REACTION OF RHODIUM (III) CHLORIDES WITH ETHYLENE IN AQUEOUS HCl SOLUTION

BY

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ABSTRACT

In the presence of iron (III) and other oxidants, HCl solutions of $RhCl_3 \cdot 3H_2O$ under mild conditions catalyze the oxidation of ethylene to acetaldehyde. The kinetics of the reaction measured by gas-uptake techniques indicate the presence of both ethylene dependent and independent steps. Hydroxy species such as $RhCl_5(OH)^{3-}$ and $RhCl_4(OH)(H_2O)^{2-}$, although present in very small concentrations, are significantly reactive towards ethylene. A mechanism based on that postulated for a similar Pd(II) system is presented. This involves the rearrangement of a rhodium (III) hydroxy π - ethylene complex to a σ - complex, followed by the production of acetaldehyde and rhodium (I). However, unlike in the Pd(II) system where the rate determining step is the conversion of the π - to σ - C_2H_4 complex, the rate determining step in the Rh(III) system is thought to involve the production of the π - complex. Iron (III) oxidizes Rh(I) back to Rh(III), giving the net reaction:

$$C_2H_4 + H_2O + 2Fe(III) \xrightarrow{Rh(III)} CH_3CHO + 2H^+ + 2Fe(II)$$

TABLE OF CONTENTS

ABSTRACT i

LIST OF TABLES iv

LIST OF FIGURES iv

ABBREVIATIONS v

ACKNOWLEDGMENTS v

CHAPTER 1. INTRODUCTION

1.1 Objectives. 1

1.2 Mechanism of Hydrogen Activation.......... 3

1.3 Rh(I)- and (III)- Catalyzed Polymerization Reactions of Olefins and Acetylenes.......... 4

1.4 Rh(I)- and (III)- Catalyzed Isomerizations of Olefins.......... 7

1.5 Catalytic Reactions in General.......... 9

1.6 Reactions of Ethylene with Rh(III), Ru(II) and Pd(II).......... 10

CHAPTER 2. APPARATUS AND EXPERIMENTAL PROCEDURE

2.1 Constant Pressure Gas Uptake Apparatus.......... 14

2.2 Gas Uptake Experimental Procedure.......... 16

2.3 Reaction Product Analysis.......... 17

2.4 Instrumentation.......... 17

2.5 Materials.......... 17

CHAPTER 3. RESULTS

3.1 Stoichiometry and Products.......... 19

3.2 Iron(III) Dependence.......... 22

3.3 Rhodium (III) Dependence.......... 23

3.4 Ethylene Dependence.......... 23

3.5 Proton and Chloride Dependences.................................... 23

3.6 Activity of Rhodium (III) Aquochloro Species.................... 28

3.7 Other Oxidizing Agents. 32

CHAPTER 4. DISCUSSION

4.1 Activity of the Pentachloro Species............................. 33

4.2 Activity of the Tetrachloro Species.............................. 39

4.3 Inverse Chloride Dependence.. 41

4.4 The Production of Acetaldehyde.................................... 43

4.5 Use of Oxidants other than Fe(III)................................ 48

4.6 Ethylene Uptake Rates in 6M Acid.................................. 48

4.7 The Ethylene : Iron(III) Stoichiometry.......................... 49

CHAPTER 5. SUMMARY AND SUGGESTIONS FOR FURTHER WORK 52

REFERENCES... 54

LIST OF TABLES

TABLE 1 Stoichiometries of Ethylene: Iron (III): Rhodium (III) 20
TABLE 2 Summary of Kinetic Data at 80° and 1 atm C_2H_4 22
TABLE 3 Summary of Ethylene Dependences. 23
TABLE 4 Summary of Proton and Chloride Dependences 25
TABLE 5 Rates of Ethylene Absorption for $RhCl_n(H_2O)_{6-n}^{(3-n)+}$ 29
TABLE 6 Summary of Proton and Ethylene Dependences for $RhCl_5^{2-}$ 30
TABLE 7 Summary of Proton and Ethylene Dependences for $RhCl_4^-$ 32
TABLE 8 Summary of Rates with Various Oxidizing Agents 32
TABLE 9 Temperature Dependence of Rate Constants k_a and k_b 38

LIST OF FIGURES

FIGURE 1 Constant Pressure Gas Uptake Apparatus 15
FIGURE 2 Uptake Plot of Ethylene Absorption 19
FIGURE 3 Visible Spectra of Reaction Solution 20
FIGURE 4 Dependence of Linear Rate on Rh(III) 23
FIGURE 5 Dependence of Linear Rate on $[C_2H_4]$. 26
FIGURE 6 Dependence of Linear Rate on $[H^+]$ at 3MCl$^-$ 26
FIGURE 7 Dependence of Linear Rate on $[H^+]$ at 2MCl$^-$ 27
FIGURE 8 Dependence of Linear Rate on $[Cl^-]$ 27
FIGURE 9 Uptake plot of Ethylene Absorption in 6MH$^+$ 28
FIGURE 10 Dependence of $RhCl_5^{2-}$ Rate on $[C_2H_4]$ at three acidities 31
FIGURE 11 Dependence of $RhCl_4^-$ Rate on $[C_2H_4]$ at two acidities 31
FIGURE 12 Dependence of C_2H_4 Independent Rate on $[H^+]$, for $RhCl_5^{2-}$ 34
FIGURE 13 Dependence of C_2H_4 Dependent Rate on $[H^+]$, for $RhCl_5^{2-}$ 34
FIGURE 14 Arrhenius Plot for reaction of $RhCl_5^{2-}$ with C_2H_4 38
FIGURE 15 Dependence of C_2H_4 Dependent Rate on $[H^+]$, for $RhCl_4^-$ 39

ABBREVIATIONS

IR: Infrared

NMR: Nuclear magnetic resonance

ESR: Electron spin resonance

(S): Solvent molecule

P^1: Partial pressure, mm.

[ ]: Concentration in moles liter^{-1}

DMA: N,N'Dimethylacetamide

ACKNOWLEDGMENTS

I wish to acknowledge the supervision of this research made possible by the extreme generosity of Dr. BRIAN R. JAMES. Also I am indebted to Miss Judy Copeland and Miss Rosalind Amies for typing this thesis.

Do you think that I'm crazy?

Out of my mind?

Do you think that I creep in the night

And sleep in a phone booth?

F Zappa

CHAPTER 1. INTRODUCTION

1.1 Objectives

In the last ten years, many platinum metal complexes in solution have been found to catalyze a wide variety of reactions. Notable among these is the activation of hydrogen for the reduction of inorganic and organic substrates. One of the earliest reactions investigated was the chlororhodium (III) - catalyzed hydrogen reduction of iron (III) in aqueous 3M hydrochloric acid at 80°[1]. The kinetics from gas uptake plots were of the form $-d[H_2]/dt = k[H_2][Rh(III)]$, and the rate determining step was thought to involve the heterolytic splitting of molecular hydrogen:

$$Rh^{III} + H_2 \underset{k_{-1}}{\overset{k_1}{\rightleftharpoons}} Rh^{III}H^- + H^+ \tag{1}$$

The metal hydride thus formed then reduces the Fe(III) substrate in a rapid step:

$$Rh^{III}H^- + 2Fe^{III} \underset{\text{fast}}{\overset{k_2}{\rightarrow}} Rh^{III} + 2Fe^{II} + H^+ \tag{2}$$

In equations (1) and (2), the Cl^- and H_2O ligands were omitted but from later spectrophotometric investigations[2], the rhodium complex in 3M HCl is likely present as $[Rh(H_2O)Cl_5]^{2-}$. Subsequently, James and Rempel[3] showed that only the anionic species $[RhCl_6]^{3-}$ to $[Rh(H_2O)_2Cl_4]^-$ are effective catalysts, with the activity decreasing with decreasing number of chloride ligands. Direct evidence for an equilibrium of the type shown in equation (1) was obtained for the corresponding ruthenium (III) system by isotopic exchange experiments using deuterium[4,5]. It was pointed out[3] that reaction (2) could involve a Rh(I) species rather than a $Rh^{III}H^-$ species since in the absence of substrate, metal was rapidly produced and this was thought to be due to the following fast reactions

$$Rh^{III}H \rightarrow Rh^{I}+H^+ \qquad (3)$$

$$2Rh^{I} \rightleftharpoons Rh^{o}+Rh^{II} \qquad (4)$$

The Rh^I state could be stabilized in the presence of olefins as a Rh^I· (olefin) complex[3].

Wilkinson and coworkers[6] found that a simple bubbling of hydrogen through neutral aqueous solutions of $RhCl_3$ gave a rapid reaction characterized by colour changes involving the production of $[Rh(H_2O)_4Cl_2]^+$ from polymeric species. Again a $Rh^{III}H$- intermediate was postulated:

$$Rh(H_2O)_3Cl_3+H_2 \rightleftharpoons Rh(H_2O)_3Cl_2H+H^++Cl^- \qquad (5)$$

$$Rh(H_2O)_3Cl_2H+H_2O \rightarrow Rh(H_2O)_4Cl_2{}^++H^- \qquad (6)$$

$$H^++H^- \rightarrow H_2 \qquad (7)$$

This catalytic substitution reaction was later observed using ethylene[7] or carbon monoxide[8] instead of hydrogen, and a more detailed investigation of this ethylene reaction in this laboratory[9] indicated that Rh(I) intermediates were involved. The postulated mechanism is outlined as

$$Rh^{III}+C_2H_4 \rightarrow Rh^{I}+CH_3CHO \qquad (8)$$

$$\begin{aligned} &Cl_nRh^{I}+Rh^{III}Cl_3 \rightarrow [Cl_nRh^{I}....Cl....Rh^{III}Cl_2] \rightarrow \\ &Rh^{I}Cl_2{}^-+Rh^{III}Cl_2{}^++(n-1)Cl^- \end{aligned} \qquad (9)$$

and is considered in more detail in section 1.6.

At the completion of this work on ethylene a paper by Rund[10] appeared which also concluded that catalytic substitution at a Rh(III) center occurs through such $Rh^{III}\!\!-\!\!-\!\!Rh^{I}$ bridged intermediates.

On considering reactions (1) and (2), and the possibility of the reduction step going via Rh(I) intermediates, a corresponding system using C_2H_4 instead of H_2 was studied in the present work. Russian workers have briefly mentioned the reaction of ethylene with $RhCl_6{}^{3-}$ in the presence of Cu(II) salts[11].

Kinetic studies of this type are also useful in determining the factors involved in the activation of a variety of gaseous molecules such as H_2[3] and CO[8] by a single transition metal complex.

This thesis describes studies on the Rhodium (III) - catalyzed ethylene reduction of iron (III). (Chapter 3).

In general, reaction (3) and the reverse reaction are thought to be important for catalysis by rhodium (III)[12]. Some pertinent literature reports will now be summarized concerning hydrogen activation (section 1.2), catalyzed reactions involving olefins and acetylenes (1.3-1.5), and reactions of ethylene with platinum metal complexes (1.6,1.7).

1.2 Mechanisms of Hydrogen Activation

Homogeneous hydrogenation reactions have been the subject of many reviews[13-19]. It is well established that there are three basic processes whereby a metal ion in a complex can activate molecular hydrogen. These are:

(a) heterolytic splitting, which involves no change in the metal oxidation state:

$$ML_n + H_2 \rightleftharpoons ML_{n-1}H^- + H^+ + L$$

In this essentially substitutional process, reactivity is governed by the substitution lability of the complex ML_n, the stability of the hydride formed, and the presence of a suitable base to stabilize the released proton.

(b) homolytic splitting, which involves an oxidation number increase of 1:

$$2ML_n + H_2 \rightleftharpoons 2ML_{n-1}H + 2L$$

(c) dihydride formation, which involves an oxidation number increase of 2:

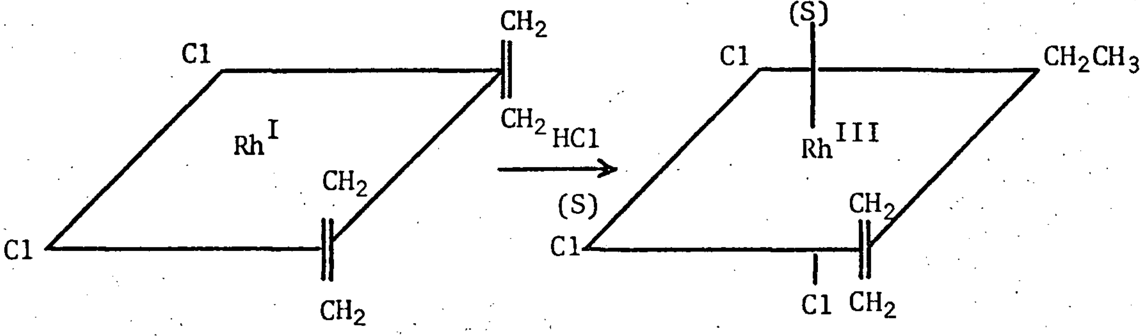
$$ML_n + H_2 \rightleftharpoons ML_nH_2$$

In cases (b) and (c), reactivity will also be dependent on the ease of metal oxidation. All the hydride intermediates are thought to contain hydrogen as an anionic ligand. The lability and thermodynamic stability of these hydrides help to determine the catalytic activity of the metal complex.

As mentioned in section 1.1, the Rhodium (III) chloride - catalyzed hydrogen reduction or iron (III)[1] in aqueous acid solution is thought to involve heterolytic splitting; a similar mechanism has been invoked for activation of hydrogen by Rh(III) species in aprotic polar solvents[20]. Rh(I) complexes activate H_2 through dihydride formation[21].

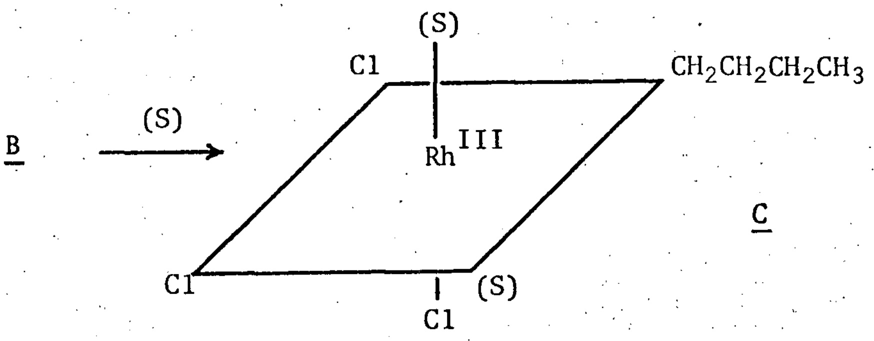
1.3 Rh(I) - and Rh(III) - catalyzed polymerization reactions of olefins and acetylenes

Cramer[22] has investigated in detail the mechanism of the rhodium (III) chloride - catalyzed ethylene dimerization in ethanolic HCl solution. Initially, when ethylene is only slowly absorbed, the active anion $[Rh^{I}Cl_2(C_2H_4)_2]^-$ is thought to be formed. This anion can be formed directly if $[Rh^{I}Cl(C_2H_4)_2]_2$ is dissolved in ethanolic HCl , no induction period is then observed in the dimerization reaction. Cramer has postulated the following four-step mechanism. The bis ethylene dichlororhodium (I) anion A is rapidly converted by reaction with HCl into an ethyl ethylene rhodium (III) complex, B:



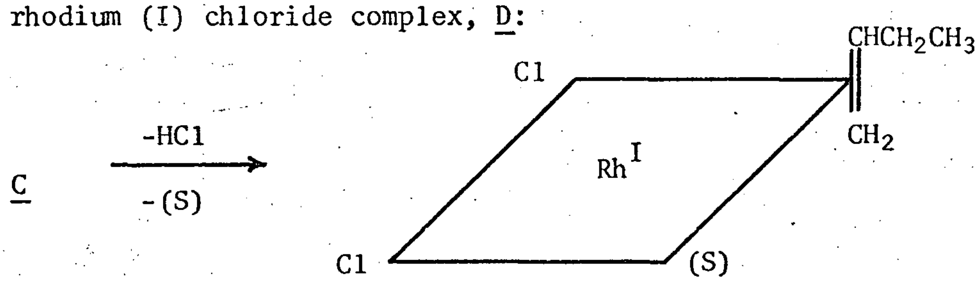
A B (10)

(S) is a molecule of water, ethanol, or chloride. B then decomposes by a slow rearrangement to an n-butyl rhodium (III) complex, C:



C (11)

Through loss of HCl and (S), C decomposes rapidly to give a 1- butene rhodium (I) chloride complex, D:



D (12)

Finally, 1- butene and a molecule of (S) in D are rapidly displaced by ethylene, and this reproduces the initial bisethylenedichlororhodium (I) anion A.

