

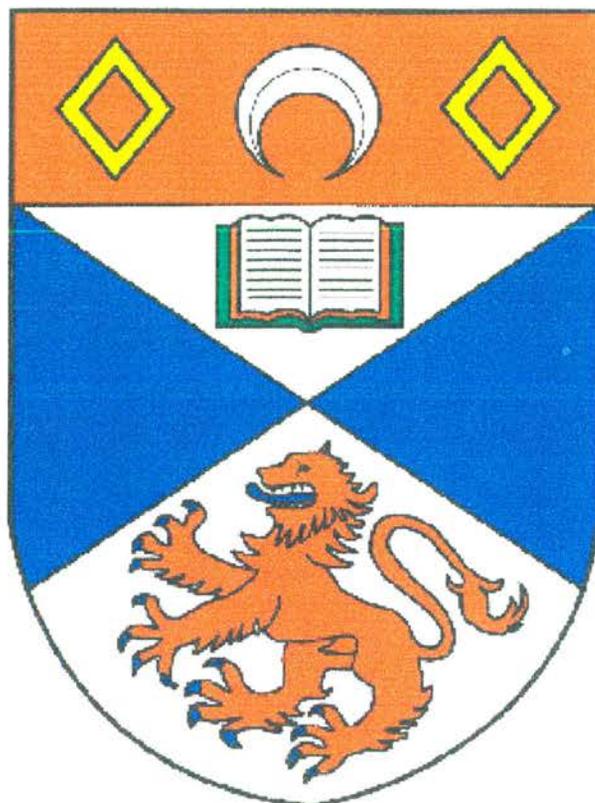
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Alternative Feedstocks for Carbonylation Catalysis

Thesis submitted in accordance with the requirements of
the University of St. Andrews for the degree of Doctor of
Philosophy by Martin John Lofthouse

April 2000



Declaration

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- (ii) I was admitted as a research student in September, 1996, and as a candidate for the degree of Doctor of Philosophy in September, 1997; the higher study for which this is a record was carried out in the University of St. Andrews between 1996 and 2000.

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Abstract: “Alternative Feedstocks for Carbonylation Catalysis”

Ethanoic acid is currently manufactured industrially by carbonylation of methanol, using a rhodium or promoted iridium catalyst. These homogeneous catalytic processes are very efficient, but there is a constant drive for even more cost-effective methods of making ethanoic acid. One approach to this problem is to use cheaper feedstocks than carbon monoxide and methanol currently used.

This thesis studies the direct formation of ethanoic acid from carbon monoxide and hydrogen (synthesis gas). Chapter two investigates the hydrogenation of carbon monoxide to methanol reaction, catalysed by iodide promoted ruthenium carbonyl species. It is shown that the reaction is active under mild conditions of 200 °C and 110 bar and the reaction is selective to methanol. Isotopic labelling studies prove that methanol is produced from CO and hydrogen gas, rather than any other source.

Chapter three studies the combination of iodide promoted ruthenium catalysed CO hydrogenation and rhodium catalysed methanol carbonylation reaction. The reaction is active at 200 °C, but at 235 °C several different hydrogenation and carbonylation products are formed and decomposition of the ruthenium catalyst is observed. Isotopic labelling studies using ^2H and ^{13}C suggest that ethanoic acid is formed from carbon monoxide and hydrogen, but scrambling effects are observed. The use of a reactor attached to a ballast vessel shows that the reaction is active for at least 3 days and more ethanoic acid is produced than can be accounted for by the reaction of iodomethane and carbon monoxide alone.

Electrospray mass spectrometry (ESMS) and *in situ* FTIR are used to study the catalytic species in chapter 4. ESMS is shown to be a very versatile technique to study catalytic solutions containing organometallic compounds. $[\text{HRu}_3(\text{CO})_{11}]^-$ and $[\text{Ru}(\text{CO})_3\text{I}_3]^-$ are observed as co-catalysts for the hydrogenation of carbon monoxide reaction, but $[\text{HRu}_3(\text{CO})_{11}]^-$ appears to be sensitive to the use of iodomethane or HI, leading to a decrease in catalytic activity.

Abbreviations

Ac	Acetyl
acac	Acetylacetonate
CATS	Catalyst Evaluation and Optimisation Service
dp	1,2-bis(diphenylphosphino)benzene
dppe	1,2-bis(diphenylphosphino)ethane
ESMS	Electrospray Mass Spectrometry
Et	Ethyl
Expt.	Experiment
FAB	Fast Atom Bombardment
FTIR	Fourier Transform Infra-red
GC	Gas Chromatography
HPLC	High Pressure Liquid Chromatography
IR	Infra-red
MS	Mass Spectrometry
Me	Methyl
NEP	N-ethylpyrrolidinone
NMP	N-methylpyrrolidinone
NMR	Nuclear Magnetic Resonance Spectroscopy
PET	Polythene terephthalate
Ph	Phenyl
ⁱ Pr	<i>iso</i> -Propyl
Syngas	Synthesis Gas
TIC	Total Ion Count
TON	Turn-over Number
WGS(R)	Water-Gas Shift (Reaction)

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For my family and friends

Walling

I've walled the in-by to the pewit's wild cry,
And the fell with the wind and the heather.
I've laid the rough stone on the hill all alone,
To shelter the yow and the wether.
Stone wall and stone drain in the wind and the rain
I've fettled, and set them together.
I've heard the snipe drum by an early pale sun,
And the grouse call a change in the weather.

I've a spade in the sack that I take on me back
And a tommy bar short and well hipped,
To clear all the fall from the gap in the wall
And dig out the founds that have slipped.
With the rack of me eye I can judge a stone's lie
And I'll never have courses that's dipped,
Yet a stone, once selected, is seldom rejected,
With courses all tight and well-nipped.

There's no fortune made at this stone-walling trade;
Ten shillings a rood is the rate.
Stoop stile and smoot hole are all reckoned as whole,
And there's still no waller paid for a mate.
Still it's gritstone for me, as rough as can be,
And I care not for shingle nor slate,
For it's faster headway, at the end of the day,
That pays for the coal in the grate.

I said to me dad, when I was a lad,
That I'd wall for a trade if I could,
For the winter storms bring your work every spring
As the drifts give the stone walls a shove.
So as man, lad and boy I've found full employ,
And when Jesus calls me up above,
I'll ask the Great Caller, does he want a waller,
For walling's the trade that I love.

Keith Scowcroft

CHAPTER 1

Introduction

1.1 Background

1.1.1 Industrial Importance of Ethanoic Acid

Ethanoic acid is one of the world's most widely used chemicals. Worldwide production capacity has risen from approximately 5.6 million tonnes per annum in 1993 ¹ to an estimated 7 million tonnes in 1996 ². This figure continues to rise as more manufacturing plants are built and existing plants are made more productive each year.

Two major producers, Hoechst Celanese and BP Amoco, each controlling approximately one third of world demand, dominate the ethanoic acid market. Until recently, the technology used by both companies had been based on the rhodium catalysed carbonylation of methanol developed by Monsanto in the late 1960s. BP Chemicals acquired the Monsanto technology in 1986, while Hoechst Celanese developed their own process based on the Monsanto system, which they had earlier used under license. The rhodium catalysed carbonylation of methanol will be discussed in detail in section 1.3.

Over the last five years, BP Amoco have developed a new iridium based system, known as Cativa, which is now being used in preference to the rhodium process on the network of ethanoic acid plants owned or licensed by BP Amoco. A discussion of this iridium-based carbonylation of methanol process can be found in section 1.4.

It has now become economically unfeasible to build a new, dedicated ethanoic acid producing plant, which uses anything other than methanol carbonylation chemistry. Oxidation of petroleum derived feedstocks (naphtha, for example) are older methods of ethanoic acid production that are still used commercially, but they represent an ever-decreasing proportion of the worldwide production. These and other historical routes to ethanoic acid will be discussed as an introduction in section 1.2.

1.1.2 Uses of Ethanoic Acid

Ethanoic acid (acetic acid) is a versatile industrial chemical with many applications³. Its major use is to form vinyl acetate monomer, which takes up to 40%² of all ethanoic acid produced. Vinyl acetate is itself in increasing demand as it is used to make a variety of polymers for the manufacture of paints, adhesives, textile treatments and paper coatings, for example.

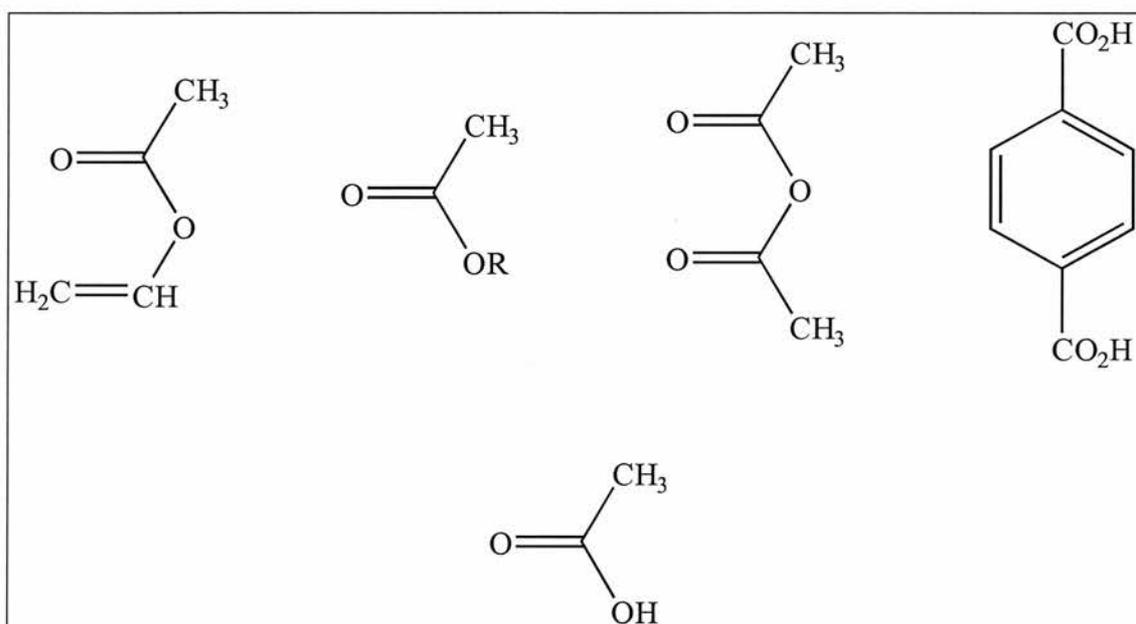


Figure 1.1; Useful chemicals from ethanoic acid; vinyl acetate, acetate esters, acetic anhydride, terephthalic acid and ethanoic acid itself.

Acetate esters are a significant class of compounds made from ethanoic acid. Ethyl acetate (ethyl ethanoate) is the most important ester in volume terms and is used to make adhesives, inks and coatings. Other simple acetate esters such as n-butyl acetate and *iso*-propyl acetate have similar uses.

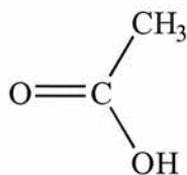
Acetic anhydride can be made by thermal dehydration of ethanoic acid or by carbonylation of methyl ethanoate; both routes are via ethanoic acid. 75% of all acetic anhydride produced is used to make cellulose acetate³, which finds applications in photographic film, pharmaceuticals and synthetic fibres.

Ethanoic acid is also used as a solvent in the production of terephthalic acid, which is used in the manufacture of polymers such as polythene terephthalate (PET). PET is an important polymer used for a variety of purposes, including packaging and drinks bottles.

Ethanoic acid, itself, can be found in vinegar, pickles and pharmaceuticals and it is also used as an acid for a variety of applications ranging from textile manufacture to electroplating.

1.1.3 Discovery and Properties

Ethanoic acid has been made from spoiled wine, in the form of vinegar, for several millennia. Indeed, wine has been made since around 10,000 BC, so vinegar has been produced since then⁴. Ethanoic acid is commonly known as acetic acid, which is derived from the Latin word *acetum*, meaning sour or sharp wine.



Ethanoic acid is an organic acid with a pKa of 4.5. Its density is 1.05 g cm⁻¹ and its relative molecular weight is 60.05. It has a boiling point of 115 °C and a melting point of 17 °C, which are relatively high for its molecular weight due to hydrogen bonding.

1.2 Historical Perspective

Ethanoic acid was originally produced by oxidation (or fermentation) of ethanol. This method is still used today to make vinegar, but it is no longer a viable economic route to quench the worldwide industrial thirst for ethanoic acid. Another route to ethanoic acid, used in the nineteenth century, was the destructive distillation of hardwood.

Other more efficient synthetic methods of production have been used since the beginning of the twentieth century. The first synthetic route to ethanoic acid was the oxidation of ethanal, produced by the catalytic hydrolysis of ethyne (acetylene) using mercuric ions⁵.

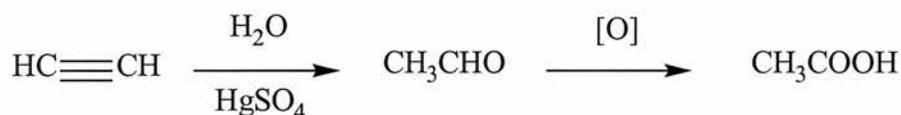


Figure 1.2; Catalytic Hydrolysis of Acetylene

This remained the major method of synthesising ethanoic acid until the late 1950s when oxidation of petroleum derived materials became important. The Wacker process uses a palladium(II)-copper(II) chloride catalyst to oxidise ethene to ethanal⁶. The ethanal produced can then be further oxidised to form ethanoic acid.

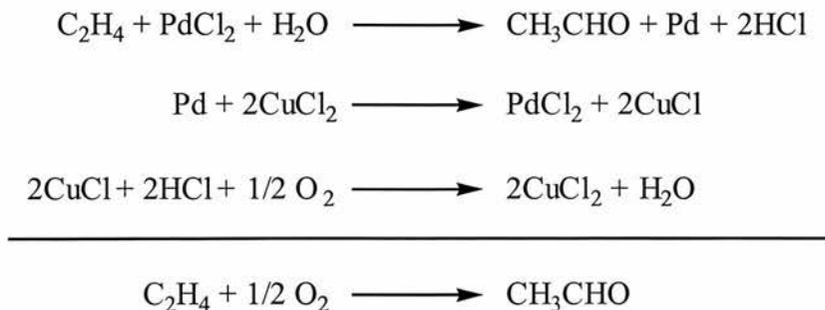


Figure 1.3; the Wacker Process

Feedstocks such as naphtha or butane can be oxidised to form ethanoic acid. A mixture of products is produced, which then must be purified by distillation before the product(s) can be used. Production plants of this type are still operated commercially today, with BP Amoco's naphtha oxidation plant at Hull being a typical example. Its economic viability arises from the fact that it already exists and needs little capital investment compared to more modern plants yet to be built. It also produces several other by-products that can also be sold.

In the 1960s BASF commercialised the first methanol carbonylation process. This had two major advantages over previous synthetic routes: cheaper feedstocks of carbon monoxide and methanol, and a higher selectivity to ethanoic acid of around 90%. An iodide promoted cobalt catalyst was used, but high pressures (600 atm) and high temperatures (230 °C) were required to achieve effective reaction rates. Compared to later catalytic advances these forcing reaction conditions, relatively low reaction rates and poor selectivity resulted in the cobalt catalysis becoming obsolete.

It is worthwhile to note certain trends in the methods of ethanoic acid production over time. Historically, there has been a gradual shift from high energy to low energy starting materials (from ethanol or ethanal to carbon monoxide and methanol). Rather than having any great chemical significance, this trend is driven by economics, reflecting the fact that high-energy chemicals are often more expensive. Today's most commercially feasible processes make significant cost savings over their corresponding earlier processes by using cheaper starting materials.

Another way to make the ethanoic acid production method more attractive from an economic point of view is one that has been utilised over the last thirty years. This is to optimise the effectiveness of the catalyst used to lower the operating temperature and pressure, allowing plants to be constructed of cheaper materials. Catalysis of methanol carbonylation, originally by cobalt, enabled methanol and carbon monoxide to be considered as a feedstock for the industrial synthesis of ethanoic acid. Further improvements in the catalyst since then will be described in the sections 1.3 and 1.4.

1.3 Rhodium Catalysed Methanol Carbonylation

Since its development in the late 1960s⁷, iodide-promoted, rhodium catalysed methanol carbonylation has been perhaps the most successful application of homogeneous catalysis in the chemical industry. Monsanto developed the technology and despite selling the process to BP Chemicals in 1986, the catalytic cycle is often referred to as the Monsanto cycle. Their first commercial production unit was opened in 1970 and triggered a revolution in industrial ethanoic acid production.

1.3.1 The Monsanto Process

The catalytic process discovered at Monsanto comprises a set of six individual reactions which combine together to form ethanoic acid from carbon monoxide and methanol, as shown in the diagram below (*Figure 1.4*). The reaction has been studied by Forster and co-workers at Monsanto^{5,8,9} and has been the subject of more recent reviews^{1,10}.

The overall reaction is made up of two closely interdependent cycles. The inner, organic cycle converts methanol to iodomethane and acetyl iodide to ethanoic acid by the reaction with HI and water respectively. In ethanoic acid as a solvent, methanol is esterified to methyl ethanoate and it is this that reacts with HI to form iodomethane and regenerate ethanoic acid. The outer, organometallic cycle is used to formally insert a carbonyl group into the C-I bond of iodomethane.

Under catalytic conditions a variety of rhodium containing catalyst precursors can be converted to $[\text{Rh}(\text{CO})_2\text{I}_2]^-$, **1**. This anion is often present in the highest standing concentration and it is the active catalytic species. The rate determining step of the overall reaction is the oxidative addition reaction of species **1** with iodomethane to form $[\text{CH}_3\text{Rh}(\text{CO})_2\text{I}_3]^-$, **2**. This methyl containing anion is relatively unstable, but has been

detected in the reaction with neat CH_3I^{11} . It quickly isomerises, via a methyl migration or carbonyl insertion step, to form $[(\text{CH}_3\text{CO})\text{Rh}(\text{CO})\text{I}_3]^-$, **3**.

Carbon monoxide is able to react with the 16 electron, anionic species **3** to form the six coordinate, 18 electron complex, $[(\text{CH}_3\text{CO})\text{Rh}(\text{CO})_2\text{I}_3]^-$, **4**. This can then lose acetyl iodide, via a reductive elimination step, to regenerate the active species **1** and complete the cycle.

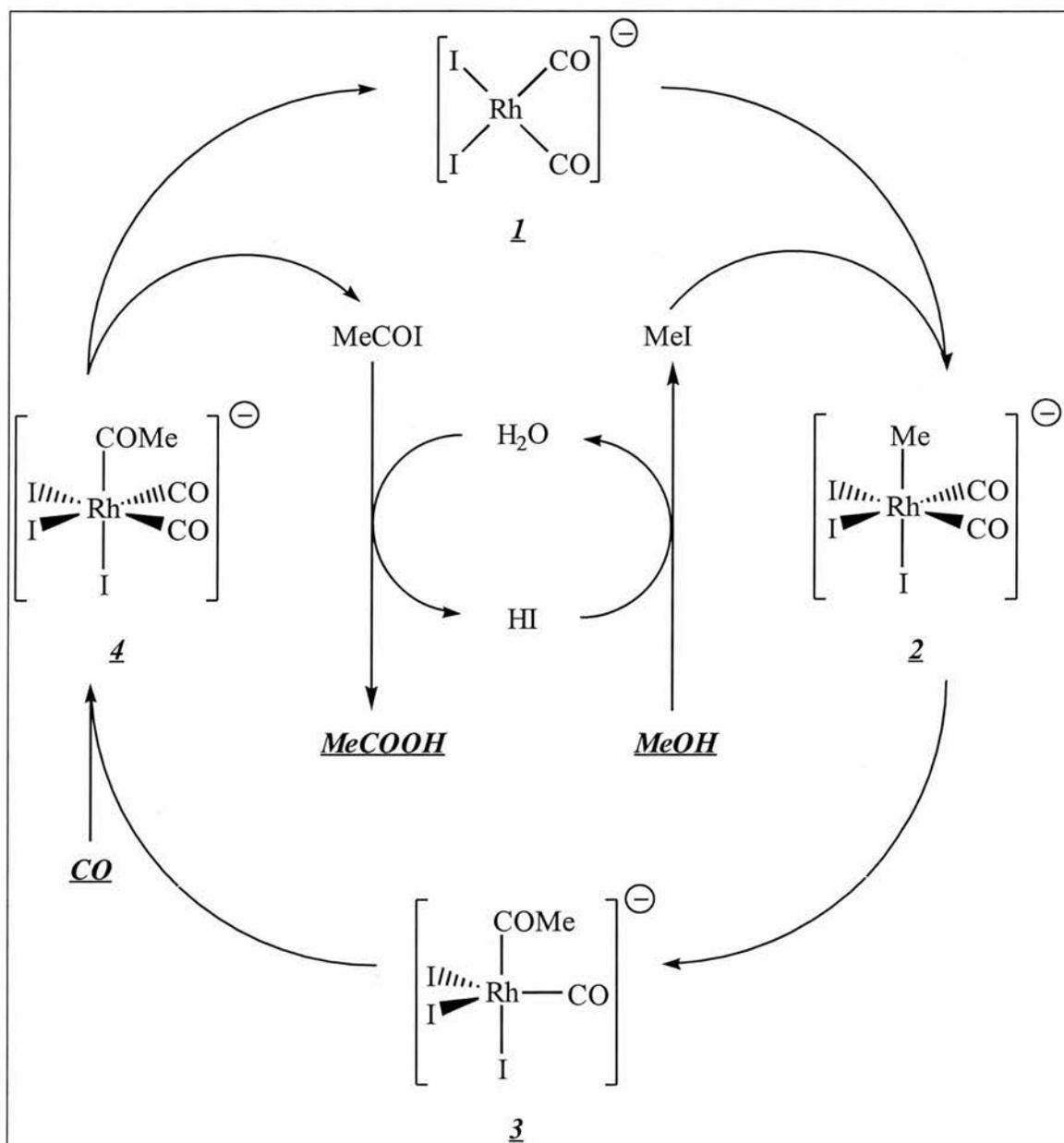


Figure 1.4; Rhodium Catalysed Methanol Carbonylation

1.3.2 Process Technology

The operating conditions, for the industrial process, are typically 150 to 200 °C and 25 to 35 bar.¹ Ethanoic acid is used as the solvent and with the presence of HI the reaction mixture is very corrosive, requiring the use of special reactor construction materials such as Hastalloy or zirconium.

The methanol carbonylation reaction is carried out industrially in a 'stirred tank' reactor. Liquid is removed from the reactor and passes into an adiabatic flash tank where the pressure is reduced rapidly, causing volatile components including ethanoic acid to be separated from the catalyst and excess ethanoic acid solvent. The catalyst is recycled; however, low carbon monoxide partial pressures can lead to loss of catalyst via the formation of insoluble RhI_3 .

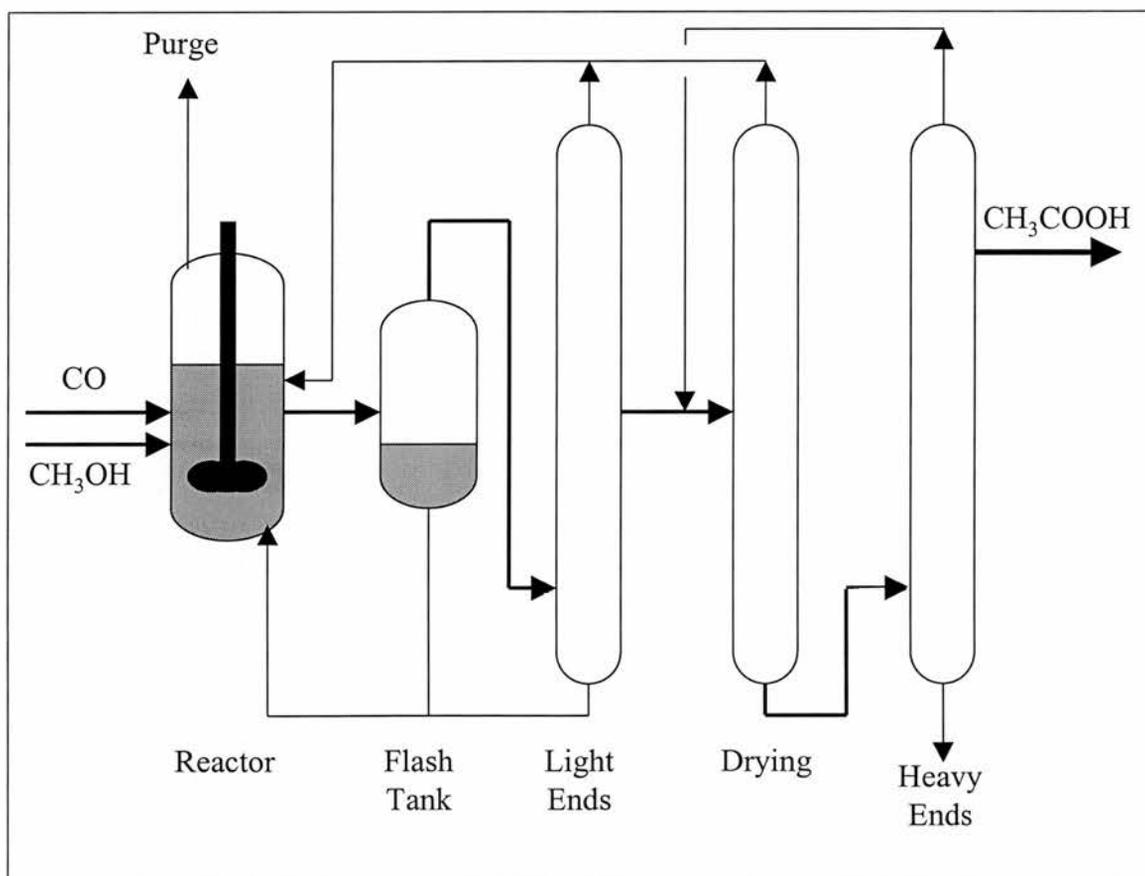


Figure 1.5; Schematic Diagram of Methanol Carbonylation Process¹²

The ethanoic acid obtained from the flash tank must then be purified. This is done using three distillation columns that separate out volatile fractions, water and heavy by-products respectively. Purification by distillation is a necessary, but very expensive process that drives the search for even more selective catalysts which are active in the presence of low water concentrations.

1.3.3 Catalyst Optimisation

The chemistry of the rhodium catalysed methanol carbonylation reaction is much more complicated than the diagram above implies. The composition of the reaction solution is a delicate balance of several equilibria, some of which can result in catalyst decomposition and others can produce alternative products. Attempts to optimise the effectiveness of the catalyst have tried to inhibit unwanted side reactions, while accelerating the rate determining step of the system; the reaction of $[\text{Rh}(\text{CO})_2\text{I}_2]^-$ with iodomethane. Three approaches to the problem are outlined below.

1.3.3.1 Electron Donating Ligands

The oxidative addition of iodomethane to $[\text{Rh}(\text{CO})_2\text{I}_2]^-$ is via nucleophilic attack by a rhodium lone pair of electrons on the electrophilic carbon of iodomethane. Thus, electron-donating ligands that increase the nucleophilic nature of the active catalyst should increase the overall rate of reaction.

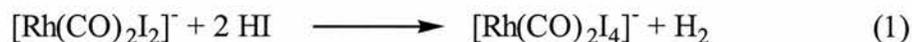
Forster⁵ studied phosphine ligands, but it was found that the phosphine complexes were unstable under reaction conditions, forming $[\text{Rh}(\text{CO})_2\text{I}_2]^-$ with the phosphine ligands

becoming quaternised by reaction with iodomethane. More recently, a triethylphosphine complex, $[\text{Rh}(\text{CO})\text{I}(\text{PEt}_3)_2]$, has been found to be more active than $[\text{Rh}(\text{CO})_2\text{I}_2]^-$ under mild conditions of 150 °C and 27 bar^{13,14}.

In order to make more stable complexes with electron donating ligands, chelating ligands with phosphorus, oxygen or sulfur donor atoms have been used¹⁵. In this study it was found that *cis*- $[\text{RhCl}(\text{CO})(\text{P}-\text{S})]$, where $(\text{P}-\text{S}) = (\text{Ph}_2\text{PCH}_2\text{P}(\text{S})\text{Ph}_2)$, was over 8 times more active than $[\text{Rh}(\text{CO})_2\text{I}_2]^-$ under industrially relevant conditions of 185 °C and 70 bar.

1.3.3.2 Water Concentration

The active species, **1**, can react with HI in an unwanted side reaction to form the rhodium (III) complex, $[\text{Rh}(\text{CO})_2\text{I}_4]^-$, **5**, as shown in equation 1 below. Furthermore, under low carbon monoxide pressures, **5** can go on to form insoluble RhI_3 . This removes rhodium from the carbonylation cycle and slows it down. However, it is possible to regenerate **1** by the reaction of **5** with water and CO according to equation 2.



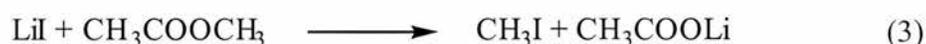
Overall, the net effect of equations 1 and 2 is the water gas shift reaction (WGSR), which competes with the carbonylation cycle for $[\text{Rh}(\text{CO})_2\text{I}_2]^-$. Water can therefore be used to maintain a high concentration of the active complex, **1**, and maximise the rate of carbonylation¹⁶.

Unfortunately, water has drawbacks too, which must be balanced with the increased rates possible. Hydrogen and carbon dioxide produced must be removed from the reactor by purging, which also carries away carbon monoxide reactant gas. In addition water is difficult to remove from the ethanoic acid product and incurs high distillation costs. It is these disadvantages that are addressed by the Celanese low water process, as well as the iridium based 'Cativa' system.

1.3.3.3 Ionic Iodide

An alternative method to maintain high concentrations of $[\text{Rh}(\text{CO})_2\text{I}_2]^-$ was developed by Hoechst Celanese in the early 1980s¹⁷. It uses the same catalytic carbonylation cycle as the Monsanto system, however, the use of high concentrations of iodide salts (LiI) cause the standing concentrations of several components to be significantly different from those observed under low iodide conditions.

Lithium iodide influences the concentration of the active anion, **1**, by reducing the acidity of the reaction mixture. The reaction is carried out with a high concentration of methyl ethanoate (from the esterification reaction of methanol with ethanoic acid). LiI replaces HI in the role of producing iodomethane, forming the basic salt lithium ethanoate according to equation 3 below.



Consequently, the concentration of HI is very low (less than 0.004 molar²), which prevents species **1** reacting according to equation 1 of the WGS cycle. More active species is then available to react via the carbonylation cycle. This means that the WGS is less significant under high iodide conditions, reducing the need to purge out

unwanted hydrogen and carbon dioxide, and allowing less water to be used, saving drying costs (see section 1.3.3.2).

An additional effect of using a high iodide concentration may be to form a small concentration of an extremely active, nucleophilic species, $[\text{Rh}(\text{CO})_2\text{I}_2(\text{L})]^{2-}$, where L^- could be I^- or $(\text{CH}_3\text{COO})^-$. This type of dianion would react faster with iodomethane, but it has not been observed directly^{2,10}. The concentrations of this dianion may be too small to detect², or the effect of iodide may be on the transition state of the reaction¹⁰.

1.3.4 Problems Associated with Rhodium Catalysis

The rhodium catalysed carbonylation of methanol is probably the most successful industrial application of homogeneous catalysis. However, there are some aspects of the reaction that can cause problems when magnified to an industrial scale.

- i. High water concentration: as described previously, water is necessary to achieve good reaction rates, but removing it from the ethanoic acid is expensive. Ionic iodide promoters can help to reduce this problem.
- ii. WGS reaction: this leads to formation of unwanted CO_2 and H_2 , causing direct loss of CO and further loss by purging to remove CO_2 and H_2 .
- iii. High HI concentration: as described earlier, HI is involved in the WGS reaction. It can also react with $[(\text{CH}_3\text{CO})\text{Rh}(\text{CO})\text{I}_3]^-$ eventually allowing the reductive elimination of CH_3CHO , rather than CH_3COI . CH_3CHO can be hydrogenated to ethanol, which can be carbonylated to form propanoic acid.
- iv. Propanoic acid formation: this impurity is formed in low levels in the reactor, but it is very difficult (and expensive) to separate by distillation from the ethanoic acid product.

1.4 Iridium Catalysed Methanol Carbonylation

Iridium was considered by Forster and co-workers at Monsanto during the development of potential catalysts for methanol carbonylation^{5,9}. It was found to be an excellent catalyst, however, the iridium system is more complicated than the rhodium equivalent⁹. They discovered that there are three distinct operating regimes, where the catalyst behaves differently.

1.4.1 Carbonylation Catalysed by Neutral Iridium Complexes

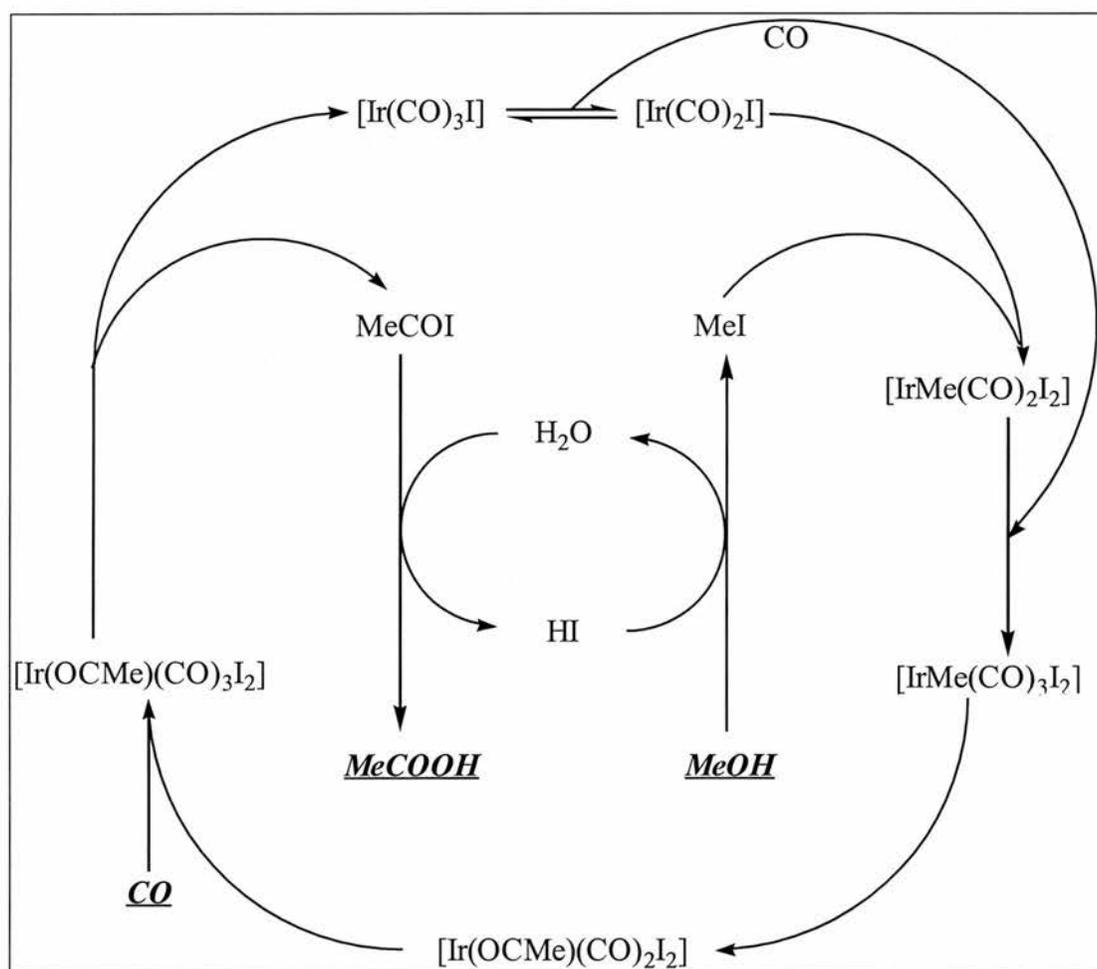
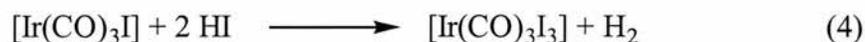


Figure 1.6; Neutral Iridium Methanol Carbonylation Cycle

In the first regime, at low iodomethane, water and ionic iodide concentrations, the principal iridium species is $[\text{Ir}(\text{CO})_3\text{I}]$, which is the active catalyst for a 'neutral' carbonylation cycle. The rate determining step in this cycle is the oxidative addition of methyl iodide to the neutral, and therefore poorly nucleophilic, $[\text{Ir}(\text{CO})_3\text{I}]$ or the more reactive $[\text{Ir}(\text{CO})_2\text{I}]$.

Oxidative addition of HI to $[\text{Ir}(\text{CO})_3\text{I}]$ can lead to a competing WGS reaction, via $[\text{Ir}(\text{CO})_3\text{I}_3]$ (equations 4 and 5), analogous to that seen for rhodium (equations 1 and 2). In this first regime, therefore, the iridium catalysed reaction is very similar to that observed for rhodium; the rate determining step is oxidative addition and there is a competing WGS reaction.



1.4.2 Carbonylation Catalysed by Anionic Iridium Complexes

By increasing the ionic iodide concentration, a second regime is encountered. Under these conditions the predominant form of iridium is the anionic complex, $[\text{CH}_3\text{Ir}(\text{CO})_2\text{I}_3]^-$. This is part of an anionic carbonylation cycle similar to the rhodium equivalent, but subtly different in important ways.

First, the rate determining step is not the oxidative addition of iodomethane to $[\text{Ir}(\text{CO})_2\text{I}_2]^-$. This step of the reaction is approximately 120 times faster for iridium than it is for rhodium¹⁰. Instead, it is the methyl migration (or carbon monoxide insertion) step which is very slow. The rate of methyl migration has been estimated to be approximately 100,000 times slower than the rhodium equivalent¹⁰. It is so slow that,

before methyl migration can take place, $[\text{CH}_3\text{Ir}(\text{CO})_2\text{I}_3]^-$ must replace an iodide ligand with the more electron withdrawing carbon monoxide ligand. It is this dissociative substitution of an iodide ligand that is the rate determining step.

The reaction rate is decreased by increasing iodide concentrations, confirming the rate determining step to be iodide dissociation. When a high concentration of iodide is used iodide dissociation and the overall carbonylation reaction rate is greatly reduced, causing a build up of $[\text{CH}_3\text{Ir}(\text{CO})_2\text{I}_3]^-$. Under these conditions the product selectivity is changed from ethanoic acid to methane and carbon dioxide formation.

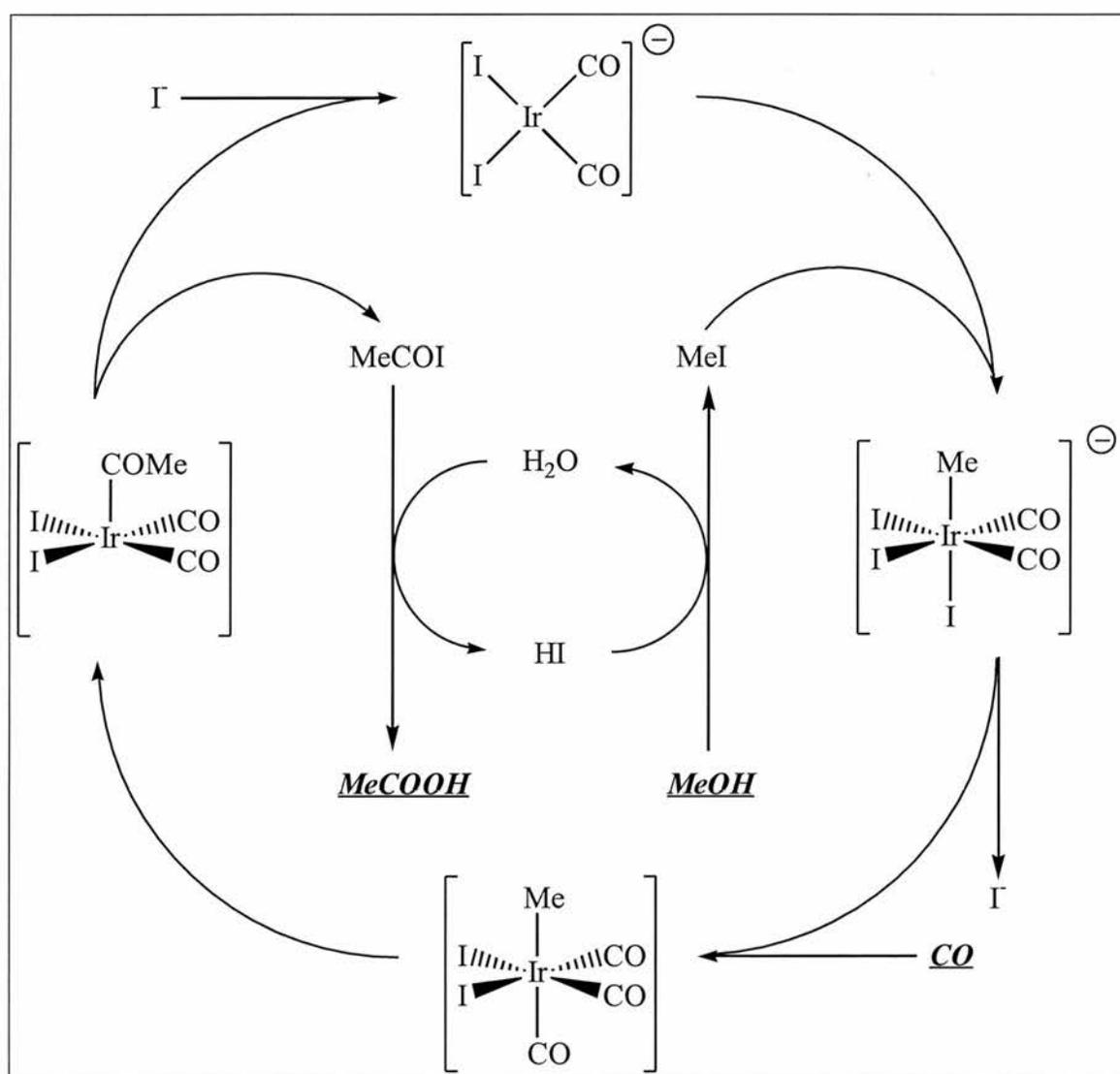
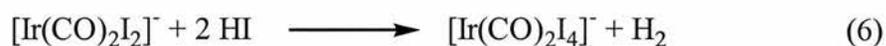


Figure 1.7; Anionic Iridium Methanol Carbonylation Cycle

As is observed for both the rhodium catalyst and the neutral iridium catalyst, a WGS cycle (equations 6 and 7) competes with the carbonylation cycle for active catalyst. The anionic iridium catalyst, however, requires a lower concentration of water to maintain high rates of carbonylation¹⁶. This is probably due to the fact that there is a lower standing concentration of $[\text{Ir}(\text{CO})_2\text{I}_2]^-$ relative to the equivalent active catalyst concentrations for both the rhodium and neutral iridium systems. Thus, the $[\text{Ir}(\text{CO})_2\text{I}_4]^-$ forming reaction (equation 6) is less active for the anionic iridium system, requiring less water to reform active catalyst via equation 7.



1.4.3 Anionic Iridium Catalysis under Specific Conditions

The third reaction regime observed by Forster and Singleton⁹ occurs at high methanol or water concentrations. Under these conditions the predominant iridium complex is part of the anionic WGS cycle, namely $[\text{HIr}(\text{CO})_2\text{I}_3]^-$. The anionic carbonylation cycle is still more active than the WGS reaction, despite $[\text{HIr}(\text{CO})_2\text{I}_3]^-$ being the predominant species. This is due to a fast equilibrium between $[\text{Ir}(\text{CO})_2\text{I}_2]^-$ and $[\text{HIr}(\text{CO})_2\text{I}_3]^-$ via the oxidative addition of HI. Addition of iodomethane to $[\text{Ir}(\text{CO})_2\text{I}_2]^-$ is slower than addition of HI, but iodomethane addition is effectively irreversible as further reaction of $[\text{CH}_3\text{Ir}(\text{CO})_2\text{I}_3]^-$ occurs via the carbonylation cycle.

