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THE HOMOGENEOUS CATALYTIC DECOMPOSITION OF ALCOHOLS
USING TRANSITION METAL COMPLEXES OF
RHODIUM AND RUTHENIUM

being a thesis presented

by

D A V I D M O R T O N

to the

UNIVERSITY OF ST. ANDREWS

in application for

THE DEGREE OF DOCTOR OF PHILOSOPHY

St. Andrews

June 1988



DECLARATION

I, David Morton, hereby certify that this thesis has been composed by myself, that it is a record of my own work, and that it has not been accepted in partial or complete fulfilment of any other degree or professional qualification.

Signed Date

I was admitted to the Faculty of Science of the University of St. Andrews under Ordinance General No. 12 on 1st October 1985, and as a candidate for the degree of Ph.D. on 1st October 1985.

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TO
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I would like to express my gratitude to Professor David Cole-Hamilton for his constant encouragement, enthusiasm and guidance throughout the period of this work. I would also like to take this opportunity to thank him for his friendship and for moving to St. Andrews.

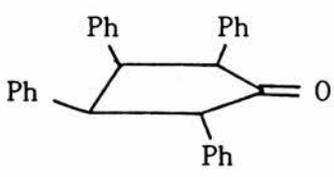
Many thanks must go to my co-workers for making my stay in St. Andrews such a happy one and for many rounds of Golf! I would also like to thank the technical staff for much needed assistance, especially Colin Smith (glass blower) in appreciation of his workmanship.

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LIST OF ABBREVIATIONS

PPh_3	triphenylphosphine
PPr_3^i	triisopropylphosphine
bipy	2,2'-bipyridine
dppp	diphenylphosphinopropane
PEt_2Ph	diethylphenylphosphine
OAc	acetate
CF_3CO	trifluoroacetate
COD	cyclo octadiene
P(OPh)_3	triphenyl phosphite
dppm	diphenylphosphinomethane
1,2-(PPh_2) C_6H_4	diphenylphosphinobenzene
$\text{PPh}_2\text{CH}_2\text{CH}_2\text{AsPh}_2$	Arphos
OAc_f	trifluoroacetate
PEtPh_2	ethyldiphenylphosphine
$\text{C}_6\text{H}_4(\text{Ph})_3\text{CO}$	
PEt_3	triethylphosphine
c- C_6H_{11}	cyclohexane

C O N T E N T S

	Page
Abstract	(i)
 Chapter 1 - HOMOGENEOUS CATALYTIC DECOMPOSITION OF ALCOHOLS	
1.1	Introduction 1
1.2	Thermodynamics of Hydrogen Production from Alcohols 3
1.3	Homogeneous Catalytic Decomposition of Alcohols 6
1.4	Complexes based on Rhodium 7
1.5	Complexes of Ruthenium 22
1.6	Complexes of Platinum 35
1.7	Homogeneous Catalysis of the Water-Gas Shift Reaction 39
1.8	Complexes of Rhodium 41
1.9	Complexes of Ruthenium 49
 Chapter 2 - THE CATALYTIC DECOMPOSITION OF ETHANOL USING TRANSITION METAL COMPLEXES OF RHODIUM AND RUTHENIUM	
2.1	Introduction 53
2.2	Results and Discussion 57
2.3	Production of CO ₂ and H ₂ from Ethanol and Water 76

	Page	
2.4	Results and Discussion	77
Chapter 3 - THE CATALYTIC DECOMPOSITION OF 1,2-ETHANEDIOL, 1,2,3-PROPANETRIOL, METHANOL, 1-PROPANOL AND 1-BUTANOL BY COMPLEXES OF RHODIUM AND RUTHENIUM		
3.1	Introduction	95
3.2	Results and Discussion	98
3.2.1.	Catalytic Dehydrogenation of 1,2-Ethenediol	98
3.2.2.	Catalytic Decomposition of 1,2,3-Propanetriol	107
3.2.3.	Catalytic Decomposition of Methanol, 1-Propanol and 1-Butanol	109
Chapter 4 - CATALYTIC DEHYDROGENATION OF 2-PROPANOL, 2,3-BUTANEDIOL, 1,3-BUTANEDIOL AND 1,4-BUTANEDIOL		
4.1	Introduction	116
4.2	Results and Discussion	118
4.2.1.	Catalytic Dehydrogenation of 2-propanol	118
4.2.2.	Catalytic Dehydrogenation of 2,3-butanediol	122
4.2.3.	Catalytic Dehydrogenation of 1,3 and 1,4-butanediol	133

Chapter 5 - CATALYTIC DEHYDROGENATION OF
SORBITOL, CELLOBIOSE AND WINE

5.1	Introduction	135
5.2	Catalytic Dehydrogenation of Sorbitol	138
5.3	Catalytic Dehydrogenation of Cellobiose	140
5.4	Catalytic Dehydrogenation of Red and White Wine	141
	Experimental	145
	References	149

ABSTRACT

The homogeneous catalytic dehydrogenation of alcohols was studied, using various group VIII metal catalysts; namely $[\text{RhCl}(\text{PPh}_3)_3]$, $[\text{RhH}(\text{PPr}_3)_3]$, $[\text{Rh}(\text{bipy})_2]\text{Cl}$, $[\text{RuH}_2(\text{PPh}_3)_4]$ and $[\text{RuH}_2(\text{N}_2)(\text{PPh}_3)_3]$. Thermal and photochemical reactions were investigated in the presence and absence of base (Sodium Hydroxide).

The dehydrogenation of ethanol involves initial formation of ethanal with all the catalysts. These catalysts have a high affinity for carbon monoxide, which is abstracted from the formed ethanal and inhibits the dehydrogenation reaction.

Irradiation with visible light can remove carbon monoxide from some complexes, promoting the more thermodynamically favourable reaction producing hydrogen, methane and carbon monoxide.

Addition of an alkanal decarbonylation catalyst, $[\text{Rh}(\text{dppp})_2]\text{Cl}$, also helps prevent catalyst poisoning.

Base has a three fold effect on the reaction:

- (a) formation of ethoxide facilitating faster substrate activation
- (b) removal of ethanal in base catalysed aldol condensation reactions
- (c) changing the mode of dehydrogenation, in some cases, to form hydrogen, methane and carbon dioxide.

Reactions with longer chain primary alcohols indicate that the rate of decarbonylation of the formed alkanal decreases with increasing chain length, thereby increasing the rate of hydrogen production.

The dehydrogenation of secondary alcohols is successful, since the product ketone is not decarbonylated. High rates of hydrogen production are obtained in the presence of base.

Dehydrogenation of diols and triols was successful - particularly where chelate stabilisation of the reactive intermediate is possible.

Preliminary studies have shown that the dehydrogenation of natural products and wine alcohol is possible.

Particular success was achieved with $[\text{Rh}(\text{bipy})_2]\text{Cl}$ and $[\text{RuH}_2(\text{N}_2)(\text{PPh}_3)_3]$ as catalysts with all the alcohols examined.

The mechanisms by which these reactions are thought to occur are discussed.

C H A P T E R O N E

HOMOGENEOUS CATALYTIC DECOMPOSITION
OF ALCOHOLS

CHAPTER 1

HOMOGENEOUS CATALYTIC DECOMPOSITION OF ALCOHOLS

1.1 INTRODUCTION

One of the consequences of the 1973 oil crisis has been the implementation of national research and development programmes directed to alternative sources of energy. The realisation that oil stocks are rapidly depleting has accelerated this search for alternative fuels and feedstocks.

Recent conservation efforts have extended the probable lifetime of oil, as a major energy source, well into the next century. However, this finite lifetime means that alternative fuels will be needed to replace oil in the not too distant future.

One possible alternative fuel, which has the advantage that it is essentially non-polluting when burnt and has a high fuel value, is hydrogen. When hydrogen is burnt, water is produced which has the advantage of not contributing to the warming of the earth by the "greenhouse" effect, which is caused by a build up of carbon dioxide in the atmosphere from the burning of fossil fuels.

The prospects for a hydrogen economy have been investigated and, although it is unlikely that hydrogen will become the

main power source on earth; it is probable that, provided hydrogen can be produced cheaply, it will make a significant contribution to our energy needs.¹

The most attractive source of hydrogen is from the photochemical dissociation of water. However, technical problems concerned with the chemistry of the process and with collection of solar energy over wide areas, suggests that hydrogen production from alternative substrates would be more favourable, particularly if the reaction can be carried out thermally.

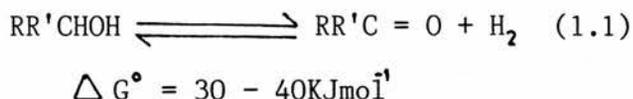
Alcohols, often available in dilute solutions as industrial waste products, are an alternative source of hydrogen. Dehydrogenation of alcohols has been demonstrated using a number of heterogeneous and homogeneous catalysts.

Biomass is also an alternative energy source. The problems associated with its conversion into energy rich fuels have received considerable attention over the last ten years. Biomass has been converted into high grade liquid fuel oil by hydrogenation at high temperature, in the presence of a heterogeneous catalyst.

Although these processes have demonstrated technical feasibility, it is clear that the economic viability would be greatly enhanced, if hydrogen could be catalytically produced from biomass, and then the biomass liquefaction performed in a one, or two stage system, in the absence of external sources of hydrogen.

1.2 THERMODYNAMICS OF HYDROGEN PRODUCTION FROM ALCOHOLS

Dehydrogenation of alcohols to produce aldehydes or ketones is the simplest method of producing hydrogen from alcohols.



It follows that, in principle, any catalyst capable of hydrogenating aldehydes or ketones will also be active for alcohol dehydrogenation.

Unfortunately, the thermodynamics of the reaction are such that in a closed system, the yields of hydrogen will be low. As the concentration of aldehyde or ketone increases, the rate of the back reaction will increase, (equation 1.1), which means that the rate of hydrogen production will be low.

The reaction has a high positive entropy change ($\Delta S^\circ = 350\text{KJmol}^{-1}$), therefore, the reaction will proceed to a greater degree as the temperature is increased.

The thermodynamics of the dehydrogenation reaction become more favourable if the alcohol is further decomposed to alkane and carbon monoxide.



For reaction (1.2), the exact equilibrium position is dependent on the structure of R. The relationship of R and ΔG° for the reaction is shown in table 1.1.

Table 1.1

Alcohol	$\Delta G^\circ / \text{KJmol}^{-1}$
Methanol	29.1
Ethanol	-13.5
1-Propanol	0.8
1-Butanol	8.4
1-Pentanol	10.5

Table 1.1 shows that ΔG° increases from -13.5KJmol^{-1} , for $R = \text{CH}_3$, as the chain length of R increases. Methanol is anomalous because $R = \text{H}$, therefore, two moles of hydrogen are produced and none of alkane, and hence the high, positive ΔG° value of 29.1KJmol^{-1} .

The most thermodynamically favourable reaction for alcohol dehydrogenation is shown in equation 1.3.



The reaction also has the advantage that two moles of hydrogen are produced per mole of alcohol. The production of highly exothermic carbon dioxide ensures that ΔG° is negative for all R.

Catalysis of all these reactions, under both thermal and photochemical conditions, with homogeneous transition metal complexes, are reviewed in this chapter and reported in subsequent chapters.

1.3 HOMOGENEOUS CATALYTIC PRODUCTION OF HYDROGEN FROM ALCOHOLS

The catalytic production of hydrogen from alcohols has been the subject of substantial research interest in recent years because it offers a means of obtaining a useful fuel from industrial waste alcohol, or of producing hydrogen from biomass derived material.

The hydrogen can then be used directly as a fuel or for the hydrogenation of biomass to a high grade liquid fuel².

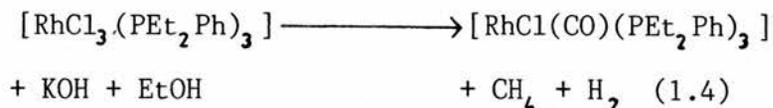
Liquid phase catalytic dehydrogenation reactions are particularly favourable because of spontaneous separation of hydrogen into the gas phase.

Much activity has focused on this type of reaction and homogeneous transition metal complexes have been shown to catalyse alcohol dehydrogenations under mild activity. Under thermal conditions, catalytic dehydrogenation gives predominantly ketones, aldehydes and methane. However, addition of base and use of photolysis have been shown to enhance the rate of dehydrogenation with carbon monoxide and carbon dioxide also being reported as products.

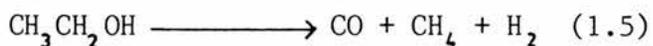
Many transition metal complexes have been studied as possible catalysts for alcohol dehydrogenation reactions.

Preparation of the Rh(I) carbonyls from the reaction of Rh complexes and alcohols was reported by Chatt and Shaw³.

The reaction is shown in equation 1.4.



It can be seen from this reaction that the alcohol appears to have been broken down as follows:



The CO remains co-ordinated to the metal; CH₄ and H₂ are evolved. Only a small quantity of H₂ was detected in the gas phase; the remaining H₂ was probably involved in reducing Rh(III) to Rh(I), and would, therefore, be present as HCl.

These were the first alcohol decomposition reactions recorded, although they were not catalytic and the H₂ was used as a reducing agent.

In 1967, Charman reported that chloro-complexes of rhodium (III) (Rh(III)) catalyse the dehydrogenation of 2-propanol to give acetone⁴ in the presence of LiCl and concentrated HCl at 83°C. The evolved gas was mainly H₂ but contained traces of 2-propylchloride and 2-propylether; probably formed by the reaction of concentrated HCl with 2-propanol since their

combined concentration increased as the concentration of HCl was increased.

During the reaction rhodium metal was precipitated, which resulted in a decrease in the rate of gas evolution. A kinetic equation was derived on the basis that the rate of dehydrogenation and the rate of metal formation were proportional to the concentration of rhodium in solution:

$$dV/dt = k' (a - x) \quad (1.6)$$

$$dx/dt = k (a - x) \quad (1.7)$$

Where:- V = volume of H_2 evolved after time t .

x = concentration of rhodium metal.

a = initial concentration of rhodium trichloride.

Integration of equation (1.7) gives (1.8) and (1.9) follows from equations (1.6) and (1.8). Integration of (1.9) gives equation (1.10) in which c is the integration constant.

$$x = a(1 - e^{-kt}) \quad (1.8)$$

$$dV/dt = k' a e^{-kt} \quad (1.9)$$

$$e = -kV/k'a + kc \quad (1.10)$$

Substitution for $t = \infty$ when $V = V_{\infty}$ gives:

$$kc = V_{\infty}/k'a \quad (1.11)$$

Substitution into (1.10) gives:

$$-kt = \ln k/k'a + \ln(V_{\infty} - V) \quad (1.12)$$

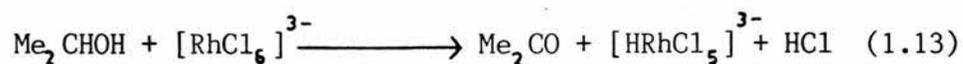
A plot of $\ln(V_{\infty} - V)$ against t gave a straight line with slope $-k$ and intercept V_{∞} at $t = 0$.

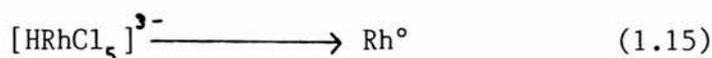
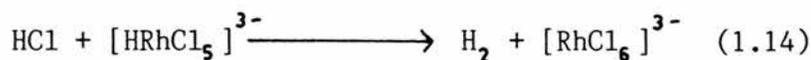
The reaction was judged to be homogeneous after consideration of the following evidence:

- (a) The reaction starts before any appreciable metal is precipitated.
- (b) The reaction stops when all the rhodium metal has been precipitated.
- (c) The rate of reaction is reduced by metal precipitation.

However, examination of these criteria does not rule out the possibility of the catalyst being colloidal rather than homogeneous.

It was suggested that the dehydrogenation catalysed by chloro-complexes of rhodium(III) proceeds via the transfer of a hydride ion from the α -carbon atom of the alcohol to the rhodium complex; which then reacts with a proton to form hydrogen or decomposes to give rhodium metal. These reactions are shown by equations (1.13), (1.14) and (1.15).

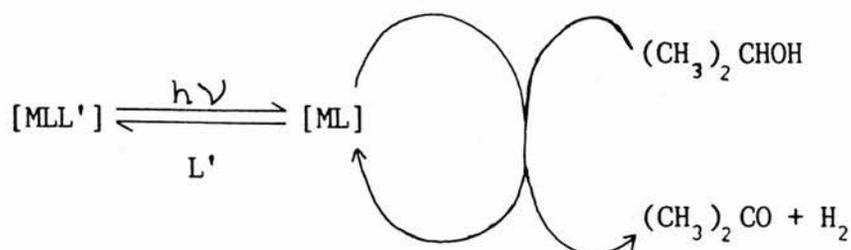




Charman continued this work in an effort to prevent concurrent formation of rhodium metal during the reaction. In 1970, he reported that the rhodium chloride catalysed dehydrogenation of 2-propanol in the presence of tin(II) chloride occurred in the absence of concurrent rhodium metal formation⁵. Tin(II)chloride replaces chloride in the complex, thus stabilising it to decomposition. As the concentration of tin(II)chloride was increased, the rate of H₂ production decreased. A build up of acetone also reduced the rate of the dehydrogenation reaction, but the rate was restored when acetone was removed by distillation.

The rate of this reaction was reported to be considerably enhanced under irradiation from low pressure mercury lamps^{6,7}. An equimolar amount of acetone, relative to the hydrogen produced, was formed confirming the mode of 2-propanol decomposition. The activation energy was calculated to be 11KJmol⁻¹, reduced from 117KJmol⁻¹. The quantum yield of the reaction was larger than unity, and the reaction had a distinct temperature dependence which suggested that photo-induced ligand elimination activates the catalyst. A mechanism was proposed, in which the generation of a co-ordinately unsaturated species by the photo-cleavage of a Rh - Sn co-ordination bond was assumed. The mechanism is shown in scheme (1.1).

Scheme 1.1



[MLL'] = Catalyst precursor.

[ML] = Catalytically active species.

L' = Dissociated ligand, SnCl₃.

L = Cl and SnCl₃ ligands.

The very high rate of hydrogen production, turnover numbers of 88h⁻¹ attained at 82.5°C, compared to thermal reactions substantiated the accelerating effect of photo-irradiation.

It is interesting to report here the more recent work on a tin(II) - co-ordinated Iridium complex⁸ with very high photoreactivity. The product of 2-propanol dehydrogenation is acetone, and the reaction proceeds to completion when acetone is removed by fractional distillation and H₂ is removed.

This system is analogous to the rhodium system^{6,7} and similar platinum and ruthenium catalysts also proved to be active for the dehydrogenation reaction.

For Iridium, the photo catalytically active solution contained trans - [IrCl₂(SnCl₃)₄]³⁻ and [IrH(SnCl₃)₅]³⁻.

At 82.1°C, the evolved gas was solely H₂ with a turnover number of 109h⁻¹. The solution retained its photo catalytic activity for more than 500 hours with a turnover number amounting to 3430, despite the rate retardation due to accumulation of acetone.

Rh₂(OAc)₄ is known to possess no catalytic activity for the dehydrogenation of isopropanol. However, in the presence of an activating ligand, PPh₃, the reaction proceeded catalytically⁹. NMR studies indicate that the catalytically active species contains co-ordinated PPh₃ both axially and equatorially to the Rh - Rh bond. The complex exhibits catalytic activity at 82.5°C for more than 10 hours under N₂, with hydrogen production corresponding to 32.8 turnovers per hour achieved.

Replacement of (OAc) by (OCOCF₃) and PPh₃ by P(OPh)₃, greatly reduced catalytic activity.

The same reaction was examined using heterogeneous catalysts prepared by immobilizing Rh₂(OAc)₄ on triphenyl phosphine derivatized silicon¹⁰. With this system, the activity was reduced compared to the homogeneous system; a maximum of 12.3 turnovers per hour observed at 82.4°C, but the reproducibility and durability of the reaction was improved by immobilizing the catalyst.

A number of the reported alcohol dehydrogenations have

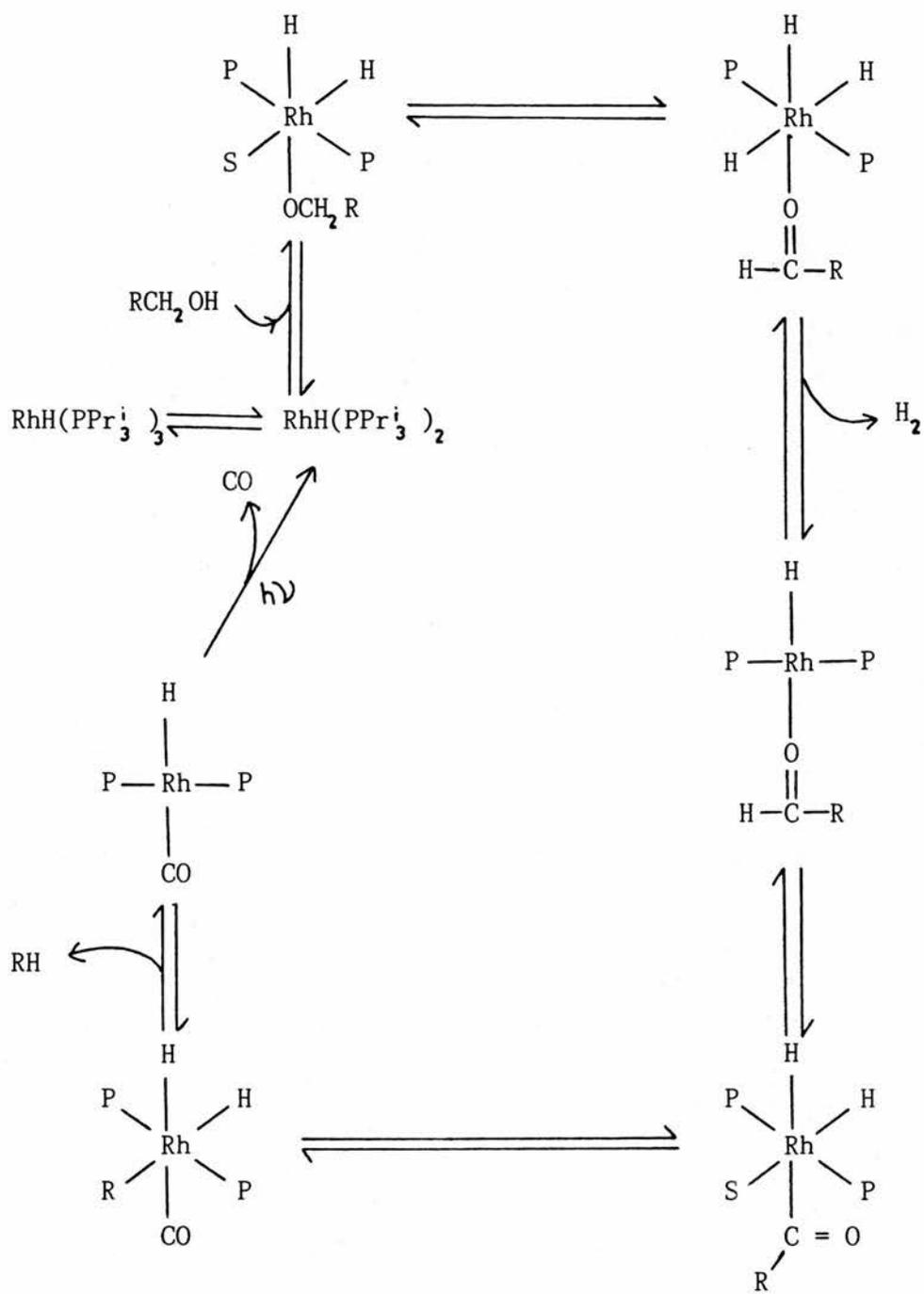
been photochemical and the substrate in most of these reactions has been 2-propanol.

Cole-Hamilton and co-workers reported the production of hydrogen, on photolysis, from both primary and secondary alcoholsⁿ. Photolysis of $[\text{RhH}(\text{PPr}^i_3)_3]$ or $[\text{RhH}(\text{CO})(\text{PPr}^i_3)_2]$ in methanol, with light from a 500W tungsten halogen lamp, catalytically produces H_2 and CO in 2:1 molar ratios. In the absence of either illumination or catalyst neither is produced.

The reaction has a moderately high activation energy indicating a slow thermal step or pre-equilibrium which is temperature dependent.

For ethanol, H_2 , CO and CH_4 are the major products. Illumination is essential for reaction and the rate increases at higher temperatures. $[\text{RhH}(\text{PPr}^i_3)_3]$ is known to react thermally with methanol to give $[\text{RhH}(\text{CO})(\text{PPr}^i_3)_2]$, therefore, the mechanism of decomposition of methanol and ethanol is probably the same for both catalysts. A mechanistic reaction scheme was suggested (scheme 1.2) with the key step being photochemical loss of CO from $[\text{RhH}(\text{CO})(\text{PPr}^i_3)_2]$ ($\lambda_{\text{max}} = 360\text{nm}$).

Scheme 1.2

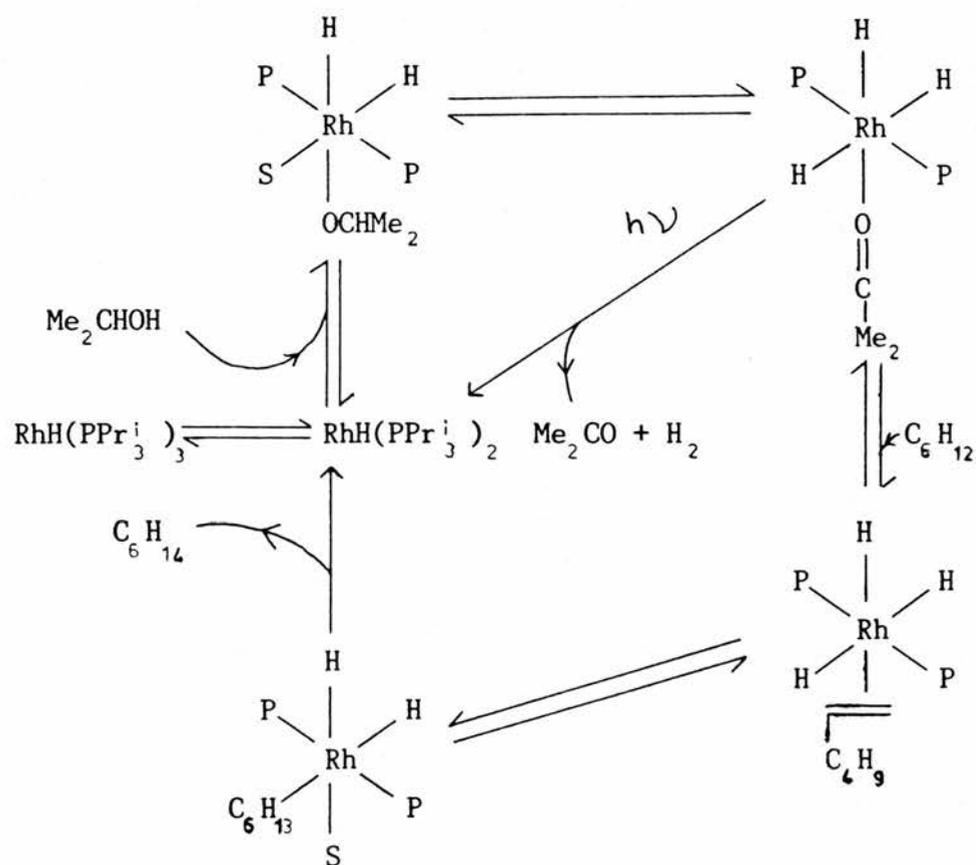


R = CH₃ or H

S = solvent

Dehydrogenation of isopropanol also occurs to give acetone as the main product. A similar mechanism to that shown in scheme 1.2 was proposed, although here hydrogen loss occurs photochemically (scheme 1.3).

Scheme 1.3



Scheme 1.3 also shows the decomposition of 2-propanol in the presence of a hydrogen acceptor, hex-1-ene.

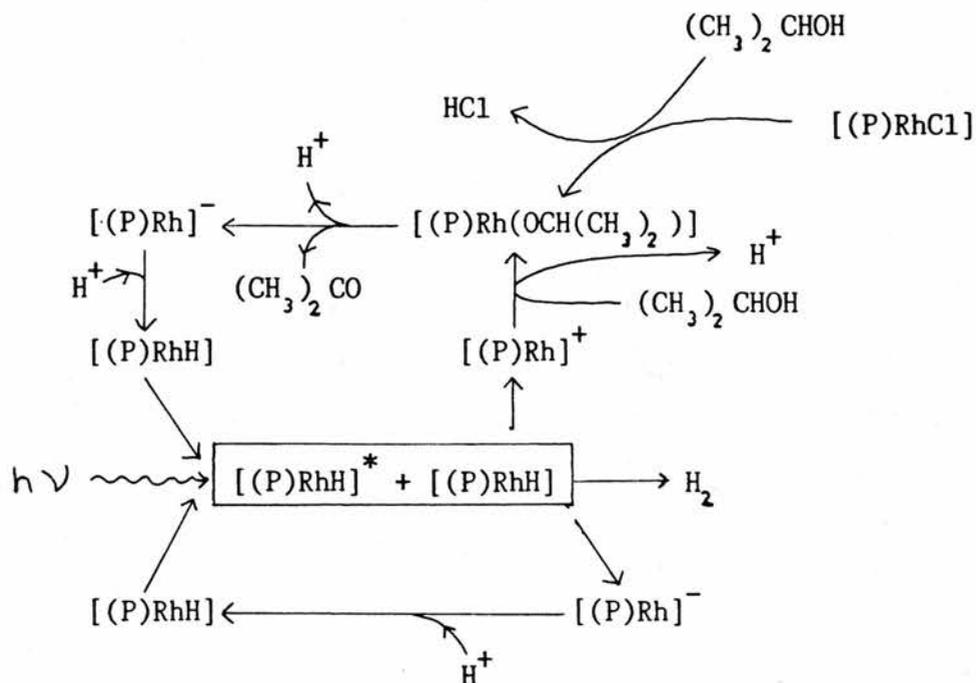
$[\text{RhH}(\text{PPr}_3)_3]$ allows hydrogen transfer from 2-propanol to give acetone and hexane thermally with 100% conversion.

Further studies on this catalytic system are described in more detail in this thesis.

Photochemical dehydrogenation of cyclohexanol and 2-propanol in the presence of a rhodium porphyrin complex, chloro(tetraphenylporphinato)rhodium(III) ($[\text{Rh}(\text{TPP})\text{Cl}]$) was reported by Japanese workers^{12,13}. The dehydrogenation of 2-propanol was studied in detail because of the potential energy-storing nature of the reaction.

Metalloporphyrin complexes are of particular interest in the utilization of solar energy because they have large molar extinction coefficients in the visible region of the spectrum. Photochemical reaction at 82.5°C under an atmosphere of argon gave acetone and hydrogen as the only products. Kinetic studies revealed that a bimolecular process, involving hydridorhodium porphyrin complexes in both the ($\pi - \pi^*$) photoexcited and ground states, was involved in the photocatalytic cycle. The mechanism proposed for hydrogen production from 2-propanol using this catalyst is shown in scheme 1.4.

Scheme 1.4



P = tetraphenylporphyrin

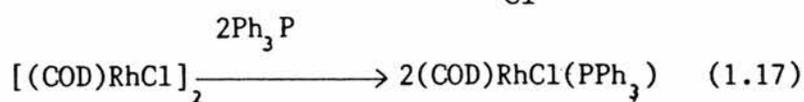
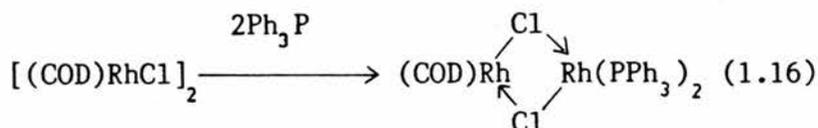
H_2 evolution is possible from the hydridorhodium porphyrin complex when it is acidified in the reduced state. Hence, addition of HCl should increase the rate of H_2 evolution, and this was found to be true.

The photocatalytic dehydrogenation of 2-propanol has been studied using Wilkinson's complex, $[RhCl(PPh_3)_3]$ as catalyst^{14,15}. Photolysis at 21°C, after exposure to air and incubation for 30 minutes, produced 312cm³ of H_2 in two hours with catalytic activity corresponding to 5415 turnovers per hour. The reaction was found to be wavelength

dependent, hydrogen was only evolved with light of $\lambda < 300\text{nm}$. Addition of free PPh_3 caused both an increase in the induction period before gas evolution and a reduction in the observed rate.

Photolysis with $[\text{RhCl}[\text{P}(\text{OPh})_3]_3]$ as catalyst showed an improved catalytic activity of 6400 turnovers per hour¹⁵. $[\text{RhCl}(\text{CO})_2]_2$ was also an efficient catalyst for this reaction.