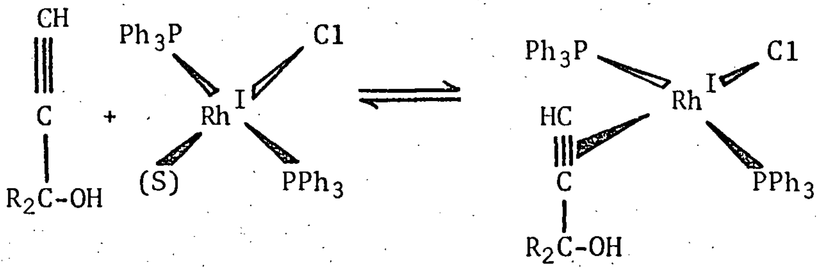
$$\underline{D} \xrightarrow{2CH_2CH_2} \underline{A} + CH_3CH_2CH{=}CH_2 + (S) \qquad (13)$$

The actual dimerization process in the second step occurs as a rate determining insertion reaction of the coordinated ethylene between the CH_2CH_3 ligand and the rhodium center. All the rhodium complex intermediates seem to be present as anions.

Singer and Wilkinson[23] showed that bis (triphenyl phosphine) chlororhodium (I) in nonpolar solvents will dimerize monosubstituted α-hydroxyacetylenes:

$$2R_2C(OH)C{\equiv}CH \rightarrow R_2C(OH)CH{=}CH{-}C{\equiv}C{-}C(OH)R_2$$

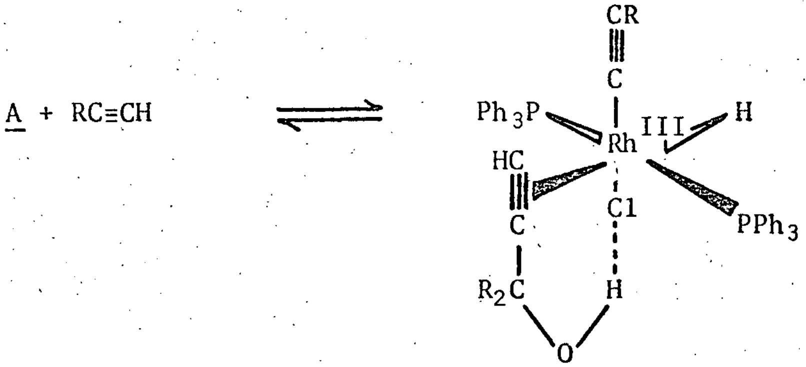
In contrast, other metal complexes usually result either in trimerization to aromatic compounds, or polymerization of the acetylene. The mechanism has been construed as follows. The α-hydroxy acetylene reacts with the solvated species $RhCl(PPh_3)_2(S)$ to give a square planar Rh(I) species with trans PPh_3 groups, A.


CH
C
R₂C-OH
+
Ph₃P
Cl
Rh
I
(S)
PPh₃
Ph₃P
Cl
Rh
I
HC
C
R₂C-OH
PPh₃

A

(14)

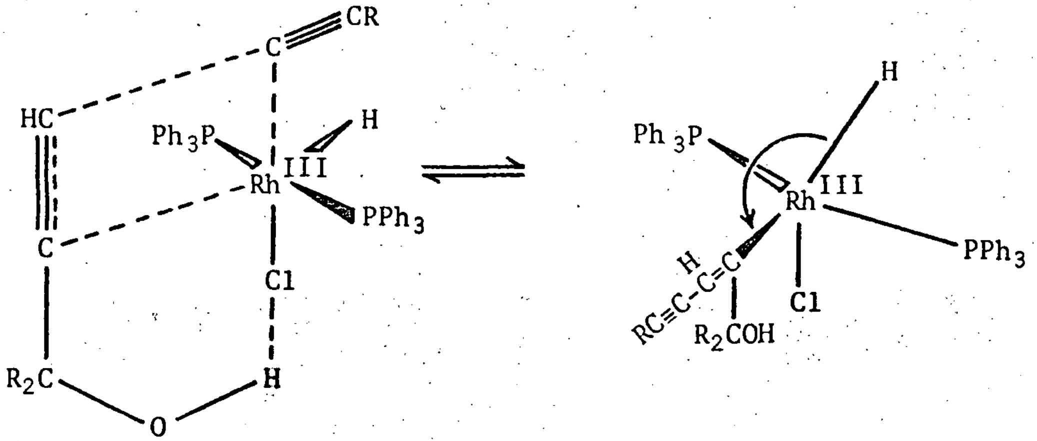
Then oxidative cis addition of a second acetylene, by edge displacement of the chloride, gives complex B.


A + RC≡CH
CR
C
Ph₃P
Rh
III
H
HC
C
Cl
PPh₃
R₂C
H
O

B

(15)

The acetylide group transfer from the metal to a carbon atom of the last-coordinated acetylene, via a four center transition state C, leads to the penta coordinate species D in which the dimer is bound by a σ bond: B →

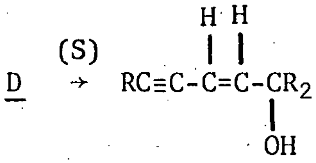

CR
C
HC
Ph₃P
H
Rh
III
PPh₃
C
Cl
R₂C
H
O
H
Ph₃P
Rh
III
PPh₃
H
RC≡C-C=C
Cl
R₂COH

(16)

C

D

Lastly, a hydride transfer via a three-center transition state produces the dimer and regenerates $RhCl(PPh_3)_2(S)$ again.



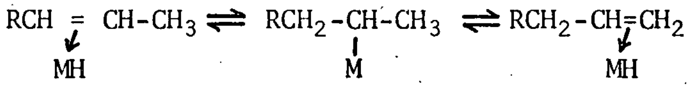
$$\underline{D} \xrightarrow{(S)} RC\equiv C-\overset{H}{C}=\overset{H}{C}-\underset{OH}{C}R_2 \qquad (17)$$

The hydroxy group is necessary for dimerization, and this may be to fulfil the stabilization of complex $\underline{B}$ through acetylene coordination.

Very recent reports of the Rh(I) - catalyzed polymerizations of olefins include the production of pentamers of allene and cyclic allene using $[RhCl(C_2H_4)_2]_2$ [24], and the di- and trimerization of norbornadiene by triphenylphosphine complexes of rhodium (I) chloride[25].

1.4 Rh(I)- and Rh(III) - catalyzed isomerizations of olefins

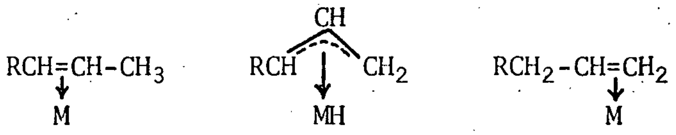
Harrod and Chalk[26] found that olefin double bond migration is catalyzed by rhodium (III) chloride. This was interpreted as a reversible addition of a hydridometal complex to the olefin:



$$\underset{MH}{RCH \swarrow\!=} CH-CH_3 \rightleftharpoons RCH_2-\underset{M}{CH}-CH_3 \rightleftharpoons RCH_2-\underset{MH}{CH\swarrow\!=}CH_2 \qquad (18)$$

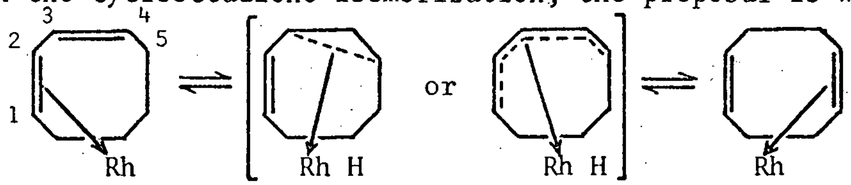
Along with this isomerization have been detected exchanges of the metal- and carbon hydrogens from deuterated metal complexes. From the variety of conditions used, and the degree of stereospecificity produced, these authors concluded that this reaction is sensitive to the metal, coordinated ligands, and the source of hydride which originates from the olefin itself or from added co-catalysts such as alcohols.

The isomerization of 1,3 to 1,5 cyclo-octadiene catalyzed by $RhCl_3$ was considered by Rinehart and Lasky[27] to involve a π-allyl intermediate. In general terms, a single migration may be represented as



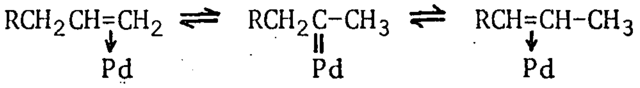
$$\underset{\mathrm{M}}{\overset{\downarrow}{\mathrm{RCH{=}CH{-}CH_3}}} \qquad \underset{\mathrm{MH}}{\mathrm{RCH}\overset{\mathrm{CH}}{\frown}\mathrm{CH_2}} \qquad \underset{\mathrm{M}}{\overset{\downarrow}{\mathrm{RCH_2{-}CH{=}CH_2}}} \tag{19}$$

In the cyclooctadiene isomerization, the proposal is written[27]



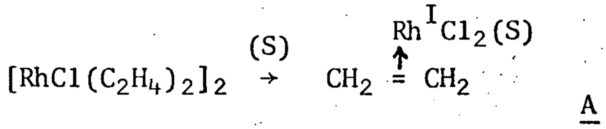
(20)

A third mechanism involving carbene intermediates has been postulated by Davies[28] for some Pd(II) - catalyzed isomerizations:

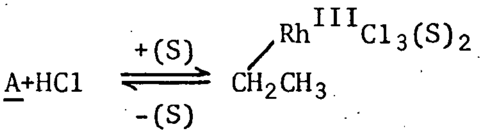


$$\underset{\mathrm{Pd}}{\overset{\downarrow}{\mathrm{RCH_2CH{=}CH_2}}} \rightleftharpoons \underset{\mathrm{Pd}}{\overset{\|}{\mathrm{RCH_2C{-}CH_3}}} \rightleftharpoons \underset{\mathrm{Pd}}{\overset{\downarrow}{\mathrm{RCH{=}CH{-}CH_3}}} \tag{21}$$

Cramer[29] has shown that linear butenes are isomerized by soluble rhodium catalysts obtained by a fast anaerobic reaction of $[\mathrm{RhCl(C_2H_4)_2}]_2$ or $\mathrm{Rh(acac)(C_2H_4)_2}$ with HCl. These inactive Rh(I) complexes are converted into a catalytically active equilibrium mixture containing Rh(III):



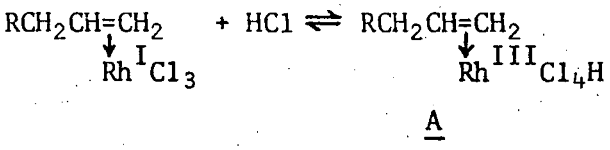
$$[\mathrm{RhCl(C_2H_4)_2}]_2 \xrightarrow{(\mathrm{S})} \overset{\mathrm{Rh^{I}Cl_2(S)}}{\overset{\uparrow}{\mathrm{CH_2 = CH_2}}} \quad \underline{\mathrm{A}} \tag{22}$$



$$\underline{\mathrm{A}}\mathrm{+HCl} \underset{-(\mathrm{S})}{\overset{+(\mathrm{S})}{\rightleftharpoons}} \overset{\mathrm{Rh^{III}Cl_3(S)_2}}{\overset{/}{\mathrm{CH_2CH_3}}} \tag{23}$$

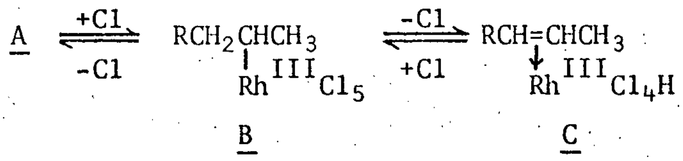
The overall reaction may be written similar to that for the ethylene dimerization given on pages 4 and 5.

(a) Starting with the product from reaction of a square planar Rh(I) complex and the olefin, the Rh(I) is oxidized by HCl to Rh(III); for simplicity all three ligands on $\mathrm{Rh^{I}L_3}$ (olefin) are written as chlorides:



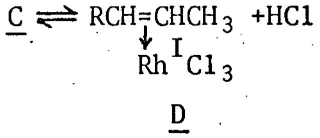
$$\underset{\mathrm{Rh^{I}Cl_3}}{\overset{\downarrow}{\mathrm{RCH_2CH{=}CH_2}}} + \mathrm{HCl} \rightleftharpoons \underset{\underline{\mathrm{A}}}{\underset{\mathrm{Rh^{III}Cl_4H}}{\overset{\downarrow}{\mathrm{RCH_2CH{=}CH_2}}}} \tag{24}$$

(b) A rearranges via an alkyl intermediate B:



$$\underline{A}\ \underset{-Cl}{\overset{+Cl}{\rightleftharpoons}}\ \underset{\underline{B}}{\begin{array}{c}RCH_2CHCH_3\\ |\\ Rh^{III}Cl_5\end{array}}\ \underset{+Cl}{\overset{-Cl}{\rightleftharpoons}}\ \underset{\underline{C}}{\begin{array}{c}RCH{=}CHCH_3\\ \downarrow\\ Rh^{III}Cl_4H\end{array}} \tag{25}$$

(c) C is reduced to a Rh(I) complex through loss of HCl:



$$\underline{C} \rightleftharpoons \underset{\underline{D}}{\begin{array}{c}RCH{=}CHCH_3\\ \downarrow\\ Rh^{I}Cl_3\end{array}} + HCl \tag{26}$$

(d) Solvolysis of D breaks off the isomerized coordinated olefin

$$\underline{D} + (S) \rightleftharpoons RCH{=}CHCH_3 + Rh^{I}Cl_3(S) \tag{27}$$

An extensive review of olefin isomerization generally covering the literature up to 1966 has been given by Orchin[30].

1.5 Catalytic reactions in General

James[12] in his extensive review on rhodium chemistry concludes that the Rh(III) - catalyzed hydrogenations, polymerizations, and isomerizations of olefins involve some or all of the following steps:

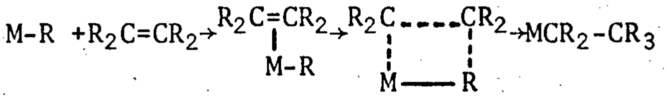
(a) the reversible oxidation of Rh(I) by a proton to give a Rh(III) hydride

(b) the lability of hydrogen in Rh(III) alkyl- and olefin complexes

(c) the importance of appropriate auxiliary ligands in the catalytic effectiveness of rhodium

(d) the insertion of a coordinated olefin between an alkyl group or hydride, and the metal ion to which it is attached.

Point (d) exemplifies an addition reaction of transition metal ions in general that produces an intermediate π-complex, which subsequently rearranges to add the elements of the original complex across the olefin's double bond:

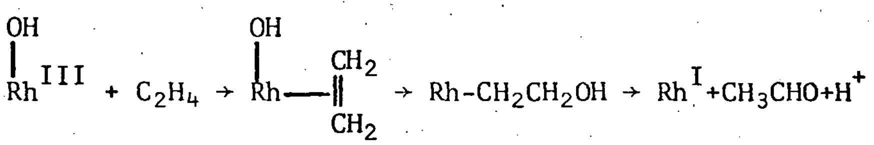


$$M{-}R + R_2C{=}CR_2 \rightarrow \begin{array}{c}R_2C{=}CR_2\\ |\\ M{-}R\end{array} \rightarrow \begin{array}{ccc}R_2C & \cdots & CR_2\\ \vdots & & \vdots\\ M & \text{—} & R\end{array} \rightarrow MCR_2{-}CR_3 \tag{28}$$

R = H, alkyl, growing chain. This type of mechanism is an example of the wide class of insertion reactions and has been suggested for numerous catalytic reactions, including hydrogenation, hydration, hydroformylation, isomerization, and polymerization[13-15,17,20,31-33].

