are known.

The paramagnetic, red-brown compound $[RuO(O_2COCEt_2)_2][Pr_4^n N]$ [113] was obtained as the product of the reaction of $[Pr_4^n N][RuO_4]$ and 2-hydroxy-2-ethylbutyric acid over twenty-four hours. The trigonal bipyrimidal anion had a short Ru=O bond (1.687 Å) and was a mild oxidant converting primary alcohols to aldehydes and secondary alcohols to ketones in acetonitrile. Catalytic turnovers of up to twenty-five were obtained for the oxidation of alcohols. A range of similar compounds $[RuO(O_2COCR^1R^2)_2][Pr_4^n N]$ (R^1R^2 = Me_2, EtMe, PhMe) showed low reactivity to organic species [114].

Ruthenium(V) mono-oxo compounds have been electrochemically generated from *trans*-$[Ru^{IV}LO(Cl)][ClO_4]$ (L = 14-TMC, 15-TMC) [115,116]. The compounds were found to oxidize benzyl alcohol to benzaldehyde catalytically with up to fifty turnovers. The compound *trans*-$[Ru(TMC)O_2][ClO_4]$ was also generated electrochemically, but it disproportionated rapidly into *trans*-$[Ru^{VI}(TMC)O_2]^{2+}$ and *trans*-$[Ru^{IV}(TMC)O(OH_2)]^{2+}$ upon dissolution in aqueous acidic solutions [88,117].

Another ruthenium(V) compound $[Ru(N_4O)O]^{2+}$ {N_4OH = bis[2-(2-pyridyl)ethyl(2-hyroxy-2-2-(2-pyridyl)ethyl]amine} was obtained as a brownish-green microcrystalline solid, which showed an intense Ru=O stretch at 872 cm^{-1}. The ion was an active oxidant, oxidizing primary alcohols to aldehydes, secondary alcohols to ketones (both reactions being completed within twenty minutes), cleaved double bonds and oxidized hydrocarbons [118]. The octahedral compound *cis*-$[RuLO_2]^+$ (L = N,N,N',N'-3,6-hexamethyl-3,6-diazaoctane-1,8-diamine) showed similar oxidation characteristics [91].

1.7. Ruthenium(IV)

The crystal structure of the cation $[RuO(py)_4Cl]^+$ showed that the oxo and chloride ligands were *trans-* co-ordinated, with the four pyridine ligands in the equatorial plane of the octahedron. The Ru=O bond distance was relatively long (1.862 Å), and exhibited a characteristic *trans*-(Ru=O) infra-red vibration at 805 cm^{-1} [119]. The complex oxidized triphenylphosphine to triphenylphosphosphine oxide in acetonitrile, but reacted with alcohols to form new ruthenium compounds [120].

The reaction of $[Ru(bipy)_2(py)O]^{2+}$ [121] with a series of alcohols in aqueous media and acetonitrile has been studied kinetically [122,123]. The study showed that tertiary alcohols were unreactive with the compound, but two-electron hydride transfer reactions were evident in the oxidation of other alcohols. The rate of such reactions followed the alcohol sequence, methyl < primary < secondary < allylic < benzylic. The potential of the complex as a catalyst could only be speculated on from the kinetic data obtained.

Trialkylphosphine compounds $[RuO(bipy)_2(PR_3)]^{2+}$ (R = Me, Et, *iso*-propyl, cyclohexyl, phenyl) have been extensively studied [124-127]. Infra-red ν(Ru=O) stretches in the range 750 cm^{-1} to 790 cm^{-1} were observed for these compounds and an increase in stability of the complexes was noticed as the number of carbon atoms in the trialkylphosphines decreased. Kinetic studies on $[RuO(bipy)_2(PPh_3)]^{2+}$ and $[RuO(bipy)_2(PEt_3)]^{2+}$ in reactions with alcohols showed mild oxidative character, with primary alcohols being oxidized to aldehydes, secondary alcohols to ketones, and aldehydes to carboxylic acids [125]. The rate of alcohol oxidation increased as the number of carbons in the alcohol increased.

A range of ruthenium(IV) epoxidation agents have been studied, among them the compound $[Ru(OH)(IO_3)(bipy)_2](PF_6)_2.\frac{1}{2}H_2O$ which epoxidized cyclooctene and *trans*-stilbene in high yield, when IO_4^- was used as co-oxidant [128]. $[RuO(tpy)(bipy)]^{2+}$ [129] and [Ru(OEP)(OROH)] {formed when $[Ru^{VI}(OEP)O_2]$ is reacted with alcohols (ROH)} [130] also behave as (mediocre) catalysts in epoxidation reactions.

$[Ru(L)O(H_2O)][ClO_4]_2.2H_2O$ (L = 1,12-dimethyl-3,4 : 9,10-dibenzo-1,12-diaza-5,8-dioxacyclo-pentadecane) [131] and $[Ru^{IV}(14\text{-}TMC)O(NCO)][ClO_4]$ [88] function as electrocatalysts for the oxidation of benzyl alcohol to benzaldehyde, the latter compound oxidizing benzyl alcohol with air as a co-oxidant. The structures of these compounds have been determined. Groves and Ahn [132] used ^1H NMR analysis to determine the formation of the ruthenium(IV) intermediate in the aerobic oxidation of $[Ru^{II}(TMP)]$ to $[Ru^{VI}(TMP)O_2]$. The paramagnetic intermediate was confidently identified as $[Ru^{IV}(TMP)O]$.

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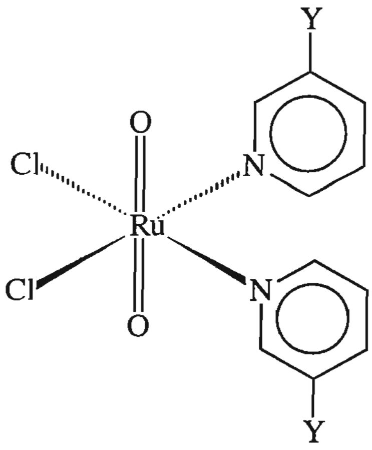
Chapter Two

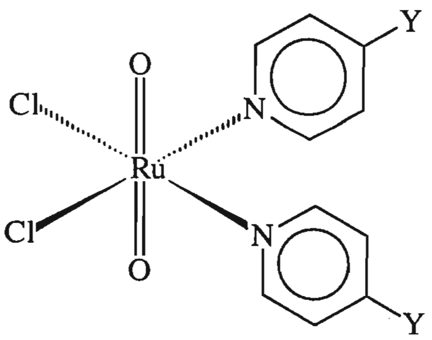
An Investigation into the Chemistry of Some Neutral Ruthenium-oxo Compounds

2.1.1. Introduction

As out-lined in Chapter One, the chemistry of ruthenium has been extensively investigated with a high degree of interest shown in ruthenium-oxo oxidation systems. However, ruthenium-oxo chemistry is still underdeveloped relative to other metals such as osmium [1-4] and rhenium [5,6]. Thus, as part of the ongoing development of new oxidation catalysts of high valent dioxoruthenium(VI), an investigation was carried out to determine how variations of substituents or ligand patterns affect oxidative ability. Compounds of the form $RuO_2(Y\text{-}py)_2Cl_2$ **1** (py = pyridine, Y = H **1a**, 4-*t*-Bu **1b**, 3-CN **1c**, 4-CN **1d**, 2-Br **1e**, 3-Br **1f**, 4-Br **1g**, 4-Cl **1h**, 4-Me **1i**, 4-$C(O)C_6H_5$ **1j**, 3-COOH **1k**, 4-COOH **1l**) and RuO_2Cl_2Z **2** (Z = bipyridine [= bipy] **2a**, phenanthroline [= phen] **2b**) (Figure 2.1.1) were prepared and the effects of the various substituents on the properties of the compounds were investigated. A comparative study of most of these as both stoichiometric and catalytic oxidants for the oxidation of 1-hexanol to hexanal was carried out. The complexes **1a**, **1b**, **1h** and **2a** have been synthesized previously [7-9].



Y = CN **1c**, Br **1f**, COOH **1k**



Y = *t*-Bu **1b**, CN **1d**, Br **1g**, Cl **1h**,
Me **1i**, $C(O)C_6H_5$ **1j**, COOH **1l**

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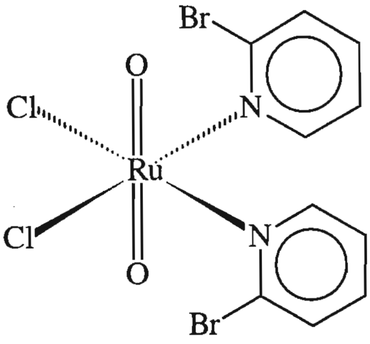
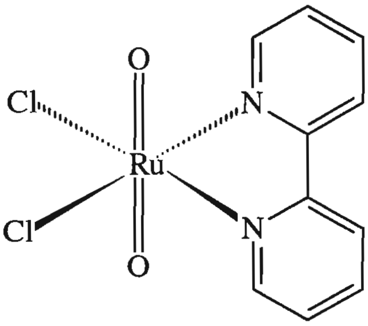
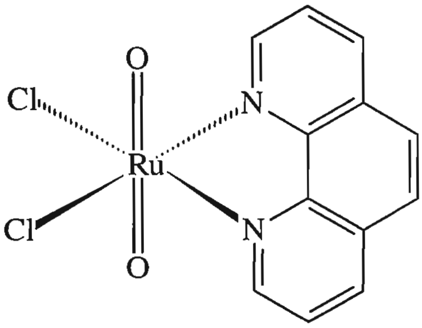


1e



2a



2b

Figure 2.1.1. Structures of the compounds **1** and **2**.

2.1.2. Results and Discussion for Compounds 1 and 2

RuO_4 was prepared by stirring $RuCl_3.3H_2O$ with $NaIO_4$ in aqueous media overnight (equation i).

$$RuCl_3.3H_2O \quad + \quad NaIO_{4(aq)} \quad \longrightarrow \quad RuO_{4(aq)} \qquad \text{(i)}$$

The RuO_4 was extracted with four portions of CCl_4. Each extract had a different colour. The first CCl_4 extract was dark brown followed by lighter shades of brown solution to the almost clear fourth extract. This was due to the varying concentrations of RuO_4 in each fraction. These four fractions were then combined in a separating flask.

The storage of the RuO_4 solution in the fumehood over a period of time would have resulted in decomposition of the ruthenium(VIII) compound [10]. Thus, an aqueous solution of sodium metaperiodate was layered above the RuO_4 solution, to enable easy re-oxidization of the ruthenium to the +VIII oxidation state by simply mixing the contents of the separating flask. This was always carried out prior to use in reactions. The final, pure solution of RuO_4 was yellow.

RuO_4 was reacted with molar NaOH to obtain sodium ruthenate, [*trans*-$RuO_3(OH)_2]^{2-}$ (equation ii), which was found to be stable at high pH's [11-13].

$$RuO_4 \quad + \quad NaOH_{(aq)} \quad \xrightarrow{\text{Room Temp.}} \quad trans\text{-}[RuO_3(OH)_2]^{2-}{}_{(aq)} \qquad \text{(ii)}$$

The compounds **1** and **2** were prepared by the reaction at 0°C of the aqueous sodium ruthenate solution with a solution of the ligand dissolved in HCl_{conc} (equations iii and iv).

$$[RuO_3(OH)_2]^{2-} \quad + \quad [H(y\text{-}py)]^+Cl^- \quad \xrightarrow{0°C} \quad RuO_2(Y\text{-}py)_2Cl_2 \qquad \text{(iii)}$$

$$[RuO_3(OH)_2]^{2-} \quad + \quad [H_2Z]^{2+}(Cl^-)_2 \quad \xrightarrow{0°C} \quad RuO_2Cl_2Z \qquad \text{(iv)}$$

The compounds precipitated out of solution instantaneously as green or yellow solids, with the yellow complexes turning green on filtration or during storage. No change in elemental analysis or in the infrared spectra accompanied the colour change.

Table 2.1.1. Yields and elemental analysis data for the novel complexes and the corresponding water of crystallization obtained for compounds **1** and **2**.

Complex	Percentage Yield	Elemental Analysis for Novel Complexes[a] %C	% H	%N	Water of Crystallization
1a	56	b	b	b	-
1b	56	c	c	c	-
1c	55	32.88 (32.80)	2.27 (2.51)	12.73 (12.75)	1.5
1d	64	33.64 (33.51)	2.07 (2.32)	13.10 (13.02)	1
1e	45	d	d	d	-
1f	65	22.35 (22.32)	1.43 (1.86)	4.80 (5.21)	1
1g	17	22.69 (22.32)	1.36 (1.86)	4.95 (5.21)	1
1h	82	c	c	c	0.5
1i	8	34.94 (35.29)	3.54 (3.92)	6.50 (6.86)	-
1j	74	48.35 (48.39)	3.04 (3.53)	4.42 (4.70)	1.5
1k	5	d	d	d	-
1l	16	d	d	d	-
2a	40	e	e	e	-
2b	47	37.06 (37.52)	2.82 (2.10)	7.19 (7.29)	-

a. Calculated values in parentheses.

b. Data in ref. [7].

c. Data in ref. [9].

d. Not obtained since the complex was too unstable.

e. Data in ref. [8].

As is evident from table 2.1.1, yields varied over a wide range from 5% to 82% depending on the ligands. Satisfactory elemental analysis (C, H, N) were obtained for all the compounds (except compounds **1k** and **1l** that were very unstable). The elemental analysis data for the new complexes are shown in table 2.1.1. Many of the complexes crystallized with between 0.5 to 1.5 water molecules. This water can be removed under vacuum in a desiccator over silica gel or KOH.

The stabilities of the compounds varied considerably. Thus, for example, compounds **1a** and **2a** decomposed over two days at room temperature, or over 4 to 5 days at –10°C, whilst *e.g.* compounds **1j** and **2b** appeared to be stable at room temperature and could be stored indefinitely at –18°C. Attempts to prepare the compounds where Y = 4-*iso*-propyl, 4-OH, 4-NH_2, 4-NMe_2 and 4-phenyl were not successful since the former four compounds decomposed in solution, and the latter compound could not be precipitated out of solution. The attempted synthesis of the 2,6-difluoropyridine and 1,2,3,4,5-pentafluoropyridine complexes also failed since no new product formation was observed.

The attempt to prepare the quinuclidine analogue of compound **1** gave a green product, in low yield, with a strong *trans*-dioxo peak observable at 887 cm^{-1} in the infrared spectrum. This peak was at a higher wavenumber than expected for neutral *trans*-dioxoruthenium(VI) species (as is evident for the other complexes in table 2.1.2) and the reaction was believed to have failed to produce $RuO_2(quinuclidine)_2Cl_2$, since the elemental analysis of the product did not fit the expected formulation.

As mentioned earlier, compounds **1a**, **1b**, **1h** and **2a** had been synthesized previously [7-9]. The infrared data obtained for these complexes during the present study, compared well with the previously published data. All the synthesized complexes showed the characteristic strong $\nu_{asym}(Ru{=}O)$ vibrations between 826 cm^{-1} and 853 cm^{-1} [14]. A single strong oxo band, characteristic of a *trans*-oxo arrangement, is observed for all the compounds except compounds **1d**, **1f** and **1i**, where two peaks are observed. This may be due to the structures of the latter three compounds not conforming to ideal symmetry, or due to a *cis*-dioxo stereochemistry. The other characteristic infrared vibrations in table 2.1.2 are for the substituted pyridine ligands and were assigned by comparison with literature values [15].

Table 2.1.2. Selected infrared data for compounds **1** and **2**.

Compound No.	**Characteristic ν_{asym}(RuO) (cm^{-1})**	**Other CharacteristicVibrations (cm^{-1})**
1a	838(vs)	1596ν(C=C),1419ν(C=C),738ν(CH)
1b	842(vs)	1617ν(C=C),1067ν(CH),569ν(CH)
1c	843(m)	2246ν(CN),1580ν(C=C),480ν(CH)
1d	840(vs), 831(s)	2243ν(CN),1486ν(C=C),480ν(CH)
1e	826(s)	1513ν(CH),1442ν(C=C),701ν(CH)
1f	848(vs), 818(s)	1592ν(C=C),1463ν(C=C),827ν(CH)
1g	841(vs)	3088ν(CN),1590ν(C=C),824ν(CH)
1h	841(vs)	1596ν(C=C),1116ν(CH), 824ν(CH)
1i	844(vs), 831(s)	810ν(CH)
1j	841(s)	1281ν(CO),746ν(CH),698ν(CH),639ν(CH)
1k	853(s)	1721ν(COOH),1429ν(C=C),758ν(CH)
1l	842(m)	1708ν(COOH),1418ν(C=C),764ν(CH)
2a	839(vs)	740ν(CH),1516ν(CH)
2b	846(vs)	3449ν(CN),1542ν(C=C),766ν(CH)

vs = very strong
s = strong
m = medium

The compounds **1** and **2** were investigated as stoichiometric oxidants in the oxidation of 1-hexanol to hexanal over a twenty-four hour period. All the oxidation reactions were carried out in Schlenk tubes, under a nitrogen atmosphere (to prevent oxidation by air) and in the dark (to prevent free radical oxidation reactions initiated by UV radiation). The reactions were monitored by gas chromatography, using an internal standard to obtain quantitative analysis data. Conversion percentages, represented as the average of at least three reactions, are presented in table 2.1.3.

Table 2.1.3. Stoichiometric oxidations of 1-hexanol to hexanal by complexes **1** and **2**.

Complex	Reaction Time	% Conversion	Complex	Reaction Time	% Conversion
1a	+ 30 Min.	45	**1g**	+ 30 Min.	47
	+ 3 Hours	55		+ 3 Hours	59
	+ 24 Hours	50		+ 24 Hours	59
1b	+ 30 Min.	34	**1h**	+ 30 Min.	49
	+ 3 Hours	38		+ 3 Hours	50
	+ 24 Hours	39		+ 24 Hours	50
1c	+ 30 Min.	21	**1i**	+ 30 Min.	33
	+ 3 Hours	37		+ 3 Hours	30
	+ 24 Hours	34		+ 24 Hours	31
1d	+ 30 Min.	37	**1j**	+ 30 Min.	38
	+ 3 Hours	40		+ 3 Hours	36
	+ 24 Hours	38		+ 24 Hours	31
1e	+ 30 Min.	31	**2a**	+ 30 Min.	26
	+ 3 Hours	73		+ 3 Hours	57
	+ 24 Hours	84		+ 24 Hours	63
1f	+ 30 Min.	58	**2b**	+ 30 Min.	<1
	+ 3 Hours	61		+ 3 Hours	2
	+ 24 Hours	63		+ 24 Hours	7

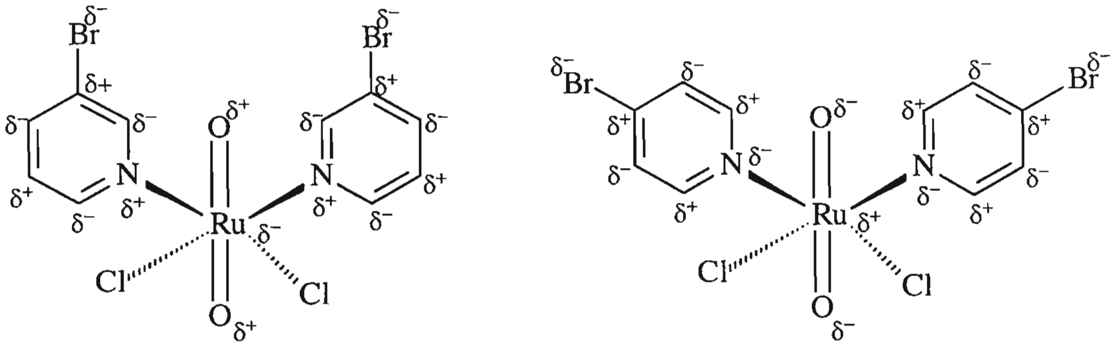
All the compounds **1** and **2** functioned as stoichiometric oxidants, although the individual activities of the complexes varied significantly. Based on the twenty-four hour conversions the compounds follow the sequence of oxidizing ability for Y-py and Z: phen < 4-Me-py < benzoyl-py < 3-CN-py < 4-CN-py < 4-*t*-Bu-py < 4-Cl-py ≈ py < 3-Br-py ≈ 4-Br-py < bipy < 2-Br. This sequence of oxidizing ability is roughly opposite to the trend of stability observed for these complexes. Thus, generally, the more thermally unstable a compound was, the more active it was as an oxidant. What is noteworthy, is the fact that the compounds $RuO_2(bipy)Cl_2$ (**2a**) and $RuO_2(phen)Cl_2$ (**2b**) are on opposite ends of the oxidation series. This reflects the vastly different stabilities of these compounds, in that **2a** decomposed fairly rapidly in air (after two days at room temperature), whilst **2b** could readily be stored. This difference in stability may in turn be due to the far greater rigidity of the phenanthroline ligand relative to the bipyridine ligand. Steric factors may also have an influence in causing the very different oxidizing abilities of compounds **2**. The compounds **1a**, **1b**, **1h** and **2a** had previously been reported to be stoichiometric oxidants for the conversion of primary alcohols to aldehydes and secondary alcohols to ketones [7-9].

