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HOMOGENEOUS RHODIUM CATALYSED HYDROCARBONYLATION REACTIONS OF ALKENES

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DOCTOR OF PHILOSOPHY

University of Durham
Department of Chemistry

1991

This work is dedicated to my family

"The rock on which I stand"

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ABSTRACT

The conversion of ethene, carbon monoxide and water to propanoic acid by the catalytic action of various rhodium species, was investigated by infra-red spectroscopy and autoclave batch reactions.

Utilisation of a high pressure infra-red cell and a Fourier Transform infra-red spectrometry enabled study of the spectra of the catalytic systems at temperatures up to 180°C, and at pressures of 10 - 150 bar. The batch autoclave reactions enable rates, yield and selectivities to be determined with the aid of Gas Chromatography and Mass Spectroscopy.

Rhodium halides were used as precursors and the effects of solvents, water, iodide initiators, were studied. It was shown that polar solvents favoured hydrocarbonylation as did hydrous conditions. Ethyl iodide and hydrogen iodide were active initiators, however hydrogen iodide was observed to poison the catalyst forming $[Rh(CO)_2I_4]^-$ and other rhodium(III) species. At temperatures above 170°C rhodium(I) species such as $[Rh(CO)_2I_2]^-$ were more prominent.

A novel catalyst system was produced by employing rhodium(III) chloride, tin(II) chloride and hydrochloric acid. The nature of this system was studied in terms of solvents, the interaction of rhodium and tin, and the role of hydrogen chloride. Infra-red studies revealed rhodium-tin species in the reaction media. Studies were conducted to ascertain the role of cations and additives. Further studies determined the activity of other metals as co-catalysts to rhodium, showing tin to be a superior co-catalyst.

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The material contained in this thesis has not been submitted for examination for any other degree or part thereof, at the University of Durham or any other institution. The material contained herein is the sole work of the author except where formally acknowledged by reference.

CHAPTER ONE

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CHAPTER 1

RHODIUM CATALYSIS

1.1 Introduction

This thesis concerns the nature of, and the factors affecting, the rhodium homogeneous catalysis of the reaction of carbon monoxide, ethene and water to form propanoic acid.

The work is concerned with the promotion of catalysis by rhodium, to achieve greater rates, yields and selectivity than previously achieved with rhodium systems. The target of the study is the elucidation of the active catalyst system by employing Fourier Transform infra-red spectroscopy to the rhodium-carbonyl species in solution at appropriate reaction temperatures and pressures. In this manner it is possible to consider catalytic, and also non-catalytic, species present in terms of their effects on rate of reaction, yield and selectivity of reaction product.

Considerable work(1, 2, 3, 4) has been aimed at model compounds and systems that may be observed by conventional analytical methods. By interfacing the available methods of approach an integrated appraisal of the systems when under catalytical conditions may be made.

1.2 Homogeneous Catalysis

By stating that a particular reaction is catalysed, it is implied that there is present in the system a moiety that provides an alternative reaction pathway; and therefore different activation energy and hence different rate than if no catalyst was present. Inherent in the usage of the term "catalysis" is the fact that the moiety concerned must be regenerated by the reaction, otherwise a different reaction would have been accomplished. In considering catalysis it is normal to divide the subject into processes with heterogeneous catalysts and those employing homogeneous catalysts. Homogeneous catalysis may be further divided into catalysis by acid/base systems and those involving transition metals. This thesis is directly concerned with homogeneous catalysis; however a survey of both heterogeneous and homogeneous catalytic systems provides a prospective background for this work. The importance of catalysis to the chemical industry cannot be ignored. It is estimated that approximately 70% of all chemicals(5, 6) produced by the industry, will be processed by a catalyst at some point in production. It is of considerable significance that over 80% of catalysts used are heterogeneous.

Before extending our comparison of these two forms of catalysis, it should be noted that there is an area of hybridisation between the two forms. Some systems thought to be homogeneous have been shown to contain a suspension of aggregates, by light scattering experiments(6). In polymerisation reactions some catalysts may become attached to the polymer. This led to research into supported catalysts(7). Furthermore the "living" catalysis employed in some polymerisation reaction may be difficult to define distinctly as being of one form or the other.

As noted the major number of industrial catalysts are heterogeneous; this may appear somewhat surprising considering the advantages of homogeneous catalysis. The most striking advantage is that of selectivity. An excellent example of this is the "Monsanto Process" for the production of ethanoic acid from methanol and carbon monoxide which is 99% selective for methanol(8). The reason for this high selectivity is concerned with the molecular nature of the catalyst. It provides specific co-ordination sites for different reactant groups. There is a controlled environment for migration and addition type reactions, and there is little chance of interaction of two or more reaction moieties under normal concentration conditions. The best example of this molecular control of energetics and steriospecific conditions is given by the work of Davies with $Cp^*Fe(CO)(PPh_3)(MeCHCO^-)$ complexes(9). Coupled with this selectivity advantage arising from the molecular nature of the catalyst is the advantage of activity; every metal atom is available for reaction in homogeneous systems. In heterogeneous systems reactivity is often limited to surface atoms or the upper few angstroms of material. A great deal of effort is dedicated to increasing the surface area of heterogeneous catalysts to reduce this problem.

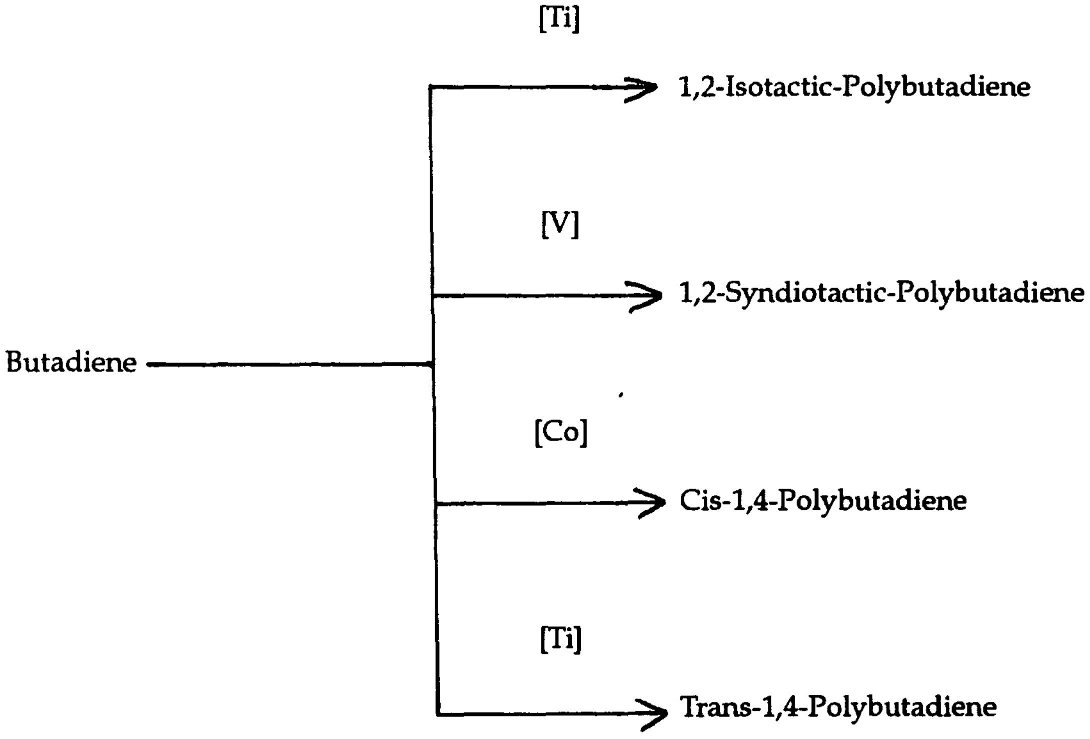
The temperature of reaction also tends to be much lower for homogeneous reactions, and economic advantage in terms of energy usage. Furthermore, recycling of energy is usually easier, as is control of temperature at the reaction site in homogeneous systems. It is more difficult to ensure the absence of localised heating in a heterogeneous system especially for an exothermic reaction(5). Reproducing the catalyst in the required manner, is far easier with homogeneous systems. This consistent reproducibility may in part be due to more detailed identification of homogeneous reaction systems. As mentioned Fourier Transform infra-red and also ultra-violet spectroscopy may be applied to homogeneous systems. In addition high pressure n.m.r. is rapidly being developed as is e.s.r. Studies on heterogeneous systems is much more complicated especially under reaction conditions. Fourier Transform infra-red can again be applied, also E.S.C.A. (X.P.S.) can also be applied to some catalyst surfaces; and work is being conducted with 111 metal crystal surfaces.

Given all the advantages of homogeneous catalysis, especially the major consideration of selectivity, it might be surprising that it is heterogeneous catalysts that are so widely used. There is a considerable single problem with homogeneous catalysis which makes it less attractive on an industrial scale. This is the separation and regeneration of the catalyst. By definition, heterogeneous catalysts are in a separate phase from reactants, and even if denatured they may often be regenerated "in situ". The separation of homogeneous catalysts often involves several chemical reactions(6) and separation processes. These additional processes can make homogeneous systems complex and uneconomical, especially considering that expensive platinum metals may be lost from the system. This has resulted in research into bridging the gap between homogeneous and heterogeneous catalysts(7). In an attempt to retain the greater activity and selectivity of homogeneous catalysts "soluble" moieties have been attached to solid supports such as crosslinked polystyrene or silica. This produces a heterogeneous catalyst with the implied advantages of separation(10).

The difficulty of catalyst recovery has meant that there are few industrial homogeneous plants in operation; however there is a potential for the exploitation of a large range of reactions. Hydrogenation, oxidation, hydrocyanation and hydrosilylation may all be catalysed homogeneously. Hydrosilylation is used to produce intermediates in the silicone industry and also in the reduction of ketones.

Du Pont have practised the hydrocyanation of butadiene yielding adiponitrile with high regioselectivity. Hydrogenation and oxidation have a greater range of applications, including the oxo-process and the Wacker process. Isomerisation, oligomerisation and polymerisation may all be catalysed homogeneously. The isomerisation of 2-methyl-3-butenenitrile to the linear nitrile is utilised industrially by Du Pont. The cyclic dimerisation and trimerisation of butadiene are practised homogeneously, and are referred to as Wilke-chemistry. In homogeneous systems polymerisation reactions can produce ordered macromolecules with a variety of different structures to that produced by radical generated polymers.

Figure 1.1



[M] infers use of a homogeneous catalyst containing the indicated metal.

Metathesis by homogeneous catalysts is used for norbornene, cycloctene and dicyclopentadiene production. Homogeneous catalysts are also employed for the synthesis of fine chemicals including heterocycles and natural products.

The major engineering requirements for any industrial process have been noted as generally disfavourable to homogeneous systems when compared to heterogeneous systems. Apart from the problem of catalyst recovery, there is an increasing trend towards processes with low energy usages. The mild conditions of homogeneous catalytic reactions will become more important as this trend continues.

Another factor of major significance when considering the potential of a process for industrial use is the availability and cost of the raw materials required.

In the recent past raw materials have been derived from crude oil but there is a growing tendency to move towards alternative feedstocks for economic, political, technological and environmental reasons. These alternative feedstocks include synthesis gas, coal, biomass and carbon dioxide. This wider range of feedstocks encourages new technology, insulates producers from fluctuations in feedstock prices, such as occurred during the oil crisis of the mid-seventies, and can reduce logistical problems if local feedstocks may be employed. Synthesis gas may be generated from natural gas, coal and biomass giving its technologies great flexibility. Furthermore, synthesis gas chemistry can be utilised in two areas of catalysis of great exploitation potential, these being Fischer-Tropsch chemistry, and methanol chemistry. Both alkanes and carbon dioxide have in the past been considered as too inert for economic reaction, but now the activation of these compounds by transition metals is being realised(11, 12).

As well as this potential for diversification in raw materials with synthesis gas chemistry, there is also the potential for diverse small tonnage processes for the pharmaceutical, agricultural and electronics industries. These high value products often require high purity and possibly sterioselectivity, an area much more suited to homogeneous catalysis. Also selectivity may become increasingly important environmentally as the waste disposal of by-products is required to meet more stringent restrictions. This also makes marketing sense as the market balance for two or more products from a process is highly unlikely to match process production. The future should see an increasing trend towards homogeneous catalysis in low tonnage high quality and speciality chemicals and probably the use of "supported" catalysts at the homogeneous/heterogeneous interface for high tonnage processes.

1.3 Chemistry of Homogeneous Rhodium Catalysis

1.3.1 Introduction

Rhodium is used in a wide range of catalytic reactions(6,13) both homogeneous and heterogeneous. The reason for this versatility lies with the catalytic reaction pathways for homogeneous catalysis which are based on the repetition of a limited number of reactions. These are co-ordinative addition, cis-migration, and oxidative addition/reductive elimination reactions. Rhodium fills the requirement of enabling all these reactive steps. The high selectivity often achieved can counter-balance its high cost.

1.3.2 Rhodium Chemistry

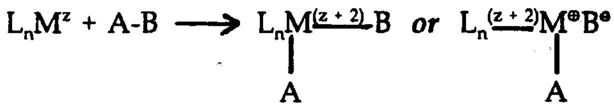
The chemistry of rhodium is largely confined to the (-I) to (III) oxidation states, higher oxidation states are confined to compounds of fluorine. The compounds of the (-I) and (O) states are those compounds formed by π-acidic ligands, particularly carbonyl ligands and ligands that may be substituted for carbonyls, such as $[Rh(CO)_4]^-$ and $[Rh(dipy)_2]^-$ (14). Rhodium(II) compounds are limited to short-lived species(15), sterically stabilised species(16) and species containing metal-metal bonds such as $[Rh_2(OCOCH_3)_4]$(17).

It is the chemistry of rhodium(I) and rhodium(III) compounds that are of particular interest to this project. Rhodium(I) compounds are exclusively those in which all or some of the ligands are "π-acidic". Rhodium(I) has a "d^8" electronic structure and in common with most low oxidation state transition metals, it has a high electron density. The "π-acidic" ligands are carbonyl, "PR_3" and ethene ligands, all of which possess empty low-lying orbitals of π nature. These π orbitals can accept electron density from the metal centre. The σ bond from carbon to metal enhances the π bonding and vice versa, thus the process is known as "synergic". The π-bond donates electron density in the opposite direction to the σ bonds, hence this is often referred to as "back bonding". Rhodium(I) compounds are known in the coordinatively saturated trigonal bipyramidal configuration. By far more common is the square planar structure which is favoured for the coordinatively unsaturated 16 electron configuration. This structure is energetically favoured in terms of d-orbital splitting, determined by the fact it has d^8 - 16 electron structure. Most complexes are 6-coordinate octahedral, coordinatively saturated and there is extensive coordination-substitution chemistry. Rhodium(III) is also highly susceptible to reduction to rhodium(I) particularly by carbon monoxide.

This ease of interconversion from rhodium(I) to rhodium(III) is the basis of a pair of reactions that have great significance for homogeneous catalysis; the couple being oxidative addition and its antithesis, reductive elimination.

1.3.3 Oxidative Addition - Reductive Elimination

The terms oxidative addition and reductive elimination have no significance in terms of mechanism, the reactions encompassed by these descriptions are wide ranging. In oxidative addition we may consider the metal centre involved as both a Lewis acid and a Lewis base. For these processes we require the metal concerned to possess two relatively stable oxidation states. For the two electron process described below these states must be formally two units apart; for the one electron process formally one state apart. In general the mechanisms are complicated by the fact they are dependent on the nature of the ligand-metal system and that of the group adding to the metal centre. For oxidative addition, as indicated earlier, there are broadly two processes. Firstly the two electron process:



$$L_nM^z + A\text{-}B \longrightarrow L_n\underset{\displaystyle A}{\underset{|}{M}}\overset{(z+2)}{-}B \quad \textit{or} \quad L_n\overset{(z+2)}{-}\underset{\displaystyle A}{\underset{|}{M}}{}^{\oplus}B^{\ominus}$$

and secondly the one electron process:

$$2M^z + A\text{-}B \longrightarrow M\overset{z+1}{-}B + M\overset{z+1}{-}A \quad \textit{or} \quad B-M\overset{z+1}{-}M\overset{z+1}{-}A$$

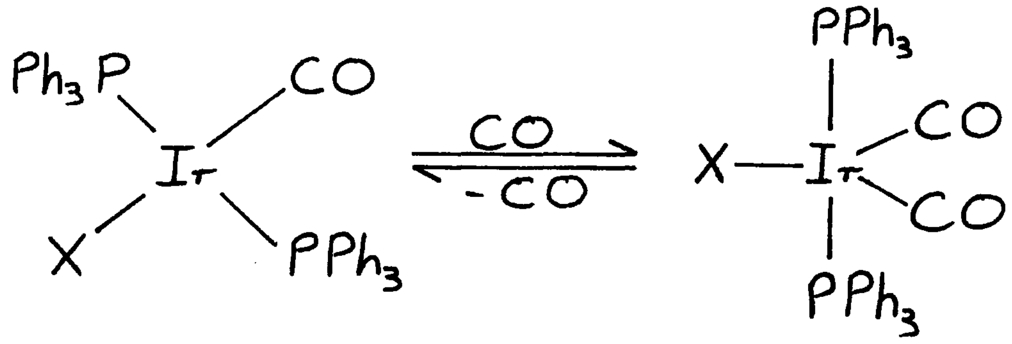
It is the former process that is of most importance to our work. It is also the more common reaction and hence the most extensively studied. For these reasons the two electron process will be considered exclusively henceforth.

The reaction of chlorocarbonyl - di(triphenylphosphine)iridate(I) has been extensively investigated by Vaska(19). The metal centre is coordinatively unsaturated and possesses the d^8 electronic configuration. When this complex undergoes oxidative addition it forms an octahedral iridium(III) complex with a d^6 electronic configuration at the metal. It should be noted that it is perfectly feasible for the coordinatively saturated 18 electron systems to undergo oxidative addition as long as a ligand is expelled from the metal ligand shell.

For example:

$$Ru^0(CO)_3(Ph_3P)_2 + I_2 \longrightarrow Ru^{II}I_2(CO)_2(PPh_3)_2 + CO$$

It should be noted that for these d^8 complexes the equilibrium between the four and five coordinate states is dependent on the ligands.



For the equilibrium above, if X = Cl, then the planar mono-carbonyl complex is stable although the dicarbonyl may be made under pressure of carbon monoxide(20). If X = I, then the five coordinate dicarbonyl is stable at room temperature and must be heated to remove one of the carbonyl ligands.

Vaska(19) studied a large number of reactions with chlorocarbonyl - di(triphenylphosphine)iridate(I). It is possible to classify the attacking groups into three classes. Broadly speaking there are firstly non polar such as H_2, RCHO, RH, ArH; secondly, molecules that remain unfragmented when added, for example O_2. Thirdly, there are polar electrophiles such as X_2, HY, RX, RCOX.

This third group, of most interest to this project, contains the Brönsted acids HY. When oxidative addition to a complex occurs, in polar solvents, the following mechanism may be envisaged:

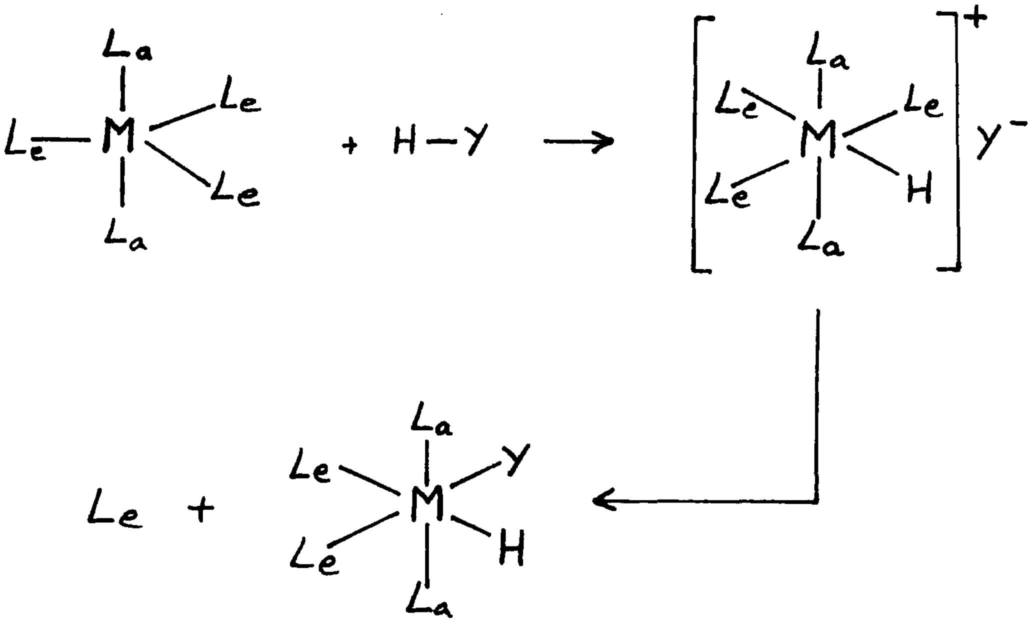
$$M^{z} + H^{\oplus} \rightarrow [M^{z} - H]^{\oplus} \xrightarrow{+B^{-}} B\text{-}M^{z+2}H$$

However it can be determined that for the addition of hydrogen chloride to the following complex the chloride anion adds first(21).

$$\mathrm{Ir(Cl)(COD)(PEtPh_2)} \xrightarrow{Cl^{-}} \mathrm{Ir(Cl)_2(COD)(PEtPh_2)^{-}} \xrightarrow{H^{+}} \text{trans - }\mathrm{HIr(Cl)_2(COD)(PEtPh_2)}$$

COD = Cyclooctadiene

The case for the five coordinate species will also be of interest to this thesis:



Le = Equatorial ligand, La = axial ligand.

In non-polar solvents it is possible to produce the cis-adduct on addition to the four coordinate species. Furthermore Vaska(19) used far-infra-red spectroscopy to show that the oxidative addition of gaseous HY to crystalline $Ir^{(I)}(CO)(PPh_3)_2Cl$ also gave cis addition. Therefore the mechanism of oxidative addition is not only dependent on the nature of the metal complex and the groups adding, but also the state of these reactants and the solvent.

The reverse reaction, reductive elimination, has not been studied so extensively, however in many catalytic homogeneous reactions it is the step that procures the organic product from the metal centre(22). There are five factors that favour intramolecular reductive elimination. Firstly, the cis orientation of the leaving groups is a prerequisite for this reaction as has been demonstrated(23) experimentally. A high formal charge on the metal in the initial complex also aids reductive elimination(24). The presence of bulky ligands can also be of aid, as reductive elimination usually decreases the coordination number, and there can be obvious steric advantages for elimination when bulky ligands are present. It is also obvious that the complex produced must have a favoured electronic configuration (eg, d^8). When the two electron process is disfavoured by this factor, then the one electron process may take place:

$$M\overset{z+1}{-}A + M\overset{z+1}{-}B \longrightarrow M\text{-}M + A\text{-}B$$

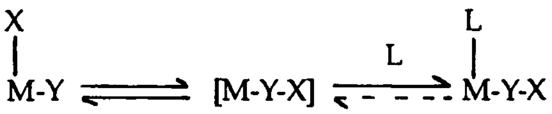
This reaction occurs in very few cases.

1.3.4 Cis-Migration

Cis migration reactions are often referred to as "insertion" reactions although the term is misleading. Two types of cis-migration reaction, intermolecular and intramolecular have been identified. Intermolecular reactions have the following form:

$$\ddot{X} + M\text{-}Y \rightarrow M\text{-}X\text{-}Y$$

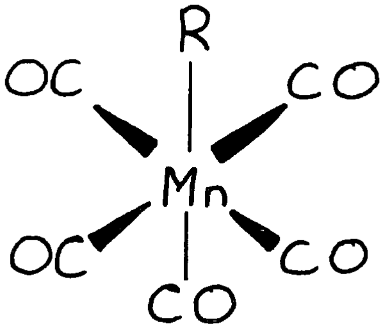
It may be seen that they are nucleophilic additions, not of interest to this project. The intramolecular "migratory insertion" of cis-migration is involved in hydrocarbonylation as well as many other catalytic processes. The form of this reaction is:

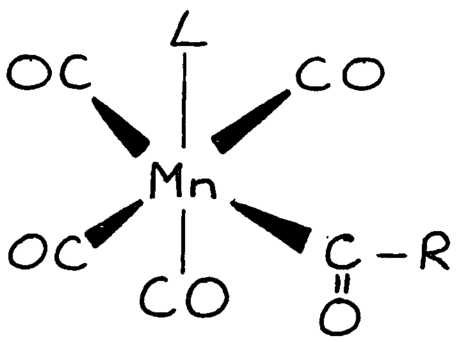


$$\overset{\displaystyle X}{\overset{|}{M}}\text{-}Y \rightleftharpoons [M\text{-}Y\text{-}X] \overset{L}{\rightleftharpoons} \overset{\displaystyle L}{\overset{|}{M}}\text{-}Y\text{-}X$$

Migration to Carbon Monoxide

This is probably the best studied reaction of this type, and of particular interest to us is the migration of alkyl groups to carbon monoxide to form an acyl group. This reaction has been studied(25) for the following system:





$L = CO, PR'_3, R_3N, X^-$

The general features of the reaction are that the alkyl is adjacent to the carbonyl ligand. Also once the alkyl has migrated there follows a separate step in which the unsaturated complex takes up a ligand in the site vacated by the migrating alkyl group. It is also a feature that a chiral alkyl group will migrate with retention of configuration.

The aptitude for a group to migrate is as follows:

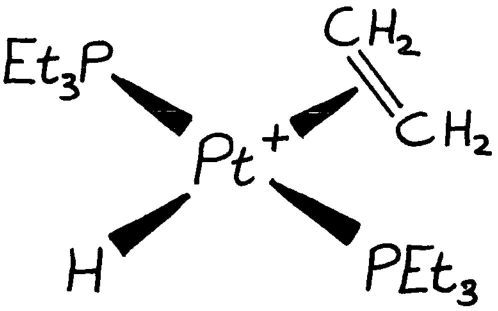
Alkyl > Benzyl > H,perfluoroalkyl,acyl

Indeed for the last three groups only, the reverse reaction is known.

As has been mentioned there is an unsaturated intermediate. If the case of the octahedral d^6 complexed metal is considered we would expect the formation of a square pyramidal intermediate as exhibited by isolated five coordinate d^6 complexes. It has been proposed(26) that the intermediate could alternatively be trigonal bipyramidal in a high spin d^6 configuration provided that the ligand field strength of all five ligands were equivalent. We have already mentioned the cis requirement for these migrations which may be demonstrated by the macrocyclic complexes of rhodium. The macrocyclic is able to coordinate at the four equatorial sites, thus preventing cis association of other ligands. Both the alkyl and acyl complexes are known but they are not interconvertible(27).

Hydride-Migration

This reaction and its reversal, β-hydrogen elimination, is of particular interest to reactions involving alkenes, being an obligatory step for alkene hydrogenation, hydroformylation and related reactions. The intramolecular migration of hydrogen to an alkene is extremely facile, a fact demonstrated by the lack of complexes containing both hydride and olefin ligands. One example is stabilised by the trans arrangement of these ligands(28).



Stereochemical and isotopic studies have shown that hydride alkene migratory insertion is highly stereospecific, suggesting that the hydride, metal and alkene are all co-planar in the intermediate. This would explain why certain catalytic hydrogenations are invariably cis.

1.4 Industrial Processes

As has been mentioned previously, only a small amount of industrial processes employ homogeneous catalysts. These processes should however be considered as several have a major bearing on the project undertaken.

1.4.1 Water Gas Shift Reaction

Synthesis gas is a mixture of hydrogen and carbon monoxide gas. It is produced by the steam reformation or partial oxidation of hydrocarbons. However the ratio of the two product gases is unlikely to be that required for the intended process (Chapter 2: Reference 13). The Water Gas Shift reaction is used to convert carbon monoxide and water to hydrogen and carbon monoxide, thus enriching the hydrogen content.

$$CO + H_2O \rightleftharpoons CO_2 + H_2$$

On a commercial scale this process uses heterogeneous catalysts, Cr_2O_3 at 350°C or Cu-Zn-Oxide at 200 - 300°C(29). However the equilibrium is catalysed by many homogeneous catalysts including $Pt(PR_3)_3$, $Ru_3(CO)_{12}$, $HFe(CO)_4^-$, and $[Rh(CO)_2I_2]^-$(30, 31, 32, 33). It is a reaction that is often responsible for side reactions, by virtue of producing hydrogen for reduction.

The catalytic cycle takes the form:

$$M^{\oplus} - CO + H_2O \xrightarrow{-H^{\oplus}} [M - (CO)OH]$$

$$[M - (CO)OH] \longrightarrow M - H + CO_2$$

$$M - H + H^{\oplus} \longrightarrow M^{\oplus} + H_2$$

$$M^{\oplus} + CO \longrightarrow M^{\oplus} - CO$$

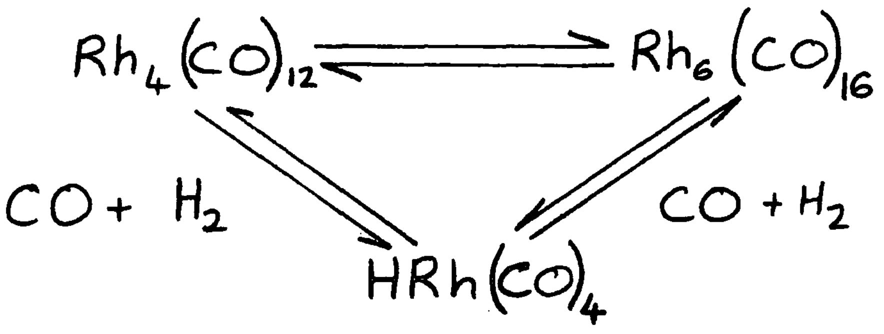
The nucleophilic attack(34) of a hydroxy group at the metal-carbonyl group produces an unstable hydroxycarbonyl group, which then loses carbon dioxide. This loss of carbon dioxide may proceed in one of two manners. Firstly(37), a coordinatively unsaturated [M-(CO)OH] complex may lose carbon dioxide by an analogue of β-hydride elimination; secondly(38), the anionic complex $[M\text{-}CO_2]^-$ can lose carbon dioxide to form the metal complex anion which combines with a proton to form the hydride. It should be noted that the loss of carbon dioxide from a complex not only arises from metal-carboxylic acids(36) but also from complexes of the formate anion:

$$M\text{–}O(CO)H \rightarrow M\text{-}H + CO_2$$

In general we must be aware that this reaction may take place in the reaction systems reported in this thesis.

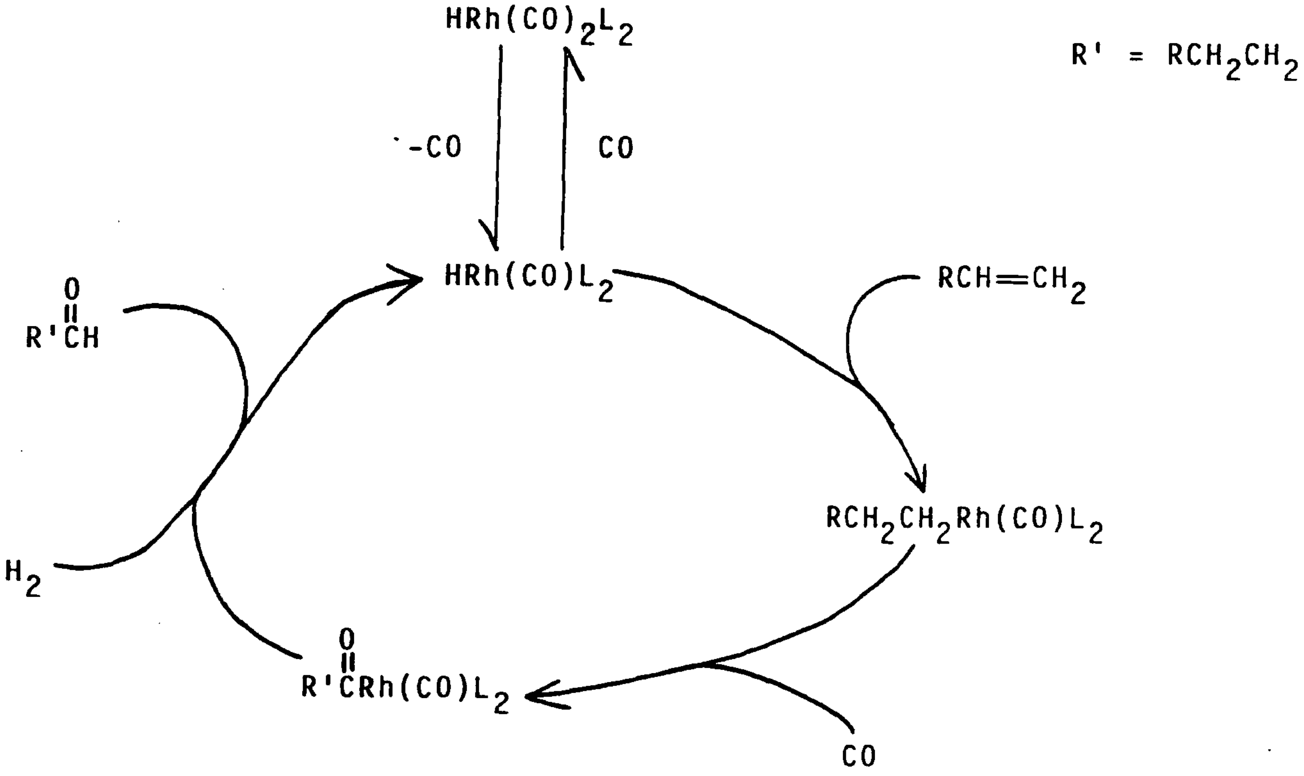
1.4.2 The "OXO" Process

This process concerns the reaction of alkenes with carbon monoxide and hydrogen. The reaction is often referred to as "Hydroformylation" despite the fact that there are no formyl intermediates. Commercially the process is used for the conversion of propylene to n-butyraldehyde and iso-butyraldehyde. Also linear alkenes such as 1-octene are converted to linear alcohols for use in detergents. The catalysts used are either complexes of cobalt or rhodium, eg $HCo(CO)_4$, $Rh(CO)(PPh_3)_3$. The rhodium carbonyls are poor catalysts for the reaction, the following equilibria being present in solution:

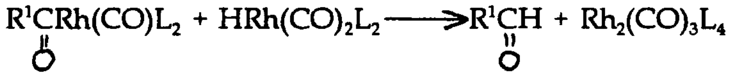


The lower of the three complexes is believed to be the active catalytic species; however it will also give rise to hydrogenated and isomerised alkenes. However the addition of phosphine to modify the catalyst produces high selectivity and reaction at room temperature and pressure. The precatalysts for the modified system include: rhodium on carbon; $Rh(CO)(Cl)(PPh_3)_2$ and Et_3N; $(acac)_2Rh(CO)_2$, and $HRh(CO)(PPh_3)_3$. These modified catalytic systems were employed by Union Carbide in 1976(39, 40). The systems were extensively studied by Wilkinson and his co-workers(41). The reaction can be undertaken at moderate condition (even in molten triphenylphosphine) at 100°C and up to 50 atmospheres of CO/H_2 pressure. It is found(42) that the triphenylphosphine present slowly degrades, probably by oxidation of the phosphorus-carbon bond. A number of studies into the phosphine modified rhodium catalysis were conducted by infra-red and N.M.R. techniques, in an attempt to elucidate the mechanism(43). These studies resulted in the mechanism proposed as shown in Figure 1.2, although there are still areas of uncertainty.

Figure 1.2



A study which attached a phosphine rhodium complex to silica to produce a "supported" catalyst showed that only rhodium complexes close enough together to achieve bi-metallic elimination were catalytically active, suggesting that the one electron reductive elimination takes place(44).



$$R^1\underset{\underset{O}{\|}}{C}Rh(CO)L_2 + HRh(CO)_2L_2 \longrightarrow R^1\underset{\underset{O}{\|}}{C}H + Rh_2(CO)_3L_4$$

$$Rh_2(CO)_3L_4 + CO + H_2 \longrightarrow 2HRh(CO)_2L_2$$

Whether this mechanism can be extended to the fully soluble systems is open to speculation.

1.4.3 The "Monsanto" Process

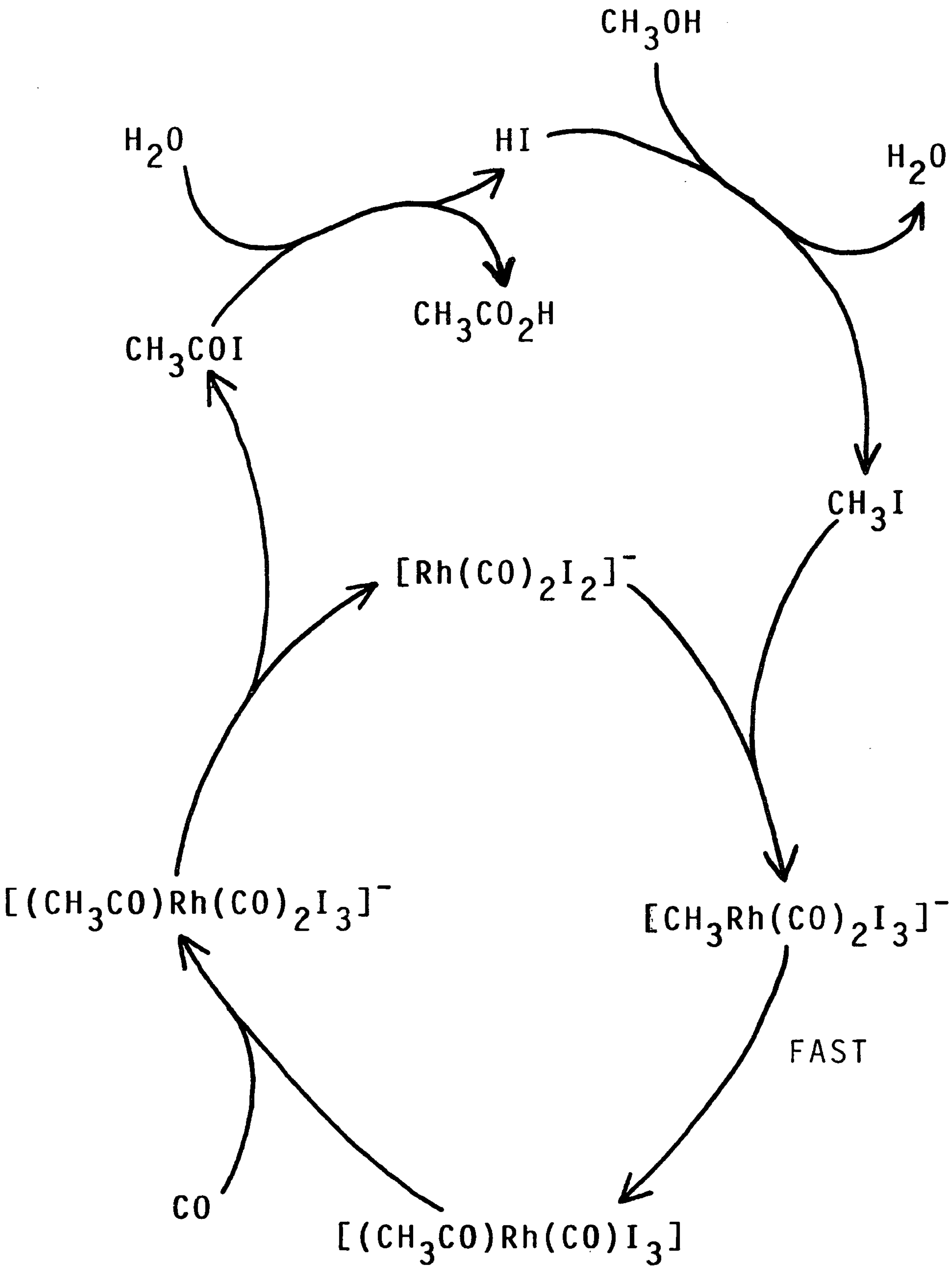
The Monsanto process involves the carbonylation of methanol to acetic acid. It is the most technologically successful of all homogeneous catalytic processes(45, 46), with rates in the enzymatic range and a selectivity with respect to methanol exceeding 99% for acetic acid.

Acetic acid was initially produced by fermentation of molasses to give ethanol which was then oxidised to acetic acid. The first major synthetic process was based on the oxidation of ethanol; produced by mercury(II) ion catalysed hydrolysis of ethene which in turn was produced from naphtha. This process continued until the 1960s when two new processes were developed. Celanese and British Petroleum introduced short-chain paraffin oxidation using manganese or cobalt catalysts(47, 48) and Walker Chemie developed palladium-copper catalysed oxidative-hydration of ethene to ethanal. 1965 saw the development of B.A.S.F.'s cobalt-iodide catalysed carbonylation of methanol. This was then superseded by the more efficient Monsanto process. The cobalt process requires conditions of 210°C and 700 atmospheres whereas the rhodium process operated at 180°C and 30 - 40 atmospheres. The process can utilise almost any form of rhodium from dichlorotetracarbonyldirhodate(I) to rhodium(III) nitrate(V). In all cases the same species is found in solution, that is diiododicarbonylrhodate(I) anion $[Rh(CO)_2I_2]^-$. Various iodide sources may also be employed from aqueous hydrogen iodide to caesium iodide. The rate determining step for the reaction may be shown to be the oxidative addition of methyl iodide to the rhodium species $[Rh(CO)_2I_2]^-$, the rate equation -

$$\text{Rate} = k[\text{Rh}]^1[\text{I}]^1[\text{MeOH}]^0[\text{CO}]^0$$

is shown to be independent of the two reactants methanol and carbon monoxide. Forster(49) reacted excess methyliodide with diiododicarbonylrhodate(I) anion and produced the 5-coordinate acyl complex, $[(CH_3CO)Rh(CO)I_3]^-$ which forms a dimer. Treatment of this complex with carbon monoxide produces the six coordinate acyl complex $[(CH_3CO)Rh(CO)_2I_3]^-$ which will then react to form ethanoic iodide and the starting rhodium(I) complex. Methyliodide is a special alkyl-iodide additive case; as not only is it expected to have the fastest rate of addition of all the alkyliodides, but it is also unable to undergo β-hydride elimination reaction. The catalytic cycle proposed for the Monsanto process is shown in Figure 1.3. The work of Forster has confirmed almost all the steps of the reaction are feasible. However under catalytic conditions only the rhodium(I) species $[Rh(CO)_2I_2]^-$ is observed.

Figure 1.3


CH_3OH
H_2O
HI
H_2O
CH_3CO_2H
CH_3COI
CH_3I
$[Rh(CO)_2I_2]^-$
$[(CH_3CO)Rh(CO)_2I_3]^-$
$[CH_3Rh(CO)_2I_3]^-$
FAST
CO
$[(CH_3CO)Rh(CO)I_3]$

1.4.4 Further Developments

Since 1983 Tennessee Eastman have used a process for the conversion of methylacetate to acetic anhydride. This employs similar catalysts to the Monsanto process but requires the presence of lithium iodide(50).

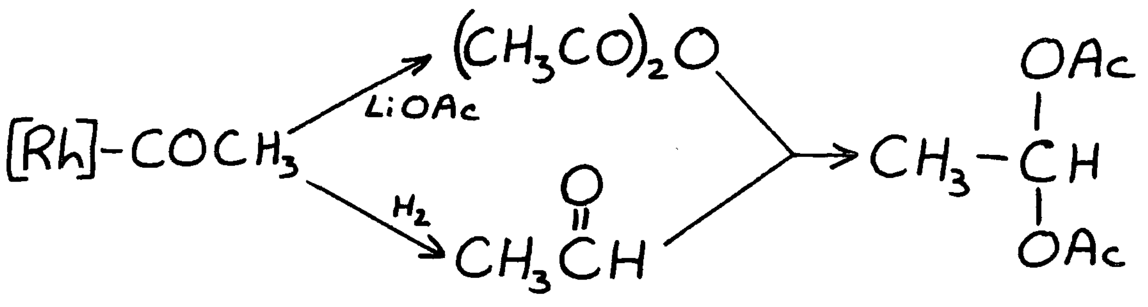
$$CH_3OAc + LiI \xrightarrow{\qquad} MeI + LiOAc$$

$$CH_3I + [Rh^{(I)}] \xrightarrow{\qquad} CH_3[Rh^{(III)}]I$$

$$CH_3[Rh^{(III)}]I \xrightarrow{CO} (CH_3CO)[Rh^{(III)}]I$$

$$CH_3CO[Rh^{(III)}]I \xrightarrow{LiOAc} (CH_3CO)_2O + LiI + [Rh^{(I)}]$$

If the reaction is conducted in the presence of hydrogen then ethylidene diacetate may be produced(51).



This product may then eliminate acetic acid to produce vinyl acetate, a very important starting material for the polymer business. Attempts have been made to produce ethylene glycol employing rhodium-carbonyls as catalysts(52). These rhodium catalysts are some ten times faster than similar cobalt catalysts, however rates are still too slow to be commercially viable. The system can afford good selectivities. High pressure and temperature infra-red studies have revealed that one or more anionic rhodium-carbonyl clusters are responsible for the formation of ethylene glycol from CO/H_2 whereas $[Rh(CO)_4]^-$ favours methanol production. In general the reaction may be summarised:

$$CO + H_2 \xrightarrow[\substack{RCO_2CH_3 \\ \text{tetraglyme} \\ \text{2-hydroxypyridine} \\ 220 - 280^\circ C \\ 40 - 70 \text{ bar}}]{Rh(CO)_2(acac)} \begin{array}{c} HOCH_2CH_2OH \\ + \\ CH_3OH \\ + \\ CH_3O(CO)H \end{array}$$

1.5 Hydrocarbonylation

Hydrocarbonylation is the subject of this thesis; in particular, the reaction of ethene with carbon monoxide and water to produce propanoic acid.

$$CH_2 = CH_2 + H_2O + CO \longrightarrow CH_3CH_2CO_2H$$

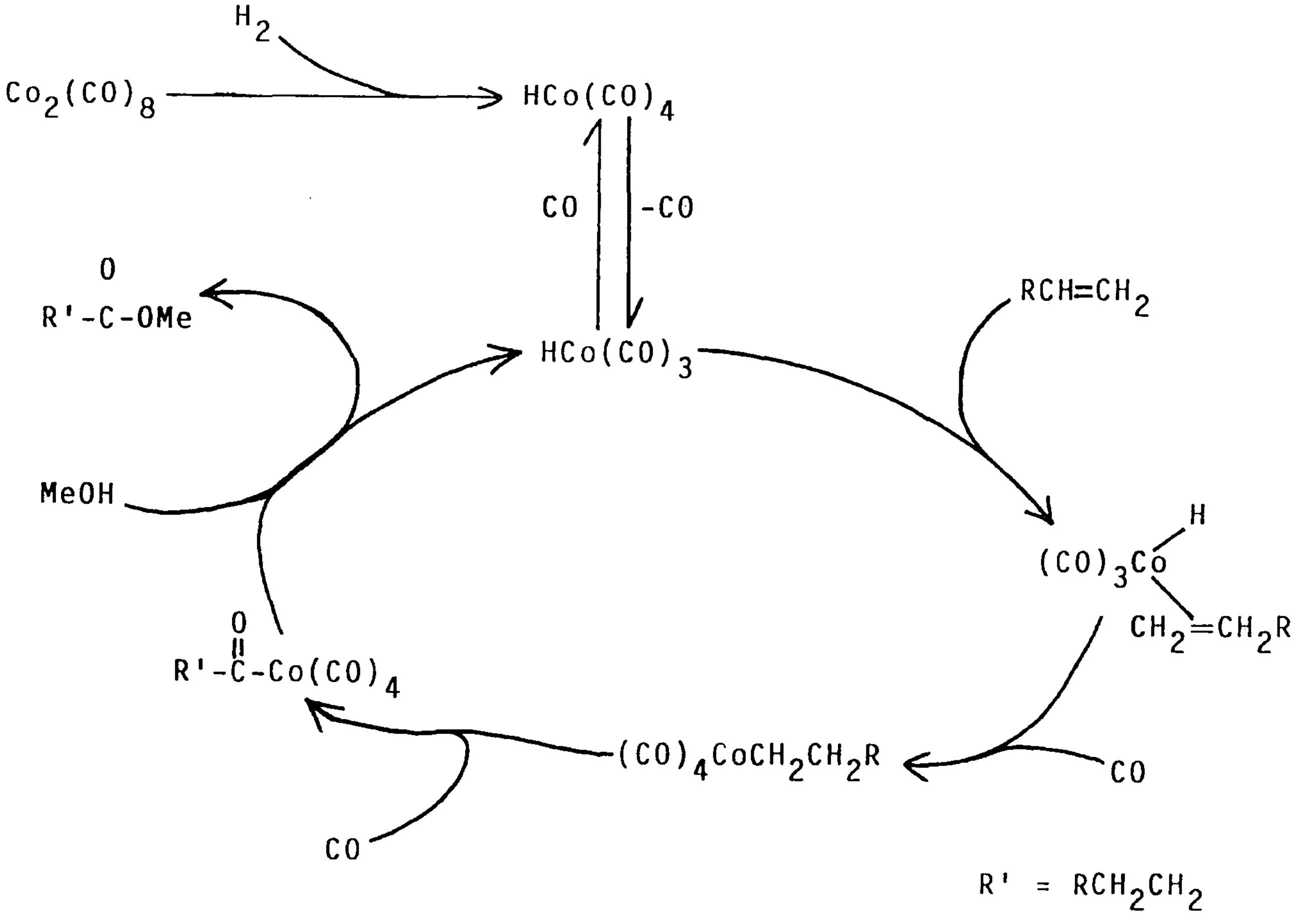
Throughout this thesis it will be referred to as hydrocarbonylation. Alternative names include hydroxycarbonylation, hydrocarboxylation, and carboalkoxylation.

Carboxylic acid derivatives have been produced from a mixture of carbon monoxide and ethene with water, alcohols and amines in a number of ways. The general reaction pathway for the reaction is considered to be the reaction of a metal hydride with ethene followed by migration to a carbonyl ligand. Thus far it mirrors hydroformylation, but at this point there is reductive elimination not hydrogenolysis.

The acid iodide formed undergoes nucleophilic attack to form the acid derivative. This process has been used to prepare fatty acids from linear olefins in which the product distribution between branched and linear products is crucial. Another problem of by-products can result from the Water Gas Shift reaction producing hydrogen that conducts hydroformylation to produce aldehydes.

One catalyst for this reaction is [$Co_2(CO)_8$]. As may be seen from Figure 1.4, an amount of hydrogen is required to initialise the catalyst[13b] and pyridine is employed, presumably to aid the elimination process.

Figure 1.4

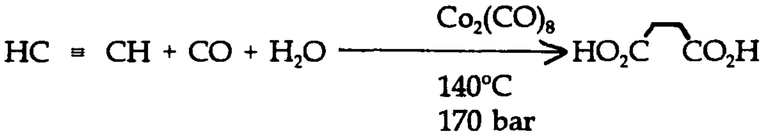


When palladium catalysts are used, two different catalytic cycles appear to operate, one in acidic and another in neutral regimes. In the presence of hydrochloric acid $Pd(PPh_3)_2Cl_2$ is the catalytic species whereas in neutral conditions tin(II) chloride is added to give $Pd(SnCl_3)_2(PPh_3)_2$ as the precatalyst(53, 54).

Nickel tetracarbonyl(6) has been employed as catalyst for a plant operated by B.A.S.F. at 280°C and 240 atmospheres of carbon monoxide/ethene gas. Poor catalyst stability, low reactivity and low selectivity plague this process. The low selectivity is due to oligomerisation of the product (see Figure 1.5). Nickel catalysts can also be employed when ethyne is the unsaturated substrate(55).

$$HC \equiv CH + CO + H_2O \xrightarrow[\substack{180^\circ C \\ 35\ bar}]{Ni(CO)_4} CH_2 = CHCO_2H$$

to produce acrylic acid. A similar reaction gives succinic acid.



In 1969 Monsanto filed a patent(56) relating to the hydrocarbonylation of primary alkenes, in the presence of rhodium or iridium, and iodide compounds. The process operated in both the vapour and liquid phases. Reaction with water and carbon monoxide occurs at temperatures ranging from 50°C - 300°C, the range 125 - 225°C being preferred. Partial pressures of carbon monoxide vary from 1 → 1000 bar, with 2 - 65 bar being preferred. As was the case with the methanol to acetic acid process, rhodium or iridium, and iodide can be added in wide-ranging forms. The preferred rhodium-iodide system had a mole ratio of these components as 1:3 to 1:300

respectively. However ratios from 1.1 to 1.2500 achieve reaction. It was noted that excess carbon monoxide and impurities such as carbon dioxide, methane, nitrogen, noble gases and paraffinic hydrocarbons, have no effect on reaction rate.

It has been suggested that the reaction mechanism for this process is related to that of the nickel system (see Figure 1.6). Oxidative addition of hydrogen iodide followed by attachment of an ethene ligand allows for hydride cis-migration followed by carbon monoxide occupying the vacant site. Alkyl cis-migration to carbon monoxide, with carbon monoxide again filling the vacant site, prepared for reductive elimination of acid iodide. Hydrolysis regenerates hydrogen iodide and the desired product. However investigation by Forster(57) shows that at 125°C and 35 bar total pressure, ethyliodide gave a rate of reaction 80 times faster than when hydrogen iodide was employed as initiator. It was also found that addition of a small amount of hydrogen iodide to the ethyliodide-promoted system, retarded the rate. Furthermore the reaction -

$$HI + C_2H_4 \rightleftharpoons C_2H_5I$$

did not equilibrate within the reaction time. This all suggests that the ethyliodide mechanism operates for the reaction, and that we observe the carbonylation of ethyliodide. This would however contradict the idea that addition of ethyliodide would be much slower than that of hydrogen iodide. Sensitive radio tracker techniques were applied to the problem and it was conclusively demonstrated that ethene hydrocarbonylation proceeds predominantly by a "HI addition" mechanism. It was also demonstrated that high levels of hydrogen iodide inhibited the rate by poisoning the catalyst, probably in the following manner:

$$[Rh(CO)_2I_2]^- + HI \rightarrow [HRh(CO)_2I_3]^-$$

$$[HRh(CO)_2I_3]^- + HI \rightarrow [Rh(CO)_2I_4]^- + H_2$$

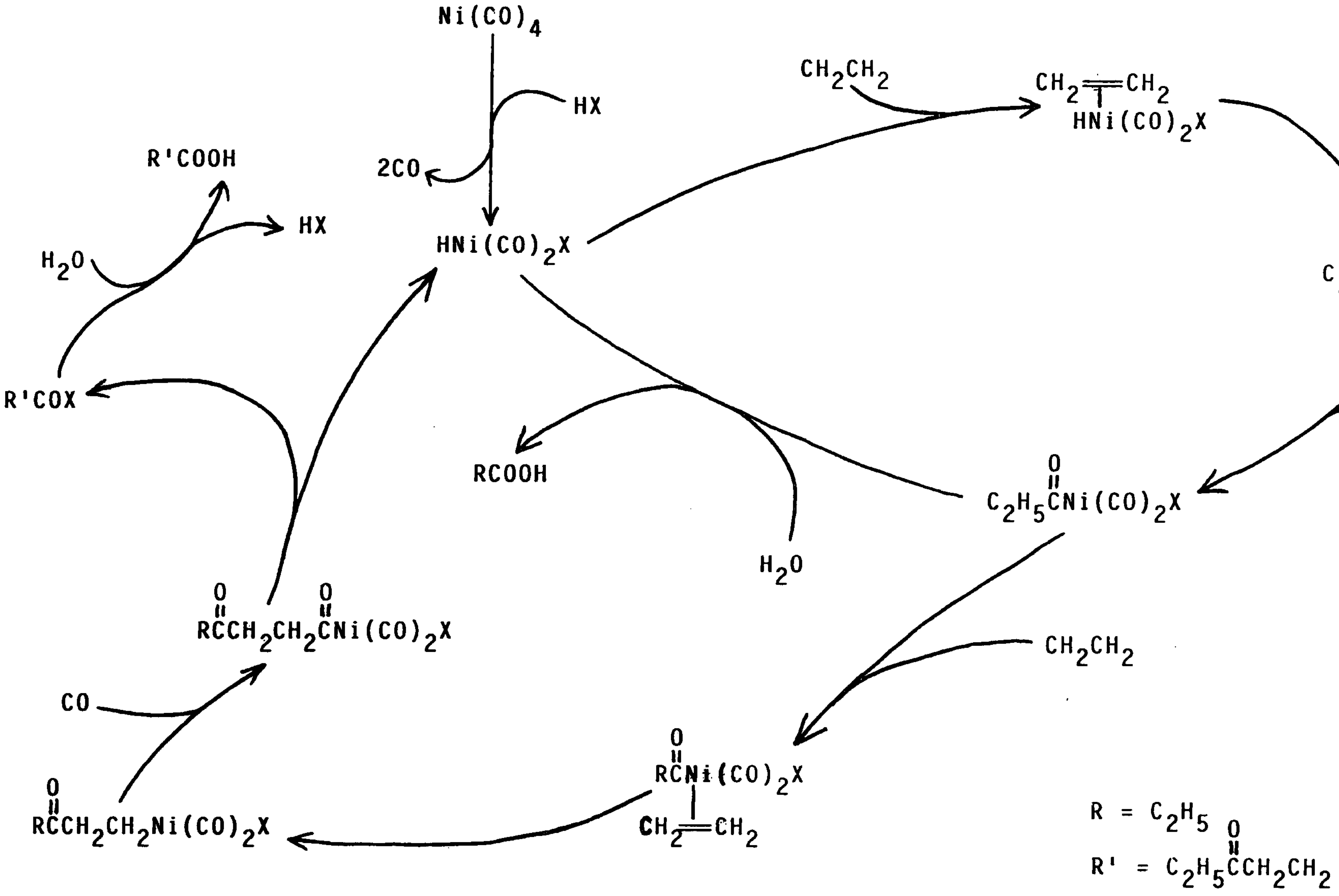
The possible sources of the hydrogen iodide during reactions involving ethyliodide as initiator, are the hydrolysis of ethanoic iodide produced by carbonylation of ethyliodide, or the β-elimination of HI from a ethyliodide adduct of rhodium. The cycle shown in Figure 1.6 will be considered in this thesis, a main aim of the research is the observation of some, or all, of the species described therein, at catalytic temperatures and pressures.

1.6 Compounds and Complexes of Rhodium

1.6.1 Introduction

Dichlorotetracarbonyldirhodate(I) $[Rh_2(CO)_4Cl_2]$ was first prepared in 1925 by Manchot and Konig(58), but it was Hieber and Lagally (1943) that provided the correct formulation, and that of the other halide analogues(59). A decade later Wilkinson et al(60) reported the rhodium analogue of ferrocene, a rhodicinium cation $[Rh(C_5H_5)_2]^{\oplus}$. In 1962, Cramer(61) isolated a rhodium complex with a mono alkene ligand, $[Rh_2Cl_2(CH_2CH_2)_4]$. A year later the first rhodium complex with a rhodium-hydrocarbon σ-bond was synthesised when Chatt and Underhill(62) synthesised $[RhBr(1\text{-naphthyl})_2(PPh_3)_2]$. Industrial and academic interest in the synthesis and chemistry of rhodium-carbon and rhodium-hydrogen compounds was greatly stimulated in 1965 by the discovery by Wilkinson et al(63) that $(RhCl(PPh_3)_3)$ would homogeneously catalyse, under mild conditions, the hydrogenation of alkenes and alkynes, and produced a rapid expansion in the investigation of rhodium chemistry.