$[\text{RhCl}(\text{COD})]_2$ was much less active for dehydrogenation, but in the presence of one mole equivalent of PPh_3 , activity comparable to $[\text{RhCl}(\text{PPh}_3)_3]$ was achieved. It was suggested that PPh_3 could have two possible modes of action:



Oxidation of Ph_3P to Ph_3PO followed by dissociation of Ph_3PO under photolysis enables both complexes to produce co-ordinatively unsaturated rhodium species. These reactions show how important oxygen is to the catalytic cycle. The experimental results provided no distinction between the two options (1.16 and 1.17) and it was suggested that both mechanisms could be operating, producing a common photocatalyst under the photocatalytic conditions.

Saito and co-workers reported that photoirradiation of both

cis-[Rh₂Cl₂(CO)₂(dppm)₂] and [Pd₂Cl₂(dppm)₂] in methanol produced considerable evolution of H₂¹⁶. Addition of acetone led to a significant increase in the rate of H₂ evolution. Photochemical of cis - [Rh₂Cl₂(CO)₂(dppm)₂] at 65°C produced H₂ with catalytic activity corresponding to 2.2 turnovers per hour. Addition of acetone led to a significant increase in the catalytic activity; a maximum of 130 turnovers per hour achieved. In the absence of acetone, the evolved gas was almost entirely H₂ with a trace of CH₄. In contrast, the gas phase products from a 9:1 mixture of methanol and acetone, under the same photochemical conditions, were in relative abundances in (%); CH₄ (90), CO (8.8) and H₂ (1.2) after reaction for 7.5 hours.

[Pd₂Cl₂(dppm)₂] showed virtually no activity in the absence of acetone, but high activity with acetone; turnover numbers of 156 per hour observed. The palladium catalyst also had an induction period and a comparatively rapid deactivation which was not the case with the rhodium catalyst.

UV experiments indicated that the active species in the palladium system was probably a cluster compound or compounds. The rhodium complex also formed catalytically active clusters after a long reaction time.

The liquid phase products were shown to be formaldehyde (1), formaldehyde dimethyl acetal (2), ethylene glycol (3), 2,3-dimethyl-2,3-butanediol (4), 2-propanol (5), and

2-methyl-1,2-propanediol (6). The following processes involving dehydrogenation, C-C coupling and intermolecular H₂ transfer were used to formally classify these products.

		Amount in m mol formed under photoirradiation at 64 °C
CH ₃ OH	→ H ₂ + HCHO	(1) 7.8
3CH ₃ OH	→ H ₂ + CH ₂ (OCH ₃) ₂ + H ₂ O	(2) 4.1
2CH ₃ OH	→ H ₂ + HOCH ₂ CH ₂ OH	(3) 15.3
2(CH ₃) ₂ CO	+ H ₂ → HOC(CH ₃) ₂ C(CH ₃) ₂ OH	(4) 0.9
(CH ₃) ₂ CO	+ H ₂ → (CH ₃) ₂ CHOH	(5) 7.7
CH ₃ OH + (CH ₃) ₂ CO	→ HOCH ₂ C(CH ₃) ₂ OH	(6) 9.4

Analysis of the liquid phase products in the absence of added catalyst shows that the catalyst does participate in the reaction in the production of (1) and (2).

Cis-[Rh₂Cl₂(CO)₂(dppm)₂] is also a catalyst for 2-propanol decomposition. The activation energy was calculated to be 14.3KJmol⁻¹ compared to 26.4KJmol⁻¹ for methanol decomposition. These values reflect the higher C-H bond dissociation energy of methanol (393KJmol⁻¹) relative to 2-propanol (381KJmol⁻¹)

indicating an increased difficulty for methanol dehydrogenation.

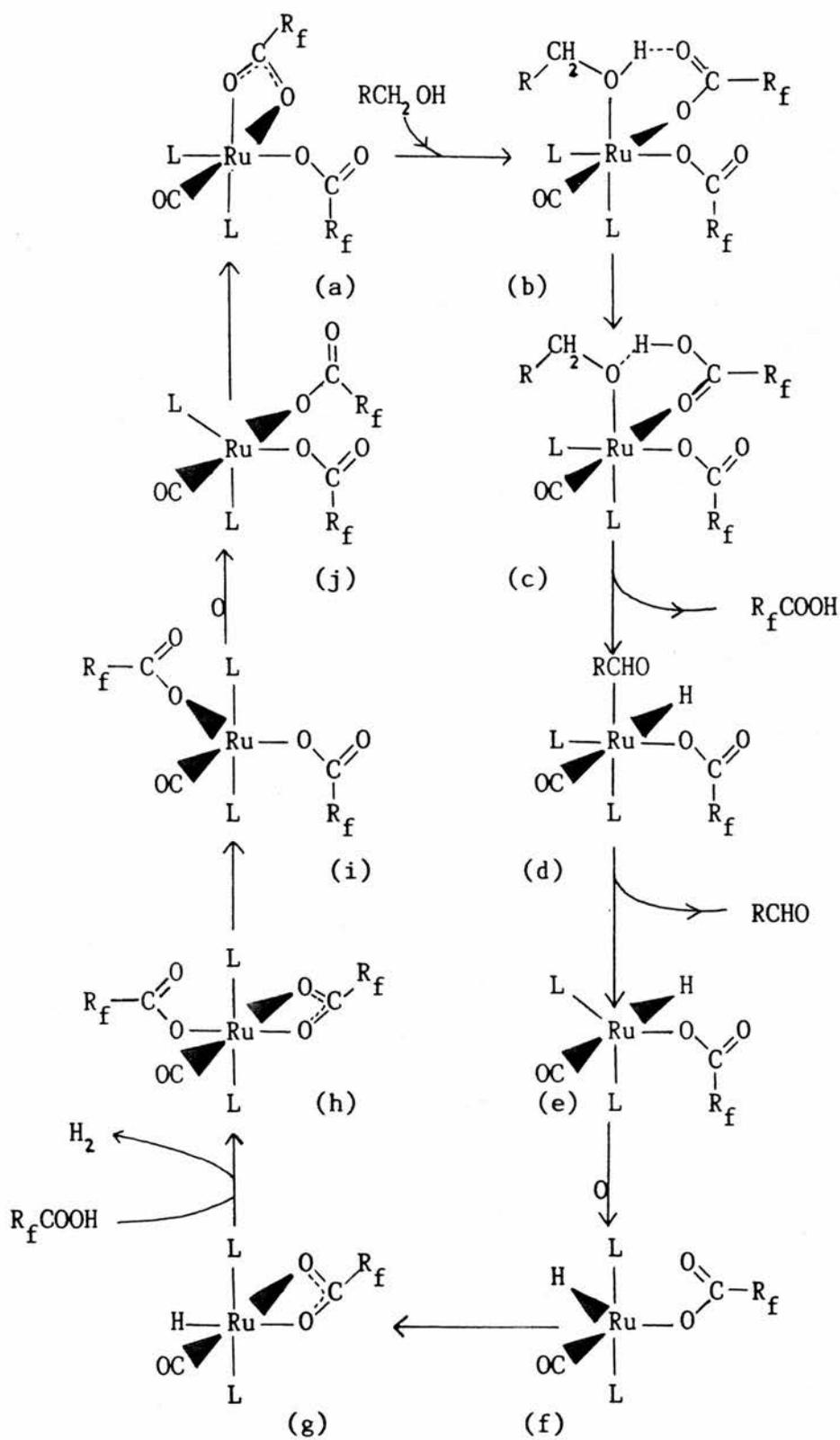
Other complexes were studied including $[\text{Pt}_2\text{Cl}_2(\text{dppm})_2]$, $[\text{Ir}_2(\mu\text{-S})(\text{CO})_2(\text{dppm})_2]$, $[\text{Mo}_2\text{Cl}_4(\text{dppm})_2]$ and $[\text{Mo}_2(\text{OAc})_4]$. None exhibited thermal catalytic activity and photochemistry was not as effective as in the rhodium and palladium cases.

1.5 COMPLEXES OF RUTHENIUM

The use of ruthenium complexes for the catalytic dehydrogenation of alcohols has been investigated. A homogeneous catalytic reaction for the dehydrogenation of primary and secondary alcohols was reported by Robinson and Dobson using ruthenium and osmium perfluorocarboxylates, $[M(OCOCF_3)_2(CO)(PPh_3)_2]$ as catalysts¹⁷. These complexes are readily attacked by alcohols to liberate aldehydes or ketones with concomitant formation of the metal hydride species. Acid attack, (CF_3COOH) , on these hydrides regenerates the parent complex and liberates H_2 , thereby completing a catalytic cycle. The reactions are shown in scheme 1.5.

The activity of the ruthenium catalyst is good with 27 turnovers per hour for ethanol dehydrogenation and 11 turnovers per hour for 2-propanol dehydrogenation reported at the reflux temperature. The efficiency of the catalysts were $Ru > Os$, and this was also dependant on the nature of the carboxylate group in the sense $CF_3 \sim C_2F_5 > C_6F_6$. The activity of the ruthenium catalyst was shown to be promoted by the addition of free acid (CF_3COOH) and hindered by the accumulation of aldehyde or ketone and by a higher concentration of acid.

Scheme 1.5



Seventeen alcohols were examined using the ruthenium catalyst, and only two, methanol and t-butanol failed to dehydrogenate. Methanol because its boiling point is too low or because the methyl C-H bonds are significantly stronger than the α C-H bonds in other primary and secondary alcohols, and the t-butanol because it lacks an α C-H group.

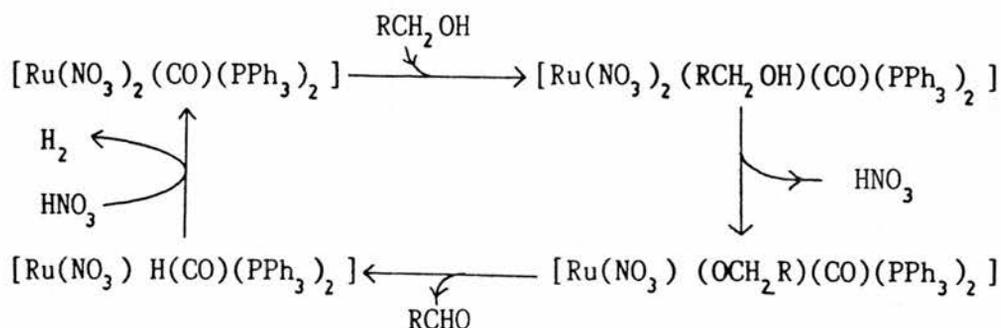
The rate of dehydrogenation was shown to be directly proportional to catalyst concentration for concentrations less than 9×10^{-4} mol/mol of alcohol. At higher catalyst concentrations the relationship is altered by precipitation of the rather insoluble catalytic intermediate $[\text{RuH}(\text{OCOCF}_3)(\text{CO})(\text{PPh}_3)_2]$ from solution.

Critchlow and Robinson reported that $[\text{Ru}(\text{NO}_3)_2(\text{CO})(\text{PPh}_3)_2]$ is also a catalyst for the dehydrogenation of primary and secondary alcohols¹⁸. The reaction was accompanied by aldehyde or ketone formation and was accelerated by the presence of base. The dehydrogenation was thought to proceed via a β -elimination mechanism similar to that shown for the corresponding perfluorocarboxylates, $[\text{Ru}(\text{OCOCF}_3)_2(\text{CO})(\text{PPh}_3)_2]$, and the reactions are shown in scheme 1.6.

In view of the apparent parallel between the activity of $[\text{Ru}(\text{OCOCF}_3)_2(\text{CO})(\text{PPh}_3)_2]$ ¹⁷ and $[\text{Ru}(\text{NO}_3)_2(\text{CO})(\text{PPh}_3)_2]$ ¹⁸ as alcohol dehydrogenation catalysts, the catalytic efficiencies of these species and the mixed complex $[\text{Ru}(\text{NO}_3)(\text{OCOCF}_3)(\text{CO})(\text{PPh}_3)_2]$ were compared¹⁸. Results for H_2 evolution showed that activity

declined by a factor of ten in the order, $[\text{Ru}(\text{OCOCF}_3)_2(\text{CO})(\text{PPh}_3)_2] \gg [\text{Ru}(\text{NO}_3)(\text{OCOCF}_3)(\text{CO})(\text{PPh}_3)_2] > [\text{Ru}(\text{NO}_3)_2(\text{CO})(\text{PPh}_3)_2]$.

Scheme 1.6



An explanation was provided by the observation that nitrate competes with methanol more favourably than perfluorocarboxylate in the alcohol solvation process, thus preventing alcohol dehydrogenation.

The dehydrogenation reaction of alcohols catalysed by $[\text{Ru}(\text{OCOCF}_3)_2(\text{CO})(\text{PPh}_3)_2]$ was also studied when this complex was attached to polystyrene functionalised with phosphine and carboxylic groups; singly or together¹⁹.

These studies were carried out in an attempt to combine the high selectivity of the homogeneous process with the ease of isolation of the catalyst in a heterogeneous system. The ruthenium complex was immobilized on polystyrene divinyl benzene resin, (PS-DVB, 3% cross-linked), functionalised with phosphine and carboxylic acid groups.

It was found that the supported catalysts had a considerable reduction in activity. The results are shown in table 1.2.

Table 1.2: Relative dehydrogenation reaction rates of alcohols catalysed by the heterogenized (IA) and homogeneous catalysts (I) [IA \equiv PPh_2 -Ru(II)].

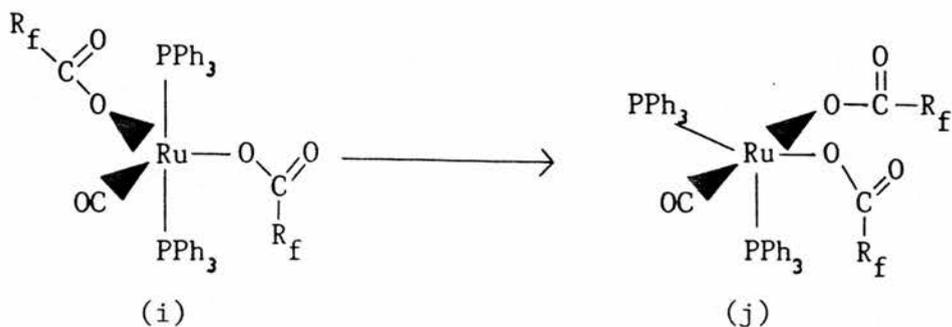
<u>Alcohol</u>	<u>Initial rate (mmol H₂/g)</u>		<u>Relative rate</u>	
	[IA]	[I]	[IA]	[I]
Ethanol	0.0383	0.116	1	1
1-Propanol	0.115	0.35	3.0	3.05
2-Propanol	0.0193	0.0511	0.5	0.44
1-Butanol	0.345	1.06	9.0	9.14

Reaction conditions: heterogenized catalyst [IA] 0.2g; homogeneous catalyst [Ru(OCOCF₃)₂(CO)(PPh₃)₂] (0.0262mol) in boiling alcohol (20ml).

The results suggested analogous mechanisms for both the heterogeneous and homogeneous systems. The heterogeneous catalysts were more stable, retaining their activity and selectivity even after repeated reactions.

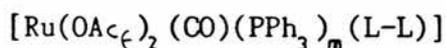
Jung and Garrou performed comparative studies on systems related to those of Dobson and Robinson. The triphenyl phosphine ligands on [Ru(OCOCF₃)₂(CO)(PPh₃)₂] were replaced with a chelating diphosphine²⁰. In the originally proposed

mechanism (scheme 1.5), an isomerisation is required whereby mutually trans phosphine ligands or intermediate (i) must rearrange to a cis configuration (j), in order to complete the catalytic cycle.



By locking the phosphines to a cis configuration using a chelating diphosphine, the rate of the reaction would be altered if the isomerisation of (i)→(j) was the rate determining step of the overall catalytic cycle.

The activities and the stability of the following catalysts were studied;



where: (L-L) = 1,2-(PPh₂)₂ C₆H₄ m = 1
 = PPh₂ CH₂ CH₂ AsPh₂ m = 1
 = Ph₂P(CH₂)_n PPh₂ n = 2, m = 0

for the dehydrogenation of primary and secondary alcohols.

The rates of conversion of cyclohexanol to cyclohexanone at 175°C using these catalysts are summarised in table 1.3, along with comparative data for other alcohols. They found that the chelate modified catalysts showed a higher activity for conversion of cyclohexanol to cyclohexanone. They also observed that all of the ruthenium complexes seemed to be specific for secondary alcohols with little or no conversion of primary alcohols to aldehydes.

In these experiments, $[\text{Ru}(\text{OAc}_f)_2(\text{CO})(\text{PPh}_3)_2]$ had a short lifetime due to thermal decomposition or side reactions yielding inactive products. The modified catalysts were much more stable to decomposition and eventual loss of activity was attributed to loss of volatile HOAc_f (b.p. 72°C) at the 175°C reaction temperature. Generally, metal complexes with chelating phosphines are more thermally stable than the analogous monodentate phosphine complex.

Although Robinson had shown that $[\text{Ru}(\text{OCOCF}_3)_2(\text{CO})(\text{PPh}_3)_2]$ was an efficient catalyst for the dehydrogenation of primary and secondary alcohols¹⁷, this work by Jung and Garrou found that this complex was specific for secondary alcohols, and was deactivated by reaction with the product aldehyde or ketone.

Table 1.3 DEHYDROGENATION OF CYCLOHEXANOL USING RUTHENIUM CATALYSTS

Catalyst	Substrate	10^5 mol of Ru	Initial Rate ^a	Rel Rate	Max % Reaction
$\text{Ru}(\text{OAc}_f)_2 (\text{CO})(\text{PPh}_3)_2$ A	Cyclohexanol ^b	2.01	1.20	1.00	4.5
$\text{Ru}(\text{OAc}_f)_2 (\text{CO})(\text{PPh}_3)[(\text{Ph}_2\text{P})\text{C}_6\text{H}_4]$ B	Cyclohexanol ^b	4.54	(8.82) ^c	1.40	5.6 ^d
$\text{Ru}(\text{OAc}_f)_2 (\text{CO})(\text{PPh}_3)(\text{Ph}_2\text{PCH}_2\text{CH}_2\text{AsPh}_2)\text{HOAc}$ C	Cyclohexanol ^b	2.06	1.68	2.30	22.0
$\text{Ru}(\text{OAc}_f)_2 (\text{CO})(\text{PPh}_3)(\text{Ph}_2\text{PCH}_2\text{CH}_2\text{PPh}_2)_2$ D	Cyclohexanol ^b	1.75	2.76(0.08)	3.50	17.0
A	Ethanol ^c	2.06	4.20		
A	Ethanol ^e	4.54	0.45		
A	1-propanol ^c	2.62	0.074		
A	1-propanol ^e	4.54	1.36		
A	2-propanol ^c	2.62	0.22		
A	2-propanol ^e	4.54	0.20		
A	1-butanol ^c	2.62	0.032		
A	1-butanol ^e	4.54	4.1		
A	1-butanol ^e	2.62	0.67		

LEGEND OF: TABLE 1.3

- a - Mol of H₂ evolved/mol of Ru/min.
- b - Reaction conditions: 175°C, 50 x 10⁻² mol of substrate,
1.3 x 10⁻⁴ mol of CF₃COOH.
- c - Ref 17: reflux temperatures, 0.134mol of substrate,
5.2 x 10⁻⁴ mol of CF₃COOH.
- d - Kinetic run arbitrarily stopped at this maximum conversion.
- e - Ref 20: reflux temperatures, 20ml of substrate,
3 x 10⁻⁴ mol of CCl₃COOH.

It was concluded that the diphosphine ruthenium complexes were more active than [Ru(OCOFC₃)₂(CO)(PPh₃)₂] and they are deactivated by a stoichiometric decarbonylation of the product aldehyde or ketone when the alcohol is high boiling. Decarbonylation did not occur for low boiling alcohols, e.g. methanol, ethanol, 2-propanol.

The first example of the thermal dehydrogenation of methanol in solution with a homogeneous complex catalyst, [Ru₂(OAc)₄Cl]-t-phosphine was reported by Saito and co-workers in 1985²¹. Previously only photocatalytic reactions had been known¹⁶.

Heating a solution of [Ru₂(OAc)₄Cl] and PR₃ dissolved in anhydrous methanol produced a mononuclear ruthenium complex found to be [Ru(OAc)Cl(PR₃)₃], (PR₃ = PPh₃, PEtPh₂). The catalytic activity of the mono and di-nuclear species were found to be similar, thus indicating that the mononuclear

complexes were the catalytically active species.

The catalyst was most active if PR_3 was $PEtPh_2$ with 0.58 turnovers h^{-1} observed over a 17 hour period at $66^\circ C$.

The reaction products were formaldehyde and hydrogen. Formaldehyde (and its dimethyl acetal) were gradually converted into secondary products which included methyl formate.

The addition of free acid (AcOH) enhanced the catalytic activity of $[Ru(OAc)Cl(PEtPh_2)_3]$. Progressive inhibition of activity was noted at high concentrations of AcOH. This behaviour was explained in terms of the protonation of a metal hydride intermediate to generate H_2 being the rate determining step. In the presence of an excess of free acid, this process would be replaced by a preceding step as the rate determining step.

Deactivation of the catalyst occurred to a small extent due to the decarbonylation of formaldehyde to form a catalytically inactive species $[RuH(Cl)(CO)_2(PEtPh_2)_2]$.

Blum and Shvo performed extensive studies on the catalytic activity²² and structure²³ of $[(\eta^4-C_6H_6)Ru(CO)_3]$ for the dehydrogenation of primary alcohols to esters (equation 1.18) and of secondary alcohols to ketones (equation 1.19) in the presence of O_2 at the refluxing temperature of the alcohol.



Esters were formed by a bimolecular dehydrogenation of primary alcohols.

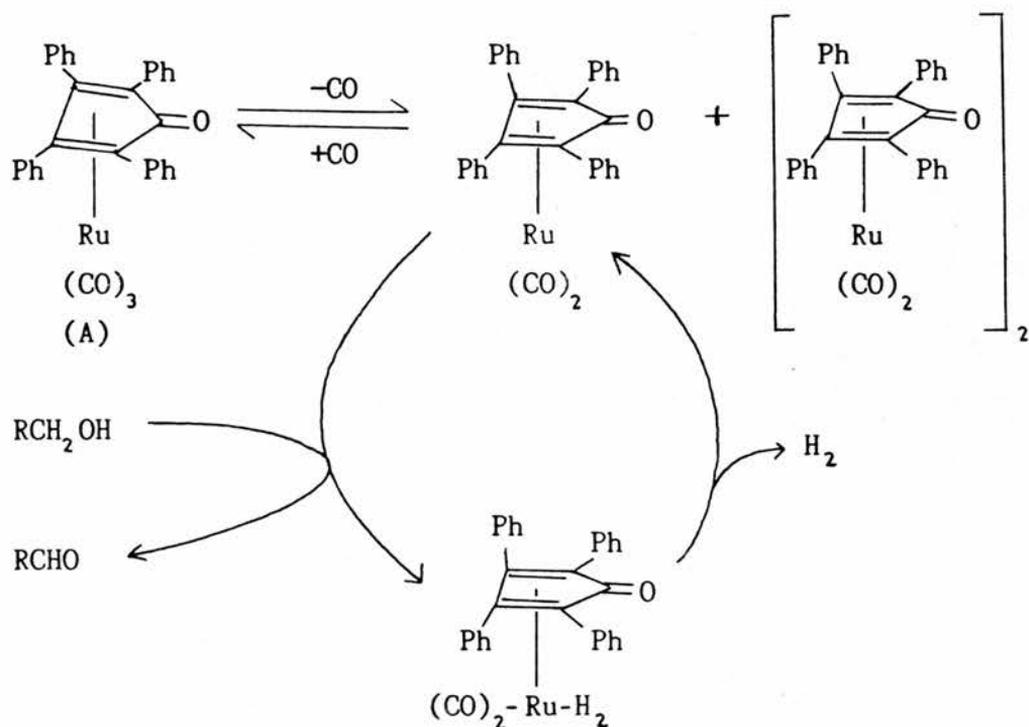
The dehydrogenation of benzyl alcohol to benzyl benzoate at 145°C, was catalysed by $[(\eta^6\text{-Ph}_4\text{C}_4\text{CO})\text{Ru}(\text{CO})_3]$ (A) and $[(\eta^6\text{-Ph}_4\text{C}_4\text{CO})\text{Ru}(\text{CO})_2]_2$ (B) in an open system generating 450 turnovers after one hour. Under similar conditions 1-pentanol yields 1-pentyl-n-pentanoate (250 turnovers in one hour).

Both of these catalysts are co-ordinatively saturated 18 electron complexes and were, therefore, regarded as catalyst precursors. The active species was deduced to be a co-ordinatively unsaturated dicarbonyl complex $[(\eta^6\text{-Ph}_4\text{C}_4\text{CO})\text{Ru}(\text{CO})_2]$. The presence of a free co-ordination site allowed this complex to oxidize a primary alcohol to an aldehyde to produce a dihydride complex which can thermally eliminate H_2 to complete the catalytic cycle.

It was established that the aldehyde was an intermediate in the formation of the ester in a second step which would involve oxidative interaction of aldehyde, alcohol and the catalyst.

A mechanism was proposed for the initial dehydrogenation step and is shown in scheme 1.7.

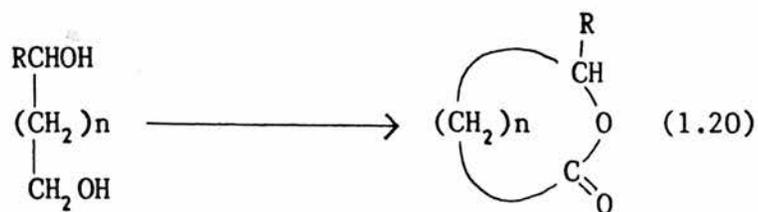
Scheme 1.7



The transformation of alcohols to esters and lactones was reported to be catalysed by a ruthenium dihydride complex, $[\text{RuH}_2(\text{PPh}_3)_4]^{24}$.

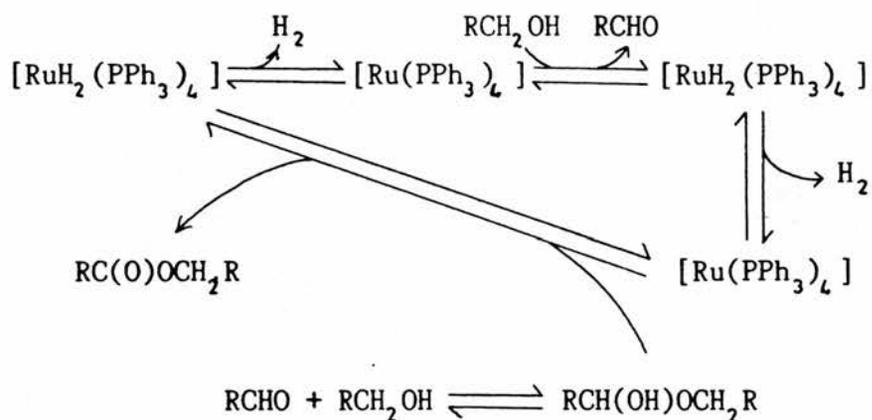
Reaction with alcohols took place at 180°C highly efficiently and the reaction was almost totally selective for ester formation from primary alcohols.

This oxidative condensation reaction can be applied to diols where lactones are the products. 1,4 and 1,5 diols are converted to γ and δ - lactones in excellent yields (equation 1.20).



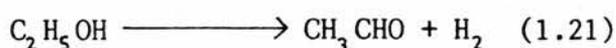
The reaction proceeds via an initial dehydrogenation of the dihydride complex which can then readily oxidatively add the alcohol. β - elimination gives the dihydride and the aldehyde as shown in scheme 1.8.

Scheme 1.8



1.6 COMPLEXES OF PLATINUM

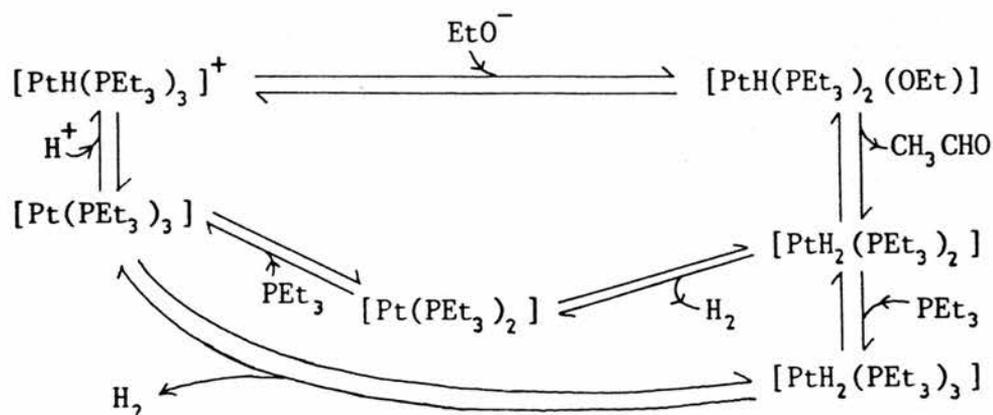
Recently Cole-Hamilton and Utuk reported the catalytic dehydrogenation of ethanol by $[\text{PtH}(\text{PEt}_3)_3]^+$ ²⁵. They showed that $[\text{PtH}(\text{PEt}_3)_3]^+$ was capable of catalysing the thermal homogeneous dehydrogenation of ethanol to ethanal in the presence of base (equation 1.21).



The reaction was found to be first order with respect to [catalyst], [ethanol] and $[\text{OH}^-]$ and to have an activation energy of 27.3KJmol^{-1} .

A likely mechanism was suggested which involved an initial attack of ethoxide ion on $[\text{PtH}(\text{PEt}_3)_3]^+$, with or without loss of PEt_3 , followed by β -H transfer; loss of H_2 and protonation (scheme 1.9).

Scheme 1.9



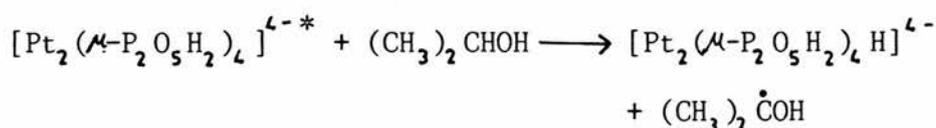
The success of the reaction is dependent upon the very high basicity²⁶ of $[\text{Pt}(\text{PEt}_3)_3]$ because it needs to be protonated in the highly alkaline reaction conditions required for successful attack of EtO^- on $[\text{PtH}(\text{PEt}_3)_3]^+$.

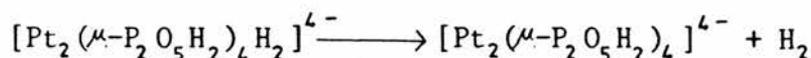
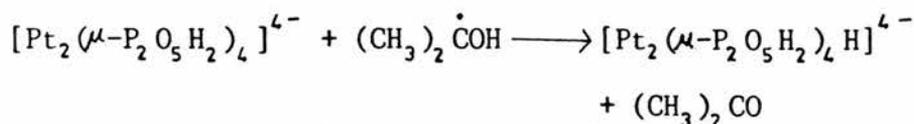
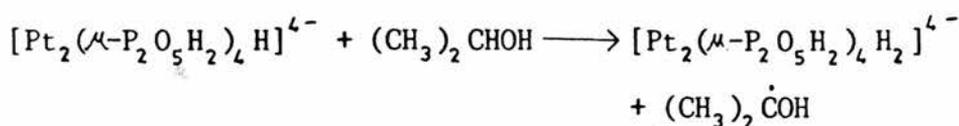
Roundhill reported the photoinduced catalytic conversion of 2-propanol into acetone and hydrogen using tetrakis (μ -pyrophosphito) diplatinum(II), $[\text{Pt}_2(\mu\text{-P}_2\text{O}_5\text{H}_2)_4]^{4-}$ ²⁷. 2-propanol reacts directly with the excited state $[\text{Pt}_2(\mu\text{-P}_2\text{O}_5\text{H}_2)_4]^{4-*}$ and removal of the light source stopped gas evolution which showed that the conversion was photoinduced rather than photocatalysed. Turnover numbers exceeding 400 were achieved over a 3 hour period.

A mechanism was proposed in which the first step was abstraction of the secondary methine H of the 2-propanol by the excited state of the platinum complex. This was followed by propagation steps to form acetone and $[\text{Pt}_2(\mu\text{-P}_2\text{O}_5\text{H}_2)_4\text{H}]^{4-}$.

Reductive elimination of H_2 completed the catalytic cycle (scheme 1.10).

Scheme 1.10

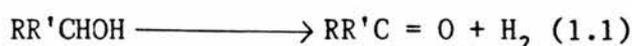




H_2 cannot be released from the complex in a concerted fashion. The reaction pathway involves an initial loss of a hydrogen atom, with H_2 formed in a stepwise manner.