It was noticed that compounds **1** and **2** decomposed with a loss of the *trans*-ruthenium oxo grouping and it was thus hoped to correlate the stability (and / or oxidizing ability) of these complexes to the strength of their *trans*-Ru=O bonds.

From the structures (**i**) and (**ii**) in figure 2.1.2, showing the localized charge dipoles on 3-Br-pyridine and 4-Br-pyridine respectively, one would expect the nitrogen atom of the pyridine ligands substituted in the 3-position by an electron withdrawing group, to be relatively more positively charged when compared to the pyridine ligands substituted in the 4-position. This localized charge distribution should result in the relative charge distribution in the complexes as shown in figure 2.1.3. As a result of this charge distribution, a stronger Ru=O bond should result in the 3-substituted compounds.

(**i**) (**ii**)

Figure 2.1.2. Localised relative charges on 3-Br-pyridine (**i**) and 4-Br-pyridine (**ii**).



1f **1g**

Figure 2.1.3. The resulting relative charge distribution in the complexes **1f** and **1g**.

The infrared data (Table 2.1.2) for the 3- and 4- substituted CN-pyridine compounds **1c** and **1d**, the 3- and 4- substituted bromo-pyridine compounds **1f** and **1g**, and the nicotinic and *iso*-nicotinic acid derivatives **1k** and **1l** confirm this by showing stronger Ru=O bond vibrations for the 3-substituted derivatives, although the differences are not large.

Attempts were made to correlate ν(Ru=O) of the compounds **1** with the pK_a's [16-18] and Hammet [19,20] or Taft [19] substituent constants of the substituted pyridines without much success. A rough trend towards higher wave numbers was observed with increasing pK_a of the substituted pyridines, however, no trend at all was observed with Hammett σ values. Since the Hammett σ value has both a resonance (σ_R) and an inductive component (σ_I), and since resonance acceptors in the 4-position make a negligible contribution to pyridinium ion acidities [18,21,22], we plotted ν(Ru=O) versus σ_I [23,24] for the compounds **1**, plotting the 3- and 4- substituted pyridine compounds separately (Figure 2.1.4).

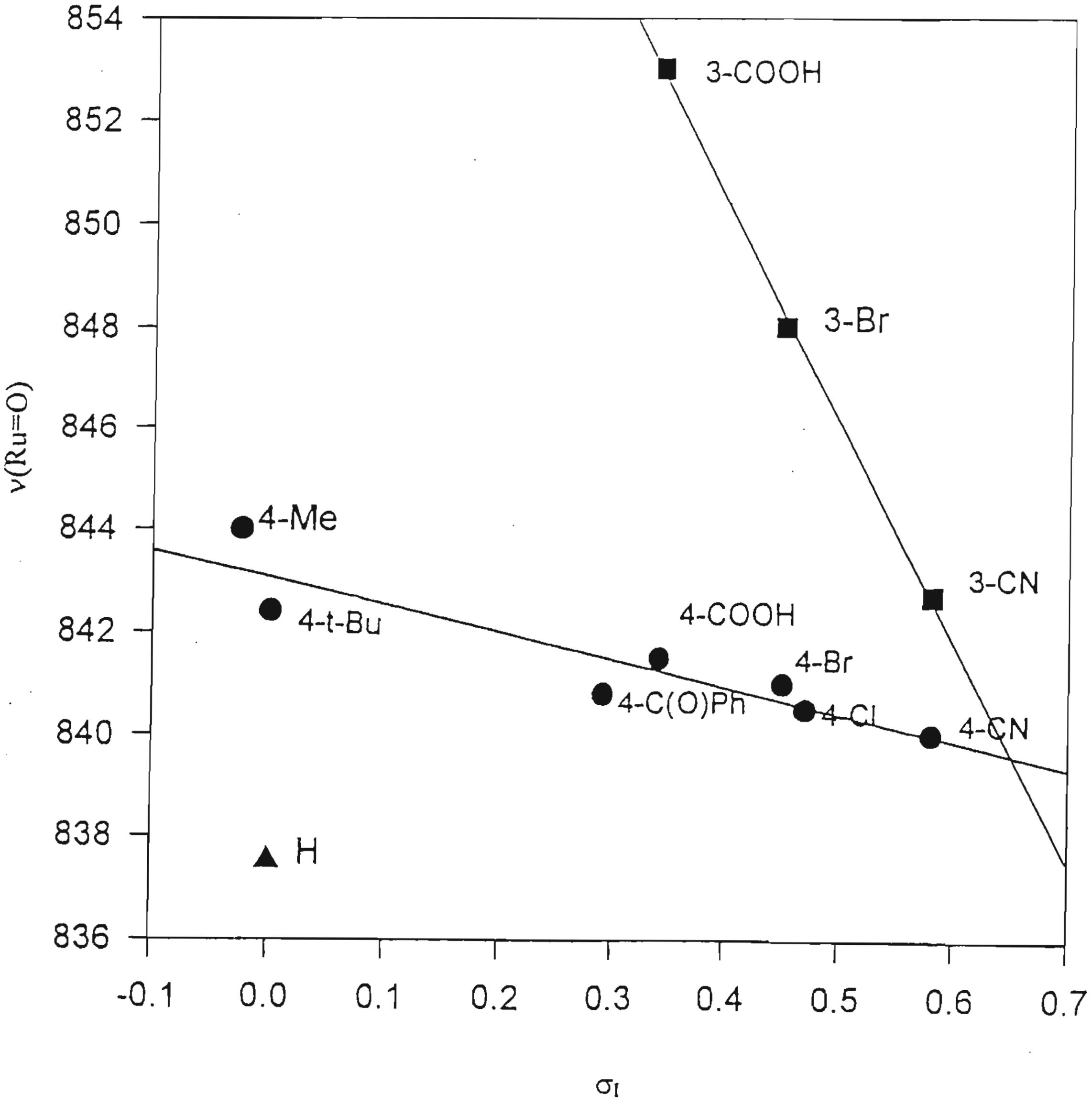


Figure 2.1.4. A plot of ν(Ru=O) versus σ_I.

As can be seen, the correlations are approximately linear ($R^2 = 0.84$ for the 4-substituted and $R^2 = 1.00$ for the 3-substituted compounds), with the slope being steeper for the pyridines substituted in the three position. The difference in slope can be rationalized by the inductive effect being a polar or field effect and thus becoming weaker with increasing distance between the substituent and the pyridine nitrogen [21]. Thus changes at the 3-position have a much stronger effect on the pyridine nitrogen and hence on the Ru=O bonds. The points for the picoline and *tertiary*-butyl-pyridine compounds are slightly off the line, probably because the methyl and *tertiary*-butyl groups act as mild resonance donor substituents, and resonance donor substituents do effect the acidity of the nitrogen [25]. What cannot be explained is the fact that the ν(Ru=O) of the unsubstituted pyridine compound **1a** does not fit on either graph. This observation is surprising since all σ values are determined relative to the substituent H.

A good linear relationship (R^2 = 0.89 for both the 3- and 4- substituted compounds) is observed between ν(Ru=O) of compounds **1** and the Pauling-type electronegativity values of the substituents (Figure 2.1.5) [26].

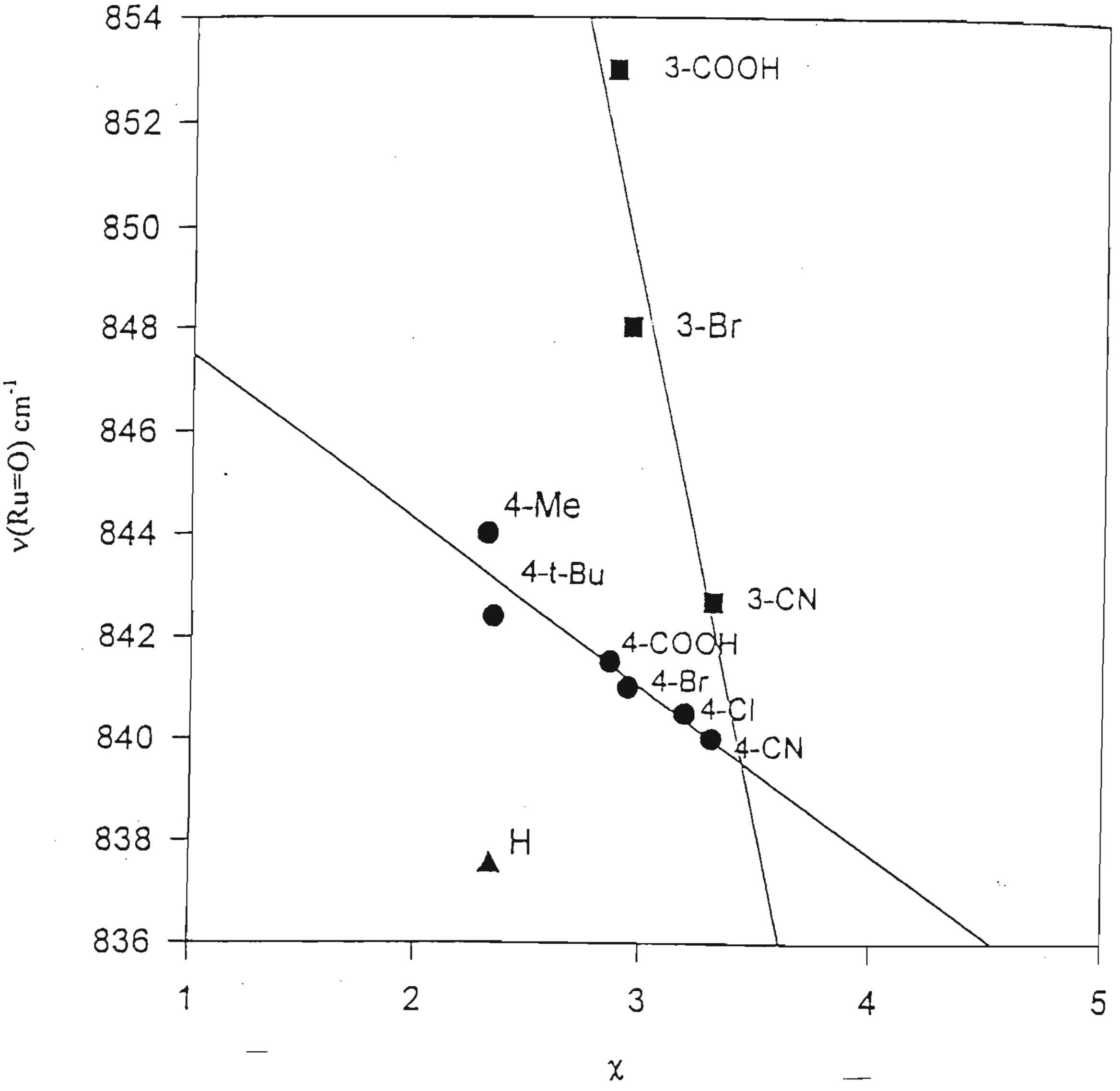


Figure 2.1.5. Plot of ν(Ru=O) versus Pauling-type electronegativity (χ).

A linear relationship is also observed between ν(Ru=O) of compounds **1** and the Swain-Lupton ℑ values [19,25]. However, the problem with the pyridine compound **1a** remains in both these cases. Consequently, the best fit between the ν(Ru=O) values of compounds **1** is probably with the Taft σ^* values ($R^2 = 0.83$ for the 4-substituted and $R^2 = 0.88$ for the 3-substituted compounds), where the methyl substituent is taken as the zero point [19,25] (Figure 2.1.6).

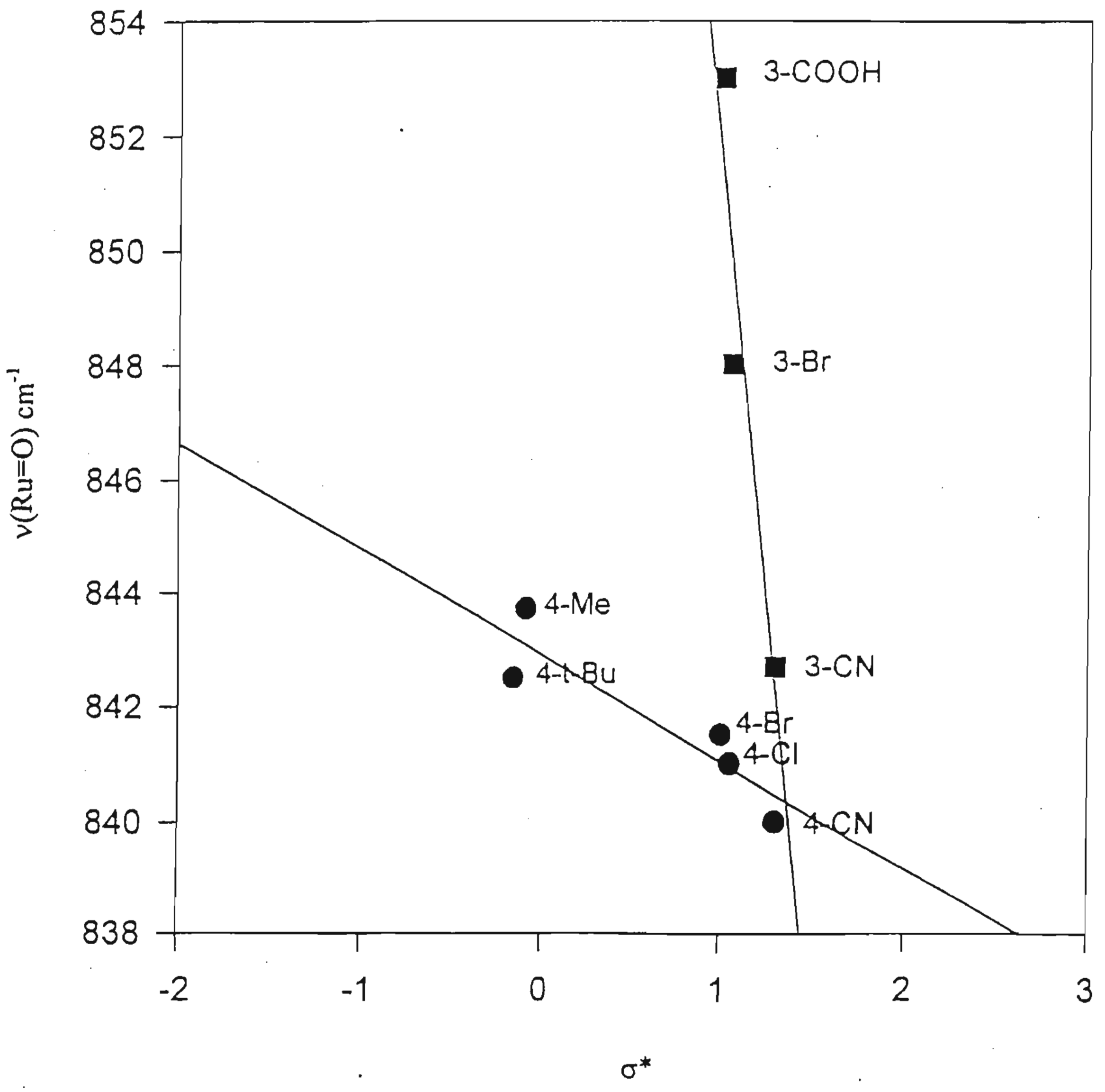


Figure 2.1.6. A plot of ν(Ru=O) versus σ^*.

In general there has been substantial interest and controversy in the interpretation of the effects of the 3- and 4-substituents on the acidities of pyridinium ions and different references quote slightly different values. The results obtained in this study imply that current substituent constants are not perfectly transferable to the system under investigation. This is not surprising, however, since substituent constant values are determined from kinetic data of chemical reactions and the use of such data to investigate structural characteristics of transition metal compounds consequently places them slightly out of context. However, the observed fit is fairly good and clearly shows a trend. There is no relationship between the stabilities of compounds **1** and their ν(Ru=O) values, nor with the pK_a's of the substituted pyridines. This confirms previous observations that, in general, the pK_a's of substituted amines do not appear to influence the stabilities of their compounds [27].

In comparing the 3- and 4-substituted pyridine compounds, one would have expected the compounds with weaker Ru=O bonds to be the stronger oxidants and thus have expected the 4-substituted pyridine complexes to be better oxidants than the corresponding 3-substituted derivatives. This, however, was not conclusive. Whereas **1d** was a better oxidant than **1c**, **1f** was equal to or better than **1g**. The differences were not large, as may have been expected from the relatively small differences in their Ru=O bond strengths.

The catalytic performance of the complexes **1b**, **1c**, **1d**, **1e**, **1f**, **1g**, **2a**, and **2b** was also investigated with 4-methylmorpholine N-oxide (NMO), hydrogen peroxide (H_2O_2), sodium hypochlorite (NaOCl) and *tertiary*-butyl hydroperoxide (*t*-BuOOH) as co-oxidants. These complexes were catalytic with at least three of the four co-oxidants investigated (Table 2.1.4)

The oxidants **1a**, **1b** and **1h** were previously reported to be "catalytic" in the presence of NMO [7-9]. Initial observations during the course of our investigations that the different substituents in **1b**, **1c** and **1d** had little effect on the catalytic conversion of 1-hexanol to hexanal using NMO as co-oxidant prompted the investigation of the direct reaction of NMO with 1-hexanol. It was found that NMO reacted directly with 1-hexanol, although in low yield (15%). This was not surprising since NMO itself has been reported to oxidize organic halides to aldehydes or ketones [28,29]. The percent conversions of many "catalytic" runs were very similar to the conversions achieved by NMO without catalyst present.

Table 2.1.4. Summary of catalytic oxidations (percentage conversions) of 1-hexanol to hexanal by complexes **1** and **2** with a range of co-oxidants. Turnover numbers are shown in parentheses.

Complex	**Reaction Time**	**H_2O_2**	**NaOCl**	***t*-BuOOH**	**NMO**
1b	+ 30 Min.	8	6	9	9
	+ 3 Hours	10	7	10	19
	+ 24 Hours	15 (2)	13 (2)	12 (1)	22 (3)
1c	+ 30 Min.	7	7	8	11
	+ 3 Hours	7	9	8	13
	+ 24 Hours	8 (1)	9 (1)	9 (1)	14 (2)
1d	+ 30 Min.	8	8	9	12
	+ 3 Hours	9	10	9	14
	+ 24 Hours	10 (1)	11 (1)	10 (1)	16 (2)
1e	+ 30 Min.	10	40	40	52
	+ 3 Hours	13	40	42	52
	+ 24 Hours	15 (2)	47 (6)	39 (5)	54 (7)
1f	+ 30 Min.	33	61	53	92
	+ 3 Hours	40	75	57	95
	+ 24 Hours	45 (6)	85 (12)	55 (8)	97 (13)
1g	+ 30 Min.	29	38	46	95
	+ 3 Hours	32	56	50	98
	+ 24 Hours	36 (5)	64 (9)	51 (7)	99 (13)
2a	+ 30 Min.	6	12	6	10
	+ 3 Hours	10	15	12	12
	+ 24 Hours	13 (1)	17 (2)	15 (1)	23 (2)
2b	+ 30 Min.	4	4	3	15
	+ 3 Hours	6	5	3	16
	+ 24 Hours	6 (1)	6 (1)	5 (1)	16 (2)

With the exception of the reactions using NMO as co-oxidant, the catalytic conversions achieved for each compound follow the same sequence as observed in the stoichiometric oxidations. The NMO results, though, need to be treated with caution since, as mentioned, NMO reacts with 1-hexanol to form hexanal and the results for **1b**, **1c**, **1d**, **2a** and **2b** may just be a combination of the separate stoichiometric oxidations of NMO and of the ruthenium compound respectively.

Compound **2a** had previously been reported to be a stoichiometric oxidant only [17], although doubts about the accuracy of that report had subsequently been expressed by the same author [30]. As is evident from table 2.1.4, compound **2a** is a catalyst, albeit with low turnovers for the entire range of co-oxidants examined.

