1974

The chloroform extraction of the alkyl and cycloalkyl ketoxime complexes of palladium (II) from aqueous acid solutions.

Patrick J. Dunn
University of Windsor

Follow this and additional works at: https://scholar.uwindsor.ca/etd

Recommended Citation
https://scholar.uwindsor.ca/etd/3790

This online database contains the full-text of PhD dissertations and Masters' theses of University of Windsor students from 1954 forward. These documents are made available for personal study and research purposes only, in accordance with the Canadian Copyright Act and the Creative Commons license—CC BY-NC-ND (Attribution, Non-Commercial, No Derivative Works). Under this license, works must always be attributed to the copyright holder (original author), cannot be used for any commercial purposes, and may not be altered. Any other use would require the permission of the copyright holder. Students may inquire about withdrawing their dissertation and/or thesis from this database. For additional inquiries, please contact the repository administrator via email (scholarship@uwindsor.ca) or by telephone at 519-253-3000ext. 3208.
THE CHLOROFORM EXTRACTION OF THE ALKYL AND CYCLOALKYL ETHER COMPLEXES OF PALLADIUM (II) FROM AQUEOUS ACID SOLUTIONS

BY

PATRICK J. DUNN

A Dissertation

Submitted to the Faculty of Graduate Studies through the Department of Chemistry in Partial Fulfillment of the Requirements for the Degree of Doctor of Philosophy at the University of Windsor

Windsor, Ontario
1974
ABSTRACT

Palladium (II) reacts with alkyl and cycloalkyl ketoximes, and the resultant complex is found extractable into chloroform.

The effect of acid concentration, chloride ion concentration, oxime concentration and hydrolysis in acid solution, as well as oxime steric effects are operable in the extraction of palladium (II) chloride after reaction with 4-heptanone oxime or 2,4-dimethyl-3-pentanone oxime into chloroform. The resultant palladium-oxime complexes are isolated and infra-red spectral shift data and elemental analyses verify the product formation. This information aids in the reaction course and equilibrium of the reactants and product. Evidence of inter- and intramolecular hydrogen bonding also verify the product formation.

Palladium (II) was also found extractable as the sulphate and nitrate salt complexes by reaction with 4-heptanone oxime. Evidence, however, shows a different reaction course and possible intermediate formation than the postulations from the chloride studies.

Gas chromatographic studies have proven that lower molecular weight symmetrical alkyl ketoximes more readily hydrolyze under specific acid as well as chloride conditions, and are found less efficient in complexing with palladium. 

ii
and extracting into chloroform. Solubility studies of the oxime in chloroform and water solutions, as well as solubility studies of the palladium complexes in chloroform were undertaken.

Steric effects of oximes play a very important role in their reaction with palladium (II) chloride, as borne out in a comparative study of 2-methyl and 4-methyl cyclohexanone oxime with 4-heptanone oxime.
ACKNOWLEDGEMENTS

I would like to thank Dr. W. J. Holland for his guidance, encouragement and friendship during the course of this research at the University of Windsor, and also my committee, including Dr. R. J. Thibert, Dr. P. E. Schmidt, Dr. R. Zak and Dr. A. W. Guyp for their reading and commenting on this dissertation.

As well, I thank Dr. Robert Walker, for his assistance throughout the course of this project.

To the University of Windsor for the teaching assistantship, and the National Research Council for summer financial aid, I express my gratitude.

Also, to the Windsor Utilities Commission for tuitional aid, I am indebted.

Finally, special thanks must be given to my family for their assistance, interest and guidance over the years; for this I am especially grateful.
# TABLE OF CONTENTS

<table>
<thead>
<tr>
<th>Section</th>
<th>Page</th>
</tr>
</thead>
<tbody>
<tr>
<td>TITLE PAGE</td>
<td>i</td>
</tr>
<tr>
<td>ABSTRACT</td>
<td>ii</td>
</tr>
<tr>
<td>ACKNOWLEDGEMENTS</td>
<td>iv</td>
</tr>
<tr>
<td>TABLE OF CONTENTS</td>
<td>v</td>
</tr>
<tr>
<td>LIST OF FIGURES</td>
<td>vii</td>
</tr>
<tr>
<td>LIST OF TABLES</td>
<td>viii</td>
</tr>
<tr>
<td>PART I</td>
<td></td>
</tr>
<tr>
<td>INTRODUCTION</td>
<td>1</td>
</tr>
<tr>
<td>PART II</td>
<td></td>
</tr>
<tr>
<td>INTRODUCTION</td>
<td>10</td>
</tr>
<tr>
<td>EXPERIMENTAL</td>
<td>10</td>
</tr>
<tr>
<td>RESULTS AND DISCUSSION</td>
<td>17</td>
</tr>
<tr>
<td>CONCLUDING REMARKS AND REACTION PATHWAY</td>
<td>34</td>
</tr>
<tr>
<td>PART III</td>
<td></td>
</tr>
<tr>
<td>INTRODUCTION</td>
<td>38</td>
</tr>
<tr>
<td>EXPERIMENTAL</td>
<td>38</td>
</tr>
<tr>
<td>DISCUSSION AND RESULTS</td>
<td>39</td>
</tr>
<tr>
<td>CONCLUDING REMARKS</td>
<td>46</td>
</tr>
<tr>
<td>PART IV</td>
<td></td>
</tr>
<tr>
<td>INTRODUCTION</td>
<td>48</td>
</tr>
<tr>
<td>EXPERIMENTAL</td>
<td>48</td>
</tr>
</tbody>
</table>
# LIST OF FIGURES

<table>
<thead>
<tr>
<th>Figure</th>
<th>Description</th>
</tr>
</thead>
<tbody>
<tr>
<td>1</td>
<td>The Effect of Hydrochloric Acid Concentration on Palladium (II) Chloride Solutions, Using a Large Excess of Oxime</td>
</tr>
<tr>
<td>2</td>
<td>The Effect of a 0.100 ( \text{M} ) Hydrochloric Acid Solution on the Mole-ratio Extraction of Palladium (II) Chloride</td>
</tr>
<tr>
<td>3</td>
<td>The Effect of a 0.628 ( \text{M} ) Hydrochloric Acid Solution on the Mole-ratio Extraction of Palladium (II) Chloride</td>
</tr>
<tr>
<td>4</td>
<td>A Mole-ratio Study of 4-Heptanone Oxime with Palladium (II) Nitrate and Palladium (II) Sulphate</td>
</tr>
<tr>
<td>5</td>
<td>The Extraction of the Chloroform Solutions of Dichlorobis (4-Heptanone Oxime) Palladium (II) in Hydrochloric and Sulphuric Acid</td>
</tr>
<tr>
<td>6</td>
<td>A Mole-ratio Study of Various Oximes with Palladium (II) Chloride</td>
</tr>
<tr>
<td>7</td>
<td>Effect of Time on the Mole-ratio Study of 4-Heptanone Oxime and 5-Nonanone Oxime with Palladium (II) Chloride</td>
</tr>
<tr>
<td>8</td>
<td>A Mole-ratio Study of Isomeric C7 Oximes with Palladium (II) Chloride</td>
</tr>
<tr>
<td>Table</td>
<td>Description</td>
</tr>
<tr>
<td>-------</td>
<td>-------------------------------------------------------------------------------------------------</td>
</tr>
<tr>
<td>I</td>
<td>Effect of pH</td>
</tr>
<tr>
<td>II</td>
<td>Effect of pH</td>
</tr>
<tr>
<td>III</td>
<td>A 1:1 Mole-ratio Extraction from a Solution 0.028 M in Hydrochloric Acid</td>
</tr>
<tr>
<td>IV</td>
<td>Extraction from a Solution 0.028 M in Hydrochloric Acid and 0.972 M in Sodium Chloride</td>
</tr>
<tr>
<td>V</td>
<td>Extraction from a Solution 0.028 M in Hydrochloric Acid and 0.972 M in Sodium Chloride</td>
</tr>
<tr>
<td>VI</td>
<td>Extraction from a Solution 1.00 M in Sodium Chloride, pH 3.00</td>
</tr>
<tr>
<td>VII</td>
<td>Extraction from a Solution 1.00 M in Sodium Chloride, pH 3.00</td>
</tr>
<tr>
<td>VIII</td>
<td>Infra-red Absorption Bands for 2,4-Dimethyl-3-Pentanone Oxime, 4-Heptanone, and Their Corresponding Palladium (II) Complexes</td>
</tr>
<tr>
<td>IX</td>
<td>Infra-red Absorption Study of the Hydrogen Bonding of 2,4-Dimethyl-3-Pentanone Oxime and Its Corresponding Palladium (II) Complex</td>
</tr>
<tr>
<td>X</td>
<td>Infra-red Absorption Study of the Hydrogen Bonding of 4-Heptanone Oxime, and Its Corresponding Palladium (II) Complex</td>
</tr>
<tr>
<td>XI</td>
<td>Extraction of Pd(NO₃)₂ and PdSO₄ at Various Acid Concentrations</td>
</tr>
</tbody>
</table>
Table

XII. Extraction of $\text{Pd(NO}_3\text{)}_2$ from a Solution 1.00 N in $\text{HNO}_3$ and 3.00 N in $\text{Na}_2\text{SO}_4$ .................. 56

XIII. Extraction of $\text{PdSO}_4$ from a Solution 1.00 N in $\text{H}_2\text{SO}_4$ and 3.00 N in $\text{Na}_2\text{SO}_4$ ......... 57

XIV. Extraction of $\text{PdCl}_2$ from a Solution 1.00 N in $\text{HCl}$ and 3.00 N in $\text{NaCl}$ .................. 59

XV. Effect of Chloride Ion Concentration on the Extractability of Oximes from Chloroform Solution to Aqueous Chloride Solution .................. 75

XVI. Effect of Chloride Ion Concentration and Total Degree of Hydrolysis of Oximes During Extraction Procedure .......... 77

XVII. Extraction Studies of a Series of Oximes at 2.00 M Chloride Ion Concentration .................. 79

XVIII. Solubility of Oxime Complexes of Palladium in Chloroform at 25.0°C .................. 87

XIX. Extraction Studies of a Series of Isomeric $\text{C}_7$ Oximes at 2.00 M Chloride Ion Concentration. 95

XX. Solubility of Oxime Complexes of Palladium in Chloroform at 25.0°C .................. 100
PART I

GENERAL INTRODUCTION
PART I

GENERAL INTRODUCTION

1. Solvent Extraction as a Separational Technique for the Noble Metals

The separation of noble metals has long challenged the analytical chemist, and the problems of interferences still continue to necessitate the development of good methods of separation. These methods are greatly enhanced by precise information concerning the effect of time, acidity, salt content and reagent susceptibility, and it is only with this data that any economical method of separation and purification of a noble metal can possibly be achieved.

Separational methods include ion-exchange, solvent extraction, chromatography; precipitation and fire assay, and such methods have been extensively reviewed within the past decade (1-6). It is the solvent extraction technique which will be studied in detail within this dissertation.

Palladium, one of the six platinum metals is found at a level of 0.005 g/ton in the earth's crust (7) and it is this metal to which this study is related.

Because the estimated production cost per ton of this metal ranks highest next to platinum (8), a suitable solvent extractive process would be ideal for its separation and purification.
Solvent extraction procedures can be industrially adaptable because they allow for continuous operation, few production stages, and the ease with which such equipment can be controlled. These advantages seem to outweigh the disadvantages of extensive laboratory study, and fire hazards in the use of organic solvents (9).

The platinum metals occur in association with the copper nickel sulphide ores in the Sudbury district of Ontario. The total content of platinum metals is only in the order of 1/2 ppm, but in view of the large tonnage of nickel produced, this proves an important source (10). Presently, International Nickel Company sends their platinum concentrates to Acton, England for final fire-assay refining; Falconbridge Mining Company concentrates go to Kristiansan, Norway for final refining (11). It would seem inevitable that within the next ten years, the solvent extraction process will be more adaptable in the separation and purification of noble metals from the lower grade iron-ore deposits of Northern Ontario.

2. Standard Palladium Determinations

Standard methods for separating large amounts of palladium from the noble metals have been extensively reviewed by Beamish (1, 2, 12). Oxime precipitants by far predominate the methods of separation in these reviews, but inorganic precipitants and reducing agents can also be selectively used for such a purpose. The application of
dimethyl glyoxime for quantitative analysis is recommended as a standard procedure for the separation and detection of palladium (13, 14).

Previous studies from this laboratory have investigated the reagent di-2-pyridyl ketoxime as a suitable chelating agent for the gravimetric determination of palladium (15). This procedure offers distinct advantages over the dimethyl glyoxime determination in that it is fast, the precipitate is easy to handle, a large gravimetric factor is present for accurate analyses, and the method is applicable over a wide pH range from three to eleven. The probable structure for the chelate formed is shown below:

![Structure Diagram]

As well, studies from this laboratory have shown that a non-chelating oxime, di-2-thienyl ketoxime was found suitable for the gravimetric determination of palladium forming the complex dichlorobis (di-2-thienyl ketoxime-N,N') palladium (II) (16). The structure of this isolated complex...
It is because of the strong co-ordinating ability of the C=N-OH oxime group and the very strong donor properties of the oxime nitrogen that the above oxime has been found so suitable in reacting selectively with metals at certain pH values.

Palladium (II) usually has a co-ordination number of four, forming square-planar complexes such as \( \text{PdCl}_4^- \), and also the structure illustrated above (17). Palladium readily co-ordinates with such ligands as amines (18) and oximes to fill two sites around the metal, the remaining two being filled by the co-ordinating anion, such as chloride, nitrate or sulphate.

