PHYSICAL AND CHEMICAL PROPERTIES OF SOME TRANSITION METAL COORDINATION COMPOUNDS. I. THE PROPERTIES OF COMPLEXES OF ETHYLENEDIAMINETETRAACETIC ACID AND SIMILAR AMINO ACIDS. II. INFRARED SPECTRAL STUDIES ON THE cis AND trans ISOMERS OF DIACIDO-BIS(ETHYLENEDIAMINE)COBALT (III) COMPLEXES

DISSERTATION

Presented in Partial Fulfillment of the Requirements for the Degree Doctor of Philosophy in the Graduate School of The Ohio State University

by

MELVIN LEE MORRIS, B. S., M. S.

The Ohio State University

1958

Approved by:

[Signature]

Adviser

Department of Chemistry
ACKNOWLEDGMENT

I would like to express my sincere appreciation to Dr. Daryle H. Busch for his guidance, encouragement, and most of all his patient understanding throughout the course of these investigations.

Furthermore, I would like to thank the Ohio State University Development Fund for the research assistantship that was given me.
# TABLE OF CONTENTS

## I. THE PROPERTIES OF COMPLEXES OF ETHYLENEDIAMINETETRAACETIC ACID AND OF SIMILAR AMINOACIDS

<table>
<thead>
<tr>
<th>Section</th>
<th>Page</th>
</tr>
</thead>
<tbody>
<tr>
<td>A. Introduction</td>
<td>1</td>
</tr>
<tr>
<td>B. Synthesis and Chemical Properties of Pentadentate Complexes of Ethylenediaminetetraacetic Acid and Hydroxyethylethlenediaminetriacetic Acid with Cobalt (III)</td>
<td>11</td>
</tr>
<tr>
<td>C. Infrared Spectra of Complexes of Ethylenediaminetetraacetic Acid and Hydroxyethylethlenediaminetriacetic Acid</td>
<td>26</td>
</tr>
<tr>
<td>1. Introduction</td>
<td>26</td>
</tr>
<tr>
<td>2. Infrared Spectra of the Complexes of Ethylenediaminetetraacetic Acid with Cobalt (III)</td>
<td>28</td>
</tr>
<tr>
<td>3. Infrared Spectra of Ethylenediaminetetraacetic Acid and Other Amino Acids with Platinum (II) and Palladium (II)</td>
<td>40</td>
</tr>
<tr>
<td>D. The Rates of Acid Hydrolysis of the Pentadentate Complexes of Ethylenediaminetetraacetic Acid and Hydroxyethylethlenediaminetriacetic Acid with Cobalt (III)</td>
<td>56</td>
</tr>
<tr>
<td>1. Introduction</td>
<td>56</td>
</tr>
<tr>
<td>2. Experimental</td>
<td>66</td>
</tr>
<tr>
<td>3. Calculations and Results</td>
<td>69</td>
</tr>
<tr>
<td>4. Discussion</td>
<td>80</td>
</tr>
</tbody>
</table>
II. INFRARED SPECTRAL STUDIES ON THE cis AND trans ISOMERS OF DIACIDO-BIS(ETHYLENEDIAMINE)-COBALT (III) COMPLEXES ............. 87
   A. Introduction ................. 87
   B. Experimental ................. 92
   C. Results and Discussion ........ 98

APPENDIX ............................................ 115
## LIST OF TABLES

<table>
<thead>
<tr>
<th>Table</th>
<th>Page</th>
</tr>
</thead>
<tbody>
<tr>
<td>I. Infrared Absorption of Cobalt (III) Complexes Containing Pentadentate Ligands</td>
<td>30</td>
</tr>
<tr>
<td>II. Infrared Absorption Spectra of Platinum (II) and Palladium (II) Complexes</td>
<td>41</td>
</tr>
<tr>
<td>III. Extinction Coefficients $10^{-2}$ as Utilized in Calculations</td>
<td>71</td>
</tr>
<tr>
<td>IV. Calculated Rate Constants</td>
<td>76</td>
</tr>
<tr>
<td>V. Calculated Values of the Frequency Factor, Entropy of Activation, and Energy of Activation</td>
<td>79</td>
</tr>
<tr>
<td>VI. Infrared Absorption Bands of Coordinated NH$_2$ and NO$_2^-$ Groups</td>
<td>88</td>
</tr>
<tr>
<td>VII. Ultraviolet Spectra of cis and trans-[Co(en)$_2$(NO$_2$)$_2$]$^+$</td>
<td>96</td>
</tr>
<tr>
<td>VIII. Infrared Spectra of cis and trans-Diacido-bis(ethylenediamine)-cobalt (III) Complexes</td>
<td>99</td>
</tr>
<tr>
<td>IX. Infrared Spectra of cis and trans-Diacido-bis(ethylenediamine)-cobalt (III) Complexes</td>
<td>103</td>
</tr>
<tr>
<td>X. Computed Values of Hydrogen Deformation Frequencies for the Gauche Form</td>
<td>105</td>
</tr>
<tr>
<td>XI - XXXII, inclusive Optical Density Measured as a Function of Time (Runs 1-44)</td>
<td>178-199</td>
</tr>
<tr>
<td>XXXIII - LXXVI, inclusive Calculated Concentrations of Reactant and Product (Runs 1-44)</td>
<td>200-243</td>
</tr>
</tbody>
</table>


<table>
<thead>
<tr>
<th>Figure</th>
<th>Page</th>
</tr>
</thead>
<tbody>
<tr>
<td>1.</td>
<td>Structure of Ethylenediaminetetraacetic Acid and Hydroxyethyl- ethylenediaminetriacetic Acid</td>
</tr>
<tr>
<td>2.</td>
<td>Structure of Hexadentate Complex of Ethylenediaminetetraacetic Acid</td>
</tr>
<tr>
<td>3.</td>
<td>Structure of Tetradeutate and Bidentate Complexes of Ethylenediaminetetraacetic Acid with Platinum (II) and Palladium (II)</td>
</tr>
<tr>
<td>4.</td>
<td>Structure of &quot;Acidic&quot; Pentadentate Complexes of Ethylenediaminetetraacetic Acid (Y^3-) with Cobalt (III)</td>
</tr>
<tr>
<td>5.</td>
<td>Structure of &quot;Neutral&quot; Pentadentate Complexes of Ethylenediaminetetraacetic (Y(^{-})) with Cobalt (III)</td>
</tr>
<tr>
<td>6.</td>
<td>Structure of Pentadentate Complexes with Hydroxyethylethylenediaminetriacetae (YOH(^{3}))</td>
</tr>
<tr>
<td>7.</td>
<td>Structure of Carboxylate-Metal Bond</td>
</tr>
<tr>
<td>8.</td>
<td>Infrared Spectra of Na([\text{Co}^{III}(\text{HY})\text{NO}_2]) \cdot \text{H}_2\text{O} and Na(_2)[\text{Co}^{III}(\text{Y})\text{NO}_2]) \cdot \text{H}_2\text{O}</td>
</tr>
<tr>
<td>9.</td>
<td>Infrared Spectra of Na([\text{Co}^{III}(\text{HY})\text{Cl})] \cdot \frac{1}{2}\text{H}_2\text{O} and Na(_2)[\text{Co}^{III}(\text{Y})\text{Cl})] \cdot \frac{1}{2}\text{H}_2\text{O}</td>
</tr>
<tr>
<td>10.</td>
<td>Infrared Spectra of Na([\text{Co}^{III}(\text{YOH})\text{NO}_2]), Na([\text{Co}^{III}(\text{YOH})\text{Cl}_2]) \cdot \frac{1}{2}\text{H}_2\text{O}, and Na([\text{Co}^{III}(\text{YOH})\text{Br}_2]) \cdot \frac{1}{2}\text{H}_2\text{O}</td>
</tr>
<tr>
<td>11.</td>
<td>Infrared Spectra of H(_4)Pt(^{II})YCl(_2) and Na(_4)Pt(^{II})YCl(_2)</td>
</tr>
<tr>
<td>12.</td>
<td>Infrared Spectra of H(_4)Pd(^{II})YCl and Na(_4)Pd(^{II})YCl</td>
</tr>
<tr>
<td>Figure</td>
<td>Description</td>
</tr>
<tr>
<td>--------</td>
<td>-------------</td>
</tr>
<tr>
<td>13.</td>
<td>Infrared Spectra of H$_2$Pd$^{II}$Y and Na$_2$PdY</td>
</tr>
<tr>
<td>14.</td>
<td>Infrared Spectra of H$_2$Pt$^{II}$Y and Na$_2$Pt$^{II}$Y</td>
</tr>
<tr>
<td>15.</td>
<td>Structure of Tyrosine and Dichloro-bis(tyrosine)platinum (II)</td>
</tr>
<tr>
<td>16.</td>
<td>Infrared Spectra of Tyrosine and Deuterated Tyrosine</td>
</tr>
<tr>
<td>17.</td>
<td>Infrared Spectra of Dichloro-bis-(tyrosine)platinum (II)</td>
</tr>
<tr>
<td>18.</td>
<td>Intramolecular Nucleophilic Substitution Process</td>
</tr>
<tr>
<td>19.</td>
<td>Unimolecular Dissociation Process</td>
</tr>
<tr>
<td>20.</td>
<td>Bimolecular Reaction with Solvent</td>
</tr>
<tr>
<td>21.</td>
<td>Stable Forms of X-CH$_2$CH$_2$X as Viewed Along the C-C Axis</td>
</tr>
<tr>
<td>22.</td>
<td>Infrared Spectra of [Co(en)$_3$]Cl$_3$ and Deuterated-[Co(en)$_3$]Cl$_3$</td>
</tr>
<tr>
<td>23.</td>
<td>Infrared Spectra of cis-[Co(en)$_2$NO$_2$]$_2$Cl and Deuterated cis-[Co(en)$_2$NO$_2$]$_2$Cl</td>
</tr>
<tr>
<td>24.</td>
<td>Infrared Spectra of trans-[Co(en)$_2$(NO$_2$)$_2$]NO$_2$ and Deuterated trans-[Co(en)$_2$(NO$_2$)$_2$]NO$_2$</td>
</tr>
<tr>
<td>25.</td>
<td>Infrared Spectra of cis-[Co(en)$_2$(NO$_2$)$_2$]NO$_2$ and Deuterated cis-[Co(en)$_2$(NO$_2$)$_2$]NO$_2$</td>
</tr>
<tr>
<td>26.</td>
<td>Infrared Spectra of trans-[Co(en)$_2$(NO$_2$)$_2$]NO$_3$ and Deuterated trans-[Co(en)$_2$(NO$_2$)$_2$]NO$_3$</td>
</tr>
<tr>
<td>27.</td>
<td>Infrared Spectra of cis-[Co(en)$_2$(NO$_2$)$_2$]NO$_3$ and Deuterated cis-[Co(en)$_2$(NO$_2$)$_2$]NO$_3$</td>
</tr>
<tr>
<td>28.</td>
<td>Infrared Spectrum of trans-[Co(en)$_2$Cl$_2$]Cl</td>
</tr>
<tr>
<td>Figure</td>
<td>Description</td>
</tr>
<tr>
<td>--------</td>
<td>-----------------------------------------------------------------------------</td>
</tr>
<tr>
<td>29.</td>
<td>Infrared Spectra of cis-([\text{Co(en)}_2\text{Cl}_2])Cl and Deuterated cis-([\text{Co(en)}_2\text{Cl}_2])Cl</td>
</tr>
<tr>
<td>30.</td>
<td>Rate of Acid Hydrolysis of Na([\text{Co(HY)Br}]) in 0.1 M NaClO(_4) at 30(^\circ)C</td>
</tr>
<tr>
<td>31.</td>
<td>Rate of Acid Hydrolysis of Na([\text{Co(HY)Br}]) in 0.05 M NaClO(_4) and 0.05 M HClO(_4) at 30(^\circ)C</td>
</tr>
<tr>
<td>32.</td>
<td>Rate of Acid Hydrolysis of Na([\text{Co(HY)Br}]) in 0.1 M HClO(_4) at 30(^\circ)C</td>
</tr>
<tr>
<td>33.</td>
<td>Rate of Acid Hydrolysis of Na([\text{Co(HY)Br})) in 0.1 M NaNO(_3) at 30(^\circ)C</td>
</tr>
<tr>
<td>34.</td>
<td>Rate of Acid Hydrolysis of Na([\text{Co(HY)Br})) in 0.1 M NaNO(_3) at 30(^\circ)C (First Order - First Order Reversible Reaction)</td>
</tr>
<tr>
<td>35.</td>
<td>Rate of Acid Hydrolysis of Na([\text{Co(HY)Br})) in 0.1 M NaNO(_3) at 30(^\circ)C</td>
</tr>
<tr>
<td>36.</td>
<td>Rate of Acid Hydrolysis of Na([\text{Co(HY)Br})) in 0.1 M NaNO(_3) at 30(^\circ)C (First Order - First Order Reversible Reaction)</td>
</tr>
<tr>
<td>37.</td>
<td>Rate of Acid Hydrolysis of Na([\text{Co(HY)Br})) in 0.1 M NaBr at 30(^\circ)C</td>
</tr>
<tr>
<td>38.</td>
<td>Rate of Acid Hydrolysis of Na([\text{Co(HY)Br})) in 0.1 M NaBr (First Order - First Order Reversible Reaction)</td>
</tr>
<tr>
<td>39.</td>
<td>Rate of Acid Hydrolysis of Na([\text{Co(HY)Br})) in 0.1 M NaNO(_3) at 30(^\circ)C</td>
</tr>
<tr>
<td>40.</td>
<td>Rate of Acid Hydrolysis of Na([\text{Co(HY)Br})) in Distilled Water at 30(^\circ)C</td>
</tr>
<tr>
<td>41.</td>
<td>Rate of Acid Hydrolysis of Na([\text{Co(HY)Br})) in 0.1 M NaNO(_3) at 40(^\circ)C</td>
</tr>
<tr>
<td>42.</td>
<td>Rate of Acid Hydrolysis of Na([\text{Co(HY)Br})) in 0.1 M NaNO(_3) at 40(^\circ)C (First Order - First Order Reversible Reaction)</td>
</tr>
<tr>
<td>Figure</td>
<td>Description</td>
</tr>
<tr>
<td>--------</td>
<td>------------------------------------------------------------------------------</td>
</tr>
<tr>
<td>43.</td>
<td>Rate of Acid Hydrolysis of Na[Co(HY)Br] in 0.1 M NaN03 at 50°C</td>
</tr>
<tr>
<td>44.</td>
<td>Rate of Acid Hydrolysis of Na[Co(HY)Br] in 0.1 M NaN03 at 50°C (First Order - First Order Reversible Reaction)</td>
</tr>
<tr>
<td>45.</td>
<td>Temperature Dependence of Na[Co(HY)Br]</td>
</tr>
<tr>
<td>46.</td>
<td>Rate of Acid Hydrolysis of Na[Co(HY)Cl] in 0.1 M NaN03 at 30°C</td>
</tr>
<tr>
<td>47.</td>
<td>Rate of Acid Hydrolysis of Na[Co(HY)Cl] in 0.1 M NaN03 at 40°C</td>
</tr>
<tr>
<td>48.</td>
<td>Rate of Acid Hydrolysis of Na[Co(HY)Cl] in 0.1 M NaN03 at 50°C</td>
</tr>
<tr>
<td>49.</td>
<td>Temperature Dependence of Na[Co(HY)Cl]</td>
</tr>
<tr>
<td>50.</td>
<td>Rate of Acid Hydrolysis of Na[Co(YOH)Cl] in 0.1 M NaN03 at 30°C</td>
</tr>
<tr>
<td>51.</td>
<td>Rate of Acid Hydrolysis of Na[Co(YOH)Cl] in 0.1 M NaN03 at 40°C</td>
</tr>
<tr>
<td>52.</td>
<td>Rate of Acid Hydrolysis of Na[Co(YOH)Cl] in 0.1 M NaN03 at 50°C</td>
</tr>
<tr>
<td>53.</td>
<td>Temperature Dependence of Na[Co(YOH)Cl]</td>
</tr>
<tr>
<td>54.</td>
<td>Rate of Acid Hydrolysis of Na[Co(YOH)Br] in 0.1 M NaN03 at 30°C</td>
</tr>
<tr>
<td>55.</td>
<td>Rate of Acid Hydrolysis of Na[Co(YOH)Br] in 0.1 NaNO3 at 30°C (First Order - First Order Reversible Reaction)</td>
</tr>
<tr>
<td>56.</td>
<td>Rate of Acid Hydrolysis of Na[Co(YOH)Br] in 0.1 M NaN03 at 40°C</td>
</tr>
<tr>
<td>57.</td>
<td>Rate of Acid Hydrolysis of Na[Co(YOH)Br] in 0.1 M NaNO3 at 40°C (First Order - First Order Reversible Reaction)</td>
</tr>
</tbody>
</table>
### LIST OF FIGURES (Continued)

<table>
<thead>
<tr>
<th>Figure</th>
<th>Description</th>
<th>Page</th>
</tr>
</thead>
<tbody>
<tr>
<td>58.</td>
<td>Rate of Acid Hydrolysis of Na[Co(YOH)Br] in 0.1 M NaNO₃ at 50°C</td>
<td>173</td>
</tr>
<tr>
<td>59.</td>
<td>Rate of Acid Hydrolysis of Na[Co(YOH)Br] in 0.1 M NaNO₃ at 50°C (First Order - First Order Reversible Reaction)</td>
<td>175</td>
</tr>
<tr>
<td>60.</td>
<td>Temperature Dependence of Na[Co(YOH)Br]</td>
<td>177</td>
</tr>
</tbody>
</table>
A. Introduction

The chemistry of the metal complexes of ethylenediaminetetraacetic acid (Fig. 1) has been studied from many varied points of view.\(^1\) \(^2\) \(^3\)

\(^1\) "Sequestrene." Alrose Chemical Company, Providence (1952).


\(^3\) Ethylenediaminetetraacetic acid will be referred to as \(H_4Y\).

Some of these investigations have been concerned with its applicability as an analytical tool in the determinations of various metal ions, such as nickel and zinc. It has been used in the separations of the rare earths, and has received wide attention and investigation for its industrial applications. However, most of this work has been concerned with solution studies. It is the purpose of this review to deal mainly with metal complexes of \(H_4Y\), which have been
Figure 1. Structure of Ethylenediaminetetraacetic Acid and Hydroxyethylenediaminetriacetic Acid
1. Ethylenediaminetetraacetic acid (Abbreviated H₄Y)

2. Hydroxyethyl ethylenediaminetriacetic Acid (Abbreviated H₃YOH)
isolated and their structures and chemical properties studied.

Pfeiffer\(^4\) and Offerman prepared the copper and cal-

cium complexes of H\(_4\)Y as early as 1942. They postulated the structure of the copper complex to involve the coordination of the two nitrogens and two carboxyl groups, each from an adjacent nitrogen atom, to the metal ion. The resulting copper complex is green and has the formula Na\(_2\) [[Cu(H\(_2\)Y)]] \(\cdot\)4H\(_2\)O. The magnesium and calcium complexes of H\(_4\)Y were also prepared by Pfeiffer and Offerman.\(^4\)

Brintzinger and Hesse\(^5\) prepared the copper, nickel,


and uranyl compounds of H\(_4\)Y. The copper complex was found to be insoluble in organic solvents but dissolved readily in hot water. Titration of this complex indicates that it is a dibasic acid, which agrees with the idea that the H\(_4\)Y is coordinated as a tetradeinate ligand. The nickel complex behaves in a manner analogous to that of the copper complex. Its stability is shown by the fact that dimethylglyoxime does not precipitate the nickel from ammoniacal
solutions of the complex. The compound UO$_2$H$_2$Y·H$_2$O was isolated; however, the UO$_2$ group gives its customary precipitation reactions. From this it was concluded that any complex formed, in this case, must be quite weak.

Brintzinger and Munkelt$^6$ studied the compounds of various metals with H$_4$Y. They concluded that Li, Be, and Y form only simple salts with H$_4$Y, while Mg, Ca, Sr, Ba, Hg, and Bi form their complex acids or salts. These conclusions were based almost entirely on chemical evidence.

Brintzinger and co-workers$^7$ prepared the compound Pb$_2$Y·H$_2$O. This product was slightly soluble in water, but gave reactions which are usual for Pb$^{+2}$ ion. For this reason they assumed that it was a salt. They also prepared Na[CoY]·4H$_2$O, H[Cr(Y)], and H[Fe(Y)]. These compounds gave none of the reactions which are usual for the metal ions. Therefore the proposed structure involved hexadentate coordination in all three cases. The general structure of these compounds is given on the following page (Fig. 2).
Figure 2. Structure of Hexadentate Complex of Ethylenediaminetetraacetic Acid

This report constituted the first study of a complex of cobalt (III) with ethylenediaminetetraacetic acid.

Schwartenbach\textsuperscript{8} prepared a number of pentadentate


6
H₄Y complexes with cobalt (III) (Fig. 4) which contained either Br⁻ or NO₂⁻ in the sixth coordination position. Aqueous solutions of these compounds had a tendency to lose bromide ion slowly, and in the presence of mercuric or silver ion, the bromide was lost more rapidly as evidenced by a color change of blue to red. He was able to isolate the red product of this reaction and found that it exhibited no acidic properties in solution. Schwartzenbach⁸ reported this product to be the hexadentate complex [CoY]⁻, which was hydrated. He also reported that when a water molecule is actually coordinated, a reversible color change, from red to blue, takes place when the pH of the solution is increased. This change of color was attributed to the formation of the mono-hydroxy complex [Co(Y)OH]⁻². The mono-aquo complex may be converted to the hexadentate complex by heating. This is shown by the fact that the reversible color change no longer takes place.

Busch and Bailar⁹ confirmed the existence of the hexadentate complex of cobalt (III) with H₄Y by use of infrared spectroscopy. They determined the infrared spectra of the pentadentate complexes of bromo and nitro-ethylenediaminetetraacetatocobaltate (III) (Fig. 4) and found that they

could show the presence of three coordinated carboxyl groups and one free carboxyl from two bands which occur in the carbonyl region. The band which corresponded to the complexed carboxyl groups was much more intense than that of the free carboxylic band. Further verification of this was found in the spectrum of sodium-ethylenediaminetetraaceta
cobaltate (III) which gave only one intense band in the carbonyl region. This was indicative of four equivalent complexed carboxyl groups.

Moeller, Moss, and Marshall\textsuperscript{10} prepared and studied the compounds of the types \( \text{H}[\text{Ln(Y)}]\cdot x\text{H}_2\text{O} \), \( \text{Na}[\text{Ln(Y)}]\cdot y\text{H}_2\text{O} \), and \( \text{Ln}[\text{Ln(Y)}]_3\cdot z\text{H}_2\text{O} \), where \( \text{Ln} \) is a rare earth or yttrium. A study of the carbonyl region of the infrared spectra of these compounds, in the same manner as Busch and Bailar\textsuperscript{9} had done previously on the cobalt complexes of \( \text{H}_4\text{Y} \), indicated that \( \text{Y}^{-3} \) was acting as a pentadentate ligand with the metal, the sixth position being occupied by a water molecule. If this postulation is correct and if the bonding in these complexes is sufficiently covalent, these complexes should be resolvable into optically active isomers. Attempts to resolve the yttrium complex failed; however,
this may have been the result of weak covalent bonding rather than an indication of the absence of an asymmetrical molecule.

Busch and Bailar\textsuperscript{11} have prepared the bidentate and tetradentate complexes of $H_4Y$ with platinum (II) and palladium (II). The structures of these are shown below (Fig. 3). $M^{\text{II}}$ is platinum or palladium.

\begin{figure}[h]
\centering
\includegraphics[width=\textwidth]{structure.png}
\caption{Structure of Tetradentate and Bidentate Complexes of Ethylenediaminetetraacetic Acid with Platinum (II) and Palladium (II)}
\end{figure}

Two strong carbonyl bands, which were observed in the spectra of both the dihydrogen-ethylenediaminetetra-acetato platinum (II) and palladium (II), were attributed to the presence of the complexed carboxyl groups and carboxylic acid groups. In the case of the bidentate complexes of platinum and palladium (II), only one strong band was observed in the carbonyl region and this was assumed to be associated with the four free carboxylic acid groups. These spectra were obtained using mulls of the compounds in Nujol.
B. Synthesis and Chemical Properties of the Pentadentate Complexes of Ethylenediaminetetraacetic Acid and Hydroxyethylethylenediaminetriacetic Acid with Cobalt (III)

The colors of the complex salts are dependent in all cases on the nature of the monodentate group $X$. They are $\text{NO}_2^-$, brick-red; $\text{Br}^-$, blue green; and $\text{Cl}^-$, blue. The colors of the complex anions are not altered by removal of proton from the uncomplexed carboxyl group to form the neutral salts in the case of the complexes with ethylenediaminetetraacetic acid. For example, the salts $\text{Na}[\text{Co(HY)}\text{NO}_2]$ (Fig. 4), and $\text{Na}_2[\text{Co(Y)NO}_2]$ (Fig. 5) are identical in color. This observation extends to the complexes of the second ligand, hydroxyethylethylenediaminetriacetic acid (Fig. 1), which coordinates through the same set of donor atoms as are used by pentadentate ethylenediaminetetraacetic acid.

The previously known cobalt (III) pentadentate complexes of ethylenediaminetetraacetic acid, $M[\text{Co(HY)}X]$, have been prepared in the course of the present investigations, and their study has been extended. The compound, in which the monodentate group is chloride,\textsuperscript{12} was prepared for the first time in these studies.

Figure 4. Structure of "Acidic" Pentadentate Complexes of Ethylenediaminetetraacetate (HY\(^{3-}\)) with Cobalt (III)

Figure 5. Structure of "Neutral" Pentadentate Complexes of Ethylenediaminetetraacetate (Y\(^{4-}\)) with Cobalt (III)
Structure of 'Acidic' Pentadentate Complexes
Ethylenediaminetetraacetate (HY$^{3-}$) with Cobalt (III).
Structure of 'Neutral' Pentadentate Complexes Ethylenediaminetetraacetate ($Y^{4-}$) with Cobalt (III).
A series of similar compounds containing hydroxy-ethylethlenediaminetriacetic acid has also been prepared. This series of compounds may be represented by the general formula $\text{Na}[\text{Co(YOH)}X]$, where $X =$ chloride, bromide, and nitrite and YOH is the trinegative anion of hydroxyethylethlenediaminetriacetic acid. The structure of this type of compound is shown in Figure 6. It is to be noted that the sixth functional group is free in each case and that the only difference in the two series of compounds is in the nature of the free group, one being a carboxylic acid group and the other, an alcoholic group. Thus, the salts $\text{Na}[\text{Co(YOH)}X]$ have the same colors as the corresponding $\text{Na}[\text{Co(HY)}X]$ salts.