The catalytic reactions of the bromopyridine compounds **1f** and **1g** with the alcohol show far higher conversions than any of the other compounds. The use of 20 mg of compound **1g** with 5.02×10^{-4} mol 1-hexanol and a 50% excess co-oxidant gave turnovers of 13 for the NMO co-oxidized reaction, 8 for NaOCl, 7 for *t*-BuOOH and 5 for H_2O_2. The highest rate of conversion for both **1f** and **1g** was with NMO as co-oxidant. Reducing the amount of compound **1g** fourfold to 5 mg, added to 5.02×10^{-4} mol 1-hexanol and 50% excess NMO, gave a 95% conversion, corresponding to a turnover of 49 (*i.e.* a four fold increase). Keeping the amount of **1g** constant at 20 mg and doubling the amount of 1-hexanol to 1.00×10^{-3} mol gave a 92% conversion, which corresponded to a turnover of 24 (*i.e.* almost doubling the turnover). In these reaction sequences, NMO definitely acts as a co-oxidant and the rates of conversion place compounds **1f** and **1g** amongst the best catalytic oxidants known for a 1-hexanol to hexanal conversion. The compounds **1f** and **1g** are mediocre stoichiometric oxidants and why they should be such successful catalysts is not clear. Apart from the results obtained from this study, NMO has been shown to be an effective co-oxidant for many reactions of other ruthenium compounds [30,31].

2.1.3. Conclusions

It can be concluded from the above study that the substituents on the pyridine influence both the strength of the Ru=O double bond and the catalytic properties of the compounds studied. The electron withdrawing substituents in the 3-position appear to have a more pronounced effect than those in the 4-position, however, no correlation between ν(RuO) and activity could be established.

An Investigation into "$RuO_4.2C_5H_5N$"

2.2.1. Introduction

Koda in 1963 obtained a greenish-black compound he claimed to be "$RuO_4.2C_5H_5N$" from the addition of a carbon tetrachloride solution of RuO_4 to pyridine at 0°C [32]. Griffith and Rossetti in 1972 used Koda's method of synthesis to obtain a dark-green, diamagnetic solid [33]. Elemental analysis and infrared data obtained for this product led the authors to reformulate Koda's complex as dihydroxodioxobis(pyridine)ruthenium(VI) [*i.e.* $RuO_2(OH)_2(py)_2$]. However, in the same year, Ishiyama and Koda used "$RuO_4.2C_5H_5N$" as starting material for the preparation of $[Ru(OH)_2(py)_2(phen)]$ and provided infrared, electronic and magnetic data as further evidence for the initial formulation of the complex [34]. In general, it is known that compounds of the form $OsO_4.L$ (L = N-donor ligand) do exist and no $OsO_4.2L$ compounds are known. RuO_4 has a smaller co-ordination sphere than OsO_4 and consequently co-ordination of two pyridine ligands to the ruthenium tetroxide moiety (as formulated in Koda's complex) is believed to be unlikely.

In 1989 Griffith refuted his claims from his earlier paper and stated that "ill defined products with variable analyses" were obtained when Koda's procedure was followed [35]. It was claimed that the dimeric, dark red powder $[Ru_2O_6(py)_4]$ [35,36], obtained from three different synthetic methods, was in fact the correct formulation for Koda's complex. However, no explanation for the distinct colour difference between the two complexes (*i.e.* green and red respectively) was offered.

To add to the controversy, in 1991, Shapley and co-workers [37] used the product synthesized by Koda's method, which they assumed to be $RuO_2(OH)_2(py)_2$, as a starting material for the synthesis of $RuO_2(py)_2\{SCH_2CHRC(O)O\}$ (R = H, NHCHO, NHCOMe) (Figure 2.2.1).

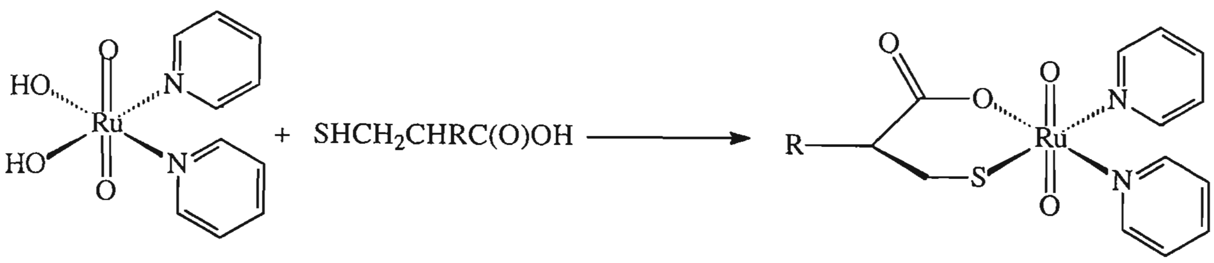


Figure 2.2.1. Schematic representation of the reaction carried out by Shapley *et al.* [37].

The products obtained are hard to rationalize if $[RuO_2(OH)_2(py)_2]$ is not the starting material. Shapley characterized the final product by comparing the *trans*-dioxo band observed in the infrared spectrum of the product to that found for the RuO_2 band in the starting material. Thus no conclusive proof for the correct formulation of Koda's reaction product has been put forward. It was decided to investigate Koda's reaction in the hope that the controversy could be laid to rest. The study resulted in the synthesis of complexes of the type $[RuO_2(OH)_2(Y\text{-}py)_2]$ **3** (py = pyridine, Y = H **3a**, 4-CN **3b**, 4-*t*-Bu **3c**) (Figure 2.2.2).

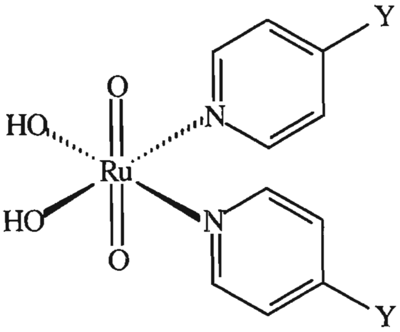


Figure 2.2.2. Structure of complexes $[RuO_2(OH)_2(Y\text{-}py)_2]$ **3** (Y = H **3a**, 4-CN **3b**, 4-*t*-Bu **3c**).

2.2.2. Results and Discussion for Compounds 3

The RuO_4 used in the preparation of the compounds **3a**, **3b** and **3c** was prepared as shown previously in equation (i) in section 2.1.2. The reaction sequence for the synthesis of compounds **3** is shown in equation (v).

$$RuO_4 + Y\text{-}py + H_2O \xrightarrow{0°C} [RuO_2(OH)_2(Y\text{-}py)_2] \quad \text{(v)}$$

The solution of RuO_4 used in the reaction was diluted with CCl_4, and the synthesis was carried out at 0°C in order to allow the reaction to proceed at as slow a rate as possible. When Koda published the results of the reaction of RuO_4 with pyridine, no mention was made about the degree of dryness of the reagents used in the synthesis [32]. Unpublished work on the syntheses of compounds **3** [38] found that the quantity of water in the reaction media was crucial. It was found that the reaction failed when perfectly dry solvents and reagents were used, with only RuO_2 forming. Excess water also leads to decomposition. It was established that a slight mole excess of water relative to the substituted pyridine ligands was required for the synthesis. Consequently, high purity solvents, KOH dried pyridine solutions and dry 4-CN-py and 4-*t*-Bu-py were used to synthesize the compounds **3a**, **3b** and **3c**.

The carbon tetrachloride solution containing a mixture of the pyridine reagent and water was layered above the RuO_4 solution under nitrogen and allowed to react without stirring. Almost immediately, a dark green precipitate began to form at the interface between the layers. The reaction was allowed to continue overnight in the dark at 0°C. The green product was filtered using a cannula, dried under vacuum and stored under nitrogen in the dark at 4°C. Every possible effort was made to prevent the decomposition of the product during the synthetic procedure, before analysis and during storage.

The infrared data for all the complexes **3a**, **3b** and **3c** show the distinctive *trans*-RuO vibration at approximately 840 cm^{-1} (Table 2.2.1). The position of this peak conforms with those observed for the other *trans*-dioxoruthenium(VI) complexes mentioned in section 2.1.2. Characteristic vibrations of constituents of the pyridine rings have also been identified from literature sources [15].

Table 2.2.1. Selected infrared data for complexes **3a**, **3b** and **3c**.

Complex	Characteristic ν_{asym}(RuO) (cm^{-1})	Other CharacteristicVibrations (cm^{-1})
3a	840(w)	3425ν(OH),1622ν(C=C),1064ν(CH),
3b	840(vs)	3438ν(OH),2241ν(CN),1615ν(C=C),1418ν(C=C),801ν(CH)
3c	839(s)	3430ν(OH),1062ν(CH),1616ν(C=C),1419ν(C=C)

vs = very strong
s = strong
w = weak

Even though the infrared data provided positive proof for the synthesis of a *trans*-dioxoruthenium(VI) complex, the elemental analysis data obtained for **3c** did not compare well with the calculated values (Table 2.2.2). However, the elemental analyses of compounds

3a and **3b** conformed to the formulations [$RuO_2(OH)_2(py)_2$] and [$RuO_2(OH)_2$(4-CN-py)$_2$], respectively. The latter is a new complex.

Table 2.2.2. The elemental analysis results for compounds **3**.

Complex	**Elemental Analysis for Complexes**[a]		
	%C	% H	%N
3a[b]	37.07 (36.90)	3.19 (3.69)	8.87 (8.62)
3b	38.86 (38.40)	2.25 (2.68)	14.85 (14.93)
3c	36.16 (49.42)	4.89 (5.99)	4.58 (6.41)

a. Calculated values for elemental analysis in parentheses.

b. Data from ref. [38].

2.2.3. Conclusions

All the complexes, **3a**, **3b** and **3c,** show the distinct green colour obtained obtained by Koda [32,34] and by Griffith and Rossetti [33]. The infrared data obtained confirms Griffith's initial speculation, and Shapley's observation [37], that these complexes have *trans*-RuO bonds. Though the elemental analyses of compound **3c** does not conform to the expected formulation for the complex, the analysis data for **3a** and **3b** show that the complexes synthesized are [$RuO_2(OH)_2(py)_2$] and [$RuO_2(OH)_2$(4-CN-py)$_2$] respectively. Attempted crystal growth is still in progress and clarification of the structure of these complexes in the near future by crystallography is all that remains to put to rest the controversy of Koda's complex.

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Chapter Three

The Chemistry of $[PPh_4][RuO_2(OCOR)Cl_2]$ ($R = CH_3, CF_3, C_6H_5, C_6F_5, C_5H_{11}$)

3.1. Introduction

Many reports of ruthenium(II) and ruthenium(III) carboxylato complexes are found in the literature and they exist mainly as dimeric or trimeric complexes. A summary of such complexes can be found in the review by Schröder and Stephenson [1]. Monomeric ruthenium monocarboxylate complexes are not common [2]. The complexes $[Ru(PPh_3)_2X_2(OCOR)]$ (X = Cl, Br; R = Me, Et, Ph, *p*-C_6H_4Cl, *o*-C_6H_4Br, *p*-C_6H_4Br, *p*-C_6H_4OMe, *o*-C_6H_4Me, *p*-C_6H_4Me, *p*-$C_6H_4NO_2$) were prepared by the reaction of $[RuX_2(PPh_3)_n]$ (n = 3 or 4) with carboxylic acids under aerobic conditions [2]. Although only a monocarboxylate is present, the ligand chelates and thus occupies two coordination sites in the complex. The vibrational spectra of these complexes have been extensively studied, but limited reaction chemistry has been carried out since many of these complexes showed poor solubility.

Robinson and Uttley obtained carboxylato derivatives from the reaction of carboxylic acids with low oxidation state hydrido- and triphenylphosphine complexes of ruthenium, in organic solvents [3]. As a result, a convenient route to a range of new and previously reported ruthenium carboxylato complexes, including $[(PPh_3)_3RuH(OCOR)]$, $[(PPh_3)_2RuCl(OCOR)(CO)]$, $[(PPh_3)_2RuH(OCOR)(CO)]$, $[(PPh_3)_2Ru(OCOR)_2(CO)]$ and $[(PPh_3)_2Ru(OCOR)_2(CO)_2]$ [R = a range of alkyl and aryl groups] was established.

Very few ruthenium-oxo carboxylates with ruthenium in the higher oxidation states exist. Perrier, Lau and Kochi synthesized the complex *trans*-$[RuO_2(py)_2(OCOR)_2]$ [$R = CH_3$, CH_3CH_2, $CH_3CH_2CH_2$, $(CH_3)_2CH$, C_6H_5] by the addition of the carboxylic acid and pyridine to a suspension of $Ba[RuO_3(OH)_2]$ in acetonitrile [4,5]. The crystal structure of the orange, diamagnetic complex *trans*-dioxobis(acetato)bis(pyridine)ruthenium(VI) showed the ruthenium(VI) coordinated to a pair of *trans*-pyridine and a pair of *trans*-acetato ligands (see figure 1.5.4). These complexes were shown to be unselective oxidants of organic substrates.

Carboxylato dioxoruthenium(VI) complexes of the form $[RuO_2(OCOR)Cl_2]^-$ ($R = CH_3$, Et, Pr, CHF_2) have been synthesized by Griffith *et al.* [6,7]. The crystal structure of the acetato anion was determined and showed a distorted octahedral structure with symmetrically bound acetato ligands and *cis*-dioxo ligands in one plane (see figure 1.5.3). The $[PPh_4][RuO_2(OCOCH_3)Cl_2]$

complexes proved to be effective two-electron oxidants in catalyzing the oxidation of primary alcohols to aldehydes, secondary alcohols to ketones, sulphides to sulphoxides and sulphones, and triphenylphosphine to triphenylphosphine oxide, using NMO as co-oxidant. Competing double bond cleavage was not observed during these reactions. The yields and turnovers achieved for the individual complexes were approximately the same for the range of substrates oxidized with NMO as co-oxidant. Griffith *et al.* recently attempted to synthesize these complexes by passing an O_3-O_2 mixture through a solution of $RuCl_3.nH_2O$ and $[PPh_4]Cl$ in carboxylic acid. The reaction failed to give the desired products in all cases. However, the new complex $[PPh_4]_2[Ru_2O(\mu\text{-}OCOEt)_2Cl_6]$ was obtained when synthesis of the propionic acid complex was attempted [8]. The complex represents the first example of a tetravalent ruthenium complex containing both a bridging oxo ligand and two bridging carboxlylate groups (Figure 3.1.1).

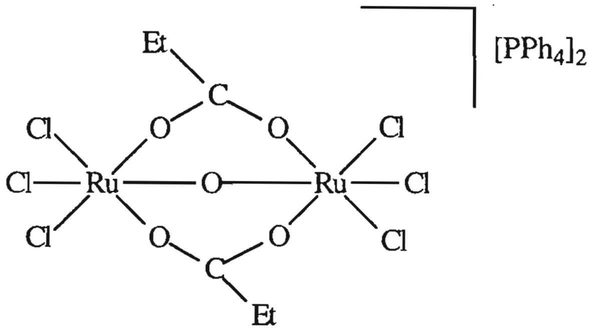


Figure 3.1.1. Structure of $[PPh_4]_2[Ru_2O(\mu\text{-}OCOEt)_2Cl_6]$.

From this background in ruthenium(VI) carboxylato complexes, the task of synthesizing and characterizing the known dioxoruthenium(VI) compound $[PPh_4][RuO_2(OCOCH_3)Cl_2]$ (**a**) [6,7] and a range of novel compounds $[PPh_4][RuO_2(OCOR)Cl_2]$ (R = CF_3 **b**, C_6H_5 **c**, C_6F_5 **d**, C_5H_{11} **e**) was undertaken (Figure 3.1.2). The fluorinated complexes **b** and **d** were compared to their protonated equivalents **a** and **c** with respect to synthetic yields and also with respect to catalytic activity for the oxidation of 1-hexanol to hexanal and 2-hexanol to 2-hexanone (with a range of co-oxidants). The complexes **c** and **d** were also investigated as catalytic oxidants for a range of alcohols with the co-oxidants tetrabutylammonium periodate and 4-methylmorpholine N-oxide. The novel compounds $[PPh_4][RuO_2(OCOC_6H_5)Cl_2]$ and $[PPh_4][RuO_2(OCOC_6F_5)Cl_2]$ were also supported on poly(4-vinylpyridine) and tested as catalytic oxidants for the oxidation of cyclohexanol to cyclohexanone, using 4-methylmorpholine N-oxide and tetrabutylammonium periodate as co-oxidants.

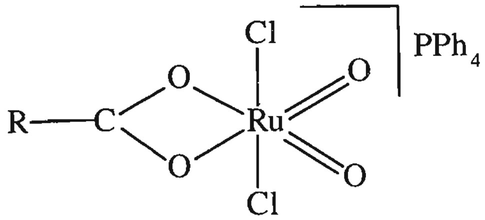


Figure 3.1.2. Structure of the complexes $[PPh_4][RuO_2(OCOR)Cl_2]$ (R = CH_3 **a**,CF_3 **b**, C_6H_5 **c**, C_6F_5 **d**, C_5H_{11} **e**).

3.2. Results and Discussion

3.2.1. Preparation and Characterization

The RuO_4 used for the synthesis of the carboxylato complexes was generated, as previously (section 2.2.1), by reaction of $RuCl_3.3H_2O$ with an excess of sodium metaperiodate overnight (equation i).

$$RuCl_3.3H_2O \quad + \quad NaIO_{4(aq)} \quad \longrightarrow \quad RuO_{4(aq)} \qquad \text{(i)}$$

Griffith and Jolliffe passed a stream of nitrogen containing RuO_4, generated as above, directly into a saturated solution of $[PPh_4]Cl$ in carboxylic acid to obtain the green dioxoruthenium(VI) carboxylate complexes $[PPh_4][RuO_2(OCOR)Cl_2]$ (R = CH_3, Et, Pr, or CHF_2) [6,7]. Thus, we initially attempted to synthesize the complex $[PPh_4][RuO_2(OCOCH_3)Cl_2]$ by this method. However, the manipulation required for this synthetic route proved to be extremely tedious, demanding extensive equipment and time to accomplish the transfer of the RuO_4 as a vapour [with the use of a stream of $N_{2(g)}$] to the vessel containing the glacial acetic acid-tetraphenylphosphonium chloride solution. We also had doubts about the safety of the above method.

Consequently, it was decided to react RuO_4 in solution in CCl_4 with a solution of $[PPh_4]Cl$ and glacial acetic acid in acetonitrile (equation ii).

$$RuO_4 + [PPh_4]Cl + H_3CCOOH \xrightarrow{\text{Room temp.}} [PPh_4][RuO_2(OCOCH_3)Cl_2] \qquad \text{(ii)}$$

The initially light yellow solution turned light green almost immediately. The reaction was stirred overnight, finally resulting in a dark green solution that was reduced in volume under reduced pressure until a green product precipitated. The precipitate was filtered off and the filtrate was again reduced in volume to yield more precipitate. The precipitate in both cases was found to be the same by comparison of infrared data. The precipitate was washed with drops of water to remove excess $[PPh_4]Cl$ and dried under vacuum. This new method was used to synthesize the novel complexes $[PPh_4][RuO_2(OCOCF_3)Cl_2]$ and $[PPh_4][RuO_2(OCOC_6F_5)Cl_2]$. Synthesis of the complexes where R = C_6H_5 and C_5H_{11} failed when this reaction was carried out at room temperature. However, when this reaction was attempted at 0°C the new complexes $[PPh_4][RuO_2(OCOC_6H_5)Cl_2]$ and $[PPh_4][RuO_2(OCOC_5H_{11})Cl_2]$ were obtained from benzoic acid and hexanoic acid respectively. The synthesis of complexes **a, b** and **d** was then repeated at 0°C and a significant increase in yield of product was obtained. It was also noticed that the fluorinated complexes were obtained in higher yield relative to the hydrogenated complexes. This is clearly evident in the summary of the analytical data obtained for these complexes in table 3.2.1.

Table 3.2.1. Summary of the analytical results for the dioxoruthenium(VI) complexes.