At first, this statement appears to contrast behaviour observed in the second regime, because in the anionic iridium carbonylation cycle the methyl anionic complex reacts very slowly as part of the rate determining step. Maitlis *et al.*^{10,18}, however, found that methanol is able to accelerate the rate of carbonylation of $[\text{CH}_3\text{Ir}(\text{CO})_2\text{I}_3]^-$, which may

explain why the methyl complex reacts faster and is not the predominant iridium complex under high methanol or water concentrations.

1.4.4 Effect of Promoters

In the rhodium system, electron donating ligands can be used to accelerate the rate determining step. In the anionic iridium catalysed carbonylation cycle, however, the change of rate determining step to dissociative substitution of an iodide ligand requires a different approach to the search for potential promoters.

1.4.4.1 Alkyl Alcohols as Promoters

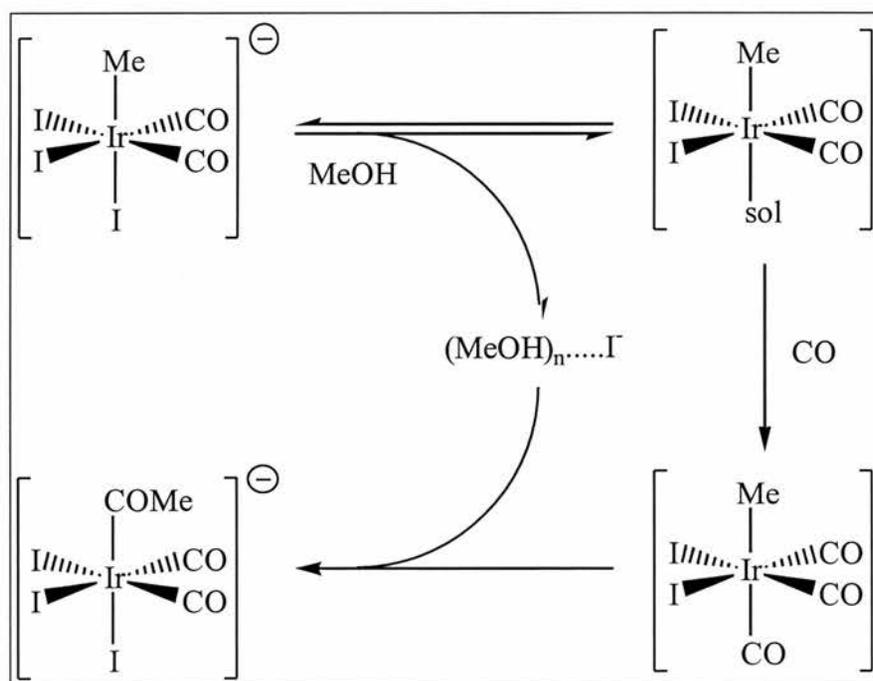


Figure 1.8; Proposed Mechanism of Methanol Promotion

The iridium catalysed carbonylation reaction is promoted by methanol and, to a lesser extent, higher alcohols^{10,18}. It is proposed that methanol, in particular, is able to aid dissociation of an iodide ligand by solvation of iodide ions in solution. Methanol may also act as a donor ligand to stabilise the resulting $[\text{CH}_3\text{Ir}(\text{CO})_2\text{I}_2]$ complex and prevent immediate iodide recombination.

1.4.4.2 Lewis Acids as Promoters

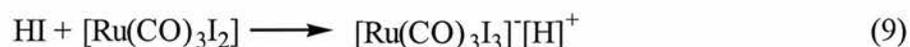
Lewis acids, such as SnI_2 , are also capable of inducing a significant increase in the rate of the methyl migration step. The adduct, $[\text{CH}_3\text{Ir}(\text{CO})_2\text{I}_2(\text{SnI}_3)]^-$, has been observed spectroscopically¹⁸. The SnI_3^- ligand has two properties that would produce an enhanced rate of methyl migration. It is a relatively labile ligand, so it could be displaced by carbon monoxide to form $[\text{CH}_3\text{Ir}(\text{CO})_3\text{I}_2]$, effectively catalysing the dissociative substitution of iodide. SnI_3^- is also a good π -acceptor ligand and has a strong *trans*-effect, which would make methyl migration more favourable. Alternatively, a Lewis acid could interact with the oxygen of a carbonyl ligand, withdrawing electrons and enabling the methyl migration step¹⁹.

1.4.4.3 Metal Carbonyl Complexes as Promoters

The promoter used by BP Amoco in their 'Cativa' process falls into this category. Various metal carbonyl complexes have beneficial effects on the iridium catalysed carbonylation reaction, but it is ruthenium that is employed in the Cativa system¹⁶. The rate enhancements obtained by using the ruthenium carbonyl promoter are most notable when low water concentrations are used.

From an industrial chemist's point of view the low water concentration afforded by the ruthenium promoter is very important, because it allows significant drying cost savings to be made as outlined in section 1.3.3.2. Ruthenium promoted iridium catalysts can be used in existing plants designed for rhodium catalysts, but faster reaction rates coupled with simplified product purification can significantly increase the plant capacity. This 'debottlenecking' process has been used to increase the annual capacity of an ethanoic acid producing plant in Korea from 200 kt to 350 kt. Alternatively, the faster rate of the new process allows new plants to use a cheaper, smaller reactor vessel.

The ruthenium promoter is believed to work by either direct interaction with $[\text{CH}_3\text{Ir}(\text{CO})_2\text{I}_3]$, or by lowering the standing concentration of HI, via equation 9 (a similar effect is observed in the LiI promoted rhodium catalysis, see section 1.3.3.3). A direct interaction of $[\text{CH}_3\text{Ir}(\text{CO})_2\text{I}_3]$ with $[\text{Ru}(\text{CO})_3\text{I}_2]$ as shown in equation 8 is proposed¹⁶. An iodide ligand is transferred from iridium to ruthenium, effectively catalysing the rate determining iodide dissociation step.



1.5 Direct Formation of Ethanoic Acid from CO and H₂

Ethanoic acid is currently made from methanol and carbon monoxide using the very efficient carbonylation catalysts discussed in sections 1.3 and 1.4. Despite this, the direct formation of ethanoic acid from carbon monoxide and hydrogen would be an attractive process if an effective, selective catalyst existed. Methanol is already manufactured from carbon monoxide and hydrogen (synthesis gas), so ethanoic acid is already made indirectly from synthesis gas.

Literature relevant to the direct formation of ethanoic acid from synthesis gas will be reviewed in chapter 3, but some of the advantages and disadvantages of such a process will be discussed here.

1.5.1 Advantages

The thermodynamics of ethanoic acid production, relative to carbon monoxide and hydrogen shows that the reaction should be possible if an efficient catalyst could be found. As shown below (Figure 1.9), at 500 K ethanoic acid formation from syngas is favourable with $\Delta G^\ominus = -24.2 \text{ kJ mol}^{-1}$.²⁰ In contrast, the formation of methanol from synthesis gas has a positive value of ΔG^\ominus (+21.3 kJ mol⁻¹), but despite this it is a commercial process (see chapter 2).

From an economic point of view, the direct formation of ethanoic acid from synthesis gas offers several potential cost savings. In the methanol carbonylation reaction, the raw materials represent one of the most important costs²¹. Carbon monoxide and hydrogen are cheaper feedstocks than methanol and carbon monoxide, so significant savings could be made. This drive to cheaper starting materials has been the driving force behind many of the changes in ethanoic acid production in the past.

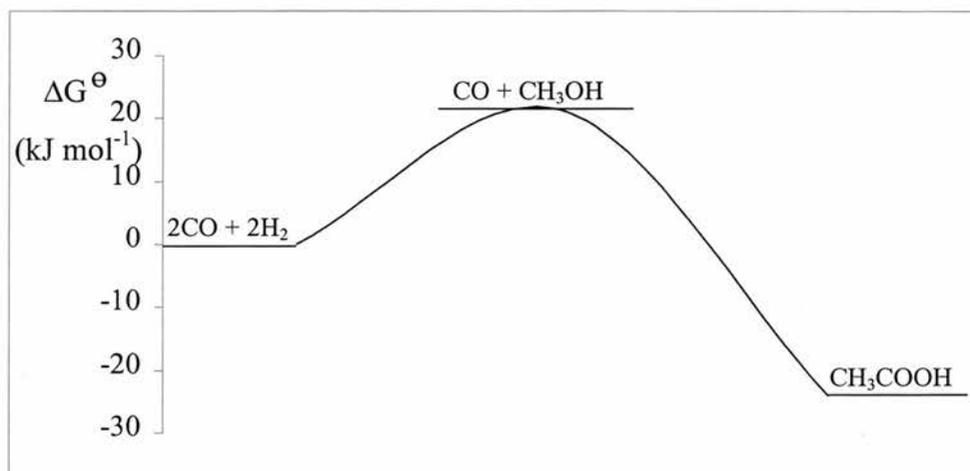


Figure 1.9; Free Energy Diagram for Ethanoic Acid Synthesis

Another significant ethanoic acid production cost is the capital cost of the plant itself²¹. Currently, one production plant is required to make methanol from synthesis gas and another is needed to carbonylate methanol to ethanoic acid. If ethanoic acid could be made directly from the synthesis gas, only one manufacturing plant would be necessary.

Synthesis gas can be obtained from a variety of sources. Coal, oil, natural gas and biomass, for example, can all be used to make synthesis gas, so as oil reserves are slowly used up synthesis gas will become an important starting material for bulk chemical manufacture. This phenomenon has already been observed whenever oil has been in short supply for political reasons. In the late 1970's the oil crisis caused world oil prices to rise sharply, which triggered a surge of research into synthesis gas processes. Also, South Africa is a world leader in synthesis gas chemistry as a trade embargo reduced the country's oil supply and forced them to look elsewhere for chemical feedstocks.

1.5.2 Disadvantages

The most significant disadvantage to the direct formation of ethanoic acid from synthesis gas process is likely to be the selectivity of the reaction. In principle, the reaction comprises the breaking of one C≡O triple bond and two H-H bonds, followed by the formation of one C=O, one C-C, one O-H and three C-H bonds. Unfortunately, having broken C≡O and H-H bonds there are many ways that the atoms can recombine to form an almost infinite number of different compounds.

Heterogeneous catalysts which essentially break CO and H₂ molecules down to surface bound atoms suffer major selectivity problems. Homogeneous catalysts are generally more selective, but selectivity is a significant concern in such a complicated reaction.

The other major disadvantage to the development of a new process for the manufacture of ethanoic acid is that the current process is efficient, well understood and in industrial use. A new process would need to be seen to have the potential to be better than the current technology before it could be developed industrially. Despite this, basic research into such a process is still of interest, both academically and industrially.

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CHAPTER 2

Carbon Monoxide Hydrogenation

2.1 Introduction

The covalent bond of the hydrogen molecule is strong. It has a bond dissociation energy of $103 \text{ kcal mol}^{-1}$ (431 kJ mol^{-1}) and a pK_a of 35^1 . This means that in hydrogen gas, under atmospheric pressure, one molecule of hydrogen is dissociated into H^+ and H^- for every 3.7 km^3 of H_2 . The challenge facing any carbon monoxide hydrogenation catalyst is to efficiently break the hydrogen molecule, then to react it selectively with carbon monoxide. Transition metal surfaces and molecules are particularly well suited for this role as they can dissociatively bind H_2 and also bind (or break) CO on the same metal atom or a neighbouring one.

The hydrogenation of carbon monoxide is an important route to a range of useful chemicals². Carbon monoxide and hydrogen (synthesis gas) can react to different degrees depending on the $\text{CO}:\text{H}_2$ ratio, the reaction conditions and the catalyst employed. The Fischer-Tropsch reaction, for example, produces a mixture of mainly linear alkanes and/or alkenes using a heterogeneous, supported transition metal (*e.g.* Fe, Co, Ni or Ru) catalyst, according to equation 10, below.



The hydrogenation of carbon monoxide to methanol is a valuable commercial process. Methanol is a very important intermediate and has a wide variety of uses. It is an intermediate in the formation of methyl methanoate, ethanol, ethanal and ethanoic acid and it can be converted catalytically to alkenes or aromatics by zeolites^{2,3}. It can even regenerate carbon monoxide and hydrogen by catalytic decomposition, effectively acting as a synthesis gas store for transport or storage.

2.1.1 Industrial Methanol Production

Methanol is synthesised industrially using a heterogeneous copper/zinc oxide catalyst. The process is very successful and produces approximately three billion kilograms of methanol per year⁴. The reaction uses synthesis gas that contains hydrogen, carbon monoxide and carbon dioxide, which is derived from natural gas by steam reforming. Water is also produced and is involved in the WGS reaction, which is also catalysed by the copper/zinc oxide catalyst.

Unlike ethanoic acid formation, as outlined in section 1.5.1, methanol formation from synthesis gas is thermodynamically unfavourable, with the equilibrium increasingly lying towards synthesis gas at high temperatures. The catalytic synthesis of methanol from carbon monoxide and hydrogen is therefore an example of how catalysis and chemical engineering can overcome problems predicted by thermodynamics. The key to the system is the ease of separation of the heterogeneous catalyst from the product stream. Methanol can then be removed from any unreacted synthesis gas, before the synthesis gas is recycled to continue the process.



$$\Delta H^\ominus = -100.5 \text{ kJ mol}^{-1}$$

$$\Delta G^\ominus = +45.4 \text{ kJ mol}^{-1}$$



$$\Delta H^\ominus = -61.6 \text{ kJ mol}^{-1}$$

$$\Delta G^\ominus = +61.8 \text{ kJ mol}^{-1}$$



$$\Delta H^\ominus = -38.7 \text{ kJ mol}^{-1}$$

$$\Delta G^\ominus = +16.5 \text{ kJ mol}^{-1}$$

(ΔH^\ominus and ΔG^\ominus values quoted at 600 K)

The position of equilibrium moves towards methanol as the temperature of the reaction decreases (Table 2.1). However, low temperatures cause a slow reaction rate and equilibrium is reached very slowly. The catalyst is therefore very important. It increases the rate of the reaction at the low temperatures required to maintain a high equilibrium amount of methanol.

Temp. (°C)	K_p (bar ⁻²)	Pressure required for 10 mol % methanol (bar)
250	2.09×10^{-3}	21.6
300	2.85×10^{-4}	58.3
350	5.29×10^{-5}	136
400	1.24×10^{-5}	281

Table 2.1; The effect of temperature on the methanol synthesis equilibrium⁵

Zinc oxide and copper are both capable of catalysing the methanol synthesis reaction individually, but only at high temperatures. Catalysts that contain both copper and zinc oxide are much more active and can be used at lower temperatures and pressures. These industrial catalysts are supported on Al₂O₃ or Cr₂O₃ typically, and may be promoted by caesium. They are used at pressures of less than 10 MPa (100 bar) and at a temperature of between 225 °C and 275 °C⁶.

Despite the position of equilibrium being on the side of synthesis gas, the reaction is exothermic. This creates another problem, because as the reaction proceeds heat is given out. If this heat is not removed from the reactor efficiently, the position of equilibrium moves back towards synthesis gas and the methanol yield drops. The industrial Cu/ZnO/Al₂O₃ methanol synthesis catalyst is so active that this large heat release is often the limiting factor, so reactor design is one of the most important considerations for the industrial methanol synthesis process.

2.1.2 Homogeneous CO Hydrogenation

Homogeneous catalysis suffers problems of separation of the catalyst from the reaction products, so it is not as well suited as heterogeneous catalysis to the methanol synthesis reaction. For a homogeneous catalyst to be competitive it would have to be active at low temperatures where methanol formation is favoured, or an alternative way of removing methanol from the system must be found. However, homogeneous CO hydrogenation catalysts do tend to preserve C-O bonds and are generally more selective to oxygen containing products than heterogeneous catalysts.

Various reviews relating to aspects of the homogeneous CO hydrogenation reaction are available. A concise review of the homogeneous mechanism with reference to specific catalytic reaction conditions is presented in "*Studies in Surface Science and Catalysis*"⁶. "*Metal carbonyl clusters in the catalytic hydrogenation of carbon monoxide*" is the topic of a review by Zwart and Snel⁷. Emphasis is placed on heterogeneous catalysts derived from clusters and their use for the formation of lower alkenes. Various reactions catalysed by homogeneous transition metal clusters involving CO and hydrogen, including hydrogenation of CO, are surveyed by Süss-Fink and Meister⁸. A recent review⁹, in Spanish, puts forward the case for homogeneous catalysis of carbon monoxide hydrogenation at low temperatures, and refers to a Brookhaven system which uses Ni(OAc)₂, Mo(CO)₆, NaH and a tertiary alcohol [(CH₃)₂C(OH)C₂H₅] in tetrahydrofuran at remarkably mild conditions of only 70 bar and 100 to 120 °C. Methoxide promoted, Ni(CO)₄ catalysed CO hydrogenation to methanol is believed to proceed via methyl methanoate and methanal¹⁰.

Homogeneous carbon monoxide hydrogenation catalysts all share a similar mechanism, which will be described in general in the next few sections. Cobalt (section 2.1.3), rhodium (2.1.4) and ruthenium (2.1.5) all show CO hydrogenation activity to different extents, with methanol, ethanol, propanol, 1,2-ethandiol and methyl methanoate being typical products. Rhenium is also able to catalyse the reaction, in the form of

$\text{Re}_2(\text{CO})_{10}$ at 700 to 750 bar and $290\text{ }^\circ\text{C}$ ¹¹. Heterogeneous rhenium catalysts have also been used¹², via methyl methanoate and a different mechanism, but CO poisoning occurs leading to the formation of $\text{Re}_2(\text{CO})_{10}$.

2.1.2.1 Carbon Monoxide and Hydrogen as Ligands

Both hydrogen and carbon monoxide molecules are weakened on binding to a metal centre. The hydrogen molecule is often broken into two discrete atomic hydrogen ligands by the binding process, although dihydrogen complexes have been observed¹³. The way in which carbon monoxide and hydrogen bind to metals is similar in that they both donate electrons to the metal centre to form part of the bond, while accepting electrons from the metal into empty orbitals to complete the bonding (see Figure 2.1).

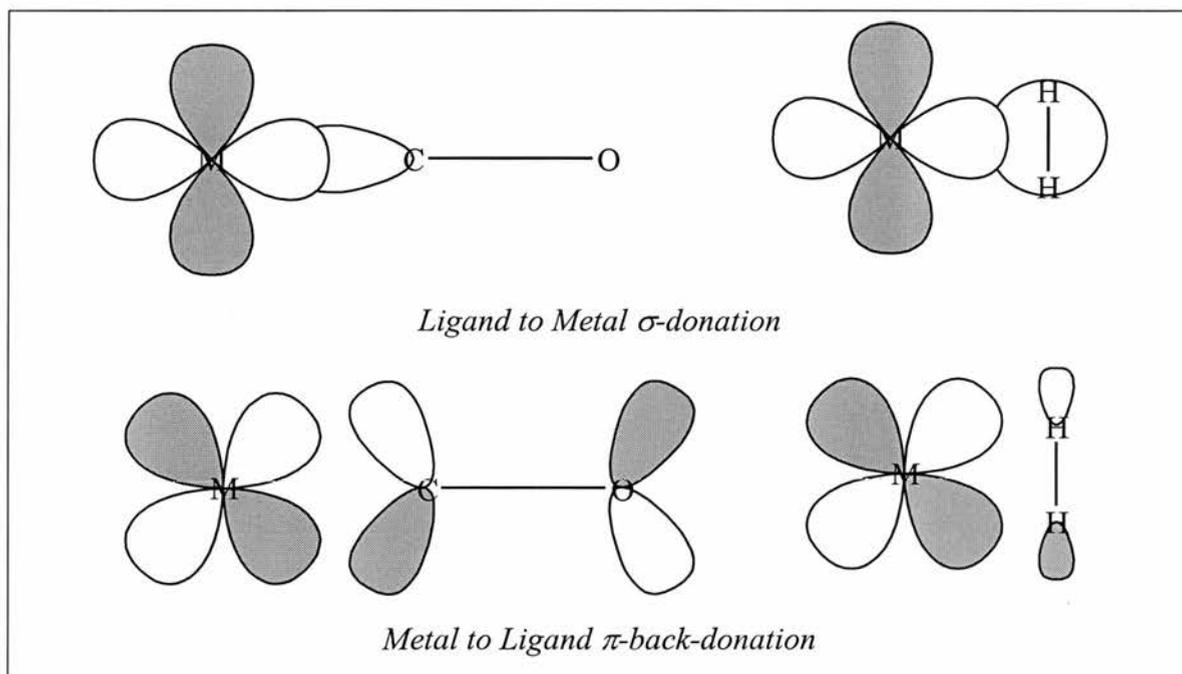


Figure 2.1; Bonding Modes of CO and H₂

The dihydrogen complex can form hydride ligands in two ways. It could be considered and intermediate in the oxidative addition of hydrogen, forming two hydride ligands and a formally oxidised metal centre. Alternatively, it can be deprotonated via a base-promoted heterolytic splitting of dihydrogen to form a hydride ligand and a proton. The latter proton transfer mechanism has been observed by NMR¹⁴.

Both carbon monoxide and hydride ligands can interact with other molecules via weak intermolecular interactions in the solid state. Thus, geometric patterns are observed, which can provide an insight into how molecules containing these ligands may approach each other prior to reaction.

Carbon monoxide ligands tend to form orthogonal CO-OC interactions¹⁵, as shown in the diagram below. This result must be treated with some caution, as carbon monoxide is relatively non-polar as a ligand, so intermolecular interactions involving carbon monoxide are relatively weak and can be distorted by other intermolecular forces. The oxygen atom of the ligand is, however, slightly basic and can interact with regions of positive charge, such as hydrogen bond donors.

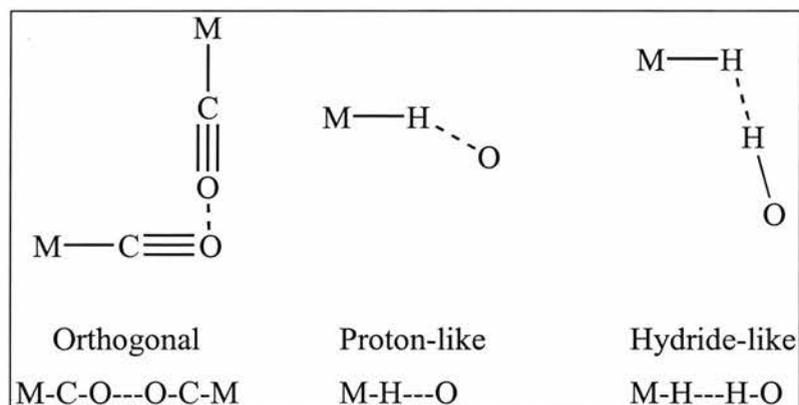


Figure 2.2; Typical inter-molecular interactions in the solid state

Hydride ligands are able to act as hydrogen bond donors or acceptors depending on the molecule in question¹⁶. Compounds containing an acidic hydride ligand, often with an overall positive charge, frequently display M-H---O interactions in the solid state.

Here, the proton acts as a hydrogen bond donor and is attracted towards the negative charge of a hydrogen bond acceptor. In other compounds, where a negative charge may be present, the hydride ligand may act less like a proton and more like a hydride. Hydrogen bonds of the type $M-H\cdots H-O$ can be observed and can be thought of as a transition state in the protonation of the hydride ligand to form a dihydrogen complex.

2.1.2.2 Reactions of Co-ordinated Carbon Monoxide

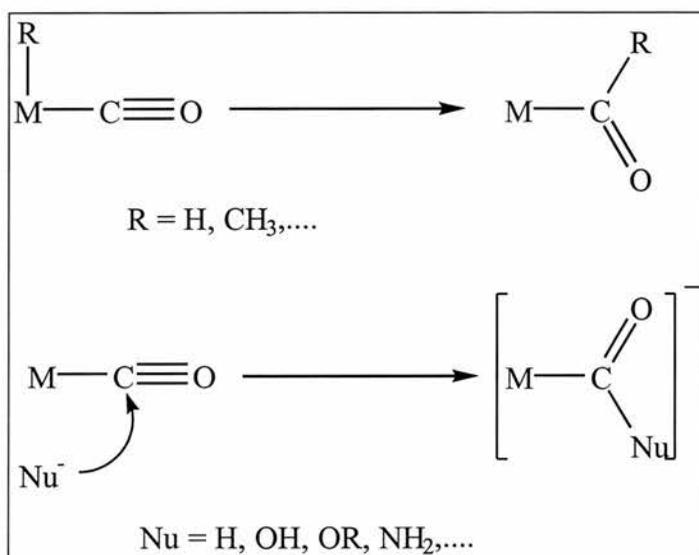


Figure 2.3; Typical reactions of bound Carbon Monoxide

The most common reaction of co-ordinated carbon monoxide is the carbon monoxide insertion reaction, or migration reaction. An example of this is the methyl migration step in the methanol carbonylation reaction (see section 1.3 and Figure 2.3) and is particularly common when the migrating group, R, is carbon based. When R is a hydride ligand, the migration reaction is much less common, but has been observed in some systems^{17,18}. This *intra*-molecular hydride transfer step is believed to occur in the homogeneous hydrogenation of carbon monoxide reaction in the absence of

promoters¹⁹. Unfortunately, this step is relatively difficult to achieve and requires high pressures to be used to sustain the reaction.

Co-ordinated carbon monoxide can also react with nucleophiles such as hydroxide or hydride in an *inter*-molecular reaction. The nucleophilic attack of hydroxide is the first step in the WGS reaction catalysed by various transition metal carbonyl compounds (including $[\text{Ru}_3(\text{CO})_{12}]$ and $[\text{Rh}(\text{CO})_2\text{I}_2]^-$), often in competition with oxidative addition of iodomethane (see section 1.3.3.2). The corresponding nucleophilic attack of hydride is believed to be the main hydride transfer step in some promoted carbon monoxide hydrogenation mechanisms, such as the iodide promoted ruthenium system (section 2.1.6.1).

The nucleophilic attack of methoxide²⁰ and chloride²¹ on $\text{Ru}_3(\text{CO})_{12}$ has been investigated by Ford, Rokicki *et al.* Methoxide reacts with a carbon monoxide ligand to form $[\text{Ru}_3(\text{CO})_{11}(\text{CO}_2\text{CH}_3)]^-$. The $-\text{CO}_2\text{CH}_3$ ligand is more labile than carbon monoxide itself and results in an increased reactivity towards dihydrogen, releasing methyl methanoate and producing $[\text{HRu}_3(\text{CO})_{11}]^-$. In contrast, chloride replaces one or two carbon monoxide ligands to form $[\text{Ru}_3(\text{CO})_{11}\text{Cl}]^-$ and $[\text{Ru}_3(\text{CO})_{10}(\mu\text{-Cl})]^-$ respectively. From a kinetic study of the reaction, the authors suggest that the chloride nucleophile may competitively attack both metal and carbonyl centres.

2.1.3 Cobalt Catalysed CO Hydrogenation

In the early 1950's, work by Du Pont²² showed that homogeneous cobalt catalysts could hydrogenate carbon monoxide using very severe conditions of 3,000 bar and 290 °C. These severe conditions deterred research into the reaction until the late 1970's when high oil prices prompted a resurgence of interest. Keim and co-workers²³ found that $[\text{HCo}(\text{CO})_4]$ was an active catalyst in toluene or N-methylpyrrolidinone (NMP) at 2,000 bar of CO/H_2 (1:1) and 230 °C. Work by Feder and Rathke²⁴ found that rates increased by a factor of 20 in polar solvents from heptane < benzene < 1,4-dioxane < 2,2,2-trifluoroethanol; however, basic polar solvents were less active as they deprotonated the active catalyst $[\text{HCo}(\text{CO})_4]$. Conditions as low as 300 bar and 200 °C were used, but the reaction was slow with turnover rates of approximately 2.5 per hour obtained.

The rate of the cobalt catalysed carbon monoxide hydrogenation reaction was found to be proportional to the concentration of $[\text{HCo}(\text{CO})_4]$ times the partial pressure of hydrogen^{25,26}. ($\text{Rate} = k \cdot [\text{HCo}(\text{CO})_4] \cdot P_{\text{H}_2}$). A kinetic isotope effect study²⁷ showed that $k_{\text{H}}/k_{\text{D}} = 0.73$ indicating that the rate determining step produces stronger bonds involving hydrogen. From this kinetic data, the rate determining step is concluded to be the oxidative addition of H_2 to a formyl containing complex $[\text{Co}(\text{CO})_3(\text{CHO})]$. This formyl complex is believed to be formed in low concentration and be in a fast equilibrium with $[\text{HCo}(\text{CO})_4]$. The acceleration of reaction rate observed when D_2 is used is attributed to the formation of two Co-H bonds, relative to the cleavage of one H-H bond.

2.1.4 Rhodium Catalysed CO Hydrogenation

Rhodium carbon monoxide hydrogenation catalysts have a tendency to produce more 1,2-ethandiol and are slightly more active than cobalt catalysts²⁸. Turnover rates of 27 per hour are observed at 500 bar and 240 °C by Watanabe *et al.*²⁹, and are typical of the system under these conditions²⁸. The mechanism of rhodium catalysis is relatively poorly understood, but anionic rhodium species are generally believed to be the active catalyst. Several rhodium-containing clusters are present under reaction conditions and the relative proportion of each is sensitive to temperature and pressure. A high pressure infra-red study of the system³⁰ showed that $[\text{Rh}(\text{CO})_4]^-$ and $[\text{Rh}_5(\text{CO})_{15}]^-$ were the major complexes under 200 °C, but at higher temperatures other higher nuclearity clusters were formed. The complexity of the rhodium system is such that it is possible that different rhodium species produce different organic products. Solutions containing $[\text{Rh}_5(\text{CO})_{15}]^-$ tend to produce 1,2-ethandiol, while solutions containing $[\text{Rh}(\text{CO})_4]^-$ produce mainly methanol.

Basic solvents that remove protons from the system and stabilise anionic rhodium complexes are beneficial³¹. Likewise, polar solvents can be used to reduce ion pairing, which is detrimental to the reaction rate^{31,32}. Anionic and cationic additives influence the reaction in a similar way³³, and amine or alkali metal carboxylates are effective additives, stabilising anionic carbonyl complexes²⁵. Complexes of the form $[\text{RhX}(\text{CO})\text{P}_2]$, where X = an anionic ligand such as PhCO_2^- and P = P^iPr_3 or $\text{P}(\text{cyclo-C}_6\text{H}_{11})_3$ have been used as catalyst precursors for the reaction³⁴. Good reaction rates are achieved at pressures of over 510 bar, although the precursor does not remain intact during the reaction, with $[\text{Rh}(\text{CO})_3\text{P}]_2$ being observed in the post-reaction solutions.

Quantum-chemical techniques have been used to investigate the mechanism of rhodium catalysed carbon monoxide hydrogenation¹⁹. The results indicate a mechanism similar to that shown in Figure 2.6, starting with the neutral complex $[\text{HRh}(\text{CO})_4]$, with oxidative addition, followed by an intramolecular proton transfer forming the methanal

ligand. The possibility of intermolecular hydride or proton transfers is not mentioned at any stage, nor are higher nuclearity rhodium clusters. An alternative mechanism, via a hydroxycarbene ($=\text{CHOH}$) intermediate, is discounted on kinetic and thermodynamic grounds, but only its formation by intramolecular proton transfer is considered. Intermolecular proton transfer from a suitable proton source may well favour the hydroxycarbene route.

2.1.5 Ruthenium Catalysed CO Hydrogenation

The hydrogenation of carbon monoxide reaction can be catalysed by unpromoted or iodide promoted ruthenium species. Unpromoted ruthenium carbonyl catalysis requires a high pressure of carbon monoxide to prevent deactivation of the catalyst. This system is discussed in section 2.1.5.1. Promotion of the catalyst by iodide appears to change the reaction mechanism, changing the selectivity in favour of 1,2-ethandiol and increasing the overall rate. The iodide promoted system will be discussed in detail in section 2.1.5.2.

2.1.5.1 Unpromoted Ruthenium System

Bradley³⁶ studied the ruthenium catalysed carbon monoxide hydrogenation reaction in 1979. He found that methanol and methyl methanoate could be formed using $[\text{Ru}(\text{acac})_3]$ as a catalyst precursor and conditions of 1,300 bar CO/H_2 (40:60) and 268 °C. The turnover rate of the reaction was approximately 30 mol products $(\text{mol Ru})^{-1} \text{h}^{-1}$. He showed that $[\text{Ru}(\text{CO})_5]$ was present during the reaction and it could be formed from $[\text{Ru}_3(\text{CO})_{12}]$ at 180°C and 265 bar CO/H_2 (1:1). At a higher temperature of 271 °C and the same pressure, further decomposition to ruthenium metal was observed. Unfortunately, this causes further complications, as ruthenium metal is able to catalyse the complete hydrogenation of carbon monoxide to methane and n-alkanes³⁷.

The unpromoted ruthenium system is believed to follow a similar mechanism to the cobalt system³⁸, with the key step being an intramolecular hydride transfer in $[\text{H}_2\text{Ru}(\text{CO})_4]$ to form a formyl species. However, the ruthenium system shows a greater selectivity to methanol and methyl methanoate than the cobalt system. It is suggested that the ruthenium system contains less acidic hydrides, which react with bound methanal to form a methoxide ligand³⁹ (see section 2.1.6).

Carboxylic acid solvents do induce a small amount of 1,2-ethandiol ester formation, although methanol (or methyl ester) is still the major product³⁸. Nitrogen bases, especially benzimidazole, are also able to promote the formation of 1,2-ethandiol, coupled with enhanced rates⁴⁰.

2.1.5.2 Iodide Promoted Ruthenium System

Addition of iodide salts to the ruthenium catalyst increases the rate of carbon monoxide hydrogenation significantly. 1,2-ethandiol is more readily produced than in the unpromoted system, but methanol remains the major product.

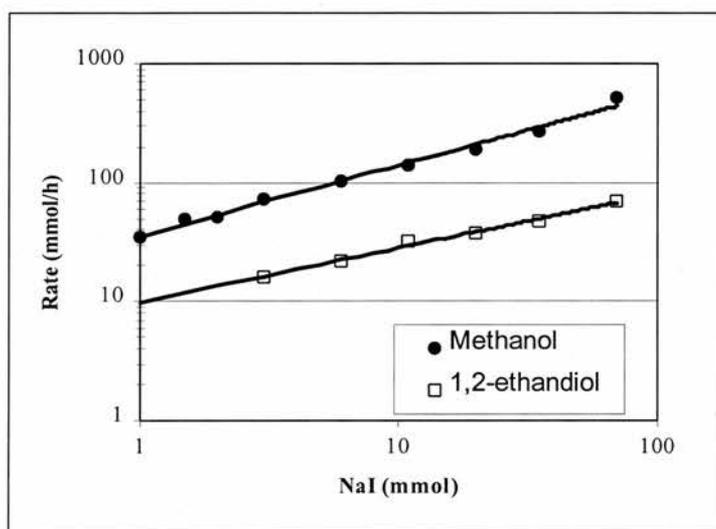
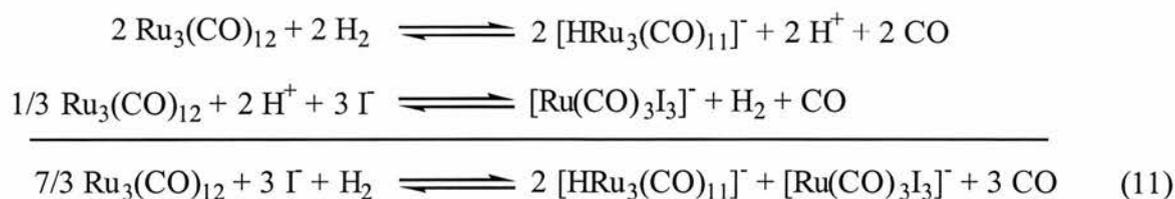


Figure 2.4; the effect of iodide concentration on the rate of hydrogenation²⁸

Conditions; 6 mmol Ru, 850 bar CO:H₂ (1:1), 230 °C, sulfolane (75 ml).

Under the reaction conditions of 850 bar of CO:H₂ (1:1), and 230 °C, two ruthenium complexes, [HRu₃(CO)₁₁]⁻ and [Ru(CO)₃I₃]⁻, are observed⁴¹. When used individually, [Ru(CO)₃I₃]⁻ shows no activity, whereas [HRu₃(CO)₁₁]⁻ is only slightly active. Only when a 2:1 ratio of the hydride cluster to the mononuclear ruthenium (II) anion is used is the maximum activity observed.

This 2:1 ratio of anionic complexes can be formed from [Ru₃(CO)₁₂] according to the following disproportionation reaction proposed by Dombek⁴¹ (equation 11). This reaction can be thought of as the heterolytic cleavage of H₂ to form the hydride complex and a proton. In the presence of iodide, [Ru(CO)₃I₃]⁻ can then be formed from Ru₃(CO)₁₂, with the regeneration of some hydrogen.



At high temperatures (above 260 °C at 850 bar) the activity of the iodide promoted system decreases⁴¹ as the catalyst breaks down, with the observed formation of $[\text{Ru}_6\text{C}(\text{CO})_{16}]^{2-}$. This is caused by the loss of carbon monoxide, eventually leading to the formation of ruthenium metal, according to the diagram below.

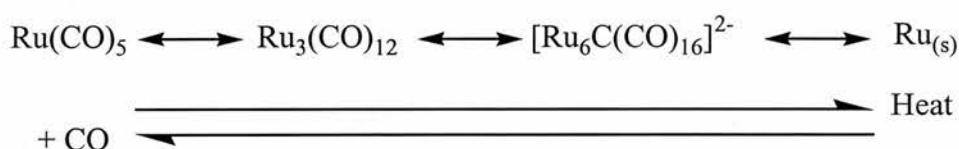


Figure 2.5; Nucleation of ruthenium carbonyl complexes

This equilibrium is effected by temperature, carbon monoxide pressure and iodide concentration. High temperature leads to carbon monoxide loss and nucleation of ruthenium species. High carbon monoxide pressure reverses this process and maintains the catalyst in the active form. In the unpromoted ruthenium system, the catalyst is less stable and breaks down to ruthenium metal at lower temperatures³⁶. Iodide effects the cluster forming process by producing the stable ruthenium (II) complex, $[\text{Ru}(\text{CO})_3\text{I}_3]^-$, which is resistant to nucleation. The formation of ruthenium metal causes further complications, because it is able to catalyse complete hydrogenation of CO, forming methane and n-alkanes³⁷.

Reactions of halides with $[\text{Ru}_3(\text{CO})_{12}]$ and equilibria between the cluster complexes formed have been studied⁴². In general, low temperatures or low carbon monoxide pressures were used, which are not consistent with catalytic reaction conditions, but the study did observe disproportionation to $[\text{HRu}_3(\text{CO})_{11}]^-$ and $[\text{Ru}(\text{CO})_3\text{I}_3]^-$ under CO and hydrogen according to equation 11.

2.1.5.3 Further Literature on the Ruthenium System

Ion pairing has an important, but poorly understood, effect on the ruthenium catalysed CO hydrogenation reaction. $[\text{Ru}(\text{CO})_3\text{I}_3]^-$ can form ion pairs with Li^+ , Na^+ , K^+ , Cs^+ , PPh_4^+ and H^+ and can effect the carbonylation and homologation of oxygenated substrates such as methanol⁴³. The strong acid hydride, $[\text{HRu}(\text{CO})_3\text{I}_3]$, is able to catalyse the homologation of methanol to ethanol, but can lead to the formation of methane if hydrogenation is faster than carbonylation. Alkali metal halides can act as Lewis acids and increase the rate of carbonylation to optimise ethanol selectivity.

The transfer of a hydride from $[\text{HRu}_3(\text{CO})_9(\text{dppe})]^-$ to *trans*- $[\text{Ru}(\text{CO})_2(\text{P-P})_2]^{2+}$ [where P-P = 1,2-bis(diphenylphosphino)ethane (dppe) or 1,2-bis(diphenylphosphino)benzene (dp)] is significantly influenced by ion pairing⁴⁴. In the presence of Na^+ ions, no *trans*- $[\text{Ru}(\text{CHO})(\text{CO})(\text{dp})_2]^+$ is produced; however, 100% conversion is observed with K^+ . The ion pairing effect is confirmed by the addition of the crown ether, 18-crown-6, to a reaction containing Na^+ leading to 100% conversion, whereas addition of excess NaClO_4 to a reaction containing K^+ totally inhibits the hydride transfer reaction. Thus, ion pairing could affect the transfer of hydride from $[\text{HRu}_3(\text{CO})_{11}]^-$ or $[\text{HRu}(\text{CO})_4]^-$.

Chloride salts and weak acids have been used as promoters for the CO hydrogenation reaction⁴⁵. Polar solvents and weak acids were found to be beneficial, with strong acids promoting homologation to ethanol. "Onium"⁴⁶ (ammonium and phosphonium) halides have been found to have an advantageous effect on the activity of 1,2-ethandiol, methanol and ethanol formation. In this case, chloride was found to be the halide of choice and moderate Lewis acidity was an important attribute of the solvent.

2.1.6 The General Homogeneous CO Hydrogenation Mechanism

The carbon monoxide hydrogenation mechanism (*Figure 2.6*) begins with the formation of a hydride-containing complex via heterolytic cleavage or oxidative addition of dihydrogen. Depending on the specific reaction conditions, the hydride then reacts with a carbon monoxide ligand via an *inter*-molecular or an *intra*-molecular hydride transfer reaction (see *Figure 2.6*). The formyl complexes formed by this reaction tend to be relatively reactive intermediates. For example, the formyl cluster complex, $[\text{Ru}_3(\text{CO})_{11}(\text{CHO})]^-$, has been observed at temperatures of less than $-50\text{ }^\circ\text{C}$ ⁴⁷, but at higher temperatures it decomposes back to $[\text{HRu}_3(\text{CO})_{11}]^-$ ^{47,48}. The stability of some anionic formyl complexes, such as $[\text{Fe}(\text{CO})_4(\text{CHO})]^-$, have been studied in the gas phase intermolecular hydride transfer reaction⁴⁹.

The inherent instability of the formyl complexes means that it is not possible to observe the formyl complexes under reaction conditions. However, the intermolecular transfer of a hydride (deuteride) from $[\text{DRu}_3(\text{CO})_{11}]^-$ to $[\text{CpRe}(\text{CO})_2(\text{NO})]^+$, forming the formyl containing complex $[\text{CpRe}(\text{CO})(\text{NO})(\text{CDO})]$, has been observed in model studies by NMR⁵⁰. Hydride transfer from $[\text{HRu}_3(\text{CO})_9(\text{dppe})]^-$ to $[\text{Ru}(\text{CO})_2(\text{dppe})_2]^{2+}$, producing the formyl complex $[\text{Ru}(\text{CHO})(\text{CO})(\text{dppe})_2]^+$ and $[\text{Ru}_3(\text{CO})_{10}(\text{dppe})]$ has also been observed⁴⁴.

The formyl ligand can react further by proton transfer (*inter*- or *intra*-molecularly) to form a coordinated methanal ligand, which can dissociate from the metal. Alternatively, reaction of a formyl ligand with a proton may occur at the oxygen centre initially, which would cause the reaction to take a slightly different route (see the following page). The formation of methanal has been observed and studied by Ishino *et al*⁵¹. They also observe 2-hydroxyethanal, an intermediate in the formation of 1,2-ethandiol.

