ACTIVATION OF HYDROGEN, OLEFINS, OXYGEN AND CARBON MONOXIDE BY RHODIUM COMPLEXES IN NON-AQUEOUS SOLVENTS

By

FLORA TAK TAK NG

B.Sc. (General), The University of Hong Kong, 1966
M.Sc., The University of British Columbia, 1968

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We accept this thesis as conforming to the required standard

THE UNIVERSITY OF BRITISH COLUMBIA
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Department of Chemistry

The University of British Columbia
Vancouver 8, Canada

Date 10th July, 1970
ABSTRACT

Kinetic studies of a number of interesting and significant reactions involving activation of hydrogen, olefins, oxygen and carbon monoxide by solutions of rhodium complexes containing sulphur and/or chloride ligands are described.

The cis 1,2,3-trichlorotris(diethylsulphide)rhodium (III) complex, RhCl$_3$(Et$_2$S)$_3$ and the corresponding dibenzyl sulphide complex, RhCl$_3$(Bz$_2$S)$_3$ in N,N-dimethylacetamide (DMA) solution were found to be effective catalysts for the homogeneous hydrogenation of maleic, fumaric and trans-cinnamic acids. The kinetic data are consistent with a dissociation of a sulphur ligand prior to the hydrogen reduction of rhodium (III) to rhodium (I). The rhodium (I) is stablized in solution by rapid complexing with the olefin to produce a Rh$^I$(olefin)L$_n$ complex ($L = auxiliary ligands$) which then reacts with H$_2$ in a rate determining step to produce the saturated paraffin and rhodium (I). In some instances, more complex kinetics resulted when one of the auxiliary ligands in the Rh$^I$(olefin)L$_n$ complex dissociates prior to reaction with H$_2$; a unique apparent zero order in catalyst concentration has been observed. Isomerization was observed in the RhCl$_3$(Et$_2$S)$_3$ catalyzed hydrogenation of fumaric acid and a mechanism involving rhodium (III) alkyl intermediate seems likely.

The cyclooctene complex, [Rh(C$_8$H$_{14}$)$_2$Cl]$_2$, in DMA was found to be a convenient source for preparing rhodium (I) complexes"in situ" by adding the desired ligands, for example, chloride or diethyl sulphide. Kinetic data obtained using such solutions are in good agreement with the hydrogenation data obtained by starting from the corresponding
rhodium (III) complexes. This result confirms that rhodium (I) intermediates are involved in the catalytic hydrogenation starting from rhodium (III) complexes.

During studies to investigate the effect of solvent on catalytic hydrogenation of olefins by rhodium (III) complexes, dimethyl sulfoxide (DMSO) was found to be catalytically reduced by hydrogen to dimethyl sulphide and water in the presence of RhCl$_3$(Et$_2$S)$_3$ and RhCl$_3$·3H$_2$O. The kinetics were consistent with a rate determining heterolytic splitting of H$_2$ by Rh$^{III}$(DMSO) to produce Rh$^{III}$(DMSO)H$^-$, which then decomposes to the products in a fast step. RhCl$_3$·3H$_2$O also catalyzed the oxidation of DMSO to dimethyl sulphone using a mixture of oxygen and hydrogen.

The solution of [Rh(C$_8$H$_{14}$)$_2$Cl]$_2$ in DMA containing LiCl was found to be a versatile catalyst, for besides the activation of hydrogen and olefins, oxygen and carbon monoxide could also be activated. The formation of a rhodium (I) molecular oxygen complex, Rh$^I$(O$_2$) and a subsequent catalyzed oxidation of the DMA solvent and cyclooctene were studied in detail. The formation of the Rh$^I$(O$_2$) complex appears to be irreversible. An E.S.R. signal, possibly due to species such as Rh$^{II}$O$_2^-$ was also observed. The kinetics of the oxidation suggest the equilibrium formation of the Rh$^I$(O$_2$) complex followed by a rate determining step to give the products. A free radical mechanism seems likely.

Solutions of [Rh(C$_8$H$_{14}$)$_2$Cl]$_2$ in LiCl/DMA readily reacted with carbon monoxide to form a Rh$^I$(CO)$_2$ species. A solution of the oxygen complex was converted more slowly to the Rh$^I$(CO)$_2$ species in a
reaction whose observed rate was determined by the dissociation of the coordinated oxygen. Preliminary studies indicated that a mixture of CO and $O_2$ is converted catalytically to $CO_2$ by a solution of $[Rh(C_8H_{14})_2Cl]_2$ in LiCl/DMA.
**TABLE OF CONTENTS**

<table>
<thead>
<tr>
<th>ABSTRACT</th>
<th>LIST OF TABLES</th>
<th>LIST OF FIGURES</th>
<th>ABBREVIATIONS</th>
<th>ACKNOWLEDGEMENTS</th>
<th>CHAPTER I. INTRODUCTION</th>
<th>1.1 General Introduction</th>
<th>1.2 Aim and Outline of the Work</th>
<th>1.3 Catalytic Activation of Molecular Hydrogen</th>
<th>1.4 Homogeneous Catalytic Hydrogenation</th>
<th>1.41 Inorganic Substrates</th>
<th>1.42 Organic Substrates</th>
<th>1.5 Molecular Oxygen Complexes and Their Role in Homogeneous Catalysis</th>
<th>1.6 Literature Reports on Catalytic Properties of Rhodium Complexes</th>
<th>1.61 Rhodium Complexes as Hydrogenation Catalysts</th>
<th>1.62 Catalytic Isomerization of Olefins</th>
<th>1.63 Polymerization of Olefins and Acetylenes</th>
<th>1.64 Carbonylation and Decarbonylation Reactions</th>
<th>1.7 Carbonyl Complexes of Rhodium</th>
<th>1.8 Molecular oxygen complexes of Rhodium</th>
</tr>
</thead>
<tbody>
<tr>
<td></td>
<td></td>
<td>xiv</td>
<td></td>
<td></td>
<td>1</td>
<td>1</td>
<td>1</td>
<td>4</td>
<td>6</td>
<td>6</td>
<td>8</td>
<td>12</td>
<td>18</td>
<td>18</td>
<td>21</td>
<td>23</td>
<td>27</td>
<td>32</td>
<td>34</td>
</tr>
<tr>
<td></td>
<td></td>
<td></td>
<td></td>
<td></td>
<td></td>
<td></td>
<td></td>
<td></td>
<td></td>
<td></td>
<td></td>
<td></td>
<td></td>
<td></td>
<td></td>
<td></td>
<td></td>
<td></td>
<td></td>
</tr>
</tbody>
</table>
# CHAPTER II. APPARATUS AND EXPERIMENTAL PROCEDURE

<table>
<thead>
<tr>
<th>Section</th>
<th>Page</th>
</tr>
</thead>
<tbody>
<tr>
<td>2.1</td>
<td>36</td>
</tr>
<tr>
<td>2.11</td>
<td>36</td>
</tr>
<tr>
<td>2.12</td>
<td>37</td>
</tr>
<tr>
<td>2.13</td>
<td>38</td>
</tr>
<tr>
<td>2.14</td>
<td>38</td>
</tr>
<tr>
<td>2.15</td>
<td>39</td>
</tr>
<tr>
<td>2.2</td>
<td>39</td>
</tr>
<tr>
<td>2.3</td>
<td>41</td>
</tr>
<tr>
<td>2.4</td>
<td>43</td>
</tr>
<tr>
<td>2.5</td>
<td>43</td>
</tr>
<tr>
<td>2.51</td>
<td>43</td>
</tr>
<tr>
<td>2.52</td>
<td>44</td>
</tr>
<tr>
<td>2.53</td>
<td>44</td>
</tr>
<tr>
<td>2.54</td>
<td>45</td>
</tr>
<tr>
<td>2.6</td>
<td>45</td>
</tr>
</tbody>
</table>

# CHAPTER III. CATALYTIC HYDROGENATION OF OLEFINIC ACIDS BY RHODIUM (III) COMPLEXES CONTAINING SULPHUR LIGANDS

<table>
<thead>
<tr>
<th>Section</th>
<th>Page</th>
</tr>
</thead>
<tbody>
<tr>
<td>3.1</td>
<td>47</td>
</tr>
<tr>
<td>3.2</td>
<td>48</td>
</tr>
<tr>
<td>3.21</td>
<td>50</td>
</tr>
<tr>
<td>3.22</td>
<td>52</td>
</tr>
</tbody>
</table>
CHAPTER IV.

Catalytic Hydrogenation and Isomerisation of Fumaric Acid Catalyzed by RhCl₃(Et₂S)₃ in DMA

4.1 Introduction ........................................ 87
4.2 Stoichiometry of the RhCl₃(Et₂S)₃/FA/H₂/DMA System ........................................ 87
4.3 Kinetics of the RhCl₃(Et₂S)₃/FA/H₂/DMA System ........................................ 89
4.31 The Initial Rate ........................................ 94
4.32 The "Hydrogenation" Region ........................................ 98
4.4 Deuteration and Stereochemistry of the H₂ or D₂ addition ........................................ 102
4.5 Hydrogenation of a Mixture of FA and MA ........................................ 104
4.6 Discussion of the Kinetic Results for the FA System ........................................ 106
4.61 The Initial Rate ........................................ 106
4.62 The "Hydrogenation" Region ........................................ 108
CHAPTER V. DISCUSSION OF THE RHODIUM (III) SULPHUR CATALYSED HYDROGENATION OF OLEFIN

5.1 General Discussion

5.11 Initial Reduction, Formation of a Rh (olefin) Complex

5.12 Catalytic Hydrogenation

CHAPTER VI. CATALYTIC HYDROGENATION OF MALEIC ACID BY RHODIUM (I) CHLORO AND SULPHUR COMPLEXES IN DMA

6.1 General Introduction

6.2 Attempted Preparations of the Rh Complexes Containing Sulphur Ligands

6.3 The Rh (Et₂S) Catalyzed Hydrogenation of MA in DMA

6.31 Kinetics of the Rh (Et₂S) Catalyzed Hydrogenation of MA

6.4 The Rh Cl Catalyzed Hydrogenation of MA

6.41 Kinetics of the Rh Cl Catalyzed Hydrogenation of MA

6.5 Discussion of the Rh Systems

6.6 Comparison of the Substrate Hydrogenation Rate in the Rh III and Rh I Systems

CHAPTER VII. HYDROGEN REDUCTION OF DIMETHYL SULPHOXIDE CATALYZED BY RHODIUM (III) COMPLEXES CONTAINING CHLORIDE AND SULPHIDE LIGANDS

7.1 General Introduction

7.2 RhCl₃·3H₂O Catalyzed H₂ Reduction of DMSO

7.3 RhCl₃(Et₂S)₃ Catalyzed H₂ Reduction of DMSO
7.4 Kinetics of the Catalyzed Reductions .......................... 165
7.5 Discussion ...................................................... 172
7.6 Catalyzed Oxidation and Reduction of DMSO by RhCl₃·3H₂O Using a Mixture of H₂ and O₂ ........................................... 178

CHAPTER VIII. ACTIVATION OF MOLECULAR OXYGEN BY BIS(CYCLO-
OCTENE)CHLORO RHODIUM (I) IN DMA ........................ 182
8.1 Introduction ..................................................... 182
8.2 Formation of the Molecular Oxygen Complex 182
8.3 Catalytic Activity of Rh⁺(O₂) in LiCl/DMA ............................... 187
8.31 Kinetics of the Catalytic Oxidation by the Rh⁺(O₂) Complex in LiCl/DMA ....... 191
8.4 Other Catalytic Systems Involving the Oxygenation Activity of [Rh(C₈H₁₄)₂Cl]₂ 200
8.5 Discussion ...................................................... 206
8.51 Formation of the Molecular Oxygen Complex 206
8.52 Formation of Molecular Oxygen Complexes in Other Solvents ................. 211
8.53 Catalytic Oxidation Catalyzed by Rh⁺(O₂) in LiCl/DMA ....................... 212
8.54 Postulated Mechanism for the Catalytic Oxidation ............................. 214

CHAPTER IX. FORMATION AND PROPERTIES OF SOME RHODIUM CARBONYL
COMPLEXES .......................................................... 222
9.1 General Introduction ............................................. 222
9.2 Reaction of [Rh(C₈H₁₄)₂Cl]₂ with CO in LiCl/DMA ........................ 222
<table>
<thead>
<tr>
<th>Section</th>
<th>Title</th>
<th>Page</th>
</tr>
</thead>
<tbody>
<tr>
<td>9.3</td>
<td>Catalytic Reaction Between the Coordinated CO and O₂</td>
<td>228</td>
</tr>
<tr>
<td>9.4</td>
<td>Reaction of RhCl₃(Et₂S)₃ with CO in DMA.</td>
<td>230</td>
</tr>
<tr>
<td>9.5</td>
<td>Discussion</td>
<td>232</td>
</tr>
<tr>
<td>9.51</td>
<td>The [Rh(C₇H₁₄)₂Cl]₂ System</td>
<td>232</td>
</tr>
<tr>
<td>9.52</td>
<td>The RhCl₃(Et₂S)₃ System</td>
<td>236</td>
</tr>
</tbody>
</table>

**CHAPTER X.**  
GENERAL CONCLUSIONS AND RECOMMENDATIONS FOR FUTURE WORK  

REFERENCES  .................................................. 244

APPENDIX I.  
SOLUBILITY DATA FOR OXYGEN IN N,N-DIMETHYL-ACETAMIDE  .................................................. 258
### LIST OF TABLES

**RhCl$_3$(Et$_2$S)$_3$ Catalyzed Hydrogenation of CA in DMA**

| I. The effect of [Rh], [H$_2$], [CA], [LiCl] and [Et$_2$S] on the initial rate | 57 |
| II. Temperature dependence of $k_1$ | 60 |
| III. The effect of [Rh], [H$_2$], [CA], [LiCl] and [Et$_2$S] on the linear rate | 63 |
| IV. Temperature dependence of hydrogenation rate | 68 |

**RhCl$_3$(Bz$_2$S)$_3$ Catalyzed Hydrogenation of MA in DMA**

| V. Dependence of initial rate on [Rh], [H$_2$], [MA], [LiCl] and [Bz$_2$S] | 74 |
| VI. Temperature dependence of $k_1$ | 78 |
| VII. Dependence of linear rate on [Rh], [H$_2$], [MA], [LiCl] and [Bz$_2$S] | 80 |
| VIII. Temperature dependence of the hydrogenation rate | 84 |

**RhCl$_3$(Et$_2$S)$_3$ Catalyzed Hydrogenation of FA in DMA**

| IX. $k'$ values for the RhCl$_3$(Et$_2$S)$_3$ catalyzed hydrogenation of FA in DMA | 90 |
| X. The effect of [Rh], [H$_2$], [FA] and additives on the initial rate | 95 |
| XI. Temperature dependence of $k_1$ | 99 |
| XII. Variation of linear rate with [FA] | 101 |
XIII. Temperature dependence of $k'$

Comparison of the Rate and Activation Parameters for the Different $\text{Rh}^{\text{III}}$ and Olefin Systems.

XIV. Rate constants and activation parameters for the $\text{Rh}^{\text{I}}$(olefin) formation from $\text{Rh}^{\text{III}}$ in DMA

XV. Rate constants and activation parameters for the hydrogenation of $\text{Rh}^{\text{I}}$(olefin) complex in DMA

Catalyzed Hydrogenation of MA by a Solution of $[\text{Rh}(\text{C}_8\text{H}_{14})_2\text{Cl}]_2$
in $\text{Et}_2\text{S/DMA}$

XVI. Kinetic data under "air free" conditions

XVII. Kinetic data at $80^\circ$

XVIII. Temperature dependence of $k_2$

Catalyzed Hydrogenation of MA by a Solution of $[\text{Rh}(\text{C}_8\text{H}_{14})_2\text{Cl}]_2$
in $0.45 \text{ M LiCl/DMA}$

XIX. Kinetic data at $80^\circ$

XX. Temperature dependence of $k_2$

XXI. Comparison of $k_2$ values and activation parameters for the $\text{Rh}^{\text{III}}$ and $\text{Rh}^{\text{I}}$ catalyzed hydrogenation of MA in DMA
RhIII Catalyzed H₂ Reduction of DMSO

XXII. Kinetic data for the RhCl₃·3H₂O catalyzed H₂ reduction of DMSO .................................................. 166

XXIII. Kinetic data for the RhCl₃(Et₂S)₃ catalyzed H₂ reduction of DMSO .................................................. 167

XXIV. Temperature dependence of k in the RhCl₃·3H₂O catalyzed H₂ reduction of DMSO .................. 170

XXV. Temperature dependence of k in the RhCl₃·(Et₂S)₃ catalyzed H₂ reduction of DMSO .................. 170

XXVI. Comparison of the activation parameters for the heterolytic splitting in RhCl₃·3H₂O and RhCl₃(Et₂S)₃ complexes in DMA and DMSO .......................................................... 176

Catalyzed Oxidation by a Solution of [Rh(C₈H₁₄)₂Cl]₂ in 0.5M LiCl/DMA

XXVII. Variation of rate with [Rh] ............................................. 192

XXVIII Variation of rate with [O₂] ............................................. 194

XXIX. Effect of additives on rate ............................................. 196

XXX. Temperature dependence of k and K ................................. 202

Activation of CO by a Solution of [Rh(C₈H₁₄)₂Cl]₂ in 0.5M LiCl/DMA

XXXI. Kinetic data for the formation of Rhᴵ carbonyl species in DMA ......................................................... 227
LIST OF FIGURES

<table>
<thead>
<tr>
<th>Figure</th>
<th>Description</th>
<th>Page</th>
</tr>
</thead>
<tbody>
<tr>
<td>1</td>
<td>Apparatus for constant pressure gas uptake measurements</td>
<td>40</td>
</tr>
<tr>
<td>2</td>
<td>Rate plots for the RhCl$_3$(Et$_2$S)$_3$ catalyzed hydrogenation of MA in DMA at 80°</td>
<td>49</td>
</tr>
<tr>
<td></td>
<td><strong>RhCl$_3$(Et$_2$S)$_3$ catalyzed hydrogenation of CA in DMA</strong></td>
<td></td>
</tr>
<tr>
<td>3</td>
<td>Rate plots at 55° for various [Rh] and [H$_2$]</td>
<td>55</td>
</tr>
<tr>
<td>4</td>
<td>Dependence of initial rate on [Rh]</td>
<td>58</td>
</tr>
<tr>
<td>5</td>
<td>Dependence of initial rate on [H$_2$]</td>
<td>59</td>
</tr>
<tr>
<td>6</td>
<td>Arrhenius plot for the initial reduction</td>
<td>61</td>
</tr>
<tr>
<td>7</td>
<td>Dependence of linear rate on [Rh]</td>
<td>64</td>
</tr>
<tr>
<td>8</td>
<td>Dependence of linear rate on [H$_2$]</td>
<td>65</td>
</tr>
<tr>
<td>9</td>
<td>Arrhenius plot for the hydrogenation</td>
<td>69</td>
</tr>
<tr>
<td></td>
<td><strong>RhCl$_3$(Bz$_2$S)$_3$ catalyzed hydrogenation of MA in DMA</strong></td>
<td></td>
</tr>
<tr>
<td>10</td>
<td>A typical rate plot at 80°</td>
<td>73</td>
</tr>
<tr>
<td>11</td>
<td>Dependence of initial rate on [Rh]</td>
<td>75</td>
</tr>
<tr>
<td>12</td>
<td>Dependence of initial rate on [H$_2$]</td>
<td>76</td>
</tr>
<tr>
<td>13</td>
<td>Arrhenius plot for the initial reduction</td>
<td>79</td>
</tr>
<tr>
<td>14</td>
<td>Dependence of linear rate on [Rh]</td>
<td>81</td>
</tr>
<tr>
<td>15</td>
<td>Dependence of linear rate on [H$_2$]</td>
<td>83</td>
</tr>
<tr>
<td>16</td>
<td>Arrhenius plot for the hydrogenation</td>
<td>85</td>
</tr>
</tbody>
</table>
RhCl$_3$(Et$_2$S)$_3$ catalyzed hydrogenation of FA in DMA

17. Rate plots at 80° for different [FA] 988
18. Rate plot and the corresponding ln plot at 80° 991
19. Variation of k' with [Rh] 992
20. Variation of k' with [H$_2$] 993
21. Dependence of initial rate on [Rh] 996
22. Dependence of initial rate on [H$_2$] 997
23. Arrhenius plot for the initial reduction 1000
24. Rate plot for the catalyzed hydrogenation of a mixture of MA and FA at 80° 1005
25. Absorption spectra of RhCl$_3$·3H$_2$O and MA in 0.5M LiCl/DMA 1009
26. Arrhenius plot for the hydrogenation 1114

Catalyzed hydrogenation of MA by a solution of [Rh(C$_8$H$_{14}$)$_2$Cl]$_2$ in Et$_2$S/DMA

27. Rate plots at 80° for a solution made up in air; and for a solution made up in the absence of air with its corresponding log plot 1331
28. Variation of linear rate with [Rh] 1338
29. Variation of linear rate with [H$_2$] 1338
30. Arrhenius plot for the hydrogenation 1340
Catalyzed hydrogenation of MA by a solution of \([\text{Rh(C}_8\text{H}_{14})_2\text{Cl}]_2\) in 0.45M LiCl/DMA

<table>
<thead>
<tr>
<th>Table</th>
<th>Description</th>
<th>Page</th>
</tr>
</thead>
<tbody>
<tr>
<td>31.</td>
<td>Rate plots at 80° for various [Rh]</td>
<td>141</td>
</tr>
<tr>
<td>32.</td>
<td>Absorption spectra of ([\text{Rh(C}<em>8\text{H}</em>{14})_2\text{Cl}]_2) in 0.5M LiCl/DMA in vacuum and under different O(_2) pressure at room temperature</td>
<td>144</td>
</tr>
<tr>
<td>33.</td>
<td>Absorption spectra of ([\text{Rh(C}<em>8\text{H}</em>{14})_2\text{Cl}]_2) and MA in 0.45M LiCl/DMA in vacuum at room temperature</td>
<td>145</td>
</tr>
<tr>
<td>34.</td>
<td>Absorption spectra of ([\text{Rh(C}<em>8\text{H}</em>{14})_2\text{Cl}]_2) and MA in 0.45M LiCl/DMA under H(_2) at room temperature</td>
<td>146</td>
</tr>
<tr>
<td>35.</td>
<td>Variation of rate with [Rh]</td>
<td>149</td>
</tr>
<tr>
<td>36.</td>
<td>Variation of rate with [H(_2)]</td>
<td>150</td>
</tr>
<tr>
<td>37.</td>
<td>Arrhenius plot for the hydrogenation</td>
<td>152</td>
</tr>
</tbody>
</table>

H\(_2\) reduction of DMSO catalyzed by \(\text{RhCl}_3\cdot3\text{H}_2\text{O}\) and \(\text{RhCl}_3(\text{Et}_2\text{S})_3\) complexes

<table>
<thead>
<tr>
<th>Table</th>
<th>Description</th>
<th>Page</th>
</tr>
</thead>
<tbody>
<tr>
<td>38.</td>
<td>Rate plots at 80°</td>
<td>162</td>
</tr>
<tr>
<td>39.</td>
<td>Variation of rate with [Rh]</td>
<td>168</td>
</tr>
<tr>
<td>40.</td>
<td>Variation of rate with p'H(_2)</td>
<td>169</td>
</tr>
<tr>
<td>41.</td>
<td>Arrhenius plots for reduction</td>
<td>171</td>
</tr>
<tr>
<td>42.</td>
<td>A rate plot for the reaction of (\text{RhCl}_3\cdot3\text{H}_2\text{O}) and DMSO using a mixture of H(_2) and O(_2) at 80°</td>
<td>179</td>
</tr>
</tbody>
</table>
E.S.R. spectra of a solution of $[\text{Rh}(C_8H_{14})_2\text{Cl}]_2$ in 0.5M LiCl/DMA under air

43. E.S.R. spectrum of $\text{Rh}^+(O_2)$ complex at room temperature .............................................. 184
44. E.S.R. spectrum of $\text{Rh}^+(O_2)$ complex at 77°C .............. 185

Catalyzed oxidation by a solution of $[\text{Rh}(C_8H_{14})_2\text{Cl}]_2$ in 0.45M LiCl/DMA

45. Rate plots for the catalyzed oxidation at 80° ...... 188
46. Dependence of rate on [Rh] ........................................ 193
47. Dependence of rate in $p'0_2$ ................................. 195
48. Variation of rate with $[C_8H_{14}]$ ......................... 197
49. Plot of $1/\text{rate-k''}$ against $1/[O_2]$ ............................. 201
50. Arrhenius plot for the oxidation ......................... 203
51. Rate plot and the corresponding log plot for the reaction of $[\text{Rh}(C_8H_{14})_2\text{Cl}]_2$ in ethanol at 50° ...... 205

Activation of CO by a solution of $[\text{Rh}(C_8H_{14})_2\text{Cl}]_2$ in 0.5M LiCl/DMA

52. Rate plot and the corresponding log plot for the formation of $\text{Rh}^+(\text{CO})_2$ at 80° ....................... 223
53. Rate plot and the corresponding log plot for the formation of Rh\textsuperscript{I}(CO)\textsubscript{2} at 80° in a solution containing the fully formed Rh\textsuperscript{I}(O\textsubscript{2}) complex ........................................... 225

54. Rate plot for the reaction of Rh\textsuperscript{I}(CO)\textsubscript{2} with O\textsubscript{2} at 80° 229

55. Rate plot and the corresponding log plot for the formation of Rh\textsuperscript{I}(CO)\textsubscript{2} in a DMA solution of RhCl\textsubscript{3}(Et\textsubscript{2}S)\textsubscript{3} at 80° ................................................................. 231

Appendix 1

56. Solubility of O\textsubscript{2} in DMA at 87°, 80°, 75°, 70° and 25° 259
ABBREVIATIONS

The following list of abbreviations, most of them are commonly adopted in chemical research literature, will be employed in this thesis.

All temperatures are in °C unless specifically denoted by °K.

acac acetylacetonate anion, CH₃COCHCOCH₃

acacen N,N'-ethylenebis(acetylacetoniminato)

atm atmosphere

bipy 2,2'-bipyridyl

b.p. boiling point

Bz benzyl, C₆H₅CH₂

CA cinnamic acid,

Calc calculated
cobaloxime  
bis(dimethylglyoximato)cobalt

\[
\text{Co} \quad \begin{array}{c}
\text{N} \\
\text{O} \\
\text{N} \\
\text{O} \\
\text{C} \\
\text{O} \\
\text{N} \\
\text{H}
\end{array}
\]

DMA  
N,N-dimethylacetamide, \( \text{CH}_3\text{CON} (\text{CH}_3)_2 \)

DMF, dmf  
\( \text{dimethylformamide, HCON(CH}_3)_2 \)

DMSO  
\( \text{dimethyl sulphoxide (CH}_3)_2\text{SO} \)

DPPH  
2,2-diphenyl-1-picrylhydrazol, \( (\text{NO}_2)_2 \text{C}_6 \text{H}_4\text{NN(C}_6\text{H}_5)_2 \)

DTH  
2,5-dithiahexane, \( \text{CH}_3\text{SCH}_2\text{CH}_2\text{SCH}_3 \)

en  
\( \text{ethylendiamine, H}_2\text{NCH}_2\text{CH}_2\text{NH}_2 \)

E.S.R.  
electron spin resonance

Et  
ethyl, \( \text{C}_2\text{H}_5 \)

FA  
fumaric acid

Fmn  
fumaronitrile,
I.R.  infrared
L   ligand
ln  natural logarithm
M   metal atom
MA  maleic acid, \(\text{HOOC}-\text{C}=\text{C}\text{-COOH}\)
Me  methyl, \(\text{CH}_3\)
Me-O-Salen  methyoxysalen
N.M.R.  nuclear magnetic resonance
\(\sigma\)-phen  \(\sigma\)-phenathroline
p'  partial pressure
Ph  phenyl, \(\text{C}_6\text{H}_5\)
Ph\(_3\)P  triphenylphosphine
Pr\(^i\)  isopropyl
pyridine

alkyl, aryl

N,N'-ethylenebis(salicylideneiminato)

N,N'-imino-di-n-propybis(salicylideneiminato)

succinic acid, $\text{HO}_2\text{CCH}_2\text{CH}_2\text{COOH}$

symmetrically

tetracyanoethylene,

triethylenetetramine, $\text{H}_2\text{NCH}_2\text{CH}_2\text{NHCH}_2\text{CH}_2\text{NHCH}_2\text{CH}_2\text{NH}_2$

halogen unless stated otherwise.

molar extinction
$\checkmark$ frequency, cm$^{-1}$

u.v. ultraviolet
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CHAPTER I
INTRODUCTION

1.1 General Introduction

In the past five years important advancements have been made in the field of homogeneous catalysis. Among the most significant developments are the discovery and elucidation of various new, and often novel, catalytic reactions of transition metal ions and compounds. New catalysts for reactions such as hydrogenation of olefins, hydroformylation of olefins (oxo process), dimerization of ethylene and polymerization of dienes, double bond migration in olefins, oxidation of olefins to aldehydes and vinyl esters (Wacker process), carbonylation and decarbonylation reactions, the hydration of acetylenes, etc. have been reported. The group VIII platinum metal complexes have been found to be particularly active for such reactions. Homogeneous catalysis has attracted much interest in recent years because of the novelty of the chemistry it reveals and its potential applications.

1.2 Aim and Outline of the Work

The main object of the present work was initially to investigate further the use of rhodium complexes particularly those containing sulphide ligands in non-aqueous solvents for the activation of molecular
hydrogen for catalytic hydrogenation reactions. In instances where
activation of molecular hydrogen was observed, the detailed kinetics
of the reactions were investigated and reaction mechanisms have been
postulated.

Some results obtained in this laboratory showed that rhodium
trichloride trihydrate, $^{1,2}$ RhCl$_3$H$_2$O, and cis 1,2,3-trichlorotris-
(diethyl sulphide) rhodium (III), $^{3,4}$ RhCl$_3$(Et$_2$S)$_3$, in dimethylacetamide
(DMA) solution were effective catalysts for the hydrogenation of olefins.
Detailed kinetic studies suggested that the rhodium (III) complexes
were activated by reduction to rhodium (I) complexes via heterolytic
splitting of the hydrogen molecule (section 1.3). The rhodium (I)
complexes were stablized in solution through rapid complexing with the
olefinic substrate. Further reaction of the rhodium (I) olefin complex
with hydrogen produced the paraffin and regenerated the rhodium (I)
catalyst. The mechanism postulated is represented below:

$$\text{Rh}^{\text{III}} + H_2 \xrightarrow{k_1} \text{Rh}^{\text{I}} + 2H^+ \quad (1.1)$$

$$\text{Rh}^{\text{I}} + \text{olefin} \xrightarrow{\text{fast}} \text{Rh}^{\text{I}}(\text{olefin}) \quad (1.2)$$

$$\text{Rh}^{\text{I}}(\text{olefin}) + H_2 \xrightarrow{k_2} \text{Rh}^{\text{I}} + \text{paraffin} \quad (1.3)$$

(ligands such as Cl$^-$, H$_2$O, Et$_2$S, DMA have been omitted).

Other than our report on the catalytic activity of RhCl$_3$(Et$_2$S)$_3$, $^{3,4}$
no other catalytic systems using rhodium complexes with sulphur ligands
have been reported, although Bailar and Tayim$^5$ have reported that
complexes of the type $\text{MX}_2(Q\text{Ph}_n)_2$ ($M = \text{Pt or Pd}$; $X = \text{halide}$; $Q = \text{P or As}$
when \( n = 3 \); and S or Se when \( n = 2 \); Ph = phenyl) catalyze the hydrogenation of nonaromatic polyolefins but only in the presence of SnCl\(_2\) as co-catalyst. In the present work, the hydrogenation of various olefinic substrates catalyzed by \( \text{RhCl}_3(\text{Et}_2\text{S})_3 \) were studied in more detail and these studies were extended to other sulphur ligand systems (Chapters III-V).

Solvent effects have been shown to be of prime importance in determining the activity of rhodium chloride hydrogenation catalysts.\(^1\) Dimethyl sulphoxide (DMSO) was used to some extent in the present work as a solvent medium in an attempt to study such effects and hydrogenation was observed in the absence of any substrate. This has been shown\(^6\) to be a catalytic reduction of the solvent and these studies will also be described (Chapter VII).

Our earlier studies\(^1-4\) suggested that rhodium (I) complexes were responsible for catalytic activity. Furthermore, chlorotris(triphenylphosphine)rhodium (I),\(^7-10\) \( \text{RhCl(Ph}_3\text{P})_3 \), had been found to be an extremely active catalyst for hydrogenation reactions. Encouraged by these reports, preparations of rhodium (I) complexes with sulphur containing ligands were attempted, with a view to investigate their catalytic properties. However, no such rhodium (I) complexes were isolated, although the bis(cyclo-octene)chloro-rhodium (I) complex \( [\text{Rh(C}_8\text{H}_{14})_2\text{Cl}]_2 \), was found to be a convenient source for preparing "in situ" this type of species, whose catalytic activity was studied (Chapter VI).

In the course of studying the catalytic activity of some rhodium (I) complexes for homogeneous hydrogenation, it was found that the solution was sensitive to traces of oxygen and that no oxidation to the rhodium(III) state was occurring. Further investigation showed that
[Rh(C\textsubscript{8}H\textsubscript{14})\textsubscript{2}Cl\textsubscript{2}] in DMA forms a 1:1 complex with molecular oxygen. The current interest in the formation and properties of molecular oxygen complexes for catalytic oxygenation reactions (section 1.5) decided us to extend our aim and study in detail the formation and catalytic activity of this molecular oxygen complex (Chapter VIII).

The activity of some rhodium (III) and rhodium (I) carbonyl complexes towards hydrogenation and oxidation were also briefly studied (Chapter IX).

A considerable amount of literature has appeared in the last few years on the activation of hydrogen and the catalytic aspects generally of rhodium complexes in solution. There are, however, relatively few reports on the activation of molecular oxygen. Some of the more pertinent data reported on general catalysis by rhodium complexes will be presented after sections on H\textsubscript{2} and O\textsubscript{2} activation.

1.3 Catalytic Activation of Molecular Hydrogen

The ability to activate molecular hydrogen homogeneously in solution has been found for a large number of transition metal ions and complexes\textsuperscript{11-17} In each case, it appears that H\textsubscript{2} is split by the catalyst, with the formation of a hydrido-transition metal complex which acts as the reactive intermediate for catalytic hydrogenation. Three distinct mechanisms for the activation of H\textsubscript{2} have been recognized\textsuperscript{11-15} and are exemplified by equations (1.4)-(1.6).

Heterolytic splitting:\textsuperscript{18}

\begin{equation}
\text{Ru}^{\text{III}}\text{Cl}_{6}^{3-} + \text{H}_2 \rightarrow \text{Ru}^{\text{III}}\text{Cl}_{3}\text{H}^{3-} + \text{H}^{+} + \text{Cl}^{-} \quad (1.4)
\end{equation}
Homolytic splitting$^{19-21}$:

$$2\text{Co}^{II}(\text{CN})_5^3^- + \text{H}_2 \rightarrow 2\text{Co}^{III}(\text{CN})_5^3^- \quad (1.5)$$

Dihydride formation$^{22,23}$:

$$\text{Ir}^1\text{ClCO(Ph}_3\text{P)}_2 + \text{H}_2 \rightarrow \text{Ir}^{III}\text{H}_2\text{Cl(CO)(Ph}_3\text{P)}_2 \quad (1.6)$$

Heterolytic splitting as exemplified by equation (1.4) is probably the most widespread mechanism for the activation of $\text{H}_2$ in solution. It is essentially a substitutional process in which one of the original ligands of the catalyst is replaced by $\text{H}^-$, without any change in the formal oxidation number of the metal atom. Reactivity towards $\text{H}_2$ in such cases is therefore governed by the stability of the hydride complex, the ease of the displacement of the original ligand and the availability of a suitable base (which may be the solvent molecule or the displaced ligand itself) to stabilize the released proton.$^{12,15}$ For example, the reactivity of copper (II)$^{24}$ and silver (I)$^{25}$ complexes show an inverse dependence on the stability of the metal-ligand bond and a direct dependence on the basicity of the ligand.

The other two mechanisms of $\text{H}_2$ splitting, namely homolytic splitting and dihydride formation, involve formal oxidation of the metal ion and the hydride formation is closely linked to the susceptibility of the metal to oxidation and the ability of the metal ion to expand its coordination shell.$^{15}$ For a given metal ion, reactivity is expected to
be enhanced by ligands which are most effective in stabilizing higher oxidation states. Thus the high reactivity of Co(CN)$_5^{3-}$ towards H$_2$, as compared with the corresponding reactivities of the isonitrile or dimethylglyoxime cobalt (II) complexes, is thought to reflect the greater effectiveness of the CN$^-$ ligands in stabilizing cobalt (III) relative to cobalt (II).\^15 Regarding dihydride formation, square planar d$^8$ complexes have been found to readily undergo oxidative addition of H$_2$ to give the corresponding d$^6$ complexes, and the ease of oxidative addition\^14,15,26,27 (subject to some modification by ligand variation) is expected to follow the approximate sequence

\[
\text{Os}^0 > \text{Ru}^0 > \text{Fe}^0, \quad \text{Ir}^I > \text{Rh}^I > \text{Co}^I, \\
\text{Pt}^{II} >> \text{Pd}^{II} >> \text{Ni}^{II}, \quad \text{Au}^{II}
\]

1.4 Homogeneous Catalytic Hydrogenation

The reactive nature of the hydrido-transition metal complexes formed by the previously described mechanisms permits them to function as intermediates in homogeneous hydrogenation reactions for both inorganic and organic substrates.

1.41 Inorganic substrates

Literature reports show that homolytic and heterolytic splitting of hydrogen are observed in the activation step for the reduction of inorganic substrates. An example of each will be given.

Calvin and Wilmarth\^28 showed that Cu$^I$ acetate, in quinoline
solution, catalyzed homogeneously the reduction of Cu$^{II}$. The rate
determining step is thought to be the homolytic splitting of H$_2$,
followed by a fast step involving reduction of the substrate. The
rate of H$_2$ uptake is proportional to the H$_2$ concentration and the
square of the Cu$^I$ concentration.

$$2Cu^I + H_2 \xrightarrow{k_1} 2Cu^{II}H \quad (1.7)$$
$$k_1$$

$$Cu^{II}H + Cu^{II} \xrightarrow{\text{fast}} 2Cu^I + H^+ \quad (1.8)$$

Harrod and Halpern$^{29}$ showed that in the reduction of Fe$^{III}$,
catalyzed by RhCl$_3$$^3$H$_2$O in aqueous 3 M HCl, the rate determining step
involved heterolytic splitting of H$_2$. The hydride intermediate,
Rh$^{III}H^-$, then reduces Fe$^{III}$ in a fast step regenerating the initial
Rh$^{III}$ species. The reaction scheme can be represented as follows:

$$Rh^{III} + H_2 \xrightarrow{k_1} Rh^{III}H^- + H^+ \quad (1.9)$$
$$k_1$$

$$Rh^{III}H^- + 2Fe^{III} \xrightarrow{\text{fast}} Rh^{III} + 2Fe^{II} + H^+ \quad (1.10)$$

Direct evidence for the equilibria in the initial step has been
obtained in the corresponding Ru$^{III}$ system by isotopic exchange
studies with deuterium.$^{18,30}$ Rhodium (III) hydrides are well known$^{31,32}$
to sometimes transform to rhodium (I) plus a proton,

$$Rh^{III}H^- \rightarrow Rh^I + H^+ \quad (1.11)$$
and the reduction of ferric could involve a rhodium (I) species. Complexes of copper (II), silver (I), mercury (II), palladium (II), ruthenium (III), cobalt (II) have also been found to be active catalysts for the hydrogen reduction of inorganic substrates via such homolytic or heterolytic processes.

1.42 Organic substrates

Homogeneous catalytic hydrogenation of organic substrates may be effected through transfer of hydrogen from hydrido-transition metal complexes. The following examples illustrate how this can be realised for each of the three mechanisms of splitting of hydrogen (heterolytic, homolytic and dihydride formation) described in section 1.3.

Heterolytic splitting of molecular hydrogen is exemplified by the chlororuthenate (II) catalyzed hydrogenation of olefinic carboxylic acids such as fumaric and maleic acids in aqueous solutions. The mechanism can be pictured as follows:

Scheme I
The rate determining step is the heterolytic splitting of \( \text{H}_2 \) by a 1:1 \( \text{Ru}^{II} \)(olefin) \( \pi \)-complex. The hydrido \( \text{Ru} \)(olefin) \( \pi \)-complex then rearranges to a Ru-alkyl \( \sigma \)-complex, through the "insertion" of the olefin into the Ru-H bond; nucleophilic attack by a proton gives the hydrogenated product and regenerates the catalyst.

Two features of this mechanism, namely coordination of the olefin to the metal as a \( \pi \)-bonded ligand and "insertion" of the olefin into a metal-hydrogen bond, are encountered in a number of other homogeneously catalyzed hydrogenation reactions.11

Pentacyanocobalt (II) is found to catalyze homogeneously the hydrogenation of conjugated olefins19-21 such as butadiene, in aqueous solution. Detailed studies by de Vries19, Kwiatek and Seyler20-21 suggested that the reaction proceeds by the following mechanism:

\[
2[\text{Co(CN)}_5]^{3-} + \text{H}_2 \rightleftharpoons 2[\text{HCo(CN)}_5]^{3-} \tag{1.12}
\]

\[
[\text{HCo(CN)}_5]^{3-} + \text{CH}_2=\text{CHCH}=\text{CH}_2 \rightarrow [\text{CH}_3\text{CH}=\text{CHCH}_2\text{Co(CN)}_5]^{3-} \tag{1.13}
\]

\[
[\text{CH}_3\text{CH}=\text{CHCH}_2\text{Co(CN)}_5]^{3-} \rightarrow \frac{[\text{HCo(CN)}_5]^{3-}}{[\text{HCo(CN)}_5]^{3-}} \rightarrow \text{CH}_3\text{CH}_2\text{CH}=\text{CH}_2 + 2[\text{Co(CN)}_5]^{3-} \tag{1.14}
\]

\[
\text{CH}_3\text{CH}=\text{CHCH}_2\text{Co(CN)}_5^{3-} \rightarrow \text{CH}_3\text{CH}=\text{CHCH}_3 + 2[\text{Co(CN)}_5]^{3-}
\]
The initial step involves homolytic splitting of H₂ by pentacyano-cobalt (II), followed by complexing of the butadiene to give the intermediate \([\text{CH}_3\text{CH}=\text{CHCH}_2\text{Co(CN)}_5]^{3-}\). This then undergoes reaction with the hydrido species in two different ways, depending on cyanide concentration, to give 1 or 2-butene. However, the \([\text{Co(CN)}_5]^{3-}\) catalyzed hydrogenation of cinnamate \([\text{C}_6\text{H}_5\text{CH}=\text{CHCO}_2^-]\) has been suggested to involve a radical anion intermediate.  

\[
2[\text{Co(CN)}_5]^{3-} + \text{H}_2 \rightleftharpoons 2[\text{HCo(CN)}_5]^{3-} \quad (1.15)
\]

\[
[\text{HCo(CN)}_5]^{3-} + [\text{C}_6\text{H}_5\text{CH}=\text{CHCO}_2^-]^- \rightarrow [\text{Co(CN)}_5]^{3-} + [\text{C}_6\text{H}_5\text{CH}_2\text{CHCO}_2^-]^- \quad (1.16)
\]

Wilkinson and coworkers reported that \(\text{RhCl(Ph}_3\text{P)}_3\) in benzene is an active catalyst for homogeneous hydrogenation of olefins containing isolated double bonds, but not ethylene itself. The mechanism of the reaction involves the formation of the cis dihydride \(\text{RhCl(Ph}_3\text{P)}_2\text{H}_2\), this then reacts with the olefin in the rate determining step to produce the paraffin. The activity of the \(\text{RhCl(Ph}_3\text{P)}_3\) complex depends on its ability to dissociate in solution to form the active species \(\text{RhCl(Ph}_3\text{P)}_2\text{S}\) where \(S\) is the solvent molecule which can be easily displaced by the olefin or hydrogen. A mechanism consistent with the kinetic data is as follows:
Wilkinson and coworkers\textsuperscript{8} showed that under their experimental conditions the $k''$ path is of negligible significance and the paraffin is produced solely by the attack of the olefin on the dihydride species. A very similar reaction scheme has been proposed by James and Memon\textsuperscript{35} for the hydrogenation of olefins using IrCl(CO)(Ph\textsubscript{3}P)\textsubscript{2} although these workers concluded that the $k''$ path is the more likely hydrogenation process. Work by Candlin and Oldham\textsuperscript{36} has indicated that hydrogenation catalyzed by RhCl(Ph\textsubscript{3}P)\textsubscript{3} can occur by both routes.

The mechanism of hydrogenation of unsaturated substrates can be regarded as one involving three steps:\textsuperscript{11} (1) hydrogen activation, (2) substrate activation, (3) hydrogen transfer. The question as to whether both olefin and hydrogen activation are required at the same time or whether only one needs to be activated has been the subject of interest for some time.\textsuperscript{11} Some recent studies have indicated that activation of both are required.\textsuperscript{9,37} The transfer of hydrogen to olefins
in the monohydride systems (or the hydrometallation step) is an example of a much wider class of "insertion type" reactions which are commonly observed in many catalytic reactions.\textsuperscript{11-15,38} The process of hydrogen transfer in the cis-dihydride systems (e.g. from \( \text{RhCl(Ph}_3\text{P)}\)\textsubscript{2}H\textsubscript{2} \) remains somewhat uncertain; this was originally thought to involve simultaneous transfer of both hydrogens, each by a three centre transition state. More recent data,\textsuperscript{39-41} however, suggest that the hydrogens are transferred consecutively, involving a \( \sigma \)-alkyl intermediate.