1.6 Reactions of Ethylene with Rh(III), Ru(II) and Pd(II)

Rhodium (III) chloroaquo complexes in aqueous solution, $RhCl_n(H_2O)_{6-n}^{(3-n)+}$, were studied by Wolsey, Reynolds and Kleinberg[2] and characterized spectrophotometrically. Neutral aqueous solutions of $RhCl_3 \cdot 3H_2O$ at ambient temperatures consist of monomeric and polymeric species[34-36]. Equilibration at room temperature for several weeks or at 80° for several days produces a mixture of $RhCl_3(H_2O)_3$ and $[RhCl_2(H_2O)_4]^+$ species[9]. It was found, however, that if ethylene is bubbled through a neutral aqueous solution of $RhCl_3 \cdot 3H_2O$ at room temperature and one atmosphere, the reaction rate due to equilibration is autocatalytic giving a rapid production of mainly $[RhCl_2(H_2O)_4]^+$ within five minutes[9]. The autocatalysis was shown not to be due to any aquochloro species of Rh(III), and it was suggested that hydroxy species were aiding the production of small amounts of Rh(I) species through a mechanism usually postulated for the ethylene reduction of metal ions[37,38].



$$\overset{\mathrm{OH}}{\overset{|}{\mathrm{Rh}}}{}^{\mathrm{III}} + C_2H_4 \rightarrow \overset{\mathrm{OH}}{\overset{|}{\mathrm{Rh}}}{-\!\!-}\begin{matrix}CH_2\\ \|\\ CH_2\end{matrix} \rightarrow Rh\text{-}CH_2CH_2OH \rightarrow Rh^{I} + CH_3CHO + H^+ \tag{29}$$

The autocatalytic nature of the substitution reaction yielding $[RhCl_2(H_2O)_4]^+$ was explained as follows. A chloride-bridged intermediate[10,39,40] is formed by reaction of a Rh(III) species with the Rh(I) chloro species produced in equation 29 with the bridging chloride originating from the substitution inert Rh(III) chloride complex:

$$\mathrm{Cl{-}Rh^{I}{-}{-}{-}Cl{-}{-}{-}Rh^{III}{-}Cl_2} \qquad (30)$$

Electron transfer then occurs, and since Rh(I) is labile while Rh(III) is substitution inert, equation 30 could yield $\mathrm{Rh^{III}Cl_2}$ and $\mathrm{Rh^{I}Cl}$ species. The Rh(I) species then reacts with more Rh(III) species. Due to reaction 29 continuing, the concentration of Rh(I) species builds up, but must remain small such as $< 10^{-6}$M [9,10] as none is detected spectrophotometrically, and no metal production via disproportionation was observed. Also no ethylene uptake or acetaldehyde was detected. A recent report[41] has indicated that aqueous solutions of some Rh(III) complexes contain small but kinetically significant amounts of Rh (I) species.

Kinetic studies in solution of the reaction of C_2H_4 with metal species to form complexes are usually complicated due to subsequent decomposition of the complex. One reaction studied that involves the production of a 1:1 π-complex without such decomposition is that of C_2H_4 with chlororuthenate (II) species in aqueous HCl solutions as reported by James and Halpern[42]. The reaction showed an inverse dependence on chloride, and a zero-to-first order dependence in ethylene with decreasing ethylene concentration. The mechanism postulated involved formation of a $\mathrm{Ru^{II}(C_2H_4)}$ complex through an initial dissociation reaction:

$$\mathrm{Ru^{II}Cl_n \underset{k_{-1}}{\overset{k_1}{\rightleftharpoons}} Ru^{II}Cl_{n-1} + Cl^-} \qquad (31)$$

$$\mathrm{Ru^{II}Cl_{n-1} + C_2H_4 \xrightarrow{k_2} Ru^{II}Cl_{n-1}C_2H_4} \qquad (32)$$

No such reactivity toward ethylene was noted for solutions containing Ru(III) or Ru(IV).

Kinetic studies similar to those of the above reaction were found by James and Rempel[38] for the ethylene reduction of $RhCl_3$ in dimethylacetamide solvent. This again suggested a two-step dissociation mechanism similar to equations 31 and 32. These were followed by faster steps such as

$$[Rh^{III}Cl_{n-1}(C_2H_4)]^{(4-n)+}+H_2O \rightarrow [Rh^{I}Cl_{n-1}]^{(2-n)+}+CH_3CHO+2H^+ \qquad (33)$$

$$[Rh^{I}Cl_{n-1}]^{(2-n)+}+2C_2H_4 \rightarrow [RhCl_{n-1}(C_2H_4)_2]^{(2-n)+} \qquad (34)$$

As in the corresponding system for Rh(III) in neutral aqueous solution (equation 29) the acetaldehyde production was again explained by the decomposition of a σ-bonded hydroxy species. No spectral or gas uptake data were found to indicate a fast initial equilibration such as

$$Rh^{III}Cl_n+C_2H_4 \rightleftharpoons Rh^{III}Cl_{n-1}(C_2H_4)+Cl^- \qquad (35)$$

as found for the Pd(II) system.[37] Such a reaction followed by a rate-determining dissociation of the complex can give the same kinetics as those observed.

The mechanism of the Pd(II) oxidation of ethylene has been studied in detail and is summarized in several reviews[43-46]. Henry[37] found that in aqueous HCl solution the overall reaction is

$$C_2H_4 +PdCl_2 +H_2O \rightarrow CH_3CHO +Pd^o +2HCl \qquad (36)$$

Gas uptake measurements indicated a rate law of the form

$$\frac{-d}{dt}[C_2H_4] = \frac{k[PdCl_4{}^{2-}][C_2H_4]}{[H^+][Cl^-]^2} \qquad (37)$$

The Pd(II) is present initially as $PdCl_4{}^{2-}$; all reactions below will be written using four-coordinate Pd(II) species.

The chloride dependence of (37) and a rapid initial uptake suggested that the first steps were the initial formation of a π-complex

$$PdCl_4{}^{2-}+C_2H_4 \xrightleftharpoons{K_1} PdCl_3C_2H_4+Cl^- \qquad (38)$$

followed by the loss of another chloride to give an aquated complex:

$$PdCl_3C_2H_4^- + H_2O \overset{K_2}{\rightleftharpoons} PdCl_2(H_2O)C_2H_4 + Cl^- \tag{39}$$

Of several subsequent reactions that have been suggested which lead to the formation of acetaldehyde, Henry[37] concluded that the inverse acid dependence results from ionization of the coordinated water molecule

$$PdCl_2(H_2O)C_2H_4 + H_2O \overset{K_3}{\rightleftharpoons} PdCl_2(OH)C_2H_4^- + H_3O^+ \tag{40}$$

Finally a slow rearrangement of the π-ethylene complex to a σ-complex

$$PdCl_2(OH)C_2H_4^- + H_2O \xrightarrow{slow} PdCl_2(H_2O)(CH_2CH_2OH)^- \tag{41}$$

is followed by a rapid decomposition which yields the products

$$PdCl_2(H_2O)(CH_2CH_2OH)^- \xrightarrow{fast} Pd^o + 2Cl^- + H_3O^+ + CH_3CHO \tag{42}$$

Weiss[47] found that added $CuCl_2$ or $FeCl_3$ favoured the homogeneous production of CH_3CHO from C_2H_4 and $PdCl_2$, since Cu(II) and Fe(III) halides oxidize Pd metal back to Pd(II). These oxidations are more effective than using molecular oxygen. However, oxygen will readily oxidize Cu(I) or copper metal in acid chloride solutions, and the following sequence below has been used for the quantitative oxidation of ethylene by oxygen to acetaldehyde:

$$C_2H_4 + PdCl_2 + H_2O \rightarrow CH_3CHO + Pd^o + HCl \tag{43}$$

$$Pd^o + 2CuCl_2 \rightarrow PdCl_2 + 2Cu^o \tag{44}$$

$$\underline{2Cu^o + 2HCl + \tfrac{1}{2}O_2 \rightarrow 2CuCl_2 + H_2O} \tag{45}$$

$$C_2H_4 + \tfrac{1}{2}O_2 \rightarrow CH_3CHO \tag{46}$$

CHAPTER 2. APPARATUS AND EXPERIMENTAL PROCEDURE

2.1 Constant Pressure Gas Uptake Apparatus

Most of the kinetic data were found by measuring gas uptake at constant pressure in the apparatus shown in Figure 1. The reaction flask A, indented for increased surface area, could be clipped to the metal piston and shaken by a Welsh variable speed electric motor; efficient stirring ensured that the reaction was not diffusion controlled. The heating bath B, of Dow Corning 550 fluid silicone oil, was thermostated with a Jumo thermoregulator and merc-to-merc relay control circuit. The oil bath was contained by a four liter beaker insulated in a plywood box. Polystyrene sections were fitted over the top of the oil bath, and by efficient stirring and 25-watt elongated light bulb heaters, the temperature could be maintained to within 0.05°C.

The reaction flask was connected by a length of pyrex glass tubing with two spring coils and a tap C, to a capillary manometer D containing a liquid of negligible vapour pressure. D was connected to a gas burette E, containing mercury and a tube N of known diameter. The manometer and burette were immersed in a rectangular perspex water bath at 25° thermostated as above. The gas burette was connected by means of an Edwards high vacuum needle valve M, to a simple gas handling system with mercury manometer F, and connections reading to a Welsh Duo Seal rotary vacuum pump G and gas inlet Y. A Lab Chron 1402 timer was used for recording reaction times.

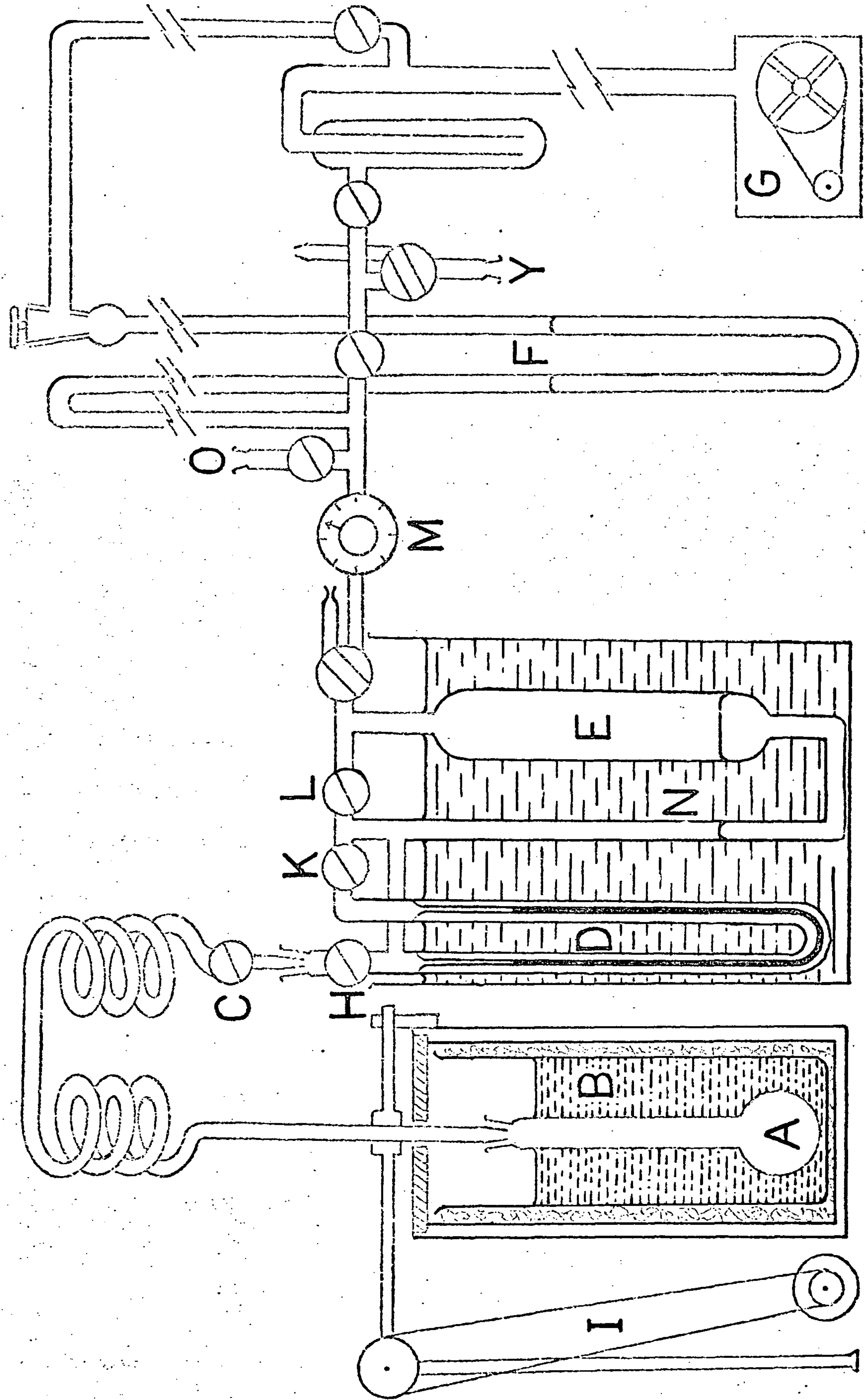

G
Y
F
O
M
E
L
N
K
D
C
H
B
A
I

FIGURE 1. Constant Pressure Gas Uptake Apparatus

2.2 Gas Uptake experimental procedure

Known amounts of reactant solutions were pipetted into the reaction flask A (in figure 1) which was then fitted with the spiral tubing containing tap C. The flask and tubing were attached at position O and the reaction solution was degassed under vacuum after freezing in liquid nitrogen. Reactant gas at a slightly greater pressure than the solvent vapour pressure at the reaction temperature was then admitted through tap Y to the reaction vessel, and then tap C was closed. The flask and spiral tubing were then disconnected from O and attached to the gas burette at H, with the flask being placed in the oil bath B and attached to the motor driven shaker I. The remainder of the system beyond tap C was then evacuated and reactant gas was introduced up to C through tap Y to a pressure slightly less than the desired reaction pressure; tap C was opened and the pressure adjusted to the desired reaction pressure through Y.

A kinetic run was started by simultaneously closing taps K and L, and starting the timer and shaker. As the reaction proceeded, gas was absorbed into solution and the oil level in the left limb of the manometer D began to rise. The oil levels were balanced to the initial reaction pressure by admitting gas into the burette through the needle valve M. This caused the mercury level in tube N to rise, and the level was measured by means of a Pye cathetometer. This height change of mercury was a direct measure of the volume of gas absorbed in ml. at 25° at the reaction pressure, and was readily converted to moles per liter of solution.

2.3 Reaction Product Analysis

To analyze the products at the end of a gas uptake experiment, the reaction was stopped and the reaction mixture quenched in liquid nitrogen. The organic products were distilled off directly from the reaction flask and then run through a gas chromatograph. Peak areas were compared with standard solutions of any suspected products, acetaldehyde, ethylene glycol, and acetic acid. Similar analyses of reaction products were done using NMR. Product yields of the ethylene oxidation reaction are discussed in Chapter 3.

Solid inorganic residue products were analyzed and characterized by infrared (nujol mull).

2.4 Instrumentation

Visible and ultraviolet absorption spectra were recorded on a Perkin Elmer 202 spectrophotometer. Matched silica cells of 1 mm path length were used. Infrared spectra were recorded on a Perkin Elmer 137. Liquid organic products were analyzed by use of a Beckman GC-2A chromatograph with a dinonyl phthalate column, and by a Varian T-60 NMR spectrometer. An AEI M S 9 mass spectrometer was used.

2.5 Materials

Rhodium (III) was obtained as $RhCl_3 3H_2O$ from Platinium Chemicals. Ethylene was obtained as C.P. grade from Matheson Co. Acetaldehyde from Eastman Organic Chemicals was distilled immediately before use each time. Inorganic salts used were $FeCl_3 6H_2O$ AR grade from Fisher Scientific, $Fe(ClO_4)_3$ $6H_2O$ from Alfa Inorganics, LiCl and $LiClO_4$ $3H_2O$ AR grades from

Allied Chemical Co. Because of the hygroscopic nature of the ferric chloride, ferric solutions were standardized by reduction to the ferrous state using a Jones Reductor, and then oxidized back to the ferric state using standard dichromate solutions. A solution made up by weighing out 0.20 M $FeCl_3 \cdot 6H_2O$ was analyzed to be 0.19 M.

