CATALYTIC OXIDATION OF CYCLOHEXANOL TO

CYCLOHEXANONE USING A COMBINATION OF RHODIUM(III),

IRON (III) AND MOLECULAR OXYGEN.

by

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ABSTRACT

The catalytic conversion of cyclohexanol to cyclohexanone using a combination of rhodium trichloride trihydrate and ferric chloride in the presence of molecular oxygen was investigated. No conversion to cyclohexanone occurred in the absence of rhodium trichloride trihydrate, but some degree of conversion was found in the absence of ferric chloride. The optimum conditions for catalytic oxidation were produced by using a combination of rhodium trichloride trihydrate and ferric chloride, and under these conditions the rate of conversion to the ketone declined steadily, until the mixture contained approximately 40% cyclohexanone.

For a fixed amount of cyclohexanol and rhodium trichloride trihydrate it was found that there was an optimum amount of ferric chloride necessary to produce the maximum yield in the shortest possible time. Addition of ferric chloride in excess of this optimum amount tended to suppress the rate of conversion to the ketone. This can probably be explained by the additional production of water and cyclohexene (see below).

Using a cyclohexanol/ferric chloride ratio in the optimum range at a given temperature, increasing the rhodium trichloride trihydrate concentration beyond a certain level did not significantly increase the final yield, or the reaction rate.

The oxidation reaction occurred under acidic conditions, this acidity being the result of interaction between ferric chloride and cyclohexanol (and cyclohexanone). The acidity of a typical system was found to decline rapidly as the reaction

progressed.

Cyclohexene was produced in a side reaction, together with water. This is presumably the result of cyclohexanol undergoing an elimination reaction under acidic conditions. Using the optimum cyclohexanol/ferric chloride ratio at 100deg, the the cyclohexene content remained at less than 10%, during the course of the reaction. Introduction of cyclohexene in amounts in excess of 20% greatly suppressed the conversion to cyclohexanone, presumably due to strong complexation of the olefin with a rhodium species.

Water was produced during the catalytic oxidation in amounts greater than could be accounted for by production of cyclohexene. This additional water content of the reaction mixture in a closed system was in good agreement with that predicted on the basis of the equation:
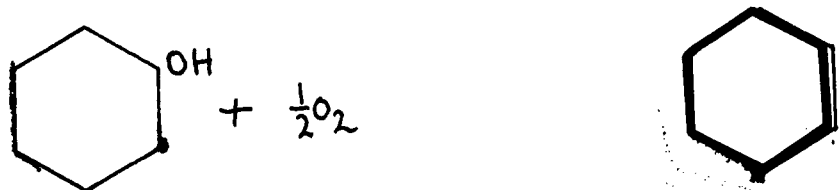
The presence of water in the reaction mixture tended to suppress the oxidation of cyclohexanol to cyclohexanone.

Using the optimum ratio of components, very little conversion to the ketone occurred in the presence of oxygen, at temperatures below 50deg. Increasing the temperature from 100deg to 150deg increased the rate of oxidation but had little effect on the final yield of cyclohexanone.

Oxygen was found to be necessary for catalytic oxidation to

occur. The measured oxygen absorption for a reaction mixture containing an optimum ratio of components, was found to be in good agreement with that predicted by the above equation.

Using an optimum ratio of components in the presence of oxygen, the conversion to cyclohexanone was limited to apprroximately 40%. This limit was probably due to an interaction between cyclohexanone and some active rhodium species essential for catalytic activity.

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ABBREVIATIONS

atm   atmosphere

b.p.   boiling point

deg   degrees centigrade

g   gram

hr   hours

in   inch or inches

min   minute or minutes

ml   millilitre

mmol   millimole

m.p.   melting point

nm   nanometres

N.T.P.   normal temperature and pressure

R.T.   room temperature

vpc   vapour phase chromatograph

ACNOWLEDGEMENTS

CHAPTER (1)

INTRODUCTION

The homogeneous catalytic oxidation of alcohols to the corresponding carbonyl compound has been studied using a variety of transition metal catalysts. The reaction mechanism appears to involve one of two pathways. It can proceed either by a catalytic dehydrogenation to produce molecular hydrogen , or by oxidation, employing oxidizing agents in combination with transition metal catalysts .

Chloro-complexes of Rh(III) have been found to catalyse the dehydrogenation of iso-propyl alcohol to acetone [1]. Hydrogen gas is evolved when iso-propyl alcohol is refluxed at 83deg with rhodium trichloride trihydrate, concentrated hydrochloric acid and lithium chloride. Rhodium metal is deposited during the reaction, and the rate of dehydrogenation decreases as rhodium is removed from solution.

The mechanism suggested for this dehydrogenation involves formation of an alkoxide, followed by the transfer of a hydride ion from the α-carbon atom of the coordinated alkoxide to the rhodium, with liberation of the ketone. The rhodium hydride intermediate then either reacts with a proton to form hydrogen or decomposes to give rhodium metal:

$$Me_2CHOH + RhCl_6^{3-} \rightleftharpoons Cl_5Rh-OCHMe_2 + H^+ + Cl^-$$

$$Cl_5Rh-OCHMe_2^{3-} \longrightarrow Cl_5Rh-H^{3-} + Me_2C=O$$

$$HCl + HRhCl_5^{3-} \rightleftharpoons H_2^- + RhCl_6^{2-}$$

$$HRhCl_5^{3-} \longrightarrow Rh^0$$
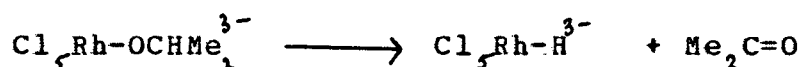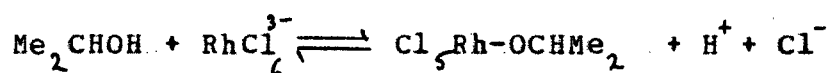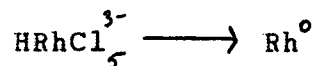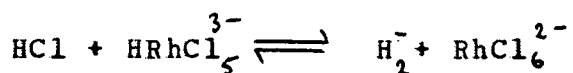
The rhodium chloride catalysed dehydrogenation of iso-propyl alcohol has also been examined in the presence of tin (II) chloride [2]. It was found that the dehydrogenation was homogeneously catalysed by rhodium-tin complexes without precipitation of the metal. The suggested mechanism followed that above and involved formation of molecular hydrogen by reaction of a rhodium hydride intermediate with protons from the solvent. However, the pi-acceptor $SnCl_3^-$ acts as a ligand to rhodium, and is thought to stabilize the hydride intermediate against decomposition to the metal. Reported conversions to acetone were low (<10%).

Dehydrogenation of primary and secondary alcohols by homogeneous catalysis to form aldehydes and ketones respectively has also been investigated more recently using ruthenium and osmium complexes of the type: $[M(OCOR)_2(CO)(PPh_3)_2]$, (R=CF$_3$, C$_2F_5$, C$_6F_5$) [3]. The mechanism suggested again involves B elimination within an alkoxide to form the corresponding carbonyl compound and a hydride. Acid attack on the hydride liberates molecular hydrogen and regenerates the catalyst. Reported yields appear to be again generally low (<10%) for oxidation of alcohols proceeding by this dehydrogenation pathway.

The second mechanistic pathway involves the use of oxidizing agents in conjunction with the transition metal catalysts. Oxidation of alcohols using tert-butyl hydroperoxide

with either vanadium or ruthenium catalysts,[4] and with chloramine-T using ruthenium has been reported [5]. Oxidation of primary and secondary alcohols using ruthenium catalysts in combination with amine N-oxides at room temperature generally gives the corresponding aldehyde or ketone in good yield. (>90% in some cases), except in the case of olefinic alcohols [6].

While the above procedures are obviously useful, they do require the consumption of expensive organic oxidants, and clearly the use of molecular oxygen in combination with a catalytic agent would be more desirable.

Homogeneous catalytic oxidation of secondary alcohols to ketones using molecular oxygen with PdCl -NaOAc as catalyst under mild conditions was recently published while the work described in this thesis was in progress [7]. By measuring the oxygen uptake, together with vpc analysis, the stoichiometry of the reported reactions was shown to be:

$$R'R''CHOH + 1/2O_2 \longrightarrow R'R''C=O + H_2O$$

Yields of ketone were generally over 90% except for olefinic alcohols (e.g. p-menth-8-en-ol), which were thought to poison the catalyst by strong complexation. In a typical example, trans 3-3-5-trimethylcyclohexanol (17mmol) was stirred with PdCl (0.170mmol) and NaOAc (8.5mmol) using ethylene carbonate as solvent at 38deg. The reaction mixture was maintained under oxygen at 1atm pressure. The conversion to ketone was 98% after 54hr. It was found that the water, which was produced in an equimolar amount with the alcohol consumed,

inhibited the reaction.

The mechanism suggested for the catalytic cycle involves complexation of the alcohol to Pd(II) and then deprotonation to give a Pd(II) alkoxide followed by the β-hydride transfer from C to Pd to yield the ketone and a Pd(II) hydride complex. This is then thought to be oxidized by oxygen to give water and regeneration of the active Pd(II) species.

The catalytic oxidation of cyclohexanol to cyclohexanone, by the Rh(III)-Fe(III)-O_2-catalyst system used in the present work , could be visualised as proceeding by either or both of the two mechanistic pathways described above.

The first pathway involves oxidation of the alcohol by molecular oxygen, and its subsequent conversion to water:
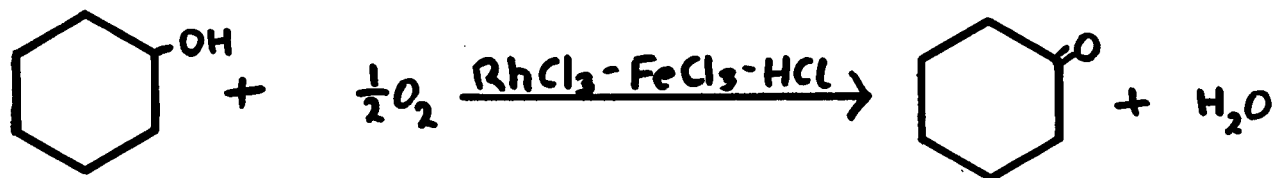
This mechanism would presumably involve initial complexation of cyclohexanol with a Rh(III) species followed by release of a proton from the coordinated alcohol to give a Rh(III)-alkoxide. A B-hydride transfer from carbon to rhodium would yield cyclohexanone and a Rh(I) hydride complex which could be oxidized by molecular oxygen to give water and an active Rh(III) species, although little is known about interaction of metal hydrides with oxygen [8].

This pathway, which will in future be referred to as reaction (1), is illustrated in Fig (1).
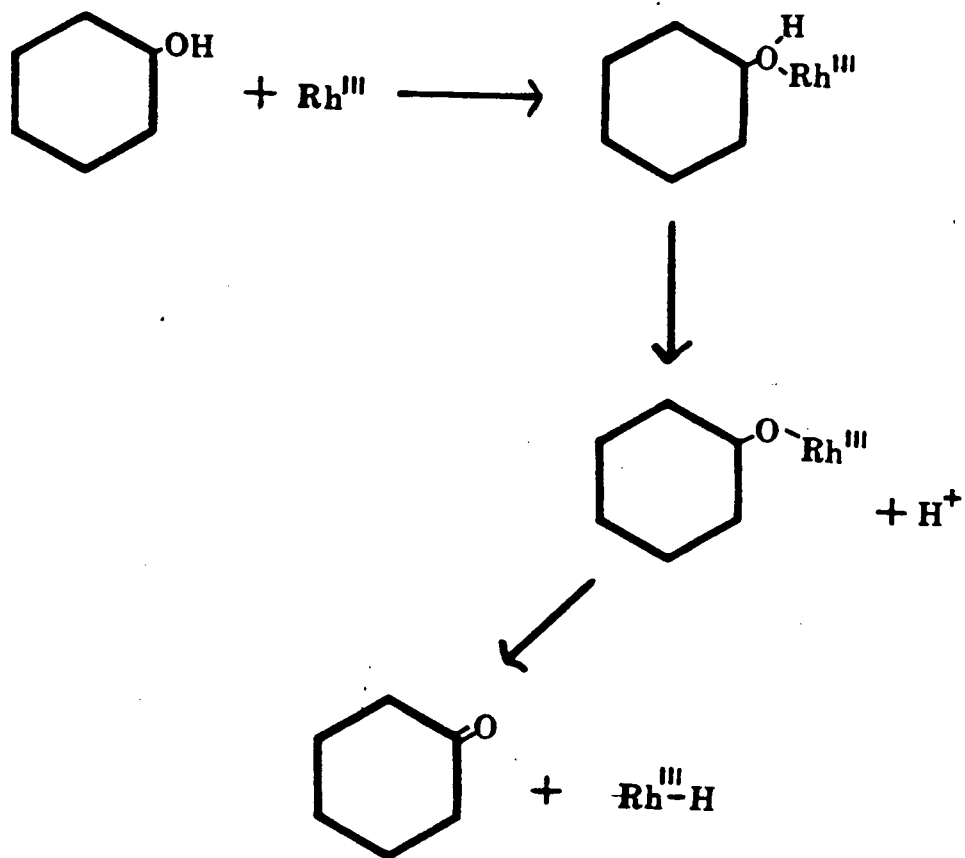
Fig (1). Mechanism (1).

In the second mechanistic pathway, cyclohexanol is catalytically oxidized to cyclohexanone with evolution of hydrogen (i.e. by dehydrogenation):

$$\text{(cyclohexanol)} \xrightarrow[O_2]{RhCl_3 - FeCl_3 - HCl} \text{(cyclohexanone)} + H_2$$
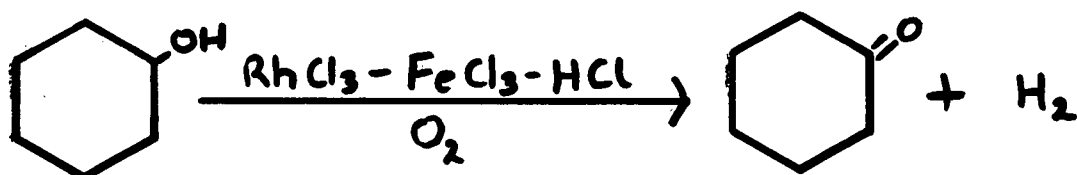
This mechanism would correspond to that shown above, at least to formation of the Rh(III) hydride, but then reaction of the hydride complex with protons produces molecular hydrogen and the active Rh(III) species:

$$Rh(III)-H \xrightarrow{H^+} Rh(III) + H_2$$
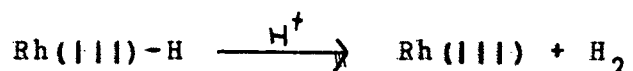
In the case of a Rh(III) hydride, there is also the possibility of the reduction of Rh(III) to Rh(I) by reductive elimination of a proton:

$$Rh(III)-H \longrightarrow Rh(I) + H^+$$
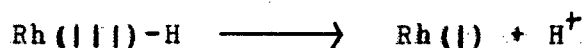
Further, there would then probably be production of rhodium metal formed by disproportionation of Rh(I)[9]:

$$2Rh(I) \longrightarrow Rh(0) + Rh(II)$$
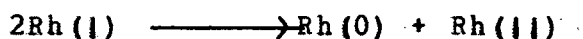
Loss of rhodium(III) via these reactions would suppress the

catalytic oxidation cycle. However, in the presence of iron in the ferric state, the Rh(I) could presumably be reoxidized to Rh(III), the ferric iron being reduced to the ferrous state:

$$Rh(I) + 2Fe(III) \longrightarrow 2Fe(II) + Rh(III)$$
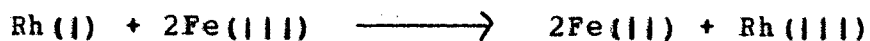
Regeneration of the iron (III) by passing oxygen through the solution appeared likely since oxidation of Fe(II) by molecular oxygen is known to occur in aqueous systems, and is dependent on the acidity of the solution.

$$2H^+ + 2Fe(II) \xrightarrow{O_2} 2Fe(III) + 2H_2O$$
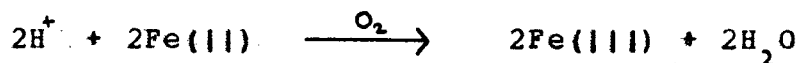
The overall process for regeneration of the Rh(III) can thus be represented as:

$$Rh(I) + 2H^+ + 1/2O_2 \longrightarrow Rh(III) + H_2O$$
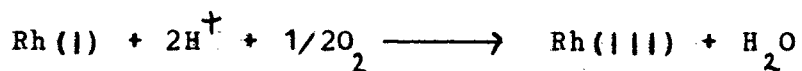
Although protons are liberated in the first stage of this mechanism, their concentration would be expected to be small, particularly as protons are consumed in the re-oxidation of iron to the Fe(III) state; this suggested that this mechanism might be facilitated by the addition of concentrated hydrochloric acid to the system. The dehydrogenation mechanism is in future referred to as reaction (2).

It was initially hoped that oxygen could be used as a direct oxidant for Rh(I) [10], but in the absence of Fe(III) the

systems were found to be inefficient.

Use of mild conditions is a feature of a homogeneous catalytic process and can lead to greater product selectivity which can have an important impact on energy and resource utilization. Homogeneous catalytic oxidation of alcohols would be of particular significance if it proceeded by dehydrogenation because of the economic value of the hydrogen gas as a fuel, especially if the reaction produced a high yield of ketone at low concentration of catalyst.

Preliminary unpublished results in this laboratory on the homogeneous catalytic oxidation of cyclohexanol to produce cyclohexanone using a combination of rhodium trichloride trihydrate, ferric chloride, and concentrated hydrochloric acid, with oxygen passing through the solution at 100-120deg and 1atm pressure had shown that a 30% conversion was attained after 6hr. However, no futher conversion was detected after an additional 12hr. This particular system was selected as the primary subject for detailed investigation and is the main topic of this thesis. Cyclohexanol was chosen for study because of the industrial importance of cyclohexanone, which is produced in large quantities by heterogeneous catalytic oxidative dehydrogenation of the alcohol at high temperature. Cyclohexanone is used as a solvent for cellulose acetate, nitrocellulose, natural resins, vinyl resins, crude rubber, waxes, fats, shellac and D.D.T. It is also converted into adipic acid which is used in the manufacture of nylon and urethan foams.

The approach to the detailed investigation was:

(1) to find the dependence of the system on such factors as

rhodium concentration, ferric chloride concentration, concentrated hydrochloric acid concentration, temperature etc.

(2) to elucidate the stoichiometry of the reaction by which oxidation occurs.

CHAPTER (2)

OXYGEN FLOW SYSTEMS

2.1 Experimental setup

The cyclohexanol sample was placed in a 100 ml three-necked round bottomed flask immersed in a constant temperature oil bath. A gas inlet tube passed through one neck and was held in place by a rubber septum. A condenser system was attached to the second neck, and the third exit was closed by a stopper, enabling samples to be withdrawn using a syringe whenever necessary.

In the early stages of this study, a major difficulty was found to arise from an inefficient condenser system, which led to significant loss of sample, carried out by the oxygen flow. The condenser system finally used was five feet in length, the upper one third containing small glass beads. The coolant used was ice-cold water, which was siphoned through the condenser between two five-gallon reservoirs.

The oxygen entering the flask was dried by being passed through a column containing drierite. The gas was then presaturated with cyclohexanol and cyclohexanone by allowing the oxygen to bubble through a flask containing equal volumes of the alcohol and ketone. The flask containing the presaturation mixture was maintained at the same temperature as the oxygen leaving the condenser system.

It was found that using this arrangement for a typical reaction system after three hours of rapid oxygen flow, and

after allowing the condenser to drain, the loss in weight was of the order of 5%. This could be accounted for by (a) cyclohexanol remaining in the condenser (cyclohexanol is a viscous liquid at room temperature) and (b) loss due to conversion to the more volatile cyclohexene.

The oxygen flow was controlled by the valve on the storage cylinder and the flow rates could be measured by channeling a small portion of the flow through a bubbler located between the supply and the drying column. Using this arrangement, flow rates could be reproduced by adjusting the regulator until the desired flow measured in bubbles per second emerged through the bubbler.

The term rapid oxygen flow used frequently in this section refers to a reproducible steady stream of oxygen through the reaction mixture, and is at the same rate in each case.

The temperature of the reaction flask could be maintained to within 1deg.

Presaturation

Before using this experimental arrangement to study the conversion of cyclohexanol to cyclohexanone, it was important to show that cyclohexanone was not transfered into the reaction system from the presaturation flask in appreciable quantities. A sample of cyclohexanol (20ml, 190mmol) was placed in the reaction flask at 100deg. Using rapid oxygen flow through the system after 1/2hr analysis (vpc) showed the solution contained approximately 1% cyclohexanone. Very little transfer of either cyclohexanol, or cyclohexanone, would be expected considering the low vapour pressures at 20deg (cyclohexanol mp 24deg, bp 161.5deg. Cyclohexanone mp -16deg, bp 156deg).

Analysis of reaction mixtures.

Samples (1-2μl) were withdrawn by syringe and analysed using a Hewlett Packard Research Gas Chromatograph. The column used was 15% FFAP on CHROM W (high performance), 80-100 mesh. The column oven temperature was maintained at 90 deg. The fastest chart speed (2 in/min) was used to produce the largest possible areas.

Ratios of weights of components in reaction systems were determined by photocopying the vpc readout, and then accurately weighing the appropriate sections of paper.

The weight of a pure compound is proportional to the area enclosed in the vpc readout corresponding to that compound. Hence having established the relationships between ratios of areas and ratios of weights of the corresponding compounds by injecting standard solutions: (cyclohexanol/cyclohexanone, cyclohexanol/water, cyclohexanol/cyclohexene), the ratios of weights of components in a reaction mixture could be determined.

Purity of cyclohexanol

Vpc analysis showed the cyclohexanol contained 1-2% cyclohexanone. This could not have been easily removed by distillation as the alcohol and ketone have almost identical boiling points. Traces of water and cyclohexene were also found to be present. As water was found to be a product of the reactions studied it was not considered necessary to remove traces of water initially present.

Miscibility of liquid components

Cyclohexanol, cyclohexanone and cyclohexene are miscible in all proportions. Up to 2ml of water is miscible with 20ml cyclohexanol or 20ml of a solution containing 60% cyclohexanol and 40% cyclohexanone. Mixtures of cyclohexanol and concentrated hydrochloric acid appear miscible in all proportions.

2.2 The cyclohexanol-rhodium trichloride trihydrate concentrated hydrochloric acid system.

The reaction mixture (cyclohexanol 20ml,190mmol; rhodium trichloride trihydrate 0.128g,0.302mmol; concentrated hydrochloric acid 0.10ml) was investigated at 100deg with rapid oxygen flow. The solution was initially red as the rhodium trichloride trihydrate dissolved. After 1hr the solution was dark reddish-brown and rhodium metal had been deposited as a black residue. The conversion to cyclohexanone was 6% after 1/2 hr and 10% after 1hr. The water content after 1hr was 0.3g,17mmol. No cyclohexene was produced.

2.3 The cyclohexanol-ferric chloride concentrated hydrochloric acid system.

The reaction mixture (cyclohexanol 20ml,190mmol; ferric chloride 1.5g,9.25mmol; concentrated hydrochloric acid 0.10ml) was investigated at 100deg with rapid oxygen flow. After 1/2hr no conversion to cyclohexanone had occurred. The cyclohexene content was 9%. The water content was 0.2g,11mmol. The solution was initially dark green becoming dark brown after 1/2hr.

The system (cyclohexanol 20ml,190mmol; ferric chloride 4.0g,24.7mmol; concentrated hydrochloric acid 0.10ml) was studied at 100deg with rapid oxygen flow. After 1/2hr no cyclohexanone had been formed. There was 20% cyclohexene present in the mixture and 0.6g,33mmol water.

The system (cyclohexanol 20ml,190mmol; ferric chloride 1.5g,9.25mmol; concentrated hydrochloric acid 2.0ml) at 100deg with rapid oxygen flow produced no cyclohexanone after 1/2hr; there was 20% cyclohexene in the reaction mixture and 1.1g,61mmol water.

It therefore seems that no oxidation of cyclohexanol to cyclohexanone takes place in the absence of rhodium trichloride trihydrate. Cyclohexene is produced by the interaction of cyclohexanol with ferric chloride presumably by elimination of water:
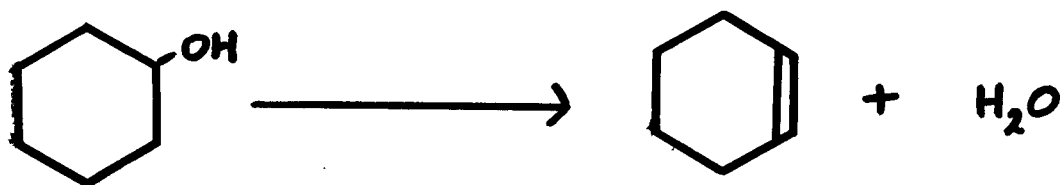
Increasing the ferric chloride content from 1.5g to 4.0g appears to increase the amount of cyclohexene and water present in the reaction mixture.

2.4 The cyclohexanol-rhodium trichloride trihydrate-ferric chloride-concentrated hydrochloric acid system

The following section describes in some detail the

oxidation of cyclohexanol to cyclohexanone using a combination of rhodium trichloride trihydrate and ferric chloride, and constitutes the major part of this thesis.