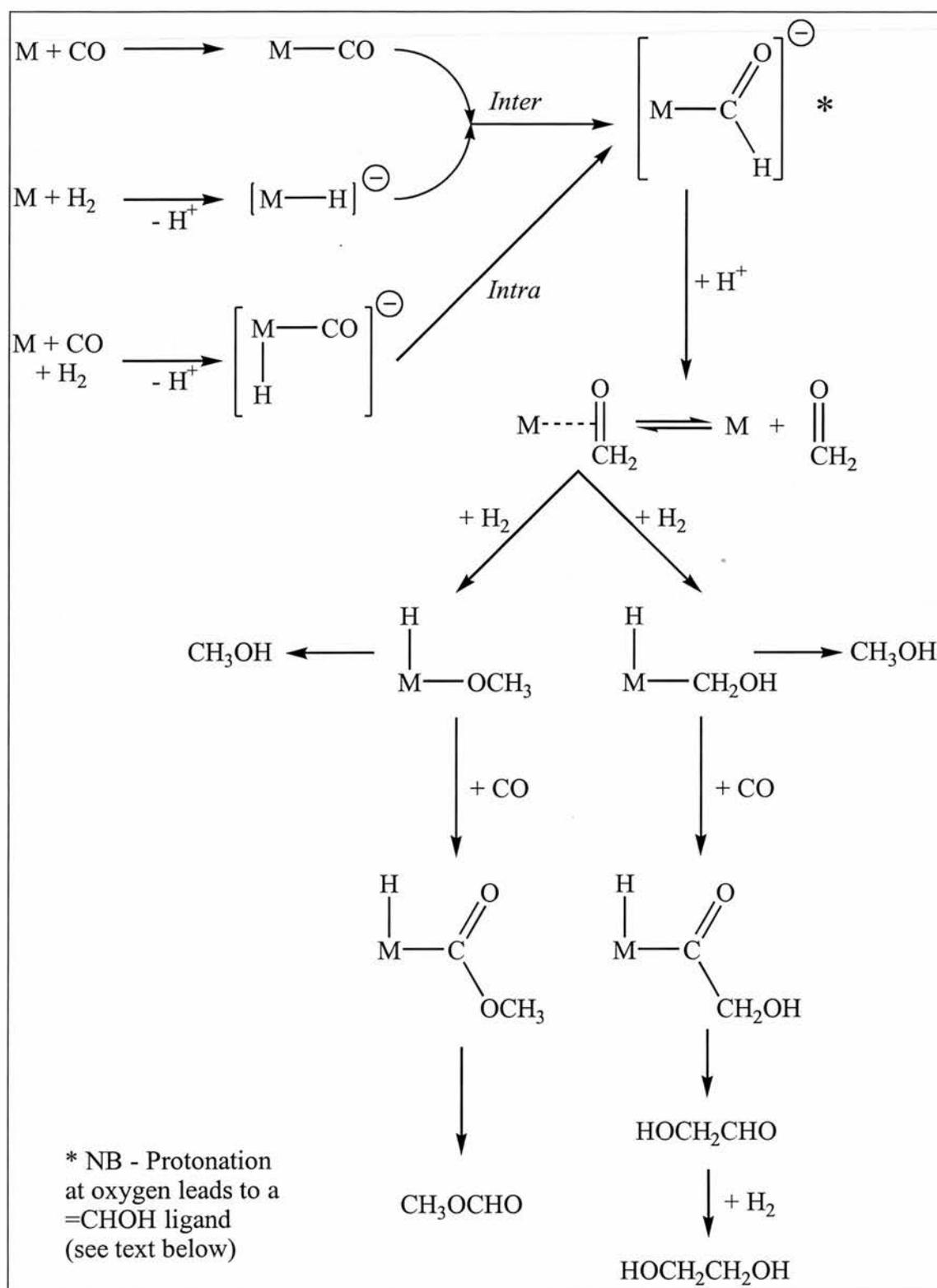


Figure 2.6; Homogeneous CO Hydrogenation Mechanism

Note; M represents a metal complex, which may or may not be part of a cluster. Other ligands omitted for clarity.

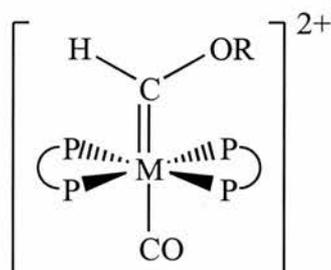
The methanal ligand is able to react with more hydride, either at carbon or oxygen. This step is likely to be an *intra*-molecular hydride transfer, but the site of hydride transfer is believed to be critical to the overall selectivity of the reaction⁴¹. If the hydride attacks the carbon atom of methanal a methoxy ligand, -OCH₃, is formed. This route leads to a high selectivity to methanol, via reductive elimination, with methyl methanoate being a minor product via a carbon monoxide insertion step prior to reductive elimination.

If hydride attack on methanal occurs at the oxygen atom, then a carbon bound hydroxymethyl ligand (-CH₂OH) is formed. This route can also form methanol via reductive elimination; however, the alternative carbon monoxide insertion step changes the selectivity towards carbon-carbon bond containing molecules. The simplest of these is 2-hydroxy-ethanal, but it is easily hydrogenated and is rarely observed. Thus, ethylene glycol (1,2-ethandiol) can be the major product of the reaction under certain reaction conditions.

At the influential hydride attack on bound methanal step, the route taken by the reaction is believed to be dependent on the acidity of the metal hydride species^{28,39}. Acidic metal hydrides, such as [HCo(CO)₄] tend to react at the more basic oxygen end of methanal, forming a hydroxymethyl ligand and leading to a bias towards 1,2-ethandiol selectivity. Less acidic hydrides, like [H₂Ru(CO)₄], produce a higher methanol selectivity, via the formation of a methoxy ligand by attack at the carbon end of methanal.

An alternative carbon monoxide hydrogenation mechanism has been proposed^{52,53}, based on the reaction of formyl ligands with electrophiles in model studies. The formyl complex formed by intermolecular attack of a hydride on a CO ligand, [Ru(CHO)(CO)(P-P)₂]⁺, where P-P = 1,2-bis(diphenylphosphino)benzene (dp), can react with electrophiles such as CF₃SO₃H or CF₃SO₃CH₃ to form complexes with a hydroxycarbene ligand. These complexes, of the form [M(CHOR)(CO)(P-P)₂]²⁺, where

M = Ru or Os and R = H or CH₃, were characterised by NMR, IR and elemental analysis and are of the form shown below. Calculations show that even in the cationic formyl complex, the oxygen is the most nucleophilic centre, leading to carbene rather than bound methanal ligands.



When R = CH₃, further reaction with hydride donors such as K[BH(OⁱPr)₃] produced the isolated complex [Ru(CH₂OCH₃)(CO)(P-P)₂]⁺. Thus, a mechanism involving stepwise reaction of a suitable carbon monoxide ligand with hydride, proton, hydride and proton to form -CHO, =CHOH, -CH₂OH and finally CH₃OH, respectively, was proposed⁵².

Figure 2.6 shows that both -OCH₃ and -CH₂OH could reductively eliminate methanol before insertion of carbon monoxide. Milstein⁵⁴ has compared the ability of the two ligands to reductively eliminate methanol and found that the preferred route was via the methoxy ligand. The hydroxymethyl ligand was found to favour β-hydride elimination to yield methanal. In the hydrogenation of carbon monoxide system, the methanal ligand would be reformed by this mechanism and be free to react via the methoxy ligand pathway.

In many cases during the 1980's, research into the area of carbon monoxide hydrogenation focused on the synthesis of 1,2-ethandiol. 1,2-ethandiol is in the top ten molecules produced in the world. It is used as a component of polyester resins and fibres and is also utilised as an antifreeze. At a time when oil prices were high, carbon-carbon bond containing molecules with functionality were seen as valuable building

blocks for the production of bulk chemicals. Consequently, most of the research in the area has been driven towards conditions conducive for 1,2-ethandiol formation, rather than methanol.

2.1.6.1 Iodide Promoted Ruthenium CO Hydrogenation Mechanism

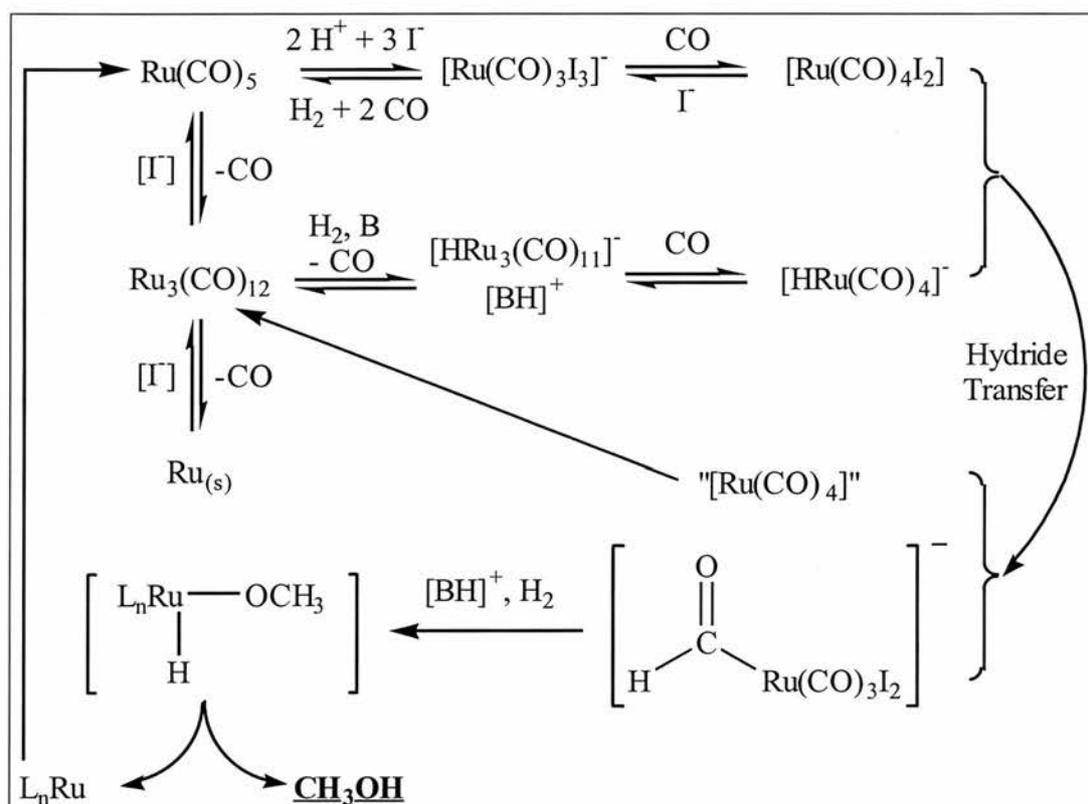


Figure 2.7; Iodide promoted ruthenium CO hydrogenation

The mechanism of the iodide promoted system differs from that of the unpromoted system in that an inter-molecular hydride transfer occurs to form a formyl ligand under high iodide conditions. It is possible that this key step in the reaction may involve $[\text{HRu}_3(\text{CO})_{11}]^-$ as the hydride donor and $[\text{Ru}(\text{CO})_3\text{I}_3]^-$ as the hydride acceptor, but it is postulated²⁸ that these complexes may be further activated before hydride transfer takes place.

Shore *et al.* showed that the hydride, $[\text{HRu}_3(\text{CO})_{11}]^-$, can act as a hydride donor⁵⁵, but its reactivity is limited. However, under reaction conditions, in particular a high pressure of carbon monoxide, $[\text{HRu}_3(\text{CO})_{11}]^-$ is believed⁴¹ to be in equilibrium with a small amount of $[\text{HRu}(\text{CO})_4]^-$ according to equation 12, below.



$[\text{HRu}(\text{CO})_4]^-$ has been shown to be a more effective hydride donor than $[\text{HRu}_3(\text{CO})_{11}]^-$ for the reduction of aldehydes⁵⁶. $[\text{HRu}(\text{CO})_4]^-$ also reacts with a carbon monoxide ligand in $[\text{CpRe}(\text{CO})_2(\text{NO})]^+$ to form $[\text{CpRe}(\text{CO})(\text{NO})(\text{CHO})]^{50}$. A rhenium hydride, $[\text{CpRe}(\text{CO})(\text{NO})\text{H}]$, is also observed. When $[\text{HRu}_3(\text{CO})_{11}]^-$ is reacted with the same cationic rhenium complex, only the rhenium hydride product is observed.

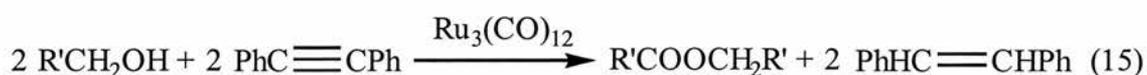
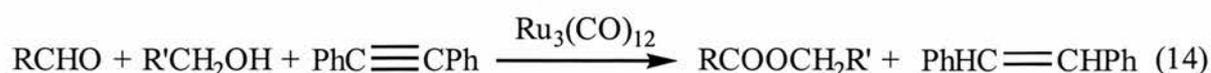
The anionic ruthenium (II) complex, $[\text{Ru}(\text{CO})_3\text{I}_3]^-$, observed in the hydrogenation of carbon monoxide reaction is not an attractive hydride acceptor because of the negative charge it carries. However, under high carbon monoxide pressures it is likely that $[\text{Ru}(\text{CO})_3\text{I}_3]^-$ is in equilibrium with $[\text{Ru}(\text{CO})_4\text{I}_2]^{41}$ (equation 13). $[\text{Ru}(\text{CO})_4\text{I}_2]$ is a very attractive hydride acceptor, because it no longer has a negative charge and the incoming hydride donor will be drawn towards the Ru^{2+} centre. $[\text{Ru}(\text{CO})_4\text{I}_2]$ reacts with $\text{LiDB}(\text{CH}_2\text{CH}_3)_3$ to form a highly unstable formyl complex, observed by NMR⁵⁰.



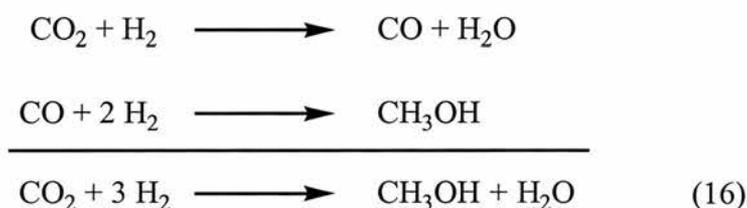
Thus, the activated hydride donor, $[\text{HRu}(\text{CO})_4]^-$, can react with the neutral Ru (II) complex, $[\text{Ru}(\text{CO})_4\text{I}_2]$, by an intermolecular hydride transfer to form a formyl ligand. The reaction has not been observed directly, because of the reactivity of the formyl ligand produced, but the evidence above suggests that such a reaction would be fast. Once formed, the formyl ligand could react in a similar way to the unpromoted ruthenium system (Figure 2.6), to form hydrogenated products.

2.1.7 Other Reactions Catalysed by Ruthenium Carbonyl

$[\text{Ru}_3(\text{CO})_{12}]$ can be used as a precursor to catalyse other reactions. In the presence of a hydrogen acceptor, such as an alkyne, $[\text{Ru}_3(\text{CO})_{12}]$ can catalyse the formation of esters from an aldehyde and an alcohol, or even from an alcohol alone⁵⁷ (equations 14 and 15).



The WGS reaction can be catalysed by unpromoted¹, chloride promoted⁵⁸ or iodide promoted⁴² ruthenium cluster complexes. The WGS reaction is the first stage in the catalysis of methanol formation from carbon dioxide and hydrogen⁵⁹ (equation 16).



In this system, the WGS reaction is proposed to be catalysed by a ruthenium cluster containing four ruthenium centres, such as $[\text{H}_2\text{Ru}_4(\text{CO})_{12}]^{2-}$. When sufficient carbon monoxide has been formed (Figure 2.8), it is hydrogenated via the iodide promoted ruthenium system. Methanol and methane are produced, with an optimal turnover number to methanol of 95 relative to $[\text{Ru}_3(\text{CO})_{12}]$. The reaction conditions of 135 bar H_2/CO_2 (3:1) and 240 °C are remarkably mild, but despite the low CO partial pressure in the system, the catalyst remains active with KI present. Temperature is a critical parameter in the reaction (Figure 2.9). Very little activity is observed at temperatures below 160 °C. At 200 °C, carbon monoxide is the major product of a three hour reaction, while methanol formation is becoming significant. At 240 °C, methanol is the

major product, but methane is also formed, while at temperatures over 260 °C the methane yield rises at the expense of methanol.

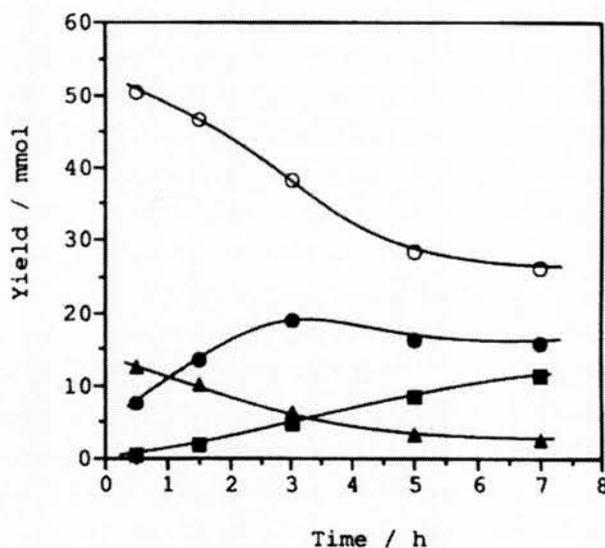


Figure 2.8; Time course of the CO_2 hydrogenation reaction

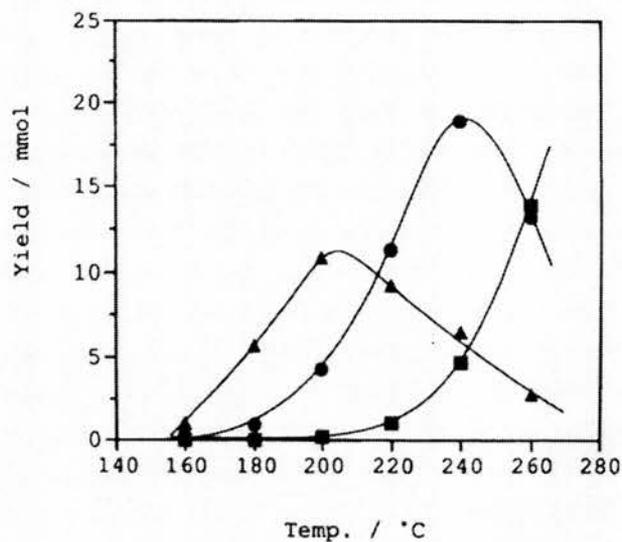


Figure 2.9; The effect of temperature on the hydrogenation of CO_2 reaction.

Conditions; $\text{Ru}_3(\text{CO})_{12}$ (0.2 mmol), KI (10 mmol), NMP (20 ml), CO/H_2 (1:3, 80 bar at 30 °C), 240 °C⁵⁹.

\square = CO_2 , \circ = CO, \bullet = CH_3OH , \triangle = CH_4

2.1.8 Bimetallic Carbon Monoxide Hydrogenation

Two different transition metals have often been used to increase the effectiveness of carbon monoxide hydrogenation. The aim has often been to improve 1,2-ethandiol selectivity by adding a metal that increases the rate of carbonylation (or homologation) to form products containing more than one carbon atom. Rhodium^{60,61,62}, cobalt^{63,64} and even rhenium⁶⁵ have been used for this purpose, in conjunction with ruthenium. Rhenium slightly increases the selectivity to 1,2-ethandiol, with little effect on the rate of methanol formation⁶⁵.

Polar solvents are generally used for the ruthenium-rhodium system. Phosphonium halides with melting points of less than 150 °C have been used⁶² and are found to enhance the rate and the selectivity to 1,2-ethandiol. Esters of methanol and 1,2-ethandiol are formed when the reaction is carried out in acetic acid^{61,66}. Nitrogen bases or alkali metal cations are effective promoters in this solvent. A third polar solvent, N-methylpyrrolidinone, has been studied by Dombek⁶⁰.

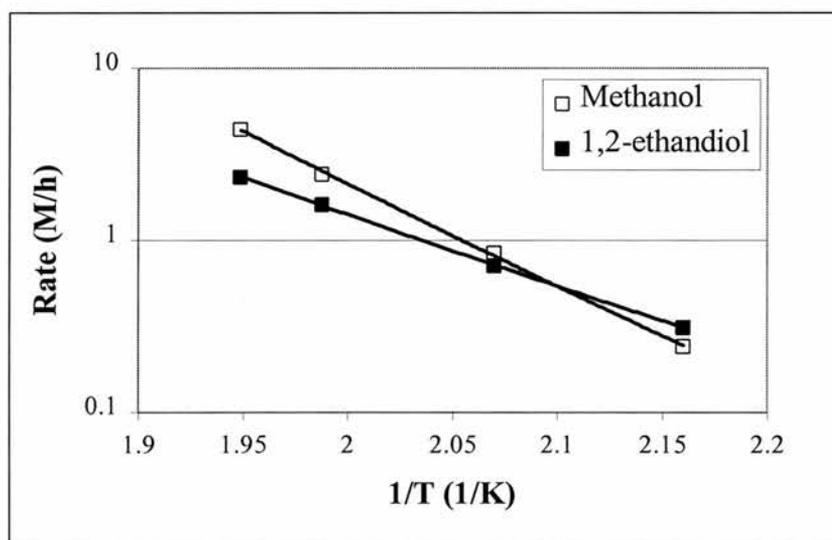


Figure 2.10; The effect of temperature on the CO hydrogenation reaction⁶⁰

Conditions: $\text{Ru}_3(\text{CO})_{12}$ (2 mmol), $\text{Rh}(\text{CO})_2(\text{acac})$ (2 mmol), NaI (18 mmol), NMP (75 ml), CO/H_2 (860 bar, 1:1).

Several features common to some or all of the different solvent systems are listed below.

- i. Increasing pressure increases the yield of both methanol and 1,2-ethandiol, with the effect being slightly more pronounced for 1,2-ethandiol. At pressures of less than 250 bar, very little 1,2-ethandiol is formed, but over 800 bar it becomes the major product^{61,60}.
- ii. Increasing temperature also increases the rate of both methanol and 1,2-ethandiol formation up to 250 °C (see Figure 2.10). This effect is more notable for methanol⁶⁰, although elevated temperatures reduce the maximum achievable yield of methanol, which is controlled by thermodynamics (see section 2.1.1).
- iii. Ruthenium only produces a low yield⁶² or low rate⁶⁰ of 1,2-ethandiol formation. Rhodium only is even less active, with maximum activity achieved with a mixture of the two metals (Ru:Rh = 1:1⁶² or 4:1⁶⁰).
- iv. Methanol production decreases with increasing rhodium mole fraction, so maximum methanol selectivity is observed with no rhodium present⁶⁰ (see Figure 2.11).

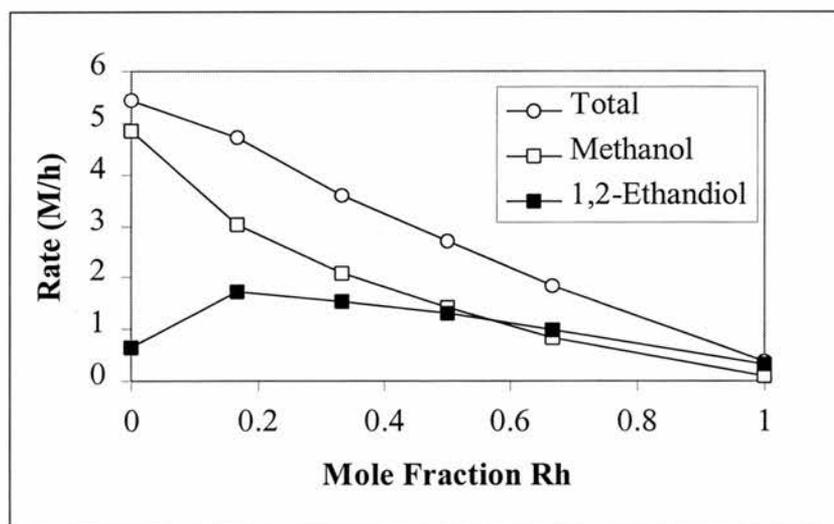


Figure 2.11; The effect of Rh/Ru ratio on the rate of CO hydrogenation⁶⁰

Conditions; 6 mmol of total metal (Rh + Ru), NaI (18 mmol), NMP (75 ml), CO/H₂ (860 bar, 1:1), 230 °C.

These features suggest that ruthenium functions as the main hydrogenation catalyst, producing mainly methanol. Rhodium has little hydrogenation activity of its own, but it is involved at some stage to form a carbon-carbon bond by a carbonylation step. Further hydrogenation then occurs, forming 1,2-ethandiol. To obtain the maximum rate and selectivity to methanol, a high Ru:Rh ratio should be used at low pressure. The temperature must be balanced between a high temperature required for maximum rate and a low temperature needed to maintain a high equilibrium concentration.

Very similar trends are observed when cobalt and ruthenium are used together^{64,63}. Overall, the reaction is less active, with a pressure of 1,000 bar required in toluene, using a phosphine promoter⁶⁴. Similarly, in N-methylpyrrolidinone and tetraglyme solvent, 850 bar has been used⁶³. Increasing cobalt concentration reduces the rate of methanol formation, as observed for rhodium, but homologation to ethanol is observed, especially when a high Co:Ru ratio is used.

Studies in this chapter will investigate the hydrogenation of carbon monoxide reaction under mild temperature and pressure conditions. A ruthenium carbonyl catalyst will be applied, using iodide promotion to stabilise the catalyst under a relatively low partial pressure of carbon monoxide. Literature on the reaction under high-pressure conditions suggests that the use of a low temperature and pressure should favour methanol, which may then be converted into ethanoic acid at a later stage. However, the conditions used represent a set of parameters where the iodide promoted, ruthenium catalysed carbon monoxide hydrogenation reaction has not been studied in the past.

2.2 Results and Discussion

The effect of varying the CO:H₂ ratio has been studied in the literature⁶², but the emphasis is generally on 1,2-ethandiol formation, with forcing conditions of over 200 bar and 200 °C used; however, methanol is the preferred product of carbon monoxide hydrogenation for the subsequent synthesis of ethanoic acid. Low pressures reduce the amount of 1,2-ethandiol formation, and although methanol production is also slowed the effect is not as significant, leading to improved methanol selectivity at low total pressure⁶⁰. The equilibrium between methanol and synthesis gas moves towards methanol at low temperatures. For these reasons, low temperature (167 °C) and low pressure (103 bar) conditions have been studied for the carbon monoxide hydrogenation reaction.

2.2.1 CO/H₂ Effects in the Homogeneous CO Hydrogenation Reaction

The diagram below (*Figure 2.12*) and *Table 2.2* show the effect of varying the CO:H₂ ratio, using a total pressure at the start of the reaction of 103 bar. No 1,2-ethandiol is produced in any of the reactions at this pressure. No activity is observed when a 1:1 ratio of CO to H₂ is used and only a trace amount of methanol is formed when the ratio is reduced to 1:2. Maximum methanol production (1.54 mmol, 13.86 mol methanol per mol [Ru₃(CO)₁₂]) is observed when a CO:H₂ ratio of 1:3 is used, but this falls when even more hydrogen is used. Since the results were observed using a reaction time of 20 hours, the maximum turnover frequency obtained is 0.69 mol methanol per mol [Ru₃(CO)₁₂] per hour.

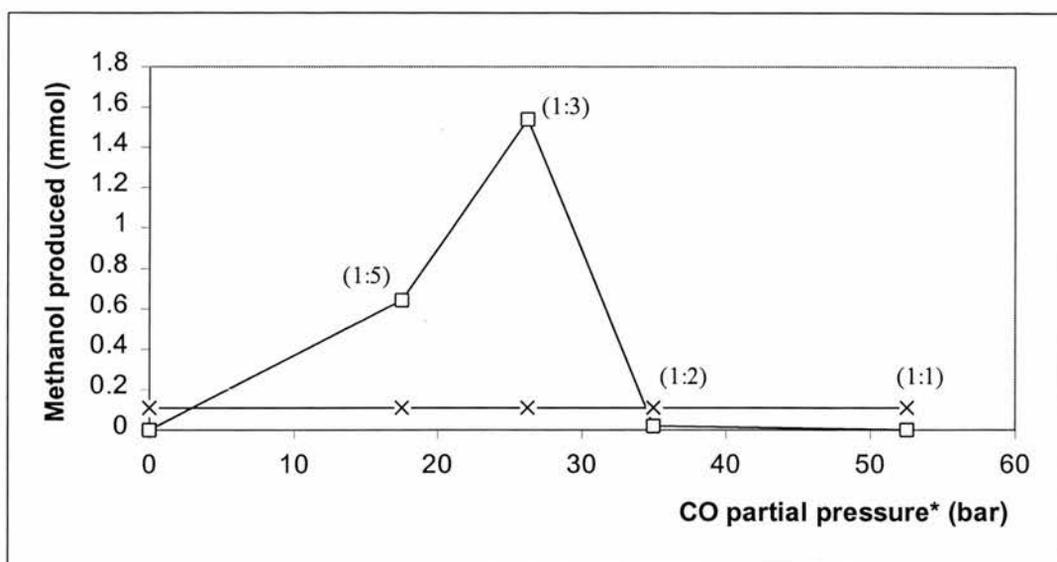


Figure 2.12; the Effect of varying CO:H₂ ratio on methanol production

□ = Methanol produced (mmol), x = [Ru₃(CO)₁₂] used (mmol) (CO:H₂ ratio in brackets)

*Total pressure = 103 bar at 167 °C, the remainder made up of hydrogen.

Conditions; NMP (5 ml), KI (0.83 g, 5 mmol), Ru₃(CO)₁₂ (0.0071 g, 0.111 mmol), 20 h.

The reaction is relatively inactive under these conditions, but the activity is consistent with extrapolation of literature results⁴¹. The low activity is not caused by the system reaching equilibrium, because Figure 2.13 shows that at conditions of 100 bar and 500 K, over 50% of the equilibrium composition is methanol. (At 167 °C, the equilibrium favours methanol even more). The amount of methanol actually produced in the reaction (1.54 mmol) is equivalent to 2% of its equilibrium concentration.

Since the equilibrium concentration of methanol is not achieved at 167 °C, the reaction is under kinetic control and the amount of methanol produced is dependent upon the rate of the reaction, assuming that the catalyst remains active. The rate of unpromoted ruthenium or cobalt catalysed CO hydrogenation is dependent on the partial pressure of H₂, and the rate of the iodide- promoted system shows a one third order in CO/H₂ pressure²⁸. The observed dependence of the amount of methanol produced on the

CO:H₂ ratio is probably caused by higher H₂ pressures leading to a higher rate. The rate increases as the partial pressure of hydrogen increases until a 1:3 CO:H₂ ratio is reached. However, as the amount of CO is decreased further, there is not enough CO to maintain the catalyst in the active form, so the amount of methanol produced decreases.

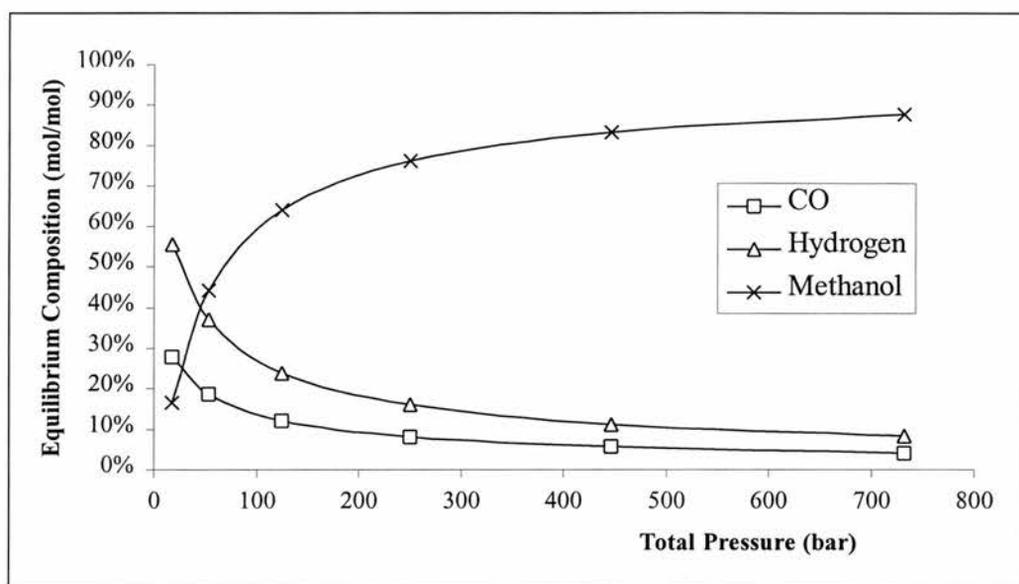


Figure 2.13; The effect of pressure on the Methanol / Synthesis gas equilibrium*

* Calculated using CO:H₂ = 1:2 and $\Delta G^\ominus = +21.3$ ⁶⁷ (at 500 K), hence $K_p = 5.95 \times 10^{-3}$.

As the reaction is under kinetic control, reducing the time of reaction lowers the amount of methanol formed. If the reaction time is reduced to 3 hours, 20 minutes, only 0.74 mmol of methanol is produced, equivalent to 2.05 mol methanol per mol [Ru₃(CO)₁₂] per hour. This is approximately half of the amount obtained if the reaction is heated for 20 hours. The slowing of the reaction over a long time period may indicate deactivation of the catalyst at the low CO partial pressure used, but as the reaction is carried out in a batch autoclave it is likely that the reaction slows as hydrogen gas is consumed.

2.2.2 The Effect of Temperature

As described in section 2.1.1, the position of equilibrium between methanol and synthesis gas moves away from methanol at high temperatures. However, this equilibrium position is irrelevant to the homogeneously catalysed reaction at 167 °C and 103 bar, because it is not reached due to the slow reaction. Raising the temperature should increase the rate of reaction, while maintaining a low pressure should deter 1,2-ethandiol formation.

Expt.	CO:H ₂	Temp. (°C)	Time (h)	Products (mmol)
1	1:1	167	24	None
2	1:2	167	20	Methanol (0.02)
3	1:3	167	20	Methanol (1.54)
4	1:5	167	20	Methanol (0.64)
5*	1:1	200	20	Methanol (3.20)
6*	1:1 (D ₂)	200	23	Methanol (6.94)
7*	0:1	200	16	N-methylpyrrolidine
8*	1:3	235	20	Methanol (12.52), Ethanol, Propanol, N-methylpyrrolidine

Table 2.2; Autoclave reaction results showing the effect of temperature

Conditions; NMP (5 ml), Ru₃(CO)₁₂ (0.0071 g, 0.111 mmol), KI (0.83 g, 5 mmol or *0.664 g, 4 mmol), 70 bar total pressure at room temp. (103 bar at 167 °C, 111 bar at 200 °C and 119 bar at 235 °C).

Using a 1:3 ratio of CO:H₂ at 235 °C with a total initial pressure at this temperature of 119 bar, the reaction is more active, with 12.5 mmol methanol produced. This is equivalent to a turnover number (TON) of 110.8 mol methanol per mol [Ru₃(CO)₁₂] and represents an 8-fold increase relative to the reaction at 167 °C. Unfortunately, the reaction produces a mixture of methanol and homologation products, ethanol and propanol, and some metallic residues were observed in the autoclave liner. The presence of ethanol and propanol indicates that the catalyst has some carbonylation activity as well as hydrogenation activity under these conditions. Decomposition of the catalyst to ruthenium metal shows that 30 bar of carbon monoxide is not enough to maintain the catalyst in its active form at this temperature. The formation of ruthenium metal causes further complications, because it is able to catalyse complete hydrogenation of CO, forming methane and n-alkanes³⁷.

Studies on the bimetallic ethanoic acid synthesis reaction (see chapter 3) suggested that a 1:3 ratio of CO:H₂ does not contain enough carbon monoxide to maintain the catalyst in the active form, even at 200 °C. However, when a 1:1 CO:H₂ ratio is used for the ruthenium catalysed CO hydrogenation reaction, no metallic residues are observed at this temperature. Under these conditions, 3.2 and 6.9 mmol methanol was produced in 20 hours, using H₂ and D₂ respectively, with no other organic products observed by GC or GCMS. This may indicate an isotopic effect, but further work would need to be carried out to confirm this.

In conclusion, temperature is just one of several parameters which can change the nature of the carbon monoxide hydrogenation reaction. Many of these parameters, such as total pressure, CO:H₂ ratio and iodide and catalyst concentrations, are interdependent. For example, the catalyst is more stable at high temperature (over 200 °C) if a high partial pressure of CO, or high iodide concentration is used. However, it has been shown that the catalyst is active for methanol formation between 165 °C and 235°C, even using a total pressure at room temperature of only 70 bar. In general, at low temperature the reaction is very slow and dependent on the CO:H₂ ratio, while at

high temperature the reaction is more active, but produces side products. A reasonable rate is observed at 200 °C, with good selectivity to methanol.

Low Temp. ←————→ High Temp

	167 °C	200 °C	235 °C
Methanol formed	1.54 mmol	6.94 mmol	12.5 mmol
TOF*	0.7	2.7	5.5
Note	Slow, rate dependent on CO:H ₂ ratio	Intermediate rate, good selectivity	Fast, poor methanol selectivity

Table 2.3; Summary table, showing the effect of temperature on the iodide promoted, ruthenium catalysed CO hydrogenation reaction

* Turnover Frequency in units of mol methanol per mol [Ru₃(CO)₁₂] per hour.

2.2.3 The Effect of KI Concentration

Dombek²⁸ has extensively studied the effect of iodide concentration on the ruthenium catalysed CO hydrogenation reaction (see *Figure 2.4*, section 2.1.5.2). The iodide promoter produces enhanced reaction rates and very high concentrations of iodide favour methanol selectivity²⁸.

Experiments 10 and 11 (*Table 2.4*) show that changing in the amount of KI has little effect on the amount of methanol produced, at the high concentrations of KI used. When a 1 molar solution of KI in NMP is used, as in experiment 10, a precipitate of KI is observed after the reaction. When 4 mmol (0.8 mol l⁻¹) KI is used, a precipitate is observed if the reaction is cooled in ice, but all of the KI dissolves at room temperature. A 0.5 molar concentration has been used in other experiments without any detrimental effects observed, such as catalyst breakdown or low activity. The lower concentrations

are preferred, because the lack of KI precipitate makes the recovery of reaction products and their quantitative analysis easier and more accurate.

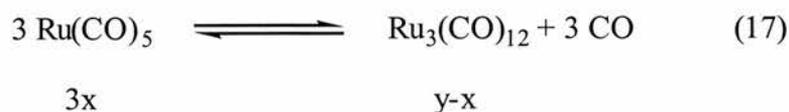
Expt.	CO:H ₂ (70 bar total at 298 K)	KI (mmol)	Time (min)	Products (mmol)
10	1:3	5.0	200	Methanol (0.75)
11	1:3	4.0	200	Methanol (0.72)

Table 2.4; The effect of varying KI concentration

Conditions; NMP (5 ml), Ru₃(CO)₁₂ (0.0071 g, 0.111 mmol), 70 bar total pressure at room temp. (103 bar at 167 °C).

2.2.4 The Effect of Catalyst Concentration

Catalysis of the carbon monoxide hydrogenation reaction by homogeneous ruthenium clusters does not show a straightforward linear dependence of rate on catalyst concentration. Whyman *et al.* found that the turnover (amount of CO consumed per unit of metal) of CO hydrogenation in a bimetallic Rh/Ru system decreases linearly with increasing catalyst concentration⁶⁶. Since nucleation to form cluster compounds is favoured at high concentrations (equation 17), it was suggested that the catalytic species was a highly dissociated metal species, perhaps a mononuclear complex, under the conditions used. [The conditions used were 1000 bar CO/H₂ (1:1), 230 °C, Et₃N promoter and ethanoic acid solvent].



where, y = amount of Ru₃(CO)₁₂ initially, $3x$ = amount of Ru(CO)₅ formed

$$K = \frac{(y - x)(pCO)^3}{27x^3}$$

At 200 °C, and a solvent volume of 5 ml, 6.94 mmol methanol was produced (expt. 6, *Table 2.2*). However, when the amount of solvent is doubled to 10 ml, 27.97 mmol methanol is produced (expt. 9). This represents a turnover number of 251 mol methanol per mol [Ru₃(CO)₁₂] (12.8 per hour) and is the most active methanol synthesis experiment carried out. The conditions used were similar to those used in *Table 2.2*, with CO:D₂ = 1:1, KI (0.83 g, 5 mmol) and a reaction time of 19 hours, 40 minutes. Thus, the concentration of KI in experiment 9 is different from that employed in experiment 6 (4 mmol in 5 ml in experiment 6 compared to 5 mmol in 10 ml used in experiment 9).

An increase in the turnover number is, therefore, observed at the lower catalyst concentration. Some of this effect may be due to low catalyst concentration favouring fragmentation of clusters, as suggested by Whyman⁶⁶, preventing the build up of inactive higher nuclearity clusters. However, the use of more solvent has other practical benefits that could increase the apparent methanol yield. The lower KI concentration is unlikely to effect the activity of the catalyst, but recovery of the reaction solution is easier because all the KI is soluble at room temperature. The use of 10 ml of solvent is also a benefit from a practical point of view, as a high proportion of it condenses within the autoclave liner, where it can be recovered under an inert atmosphere.

2.2.5 Deuterium Labelling Studies

It is important to confirm that the methanol produced in the hydrogenation of carbon monoxide has been formed from carbon monoxide and hydrogen gases. It is conceivable that the N-methylpyrrolidinone solvent could provide protons or even methyl groups for incorporation into methanol.

Isotopic labelling studies using deuterium gas as the only source of deuterium can provide a useful insight into the reaction. Any deuterium observed in products, intermediates, metal complexes or the solvent must have come from the deuterium gas rather than any other source.

2.2.5.1 Methods of Quantitative Methanol Isotopomer Analysis

The mass spectrum of methanol has 5 peaks between $m/z = 28$ and 32 , corresponding to CH_xO^+ fragments, where x ranges from 0 to 4. The largest peak is at $m/z = 31$ and there are two other large peaks, the molecular ion ($m/z = 32$) and $m/z = 29$. The other fragments, with $m/z = 28$ and 30 , are only present in small amounts. The mass spectra for CH_3OH and CD_3OH can be found in a database of spectra⁶⁸ and are shown in *Figure 2.14*. (Mass spectra for the other isotopomers of methanol are calculated from the mass spectra for CH_3OH and CD_3OH and used in analysis method 3)

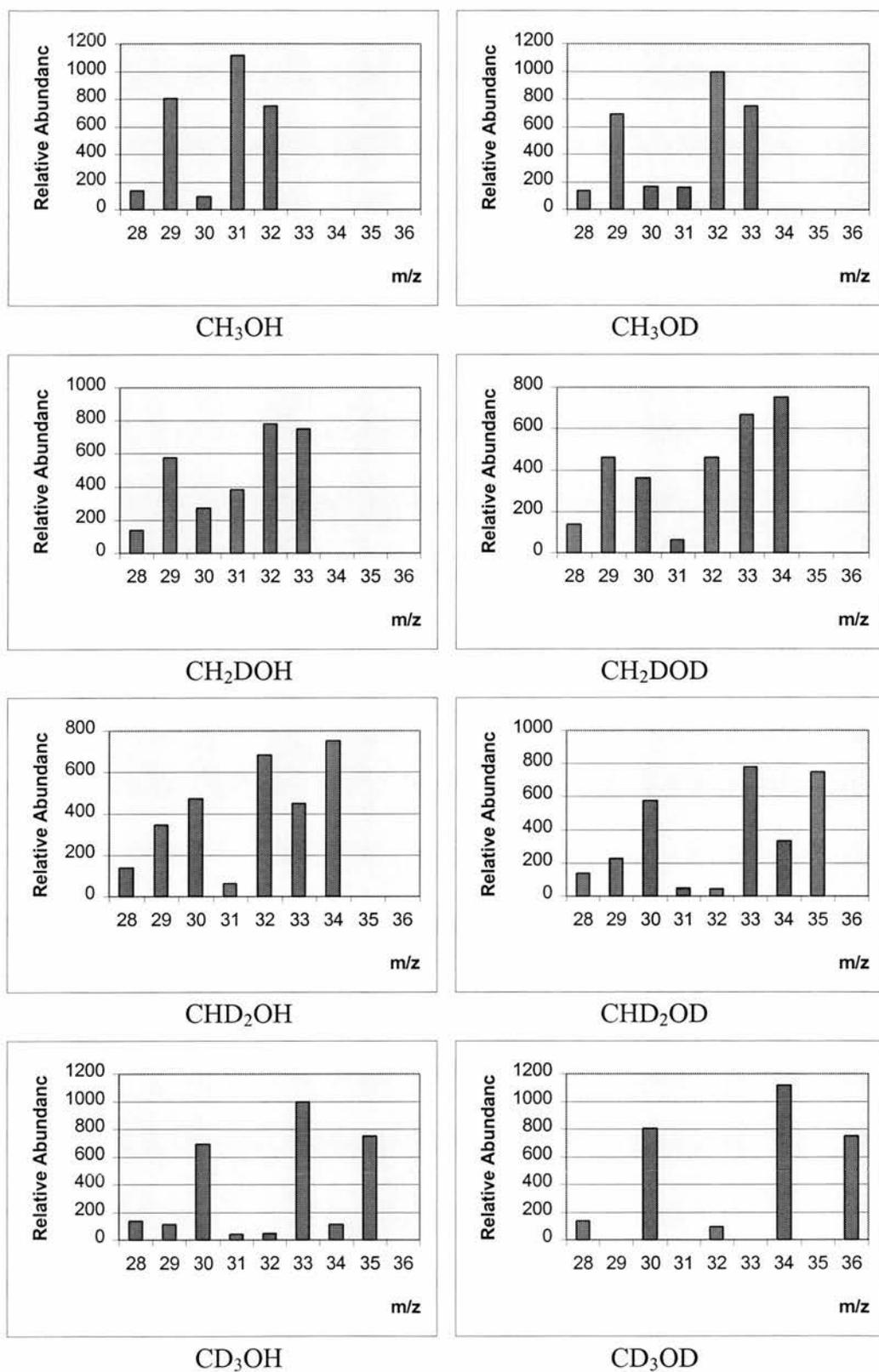


Figure 2.14; Mass spectra for isotomers of methanol⁶⁸.