The solubilities of the complex salts are profoundly affected by the nature of the free group. The salts containing a free carboxylic acid group are relatively simple to crystallize and may generally be caused to crystallize by the addition of a strong acid to their solutions. In contrast, the salts having a free hydroxyethyl group are very soluble and, in the case of the chloro complex, may be obtained in the solid form only by the use of mixed solvents or by evaporation to dryness. The latter procedure is often complicated by the deposition of the complex as a tar-like film. The effect of the monodentate anion $X$ also
Figure 6. Structure of Pentadentate Complexes with Hydroxyethylentriaminediacetate (YOH⁻)
Structure of Pentadentate Complexes with Hydroxyethylethylenediaminetriacetate ($\text{YOH}^3^-$).
appears very distinctly in the solubilities, especially in the case of the compounds of the formula Na[Co(YOH)X]. Whereas the chloro complex presents considerable difficulty in its crystallization, the corresponding bromo complex has a solubility low enough to permit its isolation from concentrated aqueous solution in crystalline form. The related nitro complex exhibits a convenient solubility in water, undergoing crystallization without difficulty.

The apparent stabilities of these compounds appear to be directly associated with the nature of the monodentate group occupying the sixth coordination position. The nitro complexes [Co(HY)NO₂⁻] and [Co(YOH)NO₂⁻] appear to be stable in solution for a period of months. When either the chloro or bromo complex is placed in aqueous solution, the color of the solution is blue. After a short period of time the color changes to a violet blue and upon further standing, it changes to a bright red. The color changes are greatly accelerated by the addition of Ag⁺ ion to a solution of the complex. These observations are logically expected to be associated with the acid hydrolysis of these complexes.

\[ \text{[Co(HY)X]}^- + \text{H}_2\text{O} \rightarrow \text{[Co(HY)H}_2\text{O}^-] + \text{X}^- \]

The rates of these reactions have been studied in the course of the present investigations.
Preparation of Sodium Hydrogen Chloro-(ethylene-diaminetetraacetato)cobaltate (III) ½-Hydrate. Ten grams of disodium dihydrogen ethylenediaminetetraacetate was dissolved in 75 ml. of distilled water. Two and fifteen-hundredths grams of sodium hydroxide, 6.37 grams of cobalt (II) chloride 6-hydrate and 12 ml. of glacial acetic acid were added. The solution was cooled to 0°C, chlorine was passed through it for approximately six hours, and it was allowed to stand overnight. The solution was filtered and the blue crystalline product was recrystallized from water, washed several times with absolute ethanol, and dried in vacuo at 80°C. Anal. Calc'd. for Na[Co(Cl0H13O8N2)Cl] ·½H2O: C, 28.90; H, 3.40; N, 6.74. Found: C, 29.02; H, 3.64; N, 6.90.

Preparation of Sodium Chloro-(hydroxyethylethylene-diaminetriacetato)cobaltate (III) 1.5-Hydrate. Twelve grams of cobalt (II) chloride 6-hydrate and 17.2 grams of trisodium hydroxyethylethylenetriacetate were dissolved in 75 ml. of distilled water and the solution was cooled to 0°C. Chlorine was passed into the solution for approximately ten hours and the solution was allowed to stand overnight. A finely divided purple product was obtained by the addition of absolute ethanol. Since this product tends to convert into a tar upon standing in the air, it
was immediately placed in a desiccator. After drying, the product was washed several times with absolute ethanol and redried in vacuo over P$_2$O$_5$. Anal. Calc'd. for Na[Co(C$_{10}$H$_{15}$O$_7$N$_2$)Cl]$\cdot$1.5 H$_2$O: C, 28.62; N, 6.68; H, 4.34. Found: C, 28.84; N, 6.64; H, 4.44.

Preparation of Sodium Hydrogen Nitro-(ethylenediaminetetraacetato)cobaltate (III) 1-Hydrate. This compound was prepared by the method of Schwartzenbach.$^8$ The analysis for the sample used here was reported in reference 9.

Preparation of Sodium Nitro-(hydroxyethylethylene-diaminetriacetato)cobaltate (III).

This substance was prepared by a method similar to that given by Schwartzenbach for the compound above. Twenty-four grams of cobalt (II) chloride 6-hydrate in 100 ml. of distilled water was mixed with a solution of 34.7 grams of trisodium hydroxyethylethylene diaminetriacetate. Fifteen grams of sodium nitrite and, after cooling to 0°C., 70 ml. of glacial acetic acid were added. The solution was allowed to stand overnight, whereupon crystallization took place. The brick-red product was purified by recrystallization from water and dried at 150°C. Anal. Calc'd. for Na[Co(C$_{10}$H$_{15}$O$_7$N$_2$)NO$_2$]: N, 10.42; H, 3.75; C, 29.79. Found: N, 10.32; H, 3.84; C, 29.77.
Preparation of Sodium Bromo-(hydroxyethylethylene-diaminetriacetato)cobaltate (III) 1-Hydrate. Seventeen and two-tenths grams of trisodium hydroxyethylethylene-diaminetriacetate and 12 grams of cobalt (II) chloride 6-hydrate were dissolved in 75 ml. of distilled water and the solution was cooled to 5°C. A solution of 4 ml. of bromine in 10 ml. of glacial acetic acid was added and the resulting solution was stirred for approximately 12 hours. The bright violet color gradually changed to blue and a bluish green precipitate formed. This product was isolated by filtration and purified by dissolving in water and precipitating with ethanol. The precipitate was filtered, washed with absolute ethanol, until the washings were colorless, and dried in vacuo at 80°C over P_2O_5. Anal. Calc'd. for Na[C_10H_15O_7N_2]Br·H_2O: C, 26.39; H, 3.77; N, 6.16. Found: C, 26.88; H, 3.41; N, 6.12.

Preparation of Sodium Hydrogen Bromo-(ethylenediaminetetraacetato)cobaltate (III). Thirty-eight and twenty-four hundredths grams of disodium ethylenediaminetetraacetate was dissolved in 100 ml. of distilled water. Ten and eighty-eight hundredths grams of sodium carbonate and twenty-four grams of cobalt (II) chloride 6-hydrate were added to this solution. The solution was cooled to 0°C. and eight ml. of bromine in twenty ml. of glacial acetic
acid was added. The solution was stirred vigorously for six hours. The product obtained was filtered and washed with absolute alcohol. It was crystallized from a solution of sodium acetate by addition of 6 ml. of concentrated hydrochloric acid and washed in alcohol, with stirring, three times. It was dried in vacuo with $P_2O_5$. **Anal.** Calc'd. for $\text{Na}[\text{Co}(\text{C}_{10}\text{H}_{13}\text{O}_8\text{N}_2)\text{Br}]$: C, 26.63; H, 2.90; N, 6.21. Found: C, 26.54; H, 3.15; N, 6.18.

**Preparation of Dihydrogen Chloro-(ethylenediaminetetraacetato)cobaltate (III).** A thick soup of potassium (ethylenediaminetetraacetato)cobaltate (III) was prepared. This solution was heated to 90°C. for about 3 to 5 minutes and cooled. Upon cooling, the product crystallized. It was purified by recrystallization from water and washed numerous times with absolute alcohol. **Anal.** Calc'd. for $\text{H}_2[\text{Co}(\text{C}_{10}\text{H}_{12}\text{O}_8\text{N}_2)\text{Cl}] \cdot 3\text{H}_2\text{O}$: C, 27.38; H, 4.60; N, 6.39. Found: C, 27.47; H, 4.01; N, 6.47.

**Preparation of Sodium (ethylenediaminetetraacetato)cobaltate (III).**

**13** F. P. Dwyer, private communication.

A mixture of eight grams of cobalt (II) chloride, 6-hydrate, thirteen and eighty-five hundredths grams of sodium acetate 3-hydrate and ten grams of ethylenediaminetetraacetic acid in 60 ml. of water was brought to nearly boiling and 30 ml. of 3% hydrogen peroxide was added slowly to the deep red solution. Absolute alcohol was added to the cooled solution and the product was isolated. The product was purified by precipitation from water with absolute alcohol. It was dried in vacuo over P₂O₅. Anal. Calc'd. for Na[Co(C₁₀H₁₂O₆N₂)]·H₂O: C, 30.94; H, 3.63; N, 7.22. Found: C, 30.49; H, 3.38; N, 7.22.

Preparation of Dichloro-(tetrahydrogen-ethylenediaminetetraacetate)palladium (II) or platinum (II). These compounds were prepared by the method of Busch and Bailar.

Preparation of Dihydrogen-(ethylenediaminetetraacetato)palladium (II) or platinum (II). These compounds were prepared by the method of Busch and Bailar.

Preparation of Disodium-(ethylenediaminetetraacetato)palladium (II) or platinum (II) and tetrasodium dichloro-(ethylenediaminetetraacetate)palladium (II) or platinum (II). Approximately four-tenths of a gram of the di- or tetra-acid palladium (II) or platinum (II)
complexes was dissolved in a minimum of water. The solution was titrated with 0.1N sodium hydroxide. The resulting solution was evaporated to dryness and a solid product was obtained. Anal. Calc'd. for

\[
\text{Na}_2\left[\text{Pd}(\text{C}_{10}\text{H}_{12}\text{N}_2\text{O}_8)\right]\cdot\text{H}_2\text{O}: \text{C}, 26.17; \text{H}, 3.08; \text{N}, 6.10.
\]

Found: C, 26.33; H, 3.59; N, 6.03. Calc'd. for

\[
\text{Na}_2\left[\text{Pt}(\text{C}_{10}\text{H}_{12}\text{N}_2\text{O}_8)\right]\cdot\text{H}_2\text{O}: \text{C}, 19.97; \text{H}, 3.36; \text{N}, 4.66.
\]

Found: C, 19.70; H, 2.86; N, 4.67. Calc'd. for

\[
\text{Na}_4\left[\text{Pt}(\text{C}_{10}\text{H}_{12}\text{N}_2\text{O}_8)\text{Cl}_2\right]\cdot\text{H}_2\text{O}: \text{C}, 17.60; \text{H}, 2.43; \text{N}, 4.10.
\]

Found: C, 17.33; H, 2.86; N, 4.13. Calc'd. for

\[
\text{Na}_4\left[\text{Pd}(\text{C}_{10}\text{H}_{12}\text{N}_2\text{O}_8)\text{Cl}_2\right]\cdot\text{H}_2\text{O}: \text{C}, 20.22; \text{H}, 2.72; \text{H}, 2.72;
\]

N, 4.72. Found: C, 20.35; H, 2.87; N, 4.65.

**Preparation of Dichloro-bis-(tyrosine)platinum (II)**\(^{15}\)

Fifteen ml. of 0.8M potassium hydroxide and 2.17 grams of tyrosine were heated with 1.24 grams of dipotassium tetra-chloro platinate (II) for two hours. Excess undissolved tyrosine was filtered off. The filtrate was boiled and 2 to 3 drops of concentrated hydrochloric acid was added. More amorphous tyrosine was precipitated. Further addition of concentrated hydrochloric acid, approximately 2 to 3 ml., precipitated an appreciable quantity of a dark

---

brown viscous mass which was allowed to settle. The
decanted supernatant liquor was filtered and treated with
5 to 6 ml. of concentrated hydrochloric acid, and boiled
2 to 3 minutes. On cooling, a yellow crystalline prod-
uct formed. It was filtered and washed with water, eth-
anol, and di-ethyl ether. Anal. Calc'd. for
Pt\textsuperscript{II}\left[\text{HOC}_6\text{H}_4\text{CH}_2\text{CH(NH}_2\text{)COOH}\right]_2\text{Cl}_2: \text{C, 34.39; H, 3.53; N, 4.46. Found: C, 34.44; H, 3.52; N, 3.38.}
C. **Infrared Spectra of the Complexes of Ethylenediaminetetraacetic Acid and Hydroxyethylethylene-diaminetriacetic Acid**

1. **Introduction**

In recent years, infrared spectroscopy has received considerable attention as a tool in the determination of the structures of complex inorganic compounds. Because of experimental difficulties, the application has been restricted, for the most part, to the study of organic functional groups and the effect which complex formation has on these groups. The carbonyl group has been the subject of several studies of this kind. The first work along this line was carried out by Douville, Duval, and Lecompte.

---


---

on the oxalato complexes of several metal ions. The study of the complexes formed by the oxalate ion has been extended recently by Sen. As a result of the investigation

---


---

of the metal complexes of glycine, Sen concluded that the link between the carboxylate group and a metal ion is largely ionic. A somewhat different view has been expressed.
by other investigators.\textsuperscript{18} According to this point of view, it is supposed that if a carbonyl group is linked to some group Z (Fig. 7), the carboxylate resonance will increase as the ionic character of the O-Z link increases.


Since an increase in carboxylate resonance imparts enhanced single-bond character to the carbonyl group, it also causes a lowering of the frequency of the C=O stretching vibration. In consequence, the C=O stretching frequency provides some information relating to the ionic character of the bond. On this basis, it has been possible to distinguish between a carboxyl group bound to a proton and a carboxyl group bound to a metal ion.\textsuperscript{9, 11} This application is reexamined and improved in the discussion to follow. As is shown in Figure 6, a carboxyl group might be present as an uncomplexed carboxylate ion.
It has recently been suggested that uncomplexed carboxylate groups may be distinguished from complexed carboxyl groups on the basis of the sharpness of the carbonyl absorption band. These studies demonstrate the applicability of infrared spectral correlations to this problem and point out certain limitations which are inherent in this technique. The infrared absorption bands of the coordinated nitro group, as reported in previous investigations, are also verified by the spectra of the compounds under considerations.

The bidentate and tetradentate complexes of ethylenediaminetetraacetic acid with Pt$^{II}$ and Pd$^{II}$ have been prepared and the structure of the compounds has been reevaluated on the basis of their infrared spectra. Dichloro-bis(tyrosine)platinum (II) has also been prepared and a confirmation of its structure given on the basis of its infrared spectrum.

2. Infrared Spectra of the Complexes of Ethylenediaminetetraacetic Acid and Hydroxyethylethlenediaminetriacetic Acid with Cobalt (III)

The infrared spectra were obtained on solid samples of the compounds in potassium bromide discs.$^{19}$ The

measurements were made with a Perkin-Elmer Model 21 Rec-
dering Spectrophotometer equipped with a sodium chloride prism.

In Table I, assignments are given for eleven absorption bands which are of diagnostic value in the study of the structures of these and similar compounds (Figures 8, 9, and 10). The bands of primary concern are those associated with the carboxyl group. Five absorptions are considered in this connection, and three of these appear only in the case of the carboxylic acid group. These are the bands of 2600-2800 cm⁻¹ (–OH stretch), 1700-1750 cm⁻¹ (C=O stretch), and 1228 cm⁻¹. The first band (2600-2800 cm⁻¹) is very weak and therefore more limited in usefulness than the other two bands. The carbon double bond oxygen stretching vibration is, of course, present in the spectrum of the carbonyl group regardless of the manner in which it may be bonded, and it is this same vibration which gives rise to two of the regions of absorption not associated with the carboxylic acid group. The third band (1228 cm⁻¹) appears to be unambiguously associated with the carboxylic acid group, as is witnessed by its presence in both complexes which contain the functional group and its absence from the other spectra. From Table I it is seen that the compounds formulated as Na[Co(HY)X] both show these three bands, thus demonstrating the presence of the free carboxylic acid group.⁹
## Table I

<table>
<thead>
<tr>
<th>Compound</th>
<th>(H\textsubscript{2}O or ROH)</th>
<th>-CH</th>
<th>1 (-OH)</th>
<th>2 (-COOH)</th>
<th>3 (COO-\textsuperscript{M})</th>
<th>4 (COO\textsuperscript{-})</th>
<th>5 (COOH)</th>
<th>(\text{NO}_2) Group</th>
<th>(1)</th>
<th>(2)</th>
<th>(3)</th>
<th>-CH\textsubscript{2}OH</th>
</tr>
</thead>
<tbody>
<tr>
<td>1. Na [Co(HY)NO\textsubscript{2}] (\cdot) H\textsubscript{2}O</td>
<td>3540</td>
<td>3040(\text{W})</td>
<td>2600-2800 (\text{vW})</td>
<td>1745(\text{M})</td>
<td>1650(\text{S})</td>
<td>--</td>
<td>1228(\text{M})</td>
<td>1415(\text{M})</td>
<td>1343(\text{M})</td>
<td>833(\text{W})</td>
<td>--</td>
<td></td>
</tr>
<tr>
<td>2. Na\textsubscript{2} [Co(Y)NO\textsubscript{2}] (\cdot) H\textsubscript{2}O</td>
<td>3580</td>
<td>3040(\text{W})</td>
<td>--</td>
<td>--</td>
<td>1650(\text{S})</td>
<td>1604(\text{M})</td>
<td>--</td>
<td>1408(\text{M})</td>
<td>1343(\text{M})</td>
<td>833(\text{W})</td>
<td>--</td>
<td></td>
</tr>
<tr>
<td>3. Na [Co(HY)Cl] (\cdot) 1/2H\textsubscript{2}O</td>
<td>3540</td>
<td>3080(\text{W})</td>
<td>2500-2700 (\text{vW})</td>
<td>1750(\text{M})</td>
<td>1650(\text{S})</td>
<td>--</td>
<td>1228(\text{M})</td>
<td>--</td>
<td>--</td>
<td>--</td>
<td>--</td>
<td></td>
</tr>
<tr>
<td>4. Na\textsubscript{2} [Co(Y)Cl]</td>
<td>3580</td>
<td>3040(\text{vW})</td>
<td>--</td>
<td>--</td>
<td>1648(\text{S})</td>
<td>1600 (\text{M, sh})</td>
<td>--</td>
<td>--</td>
<td>--</td>
<td>--</td>
<td></td>
<td></td>
</tr>
<tr>
<td>5. Na [Co(YOH)NO\textsubscript{2}]</td>
<td>3610</td>
<td>3040(\text{W})</td>
<td>--</td>
<td>--</td>
<td>1652(\text{S})</td>
<td>--</td>
<td>--</td>
<td>1408(\text{M})</td>
<td>(342(\text{M})</td>
<td>833(\text{W})</td>
<td>1080</td>
<td></td>
</tr>
<tr>
<td>6. Na [Co(YOH)Cl] (\cdot) 1 1/2 H\textsubscript{2}O</td>
<td>3580</td>
<td>3080(\text{W})</td>
<td>--</td>
<td>--</td>
<td>1658(\text{S})</td>
<td>--</td>
<td>--</td>
<td>--</td>
<td>--</td>
<td>--</td>
<td>1030</td>
<td>1070</td>
</tr>
<tr>
<td>7. Na [Co(YOH)Br] (\cdot) H\textsubscript{2}O</td>
<td>3640</td>
<td>3040(\text{W})</td>
<td>--</td>
<td>--</td>
<td>1654(\text{S})</td>
<td>--</td>
<td>--</td>
<td>--</td>
<td>--</td>
<td>--</td>
<td>1032</td>
<td>1070</td>
</tr>
</tbody>
</table>

The following abbreviations are used in the table: Y, ethylenediaminetetraacetate anion; YOH, hydroxyethylendiaminetriacetate anion; v, very; W, weak; M, moderate; S, strong; sh, shoulder.
Figure 8. Infrared Spectra of
Na[CoIII(HY)NO₂]·H₂O and Na₂[CoIII(Y)NO₂]·H₂O

Figure 9. Infrared Spectra of
Na[CoIII(HY)Cl]·½H₂O and Na₂[CoIII(Y)Cl]

Figure 10. Infrared Spectra of
Na[CoIII(YOH)NO₂], Na[CoIII(YOH)Cl]½H₂O, and Na[CoIII(YOH)Br]·H₂O
Infrared Spectra

$\text{Na}_2\text{[CO}^{\text{III}}\text{(HY)NO}_{2}\text{]}\text{H}_2\text{O}$

$\text{Na}_2\text{[CO}^{\text{II}}\text{(Y)NO}_{2}\text{]}\text{H}_2\text{O}$
Absorbance (optical density)

Wave Numbers (cm⁻¹)

Infrared Spectra
Na[CO₃(HY)Cl] ½H₂O
Na₂[CO₃(YCl)]
The two remaining bands associated with the carboxyl group are both manifestations of the carbon double bond oxygen stretching vibration. The first of these (1648-1658 cm\(^{-1}\)) arises from the complexed carboxyl group as is indicated by its presence in the spectra of all of the complexes reported. This band shows little variation in its frequency in this series of cobalt (III) complexes.

The preceding correlations have been discussed, in part, previously;\(^9\),\(^11\) however, the fifth region of absorption has not been considered in connection with complex compounds of cobalt (III) with ligands of this kind. This band is associated with the carbon double bond oxygen stretching vibration of the uncomplexed carboxylate ion. The structures of the compounds having this group (lines 2 and 4, Table I and structure) are inferred from the known structures of the starting materials from which they are prepared, from the simple reactions leading to their formation and from their properties as described above. On the basis of correlations appearing in the literature,\(^20\) the carboxylate ion is expected to absorb in the region from 1550 to 1600 cm\(^{-1}\). The compounds of general formula \(\text{Na}_2[\text{Co}(\text{Y})\text{X}]\) would, therefore, be expected to exhibit two
absorption bands, one in the region around 1650 cm$^{-1}$ corresponding to the complexed carboxyl group and a second in the region from 1550 to 1600 cm$^{-1}$ arising from the free carboxylate ion. Furthermore, if the inferred structures of these compounds are correct, there should be three complexed carboxyl groups and one free carboxylate group so that the 1650 cm$^{-1}$ band should be much more intense than the band in the range 1550 to 1600 cm$^{-1}$.

In Table I, two such bands are reported for the compound Na$_2$[Co(Y)NO$_2$], and the relative intensities vary in the manner expected. This compound, therefore, provides an ideal demonstration of the identification of a free, ionic carboxylate group in a compound which also contains complexed carboxyl groups. The certainty of this conclusion is enhanced by the assignment of all the bands not found in most of the other complex compounds listed in Table I to the nitro group, in accord with previous reports on the positions of the bands of complexed nitro groups$^{21,22}$ and with the spectra of the other nitrite-containing complexes reported here (compare lines 1, 2,


and 5 of Table I). Along with the appearance of the moderately strong 1604 cm\(^{-1}\) band, the three bands associated with the carboxylic acid group vanish (compare lines 1 and 2 of Table I), thus further confirming the conclusion.

The second compound studied in connection with the uncomplexed carboxylate ion is Na\(_2[\text{Co(Y)Cl}]\). In this case, it is also obvious that no carboxylic acid group is present since the three bands identifying the group in Na[Co(HY)Cl] do not appear in the spectrum of the neutral salt. However, the C=O stretching vibrations are not split distinctly into two bands. Instead, a single strong band appears at 1648 cm\(^{-1}\), and this band has a rather well developed shoulder of moderate intensity at 1600 cm\(^{-1}\). In light of the absence of ambiguity in the preceding case, it is quite logical to assign these bands to the carbonyl of the three complexed carboxyl groups and the carbonyl of a single carboxylate ion, respectively.

The spectra of the cobalt (III) complexes of hydroxy-ethylethlenediaminetriacetic acid provide further substantiation for the interpretation set forth above. These compounds, which are of the general formula Na[Co(YOH)X], presumably have the structure shown in Figure 6. This structure involves three complexed carboxyl groups, but neither free carboxylic acid nor uncomplexed carboxylate ion. The data given in Table 1 reveal that only one of
the absorption bands derived from carboxyl groups appears in their spectra, and this is the band at approximately 1650 cm\(^{-1}\) which arises from the complexed carboxyl group. The band is sharp and symmetrical. The absorptions of the nitro group in Na\(\left[\text{Co(YOH)}\text{NO}_2\right]\) are also reported in Table I, and bands in the range from 1030 to 1085 cm\(^{-1}\) have been assigned to the \(-\text{CH}_2\text{OH}\) group.

In the discussion immediately preceding, positive evidence has been given to show the feasibility of detecting complexed carboxyl groups and uncomplexed carboxylate ions in the presence of each other. It has been shown that separations as great as 54 cm\(^{-1}\) may exist between the C\(=\)O stretching vibrations of a free carboxylate ion and a carboxyl group bonded to a cobalt (III) ion. In other cases where a separation of this magnitude can be anticipated, it would seem reasonable to consider the presence or absence of a band in the 1550-1600 cm\(^{-1}\) range as evidence of the state of bonding of a carboxyl group which might otherwise remain in question. The second example given above leads to two limitations which are significant in this respect. The frequency of the complexed carboxyl group will differ from compound to compound even with the same metal ion, and more markedly in going from one metal ion to another. Similarly, variations in the frequency of the carboxylate anion may complicate the matter. In
the compound Na₂\([\text{Co(Y)Cl}]\), the separation between the shoulder (1600 cm⁻¹) and the band of the complexed carboxyl group (1648 cm⁻¹) is 48 cm⁻¹, a decrease of only 6 cm⁻¹ from that mentioned for the nitro complex; however, the decrease is sufficient to merge the two bands into a single band with a shoulder. It might be expected that a further decrease in this interval by 10 to 15 cm⁻¹ would cause the complete disappearance of the shoulder, leaving only a single sharp band which might be only very slightly unsymmetrical. From this it is concluded that the resolution of the average infrared spectrophotometer may not be adequate to guarantee that a distinction can be made between a complexed carboxyl group and a free carboxylate ion. Whether or not such a distinction can be made would seem to depend largely on the nature of the central metal ion in the complex, since it has been shown that the C=O frequency of the complexed carboxyl group depends on the metal ion,¹⁶, ²² while the free carboxylate ion should be relatively independent of the nature of the metal ion. A separate band for free carboxylate ion should therefore appear in the infrared spectrum on any complex of this type having no interfering complexed carboxyl group which absorbs below 1650 cm⁻¹.
3. Infrared Spectra of Ethylenediamine-tetraacetic Acid and Other Amino Acids with Platinum (II) and Palladium (II)

The infrared spectra of $[\text{M}^{\text{II}}(\text{H}_4\text{Y})\text{Cl}_2]$ and $[\text{M}^{\text{II}}(\text{H}_2\text{Y})]$ have been reported in Nujol. However, when the spectra of these compounds were confirmed, using KBr discs, several unreported absorption bands were observed. The necessary absorption bands of these compounds are given in Table II. Compounds of the general type $[\text{M}^{\text{II}}(\text{H}_4\text{Y})\text{Cl}_2]$, where M is platinum or palladium, would be expected to give one band in the region of about 1750 cm$^{-1}$. Another rather strong band should be present in the region of 1200 cm$^{-1}$. These absorption bands would be associated with the vibrational modes of the four free carboxylic acid groups. In Table II, these two bands are reported. In the case of $[\text{P}^{\text{II}}(\text{H}_4\text{Y})\text{Cl}_2]$(Fig. 11), they appear at 1748 cm$^{-1}$ and 1218 cm$^{-1}$, and those for $[\text{Pd}(\text{H}_4\text{Y})\text{Cl}_2]$ (Fig. 12) appear at 1768 cm$^{-1}$ and 1198 cm$^{-1}$. However, an unreported band appears at 1638 cm$^{-1}$ for the platinum complex and 1655 cm$^{-1}$ for the palladium complex.