2.4a Dependence on initial ferric chloride concentration

A series of experiments was carried out at 100deg using rapid oxygen flow in which different amounts of ferric chloride were initially added to the following system: (cyclohexanol 20ml,190mmol; rhodium trichloride trihydrate 0.128g,0.302mmol; concentrated hydrochloric acid 0.10ml). The following initial weights of ferric chloride were used: 1.5g,9.25mmol; 2.0g,12.3mmol; 3.0g,18.5mmol; 4.0g,24.7mmol; 1.0g,1.54mmol; 0.25g,1.54mmol. In each case the solution was initially dark green, becoming darker as the reaction progressed. After 3hr the solutions were dark brown in colour, and contained some dark solid matter. The variation in composition was investigated for each mixture over a 3hr period by withdrawing samples at 1/2hr intervals. Each reacting system was found to contain cyclohexanol, cyclohexanone, cyclohexene and water. The ratio of weights of the organic components present was determined and expressed as a percentage of the total. The water content was determined as the total weight and hence the total number of moles of water present.

The rate of cyclohexanone formation over a 3hr period is shown for each amount of ferric chloride present in Graphs (1)-(6). Inspection of these graphs shows that the initial rate of reaction and the final yield are both dependent on the weight of ferric chloride used. Graphs (1),(2) and (5) corresponding to 1.5g, 2.0g and 1.0g of ferric chloride, respectively, are very

similar and it appears that there exists an optimum range for ferric chloride addition from 1.0-2.0g. In each case the reaction rate declines steadily as time progresses, and the production of cyclohexanone after 3hr is negligible, at which time there is approximately 40% cyclohexanone in the mixture.

When initial quantities of ferric chloride are in excess of this optimum range, the initial reaction rate is lowered and the cyclohexanone content after a 3hr period is reduced. This is illustrated in Graphs (3) and (4) corresponding to 3.0g and 4.0g of ferric chloride respectively.

Graph (6), corresponding to 0.25g ferric chloride, shows that for initial weights of ferric chloride substantially lower than 1.0g the initial reaction rate is reduced and the production of cyclohexanone appears to be terminated after 1.50hr when the system contains only 20% ketone.

For purposes of comparison, the results for these systems containing 0.25-4.0g ferric chloride are shown together in Graph (7). Results for 1.0g, 1.5g and 2.0g lie within the shaded envelope.

The system containing 1.5g ferric chloride, i.e. in the centre of the optimum range, will hereafter be refered to as system (1). The experiment using system (1) was repeated under the same conditions as above to show the reproducibility of the results. Graph (1a) shows the two sets of data corresponding to system (1) at 100deg and it can be seen that the points are reproducible to within 2%.

The experiment using system (1) was repeated using 20.0g,200mmol cyclohexanol instead of 20ml,190mmol. After 3hr
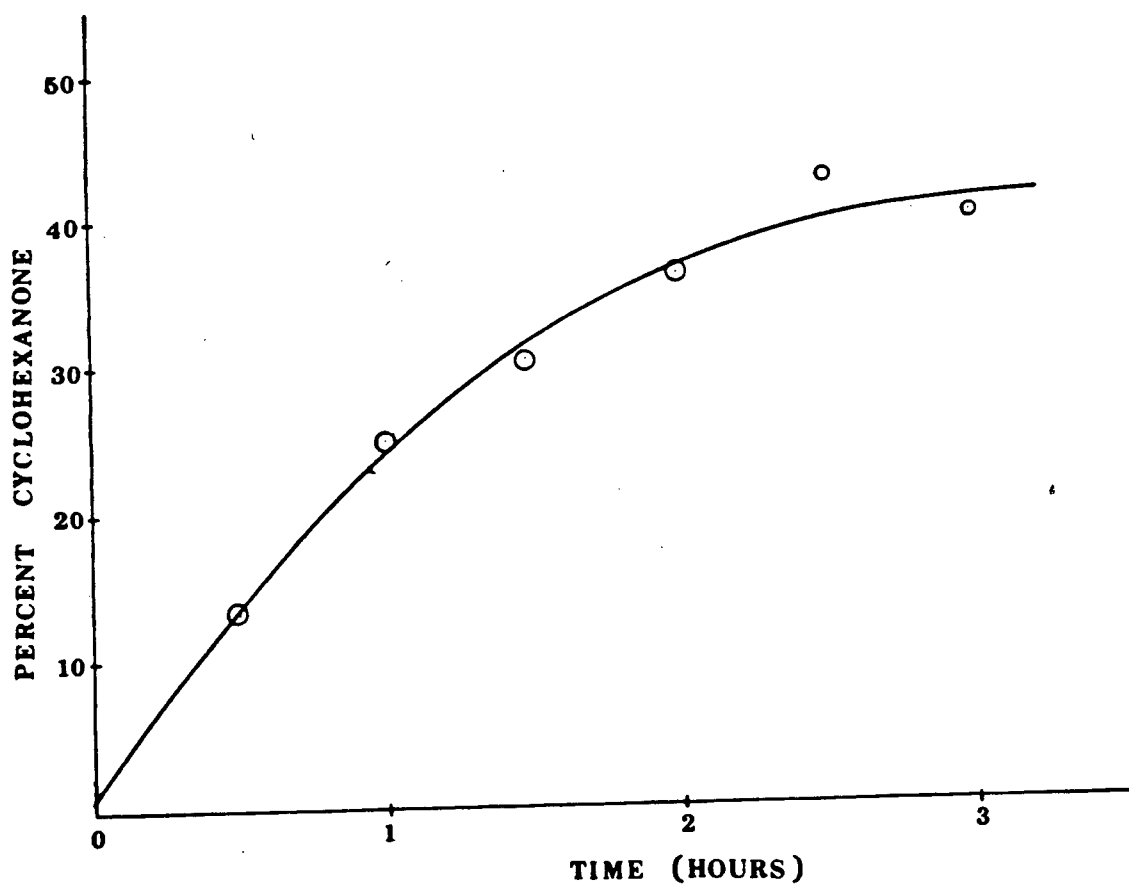
Graph (1). Rate of cyclohexanone formation for the system: Cyclohexanol (190mmol), $RhCl_3 3H_2O$ (0.302mmol), $FeCl_3$ (9.25mmol), HCl (0.10ml), at 100deg.
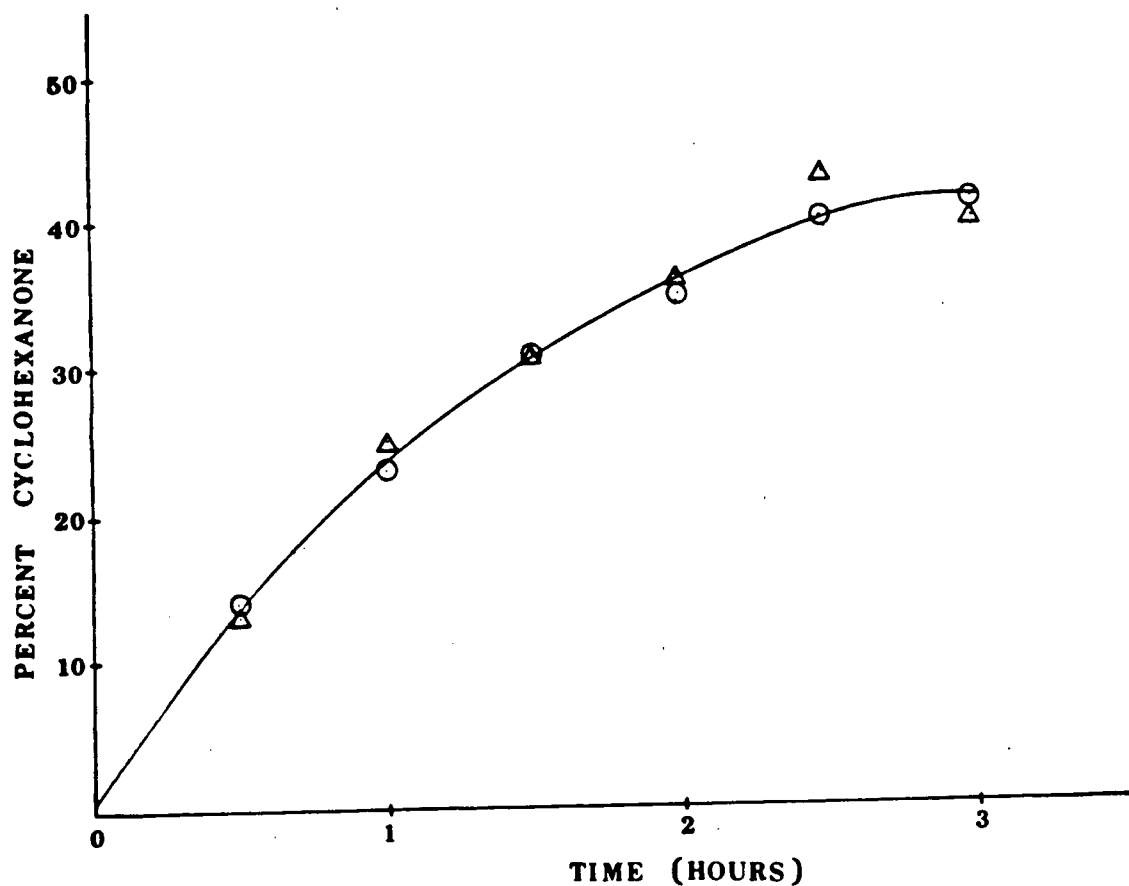
Graph (1a). Rate of cyclohexanone formation for the system: Cyclohexanol (190mmol), $RhCl_3 3H_2O$ (0.302mmol), $FeCl_3$ (9.25mmol), HCl (0.10ml), at 100deg. Reproducibility of results.
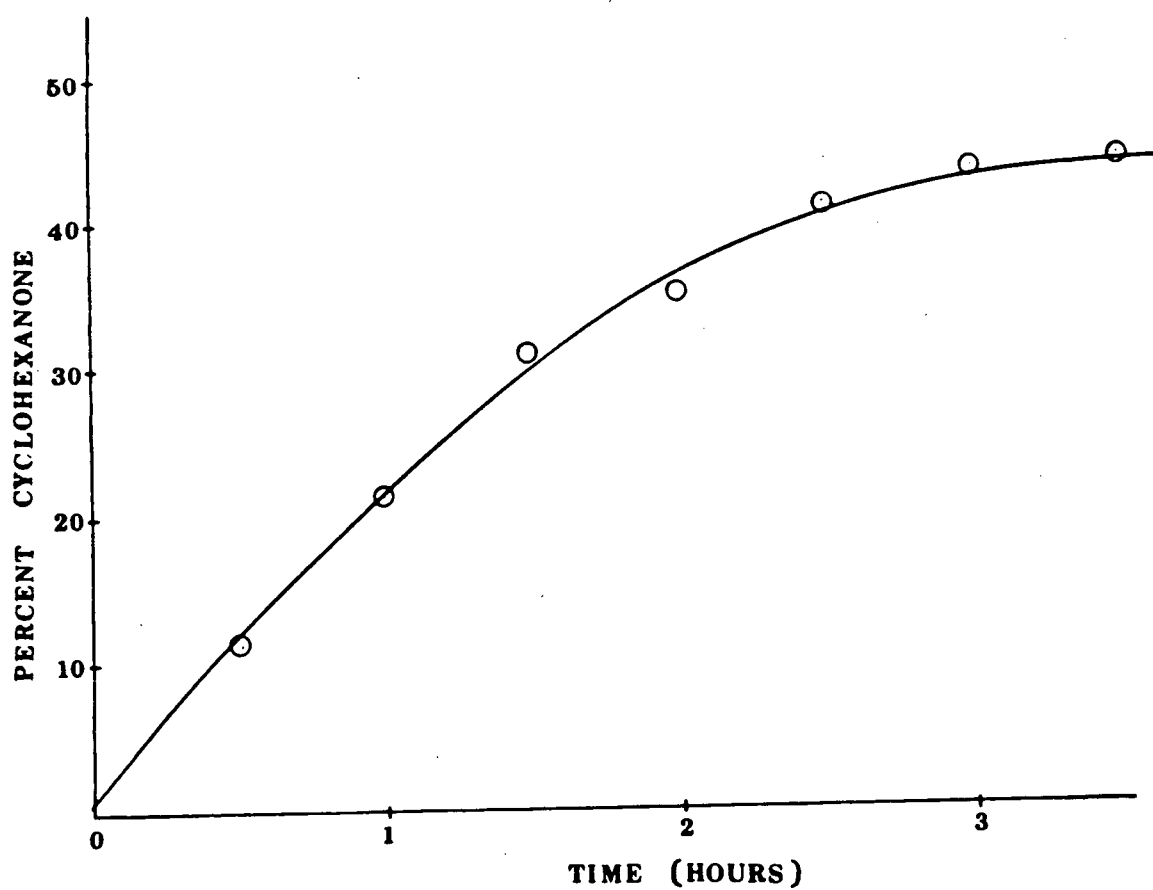
Graph (2). Rate of cyclohexanone formation for the system: Cyclohexanol (190mmol), RhCl$_3$3H$_2$O (0.302mmol), FeCl$_3$ (12.3mmol) HCl (0.10ml), at 100deg.
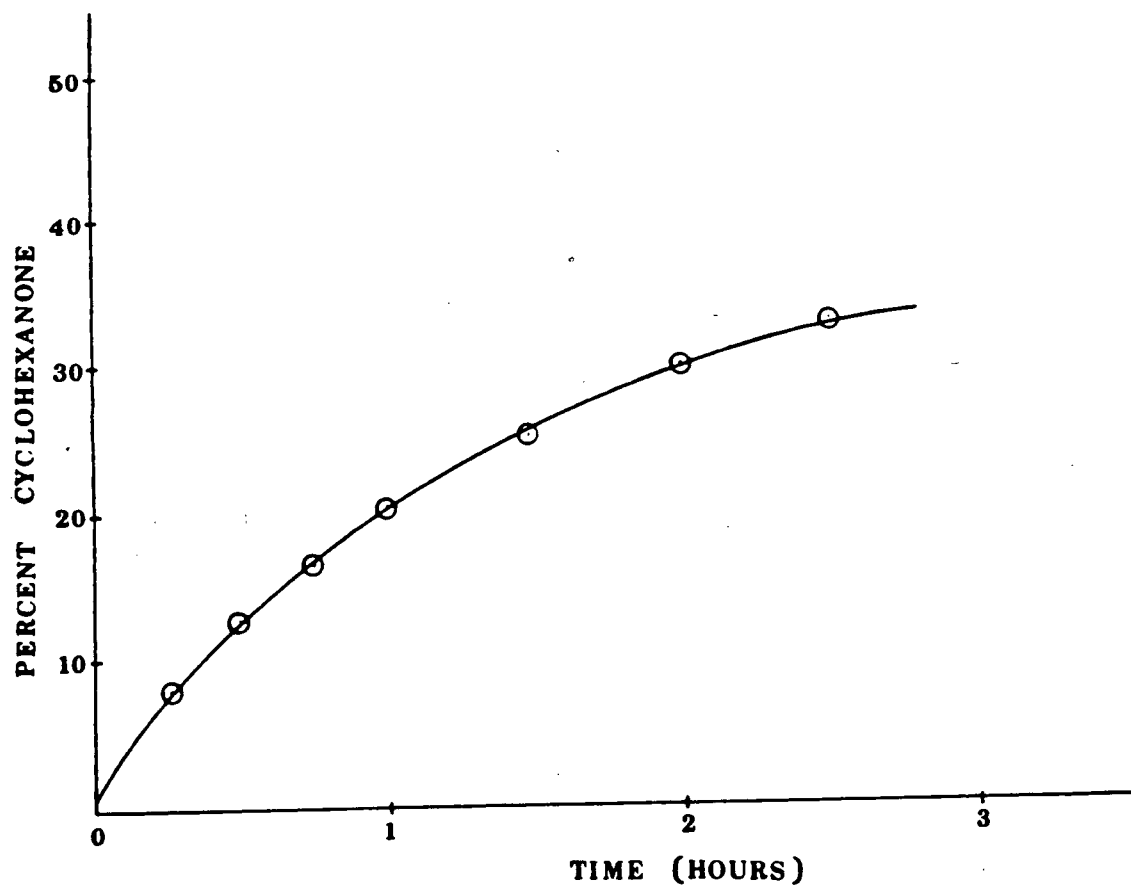
Graph (3). Rate of cyclohexanone formation for the system: Cyclohexanol (190mmol), RhCl₃3H₂O (0.302mmol), FeCl₃ (18.5mmol) HCl (0.10ml), at 100deg.
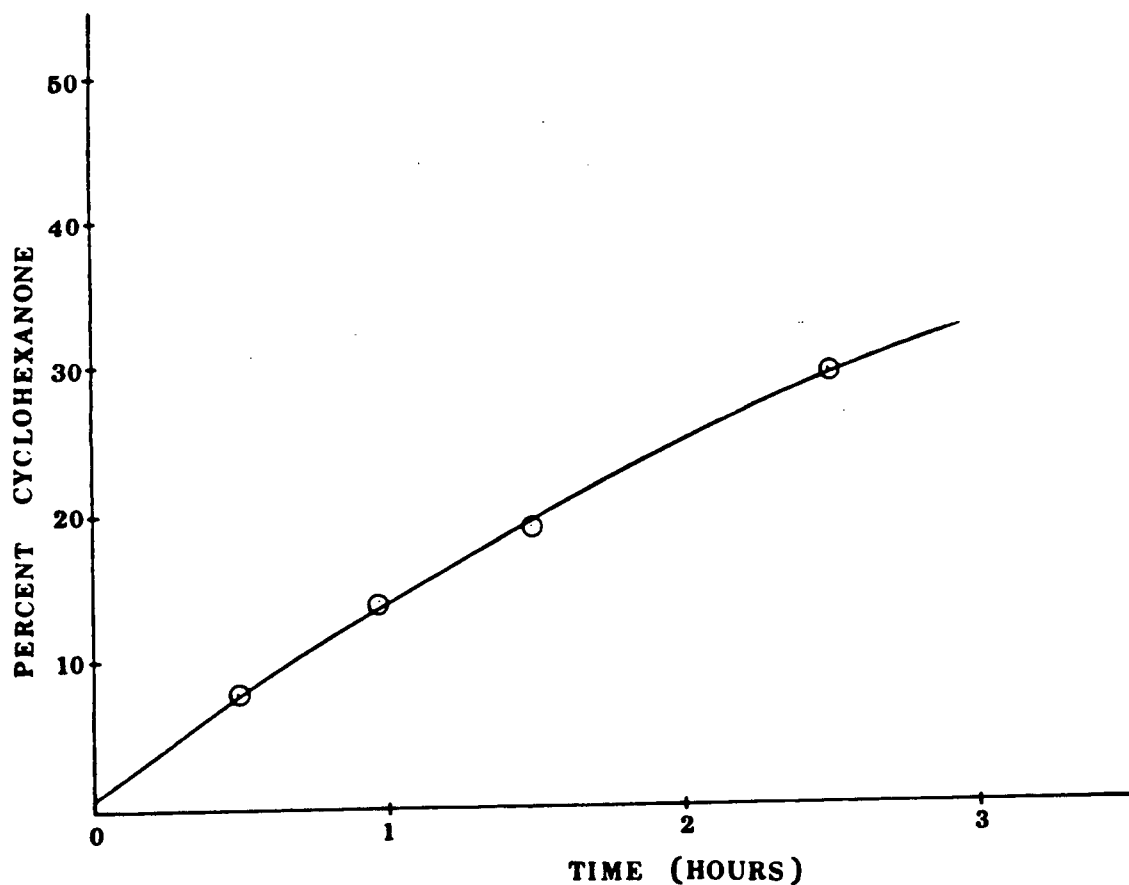
Graph (4). Rate of cyclohexanone formation for the system: Cyclohexanol (190mmol), $RhCl_3 3H_2O$ (0.302mmol), $FeCl_3$ (24.7mmol) HCl (0.10ml), at 100deg.
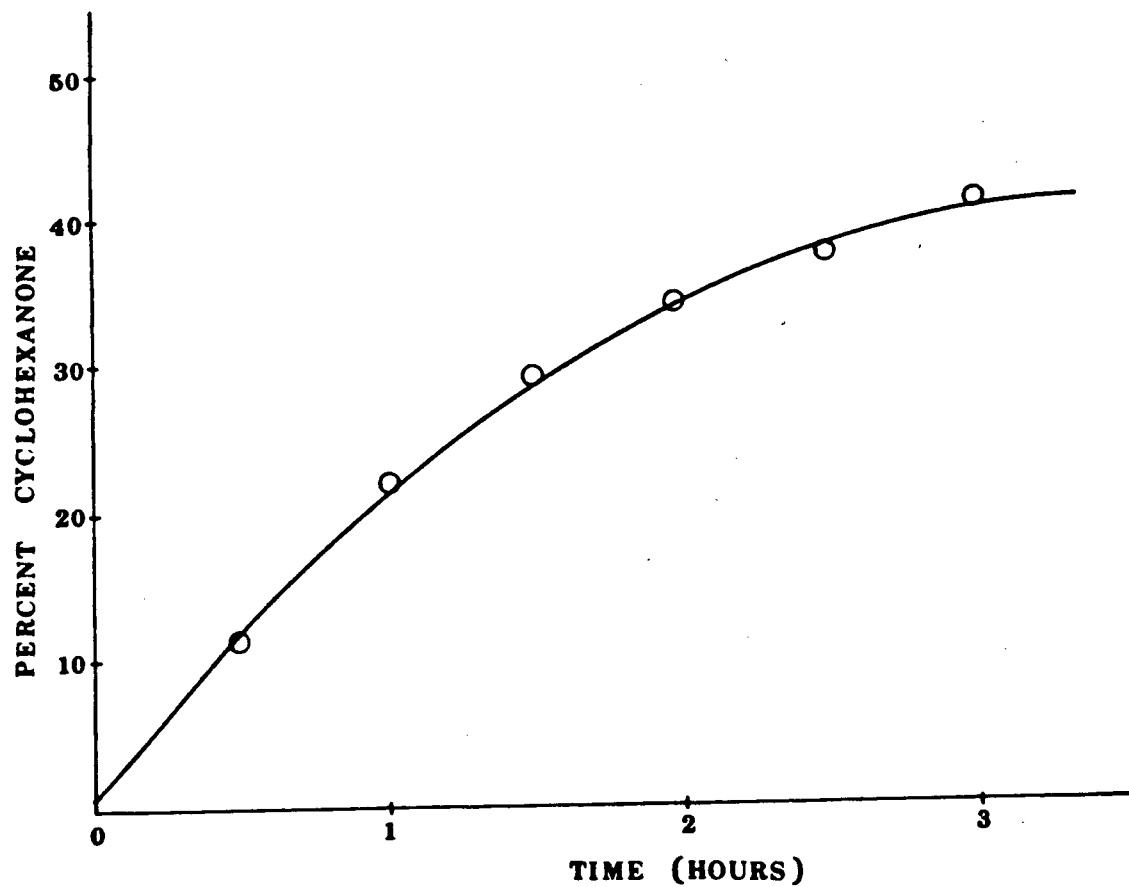
Graph (5). Rate of cyclohexanone formation for the system: Cyclohexanol (190mmol), $RhCl_3 3H_2O$ (0.302mmol), $FeCl_3$ (6.17mmol) HCl (0.10ml), at 100deg.
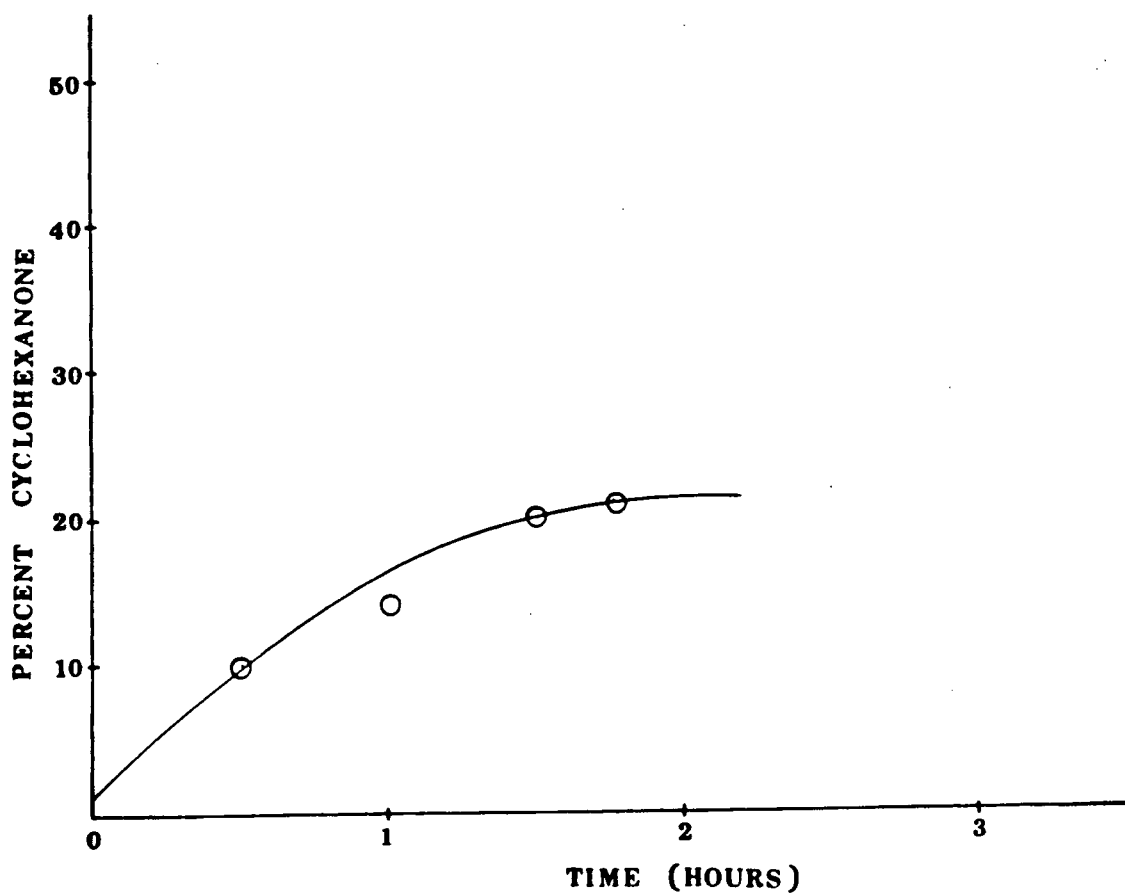
Graph (6). Rate of cyclohexanone formation for the system:
Cyclohexanol (190mmol), $RhCl_3 3H_2O$ (0.302mmol), $FeCl_3$ (1.54mmol)
HCl (0.10ml), at 100deg.
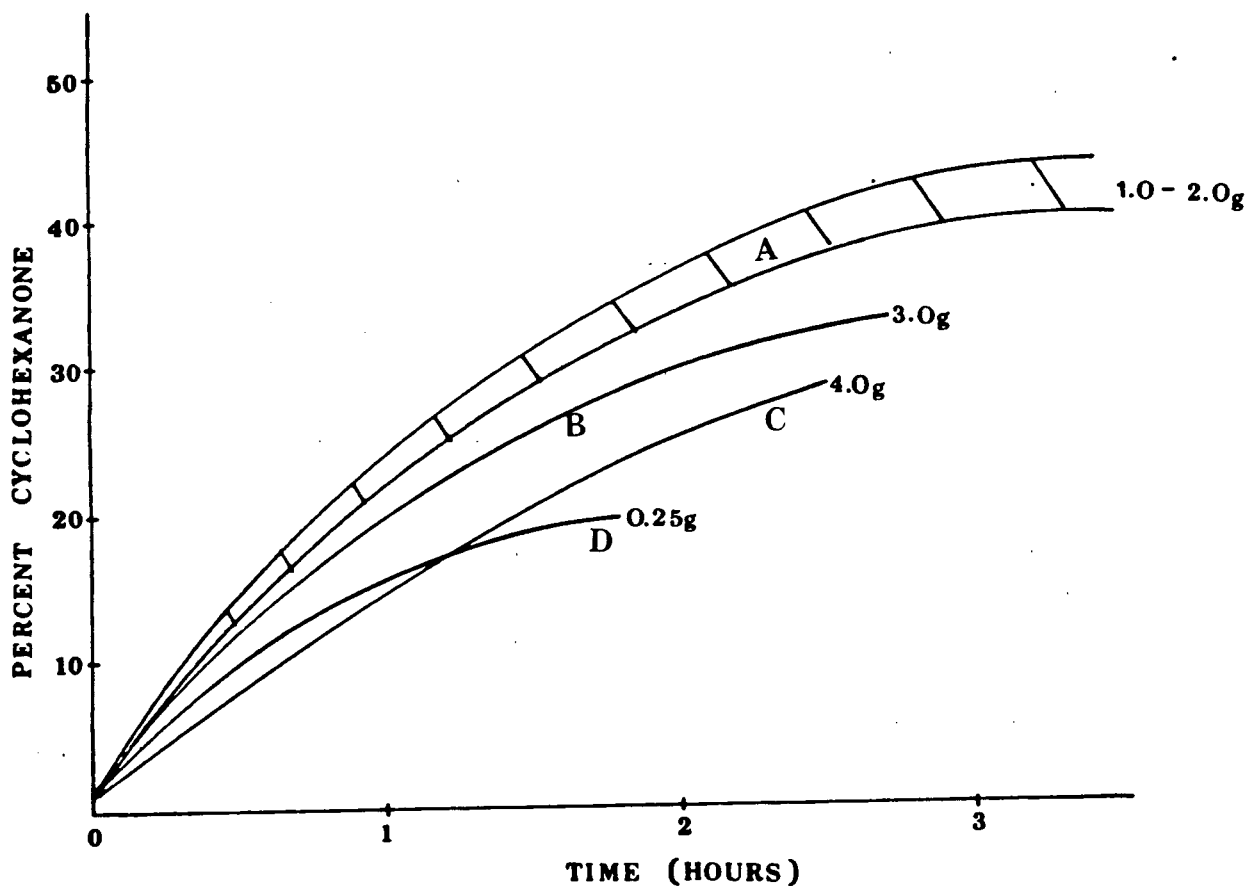
Graph (7). Rates of cyclohexanone formation for the systems:
Cyclohexanol (190mmol), RhCl$_3$3H$_2$O (0.302mmol), FeCl$_3$ A: (6.17-
12.3mmol), B: (18.5mmol), C: (24.7mmol), D: (1.54mmol):
HCl (0.10ml), at 100deg.