Analysis Method 1

One way to analyse the mass spectrum of a mixture of isotopomers of methanol is to calculate the exact proportion of each isotopomer using simultaneous equations. To illustrate this method, consider the three most significant peaks at $m/z = 31, 32$ and 29 , which are caused by the fragments CH_2OH^+ , CH_3OH^+ and CHO^+ respectively. [Later studies and the mass spectrum of CD_3OH confirm this assignment]. To simplify the problem, a relative peak intensity of 7:5:4 will be used for ions with $m/z = 31, 32$ and 29 , respectively. Other fragment ions are ignored and it is assumed that other methanol isotopomers produce the same distribution of fragment ions.

Thus, the simplified mass spectra for all 8 different isotopomers of methanol can be calculated. By considering the amount that each isotopomer contributes to each individual mass unit of the mass spectrum, a series of 8 equations can be derived: one for each of the mass units between 29 and 36. For example, the only fragment ion of any isotopomer of methanol that gives a signal at $m/z = 36$ is CD_3OD^+ . This is a molecular ion, so its relative peak intensity is 5, compared to CD_2OD^+ (at $m/z = 34$) with a peak intensity of 7. Hence, $5 \times [\text{CD}_3\text{OD}] = P_{36}$, where $[\text{CD}_3\text{OD}]$ is the relative concentration of CD_3OD in the mixture of isotopomers and P_{36} is the size of peak at $m/z = 36$. The other equations are more complicated and are listed below.

$$5[\text{CD}_3\text{OD}] = P_{36}$$

$$5\{[\text{CHD}_2\text{OD}] + [\text{CD}_3\text{OH}]\} = P_{35}$$

$$5\{[\text{CH}_2\text{DOD}] + [\text{CHD}_2\text{OH}]\} + 7/3\{[\text{CHD}_2\text{OD}] + 3[\text{CD}_3\text{OD}]\} = P_{34}$$

$$5\{[\text{CH}_3\text{OD}] + [\text{CH}_2\text{DOH}]\} + 7/3\{2[\text{CH}_2\text{DOD}] + [\text{CHD}_2\text{OH}] + 2[\text{CHD}_2\text{OD}] + 3[\text{CD}_3\text{OH}]\} = P_{33}$$

$$5[\text{CH}_3\text{OH}] + 7/3\{3[\text{CH}_3\text{OD}] + 2[\text{CH}_2\text{DOH}] + [\text{CH}_2\text{DOD}] + 2[\text{CHD}_2\text{OH}]\} = P_{32}$$

$$7/3\{3[\text{CH}_3\text{OH}] + [\text{CH}_2\text{DOH}]\} = P_{31}$$

$$4/3\{[\text{CH}_2\text{DOH}] + [\text{CH}_2\text{DOD}] + 2[\text{CHD}_2\text{OH}] + 2[\text{CHD}_2\text{OD}] + 3[\text{CD}_3\text{OH}] + 3[\text{CD}_3\text{OD}]\} = P_{30}$$

$$4/3\{3[\text{CH}_3\text{OH}] + 3[\text{CH}_3\text{OD}] + 2[\text{CH}_2\text{DOH}] + 2[\text{CH}_2\text{DOD}] + [\text{CHD}_2\text{OH}] + [\text{CH}_2\text{DOD}]\} = P_{29}$$

Note, $[\text{CX}_3\text{OX}]$ is the relative conc. of CX_3OX and P_y is the peak size at $m/z = y$

The sizes of peaks (P_{29} to P_{36}) can be read from the mass spectrum of a mixture of isotopomers of methanol, which allows the equations to be solved simultaneously to give the relative concentrations of each isotopomer. Unfortunately, this method can often produce mathematically correct, but physically impossible solutions to the equations. Negative amounts of an individual isotopomer can be implied, which are not only impossible, but distort the relative amounts of other isotopomers present, so it is not possible to simply ignore negative values. This problem is caused by the rigidity of the simultaneous equations failing to allow for small experimental errors. It would still occur if a more accurate mass spectrum for each isotopomer was used (i.e. taking into account more fragment ions instead of just 3), but the calculations would be more complicated than the simplified version used.

Analysis Method 2

Another method is to calculate the OH:OD ratio in any water present after the reaction by using the relative intensities of ions at $m/z = 18, 19$ and 20 . Assuming that this is the same in the $-OH$ group of each set of isotopomers of methanol (CH_xD_yOH) it is possible to start with the size of the $m/z = 36$ peak to obtain the amount of CD_3OD present, then calculate the amount of CD_3OH using the OH:OD ratio. This information can be used, with the size of the $m/z = 35$ peak, to calculate the amount of CHD_2OD present, since this peak arises from CHD_2OD^+ and CD_3OH^+ alone. By further use of the OH:OD ratio and the relative sizes of other peaks in the mass spectrum, the relative amounts of each isotopomer of methanol can be calculated.

This method is less rigid than the first, and often results in plausible mixtures of isotopomers. Negative amounts are rarely found, and can be avoided by using different peaks of the mass spectrum, since not all of the peaks between 29 and 36 are necessary to produce a solution. Although the resulting mixture fits the observed mass spectrum

for all of the m/z values used to generate the solution, it is possible that other m/z values are not simulated well by the solution.

Analysis Method 3

A third method is to calculate the mass spectra for the 8 isotopomers of methanol, using literature mass spectra for CH_3OH and CD_3OH ⁶⁸ (*Figure 2.14*). It is assumed that isotope effects do not effect the fragmentation patterns for each isotopomer. This assumption may not be completely valid, so the simulated mass spectra should be treated as a useful guide to the analysis of mass spectra of mixtures of isotopomers, rather than a method of calculating the exact amount of each isotopomer present. The mass spectra for each isotopomer can be put into a spreadsheet, allowing simulated mass spectra to be calculated for any mixture of isotopomers. Comparison of the actual mass spectrum with the simulated one reveals the amount of each isotopomer present in the mixture.

Using this method, all of the peaks between 28 and 36 can be compared with the actual mass spectrum and negative amounts of any isotopomer can be ruled out. A reasonable first estimate of the components of the mixture is required before refinement to a final solution is possible. This first estimate could come from the results of using one of the other methods, or it could be based on knowledge of the mass spectra of individual isotopomers. Other rules, such as fixing the OH:OD ratio for each of the $\text{CH}_x\text{D}_y\text{OH/D}$ pairs of isotopomers to the OH:OD ratio of any water present, can also be applied to the mixture of isotopomers being simulated.

2.2.5.2 CO Hydrogenation Using D₂

In a reaction using deuterium as the only source of deuterium (expt. 12), 1.32 mmol of methanol was produced. The conditions used were Ru₃(CO)₁₂ (0.0719 g, 0.112 mmol), CO/D₂ (69 bar, 2:1), KI (0.8391 g, 5.055 mmol) and N-methylpyrrolidinone (10 ml), at a temperature of 200 °C for 17 hours.

The mass spectrum of the methanol produced is shown below and has large peaks at $m/z = 30, 33, 34, 35$ and 36 . The NMP solvent is not deuterated under these reaction conditions.

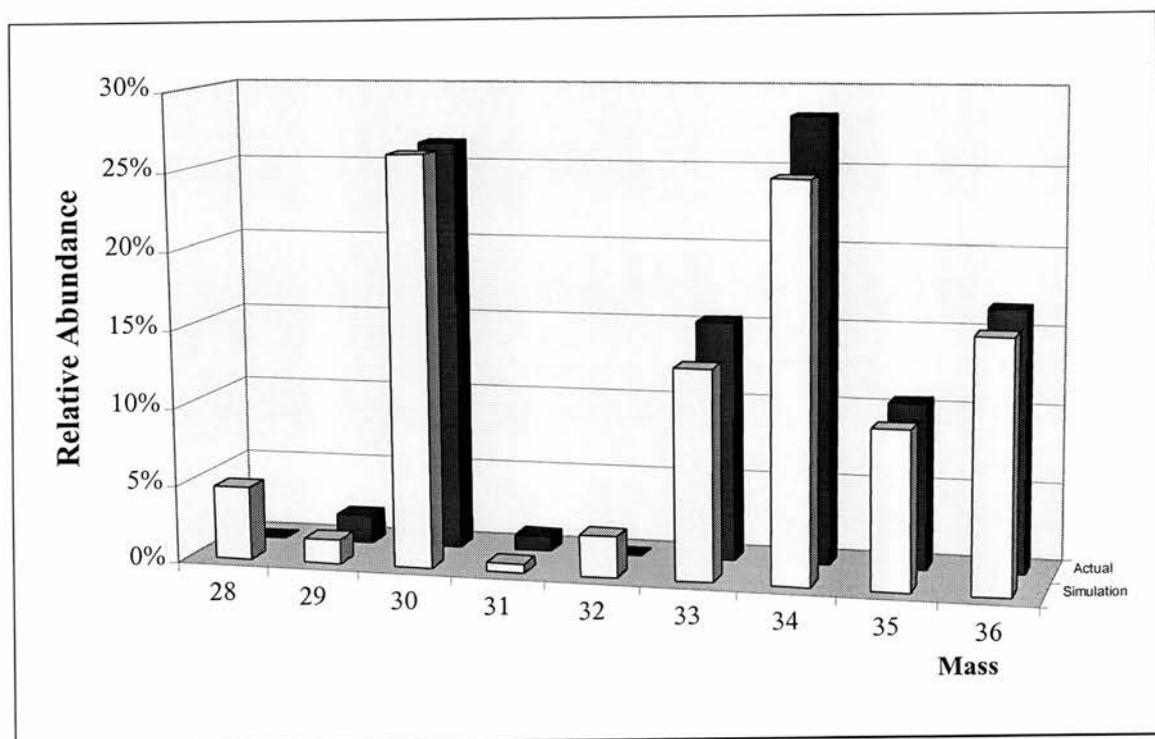


Figure 2.15; Observed and Simulated mass spectra for D₂ reaction

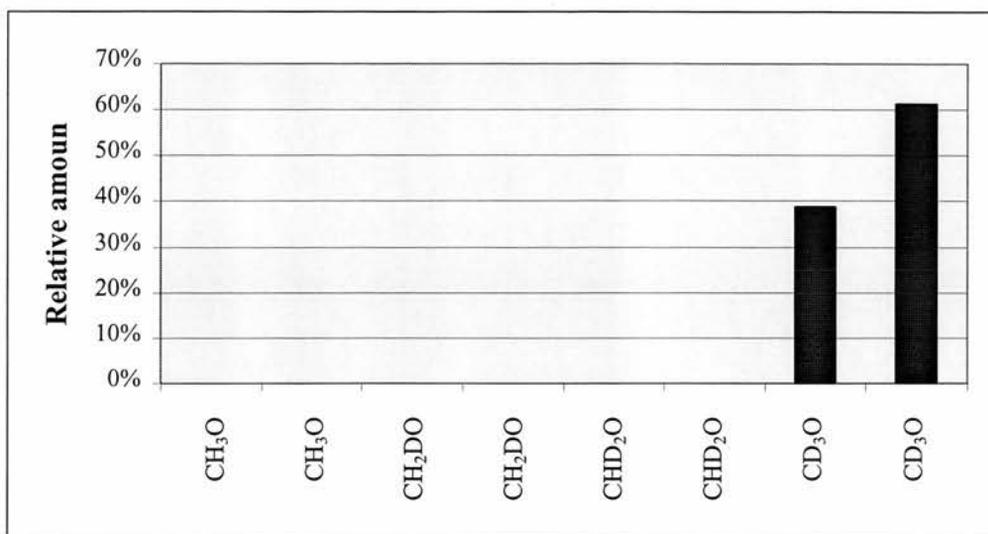


Figure 2.16; Isotopomer mixture used in simulation

The mass spectrum is characteristic of a mixture of CD₃OH and CD₃OD alone (38.8% and 61.2% respectively, derived from the relative sizes of peaks at $m/z = 35$ and 36), as shown by the simulated mass spectrum. Thus, deuterium gas has been incorporated into the methyl group of all of the methanol formed, and proves that *the methyl protons of methanol are only derived from hydrogen gas in the hydrogenation of carbon monoxide reaction.*

When the first method of calculating the amounts of each isotopomer present is used, using 8 simultaneous equations, the following mixture is obtained (Figure 2.17). This is an example of the first analysis method failing to produce a reasonable mixture of isotopomers. Negative amounts of both CD₃OH and CH₃OH are implied and the amounts of other isotopomers are distorted.

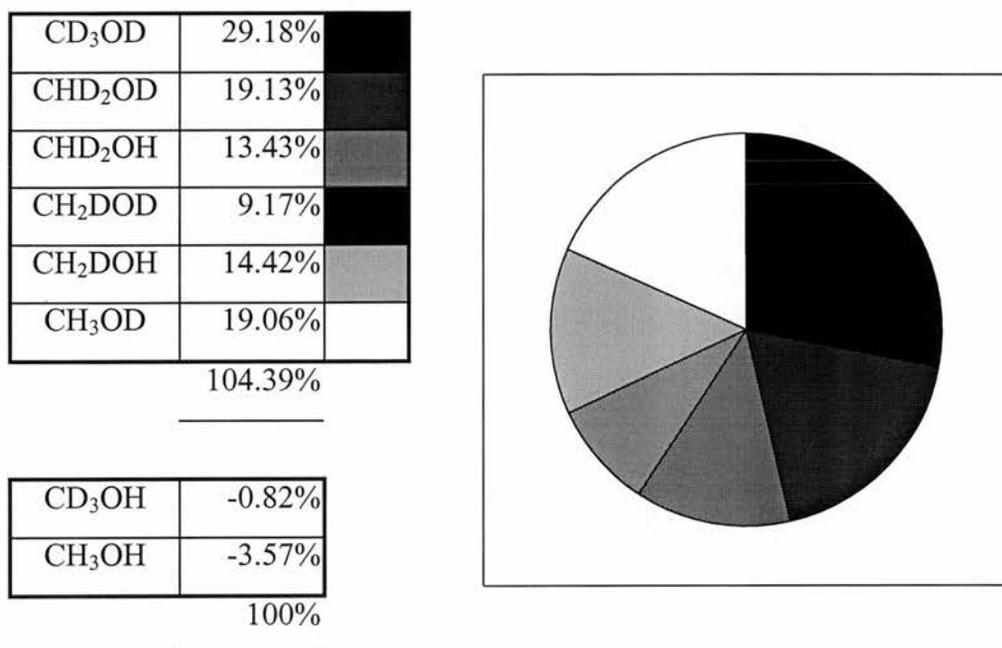


Figure 2.17; Impossible Mixture of Isotopomers Calculated using Method 1

2.2.5.3 CO Hydrogenation Using D₂ and H₂O

Water is not necessary for the hydrogenation of carbon monoxide reaction, but it is a component of the methanol carbonylation reaction. Unlabelled water was added to a hydrogenation of carbon monoxide reaction using deuterium gas as the only source of deuterium (expt. 13) to observe its effect on the mixture of methanol isotopomers produced. The conditions used were; Ru₃(CO)₁₂ (0.0715 g, 0.112 mmol), KI (0.843 g, 5.08 mmol), NMP (10 ml), H₂O (1 ml), CO/D₂ (66 bar, 1:1), 200 °C for 16 hours.

The methanol produced contained mainly CD₃OD and CD₃OH isotopomers (Figure 2.18), but some protons were also observed in the methyl group, with the overall

isotopomer distribution calculated using analysis method 2 shown in *Figure 2.19*. After this reaction, deuterium was found by GCMS in the water (more D than H) and, to a small extent, in the NMP solvent. It is likely that the WGS reaction is active when water is present, forming carbon dioxide and hydrogen from water and CO. The hydrogen formed by this route would be unlabelled and would cause some H/D scrambling in any methanol produced. The back-reaction could also occur, forming the labelled water observed and allowing labelled NMP to be formed by exchange of acidic proton(s).

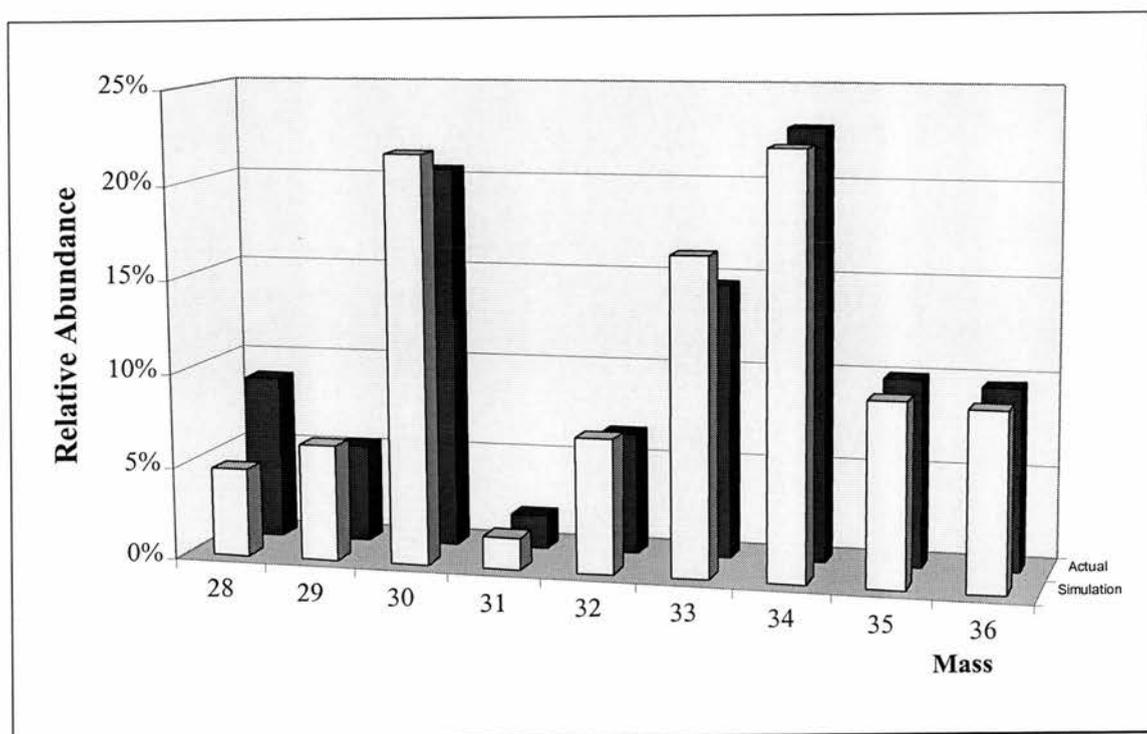


Figure 2.18; Observed and simulated mass spectra for D_2/H_2O reaction

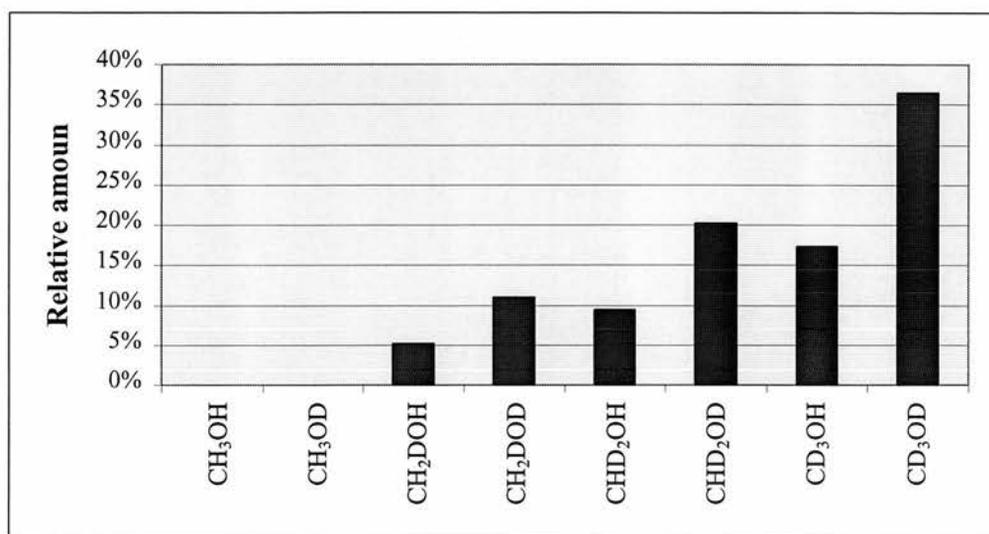


Figure 2.19; Isotopomer mixture used in simulation

The effect of water on the CO hydrogenation reaction is confirmed by another reaction, using H₂ and D₂O, rather than D₂ and H₂O. When H₂ and D₂O are used, the inverse result is obtained, with CH₃OH and CH₃OD being produced. Figure 2.21 shows the simulated mass spectrum using the inverse isotopomer distribution (Figure 2.20) to that used for the D₂/H₂O reaction (Figure 2.19). Some methanol isotopomers with deuterium atoms in the methyl group are observed, with more H₂O than D₂O found after the reaction.

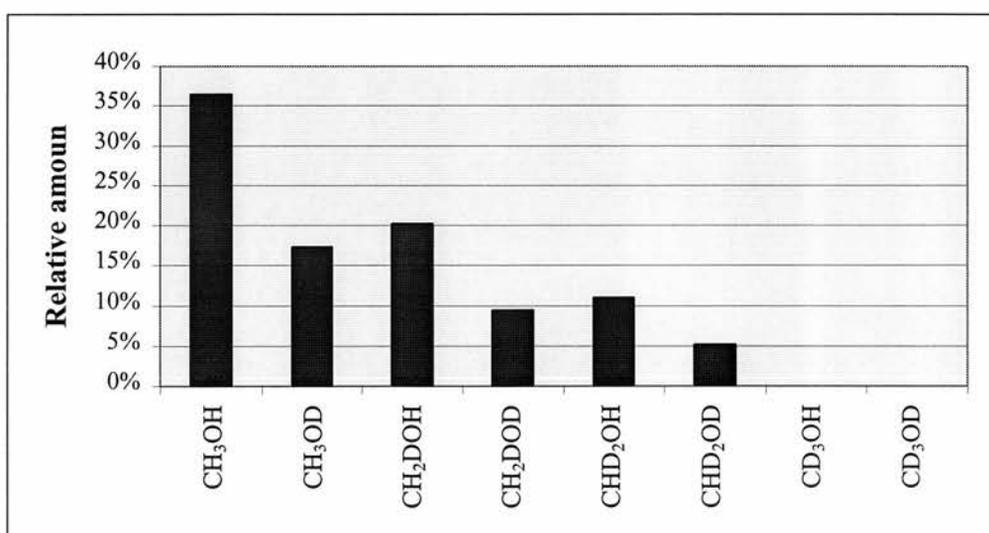


Figure 2.20; Isotopomer distribution used for H₂/D₂O simulation

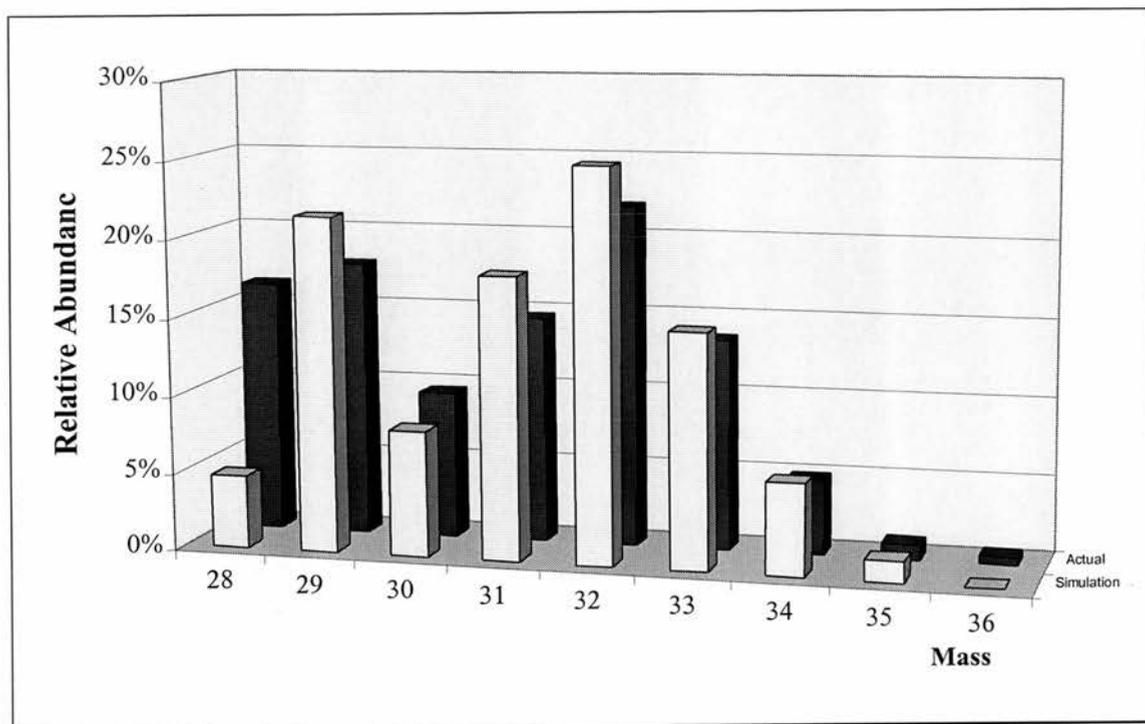


Figure 2.21; Observed and simulated mass spectrum for H_2/D_2O reaction

2.3 Conclusions

The hydrogenation of carbon monoxide by homogeneous catalysts is rarely studied, because of the efficiency of the industrial process catalysed by heterogeneous catalysts. However, the iodide promoted ruthenium system is able to catalyse the reaction in solution, even at a total pressure of only 110 bar and at 200 °C. Under these mild conditions the reaction is selective to methanol, but sensitive to changes in the partial pressure of CO and hydrogen. The rate of the reaction is dependent on the partial pressure of H_2 , but CO is required to prevent nucleation of the ruthenium cluster catalyst and the formation of ruthenium metal. The use of a high concentration of ionic iodide helps to maintain the catalyst in its active form even under the relatively low

partial pressure of carbon monoxide. The catalyst concentration also effects the amount of cluster formation, with low concentration preventing the build up of large and inactive ruthenium carbonyl clusters.

At the low partial pressures of CO used, temperature is another critical parameter. At low temperatures the reaction rate is very slow, but the catalyst breaks down and selectivity is very poor above 230 °C. Deuterium studies prove that the methanol produced is formed from gaseous hydrogen, rather than any other source of protons (such as the solvent), but addition of water causes some scrambling to be observed.

2.4 Experimental

2.4.1 General Techniques

Batch autoclave experiments were carried out within a glass liner in a 250 ml stainless steel or Hastalloy autoclave. A glass funnel was placed on top of the glass liner to help to maintain the contents within the liner. A 'turbo-effect' magnetic stirrer bar was used to aid mixing of gaseous reagents. For each experiment a new 'Elast-o-lion' O-ring was fitted, which was found to be suitable at temperatures of 200 °C or over.

Before the autoclave was sealed, the solid catalyst and KI were placed inside the glass liner. The autoclave was then fitted with stirrer bar, glass funnel and O-ring before being sealed. It was then gently flushed with argon 3 times, before the pre-mixed solvent and other liquids were added from a Schlenk tube. The autoclave was then flushed with the reagent gas [usually CO/H₂ (1:1)] three times, before being filled to the desired fill pressure (usually 70 bar). The autoclave was then heated using a heating band controlled electronically via an external thermocouple. (Typical internal autoclave

temperature profiles are shown below [Figure 2.22]. The temperatures quoted in the text are internal autoclave temperatures.)

After each reaction, the heating band was switched off and the autoclave allowed to cool to *ca.* 100 °C, before placing in an ice/water bath. When cool, the reaction mixture was removed via syringe, if possible, and stored under argon. The reaction products were analysed quantitatively using a Phillips PU4500 gas chromatograph fitted with a 25 m dimethylpolysiloxane stationary phase column. Either a Hewlett Packard 5890 GC attached to a Finnigan MAT INCOS 50 mass spectrometer, or a Hewlett Packard 5890 Series II Plus GC attached to a HP 5972 Series mass selective detector were used where appropriate. Methods of analysis of mass spectra of mixtures of methanol isotopomers are outlined in section 2.2.5.1.

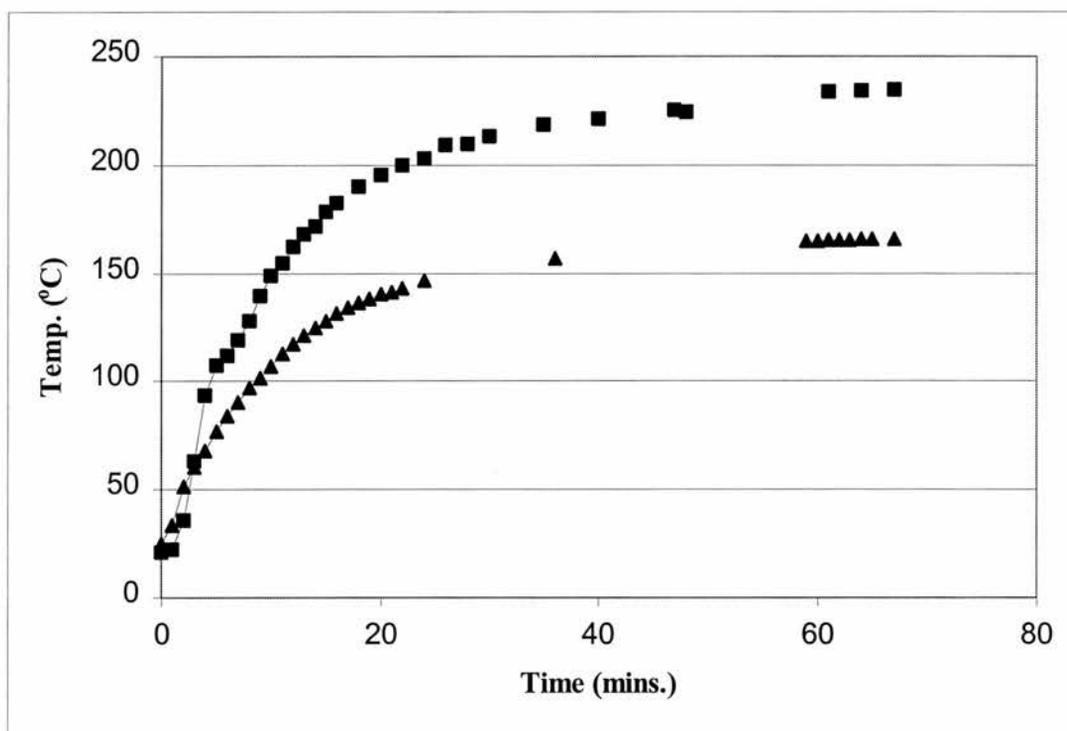


Figure 2.22; Internal autoclave temperature profiles (167 and 235 °C)

2.4.2 Materials

$\text{Ru}_3(\text{CO})_{12}$ was obtained from Strem, stored in its container over silica gel, and used without further purification. Potassium iodide was stored in an oven at 140 °C. NMP was purchased from Aldrich, dried by distillation under reduced pressure and stored in a Schlenk tube under dry argon. CO , CO/H_2 (1:1) H_2 and D_2 were purchased from BOC Gases. CO/H_2 (1:1) was sometimes passed through a carbon filter to remove trace impurities such as $\text{Fe}(\text{CO})_5$, but this was found to have no appreciable effect on the activity of the catalyst.

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CHAPTER 3

Direct Formation of Ethanoic Acid from Carbon Monoxide and Hydrogen

3.1 Introduction

Carbon monoxide and hydrogen represent a cheap and readily available feedstock for the synthesis of alkanes, alkenes and oxygen containing species such as alcohols, aldehydes and carboxylic acids. Many of these products (except methanol at moderately high temperatures) benefit from having negative standard Gibbs free energy changes relative to carbon monoxide and hydrogen. This means that catalytic synthesis processes for many bulk chemicals (including ethanoic acid) are thermodynamically feasible, should a suitable catalyst be available.

		ΔG^\ominus (kJ mol ⁻¹) ¹
CO + 3H ₂	→ CH ₄ + H ₂ O	-96.3
2CO + 5H ₂	→ C ₂ H ₆ + 2H ₂ O	-122.2
3CO + 7H ₂	→ C ₃ H ₈ + 3H ₂ O	-156.1
4CO + 9H ₂	→ n-C ₄ H ₁₀ + 4H ₂ O	-193.1
2CO + 4H ₂	→ C ₂ H ₄ + 2H ₂ O	-46.5
6CO + 12H ₂	→ 1-C ₆ H ₁₂ + 6H ₂ O	-201.5
CO + 2H ₂	→ CH ₃ OH	+21.3
2CO + 4H ₂	→ C ₂ H ₅ OH + H ₂ O	-28.4
2CO + 2H ₂	→ CH ₃ COOH	-24.2
2CO + 3H ₂	→ CH ₃ CHO + H ₂ O	-16.9

Since there are so many different products that can be made from carbon monoxide and hydrogen, processes that use synthesis gas as a feedstock can suffer selectivity problems. Even the industrially important Fischer-Tropsch process produces a mixture of different hydrocarbon products, despite attempts to make the reaction more selective. The direct formation of ethanoic acid from synthesis gas is likely to be even more

sensitive to selectivity problems, because it requires some (but not all) carbon-oxygen bonds to be broken.

Unlike many of the products that can be formed from synthesis gas, stoichiometry suggests that ethanoic acid can be made using a 1:1 ratio of CO and H₂, with no loss of material via side-product formation. This is significant because no synthesis gas is wasted by the formation of water or carbon dioxide. The ratio of CO to H₂ in the synthesis gas is also important. Synthesis gas derived from coal by steam reforming usually has a CO:H₂ ratio of 1:1 and would require no further adjustment to be used to make ethanoic acid. Methanol formation requires a CO:H₂ ratio of 1:2 and is well suited to synthesis gas derived from methane, which has a 1:2 ratio².

The formation of industrial chemicals from carbon monoxide and hydrogen is the subject of several reviews. An entire ACS Symposium Series volume is dedicated to "*Industrial Chemicals via C₁ processes*". Many aspects of synthesis gas chemistry are covered, with several chapters²⁻⁷ being particularly relevant to the production of ethanoic acid and methanol. The direct⁸ and indirect⁹ formation of C₂ compounds from synthesis gas is reviewed, with particular emphasis on the use of organometallic catalysts. Synthesis gas conversion processes catalysed by heterogeneous catalysts are briefly reviewed in reference 1.

Although reactions involving CO tend to require a catalyst, the direct reaction of carbon monoxide with aqueous HI can remarkably form ethanoic acid¹⁰. Using conditions of aqueous HI (65%, 40 ml) and 260 bar of CO pressure for 2 hours at 250 °C, ethanoic and methanoic acids were formed (0.05 g and 0.06 g respectively). A control reaction showed that the mechanism is unlikely to proceed via methanol or iodomethane. Further work¹¹ showed that methanal alone, or methanal and methanoic acid react with aqueous HI (65%) in the absence of CO at 130 °C to form ethanoic acid. It is likely that the reaction of CO with HI proceeds via methanal.

3.1.1 Bimetallic Homogeneous Catalysts Producing C₂ Products from CO/H₂

Various attempts have been made to change the selectivity of carbon monoxide hydrogenation catalysts to products containing two or more carbon atoms. Generally, this involves adding another metal to the hydrogenation catalyst to promote the carbonylation process. Depending on the nature of the carbonylated species and the amount of subsequent hydrogenation, different products can be formed. These include ethanol (via homologation of methanol), methyl methanoate (carbonylation of a methoxy-intermediate), 1,2-ethandiol (carbonylation of a hydroxy-methyl-intermediate followed by partial hydrogenation) and ethanoic acid (carbonylation of methanol or a methyl-intermediate). Any one of these processes would be of interest if the reaction could be made both active and selective to one product.

3.1.1.1 Formation of 1,2-ethandiol from CO/H₂

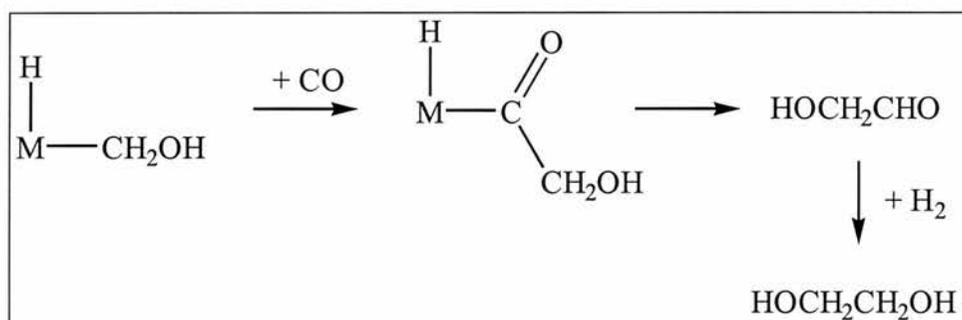


Figure 3.1; The carbonylation step favoured by Rh, producing 1,2-ethandiol

Addition of rhodium to the iodide-promoted ruthenium CO hydrogenation reaction has the effect of reducing the overall activity (Figure 3.2), but 1,2-ethandiol can become the major product^{4,12,13,14}. The rhodium catalyst is believed to aid carbonylation, particularly of a hydroxymethyl intermediate formed as part of the CO hydrogenation reaction (Figure 3.1), to form 2-hydroxyethanal that can react further to 1,2-ethandiol.

Standing concentrations of $[\text{HRu}_3(\text{CO})_{11}]^-$, $[\text{Ru}(\text{CO})_3\text{I}_3]^-$ and $[\text{Rh}(\text{CO})_2\text{I}_2]^-$ are observed. The rhodium complex is the active catalyst in the methanol carbonylation reaction (Figure 1.4), but it cannot act as a methanol carbonylation catalyst because no iodomethane or HI is present. The system is active at 230 °C and 800 bar of CO/H₂ (1:1) and requires these forcing conditions because of the decrease in overall activity caused by the use of the rhodium catalyst.

If the conditions of the CO hydrogenation reaction could be changed, so that the rhodium present would function as a methanol carbonylation catalyst, a high selectivity to methanol (rather than 1,2-ethandiol) would be preferred. The methanol produced would then be carbonylated by the rhodium catalyst to produce a high overall selectivity to ethanoic acid. Work by Dombek¹² suggests that a low mole fraction of rhodium causes the CO hydrogenation reaction to produce a high selectivity to methanol (Figure 3.2).

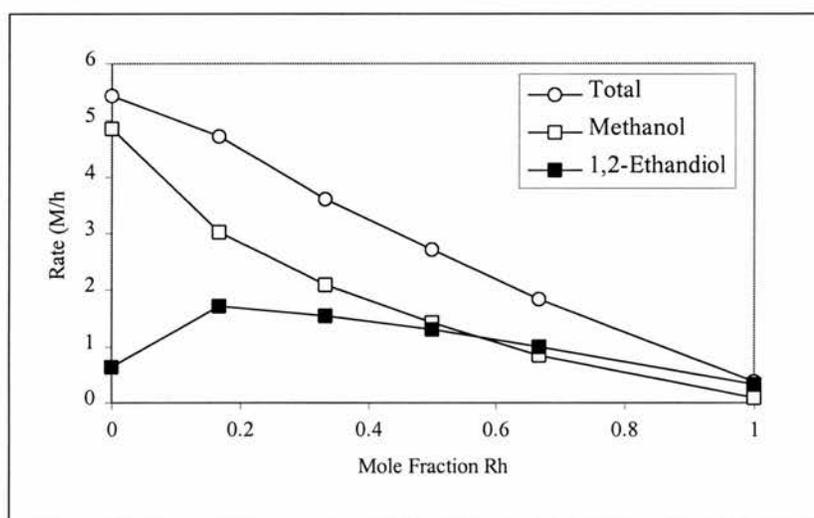


Figure 3.2; The effect of Rh mole fraction on the rates of methanol and 1,2-ethandiol formation¹²

Conditions; 6 mmol of total metal (Rh + Ru), NaI (18 mmol), NMP (75 ml), CO/H₂ (860 bar, 1:1), 230 °C.

Ethanoic acid is found to be a suitable solvent for the CO hydrogenation to 1,2-ethandiol reaction⁴, but private discussion¹⁵ suggests that it can inhibit the reaction if no promoters are used. Nitrogen-containing bases and alkali metal cations were found to have a beneficial effect on both the overall activity of the reaction and the selectivity to 1,2-ethandiol esters⁴. This effect may be due to the reduced acidity when these promoters are used, coupled with their polar nature, stabilising the hydride complexes required and preventing the formation of ion-pairs. Strong pressure dependence is observed, particularly for the formation of 1,2-ethandiol esters, highlighting the difficulty of forming C₂ products at low pressures.

3.1.1.2 Formation of Ethanoic Acid from CO/H₂

Bimetallic homogeneous catalysis has been used by Knifton^{3,16} to produce ethanoic acid from synthesis gas. The reaction proceeds via methanol and up to 95 wt% selectivity was achieved. Knifton investigated [Ru₃(CO)₁₂], [Ru(acac)₃] and RuO₂, with halide promoters to catalyse the hydrogenation of carbon monoxide reaction. Cobalt sources such as CoI₂ that formed [Co(CO)₄]⁻ under reaction conditions were then used to carbonylate the methanol to ethanoic acid. It was found that cobalt iodide produced the best selectivity to ethanoic acid, but other halides had comparable activity. Surprisingly, addition of I₂ or iodomethane suppressed the activity, with iodomethane almost completely inhibiting the reaction. The process was carried out using conditions of 482 bar and 220 °C in a low melting phosphonium halide (Bu₄PBr) solvent.

Unlike the iodide-promoted ruthenium catalysed CO hydrogenation only reaction, Knifton's bimetallic system is active even in the apparent absence of [HRu₃(CO)₁₁]⁻. [Ru(CO)₃I₃]⁻ is observed as the dominant ruthenium species. [HRu₃(CO)₁₁]⁻ is only detected at low iodide concentrations, where the methanol carbonylation step is slow, leading to alcohol products rather than ethanoic acid or ethanoate esters.