The tetrasodium salts of these complexes should contain only one absorption band in the 1600-1650 cm$^{-1}$ region. This band is observed at 1623 cm$^{-1}$ for the platinum complex (Fig. 11) and at 1628 cm$^{-1}$ for the palladium complex (Fig. 12). It is associated with the carbonyl of the four free carboxylate ions.
### Table II

**INFRARED SPECTRA OF PLATINUM (II) AND PALLADIUM (II) COMPLEXES**

<table>
<thead>
<tr>
<th>Compound</th>
<th>$\text{H}_2\text{O}$</th>
<th>$-\text{CH}$</th>
<th>$-\text{OH}$</th>
<th>$-\text{COOH}$</th>
<th>$-\text{COOM}$</th>
<th>$-\text{COO}^-$</th>
<th>$-\text{COOH}$</th>
<th>COOHM</th>
</tr>
</thead>
<tbody>
<tr>
<td>$\text{H}_2\text{PtY}$</td>
<td>3690</td>
<td>3070</td>
<td>2600-2700 (vW)</td>
<td>1765 (M)</td>
<td>1650 (S)</td>
<td>-</td>
<td>1215 (W)</td>
<td>1665 (sh)</td>
</tr>
<tr>
<td>$\text{Na}_2\text{PtY}$</td>
<td>3560</td>
<td>3040</td>
<td>-</td>
<td>-</td>
<td>1630 (S)</td>
<td>-</td>
<td>-</td>
<td>-</td>
</tr>
<tr>
<td>$\text{H}_2\text{PdY}$</td>
<td>3600</td>
<td>3080</td>
<td>-</td>
<td>1772 (M)</td>
<td>1638 (S)</td>
<td>-</td>
<td>1200-1210 (vW)</td>
<td>1713 (M)</td>
</tr>
<tr>
<td>$\text{Na}_2\text{PdY}$</td>
<td>3680</td>
<td>3040</td>
<td>-</td>
<td>-</td>
<td>1648 (vS)</td>
<td>-</td>
<td>-</td>
<td>-</td>
</tr>
<tr>
<td>$\text{H}_4\text{PtYCl}_2$</td>
<td>3580</td>
<td>3020</td>
<td>2680 (W)</td>
<td>1748 (vS)</td>
<td>-</td>
<td>-</td>
<td>1218 (S)</td>
<td>1638 (w)</td>
</tr>
<tr>
<td>$\text{Na}_4\text{PtYCl}_2$</td>
<td>3600</td>
<td>3080</td>
<td>-</td>
<td>-</td>
<td>1623 (S)</td>
<td>-</td>
<td>-</td>
<td>-</td>
</tr>
<tr>
<td>$\text{H}_4\text{PdYCl}_2$</td>
<td>3580</td>
<td>3080</td>
<td>-</td>
<td>1768 (vS)</td>
<td>-</td>
<td>-</td>
<td>1198 (M)</td>
<td>1655 (W)</td>
</tr>
<tr>
<td>$\text{Na}_4\text{PdYCl}_2$</td>
<td>3580</td>
<td>3090</td>
<td>-</td>
<td>-</td>
<td>1628 (S)</td>
<td>-</td>
<td>-</td>
<td>-</td>
</tr>
<tr>
<td>$[\text{Pt}{\text{HOC}_6\text{H}_4\text{CH}_2\text{CH(NH}_2\text{)COOH}}_2\text{Cl}_2]$</td>
<td>3077</td>
<td>2600 (W)</td>
<td>1704 (S)</td>
<td>-</td>
<td>-</td>
<td>1206 (vS)</td>
<td>-</td>
<td>-</td>
</tr>
<tr>
<td>$\text{C}_6\text{H}_5\text{CH(COOH)NH}_2$</td>
<td>-</td>
<td>-</td>
<td>-</td>
<td>-</td>
<td>-</td>
<td>1590 (vS)</td>
<td>-</td>
<td>-</td>
</tr>
</tbody>
</table>

The following abbreviations are used in the table: Y, ethylenediaminetetraacetate anion; v, very; W, weak; M, moderate; S, strong; sh, shoulder.
Figure 11. Infrared Spectra of $H_4Pt^{II}YCl_2$ and $Na_4Pt^{II}YCl_2$

Figure 12. Infrared Spectra of $H_4Pd^{II}YCl_2$ and $Na_4Pd^{II}YCl_2$
Infrared spectra

- $\text{H}_4\text{Pt}^\text{II}\text{YCl}_2$
- $\text{Na}_4\text{Pt}^\text{II}\text{YCl}_2$

Wave numbers (cm$^{-1}$)

Transmittance (% transmission)
The results obtained suggest that in the case of the $[\text{M}^\text{II}(\text{H}_4\text{Y})\text{Cl}_2]$ complexes there is some form of weak bonding between the free carboxylic acid groups and that of the central metal ion. Such an interaction would account for the unexpected band which appears at 1638 cm$^{-1}$ for the platinum complex and 1655 cm$^{-1}$ for the palladium complex. However, it appears that the free carboxylate ions do not associate with the central metal ion, since single sharp absorptions were observed in the region usually associated with the presence of free carboxylate ions.

The carboxyl groups of the tetradeinate complexes of platinum and palladium should exhibit three characteristic absorption bands. There should be one at approximately 1750 cm$^{-1}$, corresponding to the carbonyl stretching vibration of the free Carboxylic acid group. Another absorption band is expected at 1650 cm$^{-1}$, corresponding to the complexed carboxyl, and the third should occur in the 1200 cm$^{-1}$ region, which is associated with the OH group of the free carboxylic acid. Table II shows that, for $\text{H}_2\text{PdY}$ (Fig. 13) these three absorption bands occur at 1772 cm$^{-1}$, 1638 cm$^{-1}$, and 1210 to 1200 cm$^{-1}$. These absorption bands also occur for $\text{H}_2\text{PtY}$ (Fig. 14) at 1765 cm$^{-1}$, 1650 cm$^{-1}$, and 1215 cm$^{-1}$. It is interesting to note that
Figure 13. Infrared Spectra of $\text{H}_2\text{Pd}^{II}Y$ and $\text{Na}_2\text{Pd}Y$.

Figure 14. Infrared Spectra of $\text{H}_2\text{Pt}^{II}Y$ and $\text{Na}_2\text{Pt}^{II}Y$. 


Infrared spectra

Transmittance (\% transmission)

Wave numbers (cm\(^{-1}\))

- \( \text{H}_2\text{Pt}^2\text{Y} \)
- \( \text{Na}_2\text{Pt}^2\text{Y} \)
the absorption peaks in the 1200 cm\textsuperscript{-1} region are extremely weak. This is interesting in view of the fact that other complexes which contain free acid groups usually give at least a band of moderate intensity in this region. There is also one unreported band which appears at 1713 cm\textsuperscript{-1} for H\textsubscript{2}PdY and a shoulder at 1665 cm\textsuperscript{-1} for the H\textsubscript{2}PtY complex.

The carboxyl groups of the disodium salts of these complexes should give two absorption bands, one at 1650 cm\textsuperscript{-1} which is the C=O stretching vibration of the complexed carboxyl, and another at 1600 cm\textsuperscript{-1}, which is associated with the carboxyl of the carboxylate ion. Only one absorption band occurs in the spectra of the disodium salts of these complexes. It appears at 1648 cm\textsuperscript{-1} for the palladium complex (Fig. 14) and 1630 cm\textsuperscript{-1} for the platinum complex (Fig. 13). It appears to be that absorption band which is associated with the complexed carboxyl. The absorption band at 1600 cm\textsuperscript{-1} which is associated with the carbonyl of the carboxylate ion is absent. Therefore, from these results it is reasonable to assume that all of the carbonyl groups are equivalent, which leads to the possibility that in the case of the disodium salts of these complexes that the metal has a coordination number of six. In a similar manner, the unexpected bands found in the spectra of [Pt(H\textsubscript{2}Y)] and [Pd(H\textsubscript{2}Y)] may be related to an expansion of the coordination numbers of the platinum and palladium.
The absorption bands for the dichloro-bis(tyrosine)-platinum (II) complex (Fig. 15) and the ligand tyrosine (Fig. 15) are given in Table II.

Figure 15. Structure of Tyrosine and Dichloro-bis(tyrosine)platinum (II)

The absorption bands at 1617 cm⁻¹ of the tyrosine (Table II, Fig. 16), correspond to the NH₃⁺ group and phenyl group, and the absorption band at 1590 cm⁻¹ is
Figure 16. Infrared Spectra of Tyrosine and Deuterated Tyrosine
indicative of the carboxylate ion. If the amine group

If the amine group


of the tyrosine is the only functional group which is coordinated to the metal ion, the spectrum of the complex should show a strong absorption band in the 1700-1750 cm\(^{-1}\) region which would be that of the C=O stretching vibration of a carboxylic acid. Likewise, a strong absorption band in the 1200 cm\(^{-1}\) region would be indicative of the OH group of a carboxylic acid. Two such bands are reported in Table II for the dichloro-bis(tyrosine)platinum (II) complex (Fig. 17). An absorption band is observed at 1704 cm\(^{-1}\), which corresponds to the C=O stretching frequency of a free carboxylic acid and a band at 1210 cm\(^{-1}\) which is associated with the OH group of a carboxylic acid. From the above results, it is reasonable to conclude that the carbonyl groups of the tyrosine are not complexed to the platinum (II), indicating that the ligand is attached through the amine group. Thus, the structure of this compound (Fig. 15), given by Volshtein and Velikanova appears to be correct.
Figure 17. Infrared Spectra of Dichloro-bis(tyrosine)platinum (II)
1. **Introduction**

The rates of acid and base hydrolysis of complexes similar to \([\text{Co(HY)}X]^-\) and \([\text{Co(YOH)}X]^-\) complexes have been studied by earlier investigators. The term "acid hydrolysis" is defined as the reaction of the complex with the solvent in the case where water is the solvent. This may be shown by the example below.

\[
[\text{Co(NH}_3\text{)}_5X]^+ + \text{H}_2\text{O} \rightarrow [\text{Co(NH}_3\text{)}_5\text{H}_2\text{O}]^3^+ + X^-.
\]

The acidopentamminecobalt (III) complexes, \([\text{Co(NH}_3\text{)}_5X]^+\) have been studied by a number of investigators. The difference between these systems and the complexes of interest in this research, \([\text{Co(HY)}X]^-\) and \([\text{Co(YOH)}X]^-\), is that there are no acidic protons on the donor atoms in the complexes of ethylenediaminotetraacetic acid and hydroxyethylendiaminetriacetic acid. This becomes extremely important in view of a postulated mechanism for base hydrolysis. The rate expression for the base hydrolysis of \([\text{Co(NH}_3\text{)}_5X]^+\) is given in the following equation

\[
\text{Rate} = k[\text{Co(NH}_3\text{)}_5\text{Cl}^{+2}][\text{OH}^-].
\]
The second order kinetics given here may indicate a bimolecular, S.N.2 mechanism or else a pre-acid base equilibrium (postulated by Garrick\textsuperscript{24}) which is then followed by a unimolecular dissociation.

\textsuperscript{24}F. J. Garrick, \textit{Nature}, \textbf{139}, 507 (1937).

\[
\begin{align*}
[\text{Co(NH}_3\text{)}_5\text{Cl}]^{+2}+\text{OH}^- &\rightleftharpoons [\text{Cl(NH}_3\text{)}_4\text{CoNH}_2]^+ + \text{H}_2\text{O} \text{ (rapid equilibrium)} \\
[\text{Cl(NH}_3\text{)}_4\text{CoNH}_2]^+ &\rightarrow [(\text{NH}_3)_4\text{Co = NH}_2]^{+2} + \text{Cl}^- \text{ (rate determining)} \\
[(\text{NH}_3)_4\text{Co = NH}_2]^{+2} + \text{H}_2\text{O} &\rightarrow [\text{Co(NH}_3\text{)}_5\text{OH}]^{+2} \text{ (fast)}.
\end{align*}
\]

This is referred to as S.N.1 C.B. (substitution, nucleophilic, first order, conjugate base).

Since there are no acidic hydrogens on the coordinated nitrogen atoms in $[\text{Co(HOY)}X^-]$ and $[\text{Co(HY)}X^-]$ complexes, this pre-acid base equilibrium could not occur. Therefore, it may be concluded that, if pre-acid base equilibrium provides a unique mechanism for the pH dependence of the rates of hydrolysis of cobalt (III) complexes, the rate constants of complexes containing no acidic protons should be independent of the pH of the solution.

Basolo and co-workers\textsuperscript{25} studied the rates of acid

and basic hydrolysis of trans-[Co(X-py)₄Cl₂]Cl, where X-py was pyridine, \( \beta \)-picoline, \( \gamma \)-picoline, and \( \gamma \)-methoxypyridine. These compounds contain no acidic hydrogens and hydrolyze at a rate which is independent of pH. This result has been cited in support of an S.N.1 C.B. mechanism.

The free carboxyl or alcoholic group provides another major difference between the \([Co(HX)X]^-\) and \([Co(HOY)X]^-\) complexes and the ammine complexes \([Co(NH_3)_5X]^+\) or \([Co(en)_2X_2]^+\), where en = ethylenediamine. The presence of the free groups opens the possibility of a reaction mechanism involving intra-molecular displacement of the monodentate group X by the free carboxyl group. The discussion of this mechanism is given in the latter part of this section.

Lamb and Marden\(^{26}\) measured the rates of hydrolysis of the acidopentammines, \([Co(NH_3)_5X]^+\), where X = bromide, nitrate, and chloride, in aqueous solution. These reactions were found to exhibit a first order rate dependence on the concentration of complex. The rate of hydrolysis of the bromopentammine was observed to be greater than that of the

corresponding chloride complex. Garrick$^{27}$ reinvestigated these systems and confirmed the first order rate law.


Since the solvent, water, is also a reactant, the kinetics will not indicate the molecularity of these reactions.

Basolo and co-workers$^{25}$ studied the effects of C-substitution on the rates of hydrolysis of some acetopentammincobalt (III) ions in aqueous solution,

$$[\text{Co(NH}_3\text{)}_5\text{(RCO}_2\text{)}]^+ + \text{H}_2\text{O} \rightarrow [\text{Co(NH}_3\text{)}_5(\text{H}_2\text{O})]^3 + \text{RCO}_2^-.$$  

They investigated the effect of base strengths by the study of trifluoro-, trichloro-, dichloro-, and monochloroacetopentammincobalt (III) nitrates. The effect of steric hindrance was investigated by successively replacing the hydrogens on the terminal carbon of the acetate group by methyl groups. The results obtained from the halo-acids showed, in general, an increase in rate of acid hydrolysis with an increase in the base strength of the coordinated acetate and a decrease in the rate of hydrolysis with an increase in base strength. However, the rates of reaction appeared to be independent of the size of the coordinated ligand. From these results it was concluded that the incoming group approaches the complex from a position opposite
to the group that is leaving or else that the substitution takes place by a dissociation mechanism.

Pearson, Boston, and Basolo\textsuperscript{28} measured the rates of aquation of several substituted ethylenediamine complexes of the type $[\text{Co}(\text{AA})_2\text{Cl}_2]^+$, where AA is a substituted ethylenediamine, and found that they aquate more rapidly than the complex containing unsubstituted ethylenediamine. Since there is more crowding around the central metal ion it was assumed that these reactions do not proceed through a seven-co\text{"o}rdinate intermediate and, hence, an S.N.2 mechanism is incorrect. They postulate an S.N.1 mechanism with the formation of a five-co\text{"o}rdinate intermediate as the rate-determining step.

Brown and Ingold\textsuperscript{29} investigated the substitution reactions of $[\text{Co(en)}_2\text{Cl}_2]^+$ in methanol. The seven anions


nitrate, chloride, bromide, and thiocyanate reactions followed first order kinetics. The nitrite, azide, and methoxide appeared, in general, to follow either mixed kinetics (nitrite) or second order kinetics (methoxide). From the information obtained, it was suggested that these reactions are bi-molecular and that they do not involve conjugate base substitutions, which are controlled by the removal of a proton from the ethylenediamine. They assume that substitution by weakly basic groups proceeds by an S.N.1 mechanism and that, as the basicity of the substituting group becomes increasingly greater, the reaction proceeds by an S.N.2 type mechanism.

From the results of investigations of similar type complexes three possible mechanisms seem plausible for the ethylenediaminetetraacetic acid and hydroxyethylethylene-triacetic acid complexes.

**Intramolecular Nucleophilic Substitution**

Compounds of the type, $[\text{Co(HY)}X]^{-1}$ and $[\text{Co(YOH)}X]^{-1}$, where $X = \text{Br}^-$ and $\text{Cl}^-$, undergo some sort of reaction in solution. Since the color of the solution produced upon long standing resembles that of the hexadentate complex, $[\text{CoY}]^{-}$, the reaction of $[\text{Co(HY)}X]^{-}$ could involve the intramolecular reaction of the free carboxyl group with the complex itself, which would be a unimolecular first order
process. Such a process would be unique in that it would resemble bimolecular S.N.2 reactions, in detail, but would be unimolecular by virtue of the fact that the nucleophilic attacking group is a part of the same molecule which contains the electrophilic center. This process is represented in Figure 18:

![Figure 18. Intramolecular Nucleophilic Substitution Process](image)

The methylene groups are not shown in this and similar figures, since they are unnecessary in showing the postulated mechanism and only tend to add an unnecessary complication to the figures.

**Unimolecular Dissociation Process**

An alternate possibility exists which would also involve a unimolecular, first order rate process. The
pentadentate complex might dissociate a bromide ion, forming a five coordinate activated intermediate, which would then combine with either the free carboxyl group or with a water molecule. These possibilities are shown in Figure 19.

Figure 19. Unimolecular Dissociation Process
Bimolecular Reaction with Solvent

The third process by which these reactions might be expected to occur, involves direct attack of the solvent molecule. This is shown in Figure 20.

![Bimolecular Reaction with Solvent](image)

Figure 20. Bimolecular Reaction with Solvent

Such a reaction would be bimolecular, but pseudo first order, since the solvent concentration would not be affected by the extent of reaction.

Intramolecular nucleophilic substitution would be dependent on the pH of the solution. In solutions of low
pH the carboxylic acid would not be highly dissociated. Therefore the complexing tendency of the carboxylate ion would be decreased and the rate of the reaction would decrease. It is possible then that an intramolecular nucleophilic substitution reaction could be shown by a variation in rate with the pH of the solution. The unimolecular dissociation process invokes the dissociation of the X group to give a five-coordinate activated species, which can react with a water molecule or, intramolecularly, with the free carboxylate group, and the bimolecular reaction invokes direct attack of solvent molecule. In both the unimolecular dissociation process and the bimolecular process, first order kinetics would be observed and the rate would be independent of pH. Therefore a unimolecular dissociation process could not be differentiated from a bimolecular process by the method employed in these kinetic studies.

In the case of the complexes with hydroxyethylendiaminetriacetic acid, the free functional group is a very poor coordinating agent, so that some indication of whether an intramolecular mechanism is operative might be obtained by studying this complex and the ethylenediaminetetraacetic acid complexes under the same conditions. For example, the free carboxyl group may act as a nucleophilic group thereby giving rise to a pH dependence. The rate of
reaction of the \([\text{Co}(\text{YOH})X]^-\) complex would be much less affected by pH, since the alcoholic group is a very weak acid. It would be reasonable to assume that with decreasing pH the rate constant of the \([\text{Co}(\text{HY})X]^-\) complex should become similar to those of the corresponding \([\text{Co}(\text{YOH})X]^{-1}\) complexes. Above pHs where the carboxylic acid is completely dissociated the reaction should be pH independent if the assumed mechanism is intramolecular substitution. This research was undertaken with the idea of gaining a further understanding of the mechanisms involved in the acid hydrolysis of cobalt complexes.

2. Experimental

Three methods were attempted in this research to determine the kinetic data. They were: (1) titration of the halogen ion with mercuric nitrate,\(^{30}\) (2) potentiometric titration of the halogen ion by use of a Beckman Model G pH meter with silver bromide glass electrodes, and (3) spectrophotometric measurements with a Beckman D.U. Spectrophotometer. The mercuric nitrate method was unsuccessful. Sodium nitroprusside was used as the turbidity indicator and because of the intense colors of the

---

solutions used it was extremely difficult to determine when the endpoint of the titration had been reached. It was also evident that all the mercuric nitrate was reacting with the bromide in the complex, as well as with the ionic bromide. The potentiometer method, utilizing silver bromide, glass electrodes, and silver nitrate solution as the titrating agent was not satisfactory because a sharp endpoint could not be obtained.

The spectrophotometric method was found to be most satisfactory for these studies. Basically, this method consists of following the change in optical density with time. The wave lengths chosen to study the rates of these reactions were 520, 540, and 600 m\(\mu\). These wavelengths provide the largest differences in absorption due to the reactants and the products. The concentrations of reactants used were approximately 0.002 molar in the majority of the experiments. The range of concentration amenable to study by this method, using 1 cm. cells, was found to be 0.001 to 0.004 molar.

The apparatus consisted of a constant temperature bath, which could be regulated to \(\pm 0.02^\circ\text{C.}\), a water pump, and a Beckman D.U. Spectrophotometer. During the experiments, a constant flow of water was maintained from the bath to the jacket surrounding the cell compartment of the spectrophotometer. The temperature of the cell compartment
was thermostated in this manner to ±0.1°C. The cells used were Beckman-Pyrex absorption cells. Cell correction measurements were made prior to each run.

The samples of reactant were weighed on an analytical balance and placed quantitatively in calibrated 100 ml. volumetric flasks, and distilled water was added. All solutions were prepared at the temperature at which the run was to be made. Ten ml. of a 1M salt solution, which in most cases was sodium nitrate, was added and the solution was brought to a volume of 100 ml. The sample solutions were placed in the constant temperature bath. At various time intervals aliquots of the solution were withdrawn and their optical densities were measured. The cells containing the solutions were allowed to remain in the thermostated cell compartment and the solutions were replaced every six hours. The runs usually lasted approximately seventy hours.

The extinction coefficients of the various reactants were determined by preparation of the samples as previously described and measuring, immediately upon dilution, their optical densities at 520, 540, and 600 mμ. The extinction coefficients of the products were determined by adding to the solution of the reactant an amount of 0.05 M Hg(NO₃)₂ equivalent to the number of moles of the sample used. Sufficient 1 M sodium nitrate was added
to make the final solution 0.1 M with respect to the total concentration of NaNO$_3$ plus Hg(NO$_3$)$_2$. Distilled water was added until a volume of 100 ml. of solution was obtained. The optical densities of these solutions were measured at 520, 540, and 600 m$\mu$. The optical densities of these solutions were constant over a period of twelve hours.

3. Calculations and Results

a) Calculation of Concentrations of Reactant and Product at Various Time Intervals. The concentration of substances in dilute solutions can be calculated from spectrophotometric$^{31}$ measurements by use of the Beer-Lambert law for a single species in solution is given as:

$$O.D. = \varepsilon_A C_A l$$

where $\varepsilon_A$ is the molar extinction coefficient, $C_A$ is the concentration of the species in moles/liter, $l$ is the path length of the cell, and $O.D.$ (optical density at any wave length) is equal to the log $\frac{I_0}{I}$, where $\frac{I_0}{I}$ is the ratio of the intensity of light passing through the cell containing only solvent ($I_0$) to the light passing through the cell containing sample and solvent ($I$).