the mixture contained 40% cyclohexanone. The dark brown solution was filtered. The filtrate weighed 19.9g and the solid brown residue weighed 0.17g after drying. The residue was insoluble in acetone but partially soluble in concentrated hydrochloric acid to give a green-yellow solution and a dark residue.

Water and cyclohexene

The nature of the vpc readout made it more difficult to determine accurately the amount or ratio of these components present as the chromatograph was operated under conditions most suited to give accurate alcohol/ketone ratios. However, the measurements corresponding to water and cyclohexene are probably of sufficient accuracy to reveal trends in their effect on the oxidation reaction. It was found for this series of experiments that both the cyclohexene and the water content of the systems remained approximately constant during the course of each experiment. Results for this series are shown in Table (1).

The importance of water and cyclohexene are discussed in detail in sections 2.4d and 2.4e.

2.4b Dependence on rhodium trichloride trihydrate concentration

A series of experiments was carried out in which different initial amounts of rhodium trichloride trihydrate were introduced into systems containing ferric chloride in the optimum range. The experiments were carried out at 100deg with rapid oxygen flow, and each contained (cyclohexanol 20ml,190mmol; ferric chloride 1.5g,9.25mmol; concentrated hydrochloric acid 0.10ml).

Table (1)

Weight of ferric chloride		%Cyclohexene	Water content	
(g)	(mmol)		(g)	(mmol)
0.25	1.54	1-2	<0.2	<11
1.0	6.17	4-5	o.3	17
1.5	9.25	6-9	0.5-0.7	28-39
2.0	12.3	11-13	0.5-0.7	28-39
3.0	18.5	14-16	0.5-0.7	28-39
4.0	24.7	12-14	1.0	56

Table (1). Variation in water and cyclohexene content with ferric chloride concentration for the system: Cyclohexanol (190mmol), $RhCl_3 3H_2O$ (0.302mmol), HCl (0.10ml), at 100deg.

Compositions of systems containing 0.050g, 0.118mmol; and 0.256g, 0.604mmol rhodium trichloride trihydrate were studied. The variation of percentage cyclohexanone in the reaction mixtures is plotted in Graph (8), together with the corresponding data for system (1).

There appears to be a general trend of increased initial reaction rate and increased conversion to ketone after 3hr as the initial concentration of rhodium trichloride trihydrate in the system is raised.

However, the increase in the final yield of cyclohexanone on doubling the initial weight of rhodium trichloride trihydrate from 0.128g to 0.256g is small. The variation in rhodium trichloride trihydrate content did not appear to greatly influence the cyclohexene content of the reaction mixtures.

2.4c Dependence on acidity

Acidity scale.

A scale of acidity in cyclohexanol was established by employing a combination glass electrode and pH meter. The acidity of a homogeneous mixture of 20ml cyclohexanol and 0.10ml concentrated hydrochloric acid was arbitrarily fixed at 3.20. Further additional volumes of concentrated hydrochloric acid were added to the mixture and meter readings taken after thorough mixing. Measurements were taken at 20deg and are presented in Table (2).

Graph (9) is a plot of the meter readings against the value Log (total volume HCl / total volume of solution). This gives a
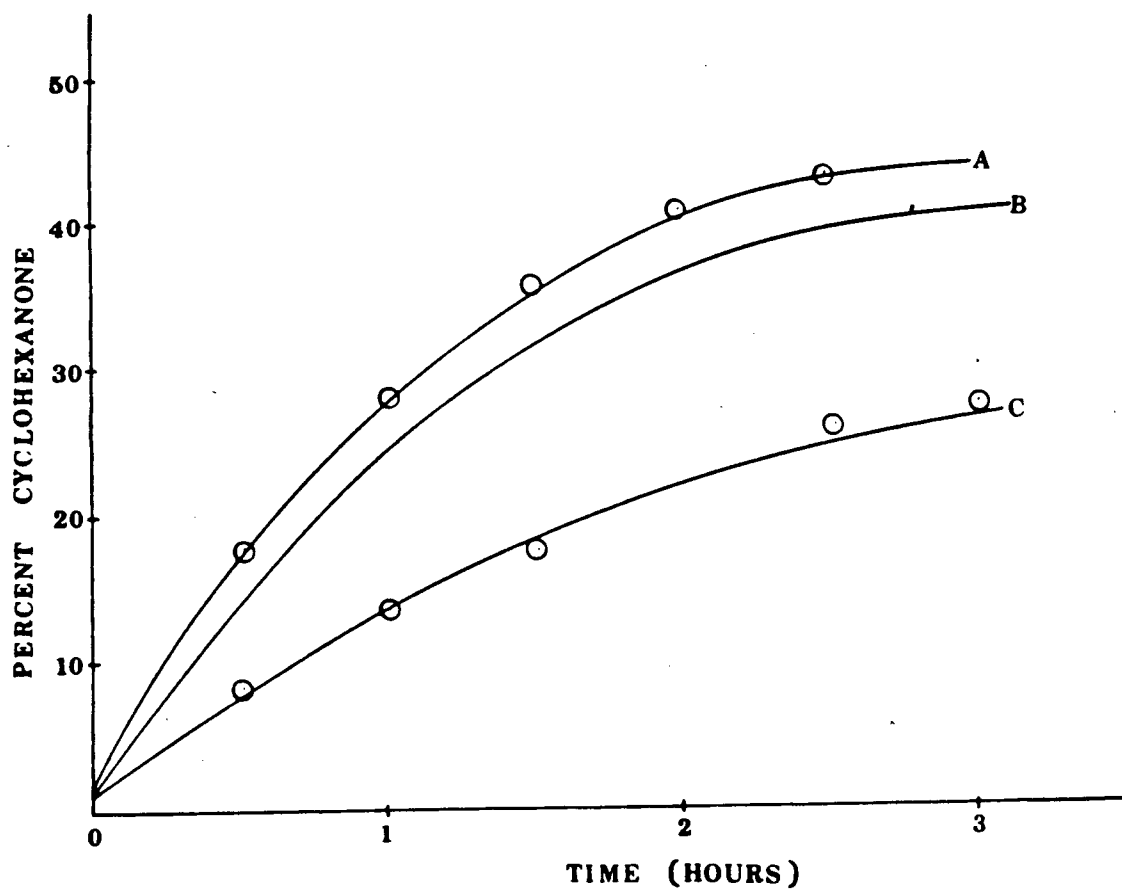
Graph (8). Rates of cyclohexanone formation for the systems: Cyclohexanol (190mmol), $RhCl_3 3H_2O$ A: (0.604mmol), B: (0.302mmol), C: (0.118mmol); $FeCl_3$ (9.25mmol), HCl (0.10ml), at 100deg.

Table (2)

Total volume conc HCl added to 20ml alcohol V (HCl) (ml)	Log $\dfrac{V(HCl)}{V(Total)}$	Meter reading pX
0.10	2.30	3.20
0.20	2.00	2.975
0.30	1.83	2.825
0.40	1.71	2.75
0.50	1.61	2.65
0.60	1.54	2.60
0.75	1.44	2.525
2.00	1.04	2.30
5.00	0.70	1.95
20.00	0.30	1.70

Table (2). Acitity of cyclohexanol/concentrated HCl mixtures.
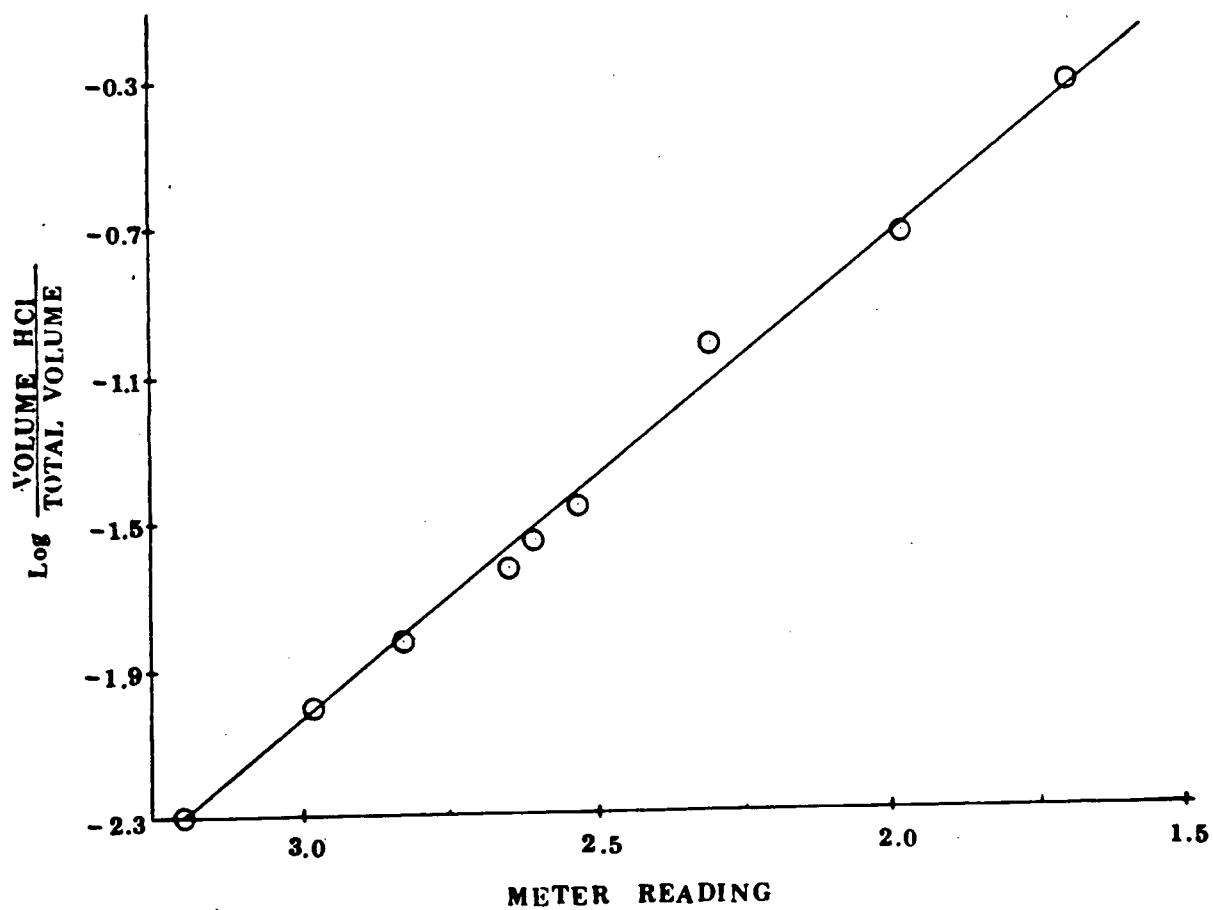
Graph (9). Acidity scale.

straight line and thus the system is behaving in a manner similar to the HCl-water system, and the meter readings can be considered analogous to the pH scale of an aqueous system. These meter readings for cyclohexanol systems are hereafter referred to as the pX. All readings were taken at 20deg.

Using this scale of acidity, cyclohexanol has a pX of 7.20 and cyclohexanone 8.00.

In order to have an approximate value of the acidity at the start of a typical cyclohexanol oxidation, mixtures of varying amounts of ferric chloride were added to 20ml,190mmol cyclohexanol and 0.10ml concentrated hydrochloric acid and each mixture heated to 100deg for approximately 1/2hr with rapid oxygen flow. The mixtures were then cooled to 20deg and the pX measured. In each case a residue was present. The results are shown in Table (3).

The effect of adding water to these systems was studied using the solution initially containing 1.5g,9.25mmol ferric chloride. Results are presented in Table (4).

The high acidities produced by the ferric chloride-cyclohexanol systems presumably arise from equilibria of the type:

$$Fe(C_6H_{11}OH) \rightleftharpoons Fe(C_6H_{11}OH)_{n-m}(C_6H_{11}O)_m + mH^+$$

$$\text{or} \quad Fe(III) + xC_6H_{11}OH \rightleftharpoons Fe(III)(C_6H_{11}O)_x + xH^+$$
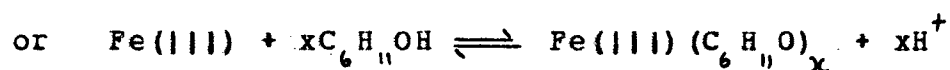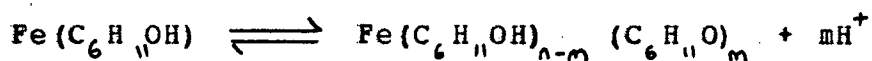
Addition of ferric chloride to cyclohexanone also produces solutions of high acidity. On mixing 1.50g,9.25mmol ferric

Table (3)

Weight of ferric chloride		pX value
(g)	(mmol)	
0.25	1.54	1.70
1.50	9.25	1.70
4.0	24.7	1.70

Table (3). Acidity of cyclohexanol/$FeCl_3$ mixtures.

Table (4)

Total water added		pX value
(ml)	(mmol)	
0	0	1.70
0.50	28	2.45
1.00	56	3.00

Table (4). Effect of water on acidity of the system: Cyclohexanol (190mmol), $FeCl_3$ (9.25mmol), HCl (0.10ml).

chloride and 20ml,190mmol cyclohexanone a tarry brown residue was formed and the solution had a pX value of 0.0. The effect of adding water to this solution is similar to the cyclohexanol system as shown in Table (5).

The high acidity of the ferric chloride-cyclohexanone mixture indicates a very strong interaction involving release of protons. Low concentrations of the enol form of cyclohexanone are known to exist in equilibrium with the keto form:

The interaction of ferric chloride with cyclohexanone could be explained in terms of equilibria of the type:

$$Fe(C_6H_9OH) \rightleftharpoons Fe(C_6H_9OH)_{n-m}(C_6H_9O) + mH^+$$
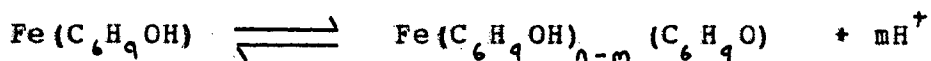
Or:
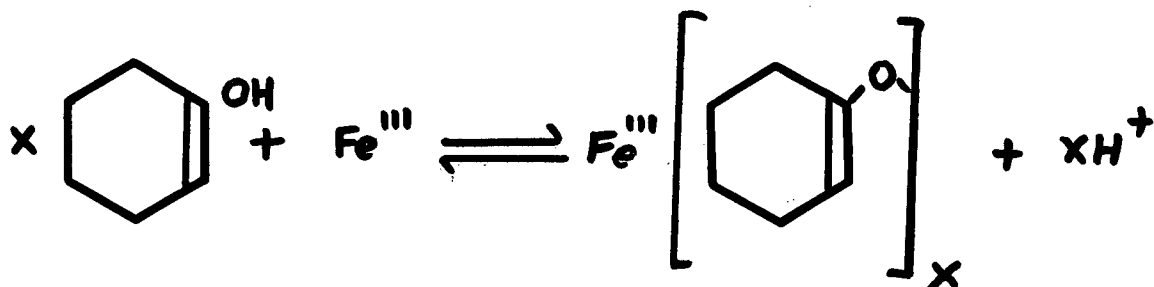
Interaction between the carbon-carbon double bond of the ring and the metal center is also possible.

Table (5)

Total water added		pX value
(ml)	(mmol)	
0	0	0.0
0.50	28	1.40
1.00	56	2.40
2.00	112	3.00

Table (5). Effect of water on acidity of the system: Cyclohexanone (190mmol), $FeCl_3$ (9.25mmol), HCl (0.10mol).

It can be readily seen from the above data that water greatly reduces the acidity of ferric chloride-cyclohexanol and ferric chloride-cyclohexanone mixtures. It is reasonable to conclude that the interaction between the metal salt and the alcohol or ketone is much weaker in the presence of water (see 2.4d below).

A series of experiments was carried out to determine how the acidity of a typical reaction mixture varied during the conversion of cyclohexanol to cyclohexanone. The system studied in each case had composition (cyclohexanol 20ml, 190mmol; rhodium trichloride trihydrate 0.128g, 0.302mmol; ferric chloride 1.5g, 9.25mmol; concentrated hydrochloric acid 0.10ml), i.e. System (1) at 100deg with rapid oxygen flow. Four different mixtures were heated at 100deg for 1/2hr, 1.00hr, 1.75hr, and 2.50hr respectively. Each was then cooled to 20deg and the acidity measured. The results are shown in Table (6) and are also represented in Graph (10).

Analysis of these mixtures at the times indicated above give compositions in good agreement with the expected values from Graph (1a). The above measurements show a steady decrease in acidity as the % cyclohexanone increases (i.e. as the rate of oxidation decreases). The change in acidity over a 2.50hr period is equivalent to the change in a solution containing 20ml concentrated hydrochloric acid in 20ml cyclohexanol to a solution containing less than 0.10ml concentrated hydrochloric acid in 20ml cyclohexanol.

Final acidity measurements on the corresponding mixtures containing 3.0g, 18.5mmol ferric chloride and 0.25g, 1.54mmol

Table (6)

Time (hrs)	pX value
0	1.70
0.5	1.85
1.0	2.10
1.75	2.40
2.50	3.95

Table (6). Variation of acidity with time for the system: Cyclohexanol (190mmol), $RhCl_3 3H_2O$ (0.302mmol), $FeCl_3$ (9.25mmol), HCl (0.10ml), at 100deg.
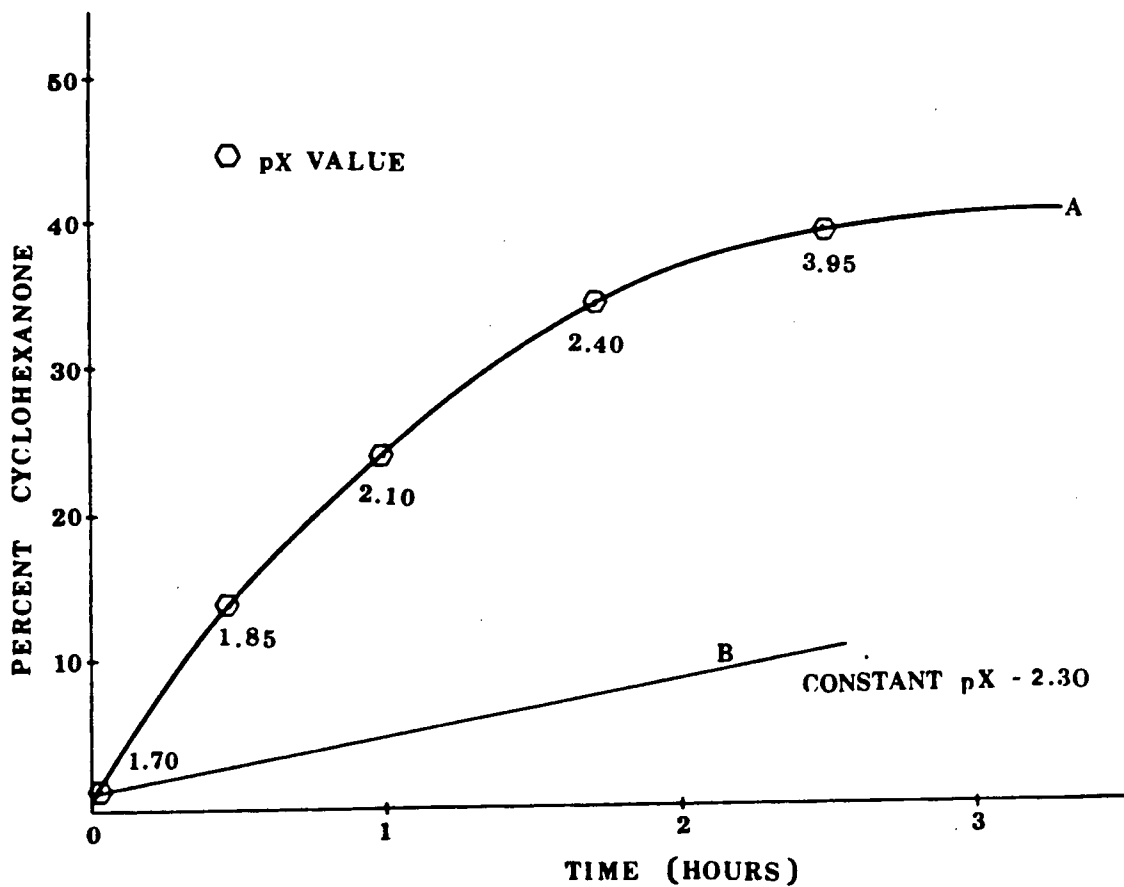
Graph (10). Variation in acidity for the systems:

Cyclohexanol (190mmol), $RhCl_3 3H_2O$ (0.302mmol), $FeCl_3$ (9.25mmol),

A: HCl (0.10ml), B: HCl (2.0ml).

ferric chloride (i.e. After 3hr and 1.50hr, respectively, also give pX values in the range 3.90-4.00.