Dioxoruthenium(VI) Complexes	**% Yield**	**Melting Point^b / °C**	**Elemental Analysis (%)^a** C	H	N
$[PPh_4][RuO_2(OCOCH_3)Cl_2]$ (**a**)	26	132	51.31 (51.84)	3.70 (3.85)	0.14 (0.00)
$[PPh_4][RuO_2(OCOCF_3)Cl_2]$ (**b**)	51	125	51.75 (47.58)	3.35 (3.07)	0.09 (0.00)
$[PPh_4][RuO_2(OCOC_6H_5)Cl_2]$ (**c**)	28	104	56.24 (56.04)	3.64 (3.79)	0.42 (0.00)
$[PPh_4][RuO_2(OCOC_6F_5)Cl_2]$ (**d**)	81	95	50.39 (49.35)	2.72 (2.67)	1.24 (0.00)
$[PPh_4][RuO_2(OCOC_5H_{11})Cl_2]$ (**e**)	43	106	52.96 (54.72)	4.10 (4.75)	0.04 (0.00)

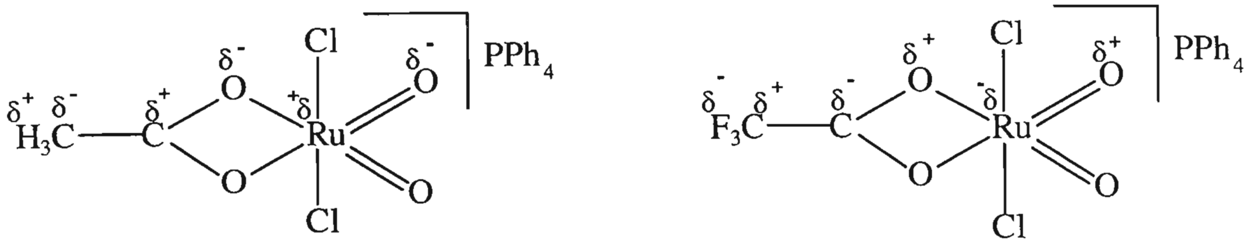
a. Calculated values in parentheses
b. Decomposed

The yields of the complexes follow the order **d** > **b** > **e** > **c** > **a**. The fluorinated complexes **b** and **d** were obtained in a distinctly higher yield than their hydrogenated equivalents **a** and **c**, with the stability of the complexes being possibly dependent on the relative charge distributions within the compounds. The relative charge distributions in the complexes result from the differences between the electronegativities of the fluorine and hydrogen atoms (which have roughly the same size) that constitute part of the ligands in these compounds. Thus, for example, in complex **b**, the electronegative fluorine atom draws electrons towards itself and becomes relatively more negative than the neighbouring carbon atom, which in turn would be relatively positive compared to the adjacent carbon atom of the carboxylate group. Similarly, in complex **a** the hydrogen atom is more positive than the neighbouring carbon atom, which is relatively negative compared to the adjacent carbon atom of the carboxylate group. These relative charge distributions are shown in figure 3.2.1. The benzoic acid complex **c** and its corresponding fluorinated equivalent **d** will show a similar, though more complex, relative charge distribution.

Satisfactory elemental analysis data were obtained for the complexes, however, the fluorinated complex $[PPh_4][RuO_2(OCOCF_3)Cl_2]$ and the alkyl complex $[PPh_4][RuO_2(OCOC_5H_{11})Cl_2]$ show elemental analysis data that do not conform completely to the calculated results, possibly due to a degree of contamination with $[PPh_4]Cl$.

All the complexes showed a distinct colour change from green to black on heating. The colour change denoted decomposition of the complex. Complex **a** and **b** showed the highest decomposition temperatures, followed by complex **e**, **c** and **d**.

All the complexes appeared to be stable at room temperature over the period of the investigation (1 year), although the complexes were preferably stored in a desiccator in the fridge, to assure that their stability was not compromised.



a b

Figure 3.2.1. Proposed relative charge distribution on $[PPh_4][RuO_2(OCOCH_3)Cl_2]$ (**a**) and $[PPh_4][RuO_2(OCOCF_3)Cl_2]$ (**b**).

The infrared data for $[PPh_4][RuO_2(OCOCH_3)Cl_2]$ in table 3.2.2 show that the very strong infrared band at 864 cm^{-1} and the weaker band at 886 cm^{-1} are assigned to the asymmetric and symmetric stretches ν_{asym}(Ru=O) and ν_{sym}(Ru=O) respectively of a *cis*-dixo unit [6,7,10,11]. The novel complexes **b**, **c**, **d** and **e** showed the characteristic ν_{sym}(Ru=O) stretch in the range 880 cm^{-1} to 884 cm^{-1}, and the ν_{asym}(Ru=O) stretch in the range 855 cm^{-1} to 864 cm^{-1}.

Table 3.2.2. Summary of infrared data for the dioxoruthenium(VI) complexes.

Dioxoruthenium(VI) Complexes	Infrared Spectra Selected Bands (cm^{-1})
$[PPh_4][RuO_2(OCOCH_3)Cl_2]$	886(w) ν_{sym}(Ru=O); 864(vs) ν_{asym}(Ru=O); 1508(s) ν_{asym}(O-C-O); 334(s) ν(Ru-Cl)
$[PPh_4][RuO_2(OCOCF_3)Cl_2]$	881(s) ν_{sym}(Ru=O); 862(m) ν_{asym}(Ru=O); 1516(m) ν_{asym}(O-C-O); 315(s) ν(Ru-Cl)
$[PPh_4][RuO_2(OCOC_6H_5)Cl_2]$	884(w) ν_{sym}(Ru=O); 859(s) ν_{asym}(Ru=O); 1538(m) ν_{asym}(O-C-O); 322(s) ν(Ru-Cl)
$[PPh_4][RuO_2(OCOC_6F_5)Cl_2]$	880(m) ν_{sym}(Ru=O); 855(w) ν_{asym}(Ru=O); 1519(s) ν_{asym}(O-C-O); 318(s) ν(Ru-Cl)
$[PPh_4][RuO_2(OCOC_5H_{11})Cl_2]$	882(w) ν_{sym}(Ru=O); 859(m) ν_{asym}(Ru=O); 1504(w) ν_{asym}(O-C-O); 320(s) ν(Ru-Cl)

vs = very strong s = strong m = medium w = weak

The ν_{sym}(Ru=O) stretches in the fluorinated complexes **b** and **d** are noticed to be relatively stronger than those of their hydrogenated equivalents. However, the opposite trend is apparent for the ν_{asym}(Ru=O) stretches. This could possibly be related to the charge distribution in the complexes as discussed previously.

As Griffith and Jolliffe noticed [7], the infrared bands of the complexes are difficult to discern beneath the bands due to $[PPh_4]^+$. However, by comparing the infrared spectrum of the unreacted salt $[PPh_4]Cl$ with the infrared spectra of the complexes, distinct peaks could be discerned apart from the $[PPh_4]Cl$ peaks. Slightly broad peaks between 1500 cm^{-1} and 1540 cm^{-1} were clearly identified in all the complexes and were assigned to the asymmetric stretch of the carboxylate group [*i.e.* ν_{asym}(O-C-O)], as identified previously in other carboxylato complexes of ruthenium [2-7]. The bands near 300 cm^{-1} in the compounds **a**-**e** were assigned to ruthenium-chloride stretches.

As mentioned, the crystal structure of $[PPh_4][RuO_2(OCOCH_3)Cl_2]$ was determined by Griffith and Jolliffe [6,7]. On the basis of the similarity of the appearance of the infrared spectra of the novel complexes **b**-**e**, with that of $[PPh_4][RuO_2(OCOCH_3)Cl_2]$, and the satisfactory elemental analysis data obtained, it is suggested that the new complexes have a similar structure to $[PPh_4][RuO_2(OCOCH_3)Cl_2]$.

The synthesis of the cyclohexanoic acid complex $[PPh_4][RuO_2(OCOC_6H_{11})Cl_2]$ was attempted and resulted in a black-green precipitate that showed a very weak ν_{asym}(Ru=O) peak in the region of 880 cm^{-1} and a correspondingly weak ν_{asym}(O-C-O) stretch. However, the elemental analysis results obtained for the product did not conform to the expected formulation $[PPh_4][RuO_2(OCOC_6H_{11})Cl_2]$. This complex was thus not studied any further during this investigation although it may be re-examined in future studies.

3.2.2. Stoichiometric Oxidations

Due to the high cost of the starting material for making ruthenium tetroxide, $RuCl_3.3H_2O$, and some of the carboxylic acids, synthesis of the complexes $[PPh_4][RuO_2(OCOR)Cl_2]$ (R = CF_3 **b**, C_6H_5 **c**, C_6F_5 **d**, C_5H_{11} **e**) is very expensive. As such it was not viable to investigate the stoichiometric oxidation reactions of all the synthesized complexes with alcohols. However, a comparison of the stoichiometric oxidation ability of the hydrogenated complex (**a**) versus the fluorinated complex (**b**) for the oxidation of 1-hexanol to hexanal over a twenty-four hour period was undertaken.

As previously, the oxidation reactions were carried out in Schlenk tubes, under a nitrogen atmosphere (to prevent any possible oxidation by air) and in the dark (to prevent free radical oxidation reactions initiated by UV radiation). The reactions were monitored by gas chromatography (using a packed column) and either *iso*-butylmethacrylate or 2-ethoxyethyl acetate were used as internal standard to obtain quantitative data (see Appendix One). Conversion percentages, represented as the average of at least three runs, are presented in table 3.2.3.

Table 3.2.3. Summary of stoichiometric oxidations of 1-hexanol to hexanal.

Complex	Reaction Time	Percentage Conversion
$[PPh_4][RuO_2(OCOCH_3)Cl_2]$	+30 Min.	61
	+ 3 Hours	60
	+24 Hours	69
$[PPh_4][RuO_2(OCOCF_3)Cl_2]$	+30 Min.	81
	+ 3 Hours	91
	+24 Hours	91

Previously, the complex $[PPh_4][RuO_2(OCOCH_3)Cl_2]$ was shown to function as a stoichiometric oxidant when 1 mol equivalent of oxidant to 1 mol of substrate was used, converting primary alcohols to aldehydes, secondary alcohols to ketones, triphenylphosphine to triphenylphosphine oxide, and sulfides to sulphoxides [7]. These results showed that the complex effectively functioned as a two-electron oxidant like other oxoruthenium(VI) complexes [10,12].

What is evident here is that the fluorinated complex $[PPh_4][RuO_2(OCOCF_3)Cl_2]$ is a better stoichiometric oxidant than the hydrogenated complex $[PPh_4][RuO_2(OCOCH_3)Cl_2]$. The fluorinated complex oxidizes 1-hexanol at a faster rate at the start of the reaction and achieves a maximum conversion of 91% within three hours. $[PPh_4][RuO_2(OCOCH_3)Cl_2]$ only achieves a 69% conversion of 1-hexanol after twenty-four hours. However, no conclusions regarding the reasons for this superiority could be made until further data was available.

3.2.3. Catalytic Oxidations

The complexes were synthesized with the intention of using them as catalysts in organic reactions, since using only small amounts of these compounds in oxidation reactions was financially viable. Furthermore, the use of catalytic quantities of the oxidant reduces the amount of inorganic waste produced.

Since only 20 mg quantities of complex were used in the catalytic reactions, all the complexes **a-e** were investigated as catalytic oxidants for the oxidation of 1-hexanol, 2-hexanol and 1-hexene to hexanal, 2-hexanone and 1,2-epoxyhexane, respectively, over a twenty-four hour period. This particular range of substrates was chosen to examine the specificity of the complexes in the catalytic oxidation reactions with a primary alcohol, a secondary alcohol and an alkene. The investigation was initially limited to substrates of a fixed carbon chain length (*i.e.* six) to overcome the potential complication of varying chain lengths on the oxidative ability of the complexes.

The co-oxidants used in this investigation were hydrogen peroxide (H_2O_2), sodium hypochlorite (NaOCl), *tertiary*-butyl hydroperoxide (*t*-BuOOH), trimethylamine-N-oxide dihydrate (TMANO), oxygen (O_2), 4-methylmorpholine N-oxide (NMO), iodosylbenzene (C_6H_5IO) and tetrabutylammonium periodate (Bu_4NIO_4). Hydrogen peroxide, sodium hypochlorite and oxygen were chosen as co-oxidants due to their low cost, ubiquitous presence and availablity in industry and research laboratories. Sodium hypochlorite though, on its own, has been found to be a selective oxidant for a range of organic substrates [13]. Hydrogen peroxide and oxygen have gained prominence as co-oxidants with the progress towards "green chemistry" [14,15]. Oxygen as a co-oxidant for the ruthenium catalyzed oxidation of alcohols has been studied recently [16-19]. *Tertiary*-butyl hydroperoxide has been used as a co-oxidant, especially for the hydroxylation of olefins [20] and the oxidation of primary alcohols to aldehydes and secondary alcohols to ketones with a range of metallo-catalysts [21-23]. Griffith *et al.*, Ley *et al.* and Sharpless *et al.* have used 4-methylmorpholine N-oxide extensively as a co-oxidant for ruthenium catalyzed oxidations of alcohols [7,15,24]. NMO, though, has been shown to react directly with activated organic halides converting them to aldehydes and ketones [25,26]. Other ruthenium catalysts have been successfully utilized with iodosylbenzene as co-oxidant for the oxidation of alcohols [27] and for the epoxidation of olefins [28].

All the co-oxidants, except iodosylbenzene, were used as supplied. Iodosylbenzene was obtained from the reaction of iodobenzene diacetate with sodium hydroxide [29]. After numerous washings of the crude product with H_2O, the yellow, solid oxidant was obtained. The product was dried under vacuum and stored under a nitrogen atmosphere in a Schlenk tube in the fridge. Iodosylbenzene was found to decompose to a hydroscopic white solid when stored in air over a few days. The purity of the oxidant was established from the distinct yellow colour, dry texture and explosive decomposition point at 210°C.

As previously, all the oxidation reactions were carried out in Schlenk tubes, under a nitrogen atmosphere and in the dark. The reactions were carried out using 0.5 mmol quantities of substrate and 0.5 mmol of either *iso*-butylmethacrylate, 2-ethoxyethyl acetate or n-hexane as internal standard to obtain quantitative data after monitoring the reaction by gas chromatography (using either a packed or capillary column). A 1.5 fold excess of co-oxidant and 20 mg catalyst was added for all the reactions. Conversion percentages, represented as the average of at least three runs, are presented in tables 3.2.4 for the conversion of 1-hexanol to hexanal and in table 3.2.5 for the conversion of 2-hexanol to 2-hexanone.

Since a fixed mass of catalyst was used for each reaction and since each catalyst (*i.e.* **a**-**e**) has a different molecular mass, different mole ratios of catalyst to substrate were used for the reactions of different catalysts. Thus, to add more meaning to the comparison of the catalytic abilities of the individual complexes, catalytic turnovers for each reaction have been included with the percentage conversion values.

The oxidation of 1-hexanol, 2-hexanol and 1-hexene was also investigated in the presence of the co-oxidants only, so as to study the degree of oxidation effected by the co-oxidants alone. These results are summarized in table 3.2.6 and show that hydrogen peroxide, trimethylamine-N-oxide and oxygen did not oxidize 1-hexanol on their own. *Tertiary*-butyl hydroperoxide and 4-methylmorpholine N-oxide show approximately the same degree of oxidation giving 18% and 15% conversions, respectively, after twenty-four hours, with iodosylbenzene showing a 20% conversion of 1-hexanol to hexanal after twenty-four hours after showing no oxidative effect initially. Sodium hypochlorite showed only a 4% conversion of 1-hexanol to hexanal after twenty-four hours, but tetrabutylammonium periodate showed a 65% conversion. All the co-oxidants, except trimethylamine-N-oxide and

Table 3.2.4. Percentage conversion of 1-hexanol to hexanal by the compounds **a-e** with various co-oxidants. Turnovers are shown in parentheses.

Complex	Reaction Time	H_2O_2	NaOCl	*t*-BuOOH	NMO	TMANO	O_2	C_6H_5IO	Bu_4NIO_4
a	+30 Min.	53(8)	64(10)	59(9)	100(15)	28(4)	0	51(8)	76(11)
	+ 3 Hours	59(9)	75(11)	55(8)	100(15)	41(6)	0	73(11)	83(13)
	+24 Hours	56(8)	83(13)	64(10)	100(15)	60(9)	0	67(10)	100(15)
b	+30 Min.	55(9)	74(13)	37(6)	87(13)	47(8)	8(1)	70(12)	96(16)
	+ 3 Hours	52(9)	90(15)	78(13)	91(14)	50(9)	11(2)	77(13)	100(17)
	+24 Hours	51(9)	91(15)	79(13)	89(13)	60(10)	10(2)	70(12)	100(17)
c	+30 Min.	60(10)	72(12)	60(10)	100(17)	20(3)	0	90(15)	100(17)
	+ 3 Hours	69(12)	68(12)	59(10)	100(17)	65(11)	6(1)	100(17)	100(17)
	+24 Hours	73(12)	77(13)	66(11)	100(17)	81(14)	9(2)	100(17)	100(17)
d	+30 Min.	30(6)	52(10)	62(12)	83(16)	34(7)	0	44(8)	100(19)
	+ 3 Hours	32(6)	61(12)	61(12)	95(18)	51(10)	0	51(10)	100(19)
	+24 Hours	36(7)	71(14)	67(13)	97(18)	58(11)	5(1)	62(12)	100(19)
e	+30 Min.	40(7)	75(13)	45(8)	93(16)	26(4)	0	52(9)	100(17)
	+ 3 Hours	50(9)	78(13)	46(8)	96(16)	43(7)	13(2)	77(13)	100(17)
	+24 Hours	53(9)	80(14)	49(8)	96(16)	62(11)	29(5)	76(13)	100(17)

Table 3.2.5. Percentage conversion of 2-hexanol to 2-hexanone by the compounds **a-e** with various co-oxidants. Turnovers are shown in parentheses.

Complex	Reaction Time	H_2O_2	NaOCl	*t*-BuOOH	NMO	TMANO	O_2	C_6H_5IO	Bu_4NIO_4
a	+30 Min.	14(2)	19(3)	23(4)	62(9)	0	0	58(9)	80(12)
	+3 Hours	16(2)	92(14)	24(4)	70(11)	29(4)	0	66(10)	100(15)
	+24 Hours	18(3)	88(13)	25(4)	63(10)	35(5)	0	73(11)	100(15)
b	+30 Min.	4(1)	31(5)	26(4)	73(12)	33(6)	0	44(8)	31(5)
	+3 Hours	4(1)	100(17)	24(4)	73(12)	37(6)	0	62(11)	48(8)
	+24 Hours	4(1)	100(17)	29(5)	68(12)	37(6)	0	63(11)	55(9)
c	+30 Min.	23(4)	47(8)	19(3)	100(17)	11(2)	0	45(8)	76(13)
	+3 Hours	25(4)	34(6)	19(3)	100(17)	32(5)	0	70(12)	80(14)
	+24 Hours	25(4)	38(7)	19(3)	100(17)	38(7)	0	78(13)	75(13)
d	+30 Min.	8(2)	36(7)	17(3)	52(10)	26(5)	0	50(10)	43(8)
	+3 Hours	10(2)	38(7)	16(3)	62(12)	33(6)	0	77(15)	41(8)
	+24 Hours	10(2)	69(13)	33(6)	67(13)	37(7)	0	77(15)	56(11)
e	+30 Min.	3(1)	62(11)	15(3)	69(12)	34(6)	0	88(15)	46(8)
	+3 Hours	12(2)	68(12)	11(2)	68(12)	36(6)	0	100(17)	100(17)
	+24 Hours	14(2)	72(12)	11(2)	72(12)	45(8)	0	100(17)	100(17)

Table 3.2.6. Percentage conversion of 1-hexanol to hexanal and 2-hexanol to 2-hexanone by co-oxidants alone.

Co-oxidant	Reaction Time	1-Hexanol	2-Hexanol
H_2O_2	+30 Min.	0	0
	+3 Hours	0	0
	+24 Hours	0	0
NaOCl	+30 Min.	0	0
	+3 Hours	1	0
	+24 Hours	4	0
t-BuOOH	+30 Min.	0	0
	+3 Hours	10	0
	+24 Hours	18	0
NMO	+30 Min.	0	0
	+3 Hours	6	0
	+24 Hours	15	0
TMANO	+30 Min.	0	0
	+3 Hours	0	7
	+24 Hours	0	14
O_2	+30 Min.	0	0
	+3 Hours	0	0
	+24 Hours	0	0
C_6H_5IO	+30 Min.	0	0
	+3 Hours	0	0
	+24 Hours	20	0
Bu_4NIO_4	+30 Min.	54	7
	+3 Hours	54	15
	+24 Hours	65	16

tetrabutylammonium periodate, showed no oxidative activity with the secondary alcohol 2-hexanol. The conversions for the latter two were low.

The compounds **a-e** showed no oxidation activity with respect to 1-hexene with all of the co-oxidants examined. No decrease in the concentration of the substrate, 1-hexene, or formation of a possible product was detected during gas chromatographic analysis of the reaction mixture over twenty-four hours. This result suggests that the compounds **a-e** do not attack the double bond in 1-hexene and thus do not form diols or epoxides. The co-oxidants used in these reactions did not oxidize the double bond on their own either. It is thus proposed that the catalysts **a**-**e** do not oxidize double bonds with the co-oxidants used in this investigation. However, this proposal needed to be tested further by examining the oxidation of unsaturated alcohols.

The compound $[PPh_4][RuO_2(OCOC_6H_5)Cl_2]$, with H_2O_2 as co-oxidant, achieves a 60% conversion of 1-hexanol to hexanal (*i.e.* 10 turnovers) within 30 minutes of the start of the reaction. This degree of oxidation is not achieved by any of the other complexes with H_2O_2, even after twenty-four hours of reaction. $[PPh_4][RuO_2(OCOC_6H_5)Cl_2]$ achieves a maximum of 73% conversion with H_2O_2 after twenty-four hours. Complexes **a** and **b** oxidize 1-hexanol to hexanal at approximately the same rate with both complexes achieving almost nine turnovers after twenty-four hours reaction. $[PPh_4][RuO_2(OCOC_6F_5)Cl_2]$ fared the worst as a catalyst with H_2O_2 since only seven turnovers were achieved after twenty-four hours. From table 3.2.6 it is noticed that hydrogen peroxide does not oxidize 1-hexanol to hexanal on its own. This implies that the role of H_2O_2 in the catalytic reactions mentioned above was purely to recycle the ruthenium catalyst. This result is significant because H_2O_2 is a cheap co-oxidant and is furthermore environmentally friendly since the decomposition products of hydrogen peroxide are water and oxygen.