If there is more than one species in solution, the

Beer-Lambert law can then be written as

\[ O.D. = \varepsilon_A C_A l + \varepsilon_B C_B l \]

where \( \varepsilon_B \) is the extinction coefficient of substance B, \( C_B \) is the concentration of B, and \( l \) is the path length of the cell. Since in these determinations the path length of the pyrex cells used were 1 cm., this equation reduces to

\[ O.D. = \varepsilon_A C_A + \varepsilon_B C_B. \]

In order to calculate the concentration of species A and B from the O.D. of a solution containing both, it is necessary to know the values of the extinction coefficients of the pure reactant and of the pure product. Henceforth, we shall refer to \( C_A \) as the concentration of reactant A and \( C_B \) as the concentration of product B. The extinction coefficients of the reactants and assumed products are given in Table III.

b) Sample Calculation of Reactant and Product. The concentrations of the reactants and products were calculated from simultaneous equations involving the O.D. at 520 m\( \mu \) and 600 m\( \mu \), and O.D. at 540 and 600 m\( \mu \).

\[ 32 \text{The optical densities of the solutions given in the tables were corrected for cell defects.} \]
### Table III

**EXTINCTION COEFFICIENTS 10^{-2} AS UTILIZED IN CALCULATIONS**

<table>
<thead>
<tr>
<th>Reactant</th>
<th>520 m(\mu)</th>
<th>540 m(\mu)</th>
<th>600 m(\mu)</th>
<th>Assumed Product^{33}</th>
<th>520 m(\mu)</th>
<th>540 m(\mu)</th>
<th>600 m(\mu)</th>
</tr>
</thead>
<tbody>
<tr>
<td>(\text{Na}[\text{Co(HY)Br}])</td>
<td>0.644</td>
<td>1.20</td>
<td>2.42</td>
<td>(\text{Na}[\text{Co(HY)Br}]) 3.02</td>
<td>3.28</td>
<td>1.38</td>
<td></td>
</tr>
<tr>
<td>Average</td>
<td>0.607</td>
<td>1.16</td>
<td>2.36</td>
<td>Average</td>
<td>3.01</td>
<td>3.26</td>
<td>1.38</td>
</tr>
<tr>
<td>(\text{Na}[\text{Co(YOH)Br}])</td>
<td>0.544</td>
<td>1.03</td>
<td>2.29</td>
<td>(\text{Na}[\text{Co(YOH)Br}]) 2.19</td>
<td>2.51</td>
<td>1.28</td>
<td></td>
</tr>
<tr>
<td>Average</td>
<td>0.519</td>
<td>1.00</td>
<td>2.29</td>
<td>Average</td>
<td>2.12</td>
<td>2.48</td>
<td>1.29</td>
</tr>
<tr>
<td>(\text{Na}[\text{Co(HY)Cl}])</td>
<td>0.690</td>
<td>1.24</td>
<td>2.25</td>
<td>(\text{Na}[\text{Co(HY)Cl}]) 2.87</td>
<td>3.11</td>
<td>1.29</td>
<td></td>
</tr>
<tr>
<td>Average</td>
<td>0.674</td>
<td>1.24</td>
<td>2.25</td>
<td>Average</td>
<td>2.88</td>
<td>3.15</td>
<td>1.30</td>
</tr>
<tr>
<td>(\text{Na}[\text{Co(YOH)Cl}])</td>
<td>1.06</td>
<td>1.55</td>
<td>1.79</td>
<td>(\text{Na}[\text{Co(YOH)Cl}]) 2.01</td>
<td>2.37</td>
<td>1.31</td>
<td></td>
</tr>
<tr>
<td>Average</td>
<td>1.08</td>
<td>1.62</td>
<td>1.79</td>
<td>Average</td>
<td>1.96</td>
<td>2.35</td>
<td>1.26</td>
</tr>
<tr>
<td>(\text{Na}[\text{Co(HY)}])</td>
<td>0.598</td>
<td>1.12</td>
<td>2.28</td>
<td>(\text{Na}[\text{Co(HY)}]) 2.78</td>
<td>3.06</td>
<td>1.28</td>
<td></td>
</tr>
<tr>
<td>Average</td>
<td>0.583</td>
<td>1.10</td>
<td>2.25</td>
<td>Average</td>
<td>2.79</td>
<td>3.06</td>
<td>1.29</td>
</tr>
<tr>
<td>(\text{Na}[\text{CoY}])</td>
<td>2.88</td>
<td>3.13</td>
<td>1.26</td>
<td>(\text{Na}[\text{CoY}]) 2.88</td>
<td>3.13</td>
<td>1.26</td>
<td></td>
</tr>
<tr>
<td>Average</td>
<td>2.80</td>
<td>3.01</td>
<td>1.23</td>
<td>Average</td>
<td>2.84</td>
<td>3.07</td>
<td>1.25</td>
</tr>
</tbody>
</table>

^{33} The products were assumed to be those of the reactions of \(\text{Hg(NO}_3\)_2\) and the complexes in solutions of composition comparable to those of the solutions subjected to kinetic study.

^{34} The extinction coefficients of all of the reactants and products were measured in 0.1 M NaNO\(_3\) except these, which were measured in 1 M HClO\(_4\).
520 m\(\mu\) and 600 m\(\mu\), and O.D. at 540 m\(\mu\) and 600 m\(\mu\).

1) \[ \text{O.D.} \, 600 = \epsilon_{A \, 600} \, C_A + \epsilon_{B \, 600} \, C_B \]

2) \[ \text{O.D.} \, 540 = \epsilon_{A \, 540} \, C_A + \epsilon_{B \, 540} \, C_B \]

Multiplying equation 1 by \(\epsilon_{B \, 540}\) and equation 2 by \(\epsilon_{B \, 600}\) yields

3) \[ (\text{O.D.} \, 600)(\epsilon_{B \, 540}) = (\epsilon_{A \, 600})(\epsilon_{B \, 540}) (C_A) + (\epsilon_{B \, 600})(\epsilon_{B \, 540}) (C_B) \]

4) \[ (\text{O.D.} \, 540)(\epsilon_{B \, 600}) = (\epsilon_{A \, 540})(\epsilon_{B \, 600}) (C_A) + (\epsilon_{B \, 540})(\epsilon_{B \, 600}) (C_B) \]

Subtracting equation 4 from equation 3 yields

5) \[ (\text{O.D.} \, 600)(\epsilon_{B \, 540}) - (\text{O.D.} \, 540)(\epsilon_{B \, 600}) = (\epsilon_{A \, 600})(\epsilon_{B \, 540}) - (\epsilon_{A \, 540})(\epsilon_{B \, 600}) \, C_A \]

Therefore,

6) \[ C_A = \frac{(\text{O.D.} \, 600)(\epsilon_{B \, 540}) - (\text{O.D.} \, 540)(\epsilon_{B \, 600})}{(\epsilon_{A \, 600})(\epsilon_{B \, 540}) - (\epsilon_{A \, 540})(\epsilon_{B \, 600})} \]

The solution of this equation for \(C_A\) then gives the concentration of reactant A at any time. The concentration
of B can be found by evaluation of C_B in either equation 3 or 4. The same method was used in calculation of concentrations using the experimental optical densities at 520 and 600 m/µ. An average value of these concentrations was used in subsequent calculations. The addition of C_A and C_B gave a check on the initial concentration of the reactant used.

c) **Determination of the Order and Rate Constants.**
The order of the initial rate of reaction was determined by the method based on the Noyes equation. The Noyes equation is as follows:

\[
n = 1 + \frac{\log t_1^h - \log t_2^h}{\log a - \log a'}
\]

where \( n \) is the order of a single reactant, \( a \) and \( a' \) are different initial concentrations of the reactant, and \( t_1^h \) and \( t_2^h \) are the half lives corresponding to the initial concentrations \( a \) and \( a' \), respectively. Solution of this equation using initial concentrations of \( 4 \times 10^{-3} \text{ M} \) and \( 1 \times 10^{-3} \text{ M} \) in sodium bromo-(ethylenediaminetetraacetato)cobaltate (III) indicated the order of the reaction, \( n \), to be 1.03.

The integrated form of the first order rate expression is:

\[
\log \frac{a}{a-x} = \frac{kt}{2303}
\]
where \( a \) is the average value of the total concentrations for a single run and \((a-x)\) is the calculated value of the reactant at any time, \( t \). It can be seen that a plot of

\[ 2.303 \log \frac{a}{(a-x)} \]

versus \( t \) should give a slope corresponding to the value of \( k \), the velocity constant. When these functions were plotted, a straight line relationship was obtained up to values amounting to between 40% and 50% of the reaction. The reasons for the change in slope of these curves will be considered in the discussion section.

In an attempt to account for the change in slope of the first order graphs, the following type of equilibrium was postulated:

\[ [\text{Co(Y)Br}]^- + \text{H}_2\text{O} \rightleftharpoons [\text{Co(Y)H}_2\text{O}] + \text{Br}^- \]

If a dissociative mechanism is operative in both forward and reverse reactions, such a process constitutes a first order – first order reversible reaction. The rate expression for such a reaction is:

\[ 2.303 \log \frac{A_0 - A_\infty}{A - A_\infty} = (k + k')t \]

where \( A_0 \) is the original concentration, \( A \) the amount of reactant remaining at a time, \( t \), and \( A_\infty \) the equilibrium concentration of the reactant. The equilibrium constant was not determined experimentally, but an approximation
was made of the ratio of the concentrations of reactant and product at equilibrium. From these values the equilibrium concentrations of A were determined in the cases of Na[Co(YOH)Br] and Na[Co(HY)Br]. The assumed equilibrium ratios of product to reactant for Na[Co(HY)Br] at 30°, 40°, and 50°C. were 2.75, 2.80, and 3.00. The equilibrium ratio for solutions of Na[Co(YOH)Br] was taken as 5.0 at 30°, 40°, and 50°C. These values were chosen so that the best straight line was obtained when a plot of \( \frac{A_0 - A_e}{A - A_e} \) versus time was made. The velocity constants obtained for a first order - first order reversible process are shown in Table IV.

d) **Determination of the Energy of Activation.** The Arrhenius activation energy can be obtained from the Arrhenius equation,

\[
k = A e^{- \frac{E_A}{RT}}
\]

where \( k \) is the velocity constant; \( E_A \), the Arrhenius activation energy; \( R \), the gas constant expressed in cal/mole °C.; and \( T \), the absolute temperature. Taking the log of this equation:

\[
\log k = \log A - \frac{E_A}{2.303 RT}
\]

Therefore, a plot of \( \log k \) against \( T^{-1} \) gives a slope equal to

\[
- \frac{E_A}{2.303 R}
\]

75
### Table IV

**CALCULATED RATE CONSTANTS**

<table>
<thead>
<tr>
<th>Compound</th>
<th>First Order (non-reversible) Reaction</th>
<th>First Order Reversible Reaction</th>
</tr>
</thead>
<tbody>
<tr>
<td></td>
<td>Run No</td>
<td>Temp. °C</td>
</tr>
<tr>
<td>$\text{Na[Co(HY)Br]}$</td>
<td>1, 2</td>
<td>30</td>
</tr>
<tr>
<td></td>
<td>3, 4</td>
<td>30</td>
</tr>
<tr>
<td></td>
<td>5, 6</td>
<td>30</td>
</tr>
<tr>
<td></td>
<td>7, 8</td>
<td>30</td>
</tr>
<tr>
<td></td>
<td>9,10</td>
<td>30</td>
</tr>
<tr>
<td></td>
<td>11,12</td>
<td>30</td>
</tr>
<tr>
<td></td>
<td>13,14</td>
<td>30</td>
</tr>
<tr>
<td></td>
<td>15,16</td>
<td>30</td>
</tr>
<tr>
<td></td>
<td>17,18</td>
<td>30</td>
</tr>
<tr>
<td></td>
<td>19,20</td>
<td>30</td>
</tr>
<tr>
<td></td>
<td>21,22</td>
<td>40</td>
</tr>
</tbody>
</table>

*Table continued*
<table>
<thead>
<tr>
<th>Compound</th>
<th>First Order (non-reversible) Reaction</th>
<th>Reversible Reaction</th>
</tr>
</thead>
<tbody>
<tr>
<td></td>
<td>Run No</td>
<td>Temp. °C</td>
</tr>
<tr>
<td>Na[Co(HY)Br]</td>
<td>23,24</td>
<td>50</td>
</tr>
<tr>
<td>Na[Co(HY)Cl]</td>
<td>25,26</td>
<td>30</td>
</tr>
<tr>
<td></td>
<td>27,28</td>
<td>40</td>
</tr>
<tr>
<td></td>
<td>29,30</td>
<td>50</td>
</tr>
<tr>
<td>Na[Co(YOH)Cl]</td>
<td>31,32</td>
<td>30</td>
</tr>
<tr>
<td></td>
<td>33,34</td>
<td>40</td>
</tr>
<tr>
<td></td>
<td>35,36</td>
<td>50</td>
</tr>
<tr>
<td>Na[Co(YOH)Br]</td>
<td>37,38</td>
<td>30</td>
</tr>
<tr>
<td></td>
<td>39,40</td>
<td>40</td>
</tr>
<tr>
<td></td>
<td>41,42</td>
<td>50</td>
</tr>
</tbody>
</table>
The values of the activation energy of the compounds measured are given in Table V.

e) Calculation of the Frequency Factor and "Thermodynamic Functions." The frequency factor, $A$, was calculated from the Arrhenius equation. The $k$ used in this calculation is a second order constant. It is first order with respect to both the solvent and the reactant. Therefore,

$$k_{2nd} = \frac{k_{first(\text{experimental})}}{[H_2O]}$$

The values calculated for the frequency factor are given in Table V.

The derived equation used in calculation of the entropies of activation is given below.

$$\Delta S^\dagger = 2.303 R \log \frac{k_r h}{k_B T} + \frac{\Delta H^\dagger}{T}$$

where $\Delta S^\dagger$ is the entropy of activation; $R$, the gas constant in cal/mole °C; $h$, Planck's constant; $k_B$, the Boltzmann constant; $T$, the absolute temperature; and $\Delta H^\dagger$, the enthalpy of activation. The enthalpy of activation was calculated from the following equation.

$$\Delta H^\dagger = E_A - RT$$

The calculated values of $\Delta S^\dagger$ are shown in Table V.
### Table V
CALCULATED VALUES OF THE FREQUENCY FACTOR, ENTROPY OF ACTIVATION, AND ENERGY OF ACTIVATION

<table>
<thead>
<tr>
<th>Compound</th>
<th>A</th>
<th>$\Delta S^\ddagger$ (cal/mole °C)</th>
<th>$E_A$ (Kcal./mole °C)</th>
</tr>
</thead>
<tbody>
<tr>
<td>Na[Co(HY)Br]</td>
<td>$2.0 \times 10^{11}$</td>
<td>-9.0</td>
<td>20.3</td>
</tr>
<tr>
<td>Na[Co(HY)Cl]</td>
<td>$3.7 \times 10^{13}$</td>
<td>-1.5</td>
<td>24.1</td>
</tr>
<tr>
<td>Na[Co(HOY)Br]</td>
<td>$1.4 \times 10^{12}$</td>
<td>-4.1</td>
<td>21.2</td>
</tr>
<tr>
<td>Na[Co(HOY)Cl]</td>
<td>$5.8 \times 10^{11}$</td>
<td>-7.5</td>
<td>21.4</td>
</tr>
</tbody>
</table>
4. **Discussion**

The rates of aquation of the cobalt (III) complexes of ethylenediaminetetraacetic acid, \([\text{Co(HY)}_x]\); and hydroxyethylethlenediaminetriacetic acid, \([\text{Co(HOY)}_x]\), where \(X = \text{chloride and bromide}\), have been measured. From the rate constants obtained, the values for the entropy of activation (\(\Delta S^\dagger\)), the frequency factor of the Arrhenius equation (A), and the energy of activation (\(E_A\)), have been calculated (Table V). The rate constants of these systems were obtained on the basis of the first order rate law. The data appear to obey this rate law up to 40\% to 50\% completion of the reaction. The order of the reaction was determined by the fractional life method (Noyes equation), and found to be unity. Since these compounds are intensely colored the maximum concentration which could be studied with one cm. pyrex cells was \(4 \times 10^{-3} \text{M}\). The lowest concentration which gave a measurable absorption was \(1 \times 10^{-3} \text{M}\). Consequently, the calculation of the order of the reaction of \(\text{Na}[\text{Co(HY)Br}]\) was based on measurements over the concentration range between \(4 \times 10^{-3} \text{M}\) and \(1 \times 10^{-3} \text{M}\).

The reactant \(\text{Na}[\text{Co(HY)Br}]\) appeared to be representative of the systems investigated. For this reason it was investigated the most thoroughly. Experiments were designed to test the effect on the rate of reaction of pH
and charge type of the supporting electrolyte. The rate of acid hydrolysis was measured in solutions having four different concentrations of hydrogen ion. These were pH = 7, 1.3, 1, and 0. The velocity constants obtained are given in Table IV. The rate of acid hydrolysis in distilled water was 0.0227 hrs.\(^{-1}\) Those in solutions 0.05, 0.1, and 1 N in perchloric acid were 0.0260, 0.0237, and 0.0297 hrs.\(^{-1}\) It appears that, in the case of the solutions which were 0.05 and 0.1 N in perchloric acid, there is a slight pH effect, which is probably within the error of measurement. However, in 1 N perchloric acid the rate constant is approximately 30% larger than that in distilled water. Therefore, in the pH range of 1-7 there appears to be little if any effect of hydrogen ion concentration. It must be noted, however, that in the case of the reactions which took place in solutions of pH equal to zero, the extinction coefficients used to give a material balance were different from those used in the calculation of concentrations at pH 1 to 7. Therefore it appears that the species in solutions of a pH of zero were not the same as the species in solution at higher pH.

The rates of reaction were measured in solutions containing 0.1 M in NaBr, NaClO\(_4\), NaNO\(_3\), and Sr(NO\(_3\))\(_2\). The rate constants obtained from reactions in these various
solutions are given in Table IV. The rate constant obtained from runs in distilled water is 0.023 hrs.\(^{-1}\). The rate constants from solutions 0.1 M in NaBr, NaClO\(_4\), NaN\(_3\), and Sr(NO\(_3\))\(_2\) were 0.023, 0.024, 0.025, and 0.030 hrs.\(^{-1}\), respectively. Therefore, there is no specific anion effect. However, the rate constant obtained from reactions in 0.1 M Sr(NO\(_3\))\(_2\) indicates that there is a small effect due to ionic strength.

In the introduction to this section, three possible mechanisms of reaction were discussed. These were intramolecular nucleophilic substitution, unimolecular dissociation, and a bimolecular process involving the solvent. Since the only mechanism postulated, which involves a pH dependence, is the intramolecular nucleophilic substitution reaction, this particular mechanism may be eliminated from further consideration. There remain two possibilities which might be used to explain the mechanism of these reactions. As has been mentioned earlier in reference to investigations on the acidopentammines, the unimolecular dissociation process has been favored by others. It appears that the data obtained here on the acid hydrolysis of the cobalt complexes of ethylenediaminetetraacetic acid and hydrolyethylaidiaminetriacetic acid are consistent with these other results.

It has been postulated that with compounds, such
as [Co(NH$_3$)$_5$X]$^{2+}$, which contain acidic hydrogens, the observed acceleration of the rate of reaction in basic solutions involves a dissociative mechanism (S.N.1 C.B.). This mechanism was discussed in the Introduction. Therefore, if the dissociative mechanism (S.N.1 C.B.) is unique for these reactions, and since the compounds [Co(HY)X]$^-$ and [Co(YOH)X]$^-$ contain no acidic hydrogens, there should be no effect of hydroxide ion concentrations on their rates. Although the rates of base hydrolysis of these compounds were not measured quantitatively, several qualitative observations were made. It appeared that in solutions above a pH of 8, a rapid acceleration, dependent on hydroxyl ion concentration, occurred. This cannot be explained on the basis of an S.N.1 C.B. mechanism. However, further investigation of these systems in solution above pH of 8 must be performed in order to confirm these results and to specify the order of hydroxide in these processes.

When the data obtained for the acid hydrolysis of [Co(HY)X]$^-$ and [Co(YOH)X]$^-$ were treated according to the first order rate law, a decrease in the rate constant was observed at long times. Two possible explanations of this behavior have been considered. An equilibrium reaction of the following type was assumed.
$\text{H}_2\text{O} + [\text{Co(HY)Br}]^- \rightleftharpoons [\text{Co(HY)H}_2\text{O}] + \text{Br}^-$

Since the equilibrium constants of this reaction could not be measured directly, an assumption was made involving the ratio of the product to the reactant at equilibrium. The ratios assumed were those which satisfied the first-order first-order reversible rate law. Such a treatment assumed unimolecular dissociation as the rate determining step in both the forward and reverse reactions. If an excess of bromide ion is added to the solution, the equilibrium should shift to the left. In a solution containing a fifty-fold excess of bromide ion, calculations using the assumed equilibrium constant indicate that the reaction should proceed to less than 5% completion. Table IV shows the effect of the addition of approximately a fifty-fold excess of bromide ion to the reaction. The results obtained show that the reaction goes to about 80% completion and that the rate constant obtained is the same as those obtained in 0.1 M NaNO₃ (Table IV) and 0.1 M NaClO (Table IV). Therefore, the postulation of an equilibrium process as the source of the curvature observed in first-order graphs seems to be invalid in this case.

Another possibility which might be responsible for the decrease in rate at longer times is the existence of
geometrical isomers. The following three isomers may be present.

In the case of isomer 2, there is distortion of the nitrogen-carbon bond angles, so that there is a strong possibility that it would not exist. However, in any event, it has been shown by previous investigations on cis and trans compounds of the diacido-bis(ethylenediamine)-cobalt (III) complexes that, in aqueous solution, the trans complex reacts faster than the cis complex. It is then possible that in solution there are two geometrical isomers which are reacting at different rates. The initial rate could then be concerned mainly with the faster reacting isomer with the rate of the other isomer predominating at longer times.
The rates of reaction of the bromo- and chloro-
(ethylenediaminetetraacetato)cobaltate (III) complexes
and the bromo- and chloro-(hydrolyethylethlenediamine-
triacetato)cobaltate (III) complexes are given in Table
IV. It can be seen that in both cases the bromo-com-
plexes react more rapidly than the chloro-complexes.
This is in agreement with the rates of the bromo- and
chloro-pentamminecobalt (III) complexes. However, an
adequate explanation for the more rapid hydrolysis of the
bromo-complexes has not yet been given.

The bromo- and chloro-complexes of ethylenediamine-
tetraacetic acid with cobalt (III) react more slowly than
the corresponding complexes with hydroxyethylethylene-
diaminetriacetic acid. This is in agreement with the ease
of preparation of the $H_4Y$ complexes in comparison to the
$H_3YOH$ complexes.
PART II

INFRARED SPECTRAL STUDIES ON THE cis AND trans
ISOMERS OF DIACIDO-BIS(ETHYLENEDIAMINE)-
COBALT (III) COMPLEXES

A. Introduction

Several methods\textsuperscript{35} have been applied with varying
degrees of success to the problem of differentiating be­
tween the cis and trans isomers of hexacovalent cobalt (III)

\textsuperscript{35}Basolo, F., Chem. Reviews, 52, 459 (1953).

complexes. Chemical approaches to the solution of this
problem have been attempted, but in general proof of struc­
ture on this basis alone is open to question. However, the
\textit{cis} isomers of compounds of the type $[\text{M(AA)}_2a_2^2]$, $[\text{M(AA)}_2ab]$, and
$[\text{M(AA)}_a_2b_2^2]$, where AA represents a bidentate ligand,
which can be resolved into their optically active antipodes,
give a definite proof of the structure. X-ray diffraction
and ultraviolet and visible absorption spectra have also
been used. Another method which might be applicable for the
determination of \textit{cis} and \textit{trans} configurations is infrared
absorption spectra.
Faust and Quagliano\textsuperscript{21} first applied infrared spectral measurements to cis and trans-diacidotetraamminecobalt (III) complexes. These investigators studied the spectra of cis and trans-dinitrotetraamminecobalt (III) ion, \([\text{Co(NH}_3\text{)}_4(\text{NO}_2\text{)}_2]^+\). The vibrations associated with the coordinated NH\(_3\) and NO\(_2\) GROUPS were assigned on the basis of the spectra of hexamminecobalt (III), \([\text{Co(NH}_3\text{)}_6]^3+\), and hexanitrocobaltate (III), \([\text{Co(NO}_2\text{)}_6]^3-\). The assignments are reported in Table VI.

<table>
<thead>
<tr>
<th>(\text{NH}_3)</th>
<th>(\text{NO}_2^-)</th>
</tr>
</thead>
<tbody>
<tr>
<td>3200 cm.(^{-1})</td>
<td>1400 cm.(^{-1})</td>
</tr>
<tr>
<td>1600 cm.(^{-1})</td>
<td>1340 cm.(^{-1})</td>
</tr>
<tr>
<td>1350 cm.(^{-1})</td>
<td>830 cm.(^{-1})</td>
</tr>
<tr>
<td>850 cm.(^{-1})</td>
<td></td>
</tr>
</tbody>
</table>

The two absorption bands in the 3200 cm.\(^{-1}\) region correspond to the NH\(_2\) stretching vibration, the absorption band at 1600 cm.\(^{-1}\) to the asymmetric deformation frequency, the band at 1350 cm.\(^{-1}\) to the symmetric deformation \(.\)
frequency, and the absorption band at 850 cm.\(^{-1}\) to the NH\(_2\) rocking frequency. These assignments have been discussed in later publications by a number of other investigators.\(^{36}\)\(^{\text{37}}\)\(^{\text{38}}\)\(^{\text{39}}\)


The infrared spectra of the cis and trans isomers studied by Faust and Quagliano were found to differ only as a consequence of the splitting of some of the low frequency bands in the case of the cis isomer. This splitting may be rationalized on the basis of the lower symmetry of the cis isomer.

Infrared spectral measurements\(^{22}\) have also been reported on the cis and trans isomers of diacido-bis(ethyl-enediamine)cobalt (III) compounds. In the case of the dinitro- and dichloro-compounds, complexities were encountered. The band at approximately 1600 cm.\(^{-1}\), which is
assigned to the asymmetric deformation mode of the NH$_2$ group, is split in the case of the cis isomer, while the trans isomer exhibits only a single band in this region.

The presence of the ethylene links in the ethylenediamine introduces a number of additional absorption bands which complicate the assignment of the too low frequency absorptions of the NH$_2$ group. The assignment of absorption bands associated with the ethylene group may be accomplished by making use of the work of Mizushima and Sweeney.$^{40, 41}$


These investigators have pointed out the fact that the ethylene group may exist in trans, gauche, or cis forms (Fig. 21). They have also shown that the trans form cannot exist in coordination compounds and that the gauche form is encountered. The bands expected of a cis form were not observed in the spectra of complex compounds containing bidentate ligands of the type X-CH$_2$-CH$_2$-X.

In the work reported here, the infrared spectra were obtained on the salts of cis and trans-dinitro-bis-(ethylenediamine)cobalt (III) and dichloro-bis(ethylene-
Figure 21. Stable Forms of $X-\text{CH}_2-\text{CH}_2-X$ as Viewed Along the C-C Axis

The assignments of bands due to the NH$_2$ groups were made unambiguous by deuteration.
B. Experimental

Preparation of Tris-(ethylenediamine)cobalt (III) Chloride.\(^{42}\) This compound was prepared by the method of J. B. Work, "Inorganic Synthesis," II, pp. 221-22 (1946).

Work. Anal. Calc'd. for \[\text{Co}(C_2H_8N_2)_3\]Cl\(_3\): C, 20.85; H, 7.00; N, 24.32. Found: C, 20.57; H, 7.06; N, 24.35.

Preparation of cis and trans-Dichloro-bis(ethylenediamine)cobalt (III) Chloride. These compounds were prepared by the method of Bailar.\(^{43}\) Anal. Calc'd. for (cis and trans)-\[\text{Co}(C_2H_8N_2)\text{Cl}_2\]Cl: C, 16.83; H, 5.65; N, 19.62. Found for trans-\[\text{Co}(C_2H_8N_2)_2\text{Cl}_2\]Cl: C, 16.72; H, 5.59; N, 19.47. Found for cis-\[\text{Co}(C_2H_8N_2)_2\text{Cl}_2\]Cl: C, 16.89, H, 5.57; N, 19.63.