These results suggested the possibility of producing an increased yield by addition of a large amount of concentrated hydrochloric acid to the system in an attempt to maintain a high acidity over a longer period. The system (cyclohexanol 10ml,95mmol; rhodium trichloride trihydrate 0.128g,0.302mmol; ferric chloride 1.5g,9.25mmol; concentrated hydrochloric acid 10.0ml) was studied at 100deg with rapid oxygen flow. The initial acidity (pX=1.70) fell to pX=2.0 after 1hr, slightly below the value for system (1) after the same time period (see Graph 9). The conversion to cyclohexanone however was only 4% and the cyclohexene content 28%.

The system (cyclohexanol 20ml,190mmol; rhodium trichloride trihydrate 0.128g,0.302mmol; concentrated hydrochloric acid 2.0ml) at 100deg with rapid oxygen flow was also studied over a 3hr period . The results are presented in Table (7). This system appears to maintain a constant acidity (pX=2.30) throughout the reaction. The rate of cyclohexanone formation is shown plotted in Graph (10). Inspection shows this plot is almost linear. However the slope is considerably less than the reaction rate for system (1), at the corresponding pX value (see Graph 10). These results indicate that other factors besides the acidity have a significant effect on the conversion of cyclohexanol to cyclohexanone, and in particular the water and cyclohexene content of a particular mixture.

It is also apparent that addition of concentrated hydrochloric acid to a system containing ferric chloride is

Table (7)

Time (hrs)	% Cyclohexanone	% Cyclohexene	Water content (g)	pX
0.5	2	14	1.0	2.30
1.0	4	17		
1.5	6	21		
2.0	8	22	1.5	
2.5	10			
3.0	10			2.30

Table (7). Variation in cyclohexanone content, cyclohexene content, water content, and acidity for the system: Cyclohexanol (190mmol), $RhCl_3 3H_2O$ (0.302mmol), $FeCl_3$ (9.25mmol), concentrated HCl(2.0ml) at 100deg.

unnecessary to produce an acidic medium as required for mechanism (2). Indeed, addition of concentrated hydrochloric acid in quantities between 0.10ml and 10.0ml to a ferric chloride-cyclohexanol mixture probably produces a lowering of pX value because of the water introduced. The addition of 0.10ml concentrated hydrochloric acid to the mixtures studied in 2.4a would therefore appear to be unnecessary. It may be predicted therefore that the difference between mixtures studied in 2.4a and the corresponding mixtures in which no concentrated hydrochloric acid is added, would be small, as the amount of water contained in 0.10ml concentrated hydrochloric acid is small.

The system (cyclohexanol 20ml, 190mmol; rhodium trichloride trihydrate 0.128g,0.302mmol; ferric chloride 1.5g,9.25mmol) at 100deg with rapid oxygen flow was studied and compared with the corresponding system in which 0.10ml concentrated hydrochloric acid was added. The results are plotted in Graph (11). It appears that the initial reaction rate is somewhat higher when the concentrated hydrochloric acid is omitted, but the final yield is very similar (2% higher).

Comparison of the system (cyclohexanol 20ml,190mmol; rhodium trichloride trihydrate 0.128g,0.302mmol; ferric chloride 0.25g,1.54mmol;) at 100deg with rapid oxygen flow, with the corresponding system initially containing 0.10ml concentrated hydrochloric acid (Graph 12), illustrates the same trend - a somewhat higher initial reaction rate but a very similar final yield of cyclohexanone.

The system (cyclohexanol 20ml,190mmol; rhodium trichloride
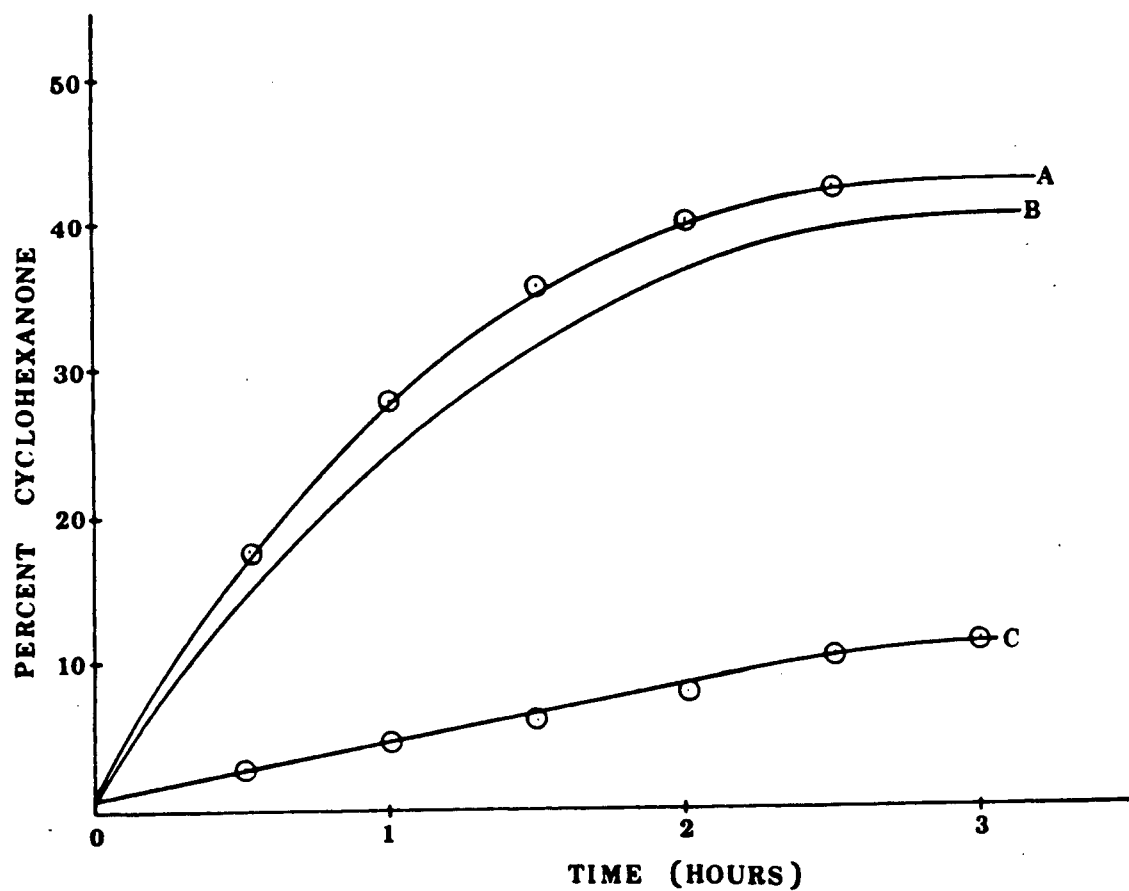
Graph (11). Rates of cyclohexanone formation for the systems:
Cyclohexanol (190mmol), $RhCl_3 3H_2O$ (0.302mmol), $FeCl_3$ (9.25mmol),
HCl A: (zero), B: (0.10ml), C: (2.0ml); at 100deg.
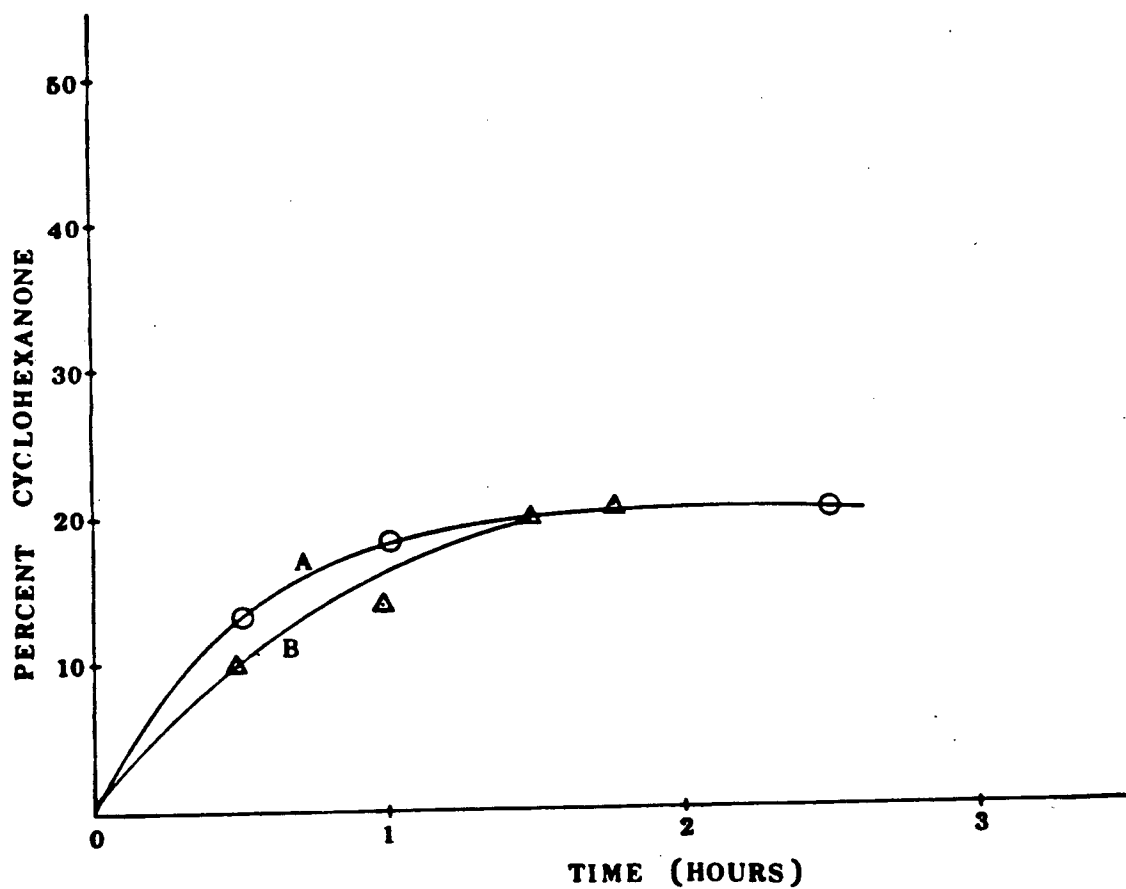
Graph (12). Rates of cyclohexanone formation for the systems:
Cyclohexanol (190mmol), $RhCl_3 3H_2O$ (0.302mmol), $FeCl_3$ (1.54mmol),
HCl A: (zero), B: (0.10ml), at 100deg.

trihydrate 0.128g,0.302mmol; ferric chloride 2.0g,12.3mmol) with rapid oxygen flow at 100deg is almost identical with the corresponding system with 0.10ml concentrated hydrochloric acid introduced initially (Graph 13).

2.4d Dependence on water content

In the previous section it was suggested that addition of large quantities of concentrated hydrochloric acid to a reaction mixture may cause a supression of the oxidation of cyclohexanol to cyclohexanone, partly because of the introduction of water into the system. Table (1) shows that for the reaction mixture (cyclohexanol 20ml,190mmol; rhodium trichloride trihydrate 0.128g,0.302mmol; ferric chloride 1.5g,9.25mmol; concentrated hydrochloric acid 0.10ml) at 100deg and rapid oxygen flow the water content remains approximately constant at approximately 0.6g,33mmol. The effect of increasing this water content by initial addition of 1.0g,56mmol water, and also presaturating the oxygen with water at 20deg, was studied for the same system. The production of cyclohexanone over a 2hr period is shown in Graph (14). At the end of this period it can be seen there was about 4% cyclohexanone present, at which time the water content had risen to about 2g,112mmol.

Another experiment was carried out in which 2.0g,112mmol water was initially added to System (1) at 100deg with rapid oxygen flow (no presaturation). The production of cyclohexanone over a 4.50hr period is shown in Graph (14). After 1.25hr the water content had fallen to 1g,56mmol. This was apparently the result of removal of water by the flow. As can be seen the

Graph (13). Rates of cyclohexanone formation for the systems: Cyclohexanol (190mmol), $RhCl_3 3H_2O$ (0.302mmol), $FeCl_3$ (12.3mmol), HCl A: (zero), B: (0.10ml); at 100deg.
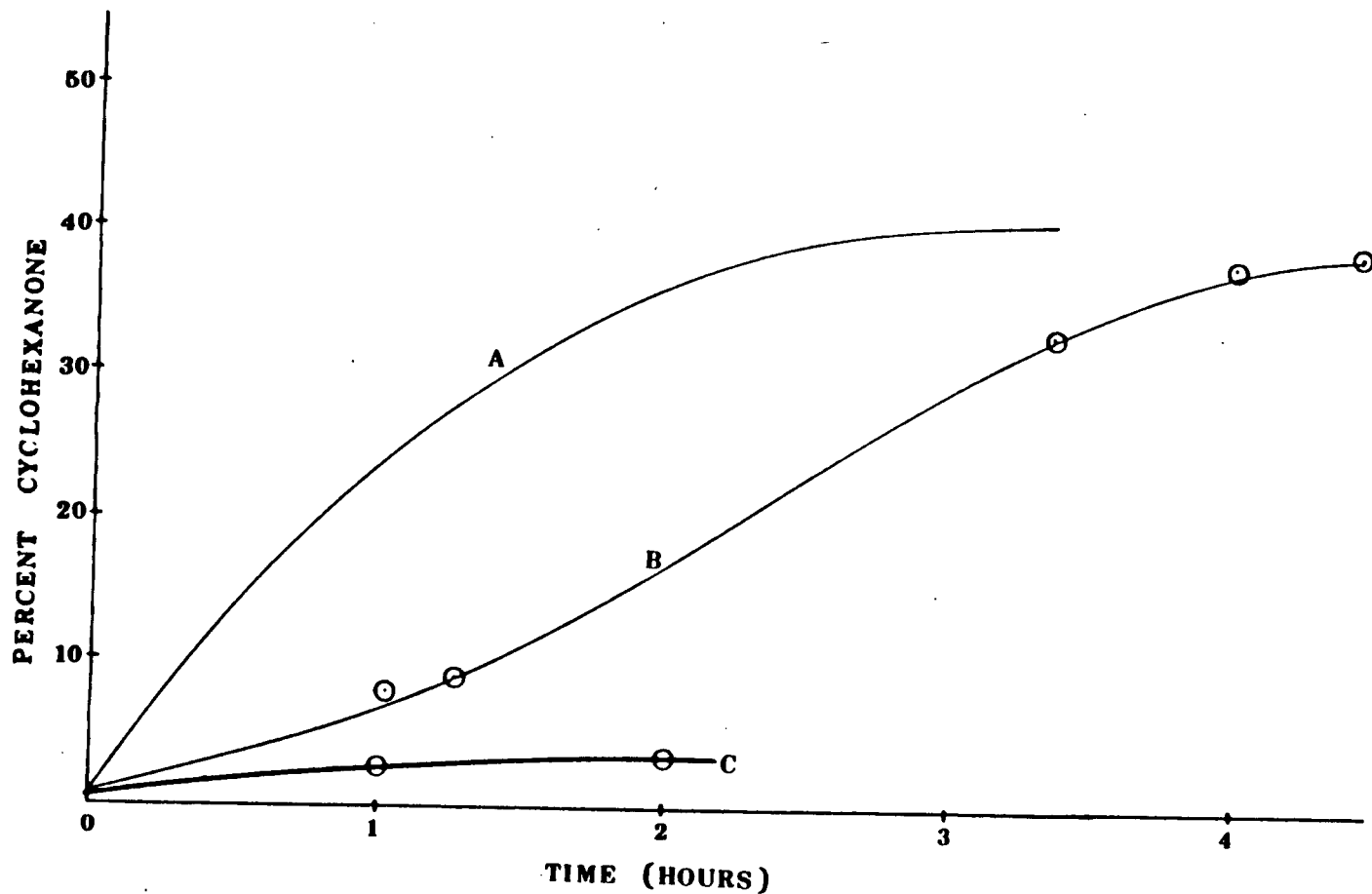
Graph (14). Rates of cyclohexanone formation for the systems: Cyclohexanol (190mmol), $RhCl_3 3H_2O$ (0.302mmol), $FeCl_3$ (9.25mmol), HCl (0.10ml), at 100deg. Initial water content A: (zero), B: (2.0ml), C: (1.0ml, with presaturation of oxygen with water).

reaction then proceeds to within a few % of the yield expected for system (1). The final acidity was pX=3.70.

The effect of addition of water to the types of systems studied thus appears to cause a suppression of the initial rate of production of cyclohexanone, even when the acidity is maintained at a high level. It would appear that when a reaction mixture similar to system (1) contains in excess of 1g,56mmol water the suppression of the oxidation reaction becomes very significant. The effect of water on conversion to cyclohexanone may partly explain the trend in systems containing in excess of 2g,12mmol ferric chloride (see section 2.4a). In systems of this type, the oxidation of the alcohol is suppressed, and this may in part be due to an increased water content.

2.4e Dependence on cyclohexene

Cyclohexene is a product of the reaction systems being described. It can be identified by its retention time on the gas chromatograph and its characteristic unpleasant smell in the oxygen flow leaving the condenser system. It is presumably produced by elimination of water from the alcohol under acidic conditions:
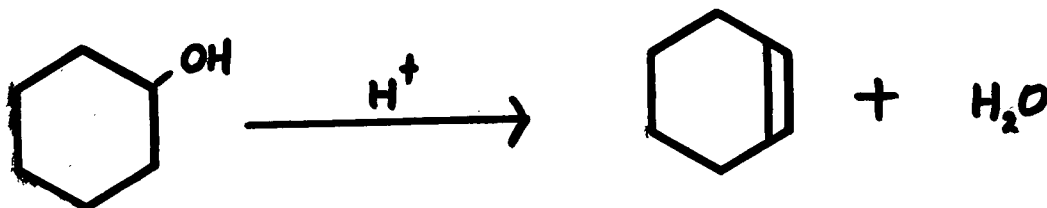
Table (1) shows that for system (1) the cyclohexene content

remains constant at approximately 6-9% during the reaction.

An experiment was carried out in which system (1) was investigated at 100deg but the rapid oxygen flow was presaturated with cyclohexene at 25deg. Graph (15) shows the variation in the cyclohexanone concentration in the mixture over a 2hr period. The rate of oxidation for the same system with no presaturation with cyclohexene is also shown. The variation in cyclohexene content for these two experiments is shown in Graph (16). It can be seen when there is no presaturation, the cyclohexene content falls steadily from about 9% to about 6% , whereas there is a steady accumulation of cyclohexene in the mixture when the oxygen is presaturated with the alkene. When presaturation was employed the reaction system was found to gain in weight by about 5g after 2hr which is approximately consistent with a cyclohexene content of 30% (vpc).

It can be readily seen that increasing the cyclohexene content of the reaction mixture above about 10% has a definite suppressing influence on the conversion of alcohol to ketone . This influence may be important in the series of experiments discussed in section 2.4a, and may partly account for the suppression of reaction rate in systems containing 3.0g,18.5mmol, and 4.0g,24.7mmol, ferric chloride, both of which appear to contain more than 10% cyclohexene. The high percentages of cyclohexene produced in the systems containing 2ml and 10ml concentrated hydrochloric acid discussed in section 2.4c (14-22% and 28% respectively) may also contribute to the inhibition of the oxidation process.

It is possible to speculate about the mechanism by which
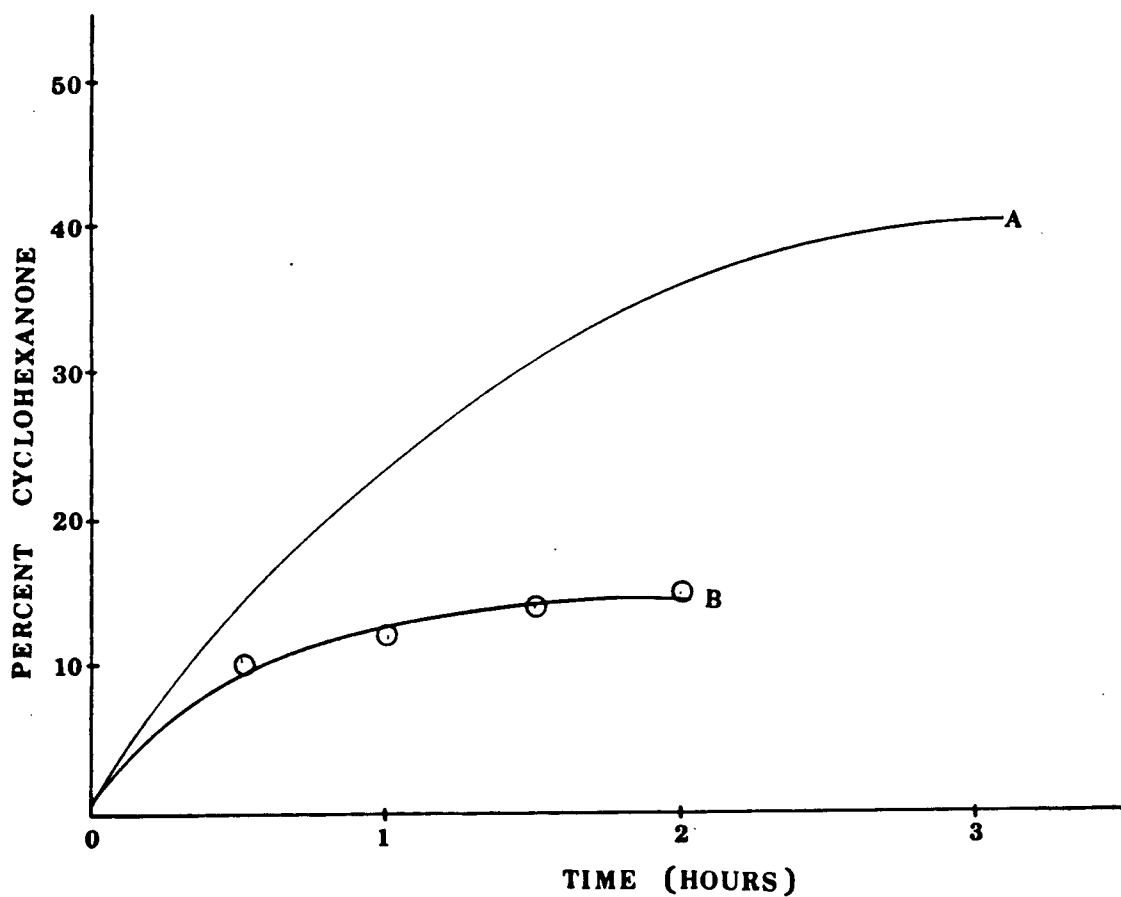
Graph (15). Rates of cyclohexanone formation for the systems:
Cyclohexanol (190mmol), $RhCl_3 3H_2O$ (0.302mmol), $FeCl_3$ (9.25mmol),
HCl (0.10ml), at 100deg. A: (no presaturation); B:
(presaturation with cyclohexene).