3. Previously-related Palladium Research

Because of the strong co-ordinating ability of oximes, an investigation of the reaction between symmetrical
alkyl ketoximes and palladium (II) was undertaken, with a preliminary study of the chloroform extraction of the resulting complexes (19). The results of this study demonstrated, from an aqueous-alcohol solution using 3-pentanone oxime, 4-heptanone oxime and 5-nonanone oxime, the chloroform extraction appeared to be quantitative with regard to palladium (II). However, the acetoxime extraction of palladium yielded approximately 89% extraction under the same reaction conditions.

This research was further projected to apply these reagents to the analytical problem of selectively separating palladium from the other base and noble metals in macro-quantitative amounts by a solvent extraction procedure.

It has been shown that palladium (II) chloride at the 18 mg per 100 ml level could be quantitatively (greater than 99.9%) extracted from 1.0 molar hydrochloric acid solutions. It has been further shown that under these acid conditions, mg amounts of copper (II), cobalt (II), iron (III), and nickel (II) were not extracted following the same palladium extraction procedure (20, 21). However, it was noted that at 0.1 molar hydrochloric acid concentration, greater than 99.0% gold (III) at the 34 mg per 100 ml level could be extracted (22).

Further studies with this same oxime showed that only trace amounts of platinum (IV) and rhodium (III) at the 30 mg per 100 ml level (0.1% and 0.03% respectively) and small amounts of iridium (IV) at the 26 mg per 100 ml level were
extracted from a 1.0 molar hydrochloric acid solution into chloroform. This study was further developed to show that microgram amounts of palladium could be separated from a hydrochloric acid solution containing milligram amounts of platinum (IV) and microgram amounts of rhodium (III) and iridium (IV) (23). This last study was found adaptable in the analysis of synthetic ore systems, as well as matte samples containing gram amounts of nickel and copper and milligram amounts of iron. Here, microgram amounts of palladium were able to be separated and detected in the presence of other trace metals (24).

4. Present Palladium Research

From a preliminary study of the reaction between palladium (II) chloride, and the symmetrical alkyl ketoximes, of which the above oxime is included, a general equation may be written:

$$2[R-\text{C-}R] + \text{PdCl}_2 \rightarrow [R-\text{C-}R]_2 \text{PdCl}_2$$

This present work constituted a comparative investigation of the effect of changing the "R" group from n-propyl to iso-propyl (i.e., 4-heptanone oxime and 2,4-dimethyl-3-pentanone oxime respectively) and analyzing data obtained with regard to oxime steric effects, oxime hydrolysis, acid concentration, oxime concentration, and chloride ion concentration on the chloroform extraction efficiency of the corresponding palladium (II) chloride
complexes (25).

These data coupled with previous infra-red data (26) as well as present hydrogen bonding infra-red data could possibly lead to an elucidation of the course of the reaction of the above equation, as well as a better appreciation of the product formed.

This research led directly into a comparative study of the effect of changing the palladium anion species, and thus the 4-heptanone oxime chloroform extraction of palladium (II) nitrate and palladium (II) sulphate was investigated. As well, the effect of large excesses of nitric and sulphuric acid, and their corresponding sodium salts was noted. A rationalization for the difference in behaviour of extractability between the chloride salts of palladium with those of nitrate and sulphate is made.

An attempt to isolate the oxime complexes of palladium (II) nitrate and palladium (II) sulphate was made, in order to justify the mole-ratio data obtained for the two palladium salts.

The effect of increasing carbon chain length with regard to ease of extractability of palladium salts was further studied. Initial studies using gas chromatographic techniques demonstrated the solubility of the oximes in both chloroform and water, under specific pH and chloride ion conditions. This data aided in an appreciation of the extent of hydrolysis of oxime to ketone under such reaction conditions, and was thus useful in predicting
The extractability of palladium (II) chloride with the unhydrolyzed oxime.

Oxime steric effects were better appreciated with a comparative study of three isomeric C₇ oximes, 4-methyl cyclohexanone oxime, 4-heptanone oxime, and 2-methyl cyclohexanone oxime.

The solubility in chloroform of the palladium complexes of a series of oximes also added to the overall understanding of extractability and efficiency of reactivity of these systems.
PART II

A COMPARATIVE STUDY OF THE EXTRACTABILITY
OF 4-HEPTANONE OXIME AND 2,5-DIMETHYL-3-PENTANONE OXIME
ON PALLADIUM (II) CHLORIDE
PART II
A COMPARATIVE STUDY OF THE EXTRACTABILITY
OF 4-HEPTANONE OXIME AND 2,4-DIMETHYL-3-PENTANONE OXIME
ON PALLADIUM (II) CHLORIDE

1. Introduction

It was felt that an investigation into the pH and acidity effects upon extractability of two isomeric oxime complexes of palladium (II) chloride might lead to some rationalization of the steric effect of changing the "R" group of the oxime. Since a study had been undertaken where C₅, C₇, and C₉ symmetrical alkyl ketoximes had demonstrated good extraction (99%) of palladium (II) chloride into chloroform (19), the C₇ oxime was arbitrarily chosen for further isomeric analyses. Thus the di-n-propyl ketoxime and the di-isopropyl ketoxime were studied in further detail.

2. Experimental
a) Apparatus

Infra-red spectra were obtained with a Beckman IR-12 Spectrophotometer. A 5-10% w/v concentration using Fisher Certified ACS Spectrophotometric chloroform was used, or in the case of some liquids, neat samples were run in potassium bromide. Solid samples were run using a one percent potassium bromide pellet. Visible spectrophotometric measurements were made on a Beckman DB Spectro-
photometer equipped with a Sargent Model SRL Recorder. A Sargent Model DR pH meter was used for all pH measurements.

b) Chemicals and reagents

All chemicals were of reagent grade. Extractions were made with Fisher Certified ACS chloroform. Baker Analyzed hydrochloric acid was used for acid concentration adjustments, while pH adjustments were made with a dilute aqueous solution of Fisher Certified ACS sodium hydroxide. Ethyl alcohol, 95%, was used for oxime dilution. The ketones, 2,4-dimethyl-3-pentanone, and 4-heptanone were obtained from Aldrich Chemical Company. Better product recovery of oxime in each case was yielded when starting ketone was redistilled prior to the oxime preparations. Both the hydroxylamine hydrochloride, used in preparing the oxime, and the anhydrous palladium (II) chloride were obtained from Fisher Scientific Company.

c) Preparation of standard palladium (II) chloride

Standard palladium (II) chloride solutions were prepared by heating a solution of 3.00 g anhydrous palladium (II) chloride in 10.0 ml of concentrated hydrochloric acid to yield a clear reddish-brown syrup. The syrup was transferred to a one-litre volumetric flask through a sintered glass crucible, and two additional portions of hot hydrochloric acid were filtered through the crucible to transfer the solution. The solution was diluted to the mark with distilled deionized water.
The solution was then standardized gravimetrically using di-2-pyridyl ketoxime (16).

The hydrochloric acid concentration of the standard palladium (II) chloride was determined by withdrawing an aliquot, adding 1.0 g sodium chloride and titrating with a previously standardized solution of sodium hydroxide to pH 5.00.

d) Preparation of 4-heptanone oxime and 2,4-dimethyl-3-pentanone oxime

Symmetrical aliphatic ketones react with hydroxylamine hydrochloride to give the corresponding oximes.

The basic reaction is:

\[
\text{R-C-R + :NH}_2\text{OH} \xrightarrow{\text{OH}} \text{R-C-R + H}_2\text{O} \xrightarrow{\text{OH}}
\]

where R=n-C\textsubscript{3}H\textsubscript{7} and iso-C\textsubscript{3}H\textsubscript{7}.

The 4-heptanone oxime was prepared as outlined by Shriner, Fuson, and Curtin (27) and infra-red analysis verified the findings of Dimenna (28).

The 2,4-dimethyl-3-pentanone oxime was prepared by refluxing 64.0 g (0.56 mole) of 2,4-dimethyl-3-pentanone with 42.0 g (0.60 mole) hydroxylamine hydrochloride dissolved in 100 ml distilled water, and 24.0 g (0.60 mole) sodium hydroxide dissolved in 100 ml distilled water. The solution was refluxed for four hours in a one-litre round-bottom flask with stirring. After cooling this solution, it was transferred to a one-litre beaker.
evaporating off the excess ethyl alcohol until two distinct layers formed. The oily top layer was separated and dried overnight with anhydrous calcium chloride. The resulting clear colourless liquid was vacuum distilled at 52-54°C with 1.60 mm Hg (29). This warm distillate was then transferred to a vacuum sublimator and 32.8 g white needles of camphoraceous odour were obtained. The melting point of the oxime was 31-33°C with the literature value being 34°C (30).

Infrared analysis indicated a C=O band at 1660 cm⁻¹ and a broad N-H stretching band centered at 3270 cm⁻¹. There was no C=O stretching band observed at the 1700 cm⁻¹ region, which indicated no ketone impurity was present in the synthesized oxime.

e) Preparation of the palladium (II) complexes of 4-heptanone oxime and 2,4-dimethyl-3-pentanone oxime

The general stoichiometric equation for oxime palladium complexation is:

\[ \text{PdCl}_2 \_ 2[R-C-R] \longrightarrow [R-C-R]_{2}\text{PdCl}_2 \]

where \( R = \text{H}, \text{C}_3\text{H}_7 \) and \( \text{iso-C}_3\text{H}_7 \).

The dichlorobis (4-heptanone oxime) palladium (II) complex was prepared following the procedure outlined by Dimenna, and gravimetric palladium determinations verified the purity of the complex (28).

The palladium complex of diisopropyl ketoxime was
prepared following the procedure outlined for the corresponding \( n \)-propyl oxime complex (11). In a 400 ml beaker was added 0.44 g of anhydrous palladium (II) chloride (10% excess) and 10 ml of 12.0 N hydrochloric acid. The mixture was heated to obtain a clear reddish-brown solution which was then cooled, the volume adjusted to 50 ml using distilled water and the pH adjusted to 3.00 using dilute sodium hydroxide.

To 10 ml of 1:3 alcohol-water mixture was added 580 mg of 2,4-dimethyl-3-pentanone oxime in a 400 ml beaker. The pH of this solution was then adjusted to 3.00 by dropwise addition of dilute hydrochloric acid.

The palladium solution was then slowly added to the alcoholic oxime mixture with stirring. A flocculent yellow precipitate appeared immediately with no appreciable change in pH upon addition of solutions. The precipitate was vacuum filtered, washed with 100 ml 5% hydrochloric acid and then with water, adjusted to pH 3.00. The yellow crystals, after being vacuum dried over anhydrous calcium sulphate overnight, melted at 199-201°C with decomposition. The product yield was 630 mg, corresponding to 62.5% of the theoretical recovery.

Analysis of the complex from Spring Micronanalytical Laboratory, Ann Arbor, Michigan is listed below:
Analysis (calculated for $C_{14}H_{20}N_2O_2Cl_2Pd$)

<table>
<thead>
<tr>
<th>Element</th>
<th>Theory</th>
<th>Found</th>
</tr>
</thead>
<tbody>
<tr>
<td>C</td>
<td>38.59</td>
<td>38.63</td>
</tr>
<tr>
<td>H</td>
<td>6.94</td>
<td>7.03</td>
</tr>
<tr>
<td>N</td>
<td>6.43</td>
<td>6.47</td>
</tr>
<tr>
<td>Cl</td>
<td>16.27</td>
<td>16.23</td>
</tr>
<tr>
<td>Pd</td>
<td>24.42</td>
<td>24.67</td>
</tr>
</tbody>
</table>

*Palladium was determined by ignition of the complex to the metal.

Infra-red analysis showed a C=N band at 1668 cm$^{-1}$ and an O-H band centered at 3290 cm$^{-1}$. A possible structure for the complex based on infra-red and elemental analysis is illustrated below:

\[
\begin{align*}
C_3H_7-N-C-C_3H_7 \\
\text{HO} \quad \text{Cl} \\
Pd \quad \text{Cl} \\
N \quad \text{OH} \\
C_3H_7-C-C_3H_7
\end{align*}
\]

f) Chloroform extraction of the palladium (II) chloride oxime complexes

A 10 ml aliquot of the standard palladium (II) chloride
solution was transferred to a 250 ml graduated separatory funnel, after appropriate adjustment of the pH or addition of a known volume of standardized concentrated hydrochloric acid. The pH adjustments were made with dropwise addition of dilute sodium hydroxide. The solution was diluted then to the 100 ml mark with distilled water of the corresponding pH or distilled water respectively. A known weight of the oxime in 5ml of alcohol was added and the mixture shaken vigorously. After standing for 10 minutes, the solution was shaken again and allowed to stand an additional 10 minutes. The mixture was extracted with two 25 ml portions of chloroform, and the chloroform extracts transferred to a 400 ml beaker. The above procedure was repeated once more with the residual water layer, and the chloroform extracts were combined.

g) Palladium analysis of the water layer

The water layer was transferred to a 400 ml beaker, 5 ml of concentrated sulphuric acid were added, and the solution evaporated to dense white fumes on a hot plate. To the residual sulphuric acid solution was carefully added 5 ml of concentrated nitric acid and 10 ml of water. The solution was again evaporated to fumes. The oxides of nitrogen were removed by repeated addition of hydrochloric acid and evaporation to fumes. This was checked by a negative test on moistened potassium iodide-starch test paper. To the cooled solution was added water and
1 ml of concentrated hydrochloric acid. After adjustment of the pH with sodium hydroxide solution, the palladium was determined spectrophotometrically (32) or gravimetrically (15) with di-2-pyridyl ketoxime.

h) Palladium analysis of the chloroform extract

The combined chloroform extracts in a 400 ml beaker were evaporated to near-dryness on a steam bath, and 5 ml of concentrated sulphuric acid and 5 ml water were added carefully to the residue. The solution was then worked up and the palladium content determined following the procedure outlined for the determination of palladium in the water layer.