At the recent Faraday Society Meeting\textsuperscript{8}, a subsidiary question of general interest was the extent of formation and lifetime of these intermediates, since reproduction of the hydrido-olefin complexes before the saturated hydrocarbon is formed can give rise to catalytic isomerization:

\[
\text{CH}_2=\text{CH-CH}_2 \rightleftharpoons \text{CH}_3-\text{CH=CH}_2 \rightleftharpoons \text{CH}_3-\text{CH} \cdot \text{CH} \text{ (1.19)}
\]

Bond and Hillyard\textsuperscript{40} reported the formation of considerable quantities of isomerized olefin during hydrogenation of 1-pentene, catalyzed by RhCl(Ph\textsubscript{3}P)\textsubscript{3}. Similar but less detailed observations were reported by Abley and McQuillin\textsuperscript{43} suggesting that alkyl complexes are indeed formed. The mechanism proposed by James and Rempel\textsuperscript{1,2,41} for maleic acid hydrogenation also involved an alkyl intermediate.

\section*{1.5 Molecular Oxygen Complexes and Their Role in Homogeneous Catalysis}

Synthetic reversible oxygen-carrying complexes have been of interest
as model compounds in the study of reversible oxygenation mechanisms involved in the very complex natural oxygen carriers, e.g. the haemoglobins and haemocyanins and as a means of separating molecular oxygen from the air. The first example of a synthetic reversible oxygen-carrying compound was bis-salicylaldehyde-ethylenediamine-cobalt (II) studied some 30 years ago.\textsuperscript{44,45} Since then a number of chelates, especially those of Co\textsuperscript{II}, have been found to be reversible oxygen carriers,\textsuperscript{46-57} but very few studies of a definitive nature have been carried out on these species because they are generally unstable or poorly characterised. Recently, there have been reports of the E.S.R. spectrum of these Co\textsuperscript{II} (oxygen) complexes.\textsuperscript{55-57}

Vaska's\textsuperscript{58} discovery of the reversible molecular oxygen carrier IrCl(CO)(Ph\textsubscript{3}P)\textsubscript{2} is of great importance since the 1:1 oxygen adduct, Ir(O\textsubscript{2})Cl(CO)(Ph\textsubscript{3}P)\textsubscript{2}, may be recrystallized and is extremely stable and well-characterised. X-ray studies\textsuperscript{59,60} have been performed on Ir(O\textsubscript{2})Cl(CO)(Ph\textsubscript{3}P)\textsubscript{2}, and the two oxygen atoms are found to be equidistant from the Ir atom, with the O-O distance (1.30 Å) longer than that of molecular O\textsubscript{2} (1.21 Å) and significantly shorter than that of O\textsuperscript{2-} (1.49 Å), and corresponding closely to O\textsuperscript{2-} (1.28 Å). The equivalence of the oxygen atoms is consistent with Griffith's\textsuperscript{61} model of the π-bonding of molecular oxygen to iron in oxyhaemoglobin (also a 1:1 oxygen carrier). The fact that oxygen uptake is reversible and that the O-O bond length is significantly shorter than that in a typical peroxide are consistent with the views of Martell and Calvin\textsuperscript{50} that reversibility probably depends upon some electron transfer from metal to oxygen, but not sufficient transfer to bring about irreversible oxidation of the metal.
In this case, this transfer seems to approximate to one electron, since the 0-0 distance corresponds closely to that in $O_2^-$. However, this predicts an oxidation state of a $d^7$ Ir$^{II}$ and yet the compound is diamagnetic. The situation is clearly more complex than simple electron transfer from the metal to the oxygen, and more recent interpretations $^{62,63}$ of the bonding involve adoption of a three-centre molecular orbital scheme for the metal and two oxygen atoms; the length of the 0-0 bond and the strength of the bonding to the metal atom are particularly sensitive to the electronegativity of the other coordinated ligands. $^{62}$ Iridium complexes are best thought of as five coordinate with a $\pi$-bonding $O_2$ molecule. $^{62,63}$ The strength of the metal-oxygen bond is related to the electron density available in the metal atom for back-bonding to the antibonding molecular orbitals on the $O_2$ molecule. $^{64}$

Since the discovery of the Ir$(O_2)Cl(CO)(Ph_3P)_2$ complex, molecular oxygen has been found to add to several reactive $d^8$ and $d^{10}$ metal complexes $^{26,65-67}$ to form diamagnetic compounds with retention of the 0-0 bond. These include complexes of Ir$^I$ $^{58-60,62-64,68-70}$, Rh$^{I}$ $^{64,71-73}$, Ru$^0$ $^{74}$, Pd$^0$ $^{75-77}$, Pt$^0$ $^{75,76,78}$, and Ni$^0$ $^{75-77,79}$.

The most significant property of some of these molecular oxygen complexes is their ability to oxygenate substrates under unusually mild conditions. Both stoichiometric and catalytic oxidations have been described. For example, autoxidations of triphenylphosphine $^{75}$ and t-butyl isocyanide $^{77,79}$ are catalyzed by oxygen complexes of palladium and nickel. Stoichiometric oxidations of gaseous non-metal oxides such as CO $^{26}$, NO $^{80}$, SO$_2$ $^{81}$, NO$_2$ $^{81}$ and CO$_2$ $^{82}$ have been observed and organic compounds such as cyclohexene and ethylbenzene have been
found to undergo autoxidations catalyzed by these molecular oxygen complexes. 80,83-85

The mechanism of these catalytic oxidations is a subject of current interest. 15 Two mechanisms, one involving a dissociative "oxygen insertion" step and the other involving free radicals have been proposed to date.

The kinetics of the catalytic oxidation of triphenylphosphine to triphenylphosphine oxide by tetrakistriphenylphosphine platinum (0) in benzene have been studied by Halpern and coworkers. 86 The mechanism of the reaction involves the initial formation of a platinum (0) molecular oxygen complex which then further reacts with excess triphenylphosphine to produce the triphenylphosphine oxide through a dissociative "oxygen insertion" step. The mechanism of the reaction is represented below:

$$\text{Pt(Ph}_3\text{P)}_4 \xrightleftharpoons[^K]{\text{benzene}} \text{Pt(Ph}_3\text{P)}_3 + \text{Ph}_3\text{P} \quad (1.20)$$

$$\text{Pt(Ph}_3\text{P)}_3 + \text{O}_2 \xrightarrow[k_1]{\text{}} \text{Pt(Ph}_3\text{P)}_2\text{O}_2 + \text{Ph}_3\text{P} \quad (1.21)$$

$$\text{Pt(Ph}_3\text{P)}_2\text{O}_2 + \text{Ph}_3\text{P} \xrightarrow[k_2]{\text{}} \text{Ph}_3\text{P}\text{Pt} \quad (1.22)$$

$$\text{Pt(Ph}_3\text{P)}_3 + 2\text{Ph}_3\text{PO} \xleftarrow[\text{fast}]{2\text{Ph}_3\text{P}} \text{Ph}_3\text{P}\text{Pt} \quad (\text{OPh})_3\text{P} \quad (\text{OPh})_3\text{P}$$
Kurkov, Pasky and Lavigne proposed that the chlorotris(triphenylphosphine)rhodium(I) catalyzed autoxidations of cyclohexene and ethylbenzene involve a free-radical chain mechanism. The chain nature of the reaction was demonstrated by the complete inhibition of the oxidation by hydroquinone. They proposed that rhodium, by analogy with cobalt, catalyzes chain initiation by a Haber-Weiss type mechanism.

\[
\text{ROOH} + \text{Rh}^I \rightarrow \text{RO}^- + \text{OH}^- + \text{Rh}^{II} \quad (1.23)
\]

\[
\text{ROOH} + \text{Rh}^{II} \rightarrow \text{ROO}^- + \text{H}^+ + \text{Rh}^I \quad (1.24)
\]

An alternative mechanism which involves a two electron transfer was also suggested:

\[
2\text{ROOH} + \text{Rh}^I \rightarrow 2\text{RO}^- + 2\text{OH}^- + \text{Rh}^{III} \quad (1.25)
\]

\[
2\text{ROOH} + \text{Rh}^{III} \rightarrow 2\text{ROO}^- + 2\text{H}^+ + \text{Rh}^I \quad (1.26)
\]

This mechanism requires termolecular reactions and is considered less likely. For the case of cobalt, it has been shown that electron transfer involves a prior complex formation between the hydroperoxide and the catalyst. Autoxidation of diphenylmethane catalyzed by \(\text{RhCl(CO)(Ph}_3\text{P)}\text{)}_2\) is also thought to go through a Haber-Weiss type mechanism involving one electron transfer.

Fallab has suggested that the polarisation of the \(O_2\) molecule as a result of the more or less labile linkage with the activator
molecule \( M \) (transition metal complex) may be sufficient to facilitate reaction with an autooxidizable substrate \( RH \):

\[
M + O_2 \rightleftharpoons M^{\delta+}O_2^{\delta-} \quad (1.27)
\]

\[
M^{\delta+}O_2^{\delta-} + RH \rightarrow M + R^\cdot + HO_2^\cdot \quad (1.28)
\]

In principle, a strongly electropositive activator \( M \) could cause heterolysis of the \( O_2 \) molecule into highly reactive atomic particles; however, such a reaction has never been observed in practice. 48

\[
M^{\delta+}O_2^{\delta-} \rightarrow M + O^+ + O^- \quad (1.29)
\]

The mechanisms of these autoxidations promoted by molecular oxygen complexes remain to be clarified. It seems likely that in many instances both the substrate and the oxygen molecule must be in the same coordination sphere for oxygenation to take place. 26 The facile oxidation of ligands such as CO, isocyanides and phosphines lends support to the above supposition. These reactions could then be considered as examples of metal ion promoted, atom transfer redox reactions. The studied autoxidations of organic substrates 80,83,84,90 seem to show a free radical mechanism. Collman 26 indicated that non-radical autoxidations may be found for organic substrates which can be incorporated in the coordinated sphere adjacent to the coordinated oxygen. The existence of numerous oxygenases, metalloenzymes, 91 which catalyze the direct oxygenation of organic substrates (at least in some instances by
non-radical pathways), sustains the expectation that non-radical, atom transfer oxidations of organic substrates by metal-oxygen complexes would be realized.

1.6 Literature Reports on the Catalytic Properties of Rhodium Complexes

A very comprehensive review, by James on the reactions and catalytic properties of rhodium complexes in solution surveyed the literature up to the middle of 1966. Since this time a considerable number of publications have appeared on this topic. Rhodium(I) and rhodium(III) complexes, particularly with coordinated phosphines and halides, have usually been involved. A literature survey of these catalytic reactions which are pertinent to the present work will be briefly described in the following sections.

1.6.1 Rhodium Complexes as Hydrogenation Catalysts

In 1939, Iguti first reported that $[\text{Rh(NH}_3]^5(H_2O)]\text{Cl}_3$, $[\text{Rh(NH}_3]^4\text{Cl}_2]\text{Cl}$ and $\text{RhCl}_3$ in aqueous acetate solution activated molecular hydrogen for reduction of quinone, fumaric acid and sodium nitrite. However, traces of metallic rhodium, a powerful heterogeneous catalyst, were found during some recently studied similar reactions, and the above systems may have been heterogeneously catalyzed. Halpern and Harrod in 1959 found that chlororhodate(III) species in aqueous solutions catalyzed homogeneously the hydrogen reduction of the ferric ion. Extension of this work by James and Rempel showed that only the anionic, labile chlororhodate(III) species were effective catalysts. The activity of the species increasing with increasing numbers of coordinated
chloride ligands. These chlororhodate(III) species in aqueous acid solutions were not effective for homogeneous hydrogenation of olefinic substances. However RhCl$_3$·3H$_2$O in DMA solution was found to catalyze the hydrogen reduction of various substituted ethylenes$^{1,2}$ as well as ethylene itself.$^{31,94}$

A number of workers, particularly Wilkinson's group, have reported the hydrogenation of olefins and acetylenes using a number of rhodium(III) and rhodium(I) complexes as homogeneous catalysts in ethanol, benzene or ethanol-benzene mixtures. These complexes include

- RhCl$_3$·3H$_2$O$^{95}$
- 1,2,6-Rh(py)$_3$Cl$_3$$^{95,96}$
- Rh$_2$Cl$_2$[SnCl$_2$·EtOH]$_4$ $^{96}$
- triphenylphosphine derivatives 1,2,3-RhCl$_3$(Ph$_3$P)$_3$$^{96,97}$
- RhCl(Ph$_3$P)$_3$ $^{7-10}$
- [RhCN(Ph$_3$P)$_2$]$_2$$^{98}$
- RhH(CO)(Ph$_3$P)$_3$$^{99-102}$
- RhCl(CO)(Ph$_3$P)$_2$$^{103,104}$

The detailed kinetics of these systems have not generally been given because the majority of these systems are quite complex: for example, hex-1-ene, a frequently used olefin substrate is catalytically isomerized by ethanolic RhCl$_3$·3H$_2$O.$^{105}$ Bond and Hillyard$^{40}$ reported the formation of considerable quantities of isomerized olefin during hydrogenation of 1-pentene catalyzed by RhCl(Ph$_3$P)$_3$.

RhCl(Ph$_3$P)$_3$$^{7-10}$ in benzene is an extremely active catalyst for the hydrogenation of compounds containing isolated olefinic and acetylenic linkages. The catalytic activity of RhX(Ph$_3$P)$_3$$^{8,9}$ increased in the order X = Cl < Br < I. Recently Candlin and Oldham$^{36}$ studied the homogeneous hydrogenation of mixed unsaturated substrates using RhCl(Ph$_3$P)$_3$ and found that the degree of selectivity achieved can be enhanced by the addition of polar solvents. They reported that the degree of participation of two kinetically indistinguishable forward routes, i.e.
via substrate attack on a hydrido intermediate, or hydrogen attack on a substrate intermediate, (see Scheme II) may also be of importance in determining the degree of selectivity. Hydrogenation of cycloalkenes using RhCl(Ph₃P)₃ were also reported by other groups.¹⁰⁶-¹⁰⁸ RhCl(Ph₃P)₃ was used in the selective reduction of steroid carbonyl groups¹⁰⁹ and in a variety of organic syntheses involving selective hydrogenation.¹¹⁰-¹¹³ RhCl(C₂H₄)(Ph₃P)₂ and RhCl₂H(Ph₃P)₃ were also found to be active catalysts for the reduction of alkynes and alkenes, the latter complex becoming active as a Rh¹⁺ species.³⁶ Rh(NO)(Ph₃P)₃ was found to catalyze the hydrogenation of terminal and cyclic olefins.¹¹⁴

The rhodium carbonyl complexes RhH(CO)(Ph₃P)₃⁹⁹-¹⁰² and RhCl(CO)(Ph₃P)₂¹⁰³,¹⁰⁴ also catalyze the hydrogenation reactions but these complexes, unlike RhCl(Ph₃P)₃ show no detectable reaction with hydrogen or olefin.⁷,⁹⁹,¹⁰⁰,¹⁰²,¹⁰³ RhH(CO)(Ph₃P)₃¹⁰⁰,¹⁰²,¹¹⁵ is active for a variety of other catalytic reactions, such as hydrogen-deuterium exchange, isomerization and hydroformylation of alkenes. The catalytic activity of RhCl(CO)(Ph₃P)₂ is much less than that of the RhCl(Ph₃P)₃ species.⁷ Substitution of CO into chlororuthenate(II) complexes similarly results in decreased activity.¹¹⁶

Wilkinson's¹¹⁷ group recently reported that the protonation of Rh₂(COMe)₄ by aqueous HBF₄ produced the green, air stable, diamagnetic ion, Rh₂⁴⁺. On addition of ligands, notably Ph₃P, the resulting cationic species provide new systems for catalytic reactions, in particular, for the hydrogenation of alkynes and alkenes. This system has an advantage over the other complexes such as RhCl(Ph₃P)₃ and RhH(CO)(Ph₃P)₃ because it will operate in polar media such as methanol.
Osborn and coworkers\textsuperscript{118} reported the Rh\textsuperscript{III} cations [RhH\textsubscript{2}(Ph\textsubscript{3}P)\textsubscript{2}S\textsubscript{2}]\textsuperscript{+} (S = (CH\textsubscript{3})\textsubscript{2}CO, C\textsubscript{2}H\textsubscript{5}OH) in tetrahydrofuran effectively catalyze the hydrogenation of olefinic and acetylenic bonds. Jardine and McQuillin\textsuperscript{119} reported that [py\textsubscript{2}(dmf)RhCl\textsubscript{2}(BH\textsubscript{4})] [py = pyridine, dmf = dimethylformamide] is an extremely active catalyst for hydrogenation of oct-1-ene and cycloalkenes, and shows high selectivity in the homogeneous hydrogenation of 3-oxo-\Delta^{4,5}-steroids. Catalytic asymmetric using optically active rhodium complexes RhCl\textsubscript{3}L\textsubscript{3}, where L = P\textsuperscript{*}PhMePr or PhP(CH\textsubscript{2}CHMeEt)\textsubscript{2} has been reported.\textsuperscript{120} Trichlorotris(4-biphenyl-1-napthylphenyl phosphine)rhodium(III)\textsuperscript{121} and the rhodium aminophosphine\textsuperscript{122} were also reported as hydrogenation catalysts.

RhCl(Ph\textsubscript{3}As)\textsubscript{3} and RhCl(Ph\textsubscript{3}Sb)\textsubscript{3} are less efficient for homogeneous hydrogenation\textsuperscript{71} compared to RhCl(Ph\textsubscript{3}P)\textsubscript{3}. No corresponding sulphide complexes appear to have been studied. However, RhCl\textsubscript{3}(Et\textsubscript{2}S)\textsubscript{3}\textsuperscript{3,4} has been shown to be an active catalyst for the hydrogenation of ethylene and substituted ethylenes in DMA, and intermediate rhodium(I) species are thought to be involved.

1.62 Catalytic Isomerization of Olefins

Of related interest to catalytic hydrogenation reactions, is the catalyzed isomerization of olefins; in some systems, isomerization may accompany hydrogenation.\textsuperscript{17,40}

Complexes of rhodium have been intensively studied as isomerization catalysts. The major contributions are those by Cramer;\textsuperscript{123-126} an active catalyst in ethanolic HCl is obtained as an equilibrium mixture containing Rh\textsuperscript{III} and Rh\textsuperscript{I} by a fast anaerobic reaction of inactive
[(C\textsubscript{2}H\textsubscript{4})\textsubscript{2}RhCl\textsubscript{2}] or (acac)Rh(C\textsubscript{2}H\textsubscript{4})\textsubscript{2} with HCl. Harrod and Chalk\textsuperscript{105} reported the isomerization of olefins catalyzed by rhodium trichloride and other platinum metal complexes. In these systems, the catalytic species were thought to be hydride complexes, and isomerization occurred via alkyl intermediates.

Reinhart and Lasky\textsuperscript{127} studied the isomerization of 1,3-cyclooctadiene to 1,5-cyclooctadiene, in the presence of RhCl\textsubscript{3} and postulated a somewhat different mechanism involving rearrangement through a \pi\-allyl hydride intermediate:

\begin{equation}
\begin{align*}
\text{-CH}_2\text{-CH=CH}_2 & \rightleftharpoons \text{-CH}\text{\-CH}_2\text{-CH}\rightarrow \text{CH} \\
& \rightleftharpoons \text{-CH=CH-CH}_3
\end{align*}
\end{equation}

A similar study involving isomerization of cis, trans 1,5-cyclocdecadiene has been explained in terms of a hydrido-alkyl intermediate\textsuperscript{128}. More recent data\textsuperscript{129} showed that \pi\-allylic complexes are intermediates in the isomerization of cyclooctadienes.

Abley and McQuillin\textsuperscript{43} found that RhCl(Ph\textsubscript{3}P)\textsubscript{3} and RhCl(CO)(Ph\textsubscript{3}P)\textsubscript{2} isomerize oct-1-ene in the absence of hydrogen. Similar studies by Biellmann and Jung\textsuperscript{39} showed that hydrogen is necessary for isomerization using RhCl(Ph\textsubscript{3}P)\textsubscript{3}, implying RhH\textsubscript{2}Cl(Ph\textsubscript{3}P)\textsubscript{2} is the active catalyst, and they proposed the formation of an alkyl rhodium hydride as an intermediate. RhCl(CO)(Ph\textsubscript{3}P)\textsubscript{2}\textsuperscript{104,130} was reported to catalyze the isomerization of 1-heptene in the presence of H\textsubscript{2}. Ugo\textsuperscript{41} suggested that at low temperatures the co-catalytic activity of hydrogen to form hydrides is necessary, but by increasing the temperature, the source of hydrogen can be the
olefin itself, via abstraction of hydrogen in the allylic position. Wells and coworkers\(^\text{130}\) studied isomerization using \(\text{RhCl}_3(\text{Ph}_3\text{P})_3\) and they believe that the catalytic species in solution are hydrides containing a "vacant site" for olefin coordination.

For the mechanism of olefin isomerization, most workers\(^\text{17,42,104,126,130,131}\) agree that a metal-alkyl must be formed. By loss of a hydrogen atom from the carbon atom other than that to which the first hydrogen atom was added, an isomerized olefin is formed and may appear as a product after discoordination (see Section 1.42, equation 1.19).

At present it cannot be firmly stated that isomerization is associated with hydrogenation, but several observations suggest that it requires (or at least is facilitated by) molecular hydrogen.\(^\text{17}\)

1.63 Polymerization of Olefins and Acetylenes

Rhodium chloride or nitrate catalyzes stereospecifically the polymerization of butadiene in water or alcohol to crystalline trans-1,4-butadiene.\(^\text{132,133}\) Butadiene polymerization is greatly accelerated on the addition of reducing agents. This suggests the participation of a lower oxidation state, possibly \(\text{Rh}^1\) or alternatively a hydride complex.\(^\text{134}\) Natta and coworkers\(^\text{135}\) reported the \(\text{RhCl}_3\) catalyzed polymerization of cyclobutenes in aqueous emulsion to a crystalline polycyclobutylenamer-2 occurring via a mechanism involving coordinated anions. Bawn and coworkers\(^\text{136}\) carried out a mechanistic study of the solution polymerization of butadiene to long chain polymers in the presence of rhodium salts, and concluded that the active species is not a rhodium(I) \(\pi\)-allylic complex but instead a \(\pi\)-allylic rhodium(III) hydride. The polymerization of butadiene catalyzed by rhodium nitrate in ethanol has also been studied by E.S.R. spectroscopy.\(^\text{137}\) A radical
was formed during polymerization, and the steady state concentration of the radical was in proportion to the concentration of nitrate added. However, a radical inhibitor such as hydroquinone did not inhibit polymerization, and also no random polymer products were obtained. The inconsistency was rationalized by postulation of a mechanism involving a coordinated radical (i.e. an allyl radical coordinated to Rh$^{2+}$).

Anderson and coworkers$^{138}$ reported the rhodium chloride catalyzed addition of ethylene and propylene to such dimers as butadiene, isoprene and 1,3-pentadiene. Rhodium derivatives were found to catalyze the dimerization of ethylene to butenes, butadiene to 2,4,6-octatriene and methyl acrylate to dimethyl 2-hexene dioate. The exclusively straight chain structures of the latter two dimers are in marked contrast to the cyclic and branched chain dimeric products formed by the other methods. Rhodium chloride$^{139}$ was also reported to catalyze the dimerizations of alkenes to a mixture of branched and straight chain isomers. Cramer$^{140}$ has investigated in detail the mechanism of the rhodium chloride catalyzed ethylene dimerization in ethanolic HCl solution; the active catalyst appears to be the anion $[(\text{C}_2\text{H}_4)_2\text{Rh}^{\text{I}}\text{Cl}_2]^-$. The anion is obtained directly by dissolution of $[(\text{C}_2\text{H}_4)_2\text{Rh}^{\text{I}}\text{Cl}]_2$ in ethanolic HCl. Cramer has postulated the following mechanism:
This involves
(a) protonation of the bis(ethylene)rhodium(I) complex to an ethyl rhodium (III) ethylene complex.
(b) the rate determining rearrangement of the ethyl-rhodium (III) ethylene complex to the butyl-rhodium (III) complex.
(c) the collapse of the butylrhodium (III) complex to rhodium (I) and butene.
(d) coordination of this resulting rhodium (I) in step (c) with two moles of ethylene to provide the initial bis(ethylene)rhodium (I) complex.
Teyssie and coworkers\textsuperscript{141} reported that RhCl\textsubscript{3} \cdot 3H\textsubscript{2}O catalyzes the polymerization of phenyl acetylene in benzene-ethanol solution. The mechanism is thought not to be of the radical type but may be similar to that of the emulsion polymerization of butadiene\textsuperscript{142}, which involves formation of a rhodium diene complex.

Rhodium (I) square planar complexes have also been found efficient for the allene polymerization in both polar and non-polar media.\textsuperscript{143-145} Maitlis and McVey\textsuperscript{146} have studied the oligomerization of diphenylacetylene by dicarbonyl complexes such as \( \pi\text{-C}_6\text{H}_5\text{Rh(CO)}_2 \) and \([\text{ClRh(CO)}_2]_2\). Collman and Kang\textsuperscript{147} have prepared a series of mononuclear acetylene complexes which are possible intermediates in metal catalyzed cyclooligomerizations and polymerizations of acetylenes. Katz\textsuperscript{148} reported the dimerization of norbornadiene catalyzed by RhCl(Ph\textsubscript{3}P)_3. Wilkinson et al\textsuperscript{149} have shown that hexafluoro-2-butyne can be oligomerized by rhodium (I) complexes, and they recently reported the dimerization of monosubstituted \( \alpha\)-hydroxy-acetylene using RhCl(Ph\textsubscript{3}P)\textsubscript{3}.\textsuperscript{150} The mechanism proposed for this latter system is represented below:

![Scheme IV](attachment://Scheme_IV.jpg)

\begin{align*}
\text{(A)} & \quad \text{RC=CH} \quad \text{Rh} \quad \text{Cl} \\
\text{(B)} & \quad \text{Cl} \quad \text{Rh} \quad \text{III} \\
\text{(C)} & \quad \text{Me}_2\text{C} \quad \text{O} \\
\text{(D)} & \quad \text{C=CH} \quad \text{Rh} \quad \text{Cl} \\
\end{align*}

(S = solvent, in (C) and (D) the Ph\textsubscript{3}P groups are omitted for clarity).
(a) the acetylene reacts with the solvated RhCl(Ph₃P)₂S to give a square planar complex of rhodium (I) with trans phosphine groups.

(b) an oxidative cis-addition of a second acetylene molecule to the d⁸ rhodium (I) complex (A).

(c) an acetylide group transfer from the metal to a carbon atom of the coordinated acetylene via a four-centre transition state (c) leads to the pentacoordinated rhodium (III) species (D) in which the dimer is bound to the rhodium by a σ bond.

(d) finally, a hydride transfer via a 3-centre transition state produces the dimer.

James,⁹² in his review on rhodium complexes, emphasized a number of points first documented by Cramer,¹⁴⁰ which are very important, in general, for reactions of coordinated olefins including hydrogenation, isomerization and polymerization. These main points are: (i) the reversible oxidation of Rh⁺ by a protonic acid to give a Rh⁺⁺ hydride, (ii) the insertion of coordinated olefin between an alkyl group and the metal ion to which it is attached, (iii) the lability of hydrogen in rhodium (III) alkyl and olefin complexes, (iv) the importance of appropriate auxiliary ligands to the catalytic effectiveness of rhodium.

The reactivity and reaction models for hydrogenation, isomerization and polymerization have been the subject of some recent reviews.⁶⁷,¹⁲⁶,¹⁵¹-¹⁵³

1.64 Carbonylation and Decarbonylation Reactions

A number of platinum metal halides have been shown to decarbonylate a variety of organic compounds, including alcohols, aldehydes,
ethers, ketones and acyl halides with the resulting formation of metal carboxyls. Rhodium (I) complexes have been found to be active for such reactions.

Tsuji and Ohno\textsuperscript{154,155} have reported that RhCl(\textsubscript{3}P)\textsubscript{3} decarbonylates aldehydes smoothly at room temperature to give the corresponding paraffin and RhCl(CO)(\textsubscript{3}P)\textsubscript{2}. Primary aldehydes and most secondary aldehydes, except aldehydes with larger steric hindrance, are decarbonylated easily. Further studies by the same workers\textsuperscript{155,156} showed that acyl halides are also decarbonylated to give the olefins and hydrogen halides. The homogeneous decarbonylation reactions can also be carried out in the presence of catalytic amounts of RhCl(CO)(\textsubscript{3}P)\textsubscript{2} at higher temperatures around 200\textdegree\textsuperscript{155,157} in contrast to RhCl(\textsubscript{3}P)\textsubscript{3} which must be used in stoichiometric quantities at a lower temperature. RhCl(CO)(\textsubscript{3}P)\textsubscript{2} was also found to decarbonylate aromatic acid halides\textsuperscript{155} to give aromatic halides. The mechanism postulated for decarbonylation of acyl halides is formulated below:\textsuperscript{155}
The first step involves reaction of RhCl(Ph₃P)₃ (A) with acyl halide in an oxidative-addition to give the five-coordinated acyl complex (E) which was isolated. When heated in absence of CO, E is converted into a six-coordinated alkylcarbonyl complex (G) by the acyl-alkyl arrangement. Finally G is converted into the olefin and RhCl(CO)(Ph₃P)₂ (B) by abstracting hydrogen at the β-position; where
there is no such hydrogen, alkyl or aryl halides are formed. The oxidative addition to form complex E from A is not reversible and decarbonylation by this complex is stoichiometric. The catalytic decarbonylation using RhCl(CO)(Ph$_3$P)$_2$ proceeds through the formation of acyl complex (F) by oxidative-addition. When F was heated in absence of carbon monoxide, CO is lost and the five-coordinate acyl complex E was formed. Then G is formed from E as before. The decarbonylation of aldehydes was explained in a similar way. Although the oxidative addition of aldehydes is not known and could not be substantiated, Tsuji and Ohno$^{155}$ concluded that complexes which are active for decarbonylation under mild conditions should satisfy the following requirements:

(a) the complex should be of a fully reduced low valence state; (b) the complex should be coordinatively unsaturated so that it can undergo oxidative-addition by acyl halides or aldehydes; (c) the complex should coordinate CO strongly to form a carbonyl complex.

Wilkinson and coworkers$^{158-160}$ also reported that RhCl(Ph$_3$P)$_3$ is efficient for decarbonylation of aldehydes and acyl halides. A detailed kinetic study$^{160}$ for the decarbonylation of aldehydes has been given. Oxidative-addition of the aldehyde is thought to be the rate determining step in the decarbonylation and the scheme postulated was very similar to that of Tsuji and Ohno.$^{155}$ No hydrido or acyl intermediate was detected in this reaction although closely related species of these types have been characterized in the reactions of olefins with RhCl$_2$H(Ph$_3$P)$_2$ and of acyl halides with RhCl(Ph$_3$P)$_3$.$^{155,159}$ The scheme$^{159}$ postulated for the decarbonylation of acyl halides followed that of Tsuji and Ohno.$^{155}$
The mechanisms postulated for decarbonylation of aldehydes and acyl halides by rhodium complexes are similar to those postulated for palladium metal.\textsuperscript{161}

Blum and coworkers\textsuperscript{162-164} reported the RhCl(Ph$_3$P)$_3$ catalyzed decarbonylation of aroyl halides to the corresponding aryl compounds. They postulated a scheme similar to that of Tsuji and Ohno although they were unable to detect the intermediate corresponding to E, $\text{RhCl}_2(COR)(\text{Ph}_3\text{P})_2$. Blum and coworkers\textsuperscript{163} questioned the assumption that the essential intermediate in the decarbonylation reaction is $\text{RhCl}(\text{CO})(\text{Ph}_3\text{P})_2$.

RhCl(Ph$_3$P)$_3$ has also been reported to decarbonylate the iron acyl complexes, $\text{C}_5\text{H}_5\text{Fe}((\text{CO})_2\text{(COR)}$, where $R = \text{CH}_3$, C$_6$H$_5$, CH(CH$_3$)$_2$, to give $\text{RhCl(}\text{CO})(\text{Ph}_3\text{P})_2$ and the corresponding iron alkyl complex.\textsuperscript{165} Isotopic labelling indicates that a terminal CO is abstracted and the final product is obtained through methyl group migration.

When RhCl$_3$(Et$_2$PhP)$_2$\textsuperscript{166,167} is heated with saturated carboxylic acids, olefins are produced; e.g. propionic acid gives ethylene, and hexanoic acid gives pent-2-ene. The final complex is $\text{RhCl(}\text{CO})(\text{Et}_2\text{PhP})_2$ but the stoichiometry appears complex since up to three molecules of olefin are formed per atom of rhodium. The first step is thought to be the formation of the carboxylate complex. Carbonylation reactions of allyl halides and benzyl halides in the presence of catalytic amounts of RhCl(Ph$_3$P)$_2$ under CO pressure have been successfully carried out,\textsuperscript{155,157} and the mechanism of the reaction is thought to be the reverse of the decarbonylation reaction.

These carbonylation and decarbonylation reactions are proving to be very useful in organic syntheses since they can be carried out.
smoothly under mild conditions.

1.7 Carbonyl Complexes of Rhodium

Hieber and Lagally found that hydrated RhCl$_3$ when heated in a stream of CO produced [Rh(CO)$_2$Cl]$_2$; the reaction was promoted by saturating the CO stream with methanol. When hydrated RhCl$_3$ was heated with CO for 24 hours at 200 atmospheres and 200°, HRh(CO)$_4$ was obtained. Stone and coworkers prepared Rh$_6$(CO)$_{16}$ by treating a dilute methanol solution of RhCl$_3$·3H$_2$O with CO at 40 atmospheres at 60°, while Chini and Martinengo reported the synthesis of Rh$_4$(CO)$_{12}$ and Rh$_6$(CO)$_{16}$ by addition of water to a solution of [Rh(CO)$_2$Cl]$_2$ in organic solvent saturated with CO at atmospheric pressure. Abel and Stone had written a very comprehensive review on the chemistry of transition metal carbonyls especially in terms of structural considerations. A large number of both mono and dicarbonyl derivatives of rhodium (I) have been prepared from the [RhCl(CO)$_2$]$_2$ dimer. These include the series of complexes RhL$_2$(CO)X where X = Ar$_3$P, Ar$_3$As, Ar$_3$Sb, (PhO)$_3$P and X = Cl, I, SCN; the anions [Rh(CO)$_2$X$_2$]$^-$, (X = Cl, Br, I) and [Rh$_2$(CO)$_2$X$_4$]$^{2-}$ (X = Br, I), the compounds [Rh(CO)$_2$X]$_2$ where X is the carboxylate, nitrate, thiocyanate, sulphate or cyanide; [Rh(CO)$_2$PR$_3$]$_n$ where R = C$_6$H$_5$; the amine complexes RhCl(amine)·(CO)$_2$ and the complexes (β-ketone) Rh(CO)$_2$. nC$_5$H$_5$Rh(CO)$_2$ and its mono and disubstituted derivatives containing phosphines, phosphites and isonitriles have been prepared. Powell and Shaw reported the preparations of Rh$_2$Cl$_2$(CO)$_2$(C$_2$H$_4$)$_2$, [RhCl$_2$Et(CO)]$_x$ and [RhCl$_2$Et(CO)(PMe$_2$Ph)$_2$]* [Rh(CO)$_2$(Ph$_3$P)(tcne)Cl] and trans[Rh(CO)$_2$LXC1] where L = pyridine or p-toluidine; x = tetracyanoethylene (tcne) and fumaronitrile (fmn) have
been recently reported. Kemmitt and Nicols reported that a variety of fluoro-olefins react with RhCl(Ph₃P)₃ and Rh₂Cl₂L₄ to give the carbonyl complexes RhCl(CO)L₂ (L = Ph₃P, (C₆F₅)₃P, (C₆F₅)₂PhP or (C₆F₅)Ph₂P) and they suggested that CO is formed by the action of traces of water present. Recently two ionic carbonyl complexes [Rh(CO)₂bipy]ClO₄ and [Rh(CO)₂O-phen]ClO₄ have been reported.

The complex RhCl(CO)(Ph₃P)₂ has been synthesized by the decarbonylation of alcohols, aldehydes, acylhalides, aroyl halides, dimethylformamide, dioxan and certain ketones using RhCl₃ in the presence of Ph₃P or by using RhCl(Ph₃P)₃ itself (see Section 1.64).

Chatt and Shaw reported the formation of rhodium carbonyl complexes by prolonged treatment of rhodium chloride solutions with CO in boiling ethanol followed by addition of the phosphine or arsine to provide RhCl(CO)L₂ where L = phosphine or arsine.

James and Rempel reported the kinetic studies of the formation of [Rh(CO)₂Cl₂]⁻ species through CO reduction of the aqueous solutions of RhCl₃·3H₂O under mild conditions. There was another later report on similar findings. However, in DMA, different kinetics for the formation of [Rh(CO)₂Cl₂]⁻ were observed and these studies show the necessity of a coordinated water (or hydroxide) on rhodium (III) for reduction by CO to occur.

Complexes such as RhCl(CO)(Ph₃P)₂ of d⁸ configuration undergo oxidative-addition reactions by adding a wide variety of covalent molecules to form hexacoordinated complexes of d⁶ configuration. The rhodium complexes have less tendency to
undergo oxidative-additions than the iridium analogues, but derivatives with $\text{SO}_2$, HCl, organic halides, halogens, tetracyanoethylene and acetylenes have been prepared. Recently Deeming and Shaw reported the oxidative-addition reactions of RX, where R = methyl, acyl, allyl or sulphonyl halides, with trans complexes of the type $\left[\text{RhX(CO)L}_2\right]$ ($X = \text{halide}, L = \text{PMe}_2\text{Ph or AsMe}_2\text{Ph}$) to give $\left[\text{RhX}_2\text{R(CO)L}_2\right]$.

Equilibria such as:

$$\text{Rh}^+\text{Cl(CO)(Ph}_3\text{P})_2 + \text{H}_2 \rightleftharpoons \text{Rh}^{\text{III}}\text{Cl(CO)(Ph}_3\text{P})_2 \text{H}_2$$ (1.31)

and the corresponding reactions with molecular $\text{O}_2$ and CO do exist, but the equilibria lie far to the left. Although rhodium (I) carbonyls may be quite stable thermodynamically they are highly labile; e.g. the ligands of $\text{RhCl(CO)(Ph}_3\text{P})_2$ undergo rapid exchange, a consequence of the facile $S_N^2$ exchange process which is possible with four-coordinate $d^8$ complexes. Substitution of CO in rhodium carbonyl complexes has been studied by various workers and both associative and dissociative mechanisms have been reported.

Of the rhodium carbonyl derivatives only $\text{RhCl(CO)(Ph}_3\text{P})_2$ and $\text{RhH(CO)(Ph}_3\text{P})_3$ have so far been reported as active catalysts for homogeneous hydrogenation (see Section 1.61).

1.8 Molecular Oxygen Complexes of Rhodium

Molecular oxygen complexes of rhodium have not been well characterized. The details of the preparations of these complexes will be presented below.
RhCl(Ph₃P)₃ in dichloromethane takes up 1 mole of oxygen yielding light brown Rh(O₂)Cl(Ph₃P)₂ (0.5 CH₂Cl₂) crystals. The oxygen can be displaced by donor ligands, such as CO to give RhCl(CO)(Ph₃P)₂. In dichloromethane, RhCl(Ph₃As)₃ readily absorbs 1 mole of O₂ per mole of Rh to give a species with possible formula RhCl(O₂)(Ph₃As)₂ nCH₂Cl₂. The O₂-containing adduct reacts with CO in chloroform to produce RhCl(CO)(Ph₃As)₂ indicating that the oxygen is most likely coordinated directly to the metal atom and that no triphenylarsine oxide is present. An unsolvated sample of the oxygen adduct having the formula RhCl(O₂)-(Ph₃As)₂ was isolated when the preparation of RhCl(Ph₃As)₃ was attempted in air.

The reaction of (1,5-cyclo-octadiene)phenyl(triphenylphosphine) rhodium (I) with gaseous oxygen in the presence of excess triphenylphosphine is reported to yield a diamagnetic product of empirical formula Rh(O₂)(Ph₃P)₃. Since this is diamagnetic it must be dimeric or have an extra ligand e.g. hydride, which was undetected. By a similar procedure, Rh(Ph₃P)(Ph₃As)₂(O₂) was also prepared.

James and Pavlis in this laboratory have shown that the dimeric anion [Rh₂Cl₂(SnCl₃)₄]⁻ in acetone solution readily absorbs molecular oxygen which is thereby activated for oxidation of triphenylphosphine.
CHAPTER II
APPARATUS AND EXPERIMENTAL PROCEDURE

2.1 Materials

2.1.1 Rhodium Complexes

The cis-1,2,3-trichlorotris(diethyl sulphide)rhodium (III), \( \text{RhCl}_3(\text{Et}_2\text{S})_3 \), was prepared according to the literature \(^{205}\) by refluxing diethyl sulphide, \( \text{Et}_2\text{S} \), with \( \text{RhCl}_3 \cdot 3\text{H}_2\text{O} \) in ethanol. The orange crystalline compound had the correct melting point of 127\( ^\circ \) and micro-analysis (C = 28.87, H = 6.44, S = 19.33, Cl = 23.3\%) was fairly consistent with that calculated for \( \text{RhCl}_3(\text{Et}_2\text{S})_3 \) (C = 30.2, H = 6.30, S = 19.42, Cl = 22.3\%). Visible and ultraviolet spectra in ethanol gave peaks at 421 \( \mu \text{m} \) (\( \varepsilon = 300 \)) and 292 \( \mu \text{m} \) (\( \varepsilon = 20100 \)) different from those reported, \(^{205}\) 424 \( \mu \text{m} \) (\( \varepsilon = 370 \)) and 292 \( \mu \text{m} \) (\( \varepsilon = 25800 \)).

The bis(cyclo-octene)chloro-rhodium (I) complex, \([\text{Rh}(\text{C}_8\text{H}_{14})_2\text{Cl}]_2\) \(^{206}\), was prepared by stirring \( \text{RhCl}_3 \cdot 3\text{H}_2\text{O} \) with cyclooctene, \( \text{C}_8\text{H}_{14} \), in ethanol. The microcrystalline yellow compound was identified from its melting point, infrared spectrum and analysis (found: C = 53.56; H = 9.71\%, Calc: C = 53.56, H = 7.81\%).

\( \mu \)-dichlorotetraethylenedirhodium (I), \( (\text{C}_2\text{H}_4)_2\text{Rh}_2\text{Cl}_2 \), was prepared according to the method of Cramer \(^{123}\) from ethylene and \( \text{RhCl}_3 \cdot 3\text{H}_2\text{O} \) in aqueous methanol solution and stored under refrigeration.
The preparation of dichlorobis(2,5-dithiahexane)rhodium (III) chloride was carried out according to literature\textsuperscript{207} but analysis of the compound even after repeated recrystallization (found: C = 18.30, H = 4.60\%, Calc: C = 21.20, H = 4.40\%) suggested the presence of some trichloro(2,5-dithiahexane)rhodium(III) (calc: C = 14.5, H = 3.0\%), which was formed first in the preparation.

A new complex trichlorotris(dibenzyl sulphide)rhodium (III), \(\text{RhCl}_3(\text{Bz}_2\text{S})_3\), was prepared by adding dibenzyl sulphide, \(\text{Bz}_2\text{S}\), to a solution of \(\text{RhCl}_3 \cdot 3\text{H}_2\text{O}\) in 100\% ethanol at room temperature in the molar ratio of 3:1 of \(\text{Bz}_2\text{S}:\text{Rh}\). A yellow crystalline precipitate was obtained immediately on slight warming and this was washed with ethanol and dried under vacuum. Analysis of the complex (C = 59.24, H = 5.05, S = 11.58, Cl = 11.47\%) agreed well with that calculated for \(\text{RhCl}_3(\text{Bz}_2\text{S})_3\) (Calc: C = 59.30, H = 4.93, S = 11.3, Cl = 11.80\%). The compound melts at 186\°C. The far I.R. spectrum of \(\text{RhCl}_3(\text{Bz}_2\text{S})_3\) showed two sharp bands at 317 cm\(^{-1}\) and 340 cm\(^{-1}\) which are in the region for (Rh-Cl) mode.\textsuperscript{207,208} The far I.R. spectrum of the known cis \(\text{RhCl}_3(\text{Et}_2\text{S})_3\) complex showed bands at 316 cm\(^{-1}\) and 344 cm\(^{-1}\). Cis complexes of this type are expected to have two infrared active (Rh-Cl) modes.\textsuperscript{207,208} Comparison of the two far I.R. spectra suggested that \(\text{RhCl}_3(\text{Bz}_2\text{S})_3\) has the cis-configuration.

\(\text{RhCl}_3 \cdot 3\text{H}_2\text{O}\) was obtained from Platinum Chemicals and stored over silica gel in a desiccator.

2.12 Organic Ligands and Substrates

Diethyl sulphide was obtained from Eastman Organic Chemicals.
Dibenzyl sulphide, cyclooctene, diphenyl sulphide, 2,5-dithiahexane were obtained from K and K Laboratories. All these were used without further purification.

Maleic acid (Eastman Kodak, C.P. grade) was recrystallized from water or water/ethanol before use. The purity was checked by melting point determination. Cinnamic acid (Eastman Organic) and fumaric acid (Fischer Scientific) were of a reagent grade and were used as such.

2.13 Gases

Purified hydrogen was obtained from Matheson Company. The hydrogen was passed through a Deoxo catalytic purifier to remove traces of oxygen before use. Carbon monoxide, deuterium and ethylene were obtained as C.P. grade from Matheson Company. Purified nitrogen and oxygen were from Canadian Liquid Air Company.

2.14 Solvents

N,N-dimethylacetamide (b.p. 165-166°) was obtained from Eastman Organic Chemicals (Kodak). Purification involved stirring over calcium hydride under nitrogen atmosphere for 40 hours, followed by distillation under a nitrogen atmosphere. The constant boiling fraction was collected directly onto Linde 4A Molecular sieve and stored under nitrogen atmosphere. Dimethyl sulphoxide (Baker analysed grade) was purified by storing over CaH₂ under N₂ for long periods, followed by distillation under reduced pressure. It was collected onto Linde 4A molecular sieve and stored under N₂.

Spectra grade benzene and dichloromethane were obtained from
Fisher Scientific. Dimethylformamide was obtained from Fischer Scientific and was used without further purification.

2.15 Other Materials

p-Toluenesulphonic acid and triphenylphosphine were A.R. grade obtained from Eastman Kodak, the latter was recrystallized from benzene-ethanol before use. Lithium chloride was A.R. grade obtained from Allied Chemical Co. 2:4-Dinitrophenylhydrazine was A.R. grade obtained from B.D.H. Laboratory.