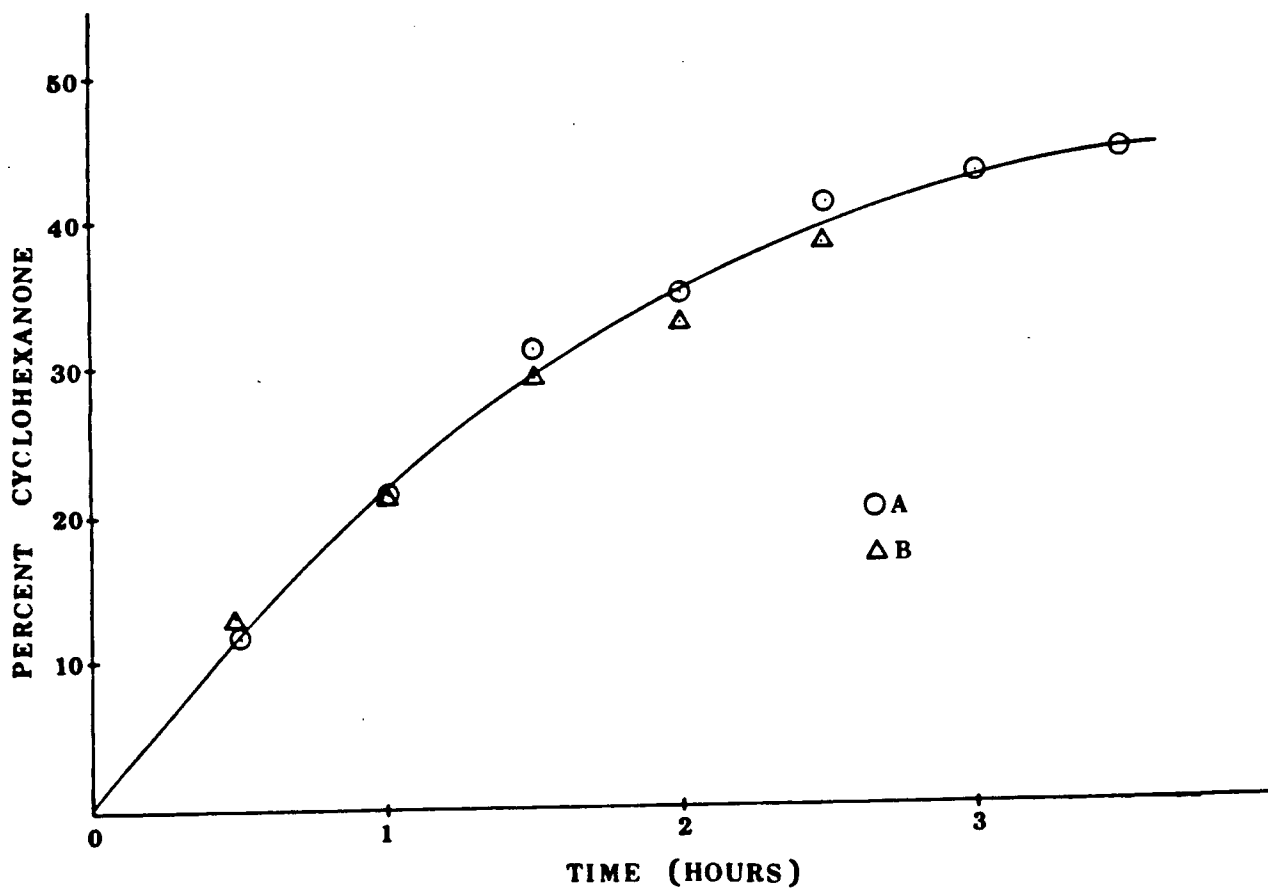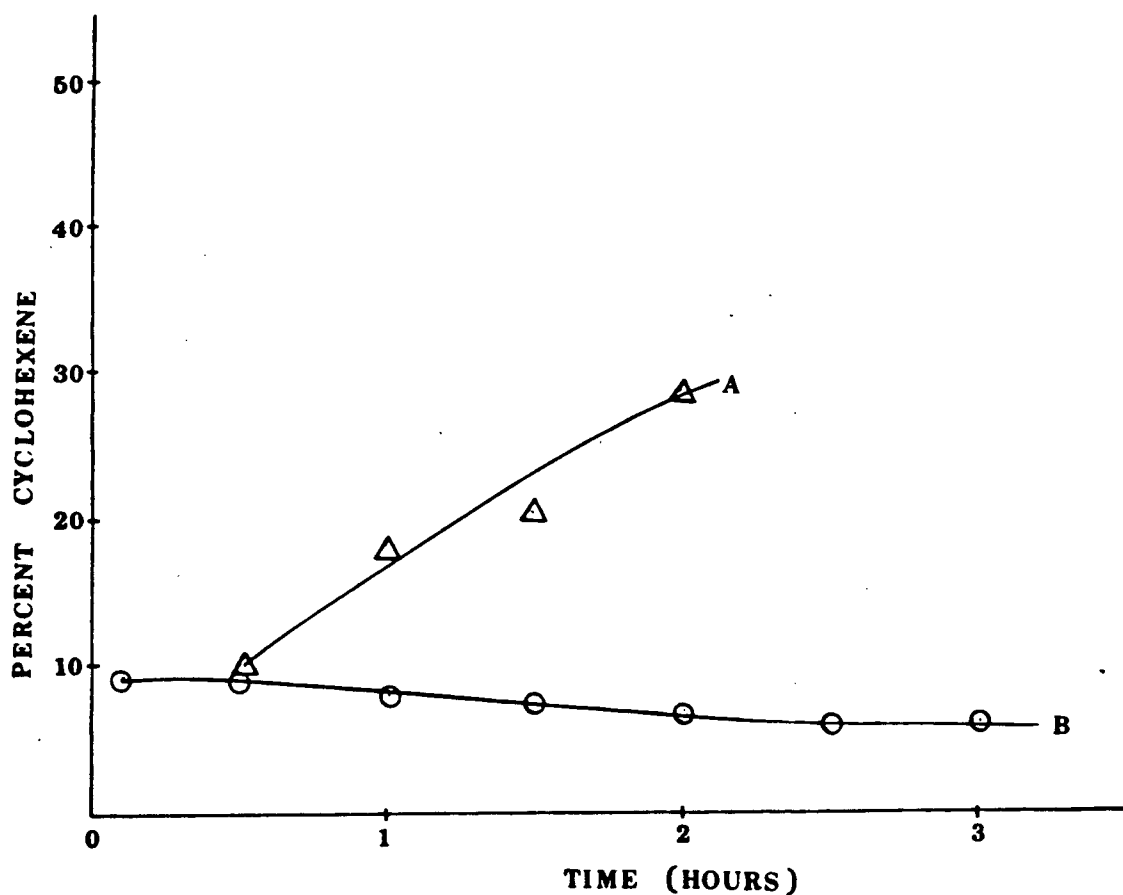Graph (16). Variation in cyclohexene concentration for the systems: Cyclohexanol (190mmol), $RhCl_3 3H_2O$ (0.302mmol), $FeCl_3$ (9.25mmol), HCl (0.10ml), at 100deg. A: oxyqen presaturatrd with cyclohexene; B: no presaturation.

the cyclohexene inhibits the conversion of cyclohexanol to cyclohexanone, and this may be the result of coordination of the olefin at a rhodium centre.

2.4f Temperature Dependence

All experiments described so far have been carried out with the reaction mixture at 100deg. The effect of increased and decreased temperature on cyclohexanone production was investigated by performing experiments using system (1) with rapid oxygen flow at 50deg and at 150deg. The results for these temperatures are plotted in Graph (17) together with results for 100deg. At 50deg the conversion proceeds very slowly indeed, having reached 4% after 4hr. At 150deg the average reaction rate during the first 1/2hr is almost doubled, but the oxidation appears to cease after 1hr, when the conversion has reached 35%.

The system (cyclohexanol 20ml,190mmol; rhodium trichloride trihydrate 0.128g,0.302mmol; ferric chloride 1.0g6.17mmol; concentrated hydrochloric acid 0.10ml) shows a similar effect on comparing data at 100deg and 150deg with rapid oxygen flow (Graph 18).

Similarly for the system (cyclohexanol 20ml,190mmol; rhodium trichloride trihydrate 0.128g,0.302mmol; ferric chloride 2.0g,12.3mmol) with rapid oxygen flow the initial reaction rate is significantly higher at 150deg compared to 100deg , but the final yield of cyclohexanone is slightly reduced (Graph 19).
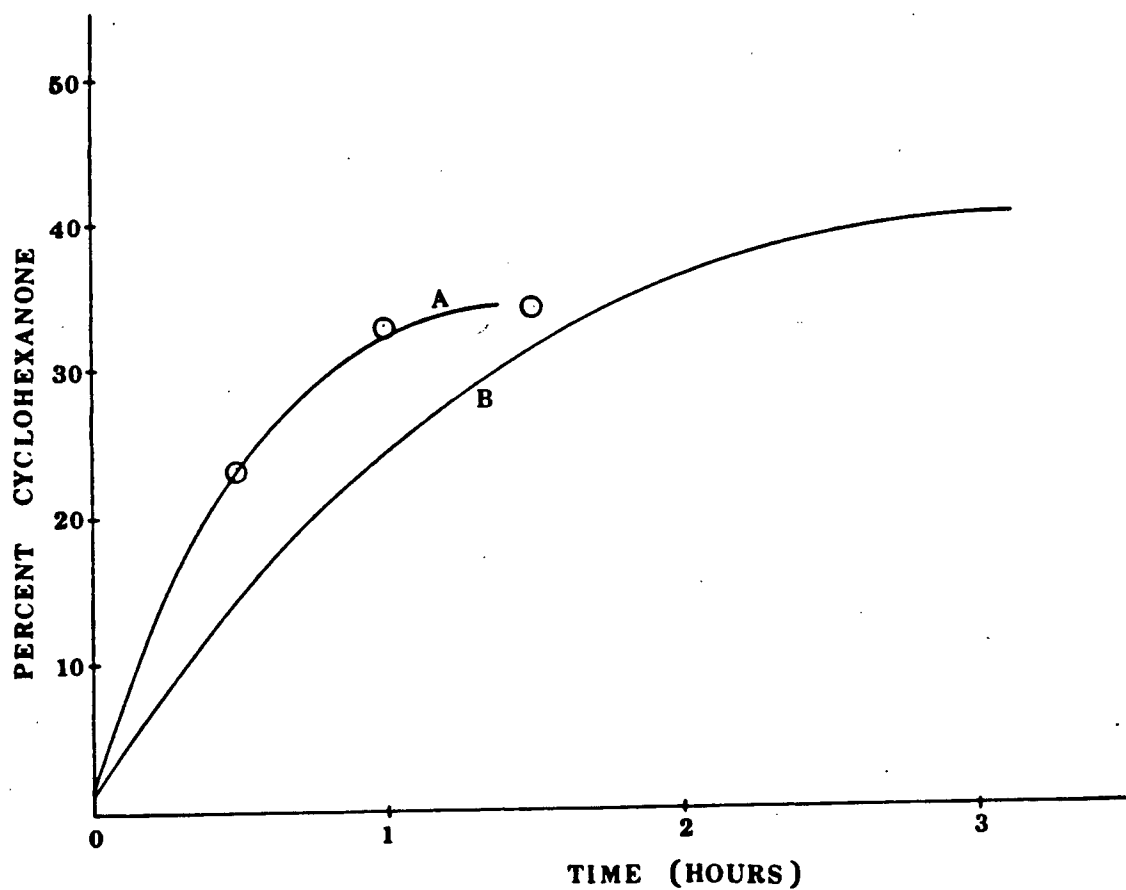
Graph (17). Rates of cyclohexanone formation for the systems: Cyclohexanol (190mmol), $RhCl_3 3H_2O$ (0.302mmol), $FeCl_3$ (9.25mmol), HCl (0.10ml),; A: (at 150deg), B: (at 100deg).
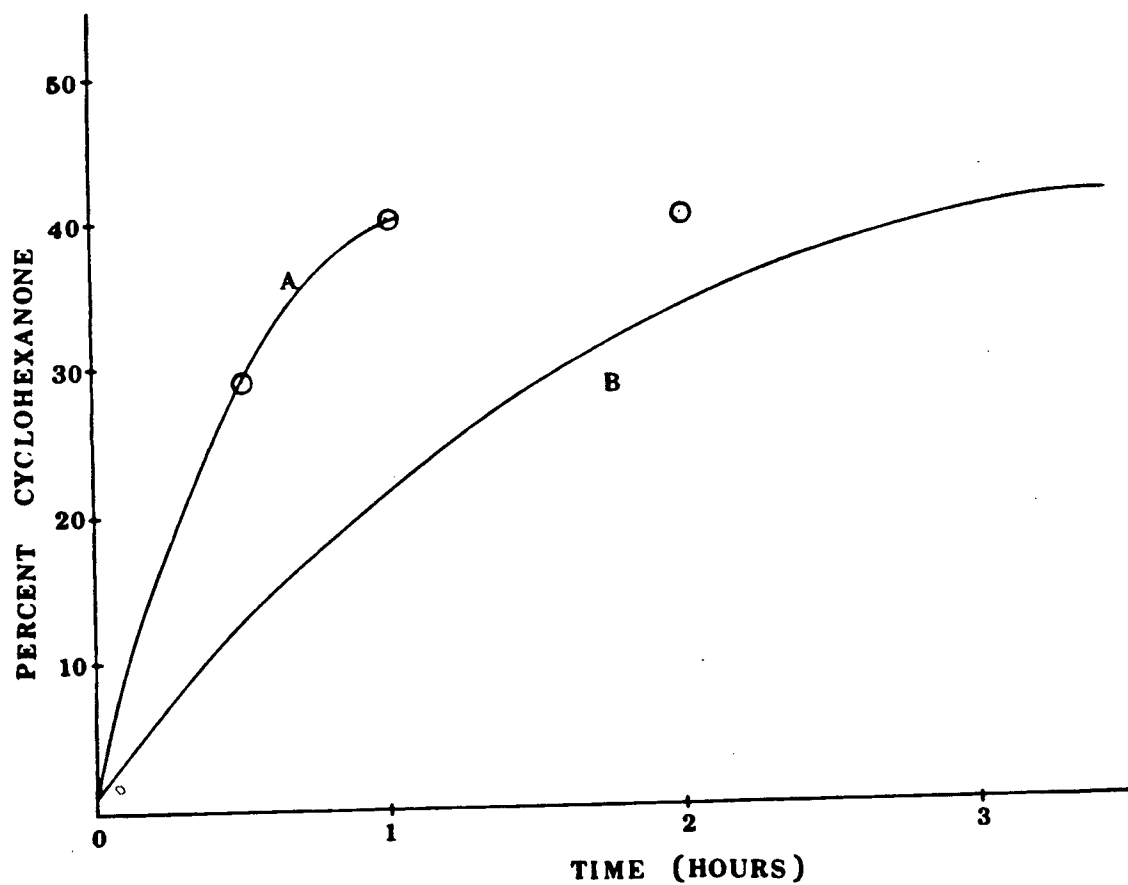
Graph (18). Rates of cyclohexanone formation for the systems:
Cyclohexanol (190mmol), RhCl$_3$3H$_2$O (0.302mmol), FeCl$_3$ (6.17mmol),
HCl (0.10ml), A: (at 150deg), B: (at 100deg).
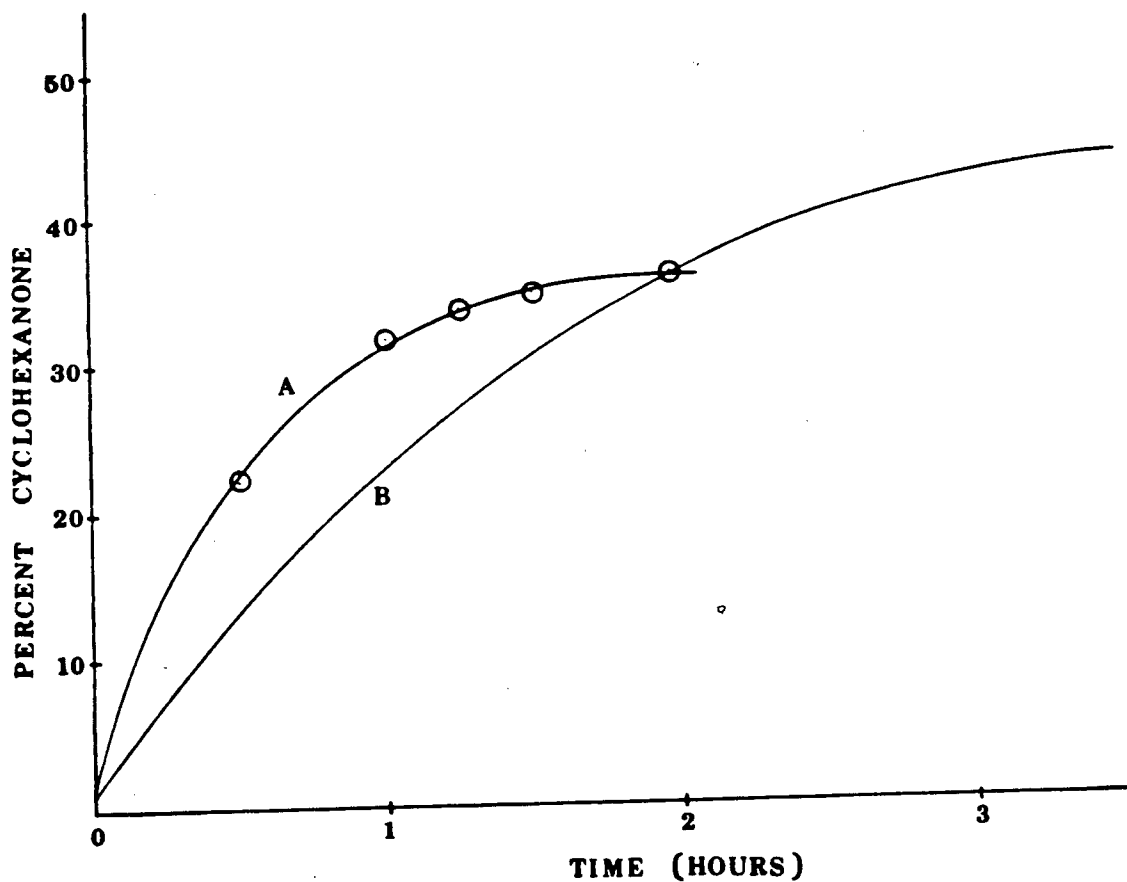
Graph (19). Rates of cyclohexanone formation for the systems:
Cyclohexanol (190mmol), $RhCl_3 3H_2O$ (0.302mmol), $FeCl_3$ (12.3mmol).
A: (at 150deg) B: (at 100deg).

2.4g Effect of addition of a phosphine

It has been found that phosphines frequently have profound effects on reactions catalysed by rhodium complexes and can coordinate to both Rh(I) and Rh(III) centres.

An approximately 1:1 molar ratio of triphenylphosphine, (PPh_3) to rhodium trichloride trihydrate was produced by adding 0.10g,0.380mmol triphenylphosphine to the system (cyclohexanol 20ml,190mmol; rhodium trichloride trihydrate 0.128g,0.302mmol; ferric chloride 2.0g,12.3mmol; concentrated hydrochloric acid 0.10ml) with rapid oxygen flow at 100deg. The results are plotted in Graph (20) together with those for the same system in the absence of the phosphine. It can be seen that addition of a phosphine does not appear to have a significant effect.

2.4h Attempt to detect hydrogen

It was found that hydrogen could be detected using the gas chromatograph employing the same column at room temperature. Hydrogen gave a pen response in the direction opposite to that for other substances, in particular oxygen and nitrogen. Rhodium trichloride trihydrate 0.128g,0.302mmol; and ferric chloride 1.5g,9.25mmol; were placed in the reaction flask. The apparatus was flushed with helium gas and 20ml,190mmol cyclohexanol injected into the flask. The reaction mixture was heated to 100deg with no gas flow through the system. No evolution of gas was seen, and analysis of a sample of gas after 1/4hr showed no hydrogen present. If reaction (2) were operating, conversion to cyclohexanone with evolution of hydrogen would be expected to occur until all the ferric chloride had been reduced to the
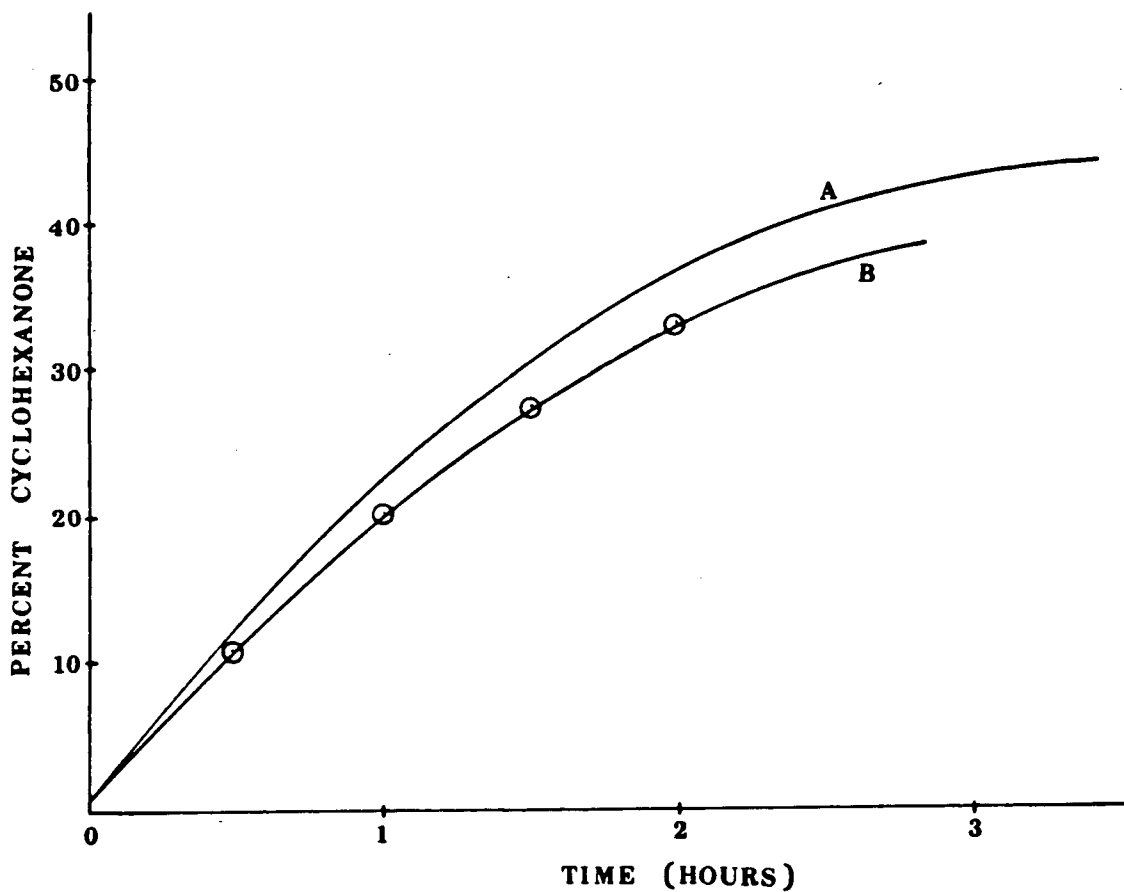
Graph (20). Rates of cyclohexanone formation for the systems: Cyclohexanol (190mmol), $RhCl_3 3H_2O$ (0.302mmol), $FeCl_3$ (12.3mmol), HCl (0.10ml), at 100deg A: (phosphine absent), B: (0.308mmol PPh_3).

ferrous state. Vpc analysis of the solution showed that no conversion to cyclohexanone had occurred.

2.4i Attempts to increase the final yield of cyclohexanone

The most successful experiments so far described produce a mixture containing approximately 40% cyclohexanone. Variations in initial ferric chloride concentration , rhodium trichloride trihydrate concentration, or temperature appear unable to increase this yield, although higher temperatures produce this final composion more rapidly.

An experiment was carried out in which a mixture containing (cyclohexanol 12ml,115mmol; cyclohexanone 8ml,75mmol) was heated to 100deg with rapid oxygen flow. The composition was ascertained by vpc analysis after ten minutes when (ferric chloride 1.5g,9.25mmol; rhodium trichloride trihydrate 0.128g,0.302mmol; concentrated hydrochloric acid 0.10ml) were added. A mixture having this composition has a pX = 1.20 at room temperature, in between that for the corresponding systems containing pure cyclohexanol and pure cyclohexanone. The final acidity of the reaction mixture after 2hr was pX=2.40. The final reaction mixture contained 4% cyclohexene and less than 0.1g,6mmolwater.

The variation in cyclohexanone content over the 2hr period is shown in Graph (21b). Graph (21a) shows the change in composition for system (1) at 100deg with rapid oxygen flow over a 3hr period. It can easily be seen that there is very little, if any, further production of the ketone in either system containing over 40% cyclohexanone, whether at high acidity
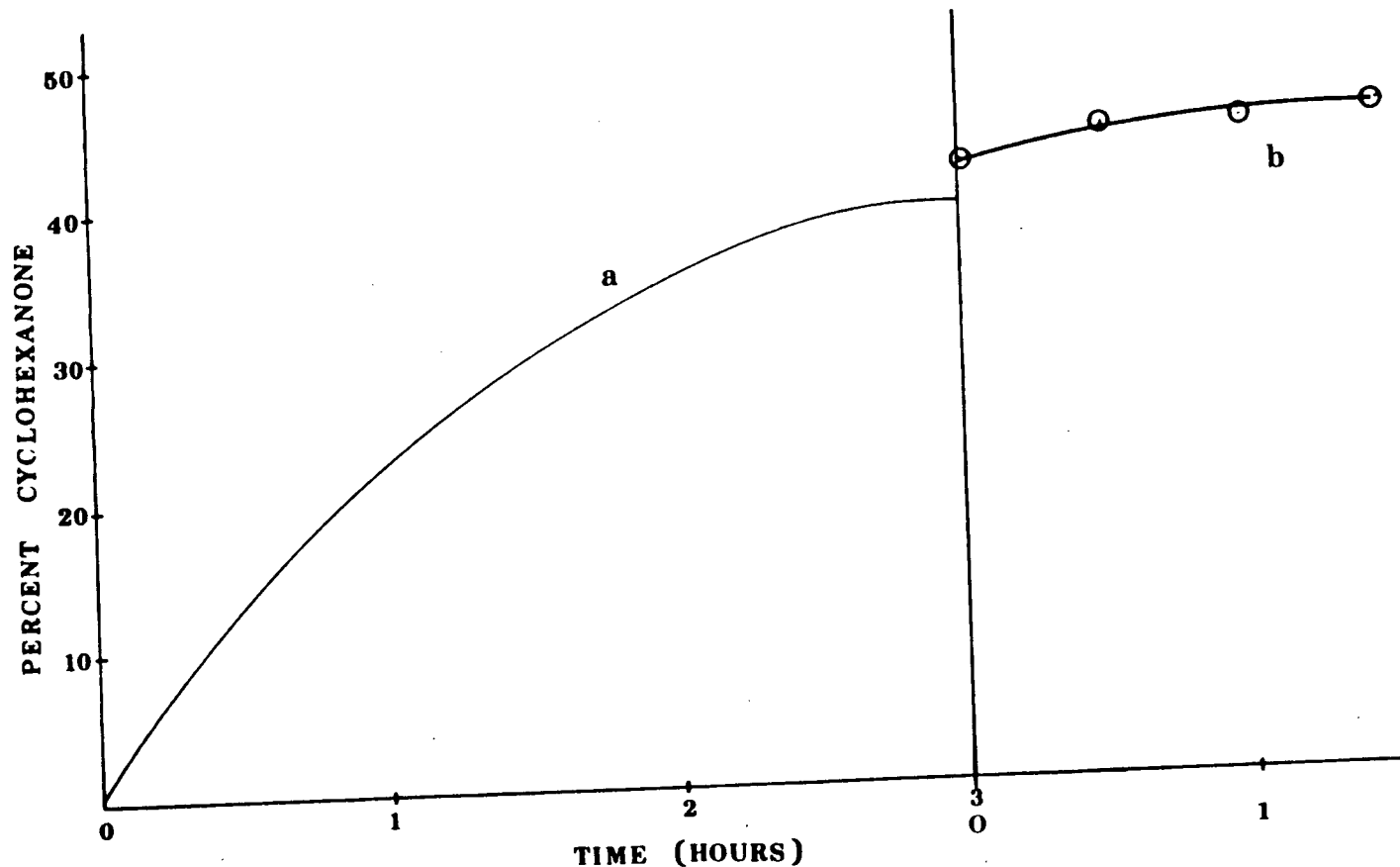
Graph (21a). Rate of cyclohexanone formation for the system: Cyclohexanol (190mmol), $RhCl_3 3H_2O$ (0.302mmol), $FeCl_3$ (9.25mmol), HCl (0.10ml), at 100deg.