Preparation of cis and trans-Dinitro-bis(ethylenediamine)cobalt (III) Nitrate. These compounds were prepared by the method of Holtzclaw, Sheetz, and
McCarthy. Anal. Calc'd. for (trans and cis)-
\[ \text{[Co(C}_2\text{H}_8\text{N}_2)_2\text{NO}_2)_2\text{]}\text{NO}_3 : \ C, 14.42; H, 4.84; N, 29.43.

\text{Found for trans-[Co(C}_2\text{H}_8\text{N}_2)_2\text{(NO}_2)_2\text{]}\text{NO}_3 : \ C, 14.47; H, 4.64; N, 29.58. \text{Found for cis-[Co(C}_2\text{H}_8\text{N}_2)_2\text{(NO}_2)_2\text{]}\text{NO}_3 : \ C, 14.39; H, 4.63; N, 29.52.

\text{Preparation of cis-Dinitro-bis(ethylenediamine)-cobalt (III) Nitrite. This compound was prepared by the method of Holtzelaw, Sheets, and McCarthy. Anal. Calc'd. for cis-[Co(C}_2\text{H}_8\text{N}_2)_2\text{(NO}_2)_2\text{]}\text{NO}_3 : \ C, 15.15; H, 5.08; N, 30.92. Found: C, 15.35; H, 5.27; N, 30.92.}

\text{Preparation of trans-Dinitro-bis(ethylenediamine)-cobalt (III) Nitrite. This compound was prepared by the method of Holtzelaw, Sheets, and McCarty. Forty-eight grams of a 10% ethylenediamine solution is added to twenty grams of potassium hexanitrocobaltate (III). The mixture is stirred constantly while it is heated slowly on a steam bath to about 70°, whereupon the reaction occurs, as evidenced by the dissolving of the yellow hexanitrocobaltate to form a dark brown solution. While it is still hot, the reaction mixture is filtered to remove...}
any traces of unreacted hexanitrocobaltate, and the filtrate is cooled in an ice-salt bath to precipitate the brown cis-dinitro-bis(ethylenediamine)cobalt (III) nitrite. The crystals are isolated by filtration.

The cis compound is converted to the trans by dissolving the cis-dinitro-bis(ethylenediamine)cobalt (III) nitrite in a minimum amount of boiling water and heating the solution for thirty minutes. The solution is cooled, filtered, and the filtrate is again heated for thirty minutes. This procedure is carried out three more times. After the final heating, the solution is filtered and the product obtained. Anal. Calc'd. for trans-
\[ \text{Co}(\text{C}_2\text{H}_8\text{N}_2)(\text{N}_2\text{O}_2)_2\text{N}_2 \text{O}_2 : C, 15.15; H, 5.08; N, 30.92. \]
Found:
\[ C, 15.82; H, 4.99; N, 31.11. \]

Preparation of cis-Dinitro-bis(ethylenediamine)cobalt (III) Chloride. This product was prepared by a modification of the method of Holtzelaw, Sheetz, and McCarty.

A mixture of 6.85 grams of 70% ethylenediamine and ten ml. of water is partially neutralized by the addition of 4 ml. of concentrated hydrochloric acid. The resulting solution is added to a solution of 9.52 grams of cobalt (II) chloride 6-hydrate and 6.0 grams of sodium nitrite in 10 ml. of water. A vigorous stream of air is
drawn through the solution. The yellow cis-dinitro-bis-(ethylenediamine)cobalt (III) chloride begins to precipitate in a few minutes and the reaction is allowed to proceed for one hour. The mixture is cooled in an ice-salt bath and filtered. The product is recrystallized from hot water and dried in the air. Anal. Calc'd. for cis-

\[
\text{[Co} (\text{C}_2\text{H}_8\text{N}_2)_2(\text{NO}_2)_2] \text{Cl: C, 15.67; H, 5.26; N, 27.41. Found: C, 15.80; H, 5.15; N, 27.28.}
\]

Ultraviolet spectra. In order to establish the geometrical configurations of the compounds containing the \([\text{Co(en)}_2(\text{NO}_2)_2]^+\) cation, their ultraviolet spectra were obtained by use of a Cary Model 10 Recording Spectrophotometer. Distilled water was used as the solvent. The wave lengths of maximum absorption of the cis and trans-

\[
\text{[Co(en)}_2(\text{NO}_2)_2] ^+\] compounds agreed quite well with those reported by Basolo.\(^{45}\)

Table VII
ULTRAVIOLET SPECTRA OF cis AND trans-\textgreek{Co}(en)_2(NO_2)_2^{4\textgreek{Co}}

<table>
<thead>
<tr>
<th>Compound</th>
<th>Solvent</th>
<th>( \lambda , \text{max.} )</th>
</tr>
</thead>
<tbody>
<tr>
<td>cis-\textgreek{Co}(en)_2(NO_2)_2\textgreek{N}_3^{45}</td>
<td>H_2O-MeOH</td>
<td>240 325 438</td>
</tr>
<tr>
<td>trans-\textgreek{Co}(en)_2(NO_2)_2\textgreek{N}_3^{45}</td>
<td>H_2O-MeOH</td>
<td>250 347 433</td>
</tr>
<tr>
<td>cis-\textgreek{Co}(en)_2(NO_2)_2\textgreek{N}_3</td>
<td>H_2O</td>
<td>239 325 437</td>
</tr>
<tr>
<td>trans-\textgreek{Co}(en)_2(NO_2)_2\textgreek{N}_3</td>
<td>H_2O</td>
<td>250 347 435</td>
</tr>
<tr>
<td>cis-\textgreek{Co}(en)_2(NO_2)_2\textgreek{N}_2</td>
<td>H_2O</td>
<td>238 325 437</td>
</tr>
<tr>
<td>trans-\textgreek{Co}(en)_2(NO_2)_2\textgreek{N}_2</td>
<td>H_2O</td>
<td>250 344 436</td>
</tr>
<tr>
<td>cis-\textgreek{Co}(en)_2(NO_2)_2\textgreek{Cl}</td>
<td>H_2O</td>
<td>240 325 437</td>
</tr>
</tbody>
</table>
**Deuteration and infrared spectral measurements.** The samples were deuterated by addition of 2 ml. of 99.5% deuterium oxide to about 10 milligrams of sample contained in a small plastic stoppered bottle. The bottle was shaken vigorously to dissolve the sample and the solution was allowed to stand overnight. The deuterated sample was isolated by distillation of the deuterium oxide. The infrared spectra of the original and deuterated samples were obtained by use of solid potassium bromide disks. The measurements were made on a Perkin-Elmer Model 21 Recording Spectrophotometer.
C. Results and Discussion

The NH$_2$ stretching frequencies, the asymmetric and symmetric deformation frequencies, and the rocking frequencies of the dichloro-bis(ethylenediamine)cobalt (III) and dinitro-bis(ethylenediamine)cobalt (III) complexes are listed in Table VIII. The NH$_2$ stretching frequencies are in the 3200 cm.$^{-1}$ range. This region includes both the symmetric and asymmetric modes. The asymmetric deformation vibration occurs at 1600 cm.$^{-1}$, the symmetric deformation at 1350 cm.$^{-1}$, and the NH$_2$ rocking vibration is at 800 cm.$^{-1}$ The infrared spectral measurements were carried out in order to determine the feasibility of a differentiation between the cis and trans isomers. A major difference in the spectra of the cis and trans isomers was observed in the NH$_2$ asymmetric deformation frequencies. In the case of the cis isomer, a splitting of this band was observed. An examination of the spectrum of trans-dichloro-bis(ethylenediamine)cobalt (III) (Figure 28, Table VIII) reveals a strong symmetric band occurring at 1596 cm.$^{-1}$ In contrast, the cis-dichloro-bis(ethylenediamine)cobalt (III) complex (Figure 29, Table VIII) exhibits a strong band at 1561 cm.$^{-1}$ and a moderate band at 1630 cm.$^{-1}$ Deuteration confirms the assignment of both bands to the asymmetric deformation mode.
## Table VIII

**INFRARED SPECTRA OF cis AND trans-DIACIDO-BIS (ETHYLENEDIAMINE)COBALT (III) COMPLEXES**

<table>
<thead>
<tr>
<th>Compound</th>
<th>NH₂Str</th>
<th>NH₂Def(a)</th>
<th>NH₂Def(S)</th>
<th>NH₂Rock</th>
<th>NO₂</th>
<th>NO₂</th>
<th>NO₂</th>
</tr>
</thead>
<tbody>
<tr>
<td>([\text{Co(en)}_3]) Cl₃</td>
<td>3172</td>
<td>1575(S)</td>
<td>1366</td>
<td>810(sh)</td>
<td>-</td>
<td>-</td>
<td>-</td>
</tr>
<tr>
<td></td>
<td>3086</td>
<td>1529(sh)</td>
<td></td>
<td>735(W)</td>
<td></td>
<td></td>
<td></td>
</tr>
<tr>
<td>cis-([\text{Co(en)}_2(NO₂)_2]) Cl</td>
<td>3227</td>
<td>1615(M)</td>
<td>1364</td>
<td>797</td>
<td>1412</td>
<td>1341</td>
<td>831</td>
</tr>
<tr>
<td></td>
<td>3138</td>
<td>1598(M)</td>
<td></td>
<td>742</td>
<td></td>
<td></td>
<td></td>
</tr>
<tr>
<td></td>
<td>3051</td>
<td>1566(S)</td>
<td></td>
<td>718</td>
<td></td>
<td></td>
<td></td>
</tr>
<tr>
<td>trans-([\text{Co(en)}_2(NO₂)_2]) NO₂</td>
<td>3245</td>
<td>1633(vW)</td>
<td>1358</td>
<td>800</td>
<td>1407(S)</td>
<td>1328</td>
<td>827</td>
</tr>
<tr>
<td></td>
<td>3227</td>
<td></td>
<td></td>
<td>778</td>
<td></td>
<td></td>
<td></td>
</tr>
<tr>
<td></td>
<td>3100</td>
<td>1617</td>
<td></td>
<td>740</td>
<td></td>
<td></td>
<td></td>
</tr>
<tr>
<td></td>
<td>1606</td>
<td></td>
<td></td>
<td></td>
<td></td>
<td></td>
<td></td>
</tr>
<tr>
<td>cis-([\text{Co(en)}_2(NO₂)_2]) NO₂</td>
<td>3204</td>
<td>1581(S)</td>
<td>1358</td>
<td>809</td>
<td>1410</td>
<td>1340</td>
<td>828</td>
</tr>
<tr>
<td></td>
<td>3171</td>
<td>1571(sh)</td>
<td></td>
<td>796</td>
<td>1394(sh)</td>
<td>1340</td>
<td>817</td>
</tr>
<tr>
<td></td>
<td>3030</td>
<td>1553(M)</td>
<td></td>
<td>774</td>
<td></td>
<td></td>
<td></td>
</tr>
<tr>
<td></td>
<td></td>
<td></td>
<td></td>
<td></td>
<td>1381(sh)</td>
<td></td>
<td></td>
</tr>
<tr>
<td>trans-([\text{Co(en)}_2(NO₂)_2]) NO₃</td>
<td>3272</td>
<td>1610(S)</td>
<td>1360</td>
<td>802</td>
<td>1428</td>
<td>1346</td>
<td>827</td>
</tr>
<tr>
<td></td>
<td>3103</td>
<td></td>
<td></td>
<td>774</td>
<td></td>
<td></td>
<td></td>
</tr>
<tr>
<td></td>
<td></td>
<td></td>
<td></td>
<td></td>
<td>1381(sh)</td>
<td></td>
<td></td>
</tr>
<tr>
<td>cis-([\text{Co(en)}_2(NO₂)_2]) NO₃</td>
<td>3272</td>
<td>1617(W)</td>
<td>obscured</td>
<td>800</td>
<td>1428</td>
<td>1345</td>
<td>827</td>
</tr>
<tr>
<td></td>
<td>3239</td>
<td>1575(S)</td>
<td></td>
<td>714</td>
<td></td>
<td></td>
<td></td>
</tr>
<tr>
<td></td>
<td>3138</td>
<td></td>
<td></td>
<td>708</td>
<td></td>
<td></td>
<td></td>
</tr>
<tr>
<td>trans-([\text{Co(en)}_2Cl₂]) Cl</td>
<td>3237</td>
<td>1596(S)</td>
<td>1386</td>
<td>805</td>
<td>-</td>
<td>-</td>
<td>-</td>
</tr>
<tr>
<td></td>
<td>3182</td>
<td></td>
<td></td>
<td>733</td>
<td></td>
<td></td>
<td></td>
</tr>
<tr>
<td></td>
<td>3061</td>
<td></td>
<td></td>
<td></td>
<td></td>
<td></td>
<td></td>
</tr>
<tr>
<td>cis-([\text{Co(en)}_2Cl₂]) Cl</td>
<td>3195</td>
<td>1630(M)</td>
<td>1366</td>
<td>785</td>
<td>-</td>
<td>-</td>
<td>-</td>
</tr>
<tr>
<td></td>
<td>3109</td>
<td>1561(S)</td>
<td></td>
<td>768</td>
<td></td>
<td></td>
<td></td>
</tr>
<tr>
<td></td>
<td></td>
<td></td>
<td></td>
<td></td>
<td></td>
<td></td>
<td></td>
</tr>
</tbody>
</table>
Upon deuteration, these bands are shifted to lower frequencies, thus indicating that they are associated with NH$_2$. The vibrational modes of the NH$_2$ groups in this region have been previously assigned to the asymmetric deformation modes.

The cis and trans-dinitro-bis(ethylenediamine)cobalt (III) complexes were also investigated. These bands were assigned to the nitro-groups.$^{12, 21}$ These were observed at approximately 1400 cm.$^{-1}$, 1340 cm.$^{-1}$, and 830 cm.$^{-1}$ in the five salts of this type which were studied. A splitting of the band in the 830 cm.$^{-1}$ region occurred in both the cis and trans-dinitro compounds. The absorption peaks occurred at 828 and 817 cm.$^{-1}$ In the case of the complexes which contained nitrate as the anion a strong peak was observed at 1376 cm.$^{-1}$, which was assigned to the nitrate ion.

Investigation of the NH$_2$ asymmetric deformation frequencies of the cis- and trans-dinitro complexes again revealed a splitting of this band in the case of the cis isomer. The trans-dinitro complex containing nitrate as the anion (Table VIII, Figure 26) showed a strong fairly symmetrical band at 1610 cm.$^{-1}$ However, as had been observed previously in the case of the cis-dichloro compound, the cis-dinitro complex (Table VIII, Figure 27) gave two peaks in this region, a strong band which occurred at
1575 cm$^{-1}$ and a weaker one at 1617 cm$^{-1}$. The chloride salt of the cis-dinitro complex gave three absorption bands in this region. These involved a strong band at 1566 cm$^{-1}$ and bands at 1615 cm$^{-1}$ and 1598 cm$^{-1}$, both of moderate intensity.

The nitrite salt of the trans-dinitro complex (Figure 24, Table VIII) however, exhibited three absorption bands in the 1600 cm$^{-1}$ region. The two strongest bands were at 1617 and 1606 cm$^{-1}$. The other band which was extremely weak, occurred at 1633 cm$^{-1}$. The band containing these peaks was, however, symmetrical. It should be noticed that in this case the strongest absorption peak is observed at 1606 cm$^{-1}$. This is 30 cm$^{-1}$ higher than any of the strong absorption bands of the cis compounds. The nitrite salt of the cis-dinitro complex (Table VIII, Figure 25) gave three bands in the 1600 cm$^{-1}$ region. The strongest band was found at 1581 cm$^{-1}$ and the others at 1571 and 1553 cm$^{-1}$. In general, examination of the spectra reveals a more distinct and a greater splitting of the asymmetric deformation modes of the NH$_2$ groups in cis isomers than is observed in the corresponding trans isomers.

Mizushima and co-workers$^{28}$ have proposed that a bidentate ligand of the type X-CH$_2$-CH$_2$-X exists in the gauche form when it is complexed. The calculated hydrogen deformation frequencies of the gauche form of NCS-CH$_2$-CH$_2$-SCN are given in Table X. These values have been used in making
assignments of the absorption peaks observed for the ethylene groups. Due to the multiplicity of the peaks observed in the spectra of the diacido-bis(ethylenediamine)cobalt (III) complexes, which could be assigned to carbon-hydrogen vibrations, the observed peaks have been categorized and assigned by region. These assignments are listed in Table IX. The absorption bands assigned fall into the general regions which are expected for the gauche form of the ethylene group. Furthermore, the low frequency rocking vibration expected of a cis-ethylene group at 740 cm$^{-1}$ is not observed. No correlation was observed between the splittings of these absorption bands and the isomeric nature of the complex ion.
<table>
<thead>
<tr>
<th>Compound</th>
<th>C-N</th>
<th>CH₂str</th>
<th>CH₂bend</th>
<th>CH₂wag</th>
<th>CH₂twist</th>
<th>CH₂rock</th>
</tr>
</thead>
<tbody>
<tr>
<td>cis-([\text{Co(en)}_2(\text{NO}_2)_2])\text{Cl}</td>
<td>1058</td>
<td>2967</td>
<td>1460</td>
<td>1307</td>
<td>1182</td>
<td>899</td>
</tr>
<tr>
<td></td>
<td></td>
<td>2908</td>
<td></td>
<td>1276</td>
<td>1171</td>
<td>890</td>
</tr>
<tr>
<td></td>
<td></td>
<td></td>
<td></td>
<td>1211</td>
<td>1131</td>
<td>883</td>
</tr>
<tr>
<td></td>
<td></td>
<td></td>
<td></td>
<td>1058</td>
<td>873</td>
<td></td>
</tr>
<tr>
<td>([\text{Co(en)}_3])\text{Cl}_3</td>
<td>1064</td>
<td>2982</td>
<td>1465</td>
<td>1331</td>
<td>1169</td>
<td>906</td>
</tr>
<tr>
<td></td>
<td></td>
<td>2895</td>
<td></td>
<td>1268</td>
<td>1157</td>
<td>895</td>
</tr>
<tr>
<td></td>
<td></td>
<td></td>
<td></td>
<td>1253</td>
<td>1110</td>
<td>890</td>
</tr>
<tr>
<td></td>
<td></td>
<td></td>
<td></td>
<td></td>
<td>1024</td>
<td></td>
</tr>
<tr>
<td>cis-([\text{Co(en)}_2(\text{NO}_2)_2])\text{NO}_2</td>
<td>1047</td>
<td>2942</td>
<td>1451</td>
<td>1337</td>
<td>1159</td>
<td>890</td>
</tr>
<tr>
<td></td>
<td></td>
<td>2878</td>
<td></td>
<td>1266</td>
<td>1129</td>
<td>870</td>
</tr>
<tr>
<td></td>
<td></td>
<td></td>
<td></td>
<td>1236</td>
<td>1098</td>
<td></td>
</tr>
<tr>
<td></td>
<td></td>
<td></td>
<td></td>
<td></td>
<td>1007</td>
<td></td>
</tr>
<tr>
<td>trans-([\text{Co(en)}_2(\text{NO}_2)_2])\text{NO}_2</td>
<td>1058</td>
<td>2953</td>
<td>1453</td>
<td>1270</td>
<td>1124</td>
<td>883</td>
</tr>
<tr>
<td></td>
<td></td>
<td>2932</td>
<td></td>
<td>1215</td>
<td>1107</td>
<td></td>
</tr>
<tr>
<td></td>
<td></td>
<td>2900</td>
<td></td>
<td></td>
<td>1000(M)</td>
<td></td>
</tr>
<tr>
<td>trans-([\text{Co(en)}_2(\text{NO}_2)_2])\text{NO}_3</td>
<td>1053</td>
<td>2992</td>
<td>1472</td>
<td>1220</td>
<td>1121</td>
<td>891</td>
</tr>
<tr>
<td></td>
<td></td>
<td>2935</td>
<td></td>
<td>1330</td>
<td>1109</td>
<td></td>
</tr>
<tr>
<td></td>
<td></td>
<td></td>
<td></td>
<td>1284</td>
<td>1002</td>
<td></td>
</tr>
<tr>
<td></td>
<td></td>
<td></td>
<td></td>
<td>1281</td>
<td></td>
<td></td>
</tr>
</tbody>
</table>

Table continued
<table>
<thead>
<tr>
<th>Compound</th>
<th>C-N (cm⁻¹)</th>
<th>CH₂str (cm⁻¹)</th>
<th>CH₂bend (cm⁻¹)</th>
<th>CH₂wag (cm⁻¹)</th>
<th>CH₂twist (cm⁻¹)</th>
<th>CH₂rock (cm⁻¹)</th>
</tr>
</thead>
<tbody>
<tr>
<td>cis-[Co(en)₂(NO₂)₂]NO₃</td>
<td>1060</td>
<td>2970</td>
<td>1469</td>
<td>1314</td>
<td>1159</td>
<td>1143</td>
</tr>
<tr>
<td></td>
<td></td>
<td>2915</td>
<td></td>
<td>1294</td>
<td>1125</td>
<td>894</td>
</tr>
<tr>
<td></td>
<td></td>
<td></td>
<td></td>
<td></td>
<td>1107</td>
<td>888</td>
</tr>
<tr>
<td></td>
<td></td>
<td></td>
<td></td>
<td></td>
<td>1047</td>
<td>875</td>
</tr>
<tr>
<td>trans-[Co(en)₂Cl₂]Cl</td>
<td>1049</td>
<td>2943</td>
<td>1446</td>
<td>1308</td>
<td>1120</td>
<td>1107</td>
</tr>
<tr>
<td></td>
<td></td>
<td></td>
<td></td>
<td>1292</td>
<td>1091</td>
<td>1047</td>
</tr>
<tr>
<td></td>
<td></td>
<td></td>
<td></td>
<td>1273</td>
<td>1002</td>
<td>869</td>
</tr>
<tr>
<td></td>
<td></td>
<td></td>
<td></td>
<td>1208</td>
<td></td>
<td></td>
</tr>
<tr>
<td>cis-[Co(en)₂Cl₂]Cl</td>
<td>1055</td>
<td>2936</td>
<td>1446</td>
<td>1318</td>
<td>1158</td>
<td>1126</td>
</tr>
<tr>
<td></td>
<td></td>
<td></td>
<td></td>
<td>1277</td>
<td>1126</td>
<td>896</td>
</tr>
<tr>
<td></td>
<td></td>
<td></td>
<td></td>
<td>1269</td>
<td>1113</td>
<td>873</td>
</tr>
<tr>
<td></td>
<td></td>
<td></td>
<td></td>
<td>1206</td>
<td></td>
<td></td>
</tr>
<tr>
<td></td>
<td></td>
<td></td>
<td></td>
<td>1193</td>
<td></td>
<td></td>
</tr>
</tbody>
</table>
Table X

COMPUTED VALUES OF HYDROGEN DEFORMATION FREQUENCIES
FOR THE GAUCHE FORM

<table>
<thead>
<tr>
<th>CH2 - bending</th>
<th>1455</th>
</tr>
</thead>
<tbody>
<tr>
<td>CH3 - wagging</td>
<td>1201</td>
</tr>
<tr>
<td></td>
<td>1332</td>
</tr>
<tr>
<td>CH2 - twisting</td>
<td>1103</td>
</tr>
<tr>
<td></td>
<td>1100</td>
</tr>
<tr>
<td>CH2 - rocking</td>
<td>911</td>
</tr>
<tr>
<td></td>
<td>858</td>
</tr>
</tbody>
</table>
Figure 22. Infrared Spectra of \([\text{Co(en)}_2]^3\text{Cl}_3\) and Deuterated-\([\text{Co(en)}_2]^3\text{Cl}_3\)

Figure 23. Infrared Spectra of \([\text{cis-}[\text{Co(en)}_2(\text{NO}_2)_2]^2\text{Cl}\) and Deuterated \([\text{cis-}[\text{Co(en)}_2(\text{NO}_2)_2]^2\text{Cl}\)

Figure 24. Infrared Spectra of \([\text{trans-}[\text{Co(en)}_2(\text{NO}_2)_2]^2\text{Cl}\) NO_2 and Deuterated \([\text{trans-}[\text{Co(en)}_2(\text{NO}_2)_2]^2\text{Cl}\) NO_2

Figure 25. Infrared Spectra of \([\text{cis-}[\text{Co(en)}_2(\text{NO}_2)_2]^2\text{Cl}\) NO_2 and Deuterated \([\text{cis-}[\text{Co(en)}_2(\text{NO}_2)_2]^2\text{Cl}\) NO_2

Figure 26. Infrared Spectra of \([\text{trans-}[\text{Co(en)}_2(\text{NO}_2)_2]^2\text{Cl}\) NO_3 and Deuterated \([\text{trans-}[\text{Co(en)}_2(\text{NO}_2)_2]^2\text{Cl}\) NO_3

Figure 27. Infrared Spectra of \([\text{cis-}[\text{Co(en)}_2(\text{NO}_2)_2]^2\text{Cl}\) NO_3 and Deuterated \([\text{cis-}[\text{Co(en)}_2(\text{NO}_2)_2]^2\text{Cl}\) NO_3

Figure 28. Infrared Spectrum of \([\text{trans-}[\text{Co(en)}_2\text{Cl}_2]^2\text{Cl}\)

Figure 29. Infrared Spectra of \([\text{cis-}[\text{Co(en)}_2\text{Cl}_2]^2\text{Cl}\) and Deuterated \([\text{cis-}[\text{Co(en)}_2\text{Cl}_2]^2\text{Cl}\)
Figure 24

Infrared spectra
- trans-[Co(en)_2(NCMe)_2]NO_2
- Deuterated trans-[Co(en)_2(NCMe)_2]NO_2

Transmittance % transmission vs. wave numbers (cm\(^{-1}\))
Figure 26

Infrared spectra

- trans - [Co(en)$_2$(NO$_2$)$_2$]NO$_3$
- Deuterated trans - [Co(en)$_2$(NO$_2$)$_2$]NO$_3$

Wave numbers (cm$^{-1}$)

Transmittance (% transmission)

0 20 40 60 80 100

4000 5000 6000 7000 8000 9000 10000
Transmittance (Transmission)

Infrared Spectra

cis-[Co(en)₂(NO₂)₂]NO₃
Deuterated-cis-[Co(en)₂(NO₂)₂]NO₃

Wave numbers (cm⁻¹)

Figure 27
Figure 28

Infrared spectra
trans-[Co(en)₂Cl₂]Cl
Infrared spectra of cis-[Co(en)$_2$Cl$_2$]Cl and deuterated cis-[Co(en)$_2$Cl$_2$]Cl.
APPENDIX

Figures 30-60, inclusive

Tables XI to LXXVI, inclusive
Figure 30. Rate of Acid Hydrolysis of NaCo(HY)Br in 0.1 M NaClO₄ at 30°C
0.1 M NaClO$_4$
$T = 30^\circ$C.