All other chemicals used were of reagent grade. Distilled water was always used when water dilutions or aqueous solution preparations were necessary.

2.2 Apparatus for Gas Uptake Measurements

A constant pressure gas uptake apparatus as shown in Figure I was used for kinetic studies.

The pyreox reaction vessel (A), which could be clipped to a metal rod shaken by motor (I) during the reaction, was connected by a spiral glass arrangement with tap (C) to the oil manometer (D) through tap (H). The oil manometer which consisted of a capillary U tube filled with butyl phthalate (a liquid of negligible vapour pressure) was connected to the gas measuring burette consisting of a mercury reservoir (E) and a precision bored tube (N) of known diameter. The gas measuring burette was in turn connected through a Edward's high vacuum needle valve (M) to the gas handling part of the apparatus, which consisted of a mercury manometer (F), the gas inlet (Y) and
Figure 1. Apparatus for constant gas-uptake measurements.
connections to the Welch Duo Seal rotary vacuum pump (G).

The reaction flask (A) was thermostated in a silicone oil (Dow Corning 550 fluid) bath (B). It consisted of a four litre glass beaker insulated by polystyrene foam on all sides and enclosed by a wooden box with a circular hole for observing the colour changes of the reaction mixture. The top of the oil-bath was well covered by polystyrene foam. The gas burette was immersed in a thermostated water bath made from a perspex rectangular tank. Both thermostat baths were operated using "Jumo" thermo regulators with "merc to merc" relay control circuits and heating provided by 25 watt elongated light bulbs. These together with mechanical stirring ensured temperature control to within ±0.1°. A vertically mounted travelling telescope was used to follow the gas uptake. A lab-chron 1400 timer was used to record the time during the kinetic experiments.

2.3 Procedure for a Typical Gas Uptake Experiment

For each experiment, the required amount of rhodium complex was weighed out or, if in solution, pipetted into reaction flask (A) and the solution was made up with the required amount of solvent. Substrate was added to the above solution if required. In experiments where the rhodium complex in solution was air sensitive, a reaction flask with a side-arm fitted with a hook at the end was used. The rhodium complex was weighed into a small glass bucket suspended from the side arm which, after removal of air from the system, was rotated to drop the bucket into the solution. The reaction flask (A) was then connected by the spiral and tap (C) to the gas-handling part of the apparatus at (0). The
reactant solution was degassed by alternate cooling with pumping and warming. The reactant gas was admitted at a pressure somewhat less than that required for the experiment and then taps (C) and (P) were closed. The whole system up to tap (H) was pumped down with taps (K), (L), (J) and (M) open. The flask and spiral arrangement were disconnected from (0) and transferred into the thermostated oil bath with the spiral connected to the oil manometer through tap (H). Tap (H) was opened and after the air between tap (H) and (C) was pumped out, tap (Q) was closed. Gas was then admitted to the rest of the gas uptake apparatus up to tap (C), which was then opened so that the pressure in the whole system was equalised. The reaction pressure required was adjusted by using the mercury manometer. Tap (J) and the needle valve (M) were closed while the initial reading of the mercury level in (N) was taken. Taps (K) and (L) were closed and the timer and shaker were started simultaneously.

As a result of any gas uptake, the oil level on the left hand side of the manometer rose and to maintain zero difference in levels, gas was admitted into the gas measuring burette through tap (J) and needle valve (M) to give a corresponding rise of mercury in (N). The change in height of the mercury was noted as a function of time. Since the diameter of (N) was known, the corresponding volume of gas used was found and an uptake plot of gas consumption in moles/litre against time could be drawn.

The use of a small volume of solution (~5 ml), a relatively large indented vessel (~30 ml) and a high shaking rate ensured the absence of diffusion control in the rate of gas consumption.
2.4 Gas Solubility Measurements

Some experiments were carried out to determine approximate gas solubilities in the solvents employed at the conditions of temperature and pressure used in kinetic experiments. These solubilities were determined by fitting the previously described gas-uptake apparatus (Figure I) with a reaction flask containing a stopcock in its neck. The entire system including the reaction flask with a measured amount of solvent was pumped down at room temperature; the solvents studied, DMA and DMSO, have low vapour pressures at room temperature. The tap on the flask was now closed and the flask placed in the oil bath B at the desired temperature. The system was now evacuated to the flask tap and then filled with the gas to the approximate pressure desired. The flask tap was now opened and the pressure adjusted immediately to that required. Taps (K) and (L) were closed and the shaker started. The uptake was measured as described in section 2.3 and the solubility of the gas in the particular solvent at the particular temperature and pressure could be evaluated. The determined solubility data are recorded in Appendix I.

2.5 Reaction Product Analyses

2.51 Solid Organic Products

For isolation of organic hydrogenation products in dimethylacetamide, the solvent was removed by pumping through a liquid nitrogen cold trap. The residue in the maleic and fumaric acid systems was heated gently while pumping was maintained. The product was sublimed onto the neck of the flask and was collected and recrystallized. The product was
identified from its melting point and I.R. spectrum (KBr disc or Nujol Mull method).

The oxidation product obtained from the catalyzed oxidation of DMSO using a mixture of H₂/O₂ was isolated by the above described method and after recrystallization was identified by I.R. and melting point.

2.52 Liquid Products

Liquid organic products, H₂O and solvent were separated from the inorganic compounds of the final reaction mixture by vacuum pumping and collected through a N₂ cold trap. Analysis was performed in a gas chromatograph with a suitable column, the retention time and peak area of each product being compared with standard solutions, and for the [Rh(C₇H₈)Cl]₂ catalyzed oxidation system, attempts were made to collect the product as it came through the column. N.M.R. and I.R. were used for identification of the product. Formation of derivatives characteristic of a particular functional group in organic compounds were also used for separation and identification of the product in the [Rh(C₇H₈)₂Cl]₂ catalyzed oxidation system.

2.53 Gaseous Products

When gaseous products were indicated or questionable in a given reaction, a gas sample was collected at the end of the reaction and was analyzed. The technique involved use of a double-necked reaction flask, one neck being connected to an evacuated sample bulb with a stopcock. At the completion of the reaction the stopcock on the bulb was opened and a gas sample collected. The sample was then analyzed.
by mass spectrometry. Chemical tests were also used to identify the gaseous product.

2.54 Solid Inorganic Products

Inorganic products were isolated by reducing the final reaction solution to low volumes by pumping through a liquid N₂ cold trap. This was sometimes followed by the addition of a complexing ligand in a small volume of an appropriate solvent. The solids, which formed immediately or on slow evaporation, were collected and recrystallised from an appropriate solvent or solvent mixture. The solids were characterised by means of some or all of the following: melting point determination, I.R. spectrum, conductance measurement and microanalysis. Microanalyses were performed by Mr. Borda of this Department.

2.6 Instrumentation

Visible and ultraviolet absorption spectra were recorded using a Perkin Elmer 202 spectrometer; this could be fitted when necessary with a thermostated cell compartment. Matched silica cells of 1 mm or 1 cm path lengths were used. A cell fitted with a micro stopcock, carrying a quickfit joint for fitting into a side arm of flasks containing the solution kept under vacuum or a particular gaseous atmosphere, was used to take spectra of such solutions.

Infrared spectra were recorded on Perkin Elmer(P.E.) 21, P.E. Infracord 137 and P.E. Infracord grating spectrophotometer 457 using KBr discs or nujol mulls. NaCl, KBr, CsI plates and liquid cells (NaCl, AgCl) of 0.1 mm or 1 mm path lengths were used. Far I.R. spectra were kindly
recorded by Mr. A.H. Hardin of this department on a double beam Perkin Elmer 301 spectrophotometer.

N.M.R. spectra were obtained on Varian H.R.-100 and A-60 nuclear magnetic resonance spectrometers. E.S.R. spectra were recorded on a Varian Associates E 3 electron spin resonance spectrometer.

An aerograph model A 90 P gas chromatograph and Beckman GC-2A chromatography unit with dinonyl phthalate column were used for analyses of the liquid samples.

Conductivity measurements were carried out using a Thomas Serfass conductivity bridge model RCM 15 BI with dip type conductivity cells of cell constants of about 0.1 cm$^{-1}$.

Melting points were determined on a Superior Electric melting point apparatus and were uncorrected. Mass spectra were recorded on an Associated Electrical Industries MS 9 mass spectrometer.
CHAPTER III

CATALYTIC HYDROGENATION OF OLEFINIC ACIDS BY RHODIUM (III) COMPLEXES CONTAINING SULPHUR LIGANDS

3.1 General Introduction

In search for effects of coordinated ligands, particularly π-acceptors, on the catalytic activity of rhodium complexes, RhCl$_3$(Et$_2$S)$_3$ had been found in this laboratory to be an efficient catalyst for the homogeneous hydrogenation of maleic acid (MA), ethylene and trans-cinnamic acid (CA). Further detailed kinetic studies using CA and fumaric acid (FA) as substrates were carried out to learn more about the factors governing the stability of the postulated intermediate Rh$^I$(olefin) complexes formed (see section 1.2) and its lability for subsequent hydrogenation. The hydrogenation of FA proved to be somewhat complex because of accompanying isomerization and is thus treated separately in Chapter IV. A new RhCl$_3$(Bz$_2$S)$_3$ complex was prepared to study the effect of other monodentate coordinating sulphur ligands on catalytic activity. The activity of a rhodium complex containing chelated sulphur ligands, dichlorobis(2,5-dithiahexane)rhodium (III) chloride, [RhCl$_2$(DTH)$_2$]Cl was also investigated.

The data obtained for the previously studied RhCl$_3$(Et$_2$S)$_3$ catalyzed hydrogenation of MA are of particular relevance to the studies to be described in this chapter and will first be summarized in section 3.2.
3.2 Summary of the Previously Studied RhCl$_3$(Et$_2$S)$_3$/MA/H$_2$/DMA System$^{3,4}$

The kinetics of the hydrogenation were studied by following H$_2$ uptake in the constant pressure gas uptake apparatus. Typical uptake plots are shown in Figure 2. The initial more rapid uptake of H$_2$ steadily decreased to a constant value which persisted up to regions approaching the end point. At later stages metallic rhodium was observed and this coincided with the observation of an increase in hydrogenation rate. The H$_2$ stoichiometry corresponded to the reduction of Rh$^{III}$ to Rh$^I$ and the complete hydrogenation of MA to succinic acid (SA). In the absence of MA, the initial Rh$^{III}$ complex was rapidly reduced by H$_2$ to the metal. No hydride intermediates were detected during these reactions.

The visible spectrum of RhCl$_3$(Et$_2$S)$_3$ in DMA at room temperature showed an absorption maxima at 426 m$\mu$ with an extinction coefficient 308, which decreased to a constant value 270 on heating the solution to 80°. When excess Et$_2$S was added to the solution essentially the same absorption peak appeared at 426 m$\mu$ ($\epsilon = 317$) but the O.D. did not change even on heating to 80°. These data suggested an equilibrium involving dissociation of a Et$_2$S ligand.

No initial complexing between the Rh$^{III}$ complex and MA was observed in DMA.

When LiCl was added in a 6:1 ratio (LiCl:Rh) to a solution of RhCl$_3$(Et$_2$S)$_3$ in DMA a steady spectrum with absorption maxima at higher wavelength ($\lambda_{\text{max}}$ 453 m$\mu$, $\epsilon = 163$, shoulder 530 m$\mu$, $\epsilon = 46.7$) was obtained on standing or heating to 80°. This indicated the presence of a
Figure 2. Rate plots for the RhCl₃(Et₂S)₃ catalyzed hydrogenation of MA in DMA, (80°, 725 mm H₂, 3.0 x 10⁻² M MA, [Rh] : (0) 8.19 x 10⁻³ M, (A) 5.15 x 10⁻³ M).
new higher chloro species.

The spectrum of a solution during the hydrogenation region showed a shoulder at 430 nm (ε 218), indicating a Rh\(^{I}\) species. Samples taken at different stages throughout the linear H\(_2\) uptake region exhibited essentially the same spectrum suggesting the presence of the same species at the linear region.

The H\(_2\) uptake plots were analyzed by measuring the initial slope and the slope of the linear region.

3.21 The Initial Rate

The initial rate was thought to involve the reduction of Rh\(^{III}\) to Rh\(^{I}\) which was stabilized by rapid complexing with MA. The initial rate was first order in [Rh] (total rhodium concentration), and [H\(_2\)] and independent of [MA]. The initial rate law was

\[
-\frac{d[H_2]}{dt} = k_1[Rh][H_2]
\]

with a mean \(k_1\) value of 1.92 M\(^{-1}\)sec\(^{-1}\) at 80°. A slight kinetic isotope effect \(k_1^H/k_1^D = 1.10\) was observed. \(k_1\) was essentially independent of added strong acid (p-toluenesulphonic acid). However, the initial rate showed an inverse dependence on added Et\(_2\)S and LiCl and with the latter a limiting rate was obtained at about a 1:1 ratio of [Cl\(^-\)] : [Rh]. These inhibitions on rate together with the spectroscopic changes suggested there was at least dissociation of Et\(_2\)S from the starting RhCl\(_3\)(Et\(_2\)S)\(_3\) complex. The findings of Dwyer and Nyholm suggested that the dissociation of Et\(_2\)S from the complex in aqueous acid...
alcoholic solutions occurs more readily than the dissociation of the
Cl⁻ ligand. The kinetic results for the initial rate analyzed well
for a pre-dissociation of Et₂S:

\[
\text{RhCl}_3(\text{Et}_2\text{S})_3 \xrightleftharpoons{K_1} \text{RhCl}_3(\text{Et}_2\text{S})_2 + \text{Et}_2\text{S} \quad (3.2)
\]

\[
\text{RhCl}_3(\text{Et}_2\text{S})_2 + \text{H}_2 \xrightarrow{k_t} \text{Rh}^{\text{III}}\text{Cl}_3(\text{Et}_2\text{S})_2\text{H}^- + \text{H}^+ \quad (3.3)
\]

\[
\text{Rh}^{\text{III}}\text{H}^- \xrightarrow{\text{fast}} \text{Rh}^{\text{I}} + \text{H}^+ \quad (3.4)
\]

\[
\text{Rh}^{\text{I}} + \text{MA} \xrightarrow{\text{fast}} \text{Rh}^{\text{I}}(\text{MA}) \quad (3.5)
\]

These reactions yielded the rate law,

\[
\text{Rate} = \frac{-d[\text{H}_2]}{dt} = \frac{K_1 k_t [\text{Rh }] [\text{H}_2]}{K_1 + [\text{Et}_2\text{S}]} \quad (3.6)
\]

Equation (3.6) is rearranged to give

\[
\frac{1}{\text{Rate}} = \frac{[\text{Et}_2\text{S}]}{K_1 k_t [\text{Rh }][\text{H}_2]} + \frac{1}{k_t [\text{Rh }][\text{H}_2]} \quad (3.7)
\]

The value of \( K_1 \) (0.047 M at 80°) and \( k_t \) (1.97 M⁻¹ sec⁻¹ at 80°) were
obtained from the plot of Rate⁻¹ against [Et₂S]; the activation para-
eters \( \Delta H_1^\ddagger = 12.9 \text{ kcal mole}^{-1} \) and \( \Delta S_1^\ddagger = -21.4 \text{ e.u.} \) were determined
for \( k_t \).

The rate inhibition by added Cl⁻, together with the spectral
data was ascribed to the presence of a new higher chloro species of
lower reactivity, possibly \([\text{RhCl}_4(\text{Et}_2\text{S})_2]\), which was expected to be less efficient towards heterolytic splitting of \(\text{H}_2\) than \(\text{RhCl}_3(\text{Et}_2\text{S})_2\text{DMA}\) because of the easier displacement of the DMA molecule in the latter.

3.22 The Linear Rate

The extended linear region of the uptake plots was associated with the hydrogenation of MA. The linear rate was first order in \([\text{Rh}]\) and \([\text{H}_2]\) and independent of \([\text{MA}]\). Addition of \(\text{Et}_2\text{S}, \text{LiCl}\) or \(\text{p-toluene sulphonic acid}\) did not affect the linear rate.

Following the production of \(\text{Rh}^{\text{I}}(\text{MA})\) represented by equations (3.2) to (3.5), a mechanistic scheme for hydrogenation consistent with the kinetic data is as follows:

\[
\begin{align*}
\text{Rh}^{\text{I}}(\text{MA}) + \text{H}_2 & \underset{k_2}{\rightarrow} \text{Rh}^{\text{I}} + \text{SA} \\
\text{Rh}^{\text{I}} + \text{MA} & \overset{\text{fast}}{\rightarrow} \text{Rh}^{\text{I}}(\text{MA})
\end{align*}
\]  

(3.8)

(3.5)

The data were fitted to a rate law of the form

\[
\frac{-d[\text{H}_2]}{dt} = k_2[\text{Rh}][\text{H}_2]
\]  

(3.9)

to give a mean \(k_2\) value of 0.34 \(\text{M}^{-1}\text{sec}^{-1}\). The activation parameters, \(\Delta H_2^\ddagger\) and \(\Delta S_2^\ddagger\), were 21.4 Kcal mole\(^{-1}\) and -1.0 e.u. respectively. A small isotope effect \((k_2^\text{H}_2/k_2^\text{D}_2 = 1.05)\) was observed.

In the absence of MA or when the amount of MA present was
insufficient to fully form the Rh\textsuperscript{I} (MA) complex, metal was produced by either one of the reactions,

\[
\text{Rh}^\text{I} \xrightarrow{\text{fast}} \text{Rh}^0 + \text{Rh}^\text{II} \quad (3.10)
\]

or \( \text{Rh}^\text{I} + \frac{1}{2} \text{H}_2 \xrightarrow{\text{fast}} \text{Rh}^0 + \text{H}^+ \quad (3.11) \)

The initially formed labile Rh\textsuperscript{I} species was thought to be of the form \( \text{RhCl}_x(\text{Et}_2\text{S})_y(\text{DMA})_z \) where \( x+y+z = 4 \). The hydrogenation was compared to the homogeneous hydrogenation of olefins catalyzed by \( \text{Ir(CO)Cl(Ph}_3\text{P)}_2 \) \textsuperscript{35} which dissolves in solution to give \( \text{Ir(CO)Cl(Ph}_3\text{P)}_2 \) and \( \text{Ph}_3\text{P} \), and was discussed in terms of the mechanism given below:

![Scheme VI](image)

Scheme VI \quad (L = ligand, including solvent)
3.3 \( \text{RhCl}_3(\text{Et}_2\text{S})_3 \) Catalyzed Hydrogenation of CA in DMA

A yellow solution of about \( 10^{-2} \) M in \( \text{RhCl}_3(\text{Et}_2\text{S})_3 \) in DMA was found to homogeneously hydrogenate CA at 55° and hydrogen pressure less than 1 atm. At higher temperatures, around 80°, metal was deposited during the reaction. CA showed no reaction with \( \text{H}_2 \) in DMA in the absence of \( \text{RhCl}_3(\text{Et}_2\text{S})_3 \).

Excess CA was added to a solution of \( \text{RhCl}_3(\text{Et}_2\text{S})_3 \) and hydrogenation was followed in the constant pressure gas uptake apparatus. Typical gas uptake plots are shown in figure 3. The stoichiometry of the \( \text{H}_2 \) uptake corresponded to the reduction of \( \text{Rh}^{\text{III}} \) to \( \text{Rh}^{\text{I}} \) and the complete hydrogenation of CA. An essentially linear plot obtained at \( 5.0 \times 10^{-3} \) M Rh, \( 3.0 \times 10^{-2} \) M CA and \( 2.40 \times 10^{-2} \) M \( \text{H}_2 \) proved to be fortuitous since more initial curvature followed by the region of linear rate was observed when [Rh] or [\( \text{H}_2 \)] was varied (Figure 3).

Addition of CA has essentially no effect on the visible spectrum of \( \text{RhCl}_3(\text{Et}_2\text{S})_3 \) in DMA (see section 3.2) suggesting there is no initial complexing between \( \text{Rh}^{\text{III}} \) and CA. A solution of CA and \( \text{RhCl}_3(\text{Et}_2\text{S})_3 \) in DMA in the linear hydrogenation region showed a shoulder at 442 m\( \mu \) (\( \varepsilon = 300 \)), indicative of a \( \text{Rh}^{\text{I}} \) species.

The kinetics of this system were examined in the initial region and the linear region separately. The initial rate is associated with the reduction of \( \text{Rh}^{\text{III}} \) to \( \text{Rh}^{\text{I}} \); the linear rate with the hydrogenation of CA as in the corresponding MA system (sections 3.2, 3.21, 3.22).

3.3.1 The Initial Rate

The initial rate could be measured with considerable accuracy and was found to be first order in [Rh] and [\( \text{H}_2 \)] and independent of [CA]
Figure 3. Rate plots for the RhCl$_3$(Et$_2$S)$_3$ catalyzed hydrogenation of CA in DMA at 55° \{(2.40 \times 10^{-3} \text{M} \text{H}_2, 3.0 \times 10^{-2} \text{M CA}, [\text{Rh}]: (O) 5.0 \times 10^{-3} \text{M}, (\Delta) 1.0 \times 10^{-2}); (a): 5.0 \times 10^{-3} \text{M Rh}, 1.92 \times 10^{-3} \text{M H}_2, 3.0 \times 10^{-2} \text{M CA}\}).
when the latter was varied between 0.03 M-0.06 M (Table I, Figures 4,5). The average value of $k_1$ at 55° is 0.50 M$^{-1}$sec$^{-1}$. There is a slight deuterium isotope effect ($k_1^{H_2}/k_1^{D_2} = 1.15$). The initial rate is inhibited by the addition of LiCl (0.0025 M to 0.05 M) reaching a limiting value at $\sim 0.01$ M; Et$_2$S also inhibited the initial rate (Table I).

A good Arrhenius rate plot was obtained for the temperature range 50-60° with activation parameters $\Delta H_1^\ddagger$ and $\Delta S_1^\ddagger$ equal to 20.0 ± 0.6 Kcal mole$^{-1}$ and 0.6 ± 2.0 e.u., respectively (Table II, Figure 6).

Inhibition by Et$_2$S suggests the solvated species RhCl$_3$(Et$_2$S)$_2$DMA is formed by dissociation of Et$_2$S as in the corresponding MA system. The $K_1$ value estimated from equation (3.7), using the single datum at 0.05 M Et$_2$S and $k_1 \approx k_t = 0.50 M^{-1}$sec$^{-1}$, was of the order of 0.01 M$^{-1}$ at 55° (c.f. $K_1 = 0.047 M^{-1}$ at 80°$^4$) which appears to be somewhat low for the observation of the good first order dependence on [Rh].

The $k_1$ value and activation parameters refer to the reduction reaction (equation 3.3). The $k_1$ value, 0.50 M$^{-1}$sec$^{-1}$ at 55°, is comparable to the $k_1$ value of 0.47 M$^{-1}$sec$^{-1}$ estimated for the corresponding MA system from the temperature dependence. Surprisingly, however, the activation parameters are quite different. This will be discussed later in Chapter V, section 5.12. The mechanism for the formation of the Rh$(I)$-(CA) complex is thought to be essentially the same as in the corresponding MA system (equations 3.2 to 3.5).
### TABLE I

**RhCl$_3$(Et$_2$S)$_3$ Catalyzed Hydrogenation of CA**

**Kinetic Data at 55° in DMA**

The effect of [Rh], [H$_2$], [CA], [LiCl] and [Et$_2$S] on the initial rate.

<table>
<thead>
<tr>
<th>[Rh] x 10$^{-3}$ M</th>
<th>[CA] x 10$^{-2}$ M</th>
<th>[H$_2$] x 10$^{-3}$ M</th>
<th>Initial Rate x 10$^6$ M sec$^{-1}$</th>
<th>$k_1$ M$^{-1}$sec$^{-1}$</th>
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</thead>
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a 0.0025 M LiCl added; b 0.005 M LiCl added; c 0.01 M LiCl added; d 0.05 M LiCl added; e D$_2$ in place of H$_2$; f 0.05 M Et$_2$S added.
Figure 4. RhCl₃(Et₂S)₃ catalyzed hydrogenation of CA in DMA at 55°.
Dependence of initial rate on [Rh], (2.40 x 10⁻³ M H₂,
3.0 x 10⁻² M CA).
Figure 5. \( \text{RhCl}_3(\text{Et}_2\text{S})_3 \) catalyzed hydrogenation of CA in DMA at 55\(^\circ\). Dependance of initial rate on \( [\text{H}_2] \), (5.0 \times 10^{-3}\text{M Rh} \\ 3.0 \times 10^{-2}\text{M CA}).
TABLE II

RhCl$_3$(Et$_2$S)$_3$ Catalyzed Hydrogenation of CA in DMA

Temperature dependence of $k_1$

$[\text{Rh}] = 5.0 \times 10^{-3}$ M, $[\text{CA}] = 3.0 \times 10^{-2}$ M

<table>
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<tr>
<th>T °C</th>
<th>$[\text{H}_2]$ x $10^3$ M</th>
<th>Initial Slope x $10^6$ M sec$^{-1}$</th>
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<td>61</td>
<td>2.38</td>
<td>10.03</td>
<td>0.84</td>
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</table>
Figure 6. $\text{RhCl}_3{(\text{Et}_2\text{S})}_3$ catalyzed hydrogenation of CA in DMA. Arrhenius plot for the initial reduction, $(5.0 \times 10^{-3}\text{M Rh, } 3.0 \times 10^{-2}\text{M CA})$. 
3.32 The Linear Rate

The kinetic data were quite different to those found for the MA system. The rate of hydrogenation increases with [Rh] at lower concentrations but approaches a constant value at about 0.015 M [Rh] (Table III, Figure 7). The rate is first order in [H₂] and independent of [MA] (Table III, Figure 8). Addition of LiCl inhibited the hydrogenation rate reaching a limiting value at 0.01 M LiCl; addition of Et₂S also inhibited the rate (Table III).

The dependence on [Rh], together with the inhibition by Et₂S or LiCl, suggests that there is dissociation of either Cl⁻ or Et₂S from the Rh²⁺(CA) complex. A general mechanistic scheme for hydrogenation, taking into account possible Cl⁻ or Et₂S dissociation, is represented below

\[ \text{Rh}^{I}(\text{CA})X \overset{K_2}{\underset{\text{II}}{\leftrightarrow}} \text{Rh}^{I}(\text{CA})X_{n-1} + X \]  
(3.12)

(\text{X stands for Et₂S or Cl⁻, DMA ligand is omitted, the total coordination number is likely to be 4})

\[ \text{Rh}^{I}(\text{CA})X_{n-1} + H_2 \overset{k_2}{\rightarrow} \text{Rh}^{I}X_{n-1} + \text{product} \]  
(3.13)

\[ \text{Rh}^{I}X_{n-1} + \text{CA} \overset{\text{fast}}{\rightarrow} \text{Rh}^{I}(\text{CA})X_{n-1} \]  
(3.14)

Following the dissociation of X, \( \text{Rh}^{I}(\text{CA})X_{n-1} \) reacts with \( H_2 \), in a rate determining step, to give the hydrogenated product and \( \text{Rh}^{I}X_{n-1} \). The rate of hydrogenation is given by
TABLE III

RhCl$_3$(Et$_2$S)$_3$ Catalyzed Hydrogenation of CA

Kinetic Data at 55° in DMA

The effect of [Rh], [H$_2$], [CA], [LiCl] and [Et$_2$S] on the linear rate

<table>
<thead>
<tr>
<th>[Rh] x 10$^{-3}$ M</th>
<th>[CA] x 10$^{-2}$ M</th>
<th>[H$_2$] x 10$^{-3}$ M</th>
<th>Linear rate x 10$^{-6}$ M sec$^{-1}$</th>
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<td>0.40$^f$</td>
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</tbody>
</table>

$^a$ 0.0025 M LiCl added; $^b$ 0.005 M LiCl added; $^c$ 0.01 M LiCl added; $^d$ 0.05 M LiCl added; $^e$ D$_2$ instead of H$_2$; $^f$ 0.05 M (Et$_2$S) added.
Figure 7. RhCl$_3$(Et$_2$S)$_3$ catalyzed hydrogenation of CA in DMA at 55°. Dependence of linear rate on [Rh] (2.40 x 10$^{-3}$M H$_2$, 3.0 x 10$^{-2}$M CA)
Figure 8. $\text{RhCl}_3(\text{Et}_2\text{S})_3$ catalyzed hydrogenation of CA in DMA at 55$^\circ$. Dependence of linear rate on $[\text{H}_2]$, (5.0 x $10^{-3}$M Rh, 3.0 x $10^{-2}$M CA).
\[-d[H_2] \frac{dt}{dt} = k_2[Rh^{I}(CA)X_{n-1}][H_2] \tag{3.15}\]

Expressing $[Rh^{I}(CA)X_{n-1}]$ in terms of $[Rh]$ gives
\[-d[H_2] \frac{dt}{dt} = \frac{k_2k_2[Rh][H_2]}{k_2 + [X]} \tag{3.16}\]

The concentration of $X$ expressed in terms of $[Rh]$, taking into account the dissociation of either Et$_2$S or Cl$^-$ during the production of the Rh$^{I}(CA)X_n$ complex (see section 3.31) is of the form

$$[X] = [II] + a[Rh] \quad (a \text{ is likely to be } 1 \text{ or } 2) \tag{3.17}$$

$$K_2 = \frac{[II][X]}{[Rh]-[II]} = \frac{([X] - a[Rh])[X]}{(a + 1)[Rh]-[X]} \tag{3.18}$$

Thus
$$[X] = \frac{(a[Rh]-K_2)\pm \sqrt{(a[Rh]-K_2)^2+4K_2(a+1)[Rh]}}{2} \tag{3.19}$$

Only the positive root is meaningful. Substitution of equation (3.19) into equation (3.16) gives
\[-d[H_2] \frac{dt}{dt} = \frac{k_2k_2[Rh][H_2]}{k_2 + a[Rh]. \frac{2}{2} + \sqrt{K_2^2 + 2(a+2)K_2[Rh] + a^2[Rh]^2}} \tag{3.20}\]

At very low $[Rh]$, equation 3.20 can be approximated to
\[-d[H_2] \frac{dt}{dt} = \frac{k_2k_2[Rh][H_2]}{k_2 + \frac{K_2}{2} + \frac{K_2}{2}} = k_2[Rh][H_2] \tag{3.21}\]
At very high \([\text{Rh.}]\) or when \([\text{Rh.}] \gg K\)

\[
-\frac{d[H_2]}{dt} = \frac{k_2 K_2 [\text{Rh.}][H_2]}{a[Rh.] + a[\text{Rh.}]} + k_2 K_2 [H_2] \quad (3.22)
\]

The mechanism based on \(\text{Et}_2\text{S}\) or \(\text{Cl}^-\) dissociation is consistent with the \([\text{Rh}]\) dependence (Figure 7) and the \(H_2\) dependence (Figure 8). \(\text{Et}_2\text{S}\) dissociation is favoured (see p. 70). The final reactive \(\text{Rh}^\text{I}(\text{CA})X_{n-1}\) complex has at least 1 coordinated \(\text{Et}_2\text{S}\) since the rates of \(\text{RhCl}^\text{I}(\text{Et}_2\text{S})^\text{3,4} \) catalyzed hydrogenation are quite different from those of the \(\text{RhCl}_3 \cdot 3\text{H}_2\text{O}^{1,2}\) systems which is attributed to the \(\text{Et}_2\text{S}\) coordination to \(\text{Rh}^\text{I}\) in the \(\text{RhCl}_3(\text{Et}_2\text{S})_3\) system and hence 'a' in equation 3.17 is very likely to be 1. From the initial slope of Figure 7, the value of \(k_2\) was found to be \(1.5 \pm 0.3 \text{ M}^{-1}\text{sec}^{-1}\) at 55\(^\circ\). The rate at 0.015 M \([\text{Rh.}]\) gave the value of \(k_2 K_2\) as \(2.8 \times 10^{-3}\text{sec}^{-1}\), hence \(K_2\) was estimated to be \(1.9 \pm 0.4 \times 10^{-3} \text{ M}\). The \(K_2\) value estimated from equation 3.7 (\(K_1\) replaced by \(K_2\)), using the single datum at 0.05 M added \(\text{Et}_2\text{S}\) ([\(\text{Et}_2\text{S}\)] equals 0.05 M plus the dissociated \(\text{Et}_2\text{S}\) arising from the production of \(\text{Rh}^\text{I}(\text{CA})X_{n-1}\)) and \(k_t \sim k_2 = 1.5 \pm 0.3 \text{ M}^{-1}\text{sec}^{-1}\), was of the order of \(1.4 \pm 0.3 \times 10^{-3} \text{ M}\). These two methods of calculating \(K_2\) agree quite well.

The dependence of rate on temperature is shown in Table IV; assuming variation in rate with temperature is due principally to the changes in \(k_2\), the reasonable Arrhenius plot (Figure 9) indicates a \(\Delta H_2^\dagger\) value of \(21.3 \pm 0.9 \text{ Kcal mole}^{-1}\) and a \(\Delta S_2^\dagger\) value of \(5.6 \pm 1.8\) e.u.
TABLE IV

RhCl$_3$(Et$_2$S)$_3$ Catalyzed Hydrogenation of CA in DMA

Temperature Dependence of the Hydrogenation Rate

[Rh] = 5.0 x 10$^{-3}$ M, [CA] = 3.0 x 10$^{-2}$ M

<table>
<thead>
<tr>
<th>T °C</th>
<th>$[H_2]$ x 10$^3$ M</th>
<th>Linear Rate x 10$^6$ M sec$^{-1}$</th>
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</tr>
<tr>
<td>61</td>
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<td>8.40</td>
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</table>
Figure 9. Arrhenius plot for the RhCl$_3$(Et$_2$S)$_3$ catalyzed hydrogenation of CA in DMA, (5.0 x 10$^{-3}$M Rh, 3.0 x 10$^{-2}$M CA).
The mechanism of the CA hydrogenation is presumably similar to that of the MA system but notable differences are the inverse dependences on both added Et₂S and Cl⁻ as well as the unusual [Rh] dependence in the CA system; addition of Et₂S or Cl⁻ did not inhibit the reaction of MA. It is possible that species (I) is involved in an equilibrium of the type shown in equation 3.12 for both systems. If \( K_2 \) is very large for the MA system, no inhibition by Et₂S or Cl⁻ would be observed. The inhibition is probably not due to any electronic effects since the two systems are not expected to be very different in this respect. However, coordinated trans-CA would give a more sterically crowded complex than the MA, perhaps blocking a prospective coordination site and the oxidative addition step (Scheme VI) requires coordination of 2 cis hydrides. In the well known RhCl(Ph₃P)₃ system, dissociation to RhCl(Ph₃P)₂(solvent) occurs before \( H_2 \) addition and it seems likely here that dissociation of Et₂S will relieve overcrowding to promote the \( H_2 \) oxidative addition reaction. Addition of Cl⁻ could block the site required by the hydride.

The reaching of a limiting rate with increasing "catalyst concentration" is most unusual, and except for a limitation by solubility, such an observation has not been observed. In the case of an active catalyst formed by dissociation, such as:

\[
ML \xrightarrow{K} M + L \quad (K \text{ small})
\]  

(3.23)

the rate will be first order at low Rh concentration and reach a limiting half order at higher Rh concentrations. The levelling off in rate (Figure 7) in the CA system results from the Et₂S liberated in
the reduction of \( \text{Rh}^{III} \) to \( \text{Rh}^+ \), inhibiting the dissociation of the \( \text{Rh}^+ \)(olefin) complex to produce the active form (equation 3.12).

3.4 Catalytic Activity of \( \text{RhCl}_3(\text{Bz}_2\text{S})_2 \) in DMA

The new \( \text{RhCl}_3(\text{Bz}_2\text{S})_3 \) complex was found to be an active catalyst for the hydrogenation of MA, FA and CA in DMA. These studies were carried out for purpose of comparison with the corresponding \( \text{Et}_2\text{S} \) systems to investigate possible steric or electronic effects on replacing the ethyl groups by benzyl groups, particularly with regard to stabilization of the \( \text{Rh}^+ \) intermediates.

A \( 10^{-2} \) M \( \text{RhCl}_3(\text{Bz}_2\text{S})_3 \) in DMA homogeneously hydrogenated MA at 80° and 1 atm of \( \text{H}_2 \); with FA and CA, metal was produced during the reaction at 80°. At 55° homogeneous hydrogenation of FA occurred, but metal was still produced during the CA hydrogenation. This was thought to be due to the lower stability of the \( \text{Rh}^+ \)(olefin) formed (see Chapter V, sections 5.1 and 5.11). The \( \text{RhCl}_3(\text{Bz}_2\text{S})_3 \) complex is reduced to the metal at 80° in the absence of substrate. The kinetics of the hydrogenation of MA were studied in detail and will be reported in section 3.5.

At room temperature, the visible spectrum of the orange solution of the complex in DMA showed absorption maxima at 430 \( \text{mu} \) (\( \epsilon = 438 \)) which changed to a steady spectrum (\( \lambda_{\text{max}} \) 440 \( \text{mu} \), \( \epsilon = 388 \)) on heating to 80° for 10 minutes. The same spectral changes were observed in the presence of MA, FA or CA indicating that these substrates do not react with the \( \text{Rh}^{III} \) complex.
3.5 Kinetics of the $\text{RhCl}_3(\text{Bz}_2\text{S})_3$ Catalyzed Hydrogenation of MA in DMA

The kinetics of this system were studied in the same way as the corresponding $\text{RhCl}_3(\text{Et}_2\text{S})_3$ catalyzed hydrogenation of MA$^{3,4}$ (see section 3.2). A typical gas uptake plot is shown in figure 10. The more rapid initial uptake is followed by a linear region which persisted until near the end point when metal deposited. The stoichiometry corresponded to the reduction of $\text{Rh}^{\text{III}}$ to $\text{Rh}^{\text{I}}$ and the complete hydrogenation of MA. The spectrum taken in the hydrogenation region showed a shoulder at 430 nm, $\varepsilon = 284$ which suggests a $\text{Rh}^{\text{I}}$ species.

3.51 The Initial Rate

The rate is first order in $[\text{Rh}]$ and $[\text{H}_2]$ and independent of $[\text{MA}]$ (Table V, Figures 11, 12). The rate law is of the form shown in equation 3.1 and refers to the reduction of $\text{Rh}^{\text{III}}$ to form a $\text{Rh}^{\text{I}}(\text{MA})$ complex. The average value of $k_1$ is $3.55 \text{ M}^{-1}\text{sec}^{-1}$. The point of metal precipitation in the uptake experiments (Figure 10) indicates that the complex is stabilized by having a minimum of 1 mole of MA per mole of Rh and the $\text{Rh}^{\text{I}}(\text{MA})$ complex is active for hydrogenation. Addition of 0.05 M p-toluenesulphonic acid had no significant effect on rate. A slight deuterium isotope effect, $k_1^H/k_1^D = 1.1$, was observed.

Addition of 0.005 M LiCl (at the 1:1 ratio of Cl$^{-}$:Rh) decreased $k_1$ markedly to a value which changed little on further addition of Cl$^{-}$; addition of $\text{Bz}_2\text{S}$ also inhibited the initial rate (Table V). These data suggest that $\text{Bz}_2\text{S}$ dissociates to provide a vacant site required for the activation of $\text{H}_2$ as in the similar $\text{RhCl}_3(\text{Et}_2\text{S})_3$ catalyzed hydrogenation of olefinic acids$^{3,4}$ (see sections 3.21, 3.31). The reactions
Figure 10. Rate plot for the $\text{RhCl}_3(\text{Bz}_2\text{S})_3$ catalyzed hydrogenation of MA in DMA at 80°, (2.5 x $10^{-3}$M Rh, 2.32 x $10^{-3}$M $\text{H}_2$, 3.0 x $10^{-2}$M MA).
TABLE V

RhCl₃(Bz₂S)₃ Catalyzed Hydrogenation of MA

Kinetic Data at 80° in DMA

Dependence of initial rate on [Rh], [H₂], [MA], [LiCl] and [Bz₂S]

<table>
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<tr>
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<th>[MA] x 10⁻² M</th>
<th>[H₂] x 10⁻³ M</th>
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---

[a] 0.005 M LiCl; [b] 0.045 M LiCl; [c] 0.05 M Bz₂S; [d] 0.10 M Bz₂S;
[e] D₂ instead of H₂; [f] 0.05 M p-toluenesulphonic acid.
Figure 11. $\text{RhCl}_3(\text{Bz}_2\text{S})_3$ catalyzed hydrogenation of MA in DMA at $80^\circ$. Dependence of initial rate on [Rh], (2.32 x 10^{-3} \text{M H}_2, 3.0 x 10^{-2} \text{M MA})$. 
Figure 12. RhCl$_3$(Bz$_2$S)$_3$ catalyzed hydrogenation of MA in DMA at 80°.
Dependence of initial rate in [H$_2$], (5.0 x 10$^{-3}$ M Rh,
3.0 x 10$^{-2}$ M MA).
for the initial reduction of the \( \text{RhCl}_3(Bz_2S)_3 \) complex are of the form shown in equations 3.2-3.5. Analysis of the data on the inhibition of initial rate by \( Bz_2S \) according to equation 3.7 gives a value of \( K_1 \), 1.6 ± 0.3 x 10^{-2} \( \text{M} \) at 80° which indicates that the complex is \( \sim 80\% \) dissociated at 0.005 \( \text{M[Rh]} \), and a \( k_t \) value of 4.3 \( \text{M}^{-1}\text{sec}^{-1} \). \( k_1 \) approaches the \( k_t \) value since the dissociation is about 80% complete (see equations 3.1 and 3.6).

Kinetic measurements over the temperature range yielded a reasonable Arrhenius rate plot (Table VI, Figure 13). The activation parameters were found to be 27.8 ± 2.4 Kcal mole\(^{-1}\) and 23.0 ± 8.0 e.u. respectively, which are thought to refer to the reaction

\[
\text{Rh}^{III}\text{Cl}_3(Bz_2S)_2 + H_2 \xrightarrow{k_t} \text{Rh}^{III}\text{Cl}_3(Bz_2S)_2H^- + H^+ \quad (3.24)
\]

The lower limiting rate with increasing chloride is very similar to that observed for the \( \text{RhCl}_3(\text{Et}_2S)_3 \) catalyzed hydrogenation of MA and CA systems. This is probably due to the production of a higher chloro species, \( [\text{RhCl}_4(Bz_2S)_2]^\text{−} \), of lower reactivity towards heterolytic splitting of \( H_2 \) as represented in equation 3.24.

3.52 The Linear Rate

The linear region in the uptake plot is associated with the hydrogenation of MA. However, the kinetics of this system are more complicated than for the corresponding \( \text{RhCl}_3(\text{Et}_2S)_3 \) system. The dependence of hydrogenation rate with \([\text{Rh}]\) is shown in Table VII and Figure 14; the rate appears to be approaching a constant value at higher \([\text{Rh}]\) which is very similar to the \( \text{RhCl}_3(\text{Et}_2S)_3 \) catalyzed
TABLE VI

RhCl$_3$(Bz$_2$S)$_3$ Catalyzed Hydrogenation of MA in DMA

Temperature Dependence of $k_1$

$[\text{Rh}] = 5.0 \times 10^{-3}$ M, $[\text{MA}] = 3.0 \times 10^{-2}$ M

<table>
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<tr>
<th>$T$ (°C)</th>
<th>$[H_2]$ ($\times 10^3$ M)</th>
<th>Initial Slope ($\times 10^6$ M sec$^{-1}$)</th>
<th>$k_1$ (M$^{-1}$ sec$^{-1}$)</th>
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Figure 13. \( \text{RhCl}_3(\text{Bz}_2\text{S})_3 \) catalyzed hydrogenation of MA in DMA, Arrhenius plot for the initial reduction, (5.0 \( \times \) 10\(^{-3} \) M Rh, 3.0 \( \times \) 10\(^{-2} \) M MA).
TABLE VII
RhCl$_3$(Bz$_2$S)$_3$ Catalyzed Hydrogenation of MA

Kinetic Data at 80° in DMA

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<th>[Rh] x 10$^3$ M</th>
<th>[MA] x 10$^2$ M</th>
<th>[H$_2$] x 10$^3$ M</th>
<th>Linear rate x 10$^6$ M sec$^{-1}$</th>
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<td>5.00$^f$</td>
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</table>

$^a$ 0.005 M LiCl; $^b$ 0.045 M LiCl; $^c$ 0.05 M Bz$_2$S; $^d$ 0.10 M Bz$_2$S;

$^e$ D$_2$ in place of H$_2$; $^f$ 0.05 M p-toluenesulphonic acid.
Figure 14. RhCl₃(Bz₂S)₃ catalyzed hydrogenation of MA in DMA at 80°. Dependence of linear rate on [Rh], (2.32 x 10⁻³ M H₂, 3.0 x 10⁻² M MA).
hydrogenation of CA (see section 3.32). The rate is first order in $[\text{H}_2]$ (Table VII, Figure 15) and independent of $[\text{MA}]$. Addition of $\text{Bz}_2\text{S}$ or $\text{LiCl}$ inhibited the rate of hydrogenation (Table VII), which contrasted with the corresponding $\text{RhCl}_3(\text{Et}_2\text{S})_3$ catalyzed hydrogenation of MA. The observed rate inhibition suggested dissociation of $\text{Bz}_2\text{S}$ or $\text{LiCl}$. Dissociation of $\text{Bz}_2\text{S}$ is thought to be more likely because this would relieve the steric crowding in the $\text{Rh}^\dagger(\text{MA})$ complex during the oxidative addition of the 2 cis hydrides (Scheme VI). Other studies have indicated that in $\text{AuCl}_3(\text{Bz}_2\text{S})^{210}$, $\text{Bz}_2\text{S}$ is more labile than the $\text{Cl}^-$, and this was attributed to steric factors. From the initial slope of Figure 14, (equation 3.21) $k_2$ was found to be $1.2 \pm 0.2 \text{ M}^{-1}\text{sec}^{-1}$. The limiting rate could be around $(11-20) \times 10^6 \text{ M sec}^{-1}$, giving $K_2$ of the magnitude $(5.7) \times 10^{-3} \text{ M}$. A value of $k_2$, $1.08 \text{ M}^{-1}\text{sec}^{-1}$, and $K_2$, of the order of $10^{-2} \text{ M}$, were obtained from the inverse dependence on $[\text{Bz}_2\text{S}]$ (Table VII) using equation 3.7 (replacing $K_1$ by $K_2$ and $k_t$ by $k_2$).