Graph (21b). Rate of cyclohexanone formation for the system: Cyclohexanol (115mmol), Cyclohexanone (75mmol), $RhCl_3 3H_2O$ (0.302mmol), $FeCl_3$ (9.25mmol), HCl (0.10ml), at 100deg.

(1.20-2.40) or at low acidity (4.0,corresponding to system 1.)

It seems reasonable to conclude that the probable reason for the oxidation reaction ceasing after reaching a 40% cyclohexanone content is that there is an inhibiting interaction between the ketone and either the ferric species or the rhodium species present.

2.4j The interaction between rhodium trichloride trihydrate and cyclohexanone

Rhodium trichloride trihydrate 0.128g,0.302mmol, was shaken with cyclohexanone 1.0ml,10mmol, until it dissolved to produce a red solution. After leaving overnight, vpc analysis showed only cyclohexanone. The mixture was heated in a small glass vial at 100deg for 1/2hr when the solution became dark brown, with red oily droplets.

This mixture was added to the system (cyclohexanol 18ml,115mmol; ferric chloride 1.5g,9.25mmol; concentrated hydrochloric acid 0.10ml) and heated at 100deg with rapid oxygen flow. The composiOn of the mixture changed from 4% cyclohexanone (vpc) after five minutes to 14% cyclohexanone after 1.50hr. (Graph 22).

These results suggest that the interaction between a rhodium species and cyclohexanone may be the cause of a decrease in the rate of conversion as the cyclohexanone content in the mixture builds up. Such an interaction may also be responsible for the apparent limit of conversion at approximately 40%.

2.4k Dependence on oxygen flow

All systems described so far have employed a constant rapid oxygen flow. In reaction (1) the molecular oxygen, having oxidized the alcohol to the ketone is converted to water. In reaction (2), the oxygen is primarily used to re-oxidize iron from the ferrous state back to the ferric state.

An experiment was carried out using system (1) at 100deg without rapid oxygen flow, but with air in the apparatus above the solution. After 2hr a 6% conversion to the ketone was found. Following rapid oxygen flow through this mixture at 100deg for 3hr, a conversion to 25% cyclohexanone was found (Graph 23). This reduced yield suggests that on standing, at raised temperature in the absence of oxygen flow, some interaction occurs which reduces later catalytic activity, in the presence of rapid oxygen flow.

An experiment, carried out using system (1) at 100deg, substituting a rapid flow of dry nitrogen for oxygen, produces a 5% conversion to cyclohexanone after 1/2hr, and no further conversion after 1hr. The acidity of the reaction mixture after 1hr had fallen to pX=1.95, indicating that the iron was probably still present in the ferric state.

If the entire 1.5g,9.25mmol, ferric chloride were converted to the ferrous state, and the oxidation were proceeding exclusively by the route involving re-oxidation of Rh(I) to Rh(III) by iron, a conversion of about 5% would be expected (9.25mmol cyclohexanol= 1.0g (approximately) i.e. 5% conversion) If reaction (1) was operating exclusively (i.e. oxidation of cyclohexanol by molecular oxygen producing water), no conversion
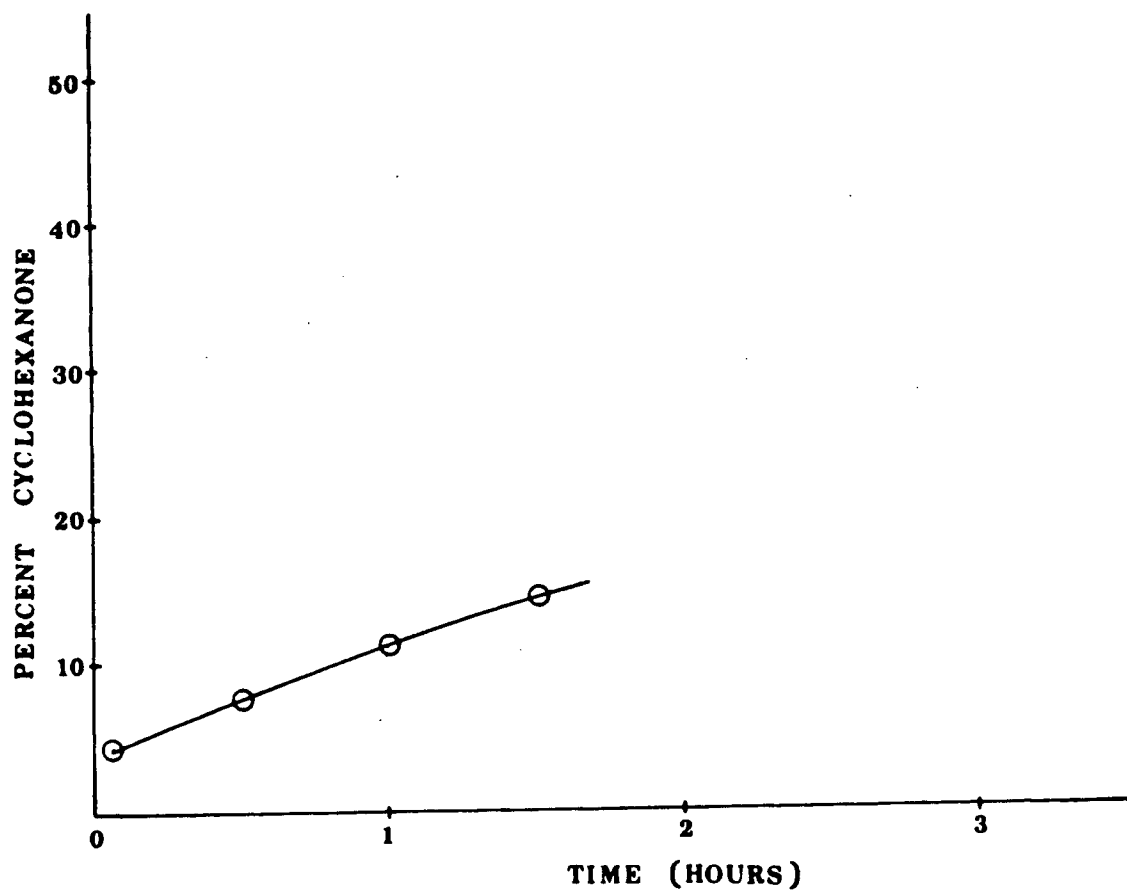
Graph (22). Effect of preheating $RhCl_3 3H_2O$ with cyclohexanone.
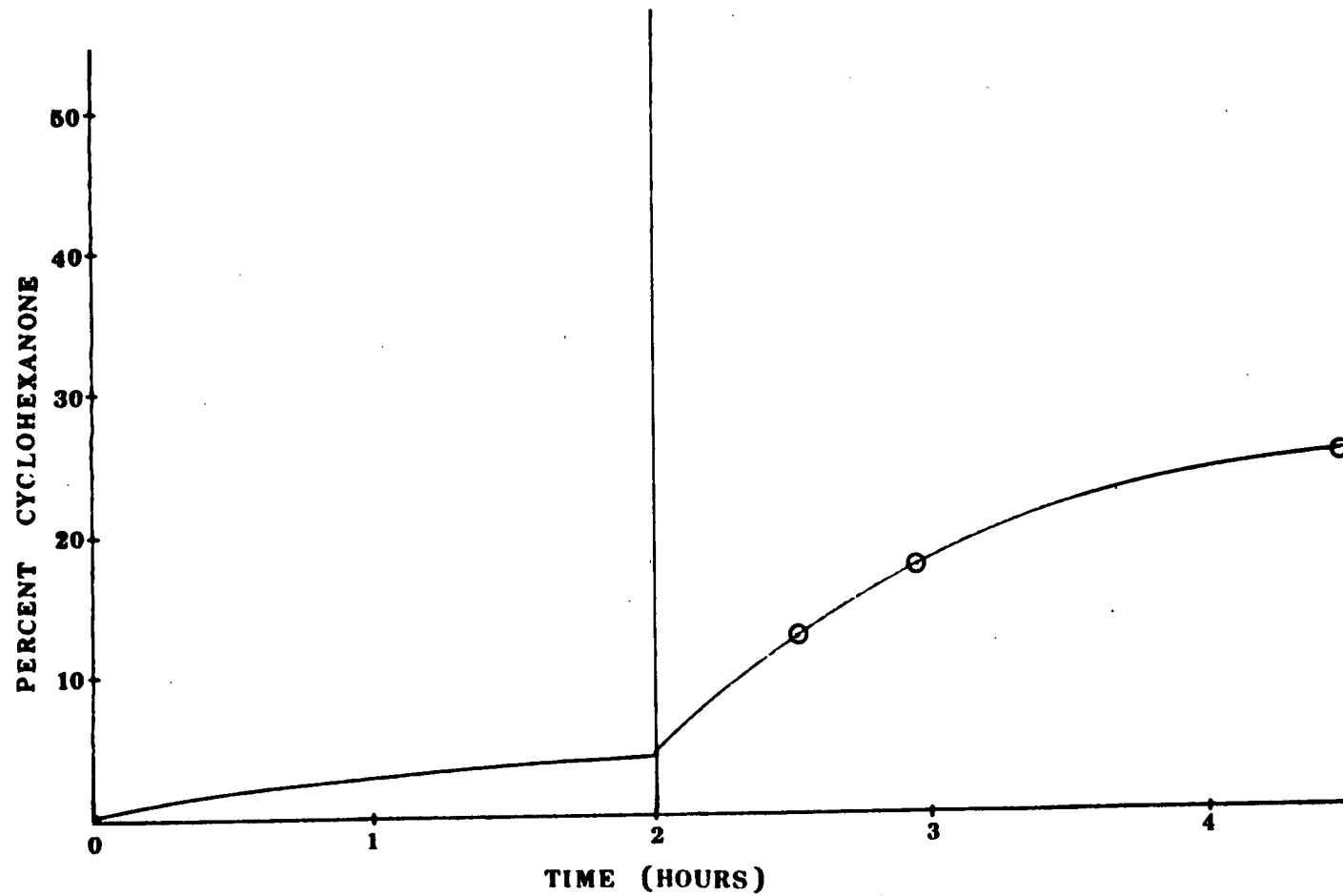
Graph (23). Dependence on oxygen flow.

to the ketone would be expected in the nitrogen flow experiment. However, the results of this experiment are by no means definitive as the original solution was not degassed and may have contained oxygen. Also, the nitrogen used may have contained traces of oxygen, enough to produce a conversion in the order of 5%. The experiment was not repeated taking measures to completely exclude oxygen because it was decided that futher investigations should be carried out employing a closed system.

2.41 Attempts to determine the ferrous/ferric ratio

Reaction (2) involves the conversion of ferric to ferrous as rhodium is re-oxidized. A possible cause of the limit of conversion to 40% cyclohexanone was at one time thought to be the complete conversion of almost all the iron present to the ferrous state with the re-oxidation by molecular oxygen proceeding very slowly. This idea was supported by acidity measurements. Considering system (1) the complete reduction of ferric chloride 1.5g,9.25mmol, to the ferrous state would produce ferrous chloride 1.17g,9.25mmol, (assuming ferrous chloride was the species present). A mixture of (ferrous chloride 1.17g,9.25mmol; cyclohexanol 12ml,115mmol; cyclohexanone 8ml,75mmol) has a pX value of 4.00, the same as system (1) after 3hr of rapid oxygen flow at 100deg. The idea of conversion to ferrous chloride is also supported by the depositing of a solid brown material on the side of the reaction flask in many experiments, apparently similar in nature to the light brown colour of anhydrous ferrous chloride.

It was thought that knowledge of the ferrous/ferric ratio during, and at the end of, a typical oxidation reaction would be very useful and might indicate something of the mechanism involved.

A standard quantitative method to determine the concentration of ferrous iron present in an aqueous solution by titration involves its oxidation to the ferric state by using potassium dichromate as oxidant and N-phenylanthranilic acid as indicator. To employ this type of method, it would of course be essential to remove the alcohol and ketone from a reaction

mixture, as both are oxidizable by potassium dichromate, and their presence would lead to erroneous results. It was found that after leaving a reaction mixture on a rotary evaporator for several hours at 100deg an oily dark brown residue remained. Heating to 150deg and pumping on a vacuum line left a tarry residue. Thus it proved very difficult to remove the organic components, again indicating a strong interaction between them and the iron species present. It was therefore decided to employ a spectophotometric method for analysis. It is well known that potassium thiocyanate, KSCN, produces a dark red colouration in aqueous solution in the presence of ferric iron; Fe(SCN) and/or Fe(SCN) may be extracted into ether[11]. This is a sensitive qualitative test for ferric iron, and has also been used previously in quantitative estimations.

Different weights of ferric chloride were mixed with cyclohexanol 20ml,190mmol, at room temperature. The mixture was then diluted with a 40:60 mixture of acetone and water and potassium thiocyanate 6g,62mmol, added. The mixture was shaken to produce a dark red solution, and made up to 1 litre, using the same solvent. After thorough shaking, 10ml of this solution was diluted to 250ml. The absorbances of the diluted soluted sotutions were measured in the range 460-480nm using a Cary 14 machine. The absorbances measured are given in Table (8).

These results indicate there is a direct relationship between the weight of ferric chloride used and the absorbance.

A solution was similarly prepared using ferrous chloride 1.17g,9.25mmol. The diluted solution had an absorbance maximum of 0.16 in the range 460-480nm.

Table (8)

| Weight of ferric chloride | | Absorbance |
(g)	(mmol)	(460-480nm)
1.50	9.25	2.16
1.00	6.17	1.36
0.50	3.08	0.69

Table (8). Absorbance of solutions after addition of KSCN to cyclohexanol/FeCl$_3$ systems.

The technique appeared to be of use in determining approximately the ferric content of a reaction mixture. It was necessary to determine whether interaction between ferric chloride and cyclohexanol at elevated temperatures would result in a change in the measured absorbance.

Ferric chloride 1.5g,9.25mmol, was heated with cyclohexanol 20ml,190mmol, at 100deg with rapid oxygen flow for 1hr. The mixture was made up as above and the absorbance measured. Insoluble particles were present in the red solution, which had an absorbance of 0.75, instead of the expected 2.16.

A similar experiment using cyclohexanone instead of the alcohol also produced solid particles in the red solution and an absorbance maximum of 0.75 in the region 460-480nm.

When ferrous chloride 1.17g,9.25mmol, was heated in cyclohexanol at 100deg with rapid oxygen flow for 1hr the acidity was found to be pX=1.70, and the colour of the solution was similar to that of ferric chloride in cyclohexanol. When the solution was made up as above and the absorbance measured, the maximum absorbance in the region 460-480nm was found to be 1.00.

It can be concluded that this technique is not useful for quantitative analysis of ferric iron because of interaction between ferric chloride and cyclohexanol at high temperature.

It also seems probable (but not certain) that ferrous chloride is converted to ferric chloride on passing molecular oxygen through a mixture of ferrous chloride and cyclohexanol at 100deg.

A possible alternative method was considered to be a spectrophotometric analysis for ferrous iron, based on formation

of the compound potassium ferrous ferricyanide. It has long been known that on treating a solution containing Fe(II) ions with hexacyanoferrate(II) a precipitate called Turnbull's blue is produced.

Standard solutions were made up by adding known weights of ferrous chloride to cyclohexanol 20ml,190mmol, diluting the solution with water and then adding potassium ferricyanide 3.1g,9.4mmol. The solutions were then diluted to 1 litre. Filtration showed all the blue compound had dissolved. This intense blue solution was diluted by a factor of 50 and the maximum absorbance measured using a Cary 14 instrument in the region of 690nm. The results are shown in Table (9).

The results indicate that the absorbance measured is proportional to the original amount of ferrous chloride used.

A solution was made up by mixing ferric chloride 1.5g,9.25mmol, and cyclohexanol 20ml,190mmol; at room temperature, diluting the mixture with water and adding potassium ferricyanide 3.1g,9.4mmol. A green solution was formed which was made up to 1 litre. A portion was diluted by a factor of two, and the maximum absorbance measured in the region of 690nm.

Another solution was made up by first heating ferric chloride 1.5g,9.25mmol, and cyclohexanol 20ml,190mmol, with rapid oxygen flow at 100deg for 1hr. This mixture was diluted with water, and potassium ferricyanide 3.1g,9.4mmol, added, to give a blue-green solution which contained insoluble particles. This solution was made up to 1 litre, a portion diluted by a factor of 50 and filtered. The maximum absorbance was measured

Table (9)

Weight of ferrous chloride		Dilution	Absorbance
(g)	(mmol)		(690nm)
1.17	9.25	50	1.30
0.585	4.68	50	0.65

Table (9). Absorbance of solutions after addition of $K_3(CN)_6$ to cyclohexanol/$FeCl_2$ systems.

Table (10)

| Weight of ferric chloride | | Temp | Dilution | Absorbance |
(g)	(mmol)	(deg)		(690nm)
1.50	9.25	R.T.	2	0.90
1.50	9.25	100	50	0.44

Table (10). Absorbance of solutions after addition of $K_3(CN)_6$ to cyclohexanol/$FeCl_3$ systems.

in the region of 690nm, and the results are presented in Table
(10).

These results show that the method may be of practical use
in an approximately determination of the ferrous iron content in
systems containing iron and cyclohexanol which have not been
heated. However, as in the thiocyanate case already discussed,
strong interaction between ferric chloride and cyclohexanol at
high temperature invalidates the method as regards analysis of
the types of reaction mixture under consideration.

CHAPTER (3)

CLOSED SYSTEMS

3.1 Experimental setup

The reaction mixture under investigation was placed in a 25ml round-bottomed flask containing a magnetic stirrer bar. The flask was immersed in an oil bath maintained at 100deg, and was connected to a condenser through which tap water flowed. The top of the condenser was connected to a manometer by means of thick walled rubber tubing.

The manometer consisted of a uniform glass tube approximately 100cm in length and 1cm in cross sectional area, joined at the lower end to a coil of tygon tubing of smaller diameter held in position in a large beaker. The glass tube had previously been calibrated by filling with water from a burette. The other end of the tygon tubing was connected to a narrower piece of uniform glass tube, approximately 20cm in length, held in a vertical position adjacent to the lower part of the 100cm tube. The manometer was filled with clean mercury such that the mercury level was visible in the upper part of the short glass tube. The system could be evacuated and filled with oxygen or nitrogen at 1atm pressure.

Gas uptake by a rapidly stirred reaction mixture could be measured by allowing the mercury level in the 100cm tube to rise a certain distance as measured by a scale , then refilling the system with gas to 1atm pressure. Normally the mercury level was allowed to rise 5.0cm, then returned to its original position by

rapid addition of oxygen until a pressure of 1atm was restored .
This cycle could then be repeated as many times as necessary.
Under these conditions the pressure under which a reaction
occurred would vary between 76.0 and 60.0cm Hg.

At the end of such a series of uptake and refilling cycles,
the shorter glass tube could be raised and the tygon tubing
uncoiled until the mercury levels in the manometer were
equivalent. The volume of gas absorbed at 1atm corresponding to
the 5.0cm change in mercury level could thus be calculated, and
hence the total volume of gas absorbed during the course of the
experiment. The water of the gas in the system was estimated to
be 25deg. Hence, the volume of gas absorbed at N.T.P could be
found.

The reaction mixture were initially degassed, then the
system filled to a pressure of 1atm. Absorbtion due to the
solubility of the gas in cyclohexanol alone was measured, so
that the volume of gas involved in a chemical oxidation process
could be calculated.

The oxygen and nitrogen used in these closed system
experiments was dried by passing through columns containing
drierite and phosphorus pentoxide.

3.2   The   cyclohexanol-rhodium   trichloride
trihydrate-concentrated hydrochloric acid system

3.2a Reaction under oxygen

The reaction mixture (cyclohexanol 10.0g,100mmol; rhodium
trichloride   trihydrate   0.064g,0.151mmol;   concentrated
hydrochloric acid 0.10ml) was investigated at 100deg under

oxygen. The solution was initially red as the rhodium trichloride trihydrate dissolved, becoming dark reddish-brown with time. No cyclohexene was produced. After 4.25hr the conversion to cyclohexanone was found to be 8% (vpc). The oxygen absorption corresponded to a 7% conversion on the basis of reaction (1). The water content at the end of the reaction was found to be 0.2g,11mmol; which agrees reasonably with the amount expected assuming reaction (1) i.e. 0.14g,8mmol.

In the absence of concentrated hydrochloric acid a cyclohexanone content of 6% (vpc) was found after 4.50hr, and the oxygen absorption corresponded to a 5% conversion.

3.2b Reaction under helium

The system (cyclohexanol 10g,100mmol; rhodium trichloride trihydrate 0.064g,0.151mmol; concentrated hydrochloric acid 0.10ml) was investigated at 100deg under helium. The solution was initially red, becoming dark brown after five minutes. After 2hr no conversion to cyclohexanone could be detected, (vpc), and no evolution or absorption of gas had occurred. At this time the solution was dark brown and rhodium metal had been deposited as a black residue.

3.3 The cyclohexanol-ferric chloride system

The reaction mixture (cyclohexanol 10.0g,100mmol;ferric chloride 0.75g,4.63mmol;) was studied at 100deg under oxygen

After ten minutes the solution was dark green and the mixture was found to contain 9% cyclohexene and 0.2g,11mmol, water. There was no conversion to cyclohexanone. The water conversion corresponds to the expected value of 0.16g,9mmol, assuming it is produced from cyclohexanol by elimination in the formation of cyclohexene.

After 2.50hr the cyclohexene content had risen to 14% and the water content to 0.4g,22mmol, rather higher than the expected value of 0.25g,14mmol. At this time the solution was dark brown and solid particles were present. There was no conversion to cyclohexanone, but there had been some oxygen absorption beyond that expected to saturate the cyclohexanol. The rather higher than expected water content and oxygen absorption may be due to some side reactions (see section 3.4). The reaction mixture (cyclohexanol 10.0g,100mmol; ferric chloride 2.0g,12.3mmol) was also investigated at 100deg under oxygen. After ten minutes the dark green solution was found to contain 14% cyclohexene and 0.5g,28mmol, water which is higher than the expected value of 0.25g,14mmol. No conversion to cyclohexene was detected. After 2hr the mixture was dark brown and contained 18% cyclohexene and 0.6g,33mmol, water. As above, there was a small amount of oxygen absorption beyond that expected to saturate cyclohexanol.