3. Results and Discussion

a) Effect of pH and acidity

A double extraction procedure was studied in order to compare the effects of changes in pH and acidity on the degree of extractability of palladium (II) chloride using 4-heptanone oxime and 2,4-dimethyl-3-pentanone oxime as complexing reagents. In each case 18.24 mg of palladium (II) was present in the separatory vessel. As well, a large excess of oxime (2 x 300 mg) was used, which constituted a 14-fold excess present to react with the palladium (II) chloride. The purpose of using ethyl alcohol was to transfer simply and easily the oxime to the separatory funnel.

Over a pH range 1.00 to 3.00 and a chloride concen-
tration range from 0.027 to 0.10 M, it was noted that greater than 99.9% of the palladium (II) taken was extracted into chloroform using the above mentioned procedure. These results are presented in Table I and Table II for the 4-heptanone oxime, and 2,4-dimethyl-3-pentanone oxime respectively.

This study was further extended into more acidic media, and by the addition of known amounts of standardized hydrochloric acid, the changes in extractability into chloroform of the oxime complexes of palladium (II) chloride could be noted. Figure 1 demonstrates this change. It was noted that using the diisopropyl ketoxime, the extractability drops from 99.9% at 0.30 M in hydrochloric acid to 99.0% at 1.00 M in acid. However, greater than 99.9% extraction of palladium (II) is obtained down as far as 1.50 M in hydrochloric acid when the 4-heptanone oxime reagent is used. Thus it would appear that the n-propyl substituent is less affected by hydrochloric acid concentration than is the isopropyl substituent.

Since it was noted that the acid concentration appeared to affect changes in the extractability of the two oximes with palladium (II) chloride, it was decided to study the extraction efficiency of these two oximes under different reaction conditions. A study was conducted whereby a mole-ratio plot of oxime to palladium (II) versus extraction efficiency was plotted.
TABLE I
EFFECT OF pH

Palladium (II) taken 18.24 mg; Total weight of 4-heptanone oxime, 600 mg (2 x 300).

<table>
<thead>
<tr>
<th>pH</th>
<th>Molarity of Chloride ion</th>
<th>Palladium (II) Found in Water Layer, μg</th>
<th>% Palladium (II) Extracted</th>
</tr>
</thead>
<tbody>
<tr>
<td>3.00</td>
<td>0.027</td>
<td>1</td>
<td>100.0</td>
</tr>
<tr>
<td>2.50</td>
<td>0.027</td>
<td>1</td>
<td>100.0</td>
</tr>
<tr>
<td>2.00</td>
<td>0.027</td>
<td>12</td>
<td>99.93</td>
</tr>
<tr>
<td>1.50</td>
<td>0.032</td>
<td>0</td>
<td>100.0</td>
</tr>
<tr>
<td>1.00</td>
<td>0.100</td>
<td>0</td>
<td>100.0</td>
</tr>
</tbody>
</table>
TABLE II
EFFECT OF pH

Palladium (II) taken 18.24 mg; Total weight of 2,4-Dimethyl-3-pentanone oxime, 600 mg (2 x 300)

<table>
<thead>
<tr>
<th>pH</th>
<th>Molarity of Chloride ion</th>
<th>Palladium (II) Found in Water Layer, μg</th>
<th>% Palladium (II) Extracted</th>
</tr>
</thead>
<tbody>
<tr>
<td>3.00</td>
<td>0.027</td>
<td>9</td>
<td>99.95</td>
</tr>
<tr>
<td>2.50</td>
<td>0.027</td>
<td>8</td>
<td>99.96</td>
</tr>
<tr>
<td>2.00</td>
<td>0.027</td>
<td>2</td>
<td>99.99</td>
</tr>
<tr>
<td>1.50</td>
<td>0.032</td>
<td>7</td>
<td>99.96</td>
</tr>
<tr>
<td>1.00</td>
<td>0.100</td>
<td>14</td>
<td>99.92</td>
</tr>
</tbody>
</table>
THE EFFECT OF HYDROCHLORIC ACID CONCENTRATION ON
PALLADIUM (II) CHLORIDE SOLUTIONS, USING A LARGE
EXCESS OF OXIME

- 4-Heptanone Oxime

- 2,4-Dimethyl-3-Pentanone Oxime

Total weight of oxime, 600 mg (2 x 300)
Palladium taken, 18.24 mg
In Figure 2, the effect of 0.10 M hydrochloric acid can be seen on the extractability of palladium (II) chloride in chloroform. It is noted that the n-propyl substituent appears to be more efficient in extractability with one hundred percent extraction being obtained at a 3:1 mole-ratio (there is a 50% excess of oxime present to complex theoretically with the palladium (II) present). This same efficiency is not reached until a 6:1 mole-ratio in the case of the 2,4-dimethyl-3-pentanone oxime (an excess of 200% oxime).

The acid concentration in each case was then altered from 0.10 M to 0.028 M in hydrochloric acid, and the same comparative study was made. It can be noted from Figure 3 that in both the extraction with 4-heptanone oxime and 2,4-dimethyl-3-pentanone oxime, one hundred percent extraction is reached very near a 2:1 mole-ratio of oxime to palladium (II). Thus, under decreased acid conditions, the extraction efficiency with each oxime is increased to its theoretical extraction level.

It was observed that for a mole-ratio plot at 0.028 M in acid, at a 1:1 mole-ratio of 2,4-dimethyl-3-pentanone oxime to palladium (II), 49% of the palladium (II) was extracted as compared to the theoretical value of 50%. However, in the case of 4-heptanone oxime, results above the 50% theoretical value were observed. Table III demonstrates these results where theoretically 52.70% of palladium should be extracted, whereas the actual
EFFECT OF A 0.100 M HYDROCHLORIC ACID SOLUTION ON THE MOLE-RATIO EXTRACTION OF PALLADIUM (II) CHLORIDE

- 4-Heptanone Oxime
- 2,4-Dimethyl-3-Pentanone Oxime

Palladium taken 18.12 mg
Molarity of Hydrochloric acid, 0.100
EFFECT OF A 0.028 M HYDROCHLORIC ACID SOLUTION ON THE
MOLE-RATIO EXTRACTION OF PALLADIUM (II) CHLORIDE

- 4-Heptanone Oxime

Δ 2,4-Dimethyl-3-Pentanone Oxime

Palladium taken, 18.04 mg
Molarity of Hydrochloric acid, 0.028.
TABLE III
A 1:1 MOLE-RATIO EXTRACTION FROM A SOLUTION
0.028 M IN HYDROCHLORIC ACID

Palladium taken 17.30 mg; Total weight of 4-heptanone
oxime added 22.11 mg (corresponding to 52.70% theoretical
extraction)

<table>
<thead>
<tr>
<th>Run</th>
<th>% Pd (II) Extracted</th>
</tr>
</thead>
<tbody>
<tr>
<td>1</td>
<td>55.15</td>
</tr>
<tr>
<td>2</td>
<td>55.60</td>
</tr>
<tr>
<td>3</td>
<td>55.14</td>
</tr>
<tr>
<td>4</td>
<td>55.15</td>
</tr>
<tr>
<td>Average</td>
<td>55.26</td>
</tr>
</tbody>
</table>
gravimetric results yield 55.26% (2.4% above the theoretical 50.0% extraction). The possibility of a small amount of presumably neutral complex having a mole-ratio of oxime to palladium (II) less than 2:1 could form and be extractable in chloroform, accounting for the high result. Such a neutral complex could possibly be of a bridged form as seen below:

![Diagram]

where Ox = 4-heptanone oxime.

b) Effect of acidity on degree of oxime hydrolysis

From the previous acid study (as seen in Figure 2 and Figure 3) it was observed that palladium oxime extraction efficiency noticeably increased as the hydrochloric acid concentration decreased. The effect of chloride ion concentration, as a salting-out agent, was thought to play a vital part in this extractability. As well, the question of what was occurring to the unreacted oxime was posed.

A study was undertaken whereby the 2:1 mole-ratio extraction of palladium (II) chloride was compared with the two different oximes, at specific chloride concentrations. The possibility of the oxime hydrolyzing to the corresponding ketone was studied by quantitative infra-red analysis. A series of oxime standards were
set up by measurement of the C=N stretching intensity, and as well, ketone standards were noted at the 1700 cm\(^{-1}\) region. Thus by noting the decrease of C=N stretching intensity relative to an increase in the C=O stretching intensity, an estimate of the degree of oxime hydrolysis could be made.

A double extraction procedure of palladium (II) chloride was studied at 0.028 M in hydrochloric acid, but the total chloride ion concentration was adjusted to 1.00 M by addition of the required amount of sodium chloride. Table IV and Table V list the extraction results under these specific conditions for the 4-heptanone oxime and 2,4-dimethyl-3-pentanone oxime respectively. Infra-red analysis indicated that in the case of the di-n-propyl ketoxime, 14% hydrolysis was observed with 75.70% of the palladium (II) chloride being extracted. However, in the case of the diisopropyl ketoxime, with 18% hydrolysis of oxime found, there is only 54.50% of the palladium (II) chloride extracted. It was noted from Figure 3, under similar acid conditions, both oximes gave very nearly 100% extraction.

A comparative study was made whereby the hydrochloric acid concentration was neutralized to a pH of 3.00 by addition of dilute sodium hydroxide, and the chloride concentration remained at 1.00 M. From Table IV - VI by decreasing the acid concentration from 0.028 M to a pH of 3.00, an increase in extraction from 75.70% to 93.00%
TABLE IV
EXTRACTION FROM A SOLUTION 0.028 M IN HYDROCHLORIC ACID AND 0.972 M IN SODIUM CHLORIDE

Palladium (II) taken, 18.04 mg; Total weight of 4-Heptanone Oxime, 43.72 mg (2 x 21.86); Hydrolysis of Oxime, 14%.

<table>
<thead>
<tr>
<th>Run</th>
<th>% Pd (II) Extracted</th>
</tr>
</thead>
<tbody>
<tr>
<td>1</td>
<td>74.11</td>
</tr>
<tr>
<td>2</td>
<td>73.95</td>
</tr>
<tr>
<td>3</td>
<td>77.72</td>
</tr>
<tr>
<td>4</td>
<td>77.00</td>
</tr>
<tr>
<td>Average</td>
<td>75.70</td>
</tr>
</tbody>
</table>
### TABLE V

**EXTRACTION FROM A SOLUTION 0.028 M IN HYDROCHLORIC ACID AND 0.972 M IN SODIUM CHLORIDE**

Palladium (II) taken 18.04 mg; Total weight of 2,4-Dimethyl-3-pentanone Oxime 43.14 mg (2 x 21.57); Hydrolysis of Oxime, 18%

<table>
<thead>
<tr>
<th>Run</th>
<th>% Pd&quot;(II) Extracted</th>
</tr>
</thead>
<tbody>
<tr>
<td>1</td>
<td>55.70</td>
</tr>
<tr>
<td>2</td>
<td>54.10</td>
</tr>
<tr>
<td>3</td>
<td>54.93</td>
</tr>
<tr>
<td>4</td>
<td>53.22</td>
</tr>
<tr>
<td><strong>Average</strong></td>
<td><strong>54.50</strong></td>
</tr>
</tbody>
</table>
### TABLE VI

**EXTRACTION FROM A SOLUTION 1.00 M IN SODIUM CHLORIDE, pH 3.00**

Palladium (II) taken 17.30 mg; Total weight of 4-Heptanone Oxime 43.80 mg (2 x 21.90); Hydrolysis of Oxime, 6%

<table>
<thead>
<tr>
<th>Run</th>
<th>% Pd (II) Extracted</th>
</tr>
</thead>
<tbody>
<tr>
<td>1</td>
<td>91.90</td>
</tr>
<tr>
<td>2</td>
<td>92.32</td>
</tr>
<tr>
<td>3</td>
<td>93.72</td>
</tr>
<tr>
<td>4</td>
<td>94.00</td>
</tr>
<tr>
<td>Average</td>
<td>93.00</td>
</tr>
</tbody>
</table>

*Illustration or figure appears at the bottom of the page.*
was seen for the 4-heptanone oxime. As well with a lesser amount of acid present, it is understandable that the acid hydrolysis of oxime is decreased from 14% to 6%.
The results of the 2,4-dimethyl-3-pentanone oxime study are seen in Table VII. An increase in extraction of palladium (II) chloride from 54.50% to 85.55% was noted, with a decrease in hydrolysis of oxime from 18% to 1%.

Thus it can be seen from these studies that an increase in acid concentration increases the degree of oxime hydrolysis, in turn decreasing the amount of palladium complex formed and found extractable into chloroform.

As well, a comparison of these studies relative to the mole-ratio study of Figure 3 shows that an increase in chloride ion concentration has the counter effect on the ability of extraction of the palladium complexes of both the di-n-propyl and diisopropyl ketoximes into chloroform.

4. Concluding Remarks and Reaction Pathway

The results presented in this part show that the four conditions of chloride ion concentration, oxime hydrolysis in acid solution, oxime concentration, and oxime steric effect are operable in the extraction of palladium (II) chloride, after reaction with 4-heptanone oxime or 2,4-dimethyl-3-pentanone oxime, into chloroform.