A similar catalytic system, using $[\text{Ru}_3(\text{CO})_{12}]$, $[\text{Co}_2(\text{CO})_8]$ and a phosphonium bromide promoter (n-heptyltriphenylphosphonium bromide) in basic solution, is also reported to produce ethanoic acid from synthesis gas¹⁷. A pressure of 460 bar CO/H_2 (1:1) at 220 °C was used (calculated from a fill pressure of 280 bar). Cobalt was found to be the only transition metal capable of promoting ethanoic acid production in association with ruthenium, although the identities of the other transition metals tested are not published.

3.1.2 Ethanoic Acid from CO/H_2 Using Heterogeneous Catalysts

Heterogeneous catalysts are known to produce ethanoic acid from carbon monoxide and hydrogen, but selectivity is a major problem. Oxide-supported rhodium catalysts are particularly active for the formation of oxygenated compounds containing two or more carbon atoms. Using a catalyst derived from Na_3RhCl_6 supported on alumina, ethanal is formed at 180 °C, even when the pressure of reactant gas is less than one atmosphere¹⁸. However, a mixture of products is obtained, including methanol, ethanol, methane, hydrocarbons and carbon dioxide.

Ethanal and methane are the major products when CO/H_2 (10 bar, 1:1) is passed over a rhodium catalyst supported on SiO_2 at 250 °C¹⁹. 15% conversion to ethanoic acid, based on carbon, is observed using SiO_2 as a support. In contrast, when the sodium form of zeolite Y is used as a support, the conversion to ethanoic acid rises to 50% under the same conditions. Several other compounds are formed, including methane, various hydrocarbons (up to at least C_6), ethanal and other oxygen containing compounds, although ethanol is not formed when NaY is used. The optimum $\text{CO}:\text{H}_2$ ratio for ethanoic acid selectivity is 3:1, when 67.8% of reacted CO is converted to ethanoic acid. Addition of water vapour causes a significant drop in both overall activity and selectivity to ethanoic acid.

The effect of the zeolite support on the selectivity of the reaction is discussed in the paper¹⁹. On the basis of results obtained, the active site is concluded to be a rhodium carbonyl cluster complex in contact with a rhodium metal cluster. The zeolite support can encourage the formation of rhodium carbonyl clusters within the pores of the zeolite, whereas SiO₂ does not favour rhodium carbonyl cluster formation. The transformation of metal particles into metal carbonyl clusters within the pores of a zeolite is discussed further in a recent paper²⁰.

Catalysts made up of rhodium nanoparticles supported on silica have been synthesised and tested for activity as carbon monoxide hydrogenation catalysts²¹. The size of each nanoparticle was found to be around 4.2 nm. Under CO hydrogenation conditions of 220 °C and a gas flow containing CO:H₂:Ar (3:6:1), methane was found to be the major product. The selectivity was found to be dependent on the rhodium content of the catalyst, with 0.6 wt% Rh producing 85.3% methane and 11.8% C₂₊ oxygenates, whereas with 3.5 wt% Rh the selectivity changed to 37.4% methane and 41.0% C₂₊ oxygenates, with the remainder comprising C₂₊ hydrocarbons. The identity of C₂₊ oxygenates is not disclosed.

Promoters can be used to change the activity and selectivity of a heterogeneous carbon monoxide hydrogenation catalyst. A rhodium catalyst promoted by MgO or CaO can produce methanol as the major product. However, MnO is able to enhance the selectivity of ethanol and ethanoic acid²². The function of the manganese sites is to stabilise bound ethanoate ligands as they are formed, inhibiting further hydrogenation or chain growth.

3.1.3 Other Alternative Feedstocks for Ethanoic Acid Production

Cheap and readily available materials such as methane or carbon dioxide represent economically attractive, but technically challenging, starting materials for the production of ethanoic acid. Methane can react with carbon monoxide and oxygen, using RhCl_3 as a catalyst precursor in water at $100\text{ }^\circ\text{C}$ ²³. The reaction can be promoted by palladium on carbon, HI, KI or HCl and labelling studies suggest that the reaction does *not* proceed via methanol. Methane can be converted to methanol at $200\text{ }^\circ\text{C}$ and 34 bar, using a platinum catalyst and sulfuric acid as an oxidising agent²⁴. The platinum catalyst (dichloro(η -2-{2,2'-bipyrimidyl})platinum(II) $[\text{Pt}(\text{bpym})\text{Cl}_2]$) produces a greater than 70% one-pass yield and a selectivity of 80%.

Methane and carbon monoxide have been used to form ethanoic acid, using ytterbium(III) ethanoate and manganese(II) ethanoate as catalysts, in the presence of sodium hypochlorite, in water²⁵. The reaction was studied using methane (20 bar) and carbon monoxide (10 bar) at just $40\text{ }^\circ\text{C}$. Unfortunately, the highest turnover number achieved was 69 (relative to ytterbium), when only $0.5\text{ }\mu\text{mol}$ of catalyst was used. In most of the experiments, when more catalyst was used, the amount of ethanoic acid tended to be similar to, or less than, the amount of ethanoate in ytterbium ethanoate and manganese ethanoate used as catalysts.

Ethanoic acid can be formed from iodomethane, carbon dioxide and hydrogen, using a homogeneous bimetallic catalyst²⁶. $[\text{Ru}_3(\text{CO})_{12}]$ and $[\text{Co}_2(\text{CO})_8]$ were used as catalyst precursors and no ionic iodide was used. The reaction was active at $150\text{ }^\circ\text{C}$, using an initial pressure of 40 bar at room temperature ($\text{CO}_2:\text{H}_2 = 1:1$). This is an interesting reaction and shows the versatility of $[\text{Ru}_3(\text{CO})_{12}]$ as a catalyst precursor. The reverse WGS reaction, forming carbon monoxide and water, followed by subsequent cobalt catalysed carbonylation of iodomethane is a likely route for the reaction mechanism. The authors, however, prefer the insertion of CO_2 into a Ru-C bond, followed by protonation to cleave the ethanoate ligand formed. Unfortunately, the amount of

ethanoic acid formed was less than the amount of iodomethane used. The highest yield of ethanoic acid was 2.5 mmol, relative to 5 mmol of iodomethane used.

Another alternative feedstock for ethanoic acid or methyl ethanoate production is methanol alone. A heterogeneous catalyst derived from $[\text{NEt}_4]_4[\text{Ru}(\text{SnCl}_3)_6]$, supported on CuO-ZnO/SiO_2 has been shown to be a potential system for this reaction²⁷. However, the activity of the system is very low, with even the most active experiment yielding less ethanoic acid and methyl acetate than the amount of ruthenium cluster impregnated onto the support.

3.1.4 Potential Benefits of a Ru/Rh Catalyst System for Ethanoic Acid Production

Knifton has achieved direct formation of ethanoic acid from carbon monoxide and hydrogen using a Ru/Co system (section 3.1.1.2). However, the conditions used for this process are relatively forcing and comparable to the conditions required for the cobalt catalysed carbonylation of methanol. Rhodium is a much more active carbonylation catalyst, capable of operating under much milder conditions than cobalt, so the use of a Rh/Ru system may allow the reaction to proceed at a lower temperature and pressure than that required by the Ru/Co system. This would make the process more attractive for industrial applications, but the use of the more active rhodium instead of cobalt has other potential benefits:

- i. Low pressure favours methanol over 1,2-ethandiol in the CO hydrogenation reaction (section 2.1.6).
- ii. Low temperature favours methanol in the equilibrium between CO, H₂ and methanol (section 2.1.1).

- iii. A fast carbonylation reaction prevents the build up of methanol, which can lead to a loss of selectivity to ethanoic acid (via homologation to ethanol, for example)

The conditions used for the Ru/Rh system must be chosen carefully, taking into account the many factors that influence the reaction. A low Rh:Ru ratio favours methanol over 1,2-ethandiol (section 3.1.1.1). High ionic iodide concentrations must be used to maintain the ruthenium catalyst in its active form under the low partial pressure of carbon monoxide used (section 2.1.5.2). The amount of water used must be balanced to maintain the rhodium catalyst in its active form for the carbonylation of methanol reaction (section 1.3.3.2). Some HI or iodomethane is required for the organic cycle within the rhodium catalysed methanol carbonylation reaction (section 1.3.1). The ruthenium catalysed CO hydrogenation reaction is also strongly influenced by the temperature and pressure used (chapter 2).

3.2 Results and Discussion

The iodide promoted, ruthenium catalysed hydrogenation reaction and the rhodium catalysed methanol carbonylation reaction are both complicated homogeneously catalysed systems. They are both dependent on several parameters to maintain the catalyst in the active form and to enable the reaction to proceed when the active catalyst is present. When the reaction is working, varying other parameters, particularly in the case of the CO hydrogenation reaction, can alter the selectivity. By combining the two systems to create ethanoic acid from carbon monoxide and hydrogen, the conditions required for each individual system must be compromised and may cause problems.

Studies on the iodide promoted, ruthenium catalysed CO hydrogenation reaction carried out in chapter 2 show that it is active (but slow) even at pressures of less than 120 bar. By adding rhodium and varying the reaction parameters, the reaction will be studied with the aim of producing ethanoic acid from carbon monoxide and hydrogen.

3.2.1 The Effect of Temperature

3.2.1.1 The Reaction at Low Temperature (167 °C)

At this temperature ethanoic acid could not be produced directly from carbon monoxide and hydrogen. From earlier work (see section 2.2.2), the hydrogenation of carbon monoxide reaction is very slow and dependent on the partial pressures of CO and hydrogen used at low temperatures. The table below shows some experiments studying the carbonylation of methanol reaction at 167 °C.

Table 3.1 shows that the rhodium catalysed carbonylation of methanol reaction is active in NMP solvent containing a high concentration of KI (expt. 14). Experiments 15 and 16 show that the reaction is still active when hydrogen and carbon monoxide are used, with ethanoic acid and esterified methyl ethanoate formed. Even when ruthenium is present, carbonylation to ethanoic acid still occurs, but ethanol is also formed (expt. 17). This proves that it is possible to form ethanoic acid from methanol, should any methanol be formed by the hydrogenation of carbon monoxide reaction. Experiment 17 also indicates that the ruthenium species can catalyse the homologation of methanol to ethanol, which can compete with carbonylation of methanol, reducing the selectivity to ethanoic acid.

Expt.	Ru ₃ (CO) ₁₂ (mmol)	Rh (mmol)	CO:H ₂ (fill pressure, bar)	Methanol (mmol)	Products
14	0	0.067	CO (70)	1.24	CH ₃ COOH (0.1 mmol)
15	0	0.077	1:1 (70)	2.47	CH ₃ COOH (2 mmol), CH ₃ COOCH ₃
16	0	0.076	1:1 (70)	12.36	CH ₃ COOH (3 mmol), CH ₃ COOCH ₃
17	0.115	0.072	1:1 (70)	12.36	CH ₃ COOH (0.1 mmol) CH ₃ CH ₂ OH

Table 3.1; The rhodium catalysed methanol carbonylation reaction

Conditions; RhCl₃.3H₂O used as the rhodium source, Ru₃(CO)₁₂ used as the ruthenium source where appropriate, NMP (5 ml), KI (0.664 g, 4 mmol), H₂O (0.1 ml, 5.56 mmol), CH₃I (40 µl, 0.64 mmol), 167 °C for 16 hours.

Expt.	Ru ₃ (CO) ₁₂ (mmol)	Rh (mmol)	H ₂ O (mmol)	CH ₃ I (mmol)	Products (mmol)
18	0.114	0.070	0	0	CH ₃ OH (0.30)
19	0.114	0.076	5.56	0	CH ₃ OH (2.00)
20	0.114	0.069	5.56	0.64	None
21	0.111	0	0	0.64	None

Table 3.2; The combined ruthenium and rhodium systems

Conditions; RhCl₃.3H₂O used as the rhodium source, Ru₃(CO)₁₂ used as the ruthenium source, NMP (5 ml), KI (0.664 g, 4 mmol), CO/H₂ (1:3, 70 bar at room temperature), 167 °C for between 14 and 19 hours.

Despite the activity of both the rhodium catalysed methanol carbonylation reaction and the ruthenium catalysed CO hydrogenation reaction at 167 °C, no ethanoic acid could be formed from CO and hydrogen using both systems at the same time. *Table 3.2* summarises results of reactions using both ruthenium and rhodium at 167 °C.

Experiments 18 and 19 show that rhodium does not effect the ability of ruthenium to catalyse the hydrogenation of carbon monoxide reaction. Methanol is formed in the presence of rhodium (and water). Unfortunately, when iodomethane is also used to enable the rhodium catalyst to carbonylate the methanol produced, neither methanol nor ethanoic acid is formed. The control reaction, experiment 21, confirms that addition of iodomethane prevents the formation of methanol under conditions otherwise previously used for the hydrogenation of CO (expt. 3, section 2.2.2).

3.2.1.2 The Reaction at High Temperature (235 °C)

At this high temperature, the ruthenium catalysed hydrogenation of carbon monoxide reaction is relatively active, but it produces methanol, ethanol and propanol (expt. 8, section 2.2.2). Unlike at 167 °C, the addition of rhodium, water and iodomethane to a reaction at 235 °C allows ethanoic acid and its methyl and ethyl esters to be formed. Metallic residues are observed on the glass liner after a reaction at this temperature. This is likely to be ruthenium metal, from decomposition of the ruthenium carbonyl catalyst. No hydrocarbons were observed in the liquid phase, but ruthenium metal is known to catalyse the complete hydrogenation of CO to methane and linear alkanes²⁸. Hydrogenation of the NMP solvent was observed, forming N-methylpyrrolidine, and indicates the powerful reducing nature of the reaction mixture at 235 °C.

Although the reaction is not selective to ethanoic acid at this temperature, the production of ethanoate groups is encouraging. The reaction is much more active at

235 °C and iodomethane does not prevent methanol formation, as it did at 167 °C. This is in contrast to the Ru/Co system studied by Knifton¹⁶, where addition of iodomethane (at 220 °C, 482 bar CO/H₂ [1:1]) is found to deactivate the catalyst and stop the reaction. This difference may be caused by the higher rate of carbonylation by rhodium, when compared to cobalt, which would prevent a build up in the standing concentration of iodomethane.

3.2.1.3 The Reaction at Moderate Temperature (200 °C)

Expt.	Temp (°C)	H ₂ O (mmol)	CH ₃ I (mmol)	NMP (ml)	Products (mmol)
20	167	5.56	0.64	5	None
22	200	27.78	0.64	5	CH ₃ OH (1.2), CH ₃ CH ₂ OH, CH ₃ COOH (trace)
23*	200	55.56	8.03	7.5	CH ₃ COOH (3)
24	235	5.56	0.64	5	CH ₃ OH (5.8), CH ₃ CH ₂ OH, CH ₃ CH ₂ CH ₂ OH, CH ₃ COOH (trace), CH ₃ COOCH ₃ , CH ₃ COOC ₂ H ₅

Table 3.3; The effect of temperature on the Ru/Rh system

Conditions; RhCl₃ (0.0147 g, 0.07 mmol), Ru₃(CO)₁₂ (0.071 g, 0.111 mmol), KI (0.664 g, 4 mmol), CO/H₂ (1:3, 70 bar at room temperature), 19 hours.

*KI (0.830 g, 5 mmol) and CO/H₂ (1:1) used.

When an intermediate temperature of 200 °C is used, ethanoic acid is often the only product observed by GC or GCMS. When a CO/H₂ ratio of 1:3 is used, methanol and ethanol have been observed, but only ethanoic acid is produced when a 1:1 CO/H₂ ratio is used. Formation of N-methylpyrrolidine, via hydrogenation of NMP, is observed when pure hydrogen or a 1:3 ratio of CO and H₂ is used, but it is less significant when the CO/H₂ ratio is 1:1.

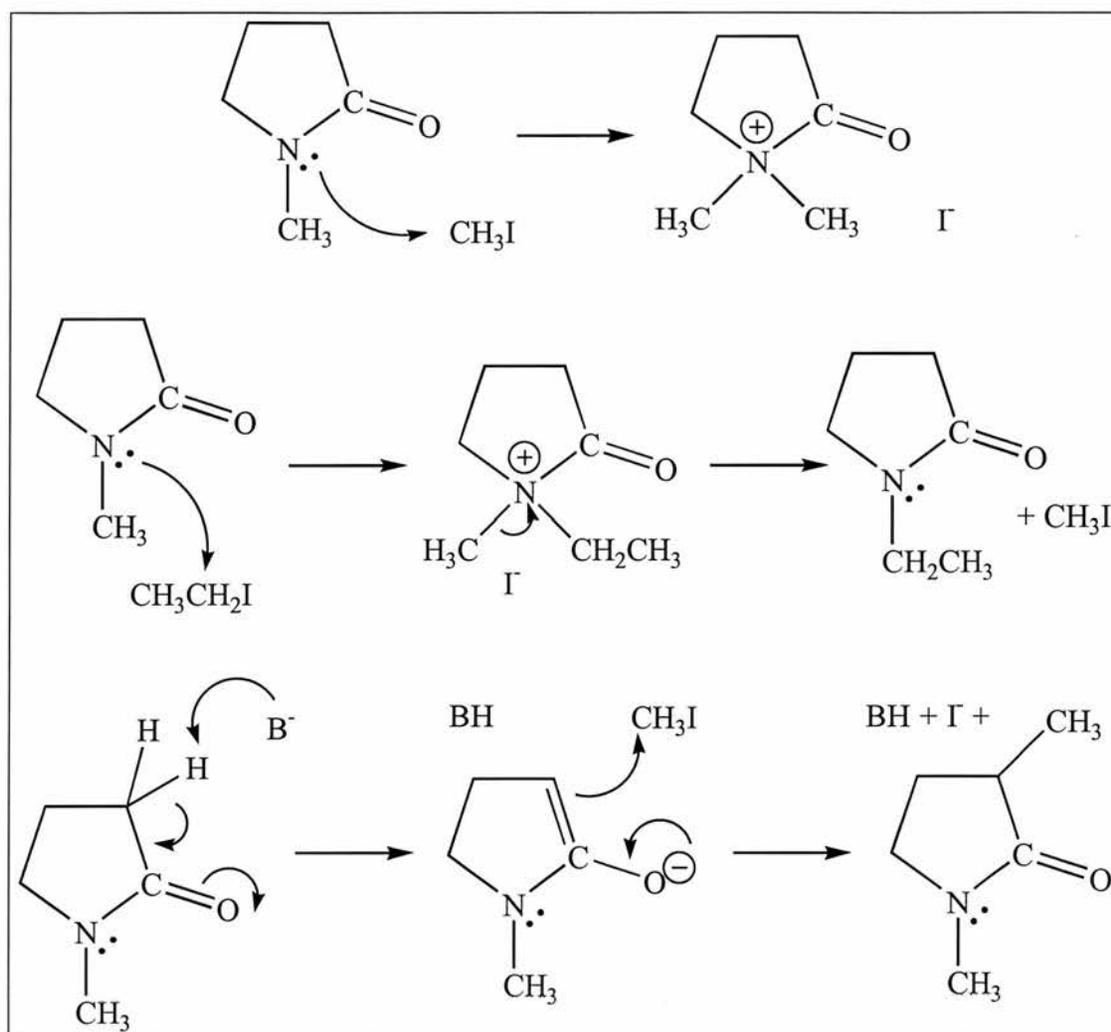


Figure 3.3; Potential solvent degradation reactions: quaternisation, substitution at nitrogen and substitution on the ring

Other solvent derived compounds with masses 14 and 28 mass units higher than NMP have also been observed at a similar retention time to NMP by GCMS, after reactions at

200 °C or above. These compounds could be N-ethyl and N-propylpyrrolidinone respectively, which would question the role of NMP as an inert solvent with no contribution to the production of ethanoic acid (or methanol). Alternatively, they could be formed by deprotonation of a ring proton of NMP, followed by electrophilic attack of iodomethane on the anion, methylating the ring (*Figure 3.3*).

3.2.2 ^2H (D) Labelling Studies

Deuterium labelling studies on the ruthenium catalysed CO hydrogenation reaction proved that the methyl protons of methanol came from hydrogen gas. Since degradation products of NMP have been observed after reactions at high temperature, or when using iodomethane or a high partial pressure of hydrogen, it is necessary to confirm that ethanoic acid is not formed from NMP under reaction conditions. It is also necessary to show that the ethanoic acid produced does not simply come from the added iodomethane alone. In order to address these problems, deuterium labelling studies have been carried out to follow the distribution of deuterium in the products.

The combined hydrogenation and carbonylation reaction is more complicated than just the hydrogenation of CO reaction. Fortunately, the mass spectrum for ethanoic acid^{29,30} has a large molecular ion signal, which is the only significant ion close to $m/z = 60$. The relative sizes of the peaks between $m/z = 60$ and 64, therefore, represents the relative amounts of isotopomers of ethanoic acid containing zero to four deuterium atoms, respectively.

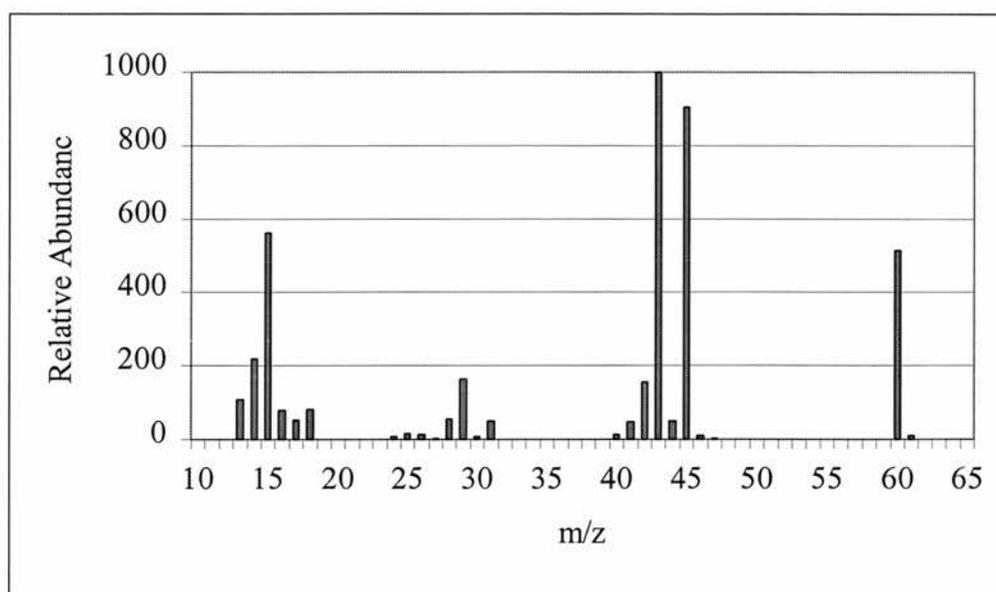


Figure 3.4; Mass spectrum of ethanoic acid^{29,30}

The precise identity of each isotopomer is more difficult to obtain by mass spectrometry. Identification of mixtures containing pairs of isotopomers with the same mass (such as CH_3COOD and CH_2DCOOH) requires the use of the fragmentation pattern between $m/z = 42$ and 46 . Major ions for CH_3COOH in this region are at $m/z = 45$ $[\text{COOH}]^+$, 43 $[\text{CH}_3\text{CO}]^+$ and 42 $[\text{CH}_2\text{CO}]^+$. The mass spectrum of a mixture of isotopomers of ethanoic acid can be simulated by using the mass spectrum for ethanoic acid to calculate the mass spectrum for each isotopomer of ethanoic acid in the m/z ranges 42 to 46 and 60 to 64 . This allows the mass spectrum of a mixture of isotopomers to be calculated, which can be compared with the observed mass spectrum. It is assumed that isotope effects do not effect the fragmentation patterns for each isotopomer. This assumption may not be completely valid, so the simulated mass spectra should be treated as a useful guide to the analysis of mass spectra of mixtures of isotopomers, rather than a method of calculating the exact amount of each isotopomer present.

3.2.2.1 The use of D₂ in the Rh/Ru System

If CD₃COOD or CD₃COOH were the only isotopomers of ethanoic acid to be produced from a reaction using D₂ as the only source of deuterium, and the solvent remained undeuterated, it would be possible to rule out NMP as a source of methyl groups in the formation of ethanoic acid. However, since CH₃I is present, some CH₃COOH(D) should be formed. No other isotopomers of ethanoic acid, containing both H and D in the methyl group, would be expected and the ratio of CH₃ to CD₃ groups would reflect the amount of ethanoic acid produced by CO hydrogenation and CH₃I carbonylation, respectively. However, when this reaction is carried out ethanoic acid is formed and its mass spectrum is shown in *Figure 3.5*. This indicates a mixture of isotopomers of ethanoic acid is formed and the calculated isotopomer distribution is shown in *Figure 3.6*. Some of the NMP solvent is also deuterated with one or two deuterium atoms.

The conditions used for this reaction were; Ru₃(CO)₁₂ (0.0722 g, 0.113 mmol), RhCl₃ (0.0177 g, 0.085 mmol), KI (0.831 g, 5.0 mmol), CH₃I (0.5 ml, 8.03 mmol), H₂O (1 ml, 55.6 mmol), NMP (7.5 ml), CO/D₂ (1:1, 70 bar at room temperature), 200 °C for 21 hours.

In this reaction, 3 mmol of ethanoic acid was produced. This is less than the amount of iodomethane used (8 mmol). It is therefore possible that all of the ethanoic acid produced could have been made by carbonylation of iodomethane, with none being formed from CO and deuterium. However, the isotopomer distribution of the ethanoic acid produced suggests that deuterium has been used to produce a significant proportion of the ethanoic acid. H/D scrambling of the methyl protons of ethanoic acid has occurred, but 80% of the ethanoic acid produced contains at least one D in the methyl group.

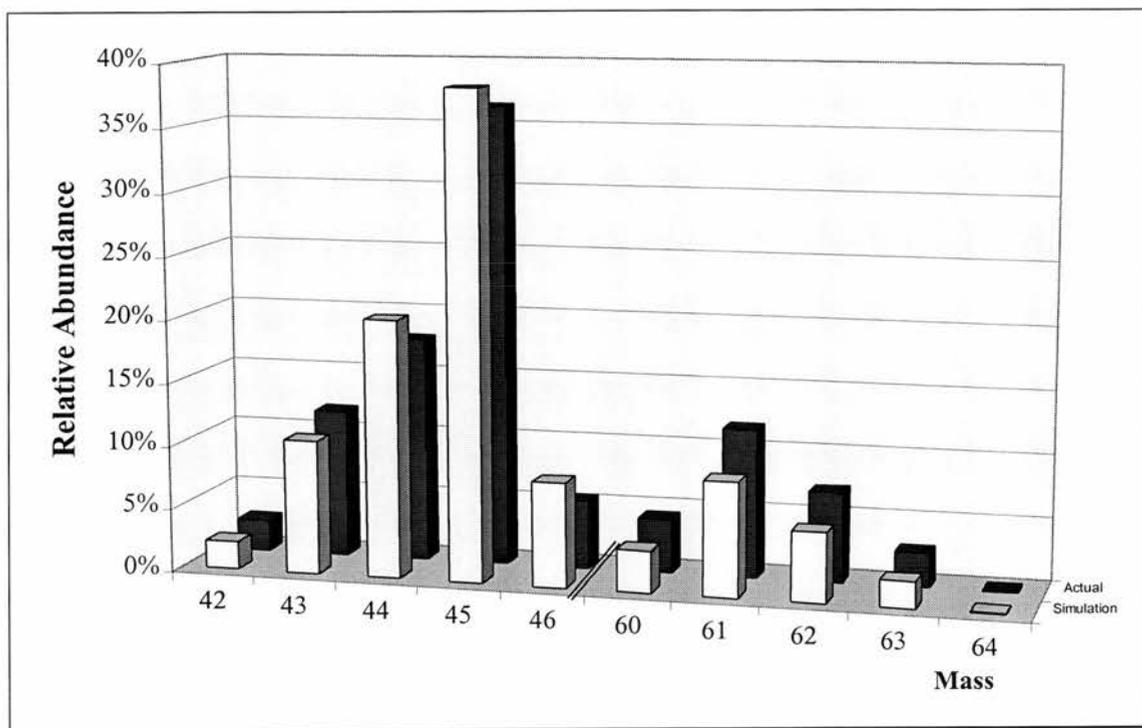


Figure 3.5; Comparison of simulated and observed MS after a reaction using D_2

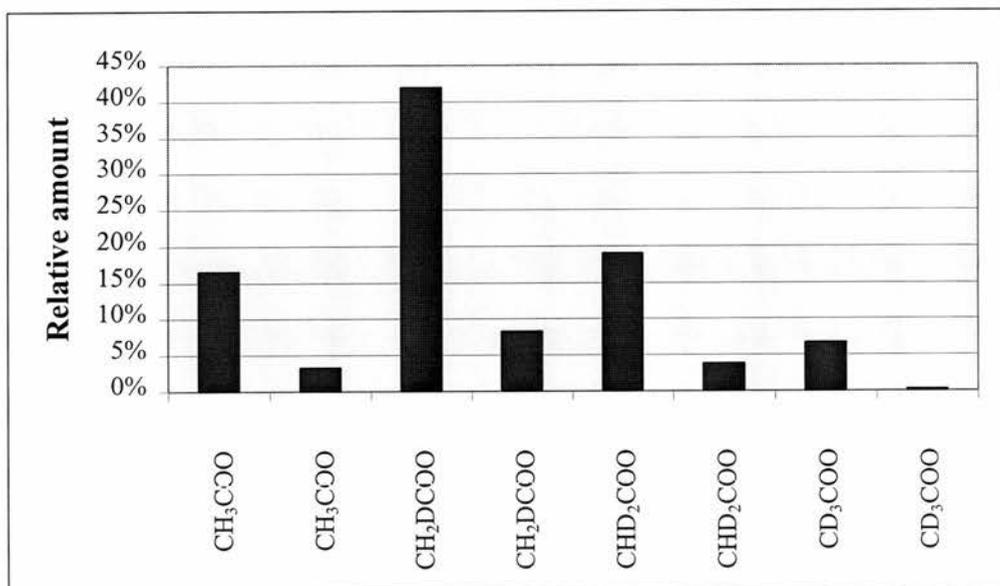


Figure 3.6; Ethanoic acid isotopomer distribution produced using D_2

Some of the H/D scrambling in the ethanoic acid produced can be attributed to unlabelled water, which causes scrambling of methyl protons in methanol formed by the hydrogenation of carbon monoxide reaction (section 2.2.5.3). However, ethanoic acid is less deuterated than would be expected by this mechanism alone. Some CH_3 containing ethanoic acid will have been formed from CH_3I , but another mechanism of H/D scrambling is exchange of protons after ethanoic acid itself has been formed. H/D exchange of methyl protons in ethanoic acid has been observed by others³¹, and has been used to prepare a variety of α -deuterated carboxylic acids, including ethanoic acid, from unlabelled acids and D_2O in basic solution at $150\text{ }^\circ\text{C}$ ³².

Before any scrambling effects, ethanoic acid produced by carbonylation of CH_3I would contain CH_3 groups, while ethanoic acid formed from CO and D_2 would contain CD_3 groups. Since unlabelled H_2O and NMP are used, scrambling of methyl protons of ethanoic acid will generally be in the direction of replacing D for H. This suggests that most of the ethanoic acid has been produced via hydrogenation of carbon monoxide, with subsequent D to H exchange, rather than simply from carbonylation of CH_3I .

It is likely that methanol is produced with an isotopomer distribution similar to that observed for the CO hydrogenation only reaction (section 2.2.5.3). This methanol is then converted into ethanoic acid with a similar distribution of isotopomers, but exchange of methyl deuterium atoms for protons from unlabelled water produces the distribution of ethanoic acid isotopomers observed.

3.2.2.2 The use of CD_3I in the Ru/Rh System

When CD_3I is used as the only source of deuterium, a mixture of isotopomers of ethanoic acid is again produced (*Figure 3.8*) and the corresponding mass spectrum is shown in *Figure 3.7*. This highlights the ability of methyl groups of ethanoic acid to exchange protons, since any methanol formed from hydrogenation of carbon monoxide would only contain CH_3 methyl groups. Any ethanoic acid produced from this methanol would also contain only CH_3 methyl groups, whereas ethanoic acid produced from CD_3I would contain only CD_3 methyl groups. Scrambling of these CH_3 or CD_3 methyl groups of ethanoic acid then takes place to produce the observed isotopomer distribution.

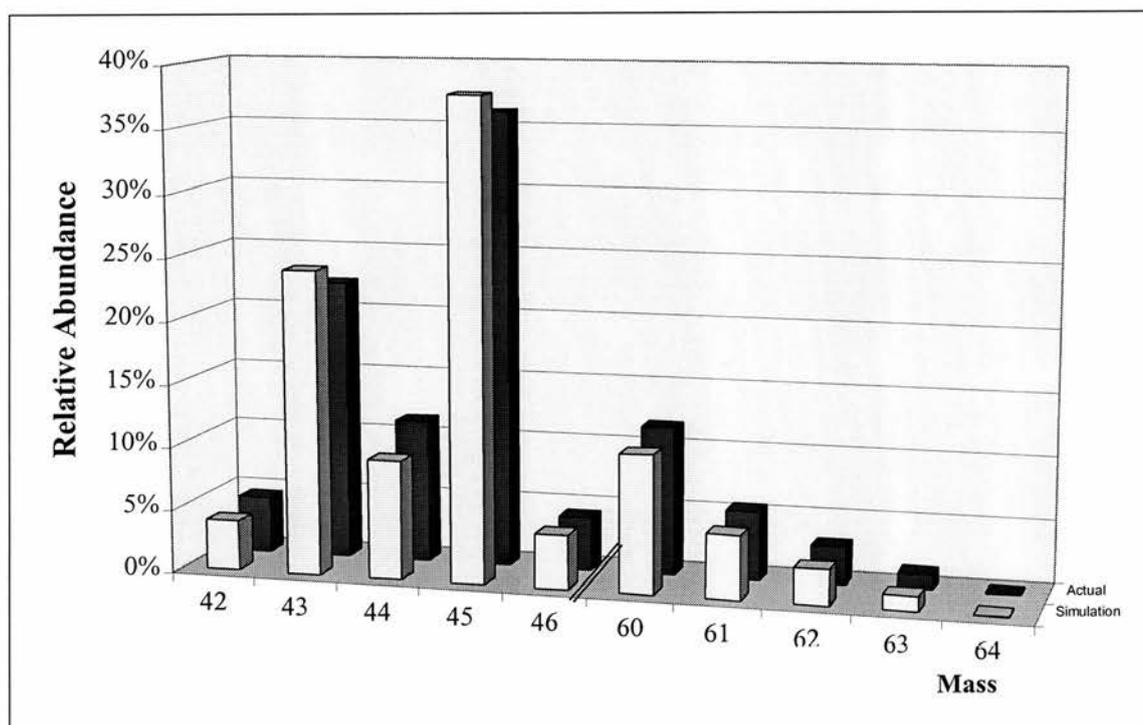


Figure 3.7; Comparison of simulated and observed MS after a reaction using CD_3I

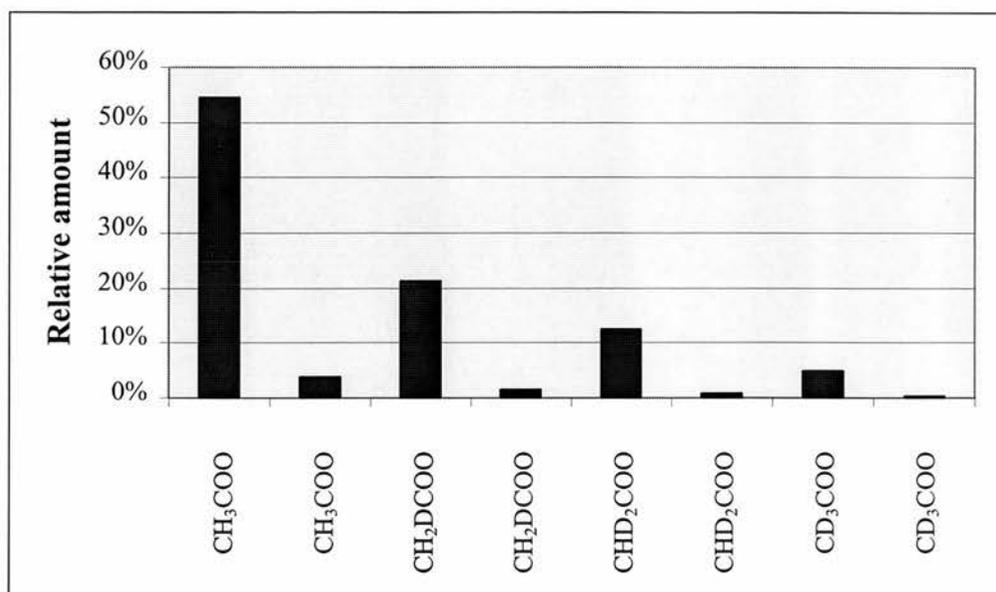


Figure 3.8; Distribution of ethanoic acid isotopomers produced using CD_3I

The conditions used for this reaction were; $Ru_3(CO)_{12}$ (0.0715 g, 0.112 mmol), $RhCl_3$ (0.0137 g, 0.066 mmol), KI (0.839 g, 5.05 mmol), CD_3I (0.5 ml, 7.9 mmol), H_2O (1 ml, 55.6 mmol), NMP (10 ml), CO/H_2 (1:1, 70 bar at room temperature), 200 °C for 18 hours.

8 mmol of ethanoic acid was produced in this reaction, which is similar to the amount of CD_3I used. It is possible that all of the ethanoic acid could come from carbonylation of the iodomethane used, but much more CH_3 containing ethanoic acid is produced in this reaction, than when D_2 and CH_3I were used (Figure 3.6), suggesting that some ethanoic acid is formed from hydrogen gas. Since unlabelled water and NMP are used, scrambling of protons would take place in the direction of replacing D for H, so unlabelled H becomes incorporated into any CD_3COOH produced from CD_3I and CO.

No deuterium was observed in the NMP, in contrast to the previous reaction, using D_2 and CH_3I . This suggests that exchange of methyl groups on NMP via reversible quaternisation with iodomethane is not significant. Instead, NMP has two protons on a carbon atom adjacent to its CO group, which are slightly acidic due to enol-like stabilisation of the corresponding anion. For deuteration to occur at this site, a high concentration of acidic deuterium atoms must be present, which is not the case when CD_3I is used as the only source of deuterium.

3.2.2.3 The use of D_2 , CD_3I and D_2O

In this reaction, the only source of unlabelled protons is the NMP solvent. Therefore, this is an inverse of a reaction using deuterated NMP as the only source of deuterium. Ethanoic acid is produced with a significant proportion of $C_2H_3DO_2$, $C_2H_2D_2O_2$ and $C_2HD_3O_2$ isotopomers, as shown by the relative sizes of the molecular ions in the mass spectrum below (*Figure 3.9*). Only trace amounts of CH_3COOH and CD_3COOD are formed. The NMP is deuterated after this reaction: mainly containing one or two deuterium atoms, but a small proportion containing 3,4 or 5 deuterium atoms.

It is clear from the mass spectrum of the ethanoic acid produced that there has been significant H/D scrambling. The lack of significant quantities of ethanoic acid containing CH_3 or CD_3 groups makes it impossible to ascertain the origins of the ethanoic acid produced. Indeed, the H/D scrambling is so great that the mass spectrum is similar to that expected for a mixture of isotopomers where the identity of each H/D is left completely to chance (*Figure 3.10*). This would produce a characteristic pattern of molecular ion peaks, with a maximum intensity at $m/z = 62$ due to the higher chance of the methyl group of ethanoic acid containing *both* H and D.

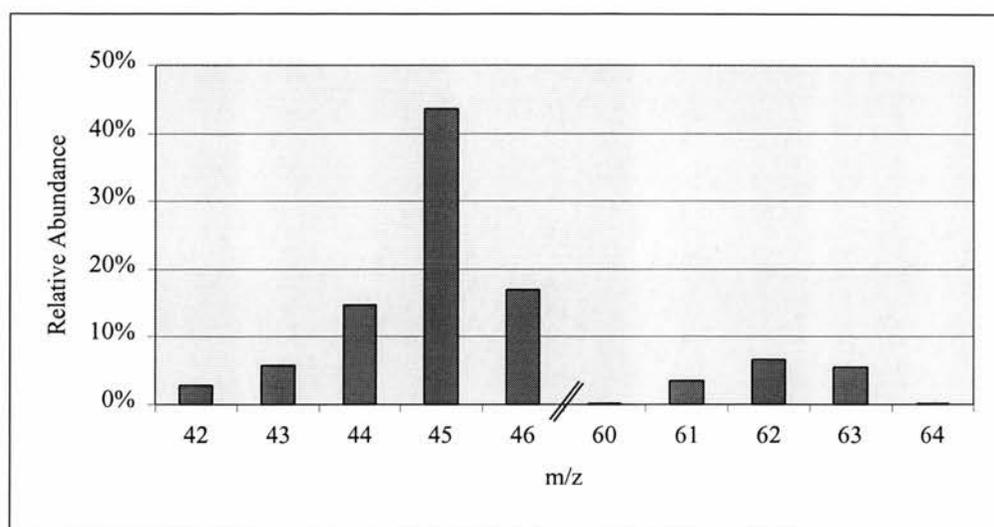


Figure 3.9; Observed MS of ethanoic acid produced

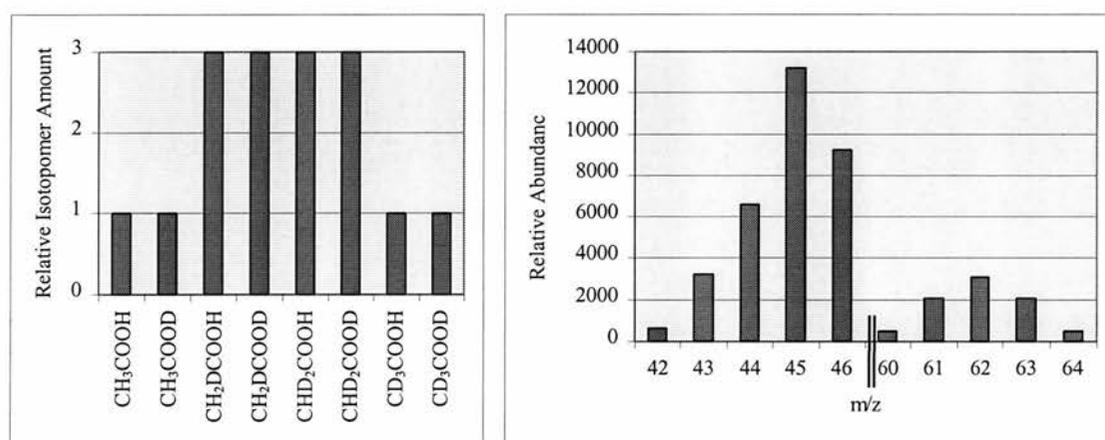


Figure 3.10; The statistical distribution of isotopomers of ethanoic acid using a H:D ratio of 1:1 and the simulated mass spectrum for this mixture

The relative sizes of peaks at $m/z = 45$ and 46 give an indication of the OH:OD ratio, as they are mainly due to the $[\text{COOH}(\text{D})]^+$ fragment ion. Thus, the OH:OD ratio in the ethanoic acid produced must be greater than one. The relative sizes of peaks at $m/z = 61$ and 63 give an indication of the overall H:D ratio. Since the 63 peak is bigger than that at 61, there is slightly more D than H in the overall mixture. Using a OH:OD ratio of 3:1 and a CH:CD ratio of 2:3 produces the isotopomer distribution shown in *Figure 3.11*, and a mass spectrum similar to that observed (*Figure 3.12*).