3.4 The cyclohexanol-rhodium trichloride trihydrate-ferric chloride system

3.4a Reaction under oxygen

The reaction mixture (cyclohexanol 10.0g,100mmol; rhodium

trichloride trihydrate 0.064g,0.0151mmol; ferric chloride 0.75g,4.63mmol) was studied at 100deg under oxygen. This mixture corresponds to the optimum conditions as determined by the oxygen flow experiments. Concentrated hydrochloric acid was not added as this appeared unnecessary. The results are shown in Graph (24), which is a plot of oxygen absorption against time. After five cycles (136 minutes), the conversion to cyclohexanone was found to be 29% (vpc) and that expected on the basis of oxygen absorption 32%. The mixture contained 8% cyclohexene. After nine cycles (469 minutes) the conversion to cyclohexanone was found to be 40% (vpc) and the oxygen absorption corresponded to a 50% conversion. At this time the oxygen absorption had not ceased. The water content was estimated to be 0.9g,50mmol, and the system had gained in weight by 0.8g. The expected water content on the basis of the reactions:
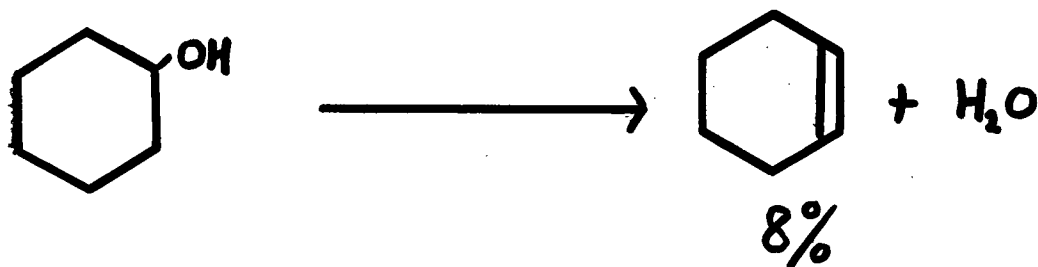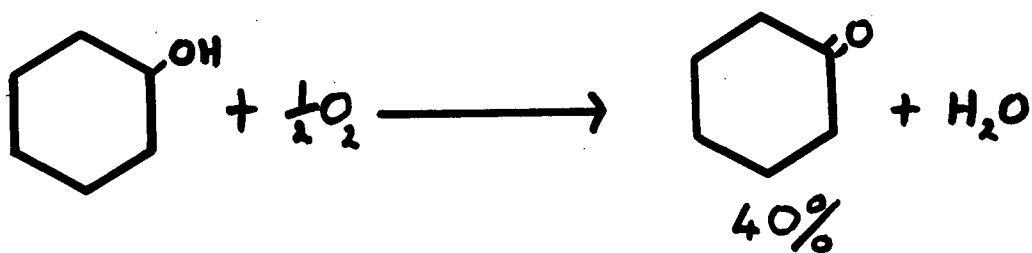
is 0.86g,47.78mmol. These reactions would predict a gain in weight of 0.7g.
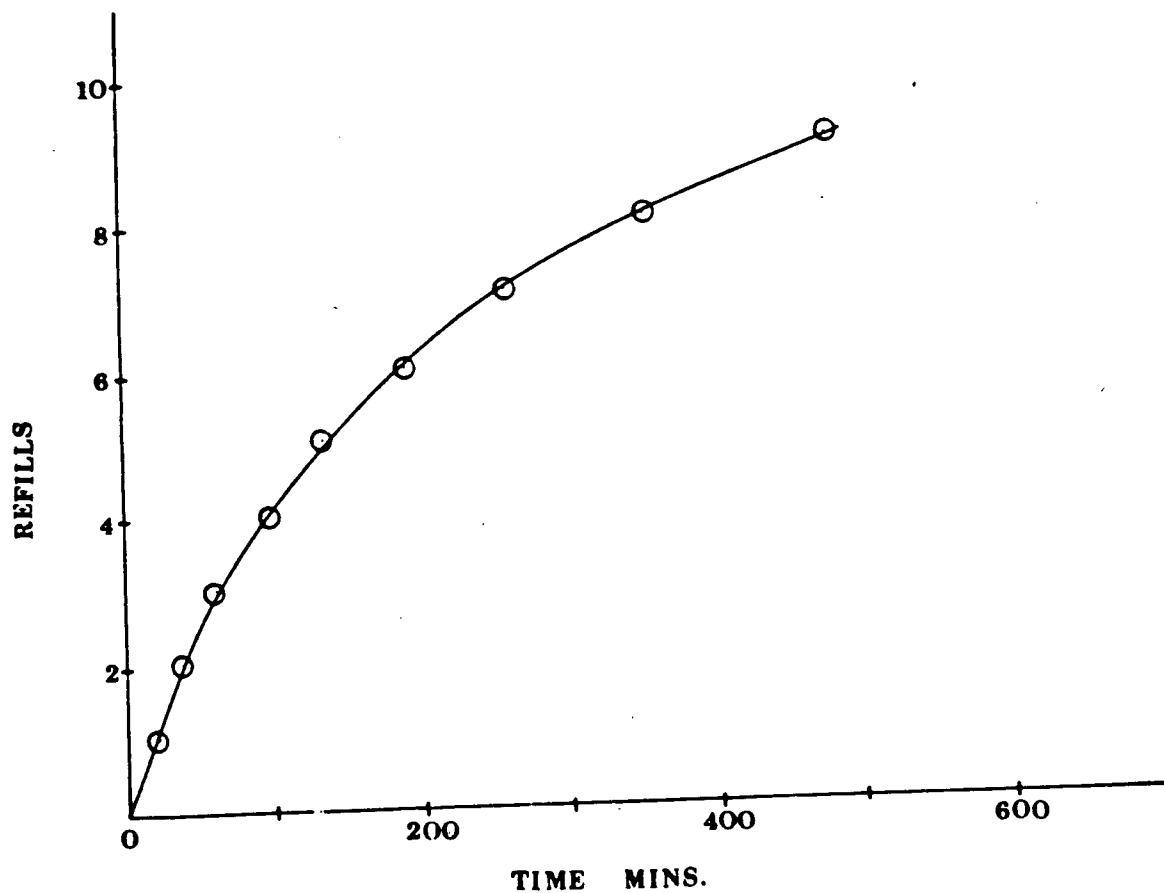
Graph (24). Rate of oxygen absorbtion for the system:
Cyclohexanol (100mmol), RhCl$_3$ 3H$_2$O (0.151mmol), FeCl$_3$ (4.63mmol),
at 100deg.

Vpc analysis of 2ul of reaction mixture was compared with 2ul of a (6:4) mixture of cyclohexanol and cyclohexanone. The ratio of the total areas of vpc readout for the experimental and known mixtures was 1.07.

The reaction mixture was allowed to absorb oxygen for another 20hr at a pressure of approximately 1atm. The mixture then contained 37% cyclohexanone and the above ratio had decreased to 0.875.

It therefore appears that, as the reaction mixture was still absorbing oxygen but no futher conversion to the ketone is seen, another oxidation process is occurring. As no additional products are detected using vpc analysis, it is possible that the products of this oxidation process are either liquids of high boiling point or solids.

The reaction mixtures (cyclohexanol 6.0g,60mmol; cyclohexanone 4.0g,41mmol; rhodium trichloride trihydrate 0.064g,0.151mmol; ferric chloride 0.75g,4.63mmol) and (cyclohexanone 10.0g,102mmol; rhodium trichloride trihydrate 0.064g,0.151mmol; ferric chloride were also studied at 100deg under oxygen. The results are shown in Graph (25) which shows that both systems absorb oxygen. The cyclohexanol-cyclohexanone system did not appear to have changed in composition after 6hr of oxygen absorption (vpc).

The most probable explanation of this oxygen absorption, with no product detected by vpc analysis, appears to be conversion of cyclohexanol and cyclohexanone to adipic acid:
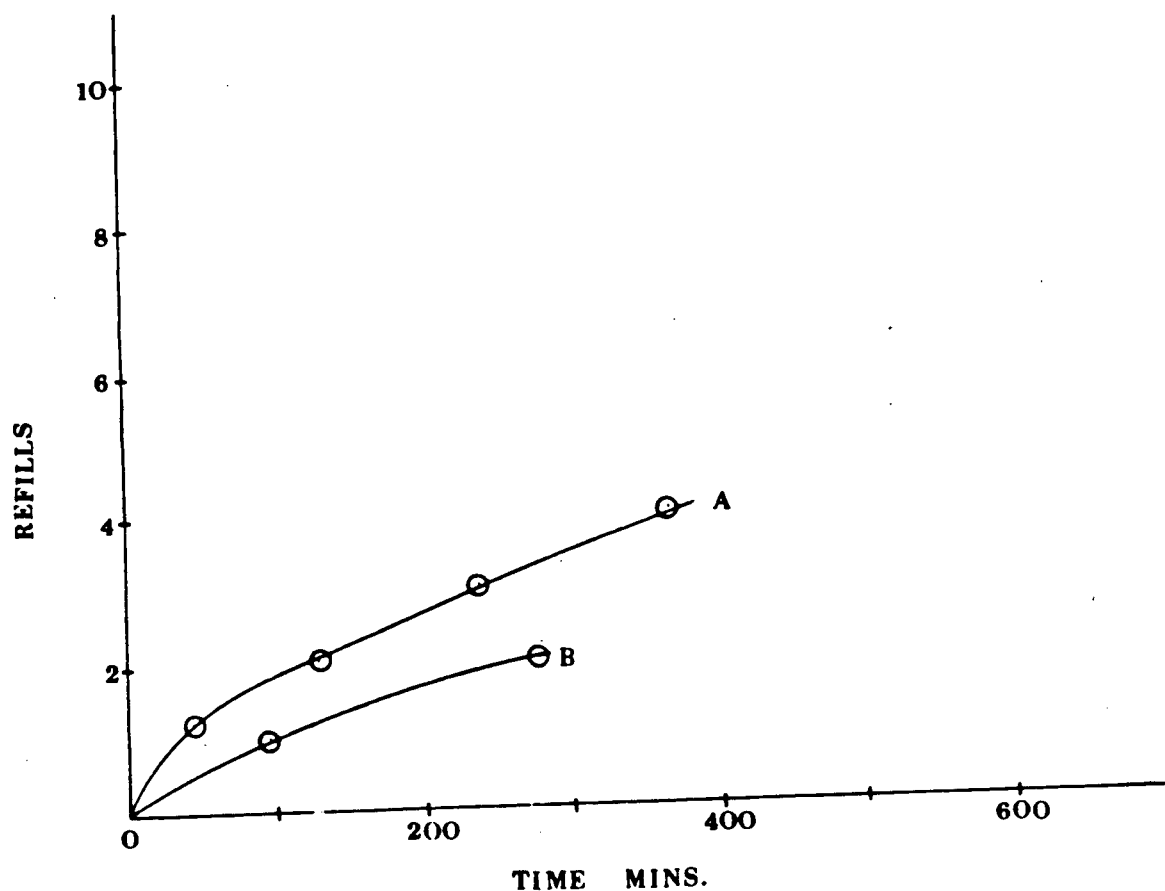
Graph (25). Rates of oxygen absorption for the systems: A: Cyclohexanol (60mmol), Cyclohexanone (41mmol), RhCl$_3$3H$_2$O (0.151mmol), FeCl$_3$(4.63mmol), at 100deg. B:Cyclohexanone (102mmol), RhCl$_3$3H$_2$O (0.151mmol), FeCl$_3$ (4.63mmol), at 100deg.
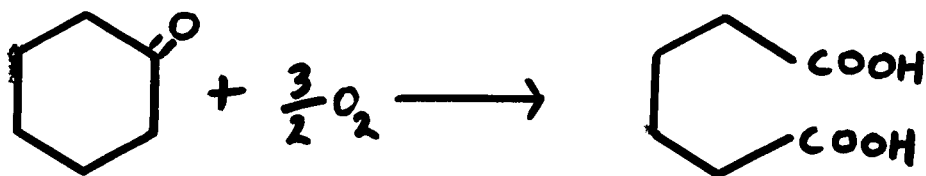
Adipic acid is a solid at normal temperature (mp 151deg) and soluble in cyclohexanol. Vpc analysis of a solution of adipic acid in cyclohexanol showed no peak other than that due to cyclohexanol, as was expected.

The literature contains a number of references to the oxidation of either cyclohexanone or cyclohexanone-cyclohexanol mixtures by air or oxygen at normal pressure in the temperature range 60-120deg. Acetic acid is usually employed as solvent, together with cyclohexane in some cases. The most common catalyst used is manganous acetate, in conjunction with other transition metal salts. Yields of adipic acid of about 70% are commonly reported after several hours. Other acids are sometimes reported as by-products of the oxidation process, e.g. glutaric, succinic, valeric and caprylic acid [12].

For example, an equimolar mixture of cyclohexanol and cyclohexanone with an equal weight of cyclohexane can be oxidized by oxygen gas using acetic acid as a solvent and a mixture of Mn, Co and Cu salts as a catalyst at 65-90deg [13]. Good yields of adipic acid are obtained after 12hr.

In another example, a cyclohexanol-cyclohexanone cyclohexane mixture was oxidized by oxygen at 60-100deg using acetic acid as solvent and a mixture of cobaltous acetate and

vanadyl acetylacetonate as catalyst [14]. Adipic acid was obtained in good yield.

Cyclohexanone, by itself, can be oxidized in acetic acid at 80deg by a stream of air using manganese acetate as catalyst to give adipic acid in 60-70% yield [15].

An attempt was made to isolate adipic acid from a reaction mixture by extraction with aqueous sodium hydroxide solution, followed by acidification. No adipic acid was recovered, perhaps because because of strong complexation between iron and the acid.

In the closed system experiment using cyclohexanol, a 40% yield of cyclohexanone was obtained using vpc analysis of the mixture. The oxygen absorption, however, corresponded to a 50% conversion. This could be explained by assuming that approximately 2.5% conversion of cyclohexanol to adipic acid had taken place:
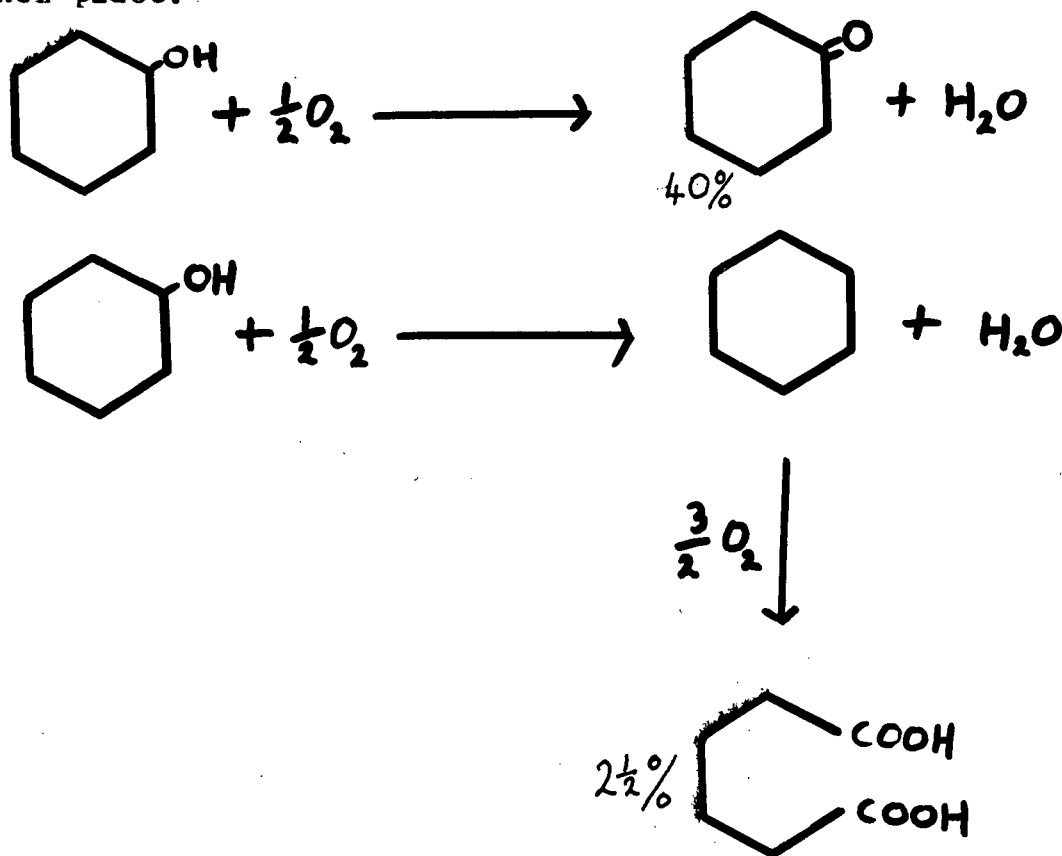
This small conversion to adipic acid is also consistent with the ratio values obtained on vpc analysis of 2ul of reaction mixture and known solution as described above. The decrease in ratio from 1.07 to 0.875 after passage of oxygen for a long period can be explained by conversion of reactants to the dicarboxylic acid which is not detected by vpc. The results for the rapid oxygen flow system and the closed system are shown together in Graph (26) for the optimum reaction mixture at 100deg. It can be seen that the rate of reaction is suppressed in the closed system. This can presumably be explained by the steady increase in water content in the closed system as the reaction progresses. An experiment employing a slow flow of oxygen through the optimum reaction mixture produced a conversion of 30% cyclohexanone after 3hr, very similar to the results for the closed system.

3.4b Reaction under nitrogen

The system (cyclohexanol 10.0g,100mmol; rhodium trichloride trihydrate 0.064g,0.151mmol; ferric chloride 0.75g,4.63mmol) was investigated under nitrogen at 100deg. After 5hr there had been no appreciable evolution or absorption. Vpc analysis showed there had been no conversion to cyclohexanone.

3.4c Effect of cyclohe^{x}ene

The system (cyclohexanol 8.0g,80mmol; cyclohexene 2.0g24mmol; rhodium trichloride trihydrate 0.064g,0.151mmol; ferric chloride 0.75g,4.63mmol) was studied under oxygen at

100deg. After 4hr the conversion to cyclohexanone was found to be 4%. (vpc), and the oxygen absorption corresponded to 4%. The cyclohexene conversion had increased to 32%. This compares with a conversion to cyclohexanone of 33% after the same period in the absence of the initially introduced cyclohexene. This result is in good agreement with the studies of the effect of cyclohexene in the oxygen flow systems.
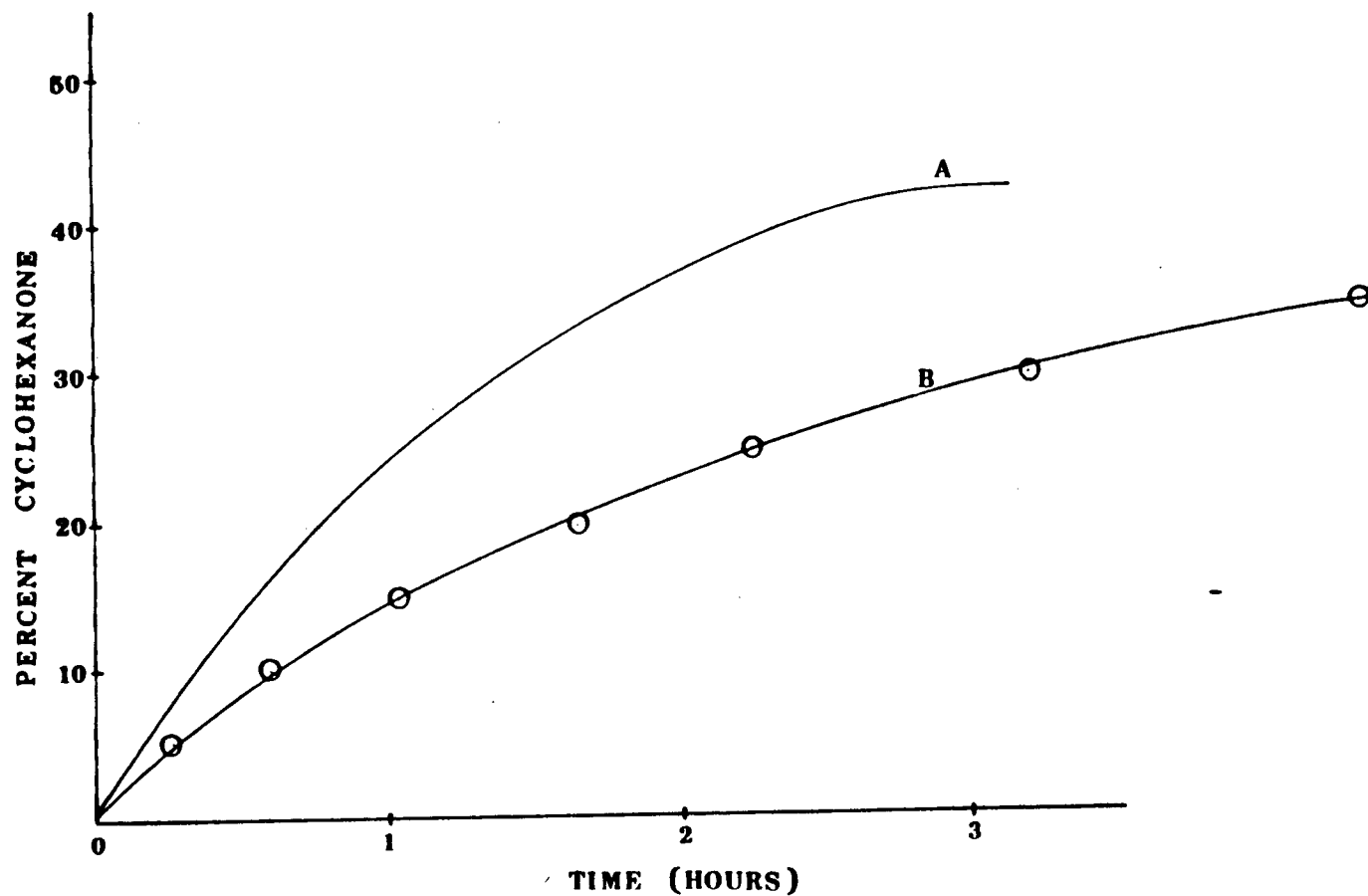
Graph (26). Rates of cyclohexanone formation for the systems: A:

Cyclohexanol (190mmol), $RhCl_3 3H_2O$ (0.302mmol), $FeCl_3$ (9.25mmol),

HCl (0.10ml), Rapid oxygen flow at 100deq.

B: Cyclohexanol   (100mmol), $RhCl_3 3H_2O$ (0.151mmol),

$FeCl_3$ (4.63mmol), Closed system at 100deq.

CHAPTER (4)

RELATED SYSTEMS

4.1 Use of other metal salts

Other systems were studied in which various metal salts were substituted for ferric chloride (e.g mercuric chloride, cupric chloride, chromic chloride). All apeared to give inferior results when compared to the ferric chloride systems already discussed.

For example, the system (cyclohexanol 20ml,190mmol; rhodium trichloride trihydrate 0.128g, 0.302mmol; cupric chloride 1.50g,11.6mmol; concentrated hydrochloric acid 0.15ml) at 100deg with rapid oxygen flow gives a 13% yield of cyclohexanone after 1.50hr. (Graph 27).

4.2 The cyclohexanol-rhodium trichloride trihydrate- p-toluene sulphonic acid monohydrate system

The exact function of the ferric chloride in the systems described in detail in chapters 2 and 3 has not been elucidated. The change in acidity as the reaction progresses was described in section 2.4c. It was suggested that the decline in the reaction rate with time might be related to the appreciable decrease in acidity from $pX=1.70$, for a typical reaction mixture, to $pX=3.90$ after a 40% conversion to cyclohexanone. Attempts to produce a constant high acidity during the reaction by addition of large amounts of concentrated hydrochloric acid were unsuccessful in increasing the final yield or initial
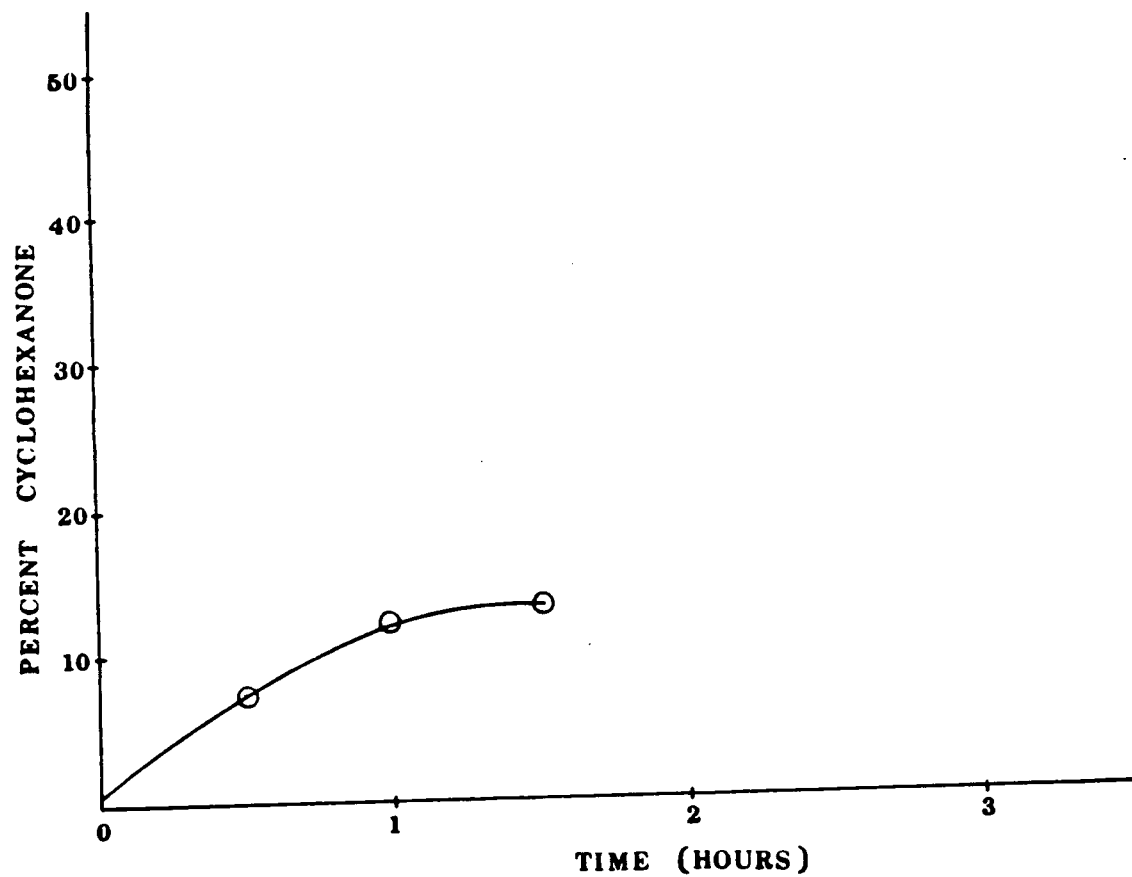
Graph (27). Rate of cyclohexanone formation for the system: Cyclohexanol (190 mmol), $RhCl_3 3H_2O$ (0.302 mmol), $CuCl_2$ (11.6 mmol), HCl (0.15ml), at 100deg.

reaction rate because of the water introduced into the system.