H_2 evolution also occurs from cyclohexanol and small quantities of the gas are produced from methanol and ethanol.

The majority of the alcohol decomposition reactions reviewed here follow a similar reaction pathway (equation 1.1)



Further catalytic decomposition of primary and secondary alcohols under thermal conditions is not normally observed. The decarbonylation of alkanals (the products of dehydrogenation of primary alcohols) by many platinum metal complexes is facile but the carbonyl complex is usually thermodynamically stable towards CO loss. The product from a secondary alcohol is normally a ketone which is not further decomposed because carbon-carbon bond breaking would have to occur which

is thermodynamically unfavourable.

CO can be lost photochemically as in the photochemical decomposition of primary alcohols catalysed by $[\text{RhH}(\text{CO})(\text{PPr}_3)_2]^+$.

An alternative answer to the thermodynamic problem would be to convert the CO into CO_2 by water-gas shift type chemistry. The overall reaction is mildly exergonic and is represented by equation 1.22.

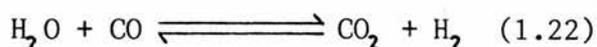


A transition metal complex is known which can readily decarbonylate alcohols and is an efficient water-gas shift catalyst under mild conditions²⁹. Also, both stoichiometric alcohol decarbonylation and water-gas shift chemistry tend to be assisted by basic reaction conditions, so the two reactions should be compatible.

Complexes of the platinum group metals which are catalysts for the water-gas shift reaction and are of relevance to the text of the thesis are reviewed here.

1.7 HOMOGENEOUS CATALYSIS OF THE WATER-GAS SHIFT REACTION

The past decade has seen a rekindling of interest in the catalytic chemistry of a classic reaction, the water-gas shift reaction (1.22).



This attention arose from the necessity to produce gaseous and liquid hydrocarbon fuels and other organic chemicals from non-petroleum sources. Virtually all schemes for such purposes require vast amounts of hydrogen for the transformation of hydrogen deficient substrates to hydrocarbons. Large amounts of hydrogen are also required for the Haber Process, in which hydrogen and nitrogen are reacted for the synthesis of ammonia.

The major source of commercially produced hydrogen is the steam reforming or partial oxidation of hydrocarbons. A different source is an obvious requirement. An old source of hydrogen is the high temperature reaction of carbon based material with water, along with the partial oxidation of the substrate, to produce a mixture of gases: H_2O , H_2 , CO and CO_2 i.e. "water gas".

The composition of the mixture can be altered via the shift reaction to give H_2 for the applications already noted or

synthesis gas with various H_2/CO ratios appropriate to the production of methanol, methane, alcohols or higher hydrocarbons.

Commercially the shift reaction is performed over heterogeneous catalysts at high temperatures²⁹. Low temperature heterogeneous catalysts are being developed but they tend to suffer from sulphur poisoning. However, development is continuing because of the lower energy requirements and the improved reaction efficiency indicated by the thermodynamics under such conditions.

Homogeneous catalysts have been discovered that are active at low temperatures, and these are attracting considerable interest because of the favourable thermodynamic equilibrium. Under ambient conditions $\Delta H_{298}^\circ = + 2.84 \text{KJmol}^{-1}$, $\Delta G_{298}^\circ = -19.92 \text{KJmol}^{-1}$, $\Delta S_{298}^\circ = + 76.57 \text{J deg}^{-1} \text{mol}^{-1}$.

However, the kinetic barriers are large and the reaction only proceeds at useful rates at elevated temperatures.

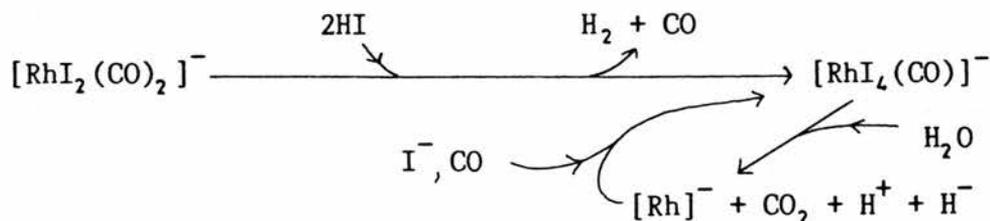
In 1977, Eisenberg and co-workers reported homogeneous catalysis of the water-gas shift reaction using a catalyst system formed from $[\text{Rh}(\text{CO})_2\text{Cl}]_2$, aqueous HI, glacial acetic acid, and concentrated HCl^{30} . When this system was charged with 0.33 - 0.53 atm of CO at 80 - 90°C the water-gas shift reaction was observed to proceed.

They found that in the absence of I^- or HCl no catalysis was observed, and reaction solutions with acetic acid present were 3 - 5 times more reactive than in its absence. The use of ^{13}C CO yielded CO_2 with the same abundance of ^{13}C label as the reactant CO.

In the absence of added CO, the catalyst solution under N_2 yielded stoichiometric amounts of H_2 and CO in a 1:1 ratio followed by slow conversion of the liberated CO into CO_2 .

A mechanism for the water-gas shift reaction was proposed and is shown in scheme 1.11.

Scheme 1.11



More detailed studies were performed by the same group in order to elucidate the mechanistic details of this reaction³¹.

The reaction was found to be first order with respect to total rhodium concentration and partial pressure of CO. The catalytically active species was a mononuclear rhodium complex. The rate of the reaction was found to be temperature dependent with an activation energy of 38.9 kJ mol^{-1} above 70°C . Between $55 - 60^\circ\text{C}$ the activation energy is $107.9 \text{ kJ mol}^{-1}$.

The Arrhenius plot, while linear at high temperatures, is concave downwards in the region of changing kinetics indicating a change in rate determining step with changes in temperature.

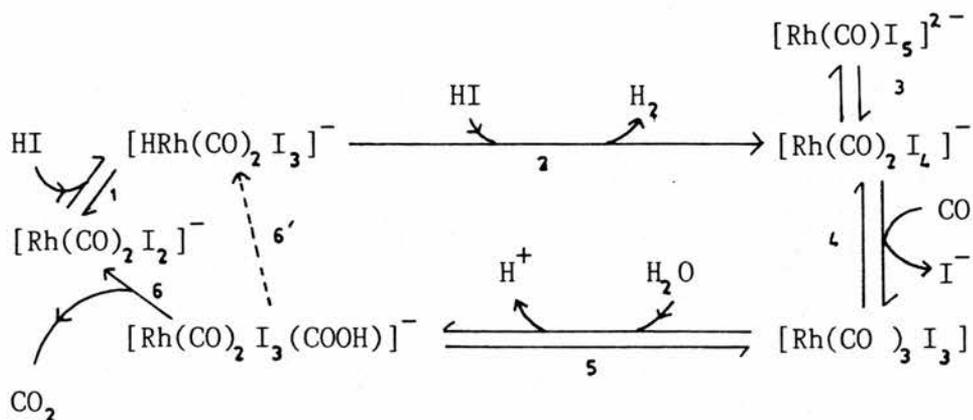
The reaction path with the higher activation energy predominates at lower reaction temperatures and is, therefore, rate-limiting at lower temperatures, while the lower activation energy process becomes rate-limiting at higher temperatures. This suggested that the change in rate-determining step occurred between consecutive reactions and was not a case of competing pathways. This was supported by experimental results on the kinetic dependence of CO, I^- and acid concentrations, which changed with temperature as expected.

These mechanistic studies led to reaction scheme 1.12 being proposed.

At high temperatures ($>80^\circ\text{C}$), step 6 is rate-limiting, while

at lower temperatures (<65°C), step 2 becomes rate-limiting.

Scheme 1.12



Eisenberg also reported that molecular A frame complexes formed from binuclear Rh(0) precursors had high catalytic activity for the water-gas shift reaction³². $[\text{Rh}_2(\mu\text{-H})(\mu\text{-CO})(\text{CO})_2(\text{dpm})_2]^+$ (0.05g) dissolved in 1-propanol with a 2 mole equivalent of LiCl and 1cm³ of H₂O, is a water-gas shift catalyst at 90°C under 1 atm of CO. The rate of catalysis corresponded to 2.5 turnovers h⁻¹ which was one of the most active catalysts then discovered.

Rhodium(I) hydrido compounds, $[\text{RhH}(\text{PEt}_3)_3]$, $[\text{RhH}(\text{PPr}_3^i)_3]$, $[\text{Rh}_2\text{H}_2(\mu\text{-N}_2)\{\text{P}(\text{c}-\text{C}_6\text{H}_{11})_3\}_4]$, $\text{trans-}[\text{RhH}(\text{N}_2)\{\text{PPh}(\text{t-Bu})_2\}_2]$ and $[\text{RhH}\{\text{P}(\text{t-Bu})_2\}_2]$ were reported to serve as catalyst precursors for the water-gas shift reaction under relatively mild conditions (19 atm CO, > 50°C)²⁸. The key intermediates appeared to be $\text{trans-}[\text{RhH}(\text{CO})\text{L}_2]$ (L = $\text{P}(\text{c}-\text{C}_6\text{H}_{11})_3$, PPr_3^i) and $\text{trans-}[\text{Rh}(\text{OH})(\text{CO})\text{L}_2]$, which in pyridine were in equilibrium with the solvated form $\text{trans-}[\text{Rh}(\text{CO})(\text{Py})\text{L}_2]\text{OH}$.

The formation of these adducts was envisaged to proceed through oxidative addition of H_2O to give $[RhH_2(Py)_2L_2]OH$ (step 1) and subsequent reaction with CO releasing H_2 (step 2).

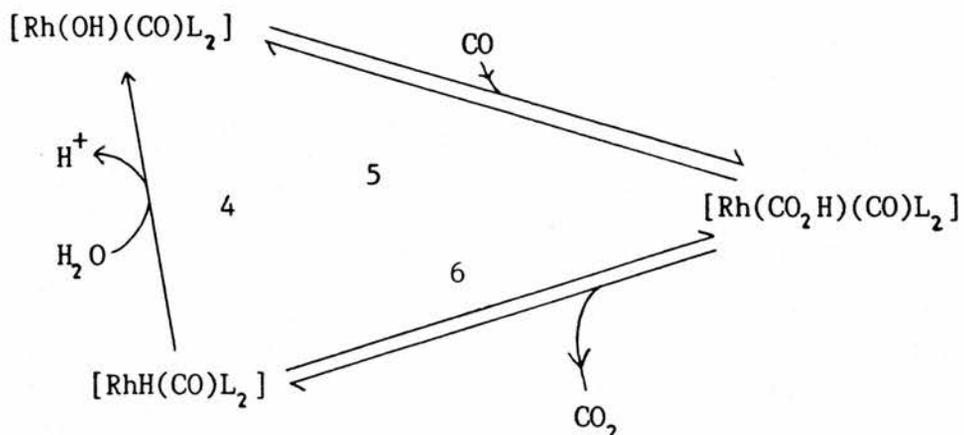
The water adducts were found to be stronger bases than NaOH in aqueous pyridine.

Alternatively, it was suggested that the catalyst precursors could react with CO first to give a Rh(0) compound such as $[Rh_2(CO)_3 \{P(Pr^i)_3\}_3]$ or $[Rh_2(CO)_4 \{P(c-C_6H_{11})_3\}_2]$ via $trans-[RhH(CO)L_2]$ (step 3). These carbonyl complexes could then react with H_2O to give $trans-[Rh(CO)(Py)L_2]OH$ with concomitant evolution of H_2 (step 4).

Under an atmosphere of CO, $trans-[Rh(OH)(CO)L_2]$ would yield $trans-[RhH(CO)L_2]$ via a nucleophilic attack of OH^- on co-ordinated CO to give $[Rh(CO_2H)(CO)L_2]$ as a transient species (step 5), followed by decarboxylation (step 6). The intermediacy of $[Rh(CO_2H)(CO)L_2]$ was suggested by isolating the closely related $trans-[Rh(CO_2CH_3)(CO)(PPr^i_3)_2]$ from the reaction of $trans-[Rh(OCH_3)(CO)(PPr^i_3)_2]$ with CO.

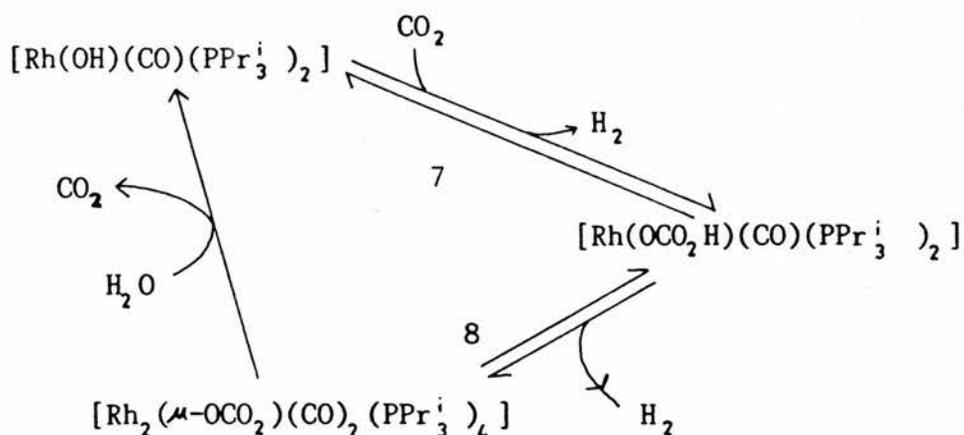
Accordingly, the authors inferred that one cycle starts from $[Rh(OH)(CO)L_2]$ and involves a sequence of steps $5 \rightarrow 6 \rightarrow 4$ for regeneration, as described above and shown in scheme 1.13.

Scheme 1.13



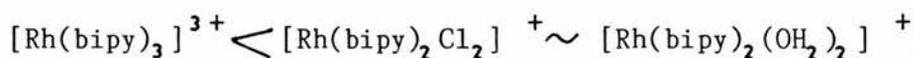
As the shift reaction proceeds another cycle becomes important. This cycle is comprised of the reaction of CO_2 and H_2O to give $[\text{Rh}(\text{OCO}_2\text{H})(\text{CO})(\text{PPr}_3)_2]$ and H_2 (step 7). The cycle is completed by transformation of this complex into $[\text{Rh}(\mu\text{-OCO}_2)(\text{CO})_2(\text{PPr}_3)_2]$ (step 8) and hydrolysis to regenerate $[\text{Rh}(\text{OH})(\text{CO})(\text{PPr}_3)_2]$ as shown in scheme 1.14.

Scheme 1.14

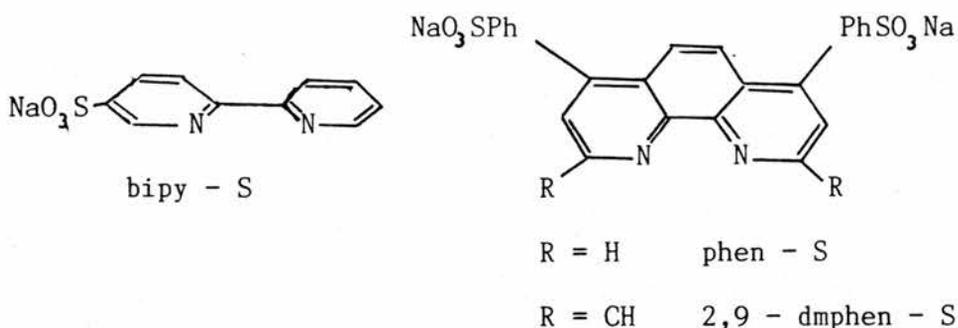


In support of the proposed reaction schemes, all the isolated rhodium compounds discussed showed catalytic activity comparable to that of the catalyst precursor.

The activity of several rhodium complexes of 2,2'-bipyridine as catalysts for the water-gas shift has been studied³³. In water, at 90°C ± 5°C under 1 atm of CO and at pH 5-8, the following sequence for the catalytic activity of the rhodium complexes studied was obtained:



The solubility and, therefore, the reactivity of the possibly active species, such as rhodium hydrides, was increased by using sulfonated bipyridine ligands:



The catalysts were generated in situ by mixing rhodium trichloride with a given amount of ligand. The most active rhodium catalyst was formed from $\text{RhCl}_3 \cdot 3\text{H}_2\text{O}$ and 2,9 - dmphen - S with a ligand to metal ratio of 2:1.

At 100°C and pH 5.4, under 1 atm of CO; turnover numbers of 23 h⁻¹ were achieved. The reaction was found to be pH dependent between pH 5 and 6 suggesting that CO oxidation and H₂ release were kinetically important as would be expected.

The most efficient catalysts were stable under the experimental conditions used with constant activity observed over several days.

Activity was also observed with analogous Iridium catalysts. Catalysts prepared from IrCl₃·3H₂O and one equivalent of 2,9 - dmphen - S in ethanol/water mixtures (4/1) were the most efficient catalysts examined with turnover numbers of up to 100h⁻¹ observed at 100°C.

Recently, homogeneous catalysis of the shift reaction under relatively mild conditions (<100°C, 1 atm CO) has been reported using various polypyridine rhodium(I) complexes as catalyst precursors in alcohol/water mixtures³⁴. The most active complex was found to be [Rh(bipy)₂]⁺. Activities of ~3 turnovers h⁻¹ were observed at 90°C.

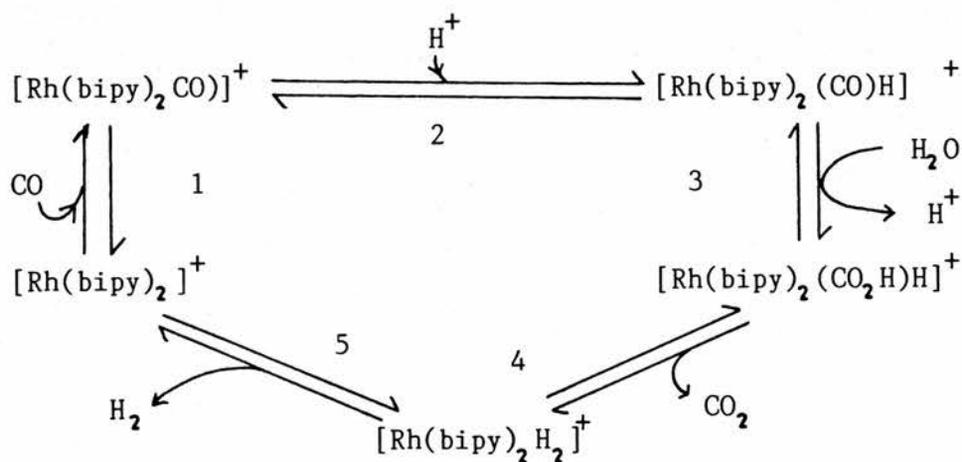
In buffered water/ethanol mixtures the rates of H₂ and CO₂ production were highest at pH 3.2, above this value the rhodium(I) species present exhibit little catalytic activity.

The pH dependance on the rates of reaction combined with

solution UV spectra indicated that $[\text{Rh}(\text{bipy})_2(\text{CO})\text{H}]^{2+}$ was the catalytically active species and this complex predominates at pH 3.2.

A mechanism was proposed and is shown in scheme 1.15.

Scheme 1.15



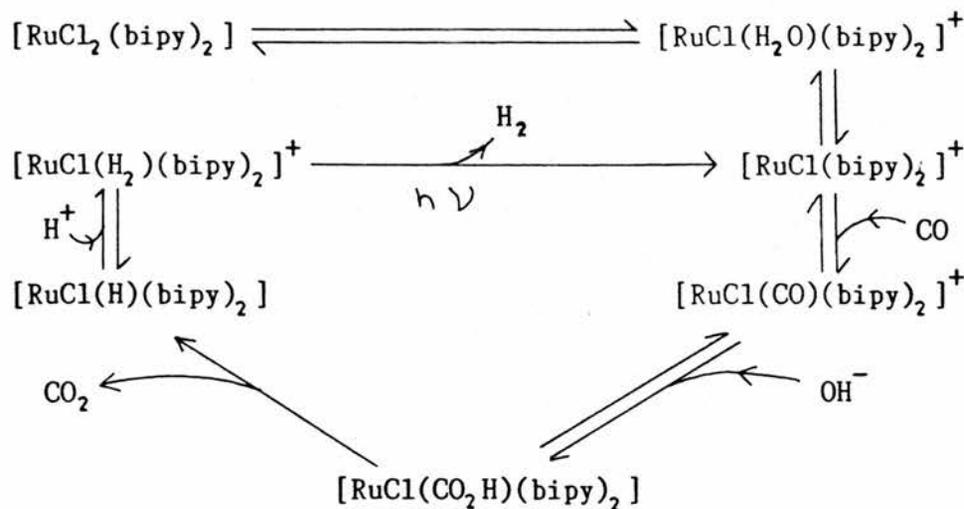
The rate determining step is either reaction 3 or 4 because of the pH dependence on the catalytic rate.

1.9. COMPLEXES OF RUTHENIUM

Cole-Hamilton and Choudhury reported the photochemical water-gas shift reaction catalysed by a ruthenium(II) complex $[\text{RuCl}(\text{CO})(\text{bipy})_2]\text{Cl}^3$. This complex was shown to be catalytically active under relatively mild conditions (1 - 3 atm CO, 100 - 160°C) with illumination by visible light. Turnover numbers of up to 20h^{-1} were observed.

They showed that CO_2 production was thermal whilst H_2 was produced in the photochemical step. Mechanistic studies showed a similar reaction mechanism to those previously reported for the shift reaction which does not involve formate decomposition. The mechanism is shown in scheme 1.16 where $[\text{RuCl}_2(\text{bipy})_2]$ is the catalyst precursor.

Scheme 1.16



The rate determining step at all pH is photochemical loss of H_2 from $[RuCl(H_2)(bipy)_2]^+$. The activation energy for the reaction is pH dependent. At pH 5.5, $E_A = 52.5 \text{ kJ mol}^{-1}$ and at pH 8.9 and 12, $E_A = 35.3 \text{ kJ mol}^{-1}$.

At high pH, the lower activation energy reflects the temperature dependence of the dominant pre-equilibrium which, at this pH, was the protonation of $[RuCl(H)(bipy)_2]$. At low pH, the activation energy is considerably higher which reflects the fact that now the dominant pre-equilibrium is attack of hydroxide ion on $[RuCl(CO)(bipy)_2]^+$. Since the temperature dependence of the two equilibria may well be different; different activation energies would be expected at high and low pH.

The activity of 20 turnovers h^{-1} compares favourably with other systems which use higher pressures of CO.

Workers in Japan reported that the same catalyst precursor $[RuCl(CO)(bipy)_2]^+$ was active for the thermal water-gas shift reaction under aqueous alkaline conditions with higher pressures of CO^{36} .

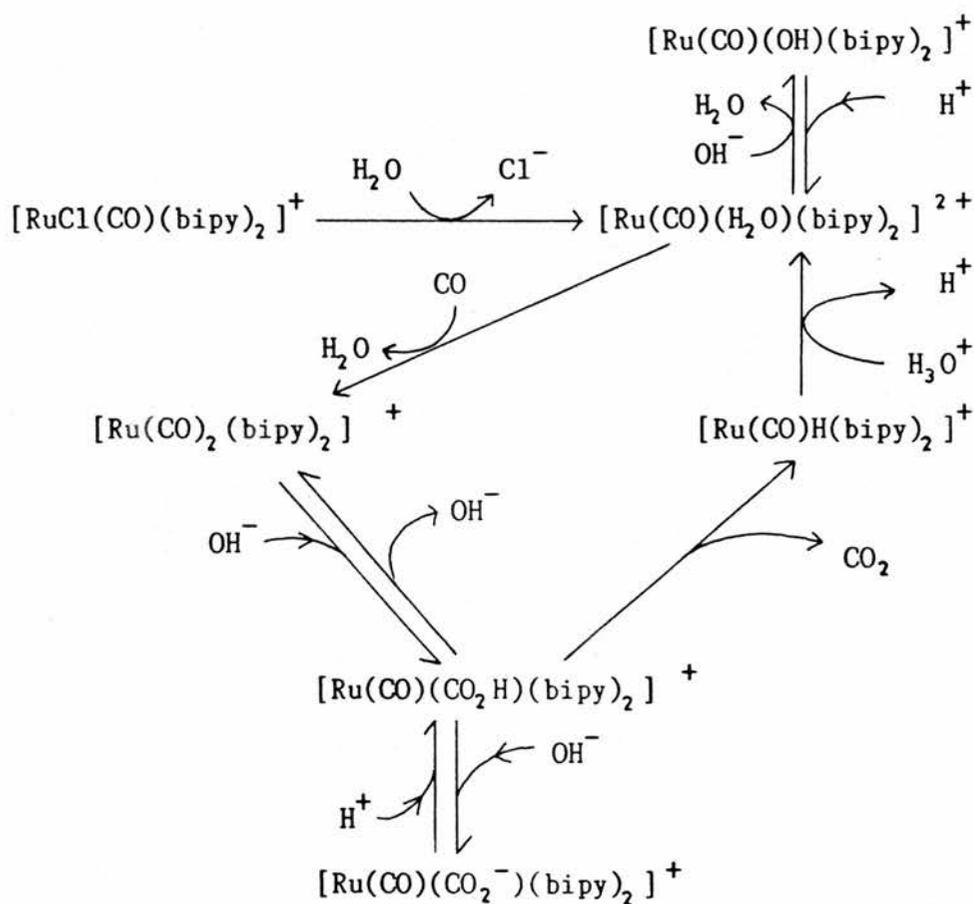
At 150°C under 4.8 atm of CO, the turnover number for hydrogen production was 112 in 20 hours. This increased to 502 at 19 atm of CO. Temperature also had a large effect on H_2 formation with double the amount of H_2 produced at 150°C compared to 100°C .

A reaction mechanism is shown in scheme 1.17.

Evidence for this proposed cycle was provided by the isolation of both $[\text{Ru}(\text{bipy})_2(\text{CO})_2]^+$ and $[\text{Ru}(\text{CO})(\text{CO}_2\text{H})(\text{bipy})_2]^+$.

This reaction scheme was validated by later work, by the same group, when they isolated or characterised by spectrophotometry all the intermediates involved in the catalytic cycle³⁷.

Scheme 1.17



Catalysis of the water-gas shift reaction by a ruthenium porphyrin has been reported³⁸. Aqueous solutions of $[\text{Ru}(\text{TPPS})\text{CO}]^{4-}$ at 100°C under 1 atm of CO produced H_2 and CO_2 with high activity.

The studies reported here have shown that in order to achieve catalysis of the water-gas shift reaction in homogeneous media, two conflicting criteria must be balanced in the choice of a suitable metal catalyst.

In general, the reaction appears to involve nucleophilic attack of hydroxide ion on a metal carbonyl. This requires an electrophilic metal complex. The next step involves protonation of a hydride intermediate which leads to the transfer of two electrons from the metal to the proton. Subsequent reductive elimination leads to the formation of hydrogen. For this hydrogen producing series of reactions to occur, the metal centre must be nucleophilic. It is perhaps this dichotomy that has led to the relatively few reports of catalytically active complexes.

C H A P T E R T W O

THE CATALYTIC DECOMPOSITION OF ETHANOL
USING TRANSITION METAL COMPLEXES
OF RHODIUM AND RUTHENIUM

CHAPTER 2

THE CATALYTIC DECOMPOSITION OF ETHANOL USING TRANSITION METAL COMPLEXES OF RHODIUM AND RUTHENIUM

2.1 INTRODUCTION

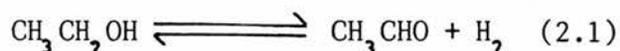
Recent studies have demonstrated that a high grade fuel oil can be produced from biomass³⁹, in the presence of heterogeneous catalysts with an external supply of hydrogen. The requirement for large amounts of hydrogen makes these reactions commercially unattractive.

This work is an attempt to identify possible processes which will allow direct dehydrogenation of biomass or of a fermentation product readily available from biomass.

Biomass and its related fermentation products contain alcoholic and aldehyde functional groups, therefore, hydrogen could be produced by dehydrogenation or dehydrocarbonylation of alcohols.

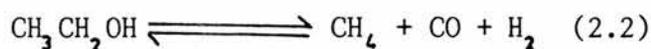
The dehydrogenation of alcohols using homogeneous transition metal catalysts has been well documented over the last ten years (see chapter one). Ethanol was chosen as a simple model for evaluating possible dehydrogenation catalysts since it is a readily available fermentation product. Relatively few transition metal complexes have been shown

to dehydrogenate ethanol. Perhaps the most successful homogeneous catalyst to date is $[\text{Ru}(\text{OCOCF}_3)_2(\text{CO})(\text{PPh}_3)_2]$ ¹⁷. Catalysis of the dehydrogenation of a variety of alcohols, including ethanol was successful. The reaction with ethanol followed equation 2.1.



These reactions usually have an inherent problem of catalyst poisoning when the substrate is a primary alcohol. This was because the catalysts that were capable of dehydrogenation tended to have a high affinity for carbon monoxide and so often decarbonylated the product alkanal¹⁸.

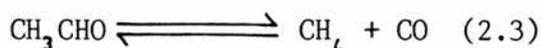
However, this type of decarbonylation reaction can be an advantage if the carbon monoxide can be released from the metal. The overall reaction is then represented by equation 2.2.



The thermodynamics for this reaction are much more favourable (see table 1.1)

Where carbon monoxide is not readily released thermally from the metal; it may be possible to dissociate carbon monoxide photochemically. Cole-Hamilton reported the photochemical decomposition of ethanol according to equation 2.2 catalysed by $[\text{RhH}(\text{CO})(\text{PPr}_3)_2]$ ¹⁹.

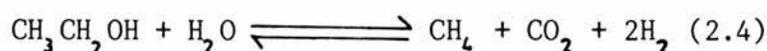
Alternatively, a second complex may be added to improve reaction rates and yields by allowing catalytic decarbonylation of aldehydes⁴⁰. Ethanal would be decarbonylated according to equation 2.3.



Therefore, the overall reaction, from a combination of equations 2.1 and 2.3 becomes as shown in equation 2.2.

Finally, attack of hydroxide ion on co-ordinated carbon monoxide will form a metallocarboxylic acid, which can release carbon dioxide and form a metal hydride. Protonation will allow removal of hydrogen. These reactions are similar to those observed in the synthesis of metal carbonyl hydrides⁴¹ and in the water-gas shift reaction (see chapter one).

In this case, the overall decomposition reaction is represented by equation 2.4.



This reaction is thermodynamically favourable and has the advantage that two molar equivalents of hydrogen are produced per mole of alcohol.

This chapter discusses a number of systems in which these various strategies are investigated for the dehydrogenation of ethanol.

Hydrogenation catalysts were investigated in an attempt to dehydrogenate ethanol according to equation 2.1.

$[\text{RhCl}(\text{PPh}_3)_3]$ ⁴², $[\text{RuH}_2(\text{PPh}_3)_4]$ ⁴³ and $[\text{RuH}_2(\text{N}_2)(\text{PPh}_3)_3]$ ⁴⁴ are all known to be hydrogenation catalysts.

The catalytic activity of these complexes for the dehydrogenation of ethanol under thermal and photochemical conditions, in the presence and absence of base was investigated.

An aldehyde decarbonylation catalyst, $[\text{Rh}(\text{dppp})_2]\text{Cl}$ ⁴⁰ was added in an attempt to facilitate decomposition according to equation 2.2.

Photochemical decomposition of ethanol by $[\text{RhH}(\text{PPr}_3)_3]$ was reinvestigated¹¹. The results are compared to those of other systems.

Decomposition according to equation 2.4 was attempted using $[\text{RhH}(\text{PPr}_3)_3]$ and $[\text{Rh}(\text{bipy})_2]\text{Cl}$ under thermal conditions in the presence of base. These reactions proved to be successful especially for $[\text{Rh}(\text{bipy})_2]\text{Cl}$.

2.2 RESULTS AND DISCUSSION

Three hydrogenation catalysts were investigated in an attempt to dehydrogenate ethanol according to equation 2.1.

The principle of microscopic reversibility ensures that any complex capable of hydrogenation will also be active for dehydrogenation. $[\text{RhCl}(\text{PPh}_3)_3]$ is known to be an efficient hydrogenation catalyst under mild conditions⁴² as is $[\text{RuH}_2(\text{PPh}_3)_4]$ ⁴³. $[\text{RuH}_2(\text{N}_2)(\text{PPh}_3)_3]$ slowly catalysed hydrogenation of alkenes⁴⁴. However, this complex was expected to react similarly to $[\text{RuH}_2(\text{PPh}_3)_4]$, with the only difference being the presence of free triphenylphosphine in solutions of $[\text{RuH}_2(\text{PPh}_3)_4]$ on account of its known dissociation of triphenylphosphine⁴⁵. A comparison of the two reactions shows the effect of free phosphine on the rate of reaction.

The catalytic activity of these complexes in the dehydrogenation of ethanol under thermal conditions was investigated. Typical results are shown in table 2.1.

These results, and all other results reported are reproducible.