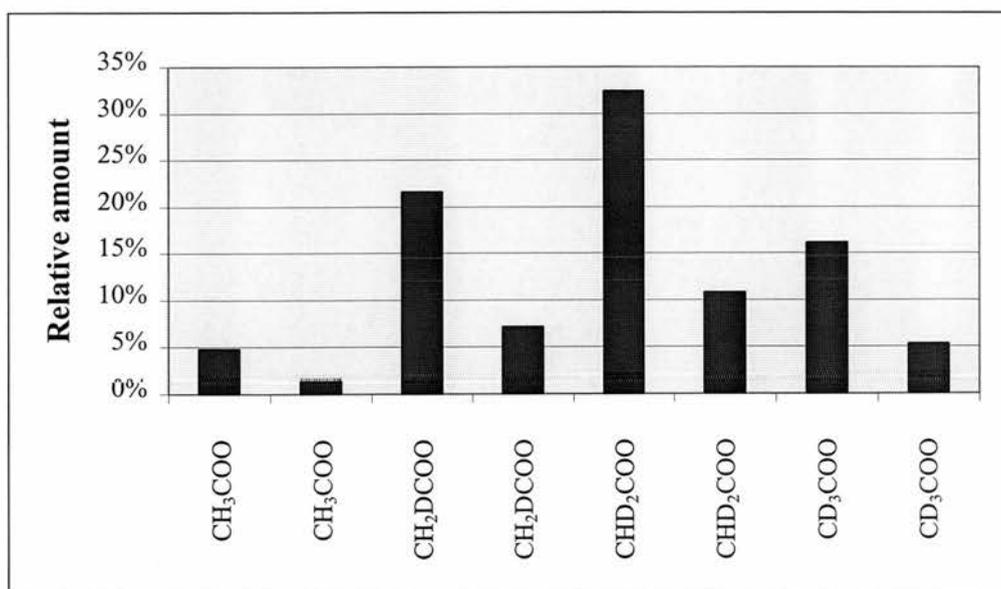


Figure 3.11; Isotopomer distribution using OH:OD = 3:1 and CH:CD = 2:3

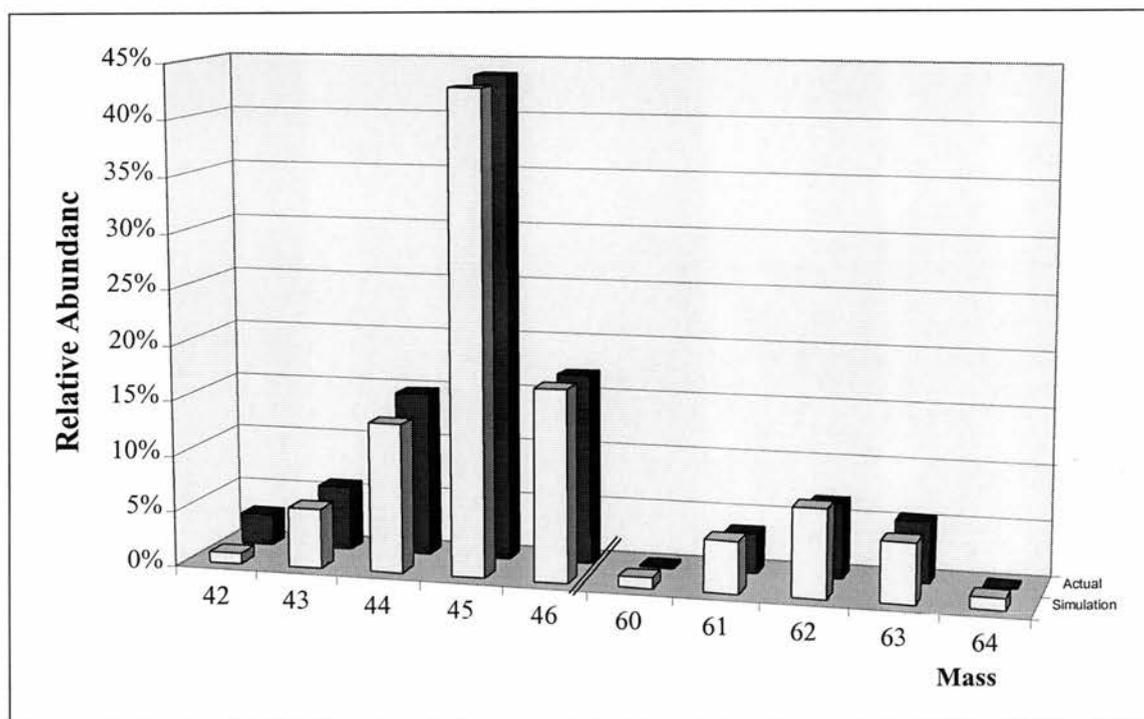


Figure 3.12; Simulated mass spectrum using OH:OD = 3:1 and CH:CD = 2:3 vs. observed MS for D₂, D₂O and CD₃I experiment

This experiment shows that H/D scrambling is significant under the conditions required for the direct formation of ethanoic acid from CO and H₂ reaction. Deuterium labelling in the NMP after the reaction shows that acidic protons and the N-methyl group can exchange during the reaction. This allows unlabelled protons to be incorporated into the ethanoic acid produced, which could continue to exchange protons after it is formed. This experiment used more deuterium than other experiments, so the overall H:D ratio is closer to one, allowing scrambling effects to be more apparent.

The deuterium labelling experiments on the direct formation of ethanoic acid from CO and hydrogen reaction are less conclusive than for the CO hydrogenation reaction. The use of water and iodomethane make more scrambling mechanisms available and the protons of ethanoic acid itself can scramble further under reaction conditions. It was hoped that deuterium labelling studies would be able to prove that NMP is not directly involved in the formation of ethanoic acid, and that ethanoic acid is produced from CO and H₂, rather than simply from carbonylation of iodomethane. Unfortunately H/D scrambling complications prevent these conclusions being drawn unequivocally, but the ethanoic acid isotopomer distributions suggest that at least some ethanoic acid is derived from hydrogen gas.

3.2.3 ^{13}C Labelling Studies

^{13}C labelling offers advantages over deuterium labelling because scrambling of labelled and unlabelled atoms is less likely. If $^{13}\text{CH}_3\text{I}$ is used as the only source of labelled carbon, the distribution of labelled carbon in ethanoic acid produced will provide evidence for the relative amount of ethanoic acid formed from hydrogenation of CO, compared to simple carbonylation of iodomethane. Scrambling of the methyl group of NMP, via quaternisation, can also be studied.

This experiment used standard conditions of $\text{Ru}_3(\text{CO})_{12}$ (0.0730 g, 0.114 mmol), RhCl_3 (0.0180 g, 0.086 mmol), KI (0.837 g, 5.04 mmol), $^{13}\text{CH}_3\text{I}$ (0.5 ml, 8.0 mmol), H_2O (1 ml, 55.6 mmol), NMP (10 ml), CO/H_2 (1:1, 70 bar at room temperature), 200 °C for 18 hours.

4.9 mmol of ethanoic acid was produced and GCMS of the reaction products reveals that 47% of the ethanoic acid produced contained no labelled carbon atoms, suggesting it originated from carbon monoxide. The remaining 53% contained one labelled carbon atom, which would be formed via carbonylation of labelled iodomethane. No labelling is observed in the NMP solvent, although a 13:1 excess of NMP over CH_3I is used, so only a small, but observable proportion would be labelled if reversible quaternisation takes place. 5.4 mmol of $^{13}\text{CH}_3\text{I}$ is not accounted for by incorporation into ethanoic acid. If all of this labelled iodomethane were to exchange for unlabelled methyl groups in NMP, the (M+1) peak in the MS of NMP would increase from a relative abundance of 5% to 10%.

3.2.3.1 Summary of Isotopic Labelling Results

Source of labelling	Conclusions
D ₂	Most of ethanoic acid produced contains at least one D in the methyl group. Scrambling in D to H direction suggests most of ethanoic acid is produced from deuterium gas, then scrambled to form distribution observed. NMP labelled with one or two D atoms.
CD ₃ I	High proportion of CH ₃ COOH produced. No labelling of NMP observed, suggesting exchange of methyl groups is not significant. More H in ethanoic acid produced than in reaction using D ₂ suggests that the hydrogen gas is incorporated, but scrambling in D to H direction exaggerates amount of H in the ethanoic acid.
D ₂ , D ₂ O and CD ₃ I	Extensive H/D scrambling. CD ₃ COOD(H) expected, but NMP supplies H to produce the isotopomer mixture observed. Labelled NMP indicates exchange of protons (and methyl groups to a lesser extent).
¹³ CH ₃ I	47:53 unlabelled and singly labelled ethanoic acid produced. No labelling observed in NMP. Suggests labelled ethanoic acid is produced from iodomethane and unlabelled product is formed from unlabelled CO.

Table 3.4; Summary of isotopic labelling experiments

3.2.4 Other Batch Autoclave Reactions

In order to probe the combined hydrogenation of carbon monoxide and subsequent carbonylation of methanol reaction, a series of reactions have been carried out, without certain components. The general reaction contains ruthenium, rhodium, KI, water, iodomethane, carbon monoxide, hydrogen and the NMP solvent. When ruthenium or hydrogen are omitted (deactivating Ru catalysed CO hydrogenation), rhodium catalysed carbonylation of iodomethane would be expected to produce some ethanoic acid. When rhodium or iodomethane are omitted, the ruthenium catalysed hydrogenation of carbon monoxide should still be active.

3.2.4.1 The Reaction in the Absence of Ru or Hydrogen

Expt.	Ru ₃ (CO) ₁₂ (mmol)	Rh (mmol)	CO/H ₂	CH ₃ COOH produced (mmol)
25	0.112	0.066	70 bar (1:1)	8.0
26	0	0.087	70 bar (1:1)	9.8
27	0.106	0.070	70 bar (CO)	11.1

Table 3.5; The effect of removing ruthenium or hydrogen

When the ruthenium catalysed CO hydrogenation reaction is prevented, by omission of either ruthenium or hydrogen (expts. 26 and 27), ethanoic acid is produced via carbonylation of iodomethane as expected. The amount of ethanoic acid produced is slightly more than the amount of iodomethane used (8 mmol), and is also more than when ruthenium is included. Iodomethane is rarely observed in the reaction products when ruthenium is present, but in experiments 26 and 27, some iodomethane is observed by GCMS after the reaction is complete. The reason for more ethanoic acid

being produced than the amount of iodomethane used is difficult to explain. It may indicate that the methyl group of NMP can react to form ethanoic acid, or it may be that the amount of ethanoic acid measured by GC is erroneously high.

3.2.4.2 The Reaction in the Absence of Iodomethane

In a reaction using $\text{Ru}_3(\text{CO})_{12}$, RhCl_3 , KI , H_2O , NMP and CO/H_2 (1:1) at 200 °C with no iodomethane present, no ethanoic acid is produced. Methanol (0.61 mmol) is produced by hydrogenation of carbon monoxide and a similar amount of 2-hydroxyethanal is observed by GCMS.

The lack of ethanoic acid production is good evidence that NMP does not contribute to ethanoic acid formation. The carbon monoxide hydrogenation reaction is active, although less methanol was produced than under similar conditions using just ruthenium, KI , NMP and CO/H_2 (section 2.2).

The formation of 2-hydroxyethanal is interesting and is only observed under these conditions. When ruthenium is the only transition metal catalyst present, methanol is the only carbon monoxide hydrogenation product at 200 °C and 110 bar of CO/H_2 . No 1,2-ethandiol is observed under these conditions, unlike at higher pressures^{13,33}, but 2-hydroxyethanal is an intermediate in the formation of 1,2-ethandiol and can be formed by hydroformylation of methanal⁸. The rhodium catalyst appears to change the selectivity of carbon monoxide hydrogenation towards the carbon-carbon bond-containing product, 2-hydroxyethanal, because of its preference for carbonylation over hydrogenation. However, when iodomethane is used as well as rhodium and ruthenium, methanol is intercepted and is carbonylated to ethanoic acid, with no methanol or 2-hydroxyethanal observed at the end of the reaction.

3.2.4.3 The Reaction in the Absence of Rhodium

When ruthenium is present, but rhodium is omitted from the reaction mixture, hydrogenation of carbon monoxide should still occur, but carbonylation to ethanoic acid is not expected. When Ru, KI, water, CO/D₂ and NMP were used, methanol was produced (section 2.2.5.3), but when Ru, KI, iodomethane, CO/H₂ and NMP were used, iodomethane was found to inhibit the reaction (expt. 21, *Table 3.2*).

However, when water *and* iodomethane are used, together with Ru, KI, CO/H₂ and NMP, a trace amount of ethanoic acid is formed, with no methanol observed. This batch autoclave result is confirmed by a reaction carried out in an autoclave fitted with a ballast vessel. The ballast vessel reaction used Ru₃(CO)₁₂ (0.7086 g, 0.43% w/w), KI (8.32 g, 5.03% w/w), NMP (135.02 g, 81.62% w/w), CH₃I (11.38 g, 6.88% w/w), H₂O (10 g, 6.04% w/w) and CO/H₂ (1:1) held at 110 bar at 200 °C; 10 times the amount of reagents, compared to the batch autoclave reaction. 17.4 mmol of ethanoic acid was produced, equivalent to 21.7% of the iodomethane used.

Ruthenium is able to catalyse the carbonylation of methanol to ethanoic acid³⁴, but it is less active than the rhodium system. The ruthenium system also reacts via a different mechanism based on [Ru(CO)₄I₂], which has been less intensively studied than the rhodium reaction. Iodomethane is not carbonylated by the ruthenium system³⁵ (as observed in expt. 21, *Table 3.2*). Instead, a proton supplier is required, which may allow the formation of a nucleophilic methyl containing cation, such as [CH₃O(H)R]⁺.³⁵ Alternatively, the proton supplier may trigger CO dissociation to form a more active catalyst³⁴. The necessity for both protons and methyl containing substrate to be present in the ruthenium catalysed carbonylation reaction explains why ethanoic acid is formed when water *and* iodomethane are present, but not when just water or iodomethane are used.

3.2.4.4 Replacement of CH₃I by HI

The use of iodomethane appeared to inhibit the formation of ethanoic acid from carbon monoxide and hydrogen at low temperatures (section 3.2.1.1). It also makes it difficult to confirm that ethanoic acid is produced from carbon monoxide and hydrogen, because carbonylation of iodomethane produces some ethanoic acid anyway. Ethanoic acid produced by this route can only be conclusively distinguished from ethanoic acid produced exclusively from carbon monoxide and hydrogen by ¹³C labelling (deuterium scrambling makes deuterium labelling less conclusive).

Iodomethane, however, is critical to the formation of ethanoic acid, as shown by the control reaction where it was left out (section 3.2.4.2). Replacement of iodomethane by HI has been tested, with the intention of generating the iodomethane required for the rhodium catalysed methanol carbonylation reaction (*Figure 1.4*) from methanol, in situ. HI is a very corrosive acid and can corrode the internal surfaces of the reaction vessel if used regularly. The o-ring is especially vulnerable to degradation by HI, particularly at the high temperatures and pressures used. Especially resistant materials are required for reactions using HI, such as a Hastalloy autoclave fitted with a durable o-ring (Elastolion for example).

Unfortunately, when HI (6.6 mmol) was used in the combined CO hydrogenation and carbonylation reaction, no reaction products are observed. The increased acidity of the reaction prevents hydrogenation of CO by the ruthenium catalyst, so no methanol is formed. HI is therefore unable to react with methanol to form iodomethane and no ethanoic acid is formed. No [HRu₃(CO)₁₁]⁻ is observed after the reaction by ESMS, as HI oxidises the hydride donor to form [Ru(CO)₃I₃]⁻, stopping the carbon monoxide hydrogenation reaction. CO hydrogenation in the presence of HI has been observed in tri-n-propylphosphine oxide solvent at 230 °C, using CO/H₂ (1:1, 850 bar), but the amount used must be carefully balanced to maintain both [HRu₃(CO)₁₁]⁻ and [Ru(CO)₃I₃]⁻ in solution³⁶.

3.2.4.5 The Use of N-Ethylpyrrolidinone (NEP) as a Solvent

Isotopic labelling experiments were less conclusive than expected, due to scrambling effects. The use of N-ethylpyrrolidinone as a solvent is another way to analyse the part that the solvent plays in the reaction. When NEP is used, ethanoic acid is produced, but ethyl methanoate is also formed and a small amount of NMP is observed. This suggests that the alkyl group attached to pyrrolidinone does effect the reaction products and confirms that it can exchange with iodomethane. The presence of ethyl methanoate suggests that the solvent has intercepted a formyl ligand or methanal intermediate.

3.2.5 Reactions Carried Out at Constant Pressure

A reactor fitted with a ballast vessel to maintain the pressure within the reactor at a constant pressure can be very useful for the kinetic study of a reaction that consumes gas. The rate of the reaction can be measured by the rate at which gas is passed from the ballast vessel to the reactor. In the carbon monoxide hydrogenation and subsequent carbonylation to ethanoic acid reaction, the use of a constant pressure may be beneficial. In a batch autoclave, the pressure drops as the reaction proceeds, but pressure itself aids the reaction, so the drop in pressure may cause the reaction to slow and stop.

Two different sets of ballast vessel equipment have been used. The first, at the BP Amoco site at Hull, was situated in a blast bay and fitted with computer controlled valves. Gases could be compressed up to 200 bar and stored in one of six ballast vessels. An automatic computer controlled valve regulated the flow of gas between the ballast vessel and reactor. The rig was also fitted with catalyst injection and gas sampling equipment. The other ballast vessel equipment is similar in principal, but on a

smaller scale, and is operated by the CATS service (Catalyst Evaluation and Optimisation Service) at St. Andrews.

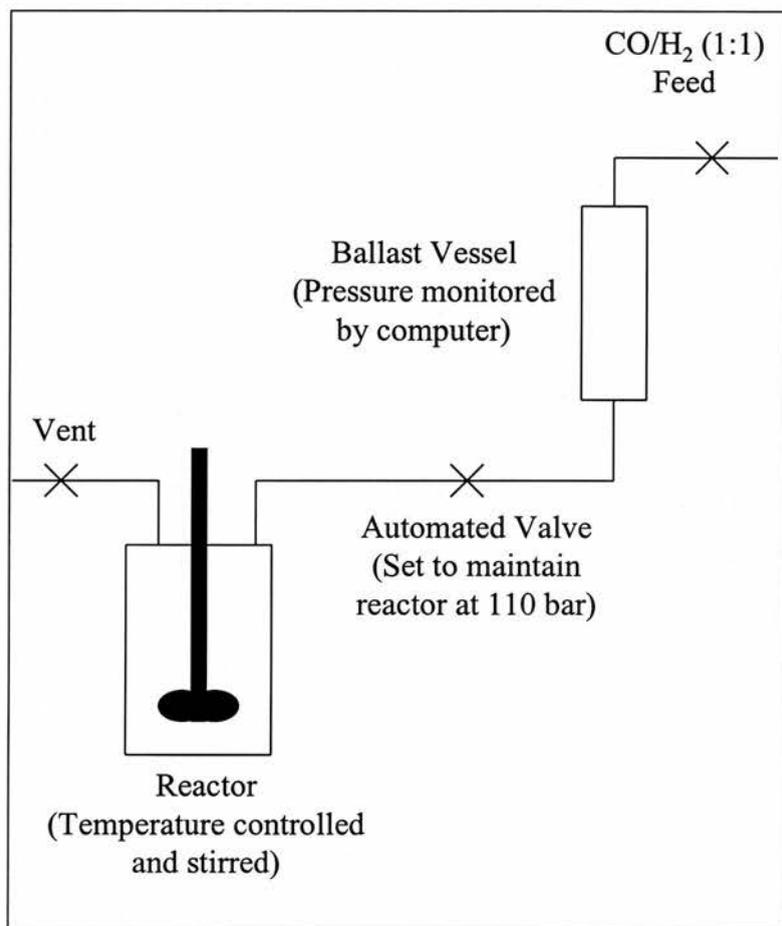


Figure 3.13; Schematic diagram of ballast vessel equipment

3.2.5.1 The General Ruthenium/Rhodium System

The conditions used for reactions of this type were $\text{Ru}_3(\text{CO})_{12}$ (0.7165 g, 1.12 mmol), RhCl_3 (0.1394 g, 0.666 mmol), KI (8.32 g, 50.1 mmol), CH_3I (11.35 g, 80.3 mmol), H_2O (10 g, 556 mmol), NMP (135 g, 130.7 ml, 1.36 mol) at a pressure of 110 bar (CO/H_2 , 1:1 at 200 °C). The volumes of the autoclave and ballast vessel used, including connecting pipes and valves, were 320 ml and 162 ml respectively.

The pressure changes in the autoclave and ballast vessel over the course of a 12 hour reaction are shown below (*Figure 3.14*). 67.5 mmol of ethanoic acid was produced in this reaction, which is equivalent to 83.5% of the iodomethane used at the start of the reaction, and is consistent with the amount of ethanoic acid formed in analogous batch autoclave reactions. Analysis of the gas at the end of the reaction showed that some methane (3.3% by volume, 33 mmol) and CO_2 (0.63% by volume, 6.2 mmol) was also produced.

The pressure in the ballast vessel fell from 177.3 bar to 166.7 bar over the course of the reaction. This would be equivalent to 76.7 mmol of gas, but it must be noted that the temperature of the ballast vessel fell from 31 °C to 25.5 °C over the 12 hour reaction period (see *Figure 3.15*). (The bay is usually maintained at a constant temperature, but it couldn't cope with one of the hottest days of the year!) This temperature drop would cause a pressure drop of 3.2 bar, and this effect can be seen in the graph of ballast vessel pressure which slopes downwards between pulses of gas to the autoclave. Thus, the amount of ballast vessel gas consumed by the reaction is more accurately 7.4 bar (53.5 mmol). This is slightly less than the amount of ethanoic acid formed. Reactions such as the WGS reaction, hydrogenation of CO to methane, carbonylation of iodomethane

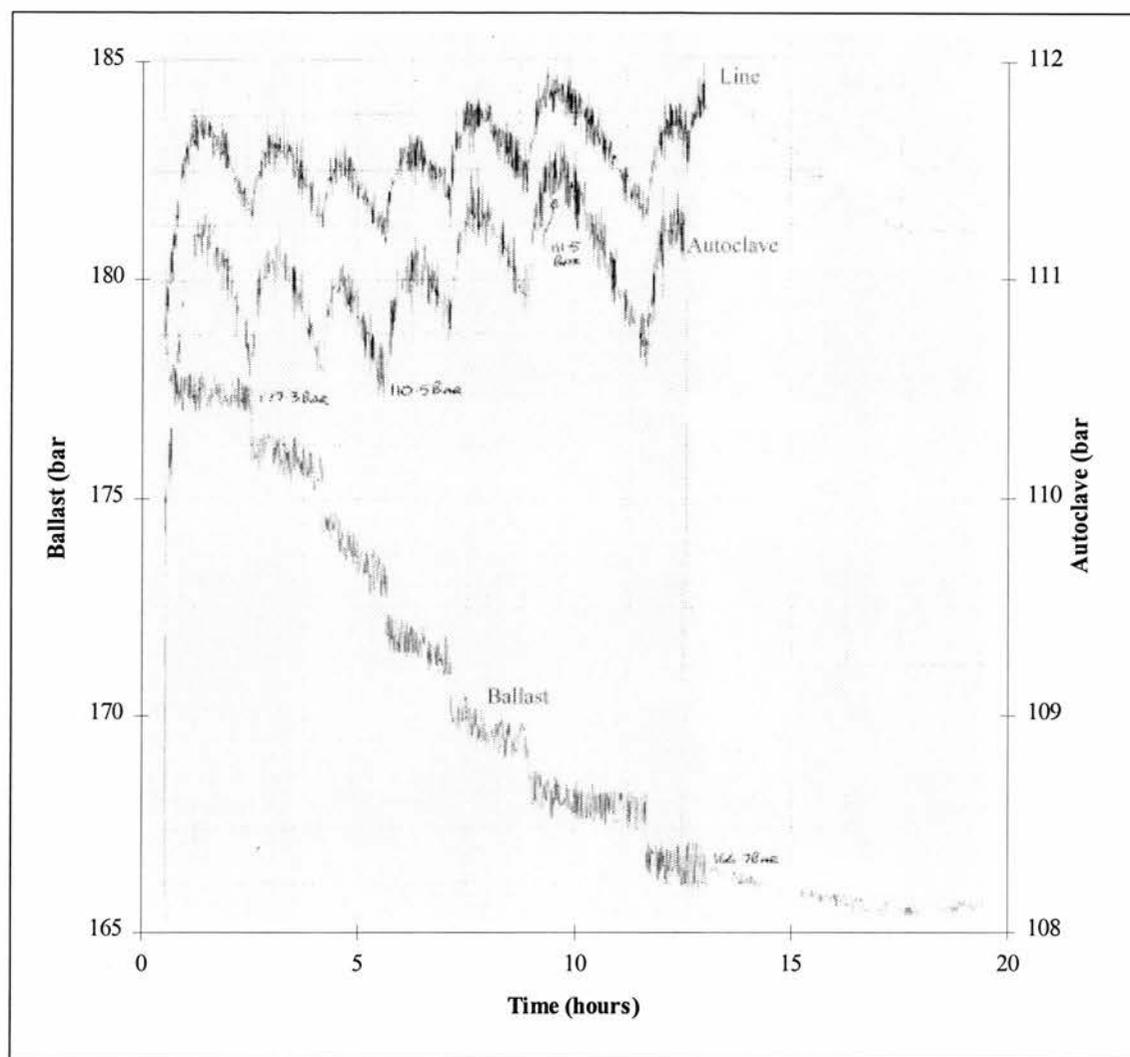


Figure 3.14; Autoclave and ballast vessel pressures over a 12 hour reaction

and the formation of ethanoic acid from CO and hydrogen all effect the amount of gas consumed. However, the relatively small amount of gas consumed suggests that ethanoic acid is formed by the carbonylation of iodomethane reaction (which consumes one mole of gas per mole of ethanoic acid produced), rather than from CO and hydrogen, where four moles of gas are consumed per mole of ethanoic acid produced.

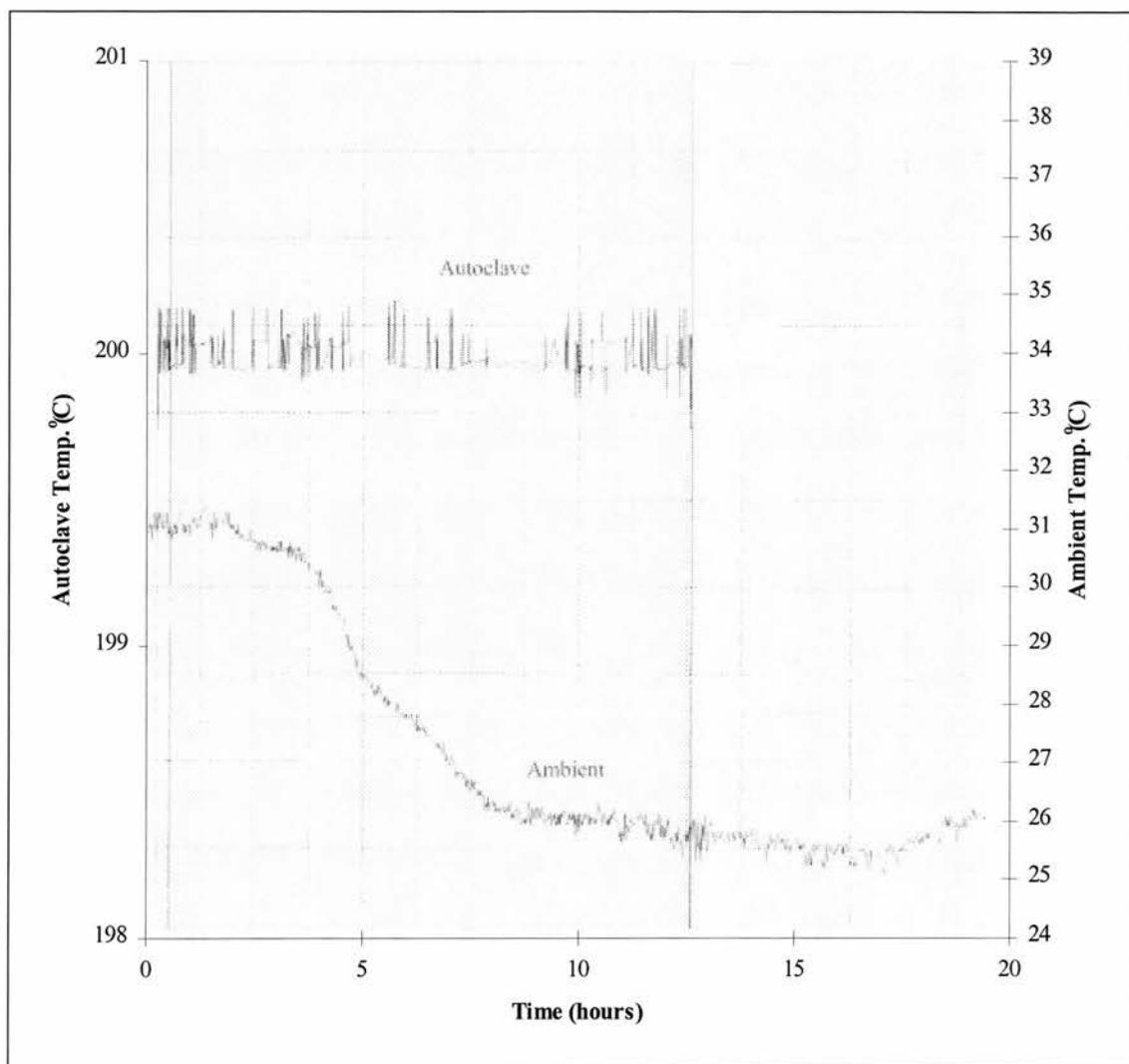


Figure 3.15; Autoclave and ballast vessel temperatures over a 12 hour reaction

The graph of the autoclave pressure over the course of the reaction is unusual for ballast vessel experiments. Rather than showing a repeating step increase in pressure as gas is fed from the ballast vessel, followed by a steady decrease in pressure as the gas is consumed, the pressure takes 30 minutes to reach its maximum after each gas feed. The temperature of the autoclave is held constant at 200 °C with a range of just 0.3 °C, so the steady pressure increase is not caused by an exothermic reaction heating the autoclave.

It is possible that an overall gas forming reaction in competition to the gas consuming carbon monoxide hydrogenation and carbonylation reaction could cause the pressure effect. Such net gas producing reactions could be the WGS reaction (if water is not completely in the gas phase at 200 °C and 110 bar), or even a solvent decomposition reaction liberating methane. However, the pressure effect may simply be an artefact caused by a faulty valve preventing immediate gas flow from the ballast vessel to the autoclave. This is supported by the fact that a 1.25 bar pressure drop in the ballast vessel should cause a 0.63 bar pressure increase in the autoclave, which is eventually observed.

The amount of ethanoic acid produced is less than would be expected if it was being formed from carbon monoxide and hydrogen as well as by carbonylation of iodomethane, perhaps suggesting that ethanoic acid is not being formed from CO and hydrogen. However, the reaction is much slower than would be expected for the rhodium catalysed carbonylation of iodomethane at this temperature.

The rate of gas consumption is also constant over the course of the reaction, as shown by the rate of decrease of autoclave pressure, taking into account the associated temperature drop. This suggests three things; i. The catalytic species is still active after 12 hours, ii. The reactant(s) have not been completely used up and iii. The rate of reaction is not dependent on a substance that is being consumed.

No iodomethane is observed by GC after the reaction. This is confirmed by the amounts of ethanoic acid and methane observed at the end of the reaction, and that quaternisation of the solvent would also remove iodomethane. Furthermore, the rate of rhodium catalysed methanol carbonylation is first order in iodomethane (and first order in $[\text{Rh}(\text{CO})_2\text{I}_2]^{37}$, so the rate of the reaction should decrease as iodomethane is used up if this is the only mechanism of ethanoic acid formation. Thus, points ii and iii suggest that rhodium catalysed carbonylation of iodomethane is not the only mechanism of ethanoic acid production.

3.2.5.2 The Ru/Rh System over a Longer Time

Studies on the combined ruthenium and rhodium system over a 12 hour period show that gas is still being consumed at the end of the reaction. If the reaction is extended to 64 hours, more ethanoic acid is produced. Using conditions similar to those in section 3.2.5.1, 116.5 mmol of ethanoic acid is produced. This is compared to 67.5 mmol formed over a 12 hour period, where both reactions initially contained 80.3 mmol of iodomethane. This confirms that the reaction is active for over 12 hours, and is further evidence that ethanoic acid is not produced from carbonylation of iodomethane alone.

Reaction Time (h)	CH ₃ I Added (mmol)	CH ₃ COOH Produced (mmol)
12	80.3	67.5
64	80.3	116.5
88	0 initially, then 80.3 added after 64 hours	178.3

Table 3.6; The effect of reaction time variation and injection of iodomethane

Conditions; Ru₃(CO)₁₂ (0.7165 g, 1.12 mmol), RhCl₃ (0.140 g, 0.67 mmol), KI (8.32 g, 50.1 mmol), H₂O (10 g, 556 mmol), NMP (135 g, 130.7 ml, 1.36 mol) at a pressure of 110 bar (CO/H₂, 1:1 at 200 °C).

In a separate reaction, iodomethane was omitted from the reaction mixture and the remaining Rh, Ru, KI, H₂O and NMP were heated to 200 °C under CO/H₂ (1:1) for 64 hours. [The hydrogenation of carbon monoxide has been shown to be active under these conditions, with the formation of methanol and 2-hydroxyethanal (section 3.2.4.2)]. Then, iodomethane (11.4 g, 80.3 mmol) was added via a catalyst injector under a slight over-pressure of CO/H₂. This reaction produced 178.3 mmol of ethanoic acid.

Ethanoic acid production is enhanced when iodomethane is added after the methanol concentration has been allowed to build up via the hydrogenation of carbon monoxide reaction. Iodomethane can have a detrimental effect on the hydrogenation of CO reaction (section 3.2.1.1), so omission of iodomethane allows methanol to build up faster than it would in other reactions where iodomethane is included from the start. Then, when iodomethane is added, the methanol produced by carbon monoxide hydrogenation can be converted into ethanoic acid relatively quickly. The overall effect of this process is to increase the amount of ethanoic acid formed.

3.2.5.3 The Reaction in the Absence of Rhodium or Ruthenium

When rhodium is not used in the reaction mixture, ethanoic acid (17.4 mmol) is still produced. No methanol is produced in this case, when iodomethane is used. This confirms earlier batch autoclave reactions, which also found that ruthenium was an active carbonylation catalyst under the conditions used (section 3.2.4.3). However, the amount of ethanoic acid formed using ruthenium only is much less than the amount of iodomethane used and the amount of ethanoic acid formed when both rhodium and ruthenium are used.

When rhodium is used as the only transition metal, and ruthenium is omitted from the reaction mixture, more ethanoic acid is formed. In fact, 108.8 mmol of ethanoic acid is formed. This is more than the amount of iodomethane used (80.3 mmol). This is more than would be expected by carbonylation of iodomethane alone, but it is consistent with equivalent batch autoclave reactions (section 3.2.4.1). Rhodium can catalyse the formation of ethanoic acid from synthesis gas under high pressure³⁸, or using zeolite catalysts¹⁹ where rhodium carbonyl species trapped within the pores of the zeolite are believed to be the active species.

3.2.5.4 The Reaction at Low Temperature

When the reaction was carried out at a relatively low temperature of 166 °C using a ballast vessel to maintain the pressure at 110 bar, ethanoic acid was formed slowly. In this experiment, using $\text{Ru}_3(\text{CO})_{12}$ (0.0355 g, 0.056 mmol), RhCl_3 (0.007 g, 0.0334 mmol), KI (0.415 g, 2.575 mmol), H_2O (0.5 g, 27.78 mmol), CH_3I (0.25 ml, 4.0 mmol) and CO/H_2 (1:1, 110 bar at 166 °C), 1.51 mmol of ethanoic acid was produced. The graph below shows the pressure of the ballast vessel during the reaction.

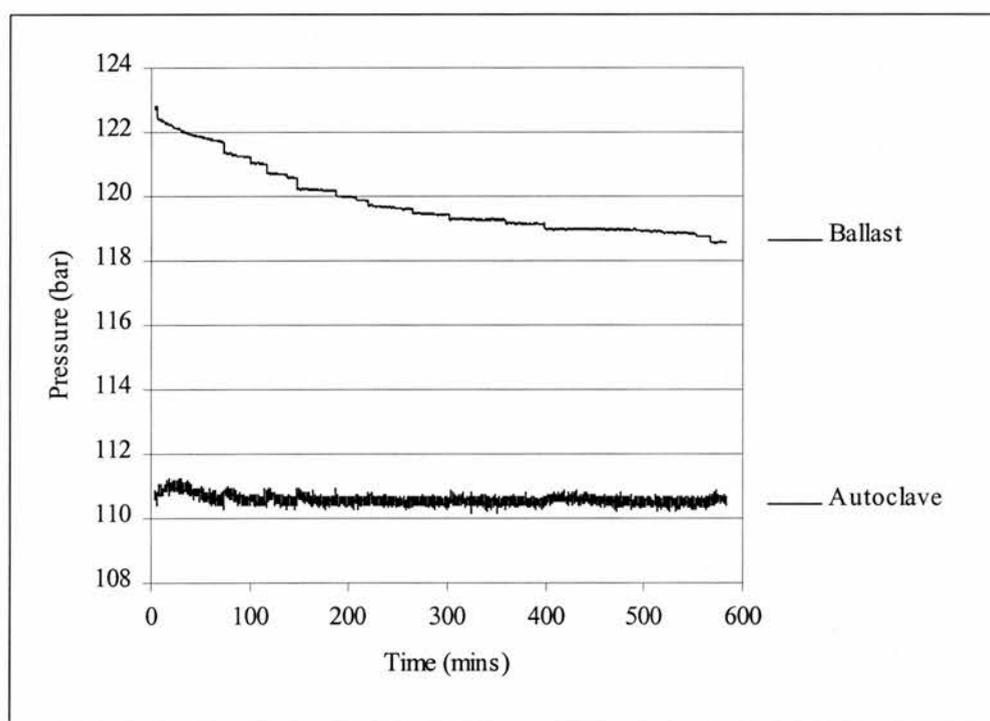


Figure 3.16; Autoclave and Ballast pressures for a reaction at 167 °C

This graph shows that 4 bar of gas is consumed during the course of the reaction. The volume of the ballast vessel in this experiment was 37.8 ml; therefore 6.75 mmol of gas has been consumed. The rate of gas consumption is not linear over time and it slows to nothing after 10 hours. No iodomethane is observed after this reaction, so it is possible that all of the ethanoic acid could have been formed by carbonylation of iodomethane.

3.2.5.5 The Reaction Using Less Water

Water is an important component of the rhodium catalysed methanol carbonylation reaction. The ruthenium catalysed carbon monoxide hydrogenation reaction does not require water, but it is still active when water is present (section 2.2.5.3). In an experiment using $\text{Ru}_3(\text{CO})_{12}$ (0.0367 g, 0.057 mmol), RhCl_3 (0.0082 g, 0.0392 mmol), KI (0.424 g, 2.554 mmol), H_2O (0.25 g, 13.9 mmol), CH_3I (0.25 ml, 4.0 mmol) and CO/H_2 (1:1, 110 bar at 200 °C) for 28 hours, 4.33 mmol of ethanoic acid was produced.

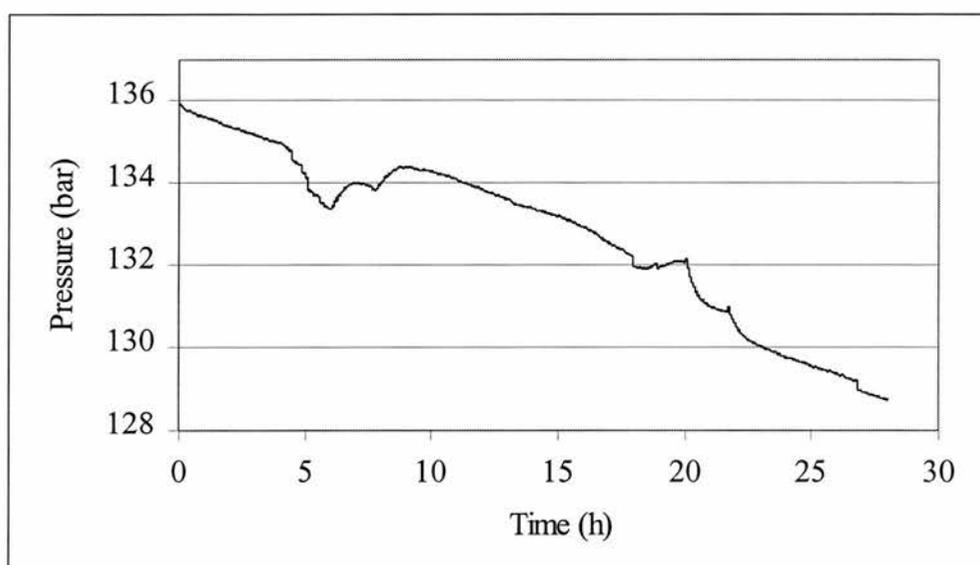


Figure 3.17; The change in ballast vessel pressure over the course of the reaction

The ballast vessel pressure shows a general downward slope as gas is consumed by the reaction, but it is affected by ambient temperature variations that cause additional pressure changes. Over a period of 28 hours, the ballast vessel pressure drops by 7 bar, which is equivalent to 11.8 mmol of gas. This suggests that at least a proportion of the ethanoic acid formed is produced from carbon monoxide and hydrogen.

This reaction used half the amount of water used for an earlier reaction, which only produced 1.883 mmol of ethanoic acid in 40 hours. The high ionic iodide concentration

required to maintain the ruthenium catalyst in its active form will also influence the rhodium based carbonylation catalyst, causing it to be more active at lower water concentrations. This effect of high iodide concentration would be similar to the Celanese low water rhodium catalysed methanol carbonylation process (see section 1.3.3.3).

3.3 Conclusions

Ethanoic acid can be produced by an iodide promoted ruthenium and rhodium system in the presence of iodomethane, water, carbon monoxide and hydrogen in NMP solvent, using a total pressure of 110 bar. The reaction is relatively slow and is inhibited by iodomethane, particularly at 167 °C, but at a temperature of 200 °C ethanoic acid is produced. No ethanoic acid is produced in the absence of iodomethane, even if HI is used instead. The amount produced is dependent on the duration of the reaction, with more ethanoic acid produced if the reaction is left for a long time (3 days). Under these conditions more ethanoic acid is formed than can be accounted for by the reaction of iodomethane with carbon monoxide alone. Catalyst decomposition is observed at 235 °C, but reaction products are still observed. Selectivity is lost, with a variety of hydrogenation and carbonylation products formed.

Isotopic labelling studies suggest that a significant proportion of the ethanoic acid produced is formed from carbon monoxide and hydrogen. However, H/D scrambling in ethanoic acid makes the results more complicated than for the hydrogenation of carbon monoxide reaction studied in chapter 2. The NMP solvent is also effected by deuterium labelling under some conditions. ¹³C labelling also suggests that ethanoic acid is formed from carbon monoxide and hydrogen.

3.4 Experimental

The procedure for batch autoclaves is outlined in section 2.4. For ballast vessel reactions, the equipment was extensively tested for leaks prior to each reaction. The reactants were mixed in the autoclave, and then the autoclave was flushed with synthesis gas. The reactor was then filled with 70 bar of the appropriate reactant gas (usually CO:H₂, 1:1) and heated to the reaction temperature (200 °C). The reactor was then topped up to 110 bar from the ballast vessel and timing started. After the reaction, the reactor was isolated from the ballast vessel and cooled, before it was carefully vented.

Ethanoic acid produced was quantitatively analysed by diluting a sample of reaction products to an ethanoic acid concentration of between 4 and 35 mM in tetrahydrofuran. 1 µl of 1-Octanol was then added as an internal standard per ml of diluted solution. This solution was then analysed using a 60 m Stabilwax GC column and compared to a calibration graph to obtain an accurate concentration of ethanoic acid.

3.4.1 Materials

Ru₃(CO)₁₂ was obtained from Strem, and RhCl₃ from Apollo Scientific. Both were stored in their containers over silica gel, and used without further purification. Potassium iodide was stored in an oven at 140 °C. NMP was purchased from Aldrich, dried by distillation under reduced pressure and stored in a Schlenk tube under dry argon. CH₃I was obtained from Aldrich and degassed by three freeze-pump-thaw cycles, then stored in a foil-wrapped schlenk tube, under argon in a fridge. CD₃I was purchased in a sealed ampoule from Aldrich and used without further purification. ¹³CH₃I was received from BP Amoco in a sealed ampoule and used without purification. CO, CO/H₂ (1:1), H₂ and D₂ were purchased from BOC Gases. CO/H₂ (1:1) was sometimes passed through a carbon filter to remove trace impurities such as Fe(CO)₅, but this was found to have no appreciable effect on the activity of the catalyst.