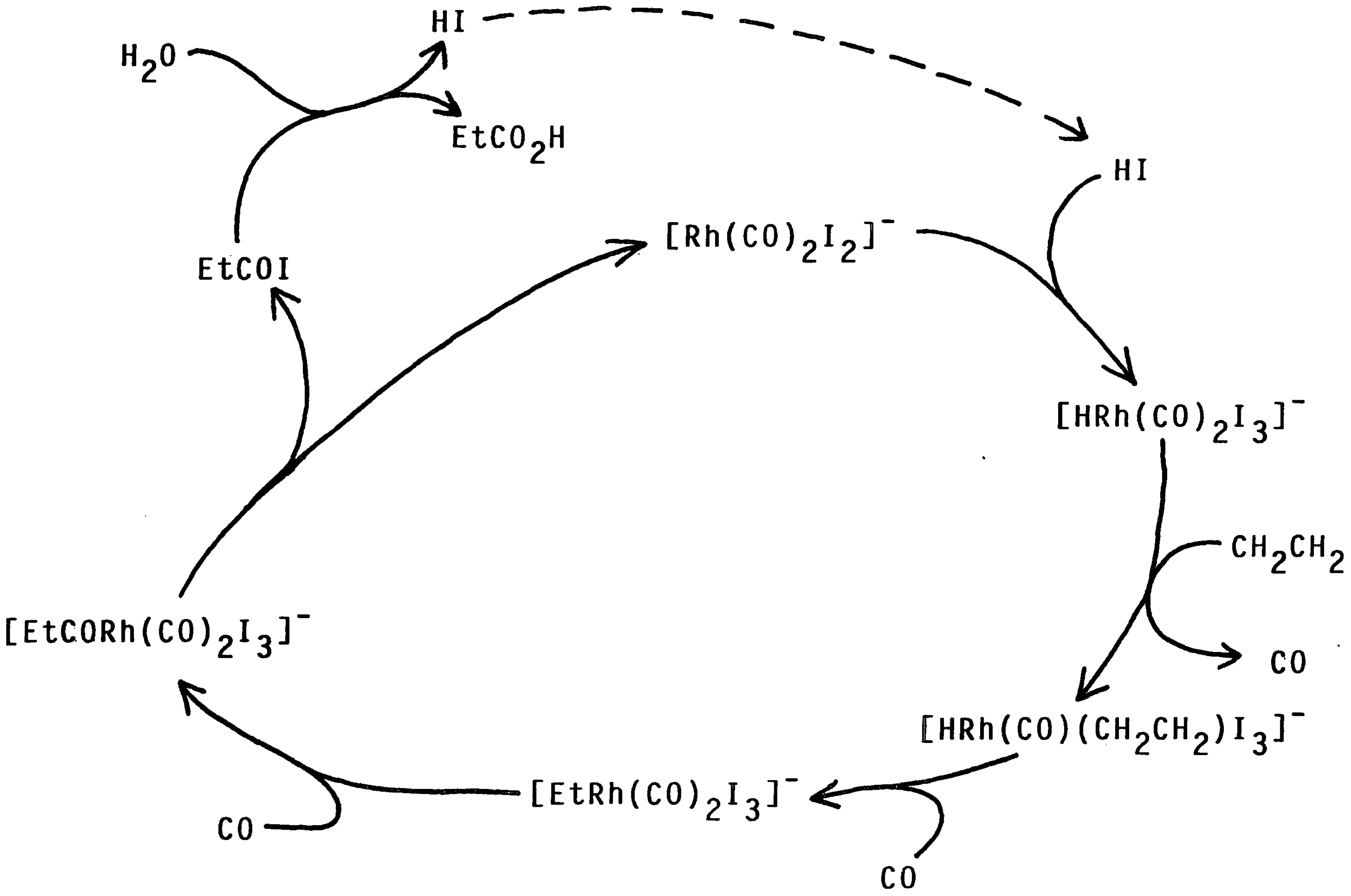
Figure 1.5: Nickel Catalysed Hydrocarbonylation



$R = C_2H_5$

$R' = C_2H_5\overset{O}{\overset{\|}{C}}CH_2CH_2$

Figure 1.6 Rhodium Catalysed Hydrocarbonylation



1.6.2. Rhodium-Halide Complexes

Halocarbonylrhodates, analogous to those known for several other transition metals, were first produced by Vallarino(64). Reaction of dichlorotetracarbonyldirhodate(I) $[Rh_2(CO)_4Cl_2]$ with hydrohalic acids followed by treatment with tetraphenylarsonium halides at 0°C in methanol produced $[Rh(CO)_2X_2]^-$ (X = Cl, Br, I). Total halogen displacement could be effected within the reaction time by the presence of the hydrohalic acid of a heavier halogen. The tetraiododicarbonyldirhodate(I) dianion $[Rh_2(CO)_2I_4]^{2-}$ was prepared by the treatment of $[Rh(CO)_2I_2]^-$ with hydrogen iodide and hypophosphoric acid $[H_3PO_2]$. The absence of $[H_3PO_2]$ led to the formation of tetraiodocarbonylrhodate(III) anion $[Rh(CO)I_4]^-$. This latter compound was also prepared by the reaction of rhodium(III) iodide with sodium iodide at 120°C and 200 atmospheres of carbon monoxide. The diiododicarbonylrhodate(I) anion is assigned a square planar structure with cis orientation of carbonyl groups on the basis of infrared data(64) (see Appendix 1A), and the complexes become increasingly less stable as we progress the series Cl > Br > I. Colton et al(70) showed the preference of iodorhodium carbonyls for the +3 oxidation state. Forster showed(65) that for rhodium(I) and also iridium(I) complexes, chloride is the favoured ligand in non-polar solvents such as dichloromethane and acetonitrile. However the addition of 10% water to acetonitrile causes iodide to be the favoured halide.

In 1968, Kingston and Scollary(66) synthesised compounds of the formula $[Rh(CO)L_2I]$ and $[Rh(CO)L_2I_3]$, (L = PR_3 etc). More interesting was the method of synthesis, by which rhodium(III) chloride trihydrate was reduced by refluxing in ethanol under an atmosphere of vaporised ethanol. The ethanol is reported as reacting as follows:

$$CH_3CH_2OH \longrightarrow CH_4 + CO + 2H^{\oplus}$$

The hydrogen atoms may reduce the rhodium(III) to rhodium(I)(67) producing $[Rh(CO)_2Cl_2]^-$. Methane was identified as a by-product of the reaction. James and Rempel(68) published kinetic work on the carbonylation of hydrous rhodium(III) chloride in 3M hydrochloric acid. The predominant species in solution was $[Rh(H_2O)Cl_5]^{2-}$; its solution absorbed carbon monoxide. The total gas uptake was equivalent to a rhodium:carbon monoxide ratio of 1:3, giving a stoichiometric equation of:

$$Rh^{(III)} + 3CO + H_2O \longrightarrow Rh^{(I)}(CO)_2 + CO_2 + 2H^{\oplus}$$

The kinetics indicate that initial reaction occurs via direct reduction of $[Rh(H_2O)Cl_5]^{2-}$ with carbon monoxide, followed by a more efficient mechanism sequence involving a bridged $Rh^{(III)}$ .... $Rh^{(I)}$ intermediate.

In 1969 Forster(69) published work based on that of Vallarino(64). Preparing salts of $[Rh(CO)_2X_2]^-$ anions by the methods of Vallarino, he noted that the reactions of $[Rh(CO)_2I_2]^-$ were complicated by the formulation of $[I_3]^-$ ions. The initial reaction of methyliodide with the $[Rh(CO)_2I_2]^-$ anion gave $[Rh(CO)(COMe)I_3]_2^{2-}$, prolonged reaction gave salts of $[Rh(CO)I_5]^{2-}$. It is also indicated that this last complex may be obtained by the reaction of $[Rh(CO)_2I_2]^-$ with hydrogen iodide in acetic acid. Colton, Farthing and Knapp(70) followed the formation of $[Rh_2(CO)_4X_2]$ and $[Rh(CO)_2X_2]^-$ by infra-red spectroscopy. They showed that the reduction of rhodium(III) chloride or bromide by formic acid-hydrohalic acid solutions preceded by the formation of the halocarbonyl anions $[Rh(CO)X_5]^{2-}$ followed by slow reduction to rhodium(I) species. Evaporation of these solutions gave $[Rh(CO)X_3]$ and the well known $[Rh_2(CO)_4X_2]$ compounds. For a similar iodo-system no reduction was observed, and only $[Rh(CO)I_3]$ and $[Rh(CO)I_5]^{2-}$ could be isolated. The preference of iodo-rhodium systems for the +3 state is again demonstrated. The spectral data for all these complexes is collected in Appendix 1A.

More recently attention has again turned to the nature of the complexes formed when hydrogen iodide and alkyl iodides oxidatively add to diiododicarbonylrhodate(I) anion $[Rh(CO)_2I_2]^-$. The work of Hickey(71) and Fulford(3) has been conducted in aprotic solvents. The investigation of the addition reaction of methyliodide showed that the presence of iodide or Lewis base promoted the reaction to form acetic anhydride. Formation of five co-ordinate species such as $[Rh(CO)_2I_3]^{2-}$ or $[Rh(CO)_2I_2(B)]^-$ (where B = Lewis base) are suggested. As mentioned in section 1.3.3. such compounds may be intermediates in oxidative addition reactions although the alternative addition of the positive species of the adduct is the more normal sequence. Fulford's(3) work involved the addition of hydrogen iodide, and iodides such as $[Bu_4N]^+I^-$, [LiI] and $[C_{12}H_{25}NH_3]^+I^-$ which bear protons. Those cations lacking N-H moieties gave spectra appropriate to $A^+(solvent)_n[Rh(CO)_2I_2]^-$. However those cations that possess N-H moieties give bands attributed to $[A^+...Rh(CO)_2I_2^-]$ ion pairs. This is also presented as the product of the addition of hydrogen iodide to diiodotetracarbonyldirhodate(I) in aprotic media. Excess hydrogen iodide produces absorption bands at 2083 cm^{-1}, either arising from $[Rh(CO)I_4]^-$ or $[Rh(CO)_2I_4]^-$. In methanol rhodium(III) iodide was produced. In general the rhodium-carbonyl-iodides are interconvertible, given pressures of carbon monoxide to reduce, or iodine sources for oxidation products(69).

1.6.3 Rhodium-Tin Chemistry

The data collected in Chapter 4 and Chapter 5 show that rhodium-tin complexes can catalyse the hydrocarbonylation of ethene to propanoic acid. A survey of tin-metal complexes therefore deserves consideration at this juncture.

Rhodium-tin complexes are known to exist in both the rhodium +1 and +3 oxidation states. The tin may also be in either of its two oxidation states tin(II) and tin(IV) both as reactant and product. Reaction occurs for both organo tin compounds(72) and also tin halides(73).

$$R_3SnBr + Na[Rh(PPh_3)_2(CO)_2] \longrightarrow (R_3Sn)Rh(PPh_3)_2(CO)_2 + NaBr$$

$$2SnCl_2 + [(norbornadiene)RhCl]_2 + 4R_3P \longrightarrow 2Rh(norbornadiene)(SnCl_3)(R_3P)_2$$

The reduction of rhodium(III) to rhodium(I) occurs in acidic solution producing $[Rh_2(Cl)_2(SnCl_3)_4]^{4-}$ as shown by Young et al(74). Complexes of this type were synthesised for ruthenium, rhodium, iridium and platinium(74). All these complexes were prepared in dilute hydrochloric acid, although the complexes of ruthenium and iridium require heating. These complexes had been used previously for analytical purposes(75). The complexes were precipitated using large tetraalkylammonium salts. The carbonyl complex $[Rh(CO)Cl(SnCl_3)_2]$ was also synthesised, as were a number of rhodium-trichlorostannate(II) complexes containing olefins and triphenylphosphine. In 1971 the studies on rhodium-tin complexes were extended to include complexes of tribromostannate(II) anion and triiodostannate(II) anion. A number of carbonyl-complexes were also studied. N.M.R. studies of this type of complexes generated a great interest as they provide the opportunity for ^{119}Sn, ^{13}C and also ^{195}Pt nuclei studies. The information this data provides was reported by Kretschmer in 1983(76).

The interest in the catalytic possibilities of these species is derived from the report(77) of hydrocarbonylation of alk-1-enes to linear alkanoic acids by platinium-tin-chloride complexes. The system displaced high selectivity both in terms of producing acids and the linearality of those acids(77). The platinium-tin-chloride system was also found to be active for the catalysis of the Water Gas Shift reaction(78). It was noted that the π accepting properties of the trichlorostannate(II) ligand prevents the reduction of Pt^{2+} ion by hydrogen but permits carbon monoxide reduction to Pt^0 (79). It is also suggested that tin species may be interconverted between the +2 and+4 oxidation states, and is active in the catalytic cycle. The role of the trichlorostannate(II) ligand in homogeneous catalysis is studied in a series of papers by Anderson et al(80). Their work concerns phenyl-platinium-tin complexes and characterise trichlorostannate(II) ligand as a leaving group and counter-anion. The complexes employed also included triphenylphosphine. The latter fact and the ambient conditions of the studies limit their usefulness in interpreting the aforementioned catalytic reactivity. However the indication that it is a good-leaving group coupled with the indication it is a π acceptor(78, 79), and its oxidative/reductive capabilities suggest it is very worthy of consideration in catalysis reaction systems.

1.6.4 Rhodium Hydrides

The existence of rhodium-hydride species is implicitly required by the "OXO" reaction, Wilkinson's hydrogenation catalyst and Forster's Catalytic cycle for hydrocarbonylation. Few have been isolated, these include [HRh(OEP)] (OEP = octaethylporphyrin), which is formed with hydrogen, as the hydride source(81). More often they are generated by action of agents such as $[BH_4]^-$. Attack of this latter reagent on $[RhCl(CO)L_2]$ (L = (PPh_3)) in the presence of excess (PPh_3) generates $[HRh(CO)(PPh_3)_3]$ with the hydride and carbonyl ligands trans to each other in a trigonal bipyramidal structure(82). Hydrides of $Rh^{(III)}$ tend to be very unstable to reductive elimination to form Rh^{I} species(83).

1.7 Conclusions

Throughout the work outlined above, it is possible to see three factors that make rhodium such a successful catalyst. Firstly, it can perform all of the reactions required for organic reaction to occur in its coordination shell. The dual oxidation states which give rise to both 16 and 18 electron structures permit oxidative addition and reductive elimination reactions, also rhodium's coordination chemistry allows for cis-migration reactions as well.

Secondly, rhodium, particularly in its +1 oxidation state, forms many complexes with π-acidic ligands. Of special interest to this thesis are carbon monoxide and ethenes. The formation of stable model complexes of these ligands enables the reaction pathway for hydrocarbonylation to be envisaged.

Finally, the wide ranging coordination chemistry enables not only reactive ligands to be varied, but also the fine tuning of catalytic activity by modifying the ligands not directly involved in reaction pathways.

The result of these factors is that rhodium homogeneous catalysts give the rapid and highly selective reaction needed to generate economic industrial processes.

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CHAPTER TWO

CONTENTS

CHAPTER 2

HIGH PRESSURE FOURIER TRANSFORM INFRA-RED STUDIES OF RHODIUM IODIDE SYSTEMS

2.1 Introduction

As work(1, 2, 13) had previously been undertaken on these systems by workers at Monsanto Plc and B.P. Chemicals Ltd, this study concentrated on infra-red investigations in the first instance.

Optimum yields of propanoic acid had been obtained by B.P. workers, using the following reaction composition(1).

$RhCl_3.3H_2O$: 150 ppm
HI : 2% w/w
H_2O : 8% w/w
$CH_3CH_2CO_2H$: 78.5% w/w
CH_3CH_2I : 11.5% w/w

To study this system, a series of systems of increasing complexity were initially investigated, until the composition of the full catalytic system was reached. In this manner, it was intended that a step by step picture of the compounds and complexes involved would be built up, so that interpretation of more complicated reactions would be simplified.

A large number of halocarbonyl-rhodium compounds have been characterised by infra-red spectroscopy (see Appendix 1). This data was used in conjunction with the less complicated reaction runs to identify species formed in catalytic reaction systems.

Early reaction studies soon demonstrated the fact that carboxylic acids were poor solvents for infra-red study in the 2500 cm^{-1} to 1800 cm^{-1} region. Although these solvents do possess a "window" for observation of rhodium-carbonyl absorption bands (as shown in Figure 2.12), the subtraction of the background leads to poor signal to noise ratio. Therefore a number of reactions were undertaken in a mixed solvent system to reduce the amount of propanoic acid present and hence the background absorbance. Dichloromethane when used in the mixed solvent systems with propanoic acid, was found to improve the spectral quality (see Figure 2.12). Some reactions were also conducted in dichloromethane only, to verify the nature of some intermediate complexes. Reactions were also conducted in ethanol to compare hydrocarbonylation reactions with the "Monsanto" chemistry of carbonylation of alcohols by rhodium-iodide systems.

The observation of certain complexes may be anticipated in light of previous work, and the projected catalytic cycles. The following compounds may be observed at some stage in the process:

trihalocarbonylrhodate(III)
dihalotetracarbonyldirhodate(I)
tetrahalodicarbonyldirhodate(I)
tetraiodocarbonylrhodate(III)
trans-tetraiododicarbonylrhodate(III)

pentaiodocarbonylrhodate(III)

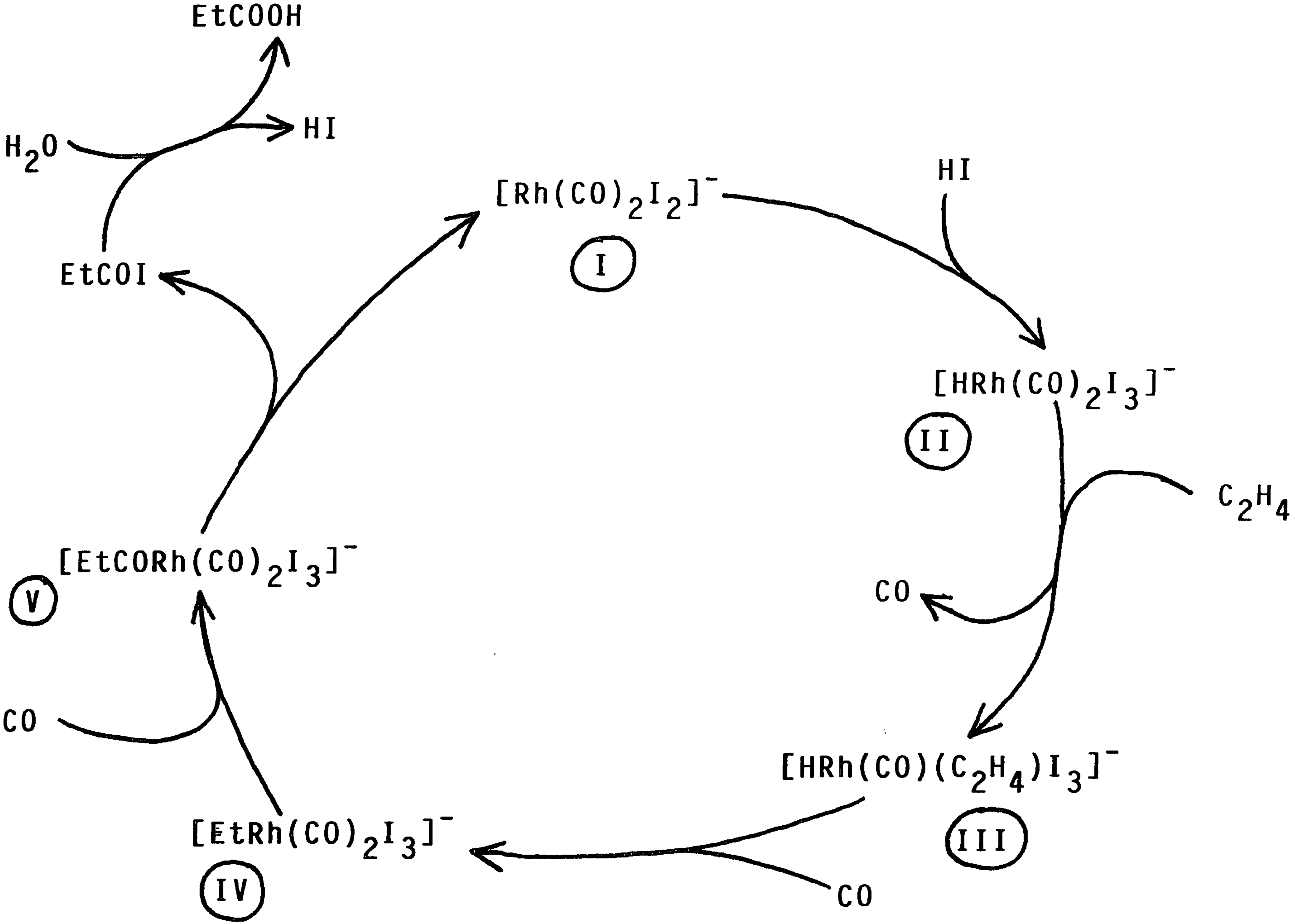
[Spectral data is given in Appendix 1]

Given Forster's work(2) on the competitive oxidative addition of hydrogen iodide and ethyliodide to diiododicarbonylrhodate(I) anion $[Rh(CO)_2I_2]^-$, the catalytic cycle of Figure 2.1 may be proposed.

It has been observed that the methyl analogue of complex V in Figure 2.1 has been observed(3). In the same study it was observed that the methyl analogue of complex IV in Figure 2.1 was transitional, and was not observed. Complex II in Figure 2.1 is of particular interest, although it has not previously been isolated or observed the iridium analogue has been reported(4).

The identification of these species is required to confirm the details of Forster's(2) proposed catalytic cycle, in particular the hydrido-species. In approaching this aim, the study is made first of straightforward systems, then of progressively more complex systems, until the full catalytic system was reached.

All the systems reported are detailed in full, with the range of reaction conditions in section 2.8. The absorption bands for the observed species are given in Appendix 1B.


EtCOOH
HI
H2O
EtCOI
[Rh(CO)2I2]⁻
I
HI
[HRh(CO)2I3]⁻
II
C2H4
CO
[HRh(CO)(C2H4)I3]⁻
III
CO
[EtRh(CO)2I3]⁻
IV
CO
[EtCORh(CO)2I3]⁻
V

2.2 Initial Systems

2.2.1 Carbonylation of rhodium systems

Reaction 2.2.1A	***Species Observed***
$RhCl_3.3H_2O$	$Rh(CO)Cl_3(ms)$
$C_2H_5CO_2H$	$Rh_2(CO)_4Cl_2(s)$
CO	$2099(vs), 2059(s)\ cm^{-1}$

This reaction produced trichlorocarbonylrhodate(III) [2135 cm^{-1}], followed by dichlorotetracarbonyldirhodate(I) [2105(w) 2029(vs) 2035(vs) cm^{-1}]. Additional peaks were observed at 2099(vs), 2059(s) cm^{-1} arising from an, as yet, unidentified species.

A further reaction was conducted using dirhodium(I)tetracarbonyldichloride as the rhodium source.

Reaction 2.2.1B	***Special Observed***
$Rh_2(CO)_4Cl_2$	$Rh_2(CO)_4Cl_2(ms)$
$C_2H_5CO_2H$	*2099(vs) 2059(s)* cm^{-1} *unidentified*
CO	*2096(w) 2086(w)* cm^{-1} *unidentified*
	2075(w) cm^{-1} *unidentified*
	2043(w) cm^{-1} *unidentified*
	2012(w) cm^{-1} *unidentified*

It is not possible at this stage to identify the weak absorption bands that were observed, however the strong absorption bands at 2099, 2059 cm^{-1} are again observed. A change in solvent to dichloromethane was employed to enable the species associated with these peaks to be studied in more detail.

Reaction 2.2.1C	***Species Observed***
$Rh_2(CO)_4Cl_2$	
CH_2Cl_2	*2099, 2059* cm^{-1}*(s)*
CO	*2075(w)* cm^{-1} *unidentified*
	$Rh_2(CO)_4Cl_2$*(vs)*

It was possible to convert $Rh_2(CO)_4Cl_2$ to the species associated with the 2099(vs) 2059(s) cm^{-1} absorption bands, by applying a pressure of carbon monoxide. The reaction may be reversed by returning to an atmosphere of nitrogen.

$$\mathrm{Rh_2(CO)_4Cl_2} \underset{\text{1 bar } \mathrm{N_2}}{\overset{\text{30 bar CO}}{\rightleftharpoons}} \text{Y (bands at 2099, 2059 cm}^{-1}\text{)}$$

(see Figure2.2)

Given this species these two species may be interconverted repeatedly. It may be concluded that this reaction is the addition of carbon monoxide which cleaves the rhodium-chloride bridge in the dimer, to produce $Rh(CO)_3Cl$, chlorotricarbonyl-rhodate(I).

To complete the series of reactions the effect of changing to dichloromethane as a solvent for the equivalent to reaction 2.2.1A.

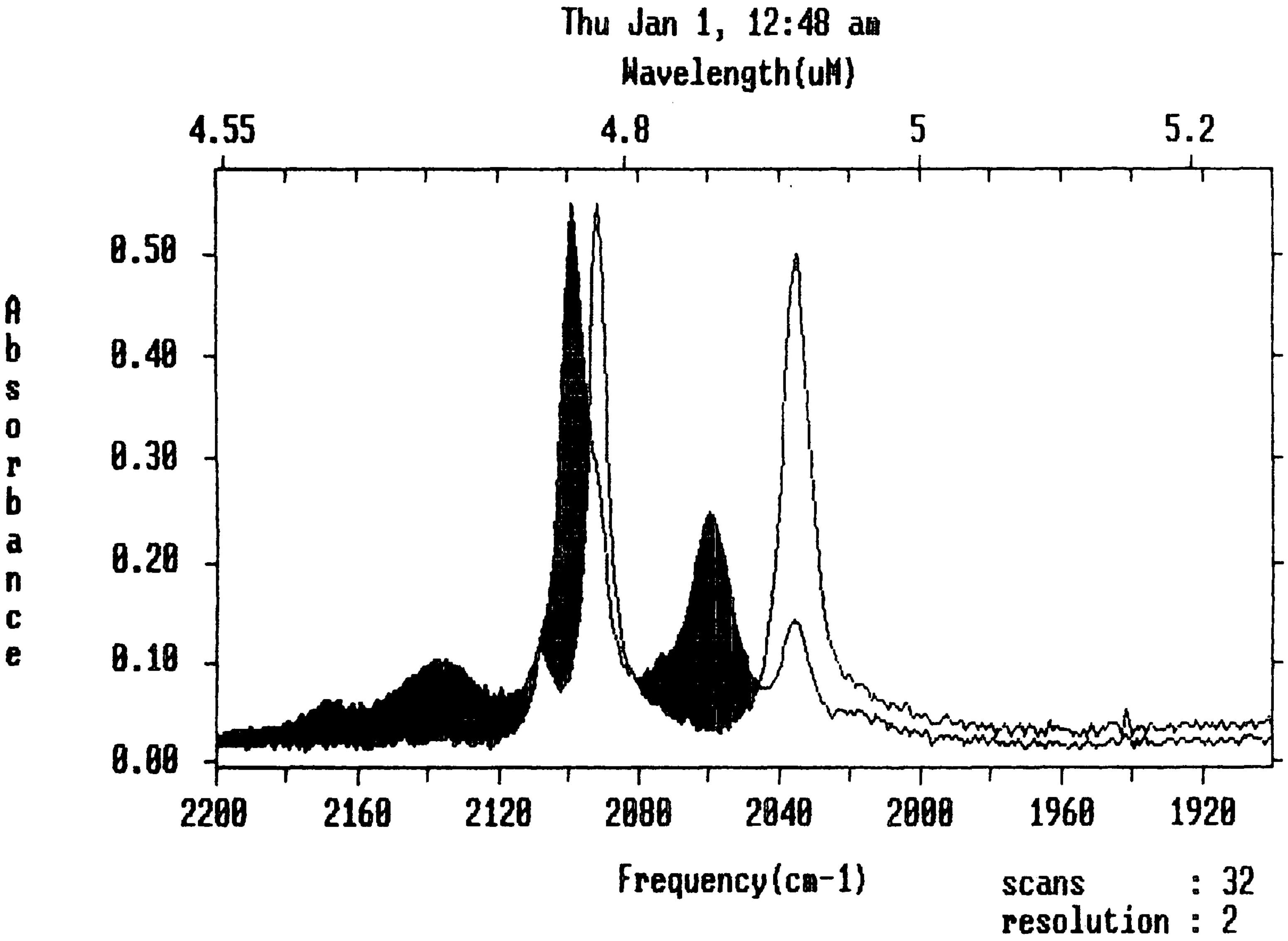


Figure 2.2 Interversion of $[Rh_2(CO)_4Cl_2]$ and $[Rh(CO)_3Cl]$

Reaction 2.2.1D	*Species Observed*
$RhCl_3.3H_2O$	$[Rh(CO)Cl_3](s)$
CH_2Cl_2	$[Rh_2(CO)_4Cl_2](vs)$
CO	$[Rh(CO)_3Cl](vs)$

Rhodium(III) carbonyltrichloride was formed initially, at 50°C. At 100°C rhodium(I) tricarbonylchloride $Rh(CO)_3Cl$ and dirhodium(I)tetracarbonyl-dichloride $Rh_2(CO)_4Cl_2$ are formed. The latter is favoured at higher temperatures, the former at lower temperatures.

Discussion

Rhodium(III) carbonyltrichloride, an intermediate in the carbonylation of rhodium(III) chloride, is observed in each of the reactions. Its identity may be confirmed by comparison with the infra-red data compiled for aqueous systems by Colton et al(5). Once this initial species has been formed, a reaction path is followed similar in nature to that expected for the standard laboratory synthesis of dichlorotetracarbonyldirhodate(I)(6).

In two of the reactions additional peaks were observed:

Reaction 2.2.1B	2096, 2080 cm^{-1}
	2075, 2043, 2012 cm^{-1}
Reaction 2.2.1C	2075 cm^{-1}

These absorbance bands may be due to mononuclear rhodium carbonyl species and/or clusters(7) which are not stable at S.T.P. under these solvent conditions. All of the bands noted are very weak and may possibly have associated bands that were not observable.

2.2.2 Addition of Tetrabutylammonium Iodide

While hydrogen iodide and ethyliodide will be the two initiators central to this study, the use of tetrabutylammonium iodide to study complexes formed prior to carbonylation or hydrocarbonylation reaction was considered to be of value.

Reaction 2.2.2A	***Species Observed***
$RhCl_3.3H_2O$ $(C_4H_9)_4NI$ $C_2H_5CO_2H$ CO	$[Rh(CO)I_5]^{2-}$*(mw)* $[Rh(CO)_2I_4]^-$*(w)*

The reaction was slowly heated to a temperature of 180°C. Until this temperature was reached no carbonyl absorbance bands were observed in the rhodium-carbonyl region. At 180°C an absorbance band at 2047 cm^{-1} was identified as $[Rh(CO)I_5]^{2-}$ and at 2084 cm^{-1} identified as $[Rh(CO)_2I_4]^-$ (see Appendix 1).

In an attempt to discern whether intermediates were formed prior to 180°C a second reaction was conducted in dichloromethane.

Reaction 2.2.2B	***Species Observed***
$RhCl_3.3H_2O$	$Rh(CO)_3Cl(s)$
$(C_4H_9)_4NI$	$[Rh_2(CO)_2I_4]^{2-}(m)$
CH_2Cl_2	$[Rh(CO)_2I_4]^{-}(m)$
CO	

Both rhodium(I) species were observed at 120°C suggesting reduction of rhodium(III) chloride to form chlorotricarbonylrhodate(I) followed by replacement of carbonyl by iodide ligands to form tetraiododicarbonyldirhodate.

Although dichlorotetracarbonyldirhodate(I) was not observed the formation of $Rh(CO)_3Cl$ suggests it was an intermediate. Therefore $[Rh_2(CO)_4Cl_2]$ was used as the rhodium source for a reaction in dichloromethane solvent.

Reaction 2.2.2C	***Species Observed***
$[Rh_2(CO)_4Cl_2$	$Rh(CO)_3Cl(s)$
$(C_4H_9)NI$	$[Rh(CO)_4Cl_2](s)$
CH_2Cl_2	*2076(m) 1997(m)* cm^{-1} *unidentified*
CO	

At room temperature the complex $Rh(CO)_3Cl$ was observed. As the temperature was raised to 120°C, it reverted to the dimer dirhodium(I)tetracarbonyldichloride. At

180°C bands were observed at 2076, 1997 cm^{-1}; there are several possible complexes that these bands may be associated with. The diiododicarbonyl-rhodate(I) anion may be associated with these peaks, however literature values are 5 to 10 cm^{-1} lower (see Appendix 1). Dichlorocarbonyl rhodate(I) anion is another possibility, however from preceding reactions we would expect halide ligand exchange. Therefore it is more likely that there is the formation of an ion pair as described by A. Fulford et al (8, 14), in this case $[Bu_4N^+ ...Rh(CO)_2I_2^-]$.

Given the possibility that the above complex is formed in reaction 2.2.2C the addition of ethene may produce rhodium-ethene complexes.

Reaction 2.2.2D	*Species Observed*
$RhCl_3.3H_2O$ $(C_4H_9)_4NI$ CH_2Cl_2 C_2H_4/CO	$Rh(CO)_3Cl(s)$ $Rh_2(CO)_4Cl_2(s)$ *2018 cm^{-1}(w) unidentified*

The species chlorotricarbonylrhodatel(I) and dichlorotetracarbonyldirhodate(I) were seen from room temperature to 120°C. Another peak at 2018 cm^{-1}(w) was seen throughout the reaction. However even at high temperatures the expected iodo-rhodium species were not seen; they may have been obscured by negative dichloromethane peaks caused by solvent loss.

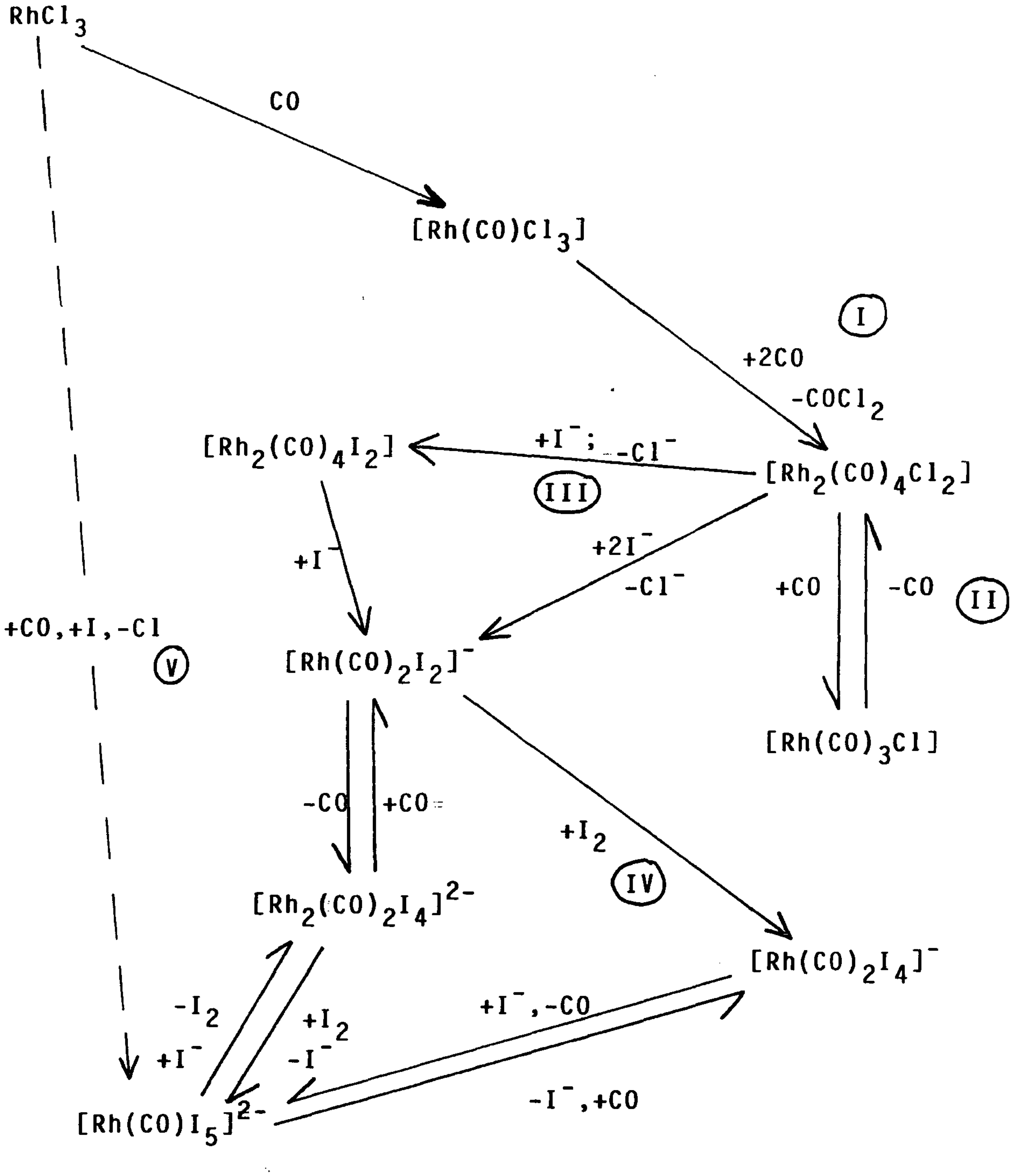
Discussion

As expected the addition of the ionic tetrabutylammonium iodide produced a range of rhodium species. A number of redox reactions are observed. In reaction 2.2.2B both rhodium(I) and rhodium(III) species are produced from rhodium(III) chloride. However in reactions 2.2.2C and 2.2.2D only rhodium(I) species are observed, despite the observation of rhodium(III) species in reaction 2.2.2A. The use of propanoic acid as solvent may have been responsible for the rhodium(III) species of reaction 2.2.2A being produced by an alternative pathway; possibly the sequence (v) in Figure 2.3.

In reaction 2.2.2B both rhodium(I) and rhodium(III) species are observed. It is possible that they are all formed by one reaction pathway. However the possibility of two reaction pathways, one to form rhodium(I) species and another to form rhodium(III) species, still remains feasible. It should be noted however that while the absence of rhodium(I) species in reaction 2.2.2A favours the existence of two distinct pathways it is possible that propanoic acid is too poor a medium for the rhodium(I) species to be observed in the infra-red spectrum.

The addition of ethene to these systems prevents the appearance of rhodium(III) carbonyliodide complexes in the infra-red spectrum. It is probable that if formed these species react with ethene to form complexes without absorbance bands in the 2300 - 1900 cm^{-1} region.

Figure 2.3



I As demonstrated for $RhCl_3(s)$, Reference 5.

II As demonstrated by Reaction 2.2.1c.

III As demonstrated , Reference 9.

IV See discussion page 53

V Possible intermediates would include species analogous to $[Rh(CO)Cl_5]^-$ (see Reference 10)

2.2.3 Ethene interaction with dichlorotetracarbonyldirhodate(I)

Probable(I) $[Rh_2(C_2H_4)_4Cl_2]$ may be synthesised by direct action of ethene on solutions of rhodium(III) chloride (see chapter 7) or by displacement of carbon monoxide from dichlorotetracarbonyldirhodate(I) $[Rh_2(CO)_4Cl_2]$ (11). This latter reaction can give intermediate complexes with a mixture of carbonyl and ethene ligands, with distinctive infra-red spectra (see Appendix 1). Two high pressure studies were considered relevant to this displacement reaction. The first was designed to monitor the replacement of carbonyl ligands with ethene. The second was to determine the effect of competition of carbon monoxide and ethene as ligands for rhodium(I) complexes.

Reaction 2.2.3A	*Species Observed*
$[Rh(CO)_2Cl]_2$ $C_2H_5CO_2H$ C_2H_4	$[Rh_2(CO)_n(C_2H_4)_{4-n}Cl_2]$ $n = 1$ to 4

Although no distinct progression from one complex to another was observed due to the co-incidence of absorbance bands common to more than one species; however the change in intensity of these peaks indicated a continuous conversion from the tetracarbonyl to tetraethene complex.

Reaction 2.2.3B	***Species Observed***
$[Rh(CO)_2Cl]_2$	$[Rh(CO)_2Cl]_2$*(ms)*
$C_2H_5CO_2H$	$[Rh(CO)_3Cl]$*(s)*
CO/C_2H_4	*2080* cm^{-1}*(w)* *2042* cm^{-1}*(w) unidentified* *2008* cm^{-1}*(w)*

When a mixture of carbon monoxide and ethene is used there is no indication of substitution of carbonyl ligands by ethene. In the infra-red spectrum carbonyl species predominate. The unidentified absorbance bands may be rhodium carbonyl carboxylates or rhodium carbonyl clusters.

Discussion

When ethene competes with carbon monoxide in the gaseous phase to form ligand to rhodium species in the solution phase, then minimal formation of ethene complexes is observed. This result, that carbon monoxide is the favoured ligand, has important implications for the hydrocarbonylation reaction. As shown in Figure 2.1, the second step involves replacement of a carbonyl ligand for ethene to facilitate the beta addition reaction with the hydride ligand. If this second step is disfavoured by the high partial pressures of carbon monoxide, then a favourable ratio should exist between the two gases to optimise for fast rates of reaction. Both gases are consumed by the reaction, and carbon monoxide is also used to form the catalytic precursors. Therefore a minimum partial pressure for carbon monoxide should exist that enables the latter two processes to proceed and yet will favour the addition of ethene by a correspondingly high partial pressure of ethene. A more detailed investigation was conducted with a system closer to that of the hydrocarbonylation reaction, reported in Chapter 3.

2.2.4 Iodine as an initiator

Having investigated the ionic tetrabutylammonium iodide as an initiator (section 2.2.2), molecular iodine was considered, for comparative purposes. We may expect the conversion of iodine to the iodide anion and the oxidation of rhodium(I) complexes to rhodium(III).

Reaction 2.2.4A	*Species Observed*
$RhCl_3.3H_2O$	$Rh(CO)Cl_3$
I_2	*2117 cm^{-1} unidentified*
CH_2Cl_2	*2108, 2094 cm^{-1} unidentified*
CO	$[Rh(CO)_3Cl](m)$

Once the trichlorocarbonylrhodate(III) complex had been formed in dichloromethane, a very sharp peak was observed at 2117 cm^{-1} (see Figure 2.4). This must be a rhodium carbonyl halide, due to its high position in the spectrum; it probably contains some chloride ions (cf. $Rh(CO)Cl_3$: 2137 cm^{-1}, $Rh(CO)I_3$ 2070 cm^{-1}) and as it is absent in reaction 2.2.1D, it is probable that iodo-ligands are present. It may be concluded, therefore, that this complex has the form $[Rh(CO)_x(Cl)_y(I)_{3-y}]$ ($x = 1$ or 2) ($y = 1, 2$). The species with bands at 2108, 2094 cm^{-1} was stable under one atmosphere of nitrogen at the end of the reaction but it was not possible to isolate any compound. The chlorotricarbonylrhodate(I) $[Rh(CO)_3Cl]$ complex was only seen after the reaction returned to room temperature under carbon monoxide pressure, and was probably formed by the reaction of previously unreacted rhodium(III) chloride with carbon monoxide.

Reaction 2.2.4B	***Species Observed***
$RhCl_3.3H_2O$	$[Rh(CO)_2I]_2(s)$
I_2	$[Rh(CO)_2I_4]^-(s)$
$C_2H_5CO_2H$	$[Rh(CO)_2I_2]^-(s)$
CO	

The early formation of diiodotetracarbonyldirhodate(I) is in marked contrast to the earlier tetrabutylammonium iodide reactions when chlorotricarbonylrhodate(I) was observed in solution. This is most probably due to the change in initiator, resulting in the rapid conversion of any chloro- complex to an iodo- complex.

Tetraiododicarbonylrhodate(III) anion $[Rh(CO)_2I_4]^-$ is first seen at 140°C. It is not surprising that the more polar solvent enables the iodine to be converted to the iodide anion, from whence the diiodotetracarbonyldirhodate(I) could be converted with iodine to the rhodium dicarbonyltetraiodide anion.

$$[Rh(CO)_2I]_2 + 2I_2 + 2I^{\ominus} \longrightarrow 2[Rh(CO)_2I_4]^{\ominus} \qquad \textit{Equation 1}$$

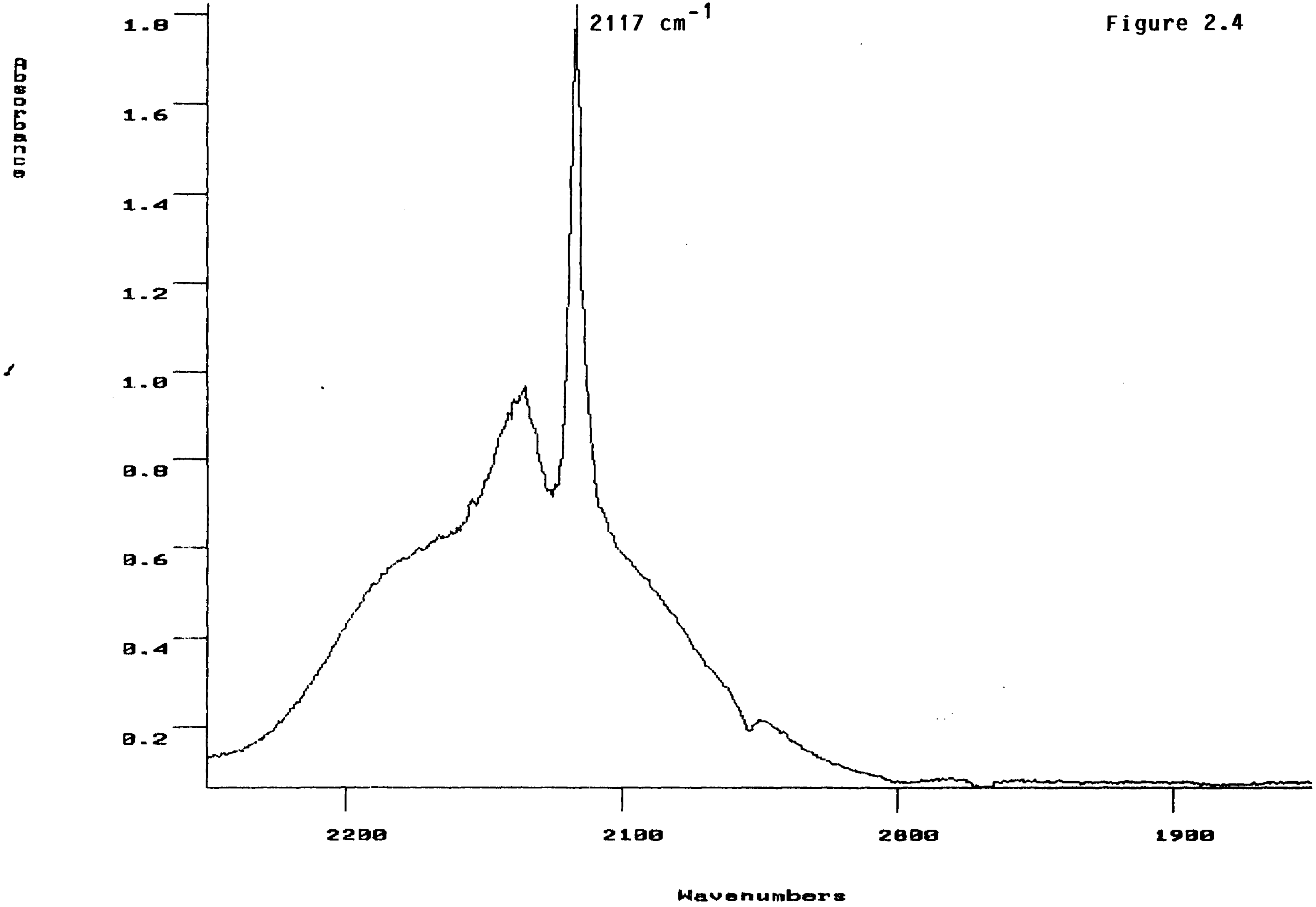

2117 cm^{-1}
Absorbance
1.8
1.6
1.4
1.2
1.0
0.8
0.6
0.4
0.2
2200
2100
2000
1900
Wavenumbers

Figure 2.4

This anion remained the only species observed up to 175°C. When the temperature was increased to 180°C the anion diiododicarbonylrhodate(I) $[Rh(CO)_2I_2]^-$ was observed. Over a period of approximately one hour at this temperature this latter species replaced the former rhodium(III) complex and then the spectrum of the rhodium(I) species is lost. Examination of the autoclave revealed the presence of plated rhodium metal.

We have shown that the compound with the absorbance band at 2117 cm^{-1} contains iodo- components (see reaction 2.2.4A), but no hydrido- component (see reaction 2.2.4B). It may however also contain a chloro- component. To confirm this the following reaction was performed using anhydrous rhodium(III) iodide.

Reaction 2.2.4C	***Species Observed***
RhI_3	
I_2	*2117* cm^{-1}*(ms)*
CH_2Cl_2	*2091* cm^{-1}*(m)*
CO	*2087* cm^{-}*(mw)*

The complex with the band at 2117 cm^{-1} must be a rhodium-carbonyl-iodide species. The data does not correspond with any complex listed in Appendix 1. The alternatives are few. Iodotricarbonylrhodate(I) would be expected to have two carbonyl absorption bands as observed for $[Ir(CO)_3I]$. Six co-ordinate species are mainly covered by known compounds. The rhodium(V) species $[Rh(CO)I_5]$ is very unlikely to occur. The rhodium(I) species $[Rh(CO)_2I]$ would rapidly dimerise or undergo addition of a carbon monoxide ligand. Triiodocarbonylrhodate(III) is the most likely candidate, however this has been characterised by Colton et al(4) and has an infra-red absorption band at 2070 - 2073 cm^{-1}. The diiodocarbonylrhodate(I) anion $[Rh(CO)I_2]^-$ would dimerise into $[Rh_2(CO)_2I_4]^{2-}$(4) with a band at 2059 cm^{-1}. Triiodocarbonylrhodate(I) dianion is a possibility, however we would expect this species' absorbance bands at around 2000 cm^{-1} from the spectra of related species. The bands at 2091 cm^{-1} and 2087 cm^{-1} are possibly analogous to those at 2107 cm^{-1} and 2108 cm^{-1} in reaction 2.2.4A.

Discussion

As may be expected, no anionic species was detected in the reaction mixture. In dichloromethane, the complex associated with the peak at 2117 cm^{-1} appears to rapidly convert to a second much more stable complex. It is somewhat surprising that neither dichlorotetracarbonyldirhodate(I) nor its iodo-analogue are produced. With trichlorocarbonylrhodate(III) present the progression to iodocarbonylrhodate anions would be expected. The change in the course of the reaction may be due to the production of the complex with the peak at 2117 cm^{-1}. This has not previously been observed, and may now start an alternate reaction sequence by-passing the dimer $[Rh_2(CO)_4X_2]$ (X = Cl, I).

In the propanoic acid solvent a different set of data is observed. In this case the dimer $[Rh_2(CO)_4I_2]$ is observed and this is then oxidised to the tetraiododicarbonylrhodate(III) anion. However at 180°C, the reduction of rhodium(III) to rhodium(I) is observed, a reaction that has not occurred in previous reactions. The tendency was to form chloro-rhodium(I) species from the rhodium(III) chloride then to form iodo-species which oxidised to rhodium(III) complexes. A possible explanation for this reduction of $[Rh(CO)_2I_4]^-$ to $[Rh(CO)_2I_2]^-$ is the Water Gas Shift reaction, Figure 2.5(12, 13). Equation 4 would explain the reduction reaction, however the only water present is the water of crystallisation in the rhodium(III) chloride. While this is quantitatively sufficient, its concentration is only approximately 3.2 x 10^{-2} molar. There is however another possible source of water, that is from the dehydration of propanoic acid to propanoic anhydride.

$$2C_2H_5CO_2H \longrightarrow (C_2H_5CO)_2O + H_2O \qquad \textit{Equation 5}$$

It should be noted that this reaction could be catalysed by a rhodium centre.

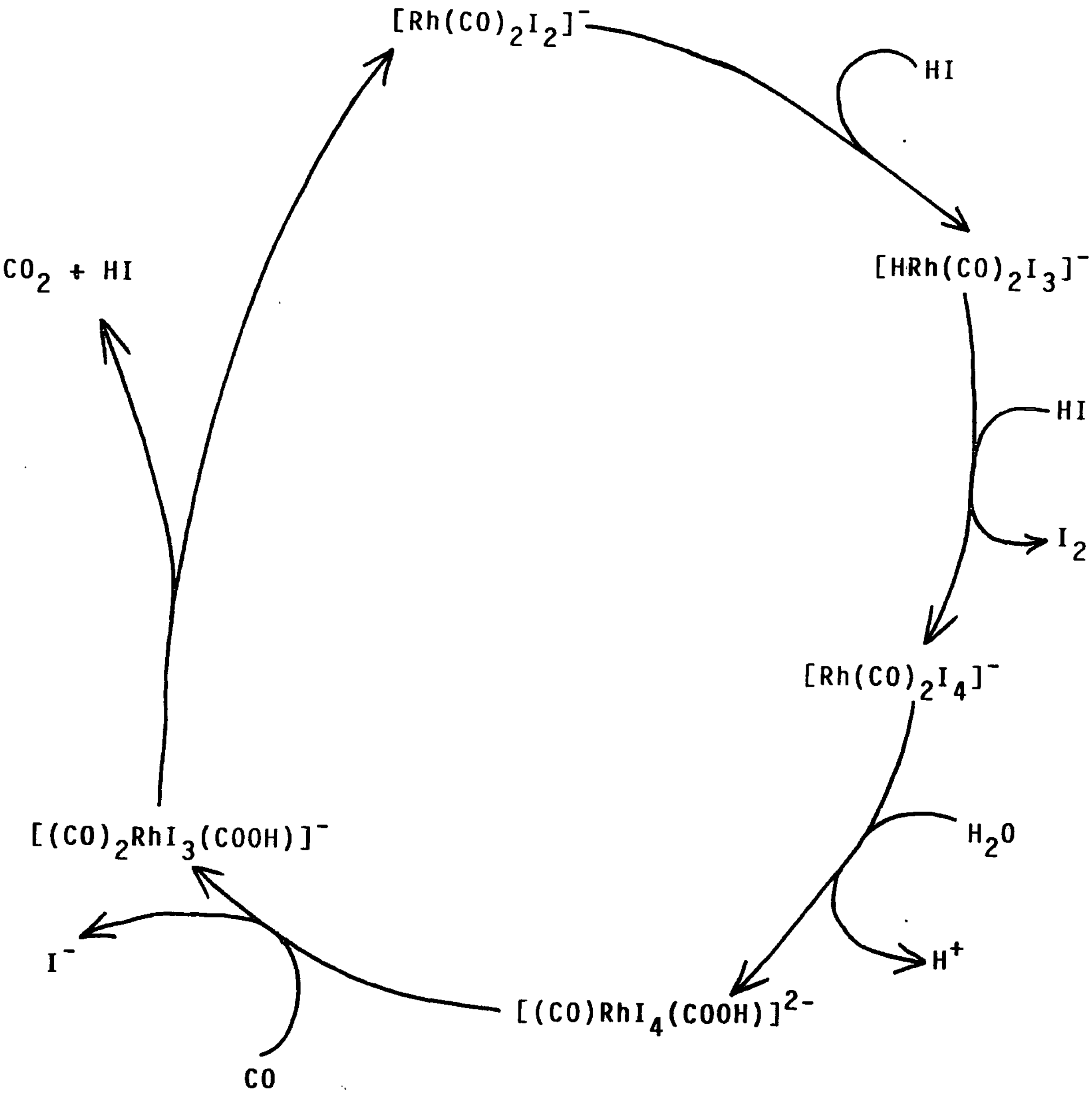
$$[Rh(CO)_2I_4]^- + C_2H_5CO_2H \longrightarrow C_2H_5I + HI + CO_2 + [Rh(CO)_2I_2]^- \qquad \textit{Equation 6}$$

The iodoethane produced by this reaction would be carbonylated to form propanoic iodide which would react to form propanoic anhydride.

$$C_2H_5COI + C_2H_5CO_2H \longrightarrow (C_2H_5CO)_2O + HI \qquad \textit{Equation 6A}$$

The combination of equations 6 and 6A give the same effect as the combination of equations 5 and 3. The two processes could only be distinguished by use of isotopically labelled carbon in the acid group, in the first case this would remain as propanoic anhydride, in the latter case it would also be present in the carbon dioxide above the reaction mixture.

Figure 2.5



$[Rh(CO)_2I_2]^- + 2HI$ --------- $[Rh(CO)_2I_4]^- + H_2$ Equation 2

$[Rh(CO)_2I_4]^- + H_2O$ ------ $[Rh(CO)_2I_2]^- + 2HI + CO_2$ Equation 3

$H_2O + CO$ --------- $H_2 + CO_2$ Equation 4

2.2.5 Alternative solvent systems

Propanoic acid, as noted in section 2.2.4, is possibly a reactant as well as a solvent. Dichloromethane was not sufficiently polar to produce anionic species, in reaction 2.2.4A, that had been seen previously. Therefore a review of other solvents, and their effect on the reaction was undertaken. Esters and ethers would be expected to react themselves under the reaction conditions and were regarded as unsuitable. Aliphatic and aromatic hydrocarbons and halo- compounds are not sufficiently polar. Ketones, aldehydes, nitriles, nitro compounds, amides and amines would also react. Iodoethane is accepted as an initiator for the hydrocarbonylation reaction. As the role of this compound in the reaction is known and is well defined, it was considered as a possible solvent. Alcohols are both reactant and solvent for the "Monsanto" process(15); study of this solvent was also considered important for comparative purposes.

Reaction 2.2.5A	*Species Observed*
$RhCl_3.3H_2O$	$Rh(CO)Cl_3(m)$
EtI	$[Rh_2(CO)_4I_2](m)$
CO	$[Rh_2(CO)_2I_4]^{2-}(m)$
	$[Rh(CO)_2I_4]^{-}(m)$
	2157 cm^{-1} unidentified
	2117 cm^{-1} unidentified

As well as trichlorocarbonylrhodate(III) a peak was seen at 2157 cm^{-1} from room temperature, right through the reaction to 180°C. It is possible that this is an analogous compound to $[(CH_3CO)Rh(CO)_2I_3]^-$ as observed by Forster(2). The compound would be expected to have another band at approximately 2085 cm^{-1}. This maybe masked by the spectra of firstly, diiodotetracarbonyldirhodate(I) $[Rh_2(CO)_4I_2]$, and later by tetraiododicarbonylrhodate(III) anion $[Rh(CO)_2I_4]^-$. The sequence of complexes, rhodium(I) followed by rhodium(III), the latter dominating the reaction, is as expected from reactions in section 2.2.2.

An absorption band is observed above 160°C at 2117 cm^{-1}, as seen in reaction 2.2.4A. It is possible that the excess iodoethane can produce the same conditions of molecular iodine excess as when iodine is added as the initiator.

Reaction 2.2.5B	***Species Observed***
$RhCl_3.3H_2O$ *EtI* *EtOH* *CO*	*$[Rh(CO)_2I_2]^-$(vs)*

In this reaction iodoethane has acted as an initiator with ethanol as a bulk solvent and reactant in the same manner as iodomethane and methanol are used in the "Monsanto" process. The only absorbance bands observed in the reaction occurred above 100°C at 2057, 1987 cm^{-1} and relate well to the predicted diiododicarbonylrhodate(I) anion $[Rh(CO)_2I_2]^-$ which is well known as the catalyst for the carbonylation of alcohols.

Reaction 2.2.5C	*Species Observed*
$RhCl_3.3H_2O$	$[Rh(CO)_2I_4]^-$*(m)*
HI	$[Rh(CO)_2I_2]^-$*(vs)*
EtOH	
CO	

When hydrogen iodide is used in place of iodoethane, the rhodium(III) complex is observed first at 100°C. It is then progressively replaced by the rhodium(I) complex which becomes the major species.

Discussion

The spectra record in iodoethane solvent are characterised by a high signal to noise ratio, and consequently small spectral changes may be undetected. In addition use of this solvent automatically produces very high levels of initiator, preventing investigation of this factor. For these reasons iodoethane was not used further as a solvent, despite several iodo-rhodium- species being detected.

When iodoethane is used in ethanol solvent diiododicarbonylrhodate(I) anion is observed as expected. As an initiator iodoethane provides a slow introduction of iodide into the reaction. It is well known that the rate of oxidative addition of hydrogeniodide and alkyliodides have the following order of rate of reaction(2).

$$\text{HI} > \text{MeI} > \text{EtI} \qquad \textit{Equation 7}$$

As iodoethane slowly adds to the rhodium(I) centre, it will release hydrogen iodide, see equation 8. Normally it would react rapidly with diiododicarbonylrhodate(I) anion to form rhodium(III) species, but in ethanol the hydrogen iodide reacts to reform iodoethane (equation 9) and consequently $[Rh(CO)_2I_2]^-$ is the only species detected.

$$\begin{tikzcd} EtI + [Rh(CO)_2I_2]^- \arrow[r] & {[EtRh(CO)_2I_3]^-} \arrow[d, "CO"] \\ & {[EtCORh(CO)_2I_3]^-} \end{tikzcd}$$

$$EtCOI \xrightarrow{EtOH} EtCO_2Et + HI \qquad \textit{Equation 8}$$

$$EtOH + HI \rightleftharpoons EtI + H_2O \qquad \textit{Equation 9}$$

When iodine-free hydrogen iodide is used as an initiator in ethanol (reaction 2.2.5C) the reaction detailed in equation 9 does not immediately reach equilibrium, and tetraiododicarbonylrhodate(III) anion is formed, possibly as shown in equation 10. It slowly declines to a minor species, this is probably due to progressive absorption of hydrogen iodide as occurs in equation 9.

$$[Rh(CO)_2I_2]^- + 2HI \longrightarrow [Rh(CO)_2I_4]^- + H_2 \qquad \textit{Equation 10}$$

2.2.6 Summary of initial systems

The expected reduction of rhodium(III) chloride produces rhodium(I) carbonyl-chloro-complexes, as predicted by Forster(11). These are preferred to the iodo- complexes. When, however, excess iodide is available rhodium(III) complexes form.