CHAPTER 3. RESULTS

3.1 Stoichiometry and Products

When excess $FeCl_3 \cdot 6H_2O$ was added to a solution of 0.1M $RhCl_3 \cdot 3H_2O$ in 3M HCl and then exposed to ethylene at one atmosphere and 80°, ethylene was absorbed. Solutions with differing chloride- and hydrogen ion concentrations were used and the reaction rate exhibited inverse chloride- and hydrogen ion dependences. For kinetic convenience, a solution of 2.0M LiCl and 0.1M HCl was used for the initial detailed studies. The manner of ethylene absorption into solution is shown in Figure 2. Such uptakes were linear up to points which corresponded to the consumption of ethylene and iron (III) in the mole ratio range 1:3.7±0.5 as shown in Table 1. At the limiting value of the linear uptake, where rhodium metal started to

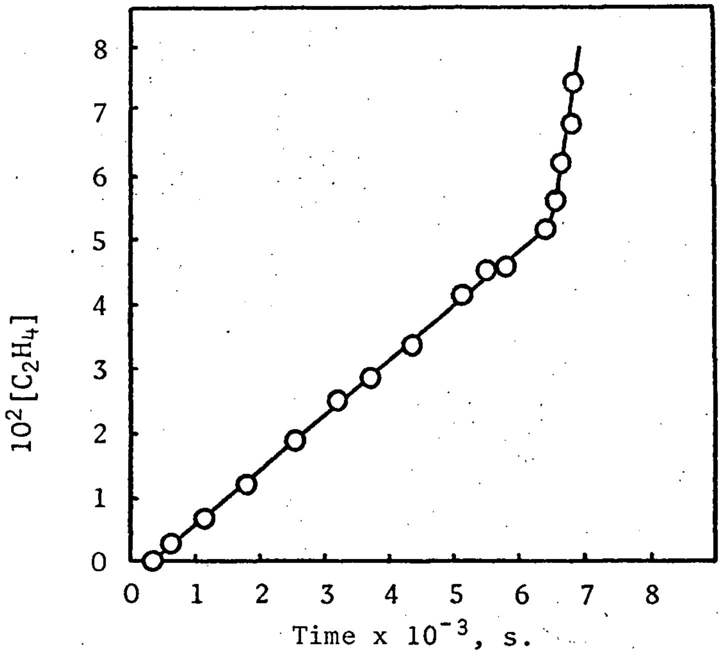


FIGURE 2. Uptake plot of ethylene absorption. Rh(III) = 0.1M, Fe(III) = 0.19M, Temperature = 80°, solvent = 2M LiCl, and 0.1M HCl, C_2H_4 = 1 atm.

appear, the plot in Figure 2 showed a sharp upward break. This will be called the end of the reaction because at this point, the spectrum of the reaction solution showed a complete loss of iron (III) chloride as seen by the loss of absorption at 422 nm. (See Figure 3.) The resulting

TABLE 1. Stoichiometries of Ethylene : Iron (III) at several [Rh(III)]. Ethylene = 1 atm, solvent = 0.1M HCl, 2M LiCl, Temperature = 80°

10^4 moles C_2H_4 [a]	10^4 moles $FeCl_3$	10^4 moles $RhCl_3$
2.2	7.6	4.0
1.0	3.8	2.0
1.0	3.8	2.0
1.1	3.8	2.0
1.2	3.8	1.0
0.9	3.8	1.0
1.1	3.8	2.0

[a] All uptake experiments yield linear ethylene dependences up to the point where rhodium is precipitated as the metal. The ethylene stoichiometry corresponds to the limit of the linear uptake.

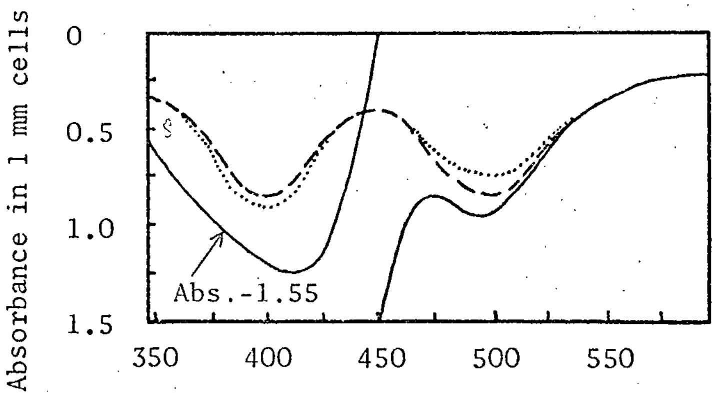


FIGURE 3. Visible spectra of reaction solution. Temperature = 80°, solvent = 2M LiCl and 0.1M HCl;- - -, 0.1M $RhCl_3$; ——, 0.1M $RhCl_3$ + 0.19M $FeCl_3$;·······, 0.1M $RhCl_3$ + $FeCl_3$ at end of reaction with ethylene, corresponding to 6000 s on Figure 2.

iron (II) has practically no absorbance between 350 and 550 nm as was shown by the spectrum of a 0.19M solution of $FeCl_2 \cdot 4H_2O$ in the same solvent.

With a total of 2.1M chloride, the predominant rhodium species is $RhCl_5(H_2O)^{2-}$ [2]. The visible spectrum of Rh(III) remained essentially unchanged over the linear region (see Figure 3) and corresponded to that of the pentachloro species. At acidities of more than 0.1M at this chloride concentration, reproducible linear uptakes were found. At lower acidities, $HClO_4$ rather than HCl was used and uptake plots were not as reproducible.

At the end of the reaction, when all the 0.19M iron (III) was consumed, the organic products which were separated by distillation to 205° and analyzed by gas chromatography and NMR, consisted only of water and acetaldehyde. Comparisons with standard solutions showed no presence of acetic acid, ethylene glycol, or paraldehyde. The distillate from a reaction using 0.1M DCl in D_2O which consumed 0.05M C_2H_4 yielded by NMR a doublet at 8.1 τ. Further additions to the NMR tube of each of the liquids above showed that only CH_3CHO was present. Comparison with standard solutions of CH_3CHO in 0.1M DCl (in D_2O) showed the reaction solution to contain 0.043M CH_3CHO.

The inorganic residue after distillation was shown by IR to contain no carbonyls.

As was pointed out earlier, the end of the reaction was signified by the loss of Fe(III) chlorides although the C_2H_4 uptake corresponded to reduction at only about one half of the iron (III) since C_2H_4 is a two-equivalent reducing agent. To check that the iron (III) had been converted to iron (II) and not to some other iron(III) species that had no absorption at 422 nm, the iron (II) produced was estimated as follows.

After an ethylene uptake experiment was done using 0.19M Fe(III), the CH_3CHO was removed by bubbling nitrogen through the solution. Then by titrating potentiometrically with $K_2Cr_2O_7$, the concentration of Fe(II) was determined to be 0.18M. This stoichiometry problem will be discussed later.

3.2 Iron (III) Dependence

As anticipated from the linear uptake plots, no dependence of the rate on [Fe(III)] was found (See Table 2). This initial Fe(III) concentration was always kept in excess, usually double the Rh(III) concentration. In the absence of Fe(III), or if Fe(III) was not present in excess, rhodium metal, a heterogeneous catalyst was slowly produced. When free rhodium metal was added to a reacting solution, an increase in the linear rate was noticed.

TABLE 2. Summary of Kinetic Data at 80° and 1 atm C_2H_4. Solvent = 0.1M HCl, 2M LiCl

$[FeCl_3]$	$[RhCl_3]$	$10^6 v$, Ms^{-1} [a]
0.0	0.10	36 s^{-1} [b]
0.095	0.10	12 [c]
0.19	0.0	0.0
0.19	0.0015	0.4
0.19	0.01	0.7
0.19	0.03	3.3
0.19	0.05	4.5
0.19	0.10	8.2 [d]
0.38	0.10	8.1
0.19	0.15	13.6
0.38	0.175	14.9

a. v is the linear rate of ethylene uptake.
b. Ethylene is consumed in a first order rate.
c. Rhodium metal precipitates early in uptake.
d. Using 0.1M DCl/D_2O, $v = 7.9 \times 10^{-6} Ms^{-1}$

3.3 Rhodium (III) Dependence

A series of ethylene uptake experiments at various Rh(III) concentrations showed that the reaction is first order in Rh(III) (see Table 2 and Figure 4).

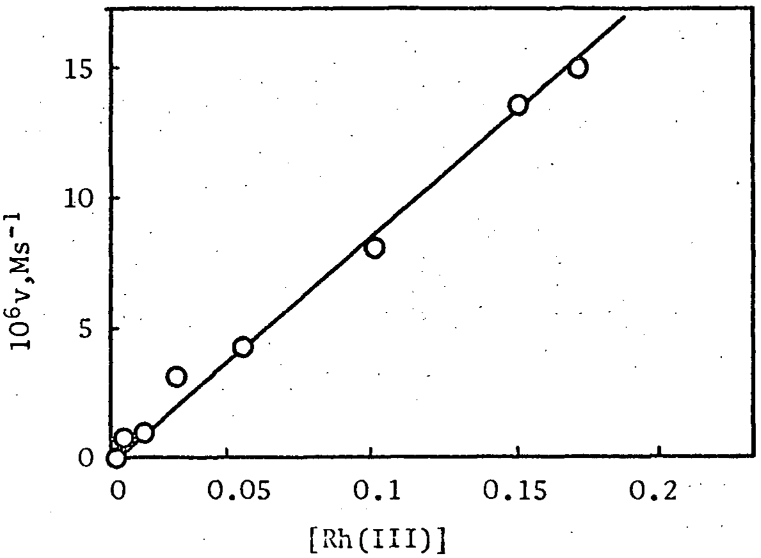


FIGURE 4. Dependence of the linear rate on [Rh(III)], using C_2H_4 at 1 atm, 80° 2M LiCl, 0.1M HCl, and 0.19M $FeCl_3$. For Rh(III) = 0.175M, $FeCl_3$ = 0.38M. v is the linear rate of ethylene consumption.

3.4 Ethylene Dependence

The kinetic dependence on ethylene was found by investigating several experiments at different ethylene pressures each at 75, 80, and 85°. The data and calculations for these uptakes are given in Table 3. A plot of linear rates versus calculated ethylene molarity is given in Figure 5.

3.5 Proton and Chloride Dependences

In an effort to establish the dependences of the rate on $[H^+]$ and on $[Cl^-]$, ethylene uptakes were studied at several acid and chloride concentrations. The results are summarized in Table 4. A plot of rate versus $[H^+]^{-1}$ at constant $[Cl^-]$ was found to be reasonably linear as shown

TABLE 3. Summary of Ethylene Dependences. Rh(III) = 0.1M, Fe(III) = 0.19M, LiCl = 2M, HCl = 0.1M, Temperatures = 75, 80, 85°

	P,mm.	$P^1_{C_2H_4}$,mm. [a]	10^6v,Ms^{-1} [b]	$10^4[C_2H_4]$ [c]
75°	330	35	2.2	0.76
	410	115	3.6	2.51
	525	230	4.6	5.02
	645	350	5.1	7.65
	760	465	7.5	10.15
	850	555	8.5	12.10
80°	380	20	2.9	0.40
	410	50	3.3	1.0
	530	170	5.1	3.4
	650	290	6.8	5.8
	760	400	8.1	8.0
	850	490	10.0	9.8
	950	590	10.5	11.8
85°	475	35	3.3	0.64
	540	100	4.6	1.81
	605	165	6.5	3.0
	760	320	9.1	5.8
	850	410	11.1	7.4

a. The partial pressures of C_2H_4 are based on the vapour pressures of the 0.1M HCl solution being 295, 360, and 440 mm at 75, 80, and 85°, from reference 48.

b. These are not observed rates but true rates, and equal to (observed rate) x (total pressure, P,mm)/(760 mm).

c. The solubility of C_2H_4 is an extrapolated value from reference 49.

TABLE 4. Summary of Proton and Chloride Dependences, at 80°, 1 atm C_2H_4, 0.19M $FeCl_3$, 0.1M $RhCl_3$

[HCl]	$[HClO_4]$	[LiCl]	$[LiClO_4]$	[Total Cl^-]^a	$10^6 v, Ms^{-1}$
6.0				6.0	0.0
3.0				3.0	0.57
0.1				0.1	10.8
0.05		2.0		2.05	10.2
0.1		0.5		0.6	9.3
0.1		2.0		2.1	8.2
	0.1	2.0		2.0	12.8
0.1		2.9		3.0	6.3
0.1		3.0		3.1	5.8
0.2		2.0		2.2	5.3
0.2		2.8		3.0	3.4
0.5		2.5		3.0	1.1
1.0		2.0		3.0	0.9
	1.0	2.0		2.0	6.4
0.1		1.0	1.0	1.1	9.7
0.1		1.0	2.0	1.1	9.3
0.1		2.0	1.0	2.1	7.1
0.1		3.0	0.0	3.1	5.8
0.05		0.1		0.15	4.4^b
0.1		0.1		0.20	3.0^b
	0.2	0.1		0.1	1.65^b
		2		2.0	16.0

a. Total chloride concentration excludes chloride from 0.1M $RhCl_3$ and from 0.19M $FeCl_3$. Using the equilibrium constants for ferric chloride complexes in 1M $HClO_4$, $K_1 = 4.2$, $K_2 = 1.3$, $K_3 = 0.04$ (reference 50), it can be shown that 0.19M $FeCl_3$ in solution yields 0.24M free chloride.

b. 0.2M $Fe(ClO_4)_3$ used rather than 0.19M $FeCl_3$.

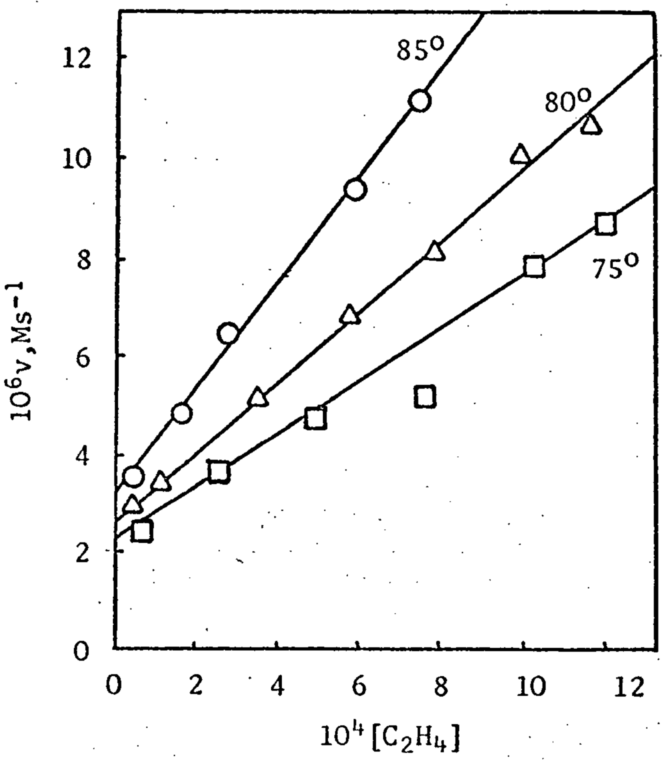


FIGURE 5. Dependence of the linear rate on $[C_2H_4]$, using 0.1M $RhCl_3$, 2M LiCl, 0.1 HCl, 0.19M $FeCl_3$ at 75, 80, and 85°

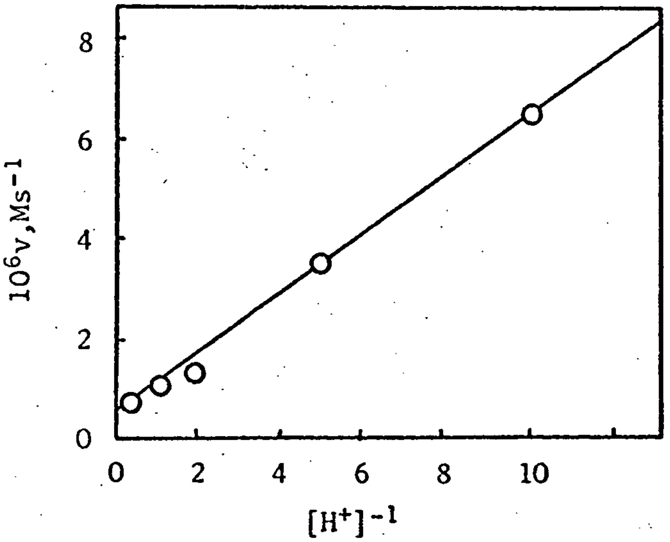


FIGURE 6. Dependence of the linear rate on $[H^+]$ as HCl, using 0.1M $RhCl_3$, 0.19M $FeCl_3$, 1 atm C_2H_4, 80°. Total $[Cl^-]$ using LiCl ≏ 3M.

in Figure 6 and 7. Plots of $(rate)^{-1}$ versus $[H^+]$, and of $(rate)^{-1}$ v. $[H^+]^{-1}$ were not linear. Graphs of rate versus $[Cl^-]^{-1}$, of $(rate)^{-1}$ versus $[Cl^-]$, and of $(rate)^{-1}$ versus $[Cl]^{-1}$ were plotted for a constant $[H^+]$ of 0.1M, and

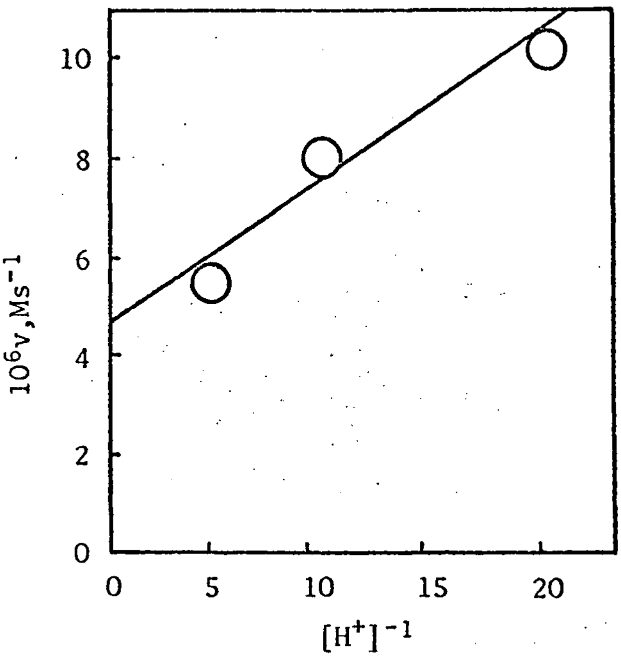


FIGURE 7. Dependence of the linear rate on $[H^+]$ as HCl, using 0.1M $RhCl_3$, 0.19M $FeCl_3$, 1 atm C_2H_4, 80°. Total $[Cl^-]$ using LiCl ≏ 2M.