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CHAPTER 4

Analysis by Electrospray-Mass Spectrometry (ESMS) and High Pressure FTIR

4.1 Introduction

FTIR spectrometry is well suited for the analysis of homogeneous catalytic solutions, especially when complexes containing carbonyl ligands are present. Using specially designed equipment it can be used *in situ* to give useful information on the nature of the catalytic species under reaction conditions. Alternatively, the reaction solution can be analysed after a reaction and can provide reasonable evidence on the nature of the catalytic species, particularly if they are relatively stable. However, the method does have some disadvantages. Spectra must be compared with those of authentic compounds, which is difficult if the catalytic species is relatively unstable or unknown. The solvent must not be strongly absorbing in the carbonyl region of the spectrum, and assignment of peaks can be difficult if there are many different carbonyl complexes present, such as in catalytic mixtures containing different metal cluster compounds.

The hydrogenation of carbon monoxide reaction, catalysed by ruthenium carbonyl clusters, has been studied by IR spectrometry. Dombek¹ found that $[\text{HRu}_3(\text{CO})_{11}]^-$ and $[\text{Ru}(\text{CO})_3\text{I}_3]^-$ are present in an active solution under reaction conditions and are still present after catalysis. Both anions were necessary for the CO hydrogenation reaction to occur. The anion $[\text{Ru}(\text{CO})_3\text{I}_3]^-$ has been studied by IR spectrometry by Braca *et al.*². The spectrum is influenced by ion pairing effects. Bands at 2102 and 2033 cm^{-1} are assigned to the tight ion-pair $[\text{KRu}(\text{CO})_3\text{I}_3]$, while the solvent separated ion-pair in aqueous tetrahydrofuran produces bands at 2095 and 2022 cm^{-1} .

In the ruthenium and cobalt catalysed synthesis of ethanoic acid from CO and hydrogen, studied by Knifton³, $[\text{Ru}(\text{CO})_3\text{I}_3]^-$ and $[\text{Co}(\text{CO})_4]^-$ are observed. Bands at 2108 and 2036 cm^{-1} are assigned to $[\text{Ru}(\text{CO})_3\text{I}_3]^-$, while $[\text{Co}(\text{CO})_4]^-$ produces a band at 1886 cm^{-1} . A ruthenium and rhodium system in ethanoic acid as solvent has been studied by Whyman *et al.*⁴ using $\text{N}(\text{C}_2\text{H}_5)_3$, rather than iodide as a promoter. $[\text{Ru}(\text{CO})_3(\text{CH}_3\text{COO})]_2$, $[\text{HRu}(\text{CO})_3(\text{CH}_3\text{COO})]$, $[\text{Ru}(\text{CO})_5]$ and $[\text{Rh}_6(\text{CO})_{15}\text{X}]$ [$\text{X} = \text{H}$ or (CH_3COO)] are all observed, and ethanoate esters of methanol, ethanol and 1,2-

ethandiol are formed. *In situ* FTIR Results of the ruthenium and rhodium catalysed hydrogenation of carbon monoxide to ethanoic acid reaction are shown in section 4.2.8.

4.1.1 Electrospray Mass Spectrometry (ESMS)

An alternative method of analysis is electrospray mass spectrometry (ESMS). This is a particularly useful technique for the analysis of ionic species in solution. Attaching a HPLC column can separate mixtures of different species, although some separation is observed without the use of a HPLC column. Another advantage is that the catalytic species do not need to be separated from the solvent. The technique is very well suited for the analysis of organometallic species, because unlike other mass spectrometry techniques the sample does not need to be volatile to be characterised. Mass spectrometry is often overlooked as an analytical method for this reason, but ESMS is becoming more popular in transition metal chemistry as more applications are studied.

4.1.1.1 The ESMS Technique

The ESMS process involves the rapid drying of a spray of ions in solution to produce ions in the gas phase. As the process does not involve heating, non-volatile ions such as transition metal complexes or clusters can be studied.

A schematic diagram of the electrospray equipment is shown below (*Figure 4.1*). The sample solution is injected into an injection port, from where it is taken to the probe using an acetonitrile/water carrier solution. The sample is carried to the tip of the probe where a spray is produced using a nebuliser gas (N_2). This produces small droplets of

solution containing the ionic species to be analysed. The solvent is then rapidly removed using a drying gas to produce bare ions in the gas phase. Strongly solvated ions can retain solvent molecules under some circumstances, and additives such as methoxide ions can be used to form adducts for the analysis of neutral complexes which would not be detected otherwise.

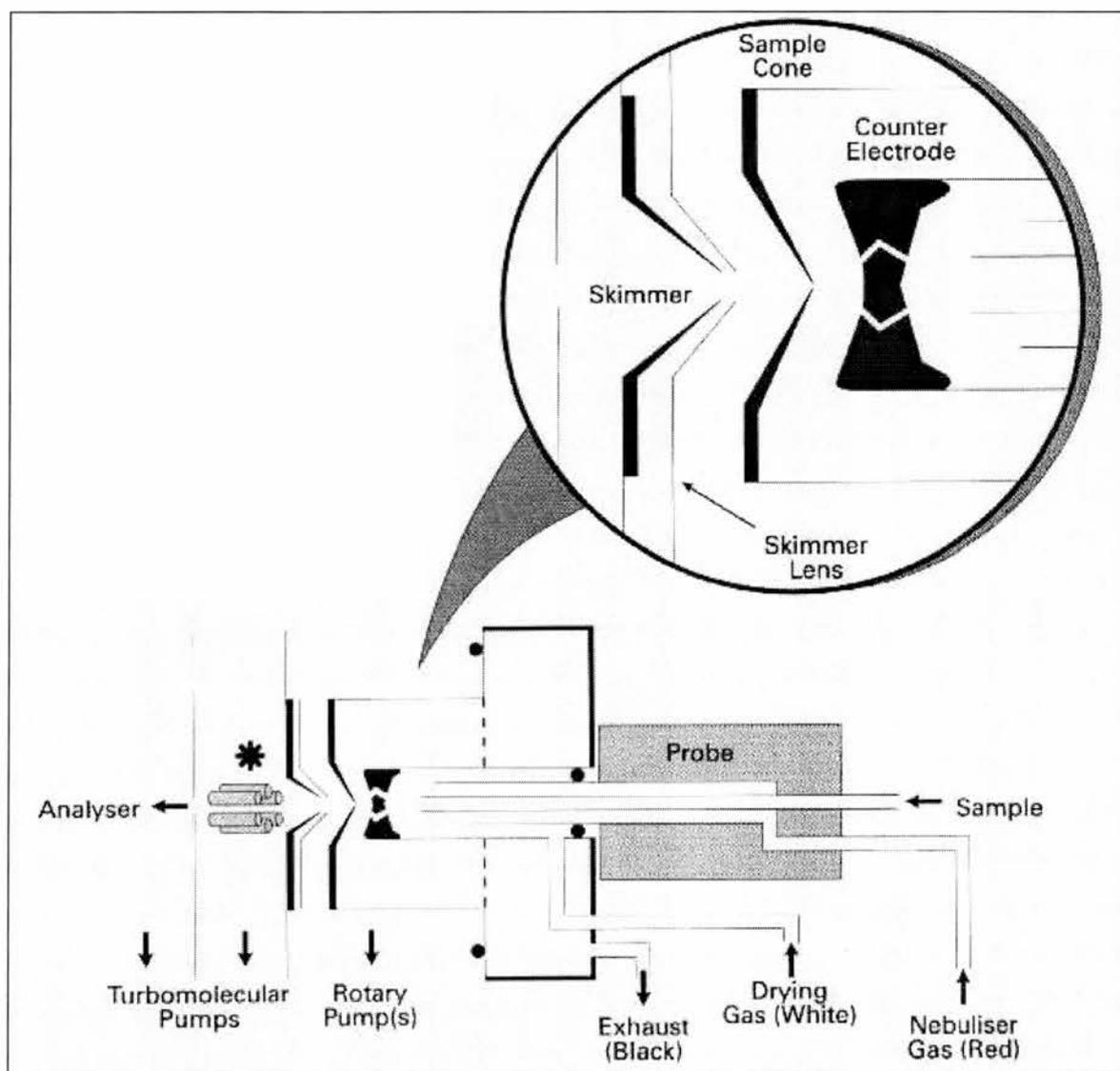


Figure 4.1; Schematic diagram of the ESMS technique - reproduced from the *Fisons Instruments, VG Platform, Users Guide*

The charged species are then accelerated using a counter electrode, which allows either positive or negative ions to be selectively analysed. A sample cone is used to focus the stream of charged species. Unlike many mass spectrometry techniques, ESMS does not use a harsh method of ionisation that causes significant fragmentation, so molecular ions are common. A skimmer lens can be used to fragment the charged species and varying the potential of the skimmer lens can change the degree of fragmentation. This is particularly useful for the characterisation of unknown species. From the skimmer lens, the charged species flow to a mass spectrometer for analysis.

4.1.1.2 Uses of ESMS

The usefulness of ESMS as an analysis tool is determined by the solubility of the sample, rather than its volatility. Thus, ESMS can be used for many samples that are non-volatile, but can be dissolved. The technique has been used to form multiply charged clusters of arginine molecules and to study the physical chemistry of the clusters formed⁵. ESMS is particularly useful for the analysis of large, thermally sensitive biological molecules. The mild ionisation conditions prevent significant fragmentation, which makes analysis possible, and multiply protonated molecular ions are observed⁶. ESMS can also be used for soluble polymeric materials such as poly(propylene glycol), $\text{H}[\text{OCH}(\text{CH}_3)\text{CH}_2]_n\text{OH}$ ⁷.

Many organometallic compounds can be analysed by ESMS and a recent review highlights some of the applications of ESMS in this area⁸. Many metal carbonyl complexes have been observed by Henderson *et al.*⁹, including neutral compounds that can be observed by adding OCH_3^- or Ag^+ ions to form adducts. When a high resolution is used, the isotopic pattern can be obtained. For many transition metal species, particularly clusters, this can produce an impressive pattern containing many peaks, each separated by one mass unit. The structure of the isotopic pattern alone can provide

information about the charge of the species (from the separation of the lines; 0.5 mass units is equivalent to a 2^+ (or $-$) charge) and the number of metal atoms present (from the relative intensity of each isotope).

Following on from the use of ESMS in the characterisation of organometallic complexes, ESMS is beginning to be used as a tool in the investigation of reactions of organometallic compounds. Exchange reactions of $[\text{Re}_2(\mu\text{-OR})_3(\text{CO})_6]^-$ ($\text{R} = \text{H}, \text{Me}$) with alcohols and phenol have been studied¹⁰. Ruthenium and osmium cluster compounds containing the phosphine, $\text{P}(m\text{-C}_6\text{H}_4\text{SO}_3\text{Na})_3$, have been synthesised and tested as water soluble catalysts for the WGS reaction¹¹. Electrospray mass spectrometry was found to be a particularly suitable method for the characterisation of the anionic complexes formed, whereas FAB mass spectrometry could only produce spectra for mono-phosphine complexes.

ESMS has recently been used to observe intermediates in the oxidative self-coupling of areneboronic acids, catalysed by palladium complexes derived from $\text{Pd}(\text{PPh}_3)_4$ ¹². Several complexes are observed, such as $[\text{ArPd}(\text{PPh}_3)_2]^+$, $[\text{ArPd}(\text{PPh}_3)_2\text{O}]^+$, $[\text{Pd}(\text{PPh}_3)_2(\text{B}(\text{OH})_2)_2]$ and $[\text{HPd}(\text{PPh}_3)_2(\text{B}(\text{OH})_2)]$ ($\text{Ar} = p\text{-NH}_2\text{C}_6\text{H}_4$), which give an insight into the mechanism of the reaction.

4.2 Results and Discussion

4.2.1 Analysis of a Mixture of Ions by ESMS

ESMS is well suited to study the species present within a homogeneous reaction solution. These solutions often contain a mixture of ions in solution, which can make analysis by IR very difficult. Although the reaction mixture cannot be studied *in situ* by ESMS, a mixture of ions can be analysed unambiguously.

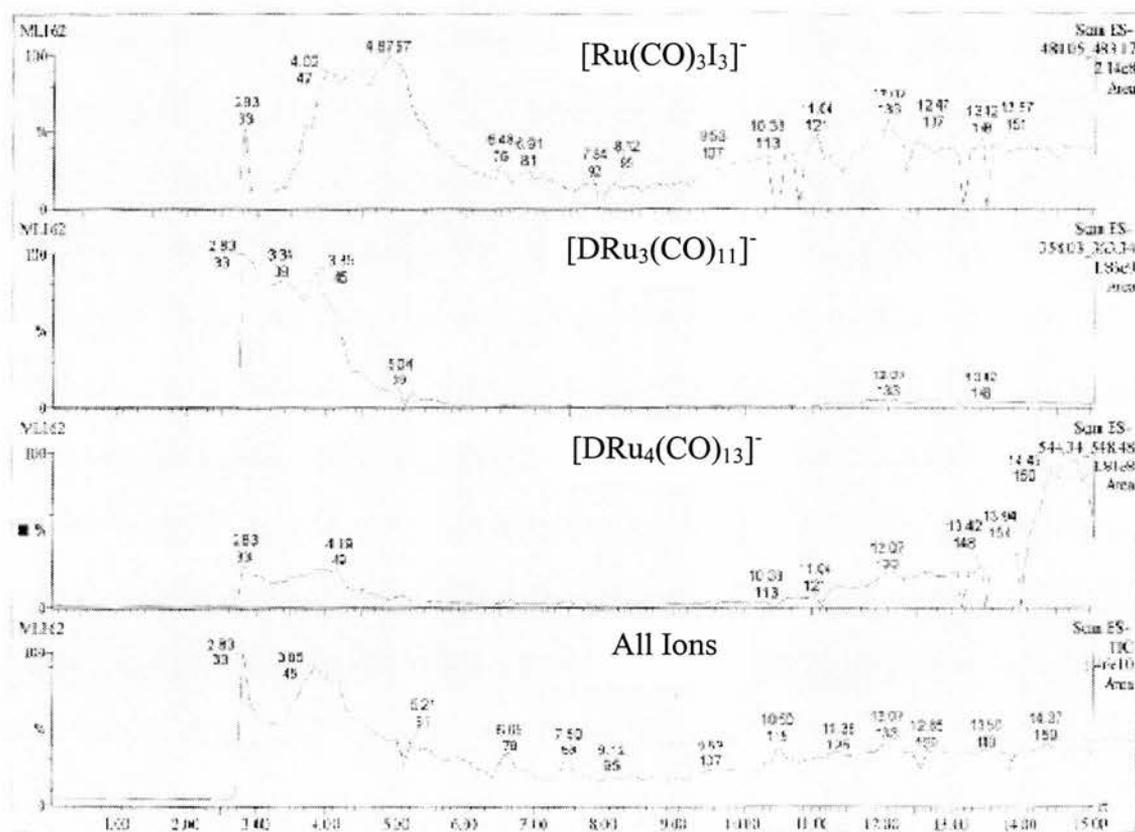


Figure 4.2; Selective ion chromatograms showing separation of individual ions

A HPLC column can be fitted to the ESMS equipment to separate ions if necessary, but the diagram above (Figure 4.2) shows that some separation occurs, even in the absence

of a HPLC column. The total ion count (TIC) shows the sum total of all the anionic species observed, including those derived from the three ruthenium complexes shown and others, notably I⁻. Selective ion chromatograms can be extracted for any anionic fragment. The selective ion chromatograms for the three ruthenium complexes present in the mixture are shown in the diagram.

The selective ion chromatograms reveal that $[\text{DRu}_3(\text{CO})_{11}]^-$ has the shortest retention time, closely followed by $[\text{Ru}(\text{CO})_3\text{I}_3]^-$, then $[\text{DRu}_4(\text{CO})_{13}]^-$ appearing after 14 minutes, with a small amount observed at the same time as $[\text{DRu}_3(\text{CO})_{11}]^-$. This separation of the mixture allows each ruthenium complex to be studied and characterised individually. For example, analysis of spectra obtained with a retention time of between 3 and 4 minutes produces a mass spectrum for $[\text{DRu}_3(\text{CO})_{11}]^-$. The other complexes can be studied in turn to provide conclusive evidence for the presence of each compound (see section 4.2.3 for the mass spectra for each complex).

Another advantage of using selective ion chromatograms to analyse a mixture of ions is that different fragment ions of the same complex can be associated to each other. If two different fragment ions have similar chromatograms, then it is likely that they are both fragment ions of the same species. This can be a very useful analytical tool, to determine which fragment ions are derived from the same complex when many ions are observed at the same time.

4.2.2 Methods for Aiding Characterisation by ESMS

4.2.2.1 Extraction Voltage Variation

The extraction voltage (or skimmer voltage) can be used to fragment ions to different extents. For example, at an extraction voltage of less than 10 V the molecular ion $[\text{HRu}_3(\text{CO})_{11}]^-$ is observed, but when the extraction voltage is increased to 150 V, $[\text{HRu}_3]^-$ is observed. This is very useful for the characterisation of an unknown species, as it produces a large amount of information about the compound.

The extraction voltage can be varied during the course of a single ESMS experiment, as shown for the analysis of $[\text{HRu}_3(\text{CO})_{11}]^-$ below. (The computer software package does not do this automatically, but it can be manually overridden). This creates a different fragmentation pattern for each extraction voltage used (*Figure 4.4*), so when the spectra are added over the whole range of retention times, an overall fragmentation pattern is obtained (*Figure 4.5*). The degree of fragmentation is dependent on the extraction voltages chosen, so the relative intensities of each fragment ion in the overall mass spectrum is of no significance and can be changed by using different extraction voltages. For example, $[\text{HRu}_3(\text{CO})_8]^-$ would appear if an extraction voltage of between 10 V and 70 V had been used.

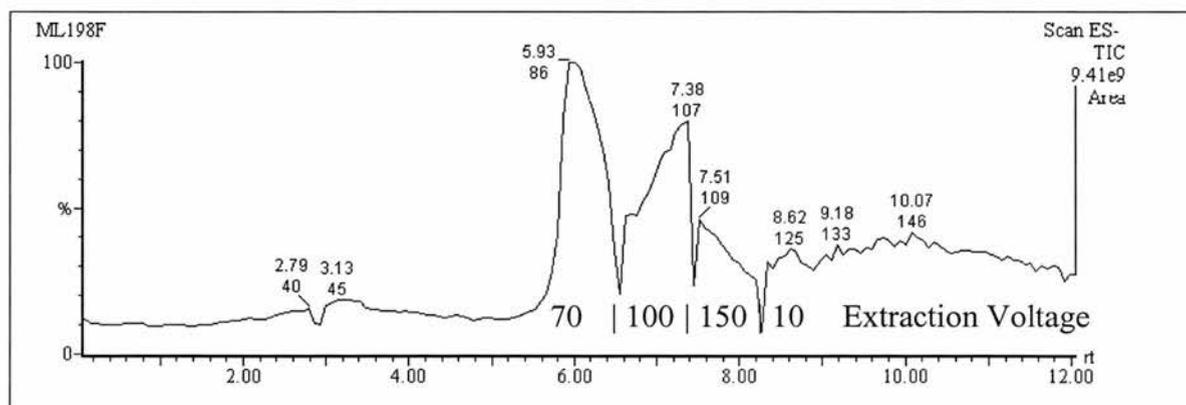


Figure 4.3; Variation of extraction voltage

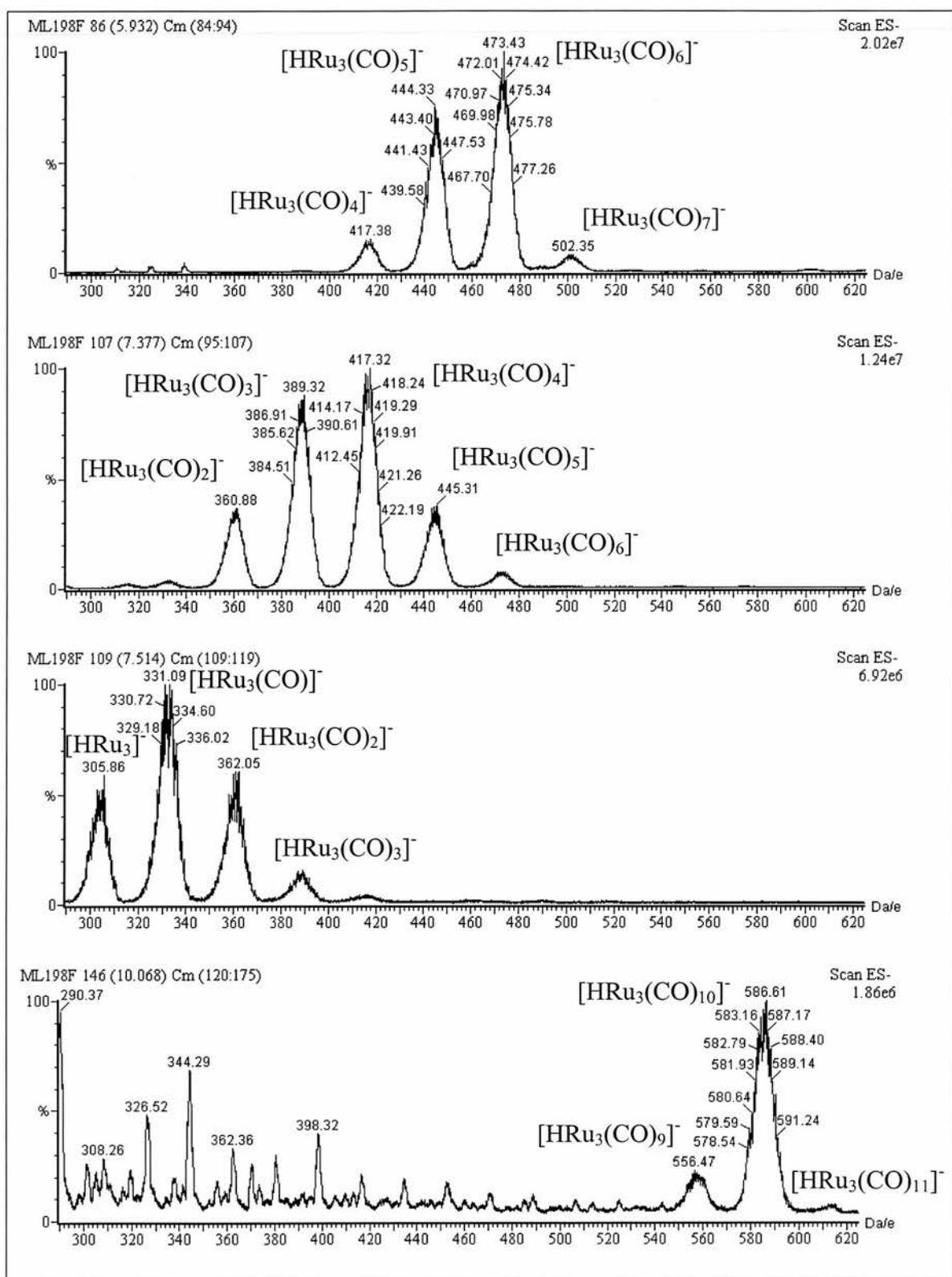


Figure 4.4; Spectra obtained for $[\text{HRu}_3(\text{CO})_{11}]^-$ at an extraction voltage of 70, 100, 150 and 10 V respectively (graphs drawn on the same m/z scale)

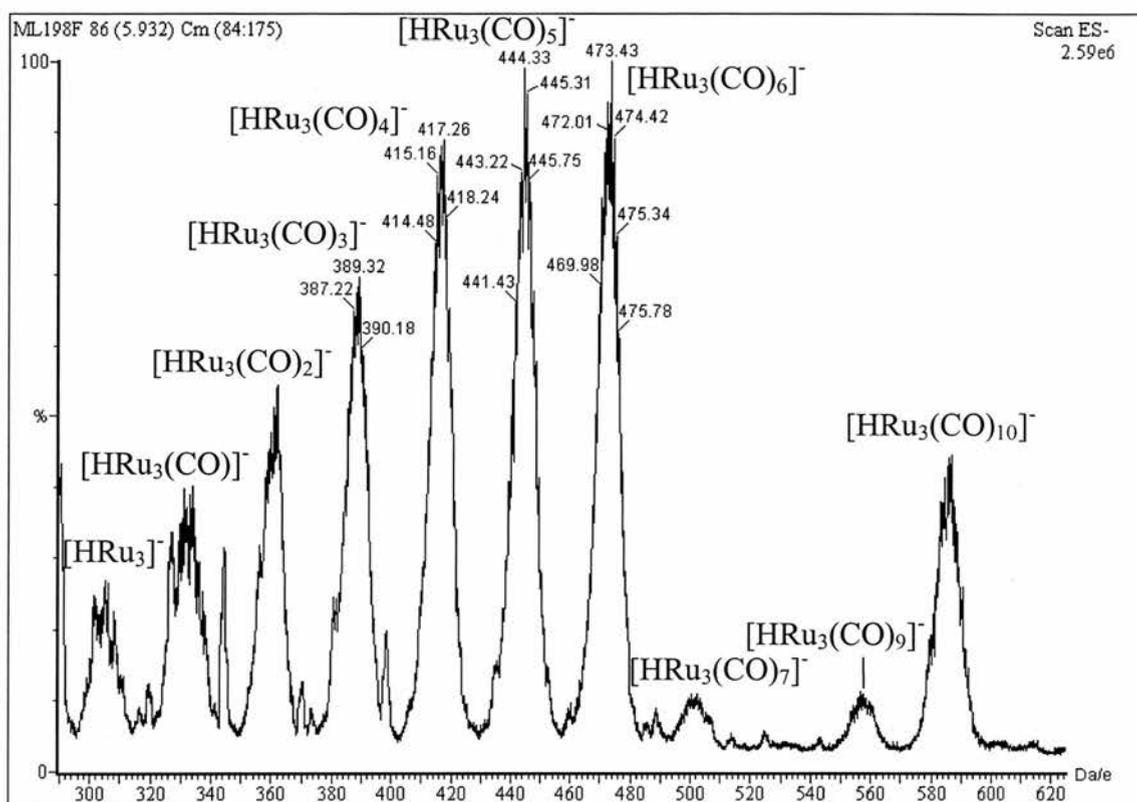


Figure 4.5; Combination of mass spectra obtained at different extraction voltages, showing $[\text{HRu}_3(\text{CO})_n]^-$ fragments

4.2.2.2 Isotopic Distribution Patterns

Another useful tool for the characterisation of transition metal complexes by mass spectrometry is the characteristic isotopic distributions for individual metals and clusters of metal atoms. Ruthenium, for example, has a very distinctive isotopic distribution, shown below (*Figure 4.6*). The isotopic distribution for clusters of ruthenium atoms is also characteristic, but the peak becomes broader and increasingly symmetrical as the number of ruthenium atoms in the cluster is increased. (See *Figure 4.14* for an example of ruthenium isotopic patterns observed by ESMS.)

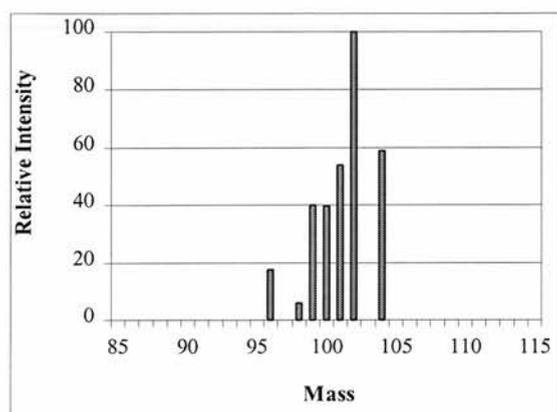
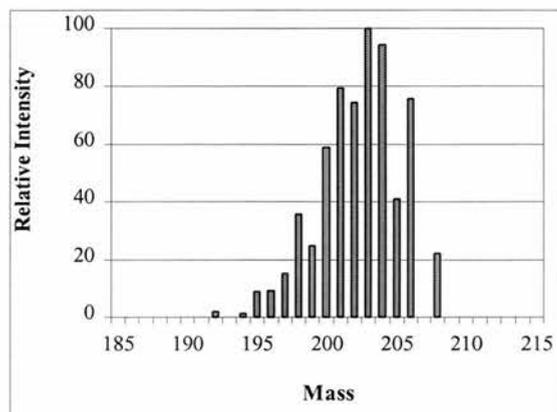
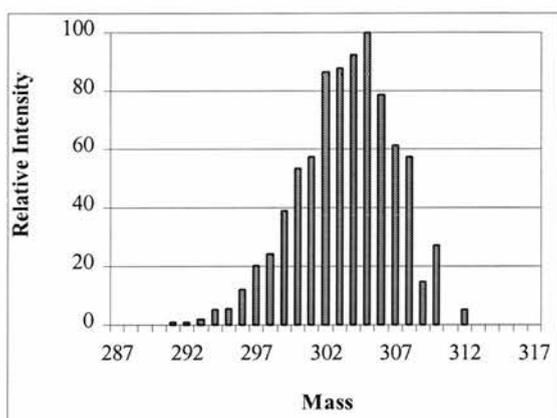
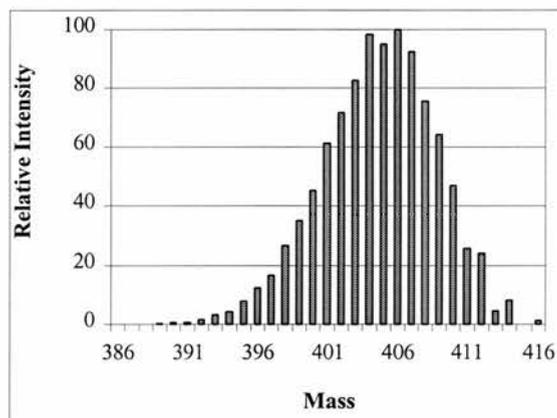
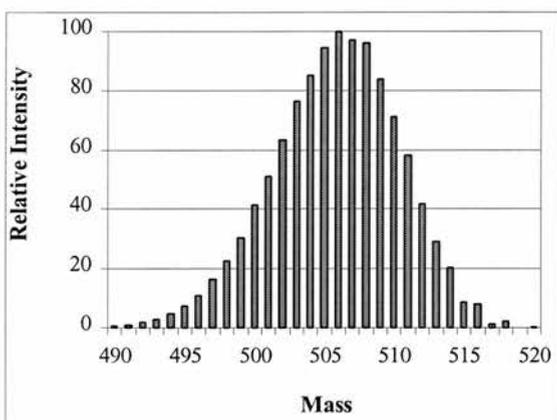
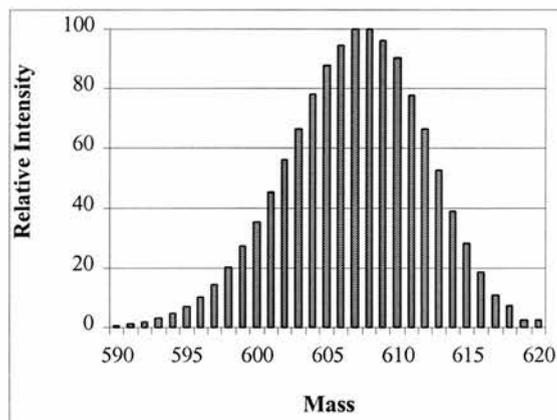
Ru₁Ru₂Ru₃Ru₄Ru₅Ru₆

Figure 4.6; Isotopic distributions for clusters containing 1 to 6 ruthenium atoms¹³

4.2.3 The Ruthenium Catalysed CO Hydrogenation Reaction

ESMS analysis of the reaction solution after a ruthenium catalysed CO hydrogenation to methanol reaction, carried out using D_2 in place of H_2 , shows the presence of three distinct anionic ruthenium species. These complexes are $[Ru(CO)_3I_3]^-$, $[DRu_3(CO)_{11}]^-$ and $[DRu_4(CO)_{13}]^-$, and their mass spectra are shown below. No cationic ruthenium complexes are observed by positive ion ESMS.

The reaction used $Ru_3(CO)_{12}$ (0.710 g, 0.111 mmol), KI (0.836 g, 5.04 mmol), NMP (10 ml) and CO/D_2 (1:1, 70 bar fill pressure) and was heated to 200 °C for 20 hours. 28 mmol of methanol was produced.

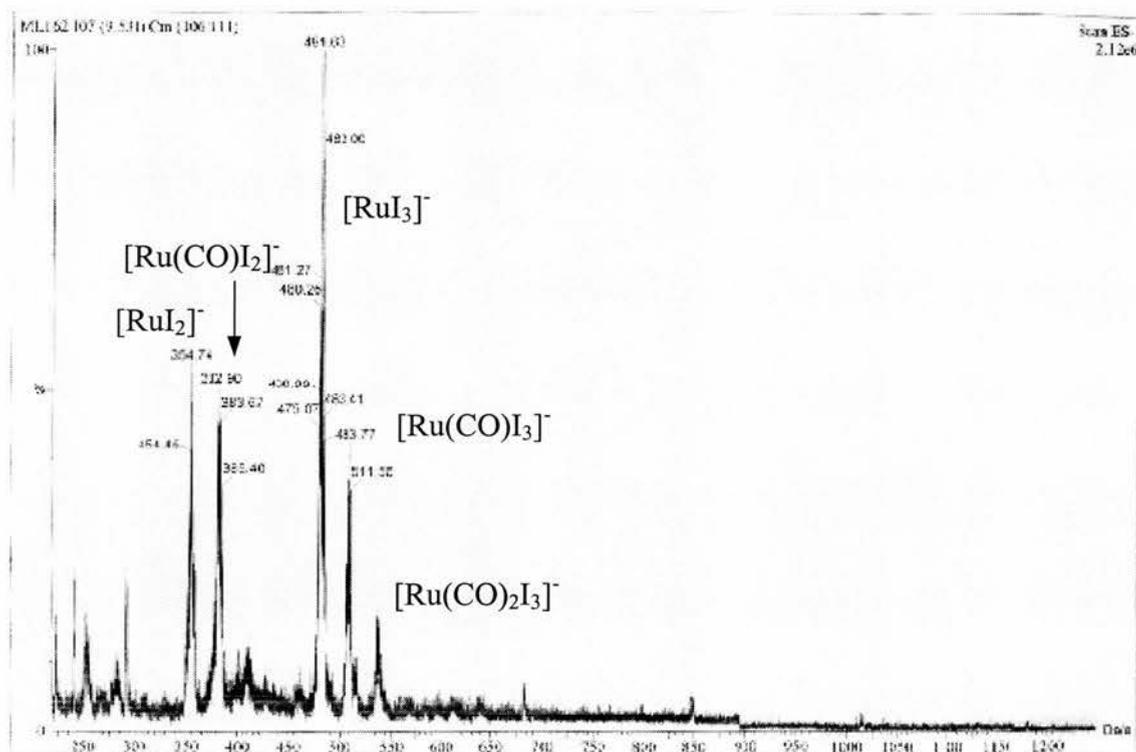


Figure 4.7; $[Ru(CO)_3I_3]^-$ observed by ESMS after a CO hydrogenation reaction

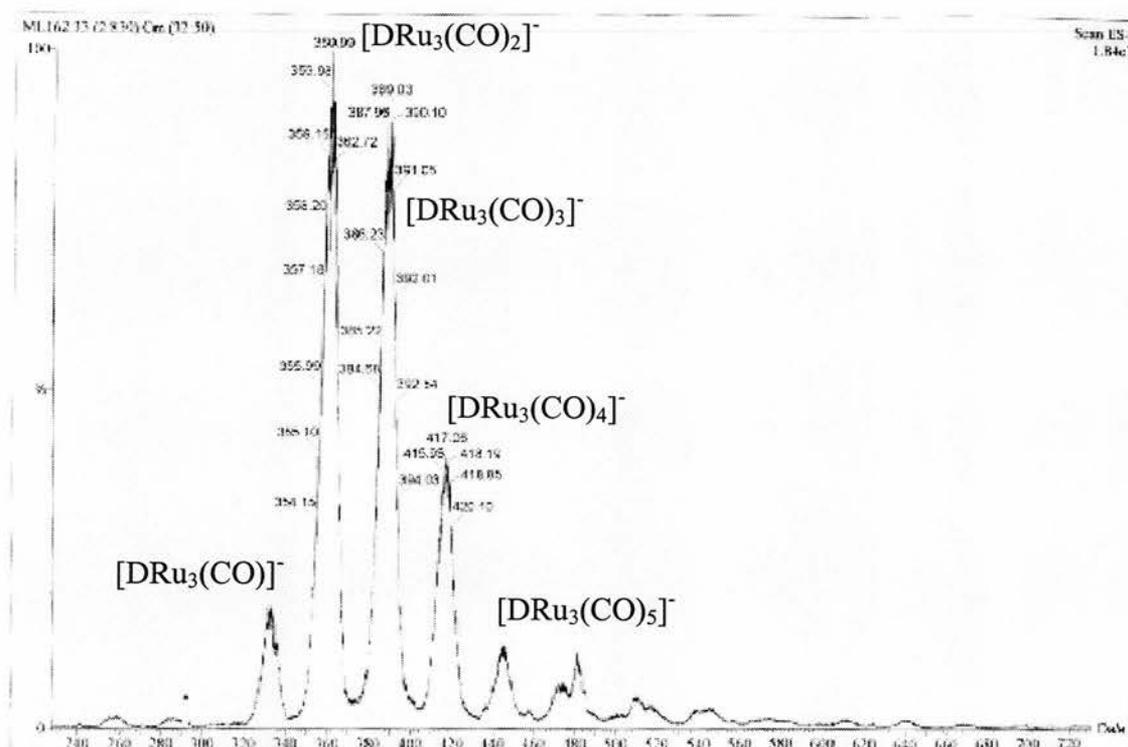
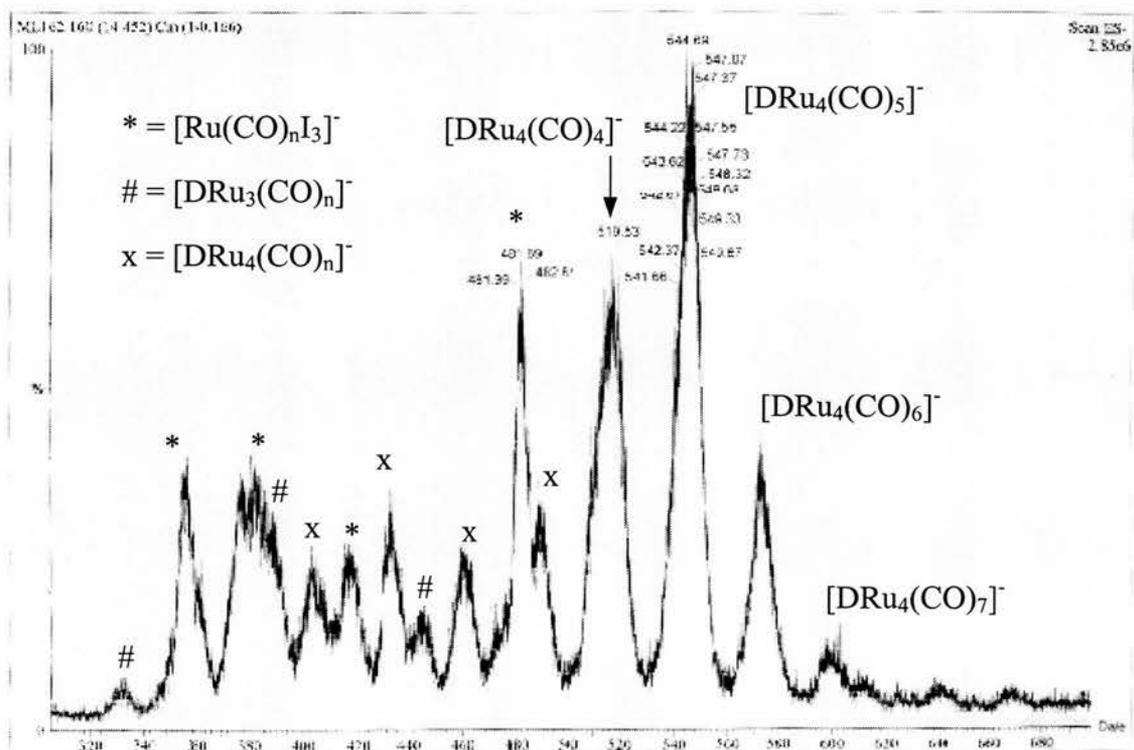


Figure 4.8; $[DRu_3(CO)_{11}]^-$ observed by ESMS after a CO hydrogenation reaction



An extraction voltage of 120 V was used to obtain these spectra. This causes a significant amount of fragmentation of the parent ion. The mass spectrum of the $[\text{DRu}_3(\text{CO})_{11}]^-$ ion (*Figure 4.8*) contains a series of peaks with a separation of 28 mass units, corresponding to the loss of different numbers of carbon monoxide ligands. Therefore, the observed fragment ions are of the form $[\text{DRu}_3(\text{CO})_n]^-$, where n can range from 0 to 11 depending on the extraction voltage used. When an extraction voltage of 120 V is used, the most abundant fragment ion is $[\text{DRu}_3(\text{CO})_2]^-$, which has a mass of 361. Fragment ions with $n = 1$ to 5 are observed under the conditions used.

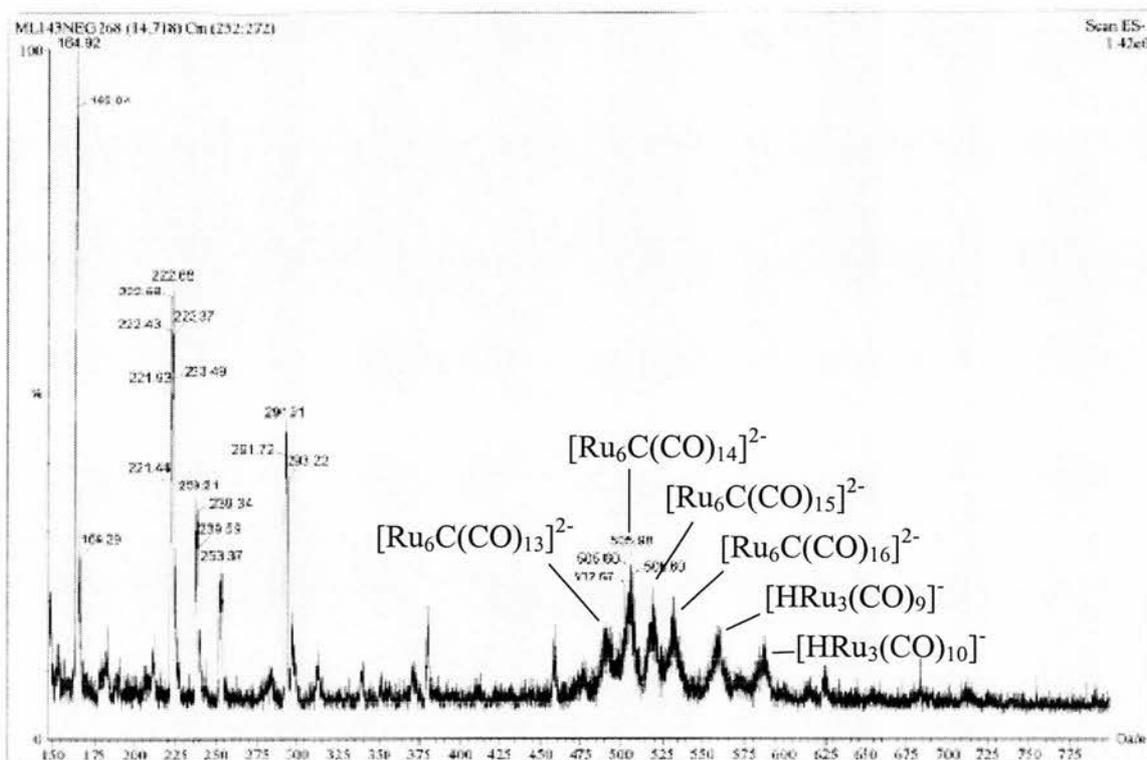
The $[\text{Ru}(\text{CO})_3\text{I}_3]^-$ ion is also fragmented using an extraction voltage of 120 V. Its mass spectrum (*Figure 4.7*) shows major peaks corresponding to $[\text{RuI}_2]^-$ ($m/z = 355$) and $[\text{RuI}_3]^-$ ($m/z = 482$). Associated peaks with one and two carbonyl ligands remaining attached are also observed, but once again the molecular ion peak is not observed using this extraction voltage. The presence of ruthenium (I) fragment ions of the form $[\text{Ru}(\text{CO})_x\text{I}_2]^-$ is slightly surprising, as they appear to arise from the loss of an iodine radical from the parent ion $[\text{Ru}(\text{CO})_3\text{I}_3]^-$.