Several complexes fundamental to this study have been detected; trans-tetraiododicarbonylrhodate(III) anion and diiododicarbonylrhodate(I) are key complexes in the predicted catalytic cycle (Figure 2.1). In propanoic acid few rhodate(I) species are detected. Additionally pentaiodocarbonylrhodate(III) dianion is observed despite high carbon monoxide pressure. Formation of the only rhodium(I) species in propanoic acid occurred at 180°C (reaction 2.2.4B) and appeared to be the reduction product from tetraiododicarbonylrhodate(III) anion $[Rh(CO)_2I_4]^-$. There have arisen two absorption bands that are unidentified, neither are stable at atmospheric pressure, and therefore the complexes are not amicable to standard methods of analysis. The band at 2157 cm^{-1} may be $[(C_2H_5CO)Rh(CO)_2I_3]^-$ but it requires an associate peak at around 2085 cm^{-1}. The absorbance band at 2117 cm^{-1} may be an intermediate in the reduction of rhodium(III) chloride, to diiodotetracarbonyldirhodate(I) but its identity has not been determined.

There has been, as expected, a marked difference in the species observed in different solvents. The less polar solvents gave spectral data of better quality and more diverse spectra. However from the species observed, it is possible that these solvents induce a different reaction pathway to that of the more polar solvents such as propanoic acid. There is a very clear distinction between the carbonylation reaction achieved in alcohols to the hydrocarbonylation reaction in alkanoic acids. The former systems show rhodium(I) species present in solution whereas the latter has the rhodium(III) complex $[Rh(CO)_2I_4]^-$ as the major species, probably due to the presence of free hydrogen iodide. The formation of this latter complex in ethyliodide reactions may be achieved by the production of butane (equation 11). This is much less likely than the production of hydrogen by hydrogen iodide (equation 10) by a three centre mechanism, Figure 2.6(12).

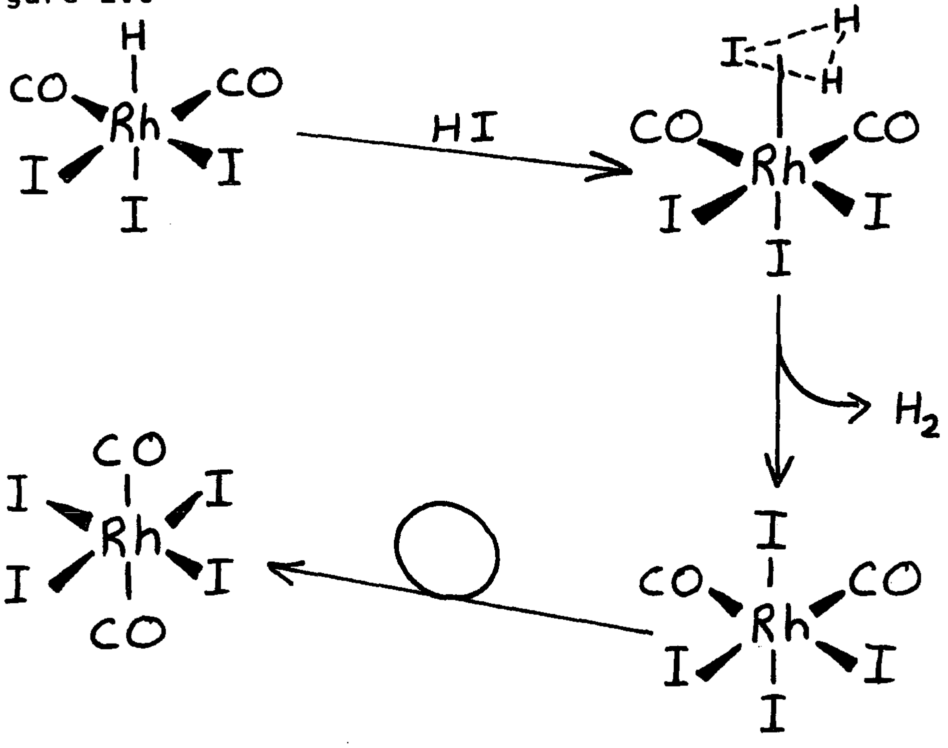
$[EtRh(CO)_2I_3]^- + EtI \longrightarrow CH_3CH_2CH_2CH_3 + [Rh(CO)_2I_4]^-$ *Equation 11*

It is however far more likely that $[EtRh(CO)_2I_3]^-$ will react with carbon monoxide to form $[(EtCO)Rh(CO)_2I_3]^-$. However in the case of hydrocarbonylation the complex $[HRh(CO)_2I_3]^-$ must first react with ethene to form $[EtRh(CO)_2I_3]^-$, thus enabling a second reaction with hydrogen iodide to form $[Rh(CO)_2I_4]^-$ before reaction with ethene and carbon monoxide.

2.3 Comparison of Iodoethane and Hydrogen Iodide as Initiators

The difference in rates of oxidative addition between iodoethane and hydrogen iodide has been noted previously (section 2.2.6). In order to determine whether the action of the two initiators could be distinguished, a series of reactions were undertaken in dichloromethane. As the presence of water or carboxylic acids would generate hydrogen iodide when iodoethane is used as initiator(2), these chemicals were avoided.

Figure 2.6



2.3.1 Iodoethane as an initiator

Reaction 2.3.1A	*Species Observed*
$RhCl_3.3H_2O$	$Rh(CO)Cl_3$*(s)*
EtI	$Rh_2(CO)_4Cl_2$*(vs)*
CH_2Cl_2	$[Rh(CO)_2I_4]^-$*(ms)*
CO	$[Rh_2(CO)_2I_4]^{2-}$*(m)*
	$[Rh_2(CO)_4I_2]$*(m)*
	2115 cm^{-1}*(m) unidentified*
	2155 cm^{-1}*(w) unidentified*
	$[Rh(CO)_2I_2]^-$*(m)*

Initially the absorption bands for trichlorocarbonylrhodate(III) are detected, but at 80 - 110°C, the first iodo-rhodium complex is observed, $[Rh(CO)_2I_4]^-$. When the temperature rises to 140 - 160°C the rhodium(I) complexes $[Rh_2(CO)_2I_4]^{2-}$ and $[Rh_2(CO)_4I_2]$ are observed, together with the unidentified species absorbing at 2115 cm^{-1} and 2155 cm^{-1}. It should be noted that the species diiodotetracarbonyldirhodate(I) would be expected to be formed before tetraiododicarbonylrhodate(III) anion. There is, therefore, the possibility that previously unreacted rhodium(III) chloride is reacting at 140°C to form $[Rh_2(CO)_4I_2]$, rather than $[Rh(CO)_2I_4]^-$ being reduced, although this latter reduction is equally feasible. When the reaction is returned to 20°C $[Rh(CO)_2I_2]^-$, $[Rh(CO)_2I_4]^-$ were detected along with absorption bands at 2117 and 2155 cm^{-1}.

Reaction 2.3.1B	*Species Observed*
$RhCl_3.3H_2O$	$Rh(CO)Cl_3$*(ms)*
EtI	$[Rh_2(CO)_4Cl_2]$*(vs)*
CH_2Cl_2	$Rh(CO)_3Cl$*(s)*
CO/CH_2CH_2	$[Rh(CO)_2I_4]^-$*(ms)*
	$[Rh_2(CO)_4I_2]$*(s)*
	$[Rh_2(CO)_2I_4]^{2-}$*(m)*
	$[Rh(CO)_2I_2]^-$*(w)*

All three chlorocarbonylrhodate complexes are observed at 20°C. At 150°C, trans-$[Rh(CO)_2I_4]^-$ and $[Rh_2(CO)_4I_2]$ are detected. Then at 160°C $[Rh_2(CO)_2I_4]^-$ forms. On raising the temperature to 180°C a small amount of $[Rh(CO)_2I_2]^-$ is observed.

Discussion

There appears to be little effect on this system by the addition of ethene; in both cases the absorption band at 2085 cm^{-1} $[Rh(CO)_2I_4]^-$ dominates the reaction.

The results of work in section 2.2 suggested that the absorption band at 2155 cm^{-1} may be due to $[(EtCO)Rh(CO)_2I_3]^-$; if this is so, we would have expected to see this absorbance band in high quantity in reaction 2.3.1B. As this band is not observed at any larger intensity, either the interpretation of the band is invalid, or the species decomposes to give propanoic chloride and $[Rh(CO)_2I_2]^{-}$(3).

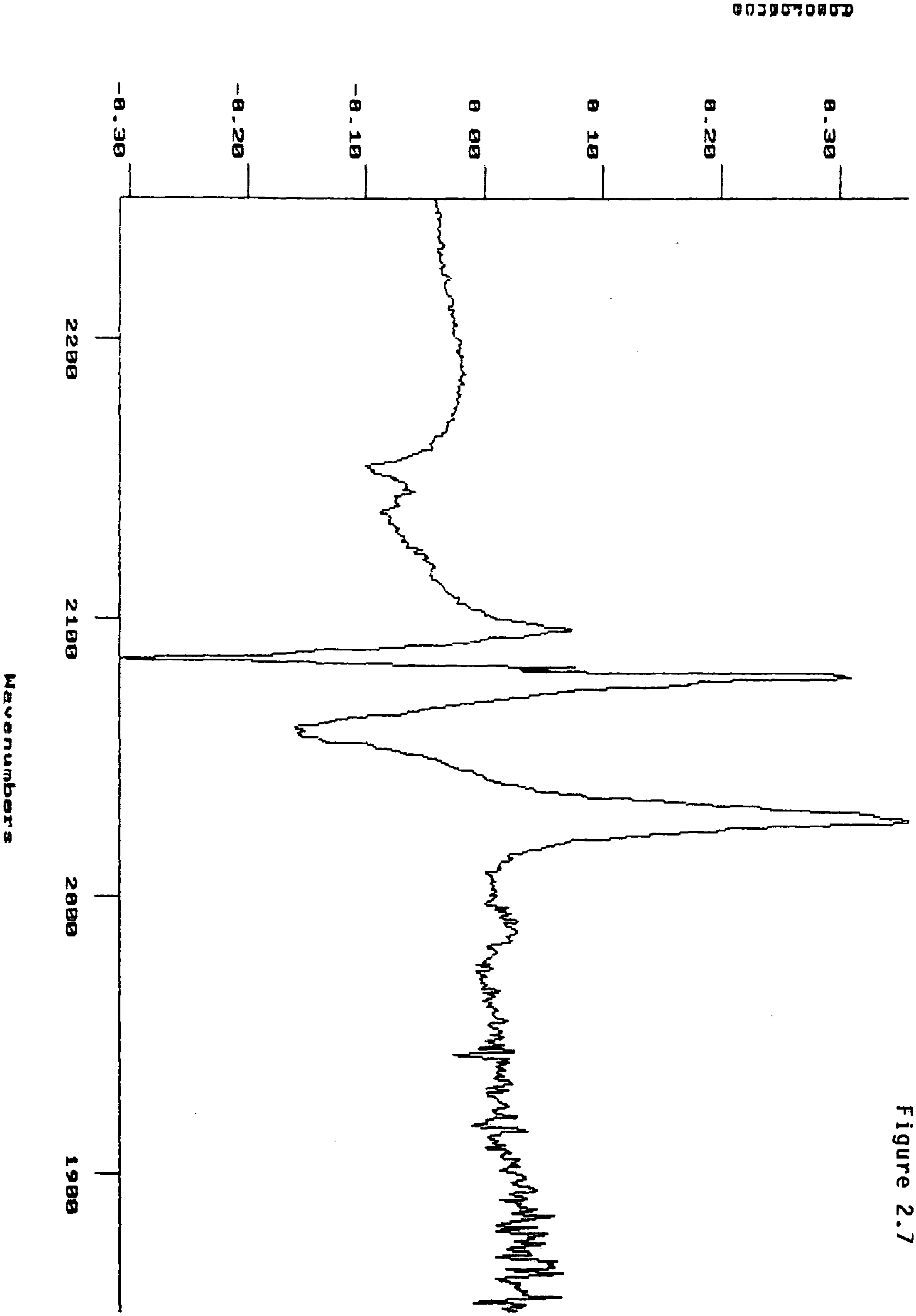

Absorbance
-0.30
-0.20
-0.10
0.00
0.10
0.20
0.30
2200
2100
2000
1900
Wavenumbers

Figure 2.7

In both reactions it is possible that a sequence of complexes are observed in the formation of $[Rh(CO)_2I_2]^-$. Carbonylation of rhodium(III) chloride followed by reduction to form chloro-carbonyl-rhodate(I) complexes $[Rh_2(CO)_4Cl_2]$ and $[Rh(CO)_3Cl]$. These react to form iodo-carbonyl-rhodate(III) anions, which are in turn reduced to iodo-carbonyl-rhodate(I) anions. In both cases however the possibility of previously unreacted rhodium(III) chloride forming each complex, at the relevant temperature, must be considered.

2.3.2 Hydrogen iodide as an initiator

Reaction 2.3.2A	*Species Observed*
$RhCl_3.3H_2O$	$Rh(CO)Cl_3$(m)
HI	$[Rh(CO)_2I_2]^-$(w)
CH_2Cl_2	2117 cm^{-1}(vs) unidentified
CO	$[Rh_2(CO)_2I_4]^{2-}$(mw)
	$[Rh_2(CO)_4I_2]$(s)
	$[Rh(CO)_2I_4]^-$(s)
	2155 cm^{-1}(w) unidentified

At 140°C trichlorocarbonylrhodate(III) and diiododicarbonylrhodate(I) anion are observed. By far the dominant species is the one associated with the band at 2117 cm^{-1}. This cannot be a hydrido- complex as it was previously observed in section 2.2.4 when iodine was the initiator in a comparable reaction. Hydrogen iodide can easily dissociate to hydrogen and iodine, the latter reacting as previously discussed in section 2.2.4. With time these complexes react to give the three complexes $[Rh(CO)_2I_4]^-$, $[Rh_2(CO)_4I_2]$, $[Rh_2(CO)_2I_4]^{2-}$; with $[Rh(CO)_2I_4]^-$ as the dominant species in the reaction mixture. An increase in temperature to 160°C gives rise to a rapid increase in $[Rh_2(CO)_4I_2]$ absorption bands (see Figure 2.7). It is surprising that this dimer is present under these conditions, as it would be expected to react with free iodide species to form the anion $[Rh(CO)_2I_2]^-$. It would appear that there is a "sink" for free iodide at this stage enabling the dimer to be formed. One possibility is the formation of iodine, combined with the reduction of another reaction component. However on return to 20°C the anions were observed again, showing that the free iodide may be returned from this "sink".

Reaction 2.3.2B	***Species Observed***
$RhCl_3.3H_2O$	$Rh(CO)Cl_3$
HI	$[Rh(CO)_2I_4]^-$
CH_2Cl_2	$[Rh(CO)I_5]^{2-}$
CO/CH_2CH_2	

This reaction gave a very limited set of absorbance bands. While it is possible that the ethene has reacted directly with the hydrogen iodide it is also likely that the ethene was reacted with some of the carbonyl complexes. The formation of pentaiododicarbonylrhodate(III) dianion $[Rh(CO)I_5]^{2-}$ may occur as in equation 12:

$$[Rh(CO)_2I_4]^- + I^- \longrightarrow [Rh(CO)I_5]^{2-} + CO \qquad \textit{Equation 12}$$

This would be disfavoured by high carbon monoxide pressure.

Figure 2.8a

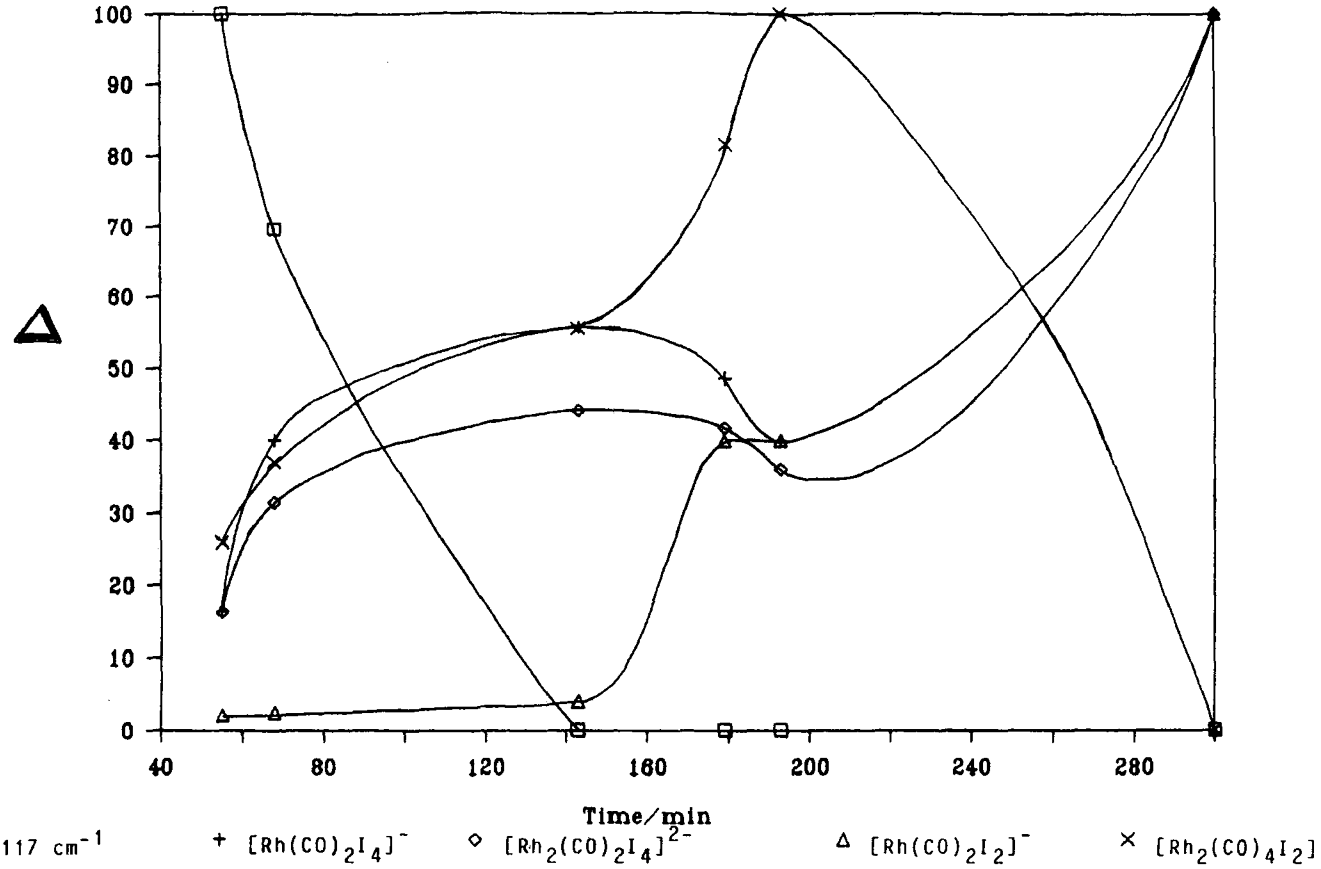
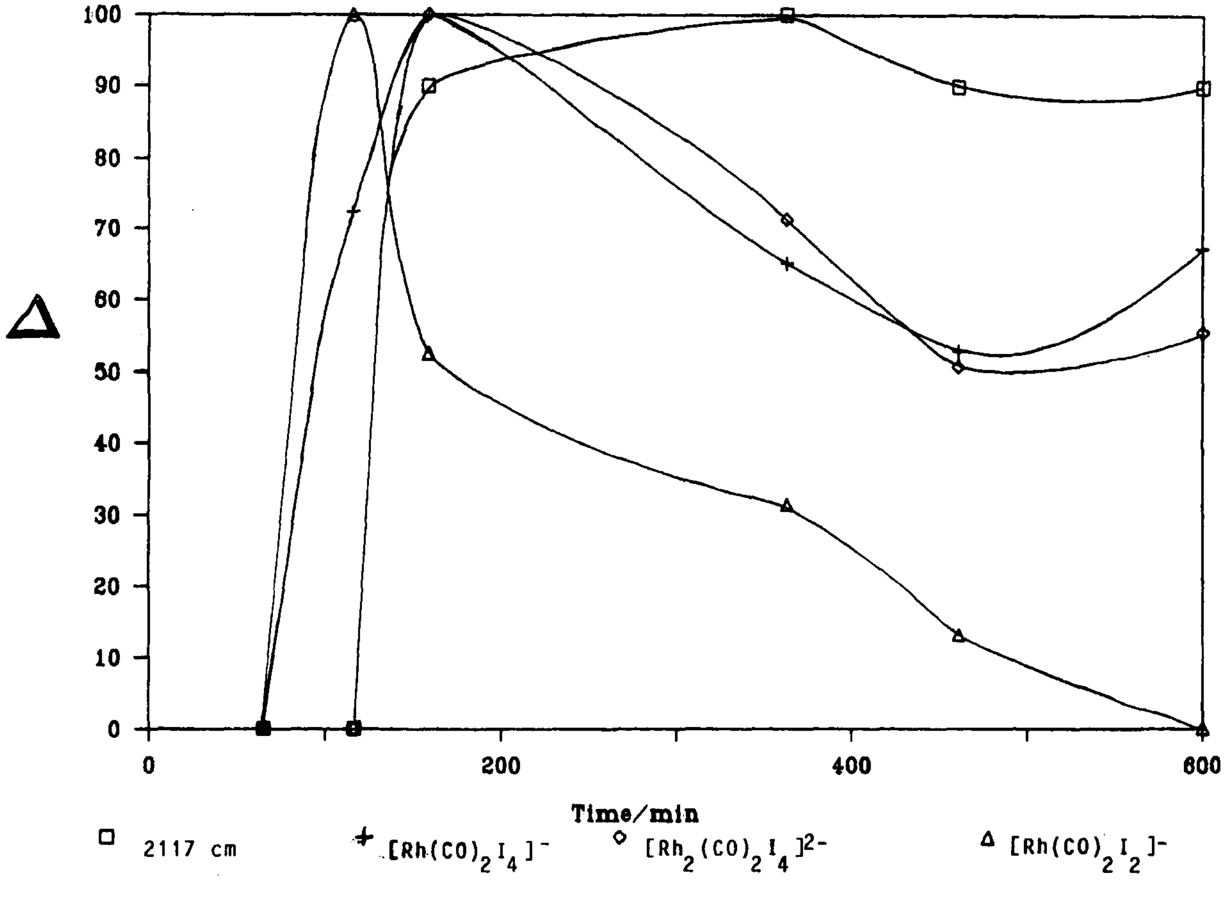


Figure 2.8b



2.3.3 Summary

The best illustration of the differences between hydrogen iodide and iodoethane as initiators comes from reactions 2.3.1A and 2.3.2A, as reaction 2.3.2B appears to be an anomaly for this series. It may be deduced from the rapid appearance of the 2117 cm^{-1} band, that hydrogen iodide rapidly introduces iodide ligands into the reaction system. Iodoethane releases its iodo- component at a steadier rate and maintains the iodocarbonylrhodate anion, whereas with hydrogen iodide there is the formation of $[Rh(CO)_4I_2]$ which suggests that the initiator is quickly consumed.

In Figure 2.8 the intensity of the spectral absorbance of complexes is plotted as Δ, Δ being a percentage defined as -

$$\Delta \equiv \frac{\text{Abs.(T)} \times 100\%}{\text{Abs.(max)}}$$

whereas Abs.(T) is the absorbance (as defined by the Beer-Lambert law) at the given time (T). Abs.(max) is the maximum absorbance observed at any time during the reaction for that complex. The intention of these diagrams is to give an impression of the changing presence of each complex throughout the reaction. Quantitative measurements would require the extinction coefficients for the complexes, which are not available for the conditions of study.

In reaction 2.3.2A with ethyliodide as initiator, it is noticeable that the component with the absorbance bands at 2117 cm^{-1} occurs much later than reaction 2.3.1A, and remains at a constant level throughout the reaction. In this first reaction, complexes appear at approximately 140°C and then follow a decay curve through the reaction. In reaction 2.3.2A $[Rh(CO)_2I_4]^-$ and $[Rh_2(CO)_2I_4]^{2-}$ form rapidly, as does the iodo-dimer $[Rh_2(CO)_4I_2]$. $[Rh(CO)_2I_2]^-$ first appears at the same time as the other complexes but only in small amounts, until the temperature reaches 160 - 170°C. Then it rapidly increases as does the dimer $[Rh_2(CO)_4I_2]$. However the absorbance of the other rhodium(I) species decreases as does the rhodium(III) complex $[Rh(CO)_2I_4]^-$.

The major differences in the two reaction diagrams concern the complexes $[Rh_2(CO)_4I_2]$ and $[Rh(CO)_2I_2]^-$. This information may be related to differences in batch autoclave reaction data reported in Chapter 3.

2.4 Action of Initiators in Propanoic Acid

Having investigated the different interaction of iodide co-catalysts in dichloromethane solvent, their behaviour in the more polar propanoic acid was studied. In section 2.2.2 it was demonstrated that tetrabutylammonium iodide only gave rise to the rhodium(III) species $[Rh(CO)I_5]^{2-}$ and $[Rh(CO)_2I_4]^-$ at 180°C without the observation of any intermediates. When iodine was used as initiator in propanoic acid (reaction 2.2.4B), it produced the intermediate dimer $[Rh_2(CO)_4I_2]$, followed by both rhodium(I) and rhodium(III) carbonyl species, with the rhodium(I) species $[Rh(CO)_2I_2]^-$ being favoured at 180°C. When iodine is used in dichloromethane only covalent species are observed. This shows that propanoic acid solvent favours the formation of ionic species. It is likely that this effect will be more pronounced for systems with iodoethane and hydrogen iodide as initiators.

2.4.1 Iodoethane as an initiator in propanoic acid

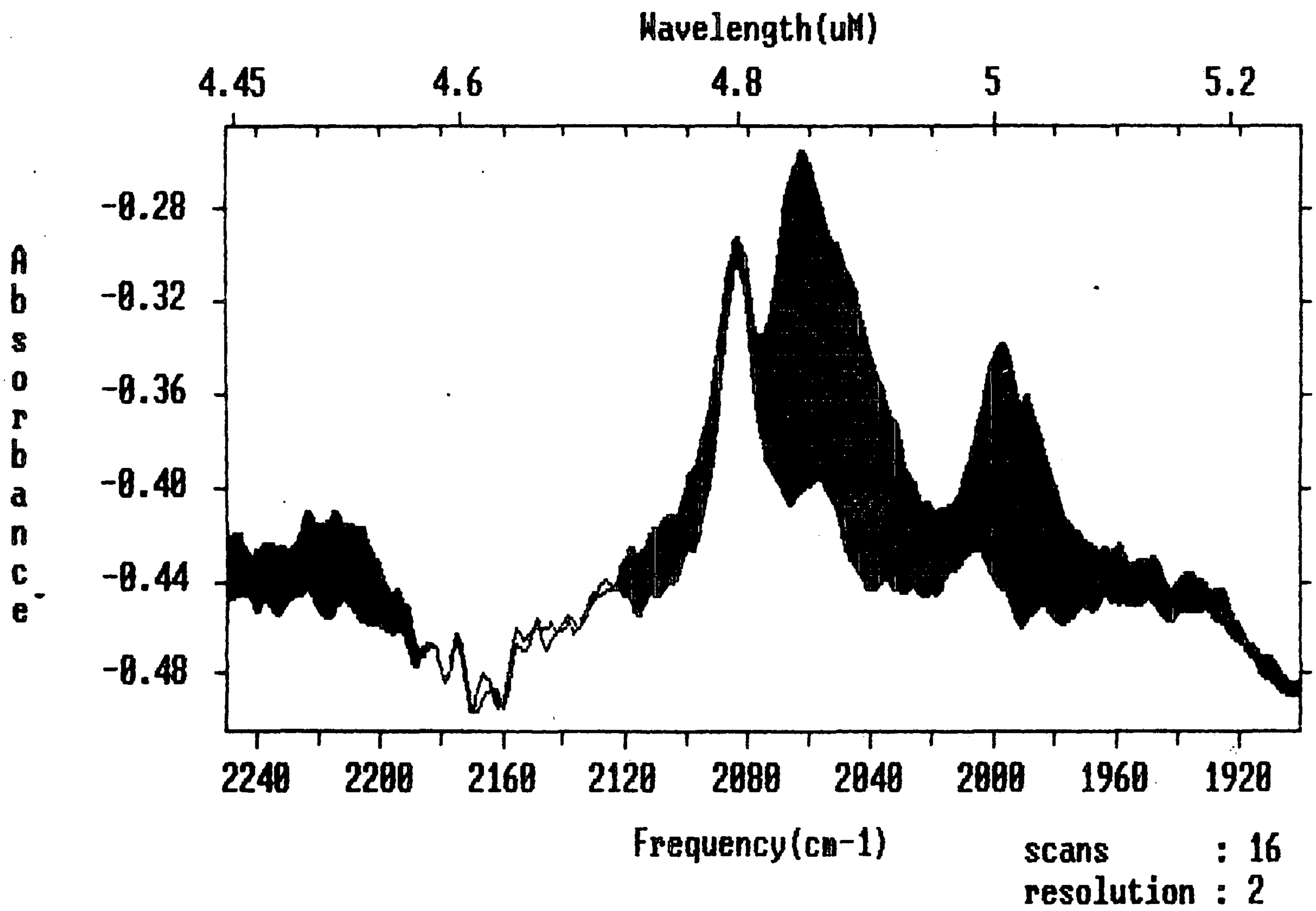
This reaction was studied in the absence of ethane. When iodoethane reacts with a rhodium(I) centre (equation 13) hydrogen iodide will be produced to react further. The rhodium-hydrogen species formed would react with ethene(2). It is possible therefore that in the absence of ethene, the hydrido- species will remain and be observable in the infra-red spectrum.

$$\mathrm{EtI + CO + ROH \xrightarrow{[Rh(CO)_2I_2]^-} EtCO_2R + HI} \qquad \textit{Equation 13}$$

Reaction 2.4.1A	*Species Observed*
$RhCl_3.3H_2O$	$[Rh(CO)_2I_2]^-$
EtI	$[Rh(CO)_2I_4]^-$
$C_2H_5CO_2H$	$[Rh(CO)I_5]^{2-}$
CO	

A marked absence of covalent rhodium(I) carbonyl species was noted and also $[Rh_2(CO)_2I_4]^{2-}$ normally seen in association with $[Rh(CO)_2I_4]^-$. A further reaction was conducted with dichlorotetracarbonyldirhodate(I).

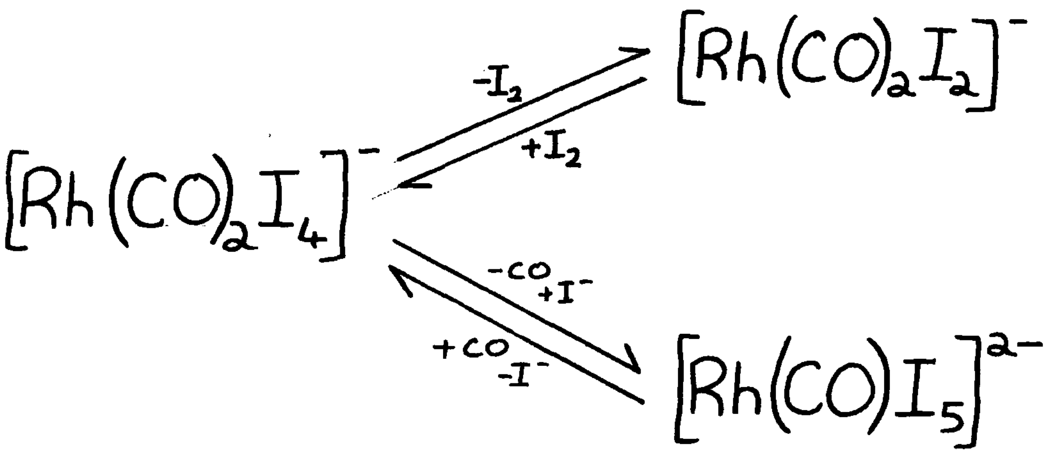
Figure 2.9


Thu Jan 1, 1:06 am
Wavelength(uM)
4.45
4.6
4.8
5
5.2
Absorbance
-0.28
-0.32
-0.36
-0.40
-0.44
-0.48
2240
2200
2160
2120
2080
2040
2000
1960
1920
Frequency(cm-1)
scans : 16
resolution : 2

Reaction 2.4.1B	***Species Observed***
$Rh_2(CO)_4Cl_2$ *EtI* *$C_2H_5CO_2H$* *CO*	*$[Rh(CO)_2I_4]^-$*

The occurrence of only one species was unexpected but may be indicative of $[Rh_2(CO)_4Cl_2]$ instability in propanoic acid. If this is the case, this would explain why only anionic species are observed in reaction 2.4.1A. In both reactions above the formation of tetraiododicarbonylrhodate(III) anion has been observed. In the former reaction where spectra had better signal to noise ratios, the rhodium(I) anion $[Rh(CO)_2I_2]^-$ was also observed at 180°C in a similar manner as when iodine was the initiator (see Figure 2.9). However in the present case we find that toward the later stages of the reaction, a rhodium(III) complex again starts to dominate the reaction, namely pentaiodocarbonylrhodate(III) dianion. It is possible that we are observing a sequence of related compounds. As all three complexes are present at the same time their interchange is via tetraiododicarbonylrhodate(III) anion.

Figure 2.10



If these two processes are competing in the hydrocarbonylation reaction, then the pentaiodocarbonylrhodate(III) dianion will form a rhodium "sink", reducing the mount of "active" catalyst available for reaction.

2.4.2 Hydrogen iodide as an initiator in propanoic acid

In using hydrogen iodide in the absence of ethene the full hydrocarbonylation reaction cannot progress. Attempts were therefore made to observe those complexes that would normally react with ethene in the catalytic cycle.

Reaction 2.4.2	*Species Observed*
$RhCl_3.3H_2O$	2080, 2010 cm^{-1}(s) *unidentified*
HI	2096 cm^{-1}(s) *unidentified*
$C_2H_5CO_2H$	$[Rh_2(CO)_2I_4]^{2-}$(m)
CO	$[Rh(CO)I_5]^{2-}$

This reaction gave rise to two absorption bands at 2080, 2010 cm^{-1} when the temperature reached 155°C. These would appear to be at too high a frequency for $[Rh(CO)_2I_2]^-$ (see Appendix 1: 2065, 1995(s) cm^{-1}). The second species at 2096 cm^{-1} appeared at the same temperature (177°) as $[Rh_2(CO)_2I_4]^{2-}$, this latter species is usually observed in conjunction with $[Rh(CO)_2I_4]^-$. However this normally exhibits an absorption band at 2085 cm^{-1} (Appendix 1). If the unidentified peaks do correspond to $[Rh(CO)_2I_4]^-$ we may expect a complementary shift in spectral frequency for the other two rhodium complexes; this shift is not observed. Alternatives to these complexes appear limited; carboxylic complexes of rhodium are a possibility, however the data obtained does not correspond to any known complex (see data in Appendix 1), nor to spectral features characteristic of these types of complexes.

$[HRh(CO)_2I_3]^-$ would be expected to possess a third band above 2100 cm^{-1} (c.f. $[HIr(CO)_2I_3]^-$ and hydrido-rhodium species, Appendix 1). One possibility is that of the ion pair reported by A. Fulford et al(14), that is $[H^+ ....Rh(CO)_2I_2^-]$. It is reported as having bands at 2072 cm^{-1} and 2003 cm^{-1}. It is possible that these bands at 2080 and 2010 cm^{-1} are a species of this form and that the additional change in frequency is caused by the propanoic acid solvent. If this is the case then the band at 2096 cm^{-1} may be $[H^+....Rh(CO)_2I_4^-]$ although there is no confirmationary evidence for the existence of a species of this nature.

2.4.3 Effect of ethene on the rhodium-iodide system in propanoic acid

The more interpretable data in the previous section was obtained using iodoethane as the initiator. Consequently studies with ethene were undertaken using iodoethane as the iodide source.

Reaction 2.4.3A	*Species Observed*
$RhCl_3.3H_2O$ EtI $C_2H_5CO_2H$ CO/C_2H_4	$[Rh(CO)I_5]^{2-}$

The absence of any absorption bands other than those due to $[Rh(CO)I_5]^{2-}$ at 180°C, was extremely surprising. It is possible that ethene has reduced the influence of carbon monoxide to stabilise the species in solution, thus destabilising the dicarbonyl complexes we would expect to see, such as $[Rh(CO)_2I_2]^-$ and $[Rh(CO)_2I_4]^-$. A further reaction was therefore conducted using $[Rh_2(CO)_4Cl_2]$.

Reaction 2.4.3B	***Species Observed***
$Rh_2(CO)_4Cl_2$	$Rh_2(CO)_4Cl_2$
EtI	$[Rh(CO)_3Cl]$
$C_2H_5CO_2H$	$[Rh(CO)_2I_4]^-$
CO/C_2H_4	$[Rh(CO)_2I_2]^-$

At first, it would appear that reaction 2.4.3B is contradictory to the data produced in reaction 2.4.3A. However the pentaiodocarbonylrhodate(III) in the first reaction may be produced directly from $RhCl_3$ without reduction first to rhodium(I) (equation 14):

$$RhCl_3 + 5I^- + CO \longrightarrow [Rh(CO)I_5]^{2-} + 3Cl^- \qquad \textit{Equation 14}$$

2.4.4. Summary

As expected from previous reactions the use of propanoic acid as a solvent has produced systems featuring mainly ionic compounds in solution. There is poor agreement between reactions however. This may in part be attributed to the poorer quality of spectra in this solvent which may prevent detection of other species.

Despite this, doubt remains about the identity of two species produced when hydrogen iodide is used as the initiator although the number of alternatives is severely limited. It is possible that the absorption bands are those of $[Rh(CO)_2Cl_3]^-$ and that the iodide concentration is not sufficient to react due to initial conversion to iodine, with the liberation of hydrogen. In the presence of ethene the suppression of complexes observable in the infra-red spectrum was not expected. Observations made in section 2.2 suggested that ethene acts as a poorer ligand than carbon monoxide and ethene is unlikely to displace carbon monoxide from a rhodium centre given an equal pressure of carbon monoxide. It is possible that in propanoic acid in the presence of iodoethane the stability of the dicarbonyl complexes is reduced.

During these reactions we have seen the interconversion of the complexes $[Rh(CO)_2I_4]^-$, $[Rh(CO)_2I_2]^-$ and $[Rh(CO)I_5]^{2-}$ (see Figure 2.9). The conversion of the former complex into either or both of the latter two is reasonable, and especially so for $[Rh(CO)I_5]^{2-}$ which involves the ligand exchange of equation 15:

$$[Rh(CO)_2I_4]^- + I^- \longrightarrow [Rh(CO)I_5]^{2-} + CO \qquad \textit{Equation 15}$$

It is also possible that pentaiodocarbonylrhodate(III) dianion decomposes to rhodium(III) iodide, which may, in turn, be reduced by carbon monoxide to re-enter the reaction system. The interconversion of tetraiododicarbonylrhodate(III) anion and diiododicarbonylrhodate(I) may be more complex. Stoichiometrically the reaction of the rhodium(I) species with iodine produces the rhodium(III) species (equation 16).

It is more likely that hydrogen iodide oxidatively adds across the rhodium centre and that further reaction with another molecule of hydrogen iodide produces the rhodium(III) complex (equation 17). The nature of the intermediate has been discussed.

$$[Rh(CO)_2I_2]^{\ominus} + I_2 \longrightarrow [Rh(CO)_2I_4]^{\ominus} \qquad \textit{Equation 16}$$

$$\begin{array}{l}
[Rh(CO)_2I_2]^{\ominus} + HI \longrightarrow [HRh(CO)_2I_3]^{\ominus} \\
[HRh(CO)_2I_3]^{-} + HI \longrightarrow [Rh(CO)_2I_4]^{\ominus} + H_2 \\
\hline
[Rh(CO)_2I_2]^{-} + 2HI \longrightarrow [Rh(CO)_2I_4]^{-} + H_2
\end{array} \qquad \textit{Equation 17}$$

The reverse conversion of rhodium(III) dicarbonyltetraiodide anion to rhodium(I) dicarbonyldiiodide anion is formally reductive elimination of iodine, it is possible that it occurs via the Water Gas Shift cycle (see Figure 2.11). This cycle has been observed for rhodium-iodide systems, but there are two points of note. Firstly there is no water added to these reaction systems; this would prevent step 2 (Figure 11) of the reduction. This would be to overlook the factor that propanoic acid can be dehydrated to form propanoic anhydride either independently or possibly by interaction such as the scheme in equation 19. It has been demonstrated that such rhodium-iodide system will under anhydrous conditions dehydrate ethanol (see Chapter 3), therefore the dehydration of propanoic acid may be expected.

$$[Rh(CO)_3I_3] + C_2H_5CO_2H \longrightarrow [(COOH)Rh(CO)_2I_3]^{-} + C_2H_5CO^{+}$$

$$C_2H_5CO^+ + C_2H_5CO_2H \longrightarrow H^+ + (C_2H_5CO)_2O$$

$$H^+ + [(COOH)Rh(CO)_2I_3]^- \longrightarrow H_2O + Rh(CO)_3I_3$$ *Equation 19*

Throughout these studies using propanoic acid there was extreme difficulty in producing quality spectra. Definition and resolution have suffered from poor signal to noise ratios. In an attempt to produce more easily interpreted spectra a mixture of solvents was used. A 5:12 v/v ratio of propanoic acid and dichloromethane was investigated and showed a decrease of approximately 20% in rate of reaction (see Chapter 3). Infra-red studies indicated a higher signal to noise ratio, so this mixture was used as an alternative solvent.

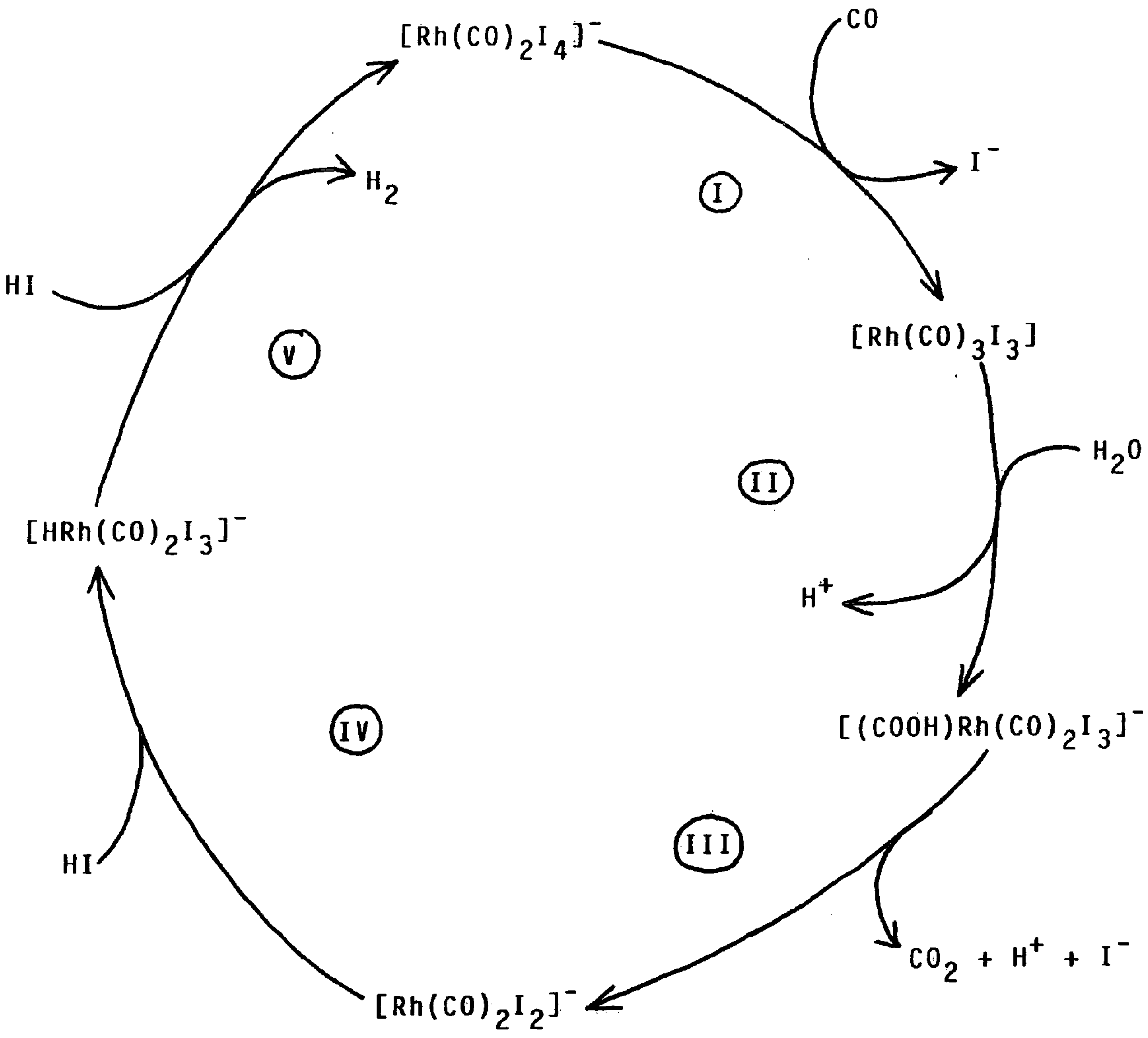
2.5 Infra-red Studies of Mixed Solvent Systems

2.5.1 Reactions of hydrated rhodium(III) chloride

As stated above the solvent systemised was a 5:12 v/v mixture of propanoic acid and dichloromethane. This solvent mixture gave an improvement in spectral quality (see Figure 2.12) although the quality achieved remained poor compared with spectra obtained in alcohols and hydrocarbon solvents.

The first reaction in this system gives a straightforward comparison with reaction 2.4.1A which was completed in pure propanoic acid.

Figure 2.11



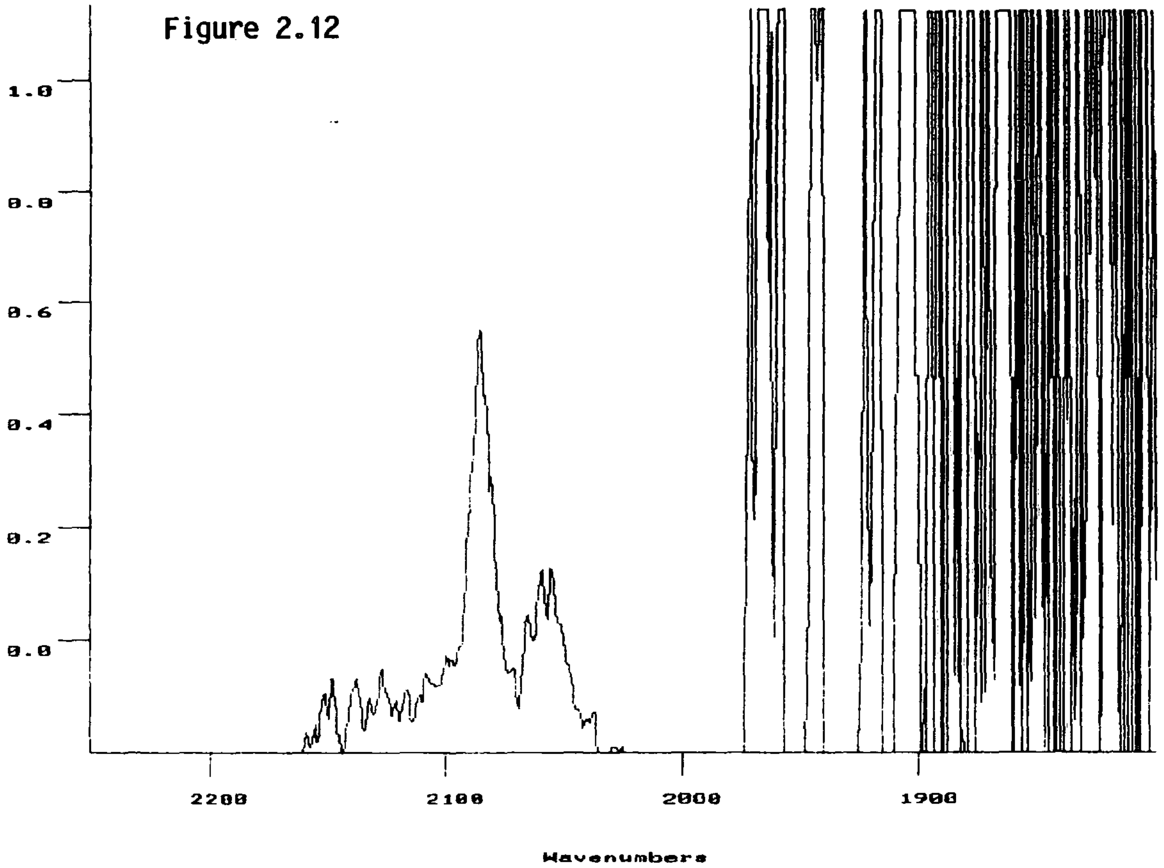
$$[Rh(CO)_2I_4]^- + CO + H_2O \longrightarrow [Rh(CO)_2I_2]^- + CO_2 + 2H^+ + 2I^-$$

$$[Rh(CO)_2I_2]^- + 2HI \longrightarrow [Rh(CO)_2I_4]^- + H_2$$

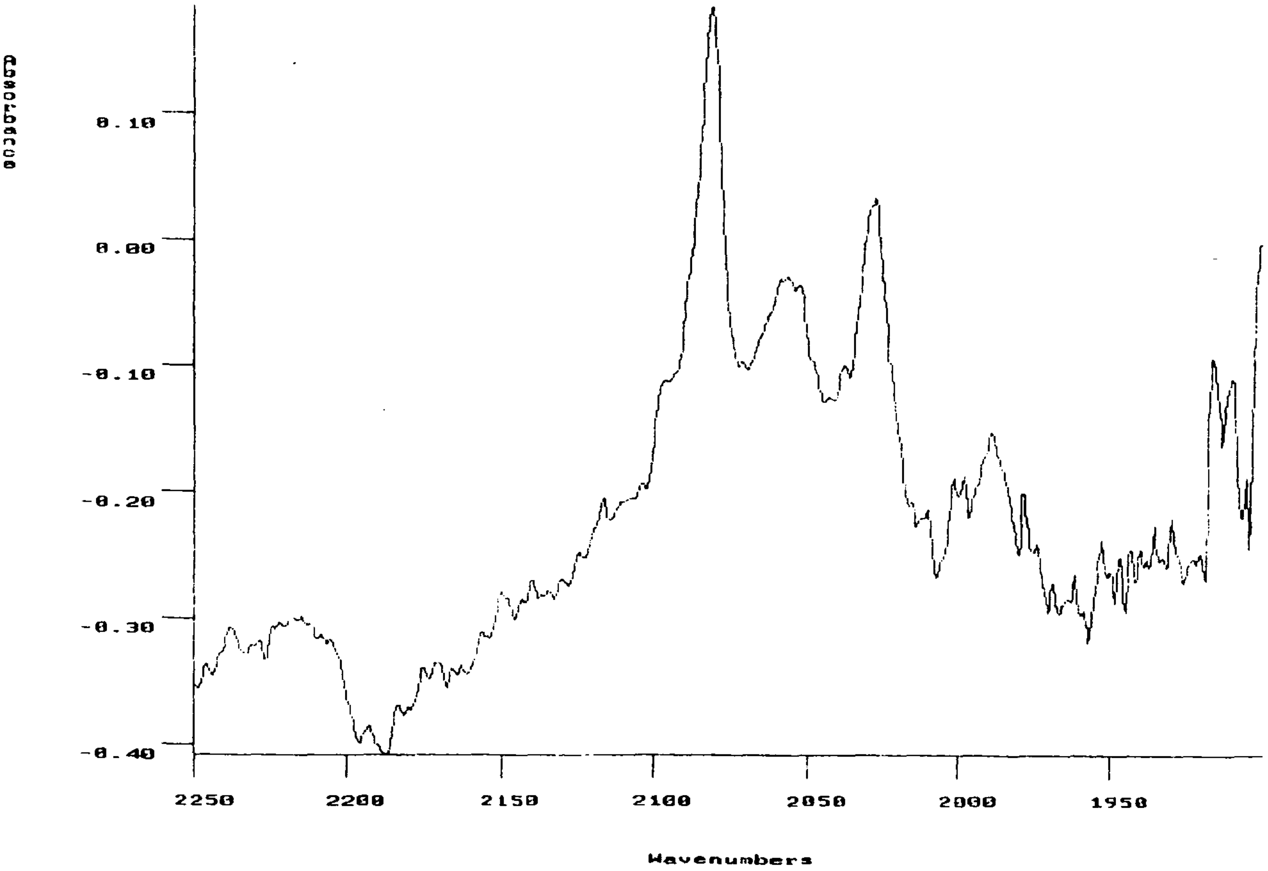
$$2HI + CO + H_2O \longrightarrow CO_2 + 2H^+ + 2I^- + H_2$$

$$\text{i.e} \quad CO + H_2O \longrightarrow CO_2 + H_2$$

Figure 2.12



a, Propanoic Acid.



b, Propanoic Acid / Dichloromethane 5:12 v/v

Reaction 2.5.1A	**Species Observed**
$RhCl_3.3H_2O$	$Rh(CO)Cl_3$
EtI	$[Rh_2(CO)_2I_4]^{2-}$
$C_2H_5CO_2H/CH_2Cl_2$	$[Rh(CO)_2I_4]^-$
CO	$[Rh_2(CO)_4I_2]$

The early complex formation of trichlorocarbonylrhodate(III) is rapidly superseded by the appearance of both $[Rh_2(CO)_2I_4]^{2-}$ and $[Rh(CO)_2I_4]^-$ at approximately 100°C. However once this reaction reaches 110 - 140°C the dimer $[Rh_2(CO)_4I_2]$ slowly becomes dominant. It would be expected that in the presence of ethyliodide there would be the opportunity for the dimer to react with iodide to form rhodiumdicarbonydiiodide anion $[Rh(CO)_2I_2]^-$. This phenomenon has already been observed when hydrogen iodide was used as initiator in reactions in dichloromethane. It is possible that this is indicative that the behaviour of this solvent system is more matched with dichloromethane than propanoic acid.

Reaction 2.5.1B	**Species Observed**
$RhCl_3.3H_2O$	$Rh(CO)Cl_3$
EtI	$[Rh(CO)_2I_4]^-$
$C_2H_5CO_2H/CH_2Cl_2$	$[Rh_2(CO)_2I_4]^{2-}$
CO/C_2H_4	$[Rh_2(CO)_4I_2]$
	$[Rh(CO)_2I_2]^-$

In section 2.4.3 the addition of ethene to a system resulted in the observation of only one species, that being pentaiododicarbonylrhodate(III) dianion $[Rh(CO)I_5]^{2-}$. In this case a sequence of species are seen. It is possible that this is again due to the presence of dichloromethane.

In this reaction, the formation of the rhodium(III) and rhodium(I) species $[Rh(CO)_2I_4]^-$ and $[Rh_2(CO)_2I_4]^{2-}$ occurs at approximately 140°C. These species do not decrease as the temperature is increased. The absorbance band at 2085 cm^{-1} (assigned to $[Rh(CO)_2I_4]^-$ appears to migrate to 2082 cm^{-1}. This coincides with the appearance of an absorbance band at 2028 cm^{-1}. Therefore the band at 2082 cm^{-1} is interpreted to be a combination of the bands associated with $[Rh(CO)_2I_4]^-$ and $[Rh_2(CO)_4I_2]$ at 2085 cm^{-1} and 2080 cm^{-1} respectively. At 150°C there is also the occurrence of very weak bands at 1990 cm^{-1} and in the region 2040 - 2060 cm^{-1}. The latter band tends to be obscured by the band associated with $[Rh_2(CO)_2I_4]$. It is surprising that there is no observation of $[Rh(CO)I_5]^{2-}$ in this reaction. The absorbance bands for this complex are also in the region of 2040 - 2050 cm^{-1}. It is possible that it is present in small amounts but unobservable. At 160°C the band at 2059 cm^{-1} is lost, indicating the reaction of $[Rh_2(CO)_2I_4]^{2-}$ although it is not apparent what is formed.

2.5.2 Reactions of anhydrous rhodium(III) iodide

Almost all of the reactions reported thus far have employed chloro- compounds as the rhodium source. Observation of chloro and chloroiodo complexes may be eliminated by the use of anhydrous rhodium(III) iodide.

Reaction 2.5.2	***Species Observed***
RhI_3	$[Rh(CO)_2I_4]^-$
EtI	$[Rh_2(CO)_2I_4]^{2-}$
$C_2H_5CO_2H/CH_2Cl_2$	$[Rh_2(CO)_4I_2]$
CO	$[Rh(CO)_2I_2]^-$

With this system the compounds observed are similar to those of the previous reactions in 2.5.1. It is interesting to note that the complex $[Rh(CO)_2I_2]^-$ is observed in this reaction but not in reaction 2.5.1A. It is possible that this is an effect caused by halide composition, but is more likely due to $[Rh(CO)_2I_2]^-$ being present but unobserved in reaction 2.5.1A.

To complete this series of reaction, rhodium(III) iodide was reacted with a mixture of carbon monoxide and ethene, but no absorbance bands were observed in the carbonyl frequency region of the infra-red spectrum. No valid explanation can be offered except that the rhodium(III) iodide was not taken into solution.

2.5.3 Summary

The use of this mixed solvent system was successful and has provided, to an extent improved spectral resolution. It has however produced some data that indicate that reaction pathways are modified by the presence of dichloromethane. This is shown by the observation of both tetraiododicarbonydirhodate(III) dianion $[Rh_2(CO)_2I_4]^{2-}$ and diiodotetracarbonyldirhodate(I) $[Rh_2(CO)_4I_2]$. Reaction 2.5.1B shows that ethene does not prevent the formation of the rhodium-carbonylhalides present in previous reactions. On the other hand reaction 2.5.2B gives no data at all. There is obviously a problem with this type of reaction utilising ethene. The problem may lie with the method of gas introduction or gas mixing. As far as the methods of monitoring that were available could discern, these gas manipulations were the same for all reactions.

In terms of chemistry we have seen an expansion of the two interconversions discussed in section 2.4.1 (see Figure 9). The absence of pentaiodocarbonylrhodate(III) dianion $[Rh(CO)I_5]^{2-}$ is probably due to the more covalent nature of the solvent system. This complex may be formed in these reactions, but immediately precipitated from solution. The other species would appear to be interconverting with each other (see Figure 13). It is noticeable that we have an initial increase in $[Rh(CO)_2I_4]^-$. After approximately 180 minutes the rhodium(I) species, $[Rh_2(CO)_2I_4]^{2-}$ and $[Rh_2(CO)_4I_2]$, both occur. There is a corresponding decrease in the absorbance bands of $[Rh(CO)_2I_4]^-$ during their formation but after 200 minutes the concentration of all three species rises to maxima and are then gradually lost from the spectra. This loss is accompanied by the appearance of $[Rh(CO)I_5]^{2-}$. These changes suggest the rhodium complexes may interconvert under equilibria above 140°C but then decompose to give the final rhodium(III) complex, $[Rh(CO)I_5]^{2-}$ and possibly rhodium(III) iodide.

2.6 Hydrous Reaction Systems

Having established the species observed in various solvents and conditions, employing different iodide sources available, it is now appropriate to consider the effects of water in the hydrocarbonylation reaction. In forming propanoic acid it is one of the reactants (equation 20) though this role may be undertaken by propanoic acid to produce propanoic anhydride (equation 21). Furthermore water may solvate rhodium species resulting in a higher catalyst concentration. As has been noted (section 2.4.4, Figure 11), it also acts in the Water Gas Shift cycle to reduce rhodium(III) to rhodium(I).