Sodium hypochlorite proved to be an effective co-oxidant for the conversion of 1-hexanol to 1-hexanal, since all the catalysts achieved ten turnovers or more after thirty minutes of reaction. $[PPh_4][RuO_2(OCOCF_3)Cl_2]$ achieved 90% conversion (*i.e.* fifteen turnovers) after three hours reaction and the complex $[PPh_4][RuO_2(OCOC_6F_5)Cl_2]$ showed the lowest conversion at 71% which equates to a turnover of fourteen. Although NaOCl on its own has previously been shown to be a selective oxidant for a range of organic substrates [13], only a 4% conversion of 1-hexanol to 1-hexanal over a twenty-four hour period was noted in the absence of catalyst.

Tertiary-butyl hydroperoxide proved to be a mild co-oxidant with the entire range of catalysts. $[PPh_4][RuO_2(OCOCF_3)Cl_2]$ achieved the highest conversion of 1-hexanol to 1-hexanal (79%) after twenty-four hours even though it showed a slow rate of oxidation at the start of the reaction. $[PPh_4][RuO_2(OCOC_6F_5)Cl_2]$ achieved a turnover of thirteen, like $[PPh_4][RuO_2(OCOCF_3)Cl_2]$, but only achieved a conversion of 67% compared to the 79%

achieved by the latter complex in the same time period, with $[PPh_4][RuO_2(OCOC_5H_{11})Cl_2]$ showing a turnover of eight (*i.e.* 49% conversion). *Tertiary*-butyl hydroperoxide converts 18% of 1-hexanol to hexanal on its own, over twenty-four hours.

The co-oxidant NMO alone also shows a 15% conversion of 1-hexanol to hexanal after twenty-four hours reaction. This ability of NMO to oxidize the primary alcohol 1-hexanol in the absence of catalyst, is in addition to the previously mentioned oxidative behaviour with respect to activated halides [25,26]. In this study, NMO was found to be an excellent co-oxidant. Complexes **a** and **c** showed 100% oxidative conversions at the initiation of the reaction, corresponding to fifteen and seventeen turnovers respectively. Complexes **d** and **e** showed percentage conversions in the upper nineties after twenty-four hours reaction, equating to eighteen and sixteen turnovers respectively.

The compound $[PPh_4][RuO_2(OCOC_6H_5)Cl_2]$ (**c**) causes an 81% conversion of 1-hexanol to 1-hexanal (*i.e.* fourteen turnovers) with TMANO as co-oxidant. The other catalysts only showed approximately 60% conversion (*i.e.* nine to eleven turnovers) over the same reaction period. The rate of oxidation is slow for all the complexes, except **c,** in the first three hours of reaction. TMANO does not oxidize 1-hexanol by itself. This thus implies that TMANO functioned only to recycle the ruthenium catalyst in the oxidation reactions.

Oxygen was a poor co-oxidant for all the catalysts examined and showed no oxidation potential on its own. $[PPh_4][RuO_2(OCOCH_3)Cl_2]$ (**a**) showed zero conversion with oxygen, even after twenty-four hours reaction. Complexes **c**, **d** and **e** showed zero activity at the early stages of the reaction, but complexes **c** and **e** showed minimal turnovers after three hours reaction. $[PPh_4][RuO_2(OCOC_5H_{11})Cl_2]$ (**e**), however, did achieve five turnovers after twenty-four hours. $[PPh_4][RuO_2(OCOCF_3)Cl_2]$ showed a low rate of oxidation from the initiation of the reaction and finally resulted in a conversion of 10% (*i.e.* two turnovers). The oxidation results utilizing oxygen as co-oxidant are disappointing from a cost and environmental point of view, since, as mentioned previously, oxygen is the most favoured co-oxidant in catalysis.

Iodosylbenzene showed a 100% conversion of 1-hexanol to 1-hexanal (*i.e.* seventeen turnovers) within three hours of the start of the reaction with $[PPh_4][RuO_2(OCOC_6H_5)Cl_2]$ (**c**). $[PPh_4][RuO_2(OCOCF_3)Cl_2]$ (**b**) achieved its maximum activity at the start of the reaction (*i.e.* 70% conversion, twelve turnovers) but failed to maintain the rapid oxidation rate.

Complexes **a** and **d** showed greater than 60% conversions (*i.e.* ten and twelve turnovers, respectively) after twenty-four hours reaction, with complex **e** showing 76% conversion (*i.e.* thirteen turnovers) in the same time period. It is noteworthy that the co-oxidant on its own only shows oxidation activity after twenty-four hours reaction. This implies that in these reactions, in the presence of the catalysts, the influence of alcohol oxidation by the co-oxidant on its own is negligible, since the highest conversions occur at the start of the reaction. Even though iodosylbenzene has been studied as a possible co-oxidant with other catalysts [27], the skill and time required for its synthesis and the instability of the pure C_6H_5IO probably limits its use as a co-oxidant.

Tetrabutylammonium periodate is the best co-oxidant for the oxidation of 1-hexanol to hexanal. Complexes **c**, **d** and **e** show 100% conversions within thirty minutes and complexes **b** and **a** within three and twenty-four hours respectively. However, Bu_4NIO_4 on its own shows a 54% conversion of 1-hexanol to hexanal within thirty minutes, and a 65% conversion by the end of the analysis period. The implication here is that the co-oxidant is itself partially responsible for the high conversions, but as is evident from table 3.2.4, most of the reactions show total conversions within thirty minutes. This means that the major role of Bu_4NIO_4 is to recycle the ruthenium catalyst.

The above reactions all involved 1-hexanol, a primary alcohol, as substrate. The carboxylic acid, hexanoic acid, was not detected as a product in any of the reactions. The carboxylic acid is produced when over-oxidation of a primary alcohol occurs, and usually when water is present in the reaction medium. This observation implied that catalysts **a-e** were specific oxidants for the oxidation of 1-hexanol to hexanal. The oxidations of further primary alcohols by the catalyst $[PPh_4][RuO_2(OCOC_6H_5)Cl_2]$ and the co-oxidants NMO and Bu_4NIO_4 will be discussed later.

Hydrogen peroxide is a poor co-oxidant for the oxidation of 2-hexanol to 2-hexanone (Table 3.2.5) by catalysts **a-e**. The highest number of turnovers was obtained by $[PPh_4][RuO_2(OCOC_6H_5)Cl_2]$ which showed four turnovers within thirty minutes. Catalysts **b**, **d** and **e** only achieved maxima of one, two and two turnovers respectively. H_2O_2 on its own showed no oxidation activity with 2-hexanol.

Sodium hypochlorite showed 100% conversion of 2-hexanol to 2-hexanone within three hours with the catalyst $[PPh_4][RuO_2(OCOCF_3)Cl_2]$ (*i.e.* seventeen turnovers). Compound **a** showed a turnover of fourteen (*i.e.* 92% conversion) after three hours, with complex **d** achieving thirteen turnovers (*i.e.* 69% conversion) after twenty-four hours. Complex **e** showed a high rate of oxidation at the start of the reaction, but showed only one further turnover over the next three hours, and thereafter showed no further activity. NaOCl showed only 4% conversion of 2-hexanol to 2-hexanone by itself.

The compound $[PPh_4][RuO_2(OCOC_6F_5)Cl_2]$ showed a low rate of conversion of 2-hexanol with *t*-BuOOH initially and finally showed a 33% conversion (*i.e.* 6 turnovers) after twenty-four hours reaction. The complexes **c** and **e** showed a maximum of only three turnovers, with complexes **a** and **b** similarly showing turnovers of four and five, respectively, with *t*-BuOOH. The co-oxidant shows no activity with 2-hexanol on its own.

NMO proved to be an efficient co-oxidant for the oxidation of 2-hexanol. $[PPh_4][RuO_2(OCOC_6H_5)Cl_2]$ with NMO achieved a 100% conversion of 2-hexanol to 2-hexanone within thirty minutes, with the other complexes showing more than fifty percent conversions in the same time interval. All the complexes showed ten or more turnovers (*i.e.* greater than 60% conversion) after twenty-four hours reaction. NMO on its own did not oxidize 2-hexanol. This is contrary to what was observed for the 1-hexanol oxidation reactions involving NMO only.

TMANO is a mediocre co-oxidant for the oxidation of 2-hexanol. With this co-oxidant $[PPh_4][RuO_2(OCOC_5H_{11})Cl_2]$ showed the highest conversion of 2-hexanol to 2-hexanone (*i.e.* 45%, eight turnovers) after twenty-four hours. $[PPh_4][RuO_2(OCOCF_3)Cl_2]$ and $[PPh_4][RuO_2(OCOC_5H_{11})Cl_2]$ showed the same rate of oxidation (*i.e.* six turnovers) at the start of the reaction, but $[PPh_4][RuO_2(OCOCF_3)Cl_2]$ did not show any major oxidation activity thereafter. Complexes **a** and **c** had low rates of oxidation in the first three hours of reaction but achieved approximately the same percentage conversion as complexes **b** and **d** after twenty-four hours. TMANO itself shows a 14% conversion of 2-hexanol to 2-hexanone after twenty-four hours.

Oxygen showed zero conversion of 2-hexanol to 2-hexanone with all the catalysts. This result, as in the 1-hexanol oxidations, was disappointing from the environmental and cost perspective.

Iodosylbenzene as a co-oxidant for the oxidation of 2-hexanol to 2-hexanone was as effective as NMO with all the catalysts. $[PPh_4][RuO_2(OCOC_5H_{11})Cl_2]$ showed a 88% conversion of 2-hexanol to 2-hexanone (*i.e.* fifteen turnovers) within thirty minutes reaction and 100% conversion after three hours reaction. Complexes **a** (nine turnovers) and **d** (ten turnovers), and **b** (eight turnovers) and **c** (eight turnovers), showed comparative oxidation rates within thirty minutes of the start of the reaction. However, after twenty-four hours, complexes **a** (eleven turnovers), **c** (thirteen turnovers) and **d** (fifteen turnovers) showed different rates of conversion. Complex **b** showed eleven turnovers in the same time period.

Both $[PPh_4][RuO_2(OCOCH_3)Cl_2]$ and $[PPh_4][RuO_2(OCOC_5H_{11})Cl_2]$ showed a 100% conversion of 2-hexanol to 2-hexanone within three hours of reaction with Bu_4NIO_4 as co-oxidant, although $[PPh_4][RuO_2(OCOCH_3)Cl_2]$ showed an 80% conversion (*i.e.* twelve turnovers) after thirty minutes compared to the 46% conversion (*i.e.* eight turnovers) shown by $[PPh_4][RuO_2(OCOC_5H_{11})Cl_2]$ in the same time period. Complexes **b** and **d** showed similar conversions after twenty-four hours reaction, but differences in the rates of oxidation at the start of the respective reactions. $[PPh_4][RuO_2(OCOC_6H_5)Cl_2]$ showed a high rate of oxidation within thirty minutes, achieving a 76% conversion of 2-hexanol to 2-hexanone, but did not show any major change thereafter. The 16% conversion of 2-hexanol to 2-hexanone obtained by Bu_4NIO_4 on its own after twenty-four hours reaction was much lower than the 65% conversion of 1-hexanol to hexanal discussed earlier.

3.2.4. Determining Catalytic Turnover Limits

The compounds $[PPh_4][RuO_2(OCOCF_3)Cl_2]$, $[PPh_4][RuO_2(OCOC_6H_5)Cl_2]$ and $[PPh_4][RuO_2(OCOC_5H_{11})Cl_2]$ were studied further to determine the level of catalytic turnovers that could possibly be achieved when the amount of alcohol substrate was doubled and the quantity of catalyst halved. $[PPh_4][RuO_2(OCOCF_3)Cl_2]$ and $[PPh_4][RuO_2(OCOC_6H_5)Cl_2]$ were chosen for this study since they performed better than their structurally equivalent complexes $[PPh_4][RuO_2(OCOCH_3)Cl_2]$ and $[PPh_4][RuO_2(OCOC_6F_5)Cl_2]$ in the catalytic oxidations of 1- and 2-hexanol.

$[PPh_4][RuO_2(OCOC_5H_{11})Cl_2]$ was chosen as a third catalyst for the investigation in order to further study the effect of varying the carboxylate ligand in the dioxoruthenium(VI) salt.

The initial study used 1-hexanol as substrate. The co-oxidants 4-methylmorpholine N-oxide and tetrabutylammonium periodate were chosen for this particular oxidation reaction since they performed best with these catalysts, as was shown in section 3.2.3 above. These reactions were again carried out with the precautions mentioned previously, and were again monitored by gas chromatography. The results of the oxidation reactions are shown in table 3.2.7.

The catalysts showed a high initial rate of conversion, with high turnovers, when NMO was used as co-oxidant. The complex $[PPh_4][RuO_2(OCOCF_3)Cl_2]$ reacted slightly faster than $[PPh_4][RuO_2(OCOC_5H_{11})Cl_2]$, which in turn reacted faster than $[PPh_4][RuO_2(OCOC_6H_5)Cl_2]$ at the start of the reaction. The reaction rate appeared to level off between the three and twenty-four hour analyses in the reactions of the compounds $[PPh_4][RuO_2(OCOCF_3)Cl_2]$ and $[PPh_4][RuO_2(OCOC_5H_{11})Cl_2]$.

Table 3.2.7. Summary of the catalytic reactions involving double quantities of 1-hexanol, 10 mg catalyst and the co-oxidants NMO and Bu_4NIO_4, showing percentage yield of hexanal. Turnovers are shown in parentheses.

Complex	Reaction Time	NMO	Bu_4NIO_4
$[PPh_4][RuO_2(OCOCF_3)Cl_2]$	+30 Min.	77(52)	40(28)
	+3 Hours	85(58)	93(64)
	+24 Hours	87(59)	90(61)
$[PPh_4][RuO_2(OCOC_6H_5)Cl_2]$	+30 Min.	65(44)	50(36)
	+3 Hours	70(48)	80(56)
	+24 Hours	78(52)	100(68)
$[PPh_4][RuO_2(OCOC_5H_{11})Cl_2]$	+30 Min.	75(51)	52(36)
	+3 Hours	82(56)	88(60)
	+24 Hours	84(56)	86(59)

The catalyst $[PPh_4][RuO_2(OCOC_6H_5)Cl_2]$ achieved a maximum of fifty-two turnovers after twenty-four hours reaction, which equated to the number of turnovers achieved by the other two complexes within thirty minutes. $[PPh_4][RuO_2(OCOCF_3)Cl_2]$ functioned as the best catalyst from those examined when NMO was used as co-oxidant, and showed fifty-nine turnovers within twenty-four hours. This result is in contrast to the earlier data in table 3.2.4 where $[PPh_4][RuO_2(OCOC_6H_5)Cl_2]$ achieved complete conversion of 1-hexanol to hexanal within thirty minutes. Actually, $[PPh_4][RuO_2(OCOCF_3)Cl_2]$ appeared to function the 'worst' for this specific oxidation reaction amongst the five catalysts examined previously. A possible reason for this behaviour is that although $[PPh_4][RuO_2(OCOCF_3)Cl_2]$ showed a slower rate of conversion of 1-hexanol to hexanal relative to the other catalysts, it has the ability to undergo more turnovers compared to its rivals. This could possibly be due to the structural stability of the fluorinated complex relative to the other complexes. This feature could increase the lifetime of the fluorinated complex during the course of the oxidation reaction and consequently allow for easier re-oxidation of the reduced catalyst to its active form.

A different trend is observed for the oxidation reactions involving tetrabutylammonium periodate. $[PPh_4][RuO_2(OCOCF_3)Cl_2]$ initially reacts relatively slowly, showing a turnover of only twenty-eight at the start of the reaction compared to the thirty-six turnovers achieved by the other two complexes. However, after three hours, $[PPh_4][RuO_2(OCOCF_3)Cl_2]$ showed a turnover of sixty four compared to the fifty-six turnovers for $[PPh_4][RuO_2(OCOC_6H_5)Cl_2]$ and the sixty turnovers for $[PPh_4][RuO_2(OCOC_5H_{11})Cl_2]$. After twenty-four hours, $[PPh_4][RuO_2(OCOC_6H_5)Cl_2]$ achieved complete conversion of the alcohol to the aldehyde with sixty-eight turnovers of the catalyst. $[PPh_4][RuO_2(OCOC_5H_{11})Cl_2]$ showed no further conversion of 1-hexanol to hexanal after three hours. The trifluoroacetic acid complex showed a three percent decrease in conversion of 1-hexanol to hexanal relative to the three hour analysis. This change is, however, within the experimental error expected for such analyses and is consequently meaningless. $[PPh_4][RuO_2(OCOC_6H_5)Cl_2]$ functioned as the best catalyst with tetrabutylammonium periodate showing a consistent increase of aldehyde product over the analysis period.

The above investigation was repeated for 2-hexanol. As is evident from table 3.2.5, no one catalyst or corresponding co-oxidant was clearly superior for this reaction. It was thus decided to examine the catalyst and co-oxidant systems that achieved maximum conversions of 2-hexanol to 2-hexanone within the shortest period of time. Thus, $[PPh_4][RuO_2(OCOCH_3)Cl_2]$ and $[PPh_4][RuO_2(OCOC_5H_{11})Cl_2]$ were used with Bu_4NIO_4,

$[PPh_4][RuO_2(OCOC_6H_5)Cl_2]$ was used with NMO and $[PPh_4][RuO_2(OCOCF_3)Cl_2]$ with NaOCl. The amount of 2-hexanol was doubled to 1.0 mmol and the quantity of catalyst was halved to 10 mg compared to the previous runs reported in table 3.2.5. The results of the gas chromatograph monitored reactions are summarized in table 3.2.8.

The compounds $[PPh_4][RuO_2(OCOCH_3)Cl_2]$ and $[PPh_4][RuO_2(OCOC_5H_{11})Cl_2]$ showed low conversions of secondary alocohol to ketone at the start of the reactions involving tetrabutylammonium periodate as co-oxidant. However, the latter complex achieved twenty turnovers compared to the eleven obtained by the former. After three hours, both complexes attained approximately the same turnover level with this trend persisting after twenty-four hours. Neither complex achieved a 100% conversion though. $[PPh_4][RuO_2(OCOCH_3)Cl_2]$ showed a 60% conversion compared to the 54% shown by $[PPh_4][RuO_2(OCOC_5H_{11})Cl_2]$. However, it must be noted that this actually equates to thirty-six turnovers for $[PPh_4][RuO_2(OCOCH_3)Cl_2]$ and thirty-seven turnovers for $[PPh_4][RuO_2(OCOC_5H_{11})Cl_2]$.

Table 3.2.8. Summary of catalytic reactions involving double quantities of 2-hexanol, 10 mg catalyst and various co-oxidants, showing percentage yield of 2-hexanone. Turnovers are shown in parentheses.