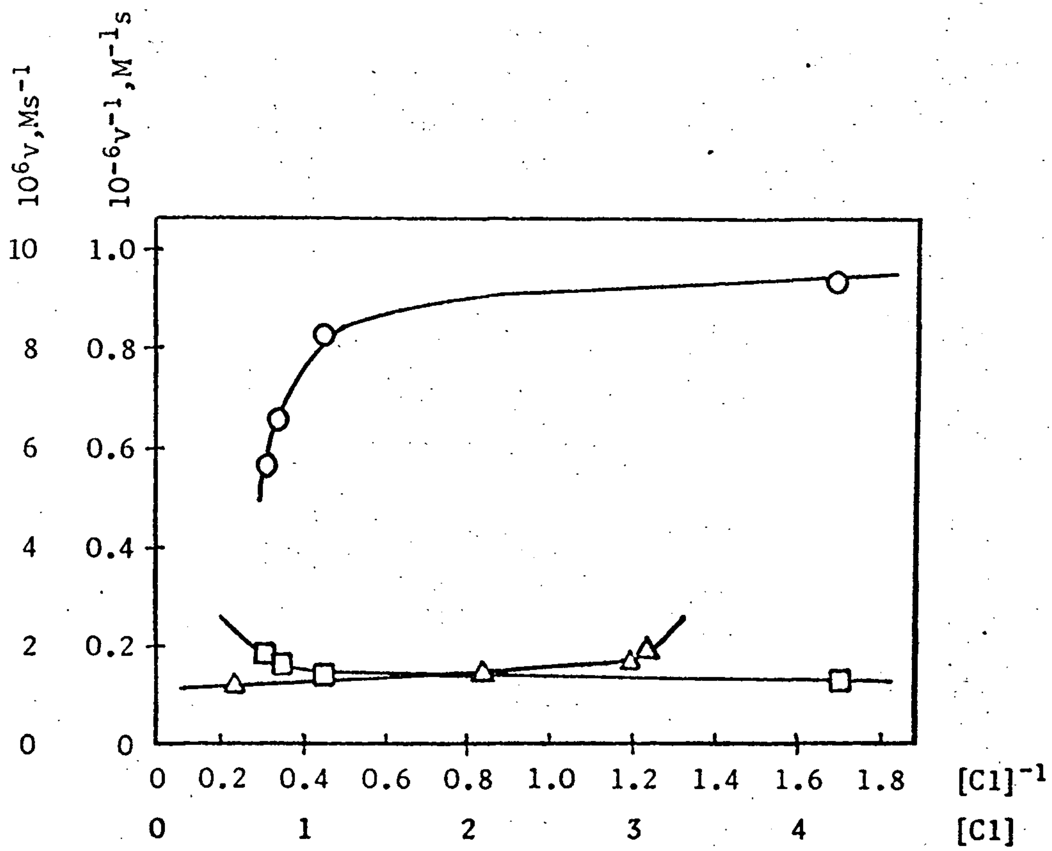


FIGURE 8. Dependence of the linear rate on $[Cl^-]$ as 0.1M HCl+LiCl, using 0.1M $RhCl_3$, 0.19M $FeCl_3$, 1 atm C_2H_4, 80°. ○, rate versus $[Cl]^{-1}$; △ rate^{-1} versus [Cl]; □, rate^{-1} versus $[Cl]^{-1}$

appear in Figure 8. These do not take into account changes in constant ionic strength (adjusted with $LiClO_4$) because rates with or without added $LiClO_4$ are quite similar (see Table 4). Addition of $LiClO_4$ up to 2.0M had little effect on the rate of reaction carried out at 0.1M H^+ and 1.1M Cl^-, indicating that variations in ionic strength were unimportant.

3.6 Activity of Rhodium (III) Aquochloro Species

The results presented so far in Figures 4 - 8 refer to solutions containing mainly the $RhCl_5(H_2O)^{2-}$ species; the activity of other aquochloro species was then studied. A series of these complexes in solution was made by varying chloride as HCl and adjusting the total acidity to 6M with $HClO_4$ [2]. A list of the reaction rates for the species $[RhCl_n(H_2O)_{6-n}]^{(n-3)-}$ is given in Table 5. The large deviation in the rates using $RhCl_5(H_2O)^{2-}$ and $RhCl_4(H_2O)_2^-$ is due to the form of the ethylene uptake plot as shown in Figure 9. This will be discussed in Chapter 4. These species were also

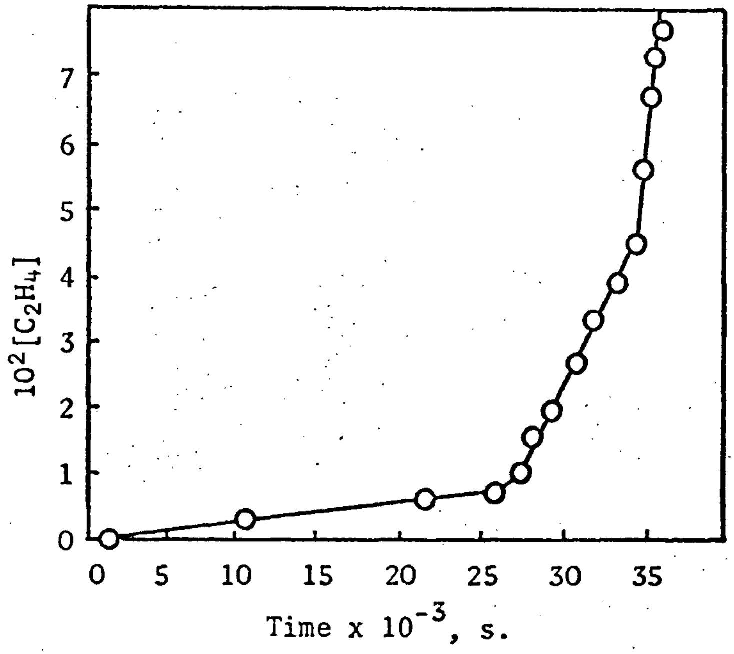


FIGURE 9. Uptake plot of ethylene absorption. Rh(III) as $RhCl_4^-$ = 0.0725M, $Fe(ClO_4)_3$ = 0.095M, H^+ = 6M as 0.17M HCl + 5.83M $HClO_4$, 80°, C_2H_4 = 1 atm.

TABLE 5. Rates of Ethylene Absorption at 1 atm, 80°, H^+ = 6M and 0.1M.

A. [Cl] controlled by $[HClO_4 + HCl]$ = 6M

Main Species	[Rh(III)]	[HCl]	[Fe(III)]	$10^6v, Ms^{-1}$
$RhCl_6{}^{3-}$	0.1	6	$0.19FeCl_3$	0
$RhCl_5(H_2O)^{2-}$	0.0725	2	$0.1Fe(ClO_4)_3$	2.4±1.1
$RhCl_4(H_2O)_2{}^-$	0.0725	0.17	$0.1Fe(ClO_4)_3$	7.2±1.6
$RhCl_3(H_2O)_3$	0.0725	0.035	$0.1Fe(ClO_4)_3$	0.8
$RhCl_3(H_2O)_3$	0.0725	0.035	$0.1Fe(ClO_4)_3$	0.9
-	-	0.035	$0.1Fe(ClO_4)_3$	0.8
$RhCl_2(H_2O)_4{}^+$	0.0725	0.02	$0.1Fe(ClO_4)_3$	0.85
$RhCl(H_2O)_5{}^{2+}$	0.0725	0.01	$0.1Fe(ClO_4)_3$	0.8
$Rh(H_2O)_6{}^{3+}$	0.0725	0.00	$0.1Fe(ClO_4)_3$	0.8

B. $[Cl^-]$ controlled by LiCl. $HClO_4$ = 0.1M

Main Species	$[RhCl_3]$	[LiCl]	[Fe(III)]	$10^6v, Ms^{-1}$
$RhCl_5(H_2O)^{2-}$	0.1	2	$0.1Fe(ClO_4)_3$	12.8
$RhCl_4(H_2O)_2{}^-$	0.1	0.2	$0.1Fe(ClO_4)_3$	42.5

found to be the most active catalysts; the ethylene dependences at varying acidities were studied for these systems. The data are summarized in Tables 6 and 7. Plots of rate versus ethylene molarity for different acidities all at 80° appear in Figures 10 and 11.

TABLE 6. Summary of Proton and Ethylene Dependence with 0.1M Rh(III) as $RhCl_5(H_2O)^{2-}$; 80°, 0.19M $FeCl_3$, 2M LiCl

[HCl]	$P_{,mm}$	$P^1_{C_2H_4,mm}$ [a]	$10^6v, Ms^{-1}$	$10^4[C_2H_4]$ [b]
0.05	410	48	5.4	0.96
0.05	560	198	7.3	3.96
0.05	760	398	10.2	7.96
0.10	380	20	2.9	0.4
0.10	410	50	3.4	1.0
0.10	530	170	5.1	3.4
0.10	650	290	6.7	5.8
0.10	760	400	8.2	8.0
0.10	850	490	10.0	9.8
0.10	950	590	10.5	11.8
0.20	410	53	1.4	1.06
0.20	560	203	3.3	4.06
0.20	760	403	5.3	8.06

a. The partial pressures of C_2H_4 are based on the vapour pressures of the 0.05, 0.10, and 0.20M HCl solutions being 362, 360, and 357 mm at 80°.

b. The solubility of C_2H_4 at 80° is an extrapolated value from reference 49 .

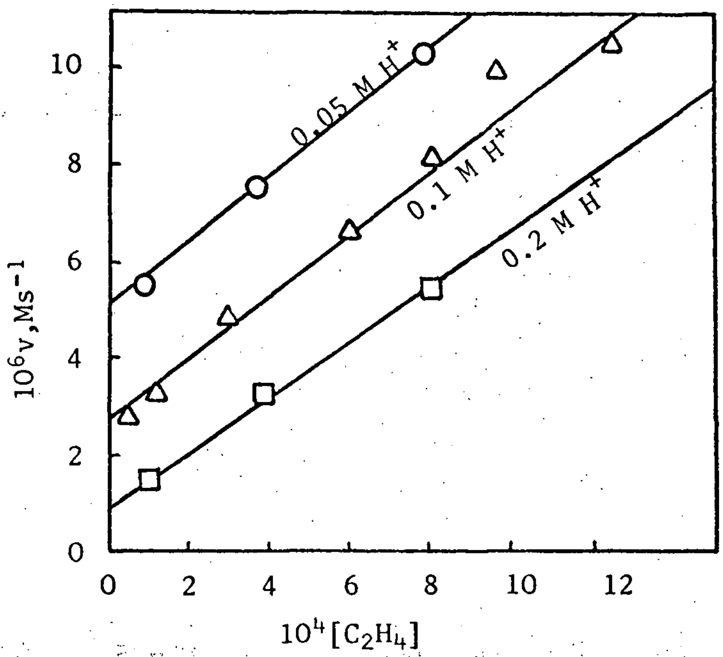


FIGURE 10 Dependence of the linear rate on $[C_2H_4]$ at three acidities as HCl, using 0.1M Rh(III) as $RhCl_5^{2-}$, 0.19M $FeCl_3$, 2M LiCl, 80°

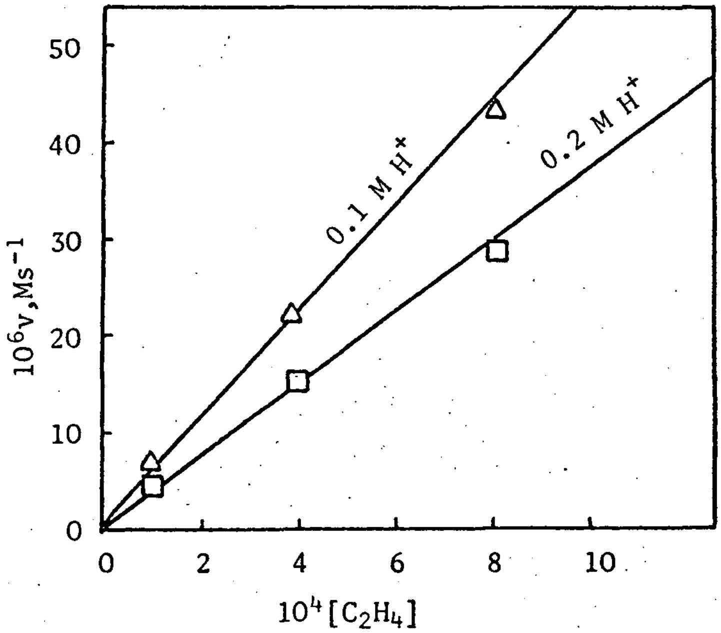


FIGURE 11 Dependence of the linear rate on $[C_2H_4]$ at two acidities as $HClO_4$, using 0.1M Rh(III) as $RhCl_4^-$, 0.2M $Fe(ClO_4)_3$, 0.2M LiCl, 80°

TABLE 7. Summary of Proton and Ethylene Dependences with 0.1M Rh(III) as $RhCl_4(H_2O)_2^-$; 80°, 0.2M $Fe(ClO_4)_3$, 0.2M LiCl.

$[HClO_4]$	P,mm	$p^1_{C_2H_4}$,mm [a]	$10^6 v$,Ms^{-1}	$10^4[C_2H_4]$ [b,c]
0.1	410	50	7	1.0
0.1	560	200	23	4.0
0.1	760	400	43	8.0
0.2	410	53	4.2	1.06
0.2	560	203	15	4.06
0.2	760	403	23	8.06

a,b. See Table 6.

c. Assuming that the solubility of ethylene is the same in $HClO_4$ as in HCl for a given set of conditions, and that the two media have similar vapour pressures.

3.7 Other Oxidizing Agents

Several other oxidants besides iron (III) were investigated for the rhodium (III) - catalyzed oxidation of ethylene. Linear rates were observed for reactions using these oxidants and are given in Table 8, along with iron (III) for comparison. The rates for the reactions with Cu(II) and Cr(IV) were independent of oxidant concentration over the range 0.2 - 0.4M.