The first of these roles is well documented and has been studied in terms of product distributed between the parent acid and its anhydride (see Chapter 3).

$$C_2H_4 + CO + H_2O \longrightarrow CH_3CH_2CO_2H \qquad \textit{Equation 20}$$

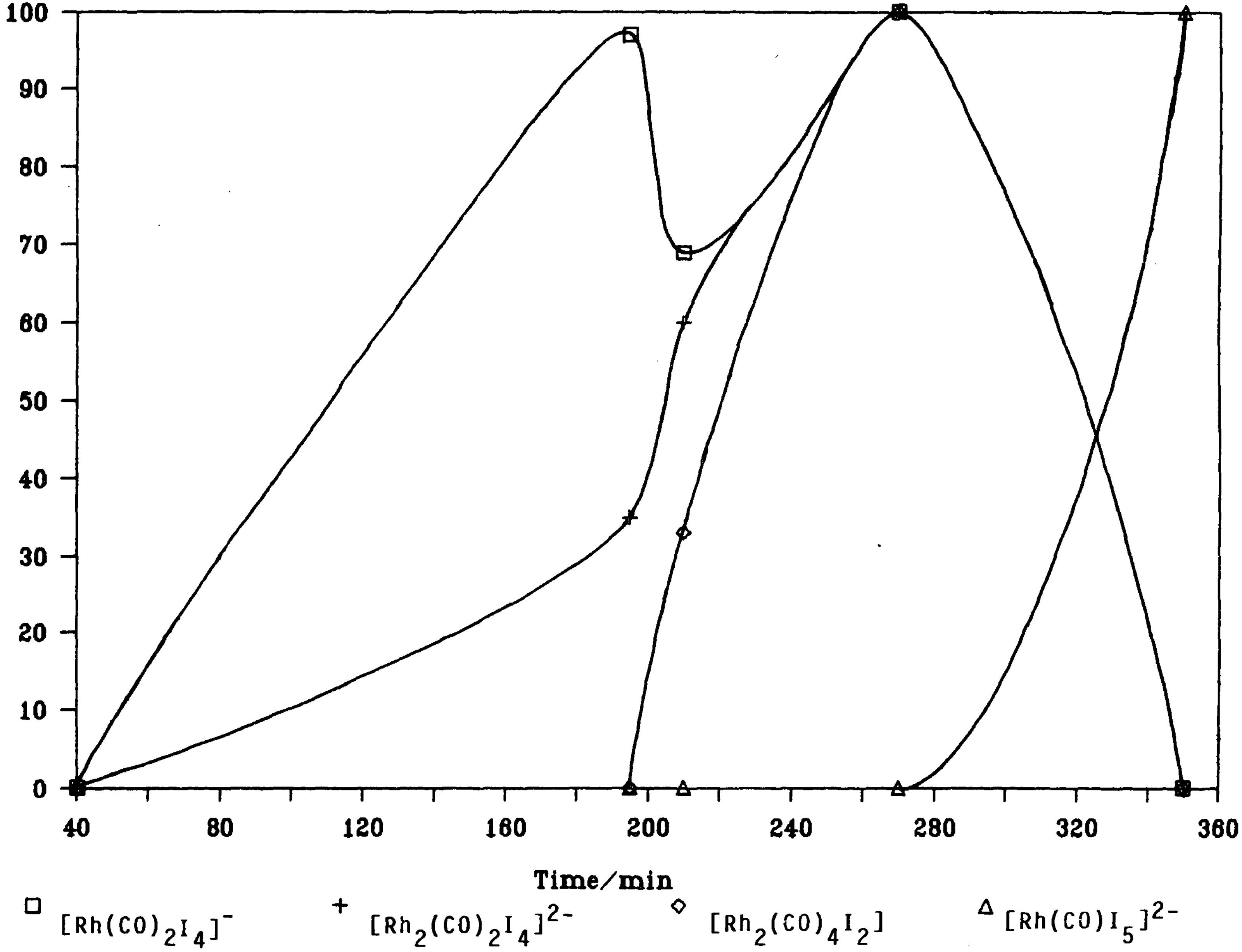
$$C_2H_4 + CO + CH_3CH_2CO_2H \longrightarrow (CH_3CH_2CO)_2O \qquad \textit{Equation 21}$$

The second role might be inferred from a general increase in infra-red absorbance for all species indicating the higher degree of solvation of rhodium species. If the Water Gas Shift reaction occurs then an increase in the proportion of $[Rh(CO)_2I_2]^-$ at the expense of $[Rh(CO)_2I_4]^-$ may be observed (see equation 22) although $[Rh(CO)_2I_4]^-$ is still likely to be present (see equation 23).

$$[Rh(CO)_2I_4]^- + H_2O \longrightarrow [Rh(CO)_2I_2]^- + 2HI + CO_2 \qquad \textit{Equation 22}$$

$$[Rh(CO)_2I_2]^- + 2HI \longrightarrow [Rh(CO)_2I_4]^- + H_2 \qquad \textit{Equation 23}$$

Figure 2.13


100
90
80
70
60
50
40
30
20
10
0
40
80
120
160
200
240
280
320
360
Time/min
□ $[Rh(CO)_2I_4]^-$
+ $[Rh_2(CO)_2I_4]^{2-}$
◇ $[Rh_2(CO)_4I_2]$
△ $[Rh(CO)I_5]^{2-}$

2.6.1 Hydrous systems excluding propanoic acid

The effect of water on reactions undertaken in dichloromethane should be to induce more polar solvent behaviour than has been demonstrated previously. While studying this solvent system, tetrahydrofuran was also studied as a water miscible solvent.

Reaction 2.6.1A	**Species Observed**
RhI_3	$[Rh(CO)_2I_4]^-(ms)$
EtI	$[Rh_2(CO)_2I_4]^{2-}(m)$
H_2O	$[Rh_2(CO)_4I_2](m)$
CH_2Cl_2	
CO/CH_2CH_2	

Although this reaction gave better spectra than observed in anhydrous dichloromethane, the species formed were unstable at 180°C and the infra-red absorptions were rapidly lost at this temperature.

Reaction 2.6.1B	**Species Observed**
$RhCl_3.3H_2O$	$[Rh(CO)_2Cl_2]^-(m)$
EtI	$[Rh(CO)_2I_2]^-(s)$
H_2O	$[Rh(CO)_2I_4](ms)$
THF	
CO/CH_2CH_2	

This reaction produced the rhodium(I) species at 180°C and the rhodium(III) species was only observed on cooling to room temperature when a small amount of rhodium(III) compound became evident. Initially this appeared to be a system worth considerable investigation. A gas liquid chromatograph of the final solution after reaction showed the presence of many components. It would appear that the tetrahydrofuran is hydrolysed to give alcohols and iodobutyl- compounds; the alcohols present returning the system to the "Monsanto" process conditions.

Given these observations, the mixed solvent system investigated in section 2.5 was again used for further studies into hydrous systems.

2.6.2 Hydrous systems employing propanoic acid

These reactions show the effects of adding water to the systems reported in section 2.5. Initially rhodium(III) iodide and iodoethane were employed.

Reaction 2.6.2A	***Species Observed***
RhI_3	$[Rh(CO)_2I_4]^-$(m)
EtI	$[Rh(CO)_2I_2]^-$(w)
H_2O	$[Rh_2(CO)_2I_4]^{2-}$(vw)
$CH_2Cl_2/CH_3CH_2CO_2H$	
CO	

This reaction was undertaken on six separate occasions. In the first instant only the first two listed compounds were observed. Spectra were poor and a second reaction was undertaken. This second reaction revealed a weak peak at 1980 cm^{-1}. To investigate this apparent anomaly between the two sets of data, the reaction was undertaken a third time; on this occasion a very strong absorbance band was formed at 1980 cm^{-1}(vs). It had an associate absorbance band at 2091 cm^{-1}(w). On cooling to room temperature the strong band remained, the weak band was lost and another weak band was formed at 2003 cm^{-1}. These two bands, 2003 cm^{-1}, 1985 cm^{-1} remained even at one atmosphere of carbon monoxide. A summary of these changes is provided by Figure 2.14. In an attempt to repeat this latter result and isolate the complex associated with these absorption bands, three further identical reactions were conducted; however in all three only a weak band was observed at 1980 cm^{-1} as in the second repetition of this reaction system.

Figure 2.14

Conditions	**Spectral Observations**
From 25°C to 170°C 40 bar CO	$[Rh(CO)_2I_4]^-$(ms) $[Rh(CO)_2I_2]^-$(mw)
At 180°C 40 bar CO	1980 cm^{-1}(vs) 2091 cm^{-1}(w)
On cooling to 25°C Pressure released to 1 Atm CO	1980 cm^{-1}(vs) 2003 cm^{-1}(w)

While it has not been possible to reproduce the reaction environment to generate large amounts of the unidentified species, in five of the six cases it has been observed, and can be considered of major importance for the hydrocarbonylation reaction.

It is possible that this unknown species is a hydrido-rhodium- compound. It was therefore considered relevant to study the effect of ethene on this reaction system.

Reaction 2.6.2B	*Species Observed*
RhI_3	$[Rh(CO)_2I_4]^-$*(w)*
EtI	$[Rh(CO)_2I_2]^-$*(w)*
H_2O	*1980* cm^{-1}*(w) unidentified*
$CH_2Cl_2/C_2H_5CO_2H$	
CO/C_2H_4	

This reaction produced spectra relating closely to that of reaction 2.6.2. Again the band at 1980 cm^{-1} was not strong. It was present in amounts corresponding to those observed in the majority of the 2.6.2A reactions, thus ethene appears not to affect the complex associated with the absorbance band at 1980 cm^{-1}. Thus it is unlikely that this complex is a hydrido-rhodium species.

Reaction 2.6.2C	**Species Observed**
$RhCl_3.3H_2O$	$Rh(CO)Cl_3(ms)$
HI	$[Rh(CO)_2I_4]^-(ms)$
H_2O	$[Rh(CO)_2I_2]^-(w)$
$C_2H_5CO_2H/CH_2Cl_2$	$[Rh_2(CO)_2I_4]^{2-}(m)$
CO/C_2H_4	$[Rh(CO)I_5]^-(mw)$
	$[Rh_2(CO)_4I_2](ms)$

This reaction produces the full range of expected species with no particular species dominating the reaction system. The presence of pentaiododicarbonylrhodate(III) dianion $[Rh(CO)I_5]^-$ suggests a loss of rhodium from solution possibly to rhodium(III) iodide. The appearance of diiodotetracarbonyldirhodate(I) may indicate that there is little free iodide in the system, again raising the possibility of an iodide "sink", possibly iodine. If this is the case then a reaction employing iodine as an initiator should show similar characteristics to the reaction employing hydrogen iodide.

Reaction 2.6.2D	**Species Observed**
$RhCl_3.3H_2O$	$[Rh(CO)_2I_4]^-(s)$
H_2O	$[Rh_2(CO)_2I_4]^{2-}(ms)$
I_2	$[Rh(CO)_2I_2]^-(mw)$
$CH_2Cl_2/CH_3CH_2CO_2H$	
CO	

All three complexes were observed when the temperature reached 150°C. On raising the temperature to 180°C there is a decrease in all bands except those related to $[Rh(CO)_2I_2]^-$.

In considering this reaction it is still possible to suggest that the iodine acts as a "sink" for iodide. The formation of two rhodium(I) compounds, despite the presence of iodine, shows that the oxidation by iodine does not necessarily proceed under these conditions. In this mixed solvent system there are three rhodium-iodide anionic complexes formed, in marked contrast to when iodine was used in dichloromethane solvent, as reported earlier in this chapter.

At this stage it was considered appropriate to study a reaction system employing the diiododicarbonylrhodate(I) anion as the rhodium and iodide source.

Reaction 2.6.2E	***Species Observed***
$[Bu_4N]^+[Rh(CO)_2I_2]^-$ H_2O $CH_2Cl_2/C_2H_5CO_2H$ CO	$[Rh(CO)_2I_4]^-$*(ms)* $[Rh_2(CO)_2I_4]^{2-}$*(m)*

In the reaction the starting complex was never observed even at 25°C. It would appear that it converts very rapidly to the rhodium(I) dimer and the rhodium(III) species under these conditions.

2.6.3 Effect of propanoate anion on hydrocarbonylation reaction

It is proposed that the addition of hydrogen iodide to diiododicarbonylrhodate(I) anion forms a hydrido-rhodium complex which may react with ethene or another iodide moiety; in the first case to undergo the hydrocarbonylation reaction, in the second case to form $[Rh(CO)_2I_4]^-$. If this is the case then we may expect the addition of a lithium propanoate to inhibit both reactions by reducing the active concentration of hydrogen iodide present. To quantify the effect of lithium cations on the reaction system a control experiment was conducted utilising lithium chloride.

Reaction 2.6.3A	***Species Observed***
$RhCl_3.3H_2O$	$[Rh(CO)_2I_4]^-$*(m)*
$LiCl$	$[Rh(CO)I_5]^{2-}$*(w)*
H_2O	
EtI	
$CH_2Cl_2/C_2H_5CO_2H$	
CO	

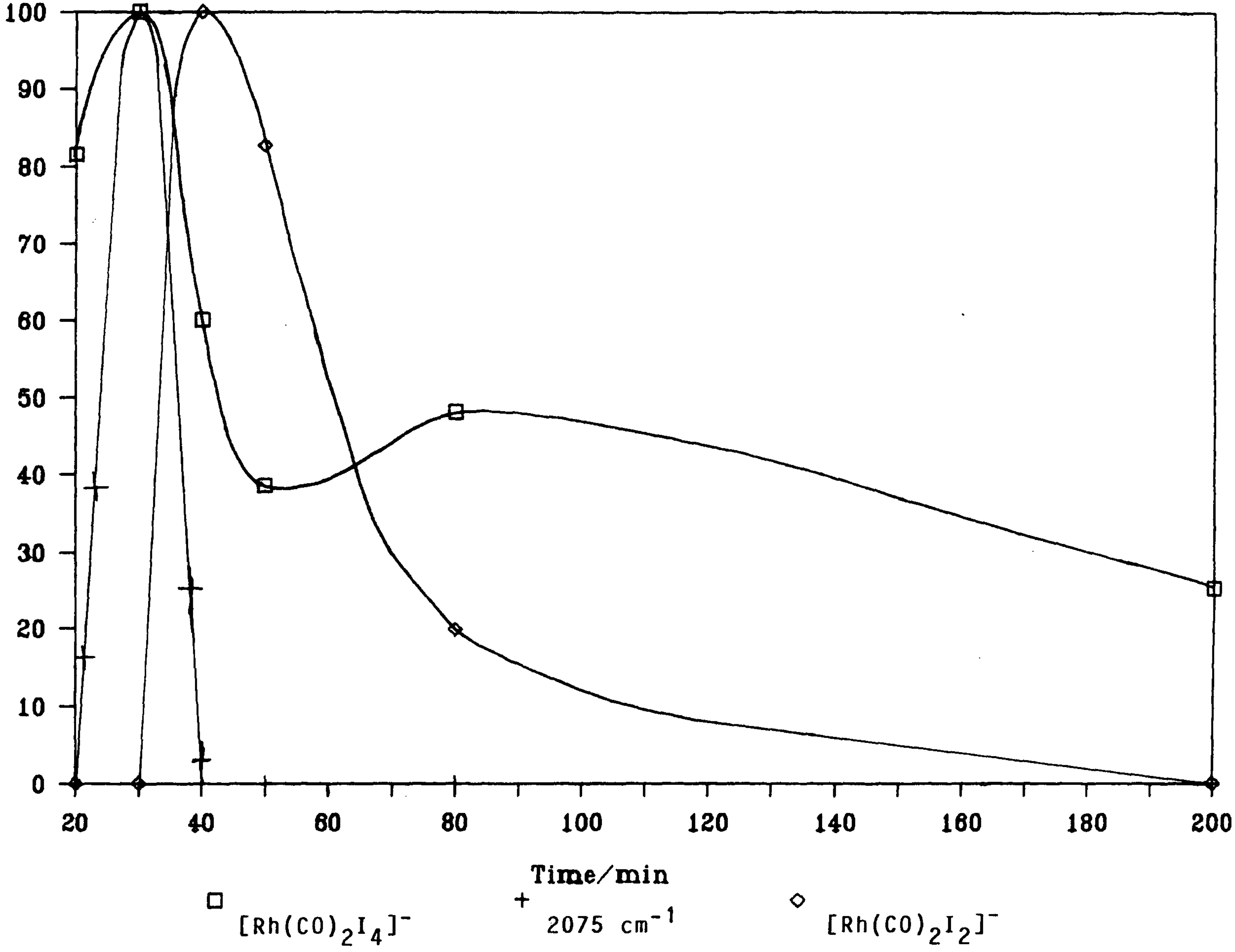
At 70°C both complexes indicated above were observed, at 125°C only $[Rh(CO)_2I_4]^-$ remained in the spectrum and at 180°C all absorbance bands were lost. It is possible that the rhodium species are being precipitated with lithium cations. The lithium propanoate reaction was then conducted to investigate the effect of propanoate anions on the reaction system.

Reaction 2.6.3B	***Species Observed***
$RhCl_3.3H_2O$	*$[Rh(CO)_2I_4]^-$(m)*
$LiO_2CC_2H_5$	*2075 cm^{-1}(s) unidentified*
H_2O	*$[Rh(CO)_2I_2]^-$(vs)*
EtI	*1983 cm^{-1}(s) unidentified*
$CH_2Cl_2/C_2H_5CO_2H$	*2091 cm^{-1}(s) unidentified*
CO	

The tetraiododicarbonylrhodate(III) anion is first observed at 60°C, but its absorbance bands are rapidly overshadowed by the unknown band at 2075 cm^{-1} when the temperature reaches 130°C. This latter band is in turn lost at 180°C when very strong absorbance bands are observed for diiododicarbonylrhodate(I) anion $[Rh(CO)_2I_2]^-$. At this time (40 - 50 minutes, see Figure 2.15) there is a complementary decrease in the absorbances of $[Rh(CO)_2I_4]^-$. As the reaction proceeds, this rhodium(III) species continues to decrease but not as rapidly as diiododicarbonylrhodate(I) anion $[Rh(CO)_2I_2]^-$. The absorbance bands for $[Rh(CO)_2I_2]^-$ in this reaction are surprisingly strong and in no other reaction, except when alcohol solvents are used, are they seen to dominate the $[Rh(CO)_2I_4]^-$ absorbance band at any point in the reaction. Therefore the presence of the propanoate anion would appear to inhibit the conversion of $[Rh(CO)_2I_4]^-$ from $[Rh(CO)_2I_2]^-$.

It is therefore likely that the conversion involves a hydrogen moiety removed from reaction by the mechanism of equation 24, wherein HB is an active moiety for the conversion and B is a Lewis base.

Figure 2.15


100
90
80
70
60
50
40
30
20
10
0
20
40
60
80
100
120
140
160
180
200
Time/min
□ $[Rh(CO)_2I_4]^-$
+ 2075 cm^{-1}
◇ $[Rh(CO)_2I_2]^-$

$$HB^{+} + CH_3CH_2CO_2^{-} \longrightarrow B + CH_3CH_2CO_2H \qquad \textit{Equation 24}$$

This of course does not exclude the possibility of a proton H^{+} being the active moiety.

When reaction 2.6.3B is cooled to 25°C after reaction two very strong absorbance bands are observed. An absorbance band at 1983 cm^{-1}, as observed in reaction 2.6.2A, is on this occasion accompanied by a very strong band at 2091 cm^{-1}. The change in relative intensities demonstrates that the two absorptions are not related to the same complex. Both complexes are likely to contain propanoate ligands.

2.7 Discussion and Conclusions

When considering the observations reported in this chapter, a clear distinction should be made between data collected during the heating process and that observed at 180°C.

It is possible to distinguish the path of formation of rhodium-carbonyl-chloride complexes from the initial reaction systems. Trichlorocarbonylrhodate(III) is formed and then reduced to dichlorotetracarbonyldirhodate(I). Under carbon monoxide pressure further carbonylation occurs to form chlorotricarbonylrhodate(I).

The route of formation for the rhodium-carbonyl-iodide complexes is much more difficult to distinguish. For many systems the tetraiododicarbonylrhodate(III) anion is the species observed first. This species is often accompanied by tetraiododicarbonyldirhodate(I) dianion, but not on all occasions. The diiododicarbonylrhodate(I) anion is only observed after the reactions reach 170°C, except in alcohol solvents. Pentaiodocarbonylrhodate(III) dianion tends to be formed toward the latter stages of reactions.

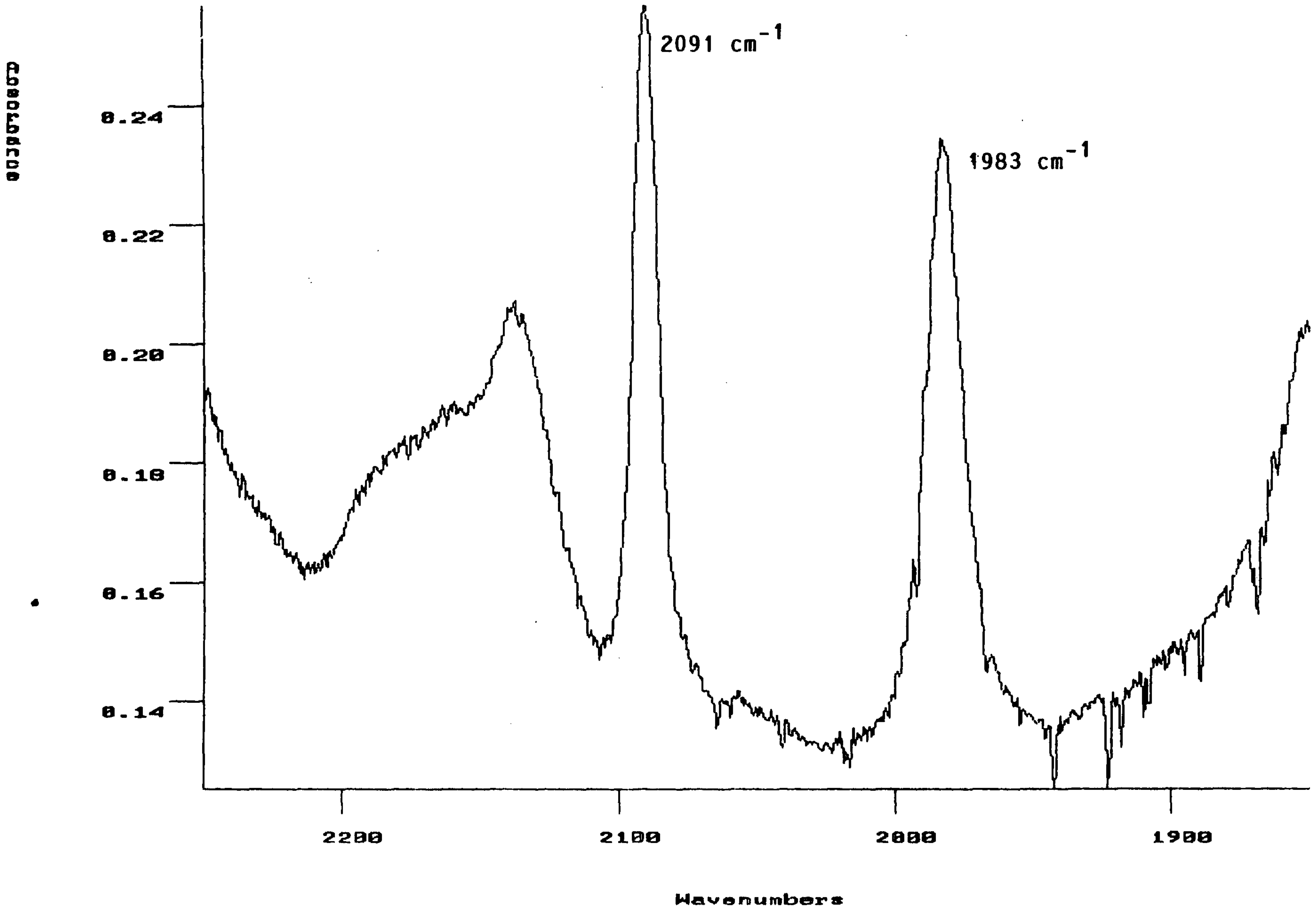
When considering solvents we should be aware that propanoic (or acetic) acid gives high rates of reaction compared with dichloromethane. The addition of water accelerates the rate of reaction in both solvents (see Chapter 3). While dichloromethane is a non-polar solvent, when it is mixed with propanoic acid it is the polar nature of the acid that is dominant. In general the presence of propanoic acid is required to produce spectra of $[Rh(CO)_2I_2]^-$, although water increases this effect (see reaction 2.6.2D).

Many known complexes have been observed including those mentioned above but many unattributed absorptions have also been observed. In reactions 2.2.2C and 2.4.2, two absorbance bands observed in the regions 2080 - 2075 cm^{-1} and 2003 - 2010 cm^{-1} are attributed to the ion- pair, $[A^+....Rh(CO)_2I_2^-]$, (where A^+ is an appropriate cation, possibly H^+) following the work of A. Fulford et al$^{(14)}$. Interestingly these absorptions are not observed in any hydrous system probably due to solvation of the cationic species by water.

An unknown absorbance band is observed at 2117 cm^{-1} in the reaction involving RhI_3 and I_2 in dichloromethane and is hence shown to be a rhodium-carbonyl-iodide complex (reaction 2.2.4C). It is unlikely to be ionic under these conditions, and may speculatively be considered as $[Rh(CO)_2I_3]$. Given this assumption, that the above species is formed, then addition of an iodide anion would give $[Rh(CO)_2I_4]^-$ and would explain why this latter species is observed first in many reactions. The absorbance band at 2157 cm^{-1} is a shoulder on the band for absorbed carbon monoxide. It may be associated with a hydrido- species but there is no consistent data for this species. On many occasions it may be obscured by the carbon monoxide band. There are also the two bands at 2091 cm^{-1} and 1983 cm^{-1} for reactions for rhodium(III) iodide in hydrous dichloromethane/propanoic acid (reactions 2.6.2A and 2.6.2B). The former band has only been observed in strength at 25°C in reaction 2.6.3B when propanoate anion was added. It was seen to a smaller extent in reaction 2.6.2A. The absorbance band at 1983 cm^{-1} has been seen in strength at the reaction temperature 180°C, and occurs both in the presence and absence of ethene. It is possible therefore that this latter species is of importance to the hydrocarbonylation reaction. To attempt to distinguish the compounds responsible for these bands would, with the data available, be purely speculative.

It has not been possible in these reactions to detect the intermediates we proposed for the catalytic cycle (see Figure 2.1). Much information has been obtained, however, on the chemistry of tetraiododicarbonylrhodate(III) anion $[Rh(CO)_2I_4]^-$ and diiodocarbonylrhodate(I) anion $[Rh(CO)_2I_2]^-$ in these systems, the mechanistic implications of which will be discussed further in Chapter 3.

Figure 2.16 : Reaction 2.6.3b



2.8 Chapter 2 - Reaction Index

Reaction Number	Reactants/Moles	Solvents	Temperature Range/°C	Pressure/ bar	Gases	Species Identified	Reaction Code
2.2.1A	$RhCl_33H_2O$, 6.35 x 10^{-4}	C_2H_5COOH	20 - 100	27 - 35	CO	$Rh(CO)Cl_3$ $Rh_2(CO)_4Cl_2$ $Rh(CO)_3Cl$	RhClPAc_1
2.2.1B	$Rh_2(CO)_4CL_2$, 2.38 x 10^{-4}	C_2H_5COOH	20 - 175	1 - 41	CO	$Rh(CO)_3Cl$	RhClCO_2
2.2.1C	$Rh_2(CO)_4Cl_2$, 3.45 x 10^{-4}	CH_2Cl_2	20 - 160	1 - 37	CO	$Rh_2(CO)_4CL_2$ $Rh(CO)_3Cl$	RhHaD_1
2.2.1D	$RhCl_3.3H_2O$, 1.92 x 10^{-4}	Ch_2Cl_2	20 - 150	28 - 66	CO	$Rh(CO)Cl_3$ $Rh_2(CO)_4Cl_2$ $Rh(CO)_3Cl$	RhICO_54
2.2.2A	$RhCl_3.3H_2O$, 2.03 x 10^{-4} $(C_4H_9)_4NI$, 1.38 x 10^{-3}	C_2H_5COOH	20 - 180	1 - 49	CO	$[Rh(CO)_2I_4]^-$ $[Rh(CO)I_5]^{2-}$	RhICO_48
2.2.2B	$RhCl_3.3H_2O$, 1.92 x 10^{-4} $(C_4H_9)_4NI$, 1.31 x 10^{-3}	CH_2Cl_2	20 - 180	1 - 56	CO	$Rh(CO)_3Cl$ $[Rh_2(CO)_2I_4]^{2-}$ $[Rh(CO)_2I_4]^-$	RhICO_51
2.2.2C	$Rh_2(CO)_4Cl_2$, 2.7 x 10^{-4} $(C_4H_9)_4NI$, 1.60 x 10^{-3}	CH_2Cl_2	20 - 180	1 - 91	CO	$[Rh(CO)_2I_2]^-$	RhClCO_8
2.2.2D	$RhCl_3.3H_2O$, 1.8 x 10^{-4} $(C_4H_9)_4NI$, 1.2 x 10^{-3}	CH_2Cl_2	20 - 180	20 - 62	C_2H_4	$[Rh_2(CO)_4]$ $[Rh(CO)_3Cl]$	RhICO_53
2.2.3A	$Rh_2(CO)_4Cl_2$, 3.2 x 10^{-4}	C_2H_5COOH	20 - 140	30 - 65	C_2H_4	$[Rh_2(CO)_n(C_2H_4)_{4-n}Cl_2]$ n = 1 to 4	RhClCO 4/5
2.2.3B	$Rh_2(CO)_4Cl_2$, 3.2 x 10^{-4}	C_2H_5COOH	20 - 120	1 - 120	CO, C_2H_4	$[Rh_2(CO)_4Cl_2]$ $[Rh(CO)_3Cl]$	RhClCO_6

2.8 Chapter 2 - Reaction Index (cont)

Reaction Number	Reactants/Moles		Solvents	Temperature Range/°C	Pressure/ bar	Gases	Species Identified	Reaction Code
2.2.4A	$RhCl_33H_2O$, I_2,	4.6×10^{-4} 1.2×10	Ch_2Cl_2	20 - 180	27 - 50	CO	$Rh(CO)Cl_3$ $Rh(CO)_3Cl$	RhICO_18
2.2.4B	$RhCl_3.3H_2O$, I_2,	1.8×10^{-4} 4.3×10^{-3}	$C_2H_5CO_2H$	20 - 180	13 - 40	CO	$[Rh_2(CO)_4I_2]$ $[Rh(CO)_2I_4]^-$ $[Rh(CO)_2I_2]^-$	RhICO_45
2.2.4C	RhI_3, I_2,	1.2×10^{-4} 1.1×10^{-3}	CH_2Cl_2	20 - 150	40 - 57	CO	-	RhICO_59
2.2.5A	$RhCl_3.3H_2O$, EtI,	4.8×10^{-4} 2.49 xx 10^{-1}	EtI	20 - 180	14 - 28	CO	$Rh(CO)Cl_3$ $[Rh_2(CO)_4I_2]$ $[Rh_2(CO)_2I_4]^{2-}$ $[Rh(CO)_2I_4]^-$	RhICO_20
2.2.5B	$RhCl_3.3H_2O$, HI, EtI,	4.2×10^{-4} 2.0×10^{-3} 2.61×10^{-2}	EtOH	20 - 160	14 - 26	CO	$[Rh(CO)_2I_2$	RhICO_24
2.2.5C	$RhCl_3.3H_2O$, HI,	4.55×10^{-4} 1.72×10^{-3}	EtOH	20 - 160	7 - 20	CO	$[Rh(CO)_2I_4^-$ $[Rh(CO)_2I_2]^-$	RhICO_25
2.3.1A	$RhCl_3.3H_2O$, EtI,	4.33×10^{-4} 1.24×10^{-2}	CH_2Cl_2	20 - 180	42 - 72	CO	$Rh(CO)Cl_3$ $Rh_2(CO)_4Cl_2$ $[Rh(CO)_2I_4]^-$ $[Rh_2(CO)_2I_4]^{2-}$ $[Rh_2(CO)_4I_2]$ $[Rh(CO)_2I_2]^-$	RhICO_4 RhICO_9

2.8 Chapter 2 - Reaction Index (cont)

Reaction Number	Reactants/Moles		Solvents	Temperature Range/℃	Pressure/ bar	Gases	Species Identified	Reaction Code
2.3.1B	$RhCl_3.3H_2O$, EtI,	4.65×10^{-4} 1.24×10^{-2}	CH_2Cl_2	20 - 170	56 - 84	CO C_2H_4	$Rh(CO)Cl_3$ $[Rh_2(CO)_4Cl_2]$ $Rh(CO)_3Cl$ $[Rh(CO)_2I_4]^-$ $[Rh_2(CO)_4I_2]$ $[Rh_2(CO)_2I_4]^{2-}$ $[Rh(CO)_2I_2]^-$	RhICO_8
2.3.2A	$RhCl_3.3H_2O$, HI,	4.29×10^{-4} 7.82×10^{-4}	CH_2Cl_2	20 - 180	28 - 38	CO	$Rh(CO)Cl_3$ $[Rh(CO)I_2]^-$ $[Rh(CO)_2I_4]^{2-}$ $[Rh(CO)_4I_2]$ $[Rh(CO)_2I_4]^-$	RhICO_16
2.3.2B	$RhCl_3.3H_2O$, HI,	2.02×10^{-4} 3.91×10^{-3}	CH_2Cl_2	20 - 180	37 - 65	CO C_2 $_{H}4$	$Rh(CO)Cl_3$ $[Rh(CO)_2I_4]^-$ $[Rh(CO)I_5]^{2-}$	RhICO_50
2.4.1A	$RhCl_3.3H_2O$, EtI,	1.81×10^{-4} 1.24×10^{-2}	C_2H_5COOH	20 - 180	43 - 54	CO	$[Rh(CO)_2I_2]^-$ $[Rh(CO)_2I_4]^-$ $[Rh(CO)I_5]^{2-}$	RhICO_58
2.4.1B	$Rh_2(CO)_4Cl_2$, EtI,	2.59×10^{-3} 1.24×10^{-2}	C_2H_5COOH	20 - 160	1 - 42	CO	$[Rh(CO)_2I_4]^-$	RhHaAc_5
2.4.2	$RhCl_3.3H_2O$, HI,	2.02×10^{-4} 1.72×10^{-3}	C_2H_5COOH	20 - 180	44 - 69	CO	$[A^+...Rh(CO)_2I_2]^-$ $[Rh_2(CO)_2I_4]^{2-}$ $[Rh(CO)I_5]^{2-}$	RhICO_56

2.8 Chapter 2 - Reaction Index (cont)

Reaction Number	Reactants/Moles		Solvents	Temperature Range/°C	Pressure/ bar	Gases	Species Identified	Reaction Code
2.4.3A	$RhCl_3.3H_2O$, EtI,	1.97×10^{-4} 1.24×10^{-2}	C_2H_5COOH	20 - 180	67 - 107	CO C_2H_4	$[Rh(CO)I_5]^-$	RhICO_57
2.4.3B	$Rh_2(CO)_4Cl_2$, EtI,	1.87×10^{-4} 1.24×10^{-2}	C_2H_5COOH	20 - 160	42 - 90	CO C_2H_4	$Rh(CO)_3Cl$ $[Rh(CO)_2I_4]^-$ $[Rh(CO)_2I_2]^-$ $[Rh_2(CO)_4I_2]$	RhICO_34
2.5.1B	$RhCl_3.3H_2O$, EtI,	4.47×10^{-4} 1.24×10^{-2}	$C_2H_5CO_2H$ CH_2Cl_2	20 - 160	34 - 55	CO C_2H_4	$Rh(CO)Cl_3$ $[Rh(CO)_2I_4]^-$ $[Rh_2(CO)_2I_4]^{2-}$ $[Rh_2(CO)_4I_2]$ $[Rh(CO)_2I_2]^-$	RhICO_15
2.5.2	RhI_3, EtI,	1.24×10^{-4} 1.24×10^{-2}	C_2H_5COOH CH_2Cl_2	20 - 170	26 - 41	CO	$[Rh(CO)_2I_4]^-$ $[Rh_2(CO)_2I_4]^{2-}$ $[Rh_2(CO)_4I_2]$ $[Rh(CO)_2I_2]^-$	RhICO_34
2.6.1A	$RhCl_3.3H_2O$, EtI, H_2O,	5.50×10^{-4} 1.24×10^{-2} 5.55×10^{-2}	CH_2Cl_2	20 - 180	25 - 52	CO C_2H_4	$[Rh(CO)_2I_4]^-$ $[Rh_2(CO)_2I_4]^{2-}$ $[Rh_2(CO)_4I_2]$	RhICO_29
2.6.1B	$RhCl_3.3H_2O$, EtI, H_2O,	4.63×10^{-4} 1.24×10^{-2} 5.55×10^{-2}	T.H.F.	20 - 180	20 - 55	CO C_2H_4	$[Rh(CO)_2Cl_2]^-$ $[Rh(CO)_2I_2]^-$ $[Rh(CO)_2I_4]^-$	RhICO_27
2.6.2A	RhI_3, EtI, H_2O,	1.24×10^{-4} 1.24×10^{-2} 2.77×10^{-2}	C_2H_5COOH CH_2Cl_2	20 - 175	20 - 48	CO	$[Rh(CO)_2I_4]^-$ $[Rh(CO)_2I_2]^-$ $[Rh_2(CO)_2I_4]^-$	RhICO_39

2.8 Chapter 2 - Reaction Index (cont)

Reaction Number	Reactants/Moles	Solvents	Temperature Range/°C	Pressure/ bar	Gases	Species Identified	Reaction Code
2.6.2B	RhI_3, 1.24×10^{-4} EtI, 1.24×10^{-2} H_2O, 2.77×10^{-2}	C_2H_5COOH CH_2Cl_2	20 - 175	20 - 48	CO C_2H_4	$[Rh(CO)_2I_4]^-$ $[Rh(CO)_2I_2]^-$	RhICO_40
2.6.2C	$RhCl_3.3H_2O$, 1.92×10^{-4} HI, 9.38×10^{-4} H_2O, 2.77×10^{-2}	C_2H_5COOH CH_2Cl_2	20 - 180	38 - 63	CO C_2H_4	$Rh(CO)Cl_3$ $[Rh(CO)_2I_4]^-$ $[Rh(CO)_2I_2]^-$ $[Rh_2(CO)_2I_4]^{2-}$ $[Rh(CO)I_5]^-$ $[Rh_2(CO)_4I_2]$	RhICO_52
2.6.2D	$RhCl_3.3H_2O$, 1.89×10^{-4} I_2, 2.49×10^{-4} H_2O, 2.77×10^{-2}	C_2H_5COOH CH_2Cl_2	20 - 180	37 - 58	CO	$[Rh(CO)_2I_4]^-$ $[Rh_2(CO)_2I_4]^{2-}$ $[Rh(CO)_2I_2]^-$	RhICO_60
2.6.2E	$[(C_4H_9)_4N]^+[Rh(CO)_2I_2]^-$, 2.15×10^{-4} H_2O, 2.77×10^{-2}	C_2H_5COOH CH_2Cl_2	20 - 180	36 - 55	CO	$[Rh(CO)_2I_4]^-$ $[Rh_2(CO)_2I_4]^{2-}$	RhICO_63
2.6.3A	$RhCl_3.3H_2O$, 1.92×10^{-4} H_2O, 2.77×10^{-2} EtI, 1.24×10^{-2} LiCl, 1.85×10^{-4}	C_2H_5COOH CH_2Cl_2	20 - 180	40 - 66	CO	$[Rh(CO)_2I_4]^-$ $[Rh(CO)I_5]^{2-}$	RhICO_61
2.6.3B	$RhCl_3.3H_2O$, 1.80×10^{-4} $LiO_2CC_2H_5$, 5.44×10^{-3} H_2O, 2.77×10^{-2} EtI, 1.24×10^{-2}	C_2H_5COOH CH_2Cl_2	20 - 180	40 - 51	CO	$[Rh(CO)_2I_4]^-$ $[Rh(CO)_2I_2]^-$	RhICO_62

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CHAPTER THREE

CONTENTS

CHAPTER 3

BATCH AUTOCLAVE REACTIONS OF RHODIUM-IODIDE SYSTEMS

3.1 Introduction

Having observed the spectral changes in the rhodium-iodide systems, a number of batch reactions were conducted in the standard autoclaves detailed below. The purpose of these experiments was to investigate the changes in rate, yield, and selectivity produced by varying the constituent components, the conditions, and the initiators.

Three autoclaves were employed:

<u>500Z</u> : 500 ml zirconium autoclave
<u>105C</u> : 105 ml hastalloy 'C' autoclave
<u>300T</u> : 300 ml hastalloy 'B' autoclave with catalyst tipping facility

Both the 500Z and 300T autoclaves have "magnedrive" stirring. The 105C was stirred by a set speed internal magnetic follower. All autoclaves were heated by external thermocouple-regulated heaters. Reactants were loaded via inlet ports at the head of the autoclave. For each reaction the autoclave was flushed with carbon monoxide and then pressurised with reactant gases.

Gas uptake was recorded for each reaction by manual or computer monitoring of pressure gauges. The reaction time for a system was considered as the period of gas uptake in all cases. On this principle the overall rate of reaction was calculated for each experiment. Gas Liquid Chromatography was conducted on the final solution of all reactions. Molar amounts of propanoic acid produced were calculated, as well as selectivity to propanoic acid. From this g.l.c. data and the observed reaction time, a calculation was made for the rate of reaction in the following terms: moles of propanoic acid produced per kilogramme of initial solution per hour of reaction. For some reactions the water content of the final solution was determined, by an automated Karls Fischer method.

3.2 Initial Systems

As indicated at the start of Chapter 2, work performed at B.P.C. Ltd, Hull, had identified that the favoured reactant composition for hydrocarbonylation is as outlined for reactions 3.2.1, using rhodium(III) chloride, a mixture of iodoethane and hydrogen iodide to initiate the reaction using propanoic acid solvent, and in the presence of water.

The following reactions were conducted to give a basis for further investigation of the effects of water and hydrogen iodide on the system.

Autoclave: 500Z *Temperature: 180°C*

Standard components: †

$RhCl_3 : C_2H_5CO_2H : CO, 50\ bar : C_2H_4, 30\ bar;$

Reaction number	*Components*	*Moles of Gas absorbed*	*Moles of Propanoic Acid produced*	*Rate (1) Bar/hr*	*Rate (2) Mol/kg/hr*
3.2.1	EtI, HI, H_2O	1.02	0.53	101	5.3
3.2.2	EtI, H_2O	0.84	0.15	44.3	0.63
3.2.3	EtI	0.55	0.40	0.32	1.16

Notes: (1) *Rate of gas absorption*

(2) *Rate of Propanoic Acid produced*

† *Full reaction compositions may be found in section 3.8 for all reactions in this chapter.*

The results obtained from these three reactions are opposed to the precedents set by section 2.6 and the work of Forster(1). These indicated that the addition of hydrogen iodide to a reaction initiated by iodoethane would retard the rate of reaction. Moreover the rate of reaction 3.2.3 is greater than reaction 3.2.2; it is expected that the previous hydrous reaction would have a greater rate of reaction than the anhydrous reaction. In taking these two observations it is possible to conclude that reaction 3.2.2 is an anomalous result, and a much greater rate of reaction should have been observed. Therefore the effects of water and also hydrogen iodide will be studied in greater detail.

As discussed in section 2.5 it was necessary to employ a mixed dichloromethane:propanoic acid solvent of 12:5 v/v for infra-red studies. Reactions 3.2.4 and 3.2.5 were conducted to compare this solvent mixture with pure propanoic acid as solvent.

Autoclave: 500Z *Temperature: 180°C*

Standard components:

RhI_3 : EtI : H_2O : CO, 30 bar : C_2H_4, 30 bar;

Reaction number	Components	Moles of Gas absorbed	Moles of Propanoic Acid produced	Rate (1) Bar/hr	Rate (2) Mol/kg/hr
3.2.4	$CH_3CH_2CO_2H$	0.77	0.55	45.0	1.55
3.2.5	$CH_2Cl_2/CH_3CH_2CO_2H$	0.40	0.30	35.4	1.24

Reactions 3.2.4 and 3.2.5 show that the difference between employing the mixed solvent system is a 20% reduction in rate when compared to using propanoic acid alone. On this basis it would appear that there is some justification in using the mixed solvent system as a model for the one using propanoic or acetic acids only.

Having conducted some reactions employing rhodium(III) chloride and some employing rhodium(III) iodide, the two rhodium source compounds were compared. Acetic acid was used as the solvent to enable greater accuracy in the determination of propanoic acid produced.

Autoclave: 105C *Temperature: 180°C*

Standard components:

EtI : H_2O : CH_3CO_2H : CO, 40 bar : CH_2CH_2, 40 bar;

Reaction number	Components	Moles of Gas absorbed	Moles of Propanoic Acid produced	Rate (1) Bar/hr	Rate (2) Mol/kg/hr
3.2.6	$RhCl_3.3H_2O$	-	0.142	415	18.1
3.2.7	RhI_3	-	0.226	218	15.7

It should be noted that reactions 3.2.6 and 3.2.7 are conducted in a different autoclave to the previous five reactions. In this thesis, reactions conducted in different autoclaves will not be compared, as no data is available on the effects of autoclave design on rate of reaction.

Reaction 3.2.6 using rhodium(III) chloride gives a greater rate of reaction than the rhodium(III) iodide analogue (reaction 3.2.7), but that the latter reaction produces a greater amount of propanoic acid. The rhodium(III) chloride reaction has a much shorter initiation time, but the rhodium(III) iodide reaction maintains a higher rate of reaction for a longer period of time. The reaction profiles are shown in Figure 3.1. Time zero is the point at which the reactions reached 180°C. It is difficult to compare the two profiles as the rhodium(III) chloride reaction starts before it reaches 180°C. A "drop catalyst" autoclave would give better comparisons for these reactions.

3.3 Alternative Solvents for the production of Propanoic Acid

While the data in section 3.2 demonstrates that propanoic and acetic acids are viable solvents for hydrocarbonylation, a brief survey of alternative solvent was conducted for comparison.

In section 2.2.5 it was demonstrated that the major complex observed in ethanol solvent was diiodocarbonylrhodate(I) anion, suggesting that carbonylation of iodoethane, produced from ethanol and hydrogen iodide, was occurring. As the predicted rate of oxidative addition(2) is -

$$\mathrm{EtI} \ll \mathrm{MeI} < \mathrm{HI}$$

a much slower rate would be expected for carbonylation as opposed to hydrocarbonylation.

Autoclave: 500Z *Temperature: 180°C*

Standard components:

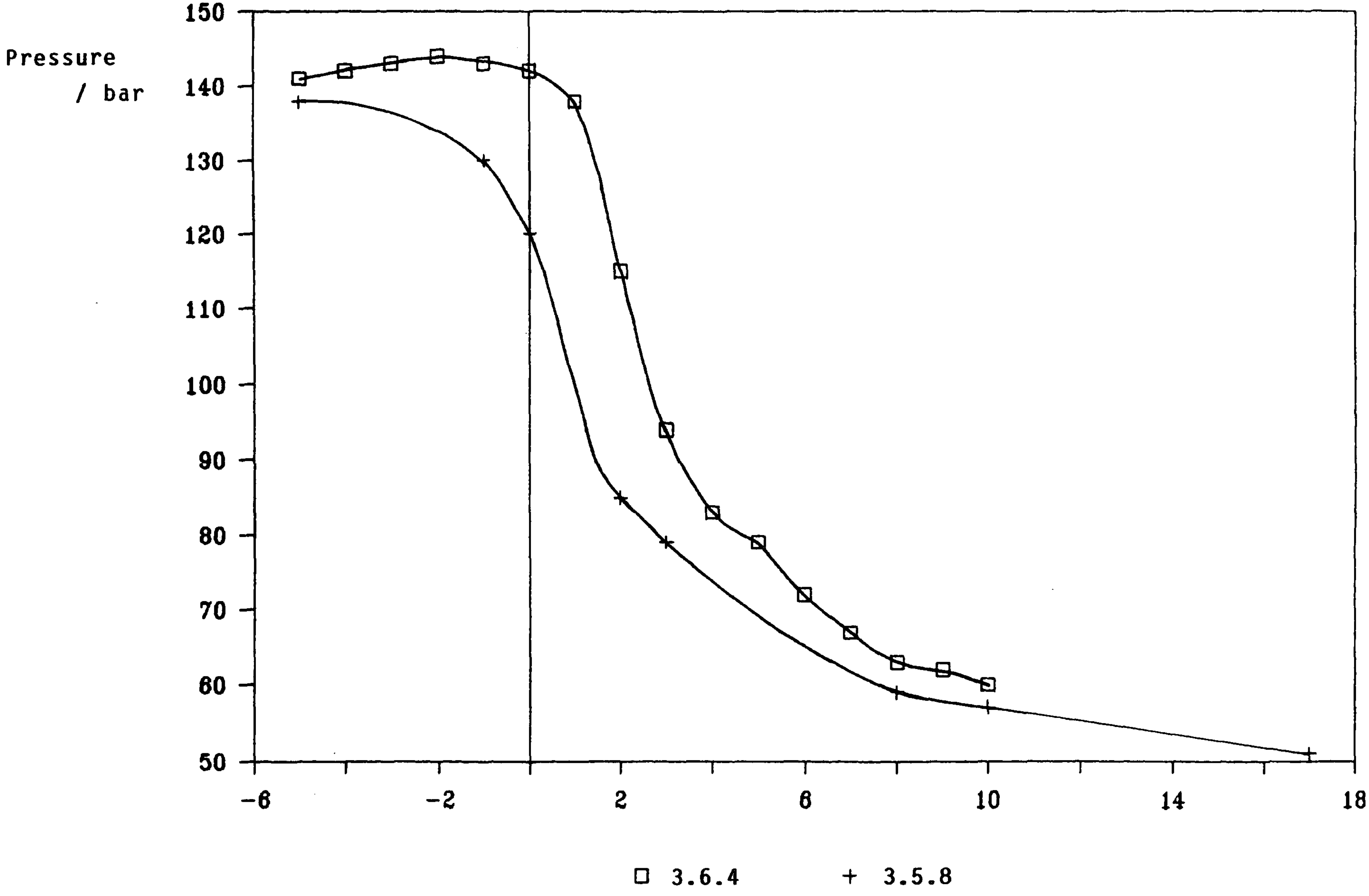
$RhCl_3.3H_2O : HI : EtI : H_2O : CO, 50\ bar : C_2H_4, 30\ bar;$

Reaction number	*Components*	*Moles of Gas absorbed*	*. Moles of Propanoic Acid produced*	*Rate (1) Bar/hr*	*Rate (2) Mol/kg/hr*
3.3.1	EtOH	0.56	0.27	4.0	0.15

This reaction's rate is 100-fold slower than reaction 3.2.1 as predicted in the preceding paragraph; however the major product of reaction was diethylether, presumably produced by the dehydration of ethanol. 0.7 moles of water were also produced. It is concluded that these anhydrous systems are able to dehydrate some solvents readily. If this includes alkanoic acids then there is a major implication for the hydrocarbonylation reaction. It becomes impossible to eliminate the Water Gas Shift reaction from any proposed reaction scheme.

Further reactions were conducted in anhydrous conditions to attempt to investigate this feature further. Two reactions, 3.3.2 and 3.3.3 were conducted, the former in the absence of ethene, as a blank reaction for assessing the level of hydrocarbonylation occurring in other reactions.

Figure 3.1


Pressure
/ bar
150
140
130
120
110
100
90
80
70
60
50
−6
−2
2
6
10
14
18
□ 3.6.4
+ 3.5.8

Autoclave: 500Z *Temperature: 180°C*

Standard components:

$RhCl_3$: *EtI : EtOH : CO, 50 bar;*

Reaction number	*Components*	*Moles of Gas absorbed*	*Moles of Propanoic Acid produced*	*Rate (1) Bar/hr*	*Rate (2) Mol/kg/hr*
3.3.2	-	0.23	0.055	3.2	0.32
3.3.3	C_2H_4:30 bar	0.87	0.64	10.5	0.99

Note that the rate was some three times as great in the presence of ethene as when ethene is absent. This suggests that despite the presence of ethanol some ethene has reacted. In both cases a large quantity of diethylether is produced again suggesting dehydration of ethanol. In both cases a considerable amount of water was produced, approximately 0.75 moles. Having observed this apparent preference for propanoic acid production by hydrocarbonylation reactions in ethanol, the effects of different initiators were studied.

Autoclave: 500Z *Temperature: 180°C*

Standard components:

$RhCl_3$: *EtOH : CO,50 bar :* C_2H_4, *30 bar;*

Reaction number	*Components*	*Moles of Gas absorbed*	*Moles of Propanoic Acid produced*	*Rate (1) Bar/hr*	*Rate (2) Mol/kg/hr*
3.3.4	EtI	0.39	0.25	3.4	0.13
3.3.5	HI	0.20	0.085	1.1	0.045

These two reactions have approximately the same molar amounts of iodide initiator (see section 3.8). Despite the indications earlier suggesting that the hydrocarbonylation reaction is proceeding, the ethyliodide promoted reaction gives rates of acid formation three times greater than that for the hydrogen iodide promoted reaction.

In an attempt to investigate the reactions producing diethylether and water a comparison was made between hydrous and anhydrous reaction systems.

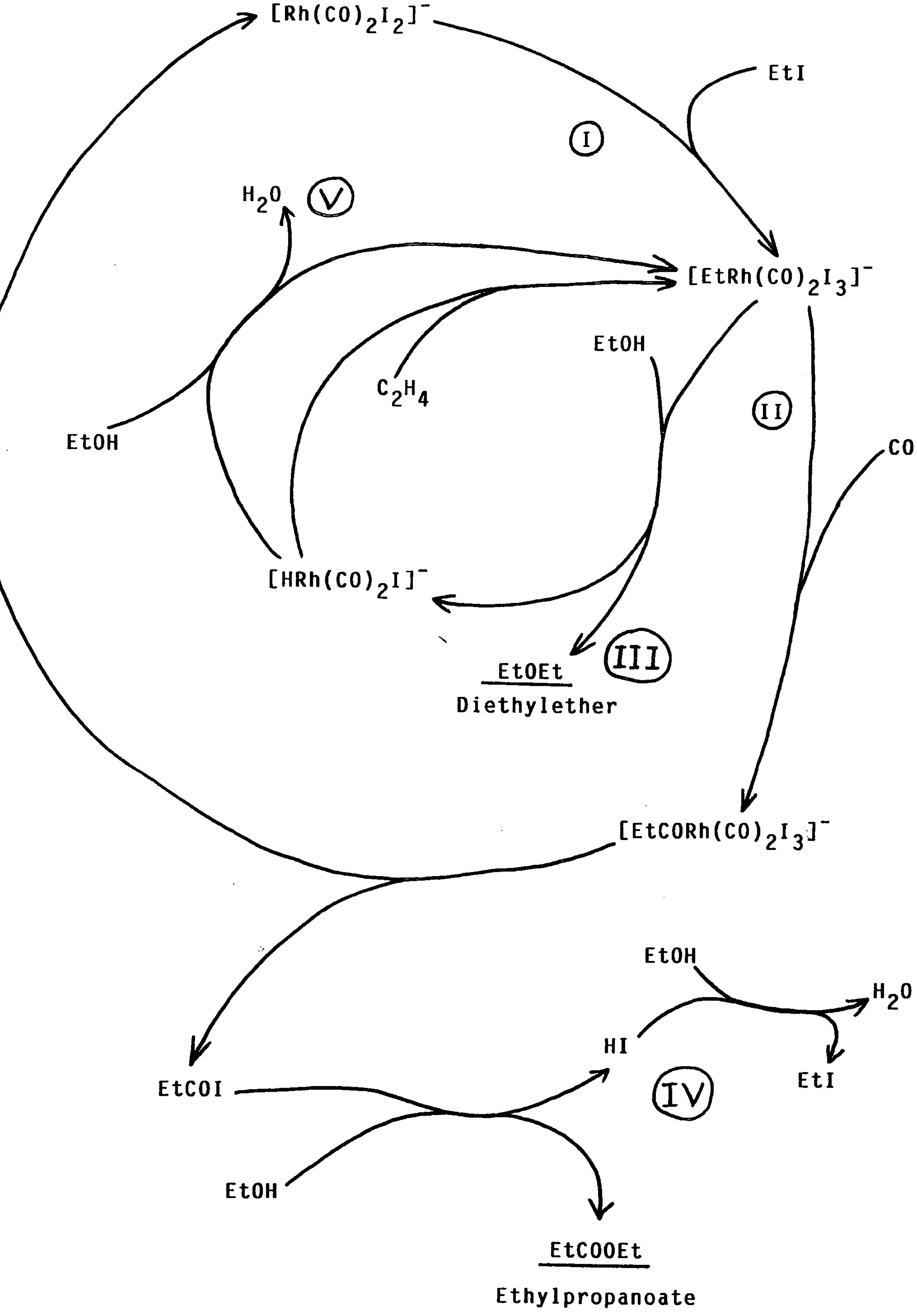
Autoclave: 500Z *Temperature: 180°C*

Standard components:

$RhCl_3.HI$: EtOH : CO, 50 bar : C_2H_4, 30 bar;

Reaction number	Components	Moles of Gas absorbed	Moles of Propanoic Acid produced	Rate (1) Bar/hr	Rate (2) Mol/kg/hr
3.3.6	-	0.20	0.085	1.1	0.045
3.3.7	H_2O	0.17	0.087	0.97	0.045

There is, for practical purposes, no difference to the rate of these reactions, in both cases there was 0.2 moles of both diethylether and water produced. In this system the presence of water does not affect the reaction mechanism. We must presume that there is a reaction mechanism for the formation of propanoic acid operating in this system that is independent of water. In considering these reactions the production of diethylether must be of major importance. In Figure 3.2 it is proposed that, as the major species observed in the infra-red studies of ethanol systems (section 2.2.5) is rhodium(I) dicarbonyldiiodide anion $[Rh(CO)_2I_2]^-$, the first step (I) would be slow.


$[Rh(CO)_2I_2]^-$
EtI
I
H_2O
V
$[EtRh(CO)_2I_3]^-$
EtOH
C_2H_4
EtOH
II
CO
$[HRh(CO)_2I]^-$
III
EtOEt
Diethylether
$[EtCORh(CO)_2I_3]^-$
EtOH
H_2O
HI
EtI
EtCOI
IV
EtOH
EtCOOEt
Ethylpropanoate

At stage (II) we may have competition between the insertion of carbon monoxide and the nucleophilic attack of ethanol to yield diethylether and the hydrido-rhodium species. It is known that the insertion of carbon monoxide is rapid(3) so we would require rapid solvolysis to compete. The hydrido species formed can rapidly be reconverted to the ethyl-rhodium species. One of the alternatives pathways for this latter process produces water (V). So does the production of ethylpropanoate (IV), the major propanoic product, produced from EtCOI reductively eliminated from $[\mathrm{EtCORh(CO)_2I_3}]^-$.

Further reactions were conducted using ethyliodide as solvent, again to parallel the infra-red work reported in section 2.2.5.

Autoclave: 500Z *Temperature: 180°C*

Standard components:

$RhCl_3$: H_2O : EtI: CO, 50 bar;

Reaction number	*Components*	*Moles of Gas absorbed*	*Moles of Propanoic Acid produced*	*Rate (1) Bar/hr*	*Rate (2) Mol/kg/hr*
3.3.8	-	*0.42*	*0.059*	*2.8*	*0.013*
3.3.9	*HI:C_2H_4, 30 bar*	*0.46*	*0.37*	*14.7*	*0.416*

In weighting the second reaction toward the hydrocarbonylation reaction we can produce much greater amounts of propanoic acid. However the rates of reaction remain poor and confirm the information implied by the infra-red work that this is a poor solvent for the hydrocarbonylation reaction.

3.4 The Effect of Carbon Monoxide to Ethene Gas Ratio on Rate of Reaction

To discover the effect of varying the ratio of ethene and carbon monoxide, five reactions were undertaken with a constant total pressure. In each case the pressure was used to determine the approximate ratio and ideal gas behaviour was assumed. It is recognised that neither gas is ideal and that absorption of gas into solution is not accounted for.

Autoclave: 500Z *Temperature: 180°C*

Standard components:

$RhI_3 : EtI : H_2O : C_2H_5CO_2H : CH_2Cl_2$;

Reaction number	*Components*	*Moles of Gas absorbed*	*Moles of Propanoic Acid produced*	*Rate (1) Bar/hr*	*Rate (2) Mol/kg/hr*
3.4.1	CO:48 bar C_2H_4:12 bar	0.44	0.24	15.0	0.99
3.4.2	CO:40 bar C_2H_4:20 bar	0.70	0.27	44.0	1.46
3.4.3	CO:30 bar C_2H_4:30 bar	0.40	0.30	35.4	1.24
3.4.4	CO:20 bar C_2H_4:40 bar	0.75	0.30	30.0	1.25
3.4.5	CO:12 bar C_2H_4:48 bar	0.42	0.085	1.54	0.04

There is clear indication that neither a four-fold excess of ethene or carbon monoxide give favourable acid formation. The region of more equal ratios is however more complex. It is apparent in Figure 3.3 that both a 2:1 and a 1:1 ratio of ethene to carbon monoxide give similar rates of propanoic acid production. The plateau is then superseded by the rate of reaction at a ratio of 2:1 carbon monoxide to ethene.

This may suggest that the step of incorporation of ethene into the catalytic cycle is either independent of the pressure of ethene, which is unlikely, or more significantly, not the rate determining step. The latter situation is consistent with the oxidative addition step being rate determining as in the Monsanto process (see Chapter 1). These reactions were conducted using a constant total pressure. A complementary set of reactions would keep the carbon monoxide pressure constant and vary the amount of ethene present, but the facilities needed were not available.