Complex	Reaction Time	NMO	Bu_4NIO_4	NaOCl
$[PPh_4][RuO_2(OCOCH_3)Cl_2]$	+30 Min.	-	19(11)	-
	+3 Hours	-	38(23)	-
	+24 Hours	-	60(36)	-
$[PPh_4][RuO_2(OCOCF_3)Cl_2]$	+30 Min.	-	-	14(10)
	+3 Hours	-	-	21(14)
	+24 Hours	-	-	25(17)
$[PPh_4][RuO_2(OCOC_6H_5)Cl_2]$	+30 Min.	69(47)	-	-
	+3 Hours	100(68)	-	-
	+24 Hours	100(68)	-	-
$[PPh_4][RuO_2(OCOC_5H_{11})Cl_2]$	+30 Min.	-	30(20)	-
	+3 Hours	-	35(24)	-
	+24 Hours	-	54(37)	-

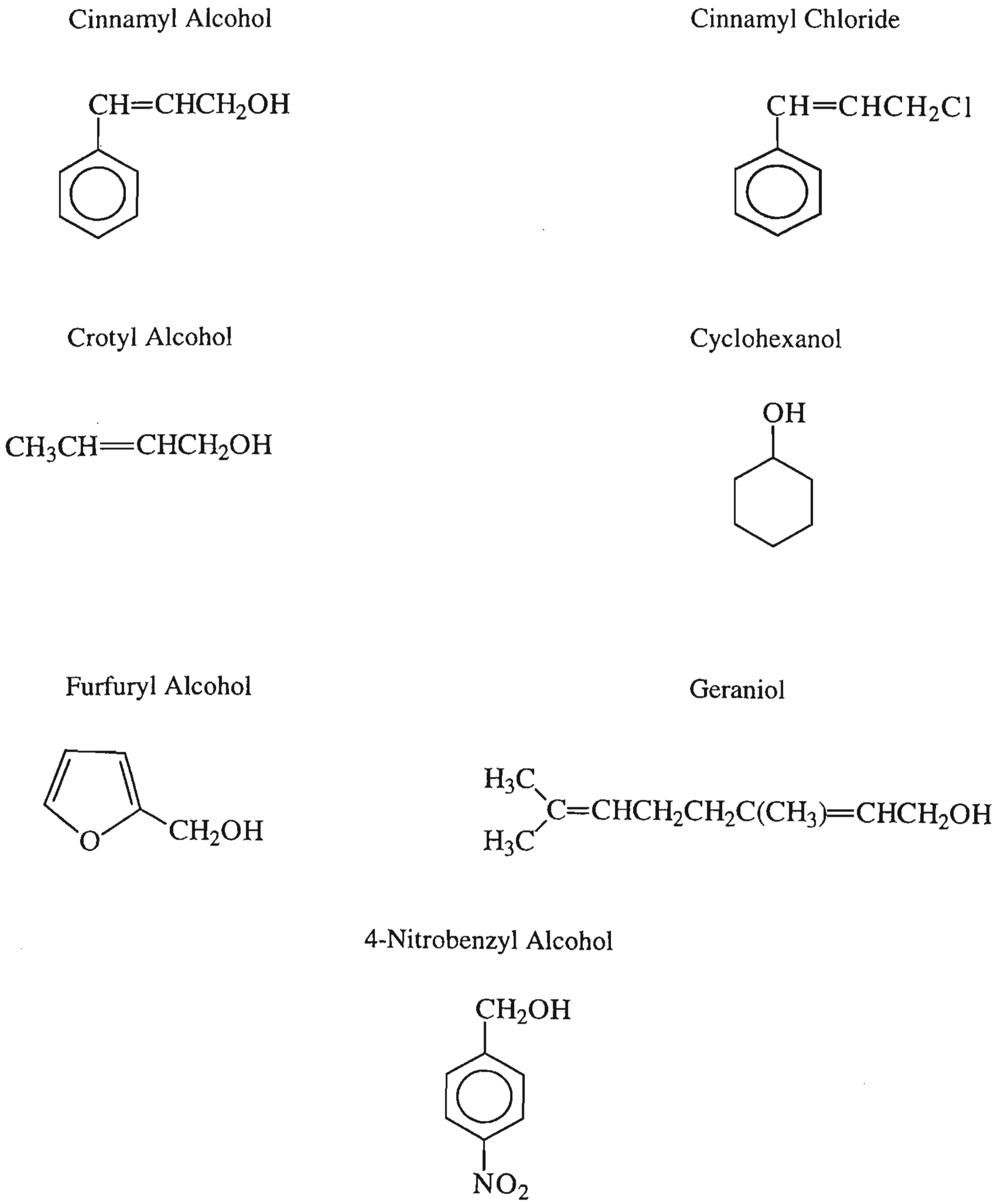
The catalyst $[PPh_4][RuO_2(OCOC_6H_5)Cl_2]$ with NMO reached forty-seven turnovers within thirty minutes of the start of the reaction and achieved total conversion of 2-hexanol to 2-hexanone (*i.e.* sixty-eight turnovers) within three hours. None of the other catalysts tested achieved this with NMO as co-oxidant.

The complex $[PPh_4][RuO_2(OCOCF_3)Cl_2]$, with the co-oxidant sodium hypochlorite, after attaining a turnover of ten at the start of the reaction, achieved fourteen after three hours but only seventeen turnovers after twenty-four hours. The maximum turnovers achieved for this reaction and the earlier one containing half the amount of alcohol and double the amount of catalyst is surprisingly the same (*i.e.* seventeen). It thus seems that $[PPh_4][RuO_2(OCOCF_3)Cl_2]$ can only obtain a maximum of seventeen turnovers for the oxidation of 2-hexanol, when sodium hypochlorite is used as co-oxidant.

3.2.5. Oxidation of a Range of Substrates by $[PPh_4][RuO_2(OCOC_6H_5)Cl_2]$ and $[PPh_4][RuO_2(OCOC_6F_5)Cl_2]$ with NMO and Bu_4NIO_4

In section 3.2.3 the complexes **a-e** were investigated to determine their potential as catalytic oxidants of 1-hexanol, 2-hexanol and 1-hexene. The results obtained suggested that the catalysts were worth further investigation since they appeared to selectively oxidize primary alcohols to aldehydes and secondary alcohols to ketones, without attacking double bonds. The study also showed that each of the catalysts's performance depended on the co-oxidant used. Although no specific trend in activity of the catalysts **a-e** could be determined, it could generally be concluded that $[PPh_4][RuO_2(OCOC_6H_5)Cl_2]$ functioned most effectively as a catalyst from the range of complexes studied. In contrast, $[PPh_4][RuO_2(OCOC_6F_5)Cl_2]$ generally was the least effective over the range of catalytic oxidations examined. Furthermore, it was noted that NMO and Bu_4NIO_4 were the most effective co-oxidants from the range examined for the systems studied. Thus, it was decided to examine $[PPh_4][RuO_2(OCOC_6H_5)Cl_2]$ and $[PPh_4][RuO_2(OCOC_6F_5)Cl_2]$ as catalysts for the oxidation of a variety of substrates using the co-oxidants NMO and Bu_4NIO_4.

The structures of the substrates examined in this study are shown in figure 3.2.2. The substrates were chosen to represent as wide a spectrum of organic alcohols as possible and further included one example of an unsaturated aromatic chloride complex. The latter substrate was used to determine whether the oxidative systems attacked halogens bonded to organic compounds. The range of substrates included the unsaturated aromatic primary alcohol (cinnamyl alcohol) and its equivalent unsaturated aromatic chloride (cinnamyl chloride), unsaturated primary alcohols (geraniol and crotyl alcohol), a saturated cyclic alcohol (cyclohexanol), a heteroatom containing aromatic primary alcohol (furfuryl alcohol) and finally a nitro-substituted aromatic primary alcohol (4-nitrobenzyl alcohol).


Cinnamyl Alcohol

Cinnamyl Chloride

Crotyl Alcohol

Cyclohexanol

Furfuryl Alcohol

Geraniol

4-Nitrobenzyl Alcohol

Figure 3.2.2. Structures of the substrates reacted with $[PPh_4][RuO_2(OCOC_6H_5)Cl_2]$ and $[PPh_4][RuO_2(OCOC_6F_5)Cl_2]$, with NMO and Bu_4NIO_4 as co-oxidants.

The results of the oxidation of these substrates by $[PPh_4][RuO_2(OCOC_6H_5)Cl_2]$ and $[PPh_4][RuO_2(OCOC_6F_5)Cl_2]$, using the co-oxidants NMO and Bu_4NIO_4, are shown in tables 3.2.9 and 3.2.10, respectively. As previously, the co-oxidants themselves were also reacted with the substrates in the absence of catalyst to determine the degree of the direct reaction. These results are shown in table 3.2.11.

Table 3.2.9. Summary of the percentage conversions of substrates to their corresponding products with $[PPh_4][RuO_2(OCOC_6H_5)Cl_2]$ and the co-oxidants NMO and Bu_4NIO_4. Turnovers are shown in parentheses.

Substrate	Product	Reaction Time	NMO	Bu_4NIO_4
Cinnamyl Alcohol	A	+30 Min.	99(17)	100(17)
		+3 Hours	100(17)	100(17)
		+24 Hours	100(17)	100(17)
Cinnamyl Chloride	A	+30 Min.	3(<1)	5(<1)
		+3 Hours	2(<1)	5(<1)
		+24 Hours	2(<1)	7(1)
Crotyl Alcohol	A	+30 Min.	51(9)	53(9)
		+3 Hours	56(10)	67(11)
		+24 Hours	57(10)	100(17)
Cyclohexanol	K	+30 Min.	100(17)	70(11)
		+3 Hours	100(17)	100(17)
		+24 Hours	100(17)	100(17)
Furfuryl Alcohol	A	+30 Min.	50(9)	89(15)
		+3 Hours	55(9)	93(17)
		+24 Hours	56(10)	98(17)
Geraniol	A	+30 Min.	92(16)	81(14)
		+3 Hours	97(17)	100(17)
		+24 Hours	98(17)	100(17)
4-Nitrobenzyl Alcohol	A	+30 Min.	99(17)	96(16)
		+3 Hours	100(17)	100(17)
		+24 Hours	100(17)	100(17)

A – corresponding aldehyde product
K – corresponding ketone product

Table 3.2.10. Summary of the percentage conversions of substrates to their corresponding products with $[PPh_4][RuO_2(OCOC_6F_5)Cl_2]$ and the co-oxidants NMO and Bu_4NIO_4. Turnovers are shown in parentheses.

Substrate	Products	Reaction Time	NMO	Bu_4NIO_4
Cinnamyl Alcohol	A	+30 Min.	100(19)	100(19)
		+3 Hours	100(19)	100(19)
		+24 Hours	100(19)	100(19)
Cinnamyl Chloride	A	+30 Min.	3(<1)	3(<1)
		+3 Hours	1(<1)	5(1)
		+24 Hours	2(<1)	9(2)
Crotyl Alcohol	A	+30 Min.	45(9)	20(4)
		+3 Hours	54(10)	47(9)
		+24 Hours	57(11)	75(14)
Cyclohexanol	K	+30 Min.	98(19)	48(9)
		+3 Hours	100(19)	98(19)
		+24 Hours	100(19)	99(19)
Furfuryl Alcohol	A	+30 Min.	52(10)	54(10)
		+3 Hours	64(12)	77(15)
		+24 Hours	67(13)	98(19)
Geraniol	A	+30 Min.	98(19)	57(11)
		+3 Hours	100(19)	100(19)
		+24 Hours	100(19)	100(19)
4-Nitrobenzyl Alcohol	A	+30 Min.	95(18)	99(19)
		+3 Hours	100(19)	100(19)
		+24 Hours	100(19)	100(19)

A – corresponding aldehyde product
K – corresponding ketone product

Both $[PPh_4][RuO_2(OCOC_6H_5)Cl_2]$ and $[PPh_4][RuO_2(OCOC_6F_5)Cl_2]$ are efficient oxidants for the oxidation of cinnamyl alcohol to cinnamyl aldehyde giving almost total conversion within thirty minutes of the start of the reaction using either NMO or Bu_4NIO_4 as co-oxidants. The double bond in cinnamyl alcohol does not appear to have been attacked by the catalysts since no product apart from cinnamyl aldehyde was detected by the gas chromatograph. NMO by itself, however, showed a 76% conversion and Bu_4NIO_4 a 46% conversion of cinnamyl alcohol to cinnamyl aldehyde after twenty-four hours reaction.

Table 3.2.11. Summary of the percentage conversions of substrates to their corresponding products by the co-oxidants NMO and Bu_4NIO_4 alone.

Substrate	Products	Reaction Time	NMO	Bu_4NIO_4
Cinnamyl Alcohol	A	+30 Min.	82	13
		+3 Hours	77	25
		+24 Hours	76	46
Cinnamyl Chloride	A	+30 Min.	18	3
		+3 Hours	16	8
		+24 Hours	30	3
Crotyl Alcohol	A	+30 Min.	0	6
		+3 Hours	3	4
		+24 Hours	3	3
Cyclohexanol	K	+30 Min.	16	6
		+3 Hours	15	13
		+24 Hours	14	12
Furfuryl Alcohol	A	+30 Min.	21	0
		+3 Hours	23	5
		+24 Hours	22	3
Geraniol	A	+30 Min.	0	4
		+3 Hours	2	5
		+24 Hours	28	10
4-Nitrobenzyl Alcohol	A	+30 Min.	70	25
		+3 Hours	65	27
		+24 Hours	64	22

A – corresponding aldehyde product
K – corresponding ketone product

The above catalysts with NMO appear to perform better than $[PPh_4][RuO_2(OCOCH_3)Cl_2]$ [6], which showed a 97% conversion of cinnamyl alcohol over a two hour period. The catalysts $(Bu_4{}^nN)[RuO_4]$ (known as TBAP) and $(Pr_4{}^nN)[RuO_4]$ (known as TPAP) with NMO achieved conversions of 91% and 75% respectively for the same oxidation over a five hour period

[30]. The $Ru(PPh_3)_3Cl_2$ / hydroquinone aerobic catalytic system used by Hanyu *et al.* [31] gave a 100% conversion of cinnamyl alcohol when oxygen was used as co-oxidant. However, the oxidation reaction was carried out at 60°C by Hanyu *et al.*, compared to the room temperature oxidation for the present study. When other catalysts [32,33] were used with Bu_4NIO_4, less than 85% oxidative conversion of cyclohexanol to cyclohexanone was achieved.

Catalytic oxidations of cinnamyl chloride by $[PPh_4][RuO_2(OCOC_6H_5)Cl_2]$ and $[PPh_4][RuO_2(OCOC_6F_5)Cl_2]$ with NMO and Bu_4NIO_4 to cinnamyl aldehyde show turnovers of one or less. These results are equal to or lower than the results obtained when the co-oxidants are used alone. This suggests that these catalysts are inactive towards the oxidation of chloride atoms in organic substrates. When NMO was used on its own, 30% of cinnamyl chloride was oxidized to cinnamyl aldehyde. This result agrees with the research that showed that NMO reacted directly with activated halides [25,26]. However, the absence of a substantial aldehyde product in the reactions containing the catalysts and NMO suggests that the catalysts inhibit the direct oxidation of organic halides by NMO.

Crotyl alcohol was progressively converted to croton aldehyde from 53% after thirty minutes, to 67% after three hours, to 100% after twenty-four hours with $[PPh_4][RuO_2(OCOC_6H_5)Cl_2]$ and Bu_4NIO_4. $[PPh_4][RuO_2(OCOC_6F_5)Cl_2]$ with Bu_4NIO_4 showed a similar yet slower reaction rate over twenty-four hours, resulting in a final conversion of 75%. NMO as a co-oxidant gave a 57% conversion for both $[PPh_4][RuO_2(OCOC_6H_5)Cl_2]$ and $[PPh_4][RuO_2(OCOC_6F_5)Cl_2]$ over a twenty-four hour period. However, for the same percentage conversion, $[PPh_4][RuO_2(OCOC_6F_5)Cl_2]$ shows eleven turnovers compared to the ten achieved by $[PPh_4][RuO_2(OCOC_6H_5)Cl_2]$. The co-oxidants by themselves converted crotyl alcohol to croton aldehyde in minimal yield (3-6%) over twenty-four hours. It was clear from the gas chromatograms and percentage conversion calculations that no other oxidation product except croton aldehyde was obtained. This suggests that the double bond in crotyl alcohol was not attacked during the oxidation process and over-oxidation to the carboxylic acid did not occur.

The catalyst $[PPh_4][RuO_2(OCOC_6H_5)Cl_2]$ causes a 100% conversion of cyclohexanol to cyclohexanone after thirty minutes with NMO and after three hours with Bu_4NIO_4 as co-oxidant. $[PPh_4][RuO_2(OCOC_6F_5)Cl_2]$ shows a similar oxidation rate giving 100% conversion with NMO and 98% conversion with Bu_4NIO_4 after three hours reaction. The co-oxidants on their own show less than fifteen percent conversion after twenty-four hours. No rupture of the cyclohexanol ring was detected from the gas chromatographic results and only cyclohexanone was detected as a product. Both catalysts perform better than known ruthenium catalysts used previously for this conversion [19,32-36] using the same co-oxidants.

The compounds $[PPh_4][RuO_2(OCOC_6H_5)Cl_2]$ and $[PPh_4][RuO_2(OCOC_6F_5)Cl_2]$ both achieve 98% conversions of furfuryl alcohol to furfuraldehyde within twenty-four hours with Bu_4NIO_4, although the former complex showed a much higher rate of oxidation than the latter complex. With NMO as co-oxidant, both catalysts initially show the same rate of oxidation. However, after the thirty minute analysis, $[PPh_4][RuO_2(OCOC_6F_5)Cl_2]$ showed a higher rate of conversion and gave a 67% conversion (*i.e.* thirteen turnovers) of furfuryl alcohol to furfuraldehyde after twenty-four hours. $[PPh_4][RuO_2(OCOC_6H_5)Cl_2]$ only achieved a 56% conversion (*i.e.* ten turnovers) in the same time period with NMO. NMO on its own gave a 21% conversion of furfuryl alcohol to furfuraldehyde after thirty minutes and did not show any substantial change thereafter. Bu_4NIO_4 alone oxidized a minimal amount of furfuryl alcohol. It was noted that there was no attack by the catalysts on the double bonds of the furfuryl ring. There was furthermore no influence on the oxygen within the structure of the aromatic ring. These observations imply that the catalyst shows specificity for the oxidation of the alcohol group in furfuryl alcohol.

The catalyst $[PPh_4][RuO_2(OCOC_6H_5)Cl_2]$ causes a 100% conversion of geraniol to citral with Bu_4NIO_4 within three hours and a 98% conversion after twenty-four hours with NMO as co-oxidant. $[PPh_4][RuO_2(OCOC_6F_5)Cl_2]$ achieved a 100% conversion within three hours with both NMO and Bu_4NIO_4. On their own, NMO and Bu_4NIO_4 show 28% and 10% conversions of geraniol to citral, respectively, after twenty-four hours. The specificity of the catalysts are again demonstrated by the absence of any other oxidation or cleavage products. These catalysts also perform better than known ruthenium catalysts that have previously been investigated for this oxidation reaction [31-35].

Both catalysts showed 100% conversions of 4-nitrobenzyl alcohol to 4-nitrobenzaldehyde after three hours reaction using either NMO or Bu_4NIO_4 as co-oxidants. NMO on its own however showed a 64% conversion of the alcohol to the aldehyde after twenty-four hours.

Bu_4NIO_4 results in a 22% conversion of the alcohol to the aldehyde in the same time period. Again no side reactions are seen, since only the expected aldehyde, 4-nitrobenzyl aldehyde, was detected without any unsubstantiated conversions being noted in percentage yield calculations, and the only peaks seen in the gas chromatogram were due to the solvent, internal standard and aldehyde.

It can be concluded from the above study that $[PPh_4][RuO_2(OCOC_6H_5)Cl_2]$ and $[PPh_4][RuO_2(OCOC_6F_5)Cl_2]$ are efficient catalysts for a range of organic substrates. They both show specificity for the oxidation of primary alcohols to aldehydes and secondary alcohols to ketones, without disruption of sensitive organic linkages like double bonds or cleavage of either aromatic or saturated rings, and show an inert behaviour to heteroatoms and chlorides in such substrates. The inertness of these catalysts to double bonds was previously postulated in section 3.2.3 when no oxidation products of 1-hexene were obtained. The results obtained show this postulate to be correct. No difference in catalytic activity is noted between the fluorinated complex $[PPh_4][RuO_2(OCOC_6F_5)Cl_2]$ and its protonated equivalent $[PPh_4][RuO_2(OCOC_6H_5)Cl_2]$.

3.2.6. Separation of Reaction Components

As mentioned in section 1.1, homogeneous catalysts exist in the same phase as the substrates they act on. The solubility of the catalyst in the solvent can become a problem when it comes to the separation of such catalysts from the reaction mixture at the end of the reaction. The reaction mixture usually contains the product of the reaction, the reduced co-oxidant and possibly unoxidized substrate, in addition to the catalyst. The catalysts $[PPh_4][RuO_2(OCOR)Cl_2]$ (R = CH_3, CF_3, C_6H_5, C_6F_5, C_5H_{11}), being homogeneous catalysts, are limited by the fact that the metal catalyst can not be simply filtered off. The separation of the components of the reaction mixture has been successfully carried out in reactions involving similar ruthenium carboxylate catalysts [7]. Separation of the mixture by column chromatography or by derivative formation of the product, with subsequent filtration of the solid, was used to separate alcohol oxidation reaction mixtures. Column chromatography, though, resulted in the loss of the catalytic salt which was retained on the column.

Separation of reaction mixtures containing the catalytic salt used in this study involved a two-step process. The first step involved the removal of the catalyst from the reaction products and the second either a distillation or a second column separation of the reaction components. The components of the mixture (*i.e.* the substrate, products and co-oxidants) dictated which of the two separation routes were followed. The separation by distillation could only be used if the reaction components had distinctly different boiling points, otherwise, the second separation was carried out by column chromatography. These separation routes could easily be combined to obtain the most appropriate method to effectively separate the reaction mixture.