The results indicate that catalytic hydrogen production occurs but that a competing process inhibits catalysis after a few catalytic cycles. $[\text{RhCl}(\text{PPh}_3)_3]$ is known to react stoichiometrically with aldehydes to form $[\text{RhCl}(\text{CO})(\text{PPh}_3)_2]$ ⁴⁶. This carbonyl complex is known to be thermally stable due to strong $d - \pi^*$ back bonding between $\text{Rh}(\text{I})$ and CO .

CH_4 is detected in small quantities in this reaction from the decarbonylation of ethanol. The rate of CH_4 production indicates that this reaction is the rate determining step for H_2 production. No CO is detected which is consistent with the formation of $[\text{RhCl}(\text{CO})(\text{PPh}_3)_2]$.

Table 2.1 THERMAL DEHYDROGENATION OF ETHANOL

Catalyst	[catalyst] /10 ⁻⁴ mol dm ⁻³	Temp /°C	Time /h	r ^a	r ^a
				H ₂	CH ₄
$\text{RhCl}(\text{PPh}_3)_3$	4.12	150	2	2.74	0.15
$\text{RhCl}(\text{PPh}_3)_3$	4.12	150	4	1.37	✓
$\text{RuH}_2(\text{PPh}_3)_4$	3.16	150	2	3.76	0.28
$\text{RuH}_2(\text{N}_2)(\text{PPh}_3)_3$	3.70	150	3	5.10	0.32

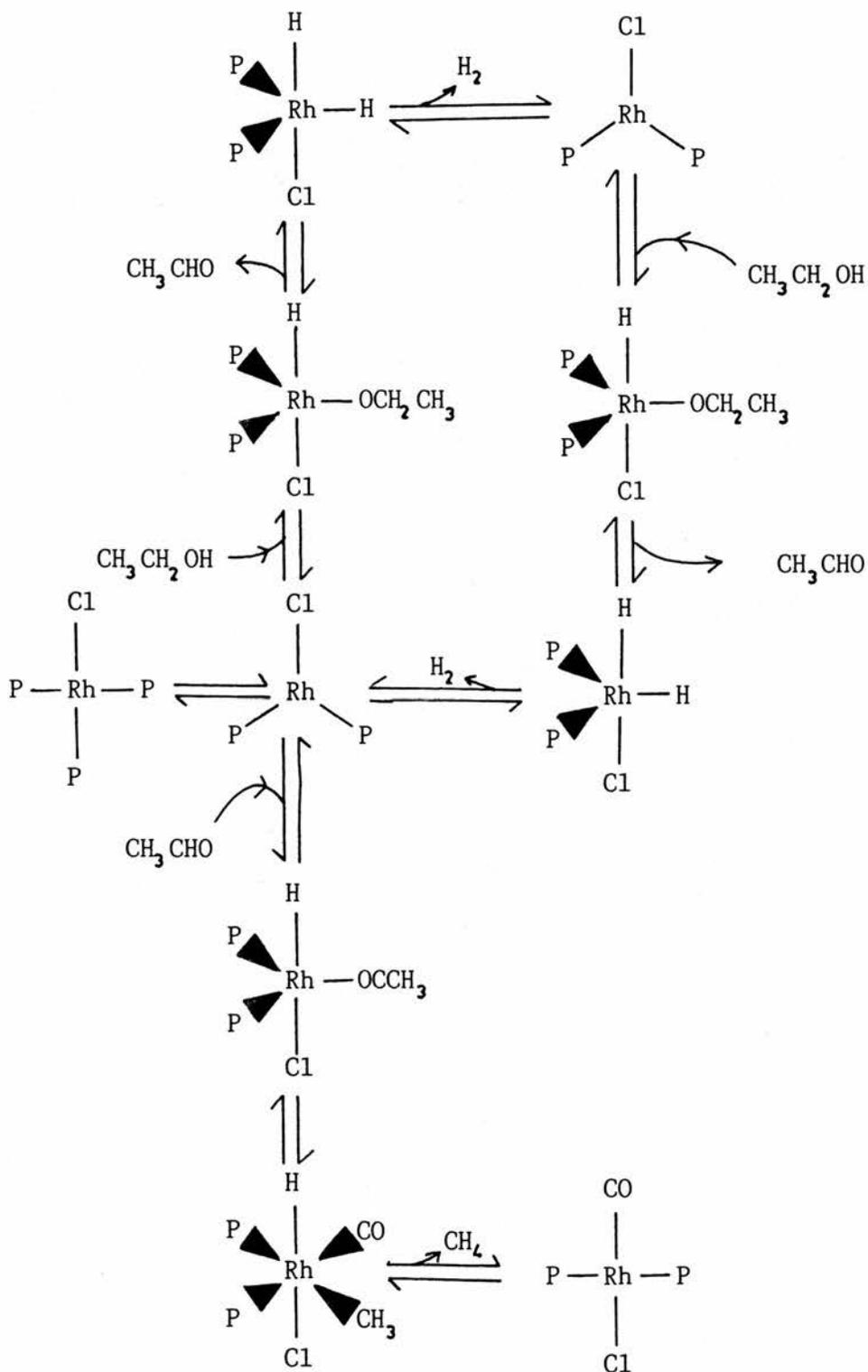
^a rate of H_2 and CH_4 production expressed as turnover number per hour (turnover number = mol of H_2 / CH_4 produced/mol of catalyst used).

Thermal reactions of $[\text{RuH}_2(\text{PPh}_3)_4]$ and $[\text{RuH}_2(\text{N}_2)(\text{PPh}_3)_3]$ also demonstrate deactivation by carbonyl complex formation. The same colourless complex is formed in both reactions and its I.R spectrum indicates that $[\text{RuH}_2(\text{CO})(\text{PPh}_3)_3]$ is the product formed.

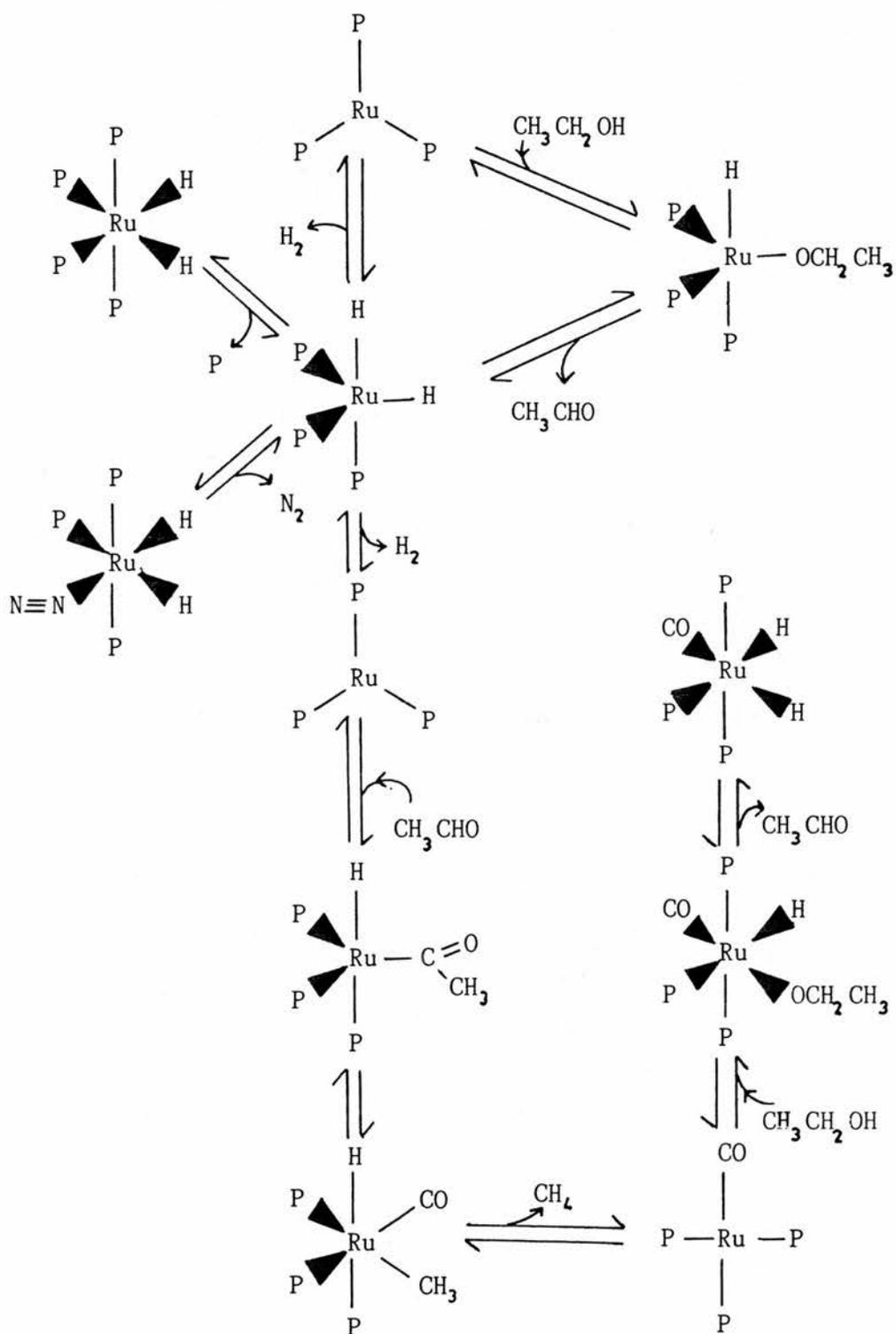
This complex was reacted under identical conditions and the rate of H_2 production was found to be comparable to that observed for $[RuH_2(N_2)(PPh_3)_3]$ with no CO detected. This suggests that the carbonyl complex is not the inactive species in these reactions, but further reaction with ethanol leads to a dicarbonyl complex which is probably inactive. The rate of H_2 production suggests that the decarbonylation reaction is very slow thus enabling catalytic hydrogen production to occur via equation 2.1.

The activity of $[RuH_2(N_2)(PPh_3)_3]$ and $[RuH_2(CO)(PPh_3)_3]$ is higher than that of $[RuH_2(PPh_3)_4]$ which is in agreement with known inhibition of catalytic reactions by the presence of free phosphine in solution⁴⁷.

Reaction mechanisms for these reactions have been proposed and are shown in schemes 2.1, 2.2 and 2.3.

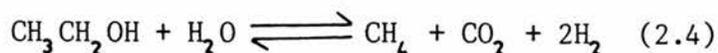


Scheme 2.2 DEHYDROGENATION OF ETHANOL CATALYSED BY



In order to facilitate catalysis by removing co-ordinated CO from the metal centre as CO_2 by nucleophilic attack of OH^- , the reactions were carried out in the presence of base. A similar reaction has been observed for many complexes in catalysis of the water-gas shift reaction (see chapter one).

The decomposition reaction would then be as shown in equation 2.4.



Results for these systems are shown in table 2.2.

Table 2.2 THERMAL DEHYDROGENATION OF ETHANOL IN THE
PRESENCE OF 1 MOLDM⁻³ OF NaOH

Catalyst	[catalyst] /10 ⁻⁴ mol dm ⁻³	Temp/°C	Time/h	Products/r		
				H ₂	CH ₄	CO
RhCl(PPh ₃) ₃	2.82	150	2	7.54	0.17	X
	2.82	150	4	11.94	✓	X
RuH ₂ (PPh ₃) ₄	2.98	150	2	23.79	0.4	X
RuH ₂ (N ₂)(PPh ₃) ₃	2.60	150	2	148.10	✓	X
	2.60	150	17	97.57	0.12	X
RuH ₂ (CO)(PPh ₃) ₃	2.82	150	2	61.99	✓	X

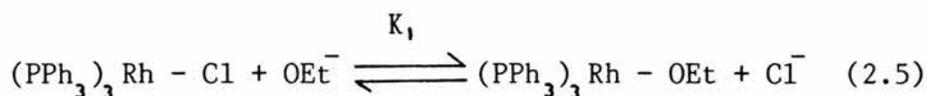
Analysis of the gaseous products by gas chromatography shows that H_2 and CH_4 are produced. The ratio of $H_2:CH_4$ appears to be of the order of 50:1, with $[RhCl(PPh_3)_3]$ and $[RuH_2(PPh_3)_4]$ and $> 800:1$ with $RuH_2(N_2)(PPh_3)_3$, with no CO or CO_2 detected due to carbonyl complex formation.

Therefore, the reaction follows equation 2.1.

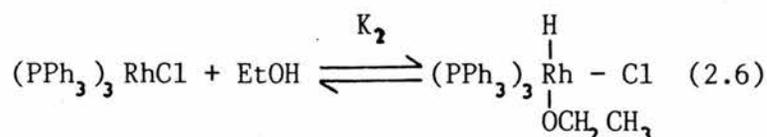
The addition of base has a substantial effect on the rate of hydrogen production with the ruthenium catalysts; especially for $[RuH_2(N_2)(PPh_3)_3]$ where the initial rate is increased 30 fold. This high activity is maintained over many hours with the observed rate retardation due to accumulation of reaction products in a closed system. Rate enhancement for $[RhCl(PPh_3)_3]$ is small but evidence has been obtained for a longer reaction lifetime.

This increase in both the rate and amount of H_2 production can be attributed primarily to base catalysed aldol condensation reactions which remove the product ethanal and hinder formation of metal carbonyl complexes. If decarbonylation does occur, CO is not released as CO_2 via attack of OH^- and the formation of a metal hydride species. i.e. Water-gas shift type chemistry does not occur.

With $[RhCl(PPh_3)_3]$ as catalyst, the effect of base will be two fold: (a) to catalyse aldol condensation reactions.
(b) to form ethoxide ion which will metathesise the Cl to form the ethoxide complex (equation 2.5).



The equilibrium constant for this reaction (K_1) will be much larger than that for direct oxidative addition of ethanol to the metal centre (K_2) shown in equation 2.6.



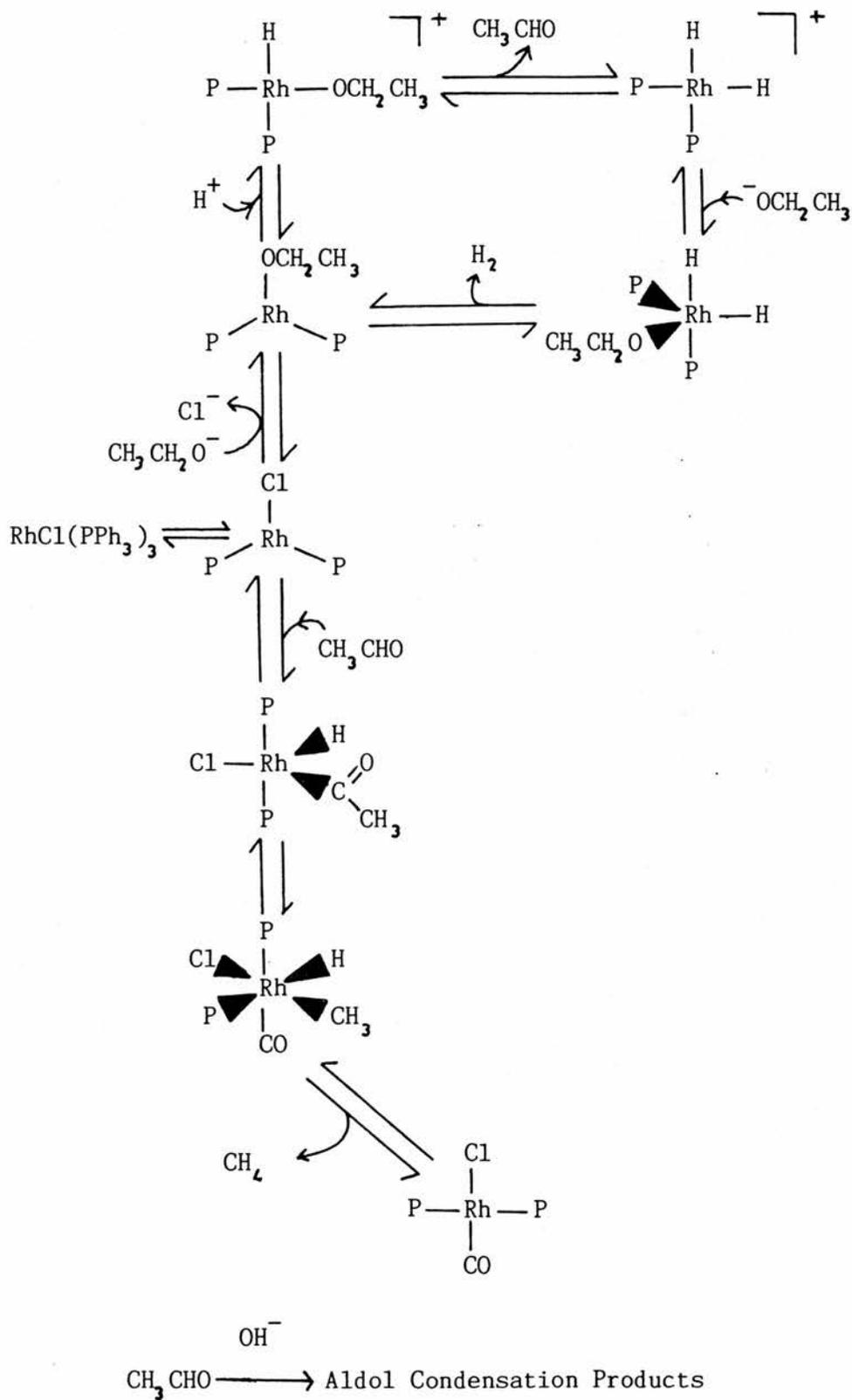
With the ruthenium catalysts, reaction with ethoxide ion will lead to the formation of $[\text{RuH}_3(\text{PPh}_3)_3]^-$. This complex is known to readily accept a proton to form $[\text{RuH}_4(\text{PPh}_3)_3]^{48}$. This tetrahydride contains co-ordinated dihydrogen and therefore loss of H_2 is rapid to reform $[\text{RuH}_2(\text{PPh}_3)_3]$, the active catalyst in these systems.

Decomposition catalysed by $[\text{RuH}_2(\text{CO})(\text{PPh}_3)_3]$ is successful in the presence of base.

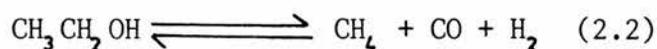
The reaction has a lower rate of hydrogen production due to the formation of the inactive dicarbonyl species by reaction with ethanal. This results in the release of free triphenyl phosphine into solution which inhibits the rate of hydrogen production by competing for vacant sites on the catalytic intermediates.

Proposed reaction mechanisms are shown in schemes 2.4 and 2.5.

Scheme 2.4: THERMAL DEHYDROGENATION OF ETHANOL CATALYSED BY $[\text{RhCl}(\text{PPh}_3)_3]$ IN THE PRESENCE OF NaOH



An alternative approach to the removal of CO from group VIII metal complexes is to employ photolysis⁴⁹. Catalytic reactions were, therefore, performed under illumination from a 500W tungsten-halogen lamp. Such a process should allow catalysis of reaction 2.2.



Photolysis was also performed in the presence of base to discover if visible light enhanced the rate of hydrogen production.

Results of these investigations are shown in table 2.3

Table 2.3 PHOTOCHEMICAL DECOMPOSITION OF ETHANOL

Catalyst	[catalyst] /10 ⁻⁴ moldm ⁻³	Temp /°C	Time /h	[NaOH] /moldm ⁻³	Rate / Products			
					H ₂	CH ₄	CO	CO ₂
RhCl(PPh ₃) ₃	3.04	150	1	0	2.11	0.31	X	X
RuH ₂ (PPh ₃) ₄	3.68	150	2	0	8.49	0.48	✓	X
RuH ₂ (N ₂)(PPh ₃) ₃	3.48	150	2	0	14.54	0.39	✓	X
RhCl(PPh ₃) ₃	4.56	150	2	1	11.40	✓	X	X
RuH ₂ (PPh ₃) ₄	2.10	150	2	1	138.37	0.90	X	X
RuH ₂ (N ₂)(PPh ₃) ₃	3.48	150	3	1	210.22	✓	X	X

Photolysis of ethanol solutions containing [RhCl(PPh₃)₃] produces no CO and has no beneficial effect on the rate of hydrogen production. This is consistent with results from recent flash photolysis studies⁴⁹ which showed that CO is

released from the metal on photolysis of $[\text{RhCl}(\text{CO})(\text{PPh}_3)_2]$ but that the back reaction is very rapid. Indeed it is known that continuous photolysis does not lead to CO evolution⁵⁰.

Photolysis of $[\text{RuH}_2(\text{PPh}_3)_4]$ and $[\text{RuH}_2(\text{N}_2)(\text{PPh}_3)_3]$ does enhance the rate of H_2 production by two and three fold respectively in the absence of base. CO is detected as a gas phase product, along with CH_4 . The decomposition does appear to be in accord with equation 2.2 although the product ratios are no 1:1:1. This is due to efficient dehydrogenation of ethanol coupled with slow decarbonylation of ethanal. When decarbonylation does occur, the CO is released by visible light thus continuing the catalytic cycle. The rate of dehydrogenation also increases on illumination due to photochemical enhanced CO loss which suggests this is the thermal rate determining step.

Photolysis in the presence of base has a dramatic effect on the rate of H_2 production. Catalysis with $[\text{RhCl}(\text{PPh}_3)_3]$ shows a five fold increase in the rate of H_2 production. The rate is similar to that obtained when base is present under thermal conditions as might be expected.

$[\text{RuH}_2(\text{PPh}_3)_4]$ also shows a five fold increase in the rate of H_2 production. This is due to photochemical evolution of CO which reacts with the base in solution to produce formate thereby preventing catalyst poisoning.

$[\text{RuH}_2(\text{N}_2)(\text{PPh}_3)_3]$ shows higher activity to that in the absence of light. The quantity of CO is greater than that produced under thermal conditions indicating that photolysis increases the rate of decarbonylation by promoting CO dissociation. This enables more hydrogen production as seen by the slightly higher rate of reaction. The high observed rates of H_2 production are due to very facile loss of H_2 from a molecular H_2 complex.

A third strategy to counter the catalyst poisoning by decarbonylation is to introduce a second catalyst that can efficiently decarbonylate aldehydes. $[\text{Rh}(\text{dppp})_2]\text{Cl}$ is known efficiently to decarbonylate aldehydes thermally⁴⁰. It was suggested that the positive charge on the metal centre results in less back electron transfer to CO through $\text{d} - \pi^*$ donation, therefore, producing a weaker metal to CO bond. Also, rechelation of a monodentate dppp will provide an entropic driving force for the expulsion of CO if the suggested mechanism of reaction is correct⁴⁰.

In this case, the overall decomposition reaction will be as in equation 2.2.

$[\text{Rh}(\text{dppp})_2]\text{Cl}$ was added to ethanol solutions containing $[\text{RhCl}(\text{PPh}_3)_3]$, $[\text{RuH}_2(\text{PPh}_3)_4]$ and $[\text{RuH}_2(\text{N}_2)(\text{PPh}_3)_3]$ in an attempt to catalyse reaction 2.2 thermally either in the presence or absence of base. The results of these experiments are shown in table 2.4.

In the absence of base, catalysis according to equation 2.2 does occur, but once again the dehydrogenation step is more efficient than the decarbonylation step, mainly because of the small concentration of ethanal produced in the reaction.

Table 2.4 THERMAL DEHYDROGENATION OF ETHANOL BY MIXED CATALYST SOLUTIONS

Catalyst	[catalyst] /10 ⁻⁴ moldm ⁻³	Temp /°C	Time /h	[NaOH] /moldm ⁻³	Rate Products		
					H ₂	CH ₄	CO
RhCl(PPh ₃) ₃	2.82	150	2	0	1.06	✓	✓
Rh(dppp) ₂ ⁺	3.32						
RuH ₂ (PPh ₃) ₄	3.50	150	2	0	4.25	0.34	✓
Rh(dppp) ₂ ⁺	3.76						
RuH ₂ (N ₂)(PPh ₃) ₃	3.04	150	2	0	8.32	0.59	✓
Rh(dppp) ₂ ⁺	3.32						
RhCl(PPh ₃) ₃	3.26	150	2	1	21.37	0.22	X
Rh(dppp) ₂ ⁺	2.70						
RuH ₂ (PPh ₃) ₄	3.68	150	2	1	53.26	✓	X
Rh(dppp) ₂ ⁺	4.38						
RuH ₂ (N ₂)(PPh ₃) ₃	3.04	150	2	1	82.37	0.35	X
Rh(dppp) ₂ ⁺	3.12						
RhCl(PPh ₃) ₃	6.30	150	24	1	17.75	✓	X
Rh(dppp) ₂ ⁺	6.04						

The combination of [RhCl(PPh₃)₃] and [Rh(dppp)₂]Cl results in the evolution of CO, which is a direct consequence of the decarbonylation of ethanal by [Rh(dppp)₂]Cl. The rate

of hydrogen production is low but activity is maintained for many hours.

Both ruthenium catalysts show increased activity although the rate enhancement of H₂ production is small. CO is detected in the gas phase from decarbonylation of ethanal by [Rh(dppp)₂]Cl thus enabling the ruthenium catalysts to continue dehydrogenation of ethanol.

The addition of base has a marked effect on the rate of H₂ production with all the catalysts. In the system with [RhCl(PPh₃)₃] the rate of hydrogen production is double that seen for the reaction without [Rh(dppp)₂]Cl and is maintained for many hours. This increase in activity must be due to competitive decarbonylation of ethanal by [Rh(dppp)₂]Cl, which leaves [RhCl(PPh₃)₃] able to dehydrogenate ethanol more efficiently.

This is also the case with [RuH₂(PPh₃)₄] where addition of [Rh(dppp)₂]Cl causes a doubling of the rate of hydrogen production. However, this system is not as efficient as photolysis of basic ethanol solutions containing [RuH₂(PPh₃)₄] with visible light. This system is highly active with 140 turnovers hour⁻¹ observed for H₂ production. Experiments showed that CO could be removed from the metal centre by photolysis and the presence of base prevents the back reaction with CO.

Addition of [Rh(dppp)₂]Cl to basic ethanol solutions

containing $[\text{RuH}_2(\text{N}_2)(\text{PPh}_3)_3]$ resulted in a ten fold increase in the rate of H_2 production compared to the same system in the absence of base. However, $[\text{RuH}_2(\text{N}_2)(\text{PPh}_3)_3]$ was a more active dehydrogenation catalyst in thermal and photochemical reactions in the presence of base. The activity of the two reactions is similar which is in complete contrast to reactions catalysed by $[\text{RuH}_2(\text{PPh}_3)_4]$. The photochemical reaction is much more efficient than the thermal reaction, possibly due to photochemical dissociation of CO from the metal centre.

The higher activity of $[\text{RuH}_2(\text{N}_2)(\text{PPh}_3)_3]$ compared to $[\text{RuH}_2(\text{PPh}_3)_4]$ can be explained in terms of the presence of free triphenyl phosphine. $[\text{RuH}_2(\text{PPh}_3)_4]$ is known to release free triphenyl phosphine into solution to form the catalytically active $[\text{RuH}_2(\text{PPh}_3)_3]$. $[\text{RuH}_2(\text{N}_2)(\text{PPh}_3)_3]$ released N_2 to form the same intermediate. The free phosphine in solutions will then compete for vacant sites on any co-ordinatively unsaturated catalytic intermediates, thus slowing such reactions as co-ordination of ethoxide and β - H abstraction. In addition it may slow down the rate of methyl migration in the proposed acyl intermediate and hence reduce the tendency for CO abstraction (i.e. catalyst poisoning).

In conclusion, the crucial role of base, light and $[\text{Rh}(\text{dppp})_2]\text{Cl}$ in the success of these reactions must be stressed. This is clearly seen if the rhodium and ruthenium systems are examined separately.

If $[\text{RhCl}(\text{PPh}_3)_3]$ is to catalyse ethanol decomposition with reasonable activity, then a number of conditions must be met. Base is needed to form ethoxide ion which metathesises the chloride to form co-ordinated ethoxide, and to catalyse aldol condensation reactions which remove the product ethanal from decarbonylation reactions thus inhibiting catalyst poisoning by carbonyl complex formation. $[\text{Rh}(\text{dppp})_2]\text{Cl}$ efficiently decarbonylates aldehydes thus inhibiting formation of $[\text{RhCl}(\text{CO})(\text{PPh}_3)_3]$. Base will react with free CO to form formate ion thereby preventing any further reaction with $[\text{RhCl}(\text{PPh}_3)_3]$.

With $[\text{RuH}_2(\text{PPh}_3)_4]$ and $[\text{RuH}_2(\text{N}_2)(\text{PPh}_3)_3]$ the important features of reaction are similar. The role of base is identical although now there is no chloride for metathesis with ethoxide. Instead attack of ethoxide followed by β -H abstraction forms $[\text{RuH}_3(\text{PPh}_3)_3]^-$ which readily picks up a proton to form $[\text{RuH}_4(\text{PPh}_3)_3]$. This complex contains co-ordinated dihydrogen which is readily released. This simple cycle enables rapid hydrogen production to take place from a molecular hydrogen complex.

Photochemical reactions are also successful because co-ordinated CO can be removed from the metal centre by irradiation with visible light.

The most important features which enable rapid H_2 production are base catalysed aldol condensation reactions which keep the metal free of CO, the formation of ethoxide ion which

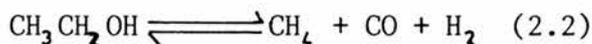
facilitates rapid substrate activation and the formation of molecular hydrogen complexes.

These reactions with $[\text{RuH}_2(\text{PPh}_3)_4]$ and $[\text{RuH}_2(\text{N}_2)(\text{PPh}_3)_3]$ show that hydrogen is lost from a molecular hydrogen complex. Therefore the assembly of the H - H bond occurs within the co-ordination sphere of the metal and the product of protonation contains H_2 already way down the reaction pathway to molecular H_2 . This is a very important feature of these catalytic systems.

INTRODUCTION

We have demonstrated that co-ordinated CO can be removed from a metal centre by photolysis with visible light. Co-ordinated CO could be removed from the metal centre by reaction with OH⁻ to form CO₂ and a metal hydride in analogous reactions to those observed in catalysis of the water-gas shift reaction.

Cole-Hamilton and co-workers showed that [RhH(CO)(PPrⁱ₃)₂] could decompose ethanol photochemically according to equation 2.2¹¹.



The products were produced in the expected ratios and the reaction proceeded smoothly under irradiation with visible light at low temperatures although the rate of H₂ production was low. The key step in the reaction was photochemical removal of CO¹¹.

We have shown that the rates and yields of H₂ production from ethanol are increased in thermal reactions by the addition of base. We show here that addition of base to [RhH(PPrⁱ₃)₃] a precursor of [RhH(CO)(PPrⁱ₃)₂] not only increases the rate and yield of H₂ production but also changes the chemistry of the process. Studies with another water-gas shift catalyst, [Rh(bipy)₂]Cl are described.

2.4 RESULTS AND DISCUSSION

Thermal reactions with $[\text{RhH}(\text{PPr}_3^i)_3]$ should be unsuccessful as the key step in the photochemical decomposition is photochemical dissociation of CO.

Thermal reactions with $[\text{RhH}(\text{PPr}_3^i)_3]$ were performed in the presence and absence of base to confirm the photochemical results and to investigate the possibility of CO_2 production by water-gas shift type chemistry. Typical results are shown in table 2.5.

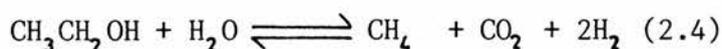
Table 2.5 THERMAL DEHYDROGENATION OF ETHANOL
CATALYSED BY $[\text{RhH}(\text{PPr}_3^i)_3]$

[catalyst] / 10^{-4} moldm $^{-3}$	Temp /°C	Time /h	[NaOH] /moldm $^{-3}$	Rate H $_2$	Products		
					CH $_4$	CO	CO $_2$
5.80	150	2	0	0.91	✓	X	X
5.16	150	2	1	5.60	0.55	X	✓

In the absence of base H $_2$ and CH $_4$ are detected as products but no CO is detected. This is consistent with previous results described by Cole-Hamilton when using $[\text{RhH}(\text{CO})(\text{PPr}_3^i)_2]$ as catalystⁿ. Indeed in this reaction, the carbonyl species is the inactive species.

When base is added to the system not only is the rate of H $_2$ production increased but the chemistry of the process changes.

H₂, CH₄ and CO₂ are the products of reaction and the decomposition reaction shown by equation 2.4.



The product ratios obtained are not as expected which is due to ethanal being removed from the system in base catalysed aldol condensation reactions, thus reducing the rate formation of [RhH(CO)(PPr₃)₂].

When the carbonyl complex is formed attack of OH⁻ to form the metalcarboxylic acid occurs and CO₂ is released very slowly. This helps to prevent catalyst deactivation.

Since the complex is known to be photochemically active the reaction was investigated under illumination with visible light in the presence and absence of base. These results are shown in table 2.6.