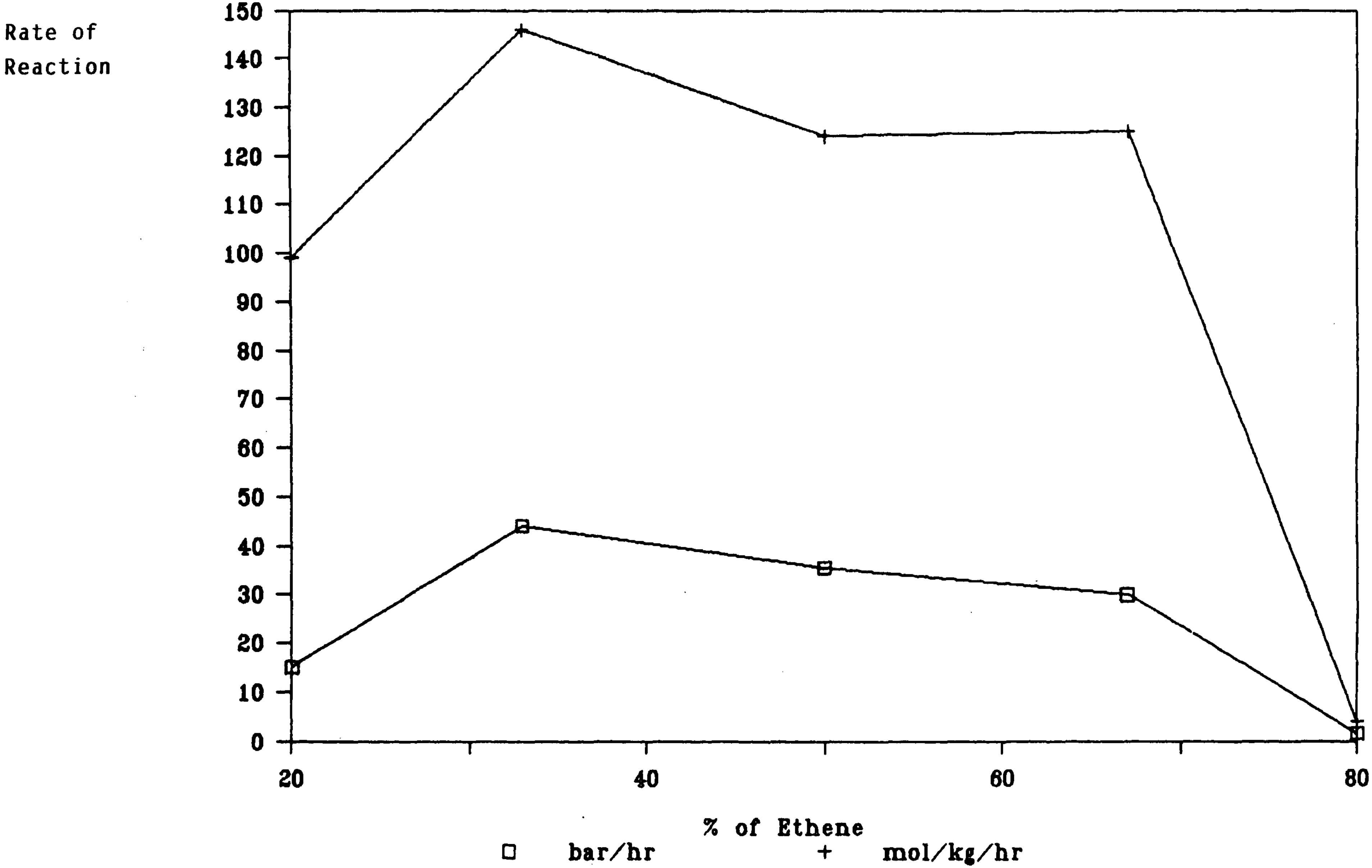
3.5 The Effects of Water Concentration

In the proposed catalytic cycle (Chapter 2, Figure 2.1) there is a reaction step to regenerate the hydrogen iodide which gives our desired reaction product:

$$RCOI + H_2O \longrightarrow RCO_2H + HI$$

Any active OH-group would serve equally well. Ethanol to give ethylpropanoate, propanoic acid to give propanoic anhydride. To investigate the relative reactivity of these three possible R-OH groups, reactions were undertaken in dichloromethane with these reagents.

Figure 3.3


Rate of
Reaction
150
140
130
120
110
100
90
80
70
60
50
40
30
20
10
0
20
40
60
80
% of Ethene
□ bar/hr
+ mol/kg/hr

Autoclave: 500Z *Temperature: 180°C*

Standard components:

$RhCl_3.3H_2O$: EtI : CH_2Cl_2 : CO, 50 bar : CH_2CH_2, 30 bar;

Reaction number	Components	Moles of Gas absorbed	Moles of Propanoic Acid produced	Rate (1) Bar/hr	Rate (2) Mol/kg/hr
3.5.1	H_2O	0.60	0.44	42	1.17
3.5.2	EtOH	0.40	0.32	3.7	0.105
3.5.3	$C_2H_5CO_2H$	0.54	0.25	4.0	0.081

In these reactions the assessment of propanoic acid production (in various forms, $EtCO_2H$, $(EtCO)_2O$, Et(CO)OEt) show a variation of less than a factor of 2. However the rate of production, when water is the R-OH moiety, is 10 to 15-fold greater. The action of water is probably more significant therefore than just as a reagent to react with CH_3CH_2COI. This step is not involved in the catalytic cycle proposed and should not affect the rate of reaction. A further study was conducted by varying the amount of water present in a series of reactions.

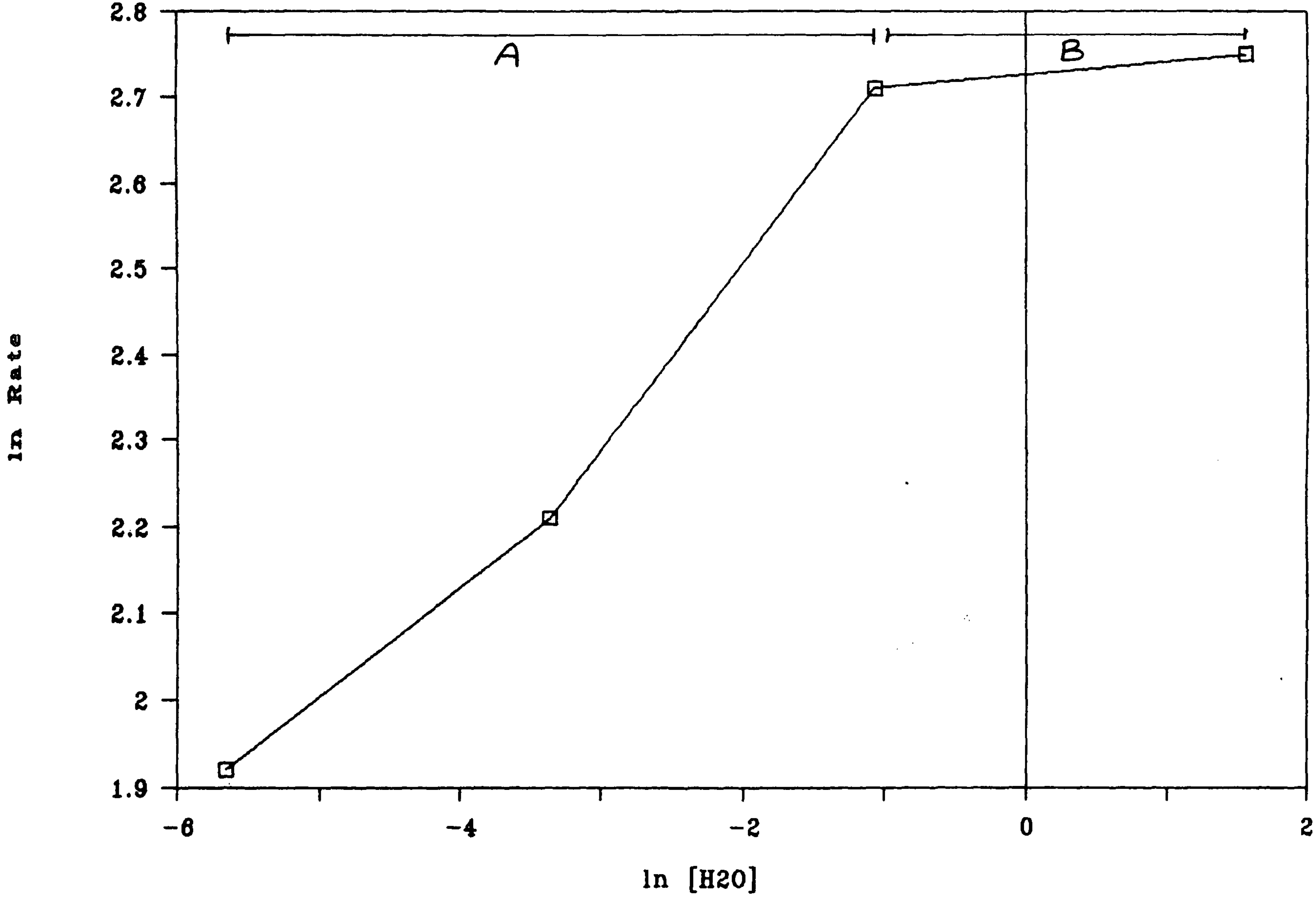
Autoclave: 105C *Temperature: 180°C*

Standard components:

RhI_3 : EtI : CH_3CO_2H : CO, 40 bar : C_2H_4, 40 bar;

Reaction number	Component/ Mole fraction	Moles of Propanoic Acid produced	Rate (1) $/bar.hr^{-}$	Rate (2) $/mol.kg^{-1}.hr^{-1}$	% selectivity
3.5.4	None	0.071	6	0.603	71.5
3.5.5	H_2O, 3.47×10^{-3}	0.090	51	6.86	59.6
3.5.6	H_2O, 3.47×10^{-2}	0.180	136	9.16	83.8
3.5.7	H_2O, 3.45×10^{-1}	0.245	185	15.0	80.1
3.5.8	H_2O, 4.76	0.226	218	15.7	82.1

Figure 3.4



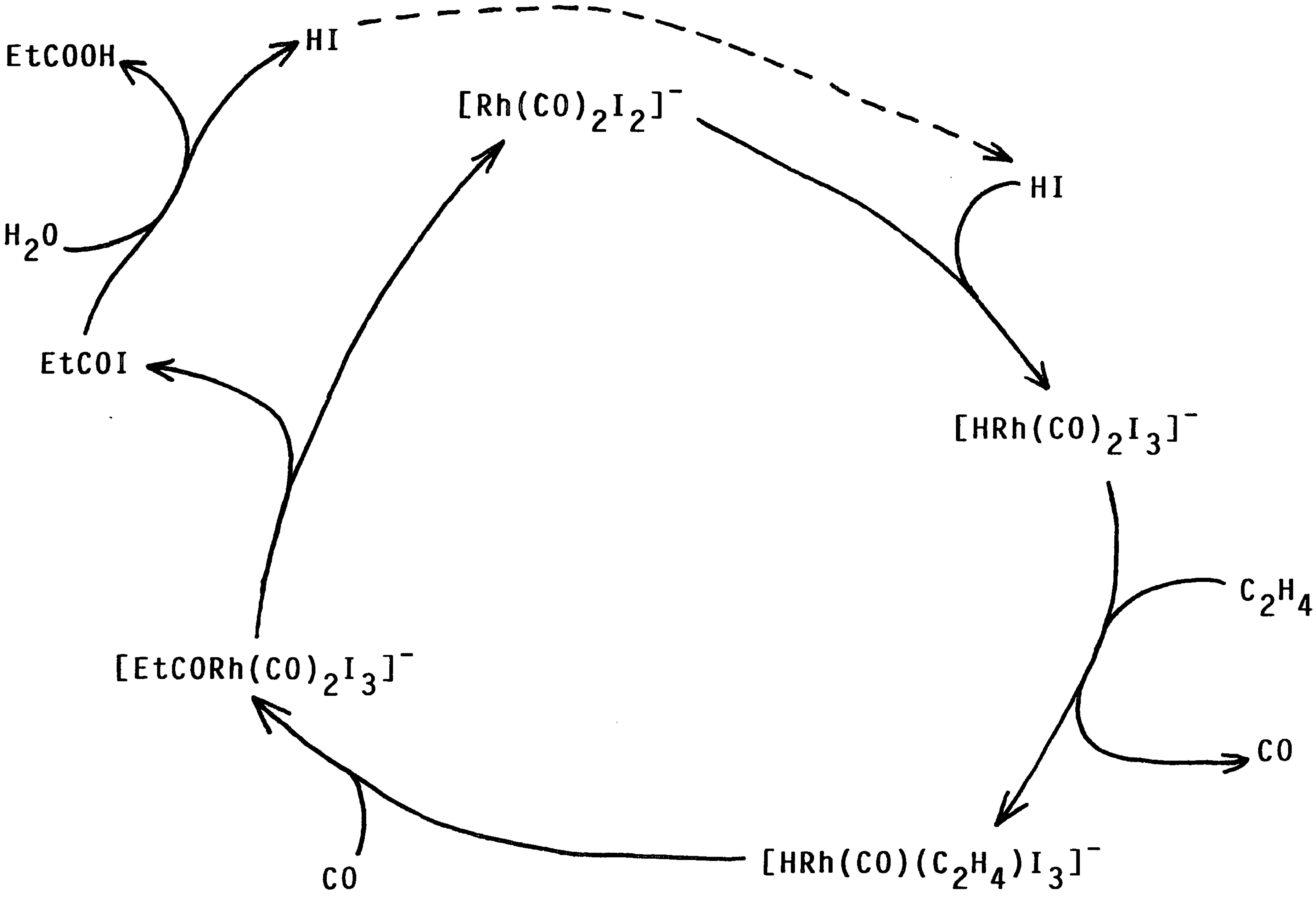
It should be noted that the addition of a very small amount of water, approximately half of the amount of rhodium present, produces a ten-fold increase in rate of reaction (reactions 3.5.4 vs 3.5.5). However the amount of acid produced is not that more than for the anhydrous reaction. If the natural logarithm of both rate (2) and concentration of water are obtained, the plot shown in Figure 3.4 is produced. There is no linear relationship, however it may be fruitful to consider the different regions of the graph.

The gradient of the graph in section "A" is approximately 0.25, a magnitude indicating some type of solvent effect. For the region high water content "B" the graph appears to plateau, and this may be caused by the amount of water present being in excess.

The area of most interest is however not shown on the graph. There is a ten-fold increase in rate from the anhydrous reaction 3.5.4 to reaction 3.5.5 in which there is a smaller molar quantity of water than rhodium. This suggests a catalytic action, by water, at this concentration. Yet in the catalytic cycle proposed (Figure 3.5) water does not feature in any of the catalytic steps. It is possible however to consider an alternative to the reductive elimination from $[EtCORh(CO)_2I_3]^-$ as shown in Figure 3.6.

At first it would appear that any ROH group would serve this function equally well. However, the reaction (Figure 3.6) would be expected to be acid catalysed as for example are the reactions of acid chlorides with water. The addition of a small amount of water may affect the acidity of glacial acetic acid significantly. Unfortunately standard acidity functions such as the Hammett function(4) do not cover the region we are studying(5, 6). It is therefore not possible to correlate acidity and rate of reaction in this region and test the hypothesis proposed above.

Figure 3.5


EtCOOH
HI
[Rh(CO)$_2$I$_2$]$^-$
HI
H$_2$O
EtCOI
[HRh(CO)$_2$I$_3$]$^-$
C$_2$H$_4$
CO
[EtCORh(CO)$_2$I$_3$]$^-$
CO
[HRh(CO)(C$_2$H$_4$)I$_3$]$^-$

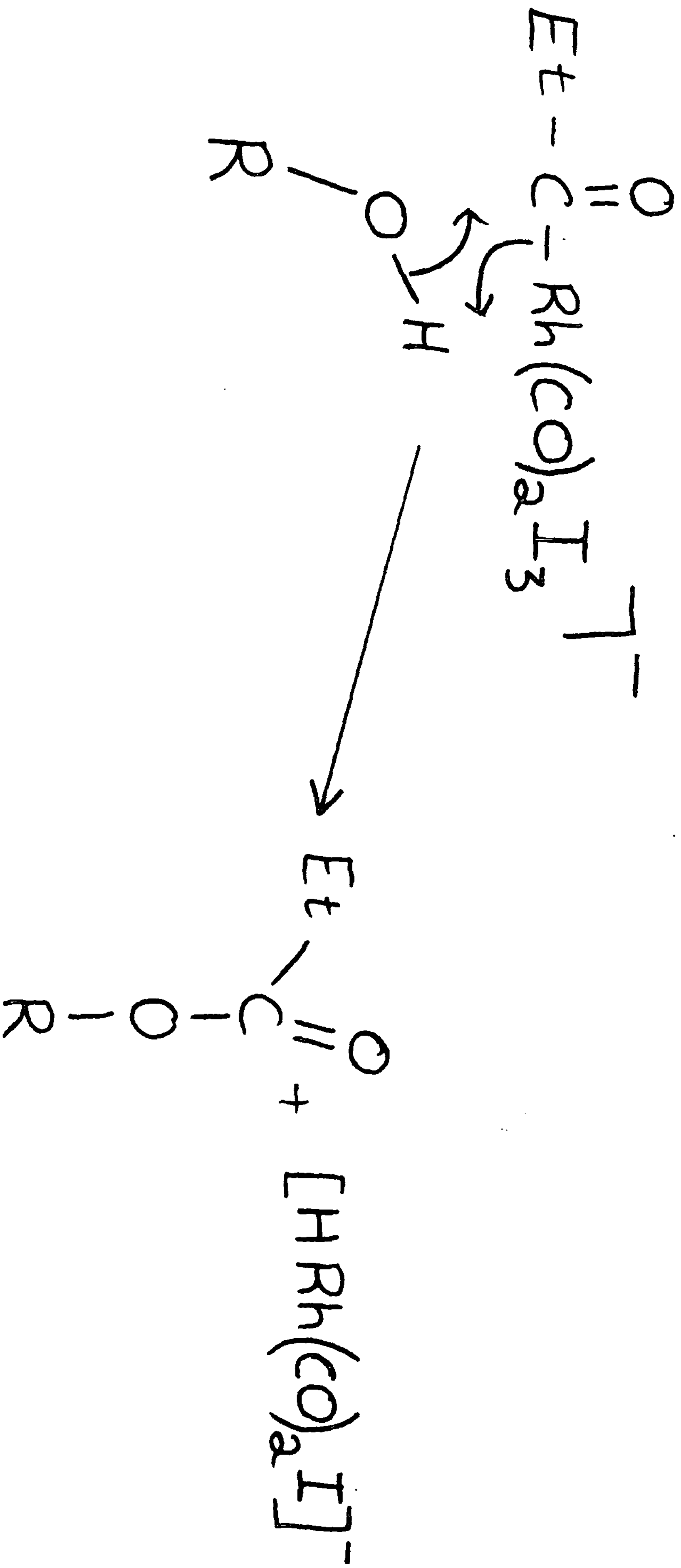


Figure 3.6

From reactions 3.5.4 to 3.5.8 the data on selectivity show that an increase above approximately 5 x 10^{-2} mol L^{-1} of water does not affect selectivity. It is expected however to negatively affect the stability of the rhodium catalyst. Thus the data shows that the more efficient systems have a water content around 1 - 3% by weight (see Figure 3.4), less than a third of the water content previously suggested (see Chapter 2, section 2.1).

3.6 Initiators

In Chapter 2 the effects of different iodide sources on the hydrocarbonylation reaction have been assessed in terms of the infra-red data. A further survey can be conducted in terms of the batch reactions reported in this chapter. Two approaches have been used; firstly a "catalyst-tip" facility was employed to compare the rates of reaction for the two most utilised initiators, hydrogen iodide and ethyl iodide. Gas absorbance was plotted against time to consider the initiation time and rates of reaction as the reaction progresses.

The second series of reactions were conducted using the standard autoclaves, and overall rates were produced. These latter reactions were to investigate the action of various additives.

Autoclave: 300T *Temperature: 180°C*

Standard components:

$RhI_3 : H_2O : C_2H_5CO_2H : CH_2Cl_2 : CO$, *20 bar* : C_2H_4, *20 bar;*

Reaction number	*Components*	*Moles of Propanoic Acid produced*	*Rate (1) Bar/hr^{-1}*	*Rate (2) Mol/kg^{-1}/hr^{-1}*
3.6.1	None	0.12	1.2	0.04
3.6.2	EtI	0.11	129	5.28
3.6.3	HI	0.11	7.9	0.68

The reaction with no initiator (Figure 3.9) is very slow and the reaction continues well beyond the first 1.5 hours shown.

For the other two reactions, it is surprising that the initial rates are the same despite the fact that HI oxidative addition should be more rapid than that of EtI. The extremely rapid rate in the presence of EtI between 60 and 80 minutes is attributed by Forster(1) to oxidative addition of hydrogen iodide generated as in equation 1.

$$EtI + CO + H_2O \xrightarrow{Rh} EtCO_2H + HI \qquad \textit{Equation 1}$$

After the initial period the amount of HI would not increase greatly as the reaction of equation 2 would dominate that of equation 1.

$$HI + C_2H_4 + CO + H_2O \xrightarrow{Rh} EtCO_2H + HI \qquad \textit{Equation 2}$$

It is therefore likely that in reaction 3.6.3 the catalyst is poisoned by an excess of hydrogen iodide. However we might expect a more classically S-shaped curve for autocatalytic process.

In the reaction 3.6.2 and 3.6.3 the initiators are used in the same molar amounts. Further reactions were conducted by keeping the molar amount of ethyliodide constant and by adding various components to the reaction mixture.

Autoclave: 105C *Temperature: 180°C*

Standard components:

$RhI_3 : EtI : H_2O : CH_3CO_2H : CO,\ 40\ bar : C_2H_4,\ 40\ bar;$

Reaction number	*Component*	*Moles of Propanoic Acid produced*	*Rate (1) /bar.hr^{-1}*	*Rate (2) /mol.kg^{-1}.hr^{-1}*	*% selectivity*
3.6.4	None	0.142	415	18.10	84.7
3.6.5	HI	0.151	164	7.69	78.7
3.6.6	I_2	0.081	258	7.30	88.8
3.6.7	H_3PO_2	0.183	45	2.34	89.3
3.6.8	$LiO(CO)C_2H_5$	0.097	59	1.98	83.4

Again the rate of reaction, when hydrogen iodide is added, decreases markedly. Two alternative modes of action of the inhibition reaction are feasible. The attack of hydrogen iodide on the proposed $[HRh(CO)_2I_3]^-$ anion would give $[Rh(CO)_2I_4]^-$ and hydrogen (see Chapter 2). The reaction of two hydrogen iodide molecules would give hydrogen and iodine. The latter could react with $[Rh(CO)_2I_2]^-$ to give $[Rh(CO)_2I_4]^-$. There is no obvious way available to us to distinguish these two pathways absolutely.

In reaction 3.6.6 a similar rate of reaction is observed to that of reaction 3.6.5 and may indicate that the oxidative addition of iodine is slowing the rate of reaction in 3.6.5. Commercial hydriodic acid is stabilised by addition of hypophosphoric acid, which acts as follows:

$$H_3PO_2 + H_2O + I_2 \longrightarrow H_3PO_3 + 2HI$$

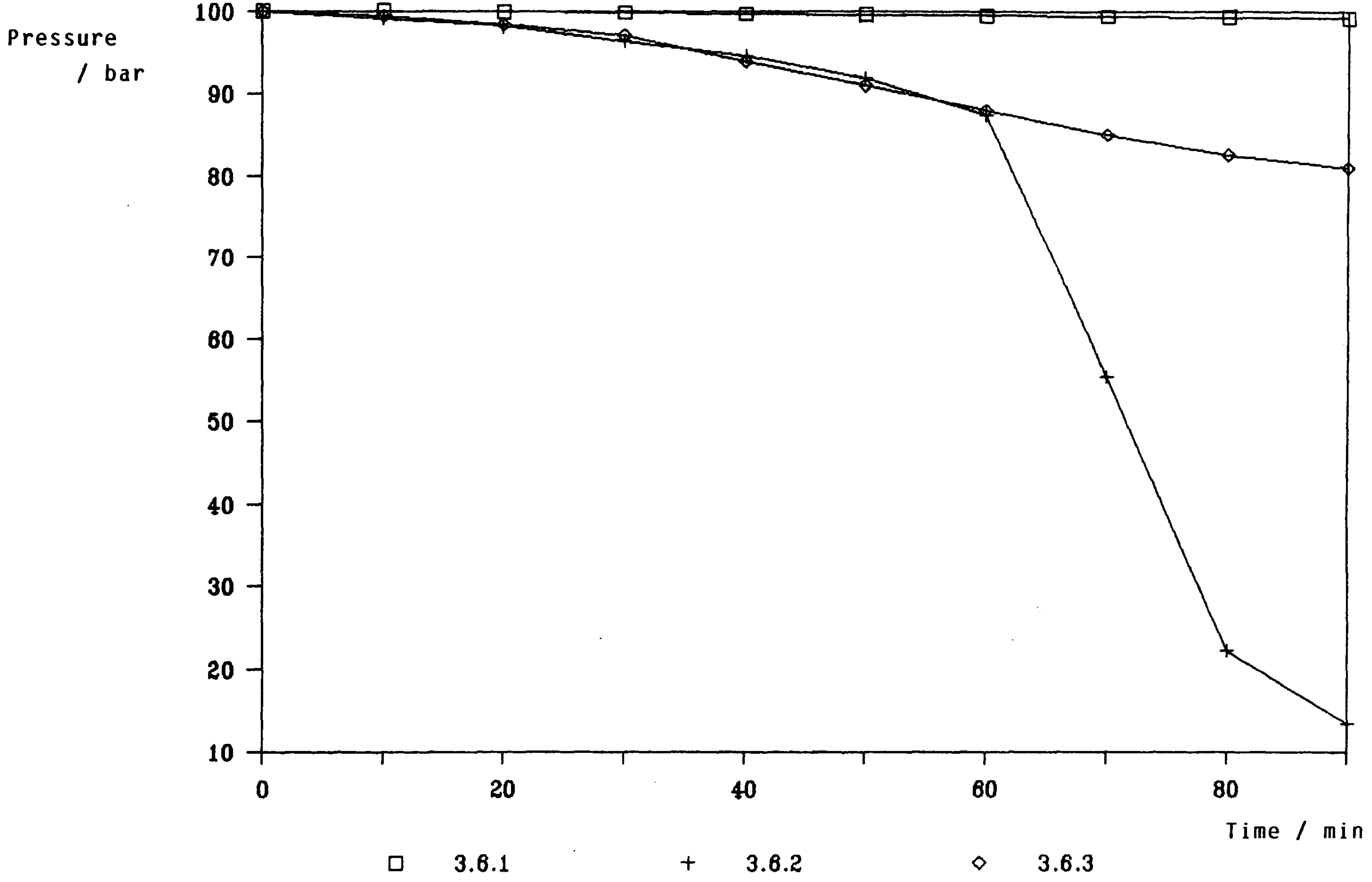
It would therefore follow that hypophosphoric acid would remove iodine from the reaction. Reaction 3.6.7 shows a marked decrease in rate compared even with reaction 3.6.6. Therefore it is probable that the inhibition of reaction 3.6.5 is due to hydrogen iodide, not iodine formed from hydrogen iodide.

We have seen previously that the addition of propanoate ion to the reaction promotes the presence of rhodium(I) species in solution at the reaction temperature (Chapter 2, section 2.6). The rate achieved for the same conditions (reaction 3.6.8) is very low. It can thus be demonstrated that the maintenance of diiododicarbonylrhodate(I) anion $[Rh(CO)_2I_2]^-$ does not necessarily increase the rate of hydrocarbonylation of ethene.

3.7 Discussion and Conclusions

Throughout Chapters 2 and 3 we have targeted certain areas for study, including the effects of initiators and water content. It is now possible to make an assessment based on both infra-red and batch reaction data.

Figure 3.7


Pressure / bar
100
90
80
70
60
50
40
30
20
10
0
20
40
60
80
Time / min
□ 3.6.1
+ 3.6.2
◇ 3.6.3

Comparing $RhCl_3.3H_2O$ and RhI_3 as rhodium sources (Figure 3.7) note that hydrous rhodium(III) chloride tends to react more rapidly initially than the insoluble rhodium(III) iodide. The infra-red data in Chapter 2 indicates that chloro-carbonyl-rhodium species are formed more rapidly, however the excess iodo- initiator produces similar spectroscopic results after the initiation period to those for rhodium(III) iodide, suggesting the only difference between the two rhodium sources to be their initial solubility.

In Chapter 2 reactions containing ethene gave varying results, the data from section 3.4 shows that an excess of carbon monoxide over ethene up to 2 to 1 produced and maintained a rapid rate of reaction.

The effect of the initiators on reaction is somewhat more complex. Forster(1) shows hydrogen iodide addition to be dominant over that of iodoethane. However as demonstrated in section 3.6 after an initial period ethyliodide produces the more rapid reaction. This fact is attributed to ethyliodide slowly producing hydrogen iodide. High levels of hydrogen iodide were found to inhibit the rate of reaction (see section 3.6).

In considering how iodoethane and hydrogen iodide affect the spectra in Chapter 2, attention must be paid to the great differences observed between protic and non-protic solvents. In dichloromethane, diiodotetracarbonyldirhodate(I) $[Rh_2(CO)_4I_2]$ is observed in the presence of hydrogen iodide, confirming Fulford's(7) observation that the protonation of this species does not proceed under these conditions. However reaction between these species is observed in propanoic acid or when water is present. In propanoic acid as the solvent, an interaction between $[Rh(CO)_2I_4]^-$ and

$[Rh(CO)_2I_2]^-$ is observed. In one case this was observed when an increase of temperature from 175°C to 180°C occurred. The importance of the species producing an absorbance band at approximately 1980 cm^{-1} must be considered. It is most easily observed when lithium propanoate is added to the reaction mixture. However the isolation of this complex was complicated by another complex with an absorbance band at 2092 cm^{-1} and isolation was not effected.

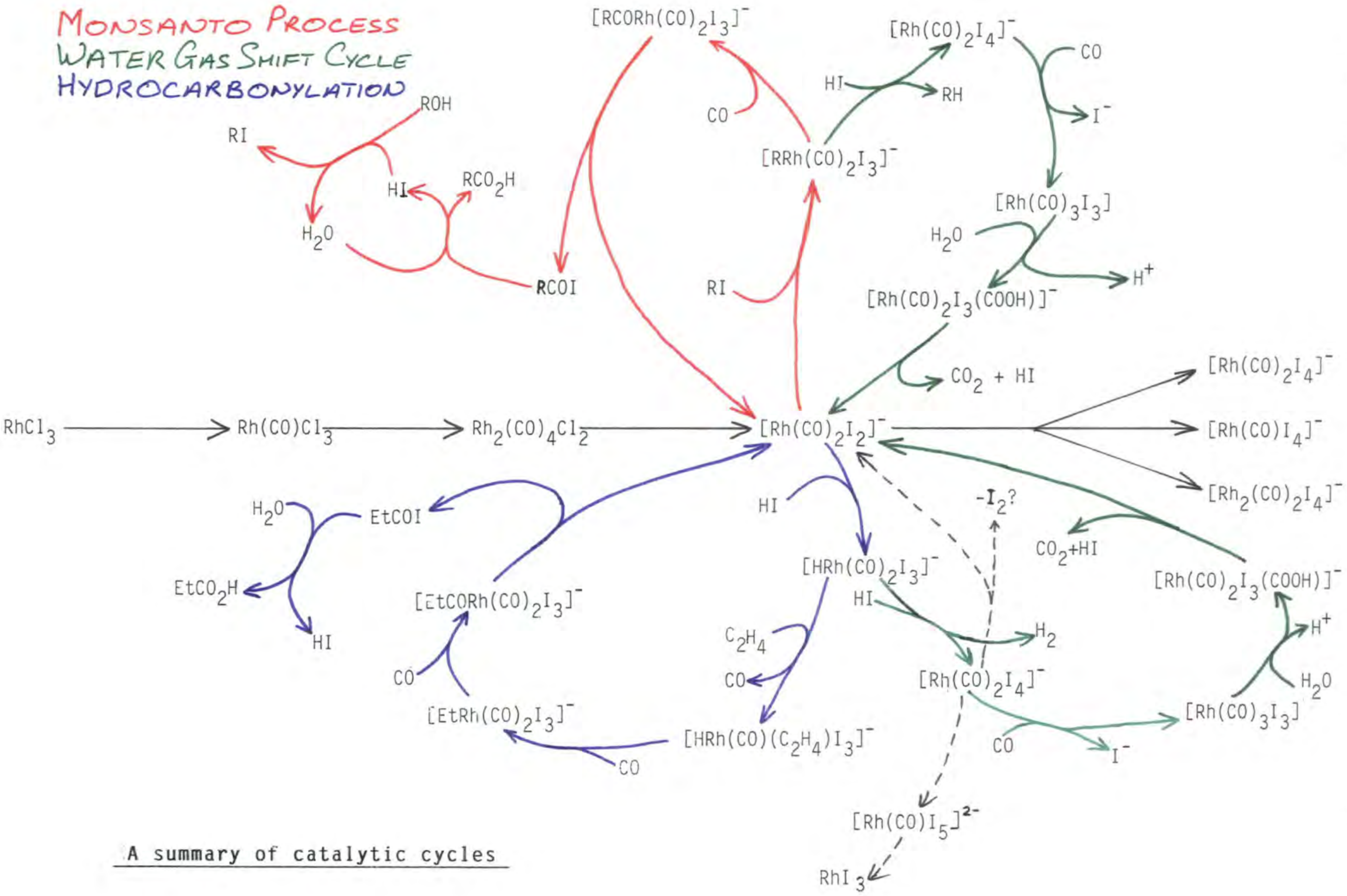
The addition of water to the reaction system shows a marked effect (see reaction 3.5.4 and 3.5.5). There was no noticeable increase in the intensity of the rhodium-carbonyl absorbance band (section 2.6) as compared with anhydrous systems. It is therefore unlikely that water acts as a solvation agent for rhodium species. The nucleophilic attack on the rhodium-acyl species has been considered, but further investigation into the pH or conductance of water/acetic acid mixture would be required to shed further light on this aspect. Another possible effect of water considered is the change of polarity of the solvent.

In considering oxidative addition in Chapter 1 (section 1.3.3) two possible mechanisms can be outlined for the oxidative addition of hydrogen iodide. Firstly addition of a proton followed by the iodide anion would produce a neutral intermediate $[HRh(CO)_2I_2]$; this would not appear to be favoured(7). The alternative initial addition of iodide anion would produce the dianion $[Rh(CO)_2I_3]^{2-}$ which would be favoured by a more polar solvent. Hickey(8) has shown the rate of this latter addition reaction for anhydrous system to be dependent on iodide anion concentration. Protic attack on the dianion would then give $[HRh(CO)_2I_3]^-$. These steps will both be favoured by a more polar solvent system.

This investigation has shown that the rhodium-iodide systems are complex and involve competing reactions to the main catalytic cycle (Figure 3.5). Figure 3.8 shows just three of these reactions and their possible interaction. The Monsanto process initiates these systems by ethyliodide carbonylation. The hydrocarbonylation reaction may then proceed, possibly via hydrogen iodide oxidative addition. The Water Gas Shift reaction may regenerate $[Rh(CO)_2I_2]^-$ from $[Rh(CO)_2I_4]^-$. Alternatively $[Rh(CO)_2I_4]^-$ may degrade to rhodium(III) iodide and then be reductively carbonylated to return the rhodium moiety to the hydrocarbonylation cycle.

It has not been possible to define the precise reaction pathway for the hydrocarbonylation reaction. The conclusions drawn do not permit an unambiguous interpretation, and must therefore be considered as individual facts. Investigation of the rhodium-chloride systems described in Chapters 4 and 5 may be of use in further interpreting these conclusions, therefore a further summary of both systems is included at the end of Chapter 5.

Figure 3.8



A summary of catalytic cycles

3.8 Chapter 3 - Reaction Index

Reaction Number	Reactants/Moles	Solvents	Temperature °C	Gases	Pressure Range/bar	Rate of Reaction mol/kg/hr	Reaction Code
3.2.1	$RhCl_3.3H_2O$, 4.99×10^{-4} HI, 3.08×10^{-2} EtI, 1.62×10^{-1} H_2O, 1.0	C_2H_5COOH	180	CO C_2H_4	80 -4	5.3	BP1R18
3.2.2	$RhCl_3.3H_2O$, 5.05×10^{-4} EtI, 6.2×10^{-2} H_2O, 5.55×10^{-1}	C_2H_5COOH	180	CO C_2H_4	80 - 17	0.63	BP1R14
3.2.3	$RhCl_3.3H_2O$, 5.12×10^{-4} EtI, 6.2×10^{-2}	C_2H_5COOH	180	CO C_2H_4	78 - 37	1.16	BP1R4
3.2.4	RhI_3, 4.98×10^{-4} EtI, 4.97×10^{-2} H_2O, 5.0×10^{-1}	C_2H_5COOH	180	CO C_2H_4	65 - 5	1.55	BP2R12A
3.2.5	RhI_3, 5.01×10^{-4} EtI, 4.97×10^{-2} H_2O, 5.0×10^{-1}	C_2H_5COOH CH_2Cl_2	180	CO C_2H_4	73 - 15	1.24	BP2R12
3.2.6	$RhCl_3.3H_2O$, 9.87×10^{-5} EtI, 3.73×10^{-2} H_2O, 1.67×10^{-1}	CH_3COOH	192	CO C_2H_4	143 - 42	18.1	D3HR69
3.2.7	RhI, 1.04×10^{-4} EtI, 3.73×10^{-2} H_2O, 1.67×10^{-1}	CH_3COOH	187	CO C_2H_4	138 - 23	15.7	

Reaction Number	Reactants/Moles	Solvents	Temperature °C	Gases	Pressure Range/bar	Rate of Reaction mol/kg/hr	Reaction Code
3.3.1	$RhCl_3.3H_2O$, 5.30×10^{-4} HI, 2.11×10^{-3} EtI, 2.48×10^{-2} H_2O, 5.55×10^{-1}	EtOH	180	CO C_2H_4	80 - 38	0.15	BP1R9
3.3.2	$RhCl_3.3H_2O$, 4.98×10^{-4} EtI, 1.24×10^{-1}	EtOH	180	CO	80 - 3	0.32	BP1R2
3.3.3	$RhCl_3.3H_2O$, 5.17×10^{-4} EtI, 1.24×10^{-1}	EtOH	180	CO C_2H_4	80 - 15	0.99	BP1R5
3.3.4	$RhCl_3.3H_2O$, 5.3×10^{-4} EtI, 6.22×10^{-3}	EtOH	180	CO C_2H_4	80 - 51	0.13	BP1R12
3.3.5 and 3.3.6	$RhCl_3.3H_2O$, 5.28×10^{-4} HI, 6.36×10^{-3}	EtOH	180	CO C_2H_4	80 - 65	0.045	BP1R6
3.3.8	$RhCl_3.3H_2O$, 4.89×10^{-4} H_2O, 5.55×10^{-1}	EtI	180	CO	80 - 49	0.013	BP1R15
3.39	$RhCl_3.3H_2O$, 5.31×10^{-4} HI, 2.13×10^{-3} $\underset{1}{H}_2O$, $5.55 \times 10^{74,34}$	EtI	180	CO C_2H_4	80 - 46	0.416	BP1R10
3.4.1	RhI_3, 5.04×10^{-4} EtI, 4.96×10^{-2} H_2O, 5.00×10^{-1}	C_2H_5COOH CH_2Cl_2	180	CO C_2H_4	83 - 27	0.99	BP2R14

3.8 Chapter 3 - Reaction Index (cont)

Reaction Number	Reactants/Moles	Solvents	Temperature °C	Gases	Pressure Range/bar	Rate of Reaction mol/kg/hr	Reaction Code
3.4.2	RhI_3, 4.95×10^{-4} EtI, 4.96×10^{-2} H_2O, 5.00×10^{-1}	C_2H_5COOH CH_2Cl_2	180	CO C_2H_4	86 - 11	1.46	BP2R15
3.4.3	RhI_3, 5.12×10^{-4} EtI, 4.96×10^{-2} H_2O, 5.00×10^{-1}	C_2H_5COOH CH_2Cl_2	180	CO C_2H_4	86 - 15	1.24	BP2R12
3.4.4	RhI_3, 4.98×10^{-4} EtI, 4.96×10^{-2} H_2O, 5.00×10^{-1}	C_2H_5COOH CH_2Cl_2	180	CO C_2H_4	78 - 5	1.25	BP2R13
3.4.5	RhI_3, 5.04×10^{-4} EtI, 4.96×10^{-2} H_2O, 5.00×10^{-1}	C_2H_5COOH CH_2Cl_2	180	CO C_2H_4	81 - 28	0.04	BP2R13
3.5.1	$RhCl_3.3H_2O$, 5.15×10^{-4} EtI, 6.2×10^{-2} H_2O, 5.55×10^{-1}	CH_2Cl_2	180	CO C_2H_4	87 - 25	1.17	BP1R3
3.5.2	$RhCl_3.3H_2O$, 5.20×10^{-4} EtI, 6.2×10^{-2} EtOH, 5.26×10^{-1}	CH_2Cl_2	180	CO C_2H_4	80 - 50	0.105	BP1R13
3.5.3	$RhCl_3.3H_2O$, 5.13×10^{-4} EtI, 6.2×10^{-2} C_2H_5COOH, 5.02×10^{-1}	CH_2Cl_2	180	CO C_2H_4	80 - 51	0.081	BP1R11

3.8 Chapter 3 - Reaction Index (cont)

Reaction Number	Reactants/Moles	Solvents	Temperature °C	Gases	Pressure Range/bar	Rate of Reaction mol/kg/hr	Reaction Code
3.5.4	RhI_3, 1.05×10^{-4} EtI, 3.73×10^{-2} H_2O, None	CH_3COOH	180	CO C_2H_4	150 - 69	0.603	D3HR77
3.5.5	RhI_3, 1.08×10^{-4} EtI, 3.73×10^{-2} H_2O, 1.11×10^{-4}	CH_3COOH	183	CO C_2H_4	124 - 64	6.86	D3HR78
3.5.6	RhI_3, 1.09×10^{-4} EtI, 3.73×10^{-2} H_2O, 1.11×10^{-3}	CH_3COOH	185	CO C_2H_4	108 - 25	9.16	D3HR79
3.5.7	RhI_3, 1.04×10^{-4} EtI, 3.73×10^{-2} H_2O, 1.11×10^{-2}	CH_3COOH	187	CO C_2H_4	110 - 35	15.0	D3HR80
3.5.8	RhI_3, 1.04×10^{-4} EtI, 3.73×10^{-2} H_2O, 1.16×10^{-1}	CH_3COOH	187	CO C_2H_4	138 - 23	15.7	D3HR76
3.6.1	RhI_3, 2.89×10^{-4} H_2O, 1.67×10^{-1}	C_2H_5COOH CH_2Cl_2	180	CO C_2H_4	48 - 10	0.04	BP2R17
3.6.2	RhI_3, 2.89×10^{-4} H_2O, 1.67×10^{-1} EtI, 1.0×10^{-2}	C_2H_5COOH CH_2Cl_2	180	CO C_2H_4	55 - 1	5.28	BP2R18

3.8 Chapter 3 - Reaction Index (cont)

Reaction Number	Reactants/Moles	Solvents	Temperature ° C	Gases	Pressure Range/bar	Rate of Reaction mol/kg/hr	Reaction Code
3.6.3	RhI_3, 3.03×10^{-4} H_2O, 1.67×10^{-1} EtI, 1.0×10^{-2}	C_2H_5COOH CH_2Cl_2	180	CO C_2H_4	50 - 27	0.68	BP2R19
3.6.4	RhI_3, 1.10×10^{-4} EtI, 3.73×10^{-2} H_2O, 1.67×10^{-1}	CH_3COOH	190	CO	144 - 28	18.10	D3HR69
3.6.5	RhI_3, 1.08×10^{-4} EtI, 2.48×10^{-2} H_2O, 1.67×10^{-1} HI, 5.26×10^{-3}	CH_3COOH	192	CO	175 - 42	7.69	D3HR70
3.6.6	RhI_3, 1.09×10^{-4} EtI, 3.73×10^{-2} H_2O, 1.67×10^{-1} I_2, 1.01×10^{-3}	CH_3COOH	191	CO	120 - 47	7.30	DrHR81
3.6.7	RhI_3, 1.06×10^{-4} EtI, 3.73×10^{-2} H_2O, 1.67×10^{-1} H_3PO_2, 1.27×10^{-3}	CH_3COOH	182	CO	160 - 39	1.98	D3HR109
3.6.8	RhI_3, 1.04×10^{-4} EtI, 3.73×10^{-2} H_2O, 1.67×10^{-1} $C_2H_5COO^-Li^+$, 1.39×10^{-3}	CH_3COOH	182	CO	160 - 39	1.98	D3HR109

CHAPTER 3 - REFERENCES

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CHAPTER FOUR

CONTENTS

CHAPTER 4

RHODIUM-TIN COCATALYST SYSTEMS FOR HYDROCARBONYLATION

4.1 Introduction

The utilisation of the trichlorostannate(I) anion $[SnCl_3]^-$ as a ligand for transition metal complexes was reported in 1964 by Young et al(1). Later Lindsey et al(2) showed the ligand to be a poor σ-donor and strong π-acceptor. This work indicates that the ligand is π-acidic in the manner that carbon monoxide and ethene were defined in Chapter 1. Furthermore it has been shown that using the criteria of Chatt(3) that $SnCl_3^-$ is a very strong trans-activating ligand(2), far stronger than the iodide ligand. Platinum-tin complexes are known as catalytic systems for a variety of reactions, including the hydrogenation of ethene and ethyne(4), the hydrocarbonylation of ethene(5) and also the Water Gas Shift reaction(6). A number of rhodium-trichlorostannate complexes have been synthesised(1, 7, 8), but of particular interest are $[Rh(CO)_2(SnCl_3)_3]^{2-}$ and $[Rh(CO)(SnX_3)X_2]^{2-}$ (X = Cl, I)(8). These rhodium(I) complexes are vulnerable to oxidative-addition as shown in Chapter 1. Given this ability these rhodium-tin complexes become viable alternatives to the $[Rh(CO)_2I_2]^-$ species central to the Monsanto and hydrocarbonylation reactions considered in Chapters 2 and 3.

4.2 Initial Systems

All reactions were conducted in the 105 ml Hastalloy C autoclave. Details of precise amounts of reactants used are listed in section 4.10 for all reactions described in this chapter.

The initial system used employed hydrous rhodium(III) chloride and hydrous tin(II) chloride in a ratio of 1:2 respectively. Tin(II) chloride is known to form $HSnCl_3$ in hydrochloric acid solution(9), therefore a small volume of concentrated hydrochloric acid was employed in addition to the acetic acid solvent.

Components:

$RhCl_3.3H_2O$: $SnCl_2.2H_2O$: HCl(aq)37% : CH_3CO_2H : CO, 40 bar : C_2H_4, 40 bar

Temperature: 180°C

Reaction Number	*Moles of Propanoic Acid produced*	*Rate (1) /bar.hr^{-1}*	*Rate (2) /mol/kg^{-1}/hr^{-1}*	*% (3) selectivity*
4.2.1	*0.101*	*21.0*	*0.89*	*80.1%*

Notes: (1) Rate of Gas Absorption

(2) Rate of Propanoic Acid production

(3) Percentage Propanoic Acid of all reaction products as determined by G.L.C.

In comparison with the reaction of the rhodium-iodide systems of Chapter 3, the rate of reaction is some 20-fold slower. The selectivity of the reaction is comparable with that of the rhodium-iodide system. To investigate the by-products of the reaction, the final solution was analysed by gas chromatograph mass spectrometry. The major by-products detected were ethylacetate and ethylpropanoate, with only trace quantities of chloroethane and ethanol. It would appear that ethene reacts by some mechanism to form an ethyl moiety, which reacts immediately with the two carboxylic acids present. It should be noted that although the ethylpropanoate moiety must have been produced by hydrocarbonylation reaction, it is not considered as product in the calculation of rate of reaction or selectivity.

There are three other minor by-products: these being butylacetate, butylpropanoate and 2-chlorobutane. The former two by-products would be formed by reaction of the carboxylic acids with the butyl moiety evidently present, as indicated by the formation of 2-chlorobutane. Therefore the by-products of this reaction are the result of the formation of ethyl or butyl moieties. There is no indication thus far, of how these ethyl and butyl moieties are formed; investigations will therefore be made in an attempt to adjust the reaction conditions and the nature of the reactants to improve rate, selectivity and yield.

A further reaction was conducted under identical conditions, but with the addition of benzyltriethylammonium chloride.

Reaction Number	*Component*	*Moles of Propanoic Acid produced*	*Rate (1) /bar.hr^{-1}*	*Rate (2)/ mol.kg^{-1}.hr^{-1}*	*% (3) selectivity*
4.2.2	$PhCH_2(Et)_3NCl$	0.121	137	5.4	88.6%

The addition of the cation has produced a six-fold increase in rate of reaction and has also increased the selectivity.

A number of test reactions were conducted without one of either rhodium(III) chloride or tin(II) chloride, in general little or no reactions occur. The results of these "blank" reactions reflected on the method employed to clean the autoclave. This indicates that trace amounts rhodium and/or tin available from the surface of the autoclave are sufficient to achieve reaction, and total cleaning of the autoclave is difficult.

The possibility that the active tin moiety may either be a tin(II) or tin (IV) compound led to a reaction being conducted with $[Bz(Et)_3N]_2$ $SnCl_6$. The conditions were as for reaction 4.2.1 with no tin(II) chloride being employed.

Reaction Number	*Moles of Propanoic Acid produced*	*Rate (1) /bar.hr^{-1}*	*Rate (2) /mol.kg^{-1}.hr^{-1}*	*% (3) selectivity*
4.2.3	*0.107*	*51.4*	*1.44*	*68.9%*

Although the rates and selectivity are relatively poor it is clearly demonstrated that both tin(II) and tin(IV) compounds are viable as precursors to the co-catalyst.

Dichlorotetracarbonyldirhodate(I) is well known as a starting compound for the synthesis of other rhodium complexes(11). Its use in place of rhodium(III) chloride as a precursor was investigated utilising the same reaction conditions and molar quantities, as reaction 4.2.2.

Reaction Number	*Moles of Propanoic Acid produced*	*Rate (1) /bar.hr^{-1}*	*Rate (2) /mol.kg.$^{-1}$.hr^{-1}*	*% (3) selectivity*
4.2.4	0.05	113	2.39	51.2%

While this reaction has a good rate of reaction, it has very poor selectivity. Rhodium(III) chloride was therefore employed in further reactions.

4.3 Effects of Solvent on Reaction Activity

As has been noted in section 4.2 and will be apparent in section 4.6, the presence of 37% hydrochloric acid is essential for reaction. This offers the possibility of employing hydrochloric acid as the solvent. A number of other solvents were also considered, as for the rhodium-iodide system (see section 3.3), and the results are summarised below.

Standard components:

$RhCl_3.3H_2O$: $SnCl_2.2H_2O$: $HCl(aq)37\%$: $Bz(Et)_3NCl$: CO, 40 bar : C_2H_4, 40 bar;

Temperature: 180^oC

Reaction Number	**Solvent**	**Moles of Propanoic Acid produced**	**Rate (1) /bar.hr^{-1}**	**Rate (2) /mol.kg$^{-1}\cdot$hr^{-1}**	**% (3) selectivity**
4.3.1	2M.HCl(aq)	0.045	6.0	0.200	59.5%
4.3.2	$HCOOCH_3$	0	0	0	0
4.3.3	$CH_3COOC_2H_5$	0.006	18.8	0.0024	6.3%
4.3.4	$(C_2H_5)_2O$	0.003	16.4	0.093	12.6%
4.3.5	$(CH_3)_2CO$	0.055	158	6.25	36.8%

It can readily be seen that all the solvents employed are much less effective than acetic acid. Only two (HCL(aq) and acetone) of the five used offer any interest. Despite poor selectivity, reaction does occur in 2M hydrochloric acid. It is possible that the active catalyst is being maintained in solution by the high chloride concentration. As tin(II) chloride is a well known reducing agent in hydrochloric acid solution, the production of rhodium metal might have been expected. Either this does not occur or we have a heterogeneous catalytic system formed "in situ".

Acetone gives excellent rates of reaction, although a number of side reactions occur. Foremost is the Aldol condensation to produce mesityloxide. Having produced this activated alkene there is the possibility of addition of $HSnCl_3$ across the double bond.

Furthermore it is just as possible that mesityloxide will be hydrocarbonylated. It is not feasible to eliminate these acid catalysed side reactions, therefore acetone is not viable as a solvent.

The following reactions investigate the possibility that co-reaction may be obtained in an alcohol solvent, to carbonylate the alcohol and hydrocarbonylate ethene. The first reaction attempts the "Monsanto" process, conversion of methanol to acetic acid. The second reaction also contains ethene to study hydrocarbonylation in alcohol solvents.

Standard components:

$RhCl_3.3H_2O : SnCl_2.2H_2O : HCl(aq)37\% : Bz(Et)_3NCl : CH_3OH;$

Temperature: 180°C

Reaction Number	***Component***	***Moles of Propanoic Acid produced***	***Rate (1) /bar.hr^{-1}***	***Rate (2) /mol.kg^{-1}hr^{-1}***	***% (3) selectivity***
4.3.6	*CO, 80 bar*	-	*- 10*	-	-
4.3.7	*CO, 40 bar: C_2H_4, 40 bar*	-	*- 7*	-	-

No carbonylation or hydrocarbonylation was observed in either case. The rise in pressure during the reactions may be attributed to either the Water Gas Shift reaction or to the production of methane by a process similar to that observed by Drury et al(10).

In attempting infra-red studies of these rhodium-tin-chloride systems, a solvent system was required which was free of absorptions in the region 2300 - 1600 cm^{-1}. A similar problem arose for rhodium-iodide systems (see section 2.5.1). Therefore a reaction was conducted employing a mixed solvent system of propanoic acid and dichloromethane. As shown, alcohols are inert when employed with this catalyst system. Therefore a mixed solvent of acetic acid and ethanol was also considered.

Standard components:

$RhCl_3.3H_2O$: $SnCl_2.2H_2O$: *HCl(aq)37%* : $Bz(Et)_3NCl$: *CO, 40 bar* : C_2H_4, *40 bar*

Temperature: 180°C

Reaction Number	*Solvent*	*Moles of Propanoic Acid produced*	*Rate (1) /bar.hr^{-1}*	*Rate (2)/ mol.kg^{-1}·hr^{-1}*	*% (3) selectivity*
4.3.8	CH_3CO_2H/C_2H_5OH	0.024	0	0.61	41.8%
4.3.9	$C_2H_5CO_2H/CH_2Cl_2$	0.067	1.88	0.515	45.0%

Neither reactions give good rates or selectivity. It may be possible to use either for infra-red studies. The fact that there is no noted change in pressure for reaction 4.3.8, despite the production of propanoic acid, suggests that gaseous by-products are formed by side-reactions during this reaction. Therefore the solvent system of reaction 4.3.9 is employed in Chapter 5.

In general the only acceptable solvents that have been employed are propanoic or acetic acid; further studies were confined to acetic acid solvent.

4.4 Investigation of Cation Effects

Reaction 4.2.2 demonstrated the beneficial effects obtained by addition of benzyltriethylammoniumchloride. In investigating the effect of other cations, an assortment of quaternary ammonium salts was used, and also salts of the alkali metals, lithium and caesium. Reaction 4.2.2 is included in the table below for comparison.

Standard components:

$RhCl_3.3H_2O$: $SnCl_2.2H_2O$: $HCl(aq)37\%$: CH_3CO_2H : CO, 40 bar, C_2H_4, 40 bar;

Temperature: 180°C

Reaction Number	*Cation*	*Moles of Propanoic Acid produced*	*Rate (1) /bar.hr^{-1}*	*Rate (2) /mol.kg^{-1}.hr^{-1}*	*% (3) selectivity*
4.2.2	$Bz(Et)_3NCl$	0.121	137	5.41	88.6%
4.4.1	Bu_4NCl	0.088	220	8.97	44.2%
4.4.2	$PPN^{\oplus}Cl^{\ominus}$ †	0	24.4	0	0
4.4.3	Li_2CO_3	0.105	48.9	1.22	97.6%
4.4.4	CsCl	0.099	67.3	3.91	87.3%

† $PPN^{\oplus} \equiv [Ph_3P = N = PPh_3]^+$

The first three reactions listed in the table above, show great variations in reactivity for the three ammonium cations employed. $PPN^{\oplus}Cl^{-}$ is obviously not effective. However tetrabutylammonium chloride gives very good rates, although the usefulness of this cation is tempered somewhat by its poor selectivity. It was noted that reaction 4.4.1 was strongly exothermic at approximately 170°C when the temperature rose to 205°C for a short period. It is possible therefore that the poor selectivity of this reaction is due to this exothermic reaction generating high temperatures which initiate other side reactions forming by-products. The effect of different temperatures on this reaction is considered later.

Turning to the reactions employing alkali metal cations, lithium gives reasonable rates of reaction but excellent selectivity. Caesium gives both rates and selectivity comparable with that of reaction 4.2.2. This would indicate that the effects of the presence of $Bz(Et)_3NCl$ are due to its cationic nature in forming ion pairs rather than its phase transfer agent nature. Therefore the difference in action between $Bz(Et)_3NCl$, Bu_4NCl and $PPN^{+}Cl^{\ominus}$ are due to their ability to act as effective cations of the groups attached to nitrogen.

During the heating period of reaction 4.4.1, a distinctly rapid temperature increase was observed, in excess of that normally due to the heating element. This suggested that a exothermic reaction occurred at approximately 150 - 170°C. Therefore a number of reactions were conducted using the tetrabutylammoniumchloride, to consider the optimum reaction temperature.

Standard components:

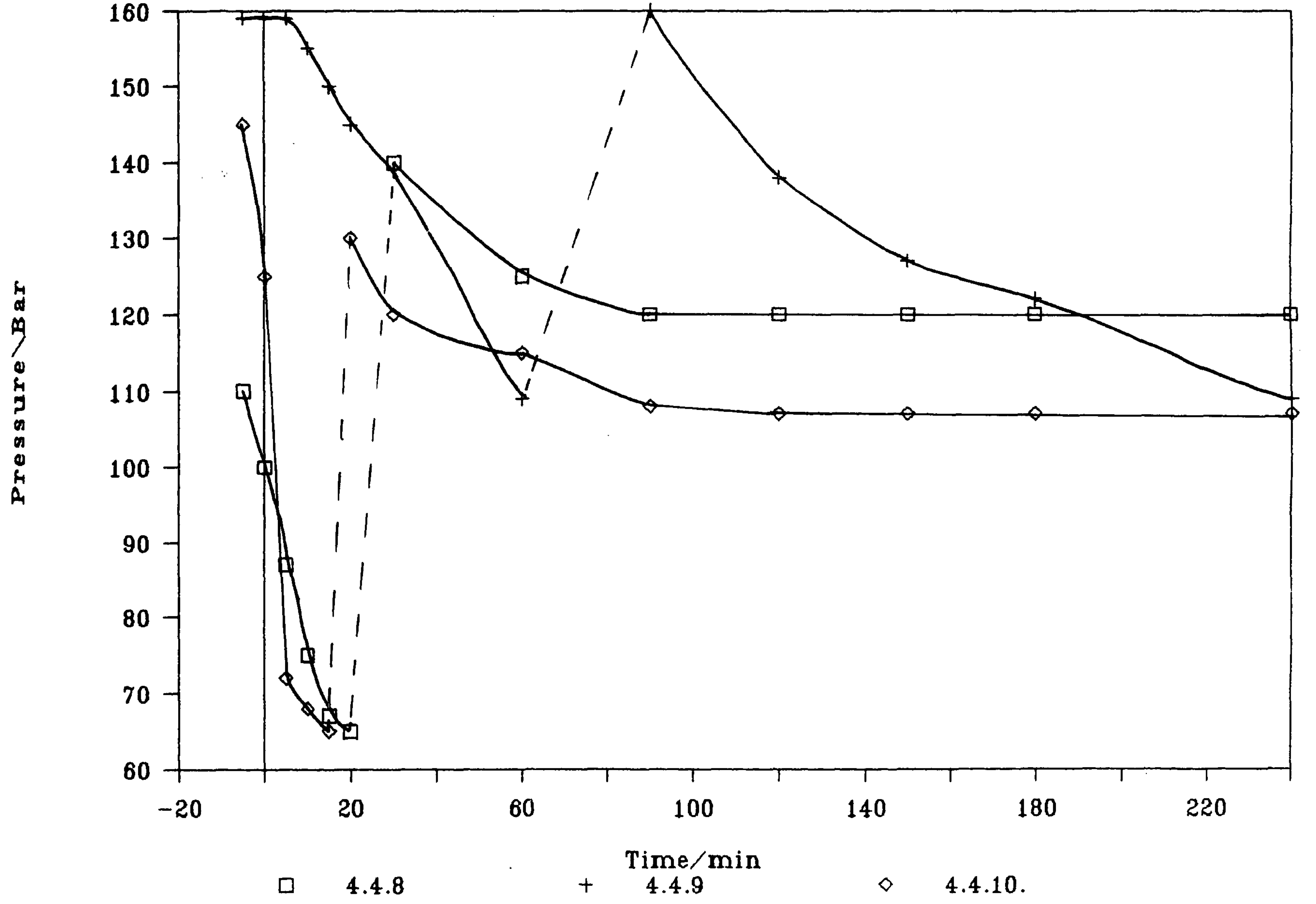
$RhCl_3.3H_2O$: $SnCl_2.2H_2O$: $HCl(aq)37\%$: Bu_4NCl : CH_3CO_2H : CO, 40 bar : C_2H_4, 40 bar;

Reaction Number	Temperature /°C	Moles of Propanoic Acid produced	Rate (1) /bar.hr^{-1}	Rate (2)/ mol.kg^{-1}.hr^{-1}	% (3) selectivity
4.4.1	180	0.088	220	8.97	44.2%
4.4.5	150	6×10^{-4}	240	0.097	0.5%
4.4.6	120	5.6×10^{-3}	102	0.17	10.1%
4.4.7	100	6.2×10^{-3}	30	0.073	4.5%

From these reactions we can see that the production of propanoic acid almost ceases when the reaction temperature is 150°C or less. However there is a large amount of gas absorbed during reactions 4.4.5 and 4.4.6, suggesting that the ethene and/or carbon monoxide react to form other products. Approximately 90 - 95% of the reaction products can be shown by G.C.M.S. to be butyl-moieties, mainly butylacetate with some 2-chlorobutane. This raises the possibility that the by-products formed in other reactions are not formed at the reaction temperature, but during the heating period of the autoclave. Therefore it is possible that the selectivity of these catalyst systems would be greater if maintained at 180°C.