- Run 1
  $a = 1.997 \cdot 10^{-3}$ m/l NaCoYBr

- Run 2
  $a = 2.044 \cdot 10^{-3}$ m/l NaCoYBr
Figure 31. Rate of Acid Hydrolysis of NaCo(HY)Br in 0.05 M NaClO₄ and 0.05 M HClO₄ at 30°C.
$0.05\text{M NaClO}_4 + 0.05\text{M HClO}_4$

$T = 30^\circ\text{C}$.

- Run 3
  $a = 2.035 \cdot 10^{-3}$ m.l. NaCoYBr

- Run 4
  $a = 2.042 \cdot 10^{-3}$ m.l. NaCoYBr
Figure 32. Rate of Acid Hydrolysis of NaCo(HY)Br in 0.1 M HClO$_4$ at 30°C.
1 M HClO$_4$
T = 30°C.

Run 5
a = 2.122 \times 10^{-3}$ m./l. NaCoYBr

Run 6
a = 2.020 \times 10^{-3}$ m./l. NaCoYBr

$log \frac{a}{a-x}$

Time (hrs.)
Figure 33. Rate of Acid Hydrolysis of NaCo(HY)Br in 0.1 M NaNO₃ at 30°C.
1 M NaNO₃

T = 30°C.

Run 7

a = 4.181 \times 10^{-3} \text{ m./l. NaCoYBr}

Run 8

a = 3.970 \times 10^{-3} \text{ m./l. NaCoYBr}
Figure 34. Rate of Acid Hydrolysis of NaCo(HY)BF$_4$ in 0.1 M NaNO$_3$, at 30°C (First Order - First Order Reversible Reaction)
$\log \frac{A_0 - A_\varepsilon}{A - A_\varepsilon}$

**Run 7**
- $A_0 = 4.181 \times 10^{-3}$ m/l. NaCoYOHBr
- $A_\varepsilon = 1.133 \times 10^{-3}$ m/l.

**Run 8**
- $A_0 = 4.181 \times 10^{-3}$ m/l. NaCoYBr
- $A_\varepsilon = 1.031 \times 10^{-3}$ m/l.

-.1 M NaNO$_3$
- $T = 30^\circ$C.
Figure 35. Rate of Acid Hydrolysis of Na[Co(HY)Br] in 0.1 M NaNO$_3$ at 30°C.
0.1M NaNO$_3$
$T = 30^\circ$ C.

- **Run 9**
  - $a = 1.124 \cdot 10^{-3}$ m./l. NaCoYBr

- **Run 10**
  - $a = 1.062 \cdot 10^{-3}$ m./l. NaCoYBr

The graph shows a plot of $\log \frac{a}{a-x}$ against time (hrs.).
Figure 36. Rate of Acid Hydrolysis of NaCo(HY)Br in 0.1 M NaNO₃ at 30°C (First Order - First Order Reversible Reaction)
1M NaNO₃
T = 30°C.

- Run 9
  \( A_0 = 1.124 \times 10^{-3} \text{ m./l. NaCoYBr} \)
  \( A_\varepsilon = 0.295 \times 10^{-3} \text{ m./l.} \)

- Run 10
  \( A_0 = 1.062 \times 10^{-3} \text{ m./l. NaCoYBr} \)
  \( A_\varepsilon = 0.288 \times 10^{-3} \text{ m./l.} \)
Figure 37. Rate of Acid Hydrolysis of NaCo(HY)Br in 0.1 M NaBr at 30°C.
1 M NaBr
T = 30°C.

Run 11
a = 2.004 \times 10^{-3} \text{m/l. NaCoYBr}

Run 12
a = 2.033 \times 10^{-3} \text{m/l. NaCoYBr}

\log \frac{a}{a-x}

Time (hrs.)
Figure 38. Rate of Acid Hydrolysis of Na₂Co(HY)Br in 0.1 M NaBr (First Order - First Order Reversible Reaction.)
1M NaBr
T = 30°C.

Run 11
\[ A_0 = 2.033 \times 10^{-3} \text{ m.} / \text{l. NaCoYBr} \]
\[ A_\epsilon = 0.549 \times 10^{-3} \text{ m.} / \text{l.} \]

Run 12
\[ A_0 = 2.004 \times 10^{-3} \text{ m.} / \text{l. NaCoYBr} \]
\[ A_\epsilon = 0.537 \times 10^{-3} \text{ m.} / \text{l.} \]
Figure 39. Rate of Acid Hydrolysis of NaCo(HY)Br in 0.1 M NaNO₃ at 30°C.
\[ .1 \text{M} \quad \text{NaNO}_3 \]
\[ T = 30^\circ \text{C.} \]

- Run 13
  \[ a = 2.044 \cdot 10^{-3} \text{ m.} / \text{l. NaCoYBr} \]

- Run 14
  \[ a = 2.026 \cdot 10^{-3} \text{ m.} / \text{l. NaCoYBr} \]
Figure 40. Rate of Acid Hydrolysis of NaCo(HY)Br in Distilled Water at 30°C.
Distilled water
T = 30°C

○ Run 15
\[ a = 2.117 \times 10^{-3} \text{ m./l. NaCoYBr} \]

● Run 16
\[ a = 2.011 \times 10^{-3} \text{ m./l. NaCoYBr} \]
Figure 41. Rate of Acid Hydrolysis of Na₂Co(HY)Br in 0.1 M NaNO₃ at 40°C.
1 M NaNO$_3$

T = 40°C.

Run 21
a = 2.173 \times 10^{-3} \text{ m/l. NaCoYBr}

Run 22
a = 2.221 \times 10^{-3} \text{ m/l. NaCoYBr}
Figure 42. Rate of Acid Hydrolysis of NaCo(HY)Br in 0.1 M NaNO₃ at 40°C (First Order - First Order Reversible Reaction.)
.1 M NaNO₃
T = 40°C.

Run 22
A₀ = 2.221 \cdot 10^{-3} \text{ m./l.}
A₁ = 588 \cdot 10^{-3} \text{ m./l.}

Run 21
A₀ = 2.173 \cdot 10^{-3} \text{ m./l.}
A₁ = 561 \cdot 10^{-3} \text{ m./l.}
Figure 43. Rate of Acid Hydrolysis of NaCo(HY)Br in 0.1 M NaNO₃ at 50°C.
0.1 M NaNO₃
T = 50°C.

Run 23
a = 1.899 \times 10^{-3} \text{ m/l NaCoYBr}

Run 24
a = 1.860 \times 10^{-3} \text{ m/l NaCoYBr}

log \frac{a}{a-x}

Time (hrs)
Figure 4. Rate of Acid Hydrolysis of NaCo(HY)Br in 0.1 M NaNO₃ at 50°C (First Order - First Order Reversible Reaction)
.1M NaNO$_3$
$T = 50^\circ$C.

- Run 23
  $A_0 = 1.899 \cdot 10^{-3}$ m./l. NaCoYBr
  $A_\varepsilon = 468 \cdot 10^{-3}$ m./l.

- Run 24
  $A_0 = 1.860 \cdot 10^{-3}$ m./l. NaCoYBr
  $A_\varepsilon = 468 \cdot 10^{-3}$ m./l.
Figure 45. Temperature Dependence of NaCo(Ni)Br
Figure 46. Rate of Acid Hydrolysis of Na[Co(HY)Cl] is 0.1 M NaNO₃ at 30°C
$0.1 \text{M} \text{NaNO}_3$
$T = 30^\circ \text{C}$.

- Run 25
  $a = 2.245 \cdot 10^{-3} \text{m.l. NaCoYCl}$
- Run 26
  $a = 2.367 \cdot 10^{-3} \text{m.l. NaCoYCl}$
Figure 47. Rate of Acid Hydrolysis of Na[Co(HY)Cl] in 0.1 M NaNO\textsubscript{3} at 40°C.
.1 M NaNO₃
T = 40°C.

○ Run 27
a = 1.809 × 10⁻³ m./l. NaCoYCl

● Run 28
a = 2.199 × 10⁻³ m./l. NaCoYCl
Figure 48. Rate of Acid Hydrolysis of Na[Co(HY)Cl] in 0.1 M NaNO₃ at 50°C.
.1 M NaNO₃
T = 50 °C.

- Run 29
  \( a = 1.814 \cdot 10^{-3} \text{ m.}/\text{l. NaCoYCl} \)

- Run 30
  \( a = 2.033 \cdot 10^{-3} \text{ m.}/\text{l. NaCoYCl} \)
Figure 49. Temperature Dependence of Na[Co(HY)Cl]
Figure 50. Rate of Acid Hydrolysis of Na\textsubscript{2}[Co(YOH)Cl] in 0.1 M NaNO\textsubscript{3} at 30°C.
.1 M NaNO₃
T = 30°C.

O Run 31
a = 2.056 \cdot 10^{-3} \text{ m./l. NaCoYHCl}

● Run 32
a = 2.335 \cdot 10^{-3} \text{ m./l. NaCoYHCl}

log \frac{a}{a-x}
Figure 51. Rate of Acid Hydrolysis of Na[Co(YOH)Cl] in 0.1 M NaNO₃ at 40°C.
1 M NaNO₃
T = 40°C.

- Run 33
  a = 2.214 \times 10^{-3} \text{ m./l. NaCoYOHCl}

- Run 34
  a = 1.694 \times 10^{-3} \text{ m./l. NaCoYOHCl}

\[ \log \left( \frac{a}{a-x} \right) \] vs. Time (hrs.)
Figure 52. Rate of Acid Hydrolysis of Na[Co(YOH)Cl] in 0.1 M NaNO₃ at 50°C.
0.1 M NaNO₃

$T = 50°C$

- Run 35
  $a = 2.030 \cdot 10^{-3} \text{ m.} / \text{l. NaCoYOHCl}$

- Run 36
  $a = 1.971 \cdot 10^{-3} \text{ m.} / \text{l. NaCoYOHCl}$
Figure 53. Temperature Dependence of $\text{Na[Co(YOH)Cl]}$. 

162
Figure 54. Rate of Acid Hydrolysis of Na[Co(YOH)Br] in 0.1 M NaNO₃ at 30°C.
\[ \log \frac{a}{a-x} \]

- \( .1 \text{ M} \) \( \text{NaNO}_3 \)
- \( T = 30^\circ C \)
- \( \text{Run 37} \)
  - \( a = 3.261 \times 10^{-3} \text{ m/l} \) \( \text{NaCoYOHB}r \)
- \( \text{Run 38} \)
  - \( a = 1.870 \times 10^{-3} \text{ m/l} \) \( \text{NaCoYOHB}r \)
Figure 55. Rate of Acid Hydrolysis of Na[Co(YOH)B₃] in 0.1 NaNO₂ at 30°C (First Order - First Order Reversible Reaction)
.1 M NaNO₃  
T = 30°C.

- Run 37  
  $A_0 = 3.261 \times 10^{-3}$ m./l. NaCoYOHBr  
  $A_\infty = .544 \times 10^{-3}$ m./l.

- Run 38  
  $A_0 = 1.870 \times 10^{-3}$ m./l. NaCoYOHBr  
  $A_\infty = .311 \times 10^{-3}$ m./l.

\[
\log \frac{A_0 - A_\infty}{A - A_\infty}
\]
Figure 56. Rate of Acid Hydrolysis of Na[Co(YOH)Br] in 0.1 M NaNO₃ at 40°C
1 M NaNO₃
T = 40°C.

- Run 39
  \( a = 1.228 \times 10^{-3} \text{ m./l. NaCoYOHBr} \)
- Run 40
  \( a = 1.819 \times 10^{-3} \text{ m./l. NaCoYOHBr} \)

\[ \log \frac{a}{a-x} \]

Time (hrs.)
Figure 57. Rate of Acid Hydrolysis of Na[Co(YOH)Br] in 0.1 M NaNO₃ at 40°C (First Order - First Order Reversible Reaction)
1.4

log \frac{A_0 - A_\infty}{A - A_\infty}

0 M NaNO_3
T = 40°C

Run 39
A_0 = 1.228 \times 10^{-3} \text{ m./l.} \ NaCoYOHB
A_\infty = .201 \times 10^{-3} \text{ m./l.}

Run 40
A_0 = 1.819 \times 10^{-3} \text{ m./l.} \ NaCoYOHB
A_\infty = .301 \times 10^{-3} \text{ m./l.}

Time (hrs)
Figure 58. Rate of Acid Hydrolysis of Na[Co(YOH)Br] in 0.1 M NaNO₃ at 50°C
0.1 M NaNO₃
T = 50°C.

- Run 41
  a = 1.709 \times 10^{-3} \text{ m./l. NaCoYOHBr}

- Run 42
  a = 2.287 \times 10^{-3} \text{ m./l. NaCoYOHBr}
Figure 59. Rate of Acid Hydrolysis of Na[Co(YOH)Br] in 0.1 M NaNO₃ at 50°C (First Order - First Order Reversible Reaction)
0.1 M NaNO₃
T = 50°C.

- Run 41
  \( A_0 = 1.709 \times 10^{-3} \text{ m./l.} \text{ NaCoYOHBr} \)
  \( A_\infty = 2.86 \times 10^{-3} \text{ m./l.} \)

- Run 42
  \( A_0 = 2.287 \times 10^{-3} \text{ m./l.} \text{ NaCoYOHBr} \)
  \( A_\infty = 3.87 \times 10^{-3} \text{ m./l.} \)
Figure 60. Temperature Dependence of Na[Co(YOH)Br]
Table XI  
ACID HYDROLYSIS OF Na\(_2\)O(HY)Br  
Optical Density Measured as a Function of Time

<table>
<thead>
<tr>
<th>Time (hrs)</th>
<th>Run 1 (\text{[NaClO] = 0.1 M} ) (a = 1.997 \times 10^{-3} \text{M})</th>
<th>Run 2 (\text{[NaClO] = 0.1 M} ) (a = 1.991 \times 10^{-3} \text{M})</th>
</tr>
</thead>
<tbody>
<tr>
<td></td>
<td>(\text{O.D. 520} )</td>
<td>(\text{O.D. 540} )</td>
</tr>
<tr>
<td>1.33</td>
<td>0.146</td>
<td>0.255</td>
</tr>
<tr>
<td>2.33</td>
<td>0.160</td>
<td>0.269</td>
</tr>
<tr>
<td>3.33</td>
<td>0.174</td>
<td>0.282</td>
</tr>
<tr>
<td>4.33</td>
<td>0.185</td>
<td>0.289</td>
</tr>
<tr>
<td>6.00</td>
<td>0.204</td>
<td>0.308</td>
</tr>
<tr>
<td>11.00</td>
<td>0.255</td>
<td>0.357</td>
</tr>
<tr>
<td>14.00</td>
<td>0.282</td>
<td>0.380</td>
</tr>
<tr>
<td>18.00</td>
<td>0.310</td>
<td>0.411</td>
</tr>
<tr>
<td>23.00</td>
<td>0.345</td>
<td>0.440</td>
</tr>
<tr>
<td>27.50</td>
<td>0.367</td>
<td>0.460</td>
</tr>
<tr>
<td>38.50</td>
<td>0.412</td>
<td>0.499</td>
</tr>
<tr>
<td>52.00</td>
<td>0.452</td>
<td>0.538</td>
</tr>
</tbody>
</table>
Table XII

ACID HYDROLYSIS OF Na[Co(HY)Br]

Optical Density Measured as a Function of Time

<table>
<thead>
<tr>
<th>Run 3</th>
<th>Run 4</th>
</tr>
</thead>
<tbody>
<tr>
<td>( [\text{NaClO}_2] = 0.05 \text{ M} )</td>
<td>( [\text{NaClO}_2] = 0.05 \text{ M} )</td>
</tr>
<tr>
<td>( [\text{HClO}_2] = 0.05 \text{ M} )</td>
<td>( [\text{HClO}_2] = 0.05 \text{ M} )</td>
</tr>
<tr>
<td>( a = 2.035 \times 10^{-3} \text{M} )</td>
<td>( a = 2.042 \times 10^{-3} \text{M} )</td>
</tr>
<tr>
<td>( T = 30^\circ \text{C} )</td>
<td>( T = 30^\circ \text{C} )</td>
</tr>
</tbody>
</table>

<table>
<thead>
<tr>
<th>Time (hrs)</th>
<th>O.D. 520</th>
<th>O.D. 540</th>
<th>O.D. 560</th>
<th>Time (hrs)</th>
<th>O.D. 520</th>
<th>O.D. 540</th>
<th>O.D. 560</th>
</tr>
</thead>
<tbody>
<tr>
<td>3</td>
<td>0.178</td>
<td>0.285</td>
<td>0.447</td>
<td>3</td>
<td>0.174</td>
<td>0.269</td>
<td>0.459</td>
</tr>
<tr>
<td>6</td>
<td>0.214</td>
<td>0.318</td>
<td>0.434</td>
<td>6</td>
<td>0.216</td>
<td>0.318</td>
<td>0.448</td>
</tr>
<tr>
<td>9</td>
<td>0.245</td>
<td>0.345</td>
<td>0.425</td>
<td>9</td>
<td>0.247</td>
<td>0.349</td>
<td>0.434</td>
</tr>
<tr>
<td>12</td>
<td>0.280</td>
<td>0.371</td>
<td>0.414</td>
<td>12</td>
<td>0.275</td>
<td>0.372</td>
<td>0.423</td>
</tr>
<tr>
<td>15</td>
<td>0.295</td>
<td>0.389</td>
<td>0.401</td>
<td>15</td>
<td>0.298</td>
<td>0.392</td>
<td>0.414</td>
</tr>
<tr>
<td>21</td>
<td>0.335</td>
<td>0.428</td>
<td>0.385</td>
<td>20</td>
<td>0.333</td>
<td>0.427</td>
<td>0.395</td>
</tr>
<tr>
<td>24</td>
<td>0.353</td>
<td>0.440</td>
<td>0.381</td>
<td>25</td>
<td>0.359</td>
<td>0.450</td>
<td>0.385</td>
</tr>
<tr>
<td>29</td>
<td>0.369</td>
<td>0.453</td>
<td>0.369</td>
<td>30.5</td>
<td>0.380</td>
<td>0.471</td>
<td>0.373</td>
</tr>
<tr>
<td>35</td>
<td>0.390</td>
<td>0.477</td>
<td>0.363</td>
<td>38</td>
<td>0.409</td>
<td>0.497</td>
<td>0.365</td>
</tr>
<tr>
<td>48</td>
<td>0.423</td>
<td>0.504</td>
<td>0.354</td>
<td>48</td>
<td>0.432</td>
<td>0.510</td>
<td>0.354</td>
</tr>
<tr>
<td>60</td>
<td>0.431</td>
<td>0.521</td>
<td>0.343</td>
<td>59</td>
<td>0.446</td>
<td>0.519</td>
<td>0.338</td>
</tr>
<tr>
<td>75</td>
<td>0.457</td>
<td>0.539</td>
<td>0.329</td>
<td>72</td>
<td>0.473</td>
<td>0.551</td>
<td>0.337</td>
</tr>
</tbody>
</table>

179
### Table XIII

**ACID HYDROLYSIS OF Na[Co(HY)Br]**

Optical Density Measured as a Function of Time

<table>
<thead>
<tr>
<th>Time (hrs)</th>
<th>Run 5 ( [\text{HClO}_4] = 0.1 \text{ M} )</th>
<th>Run 6 ( [\text{HClO}_4] = 0.1 \text{ M} )</th>
</tr>
</thead>
<tbody>
<tr>
<td></td>
<td>( a = 2.122 \times 10^{-3} \text{M} )</td>
<td>( a = 2.020 \times 10^{-3} \text{M} )</td>
</tr>
<tr>
<td></td>
<td>( T = 30^\circ \text{C} )</td>
<td>( T = 30^\circ \text{C} )</td>
</tr>
<tr>
<td>O.D. 520</td>
<td>O.D. 540</td>
<td>O.D. 600</td>
</tr>
<tr>
<td>3</td>
<td>0.183</td>
<td>0.290</td>
</tr>
<tr>
<td>6</td>
<td>0.221</td>
<td>0.328</td>
</tr>
<tr>
<td>9</td>
<td>0.257</td>
<td>0.358</td>
</tr>
<tr>
<td>12</td>
<td>0.286</td>
<td>0.385</td>
</tr>
<tr>
<td>15</td>
<td>0.303</td>
<td>0.401</td>
</tr>
<tr>
<td>20</td>
<td>0.338</td>
<td>0.436</td>
</tr>
<tr>
<td>25</td>
<td>0.364</td>
<td>0.458</td>
</tr>
<tr>
<td>30.5</td>
<td>0.396</td>
<td>0.484</td>
</tr>
<tr>
<td>38</td>
<td>0.419</td>
<td>0.504</td>
</tr>
<tr>
<td>48</td>
<td>0.440</td>
<td>0.523</td>
</tr>
<tr>
<td>59</td>
<td>0.449</td>
<td>0.530</td>
</tr>
<tr>
<td>72</td>
<td>0.474</td>
<td>0.553</td>
</tr>
</tbody>
</table>
Table XIV

ACID HYDROLYSIS OF Na[Co(HY)Br]

Optical Density Measured as a Function of Time

<table>
<thead>
<tr>
<th>Time (hrs)</th>
<th>Run 7</th>
<th>Run 8</th>
</tr>
</thead>
<tbody>
<tr>
<td></td>
<td>[NaNO₃] = 0.1 M</td>
<td>[NaNO₃] = 0.1 M</td>
</tr>
<tr>
<td></td>
<td>a = 4.181 x 10⁻³ M</td>
<td>a = 3.970 x 10⁻³ M</td>
</tr>
<tr>
<td>T = 30°C</td>
<td></td>
<td></td>
</tr>
<tr>
<td>O.D. 520</td>
<td>O.D. 540</td>
<td>O.D. 600</td>
</tr>
<tr>
<td>3.5</td>
<td>0.364</td>
<td>0.593</td>
</tr>
<tr>
<td>6.5</td>
<td>0.442</td>
<td>0.662</td>
</tr>
<tr>
<td>9.5</td>
<td>0.503</td>
<td>0.713</td>
</tr>
<tr>
<td>12.5</td>
<td>0.560</td>
<td>0.762</td>
</tr>
<tr>
<td>15.5</td>
<td>0.608</td>
<td>0.805</td>
</tr>
<tr>
<td>18.5</td>
<td>0.644</td>
<td>0.839</td>
</tr>
<tr>
<td>21.5</td>
<td>0.683</td>
<td>0.877</td>
</tr>
<tr>
<td>23.5</td>
<td>0.740</td>
<td>0.937</td>
</tr>
<tr>
<td>33.5</td>
<td>0.799</td>
<td>0.981</td>
</tr>
<tr>
<td>38.5</td>
<td>0.825</td>
<td>1.001</td>
</tr>
<tr>
<td>44.5</td>
<td>0.852</td>
<td>1.031</td>
</tr>
<tr>
<td>50.5</td>
<td>0.879</td>
<td>1.041</td>
</tr>
<tr>
<td>71</td>
<td>0.885</td>
<td>1.033</td>
</tr>
</tbody>
</table>
Table XV

ACID HYDROLYSIS OF Na[Co(HY)Br]

Optical Density Measured as a Function of Time

<table>
<thead>
<tr>
<th>Time (hrs)</th>
<th>Run 9</th>
<th>Run 10</th>
</tr>
</thead>
<tbody>
<tr>
<td></td>
<td>[NaNO_3] = 0.1 M</td>
<td>[NaNO_3] = 0.1 M</td>
</tr>
<tr>
<td></td>
<td>a = 1.124 x 10^{-3} M</td>
<td>a = 1.062 x 10^{-3} M</td>
</tr>
<tr>
<td></td>
<td>T = 30°C</td>
<td>T = 30°C</td>
</tr>
<tr>
<td>2</td>
<td>0.077</td>
<td>0.084</td>
</tr>
<tr>
<td></td>
<td>0.138</td>
<td>0.140</td>
</tr>
<tr>
<td></td>
<td>0.260</td>
<td>0.255</td>
</tr>
<tr>
<td>4</td>
<td>0.040</td>
<td>0.096</td>
</tr>
<tr>
<td></td>
<td>0.147</td>
<td>0.150</td>
</tr>
<tr>
<td></td>
<td>0.251</td>
<td>0.249</td>
</tr>
<tr>
<td>6</td>
<td>0.102</td>
<td>0.108</td>
</tr>
<tr>
<td></td>
<td>0.160</td>
<td>0.162</td>
</tr>
<tr>
<td></td>
<td>0.245</td>
<td>0.244</td>
</tr>
<tr>
<td>8</td>
<td>0.114</td>
<td>0.120</td>
</tr>
<tr>
<td></td>
<td>0.173</td>
<td>0.174</td>
</tr>
<tr>
<td></td>
<td>0.239</td>
<td>0.239</td>
</tr>
<tr>
<td>10</td>
<td>0.127</td>
<td>0.136</td>
</tr>
<tr>
<td></td>
<td>0.183</td>
<td>0.184</td>
</tr>
<tr>
<td></td>
<td>0.237</td>
<td>0.236</td>
</tr>
<tr>
<td>12</td>
<td>0.147</td>
<td>0.148</td>
</tr>
<tr>
<td></td>
<td>0.200</td>
<td>0.198</td>
</tr>
<tr>
<td></td>
<td>0.232</td>
<td>0.229</td>
</tr>
<tr>
<td>16</td>
<td>0.165</td>
<td>0.158</td>
</tr>
<tr>
<td></td>
<td>0.218</td>
<td>0.208</td>
</tr>
<tr>
<td></td>
<td>0.229</td>
<td>0.221</td>
</tr>
<tr>
<td>23</td>
<td>0.185</td>
<td>0.177</td>
</tr>
<tr>
<td></td>
<td>0.237</td>
<td>0.227</td>
</tr>
<tr>
<td></td>
<td>0.219</td>
<td>0.210</td>
</tr>
<tr>
<td>29</td>
<td>0.198</td>
<td>0.190</td>
</tr>
<tr>
<td></td>
<td>0.247</td>
<td>0.236</td>
</tr>
<tr>
<td></td>
<td>0.212</td>
<td>0.203</td>
</tr>
<tr>
<td>35</td>
<td>0.209</td>
<td>0.203</td>
</tr>
<tr>
<td></td>
<td>0.257</td>
<td>0.249</td>
</tr>
<tr>
<td></td>
<td>0.206</td>
<td>0.197</td>
</tr>
<tr>
<td>46</td>
<td>0.226</td>
<td>0.216</td>
</tr>
<tr>
<td></td>
<td>0.272</td>
<td>0.261</td>
</tr>
<tr>
<td></td>
<td>0.197</td>
<td>0.189</td>
</tr>
<tr>
<td>59</td>
<td>0.241</td>
<td>0.231</td>
</tr>
<tr>
<td></td>
<td>0.284</td>
<td>0.271</td>
</tr>
<tr>
<td></td>
<td>0.192</td>
<td>0.183</td>
</tr>
<tr>
<td>71</td>
<td>0.247</td>
<td>0.238</td>
</tr>
<tr>
<td></td>
<td>0.295</td>
<td>0.279</td>
</tr>
<tr>
<td></td>
<td>0.186</td>
<td>0.178</td>
</tr>
</tbody>
</table>
Table XVI