Addition of p-toluenesulphonic acid had practically no effect on the rate. There is a slight deuterium isotope effect when $\text{D}_2$ is used in place of $\text{H}_2$ (Table VII).

The temperature dependence of rate of hydrogenation is shown in Table VIII. Assuming variation in rate with temperature is due principally to changes in $k_2$, the good Arrhenius rate plot (Figure 16) gave $\Delta H_2^\dagger$ and $\Delta S_2^\dagger$ as $21.0 \pm 0.9 \text{ Kcal mole}^{-1}$ and $0.5 \pm 2.5 \text{ e.u.}$, respectively.
Figure 15. \( \text{RhCl}_3(\text{Bz}_2\text{S})_3 \) catalyzed hydrogenation of MA in DMA at 80°. Dependence of linear rate on \([\text{H}_2]\), (5.0 \times 10^{-3} \text{ M Rh, } 3.0 \times 10^{-2} \text{ M MA}).
TABLE VIII
RhCl$_3$(Bz$_2$S)$_3$ Catalyzed Hydrogenation of MA in DMA

Temperature Dependence of the Hydrogenation Rate
[Rh] = 5.0 x 10$^{-3}$ M, MA = 3.0 x 10$^{-2}$ M

<table>
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<th>T $^\circ$C</th>
<th>$[H_2]$ x 10$^3$ M</th>
<th>Rate of Hydrogenation x 10$^6$ M sec$^{-1}$</th>
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<tbody>
<tr>
<td>70</td>
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<tr>
<td>90</td>
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Figure 16. Arrhenius plot for the RhCl$_3$ (B$_2$S)$_3$ catalyzed hydrogenation of MA in DMA, (5.0 x $10^{-3}$ M Rh, 3.0 x $10^{-2}$ M MA).
3.6 The Catalytic Activity of [RhCl\(_2\)(DTH)\(_2\)]Cl

No pure sample of the complex was obtained (see Chapter II, section 2.11). Preliminary studies using the somewhat impure starting material indicated that the complex in DMA is not active for homogeneous hydrogenation of MA at 80°. Hence no further attempt was made to purify the complex.

3.7 Conclusion

Rh\(^{III}\) complexes containing monodentate sulphur ligands in DMA are active catalysts for homogeneous hydrogenation of olefins. The basic mechanism involves reduction of Rh\(^{III}\) to Rh\(^I\) which is stabilized in solution by the olefin. The active species for hydrogenation are the Rh\(^I\)(olefin) complexes. The stability and lability of these Rh\(^I\)(olefin) complexes and the detailed mechanism of hydrogenation will be described in Chapter V, sections 5.11-5.12 Further support for the Rh\(^I\)(olefin) complexes being the active catalysts is shown in Chapter VI.

The inactivity of [RhCl\(_2\)(DTH)\(_2\)]Cl in DMA for homogeneous hydrogenation is almost certainly due to the chelating sulphur ligands; no dissociation is possible to provide the "vacant" site necessary for activity. In general, complexes with chelating ligands are not active catalysts. Walton\(^{207}\) reported that [RhCl\(_2\)(DTH)\(_2\)]Cl is unable to form hydride species and the Rh\(^{III}\)-S bond is very stable to reduction by Ph\(_3\)P in ethanol, i.e. RhCl\(_3\)(DTH)(Ph\(_3\)P) was isolated instead of RhCl(Ph\(_3\)P)\(_3\). It was suggested that the mechanism for the production of RhCl\(_3\)(DTH)(Ph\(_3\)P) goes via a species such as [RhCl\(_2\)(DTH)\(_2\)(Ph\(_3\)P)]\(^+\) in which one of the DTH molecules is monodentate, followed by the loss of that DTH molecule and formation of the new Rh-Cl bond.
CHAPTER IV

CATALYTIC HYDROGENATION AND ISOMERIZATION OF FUMARIC ACID

CATALYZED BY RhCl$_3$(Et$_2$S)$_3$ IN DMA

4.1 Introduction

As described in section 3.1, FA was used as one of the substrates in the study of hydrogenations catalyzed by RhCl$_3$(Et$_2$S)$_3$ in DMA. The kinetics of the hydrogenation of FA proved to be quite complex due to an accompanying isomerization. Isomerization has been found previously to accompany hydrogenation catalyzed by rhodium complexes (sections 1.42 and 1.62). The following describes such a study in detail.

4.2 Stoichiometry of the RhCl$_3$(Et$_2$S)$_3$/FA/H$_2$/DMA System

A yellow solution of about 10$^{-2}$ M RhCl$_3$(Et$_2$S)$_3$ in DMA, containing excess FA, was found to absorb hydrogen at convenient rates from 40-80° and hydrogen pressure of about 1 atmosphere. The rate of H$_2$ uptake was measured in the same way as the RhCl$_3$(Et$_2$S)$_3$ catalyzed hydrogenation of MA (section 3.2). Typical H$_2$ uptake plots are shown in Figure 17; the stoichiometry at the point of metal precipitation corresponded to the reduction of Rh$^{III}$ to Rh$^I$ and the complete hydrogenation of FA. At 0.03 M FA (Figure 17) the fast initial uptake of H$_2$ was followed by a continually decreasing rate with no linear region as observed in the corresponding MA$^{3,4}$ system (Figure 2); a linear region was observed.
Figure 17. Rate plots for the RhCl$_3$(Et$_2$S)$_3$ catalyzed hydrogenation of FA in DMA at 80°. (725 mm H$_2$, 5.0 x 10$^{-3}$ M Rh, [FA]: (O) 3.0 x 10$^{-2}$ M, (Δ) 9.0 x 10$^{-2}$ M).
however, at higher [FA] (Figure 17). A solution sample taken during the initial part of a hydrogenation reaction showed a very broad absorption at 1960 cm\(^{-1}\) which could indicate a Rh-H stretch.

There was no evidence of complexing between FA and Rh\(^{III}\) as there was practically no change in the visible spectrum on adding FA to a solution of RhCl\(_3\)(Et\(_2\)S)\(_3\) in DMA. A solution of RhCl\(_3\)(Et\(_2\)S)\(_3\) and FA in DMA which had reacted with H\(_2\) for \(\approx\) 1 min at 80° showed a shoulder at 430 mu (\(\varepsilon = 338\)); a solution sample in which about 2/3 of the FA had been hydrogenated showed a slight shoulder at 440 mu (\(\varepsilon = 236\)). These solutions were sensitive to air. Rh\(^{II}\) is probably present in such solutions.

4.3 Kinetics of the RhCl\(_3\)(Et\(_2\)S)\(_3\)/FA/H\(_2\)/DMA System

In experiments with 0.03 M [FA], the uptake plots analyzed well for first order dependence on total H\(_2\) uptake, i.e. reduction of Rh\(^{III}\) to Rh\(^{II}\) and hydrogenation of FA to SA (Table IX, Figure 18). This implies a first order decrease in [FA] since the reduction of Rh\(^{III}\) has been shown to be first order.\(^3,4\) In any case, the relatively small amount of H\(_2\) required to reduce Rh\(^{III}\) to Rh\(^{II}\) is unlikely to significantly affect the ln plot, which must demonstrate a first order dependence on [FA] at < 0.03 [FA]. The pseudo first order constants \(k'\), obtained from the ln plots, are shown in Table IX, they showed an approximate first order dependence on [Rh] (Figure 19) and an approximate first order dependence on [H\(_2\)] (Figure 20). A small isotope effect \(k'_{H_2}/k'_{D_2}: 1.1\) and an enhancement of rate by added acid were measured. Addition of 0.005 M LiCl markedly inhibited the rate and a
### TABLE IX

$k'$ Values for the $\text{RhCl}_3(\text{Et}_2\text{S})_3$ Catalyzed Hydrogenation of FA in DMA at $80^\circ$, $[\text{FA}] = 3.0 \times 10^{-2} \text{ M}$

<table>
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<th>[Rh] $\times 10^3 \text{ M}$</th>
<th>[H$_2$] $\times 10^3 \text{ M}$</th>
<th>$k'$ $\times 10^3 \text{ sec}^{-1}$</th>
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$^a$ $D_2$ in place of $H_2$; $^b$ 0.10 M p-toluenesulphonic acid; $^c$ 0.005 M [LiCl]; $^d$ 0.005 M [Et$_2$S].
Figure 18. Rate plot and the corresponding ln plot for the RhCl$_3$(Et$_2$S)$_3$ catalyzed hydrogenation of FA in DMA at 80°. (2.5 × 10$^{-3}$M Rh, 2.32 × 10$^{-3}$M H$_2$, 3.0 × 10$^{-2}$M FA). (O) H$_2$ absorbed; (△) ln [Rh$_{III}$ + FA].
Figure 19. RhCl$_3$(Et$_2$S)$_3$ catalyzed hydrogenation of FA in DMA at 80°C. Variation of $k'$ with [Rh], (2.32 x 10$^{-2}$M H$_2$, 3.0 x 10$^{-2}$M FA).
Figure 20. $\text{RhCl}_3(\text{Et}_2\text{S})_3$ catalyzed hydrogenation of FA in DMA at 80°.
Variation of $k'$ with $[\text{H}_2]$, $5.0 \times 10^{-3} \text{ M Rh, } 3.0 \times 10^{-2} \text{ M FA}$. 
slight decrease in rate was observed on addition of 0.005 M Et₂S. At higher [FA], the rate plots (Figure 17) did not analyze for first order.

An overall first order ln plot appeared to be incompatible with the two rate determining steps, namely the initial reduction of Rh⁺⁺⁺ followed by hydrogenation as postulated for the other Rh⁺⁺⁺ catalyzed hydrogenations in DMA¹,⁴ (see Chapter III). Hence by analogy with the analysis of the Rh⁺⁺⁺ systems in Chapter III, all the uptake plots were analyzed by measuring the initial slope, thought to involve reduction of Rh⁺⁺⁺ to Rh⁺, and when possible, the rates of the extended linear region associated with the hydrogenation process.

4.31 The Initial Rate

The initial rate is seen to be first order in [Rh.] and [H₂], (Table X, Figures 21, 22) and essentially independent of [FA] while the latter was varied from 0.03-0.12 M. Thus the rate law initially is

\[
\frac{-d[H₂]}{dt} = k₁[Rh][H₂] \tag{4.1}
\]

Values of \(k_1\) at 80° are given in Table X, the mean value being 7.40 M⁻¹ sec⁻¹. There is a slight kinetic isotope effect (\(k_1^{H₂}/k_1^{D₂} = 1.1\)). Addition of p-toluenesulphonic acid had little effect on the rate; while addition of Et₂S and LiCl retarded the rates (Table X) as in the RhCl₃(Et₂S)₃ catalyzed hydrogenation of MA. As before \(k_1\) can be considered as a combination of \(k_t\) and \(K₁\) as represented in equations 3.1-3.3 and 3.6.
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<td>2.32</td>
<td>1.2</td>
<td>1.16$^a$</td>
</tr>
<tr>
<td>5.0</td>
<td>3.0</td>
<td>2.32</td>
<td>7.2</td>
<td>6.20$^b$</td>
</tr>
<tr>
<td>5.0</td>
<td>3.0</td>
<td>2.32</td>
<td>1.3</td>
<td>1.10$^c$</td>
</tr>
<tr>
<td>5.0</td>
<td>3.0</td>
<td>2.32</td>
<td>8.0</td>
<td>6.90$^d$</td>
</tr>
<tr>
<td>5.0</td>
<td>3.0</td>
<td>2.32</td>
<td>8.0</td>
<td>6.90$^e$</td>
</tr>
</tbody>
</table>

$^a$ 0.005 M LiCl; $^b$ 0.005 M Et₂S; $^c$ 0.05 M Et₂S; $^d$ D₂ instead of H₂; $^e$ 0.1 M p-toluenesulphonic acid.
Figure 21. RhCl$_3$(Et$_2$S)$_3$ catalyzed hydrogenation of FA in DMA. Dependence of initial rate on [Rh], (2.32 x 10$^{-3}$ M H$_2$, 3.0 x 10$^{-2}$ M FA).
Figure 22. $\text{RhCl}_3(\text{Et}_2\text{S})_3$ catalyzed hydrogenation of FA in DMA at 80°. Dependence of initial rate on $[\text{H}_2]$, ($5.0 \times 10^{-3}$ M Rh, $3.0 \times 10^{-2}$ M FA).
A $K_1$ value of 0.07 M at 80° for the dissociation of RhCl$_3$(Et$_2$S)$_3$ to RhCl$_3$(Et$_2$S)$_2$ and Et$_2$S (equation 3.2) was obtained from the rate at 0.05 M added Et$_2$S using equation 3.7 and $k_t = k_1 = 7.4 \text{ M}^{-1}\text{sec}^{-1}$. The $K_1$ value is comparable to that determined for the MA system, 0.047 M at 80°.

Kinetic measurements of $k_1$ over the temperature range 70-84° (Table XI) gave a good Arrhenius rate plot (Figure 23). The activation parameters $\Delta H_1^\dagger$ and $\Delta S_1^\dagger$, 14.3 ± 0.5 Kcal mole$^{-1}$ and $-14.4 \pm 3.8$ e.u., refer to the reaction

$$\text{RhCl}_3(\text{Et}_2\text{S})_2 + \text{H}_2 \rightarrow \text{Rh}^{III}\text{Cl}_3(\text{Et}_2\text{S})_2\text{H}^- + \text{H}^+ \quad (3.3)$$

4.32 The "Hydrogenation" Region

After the initial rapid uptake of H$_2$ for the first 500 sec. the latter part of the uptake must be associated mainly with a hydrogenation process.

The kinetic data at FA > 0.06 M were analyzed by measurement of the linear slope (Table XII); the rate perhaps decreased somewhat with increasing [FA], apparently approaching a limiting value at 0.5 M [FA].

For data at 0.03 M [FA], the $k'$ values associated with the hydrogenation are shown in Table IX, and the dependences on [Rh] and [H$_2$] are shown in Figures 19 and 20 (see section 4.3).

Addition of 0.05 M Et$_2$S to 0.03 FA resulted in a linear region with slope $1.8 \times 10^{-5}$ M sec$^{-1}$ (Table XII) which was greater than the initial rate ($1.3 \times 10^{-5}$ M sec$^{-1}$).
TABLE XI

RhCl$_3$(Et$_2$S)$_3$ Catalyzed Hydrogenation of FA in DMA

Temperature Dependence of $k_1$

$[\text{Rh}^{\text{III}}] = 5.0 \times 10^{-3}$ M, $[\text{FA}] = 3.0 \times 10^{-2}$ M

<table>
<thead>
<tr>
<th>$T$ (°C)</th>
<th>$[\text{H}_2]$ ($\times 10^3$ M)</th>
<th>Initial Rate ($\times 10^5$ M sec$^{-1}$)</th>
<th>$k_1$ (M$^{-1}$ sec$^{-1}$)</th>
</tr>
</thead>
<tbody>
<tr>
<td>70</td>
<td>2.36</td>
<td>4.40</td>
<td>3.70</td>
</tr>
<tr>
<td>74.5</td>
<td>2.34</td>
<td>5.60</td>
<td>4.80</td>
</tr>
<tr>
<td>80</td>
<td>2.32</td>
<td>8.40</td>
<td>7.25</td>
</tr>
<tr>
<td>84</td>
<td>2.30</td>
<td>12.50</td>
<td>10.00</td>
</tr>
</tbody>
</table>
Figure 23. RhCl$_3$(Et$_2$S)$_3$ catalyzed hydrogenation of FA in DMA.
Arrhenius plot for the initial reduction (5.0 x 10$^{-3}$ M Rh, 3.0 x 10$^{-2}$ M FA).
TABLE XII

RhCl$_3$(Et$_2$S)$_3$ Catalyzed Hydrogenation of FA in DMA

Kinetic Data at 80°

Variation of Linear Rate with [FA]

<table>
<thead>
<tr>
<th>[Rh] $\times 10^3$ M</th>
<th>[FA] $\times 10^2$ M</th>
<th>[H$_2$] $\times 10^3$ M</th>
<th>Linear Rate $\times 10^5$ M sec$^{-1}$</th>
<th>$k_2$ M$^{-1}$ sec$^{-1}$</th>
</tr>
</thead>
<tbody>
<tr>
<td>5.0</td>
<td>6.0</td>
<td>2.32</td>
<td>~1.80$^*$</td>
<td>1.55</td>
</tr>
<tr>
<td>5.0</td>
<td>9.0</td>
<td>2.32</td>
<td>1.34</td>
<td>1.15</td>
</tr>
<tr>
<td>5.0</td>
<td>12.0</td>
<td>2.32</td>
<td>1.56</td>
<td>1.34</td>
</tr>
<tr>
<td>5.0</td>
<td>50.0</td>
<td>2.32</td>
<td>1.12</td>
<td>0.97</td>
</tr>
<tr>
<td>5.0</td>
<td>3.0</td>
<td>2.32</td>
<td>1.84$^a$</td>
<td>--</td>
</tr>
</tbody>
</table>

$^a$ 0.05 M [Et$_2$S].

* Certainly not a first order plot, but there is no well-defined linear region.
4.4 Deuteration and Stereochemistry of the H$_2$ or D$_2$ Addition

Following the production of Rh$^I$ from the initial reduction (section 4.31, equations 3.2-3.4) the Rh$^I$(FA) complex is thought to be the active catalyst for hydrogenation as in the corresponding MA system. However, the dependence on [FA], i.e. first order dependence at < 0.03 M [FA] and independence of [FA] at higher [FA], suggested that some equilibrium is involved in the formation of the Rh$^I$(FA) complex and this could readily give rise to the observed kinetics

$$\text{Rh}^I + \text{FA} \xrightarrow{K_F} \text{Rh}^I(\text{FA}) \quad (4.2)$$

This equilibrium would, however, leave some "free" Rh$^I$ in solution, which under H$_2$ is known to readily decompose to metal. However, no metal was observed in the FA system except at the end of the reaction. Hence some stabilizing ligand other than FA must be present in the system. MA seemed an attractive possibility since FA might be isomerized to MA under the hydrogenation conditions. Hence a deuteration study was undertaken to investigate such a possibility.

In the FA system, the deutosuccinic acid obtained showed sharp bands at 8.12 $\mu$, 8.23 $\mu$ and 8.39 $\mu$ indicating a mixture of meso-symmetrically dideuterated, DL-symmetrically dideuterated and unsymmetrically dideuterated SA. The existence of the meso-symmetrically dideuterated SA is consistent with isomerization of FA during hydrogenation assuming cis addition of the D$_2$ (see Chapter V,
TABLE XIII

RhCl$_3$(Et$_2$S)$_3$ Catalyzed Hydrogenation of FA in DMA

Temperature Dependence of $k'$

$[\text{Rh}] = 5.0 \times 10^{-3}$ M, $[\text{FA}] = 3.0 \times 10^{-2}$ M

<table>
<thead>
<tr>
<th>T $^\circ$C</th>
<th>$[\text{H}_2]$ $\times 10^3$ M</th>
<th>$k'$ $\times 10^3$ sec$^{-1}$</th>
</tr>
</thead>
<tbody>
<tr>
<td>70</td>
<td>2.36</td>
<td>0.70</td>
</tr>
<tr>
<td>74.5</td>
<td>2.34</td>
<td>1.00</td>
</tr>
<tr>
<td>80</td>
<td>2.32</td>
<td>1.80</td>
</tr>
<tr>
<td>84</td>
<td>2.30</td>
<td>2.15</td>
</tr>
</tbody>
</table>
section 5.12). The deuterosuccinic acid obtained from the deuteration of MA catalyzed by RhCl$_3$(Et$_2$S)$_3$ showed sharp bands at 8.10 $\mu$ and 8.39 $\mu$ consistent with a mixture of meso symmetrically dideuterated and unsymmetrically dideuterated SA. No isomerization of MA is evident from the deuterated product assuming cis addition of D$_2$; the simpler kinetics in the MA system supports this conclusion.

4.5 Hydrogenation of a Mixture of FA and MA

The observed FA isomerization prompted the study of the kinetics of the hydrogenation of a mixture of MA and FA.

The H$_2$ uptake plot for the hydrogenation of a mixture of FA (0.03 M) and MA (0.03 M) catalyzed by RhCl$_3$(Et$_2$S)$_3$ consisted of a rapid initial uptake followed by two consecutive linear regions (Figure 24). The initial slope measured was $2.2 \times 10^{-5}$ M sec$^{-1}$([Rh] = 5.0 x $10^{-3}$ M, [H$_2$] = 2.32 x $10^{-3}$ M, T = 80°). Assuming the rate is first order in [Rh], [H$_2$] and independent of [MA] and [FA], $k_1$ was found to be 1.89 M$^{-1}$sec$^{-1}$ which is almost identical to the $k_1$ value (1.92 M$^{-1}$sec$^{-1}$) found in the MA system. The first linear rate was $3.0 \times 10^{-6}$ M sec$^{-1}$ and the second linear rate was $4.5 \times 10^{-6}$ M sec$^{-1}$. The stoichiometry of H$_2$ uptake at the break off region in the first linear rate corresponded to either complete hydrogenation of MA or FA and complete reduction of Rh$^{III}$ to Rh$^{I}$. When the ratio of [FA] to [MA] was changed to 0.045M:0.03 M, and hydrogenation carried out under the same conditions, an initial rate of $2.2 \times 10^{-5}$ M sec$^{-1}$ was observed followed by a linear region with first linear rate of $3.2 \times 10^{-6}$ M sec$^{-1}$ and a slightly higher linear
Figure 24. Rate plot for the RhCl$_3$(Et$_2$S)$_3$ catalyzed hydrogenation of a mixture of MA and FA in DMA at 80°, (5.0 x 10$^{-3}$M Rh, 2.32 x 10$^{-3}$M H$_2$, [MA] = [FA] = 3.0 x 10$^{-2}$M).
rate, $4.4 \times 10^{-6}$ M sec$^{-1}$. The stoichiometry of $H_2$ uptake at the break off region of the first linear rate corresponded to the complete hydrogenation of MA to SA and reduction of $Rh^{III}$ to $Rh^{I}$. Assuming the rate is first order in $[Rh]$, $[H_2]$ and independent of $[MA]$ or $[FA]$, the average of the first linear rates gave a $k_1$ value of $0.27$ M$^{-1}$sec$^{-1}$ and the average of the second linear rates gave a $k_2$ value of $0.38$ M$^{-1}$sec$^{-1}$.

Deuterated product obtained from the mixture of FA and MA showed sharp bands at 8.10 $\mu$, 8.23 $\mu$ and 8.40 $\mu$ consistent with a mixture of meso- and DL-symmetrically dideuterated SA and unsymmetrically dideuterated SA.

4.6 Discussion of the Kinetic Results for the FA System.

4.61 The Initial Rate

The initial reduction is thought to be the same as in the corresponding MA system which involves a solvent assisted dissociation of $RhCl_3(Et_2S)_3$ followed by the rate determining heterolytic splitting of $H_2$.

$$RhCl_3(Et_2S)_3 \overset{k_1}{\rightarrow} RhCl_3(Et_2S)_2 + Et_2S$$

(3.2)

$$RhCl_3(Et_2S)_2 + H_2 \overset{k_1}{\rightarrow} Rh^{III}Cl_3(Et_2S)_2H^- + H^+$$

(3.3)

It is not clear why the initial rates should differ for the FA and MA systems ($k_1^{FA} = 7.40$ M$^{-1}$sec$^{-1}$, $k_1^{MA} = 1.92$ M$^{-1}$sec$^{-1}$). An independent measurement for the reduction of $RhCl_3(Et_2S)_3$ by $H_2$ at $80^\circ$ to give metal
gave a first order dependence on \([H_2]\), with a \(k_1\) value of 3.00 M\(^{-1}\) sec\(^{-1}\). The value of \(k_1\) obtained by initial slope method was 2.40 M\(^{-1}\) sec\(^{-1}\). Some error is expected from the initial slope measurement but the \(k_1^{PA}\) value of 7.40 M\(^{-1}\) sec\(^{-1}\) seems too large to be accounted for by the assumption of a "build up" in the initial rate due to ensuing hydrogenation.

There is a possible rationalization for the apparent discrepancy. It is possible that once small amounts of \(\text{Rh}^I\) species are produced, a catalytic substitution process occurs at the \(\text{Rh}^{III}\) centre to give a \(\text{Rh}^{III}\) (olefin) complex. Such reactions are well substantiated for \(\text{Rh}^{III}-\text{Rh}^I\) systems\(^{187,212-216}\) and may require the presence of as little as 10\(^{-6}\) M \(\text{Rh}^I\). The overall reaction is depicted below:

\[
\begin{align*}
\text{Rh}^{III} + H_2 & \xrightleftharpoons[k_1]{\text{2e}} \text{Rh}^I + 2H^+ \quad (4.3) \\
\text{Rh}^I + \text{olefin} & \rightleftharpoons \text{Rh}^I(\text{olefin}) \quad (4.4) \\
\text{Rh}^I(\text{olefin}) + \text{Rh}^{III} & \xrightarrow{\text{Rh}^{III} \text{-Rh}^I \text{Cl-Rh}} \text{Rh}^{III}(\text{olefin}) + \text{Rh}^I \quad (4.5) \\
\text{Rh}^{III}(\text{olefin}) + H_2 & \xrightarrow[k_1]{\text{"intermediate"}} \quad (4.6)
\end{align*}
\]

The "intermediate" would be expected to finally produce the \(\text{Rh}^I(\text{olefin})\) complex. The initial rate being measured could thus include some contribution from equation 4.6. Cramer\(^{123-126}\) has postulated the existence of \(\text{Rh}^{III}\) (olefin) complexes in the catalyzed hydrogenation of olefins.

An attempt was made to obtain some evidence for the production of
such a Rh III (olefin) complex. The changes in spectra of a solution of RhCl₃·3H₂O and MA in DMA after subjection to H₂ at 80° for ~ 200 sec and then evacuation were studied (Figure 25). There was no measurable H₂ uptake during the 200 sec but the initial spectrum (Curve 1) changed somewhat (curve II); on standing in vacuum, the spectrum changed to that shown in curve III. An isosbestic point at 458 mυ was observed indicating a mixture of 2 species, possibly Rh III and Rh III (MA) (Cl⁻, H₂O, DMA ligands are omitted). The possibility of spectra II and III being a mixture of Rh III and Rh I (MA) cannot be excluded, however, since on further subjection to H₂ and the measured uptake corresponded to 40% reduction of Rh III to Rh I, the recorded spectrum is that shown in curve IV which also passed through the isosbestic point.

4.62 The "Hydrogenation" Region

A mechanism (mechanism I) which can explain at least qualitatively the first order dependence on [FA] at 0.03 M [FA] and independence of [FA] at higher [FA], isomerization of the FA to MA, and first order dependence on [Rh ] and [H₂] is as follows

\[ \text{Rh}^\text{III} + \text{H}_2 \xrightleftharpoons[k_1]{k_{-1}} \text{Rh}^\text{III}^\text{H}^- + \text{H}^+ \]  \hspace{1cm} (4.7)

\[ \text{Rh}^\text{III}^\text{H}^- \xrightarrow{\text{slow}} \text{Rh}^\text{I} + \text{H}^+ \]  \hspace{1cm} (4.8)

\[ \text{Rh}^\text{III}^\text{H}^- + \text{FA} \xleftrightarrow{\text{fast}} \text{Rh}^\text{III(alkyl)} \xrightarrow{\text{slow}} \text{Rh}^\text{III}^\text{H}^- + \text{MA} \]  \hspace{1cm} (4.9)

\[ \downarrow \text{+H}^+ \]

\[ \text{Rh}^\text{III} + \text{SA} \]
Figure 25. Absorption spectra of RhCl$_3$·3H$_2$O and MA in 0.5M LiCl/DMA.

(I) initial spectrum in air, A; (II) A treated with H$_2$ for 200 sec at 80°, B;
(III) B left in vacuum for 5 hours, C; (IV) C treated with H$_2$ with 40% reduction
of Rh$^{III}$ to Rh$^{I}$. 
The rate of hydrogenation is given by

\[
\frac{-d[H_2]}{dt} = k_2[H_2][Rh^{I}(FA)] + k_3[H_2][Rh^{I}(MA)]
\]  

\[
= k_2K_F[Rh^{I}][FA][H_2] + k_3K_M[Rh^{I}][H_2][MA]
\]

\[
[Rh, ] = [Rh^{I}] + [Rh^{I}(FA)] + [Rh^{I}(MA)]
\]

\[
= [Rh^{I}] + K_F[Rh^{I}][FA] + K_M[Rh^{I}][MA]
\]

\[
= [Rh^{I}](1 + K_F[FA] + K_M[MA])
\]

Hence equation 4.13 becomes

\[
\frac{-d[H_2]}{dt} = \frac{(k_2K_F[H_2][FA] + k_3K_M[H_2][MA])[Rh^{I}]}{1 + K_F[FA] + K_M[MA]}
\]  

Whether reaction 4.11 or 4.12 predominates will depend on the relative value of \(k_2K_F[FA]\) and \(k_3K_M[MA]\) and this will in turn depend on the
isomerization rate which determines the relative amounts of [FA] and [MA]. The faster rates in the FA system together with the result of the FA/MA mixture strongly suggest that $k_2 > k_3$ and that $k_F < K_M$ (see also later discussion). The isomerization rate will be determined by the equilibria defined in equation 4.9 but it must be of the same order as the hydrogenation rate because of the observed complex kinetics and deuterated products.

The linear rates observed at higher [FA] are thought to be due to the hydrogenation of FA since the measured rates are some three times greater than the MA system under corresponding conditions. Presumably in this linear region the complex is present almost entirely as Rh$^\text{I}$ (FA), i.e. $K_F[FA] > K_M[MA]$ and equation 4.15 reduces to simply

$$-\frac{d[H_2]}{dt} = k_2[H_2][\text{Rh.}]$$

(4.16)

The $k_2$ value so calculated are given in Table XII; the value given at highest [FA], 0.97 M$^{-1}$ sec$^{-1}$, is likely to be the best value for reaction 4.11.

At the lower [FA], the kinetics will be more complicated since as the MA is produced, it will compete for the coordination with Rh$^\text{I}$ and since the Rh$^\text{I}$ (MA) complex hydrogenates more slowly a continually decreasing rate will be observed (the data in fact analyze for first order plots). As the reaction proceeds the $k_F K_M[H_2][\text{MA}]$ term in the numerator and the $K_M[\text{MA}]$ term in the denominator of equation 4.15 will increase in value while the $K_F[FA]$ term will decrease. Since $k_2 > k_3$ it is possible that the $k_2 K_F[H_2][FA]$ term still predominates in the
numerator. The rate law essentially reduces to

\[
\frac{-d[H_2]}{dt} = \frac{k_2 K_F [H_2] [FA][Rh]}{1 + K_M [MA] + K_F [FA]} \quad (4.17)
\]

The first order plots which demonstrate essentially first order in substrate could be consistent with equation 4.17; it depends on what happens to the value of \(K_M [MA] + K_F [FA]\) as the reaction proceeds. If this remains essentially constant the rate will be first order in [FA]. The [FA] term will be decreased by isomerization to MA and reduction to SA; the [MA] is expected to increase due to the isomerization. Depending on the relative magnitude of \(K_M\) and \(K_F\), the denominator could be reasonably consistent over a fair portion of the reaction. The \(k'\) values obtained for the \(\ln\) plots then become equal to

\[
k' = \frac{k_2 K_F [H_2] [Rh]}{1 + K_F [FA] + K_M [MA]} \quad (4.18)
\]

The \(k'\) values are listed in Table IX.

The dependence on [Rh] (figure 19) although approximately first order does show a definite tendency to lower order with increasing Rh concentration. This could result from a greater contribution from the isomerization reaction reflected in a higher [MA] term in equation 4.18 or a contribution from the \(k_3 K_M [MA][H_2]\) term in equation 4.15.

The kinetics are clearly difficult to analyze quantitatively without knowledge of the rate of the accompanying isomerization but the data observed are in semiquantitative agreement with the proposed reaction scheme.
Assuming that the variation in k' with temperature is due principally to variation in k₂, the reasonable Arrhenius rate plot (Table XIII, Figure 26) yielded ΔH₂⁺ and ΔS₂⁺ values of 20.7 ± 1.5 Kcal mole⁻¹ and -0.8 ± 4.2 e.u. respectively.

The increase in rate on adding 0.1 M p-toluenesulphonic acid, which is a unique observation for the FA hydrogenation system, could be of significance since addition of H⁺ could enhance the hydrogenation by protonation of the Rh³⁺ alkyl intermediate (equation 4.9). A recent paper has reported such a reaction using Pt²⁺alkyls.²¹⁷

A more obvious mechanism (mechanism II) which would also account for the continual decrease in hydrogenation rate and the isomerization of FA to MA is as follows:

\[
\begin{align*}
\text{Rh}^{\text{III}} + \text{H}_2 & \rightarrow \text{Rh}^{\text{I}} + 2\text{H}^+ \\
\text{Rh}^{\text{I}} + \text{FA} & \stackrel{k_P}{\leftrightarrow} \text{Rh}^{\text{I}}(\text{FA}) + \text{H}_2 \stackrel{k_2}{\rightarrow} \text{Rh}^{\text{I}} + \text{SA} \\
\text{Rh}^{\text{I}} + \text{MA} & \stackrel{k_M}{\leftrightarrow} \text{Rh}^{\text{I}}(\text{MA}) + \text{H}_2 \stackrel{k_3}{\rightarrow} \text{Rh}^{\text{I}} + \text{SA}
\end{align*}
\]

Isomerization could occur directly via conversion of \( \text{Rh}^{\text{I}}(\text{FA}) \) to \( \text{Rh}^{\text{I}}(\text{MA}) \) by rotation about the double bond which is weakened by coordination to the metal centre. Then, the hydrogenation rate is given by
Figure 26. \( \text{RhCl}_3(\text{Et}_2\text{S})_3 \) catalyzed hydrogenation of FA in DMA

Arrhenius plot for the hydrogenation \((5.0 \times 10^{-3} \text{ M Rh}, 3.0 \times 10^{-3} \text{ M FA})\).
\[-\frac{d[H_2]}{dt} = \frac{d[SA]}{dt} = k_2[I][H_2] + k_3[II][H_2] \]  

(4.20)

Assuming that the contribution from the reaction between Rh\(^{I}(MA)\) and \(H_2\) is relatively small, and putting

\[I = I_0 e^{-k_4t} = [Rh] e^{-k_4t} \]

(4.21)

equation (4.20) becomes

\[\frac{d[SA]}{dt} = k_2[H_2][Rh]e^{-k_4t} \]

(4.22)

\[[SA] = \frac{k_2[H_2][Rh]}{k_4} [1 - e^{-k_4t}] \]

(4.23)

However, equation 4.23 does not account for the kinetic data, i.e. a first order decrease of [FA] (Figure 18); hence mechanism II is thought to be less likely.

In mechanism I, isomerization goes through a Rh\(^{III}H^-\) intermediate whereas in mechanism II, isomerization goes through Rh\(^I\). It seemed that a choice could be made between the two mechanisms by carrying out experiments starting with a Rh\(^I\) solution.

A stock solution of \([Rh(C_8H_{14})_2Cl_2]_2\) in Et\(_2\)S/DMA, Et\(_2\):Rh = 2:1, \(A\), was found to be a convenient source for Rh\(^I(Et_2S)\) species (see Chapter VI for details). When FA was added to \(A\) and hydrogenation attempted at 80\(^\circ\), an initial induction period followed by a linear region (rate = 3.5 x 10^{-5} M·sec\(^{-1}\), \([Rh] = 5.0 \times 10^{-3} \) M, \([FA] = 3.0 \times 10^{-2}\) M, \(H_2 = 1\) atm) was observed till about half of the FA was
hydrogenated; metal was then produced. If MA is used instead of FA, a linear rate persistent up to almost complete hydrogenation of MA without metal production was observed (Chapter VI). When 0.01 M LiCl was added to A (to give a chloride concentration equal to that present in the corresponding Rh

\[ \text{III system} \] and hydrogenation attempted under the same conditions, ([Rh] = 5.0 x 10^{-3} M, [FA] = 3.0 x 10^{-2} M, H_2 = 1 \text{ atm}, \ T = 80^\circ), an initial induction period followed by a linear region (rate = 1.16 x 10^{-5} \text{ M sec}^{-1}) was observed which persisted up to about 80% hydrogenation of FA. The linear rate was almost identical to the hydrogenation of FA at high [FA] (Table XII, [Rh] = 5.0 x 10^{-3} M, [FA] = 0.5 M, H_2 = 1 \text{ atm}, \ T = 80^\circ, \text{rate} = 1.12 x 10^{-5} \text{ M sec}^{-1}). These results show that (a) Rh^{I}(FA) is a weaker complex than Rh^{I}(MA) i.e. \( K_F < K_M \) and (b) that isomerization is not occurring via Rh^{I}. Wilkinson et al. reported that RhCl(Ph_3P)_3 did not catalyze the cis-trans isomerization of a 1:1 mixture of cis and trans hex-2-enes or isomerization of hex-1-ene.

Thus mechanism I is concluded to be the one responsible for the hydrogenation and isomerization of FA catalyzed by RhCl_3(Et_2S)_3 in DMA. Mechanism I also accounts for the hydrogenation of MA catalyzed by RhCl_3(Et_2S)_3 \cite{3,4} (see section 3.2, 3.21 and 3.23). The equilibrium constant for the formation of the Rh^{I}(MA) complex is thought to be greater than that for the Rh^{I}(FA) complex for steric reasons. In some Ag^{I}(olefin) complexes, the cis form is known to be more stable than the trans.\textsuperscript{218,219} The stability of the Rh^{I}(MA) complex is thought to drive equation 4.8 completely to the right and hence no Rh^{III}H would be present to give rise to the isomerization path.
The results on the hydrogenation of the mixture of FA and MA are particularly interesting. Initially the concentration of FA and MA are such that the Rh* will be present mainly as Rh*(MA) since K_M > K_F. Thus the Rh*(MA) complex will be hydrogenated first even though k_2 is greater than k_3 and the first linear rate (Figure 24) of 3.0 x 10^-6 M sec^-1 is close to that for the hydrogenation of MA, (4.25 x 10^-6 M sec^-1) for the same conditions. The inflexion in the curve of Figure 24 indicates a reasonably selective hydrogenation of the substrate (presumably MA) and this could give rise to the meso-symmetrically dideuterated SA. The second linear region is presumably connected with the isomerization and hydrogenation of FA. It is not clear why this region is so linear and why the rate (4.4 x 10^-6 M sec^-1) is close to that of the hydrogenation of MA. This suggests that FA is isomerized to MA in this system before the hydrogenation starts and yet the isolated DL-sym-dideuterated SA should result from cis D_2 addition to FA. Candlin and Oldham have also indicated that individual rates of hydrogenation are the wrong criteria to predict which substrate will hydrogenate most rapidly in a mixture. The same workers have also observed that the individual hydrogenation rate of a substrate in a mixture may be different from that when the single substrate is being hydrogenated.
CHAPTER V

DISCUSSION OF THE RH\textsc{III} SULPHUR CATALYZED HYDROGENATION
OF OLEFINS

5.1 General Discussion

RhCl\(_3\)(Et\(_2\)S)\(_3\) and RhCl\(_3\)(Bz\(_2\)S)\(_3\) are active catalysts for the
homogeneous hydrogenation of maleic,\(^3,4\) fumaric and trans-cinnamic
acid. The more rapid metal production in systems using fumaric and
trans-cinnamic acid suggests that trans-olefins form less stable complexes
with Rh\textsuperscript{I}. This can be rationalized in terms of steric and electronic
effects, although the steric factor is probably more important.\(^{219}\) The
Rh\textsuperscript{I} produced in the RhCl\(_3\cdot3\text{H}_2\text{O}/\text{olefin}/\text{H}_2/\text{DMA systems}^{1,2}\) formed stable
complexes with maleic acid, while with fumaric and trans-cinnamic acid,
metal was produced more readily.\(^{1,2}\) The lability and stability of these
Rh\textsuperscript{I}(olefin) complexes are major factors in determining the rate of hydro­
genation. If the Rh\textsuperscript{I}(olefin) complex is too stable, hydrogenation might
become very slow. This has been observed for the RhCl\(_3\cdot3\text{H}_2\text{O} catalyzed
hydrogenation of substituted ethylenes\(^1,2\) and in the RhCl(Ph\(_3\)P)\(_3\)
catalyzed hydrogenation of tetrafluoroethylene.\(^8\) In the present
systems, if the Rh\textsuperscript{I}(olefin) complex is not sufficiently stable,
significant amounts of "free" Rh\textsuperscript{I} are present and metal is produced.
In the RhCl(Ph\(_3\)P)\(_3\)\(^7,10\) systems, the Rh\textsuperscript{I} is stabilized against
reduction or disproportionation to metal even in the absence of olefins
by the Ph$_3$P which is a better π-acceptor than Et$_2$S or Bz$_2$S. The electronic and steric factors of auxiliary ligands, namely Cl$^-$, DMA, R$_2$S (R = Et or Bz) in the systems reported in this work, seem to be of importance in promoting or inhibiting catalytic activity.

Isomerization has been observed to accompany hydrogenation. The isomerization of FA involves an alkyl intermediate via insertion of the olefin into the Rh$^{	ext{III}}$-H bond (equation 4.9). Such isomerization is commonly thought to go through alkyl intermediates, $^{17,39,43}$ (sections 1.42 and 1.62). A Rh$^{	ext{III}}$ alkyl, (Rh$^{	ext{III}}$Cl$_2$Et(CO)$_x$, where $x > 2181$) has been isolated by Powell and Shaw, although the analysis is not too good. Wilkinson's group $^{220}$ have isolated pure crystalline salts, [RhEt(NH$_3$)$_5$]$^{2+}$X$_y$ (X = Br$^-$, I$^-$, ClO$_4^-$ and SO$_4^{2-}$; y = 1 or 2), in which the Et group is σ-bonded to Rh.

The detailed mechanism for the initial reduction of Rh$^{	ext{III}}$ and subsequent hydrogenation of the substrate will be discussed in the next two sections.

5.11 Initial Reduction, Formation of a Rh$^{	ext{I}}$(olefin) Complex

The kinetics of the initial reduction for all the systems studied (Chapters III or IV) are first order in [Rh] and [H$_2$] and independent of the olefin. Solvent assisted dissociation of the Et$_2$S$^{3,4}$ or Bz$_2$S ligand provides an active site for the activation of H$_2$ to form a Rh$^{	ext{I}}$(olefin) complex. The donor strength of the solvent is thought to be important. The inactivity of RhCl$_3$(Et$_2$S)$_3$ in benzene is due in part to the lack of the solvent assisted dissociation of the Et$_2$S$^{3,4}$. DMSO was also used for the hydrogenation in an
attempt to study the effect of solvent in these systems and will be
discussed separately in Chapter VII, since a novel reduction of the
solvent was observed.

The rate determining steps for formation of the Rh\textsuperscript{I}(olefin)
complex in the RhCl\textsubscript{3}(Et\textsubscript{2}S\textsubscript{3})\textsubscript{3} andRhCl\textsubscript{3}(Bz\textsubscript{2}S\textsubscript{3})\textsubscript{3} systems are represented
in equations 5.1 and 5.2.

\begin{align*}
\text{RhCl}_3(\text{Et}_2\text{S})_2 + \text{H}_2 & \underset{k_1}{\rightarrow} \text{Rh}^{\text{III}}\text{Cl}_3(\text{Et}_2\text{S})_2\text{H}^- + \text{H}^+ \quad (5.1) \\
\text{RhCl}_3(\text{Bz}_2\text{S})_2 + \text{H}_2 & \underset{k_1}{\rightarrow} \text{Rh}^{\text{III}}\text{Cl}_3(\text{Bz}_2\text{S})_2\text{H}^- + \text{H}^+ \quad (5.2)
\end{align*}

Previous studies\textsuperscript{1-4} suggested that heterolytic splitting is the
most probable path for activation of H\textsubscript{2} in the initial reduction. DMA
is a moderately polar solvent and heterolytic splitting is favoured.
The absence of any measurable D\textsubscript{2} isotope effect suggests that the
breaking of the H-H bond and making of the Rh-H bond occur in a
concerted process.

Heterolytic splitting for the activation of H\textsubscript{2} by Rh\textsuperscript{III} has been
observed by the other groups.\textsuperscript{29,31} Activation of H\textsubscript{2} by the octahedral
species Rh(py)_3Cl\textsubscript{3} in ethanol results in the elimination of HCl and
formation of Rh(py)_3Cl\textsubscript{2}H.\textsuperscript{71} Other Rh\textsuperscript{III} hydrides such as [Rh(NH\textsubscript{3})\textsubscript{5}H]\textsuperscript{2+},
[Rh(CN\textsubscript{4})(H\textsubscript{2}O)H]\textsuperscript{2-} and [Rh(trien)ClH]\textsuperscript{+} have been reported.\textsuperscript{92}

The general mechanism for the formation of the Rh\textsuperscript{I}(olefin)
complex is represented below.

\begin{align*}
\text{Rh}^{\text{III}} + \text{H}_2 & \underset{k_1}{\rightarrow} \text{Rh}^{\text{III}}\text{H}^- + \text{H}^+ \quad (5.3)
\end{align*}
\[
\text{Rh}^{III}\text{H}^{-} \xrightleftharpoons[4]{K_4}[3]{K_3} \text{Rh}^I + \text{H}^+ \quad (5.4)
\]

\[
\text{Rh}^{III}\text{H}^{-} + \text{olefin} \xrightarrow[K_2]{\text{Rh}^{III}(\text{alkyl})} \xrightarrow[K_3]{\text{Rh}^{III}\text{H}^{-}} \text{isomerized olefin} \quad (5.5)
\]

\[
\text{Rh}^I + \text{olefin} \xrightarrow[K_4]{\text{Rh}^I(\text{olefin})} \quad (5.6)
\]

(coordinated ligands such as Cl\(^-\), Et\(_2\)S, Bz\(_2\)S, DMA are omitted).

The magnitude of \(K_4\) is thought to determine the probability of isomerization and the complexity of the kinetics of the system.