There are two methods to confirm this hypothesis, unfortunately neither were available to this study. Firstly, a constant flow autoclave system could be used and the product heating period isolated from the analysis of the reaction. Secondly, a catalyst tip autoclave, such as that described in Chapter 7, would isolate both rhodium and tin from the reaction mixture until the reaction reached 180°C.

Figure 4.1


Pressure\Bar
160
150
140
130
120
110
100
90
80
70
60
−20
20
60
100
140
180
220
Time/min
□ 4.4.8
+ 4.4.9
◇ 4.4.10.

In considering the effect of these cations, it is possible that they stabilise the catalytic species. If this is the case then it is possible that, once reaction has taken place, re-introduction of the reactant gases, carbon monoxide and ethene, will produce further reaction.

Figure 4.1 shows the pressure profiles for three such reactions. Reaction 4.4.8 has the same composition as reaction 4.4.1 (see section 4.10 for details) and was repressurised when the pressure approached 60 atmospheres, the region at which reaction often finished. Reaction 4.4.9 is a similar reaction system (see section 4.10). However lithium replaces benzyltriethylammoniumchloride as the cation. For comparison a rhodium-iodide system similar to reaction 3.2.6 (see sections 3.8 and 4.10) has its profile presented in Figure 4.1 as reaction 4.4.10.

The figure shows that the tetrabutylammoniumchloride, rhodium-tin-chloride system behaves in a similar manner to that of the rhodium-iodide system. However the lithium system appears to retain its activity longer than the other systems. While the rate of reaction is much slower initially, and also this reaction started at higher pressure, it would still appear that reaction 4.4.9 is the more stable catalyst system.

4.5 Rhodium-Tin Ratio

So far all reactions employing rhodium and tin have involved a rhodium to tin ratio of 1:2. The synthesis of $[Rh_2Cl_2(SnCl_3)_4]^{4-}$ (11) employs a ratio of 1:3 to permit the reduction of rhodium(III) to rhodium(I) by one equivalent of tin(II). Consequently a study of the relative activity of systems containing varying ratios of rhodium to tin was undertaken to investigate the action of tin in the catalytic process.

Standard components:

$RhCl_3.3H_2O$: $SnCl_2.2H_2O$: $HCl(aq)37\%$: $Bz(Et)_3NCl$: CH_3CO_2H : $CO, 40$ *bar* : $C_2H_4, 40$ *bar;*

Temperature: *180°C*

Reaction Number	*Rhodium:Tin Ratio*	*Moles of Propanoic Acid produced*	*Rate (1) /bar.hr^{-1}*	*Rate (2) /mol.kg^{-1}.hr^{-1}*	*% (3) selectivity*
4.5.1	2:1	0.080	54.5	2.88	93.0%
4.5.2	1:1	0.115	63.0	2.97	91.4%
4.5.3	1:2	0.116	88.0	5.72	79.6%
4.5.4	1:4	0.016	160	1.69	50.7%
4.5.5	1:6	0.037	41.9	0.72	42.9%

As can be seen from Figure 4.2, while the rhodium to tin ratios of 2:1 and 1:1 give good reaction rates they are almost half that achieved by the 1:2 ratio, that has previously been employed. When the ratio is increased to 1:4 and above there is a marked decrease in activity. In contrast Figure 4.3 shows the continual decrease in selectivity for the same series of reactions. These conflicting trends mean that optimum conditions are to be found in the region of a ratio of 1:2. It seems probable therefore that two trichlorostannate ligands are involved in the hydrocarbonylation reaction. It is obvious from Figure 4.3 that more by-products are formed as the amount of tin present increases. Investigation of reaction 4.5 by G.C.M.S. shows the major by-products to be butylacetate and 2-chlorobutane, whereas G.C.M.S. has

Figure 4.2

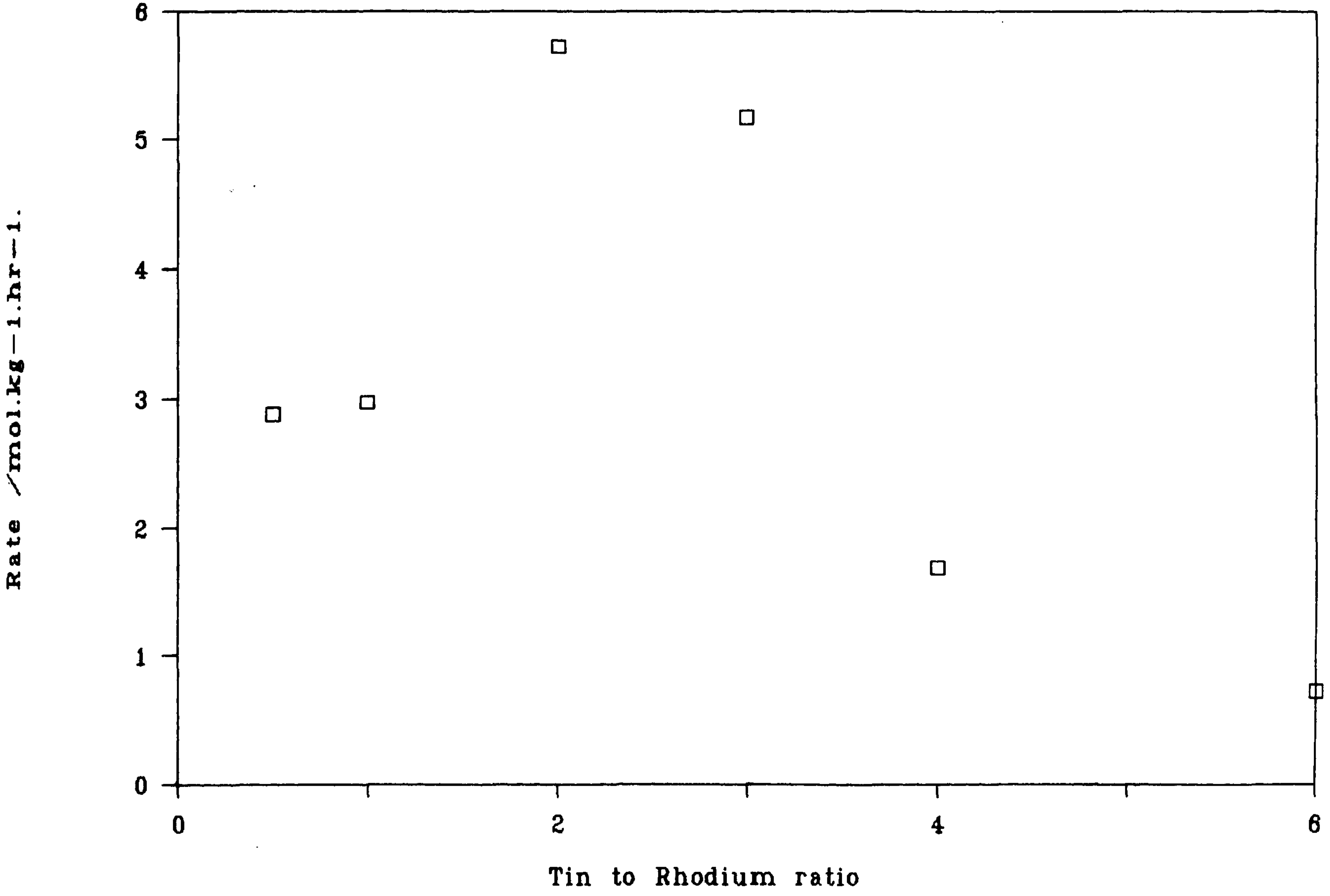
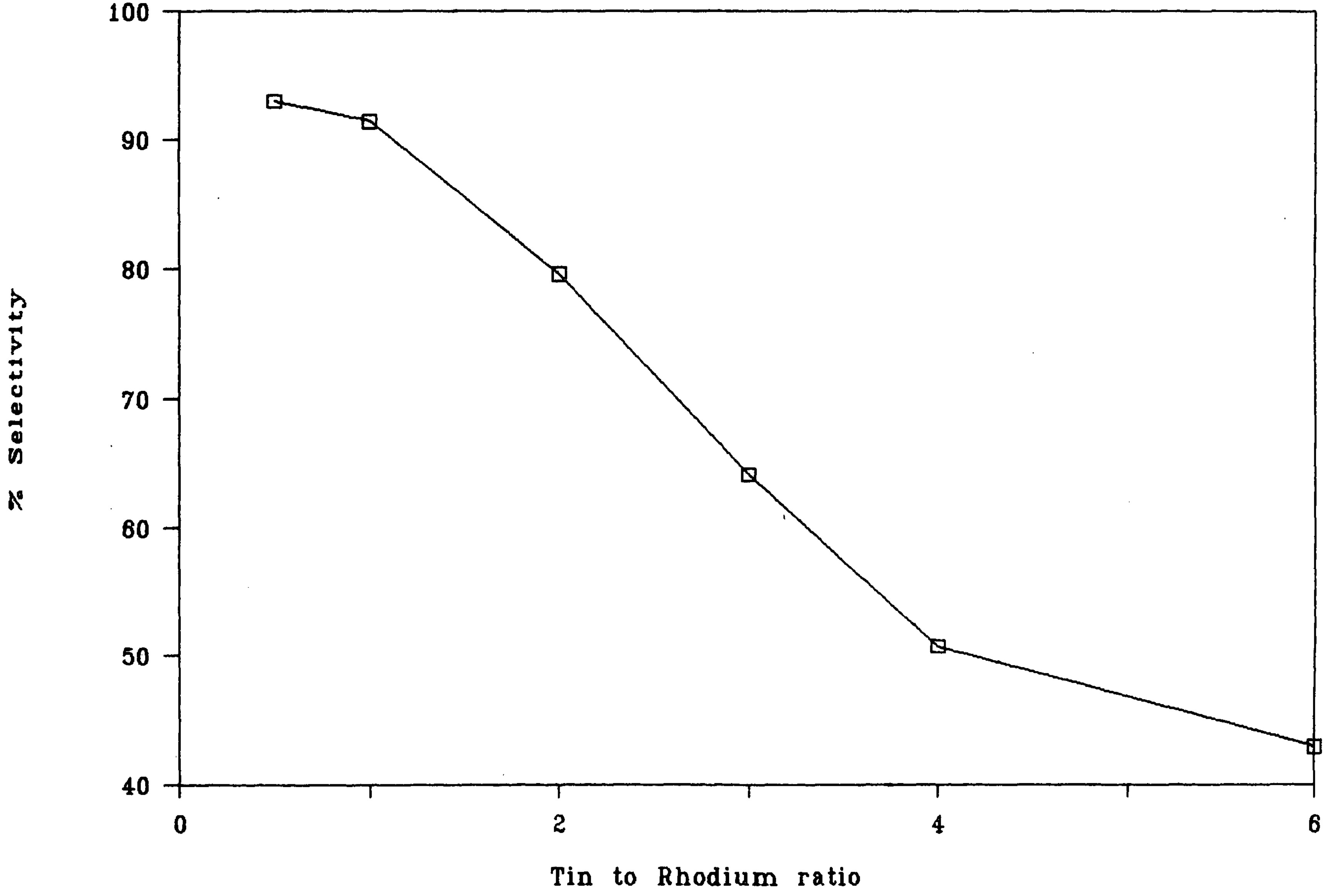


Figure 4.3



shown that the major impurities for reaction 4.2.1 were chloroethane and ethylacetate. It would therefore seem likely that side reactions form chloro-ethyl or chloro-butyl moieties are dependent on the presence of tin. It is possible that either the extreme conditions or the presence of rhodium activates one or more ethene molecules to attack by $HSnCl_3$, producing $C_2H_5SnCl_3$ or $C_4H_9SnCl_3$ would then react with hydrogen chloride or alkanoic acids to generate chloroalkanes or alkylalkanoic acid respectively to regenerate $HSnCl_3$.

More significantly it is conceivable that $EtSnCl_3$ oxidatively adds to a rhodium(I) complex prior to carbonylation. This oxidative addition is equally feasible for chloroethane (if formed from HCl and C_2H_4) both possibilities are shown in Figure 4.4.

As rhodium(III) chloride is generally accepted to be inert to oxidative addition, the possibility that chloroethane or $C_2H_5SnCl_3$ oxidatively adds to a rhodium-tin complex must also be considered. Thus it is possible to produce complex (i) (Figure 4.4) by a number of different pathways.

In all of these postulated cases it should be noted that only carbonylation occurs at the rhodium centre, not hydrocarbonylation, as in the case of the rhodium-iodide case demonstrated by Forster(12).

Following the formation of complex (i) (Figure 4.4) two alternative reductive elimination routes may be envisaged (Figure 4.5). $[SnCl_3]^-$ is known to be a very good leaving group(2, 13) and it is possible that it is in this role that the $[SnCl_3]^-$ ligand acts to catalyse the reaction. However in such protic and hydrous conditions it is unlikely that reductive elimination is rate determining as it has been shown in the Monsanto process that oxidative addition is rate limiting(14). Forster's work on ethyliodide and hydrogen iodide addition(12) suggests this is also the case for hydrocarbonylation. Rhodium-chloride catalyst systems are not very active for the hydrocarbonylation process. This would be interpreted as due to the slow oxidative addition of hydrogen chloride to $[Rh(CO)_2Cl_2]^-$. While two possible alternative oxidative additions have been outlined in Figure 4.4, there are also three other possibilities: (i) oxidative addition of $HSnCl_3$ to a rhodium complex; (ii) $HSnCl_3$ addition to a rhodium-tin complex, and (iii) oxidative addition of hydrogen chloride to a rhodium-tin complex.

(i) $HSnCl_3 + Rh^{(I)}L_x \longrightarrow HRh^{(III)}L_x(SnCl_3)$

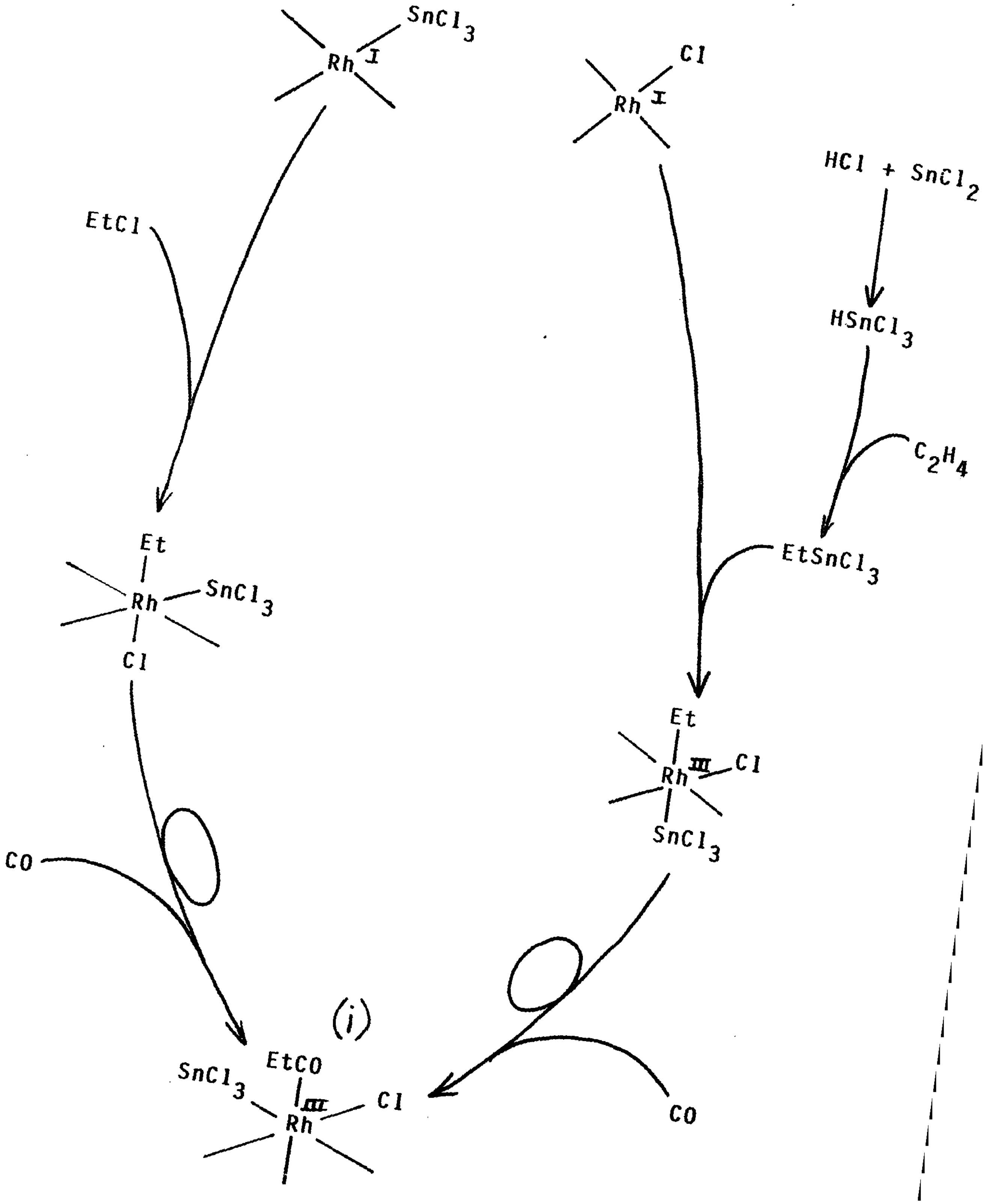
(ii) $HSnCl_3 + Rh^{(I)}(SnCl_3)L_{x-1} \longrightarrow HRh^{(III)}L_{x-1}(SnCl_3)_2$

(iii) $HCl + Rh^{(I)}L_y(SnCl_3)_z \longrightarrow HRh^{(III)}L_y(SnCl_3)_zCl$

$x = 4$ or 5, $y + z = x$

In investigating these alternatives the possibility that hydrochloric acid may additionally stabilise $HSnCl_3$ and stop formation of tin oxides must be considered. Poor reaction in the absence of hydrogen chloride may be due to this latter role and not necessarily an oxidative addition role. The first line of investigation will consider the attack of ethylchloride and possibly $EtSnCl_3$ on a rhodium or rhodium-tin complex (see section 4.6).

Figure 4.4


SnCl$_3$
Rh^{I}
Cl
Rh^{I}
EtCl
HCl + SnCl$_2$
HSnCl$_3$
C$_2$H$_4$
EtSnCl$_3$
Et
Rh
SnCl$_3$
Cl
Et
Rh^{III}
Cl
SnCl$_3$
CO
(i)
EtCO
SnCl$_3$
Rh^{III}
Cl
CO

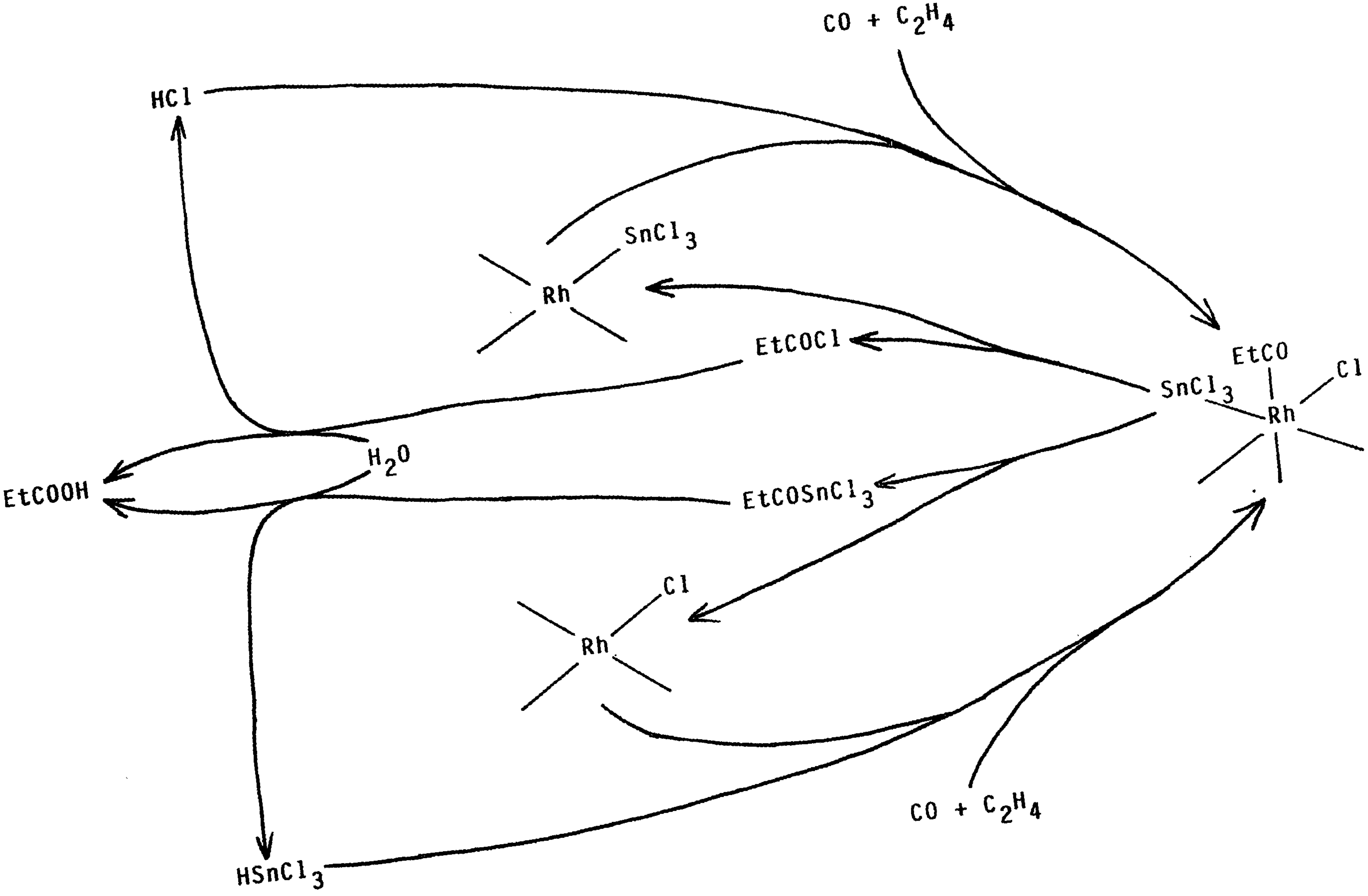

CO + C_2H_4
HCl
$SnCl_3$
Rh
EtCOCl
EtCO
Cl
$SnCl_3$
Rh
H_2O
EtCOOH
$EtCOSnCl_3$
Cl
Rh
CO + C_2H_4
$HSnCl_3$

Figure 4.5

If oxidative addition involves "$SnCl_3$" moieties, we would expect to see an increase in reactivity as the amount of tin(II) chloride present increases. As shown in Figure 4.2 this does not occur, and may be due to the $SnCl_3$ ligand occupying many of the available co-ordination sites, as occurs possibly for platinium(2).

This action may block co-ordination sites towards attachment of carbon monoxide or ethene, thus inhibiting the hydrocarbonylation reaction.

4.6 Reactions of Chloroethane

As has been indicated, the oxidative-addition of chloroethane, or possibly $EtSnCl_3$, to a rhodium centre, could be the initial step in the rhodium-tin-chloride catalyst systems. Two reactions were conducted, with and without added hydrochloric acid, employing chloroethane in the absence of ethene.

Standard components:

$RhCl_3.3H_2O : SnCl_2.2H_2O : Bz(Et)_3N^{\oplus}Cl : CH_3CO_2H : CO$, *50 bar*

Temperature: 180°C

Reaction Number	**Component**	**Moles of Propanoic Acid produced**	**Rate (1) /bar/hr^{-1}**	**Rate (2) /mol.kg^{-1}.hr^{-1}**	**% (3) selectivity**
4.6.1	EtCl	0.015	0	0.38	38.7%
4.6.2	EtCl:HCl(aq)37%	0.050	0	1.53	73.5%

In both reactions there was no observable pressure drop, however G.L.C. data indicated the formation of propanoic acid. The rate of reaction is very slow in reaction 4.6.1 and the yield is approximately 10% of some previous reactions. The second reaction, in the presence of hydrochloric acid, does seem to produce good results. The rate is 25 - 35% of the best reaction so far, and possesses a reasonable selectivity. These results would seem to suggest that the oxidative addition of chloroethane is promoted by the presence of tin(II) chloride in the reaction system.

To study the side reactions occurring, reaction systems were considered for ethene, in the absence of carbon monoxide. The second reaction system, which did not include rhodium, was to test whether side-reactions were dependent only on the presence of tin(II) chloride, or whether both rhodium and tin was required.

Standard components:

$SnCl_2.2H_2O$: $Bz(Et)_3NCl$: $HCl(aq)37\%$: CH_3CO_2H :C_2H_4, *45 bar*

Temperature: 180°C

Reaction Number	*Component*	*Moles of Propanoic Acid produced*	*Rate (1) /bar.hr^{-1}*	*Rate (2) /mol.kg^{-1}.hr^{-1}*	*% (3) selectivity*
4.6.3	$RhCl_3.3H_2O$	*0.054*	*0*	*0.914*	*(30.4%)*
4.6.4	-	*0.041*	*0*	*0.696*	*(55.4%)*

In both of these reactions we appear to produce propanoic acid, despite the absence of carbon monoxide. It is possible that decarbonylation of acetic acid occurs to produce carbon monoxide. However reaction 4.6.3 was investigated by G.C.M.S. to identify the by-products.

G.C.M.S. revealed that no propanoic acid was present in the reaction solution. The mass spectrum showed the presence of a species, that may be either butylpentanoate or 1-methylpentylpropanoate. The latter is more probable, due to a peak at 73 m/e. In addition butane and chlorobutane were present. Mass spectra of other reactions in this chapter (4.2.1, 4.5.5, 4.4.4, 4.4.3, 4.8.2) show that propanoic acid is produced when carbon monoxide is present. The confusion of the C_9 ester with propanoic acid in the G.C. of the reaction solution is therefore confined to these reactions.

From the reactions described in this section, ethylchloride has been shown to oxidatively add to rhodium to facilitate carbonylation. However, even when hydrochloric acid is present the rate of reaction is only one quarter of that for hydrocarbonylation of ethene (reaction 4.6.2 vs reaction 4.2.2). It therefore seems likely that hydrogen chloride oxidatively adds to a rhodium-tin complex, followed by hydrocarbonylation of ethene. Given this premise the reactions of hydrogen chloride were investigated further.

4.7 Reactions of Hydrogen Chloride

Throughout the series of reactions conducted thus far, the amount of concentrated hydrochloric acid used has been standardised at 2.4 ml (see section 4.10). In the following reaction the amounts of hydrogen chloride and water were varied.

Standard components:

$RhCl_3.3H_2O$: $SnCl_2.2H_2O$: $Bz(Et)_3NCl$: CH_3CO_2H :CO, 40 bar : C_2H_4, 40 bar;

Temperature: 180°C

Reaction Number	***Component***	***Moles of Propanoic Acid produced***	***Rate (1) /bar.hr^{-1}***	***Rate (2)/ mol.kg^{-1}.hr^{-1}***	***% (3) selectivity***
4.7.1	*2.4ml.2M.HCl(aq)*	*0.047*	*66.2*	*0.97*	*88.1%*
4.7.2	*2.4ml.2M.HCl + 7.6ml H_2O*	*0.013*	*15.0*	*0.27*	†

† *The sensitivity of the G.L.C. system was insufficient to produce a selectivity result at the trace levels of propanoic acid present.*

The four-fold decrease in hydrogen chloride present has reduced the rate to approximately one fifth of reaction 4.2.2. It would appear that the rate is directly linked to the amount of hydrogen chloride present. The second reaction shows a distinct decrease in rate of reaction. There are two possible causes for this drop in rate; either the decrease in concentration of hydrogen chloride or the destabilisation of rhodium complexes involved in the reaction system.

The dependence of rate on the amount of HCl present was studied in the following series of reactions.

Standard components:

$RhCl_3.3H_2O$: $SnCl_2.2H_2O$: $Bz(Et)_3NCl$: CH_3CO_2H :CO, 40 bar : C_2H_4, 40 bar;

Temperature: 180°C

Reaction Number	Volume of 37% HCl(aq)	Moles of Propanoic Acid produced	Rate (1) /bar.hr^{-1}	Rate (2)/ mol.kg^{-1}.hr^{-1}	% (3) selectivity
4.2.2	2.4 ml	0.121	137	5.4	88.6%
4.7.3	4.0 ml	0.039	75	0.77	42.9%
4.7.4	10 ml	0.072	164	2.8	43.8%

These results show no proportional relationship between rate or selectivity and the amount of concentrated hydrochloric acid. However reaction 4.2.2 has been by far the highest rate in terms of propanoic acid produced. It is interesting to note that the selectivity of reactions 4.7.3 and 4.7.4 are approximately the same. This suggests that above a given point the side-reactions are not dependent on the amount of hydrogen chloride present. This would confirm, in conjunction with section 4.5 results, that tin(II) chloride is involved in the side reactions. It is also possible that the increase in the amount of water present affects the selectivity, destabilising the complexes involved in the catalytic reaction. To investigate this possibility, two reactions were conducted in the presence of acetic anhydride in glacial acetic acid as solvent. The acetic anhydride was intended to react with water of crystallisation of rhodium(III) chloride and hence provide an anhydrous medium for reaction. The first reaction had no hydrogen chloride present, the second had gaseous hydrogen chloride added directly into the autoclave. Control of addition of the hydrogen chloride was poor, the amount used was therefore approximately (see section 4.10) ten-fold that used in reaction 4.2.2.

Standard components:

$RhCl_3.3H_2O$: $SnCl_2.2H_2O$: $Bz(Et)_3NCl$: $(CH_3CO)_2O$:CH_3CO_2H : CO,40 bar : C_2H_4,40 bar;

Temperature: 180°C

Reaction Number	***Component***	***Moles of Propanoic Acid produced***	***Rate (1) /$bar.hr^{-1}$***	***Rate (2)/ $mol.kg^{-1}.hr^{-1}$***	***% (3) selectivity***
4.7.5	-	*0*	*45*	*0*	*0*
4.7.6	*HCl(g)*	*0.053*	*236*	*5.55*	*46.5%*

Note: The final solutions of these reactions were reacted with water to give propanoic acid for G.L.C. analysis.

As may have been predicted from reaction 2.7.3 there is no reaction in the absence of hydrogen chloride. In reaction 4.7.6 despite the vast quantity of hydrogen chloride present in the reaction, the rate is approximately the same as for reaction 4.2.2. The selectivity is only half that of the hydrous system. This would confirm that an amount of water is beneficial to the production of propanoic acid. We have seen from reaction 4.6.4 that by-products can be produced in the absence of rhodium moieties; in particular chloroethane and chlorobutane. It would appear that hydrogen chloride, tin(II) chloride and ethene all react in a manner to produce these by-products.

As noted in Chapter 1, oxidative addition of AB may proceed by two pathways, either by addition of the anionic moiety B^- of the adding group, or the cationic moiety A^+.

To consider the possibility of a proton adding to the catalytic species in these reactions, a reaction was undertaken in such a manner as to reduce to a minimum the chloride content of the reaction. The protic species was introduced to the reaction by employing tetrafluoroboric acid as the acid reagent.

Standard components:

$RhCl_3.3H_2O$: $SnCl_2.2H_2O$: Et_4NOH : CH_3CO_2H : *CO, 40 bar* : C_2H_4, *40 bar;*

Temperature: 180°C

Reaction Number	*Component*	*Moles of Propanoic Acid produced*	*Rate (1) /bar.hr^{-1}*	*Rate (2)/ mol.kg^{-1}.hr^{-1}*	*% (3) selectivity*
4.7.7	HBF_4(aq)40%	0.007	13.3	0.113	4.8%

This reaction shows that hydrochloric acid is an active component in the catalytic system and suggests that a cationic hydride complex is not the catalyst.

It has been shown throughout this section that the hydrocarbonylation reaction, utilising a rhodium-tin-chloride catalyst system, requires the presence of hydrogen chloride. The anhydrous reaction proceeds at a respectable rate, but aqueous hydrochloric acid gives better results. Excess concentrated hydrochloric acid gives rise to an increase in the formation of chloroalkane by-products or their derivatives.

4.8 Additives for the Catalytic System

Several additives used elsewhere for promoting and stabilising catalytic systems were tested and the results presented below.

Acetone was a good solvent in section 4.3, but underwent the aldol condensation. A ketone inert to this condensation reaction was used as an additive.

Standard components:

$RhCl_3.3H_2O$: $SnCl_2.2H_2O$: HCl(aq)37% : $Bz(Et)_3NCl$: CH_3CO_2H : CO,40 bar:C_2H_4,40 bar;

Temperature:. 180°C

Reaction Number	*Component*	*Moles of Propanoic Acid produced*	*Rate (1) /bar.hr^{-1}*	*Rate (2)/ mol.kg^{-1}.hr^{-1}*	*% (3) selectivity*
4.8.1	$(C_6H_5)_2CO$	0.043	70.2	1.67	61.1%

These results show that the added ketone has a detrimental effect with regard to the comparable reaction 4.2.2.

Another additive that has been used as a stabilising agent commercially, is triphenylphosphine, which is added to the "Oxo" process as discussed in Chapter 1. Reaction 4.8.2 involves the use of Ph_3P at 180 C, reaction 4.8.3 was carried out at 140 C, since an exothermic reaction in some Rh/Sn hydrocarbonylation at 150 - 170 C (see section 4.4 and reaction 4.4.1) and stabilisation before this temperature rise, was of interest.

Standard components:

$RhCl_3.3H_2O$:$SnCl_2.2H_2O$:HCl(aq)37%:Bz(Et)$_3$NCl:Ph_3P:CH_3CO_2H:CO,40 bar:C_2H_4,40 bar;

Reaction Number	***Temperature /°C***	***Moles of Propanoic Acid produced***	***Rate (1) /bar.hr^{-1}***	***Rate (2)/ mol.kg^{-1}.hr^{-1}***	***% (3) selectivity***
4.8.2	*180*	*0.013*	*42.8*	*0.50*	*9.1%*
4.8.3	*140*	*0.013*	*120*	*1.00*	*27.0%*

In both cases, the rhodium:triphenylphosphine:tin ratio was 1:2:4. Both reactions give poor rates of reaction and poor selectivity compared with reaction 4.5.4 which also had a rhodium to tin ratio of 1:4.

If however we consider the role of the triphenylphosphine we must assume that it acts as a ligand to rhodium. It was suggested by the reactions of section 4.5 that additional ligands may block the co-ordination sites of rhodium. Another reaction was conducted employing a rhodium:triphenylphosphine:tin ratio of 1:1:1 enabling either a rhodium-tin-triphenylphosphine complex, or a rhodium-triphenylphosphine complex to form.

Standard components:

$RhCl_3.3H_2O:SnCl_2.2H_2O:PPh_3:HCl(aq)37\%:Bz(Et)_3NCl:Ph_3P:CH_3CO_2H:CO,40$ bar:$C_2H_4,40$ bar;

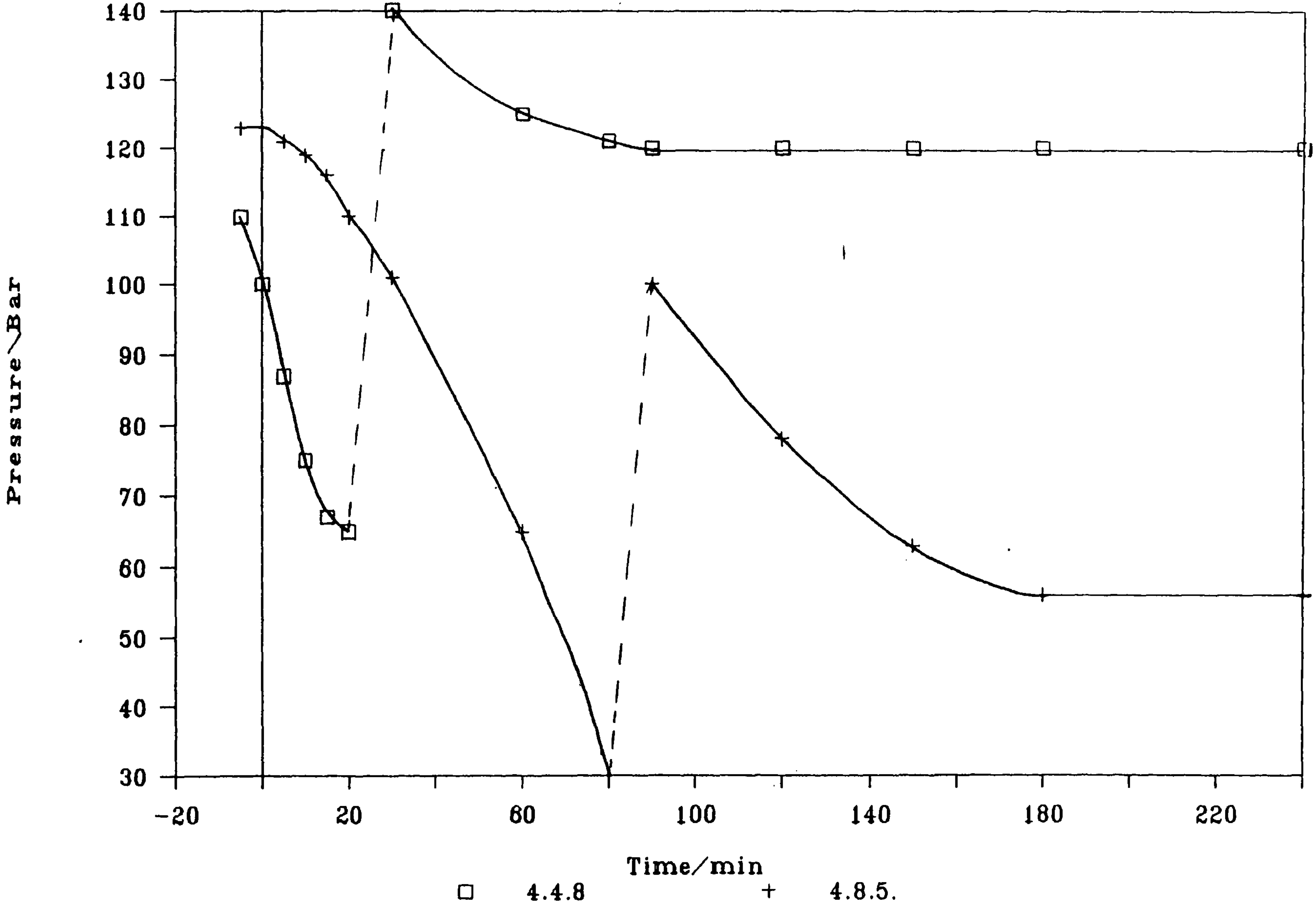
Temperature: 180°C

Reaction Number	*Moles of Propanoic Acid produced*	*Rate (1) /bar.hr^{-1}*	*Rate (2) /mol.kg^{-1}.hr^{-1}*	*% (3) selectivity*
4.8.4	0.073	66.0	1.39	95.8%

This reaction proceeds at a faster rate than the 1:2:4 reaction, although it is still not as great as 4.2.2. However the selectivity is excellent. It is possible that the triphenylphosphine encourages hydrocarbonylation at lower temperatures (see reaction 4.8.3) and hence inhibits side-reactions which reduce selectivity. If this is the case, then it would confirm the proposition in section 4.4 that by-products are formed during the heating period and not at reaction temperature.

In employing triphenylphosphine, it was intended that this additive would stabilise the catalytic system. To assess the ability of triphenylphosphine in this regard, reaction 4.8.5 was conducted, and the system replenished with CO/C_2H_4. The pressure profile is shown in Figure 4.6 together with the profile of reaction 4.4.8 for comparison. The rate after repressurisation of 4.8.5 is approximately half that of the initial rate. This suggests that while Ph_3P is not completely successful as a stabilising agent, it does improve catalyst stability and the selectivity of these reactions suggests that further investigation is worthwhile.

Figure 4.6



140
130
120
110
100
90
80
70
60
50
40
30
Pressure\Bar
−20
20
60
100
140
180
220
Time/min
□ 4.4.8
+ 4.8.5.

The complex $Rh(PPh_3)_3Cl$ is known to be an active hydrogenation catalyst. Furthermore it is known to effect the decarbonylation of alkanoic chlorides⁽¹⁵⁾.

$$Rh(PPh_3)_3Cl + RCOCl \longrightarrow RCl + Rh(CO)(PPh_3)_2Cl + PPh_3$$

It is also known to co-ordinate ethene as a ligand⁽¹⁶⁾.

$$Rh(PPh_3)_3Cl + C_2H_4 \longrightarrow (C_2H_4)Rh(Ph_3P)_2Cl + PPh_3$$

It is therefore very likely that the hydrocarbonylation reaction could proceed without the presence of tin. Reaction 4.8.6 tests the ability of $Rh(Ph_3P)Cl$ to act as a hydrocarbonylation, whereas reaction 4.8.7 tests the efficiency of a system of rhodium:triphenylphosphine ratio of 1:1.

Standard components:

$Bz(Et)_3NCl$: $HCl(aq)$37% : CH_3CO_2H : CO, 40 bar : C_2H_4, 40 bar;

Temperature: 180°C

Reaction Number	*Catalyst*	*Moles of Propanoic Acid produced*	*Rate (1) /bar.hr^{-1}*	*Rate (2)/ mol.kg^{-1}.hr^{-1}*	*% (3) selectivity*
4.8.6	*$Rh(Ph_3P)_3Cl$*	*0.090*	*28.3*	*1.53*	*99.2%*
4.8.7	*$RhCl_3.3H_2O:PPh_3$*	*0.108*	*75.4*	*2.35*	*78.8%*

While the very high selectivity of reaction 4.8.6 looks promising, the rate of reaction is considerably slower than that of reaction 4.8.7. This seems to suggest that more than two potential ligands, eg PPh_3, $SnCl_3^-$ block the reaction to some extent. This also appeared to be the case in section 4.5 and also for reaction 4.8.2. However the selectivity of reaction 4.8.7 is approximately that of the best of the reactions of rhodium-tin(II) chloride systems.

It seems likely from this information that in the mixed triphenylphosphine:tin(II) chloride systems that have been studied in this section, two separate catalytic processes are occurring simultaneously. If this is the case then we can expect that there is competition between the two processes. This is demonstrated to an extent in reactions 4.8.8 and 4.8.9 below. In both reactions $Rh(Ph_3P)_3Cl$ is employed as the catalyst. The first reaction has tin(II) chloride in the ratio to rhodium of 1:1, in the second case the ratio is 1:4. The intention being that the first reaction should be dominated by the Rh-PPh_3 catalyst system and that the Rh-$SnCl_2$ system should dominate in the second reaction.

Standard components:

$Rh(Ph_3P)_3Cl$: $SnCl_2.2H_2O$: $Bz(Et)_3NCl$: HCl(aq)37% : CO, 40 bar : C_2H_4, 40 bar;

Temperature: 180°C

Reaction Number	***Rhodium to tin ratio***	***Moles of Propanoic Acid produced***	***Rate (1) /bar.hr^{-1}***	***Rate (2)/ mol.kg^{-1}.hr^{-1}***	***% (3) selectivity***
4.8.8	*1:1*	*0.082*	*62.3*	*1.40*	*96.1%*
4.8.9	*1:4*	*0.142*	*92.0*	*3.60*	*81.1%*

Reaction 4.8.8 has a rate of reaction that is typical for the rhodium-tin systems but a very high selectivity. Reaction 4.8.9 has a typical selectivity and double to three times the rate of reaction. It seems that there is a counter-complementary effect between these two desirable reaction characteristics making optimisation of the system difficult. A much more detailed study may be needed for this system.

It has been reported that Ph_3P undergoes oxidation at the carbon-phosphorus bond during the "Oxo" process(17), therefore alternative additives were investigated.

Triethylamine was used as an additive, although it should be noted that there is also the likelihood that it will react with HCl to form $Et_3HN^+Cl^-$ and act as a cationic species for the system.

Two reactions were conducted utilising Et_3N. The first reaction employs lithium as a cation as the amine will form $Et_3HN^+Cl^-$ with hydrochloric acid. In an attempt to distinguish if the free amine or the quaternary ammonium cation are acting as agent, the second reaction was conducted with $Bz(Et)_3NCl$ present.

Standard components:

$RhCl_3.3H_2O$:$SnCl_2.2H_2O$:HCl(aq)37%:Et_3N:CH_3CO_2H:CO,40 bar:C_2H_4,40 bar;

Temperature: 180°C

Reaction Number	*Component*	*Moles of Propanoic Acid produced*	*Rate (1) /bar.hr^{-1}*	*Rate (2)/ mol.kg^{-1}.hr^{-1}*	*% (3) selectivity*
4.8.10	LiCl	0.124	59.3	2.10	92.3%
4.8.11	$Bz(Et)_3NCl$	0.074	58.7	1.18	98.1%

It should be noted that there is an effective decrease in rate of reaction in reaction 4.8.11 compared with reaction 4.2.2 which is the comparable reaction without triethylamine. However the selectivity in reaction 4.8.11 is excellent, greater by 10% than that of reaction 4.2.2. Reaction 4.8.10 shows a better rate than reaction 4.4.3 which employs lithium as a cation in the absence of triethylamine. It would appear that there is indeed the formation of $Et_3NH^+Cl^-$ in solution, and this prevents the absolute evaluation of triethylamine as a ligand for the rhodium centre in these reactions.

4.9 Conclusions

It has been demonstrated that tin(II) chloride activates the rhodium-chloride system for catalysis of the hydrocarbonylation of ethene. This action is also observed for tin(IV) compounds. The activity of this system is greatly enhanced by the presence of a cation, either a quaternary ammonium cation or an alkali metal cation. Benzyltriethylammonium chloride gives a better selectivity but slow rate than tetrabutylammoniumchloride, though selectivity is far better for the former cation. The same antagonistic trends in behaviour for selectivity against rate can be seen for the lithium and caesium reactions, the lithium reaction being slower but more selective than the caesium reaction.

From the reactions of section 4.5, involving rhodium and tin, the best rates are achieved with rhodium to tin ratios of 1:2. This is consistent with the formation of complexes such as $[Rh(CO)_2(SnCl_3)_2]^-$ and $[Rh(CO)_2(SnCl_3)_3]^{2-}$, which could then undergo oxidative addition of hydrogen chloride. There remains the possibility that

$HSnCl_3$ oxidatively adds to either $[Rh(CO)_2(SnCl_3)Cl]^-$ or $[Rh(CO)_2(SnCl_3)_2Cl]^{2-}$ which has not been eliminated.

The major point of interest to arise from the investigation of different reaction temperatures in section 4.4 is the possible occurrence of the majority of side-reactions before the reaction temperature was reached. In an industrial constant-flow process, higher selectivities may be achievable.

In section 4.6 chloroethane is shown to oxidatively add to the catalytic species, and undergo carbonylation and generate propanoic acid. It was noticeable that this process proceeds to a much greater extent in the presence of hydrochloric acid. It is surprising therefore that no reaction occurs when alcohols are used as solvents. No carbonylation of the alcohol occurs and hydrocarbonylation is also inhibited. It appears that the total removal of hydrogen chloride prevents reaction from occurring.

These reactions show that hydrogen chloride is vital for the hydrocarbonylation reaction.

The stability of the rhodium/tin catalyst is enhanced by the addition of the lithium cation and/or the use of triphenylphosphine. However, the use of additives such as triphenylphosphine and triethylamine is complicated by the competition between ligands and also the formation of quaternary alkyl-group V salts.

The areas for improvement are greatly dependent on the question of whether or not the majority of by-product formation occurs during the heating period. It is thought that greater rates may be achieved for constant temperature and flow systems by increasing concentrations of hydrogen chloride and/or tin(II) chloride. When the latter adjustments have been attempted in batch reactions the selectivity has suffered greatly.

Furthermore a wider ranging study of the effects and action of different cations and additives may lead to improvements in rates and selectivity.

4.10 Chapter 4 - Reaction Index

Reaction Number	Reactants/Moles		Solvents	Temperature ° C	Gases	Pressure Range/bar	Rate of Reaction mol/kg/hr	Reaction Code
4.2.1	$RhCl_3.3H_2O$, $SnCl_2.2H_2O$, HC1.37%(aq),	9.8×10^{-5} 2.0×10^{-4} 2.8×10^{-2}	CH_3COOH	180	CO C_2H_4	121 - 36	0.89	D3HR5
4.2.2	$RhCl_3.3H_2O$, $SnCl_2.2H_2O$, HC1.37%(aq), $PhCH_2(Et)_3NCl$,	9.8×10^{-5} 2.0×10^{-4} 2.8×10^{-2} 2.9×10^{-4}	CH_3COOH	180	CO C_2H_4	125 - 15	5.4	D3HR6
4.2.3	$RhCl_3.3H_2O$, HC1.37%(aq), $[PhCH_2(Et)_3N]_2SnCl_6$,	1.0×10^{-4} 2.8×10^{-2} 2.2×10^{-4}	CH_3COOH	181	CO C_2H_4	163 - 22	1.44	D3HR61
4.2.4	$[Rh_2(CO)_4Cl_2]$, HC1.37%(aq), $PhCH_2(Et)_3NCl$, $SnCl_2.2H_2O$,	5.2×10^{-5} 2.8×10^{-2} 2.3×10^{-4} 1.9×10^{-4}	CH_3COOH	200	CO C_2H_4	158 - 40	2.39	D3HR34
4.3.1	$RhCl_3.3H_2O$, $SnCl_2.2H_2O$, HC1.37%(aq), $PhCH_2(Et)_3NCl$,	9.8×10^{-5} 2.0×10^{-4} 2.8×10^{-2} 2.8×10^{-4}	2M,HCl(aq)	180	CO C_2H_4	123 - 52	0.2	D3HR29
4.3.2	$RhCl_3.3H_2O$, $SnCl_2.2H_2O$, $PhCH_2(Et)_3NCl$, HC1.37%(aq),	1.0×10^{-4} 2.3×10^{-4} 3.8×10^{-4} 2.8×10^{-2}	$HCOOCH_3$	180	CO C_2H_4	108 - 40	0	D3HR17

4.10 Chapter 4 - Reaction Index (cont)

Reaction Number	Reactants/Moles		Solvents	Temperature ° C	Gases	Pressure Range/bar	Rate of Reaction mol/kg/hr	Reaction Code
4.3.3	$RhCl_3.3H_2O$, $SnCl_2.2H_2O$, $PhCH_2(Et)_3NCl$, HCl.37%(aq),	1.0 x 10^{-4} 2.3 x 10^{-4} 2.5 x 10^{-4} 2.8 x 10^{-2}	$CH_3COOC_2H_5$	180	CO C_2H_4	129 - 37	0.0024	D3HR60
4.3.4	$RhCl_3.3H_2O$, $SnCl_2.2H_2O$, $PhCH_2(Et)_3NCl$, HCl.37%(aq),	1.0 x 10^{-4} 2.3 x 10^{-4} 2.8 x 10^{-4} 2.8 x 10^{-2}	$(C_2H_5)_2CO$	180	CO C_2H_4	218 - 68	0.093	D3HR53
4.3.5	$RhCl_3.3H_2O$, $SnCl_2.2H_2O$, $PhCH_2(Et)_3NCl$, HCl.37%(aq),	9.8 x 10^{-5} 2.0 x 10^{-4} 2.1 x 10^{-4} 2.8 x 10^{-2}	$(CH_3)_2CO$	180	CO C_2H_4	119 - 59	6.25	D3HR21
4.3.6	$RhCl_3.3H_2O$, $SnCl_2.2H_2O$, $PhCH_2(Et)_3NCl$, HCl.37%(aq),	9.8 x 10^{-5} 2.3 x 10^{-4} 3.0 x 10^{-4} 2.8 x 10^{-2}	CH_3OH	180	CO	132 - 83	0	D3HR24
4.3.7	$RhCl_3.3H_2O$, $SnCl_2.2H_2O$, $PhCH_2(Et)_3NCl$, HCl.37%(aq),	1.0 x 10^{-4} 2.3 x 10^{-4} 2.8 x 10^{-4} 2.8 x 10^{-2}	CH_3OH	180	CO C_2H_4	140 - 62	o	D3HR28
4.3.8	$RhCl_3.3H_2O$, $SnCl_2.2H_2O$, $PhCH_2(Et)_3NCl$, HCl.37%(aq),	1.0 x 10^{-4} 2.8 x 10^{-4} 2.6 x 10^{-4} 2.8 x 10^{-2}	CH_3COOH C_2H_5OH	180	CO C_2H_4	119 - 63	0.61	D3HR97

4.10 Chapter 4 - Reaction Index (cont)

Reaction Number	Reactants/Moles		Solvents	Temperature °C	Gases	Pressure Range/bar	Rate of Reaction mol/kg/hr	Reaction Code
4.3.9	$RhCl_3.3H_2O$, $SnCl_2.2H_2O$, $PhCH_2(Et)_3NCl$, $HCl.37\%(aq)$,	9.8×10^{-5} 2.3×10^{-4} 2.3×10^{-4} 2.8×10^{-2}	CH_3COOH CH_2Cl_2	180	CO C_2H_4	120 - 20	0.52	D3HR1
4.4.1	$RhCl_3.3H_2O$, $SnCl_2.2H_2O$, $(C_4H_9)_4NCl$, $HCl.37\%(aq)$,	9.8×10^{-5} 2.3×10^{-4} 2.0×10^{-4} 2.8×10^{-2}	CH_3COOH	180	CO C_2H_4	115 - 37	8.97	D3HR7
4.4.2	$RhCl_3.3H_2O$, $SnCl_2.2H_2O$, $(Ph_3P)_2NCl$, $HCl.37\%(aq)$,	1.0×10^{-4} 2.3×10^{-4} 2.1×10^{-4} 2.8×10^{-2}	CH_3COOH	180	CO C_2H_4	82 - 35	0	D3RH12
4.4.3	$RhCl_3.3H_2O$, $SnCl_2.2H_2O$, $LiCO_3$, $HCl.37\%(aq)$,	1.0×10^{-4} 2.9×10^{-4} 1.0×10^{-4} 2.8×10^{-2}	CH_3COOH	180	CO C_2H_4	155 - 19	1.22	D3RH56
4.4.4	$RhCl_3.3H_2O$, $SnCl_2.2H_2O$, $CsCl$, $HCl.37\%(aq)$,	1.1×10^{-4} 2.3×10^{-4} 1.1×10^{-4} 2.8×10^{-2}	CH_3COOH	180	CO C_2H_4	146 - 18	3.91	D3HR58
4.45	$RhCl_3.3H_2O$, $SnCl_2.2H_2O$, $(C_4H_9)NCl$, $HCl.37\%(aq)$,	1.0×10^{-4} 2.8×10^{-4} 2.0×10^{-4} 2.8×10^{-2}	CH_3COOH	150	CO C_2H_4	120 - 65	0.097	D3HR10

Reaction Number	Reactants/Moles	Solvents	Temperature °C	Gases	Pressure Range/bar	Rate of Reaction mol/kg/hr	Reaction Code
4.4.6	$RhCl_3.3H_2O$, 1.0×10^{-4} $SnCl_2.2H_2O$, 2.8×10^{-4} $(C_4H_9)NCl$, 1.9×10^{-4} HCl.37%(aq), 2.8×10^{-2}	CH_3COOH	120	CO C_2H_4	100 - 40	0.17	D3HR9
4.4.7	$RhCl_3.3H_2O$, 1.0×10^{-4} $SnCl_2.2H_2O$, 2.8×10^{-4} $(C_4H_9)NCl$, 2.0×10^{-4} HCl.37%(aq), 2.8×10^{-2}	CH_3COOH	100	CO C_2H_4	128 - 63	0.073	D3HR11
4.5.1	$RhCl_3.3H_2O$, 1.0×10^{-4} $SnCl_2.2H_2O$, 5.1×10^{-5} $PhCH_2(Et)_3NCl$, 2.0×10^{-4} HCl.37%(aq), 2.8×10^{-2}	CH_3COOH	180	CO C_2H_4	120 - 40	2.88	D3HR33
4.5.2	$RhCl_3.3H_2O$, 1.1×10^{-4} $SnCl_2.2H_2O$, 1.1×10^{-4} $PhCH_2(Et)_3NCl$, 2.5×10^{-4} HCl.37%(aq), 2.8×10^{-2}	CH_3COOH	180	CO C_2H_4	139 - 20	2.97	D3HR84
4.5.3	$RhCl_3.3H_2O$, 1.0×10^{-4} $SnCl_2.2H_2O$, 2.3×10^{-4} $PhCH_2(Et)_3NCl$, 2.9×10^{-4} HCl.37%(aq), 2.8×10^{-2}	CH_3COOH	180	CO C_2H_4	115 - 58	5.72	D3HR23
4.5.4	$RhCl_3.3H_2O$, 9.8×10^{-5} $SnCl_2.2H_2O$, 4.1×10^{-4} $PhCH_2(Et)_3NCl$, 2.3×10^{-4} HCl.37%(aq), 2.8×10^{-2}	CH_3COOH	180	CO C_2H_4	140 - 57	1.69	D3HR32

Reaction Number	Reactants/Moles		Solvents	Temperature ° C	Gases	Pressure Range/bar	Rate of Reaction mol/kg/hr	Reaction Code
4.5.5	$RhCl_3.3H_2O$, $SnCl_2.2H_2O$, $PhCH_2(Et)_3NCl$, HCl.37%(aq),	1.0×10^{-4} 5.7×10^{-4} 2.0×10^{-4} 2.8×10^{-2}	CH_3COOH	180	CO C_2H_4	120 - 62	0.72	D3HR22
4.6.1	$RhCl_3.3H_2O$, $SnCl_2.2H_2O$, $PhCH_2(Et)_3NCl$, EtCl,	1.2×10^{-4} 2.3×10^{-4} 2.8×10^{-4} 5.6×10^{-2}	CH_3COOH	180	CO	75 - 47	0.38	D3HR88
4.6.2	$RhCl_3.3H_2O$, $SnCl_2.2H_2O$, $PhCH_2(Et)_3NCl$, EtCl, HCl.37%(aq),	1.2×10^{-4} 2.3×10^{-4} 2.4×10^{-4} 1.1×10^{-1} 2.8×10^{-2}	CH_3COOH	180	CO	80 - 45	1.53	D3HR90
4.6.3	$RhCl_3.3H_2O$, $SnCl_2.2H_2O$, $PhCH_2(Et)_3NCl$, HCl.37%(aq),	1.2×10^{-4} 2.3×10^{-4} 2.9×10^{-4} 2.8×10^{-2}	CH_3COOH	180	C_2H_4	42 - 17	-	D3HR83
4.6.4	$SnCl_2.2H_2O$, $PhCH_2(Et)_3NCl$, HCl.37%(aq),	2.8×10^{-4} 3.0×10^{-4} 2.8×10^{-2}	CH_3COOH	180	C_2H_4	61 - 18	-	D3HR86
4.7.1 and 4.7.2	$RhCl_3.3H_2O$, $SnCl_2.2H_2O$, $PhCH_2(Et)_3NCl$, HCl.2M (aq),	9.8×10^{-4} 2.3×10^{-4} 2.3×10^{-4} 4.8×10^{-3}	CH_3COOH	180	CO C_2H_4	145 - 41	4.71:0.97 4.72:0.27	D3HR41 D3HR42

4.10 Chapter 4 - Reaction Index (cont)

Reaction Number	Reactants/Moles		Solvents	Temperature °C	Gases	Pressure Range/bar	Rate of Reaction mol/kg/hr	Reaction Code
4.7.3	$RhCl_3.3H_2O$, $SnCl_2.2H_2O$, $PhCH_2(Et)_3NCl$, HCl.37%(aq)	1.2×10^{-4} 2.2×10^{-4} 2.2×10^{-4} 4.7×10^{-2}	CH_3COOH	183	CO C_2H_4	105 - 65	0.77	D3HR26
4.7.4	$RhCl_3.3H_2O$, $SnCl_2.2H_2O$, $PhCH_2(Et)_3NCl$, HCl.37%(aq),	1.0×10^{-4} 2.5×10^{-4} 2.2×10^{-4} 1.2×10^{-1}	CH_3COOH	185	CO C_2H_4	168 - 22	2.8	D3HR37
4.7.5	$RhCl_3.3H_2O$, $SnCl_2.2H_2O$, $PhCH_2(Et)_3NCl$,	9.8×10^{-4} 2.9×10^{-4} 2.2×10^{-4}	CH_3COOH $(CH_3CO)_2O$	180	CO C_2H_4	142 - 61	0	D3HR40
4.7.6	$RhCl_3.3H_2O$, $SnCl_2.2H_2O$, $PhCH_2(Et)_3NCl$, HCl(g)	1.0×10^{-4} 2.8×10^{-4} 2.3×10^{-4} 2.3×10^{-1}	CH_3COOH $(CH_3CO)_2O$	180	CO C_2H_4	120 - 20	5.55	D3HR39
4.7.7	$RhCl_3.3H_2O$, $SnCl_2.2H_2O$, Et_4NOH, HBF_4.40%(aq),	1.2×10^{-4} 2.3×10^{-4} 1.4×10^{-4} 2.5×10^{-2}	CH_3COOH	180	CO C_2H_4	136 - 64	0.113	D3HR95
4.8.1	$RhCl_3.3H_2O$, $SnCl_2.2H_2O$, $PhCH_2(Et)_3NCl$, HCl.37%(aq), Ph_2CO,	9.8×10^{-5} 2.4×10^{-4} 4.2×10^{-4} 2.8×10^{-2} 3.8×10^{-4}	CH_3COOH	180	CO C_2H_4	108 - 35	1.67	D3HR19

Reaction Number	Reactants/Moles		Solvents	Temperature °C	Gases	Pressure Range/bar	Rate of Reaction mol/kg/hr	Reaction Code
4.8.2	$RhCl_3.3H_2O$, $SnCl_2.2H_2O$, $PhCH_2(Et)_3NCl$, HCl.37%(aq), Ph_3P,	9.8×10^{-5} 2.3×10^{-4} 2.8×10^{-4} 2.8×10^{-2} 8.0×10^{-4}	CH_3COOH	180	CO C_2H_4	118 - 40	0.5	D3HR25
4.8.3				140		97 - 26	1.0	D3HR27
4.8.4	$RhCl_3.3H_2O$, $SnCl_2.2H_2O$, $PhCH_2(Et)_3NCl$, HCl.37%(aq), Ph_3P,	1.0×10^{-4} 2.8×10^{-4} 2.5×10^{-4} 2.8×10^{-2} 2.1×10^{-4}	CH_3COOH	180	CO C_2H_4	108 - 10	1.39	D3HR87
4.8.6	$Rh(Ph_3P)_3Cl$, $PhCH_2(Et)_3NCl$, HCl.37%(aq),	1.3×10^{-4} 2.8×10^{-4} 2.8×10^{-2}	CH_3COOH	180	CO C_2H_4	103 - 40	1.53	D3HR106
4.8.7	$RhCl_3.3H_2O$, Ph_3P, HCl.37%(aq), $PhCH_2(Et)_3NCl$,	1.0×10^{-4} 1.0×10^{-4} 2.8×10^{-2} 2.6×10^{-4}	CH_3COOH	180	CO C_2H_4	110 - 13	2.35	D3HR98
4.8.8	$Rh(Ph_3P)_3Cl$, $SnCl_2.2H_2O$, $PhCH_2(Et)_3NCl$, HCl.37%(aq),	1.0×10^{-4} 1.1×10^{-4} 2.8×10^{-4} 2.8×10^{-2}	CH_3COOH	180	CO C_2H_4	114 - 20	1.40	D3HR91
4.8.9	$Rh(Ph_3P)_3Cl$, $SnCl_2.2H_2O$, $PhCH_2(Et)_3NCl$, HCl.37%(aq),	1.1×10^{-4} $4.2. \times 10^{-4}$ 2.5×10^{-4} 2.8×10^{-2}	CH_3COOH	180	CO C_2H_4	105 - 18	3.60	D3HR96

4.10 Chapter 4 - Reaction Index (cont)

Reaction Number	Reactants/Moles	Solvents	Temperature ° C	Gases	Pressure Range/bar	Rate of Reaction mol/kg/hr	Reaction Code
4.8.10	$RhCl_3.3H_2O$, 1.1×10^{-4} Et_3N, 2.2×10^{-4} LiCl, 1.9×10^{-4} $SnCl_2.2H_2O$, 2.3×10^{-4} HCl.37%(aq), 2.8×10^{-2}	CH_3COOH	180	CO C_2H_4	109 - 20	2.10	D3HR108
	$RhCl_3.3H_2O$, 1.0×10^{-4} Et_3N, 2.1×10^{-4} $PhCH_2(Et)_3NCl$, 2.5×10^{-4} $SnCl_2.2H_2O$, 2.5×10^{-4} HCl.37%(aq), 2.8×10^{-2}	CH_3COOH	180	CO C_2H_4	120 - 28	1.18	D3HR111

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CHAPTER FIVE

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CHAPTER FIVE

INFRA-RED STUDIES OF THE RHODIUM-TIN-CHLORIDE CATALYTIC SYSTEMS

5.1 Introduction

As has been noted in Chapter 2, the use of Fourier Transform Infra-red spectroscopy to probe a high pressure autoclave reaction, reveals the nature of the species in solution. While the species observed may not be the catalytic species, they will reveal much about the chemistry and the nature of the reactions undertaken.