The results referred to and the elemental analyses of the isolated complexes indicate the following reaction course:
TABLE VII
EXTRACTION FROM A SOLUTION 1.00 M IN SODIUM CHLORIDE, pH 3.00

Palladium (II) taken 17.30 mg; Total weight of 2,4-Dimethyl-3-Pentanone Oxime 43.80 mg (2 x 21.90); Hydrolysis of Oxime, 1%

<table>
<thead>
<tr>
<th>Run</th>
<th>% Pd (II) Extraction</th>
</tr>
</thead>
<tbody>
<tr>
<td>1</td>
<td>84.56</td>
</tr>
<tr>
<td>2</td>
<td>86.30</td>
</tr>
<tr>
<td>3</td>
<td>86.01</td>
</tr>
<tr>
<td>4</td>
<td>85.32</td>
</tr>
<tr>
<td>Average</td>
<td>85.55</td>
</tr>
</tbody>
</table>
\[
PdCl_4^- \rightarrow PdCl_3^- + Cl^-
PdCl_3^- \rightarrow PdCl_2 + Cl^-
PdCl_2 + 2[R-C-R] \rightarrow [R-C-R]_2 \cdot PdCl_2
\]

where R=n-propyl or isopropyl

On extraction, the resulting equilibria are displaced to the right by an excess of oxime, a low chloride ion concentration, a low acid concentration, and solubility of the neutral complexes in chloroform. A difference in extraction behaviour of the two oximes is attributed to steric effects.
PART III

CHARACTERIZATION OF INFRA-RED DATA
PART III
CHARACTERIZATION OF INFRA-RED DATA

1. Introduction
Infra-red spectral data can provide valuable information about the molecular structure and chemical bonding in coordination compounds (33). Thus, it is very useful to compare the infra-red spectra of the free and complexed ligands in order to determine the type of bonding within the metal complex. Any noticeable vibrational frequency shifts between the complexed ligand relative to the free ligand can be attributed to a metal-ligand bond formation (34). The prime absorption peaks are the free oxime functional group C=N=OH, as well as the bonded functional group (i.e., the bond co-ordinating the free functional group to the palladium (II) ion).

2. Experimental
a) Apparatus
Infra-red spectra were obtained with a Beckman IR-12 Spectrophotometer. Infra-red absorption bands for the free and complexed oximes were obtained in KBr cells, and KBr pellets, using Fisher Certified ACS Spectrophotometric chloroform for dilution. Hydrogen bonding studies were conducted using variable path-length KBr cells, supplied from Research and Industrial Instruments Company, England.
b) Chemicals

The oximes, 4-heptanone oxime, 2,4-dimethyl-3-pentanone oxime, and their corresponding dichloro palladium (II) complexes were prepared as outlined in Part II.

3. Discussion and Results

a) Band assignments for oximes and their palladium (II) complexes

The 4-heptanone oxime was analyzed using a neat sample, but the 2,4-dimethyl-3-pentanone oxime, being a solid, was analyzed in a KBr pellet. The dichloro palladium (II) complexes of each oxime were analyzed using a 5-10% w/v solution in chloroform. These data are seen in Table VIII. The absorption bands near 1660 cm\(^{-1}\) for both the oximes and their palladium (II) complexes were assigned as C=O stretching (35), with a broad band near 3300 cm\(^{-1}\) ascribed as the associated O-H stretching frequency arising from intermolecular bonding between the molecules of the oximes.

The frequency arising in the 950-1020 cm\(^{-1}\) region is assigned as N-O stretching modes. A noticeable shift is observed with regard to this N-O stretching of the free oxime relative to the palladium (II) complex. The N-O stretching frequency of the free di-n-propyl, and diisopropyl oxime are seen at 945 cm\(^{-1}\) and 960 cm\(^{-1}\), respectively. This frequency is shifted for the complexed oxime to 1006 cm\(^{-1}\) and 1020 cm\(^{-1}\) respectively.
<table>
<thead>
<tr>
<th>Compound</th>
<th>C=N Bond (cm(^{-1}))</th>
<th>N-O Bond (cm(^{-1}))</th>
<th>O-H Stretching Bond (cm(^{-1}))</th>
</tr>
</thead>
<tbody>
<tr>
<td>2,4-Dimethyl-3-Pentanone Oxime</td>
<td>1665</td>
<td>945</td>
<td>3220 (Broad)</td>
</tr>
<tr>
<td>Dichlorobis (2,4-Dimethyl-3-Pentanone Oxime) Palladium (II)</td>
<td>1660-1670</td>
<td>1006</td>
<td>3285 (Sharp)</td>
</tr>
<tr>
<td>4-Heptanone Oxime</td>
<td>1665-1670</td>
<td>960</td>
<td>3280 (Broad)</td>
</tr>
<tr>
<td>Dichlorobis (4-Heptanone Oxime) Palladium (II)</td>
<td>1665</td>
<td>1020</td>
<td>3300 (Sharp)</td>
</tr>
</tbody>
</table>
This increased frequency is indicative of an increase in bond strength (36). It has been rationalized that the increased strength of the N-O bond in the complexed oxime is due to the donation of electrons from the oxygen atom in the direction of the N-O bond, in order to offset the slight positive character which the N attains upon co-ordination. A covalent bond of Pd-N is formed as N donates its unpaired electrons during complexation (37). This rationalization has been illustrated schematically by Dimenna, as seen below:

![Chemical Structure Diagram]

It was noted that the C=N absorption peaks of both the oxime and the complexed oxime are in the same region, which tends to demonstrate that co-ordination seems to have little effect on the C=N stretching frequency. This is understandable with such high electron density of the C-to-N double bond.

In the free oxime, broad intense bands occurred in the 3200-3300 cm⁻¹ region which are characterized as associated O-H stretching modes of the free oxime. However, in the complexed oxime, similar but sharper peaks
were observed in the 3285-3300 cm$^{-1}$ region. It was also noted that a medium band near 3600 cm$^{-1}$ associated with free N-H stretching was found for the oximes, but absent in the complexed oximes.

b) Hydrogen bonding study of the oximes and their palladium (II) complexes

Hydrogen bonding which could occur between the labile hydrogen of the oxime functional group and the chloride atom of the palladium (II) chloride molecule during complexation was further investigated.

Intermolecular hydrogen bonding increases as the concentration of the solution increases and often additional bands start to appear at lower frequencies (38). For comparison of this type of bonding, the path-length of the cell must be altered with changing concentration so as the same number of absorbing molecules will be present in the infra-red beam at each concentration. However, weak intramolecular bonding frequently can occur when a hydroxyl group is situated adjacent to a proton acceptor group (38). Since there is a chloride proton acceptor group situated relatively close to the hydroxyl group of the oxime, there is a strong possibility for the occurrence of intramolecular hydrogen bonding. This type of bonding, which is independent of concentration, is characterized by a slight shift in absorption to longer wavelength, and is generally a sharp peak. It is only
with high resolution and very dilute solutions that such bonding can be detected without interference from intermolecular hydrogen bonding.

A study was conducted using very dilute oxime and palladium (II) complex solutions in Fisher ACS Spectrophotometric chloroform. The chloroform prior to use in dilution of samples was passed through a silica-gel column to eliminate any traces of water or preservative ethanol. The results of this study for the 2,4-dimethyl-3-pentanone oxime and its dichloro palladium (II) complex can be seen in Table IX. The corresponding di-n-propyl ketoxime study is shown in Table X.

It was noted that for both of the palladium (II) complexes, the free sharp O-H stretching peak at the 3600 cm⁻¹ region was absent, while it was very noticeable for the free oxime.

It was also observed that at decreased concentrations, the peak of the palladium (II) complex shifts from 3350 cm⁻¹ to 3370 cm⁻¹ for the isopropyl, and from 3305 cm⁻¹ to 3370 cm⁻¹ for the di-n-propyl oxime. This peak has also become sharper than the broad O-H peak present in the free oxime. This evidence tends to verify the possibility of intramolecular hydrogen bonding between the labile hydrogen of the oxime with the chloride of the palladium (II) chloride molecule during co-ordination. This occurrence can be illustrated as seen below:
<table>
<thead>
<tr>
<th>Run No.</th>
<th>Path Length of Cell mm</th>
<th>Concentration (moles/litre)</th>
<th>O-H Band</th>
</tr>
</thead>
<tbody>
<tr>
<td>(a) 2,4-Dimethyl-3-Pentanone Oxime</td>
<td></td>
<td></td>
<td></td>
</tr>
<tr>
<td>1</td>
<td>0.25</td>
<td>0.0125</td>
<td>3200 (broad) 3590 (sharp)</td>
</tr>
<tr>
<td>2</td>
<td>0.50</td>
<td>0.0063</td>
<td></td>
</tr>
<tr>
<td>3</td>
<td>1.00</td>
<td>0.0031</td>
<td></td>
</tr>
<tr>
<td>4</td>
<td>2.00</td>
<td>0.0015</td>
<td></td>
</tr>
<tr>
<td>(b) Dichlorobis (2,4-Dimethyl-3-Pentanone Oxime) Palladium (II)</td>
<td></td>
<td></td>
<td></td>
</tr>
<tr>
<td>1</td>
<td>0.25</td>
<td>0.0125</td>
<td>3550 (med) no 3600</td>
</tr>
<tr>
<td>2</td>
<td>0.50</td>
<td>0.0063</td>
<td>3550 (med) no 3600</td>
</tr>
<tr>
<td>3</td>
<td>1.00</td>
<td>0.0031</td>
<td>3350, 3510 no 3600</td>
</tr>
<tr>
<td>4</td>
<td>2.00</td>
<td>0.0015</td>
<td>3370, 3510 no 3600</td>
</tr>
</tbody>
</table>
TABLE X

INFRARED ABSORPTION STUDY OF THE HYDROGEN BONDING OF
4-HEPTANONE OXIME, AND ITS CORRESPONDING
PALLADIUM (II) COMPLEX

<table>
<thead>
<tr>
<th>Run No.</th>
<th>Path Length</th>
<th>Concentration (mole/litre)</th>
<th>O-H Band</th>
</tr>
</thead>
<tbody>
<tr>
<td></td>
<td>of Cell in cm</td>
<td></td>
<td></td>
</tr>
<tr>
<td>(a) 4-Heptanone Oxime</td>
<td></td>
<td></td>
<td></td>
</tr>
<tr>
<td>1</td>
<td>0.25</td>
<td>0.0125</td>
<td>3280 (broad) 3595</td>
</tr>
<tr>
<td>2</td>
<td>0.50</td>
<td>0.0063</td>
<td>3280 (broad) 3600</td>
</tr>
<tr>
<td>3</td>
<td>1.00</td>
<td>0.0051</td>
<td>3280 (broad) 3600</td>
</tr>
<tr>
<td>4</td>
<td>2.00</td>
<td>0.0015</td>
<td>3280 (broad) 3605</td>
</tr>
<tr>
<td>(b) Dichlorobis (4-Heptanone Oxime) Palladium (II)</td>
<td></td>
<td></td>
<td></td>
</tr>
<tr>
<td>1</td>
<td>0.25</td>
<td>0.0125</td>
<td>3505</td>
</tr>
<tr>
<td>2</td>
<td>0.50</td>
<td>0.0063</td>
<td>3325</td>
</tr>
<tr>
<td>3</td>
<td>1.00</td>
<td>0.0051</td>
<td>3360</td>
</tr>
<tr>
<td>4</td>
<td>2.00</td>
<td>0.0015</td>
<td>3370</td>
</tr>
</tbody>
</table>
4. Concluding Remarks

From the evidence obtained, it is reasonable to conclude that the oxime ligands bond to bivalent palladium through the nitrogen donor atom. Further infra-red studies tend to verify the possibility of intramolecular hydrogen bonding between the labile hydrogen of the oxime with the chloride of the palladium (II) chloride molecule. As well, evidence allows for associated intermolecular bonding between the molecules of the oximes.
PART IV

EXTRACTION OF PALLADIUM (II) SULPHATE AND
PALLADIUM (II) NITRATE WITH 4-HEPTANOIC OXIME.
PART IV

EXTRACTION OF PALLADIUM (II) SULPHATE AND PALLADIUM (II) NITRATE WITH 4-METHANONE OXIME

1. Introduction

From Part II, it was learned that palladium (II) chloride was extractable into chloroform after reaction with certain oximes. It was further noted that both the acid concentration as well as the chloride concentration had a noticeable effect on the degree of oxime-palladium complexation and thus the degree of extractability of this complex into chloroform. Since the resulting equilibria of the reaction tended to be affected, it was decided to study the effect of changing acid species as well as anion species in the palladium (II) system. Thus the extractions of palladium (II) nitrate and palladium (II) sulphate were carried out under specific nitric acid and nitrate salt concentrations as well as sulphuric acid and sulphate salt concentrations respectively. It was felt that this investigation might further clarify the reaction course and equilibria established during reaction, as established from the palladium (II) chloride study.