TABLE 8. Summary of rates with various oxidizing agents, with 0.1M HCl, 2M LiCl, 0.1M $RhCl_3$, 80°, 1 atm C_2H_4.

oxidizing agent	$p^1_{C_2H_4}$,mm	10^6 rate, Ms^{-1}
0.19M $FeCl_3 \cdot 6H_2O$	400	8.2
	100	3.4
0.2 M $CuCl_2 \cdot 2H_2O$	400	14.3
0.2 M $K_2Cr_2O_7$	400	9.7
300 mm. O_2	100	1.2

CHAPTER 4. DISCUSSION

4.1 Activity of the Pentachloro Species

The rate versus $[C_2H_4]$ plot in Figure 5 shows an intercept at $[C_2H_4] = 0$ so there is a contribution to the overall rate, which is independent of C_2H_4. Since the starting catalytic species is $RhCl_5^{2-}$, we have immediately the expression

$$\text{rate} = -\frac{d}{dt}[C_2H_4] = k_a[RhCl_5^{2-}] + k_b[RhCl_5^{2-}][C_2H_4] \tag{47}$$

where k_a and k_b are pseudo first and second order rate constants containing all dependences except those of rhodium and ethylene. k values used subsequently are for 80° unless otherwise stated.

In Table 5, the only other active catalytic rhodium chloro-species besides $RhCl_5^{2-}$ seems to be $RhCl_4^-$, so we might assume that the C_2H_4 independent step involves a dissociation from $RhCl_5^{2-}$ to $RhCl_4^-$. We now have for the two rate-determining steps

$$RhCl_5^{2-} \xrightarrow{k_a} RhCl_4^- + Cl^- \tag{48}$$

$$RhCl_5^{2-} + C_2H_4 \xrightarrow{k_b} \text{products} \tag{49}$$

Using Figure 10, for $[H^+] = 0.1$ and $[Rh(III)] = 0.1$, the intercept gives $k_a = 2.8 \times 10^{-5}\ s^{-1}$, and the slope gives $k_b = 6.7 \times 10^{-2}\ M^{-1}s^{-1}$. The $RhCl_4^-$ must then react with C_2H_4 in a faster step than the dissociation governed by k_a. Also, the rhodium species from the products must finally be regenerated as $RhCl_5^{2-}$ after the faster steps to explain the observed linear rates in (47).

Experiments using $RhCl_5^{2-}$ as a reactant show the following.

(a) the C_2H_4 independent rate is acid dependent because the intercepts in Figure 10 are not equal. An inverse acid dependence is observed, and a plot of these intercepts versus $[H^+]^{-1}$ goes essentially through the origin as shown in Figure 12 below. This suggests that by far the

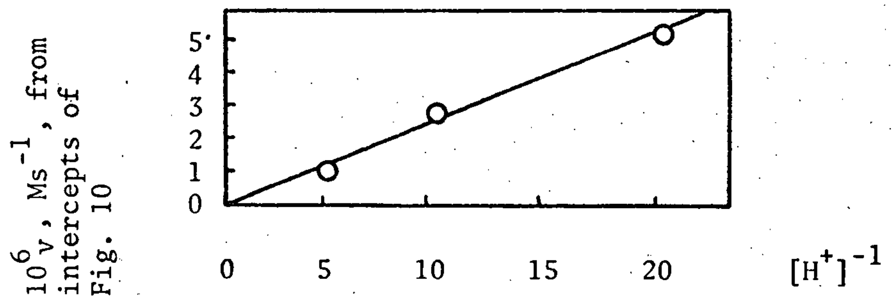


FIGURE 12. Dependence of the C_2H_4 independent rate on $[H^+]$ as HCl, using 0.1M $RhCl_5^{2-}$, 0.19M$FeCl_3$, 2M LiCl, 80°.

major contribution to k_a in (48) is one involving hydroxy species:

$$RhCl_5(OH)^{3-} + H_2O \xrightarrow{k_1} RhCl_4(OH)(H_2O)^{2-} + Cl^- \tag{50}$$

But we cannot completely exclude the possibility that a smaller contribution involving purely aquo species also occurs:

$$RhCl_5(H_2O)^{2-} + H_2O \xrightarrow{k_2} RhCl_4(H_2O)_2^- + Cl^- \tag{51}$$

This acid independent step requires that Figure 12 shows a positive intercept on the ordinate axis.

(b) The rate versus C_2H_4 plots in Figure 10 indicate that the C_2H_4 dependent rate is essentially acid independent because the slopes at the different acidities are practically equal. A plot of the slopes of Figure 10 - that is, the contribution by the C_2H_4 dependent step to the overall reaction in (47) - versus $[H^+]^{-1}$ is shown in Figure 13; the intercept $\hat{=}$ 5.9 x

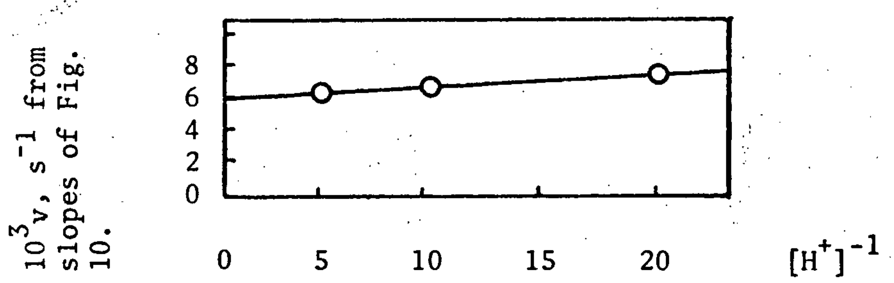


FIGURE 13. Dependence of the C_2H_4 dependent rate on $[H^+]$ as HCl, using 0.1M $RhCl_5^{2-}$, 0.19M $FeCl_3$, 2M LiCl, 80°.

$10^{-3}s^{-1}$ and the slope value $\simeq 9 \times 10^{-5}Ms^{-1}$. Thus mainly aquo species are involved but there appears to be a small contribution from hydroxy species:

$$RhCl_5(H_2O)^{2-} + C_2H_4 \xrightarrow{k_3} \text{products} \qquad (52)$$

$$RhCl_5(OH)^{3-} + C_2H_4 \xrightarrow{k_4} \text{products} \qquad (53)$$

Equation (47) can now be expanded to include the acid dependence.

$$\text{rate} = \{\frac{k_1K_a{}^5}{[H^+]} + k_2\}[RhCl_5(H_2O)^{2-}]+\{k_3+\frac{k_4K_a{}^5}{[H^+]}\}[RhCl_5(H_2O)^{2-}][C_2H_4] \qquad (54)$$

where $K_a{}^5 = [RhCl_5(OH)^{3-}][H^+]/[RhCl_5(H_2O)^{2-}]$. Using the data at $[H^+] = 0.1$ and $[RhCl_5(H_2O)^{2-}] = 0.1$, Figure 10 gives

$$\text{rate} = 2.8 \times 10^{-6} + 6.7 \times 10^{-3}[C_2H_4]\ Ms^{-1} \qquad (55)$$

For example, when $[C_2H_4] = 8 \times 10^{-4}$ (for 1 atm), the rate is calculated to be $8.2 \times 10^{-6}Ms^{-1}$ which is consistent with the same value given in Table 6.

Equation (47) can also be expanded as the plot of rate versus $[H^+]^{-1}$ shown in Figure 7.

$$\text{rate} = \{k_2+k_3[C_2H_4]\}[RhCl_5(H_2O)^{2-}] + \frac{\{k_1+k_4[C_2H_4]\}K_a{}^5[RhCl_5(H_2O)^{2-}]}{[H^+]} \qquad (56)$$

With $[RhCl_5(H_2O)^{2-}] = 0.1$

and $[C_2H_4] = 8 \times 10^{-4}$, the relationship becomes

$$\text{rate} = 4.5 \times 10^{-6} + \frac{3.1 \times 10^{-7}}{[H^+]}\ Ms^{-1} \qquad (57)$$

The reaction rate involving rhodium aquo species is given by the value $4.5 \times 10^{-6}Ms^{-1}$ in (57). From (56), this rate results from the k_2 and k_3 terms, namely $4.5 \times 10^{-6} = \{k_2+k_3[C_2H_4]\}[RhCl_5(H_2O^{2-}]$ (58)

Figure 12 indicates that the k_2 path is not important. Therefore, neglecting k_2 in (58) gives $k_3 = 5.6 \times 10^{-2} M^{-1} s^{-1}$. The intercept in Figure 13 gives a direct measurement of k_3 as $5.9 \times 10^{-2} M^{-1} s^{-1}$. The ethylene dependent contribution given by (54) and (55) be written as

$$6.7 \times 10^{-3} = \frac{\{k_3 + k_4 K_a^5\}[RhCl_5(H_2O)^{2-}]}{[H^+]} \qquad (59)$$

Using the k_3 value derived from (58), (59) gives $k_4 K_a^5 = 1.1 \times 10^{-3} s^{-1}$. The slope of Figure 13 gives a value of $k_4 K_a^5$ of $0.9 \times 10^{-3} s^{-1}$.

The contribution to the ethylene dependent rate from hydroxy species is given by (56) and (57):

$$3.1 \times 10^{-7} = \{k_1 + k_4[C_2H_4]\}K_a^5 [RhCl_5(H_2O^{2-}] \qquad (60)$$

Using the $k_4 K_a^5$ value above, (60) gives $k_1 K_a^5 = 2.2 \times 10^{-6}\ Ms^{-1}$. Lastly, the ethylene independent rate using (54) and (55) can be written as

$$2.8 \times 10^{-6} = \frac{\{k_1 K_a^5 + k_2\}[RhCl_5(H_2O)^{2-}]}{[H^+]} \qquad (61)$$

The $k_1 K_a^5$ value above gives $k_2 = 6 \times 10^{-6} s^{-1}$.

K_a^5 is given in reference 8 as approximately $10^{-8}M$ so that the values of k_1 and k_4 are of the order of $2.2 \times 10^2 s^{-1}$ and $1.1 \times 10^5 M^{-1} s^{-1}$. In any case this indicates that in the ethylene independent steps, the hydroxy species are roughly 10^8 more reactive than aquo species. The reactions involved are shown in (50) and (51), and the conclusion is that the hydroxy complex $RhCl_5(OH)^{3-}$ undergoes aquation with the loss of a chloride some 10^8 times faster than the aquo complex $RhCl_5(H_2O)^{2-}$.

This finding is probably quite significant. The strong labilizing effect of the hydroxy group in octahedral coordination chemistry is well known[51]. In the well-studied cobalt (III) system below, the rate

$$Co(en)_2LCl^+ + H_2O \longrightarrow Co(en)_2L(H_2O)^{2+} + Cl^- \qquad (62)$$

constant for L = cis-OH^- is some 10^4 times that for the reaction with L = cis H_2O[51]. This has been rationalized in terms of the strong π-donor ability of -OH^- to stabilize a trigonal bipyramidal transition state via the initial dissociation of the chloride in (62) — that is, an S_N1 mechanism. Cobalt (III) substitution reactions generally occur through a dissociative mechanism. Corresponding rhodium (III) systems have been little studied, but the data have generally been interpreted in terms of more S_N2 character although the evidence is not strong[52,53]. The most rational explanation for the OH^- effect is that the mechanism of (50) follows that of some Cobalt (III) systems and goes through an initial S_N1 dissociation of a chloride ligand.

Robb and Steyn[54] have determined the value of k_2 directly and give a value of $8 \times 10^{-5} s^{-1}$ at 30° in perchloric-hydrochloric acid media of constant ionic strength $\mu = 4.00$. Considering the completely different nature of the studies and the uncertainty of the C_2H_4 solubility in the present work, the agreement is reasonable. The present k_2 value could in fact be subject to considerable error since its estimation in (61) depends on the difference between two quite similar numbers 2.8×10^{-6} and 2.2×10^{-6}. The former is the intercept of Figure 10 which should be reasonably correct; the latter is estimated through equations (58) to (60) with some uncertainty.

The data also shows that C_2H_4 reacts 10^5-10^6 times more rapidly with $RhCl_5(OH)^{3-}$ than with $RhCl_5(H_2O)^{2-}$. The same hydroxy species has been shown[8] to be 10^6 - 10^8 times as reactive as the aquo species towards carbon monoxide. The second order rate constant for reaction (63) has been determined as $0.2\ M^{-1}s^{-1}$ at 80° in 3M HCl which is comparable to

$$RhCl_5(H_2O)^{2-} + CO \longrightarrow RhCl_4(CO)(H_2O)^- + Cl^- \qquad (63)$$

the value of 0.056 $M^{-1}s^{-1}$ for k_3 determined in this work for the corresponding ethylene reaction (52).

Measurements over the range 75-85° yielded the temperature dependence of the rate constants for the two-term law in (47) and (54) from the slope and intercepts of Figure 5. (See Table 9.)

TABLE 9. Temperature dependence of rate constants k_a and k_b for the reaction of 0.1M $RhCl_5^{2-}$ with C_2H_4. $FeCl_3$ = 0.19M, HCl = 0.1M, LiCl = 2M.

T°C	$10^5k_a, s^{-1}$	$10^2k_b, M^{-1}s^{-1}$
75	2.4	5.6
80	2.8	6.7
85	3.2	11.2

The k_a values cannot be determined with any accuracy but the data suggest that they vary little with temperature. The temperature dependence of k_a will be mainly governed by variation in k_1 in (54), suggesting a low activation energy for (50) which could be consistent with the mechanism discussed above.

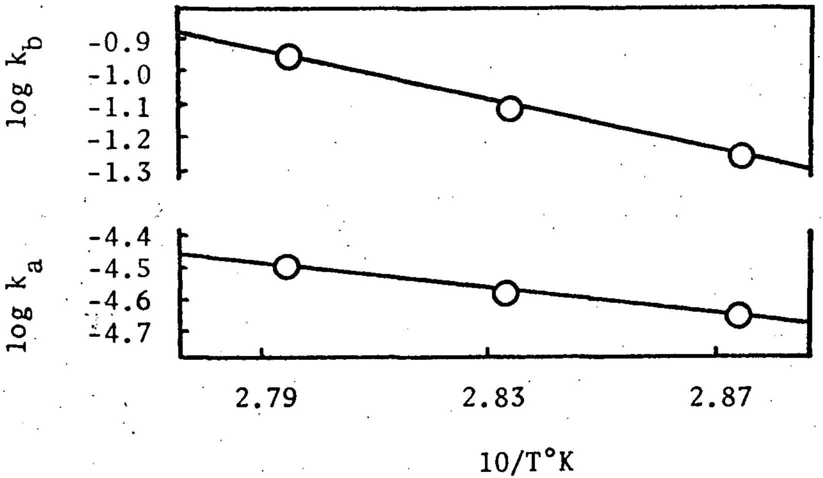


FIGURE 14. Arrhenius plot for the reaction of 0.1M $RhCl_5^{2-}$ with C_2H_4. $FeCl_3$ = 0.19M, HCl = 0.1M, LiCl = 2M.

From the Arrhenius plot in Figure 14, the enthalpies of activation are $\Delta H_a^{\ddagger} = 5.8$ kcal., and $\Delta H_b^{\ddagger} = 16.9$ kcal. Assuming that variation of k_a with temperature is mostly due to variation in k_1, and k_b to k_3, the entropies are $\Delta S_1^{\ddagger} \hat{=} -32$ e.u., and $\Delta S_3^{\ddagger} \hat{=} -17$ e.u.

4.2 Activity of the Tetrachloro Species. Experiments using $RhCl_4^-$ as a reactant show the following:

(a) There is no appreciable C_2H_4 independent rate as shown by the absence of an intercept in Figure 11. That is, a strictly first order dependence on C_2H_4 is observed. Any possible small intercept would likely be due to the presence of small amounts of $RhCl_5^{2-}$ in the reactant. The only reaction of $RhCl_4^-$ that need be considered is one involving C_2H_4.