ACID HYDROLYSIS OF Na[Co(HY)Br]

Optical Density Measured as a Function of Time

<table>
<thead>
<tr>
<th>Time (hrs)</th>
<th>0.D. 520</th>
<th>0.D. 540</th>
<th>0.D. 600</th>
<th>Time (hrs)</th>
<th>0.D. 520</th>
<th>0.D. 540</th>
<th>0.D. 600</th>
</tr>
</thead>
<tbody>
<tr>
<td>3</td>
<td>0.170</td>
<td>0.281</td>
<td>0.479</td>
<td>3</td>
<td>0.168</td>
<td>0.278</td>
<td>0.472</td>
</tr>
<tr>
<td>6</td>
<td>0.196</td>
<td>0.310</td>
<td>0.463</td>
<td>6</td>
<td>0.205</td>
<td>0.304</td>
<td>0.460</td>
</tr>
<tr>
<td>9</td>
<td>0.231</td>
<td>0.335</td>
<td>0.452</td>
<td>9</td>
<td>0.231</td>
<td>0.334</td>
<td>0.449</td>
</tr>
<tr>
<td>12</td>
<td>0.256</td>
<td>0.357</td>
<td>0.438</td>
<td>12</td>
<td>0.354</td>
<td>0.351</td>
<td>0.425</td>
</tr>
<tr>
<td>15</td>
<td>0.280</td>
<td>0.375</td>
<td>0.428</td>
<td>15</td>
<td>0.279</td>
<td>0.369</td>
<td>0.418</td>
</tr>
<tr>
<td>21</td>
<td>0.322</td>
<td>0.422</td>
<td>0.407</td>
<td>21</td>
<td>0.315</td>
<td>0.412</td>
<td>0.398</td>
</tr>
<tr>
<td>24</td>
<td>0.339</td>
<td>0.431</td>
<td>0.403</td>
<td>24</td>
<td>0.329</td>
<td>0.421</td>
<td>0.393</td>
</tr>
<tr>
<td>29</td>
<td>0.362</td>
<td>0.451</td>
<td>0.390</td>
<td>29</td>
<td>0.348</td>
<td>0.434</td>
<td>0.383</td>
</tr>
<tr>
<td>35</td>
<td>0.393</td>
<td>0.482</td>
<td>0.384</td>
<td>35</td>
<td>0.375</td>
<td>0.464</td>
<td>0.371</td>
</tr>
<tr>
<td>48</td>
<td>0.428</td>
<td>0.509</td>
<td>0.369</td>
<td>48</td>
<td>0.411</td>
<td>0.491</td>
<td>0.358</td>
</tr>
<tr>
<td>60</td>
<td>0.442</td>
<td>0.522</td>
<td>0.349</td>
<td>60</td>
<td>0.434</td>
<td>0.515</td>
<td>0.341</td>
</tr>
<tr>
<td>75</td>
<td>0.462</td>
<td>0.541</td>
<td>0.336</td>
<td>75</td>
<td>0.452</td>
<td>0.534</td>
<td>0.333</td>
</tr>
</tbody>
</table>
XVII Table

ACID HYDROLYSIS OF Na[Co(HY)Br]

Optical Density Measured as a Function of Time

---

<table>
<thead>
<tr>
<th>Time (hrs)</th>
<th>O.D. 520</th>
<th>O.D. 540</th>
<th>O.D. 600</th>
<th>Time (hrs)</th>
<th>O.D. 520</th>
<th>O.D. 540</th>
<th>O.D. 600</th>
</tr>
</thead>
<tbody>
<tr>
<td>Run 13</td>
<td></td>
<td></td>
<td></td>
<td>Run 14</td>
<td></td>
<td></td>
<td></td>
</tr>
<tr>
<td>[NaNO₃] = 0.1 M</td>
<td>a = 2.044 x 10⁻³ M</td>
<td>[NaNO₃] = 0.1 M</td>
<td>a = 2.026 x 10⁻³ M</td>
<td></td>
<td></td>
<td></td>
<td></td>
</tr>
<tr>
<td>T = 30°C</td>
<td></td>
<td></td>
<td></td>
<td>T = 30°C</td>
<td></td>
<td></td>
<td></td>
</tr>
<tr>
<td>3</td>
<td>0.177</td>
<td>0.286</td>
<td>0.483</td>
<td>3</td>
<td>0.169</td>
<td>0.273</td>
<td>0.474</td>
</tr>
<tr>
<td>6</td>
<td>0.209</td>
<td>0.316</td>
<td>0.473</td>
<td>6</td>
<td>0.200</td>
<td>0.304</td>
<td>0.465</td>
</tr>
<tr>
<td>10</td>
<td>0.244</td>
<td>0.345</td>
<td>0.449</td>
<td>10</td>
<td>0.240</td>
<td>0.340</td>
<td>0.443</td>
</tr>
<tr>
<td>15</td>
<td>0.282</td>
<td>0.379</td>
<td>0.429</td>
<td>15</td>
<td>0.278</td>
<td>0.374</td>
<td>0.421</td>
</tr>
<tr>
<td>18</td>
<td>0.309</td>
<td>0.406</td>
<td>0.421</td>
<td>18</td>
<td>0.307</td>
<td>0.399</td>
<td>0.414</td>
</tr>
<tr>
<td>21</td>
<td>0.321</td>
<td>0.417</td>
<td>0.413</td>
<td>21</td>
<td>0.322</td>
<td>0.415</td>
<td>0.411</td>
</tr>
<tr>
<td>26</td>
<td>0.339</td>
<td>0.441</td>
<td>0.402</td>
<td>26</td>
<td>0.351</td>
<td>0.445</td>
<td>0.401</td>
</tr>
<tr>
<td>30.5</td>
<td>0.371</td>
<td>0.464</td>
<td>0.391</td>
<td>30.5</td>
<td>0.367</td>
<td>0.462</td>
<td>0.388</td>
</tr>
<tr>
<td>37.5</td>
<td>0.390</td>
<td>0.476</td>
<td>0.382</td>
<td>37.5</td>
<td>0.389</td>
<td>0.481</td>
<td>0.383</td>
</tr>
<tr>
<td>47</td>
<td>0.426</td>
<td>0.514</td>
<td>0.377</td>
<td>47</td>
<td>0.422</td>
<td>0.510</td>
<td>0.375</td>
</tr>
<tr>
<td>64.5</td>
<td>0.456</td>
<td>0.540</td>
<td>0.355</td>
<td>64.5</td>
<td>0.448</td>
<td>0.531</td>
<td>0.353</td>
</tr>
<tr>
<td>75.5</td>
<td>0.474</td>
<td>0.554</td>
<td>0.348</td>
<td>75.5</td>
<td>0.462</td>
<td>0.544</td>
<td>0.344</td>
</tr>
</tbody>
</table>

184
Table XVIII

ACID HYDROLYSIS OF Na[Co(HY)Br]

Optical Density Measured as a Function of Time

<table>
<thead>
<tr>
<th>Time (hrs)</th>
<th>Run 15 Distilled Water</th>
<th>Run 16 Distilled Water</th>
</tr>
</thead>
<tbody>
<tr>
<td></td>
<td>(a = 2.117 \times 10^{-3}\text{M})</td>
<td>(T = 30^\circ\text{C})</td>
</tr>
<tr>
<td>3</td>
<td>0.166 0.286 0.494</td>
<td>3 0.160 0.268 0.468</td>
</tr>
<tr>
<td>6</td>
<td>0.194 0.317 0.477</td>
<td>6 0.185 0.289 0.455</td>
</tr>
<tr>
<td>13</td>
<td>0.270 0.376 0.447</td>
<td>13 0.256 0.352 0.427</td>
</tr>
<tr>
<td>16</td>
<td>0.295 0.396 0.441</td>
<td>16 0.283 0.371 0.420</td>
</tr>
<tr>
<td>20</td>
<td>0.324 0.425 0.437</td>
<td>20 0.302 0.396 0.406</td>
</tr>
<tr>
<td>24</td>
<td>0.343 0.440 0.421</td>
<td>24 0.330 0.417 0.401</td>
</tr>
<tr>
<td>31</td>
<td>0.380 0.477 0.414</td>
<td>31 0.353 0.441 0.382</td>
</tr>
<tr>
<td>38</td>
<td>0.399 0.490 0.396</td>
<td>38 0.376 0.460 0.372</td>
</tr>
<tr>
<td>45</td>
<td>0.417 0.516 0.388</td>
<td>45 0.396 0.482 0.363</td>
</tr>
<tr>
<td>53</td>
<td>0.439 0.534 0.371</td>
<td>53 0.421 0.498 0.351</td>
</tr>
<tr>
<td>63</td>
<td>0.460 0.549 0.364</td>
<td>63 0.440 0.512 0.347</td>
</tr>
<tr>
<td>74.25</td>
<td>0.476 0.560 0.361</td>
<td>74.25 0.451 0.531 0.344</td>
</tr>
</tbody>
</table>
Table XIX

ACID HYDROLYSIS OF Na[Co(HY)Br]

Optical Density Measured as a Function of Time

Run 17
\[
\begin{align*}
\text{NaNO}_3 & = 0.1 \text{ M} \\
\text{NaCoY} & = 0.886 \times 10^{-3} \text{ M} \\
a & = 1.643 \times 10^{-3} \text{ M} \\
T & = 30^\circ \text{C}
\end{align*}
\]

<table>
<thead>
<tr>
<th>Time (hrs)</th>
<th>O.D. 520</th>
<th>O.D. 540</th>
<th>O.D. 600</th>
</tr>
</thead>
<tbody>
<tr>
<td>3</td>
<td>0.388</td>
<td>0.501</td>
<td>0.506</td>
</tr>
<tr>
<td>6</td>
<td>0.417</td>
<td>0.524</td>
<td>0.494</td>
</tr>
<tr>
<td>9</td>
<td>0.445</td>
<td>0.551</td>
<td>0.485</td>
</tr>
<tr>
<td>12</td>
<td>0.485</td>
<td>0.595</td>
<td>0.461</td>
</tr>
<tr>
<td>17</td>
<td>0.513</td>
<td>0.614</td>
<td>0.445</td>
</tr>
<tr>
<td>22</td>
<td>0.535</td>
<td>0.630</td>
<td>0.441</td>
</tr>
<tr>
<td>28</td>
<td>0.551</td>
<td>0.6478</td>
<td>0.430</td>
</tr>
<tr>
<td>34</td>
<td>0.570</td>
<td>0.664</td>
<td>0.422</td>
</tr>
<tr>
<td>42</td>
<td>0.592</td>
<td>0.682</td>
<td>0.416</td>
</tr>
<tr>
<td>54</td>
<td>0.614</td>
<td>0.696</td>
<td>0.403</td>
</tr>
<tr>
<td>64</td>
<td>0.621</td>
<td>0.706</td>
<td>0.394</td>
</tr>
</tbody>
</table>

Run 18
\[
\begin{align*}
\text{NaNO}_3 & = 0.1 \text{ M} \\
\text{NaCoY} & = 1.133 \times 10^{-3} \text{ M} \\
a & = 1.503 \times 10^{-3} \text{ M} \\
T & = 30^\circ \text{C}
\end{align*}
\]

<table>
<thead>
<tr>
<th>Time (hrs)</th>
<th>O.D. 520</th>
<th>O.D. 540</th>
<th>O.D. 600</th>
</tr>
</thead>
<tbody>
<tr>
<td>3</td>
<td>0.444</td>
<td>0.556</td>
<td>0.505</td>
</tr>
<tr>
<td>6</td>
<td>0.471</td>
<td>0.583</td>
<td>0.487</td>
</tr>
<tr>
<td>9</td>
<td>0.494</td>
<td>0.602</td>
<td>0.484</td>
</tr>
<tr>
<td>12</td>
<td>0.542</td>
<td>0.643</td>
<td>0.465</td>
</tr>
<tr>
<td>17</td>
<td>0.565</td>
<td>0.663</td>
<td>0.452</td>
</tr>
<tr>
<td>22</td>
<td>0.585</td>
<td>0.682</td>
<td>0.448</td>
</tr>
<tr>
<td>28</td>
<td>0.603</td>
<td>0.693</td>
<td>0.435</td>
</tr>
<tr>
<td>34</td>
<td>0.616</td>
<td>0.706</td>
<td>0.431</td>
</tr>
<tr>
<td>42</td>
<td>0.635</td>
<td>0.734</td>
<td>0.428</td>
</tr>
<tr>
<td>54</td>
<td>0.640</td>
<td>0.736</td>
<td>0.407</td>
</tr>
<tr>
<td>64</td>
<td>0.661</td>
<td>0.748</td>
<td>0.403</td>
</tr>
</tbody>
</table>

186
Table XX

ACID HYDROLYSIS OF Na[Co(HY)Br]

Optical Density Measured as a Function of Time

<table>
<thead>
<tr>
<th>Time (hrs)</th>
<th>Run 19</th>
<th>Run 20</th>
</tr>
</thead>
<tbody>
<tr>
<td></td>
<td>[HClO₄] = 1.0 M</td>
<td>[HClO₄] = 1.0 M</td>
</tr>
<tr>
<td></td>
<td>a = 1.997 x 10⁻³ M</td>
<td>a = 2.017 x 10⁻³ M</td>
</tr>
<tr>
<td>T = 30°C</td>
<td></td>
<td></td>
</tr>
<tr>
<td></td>
<td>O.D. 520</td>
<td>O.D. 540</td>
</tr>
<tr>
<td>3</td>
<td>0.167</td>
<td>0.268</td>
</tr>
<tr>
<td>6</td>
<td>0.202</td>
<td>0.305</td>
</tr>
<tr>
<td>9</td>
<td>0.223</td>
<td>0.327</td>
</tr>
<tr>
<td>12</td>
<td>0.248</td>
<td>0.345</td>
</tr>
<tr>
<td>15</td>
<td>0.270</td>
<td>0.367</td>
</tr>
<tr>
<td>21</td>
<td>0.302</td>
<td>0.396</td>
</tr>
<tr>
<td>24</td>
<td>0.311</td>
<td>0.409</td>
</tr>
<tr>
<td>30</td>
<td>0.326</td>
<td>0.420</td>
</tr>
<tr>
<td>38</td>
<td>0.345</td>
<td>0.435</td>
</tr>
<tr>
<td>48</td>
<td>0.363</td>
<td>0.454</td>
</tr>
<tr>
<td>59</td>
<td>0.379</td>
<td>0.469</td>
</tr>
<tr>
<td>74</td>
<td>0.404</td>
<td>0.484</td>
</tr>
</tbody>
</table>

187
Table XXI

ACID HYDROLYSIS OF Na[Co(HY)Br]

Optical Density Measured as a Function of Time

<table>
<thead>
<tr>
<th>Time (hrs)</th>
<th>O.D. 520</th>
<th>O.D. 540</th>
<th>O.D. 600</th>
</tr>
</thead>
<tbody>
<tr>
<td>Run 21</td>
<td></td>
<td></td>
<td></td>
</tr>
<tr>
<td>[NaNO₃] = 0.1 M</td>
<td>a = 2.173 x 10⁻³ M</td>
<td>T = 40°C</td>
<td></td>
</tr>
<tr>
<td>1.50</td>
<td>0.191</td>
<td>0.301</td>
<td>0.487</td>
</tr>
<tr>
<td>3.00</td>
<td>0.257</td>
<td>0.361</td>
<td>0.476</td>
</tr>
<tr>
<td>4.5</td>
<td>0.300</td>
<td>0.404</td>
<td>0.454</td>
</tr>
<tr>
<td>6.0</td>
<td>0.331</td>
<td>0.428</td>
<td>0.426</td>
</tr>
<tr>
<td>7.5</td>
<td>0.355</td>
<td>0.455</td>
<td>0.416</td>
</tr>
<tr>
<td>9.0</td>
<td>0.378</td>
<td>0.474</td>
<td>0.408</td>
</tr>
<tr>
<td>10.5</td>
<td>0.398</td>
<td>0.491</td>
<td>0.398</td>
</tr>
</tbody>
</table>

<table>
<thead>
<tr>
<th>Time (hrs)</th>
<th>O.D. 520</th>
<th>O.D. 540</th>
<th>O.D. 600</th>
</tr>
</thead>
<tbody>
<tr>
<td>Run 22</td>
<td></td>
<td></td>
<td></td>
</tr>
<tr>
<td>[NaNO₃] = 0.1 M</td>
<td>a = 2.221 x 10⁻³ M</td>
<td>T = 40°C</td>
<td></td>
</tr>
<tr>
<td>1.50</td>
<td>0.214</td>
<td>0.327</td>
<td>0.503</td>
</tr>
<tr>
<td>3.00</td>
<td>0.274</td>
<td>0.378</td>
<td>0.489</td>
</tr>
<tr>
<td>4.5</td>
<td>0.310</td>
<td>0.414</td>
<td>0.461</td>
</tr>
<tr>
<td>6.0</td>
<td>0.344</td>
<td>0.445</td>
<td>0.439</td>
</tr>
<tr>
<td>7.5</td>
<td>0.368</td>
<td>0.466</td>
<td>0.430</td>
</tr>
<tr>
<td>9.0</td>
<td>0.391</td>
<td>0.490</td>
<td>0.422</td>
</tr>
<tr>
<td>10.5</td>
<td>0.413</td>
<td>0.509</td>
<td>0.416</td>
</tr>
</tbody>
</table>
Table XXII

ACID HYDROLYSIS OF Na[Co(HY)Br]

Optical Density Measured as a Function of Time

<table>
<thead>
<tr>
<th>Time (hrs)</th>
<th>O.D. 520</th>
<th>O.D. 540</th>
<th>O.D. 600</th>
<th>Time (hrs)</th>
<th>O.D. 520</th>
<th>O.D. 540</th>
<th>O.D. 600</th>
</tr>
</thead>
<tbody>
<tr>
<td>Run 23</td>
<td></td>
<td></td>
<td></td>
<td>Run 24</td>
<td></td>
<td></td>
<td></td>
</tr>
<tr>
<td>( [\text{NaN}_3] = 0.1 \text{ M} )</td>
<td>( a = 1.899 \times 10^{-3} \text{ M} )</td>
<td>( T = 50^\circ\text{C} )</td>
<td>( [\text{NaN}_3] = 0.1 \text{ M} )</td>
<td>( a = 1.860 \times 10^{-3} \text{ M} )</td>
<td>( T = 50^\circ\text{C} )</td>
<td></td>
<td></td>
</tr>
<tr>
<td>1</td>
<td>0.218</td>
<td>0.312</td>
<td>0.400</td>
<td>1</td>
<td>0.217</td>
<td>0.311</td>
<td>0.406</td>
</tr>
<tr>
<td>2</td>
<td>0.277</td>
<td>0.363</td>
<td>0.375</td>
<td>2</td>
<td>0.276</td>
<td>0.364</td>
<td>0.376</td>
</tr>
<tr>
<td>2.5</td>
<td>0.302</td>
<td>0.387</td>
<td>0.370</td>
<td>2.5</td>
<td>0.302</td>
<td>0.387</td>
<td>0.372</td>
</tr>
<tr>
<td>3.0</td>
<td>0.322</td>
<td>0.406</td>
<td>0.358</td>
<td>3.0</td>
<td>0.325</td>
<td>0.407</td>
<td>0.362</td>
</tr>
<tr>
<td>3.5</td>
<td>0.337</td>
<td>0.423</td>
<td>0.355</td>
<td>3.5</td>
<td>0.339</td>
<td>0.423</td>
<td>0.357</td>
</tr>
<tr>
<td>4.5</td>
<td>0.378</td>
<td>0.454</td>
<td>0.333</td>
<td>4.5</td>
<td>0.370</td>
<td>0.456</td>
<td>0.331</td>
</tr>
<tr>
<td>5.5</td>
<td>0.388</td>
<td>0.471</td>
<td>0.329</td>
<td>5.5</td>
<td>0.383</td>
<td>0.463</td>
<td>0.328</td>
</tr>
<tr>
<td>9.75</td>
<td>0.440</td>
<td>0.514</td>
<td>0.318</td>
<td>9.75</td>
<td>0.433</td>
<td>0.507</td>
<td>0.313</td>
</tr>
</tbody>
</table>
Table XXIII
ACID HYDROLYSIS OF Na[Co(HY)Cl]
Optical Density Measured as a Function of Time

<table>
<thead>
<tr>
<th>Time (hrs.)</th>
<th>Run 25</th>
<th>Run 26</th>
</tr>
</thead>
<tbody>
<tr>
<td></td>
<td>[NaNO₃] = 0.1 M</td>
<td>a = 2.245 \times 10^{-3} M</td>
</tr>
<tr>
<td></td>
<td>O.D. 520</td>
<td>O.D. 540</td>
</tr>
<tr>
<td>3</td>
<td>0.161</td>
<td>0.289</td>
</tr>
<tr>
<td>5</td>
<td>0.170</td>
<td>0.297</td>
</tr>
<tr>
<td>7.5</td>
<td>0.181</td>
<td>0.306</td>
</tr>
<tr>
<td>10</td>
<td>0.191</td>
<td>0.314</td>
</tr>
<tr>
<td>13</td>
<td>0.196</td>
<td>0.318</td>
</tr>
<tr>
<td>17</td>
<td>0.208</td>
<td>0.329</td>
</tr>
<tr>
<td>24</td>
<td>0.232</td>
<td>0.351</td>
</tr>
<tr>
<td>29</td>
<td>0.252</td>
<td>0.366</td>
</tr>
<tr>
<td>34</td>
<td>0.267</td>
<td>0.377</td>
</tr>
<tr>
<td>39</td>
<td>0.278</td>
<td>0.399</td>
</tr>
<tr>
<td>50.5</td>
<td>0.318</td>
<td>0.421</td>
</tr>
</tbody>
</table>
Table XXIV

ACID HYDROLYSIS OF Na[Co(HY)Cl]

Optical Density Measured as a Function of Time

<table>
<thead>
<tr>
<th>Time (hrs)</th>
<th>O.D. 520</th>
<th>O.D. 540</th>
<th>O.D. 600</th>
<th>Time (hrs)</th>
<th>O.D. 520</th>
<th>O.D. 540</th>
<th>O.D. 600</th>
</tr>
</thead>
<tbody>
<tr>
<td>1.25</td>
<td>0.139</td>
<td>0.240</td>
<td>0.413</td>
<td>1.25</td>
<td>0.164</td>
<td>0.286</td>
<td>0.490</td>
</tr>
<tr>
<td>2.75</td>
<td>0.148</td>
<td>0.245</td>
<td>0.393</td>
<td>2.75</td>
<td>0.181</td>
<td>0.301</td>
<td>0.479</td>
</tr>
<tr>
<td>4.25</td>
<td>0.161</td>
<td>0.257</td>
<td>0.390</td>
<td>4.25</td>
<td>0.200</td>
<td>0.314</td>
<td>0.469</td>
</tr>
<tr>
<td>5.75</td>
<td>0.178</td>
<td>0.271</td>
<td>0.386</td>
<td>5.75</td>
<td>0.216</td>
<td>0.327</td>
<td>0.463</td>
</tr>
<tr>
<td>7.25</td>
<td>0.196</td>
<td>0.285</td>
<td>0.384</td>
<td>7.25</td>
<td>0.233</td>
<td>0.344</td>
<td>0.459</td>
</tr>
<tr>
<td>9.25</td>
<td>0.211</td>
<td>0.303</td>
<td>0.380</td>
<td>9.25</td>
<td>0.258</td>
<td>0.368</td>
<td>0.450</td>
</tr>
<tr>
<td>11.25</td>
<td>0.226</td>
<td>0.317</td>
<td>0.367</td>
<td>11.25</td>
<td>0.284</td>
<td>0.389</td>
<td>0.440</td>
</tr>
<tr>
<td>13.25</td>
<td>0.243</td>
<td>0.327</td>
<td>0.359</td>
<td>13.25</td>
<td>0.296</td>
<td>0.400</td>
<td>0.432</td>
</tr>
<tr>
<td>15.25</td>
<td>0.255</td>
<td>0.336</td>
<td>0.351</td>
<td>15.25</td>
<td>0.314</td>
<td>0.418</td>
<td>0.425</td>
</tr>
<tr>
<td>27.25</td>
<td>0.318</td>
<td>0.400</td>
<td>0.319</td>
<td>27.25</td>
<td>0.400</td>
<td>0.495</td>
<td>0.381</td>
</tr>
<tr>
<td>39.75</td>
<td>0.290</td>
<td>0.450</td>
<td>0.291</td>
<td>39.75</td>
<td>0.483</td>
<td>0.565</td>
<td>0.369</td>
</tr>
</tbody>
</table>
Table XXV

ACID HYDROLYSIS OF Na\[\text{Co(HY)Cl}\]