Comparison of the \(k_1\) values and activation parameters for the formation of the various \(\text{Rh}^I(\text{olefin})\) complexes and the equilibrium constants for the initial dissociation are shown in Table XIV. The \(k_1\) value, \(7.4 \text{ M}^{-1} \text{sec}^{-1}\), for the FA system seems somewhat high compared to the MA system. Similar discrepancies in the \(k_1\) values for different olefins have been observed for the \(\text{RhCl}_3\cdot3\text{H}_2\text{O}\) catalyzed hydrogenation of olefins in DMA.\(^1\,2\) These may be rationalized by the formation of the \(\text{Rh}^{III}(\text{olefin})\) complexes in the initial reduction through catalytic substitution involving \(\text{Rh}^I\); and in such cases \(k_1\) values, i.e. rate of heterolytic splitting of \(\text{H}_2\) in the initial step, will be dependent on the olefin. The activation parameters for the \(\text{RhCl}_3(\text{Et}_2\text{S})_3\) systems involving FA and MA are not very different however. Although the \(k_1\) value obtained for the \(\text{RhCl}_3(\text{Et}_2\text{S})_3\) catalyzed hydrogenation of MA, mixture of MA and FA, and CA are comparable and close to the \(k_1\) value for the hydrogen reduction of \(\text{RhCl}_3(\text{Et}_2\text{S})_3\) in the absence of olefin, this seems fortuitous since the activation
TABLE XIV
Rate Constants and Activation Parameters for Rh\textsuperscript{III}(olefin)
Complex Formation from Rh\textsuperscript{III} in DMA

<table>
<thead>
<tr>
<th>Initial Complex</th>
<th>Olefin</th>
<th>T °C</th>
<th>$k_1$ M\textsuperscript{-1}sec\textsuperscript{-1}</th>
<th>$\Delta H_1^\dagger$ Kcal mole\textsuperscript{-1}</th>
<th>$\Delta S_1^\dagger$ e.u.</th>
<th>$K_1$ M</th>
</tr>
</thead>
<tbody>
<tr>
<td>RhCl\textsubscript{3}(Et\textsubscript{2}S)\textsubscript{3}</td>
<td>MA</td>
<td>80</td>
<td>1.92</td>
<td>12.9</td>
<td>-21.4</td>
<td>0.047</td>
</tr>
<tr>
<td></td>
<td></td>
<td>55</td>
<td>0.47\textsuperscript{a}</td>
<td>-</td>
<td>-</td>
<td>-</td>
</tr>
<tr>
<td></td>
<td>MA + FA</td>
<td>80</td>
<td>1.89</td>
<td>-</td>
<td>-</td>
<td>-</td>
</tr>
<tr>
<td>RhCl\textsubscript{3}(Et\textsubscript{2}S)\textsubscript{3}</td>
<td>FA</td>
<td>80</td>
<td>7.4</td>
<td>14.3</td>
<td>-14.4</td>
<td>0.073</td>
</tr>
<tr>
<td>RhCl\textsubscript{3}(Et\textsubscript{2}S)\textsubscript{3}</td>
<td>CA</td>
<td>55</td>
<td>0.50</td>
<td>20.0</td>
<td>0.6</td>
<td>0.010</td>
</tr>
<tr>
<td>RhCl\textsubscript{3}·3H\textsubscript{2}O</td>
<td>MA</td>
<td>80</td>
<td>1.67</td>
<td>17.3</td>
<td>-9.2</td>
<td>-</td>
</tr>
<tr>
<td>RhCl\textsubscript{3}·3H\textsubscript{2}O*</td>
<td>MA</td>
<td>80</td>
<td>0.74</td>
<td>17.3</td>
<td>-10.8</td>
<td>-</td>
</tr>
<tr>
<td>RhCl\textsubscript{3}(Bz\textsubscript{2}S)\textsubscript{3}</td>
<td>MA</td>
<td>80</td>
<td>3.55</td>
<td>27.8</td>
<td>23.0</td>
<td>0.016</td>
</tr>
<tr>
<td>RhCl\textsubscript{3}(Et\textsubscript{2}S)\textsubscript{3}</td>
<td>Nil</td>
<td>80</td>
<td>2.4\textsuperscript{b}</td>
<td>-</td>
<td>-</td>
<td>-</td>
</tr>
<tr>
<td></td>
<td></td>
<td></td>
<td>3.0\textsuperscript{c}</td>
<td>-</td>
<td>-</td>
<td>-</td>
</tr>
</tbody>
</table>

* 1.2 M LiCl/DMA media.

\textsuperscript{a} Value obtained by direct calculation from the $k_1$ value at 80°C, assuming the Arrhenius rate equation holds for the temperature range 55-80°C.

\textsuperscript{b} Initial slope method.

\textsuperscript{c} From first order log plot.
parameters for the CA and MA systems are quite different. The more unfavourable $\Delta H^\ddagger_1$ value in the CA system is compensated by the more positive $\Delta S^\ddagger_1$ value. The activation parameters for the $\text{RhCl}_3(\text{Et}_2\text{S})_3$ catalyzed hydrogenations of MA and FA are similar to those of the $\text{RhCl}_3\cdot 3\text{H}_2\text{O}^{1,2}$ catalyzed hydrogenation of MA which is again thought to involve heterolytic splitting by $\text{Rh}^{\text{III}}$ as the rate determining step.

The large and positive $\Delta S^\ddagger_1$ value for the formation of the $\text{Rh}^{\text{I}}(\text{MA})$ complex in the $\text{RhCl}_3(\text{Bz}_2\text{S})_3$ system accounts for the faster rate compared to the $\text{Et}_2\text{S}$ and the chloride systems. The reason for quite different activation parameters in this system is not obvious, it does suggest that a different mechanism is operating. There have been suggestions recently$^{221,222}$ that the so-called heterolytic splitting of $\text{H}_2$ by $\text{Ru}^{\text{II}}$ complexes may proceed in some cases via dihydride formation.

\begin{equation}
\text{Rh}^{\text{II}}\text{Cl}_2\text{P}_3 + \text{H}_2 \longrightarrow [\text{Ru}^{\text{IV}}\text{Cl}_2\text{H}_2\text{P}_3] \rightarrow \text{Ru}^{\text{II}}\text{ClHP}_3 + \text{HCl}
\end{equation}

where $P = \text{Ph}_3\text{P}$

A similar reaction here would involve a $\text{Rh}^{\text{V}}$ state, a reasonably well substantiated valence state$^{223}$ and would be expected to have a high activation energy because of the contribution of the promotion energy of the valence electrons. Although reactions said to proceed via heterolytic splitting of $\text{H}_2$ usually have a small isotope effect$^{11}$ this may not be a useful criteria since the kinetic isotope effect for the oxidative addition of $\text{H}_2$ to $\text{Ir}^{\text{I}}$ complexes is also small.$^{23}$
5.12 Catalytic Hydrogenation

The three basic steps of hydrogenation, \((i)\) substrate activation \((ii)\) hydrogen activation \((iii)\) hydrogen transfer (see sections 1.4 to 1.42) are thought to be involved in the \(\text{RhCl}_3(\text{Et}_2\text{S})_3\) and \(\text{RhCl}_3(\text{Bz}_2\text{S})_3\) catalyzed hydrogenations of MA, FA and CA.

The substrate (olefin) is activated through coordination to \(\text{Rh}^\text{I}\). \(\text{Rh}^\text{I}(\text{olefin})\) then reacts with \(\text{H}_2\) in a rate determining step to produce the paraffin (after \(\text{H}_2\) transfer) and \(\text{Rh}^\text{I}\) which is stabilized by complexing with further olefin. The mechanism is represented below

\[
\text{Rh}^\text{I} + \text{olefin} \xrightleftharpoons[\text{K}_4]{\text{K}_2} \text{Rh}^\text{I}(\text{olefin}) \tag{5.6}
\]

\[
\text{Rh}^\text{I}(\text{olefin}) + \text{H}_2 \xrightarrow[\text{K}_2]{\text{K}_4} \text{Rh}^\text{I} + \text{paraffin} \tag{5.8}
\]

(coordinated ligands such as Cl\(^-\), Et\(_2\)S, Bz\(_2\)S, DMA are omitted).

If the \(K_4\) value in equation 5.6 is sufficiently large, a first order dependence on \([\text{Rh}^\text{I}]\) and \([\text{H}_2]\) would be observed as in the \(\text{RhCl}_3(\text{Et}_2\text{S})_2\) catalyzed hydrogenation of MA.\(^{3,4}\) If one of the auxiliary ligands in the \(\text{Rh}^\text{I}(\text{olefin})\) complex dissociates prior to reaction with \(\text{H}_2\), e.g. in the \(\text{RhCl}_3(\text{Et}_2\text{S})_3\) catalyzed hydrogenation of CA and the \(\text{RhCl}_3(\text{Bz}_2\text{S})_2\) catalyzed hydrogenation of MA, a complex dependence on \([\text{Rh}^\text{I}]\) results (see sections 3.32 and 3.52). If the \(K_4\) value shown in equation 5.6 is smaller than the equilibrium shown in equation 5.5, isomerization of olefin may occur through the \(\text{Rh}^{\text{III}}(\text{alkyl})\) intermediate as in the \(\text{RhCl}_3(\text{Et}_2\text{S})_3\) catalyzed hydrogenation of FA and there will be a between zero and first order dependence on the olefin.
Following the reasoning of James and Rempel,\textsuperscript{1,2} activation of $H_2$ through dihydride formation is preferred (section 3.22, Scheme VI). Hydride formation is accompanied by formal oxidation of the metal, the second step involves hydrometallation of the olefinic bond.

Similar mechanisms have been proposed for the IrCl(CO)(Ph$_3$P)$_2$\textsuperscript{35}, RhCl$_3$·3H$_2$O \textsuperscript{1,2} and RhCl$_3$(Et$_2$S)$_3$ \textsuperscript{3,4} catalyzed hydrogenation of MA in DMA, and the RhCl(Ph$_3$P)$_3$ \textsuperscript{7-10} catalyzed hydrogenation of olefins in benzene. In the latter, however, the dihydride is thought to form prior to reaction with the olefin.

Hydrogenation is completed by hydrogen transfer. The actual process of transfer is uncertain. Wilkinson \textsuperscript{8} et al have suggested that the transfer of both hydrides is simultaneous, each by a three centre transition state if the olefin occupies a position cis to both Rh-H bonds.

\begin{equation}
\begin{array}{c}
\text{Rh} \quad \text{C} \\
\text{H} \\
\text{H}
\end{array}
\rightarrow
\begin{array}{c}
\text{Rh} \quad \text{C} \\
\text{H} \\
\text{H}
\end{array}
\rightarrow
\begin{array}{c}
\text{Rh} \\
\text{H}
\end{array}
+ \begin{array}{c}
\text{H} \quad \text{C} \\
\text{C} \\
\text{H}
\end{array}
\end{equation}

(5.9)

More recent data \textsuperscript{17,39,42,106,107} suggest that the hydrides are transferred consecutively, via alkyl intermediates.

Cis addition is generally thought to be operative in catalyzed hydrogenations.\textsuperscript{8,9,224} One definite instance of trans addition has been reported in the reduction of diphenyl acetylene using a py$_3$RhCl$_3$·Me$_2$NCHO-NaBH$_4$ catalyst system.\textsuperscript{225} The unsymmetrically deuterated SA obtained from the deuteration studies probably arises from the equilibria involving cis addition of the D$_2$ through alkyl
intermediates

\[
\begin{align*}
\text{CHR-CD} & \quad \text{CHR-CHDR} \\
\text{CH}_2\text{R-CD}_2\text{R} & \quad \text{D} \\
& \quad \text{CHR-CD}_2\text{R}
\end{align*}
\]

Scheme VII

\[R = \text{COOH}, \text{this scheme also holds for } \]

The small deuterium isotope effect observed with \(k_2\) in the present studied systems is similar to that observed for the oxidative addition of \(\text{H}_2\) (\(\text{D}_2\)) to the square planar \(\text{IrCl}(\text{CO})(\text{Ph}_3\text{P})_2\) complex. But the small isotope effect has also been attributed to the hydrogen transfer step.

Comparison of the \(k_2\) values and activation parameters for the different \(\text{Rh}^{\text{III}}\) sulphur and chloride catalyzed hydrogenations are shown in Table XV. Good \(\sigma\) donor ligands are thought to promote oxidative additions and this is possibly reflected in the higher \(k_2\) value for the \(\text{RhCl}_3 \cdot 3\text{H}_2\text{O}\) catalyzed hydrogenation of MA compared to the
TABLE XV
Rate Constants and Activation Parameter for Hydrogenation
of Rh(I)(olefin) Complex in DMA

<table>
<thead>
<tr>
<th>Initial Complex</th>
<th>Olefin</th>
<th>T (°C)</th>
<th>$k_2$ (M$^{-1}$ sec$^{-1}$)</th>
<th>$\Delta H_2^\dagger$ (Kcal mole$^{-1}$)</th>
<th>$\Delta S_2^\dagger$ (e.u.)</th>
<th>$K_2$</th>
</tr>
</thead>
<tbody>
<tr>
<td>RhCl$_3$(Et$_2$S)$_3$</td>
<td>MA</td>
<td>80</td>
<td>0.33</td>
<td>21.4</td>
<td>-1.0</td>
<td>-</td>
</tr>
<tr>
<td>RhCl$_3$(Et$_2$S)$_3$</td>
<td>FA</td>
<td>80</td>
<td>0.97</td>
<td>20.7</td>
<td>-0.8</td>
<td>-</td>
</tr>
<tr>
<td>RhCl$_3$(Et$_2$S)$_3$</td>
<td>CA</td>
<td>55</td>
<td>1.20</td>
<td>21.3</td>
<td>+5.6</td>
<td>0.19</td>
</tr>
<tr>
<td>RhCl$_3$·3H$_2$O</td>
<td>MA</td>
<td>80</td>
<td>-</td>
<td>-</td>
<td>-</td>
<td>-</td>
</tr>
<tr>
<td>RhCl$_3$·3H$_2$O$^a$</td>
<td>MA</td>
<td>80</td>
<td>1.54</td>
<td>18.4</td>
<td>-6.1</td>
<td>-</td>
</tr>
<tr>
<td>RhCl$_3$(Bz$_2$S)$_3$</td>
<td>MA</td>
<td>80</td>
<td>1.20</td>
<td>21.0</td>
<td>+0.5</td>
<td>0.10</td>
</tr>
</tbody>
</table>

$^a$ 1.2 M LiCl/DMA media. $K_2$ = dissociation constant of Rh(I)(olefin).
RhCl$_3$(Et$_2$S)$_3$ and RhCl$_3$(Bz$_2$S)$_3$ systems since chloride is a better σ donor than Bz$_2$S or Et$_2$S. Bz$_2$S and Et$_2$S are thought to be very similar in their σ donor properties. The $k_2$ value (1.20 M$^{-1}$sec$^{-1}$) for the dibenzyl system is some 4 times higher than the diethyl system ($k_2 = 0.33$ M$^{-1}$sec$^{-1}$) but the Bz$_2$S system involves a Rh$^I$ species with one less coordinated sulphur ligand than the Et$_2$S system.

The rate of hydrogenation of different olefins catalyzed by RhCl$_3$(Et$_2$S)$_3$ is in the order, trans-cinnamic acid > fumaric acid > maleic acid (Table XV) which is probably in the reverse order of the stability of the Rh$^I$(olefin) complex. The trend is the opposite to that observed in the RhCl(Ph$_3$P)$_3$ catalyzed hydrogenation where the sterically hindered and trans substituted olefins are less prone to hydrogenation than the less sterically hindered and cis substituted alkenes, e.g. cyclohexene is hydrogenated fifty times faster than a 1-methylcyclohexene, and cis-4-methylpent-2-ene is hydrogenated four times faster than the trans-isomer. In the present systems, FA (trans) is hydrogenated three times faster than the MA (cis). It should be noted, however, that these workers postulate that the complexing between the olefin and the Rh$^I$ is the rate determining step. It seems likely that the ease of complex formation decreases with the presence of bulky substituents on the olefin and the trans olefin is more hindered than the cis olefin since only certain directions of approach of the olefin to the metal will permit complexing to take place. In the present systems, however, the rate determining step of hydrogenation is thought to involve dihydride formation and the Rh$^I$(olefin) complex is thought to be formed in a fast step prior to dihydride formation. The stability of the Rh$^I$(olefin)
complexes are clearly crucial factors in determining catalytic activity. The \( \text{Rh}^{\text{I}}(\text{FA}) \) complex is less stable than the \( \text{Rh}^{\text{I}}(\text{MA}) \) complex and hence the rate of hydrogenation of \( \text{Rh}^{\text{I}}(\text{FA}) \) is enhanced. Substrates containing electron withdrawing substituents, e.g. nitrite, carboalkoxy are hydrogenated extremely rapidly using the \( \text{RhCl(Ph}_3\text{P)}_3 \) catalyst.\(^{36}\)

The activation parameters for the hydrogenation (Table XV) are in the normal range for a bimolecular reaction in solution between an ion and a neutral molecule. Such reactions are expected to be favoured in a medium of lower dielectric constant due to greater attraction between the ion and the induced dipole of the molecule.\(^{227}\)

An intermediate in which both the olefin and \( \text{H}_2 \) are coordinated to the atom seems necessary for hydrogenation to begin. Species which can activate molecular hydrogen quite rapidly and reversibly, e.g. \( \text{IrCl(CO)(Ph}_3\text{P)}_2 \)\(^{35,228}\) in benzene and \( \text{RhCl(Ph}_3\text{P)}_3 \)\(^8\) in pyridine or toluene are unable to catalytically hydrogenate olefins at 25° or 1 atmosphere of \( \text{H}_2 \) or do so only very slowly. A dihydride species which forms is coordinatively saturated and there is no vacant site for olefin coordination. If a solvent assisted dissociation of one of the \( \text{Ph}_3\text{P} \) ligand occurs, the complex becomes active for hydrogenation.\(^8,35\)

Addition of excess \( \text{Ph}_3\text{P} \) in the above systems reverses the dissociation and hydrogenation is inhibited.
CHAPTER VI

CATALYTIC HYDROGENATION OF MALEIC ACID BY RHODIUM (I) CHLORO AND SULPHUR COMPLEXES IN DMA

6.1 General Introduction

Rh\(^{I}\) complexes are known to be active catalysts for hydrogenation especially when stabilized by Ph\(^{3}P\) ligands.\(^{8-10,36,106}\) Rh\(^{I}\)(olefin) complexes with chloro\(^{1,2}\) and sulphur ligands\(^{3,4}\) formed "in situ" in DMA via reduction of the Rh\(^{III}\) complexes (see Chapter:III,IV) are thought to be the active species for catalytic hydrogenation of olefins. Thus, preparations of Rh\(^{I}\) chloro and sulphur complexes were attempted and, where successful, the catalytic activity was investigated. These studies would give further insight into the mechanism of hydrogenation of olefins catalyzed by Rh\(^{III}\) complexes in DMA and the effect of ligands on catalytic activity.

6.2 Attempted Preparations of Rh\(^{I}\) Complexes Containing Sulphur Ligands

No Rh\(^{I}\) complexes with R\(_2\)S type ligands (R = alkyl, phenyl or aryl) appear to have been reported. Since Rh\(^{I}\) forms complexes with ligands like Ph\(^{3}P\),\(^{7-10}\) Ph\(^{3}As\)\(^{7-10,71}\), and Ph\(^{3}Sb\)\(^{7-10,11}\), \(\pi\)-acceptor ligands such as Ph\(_2\)S, Bz\(_2\)S and Et\(_2\)S, were thought likely to form stable Rh\(^{I}\) complexes.
However, we could not isolate any such complexes.

The attempted methods of preparation were as follows. Stoichiometric amounts of ligands were added to ethanolic solutions of RhCl₃ · 3H₂O in the 1:2 or 1:3 ratio of Rh:ligand. No visible change in colour was observed in cold ethanolic solutions. On gentle warming, the solution with Bz₂S yielded a yellow precipitate of RhCl₃(Bz₂S)₃ (Chapter II, section 2.11), while no changes were observed in solutions containing Ph₂S and Et₂S. When the solutions were refluxed metal was deposited in solutions containing Ph₂S and Et₂S. When H₂ was passed through the cold ethanolic solutions, no visible change was observed; but at 60° metal was deposited in all the solutions. The above preparations were also attempted in DMA but there was either no visible change or else metal was found.

Since no simple and convenient method was found for the preparation of RhI complexes containing R₂S ligands, preparations of such complexes "in situ" were attempted. [Rh(C₂H₄)₂Cl]₂ and [Rh(C₈H₁₄)₂Cl]₂ were used as starting materials. [Rh(C₂H₄)₂Cl]₂ was found to be less amenable for use because of the slow decomposition of the complex in solid state. [Rh(C₈H₁₄)₂Cl]₂ was found to be very useful for preparing "in situ" RhI(Et₂S), RhI(Bz₂S) or RhICl complexes in DMA; with Ph₂S, a black precipitate, probably metal, was obtained and this was not studied further. A gas chromatogram of the solvent pumped off from the DMA solution of [Rh(C₈H₁₄)Cl]₂ with added Et₂S or Cl⁻ showed the presence of 2 moles of cyclooctene per mole of Rh (Beckman G.C. 2A instrument, dinonyl phthalate column, retention time = 12 min, 160 ma, 160°, pressure gauge setting = 10).
6.3 The Rh\textsuperscript{I}(Et\textsubscript{2}S) Catalyzed Hydrogenation of MA in DMA

[Rh(C\textsubscript{8}H\textsubscript{14})\textsubscript{2}Cl\textsubscript{2}] \textsubscript{2} is sparingly soluble in DMA, but on addition of Et\textsubscript{2}S, Rh:Et\textsubscript{2}S = 1:2, in air, an orange red solution was obtained which showed a continuum in the visible region at least down to 350 \textmu m; \varepsilon at 450 \textmu m is 460. The orange-red solution was stable to air at room temperature and on adding excess MA, \varepsilon at 450 \textmu m decreased to 400 suggesting complexing between Rh\textsuperscript{I} and MA. The spectra indicate the presence of Rh\textsuperscript{I} species. Such Rh\textsuperscript{I}(Et\textsubscript{2}S) solutions were found to hydrogenate MA at 80° and 1 atm of \textsubscript{2}H. A typical gas uptake plot is shown in Figure 27, there is an initial induction period followed by a linear region. The spectrum of the solution during the hydrogenation region was a continuum and essentially the same as the solution before hydrogenation (\varepsilon = 390 at 450 \textmu m). Hydrogenation carried out in the special "air-free" device (see section 2.3) in which a solution of MA and Et\textsubscript{2}S was carefully degassed before introducing [Rh(C\textsubscript{8}H\textsubscript{14})\textsubscript{2}Cl\textsubscript{2}] showed a continual decrease in rate. The discrepancy in two rate plots of this kind led to the finding that [Rh(C\textsubscript{8}H\textsubscript{14})\textsubscript{2}Cl\textsubscript{2}] in LiCl/DMA and possibly the Rh\textsuperscript{I}(Et\textsubscript{2}S) complex form molecular oxygen complexes (Chapter VIII). Under \textsubscript{2}H\textsubscript{2} in the absence of MA, the Rh\textsuperscript{I}(O\textsubscript{2}) complex readily loses the \textsubscript{2}O\textsubscript{2} and reverts back to a Rh hydride species (Chapter VIII). The stoichiometry of \textsubscript{2}H\textsubscript{2} uptake for both uptake plots in Figure 27 at the point of metal precipitation corresponded to complete hydrogenation of MA to SA.

An unexpected amount of \textsubscript{2}H\textsubscript{2} uptake was observed after the metal had appeared. In the absence of MA, the Rh\textsuperscript{I}(Et\textsubscript{2}S) solution was rapidly reduced by \textsubscript{2}H\textsubscript{2} to the metal and an uptake more than the reduction of
Figure 27. Rate plot for the Rh$^\text{I}$ (Et$_2$S) catalyzed hydrogenation of MA in DMA at 80°,
(5.0 x 10$^{-3}$ M Rh, 2.32 x 10$^{-3}$ M H$_2$, 3.0 x 10$^{-2}$ M MA) (O) solution made up in air,
(Δ) solution made up in absence of air, (□) log [MA]
Rhὴ to Rh⁰ was again observed. The Rh⁺(E₂S) solution was inactive for homogeneous hydrogenation of cyclooctene; metal was rapidly produced together with a very fast H₂ absorption. The uptake observed after metal production is probably due to the heterogeneous reduction of C₈H₁₄. More quantitative data on this extra H₂ uptake in the Rh⁺Cl system is in agreement with this conclusion (section 6.4).

When the Rh⁺(E₂S) solution was kept under N₂ at 80° for 5000 sec, no gas uptake was observed and metal was produced, possibly through disproportionation (equation 3.10). The molar conductances for a 5.0 × 10⁻³ M and 2.0 × 10⁻² M stock solution of Rh⁺(E₂S) were 0.7 ohm⁻¹ cm⁻² mole⁻¹ and 1.3 ohm⁻¹ cm⁻² mole⁻¹, respectively. The molar conductance for a 1:1 electrolyte in DMA is around 46-60 ohm⁻¹ cm⁻² mole⁻¹.

6.31 Kinetics of the Rh⁺(E₂S) Catalyzed Hydrogenation of MA

In all these studies, the [Rh] is expressed in terms of molarity of monomeric rhodium species (i.e. twice the dimer concentration). A few reactions were carried out in the special air-free device. At 2.5 × 10⁻³ and 5.0 × 10⁻³ M [Rh], the rate plots analyzed for first order on H₂ consumption (Figure 27) i.e. first order dependence on [MA], and the pseudo first order rate constants (k') show an approximate second order dependence on [Rh] (Table XVI). At 1.0 × 10⁻² M [Rh], the rate plot did not analyze for first order dependence on [MA]. The k' value showed between first and zero order dependence on H₂ (Table XVI). At 0.06 M [MA], k' = 1.4 × 10⁻⁴ sec⁻¹ which was different from that at 0.03 M [MA], 3.7 × 10⁻⁴ sec⁻¹, when all the other variables are kept the same (Table XVI). Because of the complicated kinetics, this system was not studied further.
TABLE XVI

Kinetic Data for the $[\text{Rh} \left( \text{C}_8\text{H}_{14} \right) \text{Cl}]_2$ Catalyzed Hydrogenation of MA in Et$_2$S/DMA Media Under "Air Free" Conditions

(\text{Rh:Et}_2\text{S} = 1:2)

<table>
<thead>
<tr>
<th>[Rh] (x 10$^3$ M)</th>
<th>[MA] (M)</th>
<th>$pH_2$ (mm)</th>
<th>$[H_2]$ (x 10$^3$ M)</th>
<th>$k'$ (x 10$^4$ sec$^{-1}$)</th>
<th>T (°C)</th>
</tr>
</thead>
<tbody>
<tr>
<td>5.0</td>
<td>0.03</td>
<td>725</td>
<td>2.32</td>
<td>10.40</td>
<td>80</td>
</tr>
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<td>1.04</td>
<td>55</td>
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<tr>
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<td>2.40</td>
<td>3.68</td>
<td>55</td>
</tr>
<tr>
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<td>725</td>
<td>2.40</td>
<td>--</td>
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<td>0.03</td>
<td>226</td>
<td>0.73</td>
<td>1.50</td>
<td>55</td>
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</table>
A more detailed study was made on the stock solutions of \( \text{Rh}^I(\text{Et}_2\text{S}) \) made up in air since simple kinetics resulted. The linear rates were measured; first order dependence on [Rh], [H\(_2\)] and independence of [MA] were observed (Table XVII, Figures 28,29). The kinetic data gave the rate law

\[
\frac{-d[H_2]}{dt} = k_2[Rh][H_2]
\]  

and the average value of \( k_2 \) as \( 2.85 \text{ M}^{-1}\text{sec}^{-1} \). There was a slight deuterium isotope effect, \( k_2^H/k_2^D = 1.2 \). p-Toluenesulphonic acid had practically no effect on the rate.

LiCl inhibited the rate of hydrogenation and a constant \( k_2 \) value of \( 0.56 \text{ M}^{-1}\text{sec}^{-1} \), was obtained on addition of 0.015-0.125 M LiCl. Addition of 0.05 M \( \text{C}_8\text{H}_{14} \) did not inhibit the rate, neither did the addition of 0.005 M \( \text{Et}_2\text{S} \) (Table XVII).

A good Arrhenius plot was obtained for the temperature range 70-84\(^\circ\) and the activation parameters \( \Delta H_2^+ \) and \( \Delta S_2^+ \) were found to be \( 14.1 \pm 0.5 \text{ Kcal mole}^{-1} \) and \( -17.4 \pm 0.4 \text{ e.u.} \) (Table XVIII, Figure 30).

6.4 The \( \text{Rh}^I\text{Cl} \) Catalyzed Hydrogenation of MA

Stock solutions of [Rh(\( \text{C}_8\text{H}_{14} \))_2\text{Cl}]_2 in 0.45 M LiCl/DMA were made up in air; a molecular oxygen complex is initially formed but this reverts to a hydride with the loss of \( \text{O}_2 \) under \( \text{H}_2 \) (Chapter VIII). Such stock solutions were efficient for the homogeneous hydrogenation of MA at 80\(^\circ\) and 1 atm \( \text{H}_2 \). Typical linear \( \text{H}_2 \) uptake plots are shown in Figure 31; the rate started to fall off in the region where the ratio
TABLE XVII
Rh(I)(Et₂S) Catalyzed Hydrogenation of MA

Kinetic Data at 80° in DMA

(Dec::Et₂S = 1:2)

<table>
<thead>
<tr>
<th>[Rh] x 10⁻³ M</th>
<th>[MA] M</th>
<th>pH₂ mm</th>
<th>[H₂] x 10⁻³ M</th>
<th>Linear Rate x 10⁻⁵ M sec⁻¹</th>
<th>k₂⁻¹ M⁻¹ sec⁻¹</th>
</tr>
</thead>
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<tr>
<td>1.0</td>
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<td>5.0</td>
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<td>0.68</td>
<td>0.58b</td>
</tr>
<tr>
<td>5.0</td>
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<td>2.32</td>
<td>0.64</td>
<td>0.55c</td>
</tr>
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<td>0.66</td>
<td>0.57d</td>
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<td>725</td>
<td>2.32</td>
<td>2.70</td>
<td>2.33i</td>
</tr>
</tbody>
</table>

a 0.45 M LiCl; b 0.125 M LiCl; c 0.03 M LiCl; d 0.015 M LiCl;
e 0.05 M p-toluenesulphonic acid; f 0.01 M p-toluenesulphonic acid;
g 0.05 M cyclooctene; h 0.005 M Et₂S; i D₂ in place of H₂.
Figure 28. Rh\textsuperscript{I}(Et\textsubscript{2}S) catalyzed hydrogenation of MA in DMA at 80°. Variation of linear rate with [Rh], (2.32 x 10\textsuperscript{-3} M H\textsubscript{2}, 3.0 x 10\textsuperscript{-2} M MA).

Figure 29. Rh\textsuperscript{I}(Et\textsubscript{2}S) catalyzed hydrogenation of MA in DMA at 80°. Variation of linear rate with [H\textsubscript{2}], (5.0 x 10\textsuperscript{-3} M Rh, 3.0 x 10\textsuperscript{-2} M MA).
TABLE XVIII

Rh\textsuperscript{1}(Et\textsubscript{2}S) Catalyzed Hydrogenation of MA in DMA

Temperature Dependence of \( k_2 \)

\([\text{Rh}] = 5.0 \times 10^{-3} \text{ M}, \ [\text{MA}] = 3.0 \times 10^{-2} \text{ M} \)

<table>
<thead>
<tr>
<th>T (^\circ\text{C})</th>
<th>( [\text{H}_2] \times 10^3 \text{ M} )</th>
<th>Linear Rate ( \text{M sec}^{-1} )</th>
<th>( k_2 \text{ M}^{-1} \text{sec}^{-1} )</th>
</tr>
</thead>
<tbody>
<tr>
<td>70</td>
<td>2.36</td>
<td>1.80</td>
<td>1.53</td>
</tr>
<tr>
<td>74.5</td>
<td>2.34</td>
<td>2.40</td>
<td>2.05</td>
</tr>
<tr>
<td>80</td>
<td>2.32</td>
<td>3.34</td>
<td>2.88</td>
</tr>
<tr>
<td>84</td>
<td>2.30</td>
<td>4.32</td>
<td>3.76</td>
</tr>
</tbody>
</table>
Figure 30. Arrhenius plot for the Rh\textsuperscript{I}(Et\textsubscript{2}S) catalyzed hydrogenation of MA in DMA, (5.0 \times 10^{-3} M Rh, 3.0 \times 10^{-2} M MA).
Figure 31. Typical rate plots for the RhCl\textsuperscript{I} catalyzed hydrogenation of MA in 0.45 M LiCl/DMA at 80°. (2.32 x 10\textsuperscript{-3} M H\textsubscript{2}, 3.0 x 10\textsuperscript{-2} M MA; [Rh]: (O) 5.0 x 10\textsuperscript{-3} M, (Δ) 1.8 x 10\textsuperscript{-3} M)
of Rh:MA is 1:1 and the stoichiometry of the H₂ uptake at the point of metal precipitation corresponded to the complete hydrogenation of MA; a faster uptake followed metal production (the stoichiometry corresponding closely to the reduction of cyclooctene). An initial induction period was also observed similar to that in the Rh\(^I\)(Et₂S) system (Section 6.4). A reaction carried out in the special "air free" device, like the Rh\(^I\)(Et₂S) system, showed a first order dependence on H₂ consumption and this was not studied further. In the absence of MA, metal was rapidly produced. Rh\(^I\)Cl did not homogeneously hydrogenate C₈H₁₄.

The visible spectrum of a stock solution of [Rh(C₈H₁₄)₂Cl]₂ in 0.45 M LiCl/DMA made up in air showed a slight shoulder at 400 μm, ε = 230. Addition of MA had little effect on the spectrum, a shoulder at 450 μm, ε = 250, was observed. The spectrum of a hydrogenated solution showed a shoulder at 450 μm, ε = 290; this changed when the solution was exposed to air at room temperature and finally after 3 days, a steady spectrum with an absorption maxima at 440 μm (ε = 420) and a broad peak at 543 (ε = 124) indicative of Rh\(^III\) chloride^{1,2} species was observed (cf. RhCl₃·3H₂O in 1.2 M LiCl/DMA, λₘₐₓ 444 μm, ε = 343, λₘₐₓ 548, ε = 115). The same changes in spectrum (λₘₐₓ 400 μm, ε = 332, λₘₐₓ 540, ε = 120) were observed after the hydrogenated solution had reacted with O₂ for 100 sec at 80° and the total O₂ uptake corresponded closely to oxidation of Rh\(^I\) to Rh\(^III\) (1.2 x 10⁻⁵ moles of O₂ per 2.5 x 10⁻⁵ moles of Rh).

Spectral studies of [Rh(C₈H₁₄)₂Cl]₂ in LiCl/DMA media with or without MA were also carried out in vacuum and under O₂ and H₂ atmospheres using the special cell attachment described in section 2.6.
to study the possible complexing between Rh\textsuperscript{I} and MA.

In vacuum, \([\text{Rh}(C_8H_{14})_2\text{Cl}]_2\) in 0.5 M LiCl/DMA gave a continuum down to 350 m\(\mu\), \(\varepsilon\) at 450 m\(\mu\) = 228. On exposing this solution to different O\(_2\) pressures, a shoulder developed at 450 m\(\mu\); at 73 mm O\(_2\), \(\varepsilon\) at 450 m\(\mu\) = 182, at 760 mm O\(_2\), \(\varepsilon\) at 450 m\(\mu\) = 168 (Figure 32).

\([\text{Rh}(C_8H_{14})_2\text{Cl}]_2\) in 0.45 M LiCl/DMA with 0.03 M MA, A, in vacuum showed a continuum initially down to 350 m\(\mu\), \(\varepsilon\) at 450 m\(\mu\) = 250. On standing at room temperature for 15 min, the spectrum changed, \(\varepsilon\) = 182 at 450 m\(\mu\); on further standing at room temperature for a few hours a shoulder developed at 450 m\(\mu\), \(\varepsilon\) = 246. Such changes were thought to be due to the slow formation of a Rh\textsuperscript{I}(MA) complex at room temperature. If the solution of A is left in air for 3 hours, B, absorption maxima at 448, \(\varepsilon\) = 266, and 544, \(\varepsilon\) = 110, were observed; and eventually after 2 days, a steady spectrum was observed (\(\lambda_{\text{max}}\) 444, \(\varepsilon\) = 404, \(\lambda_{\text{max}}\) 550, \(\varepsilon\) = 126) (Figure 33). When B was treated with H\(_2\) at 80\(^\circ\) for 500 sec, a slight shoulder at 430 m\(\mu\) is observed, \(\varepsilon\) at 450 m\(\mu\), is 290 m\(\mu\).

When A was made up under H\(_2\) at room temperature, a shoulder at 468 m\(\mu\) was observed, \(\varepsilon\) = 188. This spectrum changed slowly with time (Figure 34), an isosbestic point was observed. After 3 hours at room temperature, a slight shoulder developed at 450 m\(\mu\), \(\varepsilon\) = 220. These changes were accelerated by heating to 60\(^\circ\) for a few minutes. Such a solution on standing in air at room temperature gave \(\lambda_{\text{max}}\) at 444 m\(\mu\), \(\varepsilon\) = 400 and \(\lambda_{\text{max}}\) at 550 m\(\mu\), \(\varepsilon\) = 124.
Figure 32. Absorption spectra of \([\text{Rh}(\text{C}_8\text{H}_{14})_2\text{Cl}]_2\) in 0.5M LiCl/DMA at room temperature. 
(I) in vacuum (II) under 73 mm \(O_2\) (III) under 760 mm of \(O_2\).
Figure 33. Absorption spectra of [Rh(C₈H₁₄)₂Cl] and MA in 0.45M LiCl/DMA in vacuum at room temperature. (I) initial spectrum, (II) after 15 min., (III) after 3 hours, (IV) the solution left in air for 2 days, B, (V) B treated with H₂ at 80° for 500 sec.
Figure 34. Absorption spectra of \([\text{Rh}(\text{C}_8\text{H}_{14})\text{Cl}]_2\) in 0.45M LiCl/DMA under H\(_2\) at room temperature. (I) initial spectrum, (II) after 1/2 hour, (III) after 3 hours, (IV) the solution left in air 2 days.
6.41 Kinetics of the Rh\textsuperscript{I}Cl Catalyzed Hydrogenations of MA

Stock solutions of Rh\textsuperscript{I}Cl made up in air were used and kinetic data were obtained by measuring the linear $H_2$ uptake plots. From 0.015-0.060 M [MA], the rate of hydrogenation was first order in [Rh], [H\textsubscript{2}], and independent of [MA] ([Rh]=monomer) (Table XIX, Figures 35, 36). The rate law is of the form shown in equation 6.1, the average $k_2$ value was found to be $2.1 \text{ M}^{-1} \text{sec}^{-1}$.

A good Arrhenius rate plot was observed for the temperature range 70-85° (Table XX, Figure 37) with activation parameters $\Delta H_2^+ = 18.0 \pm 0.5 \text{ Kcal mole}^{-1}$ and $\Delta S_2^+ = -6.8 \pm 1.4 \text{ e.u.}$

6.5 Discussion of the Rh\textsuperscript{I} Systems

The u.v. and visible spectrophotomeric and kinetic data i.e. pseudo zero order kinetics (cf. Chapter III) suggest that the hydrogenations of MA described in section 5.3 and 5.4 were catalyzed by Rh\textsuperscript{I}(Et\textsubscript{2}S) and Rh\textsuperscript{I}Cl species, respectively. The easy displacement of C\textsubscript{8}H\textsubscript{14} from [Rh(C\textsubscript{8}H\textsubscript{14})\textsubscript{2}Cl]\textsuperscript{206} has provided a general method for preparing other Rh\textsuperscript{I} complexes, e.g. RhCl(Ph\textsubscript{3}P)\textsubscript{8,10}. The observed first order dependences on [Rh], using stock solutions of Rh\textsuperscript{I}(Et\textsubscript{2}S) and Rh\textsuperscript{I}Cl, give no evidence for a dimer $\rightleftharpoons$ monomer equilibrium and indicates either the dimeric species is active or else that the dimer dissociates completely to active monomer under these experimental conditions. The latter seems much more likely; there are no clear cases of hydrogenation through dimeric catalytic species. Et\textsubscript{2}S or Cl\textsuperscript{-} are likely to cleave the chloride bridges in [Rh(C\textsubscript{8}H\textsubscript{14})\textsubscript{2}Cl]\textsubscript{2} in DMA to give monomeric Rh\textsuperscript{I} species. Complexes such as [Rh(CO)\textsubscript{2}Cl]\textsubscript{2} are readily
TABLE XIX
RhCl\textsuperscript{I} Catalyzed Hydrogenation of MA
Kinetic Data at 80° in 0.45 M LiCl/DMA

<table>
<thead>
<tr>
<th>[Rh] x 10\textsuperscript{-3} M</th>
<th>[MA] M</th>
<th>pH\textsubscript{2} mm</th>
<th>[H\textsubscript{2}] x 10\textsuperscript{-3} M</th>
<th>Linear Rate x 10\textsuperscript{5} M sec\textsuperscript{-1}</th>
<th>k\textsubscript{2} M\textsuperscript{-1} sec\textsuperscript{-1}</th>
</tr>
</thead>
<tbody>
<tr>
<td>1.0</td>
<td>0.03</td>
<td>725</td>
<td>2.32</td>
<td>0.48</td>
<td>2.06</td>
</tr>
<tr>
<td>1.8</td>
<td>0.03</td>
<td>725</td>
<td>2.32</td>
<td>0.76</td>
<td>1.84</td>
</tr>
<tr>
<td>2.5</td>
<td>0.03</td>
<td>725</td>
<td>2.32</td>
<td>1.16</td>
<td>2.07</td>
</tr>
<tr>
<td>4.0</td>
<td>0.03</td>
<td>725</td>
<td>2.32</td>
<td>1.90</td>
<td>2.04</td>
</tr>
<tr>
<td>5.0</td>
<td>0.03</td>
<td>725</td>
<td>2.32</td>
<td>2.48</td>
<td>2.14</td>
</tr>
<tr>
<td>2.5</td>
<td>0.03</td>
<td>214</td>
<td>0.70</td>
<td>0.33</td>
<td>1.86</td>
</tr>
<tr>
<td>2.5</td>
<td>0.03</td>
<td>371</td>
<td>1.18</td>
<td>0.58</td>
<td>1.96</td>
</tr>
<tr>
<td>2.5</td>
<td>0.03</td>
<td>459</td>
<td>1.48</td>
<td>0.73</td>
<td>1.96</td>
</tr>
<tr>
<td>2.5</td>
<td>0.03</td>
<td>636</td>
<td>2.04</td>
<td>1.06</td>
<td>2.08</td>
</tr>
<tr>
<td>2.5</td>
<td>0.03</td>
<td>783</td>
<td>2.51</td>
<td>1.31</td>
<td>2.08</td>
</tr>
<tr>
<td>2.5</td>
<td>0.06</td>
<td>725</td>
<td>2.32</td>
<td>1.00</td>
<td>1.72</td>
</tr>
<tr>
<td>2.5</td>
<td>0.015</td>
<td>725</td>
<td>2.32</td>
<td>1.20</td>
<td>2.07</td>
</tr>
</tbody>
</table>
Figure 35. RhCl catalyzed hydrogenation of MA in 0.45M LiCl/DMA at 80°. Variation of rate with [Rh], (2.32 x 10^-3 M H₂, 3.0 x 10^-2 M MA).
Figure 36. $\text{Rh}^1\text{Cl}$ catalyzed hydrogenation of MA in 0.45M LiCl/DMA at 80°. Variation of rate with $[\text{H}_2]$, (2.5 $\times$ 10^{-3} M Rh, 3.0 $\times$ 10^{-2} M MA).
TABLE XX

Rh\textsuperscript{I}Cl Catalyzed Hydrogenation of MA in 0.45 M LiCl/DMA

Temperature Dependence of $k_2$

$[\text{Rh}] = 2.5 \times 10^{-3}$ M, $[\text{MA}] = 0.03$

<table>
<thead>
<tr>
<th>$T$ (°C)</th>
<th>$[\text{H}_2]$ ($\times 10^3$ M)</th>
<th>Linear Rate ($\times 10^5$ M sec\textsuperscript{-1})</th>
<th>$k_2$ (M\textsuperscript{-1} sec\textsuperscript{-1})</th>
</tr>
</thead>
<tbody>
<tr>
<td>70</td>
<td>2.36</td>
<td>0.56</td>
<td>0.95</td>
</tr>
<tr>
<td>75.2</td>
<td>2.34</td>
<td>0.88</td>
<td>1.50</td>
</tr>
<tr>
<td>80</td>
<td>2.32</td>
<td>1.16</td>
<td>2.07</td>
</tr>
<tr>
<td>85</td>
<td>2.30</td>
<td>1.80</td>
<td>3.13</td>
</tr>
</tbody>
</table>
Figure 37. Arrhenius plot for the Rh<sup>III</sup>Cl catalyzed hydrogenation of MA in 0.45M LiCl/DMA, (2.5 x 10<sup>-3</sup> M Rh, 3.0 x 10<sup>-2</sup> M MA).
cleaved by donor ligands, including the Cl\textsuperscript{-} ion.\textsuperscript{174,175,230} The fact that dimeric [Rh(C\textsubscript{8}H\textsubscript{14})\textsubscript{2}Cl\textsubscript{2}] is only slightly soluble in DMA but dissolves readily on addition of Et\textsubscript{2}S or Cl\textsuperscript{-} agrees with this. C\textsubscript{8}H\textsubscript{14} has been shown to dissociate completely from the initial complex in solution hence Cl\textsuperscript{-}, DMA or Et\textsubscript{2}S will occupy the vacant coordination sites. Added C\textsubscript{8}H\textsubscript{14} did not interfere with the catalytic hydrogenation activity of such solutions.

Wilkinson et al\textsuperscript{10} found that a solution containing Ph\textsubscript{3}P and [Rh(C\textsubscript{8}H\textsubscript{14})Cl\textsubscript{2}] (Ph\textsubscript{3}P:Rh = 3:1) in benzene gave the same kinetic results for hydrogenation of olefins as using RhCl(Ph\textsubscript{3}P)\textsubscript{3} crystals in benzene.