Table 2.6 PHOTOCHEMICAL DECOMPOSITION OF ETHANOL
CATALYSED BY [RhH(PPr₃)₂]

[catalyst] /10 ⁻⁴ moldm ⁻³	Temp /°C	Time /h	[NaOH] /moldm ⁻³	Rate H ₂	Products		
					CH ₄	CO	CO ₂
3.10	150	2	0	6.24	0.48	✓	X
4.14	150	2	1	23.11	1.85	X	✓

The photochemical reaction proceeds as expected in the absence of base with H_2 , CH_4 and CO detected as gaseous products.

In the presence of base the rate and yield of H_2 and CH_4 is increased four fold. CO_2 is detected after acidification with HCl .

In the absence of base the ratio of $H_2:CH_4$ is not 1:1 as expected from equation 2.2. This must be due to release of ethanal from the metal centre during the catalytic cycle and preferential reaction with the more abundant ethanol.

With base, the ratios of $H_2:CH_4:CO_2$ will not be 2:1:1 due to base catalysed aldol condensation reactions removing ethanal from reaction with the catalyst. When decarbonylation does occur CH_4 is produced in the same ratio as in reaction in the absence of base.

We suggest that the rate of H_2 production in the reaction without base is higher than it should be due to dissolved sodium hydroxide on the surface of the glass reaction vessel causing aldol condensation reactions to occur and ethoxide formation which reacts more readily than ethanol.

Addition of $[Rh(dppp)_2]Cl$ and base results in an efficient thermal reaction with $[RhH(PPR_3^i)_3]$ as shown in table 2.7.

Table 2.7 THERMAL DEHYDROGENATION OF ETHANOL CATALYSED
BY [RhH(PPrⁱ₃)₃] AND [Rh(dppp)₂]Cl

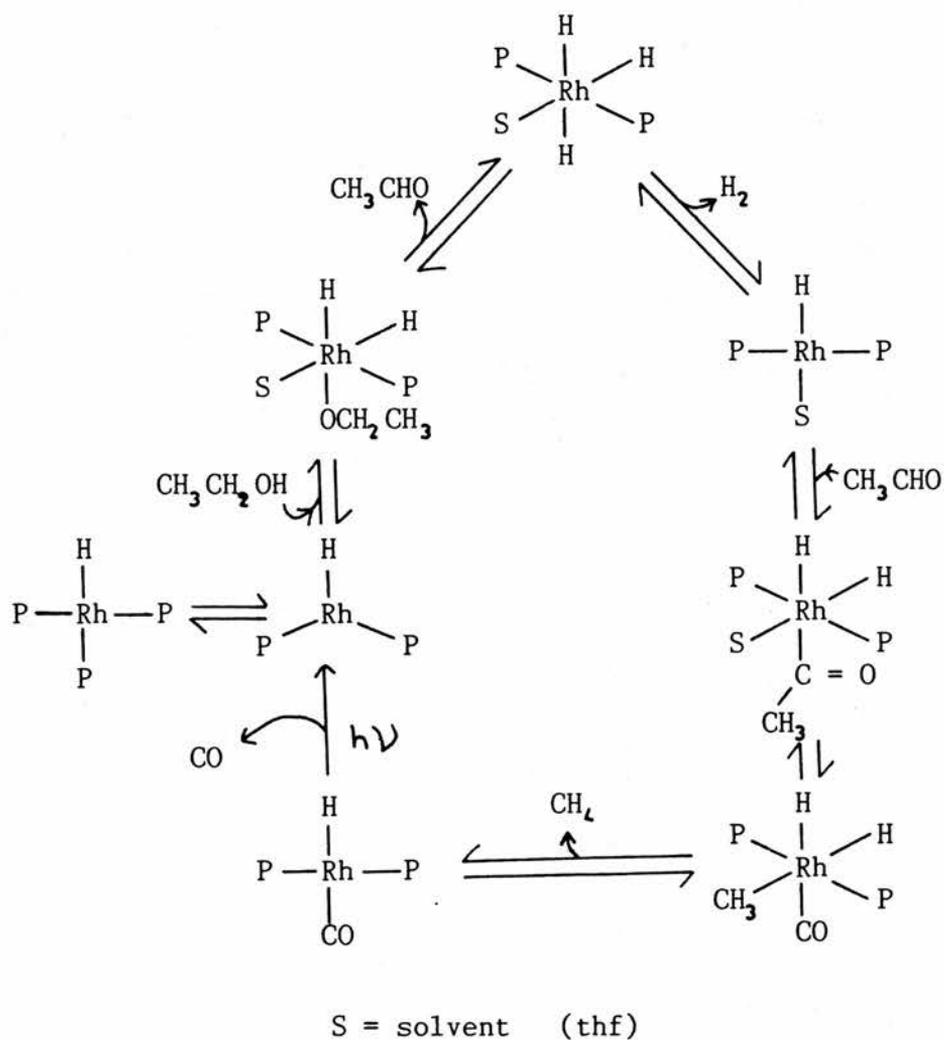
Catalyst	[catalyst] /10 ⁴ mol dm ³	Temp /°C	Time /h	[NaOH] / mol dm ³	Rate H ₂	Products		
						CH ₄	CO	CO ₂
RhH(PPr ⁱ ₃) ₃	4.48	150	2	1	17.14	/	X	/
Rh(dppp) ₂ ⁺	2.70							

These results show that in the absence of base, light is needed to drive the reaction with the key step being photochemical dissociation of CO. In the absence of light catalysis stops and no CO is observed. The proposed reaction mechanism is shown in scheme 2.7. The decomposition is in accordance with equation 2.2.

When base is present the decomposition reaction changes and is represented by equation 2.4. The rate of reaction is comparable to the photochemical reaction. The efficiency of the reaction is greatly increased by the combined effect of base and light. Now there are two methods of removing co-ordinated CO. Water-gas shift type chemistry occurs to produce CO₂ and photochemical dissociation of CO will also occur. CO is not detected because of the reaction with base to produce formate.

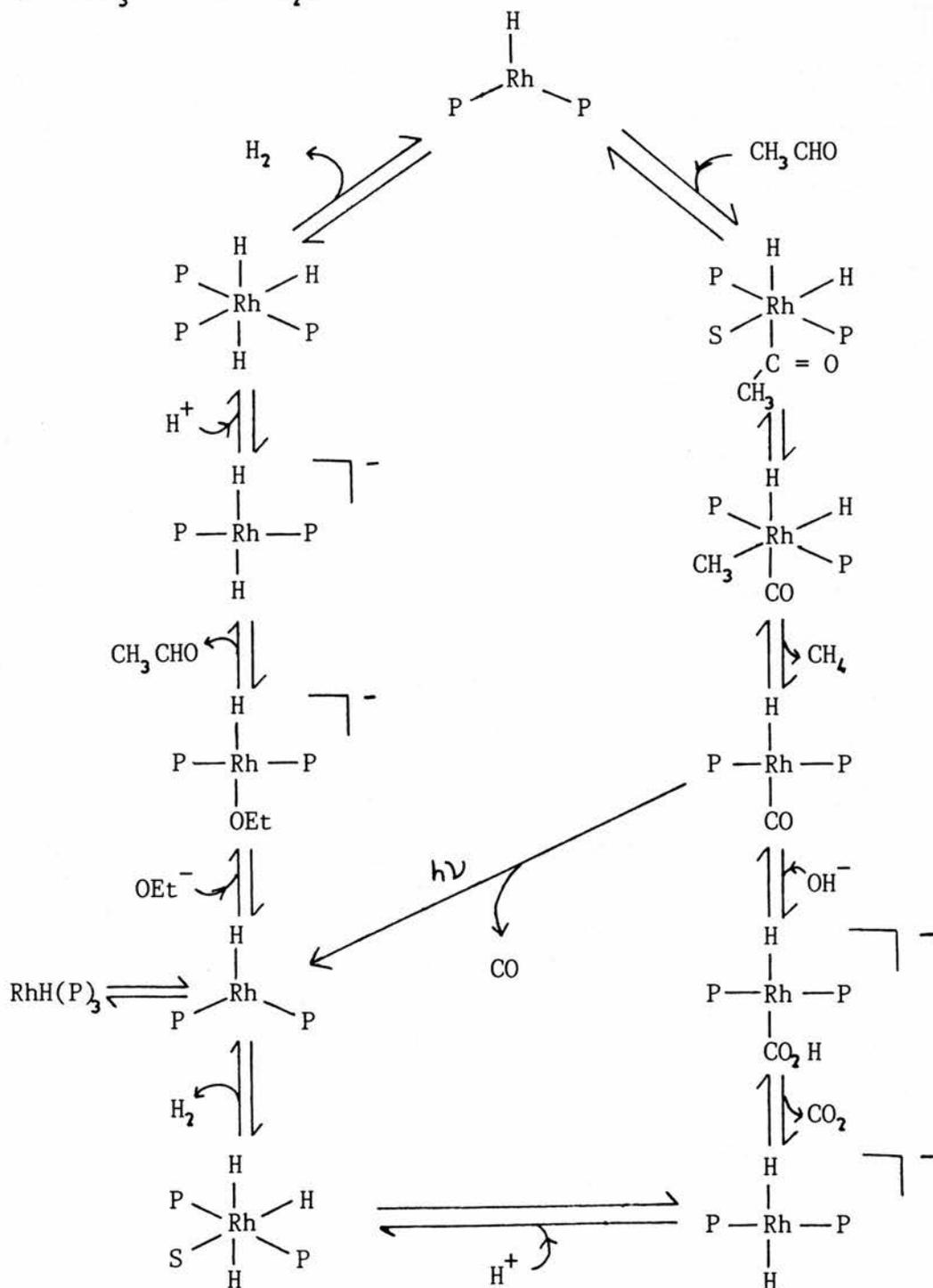
The proposed reaction scheme is shown in scheme 2.8

Scheme 2.7 PHOTOCHEMICAL DECOMPOSITION OF ETHANOL
CATALYSED BY $[\text{RhH}(\text{PPr}_3)_3]$



Scheme 2.8 PHOTOCHEMICAL DEHYDROGENATION OF ETHANOL
CATALYSED BY $[\text{RhH}(\text{PPr}_3)_3]$ IN THE PRESENCE
OF BASE

$\text{P} = \text{PPr}_3$ $\text{S} = \text{H}_2\text{O}$



[RhH(PPr₃)₃] was successful in the catalysis of reaction 2.4 but was more efficient in photochemical reactions. We investigated another water-gas shift catalyst, [Rh(bipy)₂]Cl, which is also known to be active for hydrogenation⁵¹. We found that [Rh(bipy)₂]Cl is a highly efficient dehydrogenation catalyst for ethanol at milder temperatures than for the other catalysts examined.

Typical results are shown in table 2.8.

Table 2.8 THERMAL DEHYDROGENATION OF ETHANOL

CATALYSED BY [Rh(bipy)₂]Cl

[catalyst] /10 ⁻⁴ moldm ⁻³	Temp /°C	Time /h	[NaOH] /moldm ⁻³	Rate H ₂	Products		
					CH ₄	CO ₂	CO
3.04	120	1	0	1.23	✓	X	X
4.78	120	2	1	120.30	✓	✓	X
9.56	120	3	1	99.85	11.82	10.71	X
4.78	120	24	1	64.42	✓	✓	X
4.78	120	2	1	90.82	✓	✓	✓
+ [Rh(dppp) ₂]Cl		24	1	59.64	✓	✓	✓

Analysis of these results shows very high rates of hydrogen production can be achieved in the presence of base over long reaction times. The reaction products are H₂, CH₄ and CO₂ indicating decomposition according to equation 2.4. The amounts of CH₄ and CO₂ detected suggest that they are formed in the same stoichiometry but at a rate only 10% of that for H₂ production. 90% of the reaction follows

equation 2.1 and is a straight forward dehydrogenation reaction to produce ethanal. This reaction is extremely rapid with $[\text{Rh}(\text{bipy})_2]\text{Cl}$ as catalyst. The formation of ethanal was confirmed by the addition of $[\text{Rh}(\text{dppp})_2]\text{Cl}$ and the detection of CO in the gas phase. Analysis of the liquid phase products showed ethanal and its higher condensation products. Analysis of a solution containing catalytic quantities of ethanal in basic ethanol showed the same products as those seen in the reaction solutions confirming that ethanal is indeed a reaction product.

Detailed studies have been performed on the kinetics of hydrogen production in this interesting reaction. The reaction is 1st order with respect to concentration of $[\text{Rh}(\text{bipy})_2]\text{Cl}$ and $[\text{ethanol}]$ as shown in figures 2.1 and 2.2. The effect of base is less clear, with saturation kinetics observed and little or no rate enhancement occurs above ca 0.25 mol dm^{-3} of NaOH. (See figure 2.3).

The Arrhenius plot (figure 2.4) gives an activation energy of $62.51 \text{ kJ mol}^{-1}$.

The production of the various products can be rationalised in terms of the processes in scheme 2.9.

Fig 2.1 Effect of $[\text{Rh}(\text{bipy})_2\text{Cl}] (10^{-4} \text{ moldm}^{-3})$ on the rate of hydrogen production (cm^3 per hour) from ethanol.

($T = 393\text{k}$, $[\text{NaOH}] = 1 \text{ moldm}^{-3}$, 1 atm N_2 , $[\text{ethanol}] = 8.6 \text{ moldm}^{-3}$)

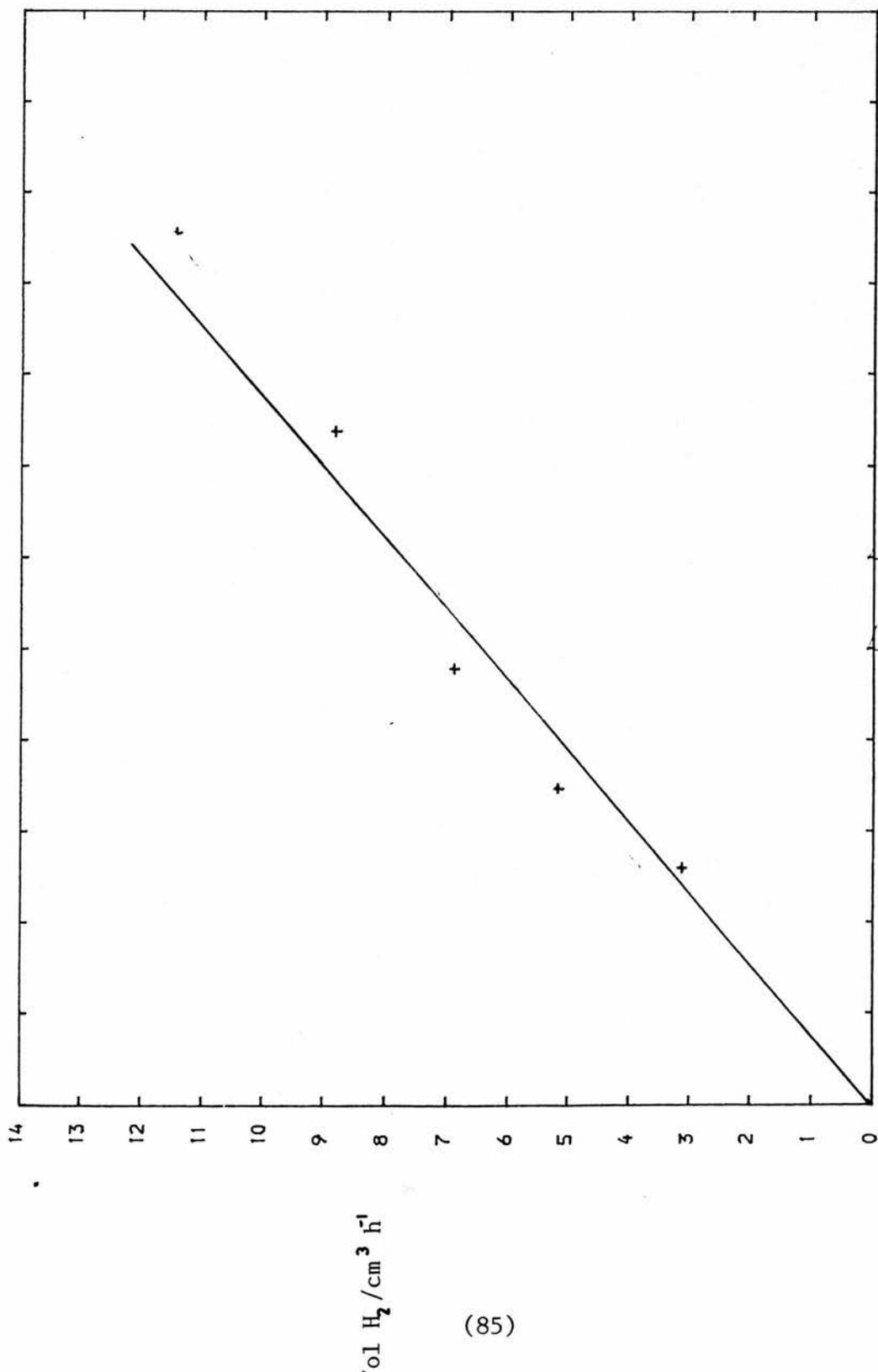


Fig 2.2 Effect of [ethanol] (mol dm^{-3}) on the rate of hydrogen production (turnover no h^{-1}) from ethanol.
 ($T = 393\text{k}$, $[\text{NaOH}] = 1 \text{ mol dm}^{-3}$, $[\text{Rh}(\text{bipy})_2]\text{Cl} = 4.78 \times 10^{-4} \text{ mol dm}^{-3}$ 1 atm N_2)

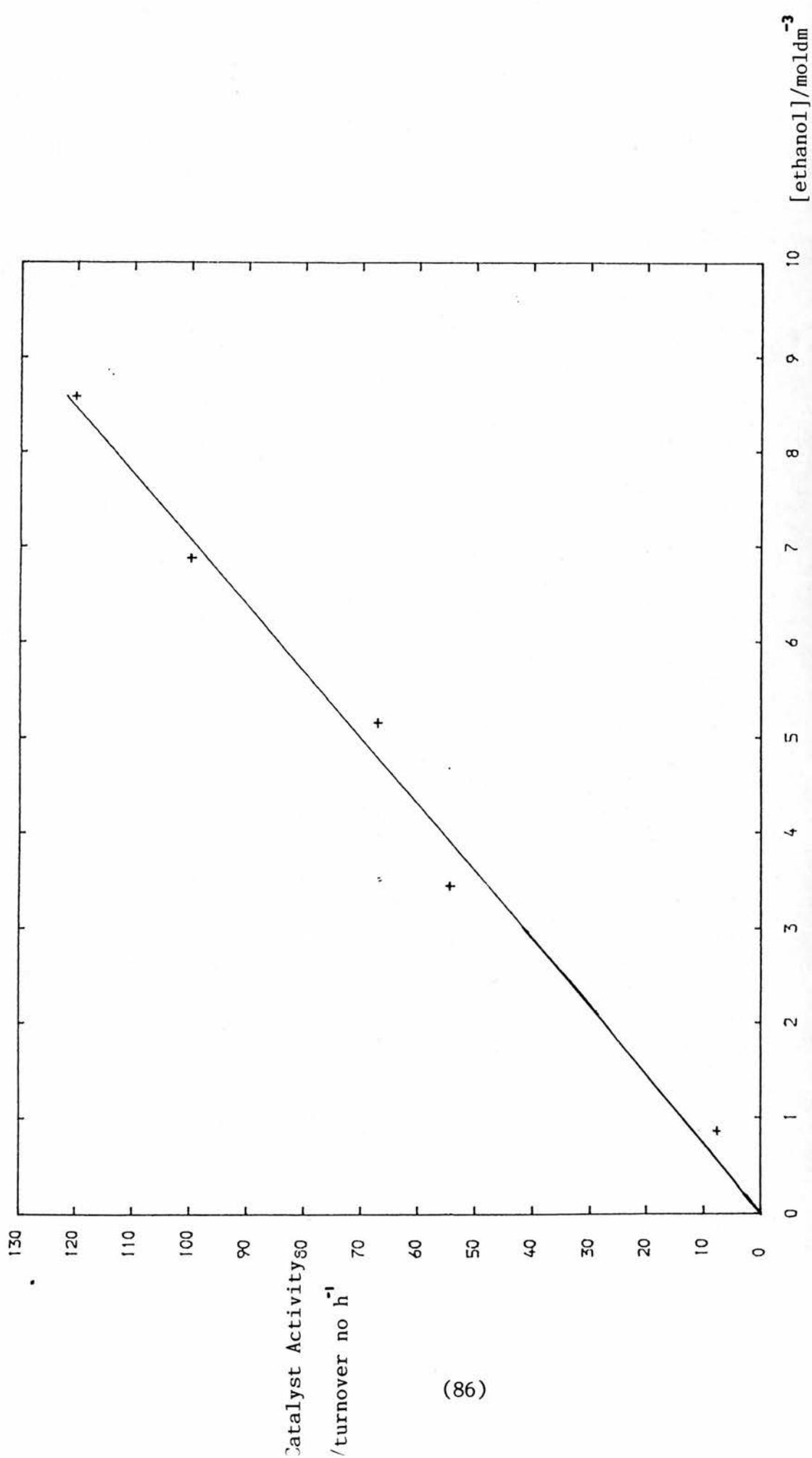


Fig 2.3 Effect of $[\text{NaOH}]$ (mol dm^{-3}) on the rate of hydrogen production (turnover no h^{-1}) from ethanol.

($T = 393\text{k}$, $[\text{ethanol}] = 8.6 \text{ mol dm}^{-3}$, 1 atm N_2)

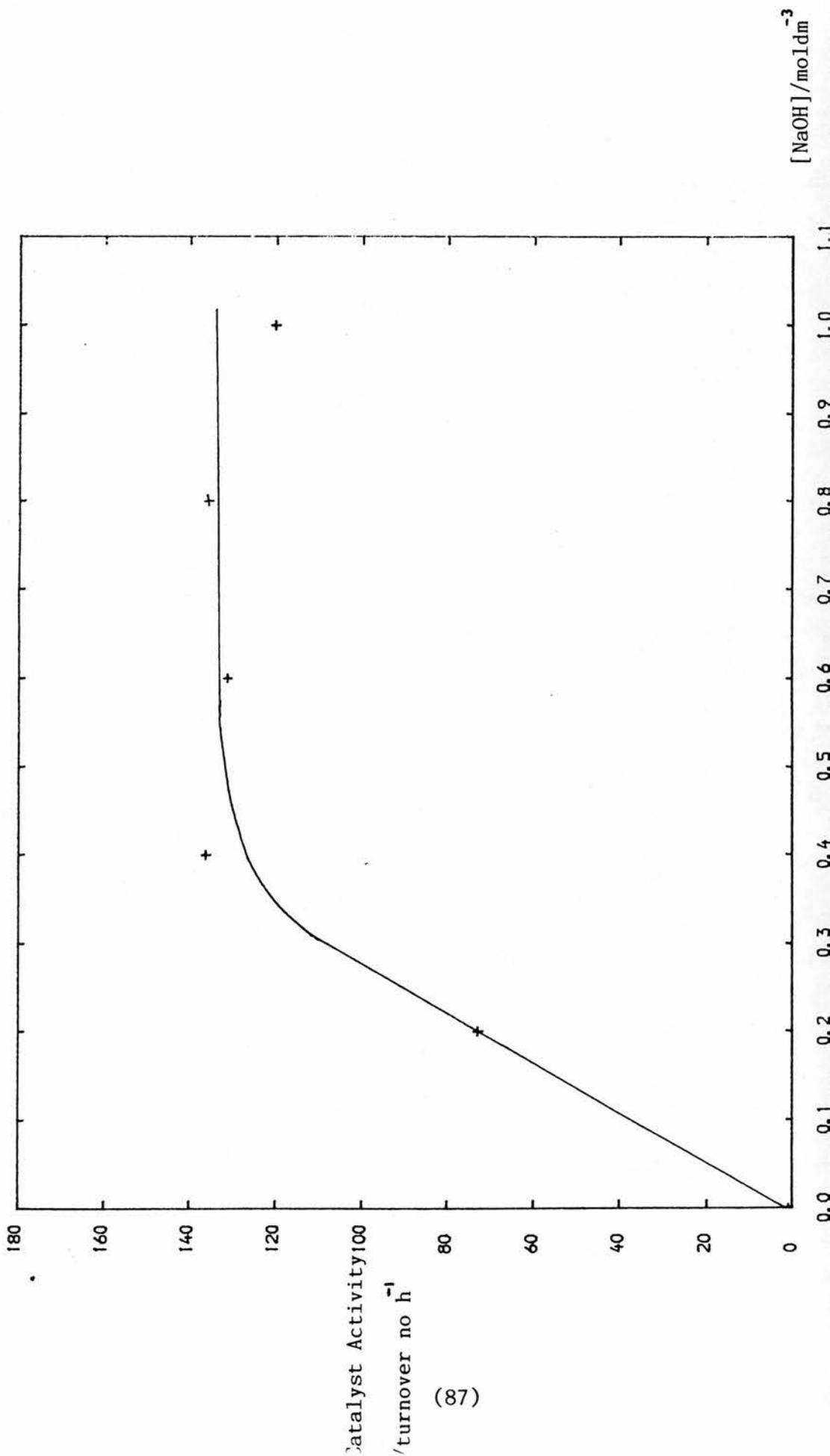
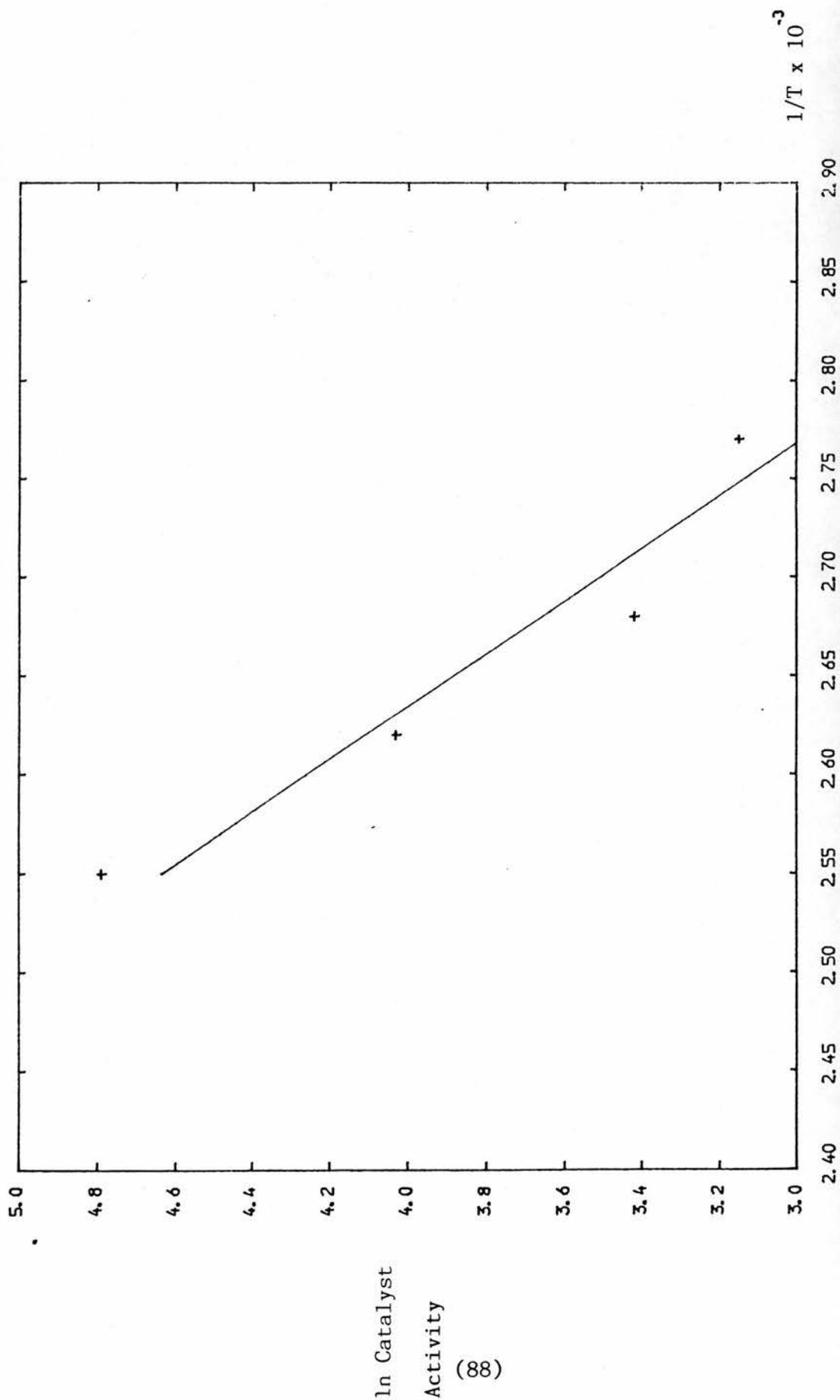


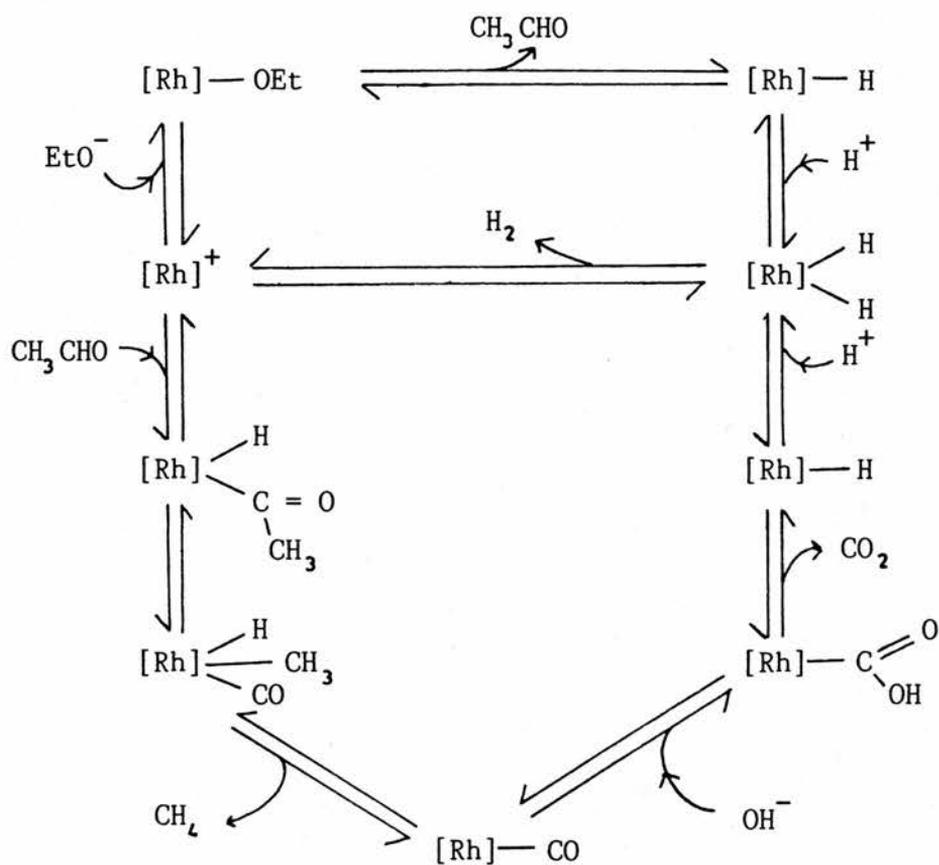
Fig 2.4 Arrhenius plot for hydrogen production (turnover no \bar{h}^{-1}) from ethanol.

($[\text{NaOH}] = 1 \text{ mol dm}^{-3}$, $[\text{Rh}(\text{bipy})_2\text{Cl}] = 4.78 \times 10^{-4} \text{ mol dm}^{-3}$, $[\text{ethanol}] = 8.6 \text{ mol dm}^{-3}$)



Scheme 2.9 THERMAL DEHYDROGENATION OF ETHANOL

CATALYSED BY $[\text{Rh}(\text{bipy})_2]\text{Cl}$



$[\text{Rh}] = \text{Rh}(\text{bipy})_2$

$\text{CH}_3\text{CHO} \xrightarrow{\text{OH}^-}$ aldol condensation reactions.

The reaction proceeds via an initial dehydrogenation of ethanol. The ethanal so produced can then undergo base-catalysed aldol condensation, decarbonylation catalysed by $[\text{Rh}(\text{dppp})_2]\text{Cl}$, or decarbonylation by $[\text{Rh}(\text{bipy})_2]\text{Cl}$. In the last case, CO is not released from the metal thermally but, instead, nucleophilic attack of OH^- on co-ordinated CO is followed by loss of CO_2 , protonation and loss of H_2 .