In the case of the rhodium-tin-chloride system investigation in Chapter 4, there are several points that still require clarification. Hydrogen chloride is obviously vital to produce a good catalytic system. It is unlikely however that its role will be determined by infra-red spectroscopy, as hydrogen chloride will not be directly observable in the region monitored (1800 - 2300 cm^{-1}). However the observation of one or more hydrido-rhodium species would give considerable insight into its role.

In Chapter 4, the considerable effect of cations on the catalytic system was demonstrated. Although the cations are not directly observable, their effect on the system may be detected by their effect on other properties. If cations stabilise some rhodium species we may expect to see stronger absorbance bands due to these species during the reactions.

Despite its ability to catalyse the hydrocarbonylation reaction, it was shown in Chapter 4 that this rhodium-tin-chloride system was inactive in alcohols and did not catalyse the carbonylation of alcohols. By observation of the species present in the alcohol solvents we may be able to discover the reason for the lack of activity in alcohols. This in turn may shed further light on the mechanism and action of the hydrocarbonylation catalyst.

5.2 Initial Systems

If rhodium(III) chloride is dissolved in a propanoic acid/hydrochloric acid mixture under a pressure of carbon monoxide, the rhodium compound that is expected to be formed is dichlorodicarbonylrhodate(I) anion$^{(1,2)}$. In order to confirm this a reaction was conducted in the absence of tin(II) chloride as follows.

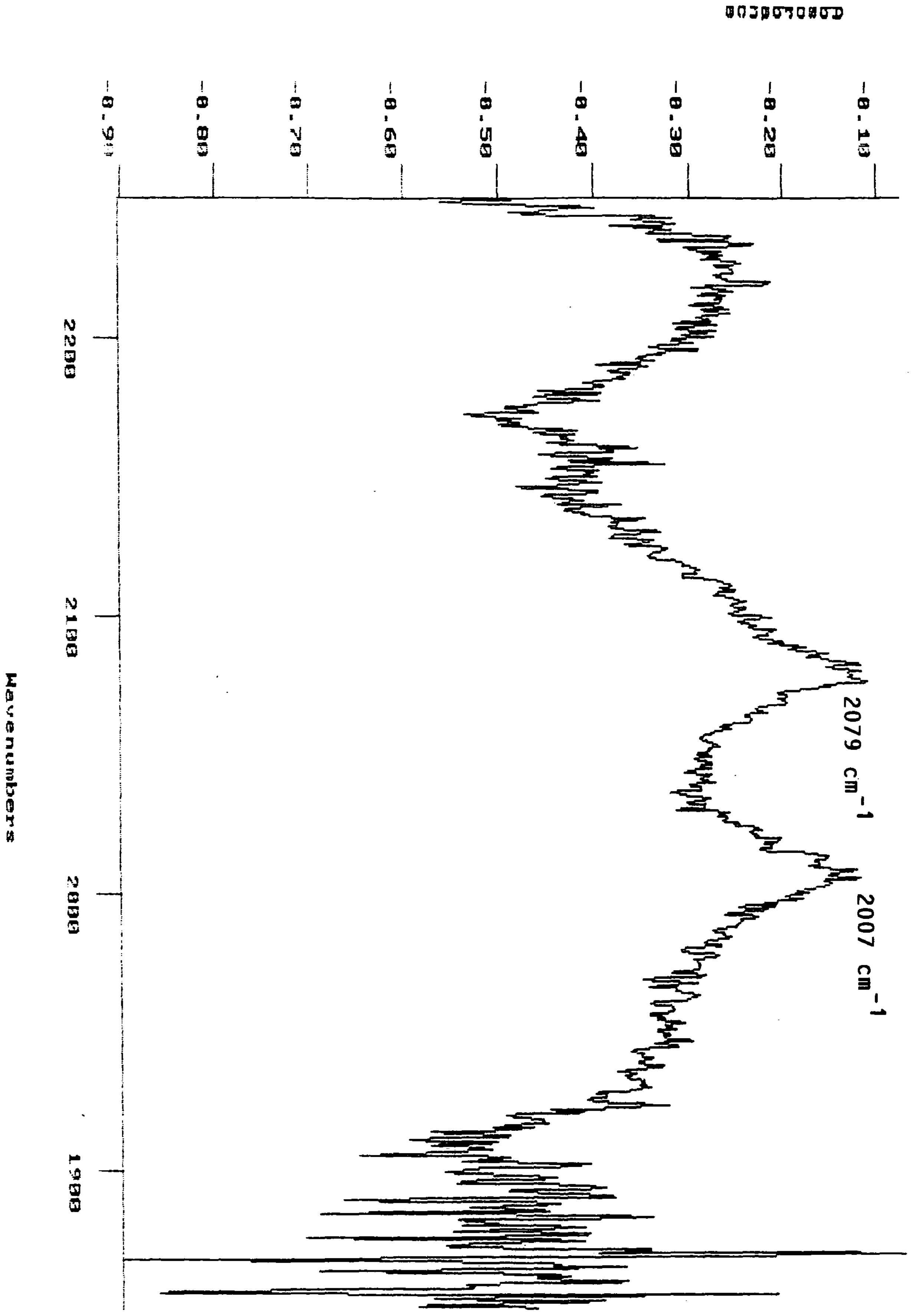
Reaction 5.2.1	*Species Observed*
$RhCl_3.3H_2O$ HCl(aq)37% CH_3CO_2H/CH_2Cl_2 CO	*2079, 2007 cm^{-1} unidentified*

Note: Details of all reaction compositions are recorded in section 5.8.

Two absorbance bands were observed from 110 - 180°C, which may be due to$[Rh(CO)_2Cl_2]^-$ (Literature value 2073, 1994 cm^{-1}, see Appendix 1). It is possible that the reaction conditions are responsible for the shift in wave number. Alternatively these absorption bands could relate to an ion pair as described by Fulford(3) for iodide systems, ie, $[H^+...Rh(CO)_2I_2^-]$. It is possible that in the present study formation of the related chloro ion-pair $[H^+....Rh(CO)_2Cl_2^-]$ occurs. The weak bands observed in reaction 5.2.1 (see Figure 5.1) show the same shift to higher frequency that Fulford observed for the corresponding iodide system. It is noticeable that these reaction observations contrast strongly with the iodide systems described in Chapter 2, when the iodide systems under high pressure and temperature conditions showed a trend in form rhodium(III) complexes. The differences between Fulford's(3) observations and those recorded in Chapter 2 may be explained by conditions and solvents used. To explain the difference between the observations recorded in Chapter 2 and reaction 5.2.1, the work of Forster(4) is of most use. Forster(4) demonstrated the tendency of chloride compounds of rhodium to favour the +1 oxidation state. In this manner the formation of chloro- analogues of the rhodium(III)-carbonyl-iodide complexes is disfavoured, leaving dichlorodicarbonylrhodate(I) $[Rh(CO)_2Cl_2]^-$ as the main species. This complex or the ion pair $[H^+....Rh(CO)_2Cl_2]^-$ may be the complex observed in reaction 5.2.1.

If the formation of an ion-pair is of importance in the process then the addition of a cation may facilitate this process. In Chapter 4 we used lithium (introduced as the carbonate) to good effect as a cation, consequently its effect on the observed solution species will be probed.

Figure 5.1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-0.20
-0.30
-0.40
-0.50
-0.60
-0.70
-0.80
-0.90
2200
2100
2000
1900
Wavenumbers
2079 cm^{-1}
2007 cm^{-1}

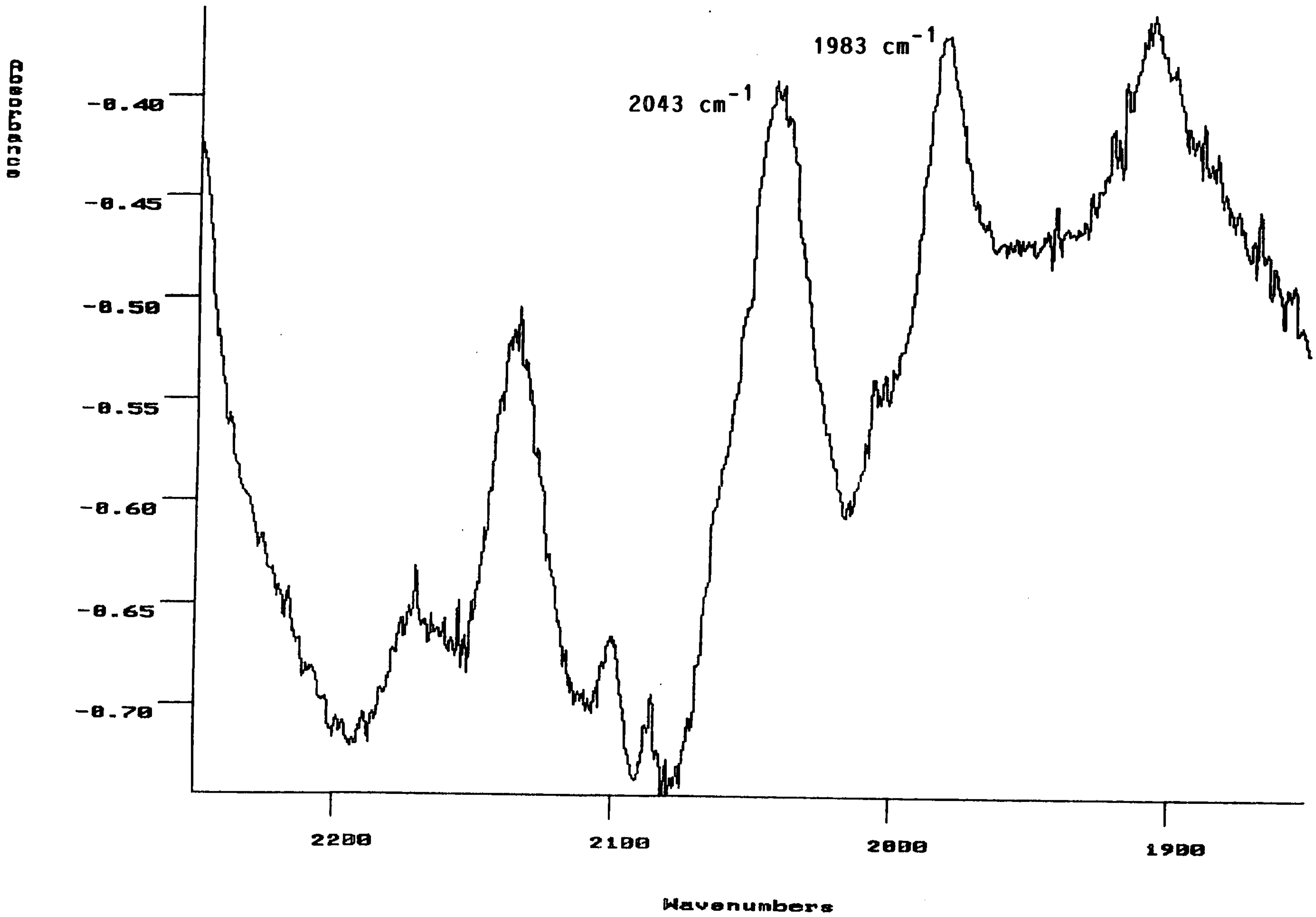

Absorbance
-0.40
-0.45
-0.50
-0.55
-0.60
-0.65
-0.70
2043 cm^{-1}
1983 cm^{-1}
2200
2100
2000
1900
Wavenumbers

Figure 5.2

Reaction 5.2.2	**Species Observed**
$RhCl_3.3H_2O$	2080, 2009 cm^{-1} unidentified
Li_2CO_3	2053 cm^{-1} unidentified
HCl(aq)37%	1985 cm^{-1} unidentified
CH_3CO_2H/CH_2Cl_2	2043, 1983 cm^{-1} unidentified
CO	

In contrast to reaction 5.2.1 an absorption band is observed at 2053 cm^{-1} in addition to those at 2080, 2009 cm^{-1}. All three bands occur at 120°C. At 180°C the band at 2053 cm^{-1} is lost and a further absorbance band occurs at 1985 cm^{-1}, with the bands at 2080, 2009 cm^{-1} still present. The band at 1985 cm^{-1} continues to strengthen with time, while the bands at 2080, 2009 cm^{-1} decrease. The band at 2053 cm^{-1} is not readily identifiable but it is probably due to a rhodium-carbonyl-chloride. However it is far too low a frequency to be either $[Rh(CO)Cl_5]^{2-}$ or $[RhCOCl_3]$, any dicarbonyl complex would be expected to show more bands. The bands observed at 2080, 2009 cm^{-1} are almost certainly the same as the ones observed in reaction 5.2.1. An additional peak was observed at 1985 cm^{-1} at 180°C. This peak would appear to be a rhodium(I) species. However the only occasion that a similar band has been observed, was in the rhodium-iodide system at 180°C and was associated with the presence of the propanoate anion (Chapter 2).

The most interesting change is observed on cooling the reaction mixture to room temperature. At this point absorbance bands are observed at 2043, 1983 cm^{-1}, as shown in Figure 5.2. These are most likely to arise from the dichlorodicarbonylrhodate(I) anion $[Rh(CO)_2Cl_2]^-$. This would infer that the absorbance bands observed at 2080, 2009 cm^{-1} must be associated with the ion-pair $[A^+....Rh(CO)_2Cl_2^-]$. In reaction 5.2.1 this is obviously the protic species. In reaction 5.2.2 however, there is the alternative of two different cations (H^+, Li^+) in the ion-pair; the small shift to high frequency between reaction 5.2.1 and 5.2.2 may suggest that lithium is present in the ion-pair, but the change is not conclusive.

5.3 Alternative Solvents

As observed in Chapter 4, alternative solvents to carboxylic acids for the rhodium-tin-chloride hydrocarbonylation catalyst system produce poor yield results. However by considering why certain solvents are poor media for the catalyst, it may be possible to show which observed species are of importance to the catalytic system.

In particular alcohol solvents are not only insusceptible to carbonylation but also inhibit all hydrocarbonylation. It is therefore unlikely that any species observed in alcohol solvents are catalytically active. The solvent used to investigate this aspect was propan-2-ol.

Reaction 5.3	*Species Observed*
$RhCl_3.3H_2O$	2081, 2017 cm^{-1} *unidentified*
$HCl(aq)37\%$	$[Rh(CO)_2Cl_2]^-$
$SnCl_2.2H_2O$	2040 cm^{-1} *unidentified*
$(CH_3)_2CHOH$	
CO/C_2H_4	

Dichlorodicarbonylrhodate(I) anion is observed at 25°C. The absorbance bands at 2081, 2017 cm^{-1} were observed from 25°C to 150°C, only above this temperature was the 2040 cm^{-1} band observed to the exclusion of all other species. It is possible that the bands observed at 2081, 2017 cm^{-1} are associated with the same species that occurs in reactions 5.2.1 and 5.2.2. If this is the case then the loss of these peaks above 150°C suggests they are involved either in generating the catalyst or in the catalytic process. However the species absorbing at 2040 cm^{-1} may be a complex with a trichlorostannate(II) ligand. Therefore further investigations of the catalytic rhodium-tin systems of Chapter 4 are required.

5.4 Rhodium-tin-chloride catalytic systems

In considering the rhodium-tin-chloride system there are a number of variables available for investigation. As lithium carbonate was used as the cation in reaction 5.2.2, a rhodium-tin system employing this cation was investigated first. This was followed by a reaction employing benzyltriethylammonium chloride. In both cases the ratio of rhodium to tin employed was 1:1. This may permit the study of systems that may not form exclusively rhodium-tin complexes. Thus it may be possible to observe at what temperature rhodium-tin complexes are favoured over rhodium-chloride complexes, and whether this coincides with the exothermic reaction observed for systems employing tetrabutylammoniumchloride (see Chapter 4, section 4.4).

For these reasons the first reaction was conducted with lithium carbonate and a rhodium-tin ratio of 1:1.

Reaction 5.4.1	***Species Observed***
$RhCl_3.3H_2O$	*2099 cm^{-1} unidentified*
Li_2CO_3	*2060 cm^{-1} unidentified*
$SnCl_2.2H_2O$	*2020 cm^{-1} unidentified*
HCl(aq)37%	*2007 cm^{-1} unidentified*
CH_3CO_2H/CH_2Cl_2	
CO	

At 180°C the first three absorbance bands are observed. As the reaction progresses they are lost. The absorbance band at 2007 cm^{-1} remains. There is no apparent relationship between these bands and any observed thus far. It is possible that the bands at 2060, 2020 cm^{-1} are associated with the same compound, possibly tri(trichlorostannate(I))dicarbonylrhodate(III) $[Rh(CO)_2(SnCl_3)_3]$. However the literature values for this species are 2060, 2010 cm^{-1} (5). If this is the case then it is possible the peak observed at 2007 cm^{-1} is tri(trichlorostannate(II))-

carbonylrhodate(III) [$Rh(CO)(SnCl_3)_3$]. In general the spectral quality was poor for this reaction. It is possible therefore that the species are being precipitated from solution at the reaction temperature.

These ideas were pursued further by a reaction employing benzyltriethylammonium-chloride instead of lithium carbonate.

Reaction 5.4.2	*Species Observed*
$RhCl_3.3H_2O$	*2077, 2003 cm^{-1} unidentified*
$Bz(Et)_3NCl$	*1985 cm^{-1} unidentified*
$SnCl_2.2H_2O$	$[Rh(CO)_2Cl_2]^-$
HCl(aq)37%	
CH_3CO_2H/CH_2Cl_2	
CO	

The absorbance bands at 2077 and 2003 cm^{-1} are first seen at 130°C (see Figure 5.3) and remain throughout the reaction. The band at 1985 cm^{-1} is observed at 180°C (see Figure 5.4) but is lost on cooling to 25°C. However the absorbance bands associated with $[Rh(CO)_2Cl_2]^-$ at 2044 and 1983 cm^{-1} emerge on return to 25°C (see Figure 5.5). This sequence of spectra shows no apparent relationship to that of reaction 5.4.1, though the same bands are seen at various stages in reactions 5.2.1, 5.2.2 and 5.3. The bands at approximately 2077, 2005 cm^{-1} are seen throughout all these three reactions and it is possible that these relate to the ion-pair $[H^+....Rh(CO)_2Cl_2^-]$.

Figure 5.3

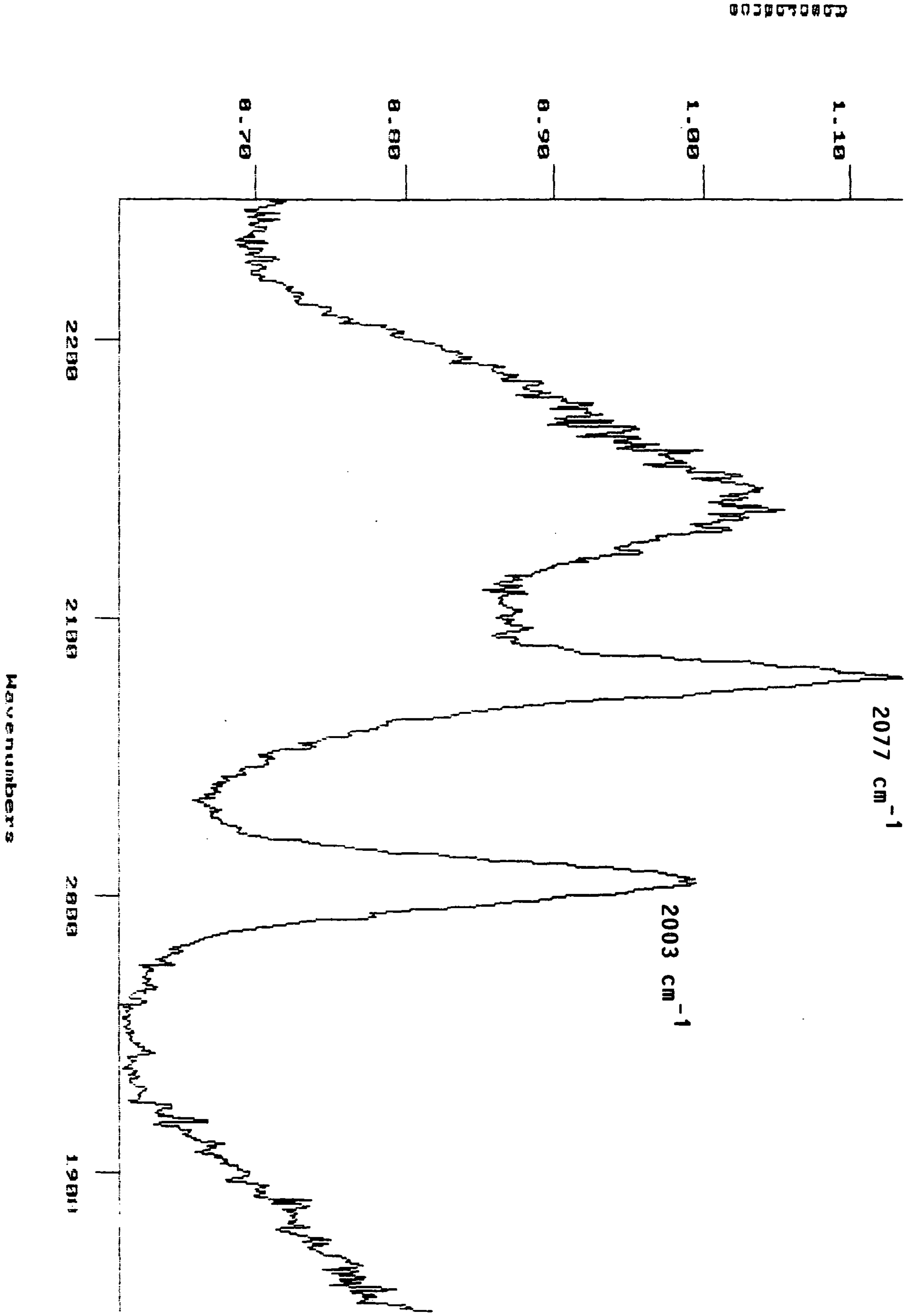
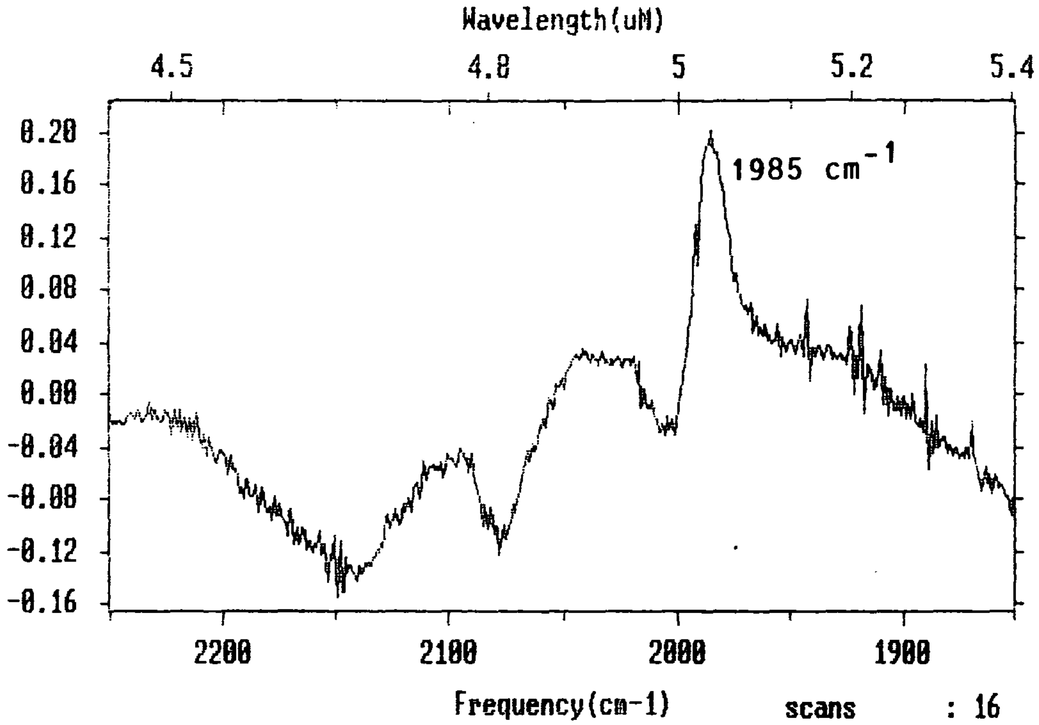

Absorbance
0.70
0.80
0.90
1.00
1.10
2200
2100
2000
1900
Wavenumbers
2077 cm^{-1}
2003 cm^{-1}

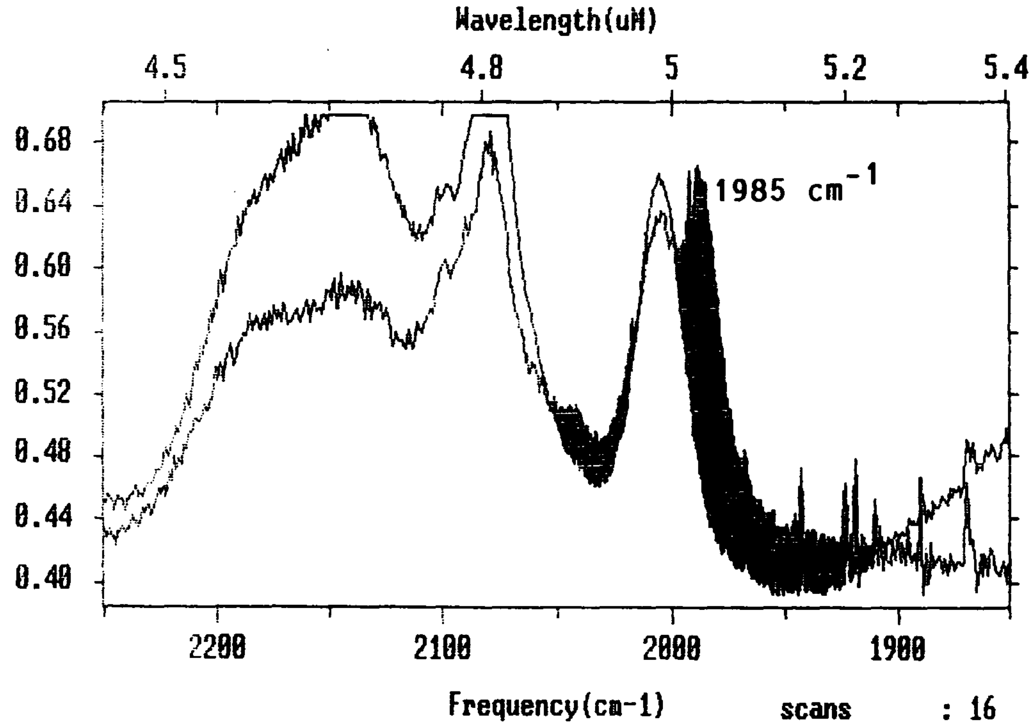
Figure 5.4



scans : 16
resolution : 2

Difference spectrum

ubtraction Factor: 1.000

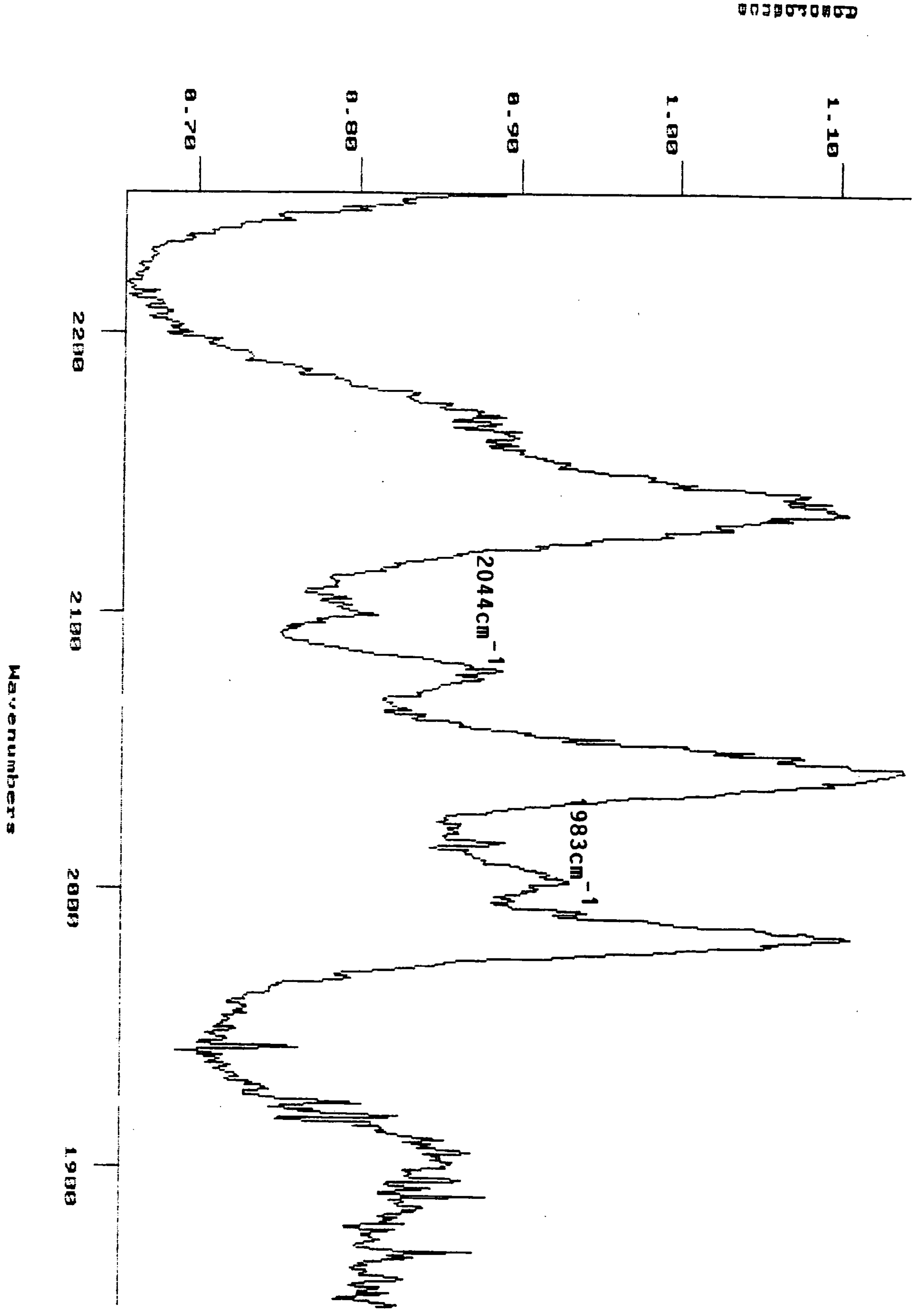


scans : 16
resolution : 2

Subtraction spectra

btraction Factor: 1.000

Figure 5.5


Absorbance
0.70
0.80
0.90
1.00
1.10
2200
2100
2000
1900
Wavenumbers
2044cm^{-1}
1983cm^{-1}

The absorbance band at 1985 cm^{-1} is again observed, as it was for reaction 5.2.2. A similar absorbance band was reported in Chapter 2. It is noted in Chapter 6 that the lithium-rhodium-chloride system is also catalytically active. Therefore it is possible that this species absorbing at 1985 cm^{-1} is important to hydrocarbonylation catalysis.

Two sets of absorbance bands are present at room temperature; the bands at 2077, 2003 cm^{-1} have been discussed, but are seen here for the first time at room temperature. It seems possible that the benzyltriethylammonium cation stabilises the species at lower temperatures than the lithium cation. This would appear to be at variance with the observations of Chapter 4, where the analysis of reaction pressure profiles suggested that the system containing a lithium cation maintained its catalytic activity for a longer period of time.

In an attempt to confirm the assignment of the bands observed in reaction 5.4.1 and 5.4.2, a further reaction was conducted with the same components as reaction 5.4.2, but with a rhodium:tin ratio of 1:2.

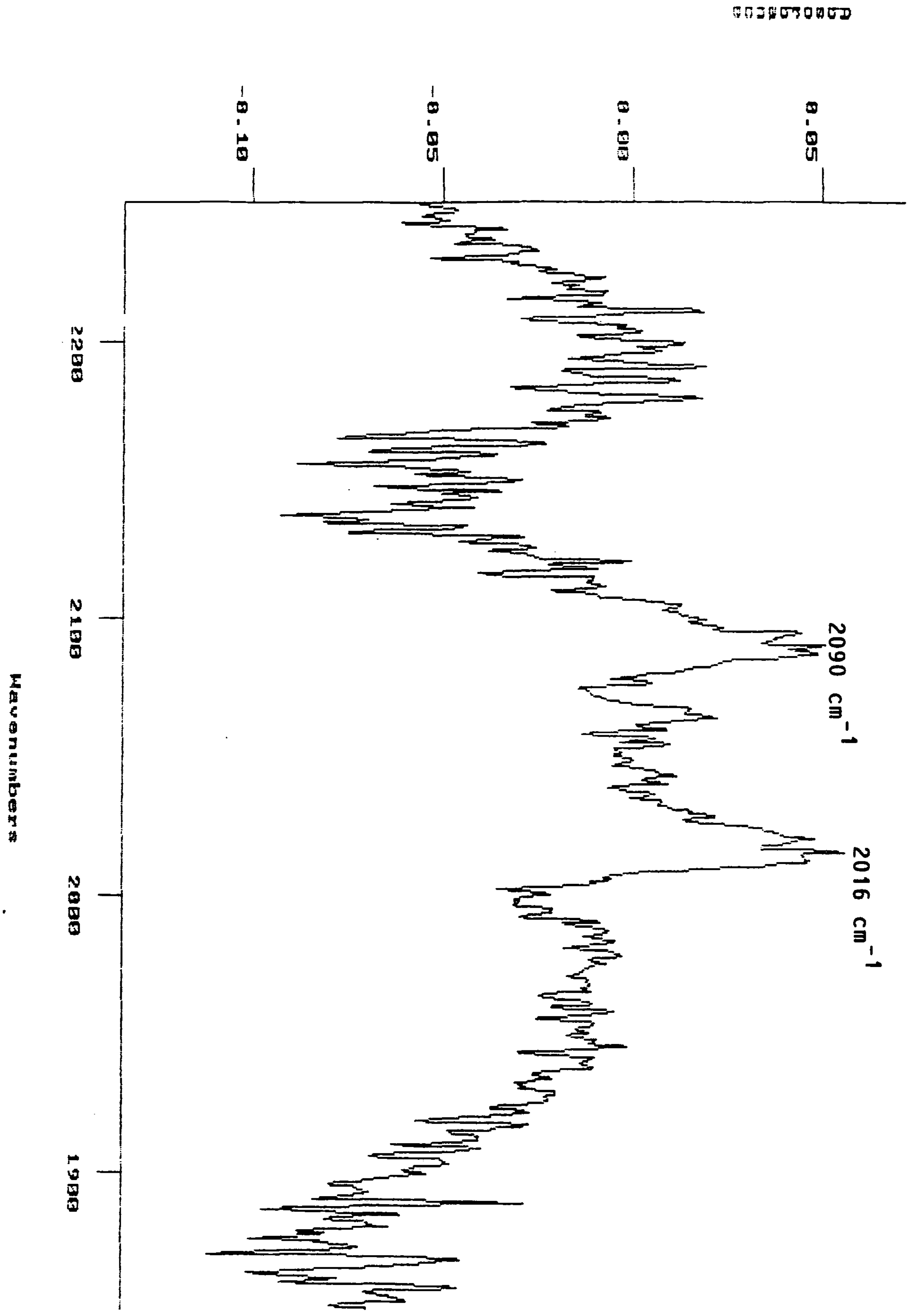
Reaction 5.4.3	***Species Observed***
$RhCl_3.3H_2O$ $Bz(Et)_3NCl$ $SnCl_2.2H_2O$ *HCl(aq)37%* CH_3CO_2H/CH_2Cl_2 *CO*	*2078, 2006 cm^{-1} unidentified* *2090, 2016 cm^{-1} unidentified*

In this reaction only two groups of absorbance bands are observed. The strong bands at 2078, 2006 cm^{-1} first arise at 155°C. It is not until 175°C that the weak absorbance bands at 2090, 2016 cm^{-1} are observed (see Figure 5.6).

The fact that the bands at 2078, 2006 cm^{-1} are apparently part of sequence, wherein the second group are those at 2090, 2016 cm^{-1}, suggests that the assignment of the 2077, 2005 cm^{-1} bands to the ion-pair $[H^+....Rh(CO)_2Cl_2^-]$ may be incorrect. It is not possible that the bands are due to a rhodium-tin complex because tin was absent from reaction 5.2.1 and 5.2.2. The following possibilities may be considered. If there is the formation of the ion-pair $[H^+....Rh(CO)_2Cl_2^-]$ [2077, 2005 cm^{-1}], then it is possible that the absorbance bands at 2090, 2016 cm^{-1} are due to either the ion-pair $[H^+....Rh(CO)_2Cl(SnCl_3)^-]$ or $[H^+....Rh(CO)_2(SnCl_3)_2^-]$. Another possibility is that the bands at 2077, 2005 cm^{-1} in reactions 5.4.2 and 5.4.3 arise from $[Rh(CO)_2Cl(SnCl_3)]^-$ with the bands at 2090, 2016 cm^{-1} corresponding to $[Rh(CO)_2(SnCl_3)_2]^-$.

In Chapter 4, studies involved the use of triphenylphosphine as an additive for the rhodium-tin-chloride catalytic system. In employing the components rhodium(III) chloride, tin(II) chloride and triphenylphosphine a ratio of 1:1:2 was used for an infra-red study.

Figure 5.6


Absorbance
-0.10
-0.05
0.00
0.05
2200
2100
2000
1900
Wavenumbers
2090 cm^{-1}
2016 cm^{-1}

Reaction 5.4.4	**Species Observed**
$RhCl_3.3H_2O$	2079, 2009 cm^{-1} unidentified
$SnCl_2.2H_2O$	2093, cm^{-1} unidentified
Ph_3P	
HCl(aq)37%	
CH_3CO_2H/CH_2Cl_2	
CO	

All of these bands were observed at 180°C. The first pair correspond to those observed in earlier sections of this chapter, due to $[H^+....Rh(CO)_2Cl_2^-]$. The third band, previously unobserved, is probably a rhodium-triphenylphosphine complex, possibly incorporating tin. These results suggest that there are two separate processes occurring in this reaction system, one involving rhodium-tin-chloride species and another rhodium-triphenylphosphine species. This explanation would appear to be compatible with the observations of section 4.8 when there appeared to be some competition between the rhodium-tin and rhodium-triphenylphosphine reactions.

5.5 A Summary of rhodium-tin-chloride reaction systems

The main feature of these reactions is the presence of the absorbance bands at approximately 2079, 2005 cm^{-1}. It has been proposed that these should be assigned to the ion-pair $[H^+....Rh(CO)_2Cl_2^-]$ (reaction 5.2.1). These peaks are observed in the presence of lithium, trichlorostannate(II) anion and triphenylphosphine. It therefore seems highly likely that the rhodium(I) species $[Rh(CO)_2Cl_2]^-$ is protonated to form the ion-pair which is attacked by an anion, which in the most reactive cases is probably the trichlorostannate(II) anion. This form of oxidative addition was considered in Chapter 1. This process produces a rhodium(III) species $[HRh(CO)_2X_3]^-$ (X = Cl and/or $SnCl_3$), which would then continue to react in the hydrocarbonylation reaction. It may be assumed that $[SnCl_3]^-$ is a much better anion for attack on the ion-pair than the chloride anion.

There is however an alternative possibility. Another set of bands is observed in reaction 5.4.3, which employed a rhodium-tin ratio of 1:2, the conditions that give the highest rate of reaction (Chapter 4). These absorbance bands at 2090, 2016 cm^{-1} may relate to the catalytical active species, only observable at these optimum conditions. If this were the case then the ion-pair $[H^+....Rh(CO)_2Cl_2^-]$ would not, despite being the major species in solution, be catalytically active itself. A parallel may be drawn to $[Rh(CO)_2I_4^-]$ in the Rh-I system, which is the inactive major species in solution. In both cases the turnover relative to rhodium must be severely reduced.

5.6 Rhodium-tin-iodide catalytic systems

Having made the observation that the addition of tin(II) chloride to the rhodium-chloride system greatly increases the catalytic activity, the question arises as to whether tin(II) chloride or possibly tin(II) iodide will increase the catalytic activity of the rhodium-iodide system. It has been noted(6) that the addition of small amounts of transition metal iodides, including iron(II), cobalt(II) and manganese(II), can greatly increase the rate of ethene hydrocarbonylation when the rhodium-ethyliodide catalytic system is employed. It seems likely therefore that the addition of tin(II) halides will increase the rate of reaction, for the rhodium iodide systems studied in Chapter 3. To deduce whether this is in fact the case, a reaction was conducted in the same manner as for the reactions of Chapter 3. The 105 ml hastalloy autoclave was used. Tin(II) chloride dihydrate was utilised as the source of tin(II) halide, however it is very unlikely that it remained as the chloride, given the high concentration of iodide in the reaction solution (see section 5.8). In addition a small amount (see section 5.8) of concentrated hydrochloric acid was added to ensure the tin(II) chloride present is stable. For comparison, details of the rhodium-iodide system, reaction 3.2.7, are quoted.

Autoclave: 500Z *Temperature: 180 C*

Standard components:

RhI_3 : EtI : H_2O : CH_3CO_2H : CO, 40 bar : C_2H_2, 40 bar;

Reaction number	*Components*	*Moles of Propanoic Acid produced*	*Rate (1) Bar/hr*	*Rate (2) /mol.kg^{-1}.hr^{-1}*	*% (3) selectivity*
5.6.1	$SnCl_2.2H_2O$/ HCl(aq)37%	0.125	384	12.8	83.5
3.2.7	-	0.226	218	15.7	82.1

Notes: (1) *Rate of gas absorption*

(2) *Rate of Propanoic Acid production*

(3) *Percentage propanoic acid of all reaction products as determined by G.L.C.*

While a much smaller amount of propanoic acid is produced the rates and selectivity in both reactions are of the same magnitude.

It is possible that the tin(II) chloride added to reaction 5.6.1 does not affect the reaction in any manner. An infra-red study of this reaction system should indicate the extent, if any, of tin involvement in the reaction.

Reaction 5.6.2	*Species Observed*
$RhCl_3.3H_2O$	$Rh(CO)_3Cl$
$SnCl_2.2H_2O$	*2097 cm^{-1} unidentified*
Bu_4NI/EtI	*2016 cm^{-1} unidentified*
H_2O	$[Rh(CO)_2I_4]^-$
CH_3CO_2H/CH_2Cl_2	$[Rh_2(CO)_2I_4]^{2-}$
CO	*2068 cm^{-1} unidentified*
	2044 cm^{-1} unidentified
	1986 cm^{-1} unidentified
	1983 cm^{-1} unidentified

The first of these absorbance bands are seen at 140°C, and shows that rhodium(III) chloride has been carbonylated to chlorotricarbonylrhodate (I), $[Rh(CO)_3Cl]$. At the same time the absorbance bands at 2087, 2016 cm $^{-1}$ are observed. These latter two bands are reminiscent of those observed in reaction 5.4.3 when they were assigned to a rhodium-tin-carbonyl chloride ion pair. While it is possible that this is the same species, it is surprising that it is observed under the conditions of this reaction. When the reaction reaches 165°C both $Rh(CO)_3Cl$ and 2087, 2016 cm^{-1} species are lost from the spectrum (see Figure 5.7). The complexes that come to prominence at this point are $[Rh(CO)_2I_4]^-$ and $[Rh_2(CO)_2I_4]^{2-}$. This is very much in line with the general trend of the rhodium-iodide systems studied in Chapter 3.

At 180°C these two rhodium-carbonyl-iodide complexes both remain, however three additional peaks are observed at 2068 cm^{-1} (w), 2044 cm^{-1} (vs), and 1986 cm^{-1} (m) (see Figure 5.8). If these three absorptions are caused by more than one species, then interpretation becomes very difficult due to the large number of possible permutations. If, alternatively only one species is responsible for these three absorptions then the species $[Rh_2(CO)_4Y_2]$ (y = SnX_3, X = Cl, I), is most likely as $[Rh_2(CO)_4I_2]$ and $[Rh_2(CO)_4Cl_2]$ have similar absorption patterns to that observed here (see Appendix 1).

In either case it is obvious that the chemistry of the reaction at 180°C has been altered by the addition of tin(II) chloride.

On returning the reaction solution to room temperature only two absorbance bands remain, these being a band at 1983 cm^{-1} seen throughout all these infra-red studies, and the band, assigned to $[Rh(CO)_2I_4]^-$ at 2085 cm^{-1}.

Only a thorough investigation of the rhodium-tin-chloride system will reveal the nature of the unidentified absorbance bands. Evaluation of this system for catalytic hydrocarbonylation of ethene as compared to the rhodium-iodide system would require a constant flow reactor, not available to this study, operating at 180°C, to provide values for selectivity and comparative rates of reaction. This would also enable the establishment of the relative stability of the two catalyst systems.

Figure 5.7

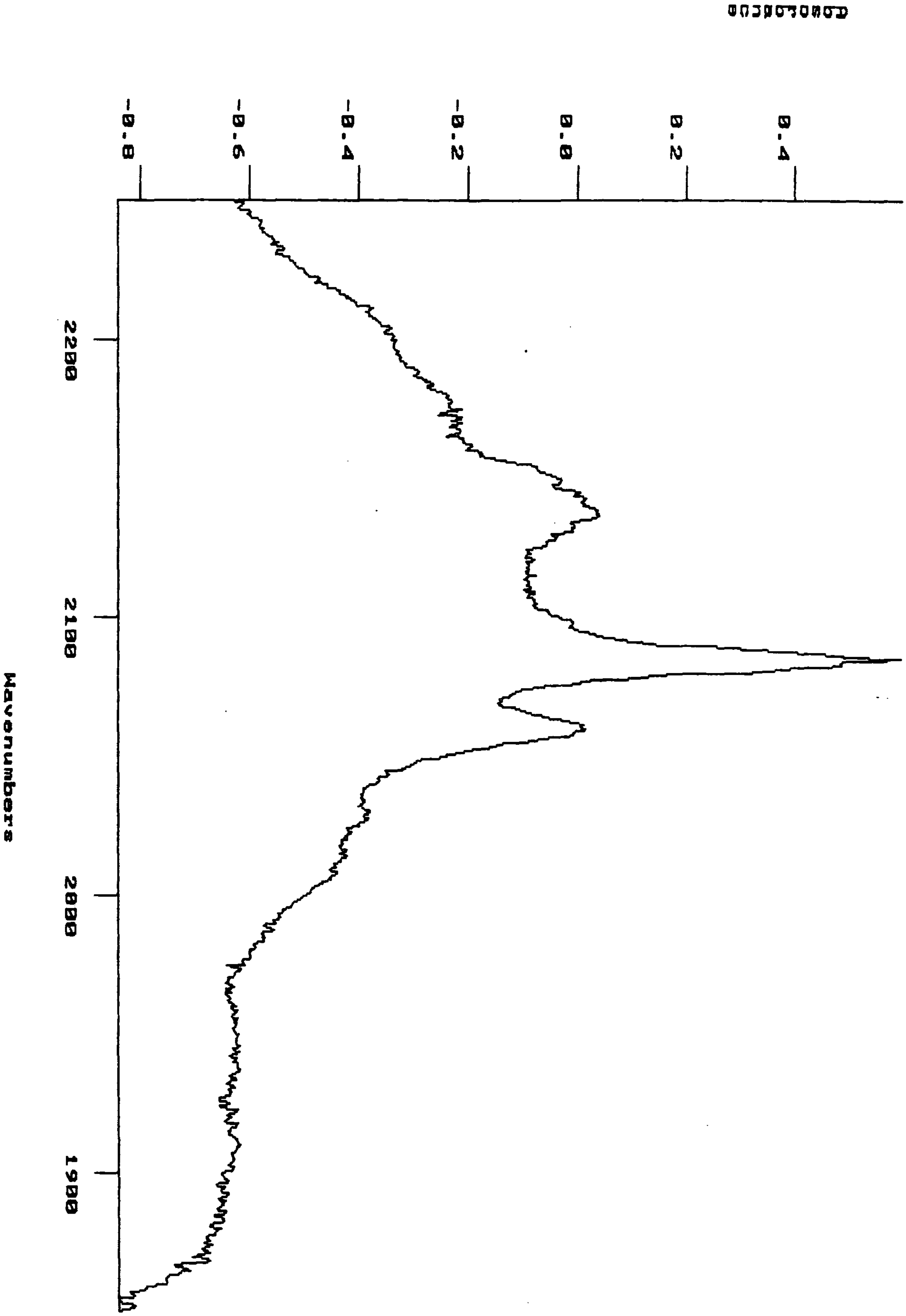
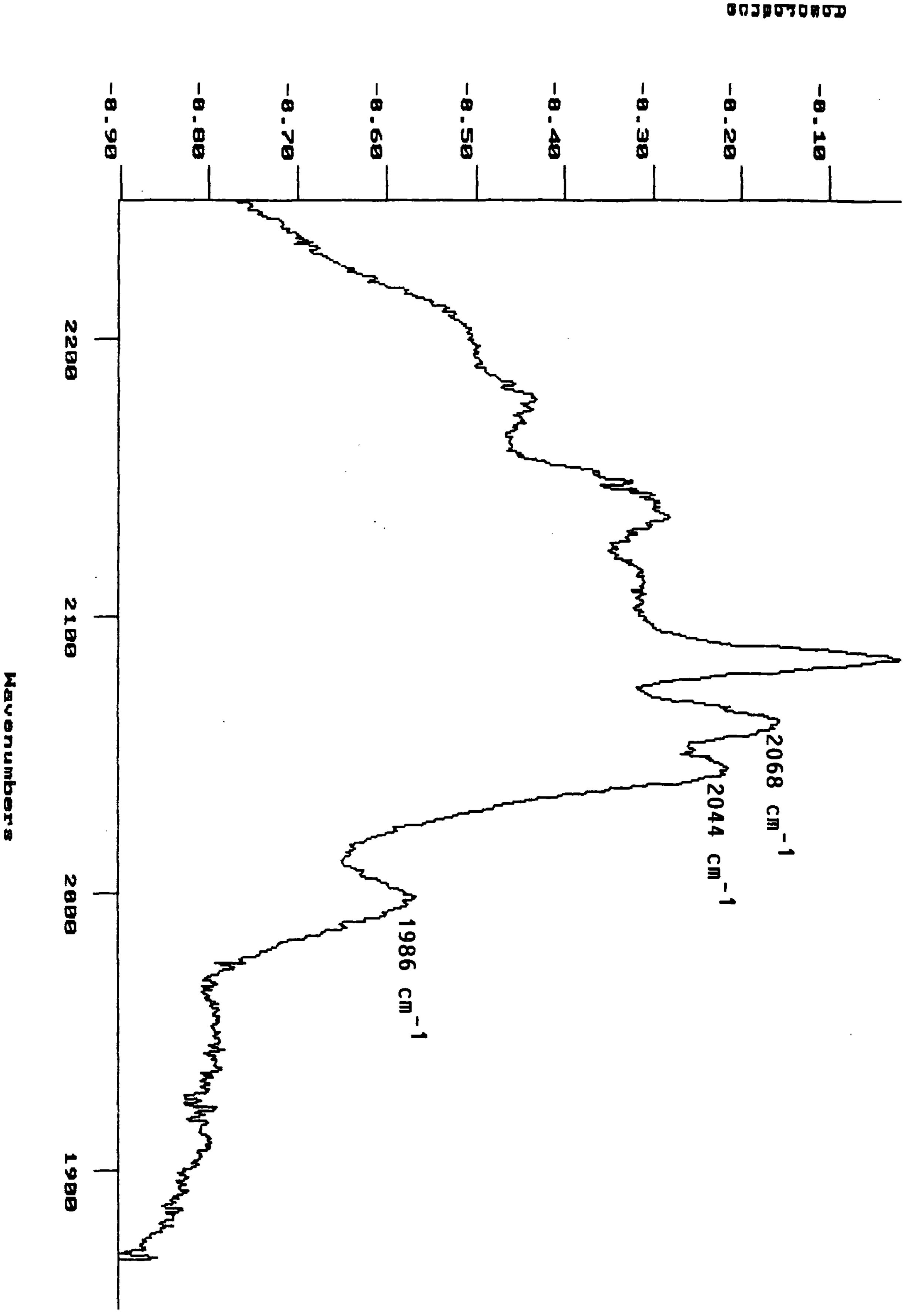

Absorbance
-0.8
-0.6
-0.4
-0.2
0.0
0.2
0.4
2200
2100
2000
1900
Wavenumbers

Figure 5.8


Absorbance
-0.90
-0.80
-0.70
-0.60
-0.50
-0.40
-0.30
-0.20
-0.10
2200
2100
2000
1900
Wavenumbers
2068 cm^{-1}
2044 cm^{-1}
1986 cm^{-1}

5.7 A summary of rhodium-halide and rhodium-tin-halide catalytic systems

When the results of Chapters 2, 3, 4 and 5 are analysed collectively, a number of areas of contrast and comparison are seen between the two systems studied.

Initial studies into the rhodium-iodide system were aimed at identifying possible hydro-intermediates in the catalytic hydrocarbonylation reaction cycle, but no such intermediates were identified although some unknowns remain. Although $[Rh(CO)_2I_2]^-$ was observed at reaction temperature, the major species observed was $[Rh(CO)_2I_4]^-$ formed either by substitution and/or addition of carbonyl and iodo-ligands to the original rhodium(III) species, or by addition of iodo- ligands to anion $[Rh_2(CO)_2I_4]^{2-}$.

A major problem encountered in the studies related to the identification of a solvent for consistent infra-red observation, particularly in the presence of ethene gas, which hampers identification of some absorbances.

A number of absorbance bands remain unassigned. One unidentified absorption occurs at 1985 cm^{-1}. It is observed throughout the whole range of reaction systems. It would appear to be formed at approximately 175 - 180 C but is then stable at room temperature while under a pressure of carbon monoxide. As this species occurs in the presence and absence of all or any of the iodo, chloro, or trichlorostannate(II) anions it is likely that it is a rhodium-carbonyl-propanoate complex. This conclusion is substantiated by the reaction employing lithium propanoate when the 1985 cm^{-1}

absorbance band is particularly strong, and have some correlation with the spectra observed by Fulford[3] (see Appendix 1).

The ion pair [A^+....$Rh(CO)_2I_2^-$] was observed only in dichloromethane solvent, in the absence of water or propanoic acid, complementing the observations of Fulford[3]. However in the rhodium-chloride and rhodium-tin-chloride reaction systems the ion pair [A^+....$Rh(CO)_2Cl_2^-$] was observed both in the presence of ethanoic acid and water. This difference in stability with regard to the rhodium(III) state is in agreement with the trends in Chapter 1 in that the iodide species form the +3 oxidation state more readily than the chloride species.

This difference may cause the two reaction systems to progress by different catalytic cycles. It seems more likely however that this difference merely makes it impossible to observe the less stable iodo- ion pair [H^+....$Rh(CO)_2I_2^-$] under the conditions used (Chapter 2).

The relevant generic catalytic cycle is shown in Figure 5.9. The action of $[SnCl_3]^-$ may be envisaged in terms of this scheme, in that it is an alternative, and more effective Y-nucleophile than the chloride anion. This would indicate that addition of a tin compound to the rhodium-iodide system would not be as beneficial as addition to the rhodium chloride system, because iodide is a far more effective Y-nucleophile than chloride.

It is not apparent, from this catalytic cycle, why a quaternary ammonium ion is so important to the rhodium-tin-chloride system, but not the rhodium-iodide system.

It is possible that this effect is due to the cation stabilising the ion pair by a general ion effect. This theory may be tested by varying the cation concentration.

While observation of the catalytic intermediates of the rhodium-iodide system has not proved possible as originally envisaged, it has been possible to propose a route of oxidative addition (Figure 5.9) by reference to the new rhodium-tin-chloride system and the work of Fulford(3).