The spectral changes of the solution of [Rh(C\textsubscript{8}H\textsubscript{14})Cl] in LiCl/DMA with MA in vacuum strongly suggest the slow complexing between MA and Rh\textsuperscript{I} at room temperature. This final solution showed a spectrum very similar to the stock solution of Rh\textsuperscript{I}Cl with MA suggesting that in the hydrogenations described, the initial species present was Rh\textsuperscript{I}(MA) formed by displacing the O\textsubscript{2} in Rh\textsuperscript{I}O\textsubscript{2} which was present initially in the stock solutions. In some molecular oxygen complexes, displacement of O\textsubscript{2} by olefin has been reported.\textsuperscript{77,80,90}

\[
\text{Rh}^\text{I}(O_2) + \text{MA} \rightarrow \text{Rh}^\text{I}(\text{MA}) + O_2 \quad (6.2)
\]

A different spectrum was observed initially when [Rh(C\textsubscript{8}H\textsubscript{14})\textsubscript{2}Cl] in 0.45 LiCl/DMA with MA was kept under H\textsubscript{2} as compared to that kept under vacuum. This suggested the presence of a Rh hydride species. On standing at room temperature for a few hours or when heated up to 60° for a few minutes the spectrum approached that of a Rh\textsuperscript{I}(MA) species.
The isosbestic point is highly suggestive of a mixture of 2 species probably \( \text{Rh}^{\text{III}}\text{H}_2 \) and \( \text{Rh}^{\text{I}}(\text{MA}) \) in solution. Hence the \( \text{Rh}^{\text{I}}(\text{MA}) \) is probably present under the hydrogenation conditions, i.e. at 80°.

All the spectral evidence strongly suggests the existence of a \( \text{Rh}^{\text{I}}(\text{MA}) \) complex in the \( \text{Rh}^{\text{I}}\text{Cl} \) system during the hydrogenation conditions; a similar \( \text{Rh}^{\text{I}}(\text{MA}) \) complex is again very likely formed in the \( \text{Rh}^{\text{I}}(\text{Et}_2\text{S}) \) system prior to hydrogenation.

The kinetics of hydrogenation for both systems using stock solutions made in air are simple with a first order dependence on [\( \text{Rh} \)], [\( \text{H}_2 \)] and independence of [\( \text{MA} \)]. The \( \text{Rh}^{\text{I}}(\text{MA}) \) complex formed in the two systems reacts with \( \text{H}_2 \) in a rate determining step to give \( \text{Rh}^{\text{I}} \) and SA; the \( \text{Rh}^{\text{I}} \) then further reacts with MA in a fast step.

\[
\text{Rh}^{\text{I}}(\text{MA}) + \text{H}_2 \xrightarrow{k_2} \text{Rh}^{\text{I}} + \text{SA} \quad (6.3)
\]

\[
\text{Rh}^{\text{I}} + \text{MA} \xrightarrow{\text{fast}} \text{Rh}^{\text{I}}(\text{MA}) \quad (6.4)
\]

These conclusions are in agreement with the results from the \( \text{RhCl}_3(\text{Et}_2\text{S})_3 \) and \( \text{RhCl}_3 \cdot 3\text{H}_2\text{O} \) catalyzed hydrogenation of MA.

The kinetic data from the few experiments performed in the "air-free" conditions for the \( \text{Rh}^{\text{I}}(\text{Et}_2\text{S}) \) system suggest that some monomer and dimer equilibrium might be involved. Oxygen and a time factor could be important in promoting the formation of monomeric species in the stock solutions. Quite similar complicated kinetics have been observed in the \( \text{RhCl}_3 \cdot 3\text{H}_2\text{O} \) catalyzed hydrogenation of MA in the absence of added LiCl and these were interpreted in terms of dimeric \( \text{Rh}^{\text{I}}(\text{MA}) \) species.
6.6 Comparison of the Substrate Hydrogenation Rates in the Rh\textsuperscript{III} and Rh\textsuperscript{I} Systems

The kinetic data obtained for the various Rh\textsuperscript{III} and Rh\textsuperscript{I} systems (excluding the data for the Rh\textsuperscript{I}(Et\textsubscript{2}S) system in "air free" conditions) are summarized in Table XXI. Hydrogenation (equation 6.3) is thought to involve the activation of H\textsubscript{2} through dihydride formation via oxidative addition for both Rh\textsuperscript{I}(Et\textsubscript{2}S) and Rh\textsuperscript{I}Cl systems (see section 5.12). The activation parameters obtained for the Rh\textsuperscript{I}Cl system are almost identical with those reported for the hydrogenation step in the RhCl\textsubscript{3}·3H\textsubscript{2}O catalyzed system in 1.2 M LiCl/DMA media.\textsuperscript{1,2} This shows that the same reactive Rh\textsuperscript{I} intermediates and the same rate determining steps are likely involved in both systems. The faster rate of hydrogenation in the Rh\textsuperscript{I}(Et\textsubscript{2}S) catalyzed system as compared with the RhCl\textsubscript{3}(Et\textsubscript{2}S)\textsubscript{3} system is reflected in the lower ΔH\textsubscript{2}^\textdagger value. Different Rh\textsuperscript{I} species are involved in the Rh\textsuperscript{I}Et\textsubscript{2}S catalyzed hydrogenations since the ratio of Rh:Cl\textsuperscript{−} is different for the two systems.

When 0.015-0.125 M Cl\textsuperscript{−} was added to the Rh\textsuperscript{I}(Et\textsubscript{2}S) system, which initially has a maximum of 1 Cl\textsuperscript{−} per mole of Rh, a lower limiting rate was obtained (Table XVII). This lower k\textsubscript{2} value (0.56 M\textsuperscript{-1}sec\textsuperscript{-1}) is more comparable to the k\textsubscript{2} value 0.33 M\textsuperscript{-1}sec\textsuperscript{-1} for the corresponding RhCl\textsubscript{3}(Et\textsubscript{2}S)\textsubscript{3} system which contains 3 Cl\textsuperscript{−} per Rh. Non-inhibition of rate on addition of 0.005 M Et\textsubscript{2}S to the Rh\textsuperscript{I}(Et\textsubscript{2}S) system is significant because this shows a maximum of 2 moles of Et\textsubscript{2}S are coordinated per mole of Rh\textsuperscript{I}. Previous studies\textsuperscript{3,4} indicated that 1 mole of Et\textsubscript{2}S dissociates per mole of RhCl\textsubscript{3}(Et\textsubscript{2}S)\textsubscript{3} prior to reduction of the complex to Rh\textsuperscript{I} (Chapter III, equations 3.2-3.5).
TABLE XXI
Comparison of $k_2$ Values and Activation Parameters for the $\text{Rh}^{\text{III}}$ and $\text{Rh}^{\text{I}}$ Catalyzed Hydrogenation of MA in DMA

<table>
<thead>
<tr>
<th>Initial Complex</th>
<th>$k_2^{\text{L}^{-1}\text{sec}^{-1}}$</th>
<th>$\Delta H_2^{\dagger}$</th>
<th>$\Delta S_2^{\dagger}$</th>
<th>$k_2^{\text{H}_2^{2}/k_2^{\text{D}_2}}$</th>
</tr>
</thead>
<tbody>
<tr>
<td>$\text{RhCl}_2(\text{Et}_3\text{S})_2$</td>
<td>0.33</td>
<td>21.4</td>
<td>-1.0</td>
<td>1.05</td>
</tr>
<tr>
<td>$\text{Rh}^{\text{I}}(\text{Et}_2\text{S})$</td>
<td>2.85</td>
<td>14.1</td>
<td>-17.4</td>
<td>1.2</td>
</tr>
<tr>
<td>$\text{Rh}^{\text{I}}(\text{Et}_2\text{S})^a$</td>
<td>0.56</td>
<td>--</td>
<td>--</td>
<td>--</td>
</tr>
<tr>
<td>$\text{RhCl}_3\cdot\text{H}_2\text{O}^b$</td>
<td>1.5</td>
<td>18.4</td>
<td>-6.1</td>
<td>1.08</td>
</tr>
<tr>
<td>$\text{Rh}^{\text{I}}\text{Cl}^c$</td>
<td>2.1</td>
<td>18.0</td>
<td>-6.8</td>
<td>--</td>
</tr>
</tbody>
</table>

$^a$ Result for addition of 0.015–0.125 M LiCl.

$^b$ in 1.2 M LiCl/DMA media.

$^c$ in 0.45 M LiCl/DMA media.
It is interesting to speculate on the active $\text{Rh}^I$ species likely to be present for reaction 4.2 in the various systems listed in Table XXI. The $\text{Rh}^I(\text{Et}_2\text{S})$ system can involve a maximum of 1 Cl$^-$ per Rh and the neutral $\text{RhCl}(\text{Et}_2\text{S})_2$(MA) complex seems likely; addition of Cl$^-$ could produce a less reactive $[\text{RhCl}_2(\text{Et}_2\text{S})\text{MA}]^-$ species. The $\text{RhCl}_3(\text{Et}_2\text{S})_3$ system could produce the $[\text{RhCl}_2(\text{Et}_2\text{S})\text{MA}]^-$ complex "in situ", with the addition of Cl$^-$ having little effect on reactivity as observed.\textsuperscript{4} The $\text{Rh}^I\text{Cl}$ or $\text{RhCl}_3$·3H$_2$O systems in 1.2 M LiCl DMA media (no Et$_2$S) could involve $[\text{RhCl}_3(\text{MA})]^2-$ or $[\text{RhCl}_2(\text{DMA})(\text{MA})]^-$ species; if the former, the data in Table XXI indicates decreasing reactivity in the trend $\text{RhCl}(\text{Et}_2\text{S})_2$MA $\rightarrow$ $[\text{RhCl}_3\text{MA}]^2-$ $\rightarrow$ $[\text{RhCl}_2(\text{Et}_2\text{S})(\text{MA})]^-$. if the latter, reactivity would decrease in the trend $\text{RhCl}(\text{Et}_2\text{S})_2$(MA) $\rightarrow$ $[\text{RhCl}_2(\text{DMA})(\text{MA})]^-$ $\rightarrow$ $[\text{RhCl}_2(\text{Et}_2\text{S})(\text{MA})]^-$.\textsuperscript{4}

Two groups have recently\textsuperscript{118,231} shown that the halide and not the diene ligand in complexes such as $[\text{Rh}(\text{C}_8\text{H}_{12})\text{Cl}]_2$ can be replaced by phosphine (L) to give cationic species such as $[\text{Rh}(\text{C}_8\text{H}_{12})\text{L}]^+$ if the reaction is carried out in polar solvents. The cationic species are also catalysts for homogeneous hydrogenation through dihydride formation.\textsuperscript{118} The conductance measurement however shows no evidence of chloride dissociation in the $\text{Rh}^I\text{Et}_2\text{S}$ system. The diene ligand is presumably more strongly attached than the monoene.

The induction period observed in the $\text{Rh}^I(\text{Et}_2\text{S})$ system and in the $\text{Rh}^I\text{Cl}$ system could be due to evolution of O$_2$ from the molecular oxygen complex present in the stock solutions which are made up in air (equation 6.2). $[\text{Rh}(\text{C}_8\text{H}_{14})_2\text{Cl}]_2$ in 0.5 M LiCl/DMA was found to form molecular oxygen complexes which under H$_2$ atmospheres lose the O$_2$.\textsuperscript{118,231}
(Chapter VIII). The formation of molecular O₂ complex by [Rh(C₈H₁₄)₂Cl]₂ in Et₂S/DMA was not studied but the system does catalyze oxidation and presumably forms an oxygen complex (Chapter VIII). The absence of the induction period for solutions made up in absence of air support this reasoning, i.e. O₂ has an initial deactivating effect presumably by occupying a coordination position required for hydride or olefin. In hydrogenations catalyzed by IrCl(CO)(Ph₃P)₂, traces of O₂ increased the rate of hydrogenation by a factor of 100. Similarly small traces of O₂ or H₂O₂ increase the activity of RhCl(Ph₃P)₂. These rate enhancements are thought to be due to the oxidation of Ph₃P to non-coordinated Ph₃PO and the resulting production of a vacant coordination site for the substrate.

RhCl₃(Et₂S)₃ in benzene is not active for homogeneous hydrogenation and this was thought to result from the inhibition of the initial reduction process (equations 3.2 and 3.3) in the non-polar media. Wilkinson et al found that addition of Et₂S to [Rh(C₈H₁₄)₂Cl]₂ in a 2:1 ratio of Et₂S:Rh in benzene gave inactive solutions for hydrogenation of cyclohexene and during attempted hydrogenations, the initial yellow solution darkened during the exposure time. This result supports further the suggestion that the stability and lability of the Rh(olefin) are important for activity of the system (section 5.1). Maleic acid is a better π-acceptor ligand than cyclohexene and complexes with Rh. The present work (sections 6.3 and 6.4) shows that maleic acid is homogeneously hydrogenated in preference to cyclooctene which fails to stabilize the Rh in DMA. Cyclooctene is thought to be similar to cyclohexene in its electronic properties and probably does
not stabilize Rh\(^{I}\) against reduction to the metal. Such reduction is probably responsible for the darkening of the reaction solution noted in Wilkinson's report.

An intermediate green solution (shoulder at 475 \(\text{m} \mu\), \(\varepsilon = 172\), broad peak at 675 \(\text{m} \mu\), \(\varepsilon = 140\)) could be obtained when the Rh\(^{I}\)Cl solution from a MA hydrogenation experiment was reacted with \(\text{O}_2\) at 80\(^\circ\) to a stage where the stoichiometry of \(\text{O}_2\) uptake was equivalent to oxidation of Rh\(^{I}\) to Rh\(^{II}\) (1/40\(_2\) per Rh). The system is quite different to the oxidation reaction of [Rh(C\(_8\)H\(_{14}\)).Cl]\(_2\) in DMA with molecular \(\text{O}_2\) in the absence of coordinated olefins (Chapter VIII). These green solutions oxidize only very slowly in air to Rh\(^{III}\). Such green solutions showed a sharp E.S.R. signal with a \(g\) value of 4.63 suggesting the presence of paramagnetic species. Some d\(^7\) transition metal complexes have been shown to have \(g\) values around 4.\(^233\) The green solutions are also active for the hydrogenation of MA, however, no detailed studies were carried out. Preliminary studies indicated that the green colour was readily converted by \(\text{H}_2\) to the orange red colour characteristic of the Rh\(^{I}\)Cl complex prior to hydrogenation of the olefin. Rh\(^{II}\) acetates\(^234,235\) are known to be green in acetic acid solutions. Thus the intermediate green solutions obtained in the present studies may well contain Rh\(^{II}\)(MA) or Rh\(^{II}\)(SA) species. The catalytic hydrogenation property of Rh\(^{4+}\)\(^117\) species has recently been reported. The present studies suggest that Rh\(^{II}\) is reduced to Rh\(^{I}\) before hydrogenation starts.
CHAPTER VII

HYDROGEN REDUCTION OF DIMETHYL SULPHOXIDE CATALYZED BY Rh\textsuperscript{III} COMPLEXES CONTAINING CHLORIDE AND SULPHIDE LIGANDS

7.1 General Introduction

The catalytic activity of platinum metal complexes as homogeneous hydrogenation catalysts is very dependent on the solvent media\textsuperscript{2,3,8,9,35} and for example, the activity of RhCl\textsubscript{3}\cdot3H\textsubscript{2}O and RhCl\textsubscript{3}(Et\textsubscript{2}S)\textsubscript{3} is very much enhanced in the coordinating aprotic solvent DMA.\textsuperscript{1-4} Investigation of such solvent effects led to the study of the catalytic activity of RhCl\textsubscript{3}\cdot3H\textsubscript{2}O and RhCl\textsubscript{3}(Et\textsubscript{2}S)\textsubscript{3} in DMSO. A hydrogenation occurred in the absence of any organic substrate; this was found to be a catalytic reduction of the solvent and these studies will be described in this chapter.

DMSO has been widely used as an advantageous medium for inorganic reactions because of its ability to dissolve fairly high concentrations of many inorganic solutes\textsuperscript{236,237} and has been used extensively as an oxidizing agent in organic synthesis. A few group III-V main group halides have been shown to reduce DMSO; most transition metal halides form coordination compounds\textsuperscript{238} although niobium and tantalum pentahalides do abstract the oxygen atom of the sulfoxide to form the
corresponding oxyhalide and halogen substituted sulphides. The present investigation shows that molecular hydrogen can be activated by Rh$^{III}$ complexes for reduction of DMSO to dimethylsulphide (DMS) and is considered important in view of the present extensive use of this solvent.

7.2 RhCl$_3$·3H$_2$O Catalyzed H$_2$ Reduction of DMSO

The visible spectrum of a solution of RhCl$_3$·3H$_2$O in DMSO changed slowly with time at room temperature, presumably due to the equilibration between complexes. This change could be accomplished rapidly by heating to 80°, and the steady spectrum of the orange solution showed absorption maxima at 360 μm (ε = 380) and 435 μm (ε = 270). Such solutions are found to absorb H$_2$ at measurable rates from 70-90° without producing metal, unlike reactions of Rh$^{III}$ complexes with H$_2$ in DMA (Chapter III and references 1-4).

The kinetics of the reduction were followed by measuring the rate of H$_2$ consumption at constant pressure. The initial concentration of Rh$^{III}$ in these experiments was in the range of 0.01-0.03 M. The partial pressure of H$_2$ was varied from 130-800 mm. The solubility of H$_2$ in DMSO is quite small, but was determined to be about 6.0 x 10$^{-5}$ M atm$^{-1}$ at 80°. A typical H$_2$ uptake plot is shown in Figure 38; a linear uptake plot is observed for 3 hours and then the rate falls off very slowly. There is no obvious stoichiometric relationship between the H$_2$ uptake and the amount of Rh used; an uptake was followed up to 1.0 M H$_2$ for a solution of 0.03 M in [Rh] and the uptake was still continuing. In the absence of the rhodium complex, there was no measurable uptake over 3 hours. No reactions other than equilibration were observed.
Figure 38. Rate plots for the Rh$^{III}$ catalyzed reduction of DMSO at 80°, (746 mm H$_2$, (Δ) 2.0 x 10^{-2} M RhCl$_3\cdot$3H$_2$O, (O) 2.0 x 10^{-2} M RhCl$_3$(Et$_2$S)$_3$)
between \( \text{RhCl}_3 \cdot 3\text{H}_2\text{O} \) and DMSO in the absence of \( \text{H}_2 \) under the conditions of kinetic experiments.

The visible absorption spectra of solution samples taken during the linear uptake region were unchanged from that of the starting solution, showing that the reaction is catalytic with respect to \( \text{Rh}^{\text{III}} \); no \( \text{Rh}^{\text{III}} \) hydrides were detected.

The reduction products of DMSO were separated from the inorganic complex by distillation and identified by gas chromatography using a dinonyl phthalate column and a proton N.M.R. spectrum. Analysis of the reaction products in solution in which 1.0 moles of \( \text{H}_2 \) had been consumed gave \( \text{Me}_2\text{S} \) and \( \text{H}_2\text{O} \), both about 1 mole for each mole of \( \text{H}_2 \) consumed.

\( \text{G.C. 2A instrument, 160°, 160 ma, pressure gauge setting=10, retention time:Me}_2\text{S (3 min), H}_2\text{O (5 min), τ for H}_2\text{O around 5.0 to 5.5). No water was detectable by N.M.R. in the starting purified DMSO. The catalyzed reaction is thus} \)

\[
(\text{CH}_3)_2\text{SO} + \text{H}_2 \rightarrow (\text{CH}_3)_2\text{S} + \text{H}_2\text{O}
\]  

The gradual fall off in the hydrogenation rate is paralleled by a decrease in the intensity of the orange solution and after a 15 hour experiment the final solution is yellow, showing a single absorption maxima at 390 m\( \mu \) (\( ε = 425 \)) indicating likely formation of the \( \text{Rh}^{\text{I}} \) state. This solution is stable in air for many hours at room temperature but on heating to 80° under oxygen overnight, an orange solution again resulted with the characteristic spectrum of \( \text{Rh}^{\text{III}} \) species (\( λ_{\text{max}} 380 \text{ mμ, } ε = 410, λ_{\text{max}} 430 \text{ mμ, } ε = 300 \)).
Attempts were made to isolate a pure inorganic complex after a long hydrogenation reaction. An orange solid was obtained by pumping off the solvent under reduced pressure. Attempts to recrystallize the solid were not successful; water was used to wash off the excess solvent from the initial gummy product. The solid residue so obtained showed strong I.R. bands at 1120, 1020 and 980 cm\(^{-1}\); a microanalysis yielded the data: C = 16.5; H = 4.2; Cl = 25.0%. The molar conductance for an approximately 0.001 M solution in DMSO was about 50 ohm\(^{-1}\)cm\(^2\)mole\(^{-1}\). The molar conductance of KCl was measured to be about 60 ohm\(^{-1}\)cm\(^2\)mole\(^{-1}\). On redissolving the isolated residue in DMSO, a spectrum characteristic of a Rh\(^{II}\) species was evident (\(\lambda_{\text{max}} = 388\), \(\varepsilon = 400\) for an approximately 0.004 M solution).

7.3 \(\text{RhCl}_3(\text{Et}_2\text{S})_3\) Catalyzed \(\text{H}_2\) Reduction of DMSO

When \(\text{RhCl}_3(\text{Et}_2\text{S})_3\) was used in place of \(\text{RhCl}_3\cdot3\text{H}_2\text{O}\) results similar to those described in the previous section were obtained although the linear rates were somewhat greater for the sulphur system. A typical \(\text{H}_2\) uptake plot is shown in Figure 38; again a fall off in linear rate after 3 hours was observed.

The initial equilibrated solution of \(\text{RhCl}_3(\text{Et}_2\text{S})_3\) in DMSO showed absorption maxima at 370 m\(\mu\) (\(\varepsilon = 500\)) and 430 m\(\mu\) (\(\varepsilon = 300\)); this spectrum remained unchanged during the linear uptake region.

The products of DMSO reduction were again \(\text{Me}_2\text{S}\) and \(\text{H}_2\text{O}\) (equation 7.1).
7.4 Kinetics of the Catalyzed Reductions

The $\text{H}_2$ uptake plots were analyzed by measuring rates in the long linear region. Tables XXII and XXIII summarize the kinetic data for the $\text{RhCl}_3 \cdot 3\text{H}_2\text{O}$ system and the $\text{RhCl}_3(\text{Et}_2\text{S})_3$ system respectively. Similar kinetics were observed for the two systems.

The rate is first order in $[\text{Rh}]$ and $[\text{H}_2]$ for both systems (Tables XXII, XXIII, Figures 39, 40). The rate law is thus

$$\frac{-d[\text{H}_2]}{dt} = k[\text{Rh}][\text{H}_2]$$ (7.2)

The values of $k$ were calculated from the slopes of the figures 39 and 40 and by direct calculation (Tables XXII, XXIII). The average value of $k$ at $80^\circ$ for the $\text{RhCl}_3 \cdot 3\text{H}_2\text{O}$ system is $1.94 \text{ M}^{-1}\text{sec}^{-1}$, and the average value of $k$ for $\text{RhCl}_3(\text{Et}_2\text{S})_3$ system is $3.35 \text{ M}^{-1}\text{sec}^{-1}$ at $80^\circ$.

Good Arrhenius rate plots were observed for both systems (Tables XXIV and XXV, Figure 41). The activation parameters for the $\text{RhCl}_3 \cdot 3\text{H}_2\text{O}$ and $\text{RhCl}_3(\text{Et}_2\text{S})_3$ systems are $\Delta H^+ = 27.0 \pm 1.0 \text{ Kcal mole}^{-1}$, $\Delta S^+ = 18.0 \pm 3.0 \text{ e.u.}$, and $\Delta H^+ = 16.8 \pm 0.5 \text{ Kcal mole}^{-1}$, $\Delta S^+ = -9.0 \pm 1.0 \text{ e.u.}$, respectively.

No measurable deuterium isotope effect, $k^\text{H}_2/k^\text{D}_2 = 0.96$, was observed for the $\text{RhCl}_3 \cdot 3\text{H}_2\text{O}$ system; addition of p-toluenesulphonic acid had no significant effect on the rate. The value of $k$ was independent of added 0.1 M Me$_2$S (Table XXII), although the linear rate fell off much more rapidly for this experiment.

Addition of up to 2.2 M $\text{H}_2\text{O}$ had no effect on $k$ for the diethyl sulphide system; higher concentrations of water (up to 40% by volume)
TABLE XXII

RhCl₃·3H₂O Catalyzed H₂ Reduction of DMSO

Kinetic Data at 80°

<table>
<thead>
<tr>
<th>[Rh] x 10⁻² M</th>
<th>H₂ mm</th>
<th>[H₂] x 10⁵ M⁻¹</th>
<th>Linear Rate x 10⁶ M sec⁻¹</th>
<th>k M⁻¹ sec⁻¹</th>
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</thead>
<tbody>
<tr>
<td>0.5</td>
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<td>6.0</td>
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<td>1.02</td>
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<tr>
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<td>6.0</td>
<td>2.28</td>
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<td>746</td>
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<td>4.30</td>
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<tr>
<td>2.0</td>
<td>746</td>
<td>6.0</td>
<td>2.30</td>
<td>1.91</td>
</tr>
</tbody>
</table>

* Solubility was estimated from the solubility of H₂ in DMSO at 746 mm, assuming Henry's law applied.

a D₂ instead of H₂
b p-Toluenesulphonic acid 0.1 M.
c 0.1 M Me₂S.
TABLE XXIII
RhCl\(_3\)(Et\(_2\)S)\(_3\) Catalyzed Reduction of DMSO
Kinetic Data at 80°

<table>
<thead>
<tr>
<th>[Rh] (\times 10^2) M</th>
<th>(p'H_2)</th>
<th>([H_2]) (\times 10^5) M*</th>
<th>Linear Rate (\times 10^6) M sec(^{-1})</th>
<th>(k) M(^{-1}) sec(^{-1})</th>
</tr>
</thead>
<tbody>
<tr>
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<td>3.35</td>
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<td>383</td>
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<td>1.07</td>
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<td>1.1</td>
<td>0.35</td>
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<td>746</td>
<td>6.0</td>
<td>2.00</td>
<td>3.33(^{a})</td>
</tr>
<tr>
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<td>746</td>
<td>-</td>
<td>4.20(^{b})</td>
<td>-</td>
</tr>
<tr>
<td>1.0</td>
<td>746</td>
<td>-</td>
<td>4.60(^{c})</td>
<td>-</td>
</tr>
</tbody>
</table>

\(^{a}\) 2.2 M H\(_2\)O; \(^{b}\) 20% (volume) H\(_2\)O; \(^{c}\) 40% (volume) H\(_2\)O.

* Solubility was estimated from the solubility of H\(_2\) in DMSO at 746 mm, assuming Henry's law applies.
Figure 39. Rh$^\text{III}$ catalyzed reduction of DMSO at 80°. Variation of rate with [Rh], (6.0 x 10$^{-5}$ M H₂, (A) RhCl$_3$·3H$_2$O (O) RhCl$_3$Et$_2$S)
Figure 40. \(\text{Rh}^{III}\) catalyzed reduction of DMSO at 80°. Variation of rate with \(p'\text{H}_2\),

\[
\text{((\triangle) 3.0 \times 10^{-2} M \text{RhCl}_3 \cdot 3\text{H}_2\text{O)}}, \ (\text{O) 1.0 \times 10^{-2} M \text{RhCl}_3(\text{Et}_2\text{S})_3)}
\]
### TABLE XXIV

RhCl₃·3H₂O Catalyzed Reduction of DMSO

Temperature Dependence of k

<table>
<thead>
<tr>
<th>T (°C)</th>
<th>p'H₂</th>
<th>[H₂] x 10⁻⁵ M</th>
<th>Linear Rate x 10⁻⁶ M sec⁻¹</th>
<th>k M⁻¹ sec⁻¹</th>
</tr>
</thead>
<tbody>
<tr>
<td>70</td>
<td>751</td>
<td>6.0</td>
<td>0.91</td>
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<tr>
<td>75</td>
<td>749</td>
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<td>1.86</td>
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<td>80</td>
<td>746</td>
<td>6.0</td>
<td>3.50</td>
<td>1.94</td>
</tr>
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<td>85</td>
<td>742</td>
<td>6.0</td>
<td>5.25</td>
<td>2.93</td>
</tr>
</tbody>
</table>

### TABLE XXV

RhCl₃(Et₂S)₃ Catalyzed Reduction of DMSO

Temperature Dependence of k

<table>
<thead>
<tr>
<th>T (°C)</th>
<th>p'H₂</th>
<th>[H₂] x 10⁻⁵ M</th>
<th>Linear Rate x 10⁻⁶ M sec⁻¹</th>
<th>k M⁻¹ sec⁻¹</th>
</tr>
</thead>
<tbody>
<tr>
<td>70</td>
<td>751</td>
<td>6.0</td>
<td>1.00</td>
<td>1.67</td>
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<tr>
<td>75</td>
<td>749</td>
<td>6.0</td>
<td>1.40</td>
<td>2.34</td>
</tr>
<tr>
<td>80</td>
<td>746</td>
<td>6.0</td>
<td>2.10</td>
<td>3.50</td>
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<tr>
<td>85</td>
<td>742</td>
<td>6.0</td>
<td>3.10</td>
<td>5.16</td>
</tr>
<tr>
<td>90</td>
<td>737</td>
<td>6.0</td>
<td>4.30</td>
<td>7.16</td>
</tr>
</tbody>
</table>
Figure 41. Arrhenius plot for the Rh$^{III}$ catalyzed reduction of DMSO, ((A) RhCl$_3$.3H$_2$O, (O) RhCl$_3$(Et$_2$S)$_3$)
increased the rate by a factor of 2.5.

7.5 Discussion

The rate law for the catalyzed reduction of DMSO (equation 7.2) together with the spectroscopic data showed that $H_2$ reacts with $\text{Rh}^{\text{III}}$ species to give an intermediate which is then decomposed to $\text{Me}_2S$, $H_2O$ and the initial $\text{Rh}^{\text{III}}$ complex.

In polar solvents such as water, ethanol and DMA, reaction of molecular $H_2$ with $\text{Rh}^{\text{III}}$ complexes can give rise to intermediate hydrides formed through heterolytic splitting of the $H_2$ molecule.\(^1,2,4,71\) In the highly polar DMSO (dielectric constant 49 at 20°) this is again likely to be the rate determining step.

\[
\text{Rh}^{\text{III}}(\text{DMSO}) + H_2 \xrightarrow{k} \frac{k}{k-1} \text{Rh}^{\text{III}}(\text{DMSO})H^- + H^+ \quad (7.3)
\]

(Cl\(^-\) and $\text{Et}_2S$ ligands are omitted)

Such reactions show little measurable isotope effect.\(^1,2,4,29\) There are no rate data on the dependence on [DMSO] but since the hydride intermediate will contain coordinated DMSO, the subsequent step must be the rapid decomposition to products with regeneration of the catalyst which rapidly coordinates with further DMSO.

\[
\text{Rh}^{\text{III}}(\text{DMSO})H^- \xrightarrow{H^+\text{fast}} \text{Rh}^{\text{III}} + \text{Me}_2S + H_2O \quad (7.4)
\]

The essential independence of $k$ on acid is consistent with the back
reaction of equation 7.3 not competing with reaction shown in equation 7.4.

Johnson and Walton\(^{241}\) have isolated the \(\text{RhCl}_3(\text{DMSO})_3\) complex from solutions of \(\text{RhCl}_3\cdot 3\text{H}_2\text{O}\) in DMSO and this species is likely to be present in the equilibrated solutions of \(\text{RhCl}_3\cdot 3\text{H}_2\text{O}\) used in the present studies. According to Gutmann,\(^{240}\) the donor strength of DMSO is greater than for water, the concentration of which will be a maximum of 0.3 M (3 times the [Rh]). \(\text{RhCl}_2\text{H}(\text{DMSO})_3\) or \([\text{RhCl}_3\text{H}(\text{DMSO})_2]^-\) are the most likely intermediates produced in the reaction (see equation 7.3). The latter is favoured since some recent work\(^{242}\) indicated that one of the DMSO ligands in \(\text{RhCl}_3(\text{DMSO})_3\) is extremely labile and can readily be displaced by \(\text{Cl}^-\).

The detailed path of reaction (equation 7.4) is uncertain. DMSO complexes of transition metals are well known to coordinate generally through the oxygen atom.\(^{243}\) Although Pt\(^{II}\),\(^{244,245}\) Pd\(^{II}\),\(^{244}\) and Ir\(^{III}\)\(^{246}\) have been shown to contain DMSO bonded through the sulphur atom; these conclusions were originally drawn from I.R. spectra particularly in the S-O stretching region, but some have been verified by X-ray work. Johnson and Walton\(^{241}\) draw no definite conclusions from the far I.R. data about the bonding in the \(\text{RhCl}_3(\text{DMSO})_3\) complex, but the existence of the strong S-O band at 1120 cm\(^{-1}\) in a sample we made during the present studies strongly suggests bonding of the DMSO through the sulphur atom. Other recent data reports that in \(\text{Na}[\text{RhCl}_4(\text{DMSO})_2]\),\(^{247}\) S-O lies at about 1113 cm\(^{-1}\), indicating bonding through the sulphur atom; in \(\text{RhCl}_3(\text{DMSO})_3\),\(^{242}\) two bands at 1140 cm\(^{-1}\) and 930 cm\(^{-1}\) were interpreted in terms of 2 sulphur bonded and 1 oxygen.
bonded DMSO ligands. The oxygen bonded DMSO in RhCl₃(DMSO)₃ is believed to be labile.²⁴² The cation Pd(DMSO)₄⁺ has been shown to contain both sulphur and oxygen bonded DMSO.²⁴⁸

A plausible mechanism for the reaction (equation 7.4) can be written for S bonding

\[
\begin{array}{c}
\text{H}^- \\ \text{Rh} \\ \text{S-CH}_3 \\
\text{CH}_3 \\ \text{H}^+ \\
\text{Rh}^* \text{S-CH}_3 \\
\text{OH} \\
\text{H}^+ \\
\text{Rh}^- \\
\text{H}_2\text{O} + \text{Me}_2\text{S} (7.5)
\end{array}
\]

Protonation of the basic oxygen atom²⁴⁹ would give II. Nucleophilic attack by the coordinated hydride (a typical insertion reaction of an unsaturated moiety into a metal hydride bond³⁸) would lead to elimination of H₂O and Me₂S, either free or coordinated depending on the stability of rhodium dimethylsulphide complexes. The constancy of the initial reaction rate and visible spectrum indicate that the Me₂S is not coordinated in this region. In the system with added Me₂S, the more rapid fall off in rate suggests that Me₂S may well coordinate as its concentration builds up (see later discussion). No effect is observed by addition of up to 2.2 M H₂O to the RhCl₃(Et₂S)₃ system; thus water does not cause the retardation in rate and is also unlikely to be coordinated to the rhodium at this concentration. Little can be said about the increase in rate at higher [H₂O]; aquo complexes may be involved and also the solubility of H₂ is some 10 times greater in H₂O than in DMSO.
An interesting possibility for the overall reduction reaction is that intermediate II is formed in a simple concerted step by the approach of the H₂ molecule to the rhodium-DMSO complex; the heterolytic splitting of the H₂ molecule would be "built into" such a mechanism which would be indistinguishable from the kinetic point of view.

The diethylsulphide system is about twice as active at 80° as the trichloride system; the visible absorption spectrum shows a different Rh III complex is initially present in solution and it must have coordinated Et₂S. Et₂S is a somewhat stronger donor ligand than Me₂S. Hence the fall off in rate (Figure 38) is not thought to be due to the coordination of Me₂S to Rh III.

The significance of the difference in the activation parameters for the two systems studied is not clear but it may be related to the difference in the charges of the reacting complex. In the Et₂S system, for example, cationic species of the type [RhCl₂(Et₂S)ₓ(DMSO)ᵧ]⁺ (x + y = 4) could be present. In some related systems in DMA, in which RhCl₃·3H₂O¹,² and RhCl₃(Et₂S)₃⁴ have been reduced to Rh I complexes through Rh III hydride intermediates, the Et₂S system again showed a lower enthalpy of activation and a more unfavourable entropy (Table XXVI).

The fall off in catalytic activity is thought to be due to the loss of Rh III hydrides which can easily dissociate into Rh I species.

\[
\text{Rh}^{III} \text{H}^- \rightarrow \text{Rh}^I + \text{H}^+ \tag{7.6}
\]

The experimental data strongly indicate that in the region of lower rate some Rh I complexes are present. The decomposition of Rh III-H⁻ to
TABLE XXVI

Comparison of the Activation Parameters for the Heterolytic Splitting in RhCl$_3$$\cdot$3H$_2$O and RhCl$_3$(Et$_2$S) Complexes in DMA and DMSO

<table>
<thead>
<tr>
<th></th>
<th>DMA$^1$-$^4$</th>
<th>DMSO$^6$</th>
</tr>
</thead>
<tbody>
<tr>
<td></td>
<td>$\Delta H^\dagger$ Kcal/mole</td>
<td>$\Delta S^\dagger$ e.u.</td>
</tr>
<tr>
<td>RhCl$_3$$\cdot$3H$_2$O</td>
<td>17.3</td>
<td>-9.2</td>
</tr>
<tr>
<td>RhCl$_3$(Et$_2$S)</td>
<td>12.9</td>
<td>-19.2</td>
</tr>
</tbody>
</table>
Rh\textsuperscript{I} is a fast reaction and the production of Rh\textsuperscript{I} will depend on the comparative rates of the decomposition of the hydride according to equation 7.6 and its reaction with DMSO according to equation 7.5. Production of Rh\textsuperscript{I} would be more favourable at higher [Me\textsubscript{2}S] since this ligand is expected to stabilize the lower valent state (more class b character).

Analysis of the inorganic residue isolated from the RhCl\textsubscript{3}·3H\textsubscript{2}O catalyzed reduction (C = 16.5; H = 4.2; Cl = 25.0%) suggested that there are 3 moles of Cl\textsuperscript{−} per mole of Rh. Plausible formulae for Rh\textsuperscript{I} complexes are [(DMSO)\textsubscript{2}H\textsubscript{2}[RhCl\textsubscript{3}(Me\textsubscript{2}S)] (calc. C = 16.8; H = 4.7; Cl = 24.8%) and [(DMSO)\textsubscript{2}H\textsubscript{2}[RhCl\textsubscript{3}(DMSO))] (C = 16.1; H = 4.5; Cl = 23.9%). A [(DMF)\textsubscript{2}H\textsubscript{2}[Pd\textsubscript{2}Cl\textsubscript{6}])\textsuperscript{251} has been reported. DMSO is a basic solvent and can easily be protonated, although no complexes with protonated DMSO as cations have been reported. The conductivity data suggest that the residue in DMSO behaves as an electrolyte although the conductivity is too low for a 2:1 electrolytic. This residue could presumably contain some neutral Rh\textsuperscript{III} species which could account for the low conductivity. However, the visible spectrum suggested the presence of Rh\textsuperscript{I} species only. The impure orange solid gave strong I.R. bands at 1120 cm\textsuperscript{−1}, 1020 cm\textsuperscript{−1} and 980 cm\textsuperscript{−1}. The first is attributed to the SO stretch of a sulphur bonded DMSO; and the latter two may be assigned to rocking modes of coordinated DMSO and Me\textsubscript{2}S although the band at 980 cm\textsuperscript{−1} may be due to oxygen bonded DMSO. There are no reports on Rh\textsuperscript{I} alkyl sulphide complexes although a Rh\textsuperscript{I}Cl(CO)(DMSO)\textsubscript{2}\textsuperscript{175} complex is known. Rh\textsuperscript{I} with its more class b character than Rh\textsuperscript{III} is thought likely to coordinate through the sulphur atom of DMSO.
The kinetic data could also be consistent with a rate determining hydrogen reduction to Rh\textsuperscript{I} through reactions shown in equations 7.4 to 7.6, followed by a rapid oxidation of Rh\textsuperscript{I} by DMSO. However, DMSO complexes of low valent transition metals such as Mn\textsuperscript{II}, Ru\textsuperscript{II}, Ir\textsuperscript{I}, Rh\textsuperscript{I} are known and the final reaction solution appears to contain Rh\textsuperscript{I}, so such a mechanism appears to be unlikely and a reaction through Rh\textsuperscript{III}H\textsuperscript{−} is highly favoured. A solution of the [Rh(C\textsubscript{8}H\textsubscript{14})\textsubscript{2}Cl\textsubscript{2}]\textsuperscript{−} complex containing the labile C\textsubscript{8}H\textsubscript{14} ligand showed no redox reaction with DMSO at 80°.

7.6 Catalyzed Oxidation and Reduction of DMSO by RhCl\textsubscript{3}·3H\textsubscript{2}O

Using a Mixture of H\textsubscript{2} and O\textsubscript{2}

The observation that the final yellow solution was oxidized slowly by O\textsubscript{2} back to Rh\textsuperscript{III} (see section 7.2) suggested the use of a H\textsubscript{2}/O\textsubscript{2} mixture might prevent the slow fall off in reaction rate. In an experiment using a mixture of 500 mm H\textsubscript{2} and 250 mm O\textsubscript{2} with 0.03 M RhCl\textsubscript{3}·3H\textsubscript{2}O in DMSO, the initial rate was that expected for the reaction in the absence of oxygen; however, the rate now showed autocatalytic behaviour before reaching a steady rate of 1.3 \times 10^{-5} M sec\textsuperscript{−1}, some 3 times faster than the initial rate, and showed no sign of falling off over a 3 hour period (Figure 42). No reaction was observed between RhCl\textsubscript{3}·3H\textsubscript{2}O dissolved in DMSO and oxygen.

The reaction products were isolated by pumping off the solvent at reduced pressure. With warming and more pumping, a white solid was isolated from the residual metal complex and was recrystallized from chloroform. The pure white solid so obtained was identified by I.R. and
Figure 42. Rate plot for the reaction of RhCl$_3$·3H$_2$O and DMSO using a mixture of H$_2$ and O$_2$ at 80°, (p'H$_2$ = 500 mm, p'O$_2$ = 300 mm, 3.0 x 10$^{-2}$ M Rh).
melting point to be dimethyl sulphone ($\text{Me}_2\text{SO}_2$). Smaller amounts of $\text{H}_2\text{O}$ and $\text{Me}_2\text{S}$ were also identified in the final reaction solution.

These reactions involving $\text{H}_2/\text{O}_2$ mixtures are particularly interesting. Trocha-Grimshaw and Henbest have reported that solutions of $\text{RhCl}_3$ or $\text{H[RhCl}_4\text{(DMSO)}_2]$ in hot propan-2-ol/water mixtures catalyze the air oxidation of DMSO to $\text{Me}_2\text{SO}_2$ although no mechanism was suggested. $\text{RhCl}_3\cdot3\text{H}_2\text{O}$ in DMSO showed no reactivity towards $\text{O}_2$ and it seems likely that the alcoholic medium is necessary to furnish intermediate hydride species. These workers state that hydrides are the most effective catalysts. $\text{Rh}^+$ complexes are known to activate molecular $\text{O}_2$ through an oxidative addition reaction and these could well be produced from $\text{Rh}^{\text{III}}\text{H}^-$ according to reaction (7.6). Hence from these considerations the increase in rate of gas uptake using the $\text{H}_2/\text{O}_2$ mixture is certainly due to an induced catalytic oxidation through $\text{Rh}^{\text{III}}\text{H}^-$ intermediate or the slowly produced $\text{Rh}^+$ species. The inactivity of either the initial $\text{Rh}^{\text{III}}$ solution or the $\text{Rh}^+$ solutions from the hydrogenation experiments towards $\text{O}_2$ indicates that $\text{Rh}^{\text{III}}\text{H}^-$ may be directly involved as oxygen carriers. Some recent work on the $\text{RuCl}_2(\text{Ph}_3\text{P})_3$ catalyzed autoxidation of ethylbenzenes has also indicated that intermediate hydrides are involved. No catalytic oxidation was observed using solutions of $\text{[Rh(C}_8\text{H}_{14})_2\text{Cl]}_2$ in DMSO, although this complex was found to activate molecular oxygen in DMA (see Chapter VIII).

DMSO in these systems plays both the part of the substrate and the solvent. Preliminary studies of the $\text{RhCl}_3(\text{Et}_2\text{S})_3$ catalyzed hydrogenation of MA in DMSO indicated that the rate plot consisted of two parts; an initial region of more rapid uptake followed by a second linear region
([Rh] = 0.01 M, [MA] = 0.03 M, pH₂ = 746 mm, T = 80°; initial rate = $2.82 \times 10^{-6}$ M sec$^{-1}$, second linear rate = $1.68 \times 10^{-6}$ M sec$^{-1}$). Comparison of the initial rate with the rate of the RhCl$_3$(Et$_2$S)$_3$ catalyzed reduction of DMSO (Table XXIII) suggested that the initial rate is possibly associated with the reduction of Rh$^{	ext{III}}$ to Rh$^{	ext{III}}^{-}$ (equation 7.3). The second linear rate is possibly due to the hydrogenation of MA. A rate constant for the RhCl$_3$(Et$_2$S)$_3$ catalyzed hydrogenation of MA in DMSO, assuming that the second linear rate is first order in [Rh] and [H$_2$], was calculated to be $2.7$ M$^{-1}$sec$^{-1}$ which was some eight times faster than the corresponding system in DMA.$^{3,4}$ Since the measurements are complicated by the catalytic reduction of the DMSO solvent, the use of DMSO as a solvent media for the RhCl$_3$(Et$_2$S)$_3$ and RhCl$_3$·3H$_2$O catalyzed hydrogenation of olefins was not further studied.
CHAPTER VIII

ACTIVATION OF MOLECULAR OXYGEN BY BIS(CYCLO-OCTENE)CHLORO RHODIUM (I)

IN DMA

8.1 Introduction

The difference in observed kinetics for the hydrogenation of olefinic substrates by [Rh(C\textsubscript{8}H\textsubscript{14})\textsubscript{2}Cl\textsubscript{2}/Et\textsubscript{2}S in DMA, using completely air free conditions instead of stock solutions, made up in air, led to the investigation of the reaction of this complex with oxygen. Reactions of transition metal complexes with molecular oxygen are of much current interest (see section 1.5). Very few kinetic studies of the formation and catalytic activity of molecular oxygen complexes have been reported and the following describes such a study.