(b) The slopes of the rate versus C_2H_4 plots in Figure 11 at the two acidities show that the rate is considerably acid dependent. Figure 15 shows the slopes of Figure 11 versus $[H^+]^{-1}$. Only two sets of data were measured; the intercept value $\hat{=} 1.8 \times 10^{-2} s^{-1}$ and the slope value $\hat{=} 4 \times 10^{-3} Ms^{-1}$. Thus as before we consider reactions of C_2H_4 which

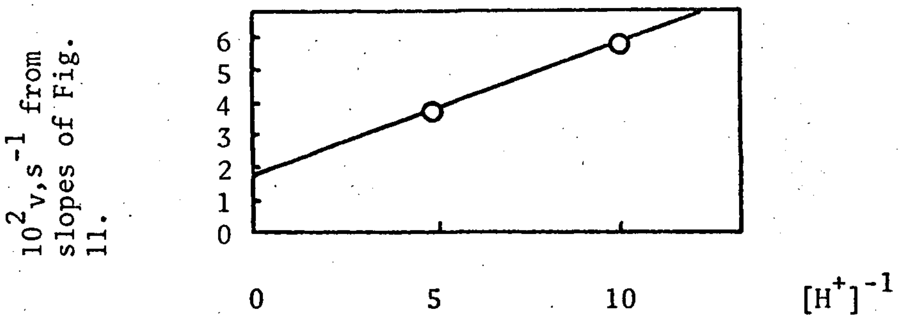


FIGURE 15. Dependence of the C_2H_4 dependent rate on $[H^+]$ as $HClO_4$, using 0.1M $RhCl_4^-$, 0.2M $Fe(ClO_4)_3$, 0.2M LiCl, 80°.

involve both aquo and hydroxy species:

$$RhCl_4(H_2O)^- + C_2H_4 \xrightarrow{k_5} \text{products} \qquad (64)$$

$$RhCl_4(OH)(H_2O)^{2-} + C_2H_4 \xrightarrow{k_6} \text{products} \qquad (65)$$

The rate law for the reaction of $RhCl_4^-$ species with ethylene is of the form

$$\text{rate} = \{k_c[RhCl_4(H_2O)_2^-]+k_d[RhCl_4(OH)(H_2O)^{2-}]\}[C_2H_4] \qquad (66)$$

where k_c and k_d are pseudo first and second order rate constants. Equation (66) can be written as

$$\text{rate} = \{k_5+\frac{k_6K_a^4}{[H^+]}\}[RhCl_4(H_2O)_2^-][C_2H_4] \qquad (67)$$

where $K_a^4 = [RhCl_4(OH)(H_2O)^{2-}][H^+]/[RhCl_4(H_2O)_2^-]$. Equation (67) is analysed directly by using the intercept and slope values obtained above from Figure 15:

$$1.8 \times 10^{-2}s^{-1} = k_5[RhCl_4(H_2O)_2^-] \qquad (68)$$

gives $k_5 = 1.8 \times 10^{-1}M^{-1}s^{-1}$, and

$$4 \times 10^{-3}Ms^{-1} = k_6K_a^4[RhCl_4(H_2O)_2^-] \qquad (69)$$

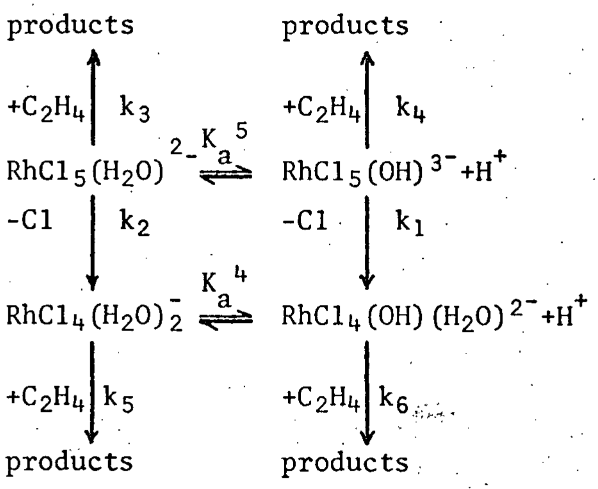
gives $k_6K_a^4 = 4 \times 10^{-2}s^{-1}$. Equation (67) is also analyzed by using the data at $[H^+] = 0.1$ and $[RhCl_4(H_2O)_2^-] = 0.1$ with the slope of Figure 11:

$$\text{rate} = 5.7 \times 10^{-2}[C_2H_4]\ Ms^{-1} \qquad (70)$$

The data are internally consistent since (68) and (69) give a summation of $5.8 \times 10^{-2}M^{-1}s^{-1}$ for $\{k_5+k_6K_a^4/[H^+]\}$ using $[H^+] = 0.1$ and $[RhCl_4(H_2O)_2^-] = 0.1$, and (67) and (70) give $5.7 \times 10^{-2}M^{-}s^{-1}$ for the same quantity.

The acidity of $RhCl_4(H_2O)_2^-$ will be somewhat higher than that of $RhCl_5(H_2O)^{2-}$ and K_a^4 is likely to be about $10^{-6}M$. Thus k_6 will be of the order of $4 \times 10^4M^{-1}s^{-1}$.

Analyses of the rate data at 80° in Sections 4.1 and 4.2 are summarized in the following Scheme:



$$\begin{aligned} k_1K_a &= 2.2\mathrm{x}10^{-6}Ms^{-1} \\ k_2 &= 6\mathrm{x}10^{-6}s^{-1} \\ k_3 &= 5.6\mathrm{x}10^{-2}M^{-1}s^{-1} \\ k_4K_a^5 &= 1.1\mathrm{x}10^{-3}s^{-1} \\ k_5 &= 1.8\mathrm{x}10^{-1}M^{-1}s^{-1} \\ k_6K_a^4 &= 4\mathrm{x}10^{-2}s^{-1} \\ \text{If } K_a^5 &= 10^{-8}M, K_a^4=10^{-6}M, \\ k_1 &= 2.2\mathrm{x}10^{2}s^{-1} \\ k_4 &= 1.1\mathrm{x}10^{5}M^{-1}s^{-1} \\ k_6 &= 4\mathrm{x}10^{4}M^{-1}s^{-1} \end{aligned} \qquad (71)$$

It now seems clear that rate paths showing no dependence on C_2H_4 concentration are indeed possible for the $RhCl_5^{2-}$ species since $k_5[C_2H_4] > k_2$ and $k_6[C_2H_4] >> k_1K_a$. That is, as mentioned on page 33 the $RhCl_4^-$ must react with C_2H_4 in a faster step than the dissociations governed by $k_a = k_1K_a^5/[H^+] + k_2$.

4.3 Inverse Chloride Dependence

The inverse chloride dependence which was seen in Table 4 but which did not analyze for any of the simple dependences shown in Figure 8, could arise in a number of possible ways. Here are three.

(a) If the composition of the rhodium chloro species changes in solution over the chloride concentration range studies (0.6 - 3.1 M) then the dependence could arise from the differing reactivities of the species. The activity of the complexes decreases in the order $RhCl_4^- > RhCl_5^{2-} > RhCl_6^{3-}$, and this could qualitatively explain the dependence. The visible spectra of the initial solutions are all essentially that of the $RhCl_5^{2-}$ species but contributions from quite small amounts of $RhCl_4^-$ at lower chloride and $RhCl_6^{3-}$ at higher chloride could be significant.

(b) Notable changes in gas solubility in chloride-perchlorate media have been observed for H_2 and CO over similar concentration ranges[3,8] and changes in ethylene solubility with the change in media here could be important although the data in Table 4 indicate that addition of $LiClO_4$ has little effect on the measured rate.

(c) It is possible that the chloride dependence arises from a genuine kinetic dependence for reactivity involving the pentachloro species. As was seen, the reactivity arises mainly from reactions (50) and (52) with a smaller contribution from (53). An inverse chloride dependence could arise if the back-reaction of (50) becomes significant. Reaction (50) would have to be written as:

$$RhCl_5(OH)^{3-} + H_2O \underset{k_{-1}}{\overset{k_1}{\rightleftharpoons}} RhCl_4(OH)(H_2O)^{2-} + Cl^- \qquad (72)$$

The contribution to the rate in (54) from (65) then becomes

$$\frac{k_1k_6[RhCl_5(OH)^{3-}][C_2H_4]}{k_{-1}[Cl^-] + k_6[C_2H_4]} \qquad (73)$$

This contribution however was independent of $[C_2H_4]$ at 2.1 M chloride which means that $k_6[C_2H_4] >> k_{-1}[Cl^-]$. Thus at lower $[Cl^-]$ no effect on the rate would be observed and indeed the rate changes very little from 0.6 to 2.1 M chloride (Table 4). It is possible that at higher $[Cl^-]$ the $k_{-1}[Cl^-]$ term will become more significant and an inverse dependence observed. But it must be remembered that at much higher $[Cl^-]$, the inactive $RhCl_6^{3-}$ may be present. In any case the overall reaction rate, neglecting k_2 terms from (51), is given by

$$\text{rate} = \frac{k_1k_6[RhCl_5(OH)^{3-}][C_2H_4]}{k_{-1}[Cl^-] + k_6[C_2H_4]} + k_3[RhCl_5(H_2O)^{2-}][C_2H_4] + k_4[RhCl_5(OH)^{3-}][C_2H_4] \qquad (74)$$

The contribution due to the last two terms at $[H^+] = 0.1$ is known to be $5.3 \times 10^{-6} Ms^{-1}$. Thus a chloride dependence would be given by

$$(\text{rate} - 5.3 \times 10^{-6})^{-1} = \frac{k_{-1}[Cl^-]}{k_1 k_6 [RhCl_5(OH)^{3-}][C_2H_4]} + \frac{1}{k_1[RhCl_5(OH)^{3-}]} \qquad (75)$$

and a plot of $(\text{rate} - 5.3 \times 10^{-6})^{-1}$ versus $[Cl^-]$ should be linear. However the data do not analyze for a linear plot, indicating that the back reaction given by k_{-1} is not significant. The independence of the rate given by (73) on $[C_2H_4]$ at 2.1M Cl^- does suggest that an increase to 3.0M Cl^- would have very little effect on the rate.

The chloride dependence then is not resolved, but contributions from the tetra- and hexachloro complexes are suspected.

4.4 The Production of Acetaldehyde

The kinetic data show that both aquo and hydroxy complexes of rhodium (III) react with ethylene.

For the ethylene independent path for the pentachloro species, the reaction sequence may be written as follows (neglecting the contribution from (51)):

$$RhCl_5(H_2O)^{2-} \xrightleftharpoons{K_a^5} RhCl_5(OH)^{3-} + H^+ \qquad (76)$$

$$RhCl_5(OH)^{3-} + H_2O \xrightarrow{k_1} RhCl_4(OH)(H_2O)^{2-} + Cl^- \qquad (50)$$

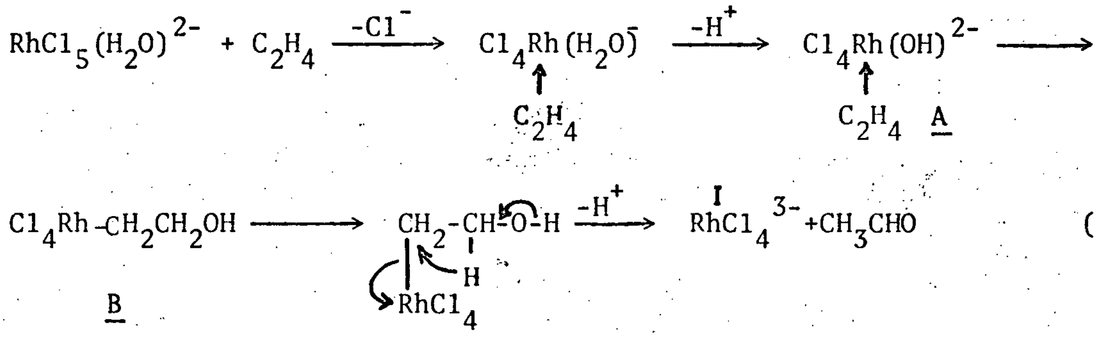
$$RhCl_4(OH)(H_2O)^{2-} + C_2H_4 \xrightarrow[\text{fast}]{k_6} \text{products} \qquad (65)$$

The ethylene dependent path involves (52) and (53) followed by faster decomposition to products:

$$RhCl_5(H_2O)^{2-} + C_2H_4 \xrightarrow[k_4]{k_3} \text{products} \qquad (52)$$

$$RhCl_5(OH)^{3-} + C_2H_4 \longrightarrow \text{products} \qquad (53)$$

On analogy with the oxidation of ethylene by other metal ions[37,38], (52) may be written in more detail as follows. This was discussed on page 10



$$RhCl_5(H_2O)^{2-} + C_2H_4 \xrightarrow{-Cl^-} \underset{\overset{\uparrow}{C_2H_4}}{Cl_4Rh(H_2O)^-} \xrightarrow{-H^+} \underset{\overset{\uparrow}{C_2H_4}\ \underline{A}}{Cl_4Rh(OH)^{2-}} \longrightarrow$$

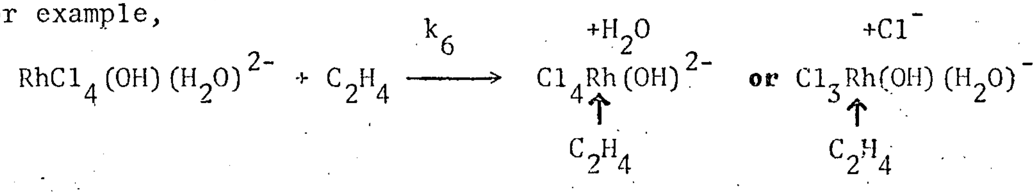
$$\underset{\underline{B}}{Cl_4Rh-CH_2CH_2OH} \longrightarrow \underset{RhCl_4}{CH_2}-\underset{H}{CH}-O-H \xrightarrow{-H^+} \overset{I}{Rh}Cl_4{}^{3-} + CH_3CHO \qquad (77)$$

Reaction (53) will produce the hydroxy intermediate A directly. Migration of the hydroxy ligand results in formation of the σ - bonded Rh(III) hydroxy ethyl intermediate B. Decomposition of B can not involve a carbonium ion formed with the production of Rh(I) because no ethylene glycol is formed by reaction with the solvent[37]. Rather, the rhodium center leaving with two more electrons assists a 1,2 hydrogen shift which directly yields acetaldehyde and a proton[37]. Since this redox step will be much faster than earlier steps, this proton liberated will not be be accounted for in the inverse acid dependence.

In Scheme (77), a coordinated Cl^- must be lost on reaction with C_2H_4 since a coordinated H_2O is necessary for subsequent reaction to products. Such a reaction mechanism also readily accounts for the complete inactivity of the hexachloro species $RhCl_6{}^{3-}$, and gives convincing evidence that a coordinated H_2O or OH^- is necessary for the formation of the hydroxy ethyl intermediate. It has been postulated by some authors[43] that attack by a non-coordinated hydroxide is involved.

Reactions (64) and (65) will follow a very similar path to that outlined in (77) although it is not immediately obvious whether C_2H_4 will replace a coordinated H_2O or Cl^-.