2. Experimental

a) Apparatus

Visible spectrophotometric results were made on a
Beckman DB Spectrophotometer equipped with a Sargent Model SRL Recorder. A Sargent Model DR pH meter was used for all pH measurements. In the case where extensive shaking periods were required, a Burrell Wrist Action Shaker was employed. This apparatus was set such that the reaction vessels being shaken were in a constant temperature water bath which was monitored at 25.0°C by use of a Haake 120 volt constant temperature heating unit.

b) Chemicals

The 4-heptanone oxime and its corresponding dichloro palladium (II) complex were prepared as outlined in Part II. The standard palladium (II) chloride solution was prepared by following the outline from Part II. Baker Analyzed hydrochloric and sulphuric acids were used after standardization for all concentration adjustments. Standardized redistilled nitric acid, available from G. Frederick Smith Chemical Company, was used for nitric acid adjustments. Fisher reagent grade sodium salts of these acids were used for anion concentration adjustments.

c) Preparation of pure palladium metal

Pure palladium metal was prepared from palladium (II) chloride following the standard procedure as outlined by Furman (39). Into a 400 ml beaker was added 5.0 g of palladium (II) chloride and approximately 10 ml concentrated hydrochloric acid. The solution was boiled
to yield a reddish-brown syrup. After the solution was cooled, sodium carbonate was added carefully until the pH was adjusted between 7.0 and 7.5. An excess of formic acid was then added and the solution boiled, which allowed the black palladium metal to precipitate out of the clear colourless solution. This black spongy metal was filtered off and washed with approximately 400 ml of hot ion-free distilled water, with traces of chloride still remaining in the wash solution. The sponge was then placed in a 2 litre beaker of hot distilled ion-free water and the solution was allowed to boil slowly overnight with stirring. The black powder was filtered and re-washed as before to obtain a product giving a negative silver nitrate test for chloride. The fine powder was then vacuum dried over anhydrous sodium sulphate overnight with 2.7 g of Pd metal being obtained.

d). Preparation of standard palladium (II) nitrate

Into a 400 ml beaker was added an accurately weighed sample of 1.80 g of palladium metal. Additions of redistilled nitric acid and distilled water were made with heating, until a clear reddish-brown solution resulted. The solution was quantitatively transferred to a 1 litre volumetric flask with the pH of the solution being adjusted to 0.0 (1.0 N in acid) and made up to volume with redistilled ion-free water adjusted to the same pH by addition of nitric acid. The solution was
standardized by taking aliquots and following the procedure of Holland, Bozic and Gerard (15).

e) Preparation of standard palladium (II) sulphate

Into a 400 ml beaker was added an accurately weighed sample of 0.90 g of palladium metal. Sulphuric acid was added and the solution was boiled to fumes on a hot plate. After cooling, 10 ml of redistilled nitric acid was added, and redistilled water, and the red precipitate slowly dissolved into a reddish-brown solution. By repeated additions of water and sulphuric acid, the solution was boiled free of the lower oxides of nitrogen. This yielded a negative test on a moistened strip of starch iodide test paper. The clear reddish-brown solution was adjusted to a pH of 0.0 (1.0 M in acid) and quantitatively transferred to a 500 ml volumetric flask where the solution was made to volume by addition of water previously pH adjusted with sulphuric acid. The resulting palladium (II) sulphate was standardized as above (15) using di-2-pyridyl ketoxime.

f) The chloroform extraction of the palladium (II) nitrate and sulphate oxime complexes

A 10 ml aliquot of standard palladium (II) solution was transferred to a 250 ml graduated separatory funnel. A known volume of standardized nitric acid or sulphuric acid was added and the volume was made up to the 100 ml mark with distilled water such that the solution would be
of an overall known molar concentration. In the case of the sodium salt addition, a weighed sample of that salt was dissolved and the solution diluted to the mark with distilled water. A 0.50 ml amount of 4-heptanone oxime was added to the separatory funnel from a graduated 1 ml pipette, and the solution shaken vigorously for 30 seconds. The mixture was then extracted with two 25 ml portions of chloroform and the chloroform extracts transferred to a 400 ml beaker. The above procedure was repeated once again with the residual water layer and the chloroform extracts were combined.

g) Palladium analysis of the water layer

The water layer was transferred to a 400 ml beaker and the volume reduced on a hot plate to approximately 5 ml. Upon cooling, a 10 ml portion of 1:1 nitric hydrochloric acid was added to the beaker and the solution was evaporated down to near dryness. Repeated additions of hydrochloric acid were made until the solution was free of the lower oxides of nitrogen. To the cooled acid solution was added water and the pH adjusted with sodium hydroxide such that the palladium could be conveniently determined spectrophotometrically (32) or gravimetrically (15) with di-2-pyridylketoxime.

h) Palladium analysis of the chloroform extract

Into a 400 ml beaker were added the combined chloroform extracts and the volume reduced to near dryness on a steam
bath. After a work-up with nitric and hydrochloric acid, the palladium content was determined following the same procedure as above.

5. Discussion and Results

a) Effect of hydrochloric and sulphuric acid on the extraction of palladium (II) with 4-heptanone oxime

It was observed that when both the palladium (II) nitrate and palladium (II) sulphate solutions were adjusted to a pH of 1.00 or above, and the extraction procedure carried out, there was considerable decomposition of the palladium-oxime complex, which tended to form a greenish-black scum at the chloroform-water interface and this made quantitative separation impossible.

The time period for extraction was altered to 30 seconds shaking, followed by immediate chloroform extraction, since it was noticed that following the 20 minute reaction period of the chloroform extraction, the entire palladium solution had decomposed with the palladium (II) being reduced to the oxide or to the elemental state. Ethyl alcohol was not used in transferring the oxime since it further hastened the reduction of the complex.

Results of the acid extraction study of palladium (II) nitrate and palladium (II) sulphate are seen in Table XI. It is seen that at the 17.69 mg level of palladium (II), as the nitrate salt, greater than 99.82% extraction with 4-heptanone oxime is achieved as far as 0.00 M in nitric
TABLE XI

EXTRACTION OF Pd(NO₃)₂ AND PbSO₄ AT VARIOUS
ACID CONCENTRATIONS

Pd(NO₃)₂ taken = 17.69 mg
PbSO₄ taken = 17.33 mg.
H₂SO₄ used for acid adjustment of Pd(NO₃)₂,
H₂SO₄ used for acid adjustment of PbSO₄.
Total weight of 4-Heptanone Oxime 1.0 g (2 x 0.5)

<table>
<thead>
<tr>
<th>Normality</th>
<th>% Pd found from Pd(NO₃)₂ extraction</th>
<th>% Pd found from PbSO₄ extraction</th>
</tr>
</thead>
<tbody>
<tr>
<td>1.50</td>
<td>99.95</td>
<td></td>
</tr>
<tr>
<td>2.00</td>
<td>99.97</td>
<td></td>
</tr>
<tr>
<td>2.50</td>
<td>99.89</td>
<td></td>
</tr>
<tr>
<td>3.00</td>
<td>99.86</td>
<td></td>
</tr>
<tr>
<td>4.00</td>
<td>99.95</td>
<td></td>
</tr>
<tr>
<td>5.00</td>
<td>99.98</td>
<td>100.1</td>
</tr>
<tr>
<td>6.00</td>
<td>99.83</td>
<td></td>
</tr>
<tr>
<td>7.00</td>
<td>99.86</td>
<td></td>
</tr>
<tr>
<td>7.50</td>
<td></td>
<td>99.51</td>
</tr>
<tr>
<td>8.00</td>
<td>99.90</td>
<td>99.44</td>
</tr>
<tr>
<td>9.00</td>
<td>99.84</td>
<td>97.64</td>
</tr>
<tr>
<td>10.00</td>
<td>97.18</td>
<td>94.01</td>
</tr>
</tbody>
</table>
acid concentration. The same efficiency is observed in studying the effect of sulphuric acid with palladium (II) sulphate at the 17.53 mg level as far as 8.00 ml in acid concentration. Relative to the hydrochloric acid effect with the palladium (II) chloride extraction as seen in Part II, a rapid drop in extraction efficiency is noted after 1.50 ml acid concentration is reached.

b) Effect of sodium salts on the extraction of palladium (II) nitrate and palladium (II) sulphate

Since such a noticeable change was observed with the effect of varying acids on the extractability of palladium (II) as the oxime complex, it was decided to compare the effect of anion concentration on the same extraction. Table XII shows the extraction results of the 4-heptanone oxime on palladium (II) nitrate. The same extraction procedure was followed as for the previous acid study, but the solution was made 1.0 M in acid and a 5.0 M concentration of sodium nitrate was also added. This solution would be equivalent in anion concentration to the 4.0 M acid extraction. It is observed that greater than 99.9% extraction of palladium (II) nitrate is achieved at the 17.69 mg level.

The same study was conducted with palladium (II) sulphate, with sodium sulphate being added to adjust the total sulphate concentration. These results are found in Table XIII. It is observed here that near
### TABLE XII

**Extraction of Pd(NO₃)₂ from a solution 1.00 N in HNO₃ and 3.00 N 1M NaNO₃**

Total weight of 4-hexanone oxime 1.0 g (2 x 0.5)

Shaking time 50 seconds

<table>
<thead>
<tr>
<th>Run No.</th>
<th>Palladium taken (mg)</th>
<th>Palladium found (mg)</th>
<th>% Palladium Extracted</th>
</tr>
</thead>
<tbody>
<tr>
<td>1</td>
<td>17.69</td>
<td>17.69</td>
<td>100.0</td>
</tr>
<tr>
<td>2</td>
<td>17.69</td>
<td>17.73</td>
<td>100.2</td>
</tr>
<tr>
<td>3</td>
<td>17.69</td>
<td>17.64</td>
<td>99.72</td>
</tr>
<tr>
<td>4</td>
<td>17.69</td>
<td>17.74</td>
<td>100.3</td>
</tr>
</tbody>
</table>

**Average**

17.70, 100.1

**Deviation**

±0.04, ±17.
TABLE XIII

EXTRACTION OF PdSO₄ FROM A SOLUTION 1.00 N IN H₂SO₄
AND 3.00 N IN Na₂SO₄

Total weight of 4-heptanone oxime 1.0 g (2 x 0.5)

Shaking time 50 seconds

<table>
<thead>
<tr>
<th>Run No.</th>
<th>Palladium taken (mg)</th>
<th>Palladium found (mg)</th>
<th>% Palladium Extracted</th>
</tr>
</thead>
<tbody>
<tr>
<td>1</td>
<td>17.33</td>
<td>17.00</td>
<td>98.10</td>
</tr>
<tr>
<td>2</td>
<td>17.33</td>
<td>17.25</td>
<td>99.42</td>
</tr>
<tr>
<td>3</td>
<td>17.33</td>
<td>17.16</td>
<td>99.02</td>
</tr>
<tr>
<td>4</td>
<td>17.33</td>
<td>17.02</td>
<td>98.21</td>
</tr>
<tr>
<td>Average</td>
<td></td>
<td>17.10</td>
<td>98.69</td>
</tr>
<tr>
<td>Deviation</td>
<td></td>
<td>± 0.09</td>
<td>± 0.53</td>
</tr>
</tbody>
</table>
99\% extraction is reached under 4.0 \% sulphate conditions, with a slight drop in extraction being noted relative to the 4.0 \% sulphuric acid conditions. The same extraction procedure was followed for palladium (II) chloride at 1.0 \% in hydrochloric acid and 5.0 \% in sodium chloride, and these results are seen in Table XIV. A noticeable drop to 91.57\% extraction is observed whereas both the nitrate and sulphate studies gave near 99\% or greater extraction. However, relative to the extraction of palladium (II) chloride at 4.0 \% in acid as extrapolated from Figure 1, it would appear that increased chloride ion as sodium chloride tends to increase the extraction of the palladium (II) chloride system.

c) Attempted preparation and isolation of the dinitrato and disulphato palladium (II) complexes of 4-heptanone oxime

The procedure for the preparation of the dichlororobis (2,4-dimethyl-3-pentanone,oxime)palladium (II) complex was followed in making the nitrate and sulphate complexes.

Into a 400 ml beaker was added 264 mg of palladium metal (a 10\% excess) which was dissolved with heating in 10 ml nitric acid solution. After cooling, 40 ml distilled water was added and the solution was adjusted to a pH of 0.00. Into another 400 ml beaker was added 580 mg 4-heptanone oxime in 100 ml of 1:3 ethanol-water solution. By dropwise addition of nitric acid, the pH
TABLE XIV

EXTRACTION OF PdCl₂ FROM A SOLUTION 1.00 N IN HCl
AND 3.00 N IN NaCl

Total weight of d-Heptanone Oxime 1.0 g (2 x 0.5)
Shaking time 30 seconds

<table>
<thead>
<tr>
<th>Run No.</th>
<th>Palladium taken mg</th>
<th>Palladium found mg</th>
<th>% Palladium Extracted</th>
</tr>
</thead>
<tbody>
<tr>
<td>1</td>
<td>17.34</td>
<td>15.98</td>
<td>92.16</td>
</tr>
<tr>
<td>2</td>
<td>17.34</td>
<td>15.72</td>
<td>90.66</td>
</tr>
<tr>
<td>3</td>
<td>17.34</td>
<td>15.84</td>
<td>91.35</td>
</tr>
<tr>
<td>4</td>
<td>17.34</td>
<td>15.83</td>
<td>91.29</td>
</tr>
<tr>
<td>Average</td>
<td></td>
<td>15.86</td>
<td>91.37</td>
</tr>
<tr>
<td>Deviation</td>
<td></td>
<td>± 0.08</td>
<td>± 0.40</td>
</tr>
</tbody>
</table>
of this solution was adjusted to 0.00. The palladium (II) solution was added to the alcoholic oxime solution with stirring and the mixture cooled in an ice bath. Orange oily beads formed on the sides of the beaker and all attempts to isolate and crystallize this oil failed. Attempts at isolating the sulphate complex following the same basic procedure proved fruitless.

Variations in acid concentration, ethyl alcohol concentration, solvents, salting out, and pH changes offered no encouragement in isolating the complexes.

It was noted that for the nitrate preparation at a pH between 0.80 and 1.20, a flocculent yellow precipitate could be seen, but any attempts in immediate filtering of the yellow complex failed, as decomposition occurred very quickly.