A small amount of $[\text{DRu}_4(\text{CO})_{13}]^-$ is also present in the reaction mixture. Due to the low concentration of this ion, relative to the other two anions, a mass spectrum containing fragment ions of $[\text{DRu}_4(\text{CO})_{13}]^-$ alone could not be obtained. However, fragment ions of the form $[\text{DRu}_4(\text{CO})_m]^-$, where $m = 0$ to 7, can be seen (*Figure 4.9*). The most abundant fragment ion using an extraction voltage of 120 V is $[\text{DRu}_4(\text{CO})_5]^-$.

These ESMS results confirm the presence of $[\text{HRu}_3(\text{CO})_{11}]^-$ and $[\text{Ru}(\text{CO})_3\text{I}_3]^-$ after a carbon monoxide hydrogenation reaction. IR studies by Dombek¹ showed that both of these anionic species were present and necessary for effective CO hydrogenation. The observation of some $[\text{DRu}_4(\text{CO})_{13}]^-$ in the reaction solution is probably caused by the relatively low CO partial pressure, allowing some aggregation of ruthenium to form these clusters containing four ruthenium atoms. The amount of this anion present could not be quantified by ESMS, however, $[\text{DRu}_4(\text{CO})_{13}]^-$ appeared to be in a lower concentration than the other two anions. This demonstrates the potential of ESMS to be

used to identify components of a reaction mixture, even if several similar complexes are present. Identification of a mixture of several cluster complexes can be very difficult by IR spectrometry, for example.

4.2.4 The CO Hydrogenation Reaction at 235 °C



dianion are observed. Some peaks associated with $[\text{HRu}_3(\text{CO})_{11}]^-$ are carried over into this spectrum, but at this extraction voltage, $[\text{HRu}_3(\text{CO})_8]^-$ is the most intense fragment ion.

4.2.5 Effects of Water, HI and Iodomethane on the Ruthenium Species

Water, HI and iodomethane are not required for the ruthenium catalysed hydrogenation of carbon monoxide reaction, but are added to the system to enable the rhodium catalyst to carbonylate any methanol produced to form ethanoic acid. Various experiments have been carried out to study the effect of these components on the ruthenium catalysed CO hydrogenation reaction and the results are discussed in chapters 2 and 3. Study of the reaction solutions by ESMS can identify the ionic transition metal complexes present, and help to explain the observed results.

4.2.5.1 The Effect of Water

Addition of water to the ruthenium catalysed hydrogenation of carbon monoxide reaction has little effect on the activity of the catalyst. Deuterium labelling studies in section 2.2.5.3 show that methanol is still produced. Some protons derived from the added water find their way into the methanol produced, whereas the methanol is produced from hydrogen derived from hydrogen gas when no water is added.

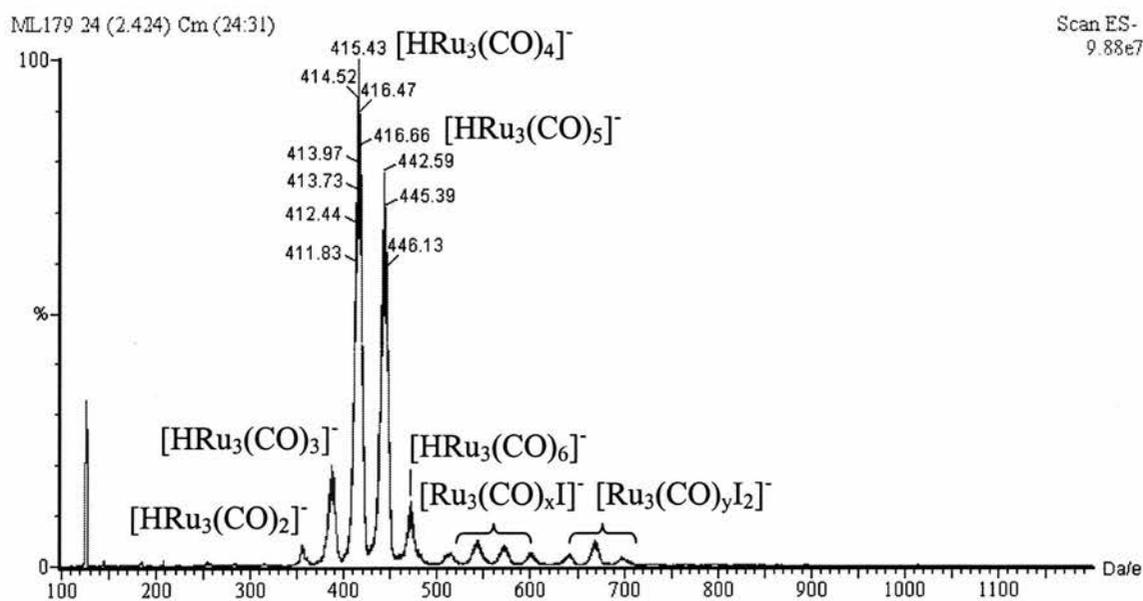


Figure 4.11; ESMS of $[\text{HRu}_3(\text{CO})_{11}]^-$ in the presence of water

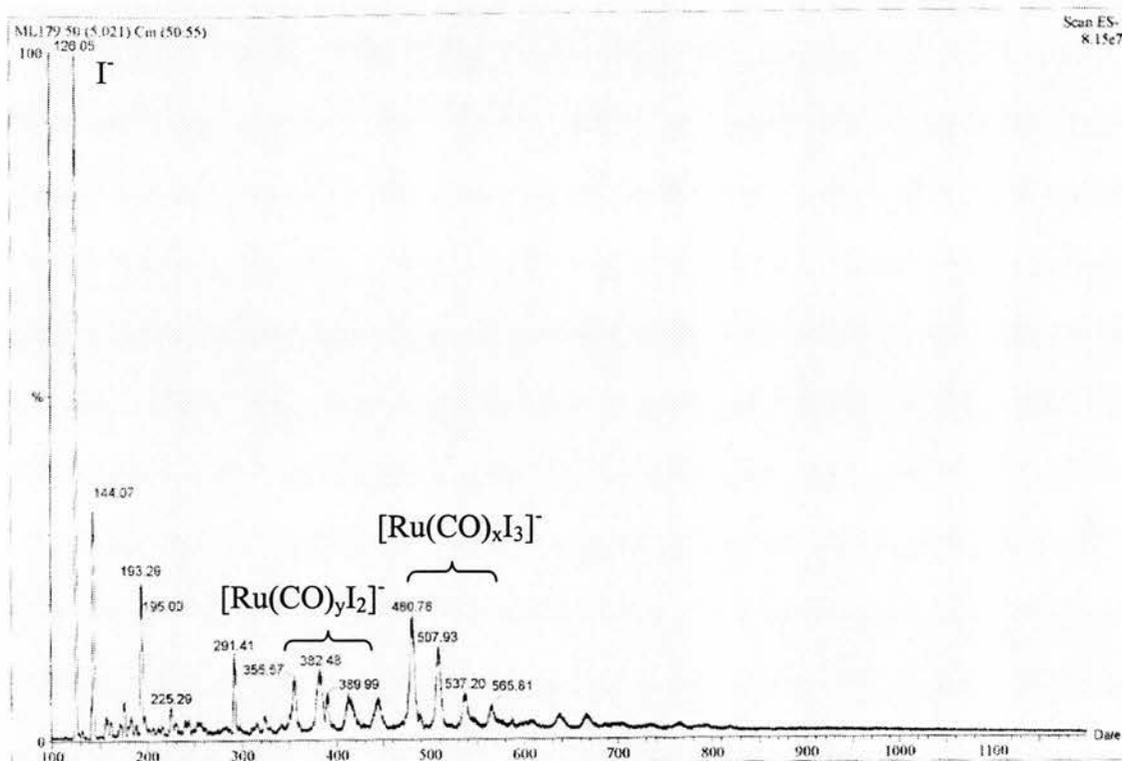


Figure 4.12; ESMS of $[\text{Ru}(\text{CO})_3\text{I}_3]^-$ in the presence of water

ESMS of the products of a reaction using $\text{Ru}_3(\text{CO})_{12}$, $\text{RhCl}_3 \cdot 3\text{H}_2\text{O}$, KI, NMP and water shows a significant amount of $[\text{HRu}_3(\text{CO})_{11}]^-$ (Figure 4.11) and some $[\text{Ru}(\text{CO})_3\text{I}_3]^-$ (Figure 4.12). These are the two co-catalysts required for the hydrogenation of carbon monoxide, which explains the production of methanol under these conditions. The presence of water (and rhodium chloride catalyst precursor) does not prevent the formation of either ruthenium co-catalyst, so the reaction proceeds normally.

No rhodium complexes are observed in this reaction solution and the rhodium added does not function as a carbonylation catalyst under these conditions, as no iodomethane is present. A small amount of catalyst decomposition is observed by the presence of peaks at $m/z = 514, 542, 570, 598$ and $m/z = 641, 669, 697$. These peaks are in two sets with peaks within each set separated by 28 mass units. The masses and peak shapes fit with complexes of the type $[\text{Ru}_3(\text{CO})_x\text{I}]^-$ and $[\text{Ru}_3(\text{CO})_y\text{I}_2]^-$, but conclusive characterisation is difficult due to their low concentration.

4.2.5.2 The Effect of Iodomethane

The effect of iodomethane on the reaction is dependent on the temperature of the reaction. At the low temperature of 167 °C it inhibits the CO hydrogenation reaction (section 3.2.1.1), but it is necessary for the formation of ethanoic acid at 200 °C. ESMS analysis of a reaction solution, where $\text{Ru}_3(\text{CO})_{12}$, KI, NMP, water and iodomethane were used at 200 °C, shows the presence of $[\text{Ru}(\text{CO})_3\text{I}_3]^-$. However, $[\text{HRu}_3(\text{CO})_{11}]^-$ is not observed (Figure 4.13).

Thus, the inhibition of the carbon monoxide hydrogenation reaction by iodomethane can be explained by the absence of the co-catalyst $[\text{HRu}_3(\text{CO})_{11}]^-$ in the reaction solution. The absence of $[\text{HRu}_3(\text{CO})_{11}]^-$ in the reaction solution is not restricted to the conditions of this individual reaction, as $[\text{HRu}_3(\text{CO})_{11}]^-$ is not observed in other

reactions where iodomethane is used. This is confirmed by high pressure FTIR results (section 4.2.8).

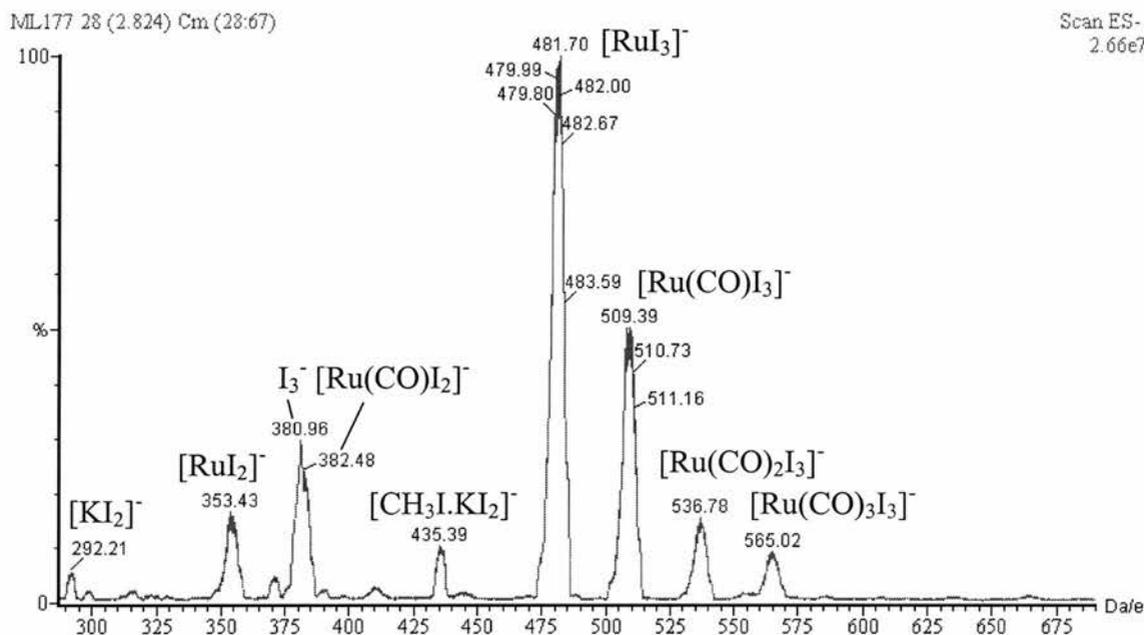


Figure 4.13; $[\text{Ru}(\text{CO})_3\text{I}_3]^-$ observed after a reaction using CH_3I

In the associated Ru/Co system for the formation of ethanoic acid from CO and hydrogen, studied by Knifton³, $[\text{HRu}_3(\text{CO})_{11}]^-$ is not observed under optimal conditions for ethanoic acid production. $[\text{Ru}(\text{CO})_3\text{I}_3]^-$ is observed and results indicate that this is the active catalyst. $[\text{HRu}_3(\text{CO})_{11}]^-$ is only detected spectroscopically when a carbon monoxide partial pressure of less than 85 bar, or a low iodide concentration is used. These conditions produce a low selectivity to ethanoic acid, favouring the formation of methanol and ethanol. The effect of iodomethane on the Ru/Co system is to completely deactivate the catalyst.

The peak at $m/z = 435$ is observed by ESMS in several reaction solutions. It does not have a characteristic ruthenium isotopic peak shape and can be found in reaction solutions that do not contain ruthenium. It is often observed at the same time as a peak at $m/z = 293$. These results suggest that the peak at $m/z = 435$ is caused by $[\text{CH}_3\text{I.KI}_2]^-$, with loss of CH_3I producing the associated peak at $m/z = 293$.

4.2.5.3 The Effect of HI

HI is an alternative to iodomethane to activate the rhodium catalysed methanol carbonylation reaction. Unfortunately, HI completely deactivates the ruthenium catalyst required for the hydrogenation of carbon monoxide (section 3.2.4.4).

ESMS of a reaction mixture where $\text{Ru}_3(\text{CO})_{12}$, RhCl_3 , KI, HI (0.5 ml, 6.65 mmol), water and NMP were used shows the presence of $[\text{Ru}(\text{CO})_3\text{I}_3]^-$ (Figure 4.14). This spectrum was obtained using a high resolution setting (HMRes = LMRes = 14.0), and the characteristic ruthenium isotope pattern can be seen clearly. The molecular ion appears at $m/z = 566$, with fragment ions associated with loss of carbon monoxide and iodide also observed.

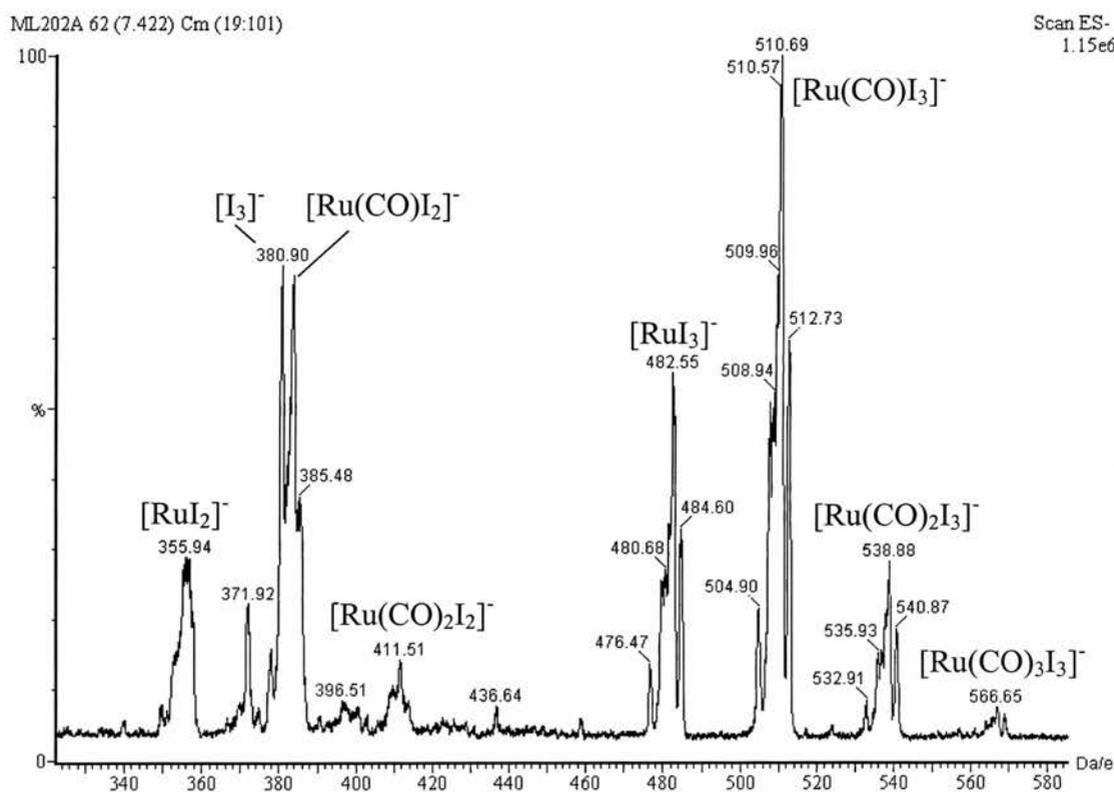


Figure 4.14; ESMS of a reaction using HI

The sharp peak at $m/z = 380.9$ is common to most negative ion ESMS experiments where a high concentration of iodide has been used and is caused by the $[I_3]^-$ ion. The peak at $m/z = 372$ does not have an isotope pattern indicative of a mono-anion containing one ruthenium atom. It is observed when ruthenium, KI, water and HI or iodomethane are used in the reaction mixture and the m/z value fits with a solvated cluster of ions of the form $[NMP.H_3O.I_2]^-$.

4.2.6 Analysis of the Rhodium Species Present

Rhodium species are not generally observed by ESMS after reactions where rhodium and ruthenium have been used together. This is partly due to the rhodium concentration being smaller than the ruthenium concentration in most reactions (a 5:1 atomic ratio in favour of ruthenium is generally used). Another problem is that anions containing rhodium could be hidden under corresponding ruthenium peaks.

The electrospray mass spectrum of a control reaction where rhodium was the only transition metal present shows several peaks from fragments of the form $[Rh(CO)_xI_y]^-$, where $x = 0$ or 1 and $y = 2, 3$ or 4 (*Figure 4.15*). This suggests that $[Rh(CO)_2I_4]^-$ is present in solution. This complex is part of the rhodium catalysed WGS reaction that is associated to the rhodium catalysed carbonylation reaction (see section 1.3.3.2). The active catalyst for the carbonylation reaction, $[Rh(CO)_2I_2]^-$, may be present, but it was not possible to distinguish its fragment ions from those of $[Rh(CO)_2I_4]^-$ by ESMS. The two biggest peaks (apart from I^- which is not shown) are at $m/z = 379$ and 435 and are caused by $[I_3]^-$ and $[CH_3I.KI_2]^-$, respectively.

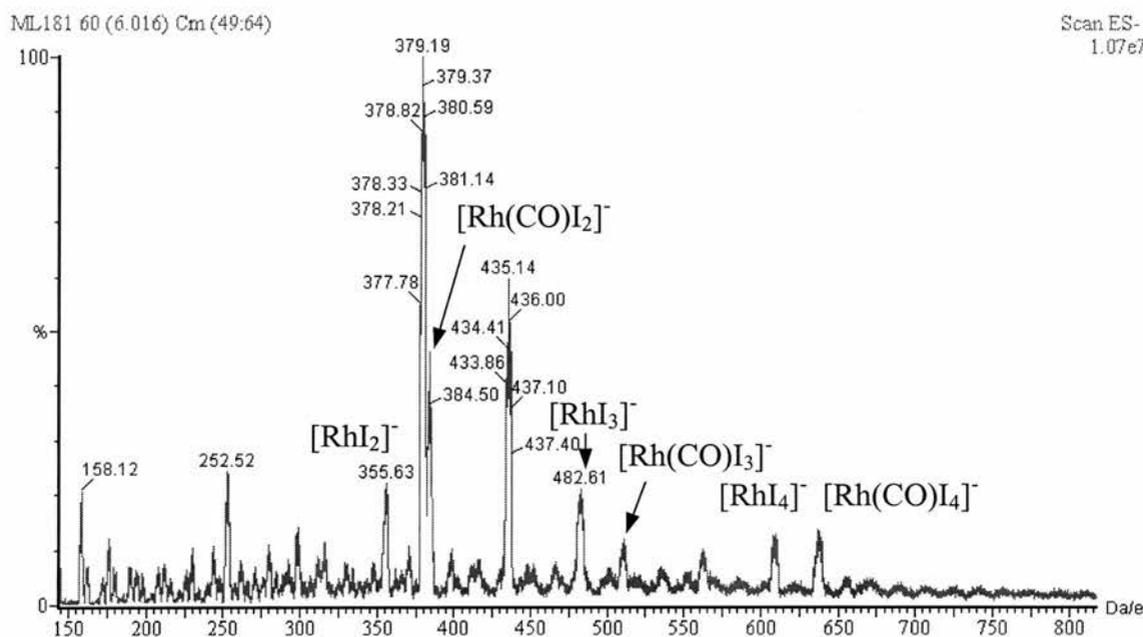


Figure 4.15; ESMS showing rhodium species present in a control reaction

Conditions: RhCl₃ (0.0181 g, 0.087 mmol), KI (0.829 g, 4.99 mmol), CH₃I (0.5 ml, 8.0 mmol), H₂O (1 ml, 55.6 mmol), NMP (10 ml) and CO/H₂ (1:1, 70 bar fill pressure) at 200 °C for 22 hours.

4.2.7 K⁺ and I⁻ Containing Species Observed by ESMS

Potassium iodide is an important component of the ruthenium catalysed CO hydrogenation reaction. Its main function is to prevent decomposition of the catalyst to clusters containing many ruthenium atoms, via loss of CO ligands. This is achieved by the formation of anionic complexes, such as [Ru(CO)₃I₃]⁻, which are stable at the reaction temperature. ESMS is particularly useful for the characterisation of [Ru(CO)₃I₃]⁻ and [HRu₃(CO)₁₁]⁻, but the gentle method of analysis allows other species containing K⁺ and I⁻ to be observed.

4.2.7.1 Species Containing K^+

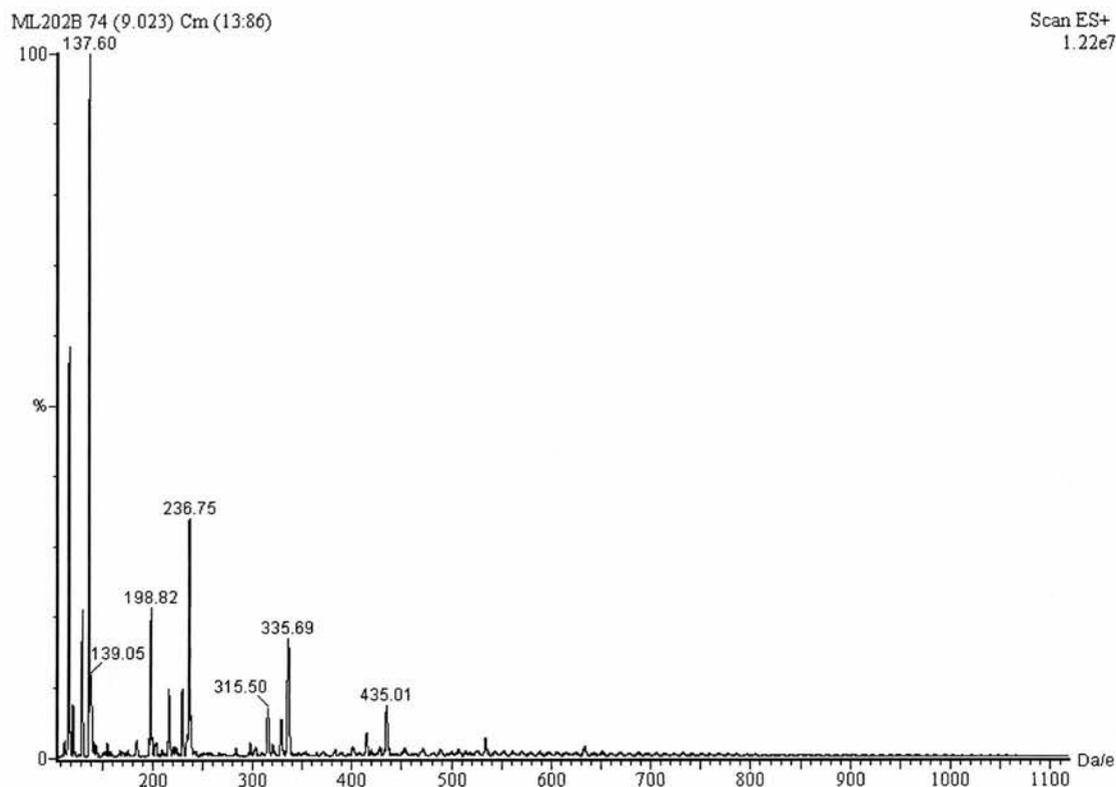


Figure 4.16; Positive ion ESMS of a reaction mixture

When reaction solutions are studied by positive ion ESMS, no transition metal complexes are observed. Instead, a series of sharp peaks is observed, starting at $m/z = 138$ and separated by 99 mass units (Figure 4.16). These are assigned to solvated potassium ions, $[K(NMP)_n]^+$. Potassium ions solvated by up to six or seven NMP molecules have been observed. This shows that NMP is capable of efficiently solvating potassium ions, which may be a reason why NMP is considered to be a good solvent for the hydrogenation of carbon monoxide reaction, catalysed by ruthenium¹⁴. By efficiently solvating potassium ions, NMP prevents the formation of ion pairs between potassium and the anionic catalytic species. Protons are also solvated by NMP, but to a lesser extent. Protons solvated by one NMP molecule is common, but generally protons surrounded by no more than two molecules of NMP are observed by ESMS.

4.2.7.2 Species Containing I

Iodide ions solvated by NMP are not observed by negative ion ESMS. However, iodide ions solvated by six or seven water molecules are often observed. Other species that are commonly seen in negative ion ESMS spectra are $[I_2]^-$ ($m/z = 254$), $[I_3]^-$ ($m/z = 381$), $[KI_2]^-$ ($m/z = 293$) and $[CH_3I.KI_2]^-$ ($m/z = 435$).

4.2.8 High Pressure FTIR Studies

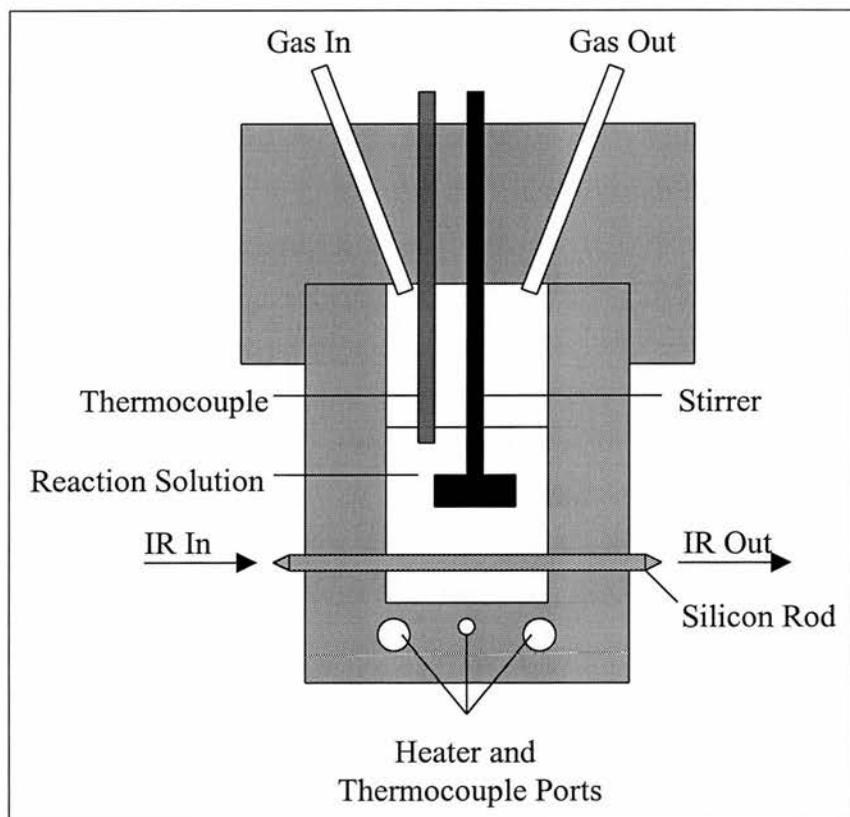


Figure 4.17; Schematic diagram of high pressure FTIR autoclave

The ruthenium and rhodium catalysed hydrogenation of CO to ethanoic acid reaction has been studied by FTIR under reaction conditions, using an autoclave fitted with a cylindrical internal reflectance rod. A diagram of this equipment is shown above (*Figure 4.17*). This method of IR study allows the reaction to be studied *in situ*, without first cooling the reaction and removing the gas.

IR spectra of the catalytic solution were taken every 5 minutes as the reaction was heated to 200 °C, then held for 3 hours. A series of background spectra were obtained by the same method, but in the absence of $\text{Ru}_3(\text{CO})_{12}$ and RhCl_3 and these were subtracted from the relevant sample spectra. The amounts of each reactant used for this reaction were in a similar proportion to other reactions carried out in batch autoclave or ballast vessel reactions, but were scaled to accommodate the high pressure FTIR equipment. (See *Table 4.1* for the amounts used). 70 bar of CO/H_2 (1:1) was added at room temperature and the total pressure was maintained at 110 bar at 200 °C using a ballast vessel.

	Reaction (g)	Reaction (mmol)	Blank (g)	Blank (mmol)
$\text{Ru}_3(\text{CO})_{12}$	0.2004	0.313	0	0
RhCl_3	0.0378	0.181	0	0
KI	2.217	13.4	2.206	13.3
CH_3I	3.056	21.5	3.025	21.3
H_2O	2.612	145.1	2.644	146.9
NMP	26.874	271.5	26.900	271.7

Table 4.1; Amounts used for the FTIR experiment

The resulting series of IR spectra show two main bands in the carbonyl region at low temperature. These are at 2049 cm^{-1} and 1978 cm^{-1} and grow slightly as the solution is heated, then remain the same sizes as the reaction is maintained at 200 °C. (*Figure 4.18*

shows spectra of the reaction mixture as it is held at 200 °C. Spectra of the mixture during heating are omitted for clarity.) These peaks are assigned as $[\text{Rh}(\text{CO})_2\text{I}_2]^-$, and are observed at 2055 cm^{-1} and 1985 cm^{-1} in CH_3I by Haynes *et al.*¹⁵. Another pair of peaks is observed at 2096 cm^{-1} and 2027 cm^{-1} . These are barely visible at first, but grow as the solution is heated and continue to grow throughout the time that the reaction is held at 200 °C. These peaks are assigned to $[\text{Ru}(\text{CO})_3\text{I}_3]^-$, which is observed at 2102 cm^{-1} and 2033 cm^{-1} in CH_2Cl_2 by Han *et al.*¹⁶.

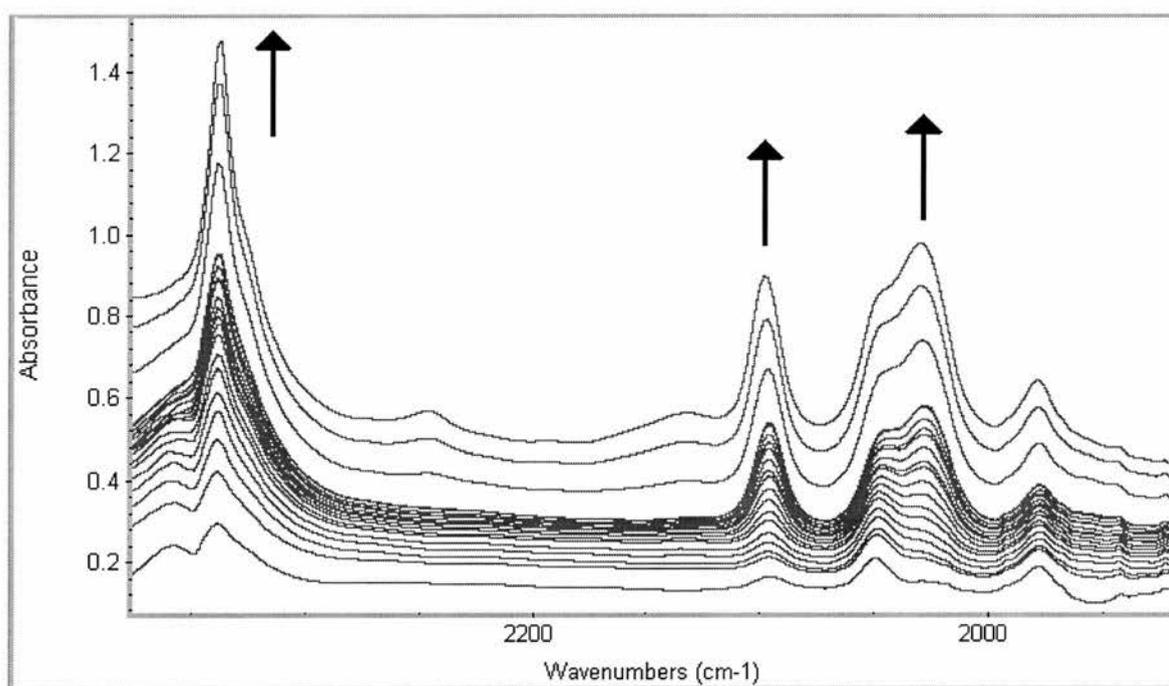


Figure 4.18; FTIR spectra of the reaction at 200 °C

Carbon dioxide evolution is observed by the increasing size of peak at 2340 cm^{-1} . This highlights the effectiveness of the catalyst to catalyse the water-gas shift reaction under the reaction conditions. Bands associated with $[\text{HRu}_3(\text{CO})_{11}]^-$, at 2072 (w) , 2016 (vs) , 1992 (vs) , 1954 (m) and $1710\text{ cm}^{-1}\text{ (w)}$ ¹⁶, are not observed. This supports ESMS results in section 4.2.5.2, where $[\text{HRu}_3(\text{CO})_{11}]^-$ is not observed when iodomethane is used (Figure 4.13).

4.3 Conclusions

Electrospray mass spectrometry is a very useful tool for the analysis of organometallic complexes in solution. It has been used to show that $[\text{HRu}_3(\text{CO})_{11}]^-$ and $[\text{Ru}(\text{CO})_3\text{I}_3]^-$ are present in reaction solutions after a ruthenium catalysed hydrogenation of carbon monoxide reaction. However, when iodomethane or HI is used in the reaction mixture only $[\text{Ru}(\text{CO})_3\text{I}_3]^-$ is observed. This result is confirmed by high pressure FTIR of the reaction solution *in situ*. Since $[\text{HRu}_3(\text{CO})_{11}]^-$ is a co-catalyst for the hydrogenation of carbon monoxide reaction, its absence explains the relative inactivity of reaction solutions containing iodomethane or HI.

$[\text{Rh}(\text{CO})_2\text{I}_4]^-$ is observed by ESMS, while $[\text{Rh}(\text{CO})_2\text{I}_2]^-$ is detected by *in situ* FTIR. This suggests that the rhodium present would act as a carbonylation catalyst if it were supplied with methanol (or iodomethane) from the hydrogenation of carbon monoxide reaction. ESMS shows that the NMP solvent has a strong affinity for solvating potassium ions. This is likely to prevent the formation of ion pairs between potassium ions and the anionic catalytic ruthenium species.

4.4 Experimental

4.4.1 Electrospray Mass Spectrometry

Electrospray analysis was carried out on a Fisons VG Platform mass spectrometer and analysed using the Mass Lynx, version 1.61, mass spectrometry data handling system. The source and mass spectrometer parameters were tuned prior to each injection and optimised settings were used. Typical parameter settings used were as follows.

Capillary Voltage = 2.00 kV

Counter Electrode (HV Lens) = 0.30 kV

Extraction Voltage = 80 V

Focus = 80 V

High Mass Resolution = 8.0

Low Mass Resolution = 1.0

Ion Energy = 2.5 V

Ion Energy Ramp = 1.0 V

Source Temperature = 60 °C

Multiplier = 792

The extraction voltage can be varied in the range 0 to 200 V to increase the extent of fragmentation of ionic complexes. Whenever the extraction voltage is changed, the focus should also be changed. It is found that the focus parameter should be set to the same value as the extraction voltage (or up to 10 V higher) to obtain optimal peak sizes. To obtain spectra with isotopic mass resolution, the high and low mass resolutions should be set to high values. (*Figure 4.14* was obtained using HMRes = LMRes = 14.0)

The general conditions for reactions studied by ESMS were, RhCl₃ (0.0140 g, 0.067 mmol), Ru₃(CO)₁₂ (0.071 g, 0.111 mmol), KI (0.83 g, 5 mmol), H₂O (1 ml, 55.56

mmol), CH₃I (0.5 ml, 8.0 mmol), NMP (10 ml), CO/H₂ (1:1, 70 bar at room temperature) at 200 °C for 20 hours. Some of the constituents may have been omitted for individual reactions, as indicated in the text.

4.4.2 High Pressure FTIR

Details of the equipment used are given in section 4.2.8. The equipment was tested for leaks under 110 bar of argon prior to the reaction. After the failure of a bursting disc and its replacement, no leaks were observed. The reaction was then carried out as described in the text.

4.5 References

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5.1 Conclusions

The hydrogenation of carbon monoxide reaction, homogeneously catalysed by iodide promoted ruthenium carbonyl complexes, has been shown to be active under relatively low pressure and temperature conditions of 110 bar and 200 °C. Under these conditions the reaction is selective to methanol and a turnover number of 250 mmol CH₃OH per mmol Ru₃(CO)₁₂ has been obtained using Ru₃(CO)₁₂ (0.0071 g, 0.111 mmol), KI (0.83g, 5 mmol), NMP (5 ml), CO:H₂ (1:1, 110 bar at 200 °C) for 19 hours, 40 minutes. One advantage of the low pressure conditions is that no 1,2-ethandiol is produced, which is beneficial for any subsequent carbonylation to ethanoic acid.

The use of mild pressure and temperature conditions causes the reaction to be particularly sensitive to factors such as the partial pressures of carbon monoxide and hydrogen, catalyst concentration and temperature. At 167 °C the reaction is especially sensitive to the partial pressure of CO and hydrogen, with a CO:H₂ ratio of 1:3 producing the most active reaction. Increasing the partial pressure of hydrogen at the expense of carbon monoxide causes some catalyst decomposition and deactivation, while increasing the amount of CO at the expense of hydrogen slows the reaction such that no methanol is formed with a CO:H₂ ratio of 1:1. At 235 °C catalyst decomposition is observed, even when a CO:H₂ ratio of 1:1 is used. However, the reaction is still active, but selectivity is lost with other hydrogenation and homologation products observed. Deuterium labelling studies prove that hydrogen gas is incorporated into the methanol produced by the ruthenium catalysed CO hydrogenation reaction. Addition of water to the reaction mixture causes a little H/D scrambling in the methanol produced, but the ruthenium catalyst is still active in the presence of water.

Electrospray mass spectrometry is a very useful MS technique for the analysis of involatile organometallic complexes in solution. It lends itself to the analysis of post catalytic solutions containing a mixture of complexes, as separation of individual complexes is achieved and characterisation is often unambiguous. This is particularly

useful when several carbonyl containing species cause the carbonyl region of the IR spectrum to be overcrowded, or literature IR spectra are unavailable.

ESMS analysis of carbon monoxide hydrogenation reaction solutions shows the presence of $[\text{HRu}_3(\text{CO})_{11}]^-$ and $[\text{Ru}(\text{CO})_3\text{I}_3]^-$, which act as hydride donor and hydride acceptor, respectively, in the CO hydrogenation reaction mechanism. After reactions at a temperature of 235 °C, or when a low partial pressure of carbon monoxide is used, larger ruthenium cluster complexes are observed by ESMS and some ruthenium metal is observed on the autoclave liner.

Addition of rhodium, iodomethane and water to the carbon monoxide hydrogenation reactants results in the formation of ethanoic acid at 200 °C. The reaction is relatively slow, but a turnover number of 159 mmol CH_3COOH per mmol $\text{Ru}_3(\text{CO})_{12}$ has been observed using a ballast vessel to maintain the total pressure at 110 bar, and only adding iodomethane after 64 hours of an 88 hour reaction. In batch autoclaves, or when a shorter reaction time is used, the amount of ethanoic acid produced is often similar to the amount of iodomethane added.

Deuterium labelling studies on the combined ruthenium and rhodium system show significant H/D scrambling within the ethanoic acid produced. The results suggest that hydrogen derived from hydrogen gas is incorporated into the ethanoic acid, but scrambling into the NMP solvent and within ethanoic acid make the results less conclusive than for the CO hydrogenation reaction. 50% of ethanoic acid produced in a reaction using $^{13}\text{CH}_3\text{I}$ contained no labelled carbon atoms suggesting that CO is the source of both carbon atoms.

Unfortunately, the use of iodomethane or HI inhibits the ruthenium catalysed CO hydrogenation reaction, especially at 167 °C. ESMS shows that CH_3I and HI, required for the rhodium catalysed carbonylation of methanol reaction, reduce the amount of $[\text{HRu}_3(\text{CO})_{11}]^-$ present in the reaction solution.

5.2 Further Work

The interaction of individual parameters within homogeneous catalytic systems can be very significant and complex. This research has studied the effect of various parameters within the combined iodide promoted ruthenium catalysed CO hydrogenation and rhodium catalysed methanol carbonylation reaction, but there is scope for further development. In particular, this research has highlighted the effect of iodomethane and HI on the ruthenium catalysed CO hydrogenation reaction, under low temperature and pressure conditions, to be especially significant.

The use of low temperature and low pressure conditions represent an area where the CO hydrogenation reaction has not been studied before and where methanol selectivity relative to 1,2-ethandiol is highest. Thus, these conditions remain attractive for the subsequent formation of ethanoic acid. Two series of experiments studying the effect of the amount of CH₃I and HI on the CO hydrogenation reaction at 110 bar and 200 °C would identify the conditions that offer optimal activity. This may translate into more ethanoic acid formed when rhodium is added if the conditions are suitable for the carbonylation catalyst. It would also be interesting to try using CO₂ and H₂, rather than CO and H₂. The ruthenium catalyst can catalyse the WGS reaction, forming CO which could then react further. However, catalyst decomposition may occur under the low initial partial pressure of CO.

Another area of potential improvement could be to use a different carbonylation catalyst, which may be active under conditions that are more suitable for the ruthenium CO hydrogenation catalyst. Iridium catalysed methanol carbonylation allows the use of low concentrations of water; while standing concentrations of CH₃I and HI are maintained at low levels due to fast oxidative addition (especially in the case of the anionic iridium carbonylation cycle). These conditions could be beneficial to the ruthenium catalyst. It would also be interesting to compare a potential Ru/Ir CO hydrogenation system with the Ru/Ir catalysed methanol carbonylation (Cativa) process.