The similarity of the last series of reactions to those of the water-gas shift reaction make a comparison of the results obtained in this work with those obtained for the water-gas shift reaction, catalysed by $[\text{Rh}(\text{bipy})_2]\text{Cl}$ pertinent. Detailed studies of the water-gas shift reaction suggest that H_2 and CO_2 should not be formed under the highly alkaline conditions employed in this work.³⁴

The failure to observe water-gas shift chemistry under alkaline conditions was attributed to the low rate of attack of OH^- on $[\text{Rh}(\text{CO})(\text{bipy})_2]^+$ compared with $[\text{RhH}(\text{CO})(\text{bipy})_2]^+$, which is only present at significantly acid pH, and to the formation of a catalytically inactive species, possibly $[\{\text{Rh}(\text{CO})(\text{bipy})_2\}_2(\text{CO})]^+$ in alkaline solution under CO ³⁴.

In these ethanol decomposition reactions the formation of the inactive species will not occur since there is insufficient CO present, and the rate of attack of hydroxide ion on $[\text{Rh}(\text{CO})(\text{bipy})_2]^+$ will be higher because of the high concentration of hydroxide ion in solution. Evidently,

the high basicity of $[\text{RhH}(\text{bipy})_2]$ ensures that it is significantly protonated even under the basic conditions employed in the reaction.

Attempts have been made to identify the rhodium species in solution. Solutions of $[\text{Rh}(\text{bipy})_2]\text{Cl}$ in basic ethanol are purple due to an intense visible absorption band at 500–530 nm. On heating these solutions become quickly pale grey and remain so during the reaction. Detailed studies on the nature of $[\text{Rh}(\text{bipy})_2]\text{Cl}$ in aqueous solutions have shown that $[\text{Rh}(\text{bipy})_2]\text{Cl}$ forms dihydrides on reaction with H_2 in ethanolic and aqueous solutions both rapidly and reversibly⁵².

In contrast, in basic ethanol with catalytic quantities of $[\text{Rh}(\text{bipy})_2]\text{Cl}$ a very pale grey solution is formed irreversibly.

The uv spectrum of this solution (210, 245 and 290 nm) is very similar to that of the solutions recovered after catalytic runs. (Figures 2.5, 2.6).

It has been reported that the colourless product obtained from $[\text{Rh}(\text{bipy})_2]\text{Cl}$ and H_2 in ethanol is $[\text{RhH}_2(\text{bipy})_2]^+$, although little is known about its pka. In basic ethanol $[\text{RhH}(\text{bipy})_2]$ is the product from deprotonation of $[\text{RhH}_2(\text{bipy})_2]^+$ and this is the major species in solution during ethanol dehydrogenation reactions catalysed by $[\text{Rh}(\text{bipy})_2]\text{Cl}$. It follows that protonation to give the dihydride is the rate-determining step of the catalytic cycle.

Fig 2.5 uv/vis spectrum of solution from the decomposition of ethanol catalysed by $[\text{Rh}(\text{bipy})_2]\text{Cl}$ in the presence of $1 \text{ mol dm}^{-3} \text{ NaOH}$

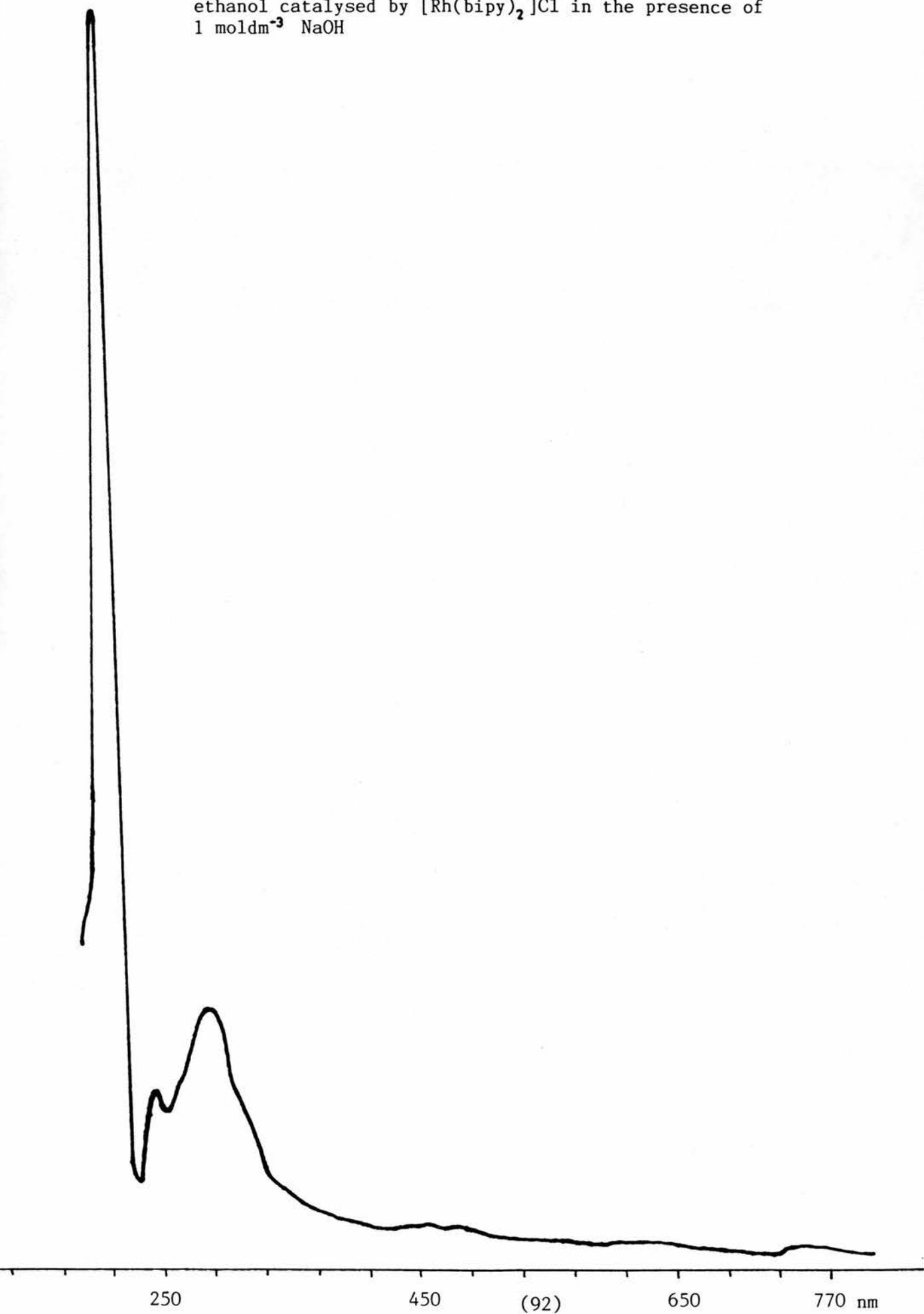
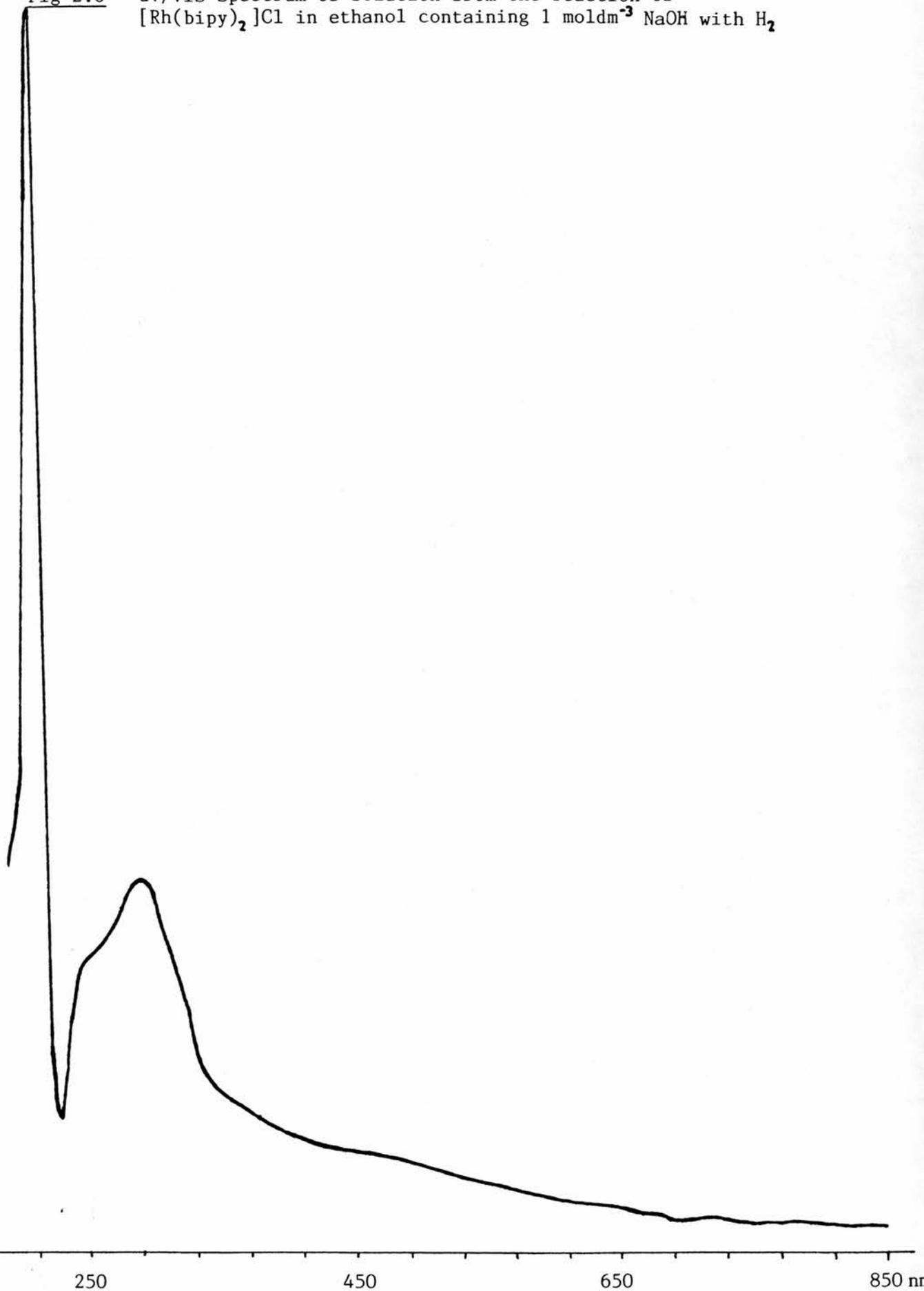


Fig 2.6 uv/vis spectrum of solution from the reaction of $[\text{Rh}(\text{bipy})_2]\text{Cl}$ in ethanol containing 1 mol dm^{-3} NaOH with H_2



In conclusion, the reasons for the success of $[\text{Rh}(\text{bipy})_2]\text{Cl}$ as a catalyst for the dehydrogenation of ethanol should be noted. $[\text{Rh}(\text{bipy})_2]\text{Cl}$ is a highly efficient alkanal hydrogenation catalyst, but we have demonstrated that this is not the only requirement for the complex to rapidly dehydrogenate alcohols.

It is important that alkanal decarbonylation is slow and/or that there is a rapid process for the removal of CO from the metal centre to prevent catalyst poisoning.

Here, it appears that CO abstraction is slow probably because the crucial intermediate in decarbonylation, $[\text{RhH}(\text{CO})(\text{CH}_3)(\text{bipy})_2]^+$ must be either 7 co-ordinate or contain a monodentate bipy ligand, both of which are high energy intermediates. Also alkanal will be removed from the system by base catalysed aldol condensation reactions.

Finally, it appears that attack of OH^- on $[\text{Rh}(\text{CO})(\text{bipy})_2]^+$ once it is formed is rapid at high pH because of the positive charge on the complex.

Together these properties make for a highly efficient catalyst for alcohol dehydrogenation.

CHAPTER THREE

THE CATALYTIC DECOMPOSITION OF 1,2-ETHANEDIOL,
1,2,3-PROPANETRIOL, METHANOL, 1-PROPANOL
AND 1-BUTANOL BY COMPLEXES OF
RHODIUM AND RUTHENIUM

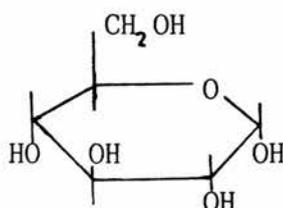
CHAPTER 3

THE CATALYTIC DECOMPOSITION OF 1,2-ETHANEDIOL, 1,2,3-PROPANETRIOL, METHANOL, 1-PROPANOL AND 1-BUTANOL BY COMPLEXES OF RHODIUM AND RUTHENIUM

3.1 INTRODUCTION

The studies described in the previous chapter on the catalytic decomposition of ethanol have shown that high rates of hydrogen production can be achieved using homogeneous rhodium and ruthenium catalysts. The reasons why these reactions were successful have been established.

Although ethanol is a successful model substrate for biomass conversion, more realistic models are required if direct dehydrogenation of biomass is to be performed. The basic biomass units are glucose molecules, which can be considered as polyols in their naturally occurring form i.e.

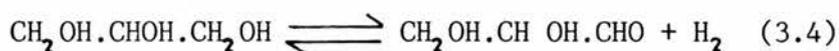
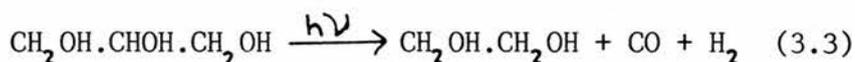
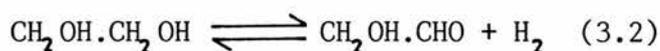
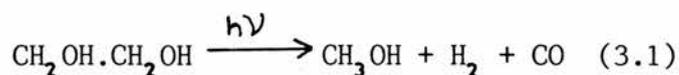


D-glucose

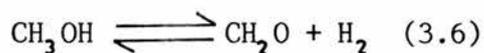
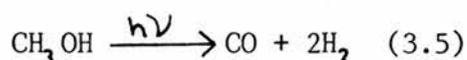
Therefore more realistic models are the simple polyols 1,2-ethanediol and 1,2,3-propanetriol.

Dehydrogenation of these alcohols was attempted using the

catalysts investigated in chapter 2. The anticipated modes of dehydrogenation are shown in equations 3.1 - 3.4:



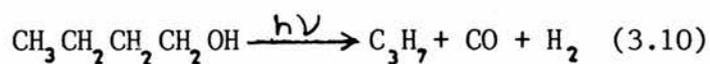
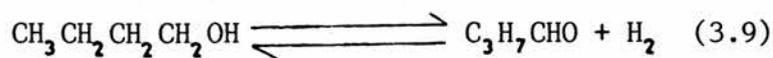
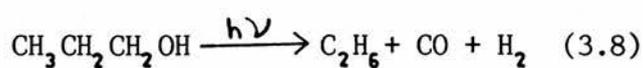
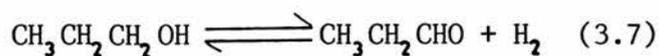
Equations 3.1 and 3.2 predict the formation of methanol. The dehydrogenation of methanol was investigated since it should be further decomposed, under the reaction conditions employed, as shown in equations 3.5 and 3.6:



The dehydrogenation was investigated under identical reaction conditions to those employed for ethanol to see if these reactions would occur at a satisfactory rate.

The higher molecular weight primary alcohols 1-propanol and 1-butanol were also used as substrates for dehydrogenation in order to investigate whether the chain length of the alcohol had any effect on the rate of hydrogen production.

The proposed decomposition reactions are shown in equations 3.7 - 3.10:



Catalysis of these reactions is discussed in this chapter.

3.2 RESULTS AND DISCUSSION

3.2.1 CATALYTIC DEHYDROGENATION OF 1,2-ETHANEDIOL

RESULTS

The results from ethanol dehydrogenation catalysed by $[\text{RhCl}(\text{PPh}_3)_3]$, $[\text{RuH}_2(\text{N}_2)(\text{PPh}_3)_3]$, $[\text{RuH}_2(\text{PPh}_3)_4]$, $[\text{RhH}(\text{PPr}_3^i)_3]$ and $[\text{Rh}(\text{bipy})_2]\text{Cl}$ have been very encouraging and have identified the reaction conditions under which each catalyst is most active.

The reaction conditions were reproduced for the dehydrogenation of 1,2-ethanediol and the results are shown in table 3.1.

Table 3.1 CATALYTIC DEHYDROGENATION OF 1,2-ETHANEDIOL

Catalyst	[catalyst] / $10^{-4} \text{ mol dm}^{-3}$	Temp / $^{\circ}\text{C}$	Time /h	$h\nu$	[NaOH] / mol dm^{-3}	H_2
$\text{RhCl}(\text{PPh}_3)_3$	4.34	150	2	X	1	46.63
$\text{Rh}(\text{dppp})_2$	3.12					
$\text{RuH}_2(\text{N}_2)(\text{PPh}_3)_3$	3.04	150	2	X	1	515.94
$\text{RuH}_2(\text{N}_2)(\text{PPh}_3)_3$	1.74	150	2	✓	1	1185.30
$\text{RuH}_2(\text{PPh}_3)_4$	3.86	150	2	X	1	149.33
$\text{RuH}_2(\text{PPh}_3)_4$	2.28	150	2	✓	1	431.03
$\text{RhH}(\text{PPr}_3^i)_3$	3.44	150	2	✓	1	9.96
$\text{RhH}(\text{PPr}_3^i)_3 + 3$	4.14	150	2	X	1	9.98
$\text{Rh}(\text{dppp})_2$	2.29					
$\text{Rh}(\text{bipy})_2^+$	6.52	150	2	X	1	43.82 ($\text{CO}_2 - 0.77$)

N.B. The reaction temperature is increased for reactions catalysed by $[\text{Rh}(\text{bipy})_2]\text{Cl}$ compared to the identical ethanol reactions.

The results show that each complex catalyses the dehydrogenation reaction and that $[\text{RuH}_2(\text{N}_2)(\text{PPh}_3)_3]$ is extremely active under thermal and, especially, photochemical conditions.

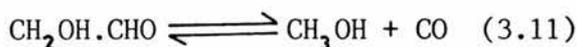
Dehydrogenation occurs according to equation 3.2 with H_2 being the only gas phase product. CO is not detected in the gas phase in the photochemical reactions due to reaction with base to produce formate ion. The rate of H_2 production is increased in all the systems compared to the identical ethanol reactions except when $[\text{RhH}(\text{PPr}_3^i)_3]$ and $[\text{Rh}(\text{bipy})_2]\text{Cl}$ are used as catalysts. In these cases the rate of hydrogen production is significantly lower than in the corresponding ethanol reactions, even more so when the higher temperature is taken into consideration for the $[\text{Rh}(\text{bipy})_2]\text{Cl}$ reaction.

Reaction catalysed by $[\text{RuH}_2(\text{N}_2)(\text{PPh}_3)_3]$ produced H_2 at an exceptionally high rate under thermal conditions and this rate is more than doubled under photochemical conditions.

DISCUSSION

Each of these catalytic systems will be treated individually in order to determine the nature of these interesting reactions.

The rate of hydrogen production from reactions catalysed by $[\text{RhCl}(\text{PPh}_3)_3]$ and $[\text{Rh}(\text{dppp})_2]\text{Cl}$ is approximately double that obtained from ethanol. Hydrogen is the only gas phase product which indicates a similar catalytic cycle to that of ethanol decomposition (scheme 2.4). The primary product of dehydrogenation will then be $\text{CH}_2\text{OH}\cdot\text{CHO}$. Decarbonylation of this bifunctional molecule is catalysed by $[\text{RhCl}(\text{PPh}_3)_3]$ stoichiometrically, however, to form $[\text{RhCl}(\text{CO})(\text{PPh}_3)_2]$ which poisons the dehydrogenation reaction. Competitive catalysis by the known decarbonylation catalyst $[\text{Rh}(\text{dppp})_2]\text{Cl}$ is highly likely as shown in equation 3.11.



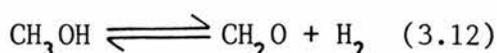
CO is not detected in the gas phase due to its removal by reaction with sodium hydroxide to produce sodium formate. Hydroxy ethanal ($\text{CH}_2\text{OH}\cdot\text{CHO}$) will also be removed from the system by base catalysed aldol condensation reactions which will be facile at these elevated temperatures.

These last two reactions, namely:

- (i) decarbonylation of $\text{CH}_2\text{OH}\cdot\text{CHO}$ catalysed by $[\text{Rh}(\text{dppp})_2]\text{Cl}$ and
- (ii) base catalysed aldol condensation reactions

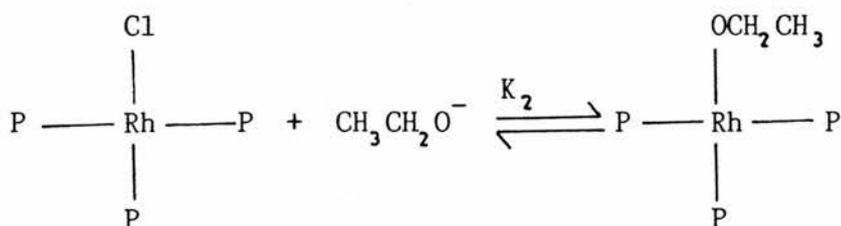
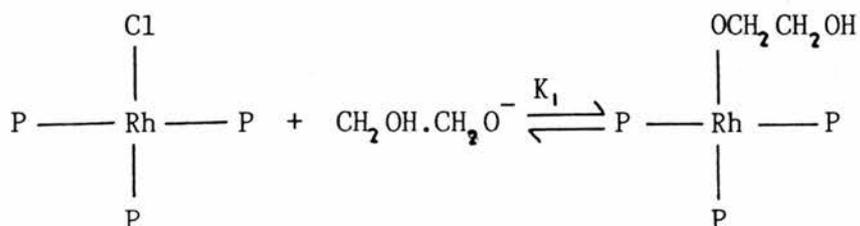
help prevent catalyst poisoning of the dehydrogenation catalyst $[\text{RhCl}(\text{PPh}_3)_3]$ which occurs when $[\text{RhCl}(\text{PPh}_3)_3]$ reacts with an aldehyde to produce $[\text{RhCl}(\text{CO})(\text{PPh}_3)_2]$.

Small amounts of methanol will be produced in this reaction and this alcohol could also be dehydrogenated under the reaction conditions employed. Then:



The results of investigations of reaction 3.12 are presented later in this chapter.

The reasons for the higher rate of hydrogen production from 1,2-ethanediol may be attributed to the much higher acidity of this alcohol compared to ethanol which results in much easier alkoxide formation and hence a higher rate of metathesis i.e.



K_1 is larger than K_2 , hence more substrate molecules can be dehydrogenated by the catalyst and therefore a higher rate of hydrogen production is observed.

Also the potential for chelate binding of the substrate is present producing a more stable reaction intermediate and therefore increasing K_1 . Both of these mechanisms will result in an increased rate of hydrogen production as observed.

Both $[\text{RuH}_2(\text{PPh}_3)_4]$ and $[\text{RuH}_2(\text{N}_2)(\text{PPh}_3)_3]$ exhibit high rates of hydrogen production under thermal conditions and extremely high activity under photochemical conditions. The maximum rate for $[\text{RuH}_2(\text{N}_2)(\text{PPh}_3)_3]$ corresponds to ca.5 litres of hydrogen per litre of catalyst solution per hour.

Base is required for reaction to occur, which implies an initial reaction involving attack of an alkoxide ion onto the ruthenium complex to give an anionic species from which an aldehyde is lost to give the known $[\text{RuH}_3(\text{PPh}_3)_3]^-$ as shown in scheme 2.5 in chapter 2. Protonation gives $[\text{RuH}_4(\text{PPh}_3)_3]$ which is the active catalytic species and contains co-ordinated molecular hydrogen which is readily replaced by neutral or anionic donors to release hydrogen.⁴³ If this is the case for the alkoxide ion, this will regenerate the required alkoxide complex and complete the catalytic cycle.

$[\text{RuH}_2(\text{N}_2)(\text{PPh}_3)_3]$ is a more reactive dehydrogenation catalyst than $[\text{RuH}_2(\text{PPh}_3)_4]$ due to the triphenylphosphine leaving group for $[\text{RuH}_2(\text{PPh}_3)_4]$. The presence of free triphenylphosphine in solution can inhibit catalysis by competing for vacant co-ordination sites on the catalytic intermediate $[\text{RuH}_2(\text{PPh}_3)_3]$.

Protonation of the trihydrido species will be facile under the basic conditions employed in the reaction due to the negative charge on the complex.⁴⁸ Hydrogen release will be rapid on account of its presence as co-ordinated dihydrogen.

Decarbonylation of the product aldehyde is not a problem in these reactions since these complexes are known⁵² to readily decarbonylate alcohols to give $[\text{RuH}_2(\text{CO})(\text{PPh}_3)_3]$ which has been shown, (in chapter 2), to be an active dehydrogenation catalyst. The increase in the rate of hydrogen production on illumination is due to photochemical enhancement of dehydrogenation catalysed by $[\text{RuH}_2(\text{CO})(\text{PPh}_3)_3]$ for which photochemical loss of dihydrogen is known.⁵³

This reaction indicates that CO abstraction is an important reaction to allow continued dehydrogenation of 1,2-ethandiol.

Small amounts of CO_2 can be detected on acidification suggesting that some of the $[\text{RuH}_2(\text{CO})(\text{PPh}_3)_3]$ can be reconverted to $[\text{RuH}_3(\text{PPh}_3)_3]^-$ by attack of OH^- on the co-ordinated CO and loss of CO_2 .

The reason for the higher activity from 1,2-ethandiol compared to ethanol is probably due to the much higher acidity of this alcohol and the potential of chelate binding of the substrate.

$[\text{RhH}(\text{PPr}_3)_3]$ exhibits low rates of hydrogen production photochemically and thermally when with $[\text{Rh}(\text{dppp})_2]\text{Cl}$.

Once again, base is required for reaction to occur which indicates initial attack of alkoxide ion to give $[\text{RhH}_2(\text{PPr}_3^i)_2]^-$ on loss of the aldehyde as shown in scheme 2.8. Protonation gives $[\text{RhH}_3(\text{PPr}_3^i)_2\text{S}]$ (S = thf) and reductive elimination of dihydrogen and attack of alkoxide ion completes the catalytic cycle. The protonation will be facile due to the negative charge on the complex.

Decarbonylation of the aldehyde will occur in both thermal and photochemical reactions. $[\text{RhH}(\text{PPr}_3^i)_3]$ is known to decarbonylate alcohols under photochemical conditions⁴⁰ to produce CO and $[\text{Rh}(\text{dppp})_2]\text{Cl}$ is a known aldehyde decarbonylation catalyst. The CO is not detected in either system due to the reaction of CO with base to produce sodium formate.

The similar rate of hydrogen production in these systems suggests that the rate of H_2 elimination is the rate determining step. Illumination removes CO from $[\text{RhH}(\text{CO})(\text{PPr}_3^i)_2]$ thus completing that catalytic cycle. In the thermal reaction $[\text{Rh}(\text{dppp})_2]\text{Cl}$ helps prevent the formation of $[\text{RhH}(\text{CO})(\text{PPr}_3^i)_2]$ and thus prevents catalyst poisoning.

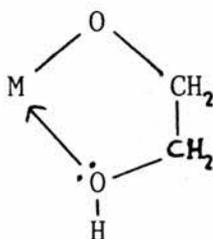
The low rate of the dehydrogenation despite the high acidity of 1,2-ethandiol suggests that chelate binding of the substrate is inhibited by the steric crowding of the PPr_3^i phosphine groups which are less labile than PPh_3 . This suggests that chelate binding is important in the systems where high rates of hydrogen production are observed. The mechanisms of these reactions are as shown in schemes 2.7 and 2.8 in chapter 2.

$[\text{Rh}(\text{bipy})_2]\text{Cl}$ shows low activity for dehydrogenation of 1,2-ethandiol compared to ethanol even though a higher temperature is used in the former reaction.

A small quantity of CO_2 is detected in the gas phase after acidification with concentrated hydrochloric acid.

The reaction mechanism will be similar to that shown in scheme 2.9. The initial attack of alkoxide ion will be rapid due to the positive charge on the metal complex. The production of hydrogen will be the rate determining step with the protonation of $[\text{Rh}(\text{bipy})_2\text{H}]$ being the dominant pre-equilibrium.

Studies on the other catalysts described above suggest that chelate binding of 1,2-ethandiol accounts for the generally high rates of hydrogen production that are observed i.e.



This mode of binding will increase the equilibrium constant for the reaction involving the co-ordination of the substrate.

For $[\text{Rh}(\text{bipy})_2]\text{Cl}$, although such a binding mode is possible, the product will be an 18 electron, 6 co-ordinate, trischelate rhodium complex, in which it will be very unfavourable to

create the vacant site required for β -hydrogen abstraction and loss of dihydrogen.

This would explain the low rates of hydrogen production observed in these reactions.

3.2.2 CATALYTIC DECOMPOSITION OF 1,2,3-PROPANETRIOL

RESULTS

The results of these dehydrogenation reactions are shown in table 3.2 and they indicate that the rate of hydrogen production is substantially lower, for all systems, than observed from 1,2-ethanediol.

Table 3.2 CATALYTIC DEHYDROGENATION OF 1,2,3-PROPANETRIOL

Catalyst	[catalyst] /mol dm ³	Temp /°C	Time /h	hν	[NaOH] /mol dm ³	H ₂	CO ₂
RhCl(PPh ₃) ₃ Rh(dppp) ₂	5.44 3.96	150	2	X	1	1.64	-
RuH ₂ (PPh ₃) ₄ RuH ₂ (PPh ₃) ₄	3.14 3.50	150 150	2 2	X ✓	1 1	18.36 22.27	- -
RuH ₂ (N ₂)(PPh ₃) ₃ RuH ₂ (N ₂)(PPh ₃) ₃	3.91 2.93	150 150	2 2	X ✓	1 1	12.42 37.58	- -
RhH(PPr ⁱ) ₃ RhH(PPr ⁱ) ₃ Rh(dppp) ₂	2.40 2.76 3.75	150 150	2 2	✓ X	1 1	3.45 4.28	0.80 1.80
Rh(bipy) ₂ ⁺	6.08	150	2	X	1	21.34	0.50

DISCUSSION

These lower results can be explained by the lack of chelate binding of the substrate. With 1,2-ethanediol a chelate 5-membered ring can be formed to stabilise the substrate in all systems except [RhH(PPrⁱ)₃] which exhibits low activity due to steric crowding from the PPrⁱ groups.

1,2,3-propanetriol would be expected to form a five membered ring but the presence of an extra CH_2OH group is likely to make this mode of bonding rather sterically congested. Hence, even though 1,2,3-propanetriol is a stronger acid than 1,2-ethanediol⁵⁴ the initial alkoxide complex is not as stable which results in a reduced rate of substrate dehydrogenation.

The mechanisms of these reactions will be as shown in chapter two for ethanol dehydrogenation.

3.2.3 CATALYTIC DECOMPOSITION OF METHANOL, 1-PROPANOL AND 1-BUTANOL

RESULTS

The catalytic dehydrogenation of methanol was attempted because this was an expected product of 1,2-ethanediol and 1,2,3-propanetriol dehydrogenation after decarbonylation occurs. These catalysts should then dehydrogenate the formed methanol.

Dehydrogenation of 1-propanol and 1-butanol was studied to investigate the effect of alcohol chain length on the rate of hydrogen production in the series methanol \rightarrow ethanol \rightarrow 1-propanol \rightarrow 1-butanol.

The results from the dehydrogenation of methanol, 1-propanol and 1-butanol are shown in table 3.3.

Table 3.3 RATES OF HYDROGEN PRODUCTION FROM STRAIGHT CHAIN ALCOHOLS CATALYSED BY VARIOUS COMPLEXES OF RHODIUM AND RUTHENIUM IN THE PRESENCE OF NaOH (1mol⁻³ dm⁻³)

Catalyst	Temp /°C	Rate of hydrogen production/catalyst turnovers h ⁻¹ (catalyst concentration/10 ⁻⁴ mol ⁻³ dm ⁻³)			
		Methanol	Ethanol	1-propanol	1-butanol
[RhCl(PPh ₃) ₃] + [Rh(dppp) ₂]Cl	150	7.97 (4.34) (3.96) ^b	21.4 (3.26) (2.7) ^b	37.60 (4.34) ^b (4.79) ^b	484.6 ^c (3.90) ^b (3.75) ^b
[RuH ₂ (PPh ₃) ₄]	150	7.53 (2.98)	23.8 (2.98)	66.15 (3.50)	526.5 (4.20)
[RuH ₂ (PPh ₃) ₄] + hν	150	27.75 (2.98)	138.4 (2.10)	161.34 (3.86)	455.9 (4.56)
[RuH ₂ (N ₂)(PPh ₃) ₃]	150	6.36 (3.90)	148.1 (2.60)	191.0 (2.82)	523.5 (3.04)
[RuH ₂ (N ₂)(PPh ₃) ₃] + hν	150	37.33 (3.90)	210.2 (3.48)	238.10 (2.60)	457.9 (2.60)
[RhH(PPr ⁱ) ₃] + hν	150	17.67 (3.10)	23.1 (3.10)	21.60 (2.76)	115.1 (1.72)
[RhH(PPr ⁱ) ₃] + [Rh(dppp) ₂]Cl	150	15.58 (3.44) (4.16) ^b	17.1 (4.48) (2.70) ^b	64.24 (4.82) ^b (3.33) ^b	370.9 (2.42) ^b (3.33) ^b
[Rh(bipy) ₂]Cl	120	7.53 ^a (7.38)	95.5 (10.0)	96.87 (3.90)	87.5 (4.12)

^a CO₂ produced after acidification. Rate = 1.75 turnovers h⁻¹

^b concentration of [Rh(dppp)₂]Cl/10⁻⁴ mol⁻³ dm⁻³

^c some metallic rhodium was observed at the end of this reaction

The results for almost all of the catalysts studied show an increase in the rate of hydrogen production as the chain length of the alcohol increases despite the fact that the effective concentration of alcohol decreases as the molecular

weight of the alcohol increases.