It was then decided that a mole-ratio plot of oxime to palladium versus extraction might lend some insight into the composition of the complex formed. This study was conducted and the results are seen in Figure 4. The mole-ratio study was conducted at 1.00:1 in acid concentration for both the nitrate and sulphate study, since any less acid very quickly led to reduction of palladium to the metallic oxide, and any greater concentration of acid further hastened the acid hydrolysis of oxime. This would lead to an inaccurate interpretation of the mole-ratio plot. It was noted that at a mole-ratio plot of 2.3:1 for palladium (II) nitrate, 100% of the
A Mole-Ratio Study of 4-Heptanone Oxime with Palladium (II) Nitrate and Palladium (II) Sulphate

\[ \text{Pd(NO}_3\text{)}_2 \text{; Palladium taken, 17.69 mg} \]

Normality of Nitric Acid 1.00

\[ \text{H}_2\text{SO}_4 \text{; Palladium taken, 17.33 mg} \]

Normality of Sulphuric Acid 1.00
complex is extracted into chloroform. This would tend to favour a structure with two moles of oxime for each palladium. The remaining two positions of the tetra-co-ordinated palladium would be presumably occupied by nitrate. A probable structure of this complex is illustrated below:

\[
\begin{align*}
\text{C}_3\text{H}_7 & \text{C} \quad \text{C}_3\text{H}_7 \\
\text{NO}_3 & \quad \text{Pd} \\
\text{HO} & \quad \text{NO}_3 \\
\text{C}_3\text{H}_7 & \text{C} \quad \text{C}_3\text{H}_7
\end{align*}
\]

From the data available in Figure 4 with regard to the sulphate study, there is no rationalization for a complex forming from a mole-ratio of palladium to oxime, which could be extrapolated at the 100% extraction level. However, this study demonstrates the efficiency of oxime complexation with palladium at this specific acid concentration.

A sulphate study was undertaken in order to offer some assistance in predicting the complex formed during the sulphate extraction. A gravimetric study of sulphate present in the chloroform layer after 100% extraction of palladium (II) sulphate with 4-hexanone oxime was
undertaken. The procedure using barium chloride as precipitant for sulphate was followed as outlined in Vogel (40). From an average of four results, the ratio of sulphate to palladium was found to be 1.96 to 1. A rationale for such results could be a bisulphate salt formed of the palladium (II) oxime complex, as illustrated below:

\[
\begin{array}{c}
\text{C}_3\text{H}_7\text{-C-}-\text{C}_3\text{H}_7 \\
\text{N} \\
\text{HO} \\
\text{OSO}_3\text{H} \\
\text{Pd} \\
\text{HO}_3\text{SO} \\
\text{N-OH} \\
\text{C}_3\text{H}_7\text{-C-}-\text{C}_3\text{H}_7
\end{array}
\]

d) Effect of hydrochloric acid and sulphuric acid on the dichlorohis (4-heptanone oxime) palladium (II) complex.

Since it was impossible to isolate the nitrato and sulphato complexes of palladium (II) in order to investigate infra-red bonding shifts and co-ordination of the ligand-metal complex, it was decided to study acid effects on the dichloro complex of palladium (II). A procedure was set up such that a specific weight of the palladium (II) complex (which was equivalent to the 18 mg level of
palladium in solution) which was dissolved in 50 ml of chloroform was shaken for one hour in a 50 ml water solution adjusted to varying acid concentrations with hydrochloric acid and sulphuric acid. The samples in a 25°C constant temperature bath were shaken on a Burrell wrist-action shaker. It was felt that this study might aid in an appreciation of the effect of a monoprotic and diprotic acid on the acid hydrolysis of the oxine after complexation. Also the degree of chloride to sulphate exchange under such conditions would be demonstrated.

The results of this study are seen in Figure 5. It is noted that the dichloro complex appears to be much more soluble in hydrochloric acid relative to sulphuric acid. As well, in each case, the solubility tends to increase as the concentration of acid increases. This chloride solubility is understandable since the chloride complex to chloride solvent exchange is much more favourable than the complex chloride to solvent sulphate interchange. However, an appreciation of acid hydrolysis in such a study is not apparent since it would be expected that similar concentrations should have the same effect on the dichloro complex. But the concentration of anionic species appears to alter this degree of hydrolysis.

4. Concluding Remarks

From the previous chloride study, a course for the
THE EXTRACTION OF THE CHLOROFORM SOLUTIONS OF
DICHLOROBIS (4-HEPTANONE OXIME) PALLADIUM (II)
IN HYDROCHLORIC AND SULPHURIC ACID

Hydrochloric Acid
Sulphuric Acid

Dichlorobis (4-Heptanone Oxime) Palladium (II), 69.98 mg
(equivalent to 17.34 mg PdCl₂)

Shaking time 1.0 hr; Temperature of shaking 25°C
reaction of palladium (II) chloride with the oxime was rationalized on the bases of acid and oxime effects on the system. It was postulated that the anionic complex species, $\text{PdCl}_4^{2-}$, was in stepwise equilibrium with the neutral $\text{PdCl}_2$. However, in the case of the sulphate and nitrate studies, it is noted that acids and salts affect the extraction to a much lesser degree than in the chloride system. Since there is no evidence of the formation of a $\text{Pd(NO}_3)_4^{2-}$ species or a $\text{Pd(SO}_4)_2^{2-}$ species, as compared to the $\text{PdCl}_4^{2-}$ anionic complex, which has been well characterized (61, 42), it is felt that the ions participating in the formation of the complex could possibly include the binding of water. The water could form a shell of oriented water dipoles around the palladium ion, such as $\text{Pd(H}_2\text{O})_4^{2+}$. Thus, in the reaction of this species with the oxime, the equilibrium is not displaced by anionic concentration as in nitrate of sulphate, or by the $\text{H}^+$ acid concentration as was noted in the chloride study.
PART V

A COMPARISON OF OXIDE SOLUBILITIES, AND THE EFFECT ON EXTRACTION OF PALLADIUM (II) CHLORIDE.
PART V
A COMPARISON OF OXIME SOLUBILITIES, AND THE EFFECT OF EXTRACTION OF PALLADIUM (II) CHLORIDE

1. Introduction

From previous studies (43) it was noted that at a pH of 3.00, near-quantitative extraction of palladium (II) chloride into chloroform could be made with 3-pentanone oxime, 4-heptanone oxime, and 5-octanone oxime at the 45 mg level, but the acetoxime reagent showed near 90% extraction under the same conditions. It was felt that some appreciation of the degree of solubility of oxime in water and chloroform could lead to reasoning behind the drop in extractability of the lower carbon group substituent of the oxime series. As well, an account of the degree of hydrolysis of oxime would perhaps further explain this extractability trend.

A recent study of carbonyl compounds as oximes was made by using gas chromatographic analyses (44). Here, a study of factors contributing to the decomposition of oximes showed that oximes were stable if heavy metals and their oxides were avoided (45). Thus it was decided that this technique could be applied to the quantitative oxime determination in chloroform and water in the absence of any palladium.

-70-
2. Experimental

a) Apparatus

Visible spectrophotometric results were obtained on a Beckman DR Spectrophotometer equipped with a Sargent Model SRL Recorder. All pH measurements were made on a Sargent Model DR pH meter. Chloroform-water solutions were shaken on a Burrell Wrist Action Shaker, set such that shaking vessels were in a constant temperature bath at 25.0°C. A Gake 120 volt constant temperature heating unit was used to maintain constant temperature.

Quantitative oxime determinations were made on a Beckman GC 45 Gas Chromatograph, which was equipped with a Flame Ionization Detector. A Beckman 10 inch. recorder equipped with automatic integrator was used in conjunction with the gas chromatograph. The column, 5 ft. by 6 mm O.D., which was packed with 0.1% Carbowax 20M supported on Glass Beads, 80/100 mesh, served to give good separation of solvent and oxime. High purity nitrogen was used as carrier gas at a flow rate of 75 cc/minute. The chromatogram was run at a temperature-rise programme rate from 10-25°C/min. depending on the resolution required and the maximum temperature needed to develop the sample. A lower temperature programme was used for the lower molecular weight oximes with the temperature programme commencing at 40-50°C immediately after sample injection.
b) Chemicals

All oximes were prepared as outlined by Dimenna (46) and were IR pure. All ketones used for gas chromatographic comparative analysis were redistilled prior to use. Distilled ion-free water which had been chloroform saturated was used with pH adjustments being made with dilute hydrochloric acid. The chloroform used in all solubility studies was treated through a silica gel column to remove any traces of preservative ethanol and then saturated with water before use. All chloride concentration adjustments were made with Fisher certified sodium chloride. Fisher certified Spectraanalyzed chloroform and n-pentane were used as solvents for oxime standard preparation and extraction.

c) General procedure

Into a 250 ml glass stoppered Erlenmeyer flask was added a weighed amount of oxime (equivalent to 50% excess of the theoretical amount to react with 18 mg of palladium if present) dissolved in 50.0 ml of chloroform. To this solution was pipetted 50.0 ml of pH adjusted chloride adjusted water. Each vessel was then shaken in a constant temperature bath for 1 hr. A series of these oxime-chloroform water solutions were run at varying times from 30 minutes through to 120 minutes and from the gas chromatographic analysis of the 4-heptanone oxime system, it was noted that maximum extraction was
reached after 30 minutes. Thus, all samples were shaken for 1 hr to ensure complete equilibrium of the oxime-chloroform water distribution. After the two layers had completely separated, a pipetted sample of the chloroform layer was transferred to a glass-stoppered volumetric flask, and anhydrous sodium sulphate added to dry the solution. Samples were injected into the gas chromatograph and results compared to previously prepared standards of oxime dissolved in chloroform. In this way, quantitative oxime distribution in the chloroform layer could be determined. Analysis of the remaining water layer entailed adding an excess of sodium chloride to saturate the water layer, followed by a triple extraction with 5 ml portions of n-pentane. This solvent was collected in a 10 ml volumetric flask, and made up to the mark with n-pentane. Anhydrous sodium sulphate was added to dry the solutions. Injections were made into the gas chromatograph with peak heights and integrated areas being compared to previously prepared standards of oxime in n-pentane. It was noted that in the case of the lower molecular weight oximes, the ketone peak could be observed as a side-arm, or often buried in the solvent peak. Thus it was possible to analyze only the total amount of oxime present in both the chloroform and water layers. Each solution was prepared and run in duplicate with at least triple gas chromatographic analyses on each layer to obtain reliable results.
3. Discussion and Results

a) Effect of chloride ion concentration on the extractability of oximes

A study was undertaken of the effect of varying amounts of chloride on the extractability of oximes into chloroform and water solutions. Specific molar amounts of sodium chloride were weighed out and dissolved in the water layer, and the pH of the solution was adjusted to 3.00. After shaking the oxime-chloroform layer with the sodium chloride solution for 1 hr, the pH of the water solution, after separation, was again noted. The amount of oxime in the chloroform layer was determined as outlined above.

The results of this study for acetoxime, 3-pentanone oxime, 4-heptanone oxime, and 5-nonanone oxime are seen in Table XV. It is noted that for the acetoxime and 3-pentanone oxime, the pH in each case appears to jump from 3.0 to 4.5-5.0. However, in the case of the 4-heptanone oxime and 5-nonanone oxime, the pH change is negligible regardless of the amount of sodium chloride present. This same change in pH is noted from solutions adjusted to a pH of 2.0. Also, the amount of oxime soluble in chloroform increases as the sodium chloride content is increased. But it is observed that from the pH 2.0 studies, much less oxime is found in the chloroform layer, than in the same pH 3.0 study. The trend of oxime solubility into chloroform appears to increase as the "R"
TABLE XV

EFFECT OF CHLORIDE ION CONCENTRATION ON THE EXTRACTABILITY
OF OXIMES FROM CHLOROFORM SOLUTION TO
AQUEOUS CHLORIDE SOLUTION

Solutions: 50 ml of 2.0 x 10^-2 M oxime in CHCl₃,
50 ml of pH adjusted Cl⁻ adjusted solution
Shaking time 1.0 hr at 25.0 °C

<table>
<thead>
<tr>
<th>Oxime</th>
<th>MCl⁻ as NaCl</th>
<th>pH (Final)</th>
<th>% Oxime from CHCl₃ layer</th>
<th>pH (Final)</th>
<th>% Oxime in CHCl₃ layer</th>
</tr>
</thead>
<tbody>
<tr>
<td>Acetoxime</td>
<td>0.0</td>
<td>4.4</td>
<td>28.4</td>
<td>2.3</td>
<td>9.59</td>
</tr>
<tr>
<td></td>
<td>0.5</td>
<td>4.7</td>
<td>35.1</td>
<td>2.7</td>
<td>16.6</td>
</tr>
<tr>
<td></td>
<td>1.0</td>
<td>4.9</td>
<td>38.1</td>
<td>2.9</td>
<td>21.6</td>
</tr>
<tr>
<td></td>
<td>2.0</td>
<td>5.1</td>
<td>45.5</td>
<td>3.2</td>
<td>31.8</td>
</tr>
<tr>
<td>3-Pentanone</td>
<td>0.0</td>
<td>5.1</td>
<td>83.8</td>
<td>2.7</td>
<td>12.8</td>
</tr>
<tr>
<td>Oxime</td>
<td>0.5</td>
<td>5.1</td>
<td>87.6</td>
<td>3.6</td>
<td>33.3</td>
</tr>
<tr>
<td></td>
<td>1.0</td>
<td>5.1</td>
<td>89.0</td>
<td>3.9</td>
<td>47.1</td>
</tr>
<tr>
<td></td>
<td>2.0</td>
<td>5.0</td>
<td>91.3</td>
<td>4.2</td>
<td>67.8</td>
</tr>
<tr>
<td>4-Heptanone</td>
<td>0.0</td>
<td>3.2</td>
<td>98.5</td>
<td>2.0</td>
<td>97.7</td>
</tr>
<tr>
<td>Oxime</td>
<td>0.5</td>
<td>2.9</td>
<td>96.3</td>
<td>1.9</td>
<td>95.8</td>
</tr>
<tr>
<td></td>
<td>1.0</td>
<td>3.1</td>
<td>97.0</td>
<td>2.0</td>
<td>96.0</td>
</tr>
<tr>
<td></td>
<td>2.0</td>
<td>3.0</td>
<td>97.7</td>
<td>2.0</td>
<td>97.5</td>
</tr>
<tr>
<td>5-Nonanone</td>
<td>0.0</td>
<td>2.9</td>
<td>93.4</td>
<td>2.1</td>
<td>96.9</td>
</tr>
<tr>
<td>Oxime</td>
<td>0.5</td>
<td>2.9</td>
<td>95.3</td>
<td>2.0</td>
<td>98.7</td>
</tr>
<tr>
<td></td>
<td>1.0</td>
<td>2.8</td>
<td>96.4</td>
<td>2.0</td>
<td>99.0</td>
</tr>
<tr>
<td></td>
<td>2.0</td>
<td>2.7</td>
<td>97.9</td>
<td>1.9</td>
<td>98.2</td>
</tr>
</tbody>
</table>
group increases on the oxime. Thus it would appear that the lower carbon atom oximes tend to hydrolyze more readily and this effect seems to level off at the 4-heptanone oxime level.

b) Effect of chloride on the degree of hydrolysis of oxime during extraction

A study was undertaken demonstrating the effect of chloride concentration on the extraction of the oximes. The total amount of oxime present in the chloroform and water layers was determined as outlined previously. It was then assumed that the oxime not accountable from this analysis had presumably hydrolyzed to the corresponding ketone.