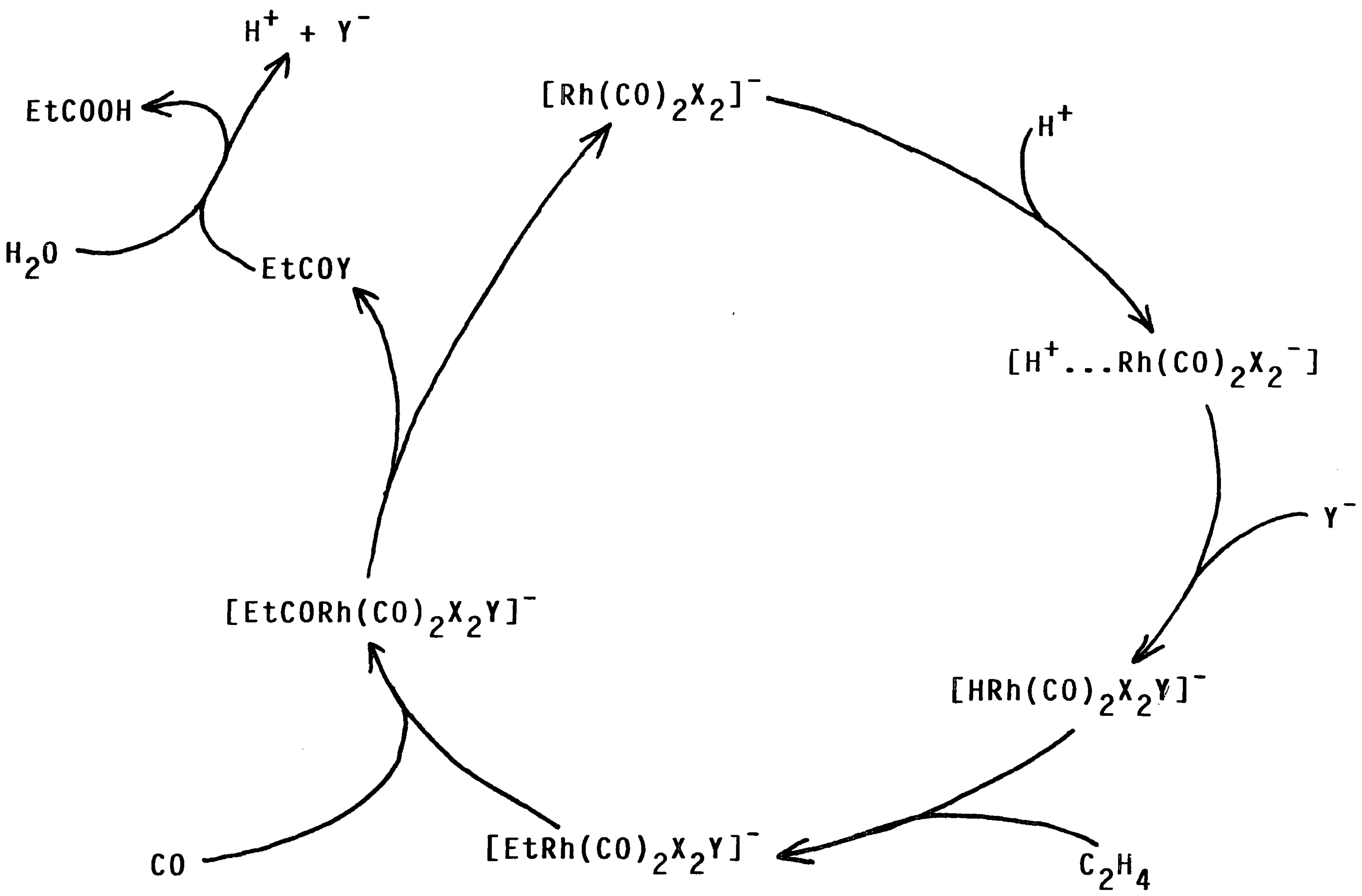

$H^+ + Y^-$
EtCOOH
$[Rh(CO)_2X_2]^-$
H^+
H_2O
EtCOY
$[H^+ ... Rh(CO)_2X_2^-]$
Y^-
$[EtCORh(CO)_2X_2Y]^-$
$[HRh(CO)_2X_2Y]^-$
CO
$[EtRh(CO)_2X_2Y]^-$
C_2H_4

Figure 5.9

5.8 Chapter 5 - Reaction Index

Reaction Number	Reactants/Moles	Solvents	Temperature Range/°C	Pressure/ bar	Gases	Species Identified	Reaction Code
5.2.1	$RhCl_3.3H_2O$, 1.9 x 10^{-4} HCl, 37%(aq), 1.4 x 10^{-2}	C_2H_5COOH CH_2Cl_2	20 - 180	41 - 72	CO	$[H^+....Rh(CO)_2Cl_2^-]$	RhSCC_11
5.2.2	$RhCl_3.3H_2O$, 2.1 x 10^{-4} HCl, 37%(aq), 1.4 x 10^{-2} Li_2CO_3, 9.3 x 10^{-5}	C_2H_5COOH CH_2Cl_2	20 - 180	41 - 66	CO	$[A^+....Rh(CO)_2Cl_2^-]$	RhSCC_12
5.3	$RhCl_3.3H_2O$, 1.9 x 10^{-4} $SnCl_2.2H_20$, 8.3 x 10^{-4}	$(CH_3)_2CHOH$	20 - 175	17 - 31	CO C_2H_4	$[Rh(CO)_2Cl_2]^-$	RhSnCO_3
5.4.1	$RhCl_3.3H_2O$, 2.0 x 10^{-4} $SnCl_2.2H_20$, 2.3 x 10^{-4} Li_2CO_3, 6.5 x 10^{-4} HCl, 37%(aq), 1.4 x 10^{-2}	C_2H_5COOH CH_2Cl_2	20 - 180	1 - 67	CO		RhSCC_13
5.4.2	$RhCl_3.3H_2O$, 2.0 x 10^{-4} $SnCl_2.2H_20$, 2.3 x 10^{-4} $PhCH_2(Et)_3NCl$, 1.9 x 10^{-4} HCl, 37%(aq), 1.4 x 10^{-2}	C_2H_5COOH CH_2Cl_2	20 - 180	1 - 70	CO	$[Rh(CO)_2Cl_2]^-$	RhSCC_14
5.4.3	$RhCl_3.3H_2O$, 2.1 x 10^{-4} $SnCl_2.2H_20$, 4.0 x 10^{-4} $PhCH_2(Et)_3NCl$, 2.1 x 10^{-4} HCl, 37%(aq), 1.4 x 10^{-2}	C_2H_5COOH CH_2Cl_2	20 - 180	1 - 56	CO		RhSCC_17
5.4.4	$RhCl_3.3H_2O$, 2.0 x 10^{-4} $SnCl_2.2H_20$, 2.5 x 10^{-4} $PhCH_2(Et)_3NCl$, 1.8 x 10^{-4} HCl, 37%(aq), 1.4 x 10^{-2} Ph_3P, 2.1 x 10^{-4}	C_2H_5COOH CH_2Cl_2	20 - 180	1 - 55	CO		RhSCC_18

5.8 Chapter 5 - Reaction Index (cont)

Reaction Number	Reactants/Moles		Solvents	Temperature Range/°C	Pressure/ bar	Gases	Species Identified	Reaction Code
5.6.2	$RhCl_3.3H_2O$, $SnCl_2.2H_20$, $(C_4H_9)_4NI$, EtI, H_2O,	2.0×10^{-4} 2.4×10^{-4} 1.7×10^{-4} 1.2×10^{-2} 2.8×10^{-2}	C_2H_5COOH CH_2Cl_2	20 - 180	38 - 65	CO	$Rh(CO)_3Cl$ $[Rh(CO)_2I_4]^-$ $[Rh_2(CO)_2I_4]^{2-}$	RhICO_64
							Rate of reaction/ mol.kg^{-1}.hr^{-1}	
5.6.1	RhI_3. $SnCl_2.2H_2O$, EtI, H_2O, HCl, 37%(aq),	1.0×10^{-4} 2.5×10^{-4} 3.6×10^{-4} 1.4×10^{-1} 8.2×10^{-3}	CH_3COOH	20 - 202	139 - 43	CO C_2H_4	12.8	D3HR85

CHAPTER 5 - REFERENCES

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2 (a) J. Chatt and B.L. Shaw, J. Chem. Soc. (A) (1966) 1437.

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6 U.S. Patent 4,132,734 (1979)

CHAPTER SIX

CONTENTS

CHAPTER 6

ALTERNATIVE METAL CO-CATALYSTS FOR THE RHODIUM-CHLORIDE SYSTEM

6.1 Introduction

In Chapter 4 lithium salts, used to provide a cation for the catalytic systems, were observed to give much slower rates than tetralkylammonium cations, but much greater selectivity (see section 4.4).

In Chapter 5 the infra-red absorptions at 2079, 2005 cm^{-1} were observed when lithium carbonate was added to a rhodium-chloride system (see Reaction 5.2.2), but not when lithium carbonate was added to a rhodium-tin-chloride system (see Reaction 5.4.1). The questions which follow are: whether lithium-rhodium-chloride systems are catalytically active, and whether the lithium-rhodium-tin-chloride systems utilise the tin present.

6.2 Group 1, 2 and 3 metals as co-catalysts

To investigate the activity of the lithium-rhodium-chloride system a batch reaction was conducted in the 105 ml hastalloy autoclave (all reactions in this chapter were conducted in the same manner as those in Chapter 4). Full details of amounts of reactants used are to be found in Section 6.4.

Standard components:

$RhCl_3.3H_2O$: $Bz(Et)_3NCl$: $HCl(aq)37\%$: CH_3CO_2H : CO, 40 bar: C_2H_4, 40 bar;

Temperature: 180°C

Reaction number	*Co-catalyst*	*Moles of Propanoic Acid produced*	*Rate (1) Bar/hr*	*Rate (2) /mol.kg^{-1}.hr^{-1}*	*% (3) selectivity*
6.2.1	Li_2CO_3	0.058	38.0	1.51	97.3

Notes: (1) *Rate of gas absorption*

(2) *Rate of Propanoic Acid production*

(3) *Percentage Propanoic Acid of all reaction products as determined by G.L.C.*

This reaction shows a slow catalytic activity, though rate and selectivity are approximately the same as for the lithium-rhodium-tin-chloride system (reaction 4.4.3).

This may indicate that the catalytic system operating in reaction 4.4.3 does not involve tin. If this is the case then the difference in rate between the reactions employing lithium and that employing benzyltriethylammonium cationic species, is easily explained by the fact that two different active catalytic species operate in these two systems.

The observation that lithium is an active co-catalyst for the rhodium-chloride system prompts an investigation of other main group metals as co-catalysts. The lithium reaction is included below for comparison.

Standard components:

$RhCl_3.3H_2O$: $Bz(Et)_3NCl$: $HCl(aq)$37% : CH_3CO_2H : CO, 40 bar: C_2H_4, 40 bar;

Temperature: 180°C

Reaction number	*Co-catalyst*	*Moles of Propanoic Acid produced*	*Rate (1) Bar/hr*	*Rate (2) /mol.kg^{-1}.hr^{-1}*	*% (3) selectivity*
6.2.1	*Li_2CO_3*	*0.058*	*38.0*	*1.51*	*97.3*
6.2.2	*$MgCl_2$*	*0.049*	*77.8*	*1.44*	*52.0*
6.2.3	*$Al(OH)_3$*	*0.040*	*32.4*	*1.27*	*†*

† *The gas liquid chromatograph showed no other products giving a theoretical value of 100%.*

There is little variation in the rate of reaction between these three reactions. However the selectivity, for both the lithium and aluminium co-catalyst reactions, is excellent.

In Chapter 4 the main method of action considered was the formation of rhodium-tin complexes. The infra-red data described in Chapter 5 suggests that the main species present in the rhodium-tin-chloride systems is the ion-pair [H^+....$Rh(CO)_2Cl_2^-$]. If this is the case then there is the possibility that the metal co-catalysts are acting in the same manner for each reaction. The oxidative addition of [$HSnCl_3$] to the rhodium centre was the method of action considered most likely for tin co-catalysts in these rhodium-chloride systems. However it is unlikely that the lithium or magnesium systems would react in this manner. While the aluminium chloride could form the ion-pair [H^+ $AlCl_4^-$], the aluminium would be co-ordinatively saturated and bonding to rhodium would be restricted to chloride bridges. Thus there is the possibility that the action of these co-catalysts is due to Lewis acid properties, which occur also for transition metals.

6.3 Transition metals as co-catalysts

In Chapter 1 the ability of both nickel and cobalt systems to catalyse the hydrocarbonylation of ethene was discussed. The cobalt system has been used industrially but requires high pressures of carbon monoxide to maintain the cobalt in solution. The nickel systems have severe selectivity problems, as several ethene insertions can occur. The problems associated with high carbon monoxide pressures make cobalt unacceptable as a co-catalyst. Various transition metals, including nickel, have however been screened as possible co-catalysts, the results being summarised below. Reactions 6.2.1 and 4.2.2 are given for comparison.

Standard components:

$RhCl_3.3H_2O$: $Bz(Et)_3NCl$: HCl(aq)37% : CH_3CO_2H : CO, 40 bar: C_2H_4, 40 bar;

Temperature: 180°C

Reaction number	Co-catalyst	Moles of Propanoic Acid produced	Rate (1) Bar/hr	Rate (2) $/mol.kg^{-1}.hr^{-1}$	% (3) selectivity
6.2.1	Li_2CO_3	0.058	38.0	1.51	97.3
4.2.2	$SnCl_2.2H_2O$	0.121	137.0	5.41	88.6
6.3.1	$FeCl_3.6H_2O$	0.100	54.5	1.44	68.7
6.3.2	$NiCl_2$	0.038	30.0	1.52	95.6
6.3.3	$CuCl_2.4H_2O$	0.013	0	0.59	58.0
6.3.4	$Zn(OAc)_2$	0.088	42.8	1.74	94.2

In considering these co-catalysts copper is noticeably poor. However lithium, iron, nickel and zinc all give similar rates of reaction, although this rate is markedly smaller than that of the tin reaction. All the metals have the ability to act as Lewis acids, furthermore they can form compounds: MCl_x^-. In discussing these co-catalysts it is worthwhile noting that, as for aluminium, there is the possibility of bi-metallic complexes containing chloride bridges:-

Rh ------ Cl ------ M

In Chapter 5 the formation of the ion pair $[H^+....Rh(CO)_2Cl_2^-]$ was detected and considered in the context of the catalytic cycle.

The formation of rhodium-tin complexes containing metal-metal bonds is detailed in Section 4.1.

From these observations it is possible to identify four feasible modes of operation for the co-catalysts studied in this chapter.

(i) Formation of $[M^+....Rh(CO)_2Cl_2^-]$
(ii) Promotion of formation of $[H^+....Rh(CO)_2Cl_2^-]$
(iii) Formation of bridged metal-metal complexes
(iv) Formation of direct metal-metal complexes.

Considering each in turn:

(i) The formation of $[M^+....Rh(CO)_2Cl_2^-]$ may promote addition of a third chloride ligand to form $[Rh(CO)_2Cl_3]^{2-}$. However the presence of M^+ seems likely to block the addition of H^+ to form $[HRh(CO)_2Cl_3]$ which would then go on to complete the hydrocarbonylation cycle. A second problem with this mode of operation is that aluminium is unlikely to form a cation species in the presence of HCl; the species $AlCl_4^-$ is expected.

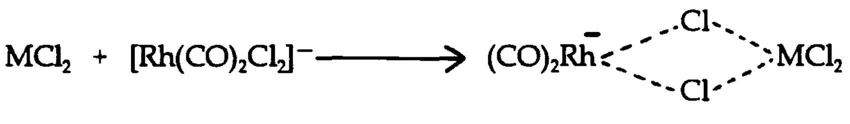
(ii) Promotion of the formation of the ion pair $[H^+....Rh(CO)_2Cl_2^-]$ is easily envisaged:

$$HCl + AlCl_3 + [Rh(CO)_2Cl_2]^- \longrightarrow [H^+....Rh(CO)_2Cl_2^-] + AlCl_4^-$$

This should however be dependent on the strength of the Lewis acid. In Chapter 4 HBF_4 was shown to give very poor rates of reaction (reaction 4.7.8). It therefore seems unlikely that this is the mode of operation for these co-catalysts.

(iii) The formation of bridged complexes would seem possible in all cases:

$$MCl + [Rh(CO)_2Cl_2]^- \longrightarrow Cl(CO)_2\overset{-}{Rh} \text{ ---- } Cl \text{ ---- } MCl$$



$$MCl_2 + [Rh(CO)_2Cl_2]^- \longrightarrow (CO)_2\overset{-}{Rh}\begin{smallmatrix} \cdot\cdot Cl \cdot\cdot \\ \\ \cdot\cdot Cl \cdot\cdot \end{smallmatrix}MCl_2$$

$$MCl_3 + [Rh(CO)_2Cl_2]^- \longrightarrow Cl(CO)_2\overset{-}{Rh} \text{ ----- } Cl \text{ ----- } MCl_3$$

Once the formation of such a complex has taken place then it is possible that oxidative addition is enhanced or that the hydride becomes more stable, thus promoting hydrocarbonylation.

(iv) As discussed in Chapter 4, section 4.1, complexes containing direct rhodium-tin bonds have been synthesised. It is much less likely that the other metals studied in this chapter will form such complexes. This is particularly the case for zinc and aluminium which would be expected to form MCl_4^{x-}.

Although there are no reactions in this chapter that achieve rates of reaction equivalent to those obtained using tin (Chapter 4), the present systems are worthy of further investigation.

The conclusions that can be drawn thus far, indicate that the formation of bi-metallic complexes is of great importance and that tin is most effective as it can form complexes with metal-metal bonds.

It seems possible that infra-red studies would be of use in confirming this theory and expanding the comparison between the co-catalysts of this chapter and tin.

6.4 Chapter 6 - Reaction Index

Reaction Number	Reactants/Moles		Solvents	Temperature °C	Gases	Pressure range/bar	Rate of reaction/ mol/kg/hr	Reaction Code
6.2.1	$RhCl_3.3H_2O$, Li_2CO_3, $PhCH_2(Et)_3NCl$, HCl, 37%(aq),	9.8×10^{-5} 2.2×10^{-4} 2.4×10^{-4} 2.8×10^{-2}	CH_3COOH	180	CO C_2H_4	153 - 50	1.51	D3HR50
6.2.2	$RhCl_3.3H_2O$, $MgCl_2$, $PhCH_2(Et)_3NCl$, HCl, 37%(aq),	1.1×10^{-4} 2.1×10^{-4} 2.5×10^{-4} 2.8×10^{-2}	Ch_3COOH	180	CO C_2H_4	110 - 39	1.44	D3HR43
6.2.3	$RhCl_3.3H_2O$, $Al(OH)_3$, $PhCH_2(Et)_3NCl$, HCl, 37%(aq),	1.0×10^{-4} 2.1×10^{-4} 2.6×10^{-4} 2.8×10^{-2}	CH_3COOH	180	CO C_2H_4	160 - 66	1.27	D3HR51
6.3.1	$RhCl_3.3H_2O$, $FeCl_3.6H_2O$, $PhCH_2(Et)_3NCl$, HCl, 37%(aq),	1.1×10^{-4} 2.2×10^{-4} 2.3×10^{-4} 2.8×10^{-2}	CH_3COOH	180	CO C_2H_4	150 - 22	1.44	D3HR48
6.3.2	$RhCl_3.3H_2O$, $NiCl_2$, $PhCH_2(Et)_3NCl$, HCl, 37%(aq),	1.0×10^{-4} 2.0×10^{-4} 2.4×10^{-4} 2.8×10^{-2}	CH_3COOH	180	CO C_2H_4	159 - 70	1.52	D3HR49
6.3.3	$RhCl_3.3H_2O$, $CuCl_2.4H_2O$, $PhCH_2(Et)_3NCl$, HCl, 37%(aq),	9.8×10^{-5} 2.3×10^{-4} 2.5×10^{-4} 2.8×10^{-2}	CH_3COOH	180	CO C_2H_4	180 - 65	0.57	D3HR47

6.4 Chapter 6 - Reaction Index (cont)

Reaction Number	Reactants/Moles		Solvents	Temperature °C	Gases	Pressure range/bar	Rate of reaction/ mol/kg/hr	Reaction Code
6.3.4	$RhCl_3.3H_2O$, $Zn(OAc)_2$, $PhCH_2(Et)_3NCl$, HCl, 37%(aq),	1.0×10^{-4} 2.1×10^{-4} 2.9×10^{-4} 2.8×10^{-2}	CH_3COOH	180	CO C_2H_4	140 - 34	1.74	D3HR52

CHAPTER SEVEN

CONTENTS

CHAPTER 7

EXPERIMENTAL PROCEDURES

7.1 Introduction

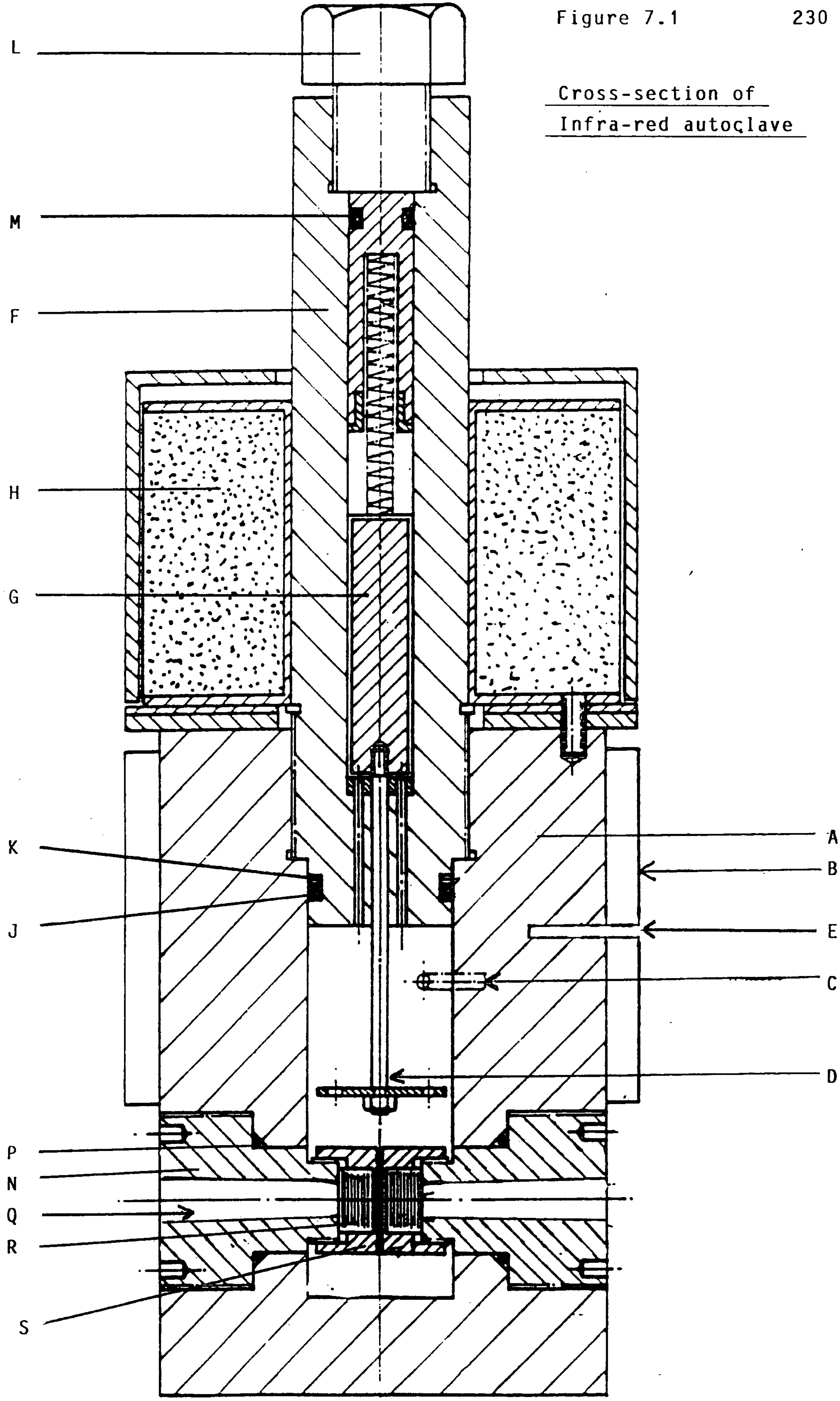
Throughout the work described in Chapters 2, 3, 4, 5 and 6 various autoclaves have been used which are described below in detail, together with the method of use. Furthermore the preparation or source of chemicals and the analytical methods used are recorded.

7.1 High Pressure Autoclaves

Of the five different autoclaves used, two were infra-red cells; both are described in detail, as there are important design changes between the two, and different construction materials are used. The three standard autoclaves are detailed in sections 7.1.2 and 7.1.3. In general all autoclaves were filled to between one-third and two-thirds of the full volume to ensure full mixing of components, both in solution and between the liquid and gas phases. The infra-red cells were disassembled between each experiment and cleaned using appropriate solvents. The standard autoclaves were not dismantled but were repeatedly washed with the reaction solvent, usually acetic acid.

Figure 7.1

Cross-section of Infra-red autoclave



7.2.1 Infra-red Autoclaves

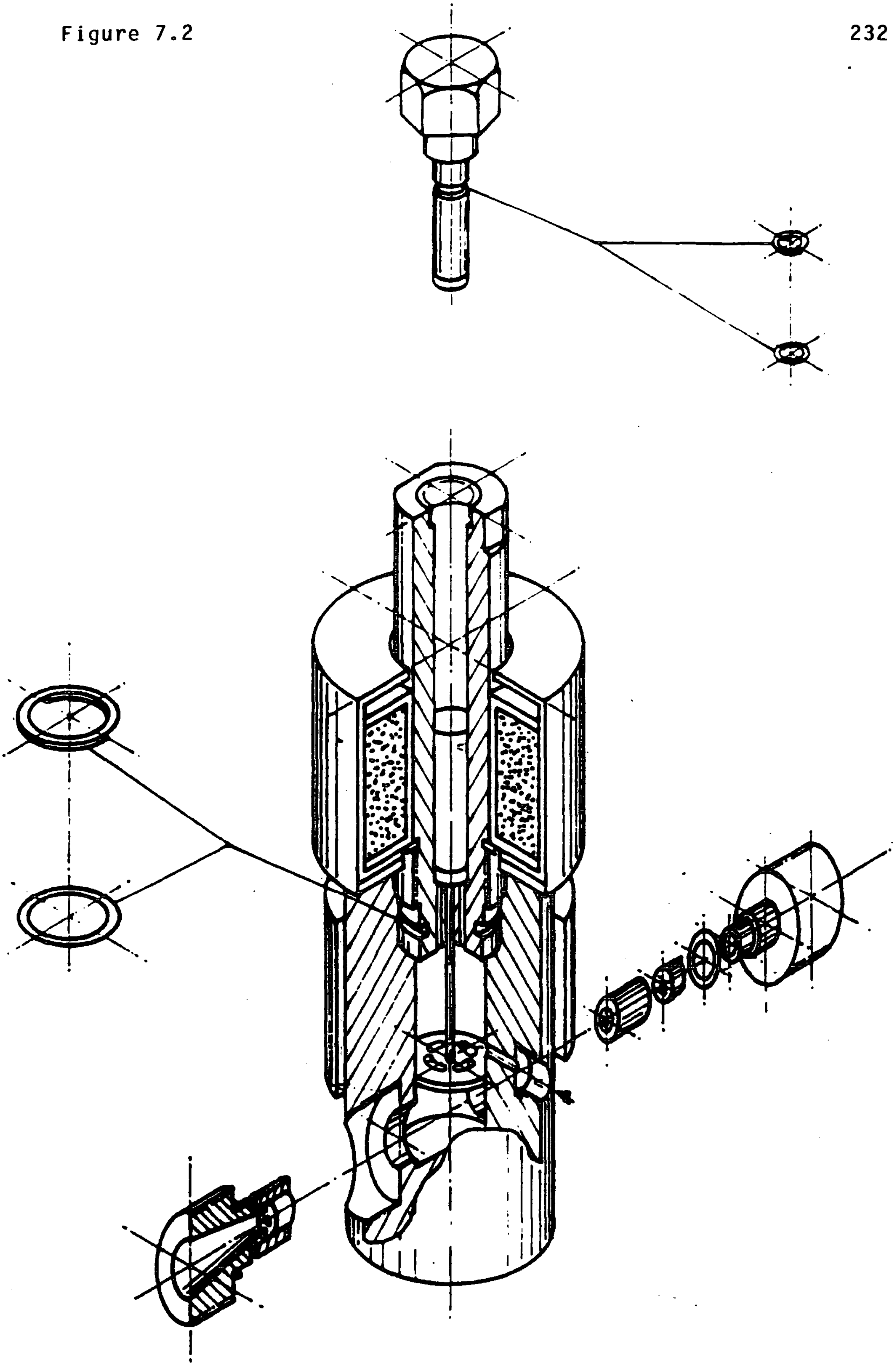
The basic design of the autoclaves is that of Whyman(1). Modifications to the design were made as noted. The autoclave used first was constructed of an alloy of titanium (Ti680), and is shown in Figure 7.1. The main body of the autoclave (A) is surrounded by an electric heating jacket (B). Gases are introduced into the autoclave via the inlet (C). The gases and solution are mixed by the "flip-flop" stirrer (D). The temperature of the autoclave was monitored by a resistance thermocouple inserted into the well at (E).

The head of the autoclave (F) contains the body of the "flip-flop" stirrer which encloses an iron core (G). Employment of a copper coil solenoid (H) causes the stirrer to oscillate. The head of the autoclave seals into the body of the autoclave by means of two "O" rings; a viton "O" ring (J) backed by one constructed of P.T.F.E. (K). The bolt closure of the head of the autoclave (L) is also sealed in this manner at (M).

The window holders (N) are screwed into the main body where they seal by means of a viton "O" ring (P). The F.T.I.R. beam passes through the channel (Q) and on through the calcium fluoride windows (R). The windows are held in place by the retaining caps (S).

Initially a fluorosilicone rubber was used to seal the calcium fluoride windows to the face of the window holders, but this sealant was deformed by the solvents used and was replaced by the "O" ring system shown in Figure 7.3.

Figure 7.2



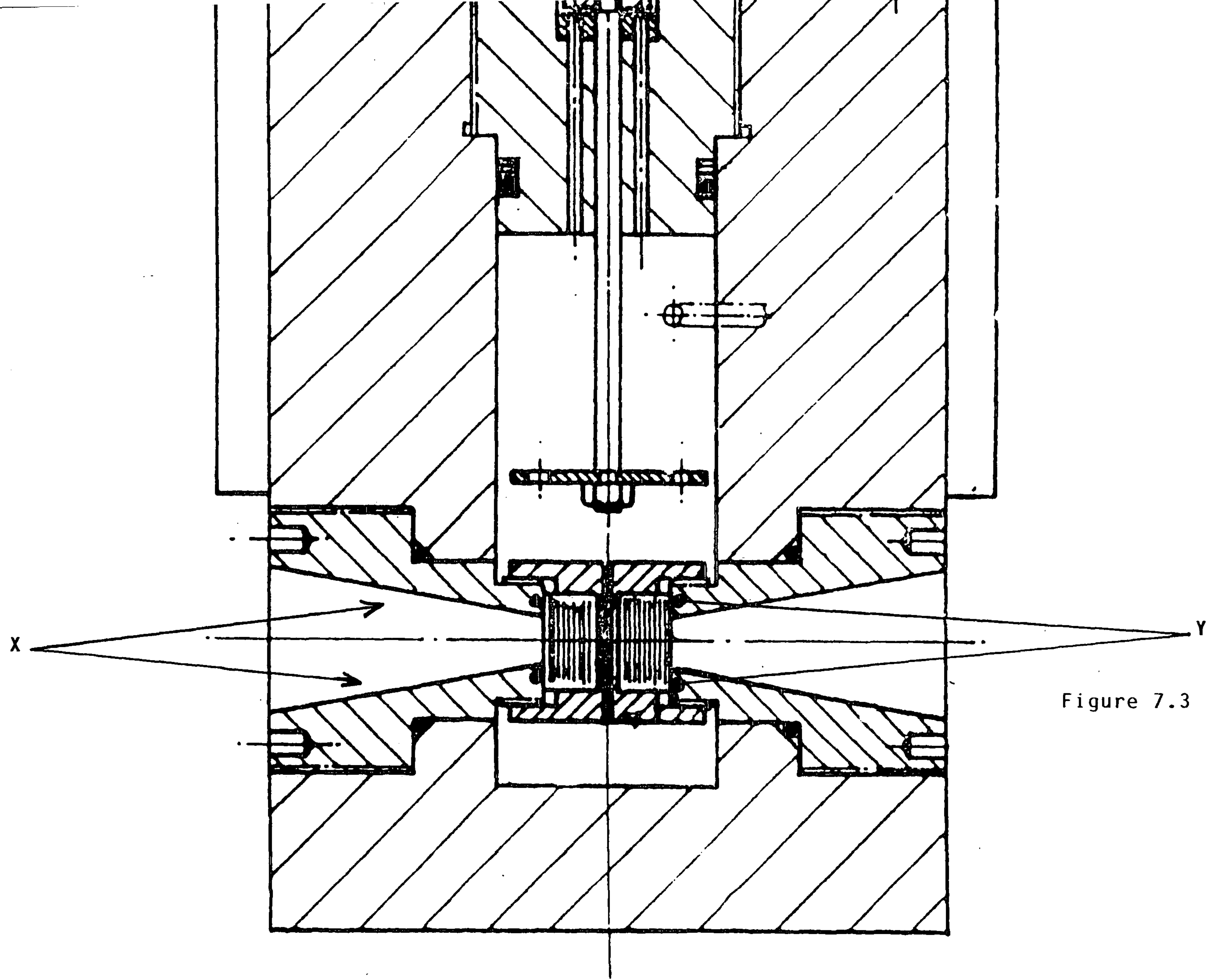


Figure 7.3

The construction of the hastalloy C infra-red cell was essentially similar as is shown in Figure 7.2. The major differences are highlighted in Figure 7.3. The expanded view shows the angled channels (X) and also the position of the viton "O" ring (Y) sealing the window against the window holder, the necessary pressure being created by the retaining cap.

Method of use

A background spectrum was acquired using the appropriate solvents and conditions of temperature and pressure. The clean autoclave was filled with the required solvents. Liquid and solid reactants were then added and the head of the autoclave screwed in place. A manifold system was used to introduce the required cases from commercial cylinders. The autoclave was flushed twice with the reaction gas, then the required pressure introduced. The required temperature was set using a "eurotherm" heater and the stirrer was switched on. Gas pressure was monitored using a standard gauge. Spectra were recorded by a Mattson "alpha centaur" F.T.I.R. spectrometer. Spectral data was transferred to an "A.T. and T." computer for recording and spectral manipulation. In general the region from 2300 - 1800 cm^{-1} was monitored at a resolution of 2 cm^{-1}, employing 16 scans.

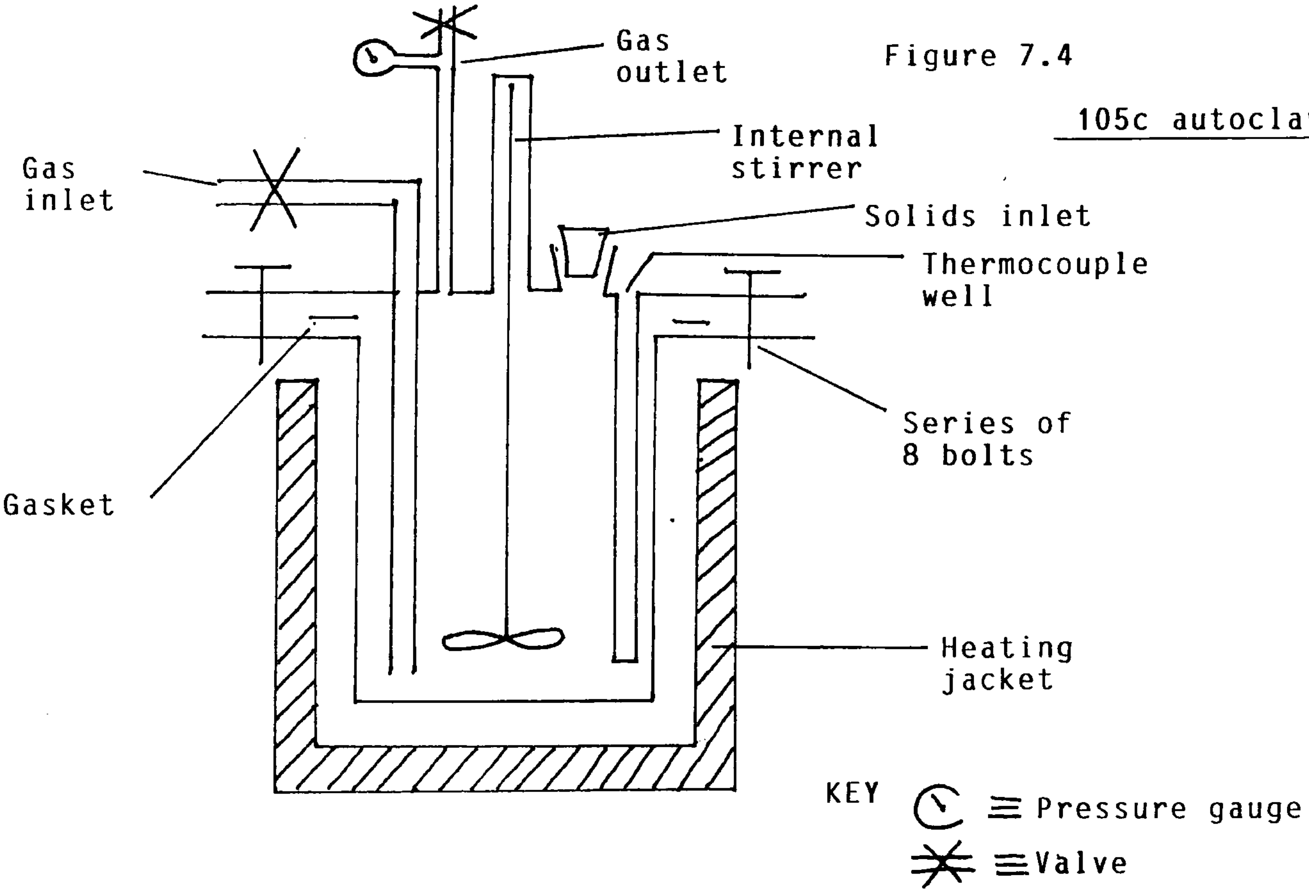


Figure 7.4

105c autoclave

7.2.2 Standard Autoclaves

The construction of both the 500Z and 105C autoclaves may be represented by the schematic diagram, Figure 7.4. Solvents and solids were introduced via the solids inlet which was then sealed. Gases were introduced via a dip-pipe and the pressure monitored via a standard gauge. The temperature was monitored and also the "eurotherm" heater controlled by a resistance thermocouple positioned in the "well".

The 500Z autoclave was constructed of Zirconium. Its volume of 500 ml resulted in a total volume of reactants of 200 ml being employed.

The 105C autoclave was constructed of hastalloy C276 alloy, a total volume of reactants of 36.4 ml being used throughout.

7.2.3 Catalyst Tip Autoclave

The catalyst-tip autoclave is shown schematically in Figure 7.5. The catalyst is held in a gelatine capsule; otherwise the autoclave is prepared as for those in section 7.2.2. Once the reaction temperature is reached, the autoclave pressure is noted on gauge P_1. Nitrogen is introduced via valve V_1 and monitored by gauge P_2 until the pressure is 2 - 5 bar greater than that of the autoclave. Valve V_2 is then opened. The resultant excess pressure within the capsule holder forces open the lid releasing the catalyst into the reaction solution. All valves are closed and the progression of the reaction monitored by gauge P_1.

The main advantage of this type of autoclave is that no catalysed reaction can occur before the reaction temperature has been reached. This can be used to determine whether by-products are formed during catalytic reaction or during autoclave "warmup". The main disadvantage of the system is that the number of valves and connections required to operate the system results in leaks, and a high proportion of runs considered void.

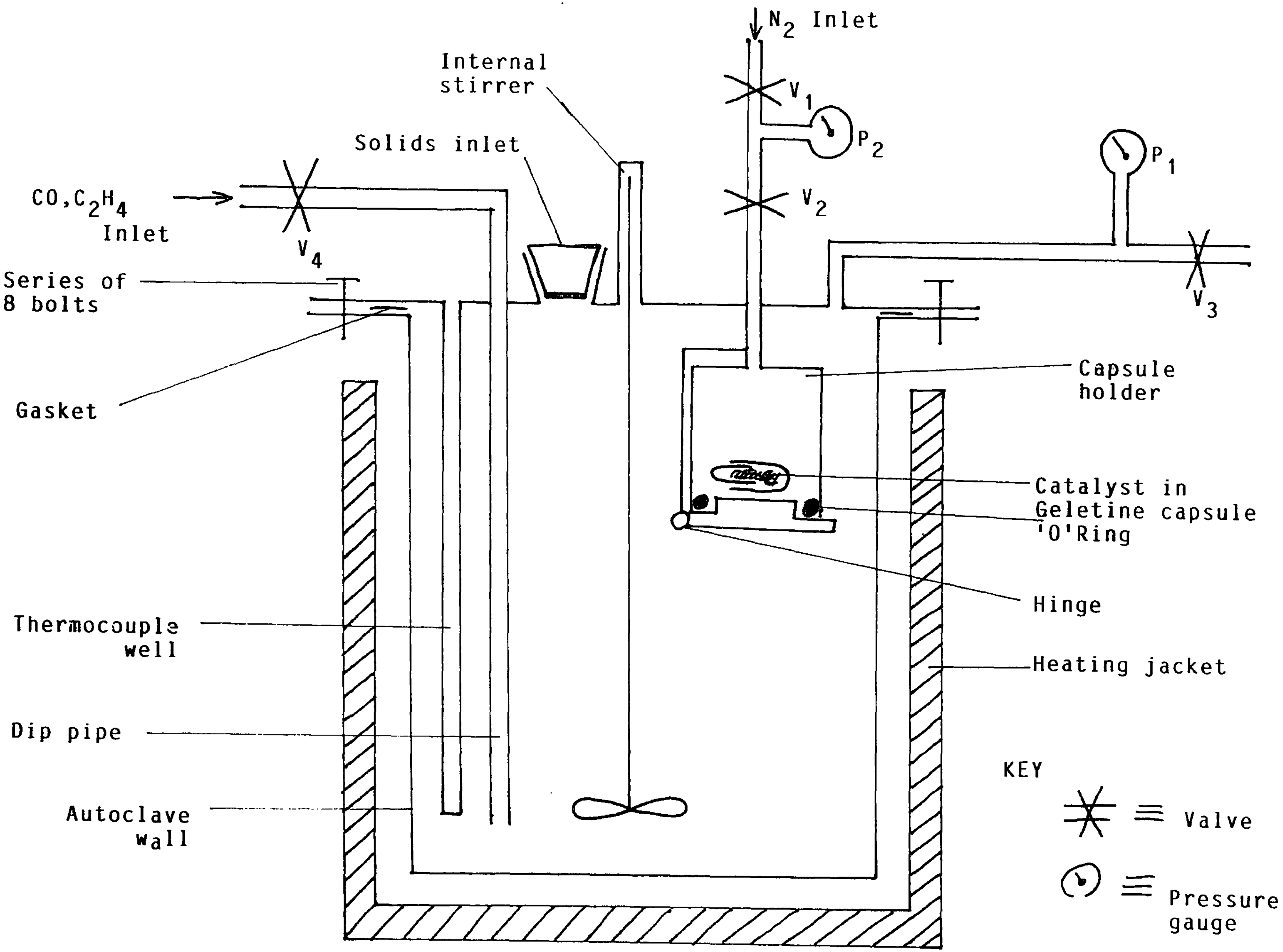


Figure 7.5 'Catalyst Tip' autoclave

7.3 Preparative Experimental Work

Rhodium(III) chloride trihydrate, rhodium(III) iodide and tris(triphenylphosphine) rhodium(I) chloride were used as obtained from Johnson Matthey, Bentron GMBH and Aldrich respectively.

Iodoethane, iodine, tetrabutylammonium iodide, benzyltriethylammonium chloride, bis(triphenylphosphine)iminium chloride and triethylamine were all used as supplied by Aldrich, 99% purity. Tin(II) chloride dihydrate and tetrabutylammonium chloride were also used as supplied by Aldrich at 96% purity. Triphenylphosphine was used as supplied by Koch-Light Ltd and chloroethane as supplied by Fluka A.G.

Solvents

Propanoic acid and dichloromethane were used as supplied by Aldrich (99% purity).

Methanol A.R. grade was dried by reaction with magnesium turnings initiated by a crystal of iodine, under a dry nitrogen flow. The resultant mixture was distilled, and methanol collected at a constant boiling point of 65°C and stored under dry nitrogen.

Glacial acetic acid and 37% aqueous hydrochloric acid were A.R. grade, as were all other named solvents.

Carbon monoxide and ethene were used direct from the cylinders as supplied by Air Products Plc.

Hydrogen Iodide

This was prepared by the reaction of tetrahydronaphthlene and iodine as described by Hoffman(2), and was passed directly into the required solvent. The yield of hydrogen iodide was determined by weight difference. Collection yield for solvents such as dichloromethane was approximately 20 to 40%. For polar solvents such as water collection yields were between 60 and 80%. The hydrogen iodide solutions were kept in light-protected vessels until ready for use. Commercial sources of hydroiodic acids were not used as they contained a stabiliser, hypophosphorous acid, which was shown to affect reactions as described in Chapter 3.

Dichlorotetracarbonyldirhodium(I)

This compound was prepared by reaction of rhodium(III) chloride trihydrate with carbon monoxide at 100°C, the method of Hieber and Lagally(3). Certain modifications were made to the experimental equipment as denoted by Figure 7.6. The ethanol bubbler is only used at the start of the reaction. Once the first traces of product are formed this bubbler is removed. The carbon monoxide passes into a reaction tube of diameter 30 mm. The forward half of the reaction tube is heated by a precalibrated heating tape to 100°C. The rhodium(III) chloride is held in a glass boat in this section of the tube. The product, fine bright red needles, crystallises in the second half of the tube which is cooled by contact with the water condenser. The product was collected and weighed in a dry nitrogen atmosphere. The apparatus was sealed and used for repeat reaction runs.

Yield = 70%

Infra-red - 2105, 2092, 2036 cm^{-1}.

Tetrabutylammoniumdiiododicarbonylrhodate(I)

This compound was prepared by the method of Fulford(4), a variation of those used by Vallarino(5) and Hickey(6). 0.5 mmol (0.2g) of dichlorotetracarbonyldirhodate(I) was dissolved in a minimum of dry degassed hexane. A tenfold excess of powdered potassium iodide (0.8g) was added and the mixture stirred under dry nitrogen for 48 hours. The resultant solution was reduced in volume under vacuum until crystallisation first occurred. The solution was cooled to 0°C in ice, then -5°C in a fridge and finally to -30°C in a freezer. The dark red crystals of diiodotetracarbonyldirhodate(I) were then filtered under a positive pressure of dry nitrogen. These crystals were then dissolved in a minimum of dry degassed methanol. Tetrabutylammonium iodide (0.175g) was added to the solution which was reduced to a small volume under vacuum. This solution was then cooled as previously described. A yellow precipitate was formed, and was separated by filtration under a positive pressure of dry nitrogen.

Yield 32.3%

ANALYSIS	Rh	C	N	H	I
Found %	12.8	35.1	2.4	4.9	39.3
Required %	15.7	33.0	2.14	5.5	38.7

Preparation of $Rh_2(CO)_4Cl_2$

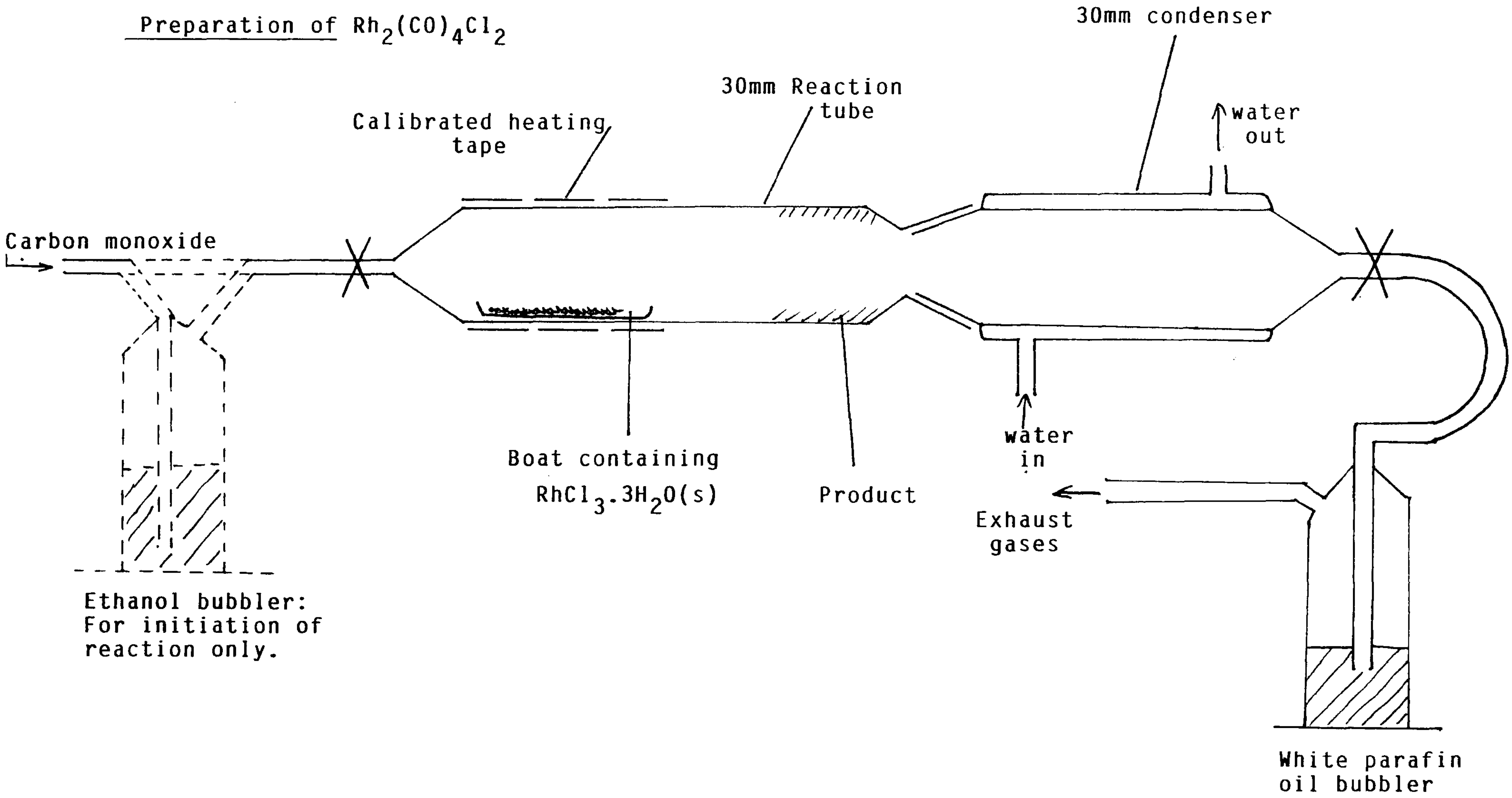


Figure 7.6

7.4 Analytical Instrumentation

Elemental Analysis

Metal analysis was conducted by atomic absorption spectrometry on a Perkin Elmer model 5000. The rhodium standard used was dichlorotetracarbonyldirhodium(I).

Carbon, hydrogen and nitrogen microanalyses were conducted using a Carlo Erba model 1106 analyser.

Chlorine and iodine analyses were performed by appropriate titration after oxygen flask combustion.

Elemental analysis was conducted by the Durham Chemistry Departmental Services.

Product Analysis

Gas liquid chromatography was conducted using a 4 foot packed chromasoris 101 column in a Varian model 3700 chromatograph. A temperature program of 10 C rise per minute from 40 C to 200 with a final time of 9 minutes was used. Integration was undertaken using a Spectro Physics "Chromojet" model integrator.

Response factors were calculated for acetic acid, dichloromethane, and propanoic acid A.R. grades. Other compounds were assumed to have a response factor of unity. Non-volatiles were removed prior to analysis by vacuum distillation.

Mass spectra were collected on a V.G. 7070E organic mass spectrometer at 70cV and 6kV accelerating voltage, by Departmental Services.

CHAPTER 7 - REFERENCES

1 W. Rigby, R. Whyman and K. Wilding, Journal of Physics E. Scientific Instruments (1970) 3 372.

2 C.J. Hoffman, Inorganic Synthesis (1963) 7 180.

3 W. Hieber and H. Lagally, Z. Anorg. Allgem. Chem. (1943) 251 98.

4 A. Fulford, Private communication.

5 L.M. Vallarino, Inorg. Chem. (1965) 4 161.

6 C.E. Hickey, Personal communication.

Infra-red data

Literature values

Compound	Data/cm^{-1}	Reference
$[Rh(CO)_2I_2]^-$	2040,1970.(KBr)	1
	2064,1989.(CH_3COOH)	1
	2063,1990.(CH_2Cl_2)	2
	2064,1989.(CH_3NO_2)	3
$[Rh(CO)_2Cl_2]^-$	2058,1974.(Nujol)	4
	2073,1994.(CH_3NO_2)	3
$Rh_2(CO)_4Cl_2$	2105,2089,2034. (^{13}C:2100,2078,2002.)	5
$Rh(CO)Cl_3$	2135	6
$Rh_2(CO)_4I_2$	2094,2078,2027. (^{13}C:2090,2068,1995.)	5
trans-$[Rh(CO)_2I_4]^-$	2092.(CH_3COOH)	1
	2084.(KBr)	7
$Rh(CO)I_3$	2070.	6
$[Rh(CO)I_4]^-$	2076.(CH_3NO_2)	3
	2072.(CH_2Cl_2)	2
$[Rh_2(CO)_2I_4]^{2-}$	2050.	1
$[Rh(CO)I_5]^{2-}$	2035.(KBr)	1
	2047.(CH_3NO_2)	3
$[CH_3CORh(CO)I_3]^-$	2062,1711.	8
$[CH_3CORh(CO)_2I]^-$	2141,2084,1708.	8
$[Rh(CO)_2Cl_4]^-$	2160,2125.	3
$[Rh(CO)Cl_5]^{2-}$	2047.	3

Compound	Data/cm^{-1}	Reference
$Rh(SnCl_3)_3(CO)_2$	2060,2010.	9
$Rh(SnCl_3)_3(CO)$	2005.	10
$[Rh(py)_4HBr]^+$	ca. 2000	11
$[Rh(py)_5H]^{2+}$	1980.	11
$[Ir(CO)_3I]$	2073,2046.	12
$[Ir(CO)_2I_2]^-$	2048,1970	12
$[Ir(CO)_3I_3]$	2185,2170,2132.	1
$[HIr(CO)_2I_3]^-$	2160,2101,2051.	13
$Rh_2(CO)_3(C_2H_4)Cl_2$	2090,2027,2020.	14
$Rh_2(CO)_2(C_2H_4)_2Cl_2$	2027,2020.	14
$Rh_2(CO)(C_2H_4)_3Cl_2$	2020.	14
$Rh_2(CO)_4(MeCO_2)_2$	2083,2067,2027,1980.	15

References

1.Journal of the American Chemical Society (1980) 102.3 1020.

2.S.A.Moffett: M.Sc Thesis University of Kent at Canterbury 1985.

3.Inorganic Chemistry (1969) 8.12 2556.

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6. Australian Journal of Chemistry (1970) 1351.

7.Journal of Inorganic Nuclear Chemistry (1969) 31 2557.

8.Journal of the American Chemical Society (1976) 98.3 846.

9.Journal of Organometallic Chemistry (1983) 241 87.

10.Journal of the Chemical Society(A) (1971) 3399.

11.Journal of the Chemical Society (1964) 5189.

12.Journal of the Chemical Society,Dalton Transactions (1979) 1643

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14.Inorganic Chemistry (1974) 13 667.

15.Journal of the Chemical Society (1965) 1900.

Infra-red data

Observed values

Compound	Data/cm^{-1}
$Rh(CO)Cl_3$	2135.
$Rh_2(CO)_4Cl_2$	2105,2092,2035.
$Rh(CO)_3Cl$	2099,2059.
$[Rh(CO)_2Cl]^-$	2043,1984.
$[A^+...Rh(CO)_2Cl_2^-]$	2080,2009.
$Rh_2(CO)_4I_2$	2095,2080,2028.
$[Rh_2(CO)_2I_4]^{2-}$	2057.
$[Rh(CO)_2I_2]^-$	2065,1992.(CH_2Cl_2/CH_3CH_2COOH)
	2060,1990.(CH_3CH_2COOH)
$[Rh(CO)_2I_4]^-$	2084.
$[Rh(CO)I_5]^{2-}$	2047.

Appendix 2

D.U.C.S. LECTURES 1986-87

MICHAELMAS TERM 1986

*Thursday, October 16th Prof. N. N. Greenwood, Leeds
Glorious Gaffes in Chemistry

Thursday, October 23rd Prof. H. W. Kroto, Sussex
Chemistry in Stars, Between Stars and in the Laboratory

Thursday, October 30th Prof. D. Detteridge, BP Research
Can Molecules Talk Intelligently

*Thursday, November 6th Dr. R. M. Scrowston, Hull
From Myth and Magic to Modern Medicine

Thursday, November 13th Prof. Sir G. Allen, Unilever Research
Biotechnology and the Future of the Chemical Industry

*Thursday, November 20th Dr. A. Milne & Mr. S. Christie, International Paints
Chemical Serendipity - A Real Life Case Study

*Thursday, November 27th Prof. R. L. Williams, Metropolitan Police Forensic Science Laboratory
Science and Crime

EPIPHANY TERM 1987

Thursday, January 22nd Prof. Ottewill, Bristol

*Thursday, February 5th Dr. P. Hubberstey, Nottingham
The Alkali Metals - Alchemists' Nightmare, Biochemists' Puzzle and Technologists' Dream (Demonstration)

*Thursday, February 12th Dr. D. Brown, ICI Billingham
Industrial Polymers from Bacteria

Thursday, February 19th Dr. M. Jarman, Institute of Cancer Research
The Design of Anti-Cancer Drugs

*Thursday, March 5th Prof. S. V. Ley, Imperial College
Fact and Fantasy in Organic Synthesis

Monday, March 9th Prof. F. G. Bordwell,

*Thursday, March 12th Dr. E. M. Goodger, Cranfield
Alternative Fuels for Transport - Chemical Energy Resources

* indicates lectures attended

D.U.C.S. LECTURES 1987-88

MICHAELMAS TERM 1987

Thursday, October 15th Dr. M. J. Winter, Sheffield
Pyrotechnics (Demonstration)

Thursday, October 22nd Prof. G. W. Gray, FRS, Hull
Liquid Crystals and their Applications

Thursday, October 29th Mrs. S. van Rose, Geological Museum
Chemistry of Volcanoes

Thursday, November 5th Dr. A. R. Butler, St. Andrew's
Chinese Alchemy

Thursday, November 12th Prof. Dr. D. Seebach, ETH Zurich
Musgrave Lecture
From Synthetic Methods to Mechanistic Insight

Thursday, November 19th Prof. P. G. Sammes, Smith, Kline and French
Society of Chemical Industry Lecture
Chemical Aspects of Drug Development

Thursday, November 26th Dr. D. H. Williams, FRS, Cambridge
Molecular Recognition

Thursday, December 3rd Dr. J. Howard, ICI Wilton
Chemistry of Non-Equilibrium Processes

EPIPHANY TERM 1988

Thursday, January 21st Dr. F. Palmer, Nottingham
Luminescence (Demonstration)

Thursday, January 28th Dr. A. Cairns-Smith, Glasgow
Clay Minerals and the Origin of Life

Thursday, February 11th Prof. J. J. Turner, FRS, Nottingham
Waddington Lecture
Catching Organometallic Intermediates

Thursday, February 18th Dr. K. Borer, UDIRL
The Brighton Bomb - A Forensic Science View

hursday, February 25th Prof. A. Underhill, Bangor
olecular Electronics

hursday, March 3rd Prof. W. A. G. Graham, Alberta
SC Centenary Lecture
hodium and Iridium Comlexes in the Activation of Carbon-Hydrogen Bonds

indicates lectures attended

Appendix 2 (cont)

D.U.C.S. LECTURES 1988-89

MICHAELMAS TERM 1988

Thursday, October 6th Prof. R. Schmutzler, Braunschweig
Fluorophosphines Revisited - New Contributions to an Old Theme

Thursday, October 18th Dr. D. R. Marshall, Bangor
The Best Bang Since the Big One

Friday, October 21st Prof. P. von Rague Schleyer, Erlangen
The Fruitful Interplay Between Calculational and Experimental Chemistry

Thursday, October 27th Prof. C. W. Rees, Imperial
Some Very Heterocyclic Compounds

Thursday, November 10th Prof. J. I. G. Cadogan, BP
From Pure Science to Profit

Thursday, November 24th Dr. R. W. Walker & Dr. R. R. Baldwin, Hull
Combustion - Some Burning Problems

Thursday, December 1st Dr. R. Snaith, Cambridge
Egyptian Mummies - What, Where, Why and How?

EPIPHANY TERM 1989

Thursday, January 26th Prof. K. R. Jennings, Warwick
Chemistry of the Masses

Thursday, February 2nd Prof. L. D. Hall, Addenbrooke's Hospital
NMR - A Window to the Human Body

Thursday, February 9th Prof. J. Baldwin, Oxford

Thursday, February 16th Prof. J B. Aylett, Queen Mary College
Silicon-Based Chips : The Chemists Contribution

Thursday, February 23rd Dr. B. F. G. Johnson, Cambridge
The Binary Carbonyls

indicates lectures attended