CO₂ is produced in reactions catalysed by [Rh(bipy)₂]Cl, but only very small amounts are observed for 1-propanol and none is produced from 1-butanol. Carbon dioxide is not a product of dehydrogenation with the other catalysts although methane is produced from ethanol and both ethene and ethane are produced from 1-propanol.

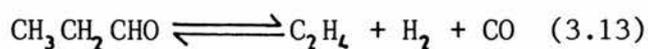
High molecular weight products are detected in solution presumably formed by aldol condensation reactions as observed in all the studied systems in the presence of base.

DISCUSSION

The mechanisms of these dehydrogenation reactions have been proposed in chapter 2 and are shown in schemes 2.4 to 2.9. The production of both ethane and ethene from 1-propanol suggests that β-hydrogen abstraction competes with reductive elimination of ethane from the alkylhydride intermediate e.g.



This is a very interesting reaction since it follows a reverse hydroformylation pathway.



The most significant result is that in all cases the rate of hydrogen production increases with increasing chain length of the alcohol. This is not due to an increased acidity of the alcohol resulting in a greater degree of protonation in the dominant pre-equilibrium that occurs just prior to H₂ loss in each case since the acidity of alcohols decreases slightly with chain length.⁵⁴ The rate of aldol condensation also decreases with increasing alkanal chain length so the extent of the back hydrogenation reaction will be higher as the chain length of the alcohol increases which should, in fact, decrease the rate of dehydrogenation.

This means that these results can only be explained by a decrease in the rate of alkanal decarbonylation, as the alkanal chain length increases, on steric grounds.

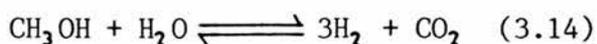
The behaviour of each catalyst shall be discussed separately to show how the rate of the dehydrogenation reaction depends on the properties of the formed carbonyl complex since CO abstraction occurs in all cases.

[RhCl(PPh₃)₃] is known to decarbonylate alkanals to give [RhCl(CO)(PPh₃)₂].⁴⁶ This is a stable carbonyl complex and its formation poisons the dehydrogenation reaction. The increase in the rate of hydrogen production as the chain length of the alcohol increases is due to a less facile decarbonylation of the longer chain alkanals, therefore, less decarbonylation and less catalyst poisoning occur hence a higher rate of hydrogen production is observed.

[Rh(dppp)₂]Cl competes for decarbonylation of the alkanal which helps attain higher rates of hydrogen production. CO is not detected in the gas phase due to the well known reaction with sodium hydroxide to form sodium formate.

[RhH(PPrⁱ)₃] is also known to decarbonylate alkanals, although the carbonyl complex formed is not a thermal alcohol dehydrogenation catalyst.¹¹ The CO can be released by photolysis so that photochemical dehydrogenation is observed.¹¹ The rate of hydrogen production from butan-1-ol is much higher than from the lower alcohols which are quite similar. This suggests that decarbonylation of 1-butanol does not occur and that CO loss is rate determining for the lower alcohols.

[Rh(bipy)₂]Cl also forms an inactive carbonyl complex on decarbonylation but in this case the CO can be removed thermally by a water-gas shift type of reaction producing CO₂.³⁴ In the dehydrogenation of methanol the expected products are shown in equation 3.14.



The stoichiometry of the observed gas phase products show that 75% of the methanal formed is decarbonylated. This contrasts with the 10% of ethanal molecules decarbonylated in the dehydrogenation of ethanol with little or no CO observed from the longer chain alcohols. This confirms that the rate of decarbonylation decreases as the chain length of the alkanal increases.

Therefore, for methanol, where a significant amount of methanal is decarbonylated, the reaction follows the bottom of scheme 2.9 which has a lower absolute rate than the top cycle. When the decarbonylation becomes kinetically insignificant ($\sim 10\%$ of the rate of hydrogen production) the rate of hydrogen production is independent of chain length. (The slight fall observed is due to the effective decrease in alcohol concentration with increasing molecular weight of the alcohol).

With $[\text{RuH}_2(\text{PPh}_3)_4]$ and $[\text{RuH}_2(\text{N}_2)(\text{PPh}_3)_3]$ decarbonylation occurs to form $[\text{RuH}_2(\text{CO})(\text{PPh}_3)_3]$ which is also an active dehydrogenation catalyst. CO_2 is not observed and it has been shown that $[\text{RuH}_2(\text{CO})(\text{PPh}_3)_3]$ is not an active water-gas shift type catalyst.⁵⁵

It is highly likely that two different catalytic cycles are operating; one involving $[\text{RuH}_2(\text{PPh}_3)_4]$ and the other $[\text{RuH}_2(\text{CO})(\text{PPh}_3)_3]$. These mechanisms are shown in schemes 2.5 and 2.6.

The cycles are very similar with the former being the reverse of that demonstrated by Halpern for hydrogenation of alkanals by $[\text{RuH}_4(\text{PPh}_3)_3]$.⁴⁸ For $[\text{RuH}_2(\text{CO})(\text{PPh}_3)_3]$, H_2 loss is known to occur photochemically and probably thermally.⁵³ The important features of the reaction are discussed below.

$[\text{RuH}_2(\text{N}_2)(\text{PPh}_3)_3]$ is a much more active dehydrogenation catalyst than $[\text{RuH}_2(\text{CO})(\text{PPh}_3)_3]$ therefore the absolute rate

of the cycle in scheme 2.5 is higher than that in scheme 2.6. We have already established that the rate of the decarbonylation reaction decreases with increasing alkanal chain length and is insignificantly slow for 1-butanol.

$[\text{RuH}_2(\text{PPh}_3)_4]$ is not as active as $[\text{RuH}_2(\text{N}_2)(\text{PPh}_3)_3]$ which is due to competitive addition of PPh_3 and alkoxide ion to $[\text{Ru}(\text{CO})(\text{PPh}_3)_3]$ thus inhibiting the rate of hydrogen production. This competing system does not operate when $[\text{RuH}_2(\text{N}_2)(\text{PPh}_3)_3]$ is used as the catalyst.

Illumination by visible light does not result in an increase in the rate of hydrogen production from 1-butanol suggesting either that light does not increase the rate of H_2 loss from $[\text{RuH}_4(\text{PPh}_3)_3]$ or that this step is not rate determining.

In conclusion, the most effective alcohol dehydrogenations involve reactions in which either the formed alkanal is not decarbonylated or where there is a thermal or photochemical mechanism to rapidly remove CO from the co-ordination sphere of the metal.

Hydrogen production is particularly successful when hydrogen is lost from a molecular hydrogen complex so that the H-H bond is formed in the ground-state co-ordinated sphere of the metal prior to rate determining loss of dihydrogen.

CHAPTER FOUR

CATALYTIC DEHYDROGENATION OF 2-PROPANOL,
2,3-BUTANEDIOL, 1,3-BUTANEDIOL
AND 1,4-BUTANEDIOL

CHAPTER 4

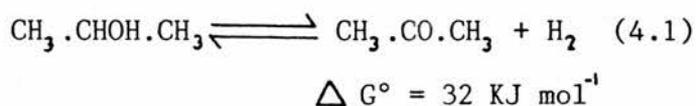
CATALYTIC DEHYDROGENATION OF 2-PROPANOL, 2,3-BUTANEDIOL, 1,3-BUTANEDIOL AND 1,4-BUTANEDIOL

4.1 INTRODUCTION

In the previous chapters of this thesis we have discussed the decomposition of primary alcohols and methods of overcoming the difficulties associated with the decarbonylation of the aldehydes produced in these dehydrogenation reactions.

An alternative approach is to employ secondary alcohols, since decarbonylation of the ketones derived from them by dehydrogenation is a non-facile process.

The dehydrogenation reaction is thermodynamically uphill according to equation 4.1.



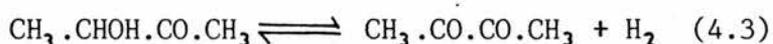
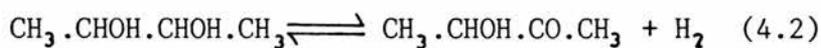
The mode of dehydrogenation has been confirmed by many research groups (see chapter one). This reaction has been studied intensely due to its potential energy storing value.

We have investigated catalysis of this reaction using $[\text{RhCl}(\text{PPh}_3)_3]$, $[\text{RhH}(\text{PPr}_i^1)_3]$ and $[\text{Rh}(\text{bipy})_2]\text{Cl}$. The use

of $[\text{Rh}(\text{dppp})_2]\text{Cl}$ was thought unnecessary because it is an aldehyde decarbonylation catalyst and does not catalyse the decarbonylation of ketones.

2,3-butanediol contains two secondary alcohol groups on adjacent carbon atoms. This alcohol is readily available from fermentation processes and is, therefore, readily available for dehydrogenation reactions. It is also a model for biomass dehydrogenation because the basic glucose unit contains many adjacent alcohol groups. It is a better model than 1,2-ethanediol because the alcohol groups are secondary as in biomass and not primary as in 1,2-ethanediol.

Catalysis of the dehydrogenation reaction should occur according to equations 4.2 and 4.3 in a sequential manner.



We have studied catalysis of these reactions by $[\text{RhCl}(\text{PPh}_3)_3]$, $[\text{RhH}(\text{PPr}_3)_3]$ and $[\text{Rh}(\text{bipy})_2]\text{Cl}$. The dehydrogenation is successful for all these catalysts.

Preliminary results suggest that $[\text{RuH}_2(\text{N}_2)(\text{PPh}_3)_3]$ is also highly active.

4.2 RESULTS AND DISCUSSION

4.2.1 CATALYTIC DEHYDROGENATION OF 2-PROPANOL

RESULTS

Catalysis of 2-propanol dehydrogenation was performed in the presence of base by $[\text{RhCl}(\text{PPh}_3)_3]$, $[\text{RhH}(\text{PPr}_3)_3]$ and $[\text{Rh}(\text{bipy})_2]\text{Cl}$. The results of these investigations are shown in table 4.1.

Table 4.1 CATALYTIC DEHYDROGENATION OF 2-PROPANOL

Catalyst	[catalyst] /10 ⁻⁴ mol dm ⁻³	Temp /°C	Time /h	[NaOH] /mol dm ⁻³	hν	Rate H ₂
$\text{RhCl}(\text{PPh}_3)_3$	4.56	120	3	0.25	X	22.42
$\text{RhH}(\text{PPr}_3)_3$	2.40	120	2	0.25	X	25.10
$\text{RhH}(\text{PPr}_3)_3$	3.10	120	2	0.25	✓	42.60
$\text{Rh}(\text{bipy})_2^+$	3.90	120	2	0.25	X	138.32

These results show high activity for each catalyst, especially when the lower temperature than that used for the dehydrogenation of primary alcohols is taken into consideration for $[\text{RhCl}(\text{PPh}_3)_3]$ and $[\text{RhH}(\text{PPr}_3)_3]$. The only gaseous product detected is H₂. G.l.c analysis of the liquid phase shows that acetone and high molecular weight condensation products are present, thus confirming that decomposition occurs according to equation 4.1. The acetone is removed from the system by base catalysed aldol condensation reactions thus enabling a high rate of dehydrogenation as the equilibrium position of the reaction is moved to the right hand side.

DISCUSSION

$[\text{RhCl}(\text{PPh}_3)_3]$ shows its highest activity in this reaction, except for the dehydrogenation of 1-butanol where some catalyst decomposition occurs. This high activity is a direct consequence of the lack of acetone decarbonylation which results in no catalyst poisoning and a high rate of dehydrogenation. Decarbonylation does not occur because a carbon-carbon bond must be broken which is highly unfavourable. The breaking of a carbon-hydrogen bond, as required for aldehyde decarbonylation, is much more favourable and is observed in many of these reactions involving primary alcohols.

This is also the case for catalysis by $[\text{RhH}(\text{PPr}_3^i)_3]$ which shows photochemical activity similar to that found for photochemical 1-butanol decomposition. The high activity of both reactions results from no or very little decarbonylation of the product ketone or aldehyde.

$[\text{Rh}(\text{bipy})_2]\text{Cl}$ shows higher activity for 2-propanol decomposition than for any other alcohol examined which is due to highly efficient dehydrogenation, coupled with no decarbonylation. The higher rate observed compared to 1-butanol decomposition is due to the higher concentration of 2-propanol used in these reactions.

In the absence of base, the reaction produces no hydrogen and the solution remains purple. When base is added, the solution rapidly becomes pale grey and hydrogen is evolved

at a high rate. This strongly suggests that the reaction follows the same dehydrogenation pathway observed for the decomposition of ethanol, scheme 2.9 (chapter 2), with $[\text{Rh}(\text{bipy})_2\text{H}]$ being the catalytically active intermediate in solution. Hydrogen loss is rate-determining and there is a dominant pre-equilibrium, namely protonation of $[\text{Rh}(\text{bipy})_2\text{H}]$ to form $[\text{Rh}(\text{bipy})_2\text{H}_2]^+$.

The role of base in these reactions is clearly to form alkoxides, which react much more readily with the electron-deficient metal centre. This is more facile than oxidative addition of the alcohol, and with $[\text{Rh}(\text{bipy})_2]\text{Cl}$, this leads to no hydrogen formation.

During these studies on the dehydrogenation of 2-propanol catalysed by $[\text{RhCl}(\text{PPh}_3)_3]$, some exceptionally high catalytic activity was recorded. This was puzzling at the time, but experiments in which the substrate was not degassed gave this high activity reproducibly. Typically 120 turnovers H_2 were observed at 120°C with 0.25 mol dm^{-3} of base. This compares extremely favourably with the 22 turnover h^{-1} recorded in table 4.1. The two systems are identical except for one crucial component - oxygen. Triphenylphosphine reacts with oxygen to form OPPh_3 which is catalysed by $[\text{RhCl}(\text{PPh}_3)_3]$. Oxygen totally inhibits⁵⁶ hydrogenation catalysed by $[\text{RhCl}(\text{PPh}_3)_3]$ but clearly something is occurring in this system which increases the rate of dehydrogenation.

A similar increase in activity is also observed for ethanol dehydrogenation, where turnover numbers of 58 h^{-1} are observed at 150°C .

These reactions certainly merit further investigation. Indeed, Griggs and Smith studied photolytic dehydrogenation of 2-propanol with $[\text{RhCl}(\text{PPh}_3)_3]$ in the presence of air or added $\text{P}(\text{OPh})_3$ ¹⁵. The activity of these catalysts were extremely high under very forcing conditions of UV light ($< 356 \text{ nm}$) at 21°C .

4.2.2 CATALYTIC DEHYDROGENATION OF 2,3-BUTANEDIOL

RESULTS

The dehydrogenation of 2,3-butanediol was investigated under basic conditions using $[\text{RhCl}(\text{PPh}_3)_3]$, $[\text{RhH}(\text{PPr}_3)_3]$ and $[\text{Rh}(\text{bipy})_2]\text{Cl}$ as catalysts. Preliminary results have been obtained from catalysis by $[\text{RuH}_2(\text{N}_2)(\text{PPh}_3)_3]$. The results of these experiments are shown in table 4.2.

Table 4.2 CATALYTIC DEHYDROGENATION OF 2,3-BUTANEDIOL

Catalyst	[catalyst] / 10^{-4} moldm $^{-3}$	Temp /°C	Time /h	[NaOH] /moldm $^{-3}$	Rate H $_2$
$\text{RhCl}(\text{PPh}_3)_3$	3.70	140	2	1	125.32
	6.08	140	2	0	0.06
	3.90	140	18	1	88.80
	3.90 ^a	140	5	1	55.40
$\text{RhH}(\text{PPr}_3)_3$	5.86	140	3	1	65.77
	2.06	140	2	0	0.32
	3.66	140	17	1	41.35
	3.66 ^a	140	6	1	42.83
$\text{Rh}(\text{bipy})_2^+$	3.68	140	2	1	184.64
	2.62	140	2	0	0.00
	3.68	140	18	1	50.77
	2.60	140	15	1	50.33
	2.60 ^a	140	5	1	56.43
$\text{RuH}_2(\text{N}_2)(\text{PPh}_3)_3$	4.56	140	2	1	217.50

a solution cooled, degassed and reheated.

DISCUSSION

The activity for hydrogen production is high for each catalyst. $[\text{RhCl}(\text{PPh}_3)_3]$ shows exceptional activity compared to that exhibited for the other alcohols over long

periods of time (the 1-butanol reaction exhibits signs of decomposition after only 2 hours).

Hydrogen is the only gaseous product due to the formation of ketones from secondary alcohol groups. This strongly suggests that decomposition occurs according to equations 4.2 and 4.3. However, attempts to identify either acetoin or 2,3-butanedione by G.l.c/mass spectrometry of reaction solutions failed due to very facile aldol condensation reactions. Indeed 2,3-butanedione forms a thick brown gel when stirred with base at room temperature. Blank solutions, containing no catalyst, but catalytic quantities of acetoin and 2,3-butanedione were heated at 140°C with base. The vessel containing acetoin was colourless while the reaction with 2,3-butanedione was dark brown like a catalytic reaction solution. This suggests that the reaction probably follows both equations 4.2 and 4.3.

Similar reaction mechanisms to those shown in chapter two can be envisaged for these reactions.

$[\text{RuH}_2(\text{N}_2)(\text{PPh}_3)_3]$ shows very high activity, approaching that observed for thermal dehydrogenation of 1,2-ethanediol. It is clear that this exciting catalyst is very versatile and further studies in both thermal and photochemical reactions are needed.

Photochemical decomposition of 2,3-butanediol has not been studied because of the preference for thermal reactions on

industrial scales. It was hoped, and indeed it proves to be the case, that these secondary alcohol dehydrogenations would proceed sufficiently rapidly to avoid the need for photochemical assistance.

$[\text{RhH}(\text{PPr}^i)_3]$ shows the lowest activity for the dehydrogenation of 2,3-butanediol. This is due to the steric hindrance of the triisopropylphosphine ligands preventing chelate stabilisation of the reactive intermediate in the catalytic cycle.

We have studied the kinetics of the dehydrogenation of 2,3-butanediol dehydrogenation catalysed by $[\text{RhCl}(\text{PPh}_3)_3]$ and $[\text{Rh}(\text{bipy})_2]\text{Cl}$ in some detail.

$[\text{RhCl}(\text{PPh}_3)_3]$ proved to be very successful as a catalyst for this reaction which appears 1st order with respect to catalyst concentration (figure 4.1). The effect of base is very similar to that observed in the dehydrogenation of ethanol catalysed by $[\text{Rh}(\text{bipy})_2]\text{Cl}$; saturation kinetics being observed above ca. 0.3 mol dm^{-3} NaOH (figure 4.2). The Arrhenius plot suggests an activation energy of $95.72 \text{ KJ mol}^{-1}$ (figure 4.3).

Similar results are obtained from studies involving $[\text{Rh}(\text{bipy})_2]\text{Cl}$ with 1st order kinetics observed with respect to catalyst concentration, (figure 4.4) and saturation kinetics observed with base above ca. 0.3 mol dm^{-3} (figure 4.5). The Arrhenius plot gives an activation energy of $91.05 \text{ KJ mol}^{-1}$ (figure 4.6). This activation energy is nearly 30 KJ mol^{-1}

Fig 4.1 Effect of $[\text{RhCl}(\text{PPh}_3)_3]$ (10^{-4} moldm $^{-3}$) on the rate of hydrogen production
 (cm 3 per hour) from 2,3-butanediol.

($T = 413\text{k}$, $[\text{NaOH}] = 1$ moldm $^{-3}$, 1 atm N_2)

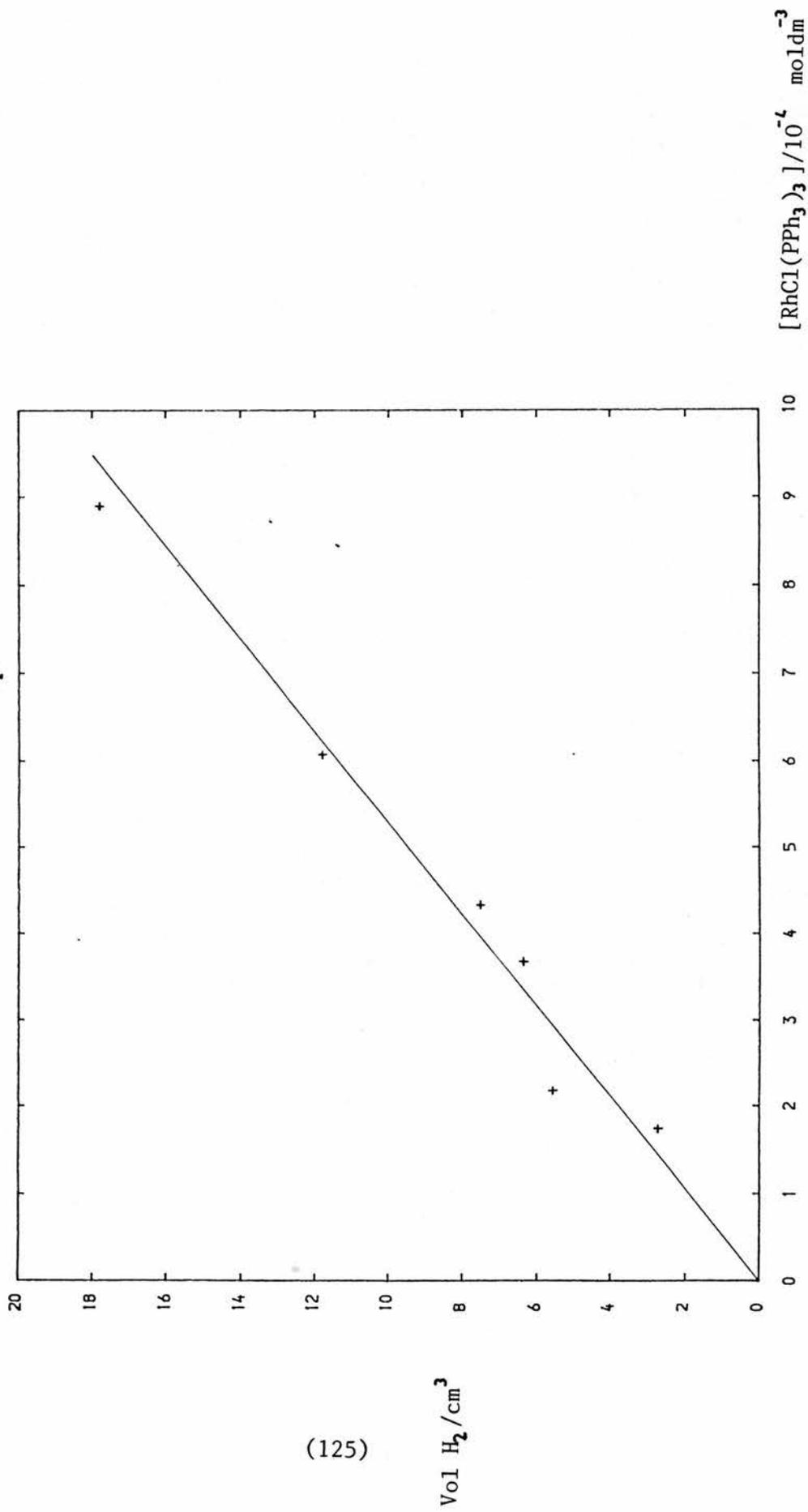


Fig 4.2 Effect of $[\text{NaOH}]$ (mol dm^{-3}) on the rate of hydrogen production (cm^3 per hour) from 2,3-butanediol catalysed by $[\text{RhCl}(\text{PPh}_3)_3]$.

$T = 413\text{k}$,
1 atm N_2

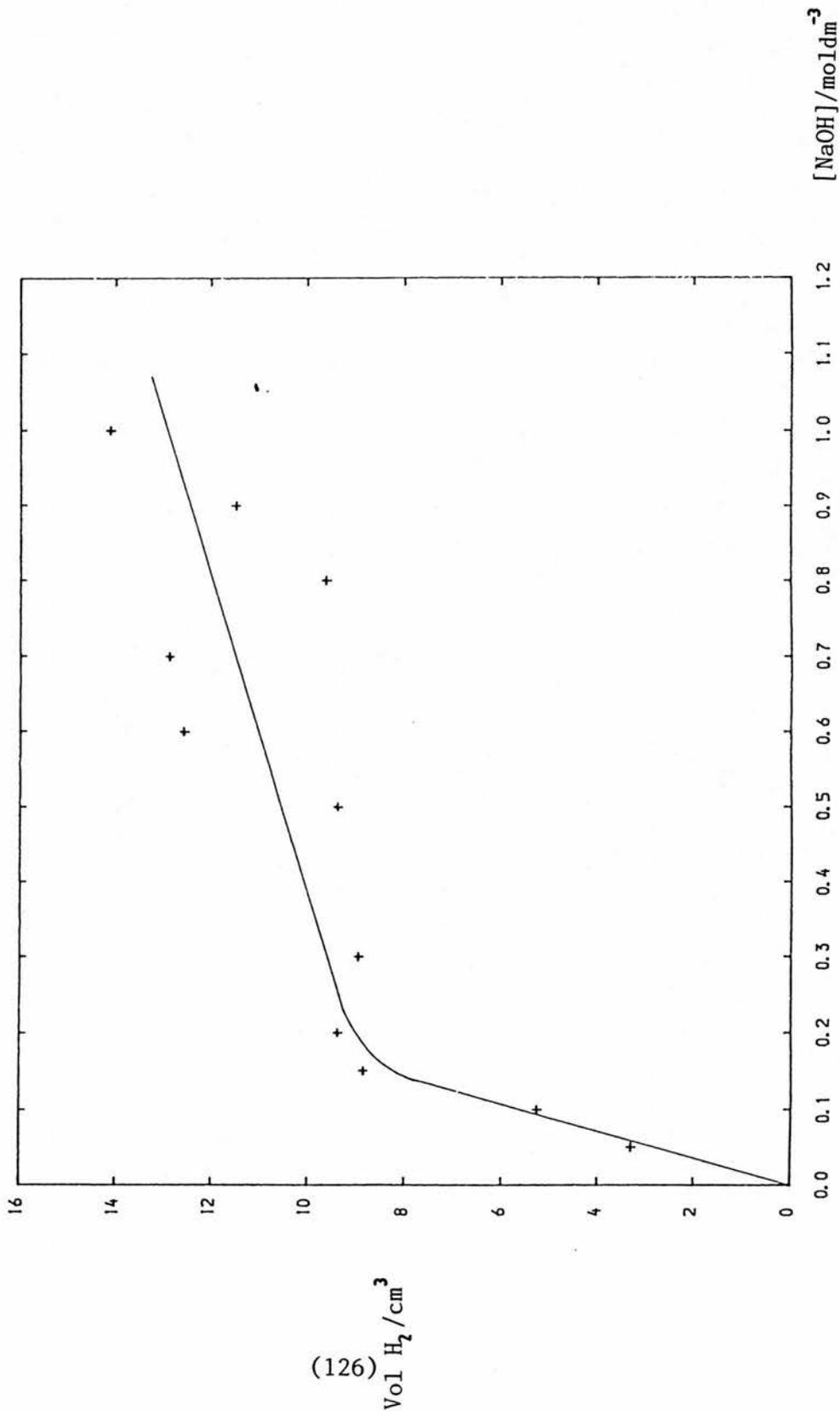


Fig 4.3 Arrhenius plot for hydrogen production (turnover no. h^{-1}) from 2,3-butanediol catalysed by $[RhCl(PPh_3)_3]$, ($[NaOH] = 1 \text{ mol dm}^{-3}$, $[RhCl(PPh_3)_3] = 4.34 \times 10^{-4} \text{ mol dm}^{-3}$, 1 atm N_2)

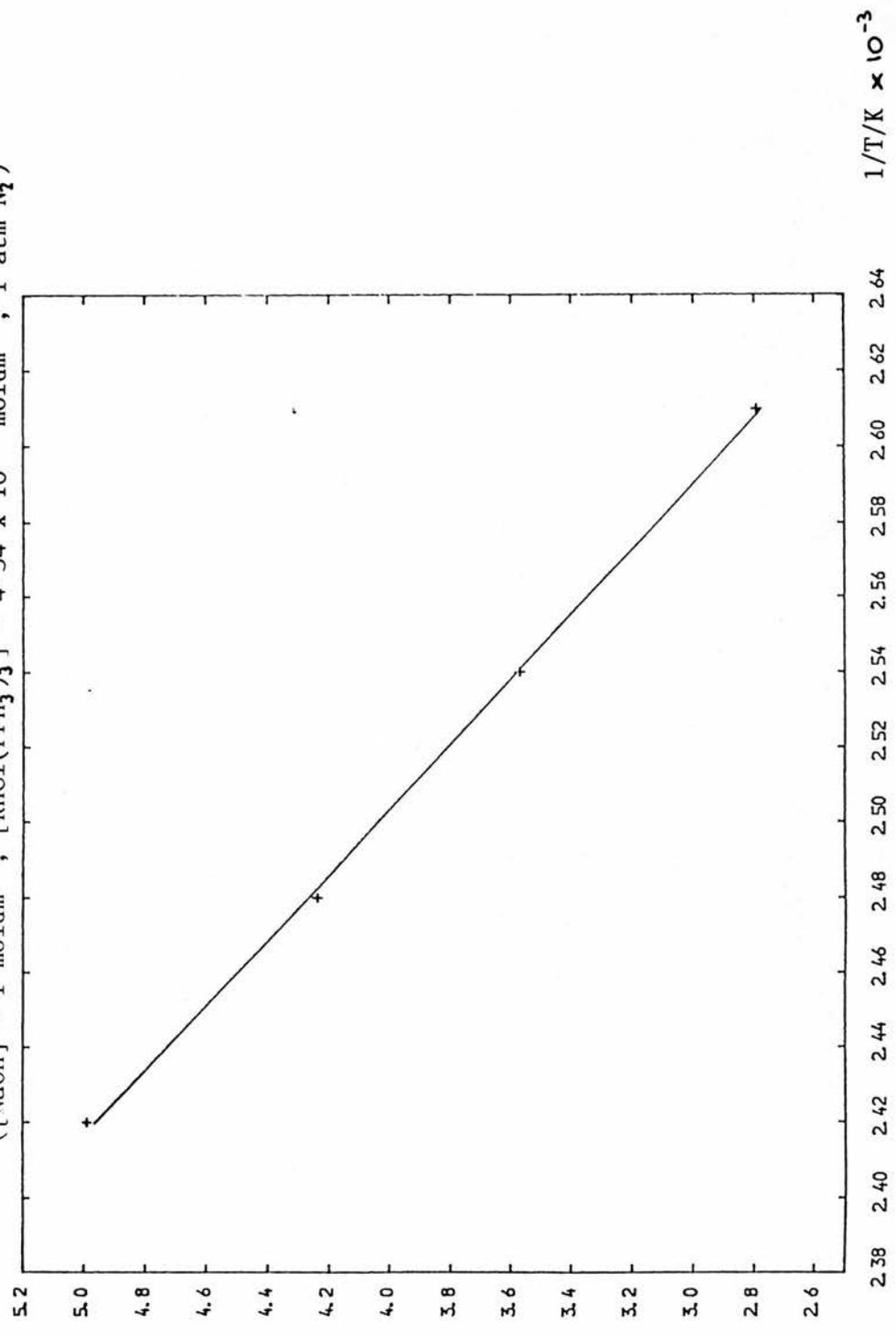


Fig 4.4 Effect of $[[\text{Rh}(\text{bipy})_2]\text{Cl}](10^{-4} \text{ moldm}^{-3})$ on the rate of hydrogen production (cm^3 per hour) from 2,3-butanediol.