Aqueous systems containing p-toluene sulphonic acid monohydrate are known to have high acidity. An attempt to produce a highly acidic medium, in the absence of water, was made by dissolving p-toluene sulphonic acid monohydrate in cyclohexanol.

p-Toluene sulphonic acid monohydrate 0.5g,2.63mmol, was added to cyclohexanol 20ml,190mmol, and the solution heated until the solid dissolved. After cooling to room temperature, the resulting solution had a pX value of 2.20. A solution of 5.0g,26.3mmol, p-toluene sulphonic acid monohydrate in 20ml,190mmol, cyclohexanol was similarly prepared, and was found to have an acidity of 2.05.

The system (cyclohexanol 20ml,190mmol; rhodium trichloride trihydrate 0.128g,0.302mmol; p-toluene sulphonic acid monohydrate 0.50g,2.63mmol) was investigated at 100deg with rapid oxygen flow. The conversion to cyclohexanone was found to be <5% after 1hr.

The system (cyclohexanol 20ml,190mmol; rhodium trichloride trihydrate 0.128g,0.302mmol; p-toluene sulphonic acid monohydrate 5.0g,26.3mmol) was also investigated at 100deg with rapid oxygen flow. After 2hr there had been no conversion to cyclohexanone and the reaction mixture contained a large amount (>50%) cyclohexene.

These results suggest that the function of the ferric chloride might not solely be to produce a high acidity in the reaction medium. However, no definite conclusions can be drawn on the basis of the results for systems containing p-toluene

sulphonic acid monohydrate as this may itself coordinate with an active rhodium species in some manner, which might inhibit efficient catalysis.

4.3 Addition of a solvent

It was thought that addition of a solvent to a reaction mixture might improve the yield of cyclohexanone. It was decided that the solvent added should be miscible with cyclohexanol and cyclohexanone, be inert to chemical reaction under the conditions used (i.e. not contain oxidizable functional groups), and have a boiling point in the same range as cyclohexanol and cyclohexanone. The solvent selected was o-xylene (bp 144deg). This also had the advantage that its vpc peak did not overlap with those of the alcohol and the ketone.

The effect of addition of 20ml,210mmol o-xylene to system (1) was studied at 100deg with rapid oxygen flow. The results are shown in Graph (28), which appears to have a slight S-shape. After 1.50 hr the conversion to cyclohexanone was 40%, compared to 31% for system (1) at 100deg. However, the rate of conversion rapidly declines when the cyclohexanone content reaches 42% after 2hr. Thus a given % conversion to the ketone appears to be attained more rapidly in the presence of an equal volume of o-xylene but the final composition remains the same (40% cyclohexanone).

An experiment using 60ml,630mmol o-xylene instead of 20ml was carried out. The results are shown in Graph (28). It can be seen that the S-shape is very pronounced. The % conversion to cyclohexanone after 2hr has declined from 42% to 30% on tripling
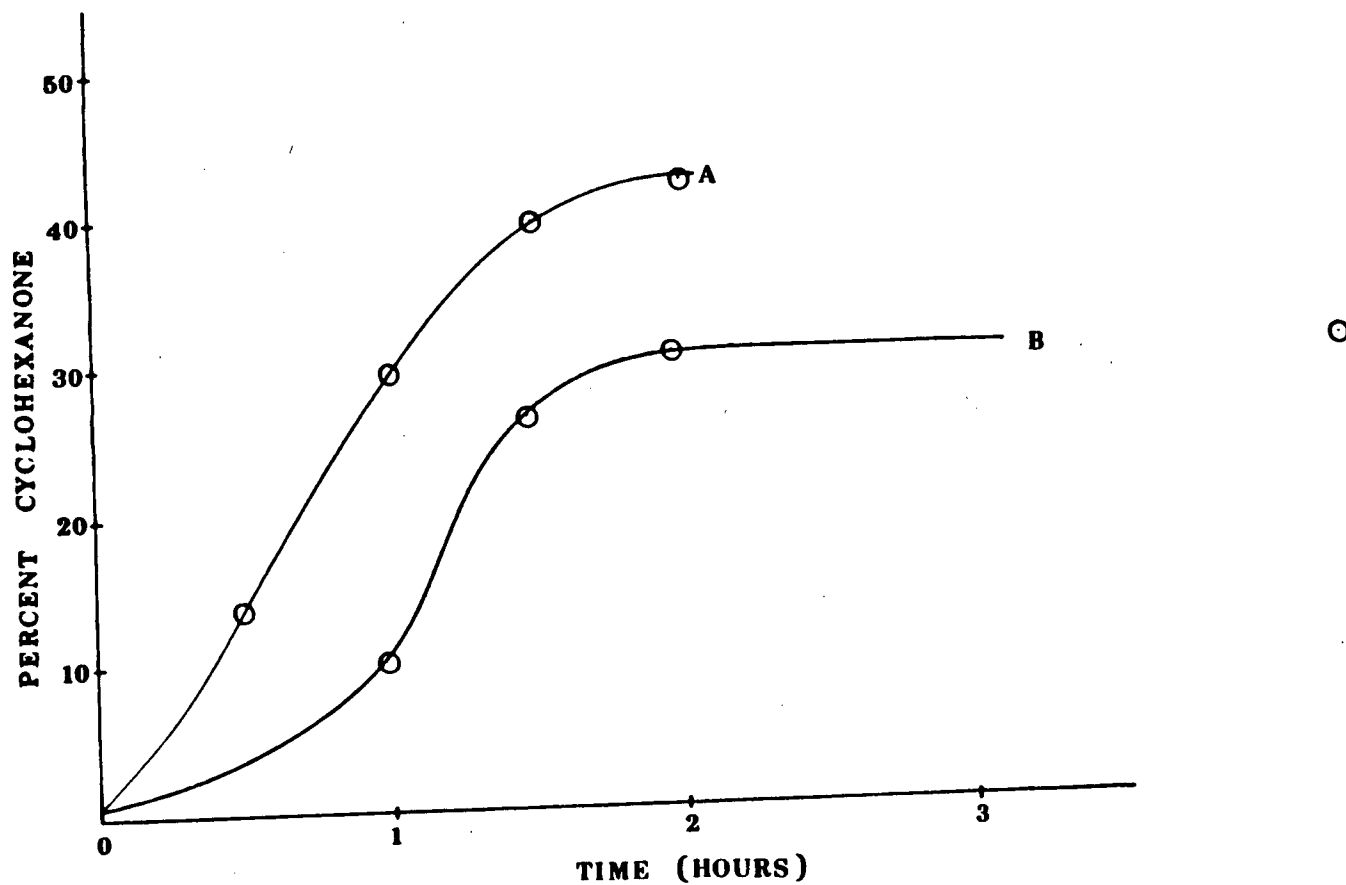
Graph (28). Rates of cyclohexanone formation for the systems:
Cyclohexanol (190mmol), $RhCl_3 3H_2O$ (0.302mmol), $FeCl_3$ (9.25mmol),
HCl (0.10ml), at 100deg; o-xylene A: (210mmol), B: (630mmol).

the amount of o-xylene.

4.4 Oxidation of cyclopentanol

The system (cyclopentanol 20ml,245mmol; rhodium trichloride trihydrate 0.128g,0.302mmcl; ferric chloride 1.5g,9.25mmol; concentrated hydrochloric acid 0.10ml) was studied at 100deg using rapid oxygen flow. The presaturation mixture contained an equal volume of cyclopentanol and cyclopentanone. The conversion to cyclopentanone was followed over a 2.50hr period and the results a plotted in Graph (29). It can be seen that the situation is very similar to the cyclohexanol case.
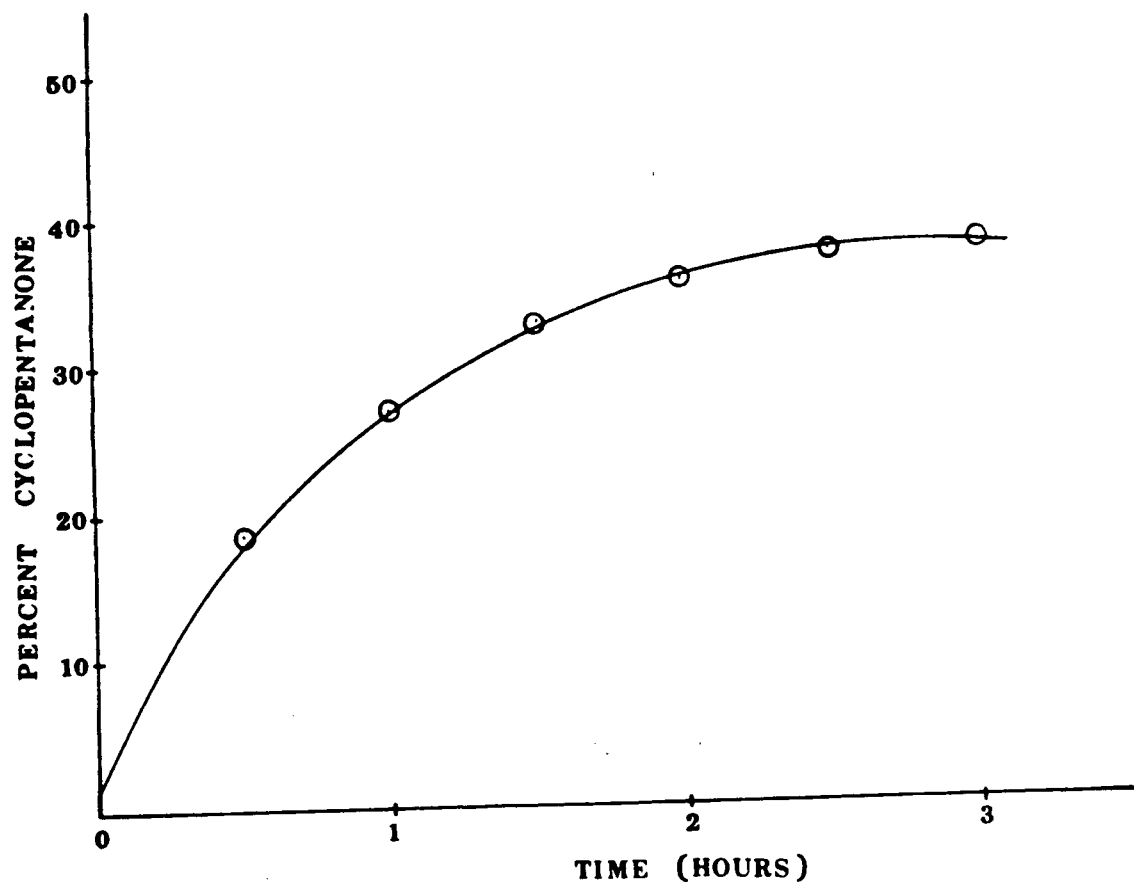
Graph (29). Rate of cyclopentanone formation for the system:
Cyclopentanol (245mmol), RhCl$_3$3H$_2$O (0.302mmol), FeCl$_3$(9.25mmol),
HCl (0.10ml), at 100deg.

CHAPTER 5

SUMMARY OF RESULTS

5.1   Reaction   mixtures   containing   the   components:
(cyclohexanol, rhodium trichloride trihydrate, ferric chloride
and concentrated hydrochloric acid) were studied in the presence
of oxygen. The nature of the reaction in which cyclohexanol was
oxidized to cyclohexanone was investigated. No conversion to
cyclohexanone occurred in the absence of rhodium trichloride
trihydrate. Some degree of conversion was found in the absence
of ferric chloride. The optimum conditions for conversion to
cyclohexanone were produced by using a combination of rhodium
trichloride trihydrate and ferric chloride. Under such
conditions the rate of conversion to the ketone declined
steadily until the mixture contained 40% cyclohexanone.

5.2   For   a   fixed   amount   of   cyclohexanol   and   rhodium
trichloride trihydrate there is an optimum amount of ferric
chloride necessary to achieve the maximum yield in the shortest
period at a given temperature . Addition of ferric chloride in
excess of this optimum amount tends to suppress the rate of
conversion to the ketone. This can probably be explained by the
additional production of water and cyclohexene (see below). The
optimum range for addition of ferric chloride is between 3 and
6mmol per 100mmol cyclohexanol.

5.3 Using a cyclohexanol/ferric chloride ratio in the optimum range at a given temperature, increasing the rhodium trichloride trihydrate concentration beyond a certain level does not significantly increase the final yield of cyclohexanone or the reaction rate.

5.4 The oxidation reaction occurs under acidic conditions. This acidity is the result of the interaction between ferric chloride and cyclohexanol (and cyclohexanone). The acidity greatly decreases as the reaction progresses. Addition of concentrated hydrochloric acid to the mixture is unnecessary and may inhibit the oxidation reaction if added in large amounts due to the water introduced (see below).

5.5 Cyclohexene is produced in a side reaction together with water. This is presumably the result of cyclohexanol undergoing an elimination reaction under acidic conditions. Using the optimum cyclohexanol/ferric chloride ratio at 100deg, the cyclohexene content of the reaction mixture is less than 10%. Introduction of cyclohexene in amounts in excess of 20% greatly suppresses the conversion to cyclohexanone. This is presumably due to strong complexation of the olefin with an active rhodium species.

5.6 Water is produced during the catalytic oxidation in amounts greater than can be accounted for by the production of cyclohexene. This additional water content of the reaction

mixture in a closed system is in good agreement with that predicted by reaction (1). The presence of water in the reaction mixture tends to supress the oxidation of cyclohexanol to cyclohexanone.

5.7 Using the optimum ratio of components, very little conversion occurs in the presence of oxygen at temperatures below 50deg. Increasing the temperature from 100deg to 150deg increases the rate of oxidation but does not increase the final yield of the ketone.

5.8 Addition of a phosphine to a system containing the optimum ratio of components in the presence of oxygen, in an attempt to stabilize possible Rh(I) intermediates, has little significant effect.

5.9 No hydrogen evolution could be detected when a system containing the optimum ratio of components was heated at 100deg under helium. This suggests reaction (2) may not be involved.

5.10 No gas evolution occurs when a reaction mixture is heated at 100deg under nitrogen. No conversion to cyclohexanone could be detected. Reaction (2) would enable some conversion to the ketone to occur until all the iron present in the ferric state had been reduced to the ferrous state. Evolution of hydrogen would also occur.

5.11   Oxygen is necessary for conversion of cyclohexanol to cyclohexanone to occur. Gas absorption is detected when a mixture containing an optimum ratio of components at 100deg is studied in a closed system containing oxygen. This suggests reaction (1) is occurring. Reaction (2) would give rise to a net evolution of gas. The measured volume of oxygen absorption is in good agreement with that predicted on the basis of reaction (1).

5.12   Using an optimum ratio of components in the presence of oxygen the conversion to cyclohexanone is limited to approximately 40%. This limit is probably due to an interaction between cyclohexanone and some active rhodium species essential for catalytic oxidation. Oxygen absorption continues after conversion to cyclohexanone has ceased. This can be accounted for by assuming another oxidation process is occurring, probably to produce adipic acid.

CHAPTER (6)

DISCUSION AND CONCLUSIONS

The oxidation of cyclohexanol to cyclohexanone in the presence of oxygen using a combination of rhodium trichloride trihydrate and ferric chloride as catalyst has been shown to have the stoichiometry:

$$\text{cyclohexanol} + \tfrac{1}{2}O_2 \xrightarrow[\text{100 deg}]{RhCl_3 - FeCl_3 \cdot HCl} \text{cyclohexanone} + H_2O$$
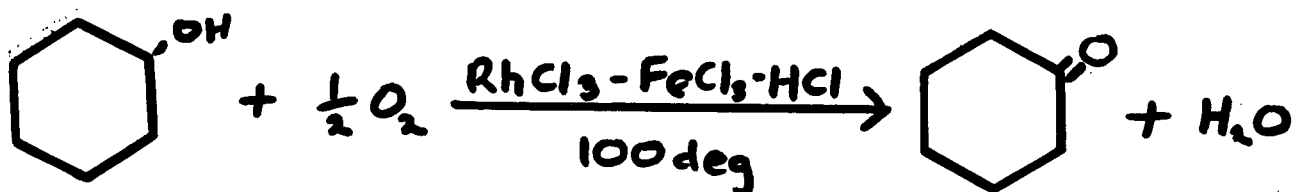
A plausible mechanism for this reaction has been discussed in the introduction.

The function of the ferric chloride has not been definitely established. As well as being a potent oxidant for Rh(I), it may be required to produce a highly acidic medium in the absence of water. However, the results for experiments discussed in section 4.2, employing p-toluene sulphonic acid monohydrate, in combination with rhodium trichloride trihydrate, tend to suggest this might not be the case. It is also possible that it may contribute to the stabilization of a Rh(I) intermediate amd prevent precipitation of rhodium metal, as in the case of the rhodium trichloride trihydrate-stannous chloride system. The complex formed between Rh(I) and tin(II) chloride has been formulated as: [16]

$$\left[\begin{array}{ccc} \text{Cl}_3\text{Sn} & \text{Cl} & \text{SnCl}_3 \\ & \text{Rh} \quad \text{Rh} & \\ \text{Cl}_3\text{Sn} & \text{Cl} & \text{SnCl}_3 \end{array} \right]^{4-}$$
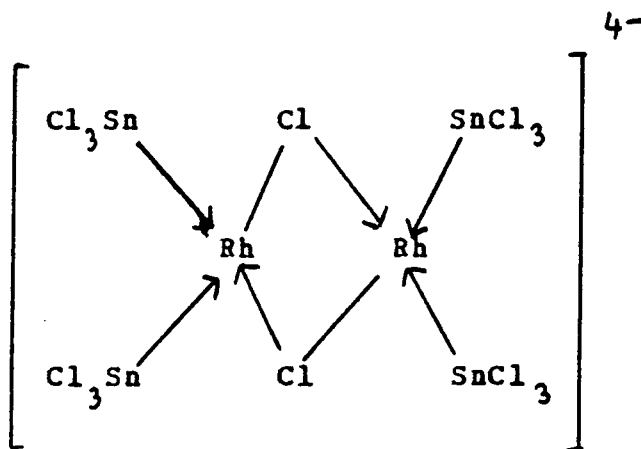
The conversion to cyclohexanone appears to be limited to approximately 40% for the rhodium trichloride trihydrate-ferric chloride system. This is possibly the result of interaction between cyclohexanone in the enolized form and the active rhodium species required for catalytic activity. The complexation between the enol and rhodium might be expected to be stronger than the complexation between the alcohol and rhodium because of the possibility of interaction between the double bond and the metal centre:
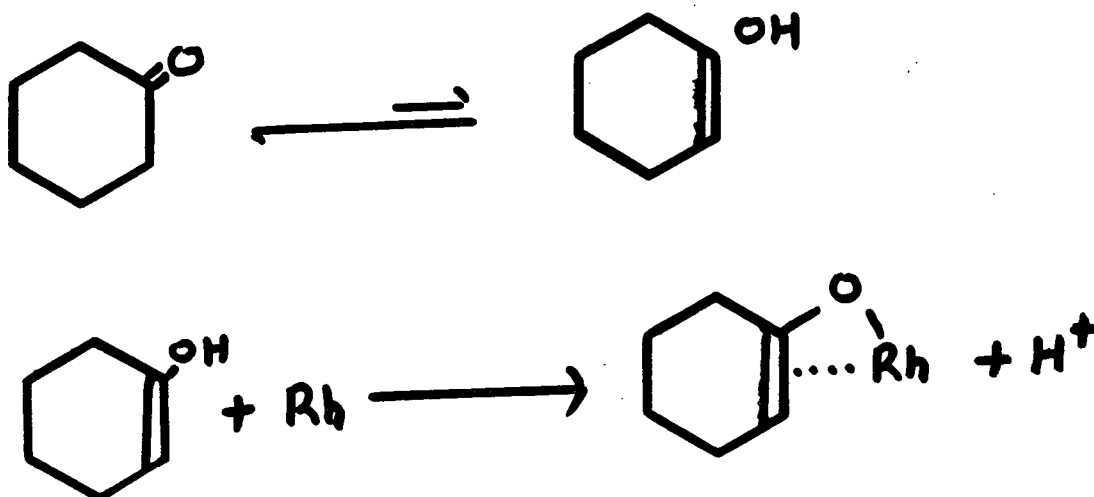
Interaction between a rhodium centre and acetone in the enolised form has also been proposed [17].

Evidence for strong interaction between rhodium and a carbon-carbon double bond is provided by the observation that addition of cyclohexene to the rhodium trichloride trihydrate-ferric chloride-cyclohexanol system can greatly inhibit catalytic oxidation. Strong complexation of olefins has also been found to poison the catalyst in the palladium chloride-sodium acetate- alcohol systems.

The rate of dehydrogenation of isopropyl alcohol by rhodium trichloride trihydrate -lithium chloride - stannous chloride-concentrated hydrochloric acid was found to be reduced as the concentration of acetone built up in the mixture but was restored when the acetone was distilled off. This was attributed to a competing hydrogenation of the acetone back to the alcohol.

Unfortunately in the present studies, it is not possible to separate cyclohexanone from cyclohexanol by simple distillation because of the similarity of their boiling points. It would be of interest to discover whether the original catalytic activity of the rhodium trichloride trihydrate-ferric chloride, combination could be restored after removal of the ketone from a reaction mixture containing 60% cyclohexanol and 40% cyclohexanone.

Water is produced during the catalytic oxidation of cyclohexanol to cyclohexanone by the rhodium trichloride trihydrate-ferric chloride system in the presence of oxygen. The accumulation of water inhibits the catalysis, as has been found in the palladium chloride-sodium acetate and palladium chloride-

cupric nitrate systems. This could result from competition between the water and the alcohol ligands for the rhodium.

It is difficult to make a meaningful comparison between the various catalytic systems for oxidation of secondary alcohols to ketones because different alcohols have been studied and at varying temperatures. Also, the effect of variation in concentration of catalyst on the oxidation process has not been published in most cases.

However, an attempt has been made to compare the 'catalytic efficiency' of a number of systems, and the data are presented in Table (11). The concentration of the catalytic species has been calculated for each system as mmol of catalyst per 100mmol of alcohol. The yield refers to the % of ketone present in the reaction mixture at the time indicated. The yield for system (m) has been calculated on the basis of the report

The 'catalytic efficiency' has been calculated in terms of the ratios mmol ketone/(mmol catalyst) and mmol ketone/(mmol catalyst)/(hr).

The % yields for systems involving dehydrogenation appear to be low (3-10%). Whether higher yields of ketone can be obtained using these catalytic dehydrogenation methods does not appear to have been investigated.

Both catalytic efficiency ratios for rhodium trichloride trihydrate-ferric chloride-oxygen systems compare favourably with the ratios for other catalytic systems. The ratio mmol ketone/(mmol catalyst) for the rhodium trichloride trihydrate-ferric chloride-oxygen system at 100deg appears to increase as the concentration of rhodium decreases.

Comparison with the palladium chloride-sodium acetate-oxygen system shows that both ratios are higher for the rhodium trichloride trihydrate -ferric chloride -oxygen combination, particularly when the time factor is considered. However, it should be noted that catalytic oxidation with the Pd system occurs at lower temperature.

It is not clear why dehydrogenation of iso-propyl alcohol occurs using a combination of rhodium trichloride trihydrate, lithium chloride and concentrated hydrochloric acid in the presence of oxygen, whereas no dehydrogenation of cyclohexanol was detected using rhodium trichloride trihydrate/concentrated hydrochloric acid, in the presence of oxygen. This could possibly be explained in terms of oxidation potentials for the conversion of alcohols to the corresponding carbonyl compounds as discussed in reference (18). In this publication it was suggested that the greater difficulty of oxidation of cyclohexanol, compared to other secondary alcohols was related to its ring structure.

Table (11).

	Catalyst	Oxidant	Alcohol	Temp deg	Time hr
a)	$RhCl_3/FeCl_3$	O_2(1atm)	Cyclohexanol	100	2.5
b)	"	"	"	100	0.5
c)	"	"	"	150	1.0
d)	"	"	"	100	3.0
e)	"	"	Cyclopentanol	100	2.5
f)	$RhCl_3$	"	Cyclohexanol	100	1.0
g)	$PdCl_2/Cu(NO_3)_2$	O_2(3atm)	"	90	2.0
h)	$PdCl_2$, NaOAc	O_2(1atm)	"	38	56
i)	"	"	Trans 3,3,5, trimethyl cyclohexanol	38	34
j)	$RuCl_2(P\phi_3)_3$	N-methyl-morpholine N-oxide	d-carverol	R.T.	2.0
k)	$RhCl_3/LiCl/$	Dehydrogenation	Isopropyl	83	6.0
l)	$RhCl_3/LiCl/$ $HCl/SnCl_2$	"	"	83	98
m)	$Ru(OCOCF_3)$ $CO(P\phi_3)_2$	"	sec-hexanol	143	0.5

Table (11). Comparison of data for catalytic oxidation of alcohols.

Table (11). Continued

	mmol catalyst/ (100mmol alcohol)	yield %ketone	mmol ketone/ (mmol catalyst)	mmol ketone/ (mmolcatalyst)/ hr
a)*	o.15	42	280	112
b)*	0.15	14	92	184
c)*	0.15	40	268	268
d)*	0.059	27	458	153
e)*	0.124	38	306	152
f)*	0.15	10	67	67
g)[9]	4	2	0.5	0.25
h)[7]		88		
i)[7]	1.0	94	94	2.8
j)[6]	0.42	94	223	112
k)[1]	0.035	10	280	47
l)[2]	1.15	9	8	0.8
m)[3]	0.033	3	91	182

* present work

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