8.2 Formation of the Molecular Oxygen Complex

At room temperature or 80°, a solution of [Rh(C\textsubscript{8}H\textsubscript{14})\textsubscript{2}Cl\textsubscript{2}] in 0.5 M LiCl/DMA, \textsubscript{14}, rapidly absorbed oxygen in a 1:1 ratio of O\textsubscript{2}:Rh ([Rh] = [monomer]). This was accompanied by a rapid colour change from red to dark brown. The I.R. spectra of the resulting oxygenated solution showed a fairly strong absorption at 893 cm\textsuperscript{-1}, in the region of the O-O stretch of a coordinated O\textsubscript{2} molecule\textsuperscript{58,71,255} which was absent in the initial red solution. On prolonged pumping of
the dark brown "oxygenated" solutions at room temperature or 80°, the initial red colour of the "unoxygenated" solution could not be restored, and such resulting "deoxygenated" solutions absorbed about 1/10 of the amount of O₂ required to fully form the Rh^I(O₂) complex. The oxidation state of the complex is written formally as Rh^I, but the exact electronic configuration may include Rh^IIO₂⁻ or Rh^III0₂⁺. An equilibrium such as:

\[
\text{Rh}^I + O_2 \rightleftharpoons \text{Rh}^I(O_2)
\]  
(8.1)

(ligands such as C₆H₁₄, Cl⁻, DMA are omitted).

probably exists but lies far to the right at room temperature and 80°.

Oxygenated and stock solutions (in air) of \( \text{I} \) showed a symmetrical E.S.R. signal at room temperature with a value, \( g_{av} \), of 2.0485 (Figure 43). At liquid N₂ temperature, the signal is split into 3 lines (Figure 44) with \( g_1, g_2 \) and \( g_3 \) values of 2.1157, 2.0367, 1.9728 respectively. The average value of \( g_1, g_2 \) and \( g_3 \) is 2.0417, very close to the \( g_{av} \) value. No E.S.R. signal was observed for a solution of \( \text{I} \) kept under vacuum and when such a solution is exposed to air or O₂, the E.S.R. signal builds up. When \([\text{Rh}(C₆H₁₄)_2\text{Cl}]_2 \) (0.02 M) was dissolved in an evacuated solution of 2,2-diphenyl-1-picryl hydrazol, DPPH,(0.06 M), in LiCl/DMA, evolution was observed and such a solution did not take up O₂ for 5000 sec at 80° and only the E.S.R. signal of DPPH was observed (g = 2.0036).

If H₂ is passed through the dark brown "oxygenated" solution at 80° for ~ 100 sec (if left under H₂ for a longer time at 80° or at
Figure 43. E.S.R. spectrum of Rh\(^I\)(O\(_2\)) complex in 0.5M LiCl/DMA at room temperature.
Figure 44. E.S.R. spectrum of Rh(I) complex in 0.5M LiCl/DNA at 77°K.
room temperature for a few hours, metal was formed), a red solution was obtained. The I.R. of this red solution showed a strong absorption at 1980 cm\(^{-1}\) and the disappearance of the 893 cm\(^{-1}\) absorption. No apparent \(\text{H}_2\) uptake was observed and this could be consistent with the following reaction.

\[
\text{Rh}^{\text{I}}(\text{O}_2) + \text{H}_2 \rightarrow \text{Rh}^{\text{III}}\text{H}_2 + \text{O}_2
\]  

(8.2)

The \(\text{Rh}^{\text{III}}\text{H}_2\) was stable at room temperature in air for several hours, as evidenced from the I.R. spectra. However, no Rh-\(\text{H}\) bond signal from 0-40 \(\tau\) units was observed in the proton N.M.R. spectra for a saturated solution at room temperature. This could be due to proton exchange occurring between the hydride and the DMA solvent.

The visible spectrum of a solution of \(\mathbf{l}\) in 0.5 M LiCl/DMA under vacuum or \(\text{N}_2\) (\(\varepsilon = 450 \text{ m}\mu\), \(\varepsilon = 228\)) changed when subjected to an atmosphere of \(\text{O}_2\) (shoulder 460 \(\text{m}\mu\), \(\varepsilon = 162\)) (Figure 32). An attempt was made to determine the equilibrium constant of the formation of the \(\text{Rh}^{\text{I}}(\text{O}_2)\) complex (equation 8.1) from the spectrophotometric data, assuming that in vacuum the spectrum obtained was that of the initial starting \(\text{Rh}^{\text{I}}\) species (\(\text{O}_2\) free); the spectra of solutions formed under \(\text{O}_2\) over the pressure range of about 200-800 mm were almost identical; indicating that the oxygen complex was fully formed over this pressure range. Only at lower pressure was complex formation incomplete and differences in spectra observed (Figure 32). The extinction coefficients \(\varepsilon_A\) and \(\varepsilon_B\) for \(\text{Rh}^{\text{I}}\) and \(\text{Rh}^{\text{I}}(\text{O}_2)\) respectively were determined at 450 m\(\mu\). The optical density at 450 m\(\mu\) of a solution treated with 71 mm \(\text{O}_2\) was measured. From the equation
\[
\text{O.D.} = \frac{(\varepsilon_A + \varepsilon_B(K)[O_2])[\text{Rh}]}{1 + K[O_2]} \tag{8.3}
\]

and taking the estimated value of \([O_2]\) to be \(0.7 \times 10^{-3}\) M (Appendix I), the value of \(K\) at room temperature was determined to be \(\approx 5.0 \times 10^3\) M\(^{-1}\). However, the procedure cannot be entirely valid since the spectra do not show the expected isosbestic point. A complication might be a monomer \rightleftharpoons \text{dimer} equilibrium involved in the air free solution.

But the complex formation does occur at oxygen pressure up to 200 mm and so \(K\) must be of that order of magnitude. Some values of \(K\), for temperatures between 70-90°, have been obtained from the kinetic data of the reaction of Rh\(^I\)(O\(_2\)) with DMA (section 8.31, Table XXX).

### 8.3 Catalytic Activity of Rh\(^I\)(O\(_2\)) in LiCl/DMA

Following the initial rapid oxygen uptake of solutions of \(\mathcal{J}\) in (section 8.2) a further slower uptake was observed which could be measured conveniently over the temperature range 70-90°. Stock solutions of \(\mathcal{J}\) (shoulder at 450 μν, \(ε = 230\)) were used in the kinetic studies. A typical gas uptake plot is shown in Figure 45 which, after an initial "instantaneous" uptake, consisted of a linear region followed by a region of gradual decreasing rate. The initial rapid uptake is associated with the completion of the formation of the Rh\(^I\)(O\(_2\)) complex.

There was no obvious stoichiometric relationship between the total \(O_2\) absorbed at the end of a reaction and the amount of Rh used. For \([\text{Rh}] = 0.001\) M, \(O_2\) uptake in excess of 10:1 mole ratio of \(O_2:\text{Rh}\) has been followed; at \(0.14\) M \([\text{Rh}]\), a 5:1 mole ratio of \(O_2:\text{Rh}\) uptake
Figure 45. Typical O₂ uptake plot for the Rh(I)(O₂) catalyzed oxidation in 0.5M LiCl/DMA at 80°, (3.75 x 10⁻²M O₂, (O) 1.0 x 10⁻²M Rh, (Δ) in the absence of Rh)
was observed; while at 0.05 M [Rh], only a 3:1 mole ration
of \( \text{O}_2 \):Rh was observed. In the absence of Rh, a very slow reaction between
\( \text{O}_2 \) and LiCl/DMA was observed, "the blank reaction" (Figure 45). The
rate of the blank reaction is practically independent of \( \text{O}_2 \) pressure
from 40 to 800 mm. In the absence of LiCl, there was essentially no
reaction between DMA and \( \text{O}_2 \).

The visible absorption spectra of solution samples taken in the
linear region were the same as that of the initial oxygenated
solution indicating that the reaction is catalytic with respect to
the initial starting rhodium species, i.e. \( \text{Rh}^\text{I}(\text{O}_2) \).

The gradual fall off in the rate of reaction is paralleled by
the appearance of a greenish tinge to the dark brown colour of the
initial solution. A broad absorption maxima at 690 my, \( \varepsilon = 86 \), was
measured for a final relatively unreactive solution.

When a final greenish brown solution was treated with \( \text{H}_2 \) at 80°,
the colour of the solution changed to red and such a solution was
found to undergo reaction with \( \text{O}_2 \) at a rate comparable to that before
the fall off in rate. Thus treatment of the less "active" Rh
species with \( \text{H}_2 \) regenerates the active initial Rh species for catalytic
oxidation. Prolonged treatment of the dark brownish green solution
with \( \text{H}_2 \) at 80° produced metal.

The identification of products proved to be very difficult;
attempts were made to identify the products in the gaseous phase,
liquid phase and the residual solid phase.

Gaseous samples after a long reaction were collected in an
evacuated glass bulb and mass spectrometry on such samples showed the
presence of 28, 32, 44, 45 and 46 peaks in the spectra after allowing
for the background. \( \text{CO}_2 \) and \( \text{Me}_2\text{NH} \) were thought to be present in the
sample. One of the major peaks for DMA (43) was absent.

I.R. spectra of the distillate pumped off from the oxidized solution showed essentially the same peaks as DMA, except for a band at 1725 cm\(^{-1}\) and another band at 820 cm\(^{-1}\) showing a \(\text{C} = \text{O}\) group and possibly a \(\text{C} = \text{C}\) or \(\text{C} - \text{C}\) group. Four peaks were obtained from the gas chromatogram using a dinonyl phthalate column; retention times were 5 min, 12 min, 23 min and 40 min respectively. (G.C. 2A instrument, 160°, 160 ma, pressure gauge setting = 10). Comparison of the retention time with that of authentic samples showed that these were due to respectively water, cyclooctene, DMA and an unknown. Attempts were made to trap the sample that came out at 40 min using an Aerograph model A90P gas chromatograph and a dinonyl phthalate column; however, not enough was collected for complete identification purposes. I.R. spectra of the "collected" sample showed the presence of a \(\text{C} = \text{O}\) group at 1725 cm\(^{-1}\). A 2,4-dinitrophenylhydrazine derivative of the unknown carbonyl compound was prepared from the distillate pumped off from the oxidized solution. The recrystallized 2,4-dinitrophenylhydrazone melted at 170° and analysis (found: C=54.66; H = 5.92; N = 18.13%) gave a molecular formula corresponding to \(\text{C}_{14}\text{H}_{18}\text{N}_{4}\text{O}_{4}\). (Calc.: C = 54.8; H = 5.88; N = 18.3%). N.M.R. spectra of the 2,4-dinitrophenyl hydrazine derivative of the unknown carbonyl in CDCl\(_3\) gave the same spectra as the 2,4-dinitrophenylhydrazine derivative of cyclooctanone, which melted at 173°. These results indicate that cyclooctanone is a product of the oxidation although retention time of an authentic sample of cyclooctanone in DMA was 70 min.

The inorganic and solid organic residue obtained after removal of
the distillate from pumping off the solvent was soluble in water. The I.R. spectra of the solid residue showed the presence of a Rh-CO stretch at 1980 cm\(^{-1}\) and another stretch at 970 cm\(^{-1}\). This latter band could be due to a NO stretch, but this could not be determined unequivocally since DMA showed a band at 960 cm\(^{-1}\) which was now absent in the I.R. of the solid residue. Bands due to DMA were observed elsewhere, however. Attempts to isolate the possible Me\(_3\)NO by adding picric acid dissolved in ethanol were unsuccessful.

8.31 Kinetics of the Catalytic Oxidation by the Rh\(^{I}(O_2)\) Complex in LiCl/DMA

The oxygen uptake plots were analyzed by measuring the rates in the linear region. Variation of rate with [Rh] gave a straight line with a positive intercept (Table XXVII, Figure 46). Use of a different stock solution (i.e. different "age" of the solution) had a slight effect on rate (Figure 46). The dependence of rate on oxygen was approximately first order at very low O\(_2\) pressure (< 50 mm) but the order decreased with increasing pressure and the rate reached a limiting value at about \(\approx\) half an atmosphere (Table XXVIII, Figure 47).

Addition of water up to 1.1 M increased the rate by a factor of \(\approx\) 2. Further addition of water up to 5.6 M had little effect (Table XXIX). Addition of cyclooctene increased the rate and the dependence of rate on added cyclooctene is perhaps approaching a limiting value at higher concentrations (Table XXIX, Figure 48). The rate decreased with increasing [Cl\(^-\)], but a limiting value was observed
TABLE XXVII

Rh\textsuperscript{I}(O\textsubscript{2}) Catalyzed Oxidation in 0.5M LiCl/DMA

Kinetic Data at 80°

Variation of Rate with [Rh]

<table>
<thead>
<tr>
<th>[Rh] x 10\textsuperscript{-3} M</th>
<th>p'O\textsubscript{2} mm</th>
<th>[O\textsubscript{2}] x 10\textsuperscript{-3} M*</th>
<th>Rate x 10\textsuperscript{6} M sec\textsuperscript{-1}</th>
</tr>
</thead>
<tbody>
<tr>
<td>1.0</td>
<td>725</td>
<td>3.75</td>
<td>1.20</td>
</tr>
<tr>
<td>2.0</td>
<td>725</td>
<td>3.75</td>
<td>1.48</td>
</tr>
<tr>
<td>4.0</td>
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<td>3.75</td>
<td>1.88</td>
</tr>
<tr>
<td>5.0</td>
<td>725</td>
<td>3.75</td>
<td>2.28</td>
</tr>
<tr>
<td>5.0\textsuperscript{a}</td>
<td>725</td>
<td>3.75</td>
<td>2.56\textsuperscript{a}</td>
</tr>
<tr>
<td>7.5</td>
<td>725</td>
<td>3.75</td>
<td>2.88</td>
</tr>
<tr>
<td>10.0</td>
<td>725</td>
<td>3.75</td>
<td>3.68</td>
</tr>
</tbody>
</table>

* see appendix 1

\textsuperscript{a} from another stock solution
Figure 46. Rh\textsuperscript{I}(O\textsubscript{2}) catalyzed oxidation in 0.5M LiCl/DMA at 80°. Dependence of rate on [Rh], (3.75 x 10\textsuperscript{-3} M O\textsubscript{2}, (Δ) a different stock solution)
TABLE XXVIII

Rh\textsuperscript{I}(O\textsubscript{2}) Catalyzed Oxidation in 0.5 M LiCl/DMA

Kinetic Data from 70-87°

Variation of Rate with \([O\textsubscript{2}]. [Rh] = 5.0 \times 10^{-3} \text{ M}\)

<table>
<thead>
<tr>
<th>(P'O\textsubscript{2}) mm</th>
<th>([O\textsubscript{2}]) x 10(^{-3}) M</th>
<th>([O\textsubscript{2}]^{-1})</th>
<th>T °C</th>
<th>Rate (x 10^6) M\textsuperscript{-1} sec\textsuperscript{-1}</th>
<th>(k'')</th>
<th>Rate-(k'') (x 10^{-5}) M\textsuperscript{-1} sec\textsuperscript{-1}</th>
<th>(\frac{1}{\text{Rate-}k''})</th>
</tr>
</thead>
<tbody>
<tr>
<td>23</td>
<td>0.13</td>
<td>7.68</td>
<td>80</td>
<td>1.16</td>
<td>0.60</td>
<td>0.56</td>
<td>17.8</td>
</tr>
<tr>
<td>44</td>
<td>0.23</td>
<td>4.35</td>
<td>80</td>
<td>1.50</td>
<td>0.60</td>
<td>0.90</td>
<td>11.1</td>
</tr>
<tr>
<td>70</td>
<td>0.38</td>
<td>2.66</td>
<td>80</td>
<td>1.82</td>
<td>0.60</td>
<td>1.22</td>
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</tr>
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<td>1.90</td>
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<td>1.48</td>
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<td>80</td>
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<td>2.36</td>
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<td>1.76</td>
<td>5.7</td>
</tr>
<tr>
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<td>3.75</td>
<td>0.27</td>
<td>80</td>
<td>2.56</td>
<td>0.60</td>
<td>1.96</td>
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</tr>
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<td>0.23</td>
<td>0.37</td>
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<tr>
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<td>0.23</td>
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<tr>
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<td>1.08</td>
<td>0.23</td>
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<td>0.23</td>
<td>0.97</td>
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<td>0.78</td>
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<td>75</td>
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<td>1.18</td>
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<td>0.24</td>
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<td>0.45</td>
<td>1.31</td>
<td>7.6</td>
</tr>
<tr>
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<td>0.20</td>
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<td>2.66</td>
<td>0.87</td>
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<td>0.87</td>
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<td>0.87</td>
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<td>3.03</td>
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<td>87</td>
<td>5.20</td>
<td>0.87</td>
<td>4.33</td>
<td>2.3</td>
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</tbody>
</table>

\(k''\) = Rate of reaction of LiCl/DMA and \(O_2\) in absence of Rh.

\(\dagger\) see Appendix I.
Figure 47. Rh\(\text{I}(O_2)\) catalyzed oxidation in 0.5M LiCl/DMA at 80°. Dependence of rate on \(p'\text{O}_2\), (5.0 \times 10^{-3}\text{ M Rh})
**TABLE XXIX**

Rh\(^I\)(O\(_2\)) Catalyzed Oxidation in LiCl/DMA

Kinetic Data at 80°

Effect of Additives on Rate

<table>
<thead>
<tr>
<th>[Rh] (x 10^3) M</th>
<th>(p^0_\text{O}_2) mm</th>
<th>(\text{O}_2) (x 10^3) M (^*)</th>
<th>Rate (x 10^6) M sec(^{-1})</th>
<th>LiCl M</th>
<th>Additive</th>
</tr>
</thead>
<tbody>
<tr>
<td>5.0</td>
<td>725</td>
<td>3.75</td>
<td>2.28(^a)</td>
<td>0.50</td>
<td>Nil</td>
</tr>
<tr>
<td>5.0</td>
<td>725</td>
<td>-</td>
<td>4.64(^b)</td>
<td>0.50</td>
<td>1.1 M H(_2)O</td>
</tr>
<tr>
<td>5.0</td>
<td>725</td>
<td>-</td>
<td>4.80(^c)</td>
<td>0.50</td>
<td>5.6 M H(_2)O</td>
</tr>
<tr>
<td>10.0</td>
<td>725</td>
<td>3.75</td>
<td>4.60(^d)</td>
<td>0.50</td>
<td>Nil</td>
</tr>
<tr>
<td>10.0</td>
<td>725</td>
<td>3.75</td>
<td>9.20(^e)</td>
<td>0.50</td>
<td>0.05 M C(<em>8)H(</em>{14})</td>
</tr>
<tr>
<td>10.0</td>
<td>725</td>
<td>3.75</td>
<td>19.20(^f)</td>
<td>0.47</td>
<td>0.50 M C(<em>8)H(</em>{14})</td>
</tr>
<tr>
<td>10.0</td>
<td>725</td>
<td>3.75</td>
<td>27.20(^g)</td>
<td>0.44</td>
<td>1.0 M C(<em>8)H(</em>{14})</td>
</tr>
<tr>
<td>5.0</td>
<td>725</td>
<td>3.75</td>
<td>2.60(^h)</td>
<td>0.50</td>
<td>Nil</td>
</tr>
<tr>
<td>5.0</td>
<td>725</td>
<td>3.75</td>
<td>1.92(^i)</td>
<td>0.50</td>
<td>0.0025 M DPPH</td>
</tr>
<tr>
<td>10.0</td>
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<td>3.66(^j)</td>
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</tr>
<tr>
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<td>1.68(^k)</td>
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<tr>
<td>10.0</td>
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<td>0.80(^l)</td>
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<tr>
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<td>5.20(^m)</td>
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<td>Nil</td>
</tr>
<tr>
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<td>725</td>
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<td>4.00(^n)</td>
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<td>Nil</td>
</tr>
<tr>
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<td>3.75</td>
<td>3.60(^o)</td>
<td>0.50</td>
<td>Nil</td>
</tr>
<tr>
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<td>725</td>
<td>3.75</td>
<td>3.60(^p)</td>
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<td>Nil</td>
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<tr>
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<td>15.50(^r)</td>
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<tr>
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<td>2.75</td>
<td>7.40(^s)</td>
<td>0.50</td>
<td>Nil</td>
</tr>
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</table>

\(^a\),\(^b\),\(^c\) are the same stock solution; \(^d\),\(^e\),\(^f\),\(^g\) are the same stock solution; \(^h\),\(^i\) are the same stock solution; \(^j\),\(^k\),\(^l\) are the same stock solution; \(^m\),\(^n\),\(^o\),\(^p\) are freshly made up solutions; \(^q\) 2 month old stock solution, greenish in colour; \(^r\),\(^s\) mixture of H\(_2\)/O\(_2\) where total pressure = 1 atm.

\(^*\) see appendix 1
Figure 48. Rh \textsuperscript{I} (O\textsubscript{2}) catalyzed oxidation if in 0.5M LiCl/DMA at 80\(^\circ\)C. Variation of rate with [C\textsubscript{8}H\textsubscript{14}], (3.75 \times 10^{-3} M O\textsubscript{2}, 1.0 \times 10^{-2} M [Rh])
from 0.5-1.0 M [Cl\textsuperscript{-}] (Table XXIX).

The oxidation reaction was not inhibited in the dark. Addition of DPPH, a free radical inhibitor, in the ratio of 0.5:1 mole ratio of DPPH:Rh (Rh = 0.005 M) slowed the oxidation by an amount equal to the blank reaction; while addition of DPPH to Rh (0.01 M) in the 1:1 and 2:1 mole ratios slowed the oxidation by a factor of 1/2 and 1/4 respectively. Addition of 10:1 mole ratio of DPPH:Rh (0.01 M) inhibited the O\textsubscript{2} uptake completely. The blank reaction was completely inhibited by the addition of 0.03 M DPPH.

When the final greenish brown solution was treated with an O\textsubscript{2}/H\textsubscript{2} mixture (345 mm O\textsubscript{2}, 380 mm H\textsubscript{2}) an increase in rate was observed without metal product at the end of 4 hours at 80° (Table XXIX). The final colour of the solution was yellowish. The linear region of the gas uptake plot was considerably longer than when O\textsubscript{2} alone was used. When a mixture richer in O\textsubscript{2} (545 mm O\textsubscript{2}, 180 mm H\textsubscript{2}) was used a slower rate was observed (Table XXIX). When the proportion of H\textsubscript{2} was in excess of O\textsubscript{2} (165 mm O\textsubscript{2}, 570 mm H\textsubscript{2}) metal was produced.

The kinetic data over the linear region could be consistent with the following mechanism

\[ L_x \text{Rh}^\text{I} + O_2 \xrightarrow{K} L_x \text{Rh}^\text{I}(O_2) \] \hspace{1cm} (8.4)

\[ L_x \text{Rh}^\text{I}(O_2) \xrightarrow{k} \text{products} + L_{x-1} \text{Rh}^\text{I} \] \hspace{1cm} (8.5)

\[ L_{x-1} \text{Rh}^\text{I} + L \xrightarrow{\text{fast}} L_x \text{Rh}^\text{I} \] \hspace{1cm} (8.6)
LiCl/DMA + O$_2$ $\xrightarrow{\text{fast}}$ LiCl/DMA/O$_2$ \hspace{1cm} (8.7)

LiCl/DMA/O$_2$ $\xrightarrow{k'}$ products \hspace{1cm} (8.8)

($L_x$ = ligands such as DMA or $C_{8}H_{14}$, Cl$^-$ omitted)

Following the formation of the $L_x$Rh$^I$(O$_2$) complex (see later, section 8.51) the rate determining step is the decomposition of $L_x$Rh$^I$(O$_2$) to give the products with the regeneration of $L_x$Rh$^I$. The blank reaction is represented by equations 8.7 and 8.8. The rate law for the above reaction mechanism (equation 8.4-8.8) is of the form

$$\text{Rate} = \frac{-d[O_2]}{dt} = k[L_x\text{Rh}^I(O_2)] + k'[\text{LiCl/DMA/O}_2]$$

$$= k[L_x\text{Rh}^I(O_2)] + k'' \hspace{1cm} (8.9)$$

Expressing the rate in terms of the total monomeric [Rh] concentration (see section 8.51) equation 8.9 becomes

$$\text{Rate} = \frac{-d[O_2]}{dt} = \frac{kK[O_2][\text{Rh}]}{1 + K[O_2]} + k'' \hspace{1cm} (8.10)$$

If $K[O_2] \gg 1$, equation 8.10 reduces to

$$\text{Rate} = \frac{-d[O_2]}{dt} = k[\text{Rh}] + k'' \hspace{1cm} (8.11)$$

The dependence of rate on [Rh] at 725 mm at 80° was analyzed according to equation 8.11 and the value of $k$ was found to be $2.96 \times 10^{-4}$ sec$^{-1}$ and $k''=0.8 \times 10^{-6}$ M sec$^{-1}$ (Figure 46). The value
of $k''$ estimated for the blank reaction at 80° (Figure 45) was $0.6 \times 10^{-6}$ M sec$^{-1}$.

Rearrangement of equation 8.10 gives

$$\frac{1}{\text{Rate}-k''} = \frac{1}{kK[O_2][\text{Rh}]} + \frac{1}{k[\text{Rh}]} \quad (8.12)$$

The dependence of rate on [O$_2$] was analyzed according to equation 8.12; taking $k''$ as $0.6 \times 10^{-6}$ M sec$^{-1}$, the values of $k$, $4.25 \times 10^{-4}$ sec$^{-1}$, and $K$, $2.96 \times 10^{-3}$ M$^{-1}$, at 80°, were obtained (Table XXVIII, Figure 49). The discrepancy between the $k$ value, as obtained from the [Rh] dependence and [O$_2$] dependence, is due to the use of different stock solutions for the two series of experiments. The rate data at different temperatures were analysed as for those at 80° (Table XXVIII); for these calculations, values of $k''$ at different temperatures were obtained from independent measurements and were found to be practically independent of O$_2$ pressure from 40 to 800 mm. The $K$ value at 70° seems anomalously low (Table XXX). An Arrhenius rate plot for the rate constant $k$ is shown in Figure 50; $\Delta H^+$ and $\Delta S^+$ for the reaction (equation 8.5) were determined to be $21.9 \pm 1.2$ Kcal mole$^{-1}$ and $-7.8 \pm 2.6$ e.u. respectively ($k = 2.96 \times 10^{-3}$ sec$^{-1}$).

8.4 Other Catalytic Systems Involving the Oxygenation Activity of [Rh(C$_8$H$_{14}$)$_2$Cl]$_2$

No oxidation of ethanol (0.06 M) or Ph$_3$P (0.03 M) was observed (no oxidation product detected) when these were used as oxidizable substrates in LiCl/DMA media. The rate of oxidation in the presence of added Ph$_3$P was $2.08 \times 10^{-6}$ M sec$^{-1}$ ([Rh] = 5.0 $\times 10^{-3}$ M,
Figure 49. Rh(I$\text{O}_2$) catalyzed oxidation in 0.5M LiCl/DMA at 80°. Plot of $\frac{1}{\text{Rate} - k''}$ against $\frac{1}{[\text{O}_2]}$, (5.0 x 10$^{-3}$M Rh)
TABLE XXX

Rh(I)(O₂) Catalyzed Oxidation in 0.5 M LiCl/DMA

Temperature Dependence of k and K

[Rh] = 5.0 x 10⁻³ M

<table>
<thead>
<tr>
<th>T (°C)</th>
<th>[O₂] x 10⁻³ M</th>
<th>k x 10⁴ sec⁻¹</th>
<th>K x 10⁻³ M⁻¹</th>
</tr>
</thead>
<tbody>
<tr>
<td>25</td>
<td>-</td>
<td>-</td>
<td>5.00</td>
</tr>
<tr>
<td>70</td>
<td>4.95</td>
<td>2.15</td>
<td>1.38</td>
</tr>
<tr>
<td>75</td>
<td>4.15</td>
<td>2.77</td>
<td>4.25</td>
</tr>
<tr>
<td>80</td>
<td>3.75</td>
<td>4.25</td>
<td>2.92</td>
</tr>
<tr>
<td>87</td>
<td>3.61</td>
<td>9.10</td>
<td>1.90</td>
</tr>
</tbody>
</table>

* See appendix 1.
Figure 50. Arrhenius plot for the Rh⁺(O₂) catalyzed oxidation in 0.5M LiCl/DMA, 5.0 × 10⁻³ M Rh.
p'\textsubscript{O}_2 = 725 \text{ mm}, 80^\circ) which was slightly lower than when no Ph\textsubscript{3}P was present (cf. Table XXVII). The rate of oxidation in the presence of added ethanol was 0.60 \times 10^{-6} \text{ M sec}^{-1} ([\text{Rh}] = 5.0 \times 10^{-3} \text{ M, p'}\textsubscript{O}_2 = 750 \text{ mm, T} = 50^\circ).  

A solution of \([\text{Rh(C}_8\text{H}_14)_2\text{Cl}]_2\) in DMF showed no catalytic oxidation properties over a period of 3 hours at 80\°. The initial orange red colour was unchanged at the end of the reaction. When the same reaction was carried out in 0.5 M LiCl/DMF media, a very slow reaction was observed. No initial rapid uptake of \text{O}_2 was apparent. Similarly, no \text{O}_2 uptake was apparent in DMSO as solvent media.

At 50\°, a solution of \([\text{Rh(C}_8\text{H}_14)_2\text{Cl}]_2\) in ethanol, made up in air, absorbed 4.1 \times 10^{-5} \text{ moles of O}_2 for 2.5 \times 10^{-5} \text{ moles of Rh} (Figure 51). The uptake analyzed fairly well for a first order on \text{O}_2 consumption with the pseudo first order constant 4.18 \times 10^{-4} \text{ sec}^{-1}

This could refer to a first order dependence on cyclooctene which was being oxidized.

\[
\text{Rh}^\ddagger + \text{O}_2 \rightleftharpoons \frac{K}{\text{Rh}^\ddagger(\text{O}_2)}\]  

\[
\text{Rh}^\ddagger(\text{O}_2) + \text{C}_8\text{H}_{14} \rightarrow \frac{k}{\text{Rh}^\ddagger + \text{oxidation products}}\]  

Therefore the rate law would be given by equation 8.14

\[
\frac{-d[\text{O}_2]}{dt} = \frac{kK[\text{Rh}][\text{O}_2][\text{C}_8\text{H}_{14}]}{1 + K[\text{O}_2]}\]  

Further studies are required on this system.
Figure 51. Rate plot and the corresponding log plot for the reaction of $[\text{Rh(C}_8\text{H}_{14})_2\text{Cl}]_2$ with $\text{O}_2$ in ethanol at $50^\circ$, $(5.0 \times 10^{-3}\text{ M Rh, 3.75 x }10^{-3}\text{ M O}_2)$ (O) $\text{O}_2$ absorbed, (A) log $[\text{C}_8\text{H}_{14}]$. 
The complex, [Rh(C₈H₁₄)₂Cl]₂, dissolves easily in solvents such as benzene, dichloromethane and chloroform, to give yellow solutions which on standing in air give brown precipitates. It seemed that molecular oxygen complexes were possibly being precipitated in such solutions.

[Rh(C₈H₁₄)₂Cl]₂ was dissolved in benzene in the absence of air at room temperature. The initial orange yellow solution darkened in two hours under O₂, 8.0 x 10⁻⁵ moles of O₂ uptake being observed for 10.0 x 10⁻⁵ moles of Rh, and a brown precipitate was obtained. I.R. of the brown precipitate showed absorption peaks at 3460 cm⁻¹, 1600 cm⁻¹ and a very broad absorption around 1100 cm⁻¹. If N₂ was used instead of O₂ under the same conditions, no uptake and no colour changes were observed in three hours; on leaving such a solution under N₂ overnight, a brown precipitate was again observed.

8.5 Discussion

8.5.1 Formation of the Molecular Oxygen Complex

The initial rapid O₂ uptake at room temperature or 80°C in a solution of ¹ is associated with the formation of a molecular complex which is probably monomeric as suggested by the kinetic data of the Rh¹ catalyzed hydrogenation (see section 6.4). The exact stoichiometry of the O₂ uptake, i.e. 1:1 mole ratio of O₂:Rh and the appearance of the 0-0 stretch typical of a mono-nuclear molecular oxygen complex are very good evidence for the formation of a 1:1 monomeric molecular rhodium oxygen complex.

The formation of this Rh¹(O₂) complex was to a very large extent
irreversible. The equilibrium constant for the formation of the Rh\textsuperscript{I}(O\textsubscript{2}) complex (equation 8.1) determined from spectroscopic and kinetic data was of the order of \((2.0-5.0) \times 10^3\) M\(^{-1}\) (Table XXX) which indicates that the Rh\textsuperscript{I}(O\textsubscript{2}) complex is formed to the extent of 90% at 760 mm O\textsubscript{2} for a 5.0 x 10\(^{-3}\) M Rh solution. Crumbliss and Basolo\textsuperscript{53} have reported that for a reversible oxygenation of Co (acacen) in DMA at -10°, the K value for

\[
\text{Co(acacen)} + \text{DMF} + O_2 \rightleftharpoons \text{Co(acacen)DMF(O}_2) \quad (8.15)
\]

was 1.3 \times 10^2 \text{ M}^{-1}. No reversible Rh(O\textsubscript{2}) complex has been reported although CO has been found to displace O\textsubscript{2} in Rh(O\textsubscript{2})(Ph\textsubscript{3}P)\textsubscript{2}Cl(0.5CH\textsubscript{2}Cl\textsubscript{2})\textsuperscript{72}.

A solution of Rh\textsuperscript{I}(O\textsubscript{2}) was found to absorb CO to produce Rh\textsuperscript{I}(CO)\textsubscript{2} (section 9.3). Kinetic data for the formation of the Rh\textsuperscript{I}(CO)\textsubscript{2} complex yielded the rate constant for the backward reaction of equation 8.1 as 0.64 \times 10^{-3} \text{ sec}^{-1} at 80° (sections 9.2 and 9.51, equations 9.1 and 9.2, Table XXXI) which combined with the K value gave the rate constant for the forward reaction of equation 8.1 as 1.87 M\(^{-1}\) sec\(^{-1}\) at 80°.

On comparison with the formulation of the oxygen complexes of other d\textsuperscript{8} systems, for example, Ir(CO)Cl(Ph\textsubscript{3}P)\textsubscript{2}(O\textsubscript{2})\textsuperscript{58-60}, possible formulae for the molecular oxygen complex are Rh(O\textsubscript{2})Cl\textsubscript{x}(DMA)\textsubscript{y} where x + y = 4. C\textsubscript{8}H\textsubscript{14} has been shown to be present as "free" ligands in solutions of \(\mathcal{L}\) (see section 6.2). The lability of the O\textsubscript{2} ligand in Rh(O\textsubscript{2})Cl\textsubscript{x}(DMA)\textsubscript{y} is shown by the rapid displacement of O\textsubscript{2} by H\textsubscript{2} (section 8.2 and equation 8.2). Maleic acid has been shown to displace O\textsubscript{2} in Rh(O\textsubscript{2})Cl\textsubscript{x}(DMA)\textsubscript{y} (section 6.5). The appearance of one Rh-H stretch for a possible dihydride formation is consistent with the formulation RhCl(DMA)\textsubscript{3}H\textsubscript{2} but with trans hydrides; a cis hydride would, however, have been anticipated, as in RhCl(Ph\textsubscript{3}P)\textsubscript{2}H\textsubscript{2}.\textsuperscript{8} The problem of stereospecificity of the addition of
diatomic molecules to square planar $d^8$ systems is presently a controversial one with the role of the solvent being particularly important; subsequent isomerization of the initial oxidative addition is a further possible complication. A very probable formula for $\text{Rh}^1(O_2)$ in LiCl/DMA media is $\text{Rh}(O_2)\text{Cl}(\text{DMA})_3$.

The irreversibility of $O_2$ uptake is largely determined by the electronegativity of the ligands around the metal. The well-known $\text{Ir}(O_2)\text{Cl}(\text{CO})(\text{Ph}_3\text{P})_2$ complex is a reversible oxygen carrier while the iodo analogue, $\text{Ir}(O_2)\text{I}(\text{CO})(\text{Ph}_3\text{P})_2$, is an irreversible one. The lower electronegativity of the iodine atom results in the oxygen molecule being bonded more strongly with resulting irreversible formation of the molecular oxygen complex. Griffith has proposed that the $O_2$ molecule in oxygenated heme is in the excited singlet state and bonding proceeds by donation of electrons from the $\pi$-orbital to a vacant orbital on the central metal ion; this sets up a dipole which reduces the extent of donation. This dipole is simultaneously reduced by back donation from the central metal ion, using its filled $d$ orbitals to the $\pi$-orbitals of the $O_2$ group. Thus the strength of attachment of oxygen to the carrier is dependent upon the availability of electrons at the central metal ion. It is therefore conceivable that, in $\text{Rh}(O_2)\text{Cl}(\text{DMA})_3$, the $O_2$ molecule will be bound irreversibly because both DMA and Cl are $\sigma$ donors and weak $\pi$-acceptors.

According to its position in the electrochemical series, molecular

\[\text{A very recent paper by D.M. Blake and M. Kubota (Inorg. Chem., 9, 989 (1970)) summarizes the relevent data.}\]
oxygen is a powerful oxidizing agent and Rh\textsuperscript{I} complexes are known to be readily oxidized to Rh\textsuperscript{III} in both aqueous and non-aqueous solvent media.\textsuperscript{1,2} The factors that govern the formation of a molecular oxygen complex in preference to oxidation is thought to be related to the reduction potentials of the metal ions.\textsuperscript{46} The reduction potentials of the metal ions can be adjusted by coordination with the proper ligands. It is therefore possible to predict which complex would act as a oxygen carrier if the reduction potentials of the ligands in the given solvent media were known and steric factors were considered. Unfortunately no such reduction potentials of rhodium and its complexes have been reported in non-aqueous solvent systems.

A striking feature of the iridium oxygen complexes, e.g., IrCl(CO)(Ph\textsubscript{3}P)\textsubscript{2}(O\textsubscript{2}) and IrI(CO)(Ph\textsubscript{3}P)\textsubscript{2}(O\textsubscript{2}), is that the ligands, with the exception of Cl\textsuperscript{−}, belong to the class of readily polarizable "soft" Lewis bases. CO and Ph\textsubscript{3}P are typical \(\pi\)-acceptors,\textsuperscript{256} (soft). O\textsubscript{2} is also soft, owing to its \(\pi\)-acceptor properties.\textsuperscript{257} Thus a complex containing only "soft" ligands will be stabilized by a "symbiotic" effect.\textsuperscript{258} Macrocyclic unsaturated ligands such as porphyrins or phthalocyanines change the coordinative properties of the metal ion, e.g. Co\textsuperscript{II} and Fe\textsuperscript{II}, to such an extent, apparently making it so soft that O\textsubscript{2} can be bound in measurable quantities.\textsuperscript{48} In the case of Co\textsuperscript{II}, the metal ion can be caused to bind O\textsubscript{2} not only by the polydentate unsaturated ligands such as (salicylaldehyde imine) but also by monodentate ligands such as CN\textsuperscript{−} or NH\textsubscript{3}.\textsuperscript{259} A large number of the recently reported mononuclear molecular oxygen complexes contain \(\pi\)-acceptor ligands such as Ph\textsubscript{3}P or Ph\textsubscript{3}As (section 1.5 and 1.8).
which may be of great importance in stabilizing the low oxidation state of the metal ion and in adjusting the metal ion to the right potential for formation of a molecular oxygen complex.

DMA is generally thought to coordinate to metal ions through the oxygen[260] but complexes containing DMA as a chelated ligand and bridging ligand[260] have been proposed in which coordination through nitrogen must be involved. A number of Co[II] chelates[46,51-57] with coordination through nitrogen and oxygen of one ligand are known to form reversible molecular oxygen complexes. Coordination of DMA in a complex such as Rh(O₂Cl(DMA))₃ could involve bonding through nitrogen atoms or chelation through oxygen and nitrogen.

The absence of an E.S.R. signal in solutions of Ω kept in vacuum, and the "build-up" of the E.S.R. signal on exposing such a solution to air or oxygen show that the signal is due to some paramagnetic species formed in the presence of air in O₂. The signal has not been identified exactly but it is probably caused by the coordination of O₂ to Rh. Further work is in progress in this laboratory on the E.S.R. aspects of the system. There are a number of reports on the E.S.R. signal of Co[II] oxygen complexes.[54-57] An eight line spectrum arising from the interaction of an unpaired electron with a single Co nucleus (I = 7/2) was observed for the systems "cobaloximes(II)",[54] Co[II](3-MeO Salen),[55] Co[II](vitamin B₁₂r)[56] and Co[II](acacen),[57] and thus support the monomeric nature of these Co[II] oxygen complexes. A fifteen line spectrum has been observed for a binuclear Co[II] oxygen species.[54] These workers[54-57] concluded from the E.S.R. spectra that
in mononuclear species the unpaired electron is largely associated with $O_2^-$ and the mononuclear $\text{Co}^{II}$ oxygen complexes are formulated as $\text{Co}^{III}O_2^-$. There are no reports on the E.S.R. spectra of $\text{Rh}(O_2)$ complexes. The E.S.R. spectrum of the present studied $\text{Rh}^{I}(O_2)$ complex seems to suggest that the signal is largely due to $O_2^-$ since its $g$ value and line shape are closely similar to some reported $O_2^-$ species. No splitting by the Rh nucleus ($I = 1/2$) is observed; with its smaller nuclear magnetic moment, the Rh nucleus is expected to cause a smaller hyper-fine splitting than the Co nucleus. Hence on analogy with the Co systems, $54-57$ $\text{Rh}^{II}O_2^-$ is the most probable electronic structure of the $\text{Rh}^{I}(O_2)$ complex. It is of interest that the molecular oxygen complexes of all the other $d^8$ and $d^{10}$ systems, $\text{Ir}^I$, $\text{Pd}^0$, $\text{Pt}^0$, $\text{Ni}^0$ have been well characterized and are diamagnetic $(p.14)$. The reported Rh complexes $64,71-73$ are ill-characterized; although $\text{Rh}(\text{Ph}_3^P)_3(O_2)^73$ was reported to be diamagnetic. The former group apparently catalyze oxygenation by atom transfer mechanism and the latter by a free radical mechanism. The oxidation in the present work will be discussed in section 8.53.

8.52 Formation of Molecular Oxygen Complexes in Other Solvents

It is surprising that no initial rapid $O_2$ uptake was apparent in solutions of $[\text{Rh}(C_8H_{14})_2\text{Cl}]_2$ in DMSO and DMF, since these are thought to be very similar to DMA in solvent properties. It is significant that addition of $\text{Cl}^-$ did promote the $O_2$ uptake in the DMF solution. Calderazzo and coworkers $52$ reported that the oxygenation of Co(Salen) was promoted in some aprotic solvents by the addition of anionic ligands, e.g. $\text{SCN}^-$, $\text{N}_3^-$ and $\text{CH}_3\text{CO}_2^-$. They also found that Co(Salen)
readily forms a binuclear molecular oxygen complex in DMF and DMSO, however, in DMA, oxygenation was hindered and this was attributed to steric factors.\textsuperscript{52} The oxygenation of [Rh(C\textsubscript{8}H\textsubscript{14})\textsubscript{2}Cl\textsubscript{2}] in DMA with no added Cl\textsuperscript{-} was not studied because the complex was only slightly soluble in DMA.

The brown precipitate obtained when solutions of [Rh(C\textsubscript{8}H\textsubscript{14})\textsubscript{2}Cl\textsubscript{2}] in chloroform, benzene or dichloromethane, were allowed to stand in air or oxygen are likely to be some sort of oxygenated Rh species. In benzene solution, an oxygen uptake in the 0.8:1 mole ratio of O\textsubscript{2}:Rh was observed but the I.R. data did not indicate the existence of an 0-0 stretch typical of the mononuclear molecular oxygen species.\textsuperscript{255} Calderazzo and coworkers\textsuperscript{52} has tentatively assigned a weak band at 1140 cm\textsuperscript{-1} to the 0-0 stretch in a monomeric Co 3-methyloxysalen, py,O\textsubscript{2} species and a band was observed at 1100 cm\textsuperscript{-1} for the brown precipitate. However, the bands at 3400 cm\textsuperscript{-1} and 1600 cm\textsuperscript{-1} are more likely attributed to the OH species. The appearance of a brown precipitate in a solution of [Rh(C\textsubscript{8}H\textsubscript{14})\textsubscript{2}Cl\textsubscript{2}] in benzene kept under N\textsubscript{2} overnight is not too conclusive; this may be due to traces of air leaking into the solution or traces of O\textsubscript{2} impurity in the N\textsubscript{2}.

8.53 Catalytic Oxidation Catalyzed by Rh\textsuperscript{I}(O\textsubscript{2}) in LiCl/DMA

The observed O\textsubscript{2} uptake after the initial molecular oxygen complex formation is due to the Rh\textsuperscript{I}(O\textsubscript{2}) catalyzed oxidation of DMA and C\textsubscript{8}H\textsubscript{14}. DMA must be oxidized since the O\textsubscript{2} uptake is in excess of that required for just the C\textsubscript{8}H\textsubscript{14} oxidation. The inhibition of the
formation of the Rh\(^{I}(O_2)\) complex in the presence of DPPH and the evolution of gases observed on adding \([\text{Rh}(_8\text{C}_8\text{H}_{14})_2\text{Cl}]_2\) to an evacuated solution of LiCl/DMA with DPPH suggests that a reaction occurs between DPPH and the \([\text{Rh}(_8\text{C}_8\text{H}_{14})_2\text{Cl}]_2\). \(N_2\) is probably evolved. The catalytic oxidation is not photosensitized but a free radical mechanism might be involved since addition of DPPH in a 10:1 mole ratio of DPPH:Rh, inhibited the catalytic oxidation completely, while addition of 0.5:1, 1:1 and 2:1 mole ratios of DPPH:Rh decreased the rate (Table XXIX). The blank reaction is almost certainly a free radical reaction since addition of 0.03 M DPPH stopped the blank reaction completely.

The observed kinetics in the linear region are simple but the overall oxidation reaction clearly becomes very complicated since CO abstraction was observed in the course of oxidation and Me\(_2\)NH was detected by mass spectrometry. The CO abstracted is thought to be catalytically oxidized to CO\(_2\) (Chapter IX). The formation of CO\(_2\) was detected in the system. The kinetics and the observed O\(_2\) uptake in linear region suggested that CO abstraction is not occurring in that region. The production of Me\(_3\)NO from the oxidation of Me\(_3\)N resulting from the CO abstraction of DMA appeared likely but attempts to isolate Me\(_3\)NO as the picrate failed.