$T = 413\text{k}, [\text{NaOH}] = 1 \text{ moldm}^{-3}, 1 \text{ atm N}_2$

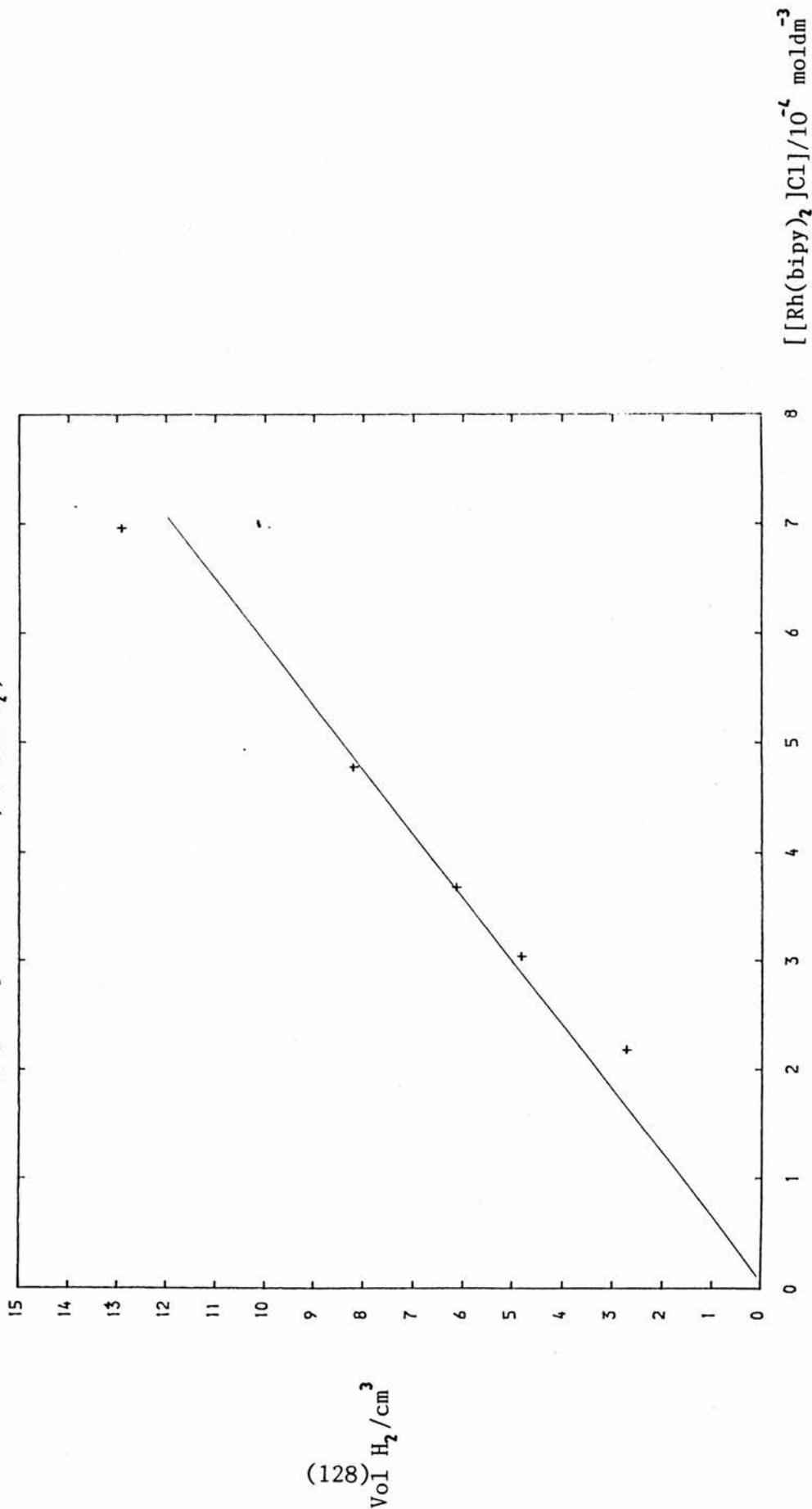


Fig 4.5 Effect of $[\text{NaOH}]$ (mol dm^{-3}) on the rate of hydrogen production
(turnover no. h^{-1}) from 2,3-butanediol catalysed by $[\text{Rh}(\text{bipy})_2]\text{Cl}$

($T = 413\text{k}$, 1 atm N_2)

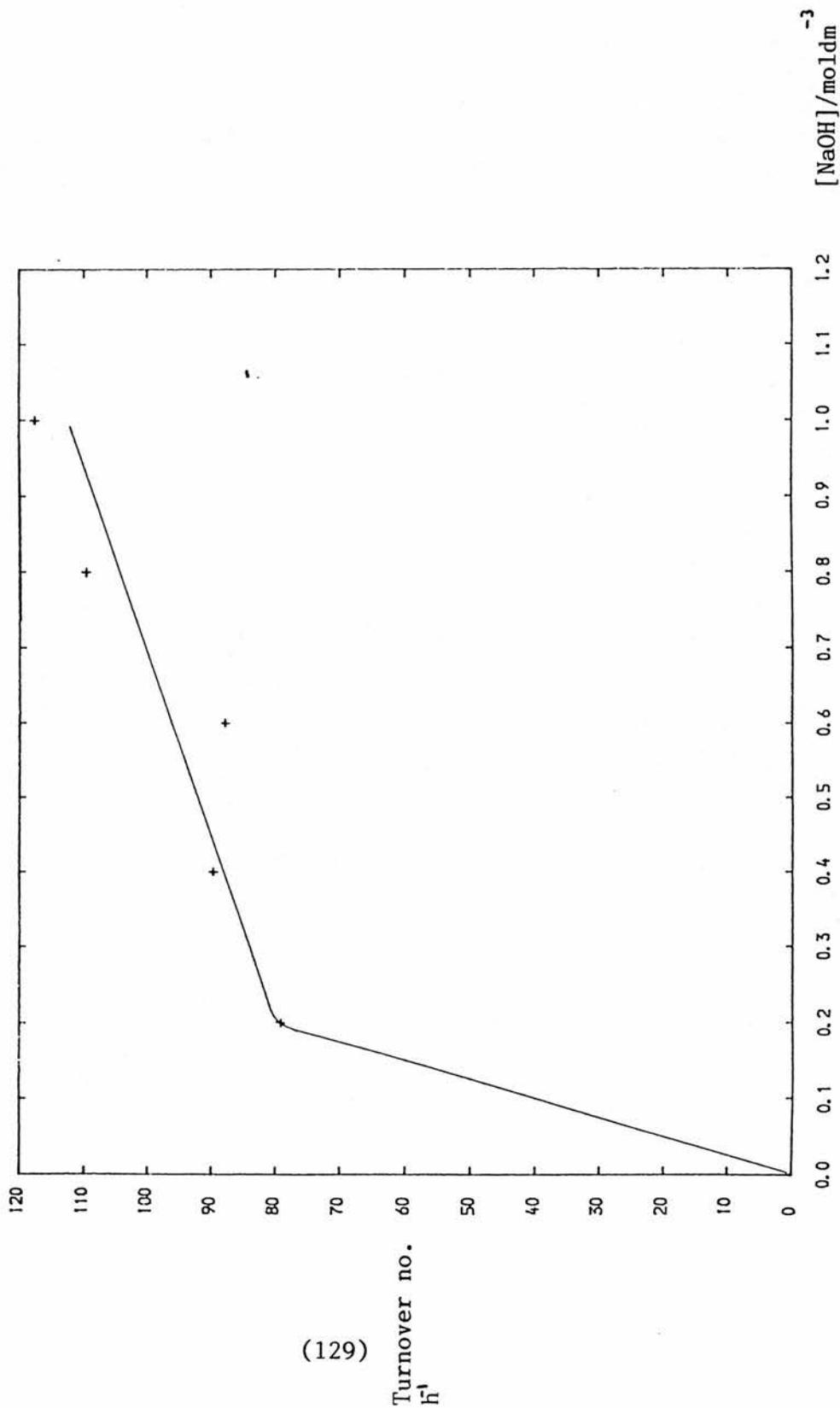
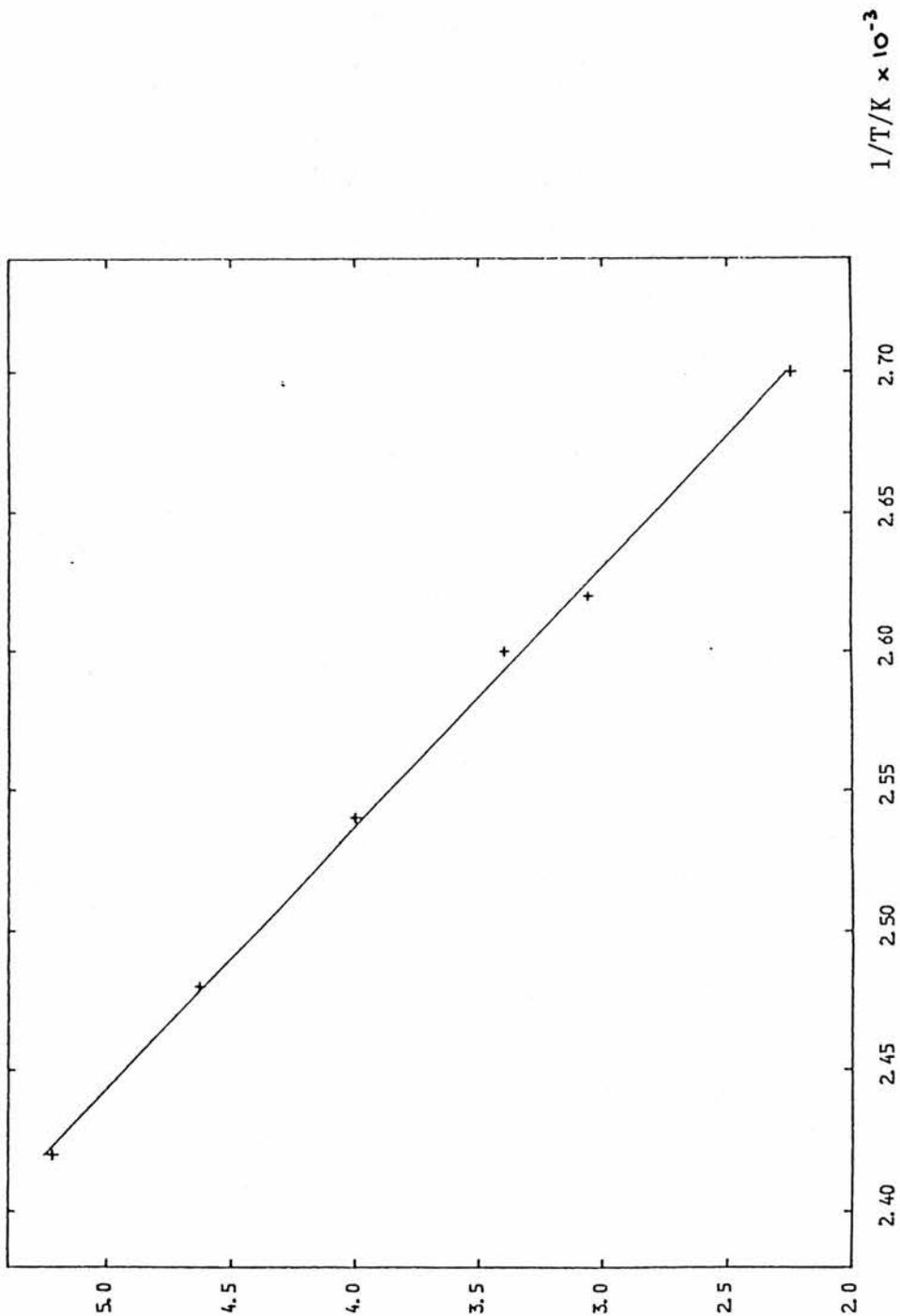


Fig 4.6 Arrhenius plot for hydrogen production (turnover no. h^{-1})
 from 2,3-butanediol catalysed by $[Rh(bipy)_2]Cl = 4.78 \times 10^{-4}$ moldm $^{-3}$
 ($[NaOH] = 1$ moldm $^{-3}$, $[Rh(bipy)_2]Cl = 4.78 \times 10^{-4}$ moldm $^{-3}$)



higher than that for the dehydrogenation of ethanol. This suggests a different rate determining step or a different dominant pre-equilibrium.

Over long reaction times the rate of hydrogen production is reduced. This rate reduction is significant and is due, in part, to the build up of hydrogen in a closed system. However, removal of the hydrogen and further reaction does not restore the original high rates of dehydrogenation. Instead, the rate is restored to that observed after ca. 18 hours or is reduced further as seen when $[\text{RhCl}(\text{PPh}_3)_3]$ is catalyst.

These results indicate that something or some process in solution is inhibiting the rate of hydrogen production. The build up of reaction products in solution should not occur due to facile base catalysed aldol condensation reactions. These products have identified as high molecular weight species from G.l.c/mass spectra of the liquid phase ($m/e > 450$). The reaction solutions become very viscous over long reaction times due to the build up of these condensation products. It seems probable that these products will inhibit the dehydrogenation reaction by retarding the rate of diffusion of the substrate alcohol to the metal centre. Also the substrate could react in acetal or ketal forming reactions in preference to reacting with the metal centre.

The reactions discussed in this chapter have demonstrated the relative ease of secondary alcohol dehydrogenation

compared to that of primary alcohols. This is due to the lack of decarbonylation of the product ketone. $[\text{RhCl}(\text{PPh}_3)_3]$ showed particularly good activity in these reactions. $[\text{Rh}(\text{bipy})_2]\text{Cl}$ exhibited similar activity in moving from primary to secondary alcohols due to kinetically insignificant or no decarbonylation. Reduced activity was observed for the diols and triol due to the lack of chelate substrate stabilisation.

The dehydrogenation of 1,3- and 1,4-butanediols should prove very interesting because of the presence of primary alcohol groups.

4.2.3 CATALYTIC DEHYDROGENATION OF 1,3 AND 1,4-BUTANEDIOL

We would expect the catalytic activity of $[\text{RhCl}(\text{PPh}_3)_3]$ to be lower in both these reactions because of the primary alcohol groups and the potential decarbonylation of the formed aldehyde. We should see an order of reactivity of $2,3 > 1,3 > 1,4$ in accordance with the number of primary alcohol groups in the molecule. However, $[\text{Rh}(\text{bipy})_2]\text{Cl}$ should show similar activity in light of the results shown in previous chapters.

RESULTS

The results of these investigations are shown in table 4.3.

Catalyst	[catalyst] / 10^{-4} mol dm $^{-3}$	Temp /°C	Time /h	Substrate Alcohol	Rate H $_2$
$\text{RhCl}(\text{PPh}_3)_3$	4.34	140	1	1,3	82.03
$\text{RhCl}(\text{PPh}_3)_3$	4.34	140	1	1,4	23.66
$\text{Rh}(\text{bipy})_2^+$	2.60	140	1	1,3	294.56
$\text{Rh}(\text{bipy})_2^+$	6.08	140	1	1,4	170.13

These preliminary results suggest that the activity of these catalysts is as expected although 1,3-butanediol dehydrogenation by $[\text{Rh}(\text{bipy})_2]\text{Cl}$ is very rapid.

DISCUSSION

Catalysis of 1,4-butanediol decomposition is relatively slow by $[\text{RhCl}(\text{PPh}_3)_3]$, due to the presence of two primary alcohol groups forming exclusively aldehydes on dehydrogenation. Decarbonylation will poison the catalyst. Dehydrogenation of 1,3-butanediol is much more facile with good activity. The activity is lower than for 2,3-butanediol due to the primary alcohol group. The activity is higher than 1,4-butanediol due to the secondary alcohol dehydrogenation being very facile.

$[\text{Rh}(\text{bipy})_2]\text{Cl}$ shows activity for hydrogen production from 1,4-butanediol comparable to that observed from 2,3-butanediol. CO_2 is observed in small quantities after acidification with concentrated hydrochloric acid but this decarbonylation is kinetically insignificant due to predominant aldol condensation reactions. Catalysis of 1,3-butanediol dehydrogenation is extremely good with very high rates of hydrogen production observed. Small quantities of CO_2 are detected as expected. An unidentified orange solid is produced which is not seen in any other reaction and clearly these interesting reactions merit further investigation.

CHAPTER FIVE

CATALYTIC DEHYDROGENATION OF
SORBITOL, CELLOBIOSE
AND WINE

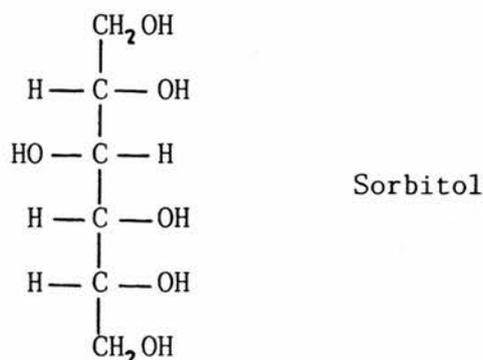
CHAPTER 5

CATALYTIC DEHYDROGENATION OF SORBITOL, CELLOBIOSE AND WINE

5.1 INTRODUCTION

Previous chapters have described a progression from the dehydrogenation of simple primary alcohols to more complex diols and triols. The work in this chapter involves a further progression in the attempt to model the reactions that would occur in the dehydrogenation of biomass.

Sorbitol is a six carbon, straight chain polyol.

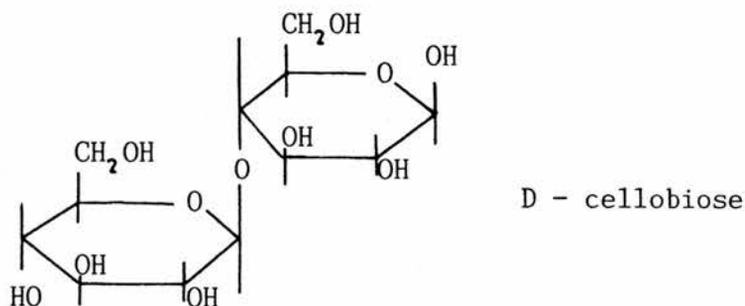


Simple dehydrogenation of one of the primary alcohol groups will give the straight chain analogue of glucose. Indeed, glucose is readily converted into sorbitol by reduction with sodium borohydride or by catalytic hydrogenation. ⁵⁷

Preliminary results on the dehydrogenation of sorbitol

catalysed by $[\text{RhCl}(\text{PPh}_3)_3]/[\text{Rh}(\text{dppp})_2]\text{Cl}$, $[\text{RhH}(\text{PPr}_3)_3]$ and $[\text{Rh}(\text{bipy})_2]\text{Cl}$ are discussed.

Cellulose is a major component of biomass but is virtually insoluble in all common solvents. However, partial acid hydrolysis gives the disaccharide cellobiose.



Cellobiose consists of two glucose units attached by a 1,4- β -glycoside linkage as seen in cellulose. Dehydrogenation of cellobiose is attractive because of the large amounts of readily available plant cellulose. We have attempted dehydrogenation using $[\text{RhH}(\text{PPr}_3)_3]$ and $[\text{Rh}(\text{bipy})_2]\text{Cl}$ and the results of these reactions are discussed.

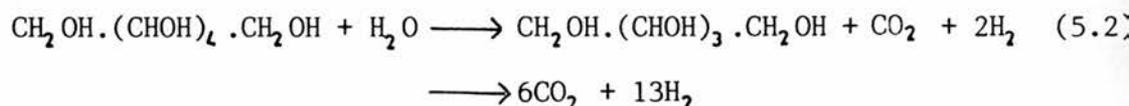
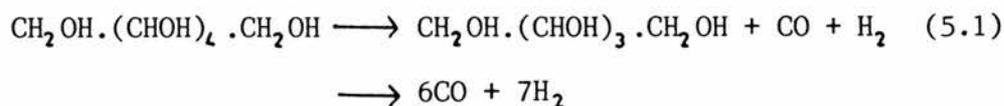
Another readily available source of alcohol, for these dehydrogenation reactions, are the E.E.C. wine lakes. Millions of gallons of surplus wine are stored throughout Europe at great expense to the community as a whole.

If hydrogen production from wine was feasible, this would be a potentially good method of making, for example, fertilisers by using the hydrogen in the synthesis of ammonia.

Preliminary investigations have been performed using $[\text{RhCl}(\text{PPh}_3)_3]/[\text{Rh}(\text{dppp})_2]\text{Cl}$, $[\text{RhH}(\text{PPr}^i)_3]$, $[\text{Rh}(\text{bipy})_2]\text{Cl}$, $[\text{RuH}_2(\text{N}_2)(\text{PPh}_3)_3]$ and $[\text{RuH}_2(\text{PPh}_3)_4]$ on both red and white wines. Some wine was distilled to remove the high boiling constituents ($> 100^\circ\text{C}$). Decomposition of the distillate has been investigated using $[\text{RhCl}(\text{PPh}_3)_3]/[\text{Rh}(\text{dppp})_2]\text{Cl}$ and $[\text{Rh}(\text{bipy})_2]\text{Cl}$ as catalysts.

The results of these reactions are discussed in this chapter.

$[\text{RhCl}(\text{PPh}_3)_3]$, $[\text{RhH}(\text{PPr}^i)_3]$ and $[\text{Rh}(\text{bipy})_2]\text{Cl}$ have all been successful catalysts for alcohol dehydrogenation in the presence of base. Sorbitol has two primary alcohol and four secondary alcohol groups in a linear molecule. Dehydrogenation could occur initially at any of the six hydroxyl groups, but if attack at one of the primary alcohol groups is envisaged then the alcohol could be systematically broken down to hydrogen and carbon monoxide or carbon dioxide as shown in equations 5.1 and 5.2.



Typically, 0.25g of sorbitol was dissolved in water, although with $[\text{Rh}(\text{bipy})_2]\text{Cl}$ 10g of sorbitol was used with 1 cm³ of water. This is possible because sorbitol melts at ca. 93°C. The results are shown in table 5.1.

RESULTS

Table 5.1 CATALYTIC DEHYDROGENATION OF SORBITOL

Catalyst	[catalyst] /10 ⁻⁴ moldm ⁻³	Temp /°C	Time /h	[NaOH] /moldm ⁻³	Rate H ₂
RhCl(PPh ₃) ₃	10.22	150	3	1	2.94
Rh(dppp) ₂	10.62				
RhH(PPr ⁱ) ₃	20.00	140	4.5	0.6	0.85
Rh(bipy) ₂ ⁺	4.78	140	2	1	2.42

DISCUSSION

These results show that the rate of hydrogen production is very low for all these catalysts. CO₂ production has not been investigated in these preliminary reactions.

The factors which will prevent rapid dehydrogenation are

- (a) low alcohol concentration and
- (b) the lack of chelate substrate stabilisation due to steric inhibition.

The combination of these factors results in low rates of hydrogen production.

5.3 CATALYTIC DEHYDROGENATION OF CELLOBIOSE

RESULTS

The dehydrogenation of cellobiose is also very slow as shown by the results in table 5.2.

Table 5.2 CATALYTIC DEHYDROGENATION OF CELLOBIOSE

Catalyst	[catalyst] /10 ⁻⁴ moldm ⁻³	Temp /°C	Time /h	[NaOH] /moldm ⁻³	Rate H ₂
RhH(PPr ₃) ₃	5.16	140	2	1	1.54
Rh(bipy) ₂ ⁺	2.60	140	2	1	0.23

DISCUSSION

Once again the rate of dehydrogenation is very slow although a direct comparison of the two systems cannot be made due to varying substrate concentrations.

Aldol type condensation reactions will be important in both the sorbitol and cellobiose systems, forming complex high molecular weight products. Such reactions could also reduce the substrate concentration.

Further study will enable elucidation of the reaction mechanisms and a maximising of the rate of hydrogen production.

RESULTS

The dehydrogenation of French red and white wine has been investigated in this work. The results of the initial investigations are shown in table 5.3.

Table 5.3 CATALYTIC DEHYDROGENATION OF RED AND WHITE WINE

Catalyst	[catalyst] /10 ⁴ moldm ³	Temp /°C	Time /h	[NaOH] /moldm ³	hν	Rate H ₂
RhCl(PPh ₃) ₃ ^a	4.34	120	2	1	X	0.10
Rh(dppp) ₂	4.16					
RhCl(PPh ₃) ₃ ^a	4.34	140	2	1	X	0.34
Rh(dppp) ₂	4.16					
Rh(bipy) ₂ ^{+a}	4.78	120	2	1	X	0.14
RuH ₂ (N ₂)(PPh ₃) ₃ ^a	3.90	150	2	1	X	0.76
RuH ₂ (N ₂)(PPh ₃) ₃ ^a	3.26	150	2	1	✓	12.68
RuH ₂ (PPh ₃) ₄ ^a	3.50	150	2	1	X	0.43
RuH ₂ (PPh ₃) ₄ ^a	4.20	150	2	1	✓	0.68
Rh(bipy) ₂ ^{+b}	3.04	120	2	1	X	0.11

a red wine

b white wine

DISCUSSION

Here, the rate of dehydrogenation is very low with all catalysts except when [RuH₂(N₂)(PPh₃)₃] is used in

photochemical reactions. Illumination with a 500 W tungsten halogen lamp increases the rate of hydrogen production significantly. This must be due to photochemical dissociation of CO from the metal centre, as seen for ethanol dehydrogenation.

One of the major problems with wine is the low concentration of ethanol, usually 12% by volume. This problem is enhanced by a high concentration of aldehydes which give the wine its flavour and aroma. These aldehydes will react with the catalysts in solution producing carbonyl complexes thus inhibiting dehydrogenation. The large concentration of aldehydes effectively stops dehydrogenation in most cases. This effect is only overcome when illumination is used when $[\text{RuH}_2(\text{N}_2)(\text{PPh}_3)_3]$ is the catalyst.

Many of the high boiling constituents of wine can be removed by distillation. This was done with constituents having boiling points of $< 100^\circ\text{C}$ being kept for dehydrogenation reactions. Initial results are shown in table 5.4.

Table 5.4 CATALYTIC DEHYDROGENATION OF WINE DISTILLATES

Catalyst	[catalyst] /10 ⁻⁴ moldm ⁻³	Temp /°C	Time /h	[NaOH] /moldm ⁻³	Rate H ₂
RhCl(PPh ₃) ₃ ^a Rh(dppp) ₂	4.34 4.16	120	2	1	1.97
RhCl(PPh ₃) ₃ ^a Rh(dppp) ₂	4.34 4.16	140	1	1	6.65
Rh(bipy) ₂ ^{+ a} RhCl(PPh ₃) ₃ ^b	3.90 4.34	120	2	1	5.45
Rh(dppp) ₂ ⁺	6.04	140	1	1	5.17

a red wine

b white wine

Removal of the high boiling constituents in wine results in a very large increase in the rate of dehydrogenation, although the rate is much less than that obtained for ethanol. However the substrate concentration is still very low. Clearly the concentration of aldehydes is still high and is still inhibiting the dehydrogenation reaction.

Further investigation with [Rh(dppp)₂]Cl added to each catalyst system would prove very interesting since in synergism with [RhCl(PPh₃)₃] a good rate of dehydrogenation is obtained. Variation of the concentration of [Rh(dppp)₂]Cl would show the effect of this catalyst on the rate of dehydrogenation.

Distillation to remove the high boiling constituents appears

to be the way to proceed in further experiments with wine. Experiments with $[\text{RuH}_2(\text{N}_2)(\text{PPh}_3)_3]$ in both thermal and photochemical dehydrogenations of these distillates should prove very interesting.

EXPERIMENTAL

I.r. spectra were measured as nujol nulls between CsI plates on a Perkin-Elmer 1310 spectrometer and n.m.r. spectra on Bruker associates WM 250 or WP 80 spectrometers operating in the Fourier Transform mode with (for ^{31}P) noise proton decoupling. For preparations of the catalysts all solvents were dried over sodium (C_6H_6) or by refluxing over sodium diphenylketyl (thf and petroleum, boiling range $40\text{--}60^\circ$).

The ethanol and sodium hydroxide were standard reagent grade and were used without further purification. $[\text{RhCl}(\text{PPh}_3)_3]^{47}$, $[\text{Rh}(\text{bipy})_2]\text{Cl}^{52}$, $[\text{RuH}_2(\text{PPh}_3)_4]$ and $[\text{Rh}(\text{dppp})_2]\text{Cl}$ were prepared by standard literature methods.

PREPARATION $\text{RuH}_2(\text{N}_2)(\text{PPh}_3)_3$

$[\text{RuCl}_2(\text{PPh}_3)_3]$ (0.5 g, 0.435 mmol) was dissolved in a mixture of benzene (30 cm^3) and methanol (50 cm^3) under N_2 . Dry, finely ground sodium borohydride (0.75 g, 0.02 mol) was added with rapid stirring. After 30 minutes the complex was precipitated as offwhite microcrystals.

Degassed methanol was added (50 cm^3) and the product filtered and dried under vacuum. It was identified as $[\text{RuH}_2(\text{N}_2)(\text{PPh}_3)_3]$ by its i.r. spectrum.

$\nu_{\text{max}}(\text{cm}^{-1})$ 2140 vs (lit 2147 br)⁵⁹, $\nu_{\text{N}\equiv\text{N}}$, 1935 wbr
(lit 1947 br)⁵⁹, 1920 wbr (lit 1917 br)⁵⁹, $\nu_{\text{Ru}-\text{H}}$

PREPARATION OF RhH(PPrⁱ₃)

RhCl₃ · 3H₂O (0.75 g) was stirred for 18 hours with PPrⁱ₃ (1.8 cm³) in thf (35 cm³) containing water (5 cm³) and a few drops of concentrated HCl, after which the solvent was removed under vacuum at 45°C. Thf (35 cm³) was added to the solid which was reduced using Na/Hg (0.3 g/6 cm³) in the presence of PPrⁱ₃ (1 cm³) for 18 hours.

When the mixture had been allowed to settle, the solution was filtered. The amalgam was washed with thf (2 x 5 cm³) and the washings added to the filtrate. The solvent was removed under vacuum and the resulting tar was extracted into petroleum (3 x 15 cm³). The volume was reduced to 10 cm³ and PPrⁱ₃ (10 drops) added prior to crystallization at -30°C.

Yellow/orange crystals grew after 5 days which were collected by filtration and dried in vacuo. These were identified at [RhH(PPrⁱ₃)₃] by their ³¹p n.m.r. and i.r. spectra.

$$\begin{aligned} &^{31}\text{p } \delta -58.8 \text{ d, } J_{\text{Rh-p}} = 157 \text{ Hz (lit } 157 \text{ Hz)}^{60} \\ &\text{i.r. } 1970 \text{ wbr cm}^{-1} \text{ (lit } 1975 \text{ cm}^{-1} \text{), } \nu_{\text{Rh-H}}^{60} \end{aligned}$$

CATALYTIC REACTIONS

All reactions were carried out in glass tubes of approximately 120 cm³ capacity fitted with a screw on cap, tap adaptor for connection to a vacuum line and septum for gas sampling.

Degassed ethanol (5 cm³) containing the catalyst (10⁻⁴ - 10⁻³ mol dm⁻³) and sodium hydroxide (0 - 1 mol dm⁻³) was placed in the vessel described above, which had previously been filled with nitrogen. The vessel was then closed and the portion of the vessel containing the liquid was placed in an oil bath at the required reaction temperature. The mixture was stirred magnetically at this temperature for the given reaction time (usually 2 h) and then cooled in air.

The gas was sampled (0.5 cm³) with a gas tight syringe and analysed by g.l.c. for H₂, CH₄ and CO. For reactions carried out in the presence of base, conc HCl (2 cm³) was added by injection through the septum and, after all gas evolution was complete, the gases were reanalysed for CO₂ by g.l.c. All reactions were carried out in duplicate and reproducibility of ± 5% was observed.

In some cases the volume of evolved gases were measured with a gas burette and were found to correspond to the volumes obtained by g.l.c.

Peak heights on the g.l.c. were converted to percentages of gas in the vessel by calibration with standards of known composition due account being taken for non-linearities in the response of the detector at different concentrations. These percentages were converted into volumes of gas evolved, knowing the volume of the reaction vessel.

In some reactions, particularly those involving long reaction times, significant increases in pressure within the reaction vessel were observed. In all cases, the reactions were sampled at the pressure within the cell as 0.5 cm³ samples at that pressure. It can readily be shown that peak heights obtained in this way relate directly to the volume of hydrogen produced - corrected to one atmosphere.

All gases were analysed as 0.5 ml samples by g.l.c. using Pye Unicam Series 104 or 204 gas liquid chromatographs and a thermal conductivity detector. Columns were molecular sieve 4A (H₂ using N₂ as carrier gas) or Chromosorb 102 (CO, CO₂ using He as carrier gas). Carbosieve 100/120S (CH₄, using N₂ carrier gas and an FID detector).

TEST FOR HOMOGENEITY

A reaction catalysed by [Rh(bipy)₂]Cl was tested for homogeneity by stirring with liquid mercury which is known to inhibit colloidal catalysis. After heating for 30 minutes the cell was analysed for H₂ (57.7 turnovers) and then cooled. Mercury was added and the reaction stirred for 10 minutes. The solution was filtered away from the mercury and the reaction re-run for 30 minutes. Hydrogen corresponding to 55.2 turnovers was detected in the gas phase, suggesting that the reaction was genuinely homogeneous.

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