With the above factors in mind an up-scaled oxidation of cyclohexanol by $[PPh_4][RuO_2(OCOC_6H_5)Cl_2]$ with the co-oxidant NMO was attempted. The reaction was carried out with the same precautions utilized previously. All the constituents in the reaction were scaled up proportionally and included gravimetric quantification of the cyclohexanol. The reaction was run over a seventy-two hour period to allow for as complete conversion of the substrate as possible. The reaction was monitored at twenty-four hour intervals by gas chromatography to determine the extent of the oxidation reaction. After seventy-two hours, it was noted that the reaction had not reached completion and showed approximately 50% conversion of cyclohexanol to cyclohexanone. However, the reaction was stopped and worked-up. Initially the entire reaction mixture was filtered through a glass frit to remove the insoluble molecular sieves. A long silica column was prepared with hexane before the dichloromethane solution containing the reaction mixture was layered onto the column. The mixture was eluted through the column with a hexane mobile phase. As the solution eluted through the column the dark green ruthenium complex was trapped on the silica stationary phase, thus giving rise to a catalyst free clear eluent. The column was flushed with hexane to ensure that all the cyclohexanol, cyclohexanone, NMO and 4-methylmorpholine (NM) (*i.e.* reduced NMO) was eluted. To further ensure complete elution of the catalyst free reaction components, the column was flushed with dichloromethane. All the eluent obtained was collected together in a round-bottomed flask.

It was established from literature [37] that the substrate cyclohexanol, the expected product cyclohexanone, the co-oxidant NMO and the reduced co-oxidant NM all had different boiling points. Consequently, a simple distillation was used to separate the mixture. The solvents dichloromethane and hexane distilled off first, followed by NM and NMO. The boiling points of cyclohexanol and cyclohexanone are relatively close to each other (*i.e.* 160°C and 155°C respectively). Thus, the distillation had to be closely monitored to ensure effective separation. All the distilled fractions were analyzed by ^1H and ^{13}C NMR and the spectra obtained were compared to spectra of commercially obtained compounds. The NMR spectra of all the fractions showed pure products and thus confirmed that the reaction mixture was successfully separated by distillation.

Gravimetric analysis of the cyclohexanone oxidation product obtained after distillation showed a yield of 42%. This was less than the quantitation obtained by gas chromatography and implied that about 8% of the product had been lost during the work-up of the reaction mixture. Even though this method did not give the quantitative separation expected, the technique of separating the reaction products overcame one of the limitations associated with homogeneous catalyzed reactions. The methodology used here can similarly be applied to the separation of the other oxidation systems examined in sections 3.2.3 and 3.2.5.

3.2.7. Supporting $[PPh_4][RuO_2(OCOC_6H_5)Cl_2]$ and $[PPh_4][RuO_2(OCOC_6F_5)Cl_2]$ on Poly(4-vinylpyridine)

As mentioned above, one of the major deterrents to the development of homogeneous catalysis is the inability to readily separate reaction products from the catalyst [38]. This becomes a significant economic problem especially when catalysts containing expensive metals like ruthenium are lost during the work-up of reaction mixtures. For years researchers have tried to combine the advantages of homogeneous catalysis with those of heterogeneous catalysis [38,39], and present research aims to support homogeneous catalysts on insoluble supports without affecting the activity and selectivity that has become synonymous with homogeneous catalysts [38-40].

In view of this trend, it was decided to undertake a preliminary study to determine whether $[PPh_4][RuO_2(OCOC_6H_5)Cl_2]$ and $[PPh_4][RuO_2(OCOC_6F_5)Cl_2]$ could be supported on the polymer poly(4-vinylpyridine) {PVP} (Figure 3.2.4).

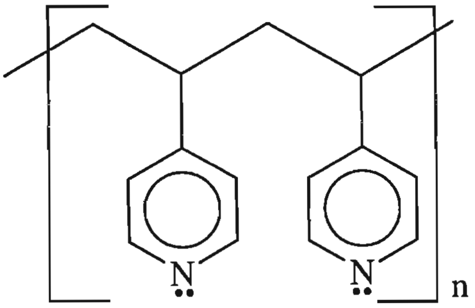


Figure 3.2.3. Structure of uncoordinated poly(4-vinylpyridine).

The compounds $[PPh_4][RuO_2(OCOC_6H_5)Cl_2]$ and $[PPh_4][RuO_2(OCOC_6F_5)Cl_2]$ were synthesized and fully characterized as previously. One gram of poly(4-vinylpyridine) was stirred for five minutes with dichloromethane before 100 mg of the homogenous catalyst was added (*i.e.* in the ratio of 1 mg catalyst : 10 mg PVP). After stirring these two components for five hours, the solvent was removed under vacuum to yield dark green polymeric beads. The product was characterized by comparing infrared spectra of the green beads with those of the unsupported catalysts and the "unloaded" PVP. A summary of the characteristic peaks are shown in table 3.2.12.

The infrared data of both supported catalysts show characteristic peaks that have been assigned. The peak in the region 3020 cm^{-1} to 3030 cm^{-1} is assigned to the aromatic ν(C-H) stretching mode of the pyridine ring and the intense peak at approximately 1597 cm^{-1} to the ν(C=C) stretch in the pyridine ring. The band at approximately 2925 cm^{-1} is due to aliphatic ν(C-H) stretching of the $-CH_2-$ group in the vinyl chain of the polymer backbone.

The strong peak at 1414 cm^{-1} represents the ν(C=N) stretching vibration in the pyridine ring, with the strong ν_{asym}(C-H) vibration at about 821 cm^{-1} being a diagnostic feature of the poly(4-vinylpyridine) backbone. The peak at approximately 683 cm^{-1} is representative of a ν(CH) aromatic bend of either the pyridine ring of the polymer, or the benzene ring from the ruthenium(VI) complex.

The peak at approximately 1105 cm^{-1} represents the ν(C-O) stretch of the carboxylate group of the carboxylic acid ligand on the ruthenium(VI) complexes. Although weak, a distinct ν_{asym} (Ru=O) stretch is observed at approximately 878 cm^{-1}. Both the ν(C-O) stretch and the ν_{asym}

(Ru=O) stretch noticed for the green beads are shifted to lower wavenumbers when compared to those observed for the unsupported complexes (see table 3.2.2).

Table 3.2.12. Infrared data of $[PPh_4][RuO_2(OCOC_6H_5)Cl_2]$ and $[PPh_4][RuO_2(OCOC_6F_5)Cl_2]$ supported on poly(4-vinylpyridine).

PVP-Supported Complex	**Selected Bands of Infrared Spectra (cm^{-1})**
$[PPh_4][RuO_2(OCOC_6H_5)Cl_2]$	3023(w) ν(C-H)-pyridine ring, 2925(m) $\nu(CH_2)$-vinyl chain, 1598(s) ν(C=C)-pyridine ring, 1414(s) ν(C=N)-pyridine ring, 822(s) ν_{asym}(C-H)-vinyl chain, 682(m) ν(C-H)-aromatic ring, 1107(m) ν(C-O)-carboxylate, 875(w) ν_{sym}(Ru=O)
$[PPh_4][RuO_2(OCOC_6F_5)Cl_2]$	3028(m) ν(C-H)-pyridine ring, 2924(s) $\nu(CH_2)$-vinyl chain, 1596(s) ν(C=C)-pyridine ring, 1414(s) ν(C=N)-pyridine ring, 821(s) ν_{asym}(C-H)-vinyl chain, 684(m) ν(C-H)-aromatic ring, 1104(m) ν(C-O)-carboxylate, 879(w) ν_{sym}(Ru=O)

s = strong m = medium w = weak

The peaks of the poly(4-vinylpyridine) support do overlap with other characteristic peaks of the ruthenium(VI) salts. However, the presence of the carboxylate and ruthenium-oxo vibrations mentioned above do prove that the complexes $[PPh_4][RuO_2(OCOC_6H_5)Cl_2]$ and $[PPh_4][RuO_2(OCOC_6F_5)Cl_2]$ are indeed associated with the support poly(4-vinylpyridine). The type of association that exists between the ruthenium(VI) complex and the polymer was not studied, however, it is believed to be some form of ionic interaction [41].

As mentioned in Chapter One, one of the major drawbacks of supporting homogeneous catalysts on insoluble supports was the possibility of the metal catalyst leaching from the support. To test whether $[PPh_4][RuO_2(OCOC_6H_5)Cl_2]$ or $[PPh_4][RuO_2(OCOC_6F_5)Cl_2]$ leached off the PVP, samples of the dark green polymeric beads were stirred overnight with dichloromethane and toluene. Dichloromethane was used as solvent since as it was established earlier that both catalysts dissolved in it when unsupported. Consequently, dichloromethane was ideal to check for leaching of the catalyst from the support. Toluene was chosen as solvent since $[PPh_4][RuO_2(OCOC_6H_5)Cl_2]$ and $[PPh_4][RuO_2(OCOC_6F_5)Cl_2]$ were not soluble in it and it was hoped that this would thus reduce the possibility of the catalyst leaching off the polymer. After twenty-four hours stirring, no green colouration (a qualitative visual test for the presence of the coloured catalyst) was observed and implied that no visible leaching occurred in these solvent systems.

The choice of solvent for use in oxidation reactions involving polymer-supported catalysts is very important as it is known that solvents influence the swelling of polymer beads [42]. Benzene as solvent was found to swell the phosphinated polystyrene polymer used by Nicolaides and Coville when the homogeneous catalyst $[RuCl_2(PPh_3)_3]$ was supported on the polymer [42]. The swelling of the polymer beads in benzene made accessibility of the active sites within the beads easier. However, the use of benzene is not recommended industrially due to its carcinogenic properties. Toluene is a methylated derivative of benzene and is regarded as a "green solvent" industrially. Thus, toluene was chosen as a solvent in our investigations on the supported catalysts. Dichloromethane does not cause swelling of the polymeric support [42]. However, it was used as a solvent to maintain consistency with the previous oxidation reactions studied.

The conversion of cyclohexanol to cyclohexanone with the co-oxidants NMO and Bu_4NIO_4 was attempted with the supported catalysts. This oxidation reaction was chosen because the unsupported $[PPh_4][RuO_2(OCOC_6H_5)Cl_2]$ and $[PPh_4][RuO_2(OCOC_6F_5)Cl_2]$ catalysts had previously shown 99-100% conversions of cyclohexanol to cyclohexanone with the same co-oxidants.

The oxidation reactions were set-up as before with the precautions regarding elimination of light and oxygen being maintained. The oxidation reactions were carried out first in dichloromethane and then repeated in toluene. The 200 mg of PVP-supported catalyst used in these reactions maintained the same mole ratio of ruthenium catalyst to substrate as before, since 100 mg of catalyst was added for every 1 g of polymer. The assumption was that with uniform stirring the catalyst was evenly distributed throughout the polymer. As such, 200 mg supported catalyst would be equivalent to 20 mg unsupported catalyst (based on the loading strategy employed above).

Samples were removed from the Schlenk tubes as before, dried over anhydrous $MgSO_4$ and filtered before analysis on the gas chromatograph. No leaching of the catalyst was observed since a clear filtrate was obtained after drying. Conversion percentages for the oxidation of cyclohexanol to cyclohexanone by $[PPh_4][RuO_2(OCOC_6H_5)Cl_2]$ / PVP (f) and $[PPh_4][RuO_2(OCOC_6F_5)Cl_2]$ / PVP (g) with NMO and Bu_4NIO_4 are shown in table 3.2.13 and 3.2.14.

Table 3.2.13. Percentage conversion of cyclohexanol to cyclohexanone by PVP-supported $[PPh_4][RuO_2(OCOC_6H_5)Cl_2]$ in dichloromethane and toluene. Turnovers are shown in parentheses.

Solvent	Reaction Time	NMO	Bu_4NIO_4
Dichloromethane	+30 Min.	14(2)	29(5)
	+3 Hours	13(2)	30(6)
	+24 Hours	17(3)	20(3)
Toluene	+30 Min.	4(<1)	3(<1)
	+3 Hours	6(1)	6(1)
	+24 Hours	40(7)	13(2)

When dichloromethane was used as solvent with both supported catalysts, mediocre conversions of cyclohexanol to cyclohexanone were obtained with NMO and Bu_4NIO_4. Fluctuations in the conversion values were observed due to stability problems experienced with the gas chromatograph. The conversion percentages achieved by the co-oxidants alone for the oxidation of cyclohexanol to cyclohexanone, *i.e.* 14% for NMO and 15% for Bu_4NIO_4 (see table 3.2.11), makes the conversions obtained by the PVP-supported catalysts in dichloromethane even more insignificant.

Both supported catalysts showed a slow rate of conversion of cyclohexanol to cyclohexanone in toluene at the beginning of the reactions with both the co-oxidants. However, the PVP-supported $[PPh_4][RuO_2(OCOC_6H_5)Cl_2]$ with NMO achieved a 40% conversion (seven turnovers) of cyclohexanol to cyclohexanone after twenty-four hours. A significantly lower conversion was obtained when Bu_4NIO_4 was used with this catalyst (*i.e.* 13% conversion [two turnovers] after twenty-four hours), or when the $[PPh_4][RuO_2(OCOC_6F_5)Cl_2]$ supported catalyst was used with either of the co-oxidants (*i.e.* ~20% conversion [approximately four turnovers] with both co-oxidants after twenty-four hours).

Table 3.2.14. Percentage conversion of cyclohexanol to cyclohexanone by PVP-supported $[PPh_4][RuO_2(OCOC_6F_5)Cl_2]$ in dichloromethane and toluene. Turnovers are shown in parentheses.

Solvent	Reaction Time	NMO	Bu_4NIO_4
Dichloromethane	+30 Min.	22(4)	15(3)
	+3 Hours	12(2)	21(4)
	+24 Hours	19(3)	17(3)
Toluene	+30 Min.	4(<1)	3(<1)
	+3 Hours	8(1)	5(1)
	+24 Hours	20(3)	21(4)

Since almost no cyclohexanol was oxidized to cyclohexanone by NMO and Bu_4NIO_4 on their own in toluene, the result obtained above suggests that the PVP supported $[PPh_4][RuO_2(OCOC_6H_5)Cl_2]$ does behave catalytically.

The observed trend of a low rate of conversion at the beginning of the oxidations in toluene suggests that a solvent influence prevails. Nicolaides and Coville observed that benzene as solvent increased accessibility to active sites of the catalyst within the phosphinated polystyrene support, due to swelling experienced by the polymer [42]. With respect to the present work, it is suggested that the poly(4-vinylpyridine) support swells in toluene over the twenty-four hours of the reaction, with a consequential increase in accessibility of the sites of the supported catalyst, and thus an increase in the rate of oxidation. This trend was not observed for the reactions carried out in dichloromethane, thus adding support to the above proposal.

The degree of oxidation observed by this system was difficult to compare to previous reactions involving $[PPh_4][RuO_2(OCOC_6H_5)Cl_2]$ and $[PPh_4][RuO_2(OCOC_6F_5)Cl_2]$, since the mole quantity of catalyst responsible for the above reaction was not known. The nature of the association between the catalyst and support was not investigated further in the present study, and a more detailed characterization of the system was not carried out since the aim of the study was merely to determine whether $[PPh_4][RuO_2(OCOC_6H_5)Cl_2]$ and $[PPh_4][RuO_2(OCOC_6F_5)Cl_2]$ could be supported on an insoluble support. It is conceivable that different co-oxidants or different supports (*e.g.* ion exchange resins) could be more effective. Further work in this field is envisaged in the near future.

3.2.8. Conclusions

The known complex $[PPh_4][RuO_2(OCOCH_3)Cl_2]$ and the novel complexes $[PPh_4][RuO_2(OCOR)Cl_2]$ (R = CF_3, C_6H_5, C_6F_5, C_5H_{11}) were successfully synthesized and characterized. The fluorinated complexes $[PPh_4][RuO_2(OCOCF_3)Cl_2]$ and $[PPh_4][RuO_2(OCOC_6F_5)Cl_2]$ were obtained in a distinctly higher yield than their hydrogenated equivalents $[PPh_4][RuO_2(OCOCH_3)Cl_2]$ and $[PPh_4][RuO_2(OCOC_6H_5)Cl_2]$. All the complexes proved to be effective catalysts for the oxidation of the primary alcohol hexanol to hexanal and the secondary alcohol 2-hexanol to 2-hexanone, with a range of co-oxidants, without attacking the double bond in 1-hexene. The complexes $[PPh_4][RuO_2(OCOC_6H_5)Cl_2]$ and $[PPh_4][RuO_2(OCOC_6F_5)Cl_2]$ were found to selectively oxidize a range of primary and secondary alcohols to aldehydes and ketones respectively without attacking double bonds, aromatic rings, saturated rings, heteroatoms or halogens with the co-oxidants NMO and Bu_4NIO_4. It was shown that the oxidation products from those reactions could be successfully separated by a combination of column chromatography and distillation, to give pure oxidation products in good yield. Preliminary studies showed that the catalysts $[PPh_4][RuO_2(OCOC_6H_5)Cl_2]$ and $[PPh_4][RuO_2(OCOC_6F_5)Cl_2]$ could be supported on poly(4-vinylpyridine) and used to catalyze the oxidation of cyclohexanol to cyclohexanone with either NMO or Bu_4NIO_4 in toluene.

3.3. References

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Chapter Four
Experimental

4.1. Experimental Chapter Two

4.1.1. Reagents Used

The substituted pyridines and quinuclidine hydrochloride were obtained variously from Aldrich, Sigma, Acros, Jansen, BDH, Unilab and Koch Light Laboratories. $RuCl_3.3H_2O$ was obtained from N.M.T. Electrodes or *NEXT* Chimica, sodium metaperiodate from M & B Laboratory Chemicals, powdered 4 Å molecular sieves from Aldrich, 1-hexanol (Sigma, 98%) and the standards 1-hexanal (Aldrich, 98%) and *iso*-butylmethacrylate (Aldrich, 99%) were used without further purification. The co-oxidants hydrogen peroxide (BDH, 30% m/v), sodium hypochlorite (Associated Chemical Enterprises, 15% m/v), *tert*-butyl hydroperoxide (Aldrich, 70%) and 4-methylmorpholine N-oxide (Aldrich, 97%) were also used as supplied.

4.1.2. Instruments Used

Infrared spectra were recorded on a Nicolet 5DX FT-spectrophotometer (4000-400 cm^{-1}) and a Pye Unicam, SP3-300 Infrared Spectrophotometer (4000-200 cm^{-1}) as KBr discs. The micro-analytical laboratory at the University of Natal, Pietermaritzburg carried out the elemental analyses. Gas chromatographic analyses were carried out on a Pye Unicam, G. C. D. Chromatograph with a flame ionization detector and a Varian, SP 4270 Integrator.

4.1.3. Column Used

Langet, stainless-steel
Outer Diameter: 3.2 mm
Inner Diameter: 2 mm
Max. Temp.: 225°C
Support: WHP (Silicalized diatomized sieves)
Length: 3 m
Mesh Range: 80 / 100
Weight %: 12.5%
Liquid Phase: FFAP (free fatty acid phase)

4.1.4. Optimized Gas Chromatograph Conditions

Column Temperature: 120°C
Detector Temperature: 180°C
Injector Temperature: 160°C
Backoff: 3.5
Range: 64 x 10^2

4.1.5. Preparation of RuO_4 [1, 2]

$RuCl_3.3H_2O$ (1.5 g, 5.7 mmol) was dissolved in 40 cm^3 of water in a 250 cm^3 round bottomed flask and stirred. Sodium metaperiodate (5.5 g, 25.7 mmol) was added to the reaction vessel before being stoppered and stirred overnight. The following day, CCl_4 (10 cm^3) was added to the vessel and stirred for half an hour. The resulting solution was poured into a separating funnel and the CCl_4 fraction (*i.e.* the lower fraction) was run into a second separating funnel. The aqueous solution was similarly extracted a further three times with 10 cm^3 aliquots of CCl_4. A solution of sodium metaperiodate (1 g) in water (20 cm^3) was layered above the combined RuO_4-CCl_4 fractions in the separating funnel and the solution was stored in the fumehood.

4.1.6. Preparation of Compounds 1 and 2

10 cm^3 of the stock RuO_4 solution (1.4 mmol) was added to 5 cm^3 NaOH (1 M) and stirred vigorously. Once the solution had turned red (indicating the formation of sodium ruthenate), the solution was cooled to 0°C and the respective ligand (3.0 mmol for compounds **1**, 1.5 mmol for compounds **2**) dissolved in a minimum of HCl_{conc} was added with stirring. A green or yellow precipitate formed almost immediately to yield compounds **1** and **2**. The precipitate was filtered off and washed dropwise with cold water and ether, with the exception of compounds **1j** and **2a** (which decomposed on washing with ether), and dried under vacuum in a desiccator over silica.

4.1.7. General Comments for the Oxidation Reactions

All organic oxidation reactions were carried out in small (length 12 cm, diameter ~1.5 cm) Schlenk tubes under nitrogen atmospheres in nitrogen saturated dichloromethane and monitored by gas chromatography (see Appendix One). Samples were dried over anhydrous $MgSO_4$ and filtered through cotton wool before analysis. All oxidations were carried out in the absence of light and repeated a minimum of three times to ensure reproducibility.