This data is seen in Table XVI. In each case, at a pH of 3.0, the amount of oxime found in the chloroform layer increases as the amount of sodium chloride increases, but this increased amount of salt in the water layer serves to decrease the oxime solubility in that layer. Very near 100% oxime is recovered in the 4-heptanone oxime and 5-nonanone oxime studies, and these oximes seem to be much less soluble in water than the lower molecular weight oximes. The increased amount of sodium chloride in the water layer, which enhances oxime solubility into chloroform, seems to allow less hydrolysis of oxime, with more oxime presumably present to react with any palladium (II).
### Table XVI

**Effect of Chloride Ion Concentration and Total Degree of Hydrolysis of Oximes During Extraction Procedure**

Solutions: 50 ml 2.0 x 10^{-2} M oxime in CHCl₃
50 ml of pH 3.0 chloride adjusted solution
Shaking time 1.0 hr at 25.0°C

<table>
<thead>
<tr>
<th>Oxime</th>
<th>CHCl₃</th>
<th>% Oxime in CHCl₃ layer</th>
<th>% Oxime in H₂O layer</th>
<th>Total Recovery of Oxime</th>
</tr>
</thead>
<tbody>
<tr>
<td>Acetoxyne</td>
<td>0.0</td>
<td>25.0</td>
<td>1.9</td>
<td>26.9</td>
</tr>
<tr>
<td></td>
<td>0.5</td>
<td>30.8</td>
<td>0.9</td>
<td>31.7</td>
</tr>
<tr>
<td></td>
<td>1.0</td>
<td>36.0</td>
<td>0.9</td>
<td>36.9</td>
</tr>
<tr>
<td></td>
<td>2.0</td>
<td>46.5</td>
<td>1.5</td>
<td>48.0</td>
</tr>
<tr>
<td>3-Pentanone</td>
<td>0.0</td>
<td>86.5</td>
<td>6.3</td>
<td>92.8</td>
</tr>
<tr>
<td>Oxime</td>
<td>0.5</td>
<td>88.9</td>
<td>4.3</td>
<td>95.2</td>
</tr>
<tr>
<td></td>
<td>1.0</td>
<td>91.1</td>
<td>4.1</td>
<td>95.2</td>
</tr>
<tr>
<td></td>
<td>2.0</td>
<td>92.0</td>
<td>2.4</td>
<td>94.4</td>
</tr>
<tr>
<td>4-Heptanone</td>
<td>0.0</td>
<td>98.5</td>
<td>1.6</td>
<td>100.1</td>
</tr>
<tr>
<td>Oxime</td>
<td>0.5</td>
<td>98.7</td>
<td>0.9</td>
<td>99.6</td>
</tr>
<tr>
<td></td>
<td>1.0</td>
<td>98.1</td>
<td>1.1</td>
<td>99.2</td>
</tr>
<tr>
<td></td>
<td>2.0</td>
<td>97.9</td>
<td>1.0</td>
<td>98.9</td>
</tr>
<tr>
<td>5-Hexanone</td>
<td>0.0</td>
<td>98.5</td>
<td>0.5</td>
<td>98.8</td>
</tr>
<tr>
<td>Oxime</td>
<td>0.5</td>
<td>98.7</td>
<td>0.6</td>
<td>99.3</td>
</tr>
<tr>
<td></td>
<td>1.0</td>
<td>100.3</td>
<td>0.3</td>
<td>100.6</td>
</tr>
<tr>
<td></td>
<td>2.0</td>
<td>99.9</td>
<td>0.6</td>
<td>100.5</td>
</tr>
</tbody>
</table>
c) Extraction study of a series of oximes at 2.00 M in chloride concentration

Since the 2.00M chloride studies of Table XV and Table XVI appeared to give best overall oxime recovery, it was decided to study this series in more detail. A set of eight solutions for each oxime were set up and analyzed as outlined previously, and the results of this study are seen in Table XVII. From the acetoxime data, an increase in pH from 3.0 to 5.1 would suggest a large degree of hydrolysis, and the overall amount of oxime found is 45.1% with 1.1% of this accounted for in the water layers. In the case of 3-pentanone oxime, there appears to be less hydrolysis, the pH changing from 3.0 to 4.7, and this is borne out with recovery of 94% of the total oxime added. In the case of the 4-heptanone oxime, and 5-nonanone oxime, the pH change is minimal with 0.5 and 0.3% of the oxime being found in the water layers, respectively. From this result it would appear that 5-nonanone oxime is much less soluble in water than is the 4-heptanone oxime.

d) A mole-ratio study of various oximes with palladium (II) chloride

From the data of Table XVII concerning the trends of oxime hydrolysis and oxime solubility, it was decided to investigate the same system, but introducing palladium (II) chloride. A mole-ratio study was undertaken at 2.00 M.
### Table XVII

**Extraction Studies of A Series of Oximes at 2.00 M Chloride Ion Concentration**

Solutions: 50 ml of 2.0 x 10^{-2} M oxime in CHCl₃

50 ml of pH 3.0 adjusted, 2.00 M chloride solution

Shaking time 1.0 hr at 25.0°C

<table>
<thead>
<tr>
<th>Oxime</th>
<th>Final % Oxime in CHCl₃</th>
<th>Deviation in CHCl₃ layer</th>
<th>Oxime in H₂O</th>
<th>Deviation in H₂O layer</th>
<th>Total Recovery of Oxime</th>
</tr>
</thead>
<tbody>
<tr>
<td>Acetoxime</td>
<td>5.1</td>
<td>+0.8</td>
<td>1.1</td>
<td>+0.08</td>
<td>45.1</td>
</tr>
<tr>
<td>3-Pentanone Oxime</td>
<td>4.7</td>
<td>93.0</td>
<td>+1.5</td>
<td>2.0</td>
<td>+0.09</td>
</tr>
<tr>
<td>4-Heptanone Oxime</td>
<td>3.0</td>
<td>*</td>
<td>0.5</td>
<td>+0.04</td>
<td></td>
</tr>
<tr>
<td>5-Nonanone Oxime</td>
<td>2.9</td>
<td>90.0</td>
<td>0.3</td>
<td>0.02</td>
<td></td>
</tr>
</tbody>
</table>

* Assumed very near total recovery of oxime from previous analyses
in sodium chloride and at a pH of 5.0 for the four
symmetrical alkyl ketoximes with palladium (II) chloride.
A variation from the previous double extraction mole-ratio
procedure was used. Into a 250 ml glass-stoppered vessel
was pipetted 50 ml of palladium (II) chloride solution
which had been adjusted with the correct weighed amount
of sodium chloride and pH adjusted. The varying amounts
of oxime were weighed out and dissolved in 50 ml of
chloroform which was added to the shaking vessel. After
the 1 hr shaking period, the chloroform layer was quanti-
tatively separated and the palladium content determined
as outlined in Part II. The results of this study are
seen in Figure 6.

The 4-hexanone oxime system appears to be most
efficient with regard to extractability at the lowest
mole-ratio, with the 3-pentanone oxime very near in
efficiency. However, there is quite a noticeable drop
in extraction efficiency for the acetoxime. But these
results tend to correlate with the previous gas chromato-
graphic results of Table XVII, with regard to the total
amount of oxime available to react with the palladium (II)
chloride.

But, from Figure 6, there appears to be a complete
misplacement of the 5-nonanone oxime, which is much less
efficient than the acetoxime, when it would be expected
to react better than the 4-hexanone oxime. It is not
A Mole Ratio Study of Various Oximes with

Palladium (II) Chloride

- O - 4-Hexanone Oxime
- △ - 3-Pentanone Oxime
- ▲ - Acetoxime
- □ - 5-Hexanone Oxime

Palladium taken, 17.33 mg
Molarity of NaCl 2.00
pH of Initial Solution 3.00
until a mole-ratio of greater than 40/1 of oxime to palladium that 100% extraction efficiency is reached for the 5-nonanone oxime system.

It was decided to increase the amount of time of sample shaking of the 5-nonanone oxime extraction, since equilibrium may not have been reached after 1 hour, as was established for the 4-heptanone oxime system of the gas chromatographic analysis. A 5:1 mole-ratio of oxime to palladium solution was introduced into the shaking vessel as before, but the shaking time was varied. This mole-ratio would ensure an excess of oxime present in the case that any hydrolysis of oxime might occur over such a long shaking period. The results of this comparative study for 4-heptanone oxime and 5-nonanone oxime are seen in Figure 7.

It is noted that after approximately 20 hours shaking, near 100% extraction is reached for the 5-nonanone oxime system. Thus this study tends to justify the positioning of the 5-nonanone oxime in Figure 6 because equilibrium of the oxime palladium system had not been reached after the 1 hour shaking period.

e) Solubility of oxime complexes of palladium (II) chloride

It was felt that the solubility of the oxime complexes of palladium (II) chloride in chloroform might be a limiting factor in the extraction study. Thus an investigation of complex solubility in chloroform was undertaken.
EFFECT OF TIME ON THE MOLE-RATIO STUDY OF 4-HEPTANONE OXIME 
AND 5-NONANONE OXIME WITH PALLADIUM (II) CHLORIDE

- 4-Heptanone Oxime
- 5-Nonanone Oxime

Palladium taken 17.34 mg/50 ml Cl⁻ solution
Molarity of Chloride (as NaCl) 2.00
4-Heptanone Oxime taken 63.4 mg*/50 ml CHCl₃
5-Nonanone Oxime taken 76.8 mg*/50 ml CHCl₃
Temperature of Shaking 25.0°C

* A 3:1 Mole-ratio of Oxime/Palladium
A large excess of the complex was dissolved into some previously treated chloroform, such that the resulting solution was well saturated with complex. The solution was prepared and allowed to equilibrate in a constant temperature bath at 25.0°C. A glass A 1/2 ml pipette was used for measurement of the solution. The pipette was equipped with a removable piece of Tygon tubing (approximately 1/2 inches in length) packed with glass wool. This acted as a filter when transferring the pipetted solution. The sample was pipetted into a previously tared evaporating dish, and the solution was allowed to evaporate slowly to dryness in a dessicator, until constant weight was reached. Duplicate samples were run for each oxime complex and these results are seen in Table XVIII. It is noted that the solubility in chloroform of the complexes very rapidly increases when comparing the acetoxime complex with that of 5-nonanone oxime.

4. Concluding Remarks

From this study the trends of oxime complex extractability, effect of chloride concentration, and the degree of hydrolysis can better be appreciated. The lower molecular weight oximes more readily hydrolyze, and thus are less efficient in complexing and being extracted into chloroform. As well, the higher molecular weight oximes are less soluble in water, with their corresponding palladium (II) complexes being more soluble in chloroform.
<table>
<thead>
<tr>
<th>Oxime Complex of Palladium</th>
<th>Solubility in CCl₃ mg/ml</th>
<th>Corresponding Pd content mg/ml</th>
</tr>
</thead>
<tbody>
<tr>
<td>Acetoxime</td>
<td>7.23</td>
<td>2.38</td>
</tr>
<tr>
<td>3-Pentanone Oxime</td>
<td>14.90</td>
<td>4.17</td>
</tr>
<tr>
<td>4-Hexanone Oxime</td>
<td>218.5</td>
<td>53.36</td>
</tr>
<tr>
<td>5-Nonanone Oxime</td>
<td>464.7</td>
<td>100.56</td>
</tr>
</tbody>
</table>

* Average of duplicate analyses
which would increase their extraction efficiency into chloroform. However, equilibrium of the palladium oxime solution plays an important part in comparing these systems, and in the case of the 5-nonanone oxime this single factor quite readily alters the apparent extraction efficiency of the system.
PART VI

A COMPARATIVE STUDY OF SOME ISOMERIC C7 OXIMES AND THEIR
REACTION WITH PALLADIUM (II) CHLORIDE
PART VI

A COMPARATIVE STUDY OF SOME ISOMERIC C7 OXIMES AND THEIR REACTION WITH PALLADIUM (II) CHLORIDE

1. Introduction

From Part II, a study was conducted comparing the steric effect of the di-n-propyl with the diisopropyl ketoxime and their extraction with palladium (II) chloride. It was decided to further this study by investigating the 2-methyl cyclohexanone oxime and 4-methyl cyclohexanone oxime, relative to the 4-heptanone oxime, with regard to extractability of palladium (II) chloride. As well, solubility studies and attempts to isolate the palladium (II) complexes might offer some aid in predicting the extractability differences due to steric effects of the different oximes.