The fall off in linear rate in the course of the catalytic oxidation is probably due to the slow oxidation of Rh\(^{I}\) to Rh\(^{II}\) which is incapable of forming the molecular oxygen complex. Regeneration of the active species by H\(_2\) treatment of the less "active" solutions supports this argument. H\(_2\)/O\(_2\) mixtures appeared to be able to maintain a longer linear and the rate of O\(_2\) uptake is comparable to that when
0\textsubscript{2} was used alone. Different stock solutions (Figure 46) showed slightly different activities possibly due to slow oxidation of Rh\textsuperscript{I} to Rh\textsuperscript{II}. In solution, the rapid deterioration of all the Co\textsuperscript{II} oxygen carrying chelates is due to the irreversible oxidation of Co\textsuperscript{II} to Co\textsuperscript{III}; similar deterioration of a Fe\textsuperscript{II} oxygen carrying chelate\textsuperscript{46} has been observed.

The dependence of rate on added C\textsubscript{8}H\textsubscript{14} is not too clear. The rate determining step in the absence of added C\textsubscript{8}H\textsubscript{14} probably involves the oxidation of DMA (equation 8.5). In the presence of added C\textsubscript{8}H\textsubscript{14}, the rate determining step may involve the oxidation of C\textsubscript{8}H\textsubscript{14} which could now be incorporated in the coordination sphere.

The increase in rate when H\textsubscript{2}O (one of the oxidation products) was added may be due to the change in dielectric constant of the media or the increased solubility of O\textsubscript{2}. In any case, the fall off in the oxidation rate is unlikely to be due to H\textsubscript{2}O production.

8.54 Postulated Mechanism for the Catalytic Oxidation

Two general paths for oxygenation of substrates catalyzed by molecular oxygen complexes have been proposed, namely; one involving "dissociative oxygen insertion" (oxygen atom transfer) and the other involving free radicals (see section 1.5). There is no strong evidence in the present work that the oxidation proceeds via a free radical mechanism; DPPH clearly reacts with the Rh\textsuperscript{I} species in the absence of O\textsubscript{2} and inhibites the reaction in this way. However, the existence of a species such as Rh\textsuperscript{II}O\textsubscript{2}\textsuperscript{-} which might readily initiate a free radical reaction and the fact that all other oxidations
catalyzed by Rh complexes have been shown to be free radical reactions suggest that the present system may involve a similar process.

A Haber-Weiss type mechanism involving one or two electron transfer has been proposed in the RhCl(Ph₃P)₃ and RhCl(CO)(Ph₃P)₂ catalyzed oxidation of organic substrates (section 1.5, equations 1.23-1.26). In the RhCl(CO)(Ph₃P)₂ catalyzed oxidation of diphenylmethane, the active catalyst is thought to be RhCl(CO)(Ph₃P)₂(O₂) or some sort of hydroperoxide.

The autoxidation of amides which may be regarded as model substances for nylon has not yet been as extensively studied as that of the hydrocarbons. Sharkey and Mochel postulated a scheme for the autoxidation of amides, of the general formula R'CONHCHR, which is analogous to that for the autoxidation of hydrocarbons. On the assumption that the C-H bond dotted in the above formula is weaker than the others, these workers postulated the hydroperoxide R'CONHCH(OOH)R² as the intermediate for the ultimate autoxidation products, particularly R'CONH₂, R²CHO and R²COOH. Riches studied the sodium anthraquinone-2-sulphonate photosensitized autoxidation of amides and concluded that a reaction mechanism involving free radicals is postulated but a chain reaction is excluded, i.e.

\[
RO₂⁻ + RH \rightarrow ROOH + R⁻ \quad (8.15)
\]

is negligible and the autoxidation products are formed mainly by a
RO₂⁻ + RO₂⁻ reaction. According to Sharkey and Mochel's scheme, CH₃CONHCH₃, HCHO and HCOOH might be expected as oxidation products of DMA. Carbonyl abstraction from CH₃CONHCH₃ would produce the observed amine product, Me₂NH. Carbonyl abstraction from HCHO and HCOOH could also occur (see section 1.64).

It is difficult to present a very realistic reaction scheme to account for the observed products particularly since the nature of the oxidation product of DMA was not substantiated. However, a scheme which is thought to contain some of the probable reactions involved is as follows:

\[
\begin{align*}
\ce{O|C-N|CH_3} & + \ce{O_2} \xrightarrow{K} \ce{O|C-N|CH_3} \quad \text{(8.16)} \\
\ce{CH_3|C-N|CH_3} & \xrightarrow{k} \text{rate determining} \quad \ce{Rh^I + OOH + |N-CH_2|CH_3CO} \quad \text{(8.17a)}
\end{align*}
\]

or \( \ce{O_2} \) insertion

\[
\begin{align*}
\ce{CH_3|C-N|CH_3} & \xrightarrow{\text{rate determining}} \text{rate determining} \quad \ce{Rh^I + N-CH_2(OOH)} \quad \text{(8.17b)}
\end{align*}
\]
\[
\begin{align*}
\text{OOH} + & \quad \text{chain propagation} \quad \text{fast} \\
\text{H} & \quad \rightarrow \quad \text{OOH} \\
& \quad \text{fast} \\
& \quad \text{H}_2O \\
& \quad \text{chain termination} \\
\end{align*}
\]
As mentioned in section 8.3, it is surprising that \( \mathrm{C_8H_{14}O} \) was identified as a product from the prepared 2,4-dinitrophenylhydrazine derivative. The retention time in the gas chromatogram indicated a keto product different from \( \mathrm{C_8H_{14}O} \) was obtained. 3-Cyclohexene hydroperoxide was postulated as the likely intermediate in the \( \mathrm{RhCl(Ph_3P)_3} \) catalyzed oxidation of cyclohexene to cyclohexene-3-one; hence production of cyclooctene-3-one (equation 8.18b) was considered very likely in the present system. Cyclooctanone could be produced via a questionable reaction such as 8.18a. Alternatively the cyclooctanone derivative could be produced from the reduction of cyclooctene-3-one by the 2,4-dinitrophenylhydrazine/HCl reagent. The possible DMA oxidation product, \((\mathrm{CH}_3\mathrm{CONCH}_3\cdot\mathrm{CH}_2)_2\cdot\mathrm{N,N'-diacetyl-N,N'-dimethylethylenediamine}\), was not identified but it could be in the solid residue. Radical dimerization of DMA by t-butyl peroxide to yield \( \mathrm{N,N'-diacetyl-N,N'-dimethylethylenediamine} \) (m.p. 90-92°) has been reported. However, no reports on the properties of this compound were found. Many fruitless attempts were made to isolate this possible compound from the solid residue of the oxidation reaction mixture. The possible \( \mathrm{CH}_3\mathrm{CONHCH}_3 \) product would be difficult to isolate and characterize from the final reaction mixture. Water was shown to be one product in these reactions (equation 8.18b).

An analogy with the other Rh catalyzed oxidation of organic substrates, \(^{84,90}\) a Haber-Weiss type mechanism involving \( \mathrm{Rh^I} \) and \( \mathrm{Rh^II} \) can be written as follows:

\[
\begin{align*}
\mathrm{CH}_3\mathrm{CO} & \quad \mathrm{N-CH}_2 \quad + \quad \mathrm{O}_2 \quad \longrightarrow \quad \mathrm{CH}_3\mathrm{CONCH}_3\cdot\mathrm{CH}_2\mathrm{OOH} \\
\mathrm{CH}_3 & \quad \mathrm{H}
\end{align*}
\]  
\[(8.23a)\]
A similar scheme for transfer of two electrons, involving Rh\textsuperscript{I} and Rh\textsuperscript{III}, is possible. In the present system, the formation of the Rh\textsuperscript{I}(O\textsubscript{2}) complex is established and the electronic structure of the molecular oxygen complex is thought to be Rh\textsuperscript{II}O\textsubscript{2}\textsuperscript{-} hence it appears that a reaction involving H abstraction or hydroperoxide formation via insertion of the coordinated oxygen (equation 8.17) is the likely rate determining step.

The blank reaction is definitely free radical in nature. Trace metal has been proposed\textsuperscript{266} for the apparently uncatalyzed autoxidation and has been invoked for reactions of the metal with molecular oxygen via a complex which involves metal, O\textsubscript{2} and substate or solvent, e.g.
\[
M^{n+}(O_2)(XH) \rightarrow M^{(n+1)+}X^- + O_2H
\]
(8.28)

(in the present system, \(M^{n+} = Li^+, XH = CH_3CONCH_3CH_2H\))

The \(\text{Rh}^{\text{I}}\) systems involving MA (Chapter VI) did not catalyze the autoxidation of DMA and \(C_8H_{14}\). This is in good agreement with the finding of Fine's group,\(^{90}\) where the catalytic effect of \(\text{RhCl(}CO)(\text{Ph}_3\text{P})_2\) in the autoxidation of diphenylmethane becomes more and more inhibited with the increased degree of complexing to a more strongly electrophilic olefin.

It has been suggested earlier (p. 213) that the fall off in catalytic activity of the oxidation is due to oxidation of \(\text{Rh}^{\text{I}}\) to \(\text{Rh}^{\text{II}}\). However, the retardation of rate may be due to a self inhibiting or auto-retardation reaction.\(^{267}\) Such retardations have been shown to be due to "in situ" formation of oxidation side products. This phenomenon introduces into any autoxidation the complicating factor that the observed rate may be determined by the rate of formation of the inhibition itself rather than the stability of the substrate. However, such retardations do not generally occur until a considerable amount of oxidation has taken place.

The catalytic oxidation activity of the \(\text{Rh}^{\text{I}}(O_2)\) complex in the present system is due largely to the reactive nature of the \(O_2\) molecule since the electronic structure of \(\text{Rh}^{\text{I}}(O_2)\) is thought to be \(\text{Rh}^{\text{II}}(O_2)^-\). Hence the \(O_2\) molecule on bonding to rhodium becomes activated and initiates oxidation. It appears therefore, in this system, both the substrate and \(O_2\) are incorporated into the coordination sphere of \(\text{Rh}\) before oxidation occurs.

The activation enthalpy of the present system is \(21.9 \pm 1.2\) Kcal
mole\(^{-1}\) which is very close to the energy difference between the ground state to the first excited state of \(O_2\), \(\Sigma \rightarrow \Delta = 22.1\) Kcal mole\(^{-1}\), although this is probably fortuitous since the activation energy of that order is very common. The observed dependence of rate on pressure is very similar to that for reactions involving free radicals, \(^{268}\) although in this present system, the dependence of rate on pressure is governed by the K value for the formation of the \(Rh^I(O_2)\) complex.
CHAPTER IX

FORMATION AND PROPERTIES OF SOME RHODIUM CARBONYL COMPLEXES

9.1 General Introduction

This chapter describes very preliminary studies of the formation of rhodium carbonyl complexes via direct carbonylation with CO in solution and via CO abstraction from the solvent. These studies were initiated to investigate the activation of CO by rhodium complexes and also to learn more of the suspected decarbonylation of solvent in the oxidation studies. (Chapter VIII) The studies show that such abstracted CO is likely to be converted to CO₂ under the oxidation conditions. The reaction between coordinated CO and gaseous O₂ seems worthy of further study. The catalytic hydrogenation activity of these rhodium carbonyl complexes was also briefly studied.

9.2 Reaction of [Rh(C₈H₁₄)₂Cl₂] with CO in LiCl/DMA

A stock solution (kept in air) of [Rh(C₈H₁₄)₂Cl₂] in 0.5M LiCl/DMA readily absorbed CO in about a 2:1 mole ratio of CO:Rh. (Figure 52) The initial brownish red solution turned pale yellow. The I.R. of the carbonylated solution showed bands at 1974 cm⁻¹ and 2053 cm⁻¹ which are very similar to that reported for [Rh(CO)₂Cl₂]⁻ (νCO = 1974, 2058 cm⁻¹).
Figure 52. Rate plot and the corresponding log plot for the formation of Rh$^+$(CO)$_2$ complex in 0.5M LiCl/DMA at 80°, (2.0 × 10$^{-2}$M [Rh(C$_8$H$_{14}$)$_2$Cl], 3.75 × 10$^{-3}$ M O$_2$) (O) gas absorbed, (△) log plot
No colour change was observed when the pale yellow solution was pumped on for a few hours at 40° and the I.R. spectrum of the resulting solution showed the same two I.R. bands at 1974 cm\(^{-1}\) and 2053 cm\(^{-1}\). No further CO uptake was observed for such a solution.

Attempts were made to isolate the possible \([\text{Rh(CO)}_2\text{Cl}]_2^-\) species by the addition of tetraphenylarsonium chloride\(^{174}\) but surprisingly the expected yellow solid was not isolated. Gas evolution was observed when \(\text{Ph}_3\text{P}\) was added to the carbonylated solution and a pale yellow powder was obtained. I.R. spectrum of this yellow powder showed CO at 1960 cm\(^{-1}\) which is very similar to that reported for \(\text{RhCl(CO)(Ph}_3\text{P)}_2\)\(^{173}\).

A typical gas uptake plot (Figure 52) for a stock solution of \([\text{Rh(C}_8\text{H}_14)_2\text{Cl}]_2\) in LiCl/DMA consisted of an initial rapid uptake followed by a region of decreasing rate; the initial rapid uptake was not observed when a solution containing the fully formed \(\text{Rh}(\text{O}_2)\) complex was used. (Figure 53) The stock solution is believed to contain some oxygen complex, i.e. \([\text{Rh}] = \text{Rh}^I + \text{Rh}(\text{O}_2)\) where \([\text{Rh}] = [\text{Monomer}]. \) (Chapter VIII) The initial rapid uptake when stock solutions were used is thought to be due to the reaction of CO with \(\text{Rh}^I\) and the latter part of the uptake due to reaction of CO with \(\text{Rh}(\text{O}_2)\). (See section 9.5) The gas uptake plots were analyzed by plotting the log (total moles of gas absorbed − moles of gas absorbed at time \(t\)) against time, \(t\). A good first order plot (Figure 53) was obtained for the experiment using a solution containing the fully formed \(\text{Rh}(\text{O}_2)\) and the pseudo first order constant, \(k\), which referred to a first order decrease in \([\text{Rh}(\text{O}_2)]\) is shown in
Figure 53. Rate plot and the corresponding log plot for the formation of Rh\(^{1}\)(CO)\(_2\) in 0.5M LiCl/DMA at 80° (1.3 x 10\(^{-2}\)M Rh\(^{1}\)(O\(_2\)), 3.75 x 10\(^{-3}\)M O\(_2\)). (O) gas absorbed, (Δ) log [Rh\(^{1}\)(O\(_2\))].
Table XXXI; a 1:1 mole ratio of gas:Rh was absorbed. I.R. spectra of the resulting pale yellow solution showed bands at 2060 cm$^{-1}$ and 1980 cm$^{-1}$. For experiments using the stock solutions, the log plot corresponding to the latter stages of the gas uptake gave a good straight line (Figure 52) from which the listed k values (Table XXXI) were determined. The first order constants showed independence on [CO] and a first order dependence on [Rh$^I$(O$_2$)].

Uptake of CO in a 1:1 mole of CO:Rh was observed for a solution of [Rh(C$_8$H$_{14}$)$_2$Cl]$_2$ in 0.5 M LiCl/DMA made up in the absence of O$_2$. The CO uptake was completed in 80 sec. at 80° ([Rh] = 1.0 x 10$^{-2}$ M, [CO] = 5.0 x 10$^{-3}$ M) and no further CO uptake was observed even after 4 hours at 80°. I.R. spectrum of the resulting pale yellow solution showed bands at 2060 cm$^{-1}$ and 1980 cm$^{-1}$; some of the initial CO uptake was probably missed. If the same reaction was carried out at 60°, the CO absorbed was equivalent to 1.5:1 mole ratio of CO:Rh. This CO uptake plot analyzed for first order decrease in [Rh$^I$] (Table XXXI). If the same reaction was carried out at room temperature, the CO absorbed was equivalent to a 2:1 mole ratio of CO:Rh; the first mole of CO was absorbed rapidly and the second mole of CO was absorbed over a period of several hours.

Addition of MA to the carbonylated solution resulted in an intense yellow solution and gas evolution was observed. On subjection to 1 atm of H$_2$ at 80°, no gas uptake was observed for two hours.
TABLE XXXI
Formation of Rh\textsuperscript{I} Carbonyl Species in DMA

Summary of Kinetic Data

<table>
<thead>
<tr>
<th>T (^{°}C)</th>
<th>[Rh] (mm)</th>
<th>CO</th>
<th>[CO] (x10^3 M)</th>
<th>(k \times 10^3 ) sec(^{-1})</th>
</tr>
</thead>
<tbody>
<tr>
<td>80</td>
<td>0.5</td>
<td>725</td>
<td>5.0</td>
<td>0.63</td>
</tr>
<tr>
<td>80</td>
<td>1.0</td>
<td>725</td>
<td>5.0</td>
<td>0.63</td>
</tr>
<tr>
<td>80</td>
<td>2.0</td>
<td>725</td>
<td>5.0</td>
<td>0.65</td>
</tr>
<tr>
<td>80</td>
<td>1.0</td>
<td>406</td>
<td>2.6</td>
<td>0.65</td>
</tr>
<tr>
<td>60</td>
<td>1.0</td>
<td>745</td>
<td>5.2</td>
<td>0.28</td>
</tr>
<tr>
<td>60</td>
<td>1.0</td>
<td>745</td>
<td>5.2</td>
<td>0.51(^a)</td>
</tr>
<tr>
<td>80</td>
<td>2.0</td>
<td>725</td>
<td>5.0</td>
<td>0.65(^b)</td>
</tr>
</tbody>
</table>

\(^a\) Data referred to stock solutions of \([\text{Rh(C}_8\text{H}_{14})_2\text{Cl}]_2\) in 0.5M LiCl/DMA

\(^b\) a solution containing the fully formed Rh\textsuperscript{I}(O\textsubscript{2}) complex.
9.3 Catalytic Reaction Between the Coordinated CO and O₂

The rhodium carbonyl complexes prepared from the \([\text{Rh(C}_8\text{H}_{14})_2\text{Cl}]_2\) complex in 0.5M LiCl/DMA were found to undergo interesting reactions with O₂. When the carbonylated solution was left at room temperature under air for a few days, a brownish red solution with an I.R. band at 2100 cm⁻¹ and a very slight shoulder at 2130 cm⁻¹ was observed. If the solution was reacted with O₂ at 80°, O₂ uptake in excess of that required for oxidation of Rh\(^{II}\) to Rh\(^{III}\) was observed. An O₂ uptake plot for a 0.01 M Rh solution is shown in Figure 54; a very slow initial uptake followed by a more linear region with a rate \((3.2 \times 10^{-5} \text{ M sec}^{-1})\) which was seven times faster than the Rh\(^{II}(O₂)\) catalyzed oxidation \((\text{c f. } 4.6 \times 10^{-6} \text{ M sec}^{-1}, \text{ Table XXVII})\) was observed. The stoichiometry of O₂ uptake at the break off region of the first linear rate corresponded closely to 1 mole of O₂ consumed per mole of coordinated CO. After the initial more rapid linear rate, a second region of linear rate \((6.6 \times 10^{-6} \text{ M sec}^{-1})\) which was close to the rate of the Rh\(^{II}(O₂)\) catalyzed oxidation was observed. The resulting greenish brown solution (shoulder at 450 m, ε = 260) suggested the presence of Rh\(^{II}(O₂)\) species. I.R. spectrum of the resulting brown solution showed bands at 1290, 1140 and 830 cm⁻¹.

A stock solution of \([\text{Rh(C}_8\text{H}_{14})_2\text{Cl}]_2\) in 0.5M LiCl/DMA \((1.0 \times 10^{-4} \text{ moles of Rh})\) reacted with a mixture of O₂ \((370 \text{ mm})\) and CO \((380 \text{ mm})\) and after 3 hours, \(1.0 \times 10^{-4} \text{ moles of gas were apparently consumed}\); and after 3 days a total of \(2.2 \times 10^{-4} \text{ moles of gas were apparently consumed}\).
Figure 54. Rate plot for the reaction of Rh(CO)$_2$ with O$_2$ in 0.5M LiCl/DMA at 80°,
(1.0 x 10$^{-2}$ M Rh, 3.75 x 10$^{-3}$ M O$_2$)
and possibly a very slow reaction was still occurring. Mass spectrometry indicated CO₂ is produced in the gaseous phase. I.R. spectrum of the pale yellow solution showed peaks at 2060 cm⁻¹ and 1960 cm⁻¹. The visible spectrum gave a λ_max at 400 μm (ε = 130).

When a solution of [Rh(C₈H₁₄)₂Cl]₂ in 0.5M LiCl/DMA was kept under N₂ for two days at 80°, no N₂ uptake was observed and the I.R. spectrum showed a band at 1940 cm⁻¹ which is attributed to Rh-CO stretch; the Rh-CO species was formed via CO abstraction from the solvent DMA. CO abstraction under O₂ atmosphere by [Rh(C₈H₁₄)₂Cl]₂ is thought to be present in the catalytic oxidation system. In the presence of O₂ at 80°, the CO abstracted is also believed to be oxidized to CO₂. (Chapter VIII)

9.4 Reaction of RhCl₃(Et₂S)₃ with CO in DMA

An orange red solution of RhCl₃(Et₂S)₃ in DMA (λ_max 426 μm, ε = 308) readily absorbed two moles of CO per mole of Rh to give a pale yellow solution (λ_max 340 μm, ε = 2730). I.R. of the resulting pale yellow solution showed two bands at 2062 cm⁻¹ and 1976 cm⁻¹. This pale yellow solution turned orange on standing for a day in air at room temperature (shoulder at 450 μm, ε = 420). The resulting orange red solution showed a Rh-CO band at 2060 cm⁻¹.

Preliminary studies indicated that the CO uptake plot (Figure 55) analyzed for a first order loss in [Rh⁺⁺⁺] and the pseudo first order constant was 7.85 x 10⁻³ sec⁻¹ at 80°. At 60°, the pseudo first order constant was found to be 1.45 x 10⁻³ sec⁻¹.
Figure 55. Rate plot and the corresponding log plot for the formation of $\text{Rh}^\text{I}(\text{CO})_2$ in DMA at $80^\circ$, $(1.43 \times 10^{-3} \text{M}, \text{RhCl}_3(\text{Et}_2\text{S}), 5.0 \times 10^{-3}\text{M CO} (\bigcirc) \ CO$ absorbed; (□) log [Rh $\text{III}$.]
Prolonged pumping (a few hours at room temperature) did not remove the CO in the rhodium carbonyl species since no CO uptake was measured on such solutions.

When MA was added to the solution containing the rhodium carbonyl species, evolution was observed and the resulting solution did not act as a homogeneous hydrogenation catalyst for MA.

9.5 Discussion

9.51 The \([\text{Rh(C}_8\text{H}_{14})_2\text{Cl}]_2\) System

Spectral evidence indicates that a \(\text{Rh}^\text{I}(\text{CO})_2\) species, \([\text{Rh(CO)}_2\text{Cl}]^-\) or possibly \(\text{RhCl(CO)}_2\text{(DMA)}\) (which would account for the lack of precipitation of \(\text{Ph}_4\text{As}^+\text{[Rh(CO)}_2\text{Cl}_2\text{]}^-\) on addition of \(\text{Ph}_4\text{As}^+\text{Cl}^-\)) is formed in the reactions of \([\text{Rh(C}_8\text{H}_{14})_2\text{Cl}]_2\) with CO in DMA. The preparation of \([\text{Rh(CO)}_2\text{Cl}]_2\) from \([\text{Rh(C}_8\text{H}_{14})_2\text{Cl}]_2\) has been reported.\(^{208}\)

Preliminary kinetic data on the reactions of stock solutions of \([\text{Rh(C}_8\text{H}_{14})_2\text{Cl}]_2\) in LiCl/DMA with CO suggest that the rate determining step is first order in \([\text{Rh}^\text{I}(\text{O}_2)]\) and independent of CO (Table XXXI). The difference in the kinetic data for reactions using stock solutions, a solution containing the fully formed \(\text{Rh}^\text{I}(\text{O}_2)\) complex and the "air free" solutions suggests that the rate determining step is the production of the "active" \(\text{Rh}^\text{I}\) species which then picks up two moles of CO in a fast step to produce the \(\text{Rh}^\text{I}(\text{CO})_2\) species. \([\text{Rh(C}_8\text{H}_{14})_2\text{Cl}]_2\) in LiCl/DMA has been shown to form the \(\text{Rh}^\text{I}(\text{O}_2)\) complex. The stock solutions of \([\text{Rh(C}_8\text{H}_{14})_2\text{Cl}]_2\) in LiCl/DMA contain some \(\text{Rh}^\text{I}(\text{O}_2)\) species. The kinetic data could be consistent with the following reactions involving stock solutions.
\[
\text{Rh}^1(\text{O}_2) \xrightarrow{k} \text{Rh}^1 + \text{O}_2 \quad (9.1)
\]
\[
\text{Rh}^1 + 2\text{CO} \xrightarrow{\text{fast}} \text{Rh}^1(\text{CO})_2 \quad (9.2)
\]

k is known to be relatively small since the equilibrium in equation 9.1 is not displaced to the right on removal of gases; the "air free" Rh\(^1\) solutions do have a high affinity for CO as seen by the very rapid CO uptake for such solutions. Starting with the stock solutions, Rh\(^1\) will absorb CO very rapidly; Rh\(^1(\text{O}_2)\) will absorb CO at a rate governed by \(k\). The reaction between Rh\(^1\) and CO has also been shown to be a fast step in the formation of [Rh(CO)\(_2\)Cl\(_2\)]\(^-\) species from RhCl\(_3\).3H\(_2\)O and CO in both aqueous and non-aqueous media.\(^1,187,189\)

The evolution of O\(_2\) (equation 9.1) could account for the somewhat low stoichiometry (-1.6:1) of the observed gas uptake in reactions involving stock solutions (see Figure 52) and the 1:1 stoichiometry for a solution containing the fully formed Rh\(^1(\text{O}_2)\) complex. The oxygen molecule in RhCl(\text{O}_2)(\text{Ph}_3\text{P})\(_2\)\(^72\) and RhCl(\text{O}_2)(\text{Ph}_3\text{As})\(_2\)\(^71\) has been found to be readily displaced by CO in dichloromethane.

The reaction between Rh\(^1(\text{CO})_2\) and O\(_2\) is of special interest in view of the recent reports on complexes containing CO\(_2\)\(^269\), CO\(_3\)\(^2\)\(^-\)\(^74,82\), and OCO\(_3\)\(^2\)\(^-\)\(^270\) as ligands. Pt(CO\(_3\)\(_2\))(\text{Ph}_3\text{P})\(^82\) has been formed by passing an O\(_2\) and CO\(_2\) mixture into a solution of Pt(\text{Ph}_3\text{P})\(_3\).

(I.R. for CO\(_3\)\(^2\)\(^-\), 1680, 1180, 815 and 760 cm\(^{-1}\)). An intermediate peroxycarbonate complex Pt(OCO\(_3\)\(_2\))(\text{Ph}_3\text{P})\(^270\) was also isolated (I.R. for OCO\(_3\)\(^2\)\(^-\), 1678, 1250, 815, and 778 cm\(^{-1}\)). A carbonate complex has also been formed by the action of molecular O\(_2\) on a coordinated CO\(^74\),
Os-CO $\xrightarrow{O_2} \overset{O}{\overset{0}{\underset{C=0}{Os}}} \quad (9.3)$

(I.R. for $CO_3^{2-}$, 1710, 1030, 760 and 662 cm$^{-1}$)

and the action of CO on a molecular $O_2$ complex$^{26}$

\[ \xrightarrow{\text{Pt}} \quad + \text{CO} \quad \rightarrow \xrightarrow{\text{Pt}} \quad (9.4) \]

The complex $[\text{Co(NH}_3)_5(\text{CO})_3]^+$ has $CO_3^{2-}$ absorption bands at 1482, 1365, 1052, 738 and 690 cm$^{-1}$. Reaction of a rhodium carbonyl complex with $O_2$ is also reported to produce a complex containing a coordinated $CO_2$ ligand.$^{269}$ (I.R. for $CO_2$, 1498, 1368 and 813 cm$^{-1}$)

\[ \text{Rh}_2(\text{CO})_4(\text{Ph}_3\text{P})_4 + O_2 \rightarrow \text{Rh}_2(\text{CO})_2(\text{CO}_2)(\text{Ph}_3\text{P})_3 + \text{CO} + \text{Ph}_3\text{PO} \quad (9.5) \]

Finally the reaction of $O_2$ with $[\text{Rh(CO)}_2\text{Cl}_2]^{-}$ in aqueous acid solution has been represented by equation 9.6.$^{188}$

\[ [\text{Rh(CO)}_2\text{Cl}_2]^{-} + O_2 \rightarrow [\text{Rh}^{III}(\text{CO}_3)(\text{CO})\text{Cl}_3]^{2-} \xrightarrow{2H^+}{\text{Cl}^-} [\text{Rh}^{III}(\text{CO})\text{Cl}_5]^{2-} + \text{CO}_2 + \text{H}_2\text{O} \quad (9.6) \]

The I.R. reported for coordinated carbonate (or peroxycarbonate) are all measured on the solid samples in nujol or KBr discs and are clearly not as unambiguously assigned as, for example, a carbonyl band. It might be difficult to detect a $CO_3^{2-}$ ligand in DMA solution.
The bands at 2130-2100 cm\(^{-1}\) in the carbonylated solution left in air at room temperature could be due to Rh\(^{III}\) carbonyl species\(^{201}\) although no bands assignable to CO\(_3^{2-}\) were evident. In the kinetic study at 80° (Figure 54) the stoichiometry of \(\text{O}_2\) uptake at the end of the first linear region (i.e. 1:1 mole ratio of coordinated CO:O\(_2\)) is probably significant, the coordinated CO is almost certainly removed as CO\(_2\) (see following discussion on the reaction involving CO and O\(_2\) mixture) but it is not clear how the stoichiometry or the nature of the uptake plot arises. The visible spectra of the final solution suggest the presence of Rh\(^{I}(O_2)\) species. This, together with the rate of \(\text{O}_2\) uptake in the later stages of the \(\text{O}_2\) uptake, suggests catalytic oxidation of DMA and C\(_6\)H\(_{14}\) could be taking place. (See Chapter VIII)

The reaction between \([\text{Rh(C}_8\text{H}_{14})_2\text{Cl}]_2\) and a mixture of CO and \(\text{O}_2\) suggest that the CO is catalytically oxidized to CO\(_2\). In the presence of both CO and \(\text{O}_2\), Rh\(^{I}(\text{CO})_2\) will be preferably formed.

The stoichiometric oxidation of coordinated CO in \([\text{Rh(CO)}_2\text{Cl}_2]^-\) by \(\text{O}_2\) in aqueous HCl is shown in equation 9.6. The mechanism was thought to involve oxidative addition of \(\text{O}_2\) to produce the octahedral intermediate \([\text{Rh}^{III}(\text{CO}_3)(\text{CO})\text{Cl}_3]^{2-}\) containing the coordinated CO\(_3^{2-}\) ion which in acid media would decompose to give CO\(_2\) and be further anated by Cl\(^-\) to form the stable \([\text{Rh}^{III}\text{Cl}_5(\text{CO})]^{2-}\) complex.

In the present studied system, formation of the \([\text{Rh}^{III}(\text{CO}_3)(\text{CO})\text{Cl}_3]^{2-}\) is possible, however there is no acid present to decompose the coordinated CO\(_3^{2-}\) to give CO\(_2\). There is also the possibility that the CO\(_2\) is produced directly from the coordinated CO and \(\text{O}_2\) (equation 9.7). The usual DMA oxidation is suppressed because
the Rh\(^{I}(O_{2})\) species is not present.

\[
\text{Rh}^{I}(\text{CO})_{2} + \frac{1}{2} \text{O}_{2} \overset{k}{\longrightarrow} \text{Rh}^{I}(\text{CO}) + \text{CO}_{2} \quad (9.7)
\]

\[
\text{Rh}^{I}(\text{CO}) + \text{CO} \longrightarrow \text{Rh}^{I}(\text{CO})_{2} \quad (9.8)
\]

Further studies are required to unravel this system.

9.52 The RhCl\(_{3}(\text{Et}_{2}S)_{3}\) System

Preliminary studies indicate that RhCl\(_{3}(\text{Et}_{2}S)_{3}\) in DMA reacts with two moles of CO to produce a Rh\(^{I}(\text{CO})_{2}\) species (ligands such as Et\(_{2}\)S and Cl\(^{-}\) are omitted) in a process involving first order decrease in [Rh\(^{III}\)]. In the reaction of RhCl\(_{3}.3\text{H}_{2}\text{O}\)\(^{189}\) with CO in DMA, [Rh(CO)\(_{2}\)Cl\(_{2}\)]\(^{-}\) was produced via two steps (i) substitution of CO to produce a chloro carbonyl rhodate (III) species followed by (ii) a slow insertion reaction involving coordinated OH\(^{-}\) to produce Rh\(^{I}\) which then picks up CO in a fast step to produce [Rh(CO)\(_{2}\)Cl\(_{2}\)]\(^{-}\). The reaction mechanism is depicted below

\[
\begin{align*}
(H_{2}O)\text{Rh}^{III} + \text{CO} & \overset{k_{1}}{\longrightarrow} (H_{2}O)\text{Rh}^{III}(\text{CO}) \quad (9.9) \\
(H_{2}O)\text{Rh}^{III}\text{CO} & \overset{k_{2}}{\longrightarrow} \text{Rh}^{III}(\text{COOH}) + H^{+} \quad (9.10) \\
\text{Rh}^{III}(\text{COOH}) & \overset{\text{fast}}{\longrightarrow} \text{Rh}^{I} + \text{CO}_{2} + H^{+} \quad (9.11) \\
\text{Rh}^{I} + 2\text{CO} & \overset{\text{fast}}{\longrightarrow} \text{Rh}^{I}(\text{CO})_{2} \quad (9.12)
\end{align*}
\]

However in the reaction of RhCl\(_{3}(\text{Et}_{2}S)_{3}\) with CO, there is no coordinated water present and the kinetics do not suggest two distinct stages in the reaction. The Et\(_{2}\)S may be responsible for the reduction of Rh\(^{III}(\text{CO})\) to
give $\text{Rh}^\text{I} (\text{CO})_2$ species.

The $\text{Rh}^\text{I} (\text{CO})_2$ species produced from the carboxylation of DMA solutions of $\text{RhCl}_3 (\text{Et}_2\text{S})_3$ and $\text{RhCl}_3 3\text{H}_2\text{O}$ reacts with $\text{O}_2$ to produce $\text{Rh}^\text{III} \text{CO}$; no continuous gas uptake was observed. It appears that both $\text{CO}$ and $\text{O}_2$ need to be activated for the catalytic oxidation to occur. $[\text{Rh}(\text{C}_8\text{H}_{14})_2\text{Cl}]_2$ has been shown to activate both $\text{O}_2$ and $\text{CO}$, whereas $\text{RhCl}_3 3\text{H}_2\text{O}$ and $\text{RhCl}_3 (\text{Et}_2\text{S})_3$ do not activate $\text{O}_2$.

$\text{CO}$ has an inhibiting effect on the catalytic hydrogenation property of $\text{Rh}^\text{I}$ species. Decrease in activity with the introduction of carbonyl groups into the metal complexes has been observed in other rhodium systems. $\text{CO}$ will withdraw electron density from the metal ion and will increase the energy required to activate molecular $\text{H}_2$ in the oxidative addition step.
CHAPTER X

GENERAL CONCLUSIONS AND RECOMMENDATIONS FOR FUTURE WORK

The work described in this thesis has involved kinetic studies of the catalytic activation of H₂, olefins, O₂ and CO by rhodium complexes containing sulphur and/or chloride ligands.

RhCl₃(Et₂S)₃ and RhCl₃(Bz₂S)₃ in DMA were found to activate H₂ for homogeneous hydrogenation of olefins, such as maleic, fumaric and trans-cinnamic acid. The kinetic data are basically consistent with a previously postulated mechanism involving an initial H₂ reduction of Rh^{III} to Rh^{I} which is then stabilized in solution by rapid complexing with the olefin; the resulting Rh^{I}(olefin)Lₙ complexes (L = auxiliary ligand) subsequently react with H₂ to produce the saturated paraffin and Rh^{I} again.

A predissociation step involving loss of a sulphur ligand from the Rh^{III} complexes occurs before reaction with H₂ in the initial reduction step. This step was originally thought to be independent of olefin, but some variation in the rate constants for this step in the RhCl₃(Et₂S)₃ catalyzed hydrogenation of FA and MA suggest that this may not be so, and some spectroscopic evidence suggests that Rh^{III}(olefin) complexes may be produced via a catalytic substitution process involving Rh^{I}(olefin)Lₙ. The spectroscopic evidence is not strong.
However, this possible production of Rh\textsuperscript{III}(olefin) complexes, using a reductant other than H\textsubscript{2} for the production of the Rh\textsuperscript{I} catalyst, seems worth further studying.

The kinetics of the olefin hydrogenation reaction depend markedly on the nature of the Rh\textsuperscript{I}(olefin)\textsubscript{L\textsubscript{n}} complex, i.e. the structure of the olefin and the ligands L on the Rh\textsuperscript{I}. In some instances, one of the sulphur ligands in the Rh\textsuperscript{I}(olefin)\textsubscript{L\textsubscript{n}} complex has to dissociate to provide a vacant site, presumably necessary for oxidative addition of H\textsubscript{2}. These conclusions resulted from a unique observation in the RhCl\textsubscript{3}(Et\textsubscript{2}S)\textsubscript{3} catalyzed hydrogenation of CA and possibly in the RhCl\textsubscript{3}(Bz\textsubscript{2}S)\textsubscript{2} catalyzed hydrogenation of MA that the rate of hydrogenation is first order at very low [Rh] and reaches a limiting value (zero order) at high [Rh]. This results from the free sulphur ligand produced in the initial Rh\textsuperscript{III} to Rh\textsuperscript{I} reduction step inhibiting the dissociation of the Rh\textsuperscript{I}(olefin)\textsubscript{L\textsubscript{n}} complex to produce the active form.

Isomerization of FA to MA was observed in the RhCl\textsubscript{3}(Et\textsubscript{2}S)\textsubscript{3} catalyzed hydrogenation of FA. Although the trans acid (FA) is more stable thermodynamically, the Rh\textsuperscript{I}(FA) complex appears to be less stable than the Rh\textsuperscript{I}(MA) complex presumably because of steric requirements in the Rh\textsuperscript{I}(olefin)\textsubscript{L\textsubscript{n}} complex. Isomerization was thought to occur through a Rh\textsuperscript{III}-H\textsuperscript{-} intermediate. The kinetics of the RhCl\textsubscript{3}(Et\textsubscript{2}S)\textsubscript{3} catalyzed hydrogenation of FA are complicated because of the accompanying isomerization.

Unsuccessful attempts were made to prepare Rh\textsuperscript{I} sulphur complexes for use as hydrogenation catalysts. However, the cyclooctene complex, [Rh(C\textsubscript{8}H\textsubscript{14})\textsubscript{2}Cl]\textsubscript{2}, in DMA proved to be a very useful source for
preparing Rh\textsuperscript{I} complexes "in situ" by adding the desired ligand, e.g. Cl\textsuperscript{-} and Et\textsubscript{2}S, since C\textsubscript{6}H\textsubscript{14} ligand was very easily displaced. Simple kinetics were observed for hydrogenation reactions using such stock solutions (which are thought to contain monomeric species) and the kinetic data are in good agreement with the hydrogenation data obtained by starting from the corresponding Rh\textsuperscript{III} systems. This result confirms that Rh\textsuperscript{I} intermediates are involved in the catalytic hydrogenation starting from Rh\textsuperscript{III} complexes. The C\textsubscript{6}H\textsubscript{14} in these Rh\textsuperscript{I} systems was not homogeneously hydrogenated and this was attributed to its weaker bonding (\(\pi\)-acceptor property) compared with MA. Hence this catalyst system could be developed usefully for selective hydrogenation since one of the major factors must be the stability of the metal-substrate complex.

A green solution obtained when the hydrogenated olefin solution (from the Rh\textsuperscript{I}Cl system) is left in air probably contains a Rh\textsuperscript{II} species. An E.S.R. signal suggest that the species is likely to be monomeric and it would be worthwhile attempting to isolate this "green" complex. The most well-established Rh\textsuperscript{II} species is the Rh\textsuperscript{II} acetate dimer, although recently some Rh\textsuperscript{II} phosphine monomers were also reported. Irreproducibility of the kinetic data in some RhCl\textsubscript{(Ph\textsubscript{3}P)}\textsubscript{2} systems is thought to be due to traces of Rh\textsuperscript{II} species. The study of the catalytic activity of the "green" solution would give further insight into the activity of rhodium species in different oxidation states.

DMSO was used primarily to study the effect of solvent on catalytic hydrogenation of olefins by Rh\textsuperscript{III} complexes; however,
RhCl\(_3\)(Et\(_2\)S)\(_3\) and RhCl\(_3\)·3H\(_2\)O were found to catalyze the reduction of DMSO to DMS and water. The kinetics indicated a rate determining heterolytic splitting of H\(_2\) by Rh\(_{\text{III}}\)(DMSO) to produce Rh\(_{\text{III}}\)(DMSO)H\(^-\) which then decomposes to Me\(_2\)S and H\(_2\)O in a fast step. An eventual fall off in catalytic activity is thought to be due to decomposition of the Rh\(_{\text{III}}\)(DMSO)H\(^-\) to Rh\(^+\). The detailed mechanism of an observed catalytic oxidation of DMSO to Me\(_2\)SO\(_2\) by RhCl\(_3\)·3H\(_2\)O using a mixture of O\(_2\) and H\(_2\) is well worth investigating since a Rh\(_{\text{III}}\)H\(^-\) species appears to be the active oxygen carrier and this offers the attractive speculation that H\(_2\)O\(_2\) might be involved in the catalyzed oxidation.

The solution of [Rh(C\(_8\)H\(_{14}\)Cl)\(_2\)] in LiCl/DMA has been found to be a very versatile catalyst, for besides the activation of H\(_2\) and olefins, O\(_2\) and CO can also be activated. The formation of a Rh\(^I\)(O\(_2\)) complex and a subsequent catalyzed oxidation of the DMA solvent and cyclooctene were studied in detail. The formation of the Rh\(^I\)(O\(_2\)) complex appears to be irreversible; an E.S.R. signal possibly due to a species such as Rh\(_{\text{II}}\)·O\(_2\)\(^-\) was also observed. Previously reported oxygen complexes of d\(^8\) and d\(^{10}\) species, Ir\(^I\), Ni\(^0\), Pd\(^0\) and Pt\(^0\) are all diamagnetic; Rh\(^I\) molecular oxygen complexes are ill-characterized although Rh(O\(_2\))(Ph\(_3\)P)\(_3\) was reported to be diamagnetic. The kinetics of the catalyzed oxidation are simple and the mechanism involves the equilibrium formation of the Rh\(^I\)(O\(_2\)) complex followed by the rate determining step to give the products. The detailed nature of the rate determining steps and the identification of all the oxidation products proved to be very difficult. A free radical mechanism seems to be likely involved although this is not proved unequivocally since the free radical inhibitor DPPH
reacts itself with Rh\(^{I}\). There is a great deal of current interest in the mechanism of oxidation through molecular oxygen complexes. Both oxygen atom transfer and free radical processes have been postulated. Oxygenation reactions with Ni\(^{0}\), Pd\(^{0}\) and Pt\(^{0}\) complexes have been considered to be atom transfer reactions, while Rh\(^{I}\) systems appears to catalyze oxygenation via free radical processes. The finding of the E.S.R. signal in the present system seems most significant and indicates that the oxidation mechanism may depend on the magnetic properties of the catalyst, since species such as Rh\(^{II}O_2\) may well initiate free radical hydroperoxide processes by proton or hydrogen atom transfer. More detailed E.S.R. studies are required to elucidate the electronic structure of the Rh\(^{I}(O_2)\) complex. The present system could be extended by using other solvent systems and a variety of other oxidizable substrates. The preliminary result on a catalyzed oxidation in ethanol is very promising.

Preliminary studies indicate that an oxygen-free solution of 
\[\text{[Rh(C}_8\text{H}_{14})_2\text{Cl}_2]\] in 0.5 M LiCl/DMA reacts rapidly with CO to produce a Rh\(^{I}(CO)_2\) species. A solution of Rh\(^{I}(O_2)\) absorbs CO more slowly and the kinetics indicate the rate determining step is the dissociation of Rh\(^{I}(O_2)\) to Rh\(^{I}\) and O\(_2\) followed by a fast step involving the reaction of Rh\(^{I}\) and CO to produce Rh\(^{I}(CO)_2\). Such Rh\(^{I}(CO)_2\) solutions react with O\(_2\) to produce CO\(_2\). A mixture of O\(_2\) and CO\(_2\) is converted catalytically by a solution of \[\text{[Rh(C}_8\text{H}_{14})_2\text{Cl}_2]\] in LiCl/DMA. The nature of this catalytic reaction, which could involve carbonate, peroxycarbonate or carbon dioxide complexes is worth further investigation, particularly in view of the present CO pollution problem.

In agreement with the results of other workers, the introduction
of coordinated CO was found to have an inhibiting effect on the catalytic hydrogenation property of rhodium (I) complexes.

Finally, possible activation of other small covalent gaseous molecules such as CO₂, SO₂, NO₂, C₂H₄, C₂H₂ etc., by [Rh(C₈H₁₄)₂Cl]₂ in DMA and other solvents is worthy of investigation.
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APPENDIX I

SOLUBILITY DATA FOR OXYGEN IN N,N'-DIMETHYLACETAMIDE

A1  The Solubility of Oxygen in DMA

The solubility of oxygen in DMA at specific temperatures and pressures were estimated by the method described in Chapter II, section 2.4. Figure 56 shows the solubility of $O_2$ from 0-800 mm at $87^\circ$, $80^\circ$, $75^\circ$, $70^\circ$, and $25^\circ$. 
Figure 56. Solubility of O₂ in DMA. (o) 87°, (o) 80°, (A) 75°, (□) 70°, (○) 25°.