4.1.8. Preparation of the Standard Solution

The standard solution was prepared by mixing dichloromethane (6 cm^3), 1-hexanol (63 μl, 0.5 mmol), *iso*-butylmethacrylate (80 μl, 0.5 mmol, internal standard) and hexanal (60 μl, 0.5 mmol). The standard solution was run daily before analyses and again after 3 hours, to ensure consistency of results.

4.1.9. Stoichiometric Oxidations

A small Schlenk tube was evacuated and filled with $N_{2(g)}$. To this was added 4 Å molecular sieves (180 mg), CH_2Cl_2 (6 cm^3), 1-hexanol (63 μl, 0.5 mmol), *iso*-butylmethacrylate (80 μl, 0.5 mmol) as internal standard and the oxidants, compounds **1** or **2** (0.5 mmol). The solutions were stirred at room temperature under a nitrogen atmosphere. The reactions were monitored by G.C. with conversions determined after 30 minutes, 3 hours and 24 hours.

4.1.10. Catalytic Oxidations

A small Schlenk tube was evacuated and filled with $N_{2(g)}$. To this was added 4 Å molecular sieves (180 mg), CH_2Cl_2 (6 cm^3), 1-hexanol (63 μl, 0.5 mmol), *iso*-butylmethacrylate (80 μl, 0.5 mmol) as internal standard, the co-oxidants (0.75 mmol) and the catalyst (20 mg). The solutions were stirred at room temperature under a nitrogen atmosphere. The reactions were monitored by G.C. with conversions determined after 30 minutes, 3 hours and 24 hours.

4.1.11. Testing Catalytic Oxidation Turnover Limits for Compound 1g

(a) A small Schlenk tube was evacuated and filled with $N_{2(g)}$. To this was added 4 Å molecular sieves (180 mg), CH_2Cl_2 (6 cm^3), 1-hexanol (63 μl, 0.5 mmol), *iso*-butylmethacrylate (80 μl, 0.5 mmol) as internal standard, the co-oxidants (0.75 mmol) and the catalyst **1g** (5 mg, 9.6×10^{-3} mmol).

(b) A small Schlenk tube was evacuated and filled with $N_{2(g)}$. To this was added 4 Å molecular sieves (180 mg), CH_2Cl_2 (6 cm^3), 1-hexanol (126 μl, 1.0 mmol), *iso*-butylmethacrylate (160 μl, 1.0 mmol) as internal standard, the co-oxidants (1.5 mmol) and the catalyst **1g** (20 mg, 3.9×10^{-2} mmol).

Both (a) and (b) were stirred at room temperature under a nitrogen atmosphere. The reactions were monitored by G.C. with conversions determined after 30 minutes, 3 hours and 24 hours.

4.1.12. Reaction of NMO with 1-hexanol

A small Schlenk tube was evacuated and filled with $N_{2(g)}$. To this was added 4 Å molecular sieves (180 mg), CH_2Cl_2 (6 cm^3), 1-hexanol (63 μl, 0.5 mmol), *iso*-butylmethacrylate (80 μl, 0.5 mmol) as internal standard and 4-methylmorpholine N-oxide (92 mg, 0.78 mmol). The solution was stirred at room temperature under a nitrogen atmosphere. The reaction was monitored by G.C. with conversions determined after 30 minutes, 3 hours and 24 hours.

4.1.13. Preparation of Compounds 3

The compound Y-py (Y = *H, 4-CN, 4-*t*-Bu) (1.0 mmol) was dissolved in $N_{2(g)}$ saturated CCl_4 (9 cm^3) before adding nitrogen saturated deionized water (0.1 cm^3). An oxygen-free environment was maintained throughout this solution by continuous bubbling of $N_{2(g)}$ through the solution. A large (length 17 cm, diameter ~2 cm) Schlenk tube was evacuated, filled with $N_{2(g)}$ and cooled in an ice-bath. A solution of RuO_4 (0.5 mmol) and $N_{2(g)}$ saturated CCl_4 (10 cm^3) was added to the Schlenk and cooled to 0°C. The pyridine / water mixture in CCl_4 was layered over the RuO_4 solution and the Schlenk tube was stoppered under a nitrogen atmosphere. The mixture was allowed to stand at 0°C for twelve hours before filtering with a cannula, washing with $N_{2(g)}$ saturated CCl_4 and drying under vacuum. The resulting green product was stored under $N_{2(g)}$ in a Schlenk tube in the fridge.

*The pyridine used was initially dried over KOH for seventy-hours.

4.2. Experimental Chapter Three

4.2.1. Reagents Used

$RuCl_3.3H_2O$ was obtained from N.M.T. Electrodes or *NEXT* Chimica and sodium metaperiodate from M & B Laboratory Chemicals. The tetraphenylphosphonium chloride (Merck, 98%), glacial acetic acid, trifluoroacetic acid, benzoic acid, pentafluorobenzoic acid (all Aldrich, 99%) and hexanoic acid (Acros, 98%) were used as supplied. The powdered 4 Å molecular sieves were obtained from Aldrich and the internal standards *iso*-butylmethacrylate (99%), 2-ethoxyethyl acetate (99%) and n-hexane (95%) from Aldrich, Acros and Lab Scan respectively. The substrates and standard products were obtained as follows: cinnamyl alcohol (Acros, 98%), *trans*-cinnamaldehyde (Acros, 99%), cinnamyl chloride (Aldrich, 95%), crotyl alcohol (Aldrich, 97%), crotonaldehyde (Acros, 99%), cyclohexanol (BDH, 98%), cyclohexanone (Kleber Chemicals, 99%), furfuryl alcohol (Fine Chemicals, 98%), furfuraldehyde (BDH, 98%), geraniol (Acros, 99%), citral (BDH, 90%), 1-hexanol (Sigma, 98%), 1-hexanal (Aldrich, 98%), 2-hexanol (Aldrich, 99%), 2-hexanone (Aldrich, 98%), 1-hexene (Merck, 96%), 1,2-epoxyhexane (Aldrich, 97%), 4-nitrobenzyl alcohol (Acros, 99%), 4-nitrobenzaldehyde (Aldrich, 98%). The polymeric support poly(4-vinylpyridine), crosslinked with 2% divinylbenzene [~60 mesh] and iodobenzene diacetate (98%) were obtained from Acros. The co-oxidants hydrogen peroxide (BDH, 30% m/v), sodium hypochlorite (Associated Chemical Enterprises, 15% m/v), *tert*-butyl hydroperoxide (Aldrich, 70%), 4-methylmorpholine N-oxide (Aldrich, 97%), trimethylamine-N-oxide dihydrate

(Acros, 98%), tetrabutylammonium periodate (Acros, 99%) and instrument grade air (Afrox) were also used as supplied.

4.2.2. Instruments Used

Infrared spectra were recorded on a Nicolet 5DX FT-spectrophotometer (4000-400 cm^{-1}) and a Pye Unicam, SP3-300 Infrared Spectrophotometer (4000-200 cm^{-1}) as KBr discs. The micro-analytical laboratory at the University of Natal, Pietermaritzburg carried out the elemental analyses. Gas chromatographic analyses were carried out on a either a Pye Unicam, G. C. D. Chromatograph with a Varian, SP 4270 Integrator, a Fisons G. C. 8000 Series (MFC 800) gas chromatograph or a Perkin Elmer, Auto System XL gas chromatograph, all fitted with flame ionization detectors.

4.2.3. Columns Used

A. Langet, stainless-steel
Outer Diameter: 3.2 mm
Inner Diameter: 2 mm
Max. Temp.: 225°C
Liquid Phase: FFAP (free fatty acid phase)
Length: 3 m
Mesh range: 80 / 100
Weight %: 12.5%
Support: WHP (Silicalized diatomize sieves)

B. SGE Capillary
Outer Diameter: 0.43 mm
Inner Diameter: 0.32 mm
Max. Temp.: 260°C
Phase: BP20 (polar)
Length: 25 m
Type: Bonded Phase
Material: Fused Silica
Film Thickness: 0.5 micron

C. SGE Capillary
Outer Diameter: 0.43 mm
Inner Diameter: 0.32 mm
Max. Temp.: 260°C
Phase: 5-CP (non-polar)
Length: 25 m
Type: Bonded Phase
Material: 5% Phenylmethyl Silica
Film Thickness: 0.5 micron

D. Perkin Elmer Megabore
Inner Diameter: 0.53 mm
Max. Temp.: 320°C
Length: 30 m
Film Thickness: 1.5 μm

4.2.4. Preparation of RuO_4

Prepared as described in section 4.1.5.

4.2.5. Preparation of $[PPh_4][RuO_2(OCOR)Cl_2]$ (R = CH_3, CF_3, C_6H_5, C_6F_5, C_5H_{11})

Tetraphenylphosphonium chloride (1.18 g, 2.8 mmol) was dissolved in acetonitrile (15 cm^3) with stirring in an ice bath (0°C, 20 minutes) before adding the carboxylic acid (1.4 mmol). The RuO_4 solution (10 cm^3, 1.4 mmol) was added carefully to the cold mixture before sealing the flask and stirring overnight in the ice bath. The next day, the resulting green solution was concentrated under reduced pressure using a Teflon vacuum pump until precipitation was observed. The precipitate was filtered off under vacuum, washed with drops of cold water, and dried over silica gel under vacuum. The filtrate was concentrated further and the resulting precipitate was worked up as above. After drying, the products were stored in a desiccator in the fridge.

4.2.6. Synthesis of Iodosylbenzene [3]

Sodium hydroxide (19 cm^3, 3 M) was added to iodobenzene diacetate (12.4 mmol) in the fumehood over 5 minutes with vigorous stirring. The yellow green product was triturated for 15 minutes before allowing the reaction mixture to stand for 45 minutes. Water (13 cm^3) was added to the mixture and the mixture was stirred for 5 minutes before filtering off the crude iodosylbenzene. The wet solid was returned to the beaker and triturated with 25 cm^3 of water. The solid was again collected by filtration, washed with 25 cm^3 water and dried under vacuum. The dry, yellow solid (Decomp. 210°C) was stored in a Schlenk tube under nitrogen in the fridge.

4.2.7. Supporting the Compounds $[PPh_4][RuO_2(OCOR)Cl_2]$ (R = C_6H_5, C_6F_5) on Poly(4-vinylpyridine)

Poly(4-vinylpyridine) (1 g) was stirred with dicholoromethane (20 cm^3) for 5 minutes before adding $[PPh_4][RuO_2(OCOR)Cl_2]$ (R = C_6H_5, C_6F_5) (100 mg). Stirring was continued for 5 hours before removing the solvent under high vacuum over a five hour period. The dry, dark green, supported homogeneous catalyst was stored in a Schlenk tube under nitrogen.

4.2.8. General Comments for the Oxidation Reactions

All organic oxidation reactions were carried out in Schlenk tubes under nitrogen atmospheres in nitrogen saturated solvents in the presence of a suitable internal standard, followed by analysis on one of a number of gas chromatographs (see Appendix One), using a range of columns and instrument conditions (see table 4.2.1). The internal standard used was either *iso*-butylmethacrylate, 2-ethoxyethyl acetate or n-hexane and was chosen to achieve base-line separation on the various columns. Samples were dried over anhydrous $MgSO_4$ and filtered through cotton wool before analysis. All oxidations were carried out in the absence of light and repeated a minimum of three times to ensure reproducibility.

4.2.9. Preparation of Standard Solutions

The standard solution was prepared by mixing the solvent dichloromethane [or toluene for the supported catalyst] (6 cm^3), substrate (0.5 mmol), internal standard [*iso*-butylmethacrylate or 2-ethoxyethyl acetate or n-hexane] (0.5 mmol) and product [either the corresponding aldehyde, ketone or epoxide] (0.5 mmol). The standard solution was run daily before analyses and again after 3 hours, to ensure consistency of results.

4.2.10. Stoichiometric Oxidations of 1-hexanol by $[PPh_4][RuO_2(OCOCH_3)Cl_2]$ and $[PPh_4][RuO_2(OCOCF_3)Cl_2]$

A small Schlenk tube was evacuated and filled with $N_{2(g)}$. To this was added 4 Å molecular sieves (180 mg), CH_2Cl_2 (6 cm^3), 1-hexanol (0.5 mmol), the internal standard (0.5 mmol) and the oxidant, $[PPh_4][RuO_2(OCOR)Cl_2]$ (R = CH_3, CF_3) (0.5 mmol). The solutions were stirred at room temperature under a nitrogen atmosphere. The reaction was monitored by G.C. with conversions determined after 30 minutes, 3 hours and 24 hours.

4.2.11. Catalytic Oxidations

4.2.11.1. Homogeneous Catalysts

A small Schlenk tube was evacuated and filled with $N_{2(g)}$. To this was added 4 Å molecular sieves (180 mg), dichloromethane (6 cm^3), substrate (0.5 mmol), internal standard (0.5 mmol), the co-oxidants (0.75 mmol) and the catalyst (20 mg). The solutions were stirred at room temperature under a nitrogen atmosphere. The reactions were monitored by G.C. with conversions determined after 30 minutes, 3 hours and 24 hours.

4.2.11.2. Supported Homogeneous Catalysts

A small Schlenk tube was evacuated and filled with $N_{2(g)}$. To this was added 4 Å molecular sieves (180 mg), dichloromethane or toluene (6 cm^3), cyclohexanol (0.5 mmol), internal standard (0.5 mmol), NMO or Bu_4NIO_4 (0.75 mmol) and the supported catalyst (200 mg). The solutions were stirred at room temperature under a nitrogen atmosphere. The reactions were monitored by G.C. with conversions determined after 30 minutes, 3 hours and 24 hours.

4.2.12. Investigating Catalytic Oxidation Turnover Limits for $[PPh_4][RuO_2(OCOR)Cl_2]$ (R = CH_3, CF_3, C_6H_5, C_6F_5, C_5H_{11})

A small Schlenk tube was evacuated and filled with $N_{2(g)}$. To this was added 4 Å molecular sieves (180 mg), CH_2Cl_2 (6 cm^3), the alcohol (1 mmol), internal standard (1 mmol), the co-oxidants (1.5 mmol) and the catalyst (10 mg). The solutions were stirred at room temperature under a nitrogen atmosphere. The reactions were monitored by G.C. with conversions determined after 30 minutes, 3 hours and 24 hours.

4.2.13. Reaction of Co-oxidants (H_2O_2, NaOCl, *t*-BuOOH, NMO, TMANO, O_2, C_6H_5IO and Bu_4NIO_4) with the Alcohols (Cinnamyl Alcohol, Crotyl Alcohol, Cyclohexanol, Furfuryl Alcohol, Geraniol and 4-Nitrobenzyl Alcohol) and Cinnamyl Chloride

A small Schlenk tube was evacuated and filled with $N_{2(g)}$. To this was added 4 Å molecular sieves (180 mg), CH_2Cl_2 (6 cm^3), the substrate (0.5 mmol), internal standard (0.5 mmol) and co-oxidant (0.75 mmol). The solution was stirred at room temperature under a nitrogen atmosphere. The reactions were monitored by G.C. with conversions determined after 30 minutes, 3 hours and 24 hours.

4.2.14. Separation of Reaction Products

A small Schlenk tube was evacuated and filled with $N_{2(g)}$. To this was added 4 Å molecular sieves (360 mg), CH_2Cl_2 (6 cm^3), cyclohexanol (9.7 mmol), NMO (14.6 mmol) and $[PPh_4][RuO_2(OCOC_6H_5)Cl_2]$ (389 mg). The solution was stirred at room temperature under a nitrogen atmosphere with the reaction being monitored by G.C. at twenty-four hour intervals. The reaction mixture was filtered after 72 hours reaction to remove the insoluble 4 Å molecular sieves. The green filtrate was passed through a silica column using hexane as solvent and the column was finally flushed with CH_2Cl_2 (50 cm^3). The clear hexane and dichloromethane fractions were combined and distilled. The distillate fractions collected in the temperature ranges 154-157°C and 159-163°C were characterized by ^1H and ^{13}C NMR.

Table 4.2.1. Summary of gas chromatographs, columns, and associated instrument conditions for the range of oxidations investigated.

Substrate	Gas Chromatograph	Column (Phase)	*Oven Temperature / °C	*Injector Temperature / °C	*Detector Temperature / °C
Cinnamyl alcohol	Fisons / Perkin Elmer	Capillary (5-CP) / Megabore (PE-5)	A	260	260
Cinnamyl chloride	Fisons / Perkin Elmer	Capillary (5-CP) / Megabore (PE-5)	A	260	260
Crotyl alcohol	Fisons / Perkin Elmer	Capillary (BP20) / Megabore (PE-5)	90 / 80	165	165
Cyclohexanol	Fisons / Perkin Elmer	Capillary (BP20) / Megabore (PE-5)	150	165	165
Furfuryl alcohol	Fisons	Capillary (BP20)	160	175	170
Geraniol	Fisons / Perkin Elmer	Capillary (BP20) / Megabore (PE-5)	A	260	260
1-Hexanol	Pye Unicam / Fissons	Langet / Capillary (BP20)	120 / 90	160 / 165	180 / 165
2-Hexanol	Pye Unicam / Fissons	Langet / Capillary (BP20)	120 / 90	160 / 165	180 / 165
1-Hexene	Pye Unicam	Langet	120	160	180
4-Nitrobenzyl alcohol	Perkin Elmer	Megabore (PE-5)	B	250	280

*Varying temperatures due to the use of different columns on the different instruments.

A. Initial Temp.: 120°C for 1 min.
Ramp 1: 20°C / min. to 180°C for 5 mins.

B. Initial Temp.: 100°C for 0 min.
Ramp 1: 15°C / min. to 180°C, hold for 2 mins.
Ramp 2: 45°C / min. to 250°C, hold for 3 mins.

4.3. References

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Appendix One

Gas Chromatography, Reference Response Factors and Turnovers

All the oxidation reactions were monitored by gas chromatography with the use of an internal standard to obtain quantitative analysis data.

Gas chromatography is used to separate and analyze components of a mixture. The technique is based on the partition of the components of a mixture between a mobile (*i.e.* gas phase) and stationary phase (*i.e.* usually a liquid that is immobilized on the surface of a solid support). The inert carrier gas (*e.g.* nitrogen) elutes components of the mixture from the column with the rate of elution being determined by the analyte distribution ratio between the gaseous and liquid phases. The more volatile components of a mixture elute faster through the column, since they spend more time in the mobile gaseous phase, with consequentially lower retention times than less volatile components [1].

The polarity of a column influences the rates of elution experienced by the components of a mixture. A polar column interacts to a greater degree with polar components in a mixture compared to non-polar components. This implies that the polar components elute at a slower rate relative to the non-polar components. The retention time of the individual components of a mixture are established before the mixture itself is analyzed on the gas chromatograph. As such, each component can be positively identified when a sample is analyzed.

A quantitative evaluation of the components of a mixture is obtained by using a standard solution and an internal standard. The standard solution contains the substrate, the expected product and the internal standard (which is inert and whose quantity does not change during the course of the reaction), all in equivalent amounts to those used in the reaction being analyzed. The standard is run daily prior to the analysis of samples. The peak area data obtained from such chromatographic analyses are used to quantify the components of the reaction mixtures. Initially, the peak area data obtained from the analysis of the standard solution is used to obtain reference response factors (RRF) (equation i).

$$\mathrm{RRF} = \frac{\text{Moles of internal standard} \quad \mathrm{X} \quad \text{Peak area of component}}{\text{Moles of component} \quad \mathrm{X} \quad \text{Peak area of internal standard}} \qquad \text{(i)}$$

The reference response factors are calculated separately for each substrate and product in a mixture, and are used to establish the number of moles of unreacted substrate and reaction product by substitution into equation (ii) below.

$$N = \frac{\text{Moles of internal standard} \ \text{X} \ \text{Peak area of component}}{\text{RRF} \ \text{X} \ \text{Peak area of internal standard}} \qquad \text{(ii)}$$

(N = number of moles of component being analyzed for)

The percentage conversion of substrate to product can thus be established from the number of moles that is calculated for each component.

The percentage of substrate converted to product is just one important factor considered when catalysts are used in catalytic oxidations. The catalytic oxidations in the present study involved a host of catalysts of varying molecular masses. Since each catalytic oxidation examined used a fixed mass of catalyst, different mole quantities of oxidant were introduced to reactions. Consequently, percentage conversion values obtained for the various oxidations could not be compared due to the different amounts of catalyst being used. As such, catalytic turnover values for the various catalysts have been included with percentage conversion values in the result tables. Catalytic turnovers (or just turnovers) are calculated from the ratio of the number of moles of product to the number of moles of catalyst (equation iii).

$$\text{Turnovers of catalyst} = \frac{\text{Moles of product}}{\text{Moles of catalyst}} \qquad \text{(iii)}$$

The turnovers achieved by specific catalysts give good indications of the performance of the catalysts in comparative catalytic studies.

References

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