For example,



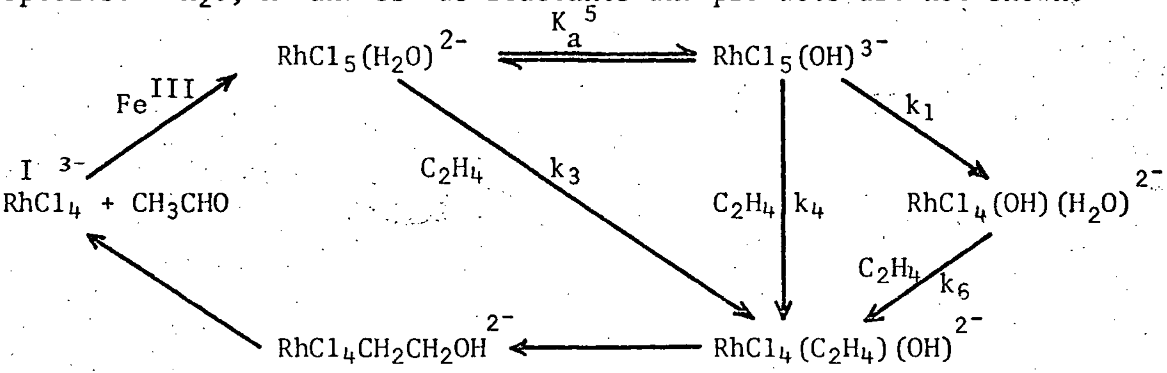
$$RhCl_4(OH)(H_2O)^{2-} + C_2H_4 \xrightarrow{k_6} \underset{\overset{\uparrow}{C_2H_4}}{Cl_4Rh(OH)^{2-}} \overset{+H_2O}{} \text{ or } \underset{\overset{\uparrow}{C_2H_4}}{Cl_3Rh(OH)(H_2O)^{-}} \overset{+Cl^-}{} \quad (78)$$

An important conclusion in these studies is that solutions containing $RhCl_4(H_2O)_2^-$ species are considerably more reactive towards C_2H_4 than are solutions containing $RhCl_5(H_2O)^{2-}$ at 0.1M acidity and 1 atm total pressure. This initially seemed unusual in that the series of aquochloro complexes becomes more labile with increasing number of coordinated chlorides[3]. The major contribution to the rate for tetrachloro system is (65) involving $RhCl_4(OH)(H_2O)^{2-}$ and C_2H_4 for which the data show $k_6K_a^4 = 4 \times 10^{-2}s^{-1}$; the major contribution to the rate for the pentachloro system is (52) involving $RhCl_5(H_2O)^{2-}$ and C_2H_4 for which $k_3 = 5.6 \times 10^{-2}M^{-1}s^{-1}$. Thus although hydroxy species are present in very small amounts in both systems at 0.1M acidity, more kinetically significant amounts are present in the tetrachloro system and this is reasonable since K_a^4 will be > K_a^5. The rates of reaction between C_2H_4 and the hydroxy species are governed by the values $k_6K_a^4 = 4 \times 10^{-2}s^{-1}$ and $k_4K_a^5 = 1.1 \times 10^{-3}s^{-1}$ (the contribution to the rate is given by $kK[Rh(III)]/[H^+]$), and at any given acidity the $k_6K_a^4$ term will be > $k_4K_a^5$. The actual rate constants are probably quite similar and in fact the present data suggest that k_4 is somewhat larger than k_6 — that is, $RhCl_5(OH)^{3-}$ is more reactive than $RhCl_4(OH)(H_2O)^{2-}$ is towards C_2H_4.

At very high acidities (theoretically at $[H^+]^{-1} = 0$), the C_2H_4 independent step for the pentachloro system becomes negligible (Figure 12) and the reaction rate will be governed purely by the rate constant $k_3 = 5.6 \times 10^{-2}M^{-1}s^{-1}$ for the reaction between $RhCl_5(H_2O)^{2-}$ and

C_2H_4. Secondly, the rate for the $RhCl_4^-$ system will be governed purely by the rate constant $k_5 = 1.8 \times 10^{-1} s^{-1}$ for the reaction between $RhCl_4(H_2O)_2^-$ and C_2H_4. The rates would thus be quite similar although as mentioned above one might have expected the $RhCl_5^{2-}$ aquo species to be somewhat more active.

The entire reaction, neglecting the very small contributions from k_2 and k_5 in (51) and (64), may now be written as a catalytic system for the production of acetaldehyde using rhodium (III) aquopentachloro species. H_2O, H^+ and Cl^- as reactants and products are not shown. (79)



The rhodium (I) species is immediately oxidized back to rhodium (III) by iron (III). Since the total chloride concentration remains constant, the $RhCl_5^{2-}$ species are regenerated as required by the kinetic and spectrophotometric data. When all the iron (III) has been consumed, or if no iron (III) on other oxidant is present, the rhodium (I) rapidly disproportionates to rhodium metal:

$$2\ Rh(I) \longrightarrow Rh(0) + Rh(II) \qquad (80)$$

This reaction has always been written to explain the production of rhodium metal from rhodium (I) especially in aqueous solutions[3,8,9] but no quantitative data have been available. However, recent work[55] involving the oxidation of ethylene by Rh(III) in the absence of any reoxidant such as Fe(III) has shown that rhodium metal is produced as well as a pale yellow solution which gives an ESR signal thought to be due to a paramagnetic Rh(II) species. This disproportionation to a possible monomeric Rh(II) species is being further studied.

When ethylene was oxidized with $RhCl_5^{2-}$ (again using 2MLiCl and 0.19M $FeCl_3$) in 0.1MDCl in D_2O, NMR measurements showed that no deuterium was incorporated into the acetaldehyde molecule. That all of the hydrogen atoms of the acetaldehyde molecule have come from the ethylene, is consistent with the hydrogen shift postulated in (77). A similar result has been observed for the Pd(II) oxidation of C_2H_4 in D_2O[37]. For the present Rh(III) reaction, the small isotope effect $k_H/k_D = 1.04$ shown in Table 2 is significant. The corresponding isotope effect measured in the Pd(II) system[37] was 4.0; this was attributed to the difference in K_a values in D_2O and H_2O, and showed that the ionization to a hydroxy species was prior to the rate determining step. The isotope effect of 1.04 in the present work indicates that the ionization is subsequent to the rate determining step at the conditions of measurement, and this is consistent with the interpretation that the reaction between $RhCl_5(H_2O)^{2-}$ and C_2H_4 in (52) prior to ionization is the major contribution for these conditions.

The present study gives no data on the fast reactions between Rh(I) and Fe(III). Both of these species are substitution labile, assuming that Fe(III) is in the high spin state. In the reaction medium there are aquo, hydroxy and chloride ligands, all of which are suitable for bridging so that an inner or outer sphere reaction is possible[56]. The mechanism of electron transfer may be similar to that suggested for Rh(I) - Rh(III) reactions involving chloro-bridged intermediates (page 11).

Spectrophotometric and gas uptake measurements showed no evidence for a rapid initial equilibrium process to form an ethylene π-complex via a reaction such as

$$RhCl_5(H_2O)^{2-} + C_2H_4 \overset{K}{\rightleftharpoons} RhCl_4(C_2H_4)(H_2O)^- + Cl^- \qquad (81)$$

as was postulated in the corresponding Pd(II) system[37]. If K is very small, such a process followed by a slow decomposition of the π-complex could equally well explain most of the kinetic data for the ethylene dependent path. However, such a mechanism should give rise to a rate inversely proportional to chloride at least for that due to the ethylene dependent path. The chloride dependence found argues against this. Also the measured isotope effect as discussed above argues against such a pre-equilibrium. In similar systems involving reactions of rhodium chlorides with C_2H_4 in DMA, and with CO in aqueous HCl, no rapid pre-equilibria were found.

4.5 Use of Oxidants Other Than Fe(III). Table 8 shows that some variation in the linear uptake rates is observed on using different oxidants to regenerate the Rh(III) catalyst. Since no Rh metal production was observed in these systems, the Rh(I) must be oxidized rapidly back to Rh(III) and thus the measured C_2H_4 linear uptake rates are expected to be independent of the nature of the oxidant used. The variation in rates upon using Fe(III), Cu(II) and Cr(VI) is not great and is probably not significant. The result for O_2 does seem low but this system should be further investigated as described in Chapter 5. Experimentally this system requires the use of uptake measurements from a gas-mixture (ethylene and oxygen) but this procedure is not well established for the usual apparatus at present.

4.6 Ethylene Uptake Rates in 6M Acid. Figure 9 shows that in 0.17 M HCl and 5.83 M $HClO_4$, linear uptake rates are not observed. An "induction period" before the reduction of Fe(III) took place, and a reduction of Rh(III) to the metal, was observed. The fact that rhodium metal is produced may indicate that Fe(III) can less easily oxidize any low-valence Rh intermediate such as Rh(I). For instance, the reduction potential of the Fe(III) - Fe(II) couple might be lower in higher acid concentration. However, Connick and McVey[57] found that the opposite is true for this and other couples in $HClO_4$ but that the couple is lower in $HClO_4$ than in HCl.

The "induction period" does consist of a small rate of ethylene uptake and this is observed for all species in $HClO_4$, such as $RhCl_n$ with $n \leqslant 3$ and even for a solution containing no rhodium (III) (Table 5). This could result from a slow hydration reaction of the ethylene. No such reaction is apparent in 6M HCl.

Thus rhodium chloroaquo species $RhCl_n$ with $n \overset{<}{-} 3$ are effectively inactive as catalysts for the reaction described in this thesis, and this is reasonable because these species are progressively more substitution inert that $RhCl_5^{2-}$ and $RhCl_4^-$. In $RhCl_6^{3-}$ there is no possibility of a coordinated H_2O or OH^- as required for the subsequent insertion reaction (29).

4.7 The Ethylene: Iron(III) Stoichiometry.

In answer to the C_2H_4:Fe(III) stoichiometry problem from section 3.1, there seemed after much deliberation to be several possibilities. The fact is that the observed C_2H_4:Fe(III) molar consumption ratio of roughly 1:4 is too low if C_2H_4 is acting as a two-equivalent reducing agent.

One answer is that Fe(III) chlorides were being removed by some way other than reduction by C_2H_4. First, there might be a further reduction by the CH_3CHO produced in solution. This would produce CH_3COOH but none was found in the reaction products; also CH_3CHO did not react with Fe(III) under the reaction conditions. The possibility that CH_3CHO reduced Fe(III) in a catalytic system through Rh(III) was also investigated. Indeed, under N_2 at 80°Rh(III) was reduced to metal (presumably via Rh(I)) by CH_3CHO, and the possibility of (82) and (83), as shown below, occuring seemed likely:

$$\mathrm{Rh(III)} + CH_3CHO \longrightarrow \mathrm{Rh(I)} + CH_3COOH \quad (82)$$

$$\mathrm{Rh(I)} + 2\mathrm{Fe(III)} \longrightarrow \mathrm{Rh(III)} + 2\mathrm{Fe(II)} \quad (83)$$

However, as mentioned earlier, no CH_3COOH was detected and also a reaction of CH_3CHO with the usual mixture of Rh(III) and Fe(III) gave no changes whatsoever. That is, neither Rh(III) nor Fe(III) was consumed. It is not at all clear why the presence of Fe(III) should inhibit a reaction such as (82).

Second, it was considered that Fe(III) chlorides might be removed by complexing with other ligands produced during the reaction. But again no acetates were found. Third, Fe(III) might have formed bridged species with Rh(III) or with itself but no evidence for either of these reactions was found spectroscopically.

No decarbonylation of the acetaldehyde by the rhodium complexes was observed. Such decarbonylation to give metal carbonyls has been observed for low valent platinum metal complexes including Rh(I) species (see, for example reference 21).

The wide variation in C_2H_4 stoichiometries for several identical experiments (Table 1) portends to an argument that the problem may not be a purely chemical one such as an unforeseen side reaction, but rather a more physical one.

The C_2H_4 was apparently consumed in a smaller quantity than that corresponding to the reduction of the Fe(III) chlorides. If some of the

CH_3CHO product (which corresponded to the amount of C_2H_4 absorbed into solution) was present in the gas phase, then the apparent overall uptake of C_2H_4 would be low since the kinetic technique measures volume changes in the gas phase. In spite of the alleged infinite solubility of CH_3CHO in hot aqueous solutions[58], the presence of CH_3CHO vapour is thought to explain the observed low C_2H_4 consumption. Some experimental data support this reasoning.

A mass spectrum of the gas above solution at the end of an uptake experiment at 80° showed the presence of CH_3CHO, and the vapour pressure of the reaction solvent + 0.05 M CH_3CHO at room temperature was found to be roughly twice that of the reaction solvent alone. (As seen in Figure 2, the C_2H_4 consumption at the end of a reaction is 0.05 M instead of the expected 0.1 M).

Literature data[62] give a value for the partial pressure p^1 of acetaldehyde at 82° as 380mm over a 0.55M aqueous acetaldehyde solution. A 0.05M solution assuming Henry's Law would have a P^1 of 35mm. The volume of the apparatus open to acetaldehyde is about 50ml mainly at room temperature, and assuming Boyle's Law, this would contain 0.9×10^{-4} moles of gaseous acetaldehyde. The amount of acetaldehyde present in the 2ml of reactant solution will be 1.0×10^{-4} moles. These calculations show that for the present apparatus, one half of the acetaldehyde produced will be in the gas phase. This causes the apparent ethylene uptake to be about one half the true uptake and explains the stoichiometry problem. It should be noted also that since the measured rates are therefore one half the true rates, the calculated rate constants are apparent ones and should be doubled to give the true values.

CHAPTER 5. SUMMARY AND SUGGESTIONS FOR FURTHER WORK

The reaction of rhodium (III) chlorides with ethylene and iron (III) in aqueous HCl at 80° and 1 atm was shown to catalytically produce acetaldehyde. Rhodium (I) is a likely intermediate, rather than a rhodium (III) hydride which was suggested for a similar reaction involving oxidation of hydrogen to protons[1].

The kinetics of the Rh(III) reaction with C_2H_4 were studied and proved to be much more complex than anticipated. A first order dependence on Rh(III) was observed but the overall reaction involved contributions from an ethylene independent path as well as the expected ethylene dependent one. Studies on the acid dependence of the contributing paths have shown that hydroxy species although present in very small concentrations are significant kinetically.

The reactions involved in the rate determining steps are summarized below:

$$
\begin{array}{lcl}
RhCl_5(H_2O)^{2-} & \xrightleftharpoons{K_a^5} & RhCl_5(OH)^{3-}+H^+ \\
RhCl_5(OH)^{3-}+H_2O & \xrightarrow{k_1} & RhCl_4(OH)(H_2O)^{2-}+Cl^- \\
RhCl_5(H_2O)^{2-}+H_2O & \xrightarrow{k_2} & RhCl_4(H_2O)_2^-+Cl^- \\
RhCl_5(H_2O)^{2-}+C_2H_4 & \xrightarrow{k_3} & RhCl_4(C_2H_4)(H_2O)^-+Cl^- \\
RhCl_5(OH)^{3-}+C_2H_4 & \xrightarrow{k_4} & RhCl_4(C_2H_4)(OH)^{2-}+Cl^- \\
RhCl_4(H_2O)_2^- & \xrightleftharpoons{K_a^4} & RhCl_4(OH)(H_2O)^{2-}+H^+ \\
RhCl_4(H_2O)_2^-+C_2H_4 & \xrightarrow{k_5} & RhCl_4(C_2H_4)(H_2O)^-+H_2O \\
 & \text{or} & RhCl_3(C_2H_4)(H_2O)_2+Cl^- \\
RhCl_4(OH)(H_2O)^{2-}+C_2H_4 & \xrightarrow{k_6} & RhCl_4(C_2H_4)(OH)^{2-}+H_2O \\
 & \text{or} & RhCl_3(C_2H_4)(OH)(H_2O)^-+Cl^-
\end{array}
$$

Values of the rate constants k_2, k_3, k_5 and the composite constants $k_1K_a^5$, $k_4K_a^5$, $k_6K_a^4$ at 80° have been determined.

Relatively fast subsequent decompositions of the C_2H_4 π- complexes are assumed to occur via a mechanism well-established for the corresponding Pd(II) system[37]. For example,

$$RhCl_4(C_2H_4)(OH)^{2-} \longrightarrow RhCl_4(CH_2CH_2OH)^{2-}$$

$$RhCl_4(CH_2CH_2OH)^{2-} \longrightarrow Rh^{I}Cl_4^{3-}+CH_3CHO+H^+.$$

Rh(I) is rapidly oxidized back to Rh(III) by the Fe(III) present, and the net reaction is

$$C_2H_4+H_2O+2Fe(III) \xrightarrow{Rh(III)} CH_3CHO+2H^++2Fe(II)$$

The reported results are considered significant since they would suggest that more efficient rates of conversion of C_2H_4 to CH_3CHO would be observed in less acid conditions where higher concentrations of Rh(III) hydroxy complexes would be present. The oxidative ability of $Cr_2O_7^{2-}$ decreases at lower acidities, and Fe(III) and Cu(II) readily give hydroxy complexes which may be less efficient oxidants. But O_2 is particularly appealing for use as an oxidant of Rh(I) since it suggests that C_2H_4/O_2 mixtures might be oxidized directly to CH_3CHO. This would give a process somewhat simpler than the Wacker Process where O_2 and Cu(II) are needed to regenerate Pd(II) from Pd metal. Oxygen is probably not very efficient as an oxidant at ordinary pressures in aqueous solution because of its low solubility, and its oxidation power does decrease with decreasing acidity[59]. However, the use of higher O_2 pressures and some other solvent system such as DMA (where the O_2 solubility is higher[60,61] and Rh(I) is more stable[38]) might prove rewarding.

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