2. Experimental

a) Apparatus

All instrumentation used in this study was as outlined in Part V.

b) Chemicals

All solvents and chemicals used were of reagent grade. The ketones, 2-methyl cyclohexanone, and 4-methyl cyclohexanone were obtained from Eastman Organic Chemical Company, Rochester, and were redistilled before use in preparing
the oximes.

c) Preparation of 2-methyl cyclohexanone oxime and 4-methyl cyclohexanone oxime

The 2-methyl cyclohexanone oxime was prepared following the outline of Shriver, Fuson and Curtin (27).

In a 500 ml round bottom flask was added 26.9 g (0.24 moles) of 2-methyl cyclohexanone, dissolved in 200 ml of 95% ethyl alcohol. As well, 18.3 g (0.26 moles) of hydroxylamine hydrochloride in 50 ml of distilled water, and 10.4 g (0.26 moles) of sodium hydroxide in 50 ml of distilled water was added to the reaction vessel. The solution was refluxed for three hours.

After cooling, the solution was transferred to a 500 ml beaker and evaporated down until two layers appeared. The oily top layer was separated and dried with anhydrous calcium chloride. After this solution was vacuum distilled and vacuum sublimed, a yellow oil resulted. This oil was crystallized from a cold ethanol-water solution, and then recrystallized, with 3.9 g of white crystals being obtained. Infra-red analysis of the product yielded a strong C=N peak at 1665 cm⁻¹ with no ketone contaminant being evident. The melting point of the product was 38-39°C with a literature value of 43°C (30).

The 4-methyl cyclohexanone oxime was prepared in exactly the same way as outlined above. A thick yellow oil was obtained by vacuum distilling the top oily layer,
and this oil was repeatedly boiled down in an ethanol-water mixture to promote crystallization. After refrigeration of the product overnight, a white solid was filtered from the remaining oil, and recrystallized from an ethanol-water solution. The product, 11.9 g of very fine white powder, after being vacuum dried, melted at 24-35°C, with a literature value of 37°C (30). Infra-red analysis of the product showed a strong C=N peak centred at 1668 cm⁻¹ with no ketone interference.

c) Preparation of the palladium complexes of 2-methyl cyclohexanone oxime and 4-methyl cyclohexanone oxime

Into a 250 ml beaker was added 440 mg of palladium (II) chloride (10% excess) and 10 ml of concentrated hydrochloric acid, which, upon heating, yielded a reddish-brown syrupy solution. After cooling, the volume was adjusted to 50 ml with distilled water and the pH adjusted to 3.0 by dropwise addition of sodium hydroxide. Into a 400 ml beaker was added 571 mg of 2-methyl cyclohexanone oxime dissolved in 100 ml of 1:3 ethyl alcohol-water solution, with the pH being adjusted to 3.0 by dropwise addition of dilute hydrochloric acid. The palladium solution was then slowly added to the ethanolic oxime solution with stirring. The solution, after being refrigerated overnight yielded a small amount of deep yellow crystalline product, which was filtered, washed with dilute hydrochloric acid and vacuum dried over anhydrous calcium sulphate.
overnight. The above procedure was repeated with a smaller amount of alcohol used to solubilize the oxime, which appeared to increase the yield slightly.

Infra-red analysis of the complex yielded a C=N peak at 1662 cm$^{-1}$ and a shift in the N=O peak to 993 cm$^{-1}$ from 945 cm$^{-1}$ for the uncomplexed oxime. The product appeared to decompose near 200$^\circ$C. Elemental analysis of the product from Spang Microanalytical Laboratory is listed below:

Analysis (calculated for $C_{14}H_{24}N_2O_2Cl_2Pd$)

<table>
<thead>
<tr>
<th>Element</th>
<th>Theory %</th>
<th>Found %</th>
</tr>
</thead>
<tbody>
<tr>
<td>C</td>
<td>39.12</td>
<td>39.52</td>
</tr>
<tr>
<td>H</td>
<td>5.59</td>
<td>6.71</td>
</tr>
<tr>
<td>N</td>
<td>6.52</td>
<td>5.86</td>
</tr>
<tr>
<td>Cl</td>
<td>16.53</td>
<td>15.48</td>
</tr>
<tr>
<td>Pd</td>
<td>24.78</td>
<td>24.38</td>
</tr>
</tbody>
</table>

No further attempts were made to purify the product since complicated procedures of separating the syn and anti isomers would be entailed.

The palladium complex of the 4-methyl cyclohexanone oxime was made following the same procedure as above, except that the oxime was dissolved in approximately 30 ml of ethanol, and the volume made up to near 60 ml with distilled water. Upon addition of the palladium solution to the pH adjusted ethanolic oxime solution, a fine yellow precipitate immediately settled out of
solution. After filtering, the yellow crystalline solid was washed with dilute hydrochloric acid and dried over anhydrous sodium sulphate overnight. The product decomposed near 200°C. Infra-red analysis showed a C=N peak at 1665 cm\(^{-1}\) with a shift in the N-O stretching frequency to 995 cm\(^{-1}\) from 960 cm\(^{-1}\) of the corresponding oxime.

Elemental analysis of the product is listed below:

Analysis (calculated for \(\text{C}_{14}\text{H}_{24}\text{N}_{2}\text{O}_{2}\text{Cl}_{2}\text{Pd}\))

<table>
<thead>
<tr>
<th>Element</th>
<th>Theory %</th>
<th>Found %</th>
</tr>
</thead>
<tbody>
<tr>
<td>C</td>
<td>39.12</td>
<td>39.25</td>
</tr>
<tr>
<td>H</td>
<td>5.59</td>
<td>5.69</td>
</tr>
<tr>
<td>N</td>
<td>6.52</td>
<td>6.65</td>
</tr>
<tr>
<td>Cl</td>
<td>16.53</td>
<td>16.49</td>
</tr>
<tr>
<td>Pd</td>
<td>24.78</td>
<td>24.55</td>
</tr>
</tbody>
</table>

e) General procedure

The gas chromatographic study was followed as outlined in Part V, with the palladium mole-ratio study and solubility analyses following that same basic procedure.

3. Discussion and Results

a) Extraction of C\(_7\) oximes at 2.00 1 in chloride concentration

A gas chromatographic study of the solubility of the 2-methyl, and 4-methyl cyclohexanone oximes in chloroform and sodium chloride solutions was compared to the results of the 4-heptanone oxime. These results are seen in Table XIX.
TABLE XIX

EXTRACTION STUDIES OF A SERIES OF ISOMERIC C₇ OXIMES AT
2.00 M CHLORIDE ION CONCENTRATION

Solutions: 50 ml of 2.0 x 10⁻² M oxime in CHCl₃
50 ml of pH 3.0 adjusted, 2.00 M chloride solution

Shaking time 1.0 hr at 25.0°C

<table>
<thead>
<tr>
<th>Oxime</th>
<th>Final % Oxime in CHCl₃</th>
<th>Deviation</th>
<th>% Oxime Deviation</th>
<th>Total Recovery of Oxime</th>
</tr>
</thead>
<tbody>
<tr>
<td>4-Heptanone Oxime</td>
<td>3.0</td>
<td>-*</td>
<td>0.5 ± .04</td>
<td>-</td>
</tr>
<tr>
<td>4-Methyl cyclohexanone oxime</td>
<td>4.3</td>
<td>95.3 ± 0.8</td>
<td>1.3 ± .13</td>
<td>96.6</td>
</tr>
<tr>
<td>2-Methyl cyclohexanone oxime</td>
<td>4.8</td>
<td>92.6 ± 1.1</td>
<td>1.0 ± .08</td>
<td>93.6</td>
</tr>
</tbody>
</table>

* Assumed very near total recovery of oxime from previous analyses
It is noted that after one hour shaking of the 4-methyl cyclohexanone oxime, the pH changes from 3.0 to 4.3 in the 2.00 M chloride solution, while with the 2-methyl cyclohexanone oxime, the pH increases to 4.8 from 3.0. Thus, the 4-methyl cyclohexanone oxime appears to be less hydrolyzed with 96.6% of that oxime being recovered, whereas the 2-methyl substituted oxime has 93.6% of the oxime recovered. The 4-methyl cyclohexanone oxime appears to be slightly more soluble in the sodium chloride solution. But both of these oximes are hydrolyzed to a greater extent than the straight chain 4-heptanone oxime.

b) A mole-ratio study of the C₇ oximes with palladium (II) chloride

Since the 4-heptanone oxime appeared to give best extraction efficiency when reacted with palladium (II) chloride, as seen in Figure 6, the extraction efficiency of the two substituted ring systems was studied to investigate the effect of steric hindrance around the C=N binding site. This study is seen in Figure 8.

Under these specific pH and chloride conditions, the three C₇ oximes are very close in extraction efficiency with palladium (II) chloride, but the 4-methyl cyclohexanone oxime appears to reach the 100% extraction level at the lowest mole-ratio. The 2-methyl cyclohexanone oxime appears to be less efficient than the 4-heptanone oxime with regard to mole-ratio extraction efficiency, and
FIGURE 8
A MOLE-RATIO STUDY OF ISOMERIC C7 OXIMES WITH
PALLADIUM (II) CHLORIDE

☐ 4-Methyl Cyclohexanone Oxime
☐ 4-Heptanone Oxime
△ 2-Methyl Cyclohexanone Oxime

Palladium taken, 17.33 mg
Molarity of NaCl 2.00
pH of Starting Solution 3.0
these results correlate with the degree of congestion of the oximes around the C=N active binding site. Thus steric effects play an important part when comparing the reactivity and extraction of these oximes with palladium (II) chloride.

c) Solubility of the C₇ palladium oxime complexes

The solubility into chloroform of the dichlorobis (4-methyl cyclohexanone oxime) palladium (II) was investigated following the same procedure of the previous chapter, with the results of this study compared to the 4-heptanone oxime complex, listed in Table XX. There is a very noticeable decrease in solubility of the methyl substituted ring-oxime complex, relative to the straight chain-oxime complex. As well, the ring complex is less soluble in chloroform than the palladium complex of 3-pentanone oxime. These results are quite surprising since polarity differences would have predicted the reverse situation. However, possible dissociation or aggregation of complex in solution may account for this noticeable solubility difference.

4. Concluding Remarks

From this study it is quite evident that steric effects play a very important part in the extraction efficiency of the palladium oxime system as well as the degree of solubility and hydrolysis of the palladium complex during reaction.
### Table XX

**Solubility of Oxime Complexes of Palladium in Chloroform at 25.0°C**

<table>
<thead>
<tr>
<th>Oxime Complex of Palladium</th>
<th>Solubility (*) in CHCl₃ mg/ml</th>
<th>Corresponding Pd content mg/ml</th>
</tr>
</thead>
<tbody>
<tr>
<td>4-Heptanone Oxime</td>
<td>218.5</td>
<td>53.36</td>
</tr>
<tr>
<td>4-Methyl Cyclo-hexanone Oxime</td>
<td>9.12</td>
<td>2.23</td>
</tr>
</tbody>
</table>

*Average of duplicate analyses*
PART VII

GENERAL CONCLUSIONS
PART VII
GENERAL CONCLUSIONS

From this study it is noted that palladium (II) has been found extractable into chloroform, after reaction with symmetrical alkyl and cycloalkyl ketoximes. The degree of reactivity and extractability of the palladium (II) ion with the oxime species is dependent upon concentration and type of acid, concentration of anionic species, concentration and hydrolysis of oxime, the steric effects of various oximes and their solubility in chloroform and water, as well as the solubility of the palladium oxime complex in chloroform. These factors appear to affect the equilibrium established between the reactive species — metal with oxime and the product — palladium oxime complex. A reaction course and possible intermediate formation can be elucidated from such information. The resulting palladium oxime complexes have been verified by elemental analyses as well as infra-red spectral shift data.

Further studies could be initiated incorporating oximes for the separation of palladium from the other noble, precious, and base metals by selective anion extraction techniques. This would inevitably extend the use of such oximes, most specifically 4-heptanone oxime, into areas of further practical analytical applications.
BIBLIOGRAPHY

2. Beamish, F. E., Ibid., 14, 991 (1967).


VITA AUCTORIS


Primary School: S.S. 7 Downie (Perth County).

Secondary School: St. Marys District Collegiate and Vocational Institute.

Post-Secondary School: Graduate Chemical Technologist from St. Clair College, Windsor, Ontario, 1968.

B.Sc., Detroit Institute of Technology, Detroit, Michigan, 1969.

One year of Graduate Studies at University of Detroit, Detroit, Michigan, 1970.

Accepted into Faculty of Graduate Studies at University of Windsor, Windsor, Ontario, June, 1970.

M.Sc., University of Windsor, Fall, 1971.

Accepted full-time position as Water Laboratory Analyst, Windsor Utilities Commission (Water Division), Windsor, Ontario, Fall 1971-Fall 1973.

Accepted in Doctoral Studies Program at University of Windsor, October, 1971.
Professional Societies: Chemical Institute of Canada

American Chemical Society