Optical Density Measured as a Function of Time

<table>
<thead>
<tr>
<th>Run 29</th>
</tr>
</thead>
<tbody>
<tr>
<td>[\text{NaNO}_3] = 0.1 M</td>
</tr>
<tr>
<td>(a = 1.814 \times 10^{-3} \text{M})</td>
</tr>
<tr>
<td>(T = 50^\circ\text{C})</td>
</tr>
<tr>
<td>Time (hrs)</td>
</tr>
<tr>
<td>0.5</td>
</tr>
<tr>
<td>1.0</td>
</tr>
<tr>
<td>1.5</td>
</tr>
<tr>
<td>2.0</td>
</tr>
<tr>
<td>2.5</td>
</tr>
<tr>
<td>3.0</td>
</tr>
<tr>
<td>4.0</td>
</tr>
<tr>
<td>6.0</td>
</tr>
<tr>
<td>8.0</td>
</tr>
<tr>
<td>11</td>
</tr>
<tr>
<td>20</td>
</tr>
<tr>
<td>27.5</td>
</tr>
</tbody>
</table>

<table>
<thead>
<tr>
<th>Run 30</th>
</tr>
</thead>
<tbody>
<tr>
<td>[\text{NaNO}_3] = 0.1 M</td>
</tr>
<tr>
<td>(a = 2.033 \times 10^{-3} \text{M})</td>
</tr>
<tr>
<td>(T = 50^\circ\text{C})</td>
</tr>
<tr>
<td>Time (hrs)</td>
</tr>
<tr>
<td>0.5</td>
</tr>
<tr>
<td>1.0</td>
</tr>
<tr>
<td>1.5</td>
</tr>
<tr>
<td>2.5</td>
</tr>
<tr>
<td>3.5</td>
</tr>
<tr>
<td>5.5</td>
</tr>
<tr>
<td>7.5</td>
</tr>
<tr>
<td>9.5</td>
</tr>
<tr>
<td>11.5</td>
</tr>
<tr>
<td>22.5</td>
</tr>
</tbody>
</table>

192
Table XXVI

ACID HYDROLYSIS OF Na[Co(YOH)Cl]

Optical Density Measured as a Function of Time

<table>
<thead>
<tr>
<th>Time (hrs)</th>
<th>O.D. 520</th>
<th>O.D. 540</th>
<th>O.D. 600</th>
</tr>
</thead>
<tbody>
<tr>
<td>Run 31</td>
<td></td>
<td></td>
<td></td>
</tr>
<tr>
<td>[NaNO₃] = 0.1 M</td>
<td>a = 2.056 x 10⁻³M</td>
<td>T = 30°C</td>
<td></td>
</tr>
<tr>
<td>3</td>
<td>0.219</td>
<td>0.326</td>
<td>0.364</td>
</tr>
<tr>
<td>6</td>
<td>0.228</td>
<td>0.329</td>
<td>0.358</td>
</tr>
<tr>
<td>9</td>
<td>0.232</td>
<td>0.336</td>
<td>0.352</td>
</tr>
<tr>
<td>12</td>
<td>0.239</td>
<td>0.345</td>
<td>0.349</td>
</tr>
<tr>
<td>22</td>
<td>0.252</td>
<td>0.356</td>
<td>0.339</td>
</tr>
<tr>
<td>27</td>
<td>0.256</td>
<td>0.359</td>
<td>0.331</td>
</tr>
<tr>
<td>32</td>
<td>0.262</td>
<td>0.363</td>
<td>0.327</td>
</tr>
<tr>
<td>37</td>
<td>0.267</td>
<td>0.372</td>
<td>0.324</td>
</tr>
<tr>
<td>46.5</td>
<td>0.281</td>
<td>0.383</td>
<td>0.315</td>
</tr>
<tr>
<td>56.5</td>
<td>0.288</td>
<td>0.386</td>
<td>0.305</td>
</tr>
</tbody>
</table>

<table>
<thead>
<tr>
<th>Time (hrs)</th>
<th>O.D. 520</th>
<th>O.D. 540</th>
<th>O.D. 600</th>
</tr>
</thead>
<tbody>
<tr>
<td>Run 32</td>
<td></td>
<td></td>
<td></td>
</tr>
<tr>
<td>[NaNO₃] = 0.1 M</td>
<td>a = 2.335 x 10⁻³M</td>
<td>T = 30°C</td>
<td></td>
</tr>
<tr>
<td>3</td>
<td>0.256</td>
<td>0.379</td>
<td>0.419</td>
</tr>
<tr>
<td>6</td>
<td>0.269</td>
<td>0.389</td>
<td>0.415</td>
</tr>
<tr>
<td>9</td>
<td>0.281</td>
<td>0.404</td>
<td>0.414</td>
</tr>
<tr>
<td>12</td>
<td>0.284</td>
<td>0.408</td>
<td>0.413</td>
</tr>
<tr>
<td>22</td>
<td>0.304</td>
<td>0.426</td>
<td>0.405</td>
</tr>
<tr>
<td>27</td>
<td>0.300</td>
<td>0.417</td>
<td>0.383</td>
</tr>
<tr>
<td>32</td>
<td>0.307</td>
<td>0.423</td>
<td>0.378</td>
</tr>
<tr>
<td>37</td>
<td>0.312</td>
<td>0.429</td>
<td>0.374</td>
</tr>
<tr>
<td>46.5</td>
<td>0.324</td>
<td>0.441</td>
<td>0.363</td>
</tr>
<tr>
<td>56.5</td>
<td>0.325</td>
<td>0.445</td>
<td>0.351</td>
</tr>
</tbody>
</table>
Table XXVII

ACID HYDROLYSIS OF Na[Co(YOH)Cl]

Optical Density Measured as a Function of Time

<table>
<thead>
<tr>
<th>Time (hrs)</th>
<th>O.D. 520</th>
<th>O.D. 540</th>
<th>O.D. 600</th>
<th>Time (hrs)</th>
<th>O.D. 520</th>
<th>O.D. 540</th>
<th>O.D. 600</th>
</tr>
</thead>
<tbody>
<tr>
<td>2</td>
<td>0.248</td>
<td>0.358</td>
<td>0.392</td>
<td>2</td>
<td>0.190</td>
<td>0.275</td>
<td>0.299</td>
</tr>
<tr>
<td>4</td>
<td>0.259</td>
<td>0.376</td>
<td>0.383</td>
<td>4</td>
<td>0.199</td>
<td>0.283</td>
<td>0.291</td>
</tr>
<tr>
<td>6</td>
<td>0.273</td>
<td>0.381</td>
<td>0.373</td>
<td>6</td>
<td>0.207</td>
<td>0.292</td>
<td>0.286</td>
</tr>
<tr>
<td>8.5</td>
<td>0.285</td>
<td>0.390</td>
<td>0.362</td>
<td>8.5</td>
<td>0.226</td>
<td>0.311</td>
<td>0.282</td>
</tr>
<tr>
<td>12</td>
<td>0.292</td>
<td>0.403</td>
<td>0.345</td>
<td>12</td>
<td>0.233</td>
<td>0.313</td>
<td>0.268</td>
</tr>
<tr>
<td>21</td>
<td>0.325</td>
<td>0.432</td>
<td>0.322</td>
<td>21</td>
<td>0.258</td>
<td>0.339</td>
<td>0.253</td>
</tr>
<tr>
<td>26</td>
<td>0.330</td>
<td>0.436</td>
<td>0.319</td>
<td>26</td>
<td>0.260</td>
<td>0.340</td>
<td>0.247</td>
</tr>
<tr>
<td>32.5</td>
<td>0.340</td>
<td>0.447</td>
<td>0.315</td>
<td>32.5</td>
<td>0.267</td>
<td>0.348</td>
<td>0.245</td>
</tr>
</tbody>
</table>
Table XXVIII

ACID HYDROLYSIS OF Na[Co(YOH)Cl]

Optical Density Measured as a Function of Time

<table>
<thead>
<tr>
<th>Time (hrs.)</th>
<th>O.D. 520</th>
<th>O.D. 540</th>
<th>O.D. 600</th>
<th>Time (hrs.)</th>
<th>O.D. 520</th>
<th>O.D. 540</th>
<th>O.D. 600</th>
</tr>
</thead>
<tbody>
<tr>
<td>Run 35</td>
<td></td>
<td></td>
<td></td>
<td>Run 36</td>
<td></td>
<td></td>
<td></td>
</tr>
<tr>
<td>[NaNO₃] = 0.1 M</td>
<td>a = 2.030 x 10⁻³ M</td>
<td>T = 50°C</td>
<td>[NaNO₃] = 0.1 M</td>
<td>a = 1.971 x 10⁻³ M</td>
<td>T = 50°C</td>
<td></td>
<td></td>
</tr>
<tr>
<td>0.5</td>
<td>0.215</td>
<td>0.315</td>
<td>0.358</td>
<td>0.5</td>
<td>0.216</td>
<td>0.316</td>
<td>0.352</td>
</tr>
<tr>
<td>1.0</td>
<td>0.227</td>
<td>0.325</td>
<td>0.353</td>
<td>1.0</td>
<td>0.225</td>
<td>0.319</td>
<td>0.346</td>
</tr>
<tr>
<td>1.5</td>
<td>0.233</td>
<td>0.331</td>
<td>0.348</td>
<td>1.5</td>
<td>0.232</td>
<td>0.331</td>
<td>0.342</td>
</tr>
<tr>
<td>2.5</td>
<td>0.253</td>
<td>0.350</td>
<td>0.334</td>
<td>2.5</td>
<td>0.252</td>
<td>0.347</td>
<td>0.326</td>
</tr>
<tr>
<td>3.5</td>
<td>0.267</td>
<td>0.358</td>
<td>0.327</td>
<td>3.5</td>
<td>0.263</td>
<td>0.354</td>
<td>0.320</td>
</tr>
<tr>
<td>5.5</td>
<td>0.279</td>
<td>0.376</td>
<td>0.313</td>
<td>5.5</td>
<td>0.277</td>
<td>0.371</td>
<td>0.306</td>
</tr>
<tr>
<td>7.5</td>
<td>0.299</td>
<td>0.395</td>
<td>0.296</td>
<td>7.5</td>
<td>0.298</td>
<td>0.393</td>
<td>0.293</td>
</tr>
<tr>
<td>9.5</td>
<td>0.307</td>
<td>0.402</td>
<td>0.289</td>
<td>9.5</td>
<td>0.306</td>
<td>0.402</td>
<td>0.286</td>
</tr>
<tr>
<td>11.5</td>
<td>0.312</td>
<td>0.406</td>
<td>0.286</td>
<td>11.5</td>
<td>0.313</td>
<td>0.411</td>
<td>0.285</td>
</tr>
<tr>
<td>22.5</td>
<td>0.327</td>
<td>0.422</td>
<td>0.270</td>
<td>22.5</td>
<td>0.330</td>
<td>0.422</td>
<td>0.268</td>
</tr>
</tbody>
</table>
Table XXIX

ACID HYDROLYSIS OF Na\([\text{Co(YOH)Br}]\)

Optical Density Measured as a Function of Time

<table>
<thead>
<tr>
<th>Run 37</th>
<th>Run 38</th>
</tr>
</thead>
<tbody>
<tr>
<td>([\text{NaNO}_3]) = 0.1 M</td>
<td>([\text{NaNO}_3]) = 0.1 M</td>
</tr>
<tr>
<td>(a = 3.261 \times 10^{-3}\text{M})</td>
<td>(a = 1.870 \times 10^{-3}\text{M})</td>
</tr>
<tr>
<td>(T = 30^\circ\text{C})</td>
<td>(T = 30^\circ\text{C})</td>
</tr>
</tbody>
</table>

<table>
<thead>
<tr>
<th>Time (hrs)</th>
<th>0.D. 520</th>
<th>0.D. 540</th>
<th>0.D. 600</th>
<th>Time (hrs)</th>
<th>0.D. 520</th>
<th>0.D. 540</th>
<th>0.D. 600</th>
</tr>
</thead>
<tbody>
<tr>
<td>3</td>
<td>0.232</td>
<td>0.384</td>
<td>0.678</td>
<td>3</td>
<td>0.138</td>
<td>0.226</td>
<td>0.405</td>
</tr>
<tr>
<td>6</td>
<td>0.287</td>
<td>0.450</td>
<td>0.643</td>
<td>5</td>
<td>0.161</td>
<td>0.254</td>
<td>0.393</td>
</tr>
<tr>
<td>9</td>
<td>0.339</td>
<td>0.503</td>
<td>0.611</td>
<td>7.5</td>
<td>0.186</td>
<td>0.278</td>
<td>0.369</td>
</tr>
<tr>
<td>12</td>
<td>0.378</td>
<td>0.539</td>
<td>0.583</td>
<td>10.0</td>
<td>0.207</td>
<td>0.302</td>
<td>0.352</td>
</tr>
<tr>
<td>22</td>
<td>0.457</td>
<td>0.630</td>
<td>0.528</td>
<td>13.0</td>
<td>0.226</td>
<td>0.327</td>
<td>0.338</td>
</tr>
<tr>
<td>27</td>
<td>0.541</td>
<td>0.733</td>
<td>0.549</td>
<td>16.0</td>
<td>0.254</td>
<td>0.351</td>
<td>0.324</td>
</tr>
<tr>
<td>32</td>
<td>0.559</td>
<td>0.750</td>
<td>0.532</td>
<td>23.0</td>
<td>0.287</td>
<td>0.391</td>
<td>0.311</td>
</tr>
<tr>
<td>37</td>
<td>0.581</td>
<td>0.763</td>
<td>0.519</td>
<td>28</td>
<td>0.311</td>
<td>0.414</td>
<td>0.303</td>
</tr>
<tr>
<td>46.5</td>
<td>0.595</td>
<td>0.774</td>
<td>0.503</td>
<td>33</td>
<td>0.303</td>
<td>0.404</td>
<td>0.279</td>
</tr>
<tr>
<td>56.5</td>
<td>0.602</td>
<td>0.794</td>
<td>0.495</td>
<td>38</td>
<td>0.378</td>
<td>0.417</td>
<td>0.279</td>
</tr>
<tr>
<td>49.5</td>
<td>0.325</td>
<td>0.427</td>
<td>0.273</td>
<td></td>
<td></td>
<td></td>
<td></td>
</tr>
</tbody>
</table>

196
### Table XXX

**ACID HYDROLYSIS OF Na[Co(YOH)Br]**

Optical Density Measured as a Function of Time

<table>
<thead>
<tr>
<th>Run 39</th>
<th>Run 40</th>
</tr>
</thead>
</table>

- **NaNO$_3$** = 0.1 M  
  - **a** = 1.228 x 10$^{-3}$ M  
  - **T** = 40°C

- **NaNO$_3$** = 0.1 M  
  - **a** = 1.819 x 10$^{-3}$ M  
  - **T** = 40°C

<table>
<thead>
<tr>
<th>Time (hrs)</th>
<th>O.D. 520</th>
<th>O.D. 540</th>
<th>O.D. 600</th>
<th>Time (hrs)</th>
<th>O.D. 520</th>
<th>O.D. 540</th>
<th>O.D. 600</th>
</tr>
</thead>
<tbody>
<tr>
<td>1.25</td>
<td>0.106</td>
<td>0.165</td>
<td>0.264</td>
<td>1.50</td>
<td>0.158</td>
<td>0.245</td>
<td>0.372</td>
</tr>
<tr>
<td>2.75</td>
<td>0.131</td>
<td>0.198</td>
<td>0.239</td>
<td>3.00</td>
<td>0.212</td>
<td>0.301</td>
<td>0.350</td>
</tr>
<tr>
<td>4.25</td>
<td>0.151</td>
<td>0.213</td>
<td>0.219</td>
<td>4.50</td>
<td>0.245</td>
<td>0.338</td>
<td>0.330</td>
</tr>
<tr>
<td>5.75</td>
<td>0.167</td>
<td>0.228</td>
<td>0.206</td>
<td>6.0</td>
<td>0.264</td>
<td>0.336</td>
<td>0.300</td>
</tr>
<tr>
<td>9.25</td>
<td>0.181</td>
<td>0.247</td>
<td>0.193</td>
<td>7.5</td>
<td>0.279</td>
<td>0.371</td>
<td>0.292</td>
</tr>
<tr>
<td>11.25</td>
<td>0.190</td>
<td>0.257</td>
<td>0.189</td>
<td>9.0</td>
<td>0.289</td>
<td>0.384</td>
<td>0.283</td>
</tr>
<tr>
<td>13.25</td>
<td>0.198</td>
<td>0.266</td>
<td>0.181</td>
<td>10.5</td>
<td>0.299</td>
<td>0.395</td>
<td>0.275</td>
</tr>
<tr>
<td>15.25</td>
<td>0.202</td>
<td>0.271</td>
<td>0.178</td>
<td></td>
<td></td>
<td></td>
<td></td>
</tr>
<tr>
<td>27.25</td>
<td>0.205</td>
<td>0.273</td>
<td>0.176</td>
<td></td>
<td></td>
<td></td>
<td></td>
</tr>
<tr>
<td>39.75</td>
<td>0.213</td>
<td>0.281</td>
<td>0.173</td>
<td></td>
<td></td>
<td></td>
<td></td>
</tr>
</tbody>
</table>

197
Table XXXI

ACID HYDROLYSIS OF Na[Co(YOH)Br]

Optical Density Measured as a Function of Time

<table>
<thead>
<tr>
<th>Time (hrs)</th>
<th>Run 41</th>
<th>Run 42</th>
</tr>
</thead>
<tbody>
<tr>
<td></td>
<td>O.D. 520</td>
<td>O.D. 540</td>
</tr>
<tr>
<td>0.5</td>
<td>0.158</td>
<td>0.243</td>
</tr>
<tr>
<td>1.0</td>
<td>0.193</td>
<td>0.281</td>
</tr>
<tr>
<td>1.5</td>
<td>0.221</td>
<td>0.310</td>
</tr>
<tr>
<td>2.0</td>
<td>0.244</td>
<td>0.332</td>
</tr>
<tr>
<td>2.5</td>
<td>0.269</td>
<td>0.359</td>
</tr>
<tr>
<td>3.0</td>
<td>0.270</td>
<td>0.362</td>
</tr>
<tr>
<td>4.0</td>
<td>0.284</td>
<td>0.376</td>
</tr>
<tr>
<td>6.0</td>
<td>0.313</td>
<td>0.404</td>
</tr>
<tr>
<td>8.0</td>
<td>0.303</td>
<td>0.397</td>
</tr>
<tr>
<td>11.0</td>
<td>0.303</td>
<td>0.397</td>
</tr>
<tr>
<td>20.0</td>
<td>0.321</td>
<td>0.414</td>
</tr>
</tbody>
</table>
Table XXXII

ACID HYDROLYSIS OF Na[Co(HY)Br]

Optical Density Measured as a Function of Time

<table>
<thead>
<tr>
<th>Time (hrs)</th>
<th>Run 43 [St(NO₃)₂] = 0.1 M (a = 2.130 \times 10^{-3}M)</th>
<th>Temperature = 30°C</th>
<th>Run 44 [St(NO₃)₂] = 0.1 M (a = 2.004 \times 10^{-3}M)</th>
<th>Time (hrs)</th>
<th>O.D. 520</th>
<th>O.D. 540</th>
<th>O.D. 600</th>
</tr>
</thead>
<tbody>
<tr>
<td>3</td>
<td>0.194 0.303 0.493</td>
<td></td>
<td>3</td>
<td>0.177 0.286 0.461</td>
<td></td>
<td></td>
<td></td>
</tr>
<tr>
<td>6</td>
<td>0.244 0.350 0.467</td>
<td></td>
<td>6</td>
<td>0.224 0.326 0.437</td>
<td></td>
<td></td>
<td></td>
</tr>
<tr>
<td>9</td>
<td>0.280 0.378 0.447</td>
<td></td>
<td>9</td>
<td>0.259 0.354 0.422</td>
<td></td>
<td></td>
<td></td>
</tr>
<tr>
<td>12</td>
<td>0.313 0.408 0.437</td>
<td></td>
<td>12</td>
<td>0.292 0.387 0.406</td>
<td></td>
<td></td>
<td></td>
</tr>
<tr>
<td>15</td>
<td>0.340 0.436 0.424</td>
<td></td>
<td>15</td>
<td>0.317 0.406 0.400</td>
<td></td>
<td></td>
<td></td>
</tr>
<tr>
<td>21</td>
<td>0.378 0.471 0.392</td>
<td></td>
<td>21</td>
<td>0.354 0.444 0.370</td>
<td></td>
<td></td>
<td></td>
</tr>
<tr>
<td>24</td>
<td>0.396 0.483 0.384</td>
<td></td>
<td>24</td>
<td>0.372 0.456 0.364</td>
<td></td>
<td></td>
<td></td>
</tr>
<tr>
<td>30</td>
<td>0.419 0.506 0.372</td>
<td></td>
<td>30</td>
<td>0.394 0.473 0.350</td>
<td></td>
<td></td>
<td></td>
</tr>
<tr>
<td>38</td>
<td>0.444 0.536 0.358</td>
<td></td>
<td>38</td>
<td>0.420 0.501 0.335</td>
<td></td>
<td></td>
<td></td>
</tr>
<tr>
<td>48</td>
<td>0.470 0.553 0.342</td>
<td></td>
<td>48</td>
<td>0.442 0.515 0.321</td>
<td></td>
<td></td>
<td></td>
</tr>
<tr>
<td>59</td>
<td>0.497 0.568 0.332</td>
<td></td>
<td>59</td>
<td>0.459 0.539 0.313</td>
<td></td>
<td></td>
<td></td>
</tr>
<tr>
<td>74</td>
<td>0.529 0.597 0.328</td>
<td></td>
<td>74</td>
<td>0.501 0.576 0.325</td>
<td></td>
<td></td>
<td></td>
</tr>
</tbody>
</table>
Table XXXIII

ACID HYDROLYSIS OF Na[Co(HY)Br]

Calculated Concentrations of Reactant and Product

Run 1

\([\text{NaClO}_4]\) = 0.1 M

Initial Concentration, \(a = 1.997 \times 10^{-3} \text{M}\)

\(T = 30^\circ \text{C}\)

<table>
<thead>
<tr>
<th>Time (hrs)</th>
<th>Calc'd conc. at 520 and 600m(\mu) Conc. (x 10^3)</th>
<th>Calc'd conc. at 540 and 600m(\mu) Conc. (x 10^3)</th>
<th>Average Concentrations Conc. (x 10^3)</th>
</tr>
</thead>
<tbody>
<tr>
<td></td>
<td>((a-x) \times \text{Total})</td>
<td>((a-x) \times \text{Total})</td>
<td>((a-x) \times \text{Total})</td>
</tr>
<tr>
<td>1.33</td>
<td>1.986 0.072 2.058</td>
<td>1.994 0.058 2.052</td>
<td>1.990 0.065 2.055</td>
</tr>
<tr>
<td>2.33</td>
<td>1.918 0.131 2.049</td>
<td>1.918 0.131 2.049</td>
<td>1.918 0.131 2.049</td>
</tr>
<tr>
<td>3.33</td>
<td>1.829 0.203 2.032</td>
<td>1.811 0.232 2.043</td>
<td>1.820 0.218 2.038</td>
</tr>
<tr>
<td>4.33</td>
<td>1.791 0.239 2.030</td>
<td>1.795 0.239 2.034</td>
<td>1.793 0.239 2.032</td>
</tr>
<tr>
<td>6.00</td>
<td>1.726 0.319 2.045</td>
<td>1.727 0.319 2.046</td>
<td>1.726 0.319 2.045</td>
</tr>
<tr>
<td>11.00</td>
<td>1.540 0.508 2.048</td>
<td>1.522 0.544 2.066</td>
<td>1.531 0.527 2.058</td>
</tr>
<tr>
<td>14.00</td>
<td>1.428 0.639 2.067</td>
<td>1.423 0.645 2.068</td>
<td>1.426 0.642 2.068</td>
</tr>
<tr>
<td>18.00</td>
<td>1.300 0.762 2.062</td>
<td>1.280 0.791 2.071</td>
<td>1.290 0.776 2.066</td>
</tr>
<tr>
<td>23.00</td>
<td>1.167 0.907 2.074</td>
<td>1.152 0.929 2.081</td>
<td>1.160 0.918 2.078</td>
</tr>
<tr>
<td>27.50</td>
<td>1.071 0.994 2.065</td>
<td>1.054 1.028 2.082</td>
<td>1.062 1.011 2.073</td>
</tr>
<tr>
<td>38.50</td>
<td>0.902 1.182 2.084</td>
<td>0.888 1.205 2.093</td>
<td>0.895 1.196 2.091</td>
</tr>
<tr>
<td>52.00</td>
<td>0.757 1.342 2.099</td>
<td>0.737 1.379 2.116</td>
<td>0.747 1.356 2.103</td>
</tr>
</tbody>
</table>

Total average = 2.063 x 10^{-3} \text{M}
Table XXXIV
ACID HYDROLYSIS OF Na[Co(HY)Br]

Calculated Concentrations of Reactant and Product
Run 2
$[\text{NaClO}_4]= 0.1 \text{ M}$
Initial Concentration, a = $1.991 \times 10^{-3} \text{ M}$

<table>
<thead>
<tr>
<th>Time (hrs.)</th>
<th>Calc'd conc. at 520 and 600 m(\mu) Conc. x $10^{-3}$ moles/liter</th>
<th>Calc'd conc. at 540 and 600 m(\mu) Conc. x $10^{-3}$ moles/liter</th>
<th>Average Concentrations Conc. x $10^{-3}$ moles / liter</th>
</tr>
</thead>
<tbody>
<tr>
<td>3</td>
<td>1.889 0.138 2.027</td>
<td>1.886 0.145 2.031</td>
<td>1.888 0.142 2.030</td>
</tr>
<tr>
<td>6</td>
<td>1.734 0.304 2.038</td>
<td>1.742 0.290 2.032</td>
<td>1.738 0.297 2.035</td>
</tr>
<tr>
<td>10</td>
<td>1.538 0.472 2.010</td>
<td>1.535 0.479 2.014</td>
<td>1.536 0.476 2.012</td>
</tr>
<tr>
<td>15</td>
<td>1.398 0.624 2.022</td>
<td>1.393 0.639 2.032</td>
<td>1.396 0.632 2.028</td>
</tr>
<tr>
<td>18</td>
<td>1.270 0.740 2.010</td>
<td>1.260 0.755 2.015</td>
<td>1.265 0.748 2.013</td>
</tr>
<tr>
<td>21</td>
<td>1.223 0.791 2.014</td>
<td>1.210 0.813 2.023</td>
<td>1.216 0.802 2.018</td>
</tr>
<tr>
<td>26</td>
<td>1.141 0.878 2.019</td>
<td>1.121 0.907 2.028</td>
<td>1.131 0.892 2.023</td>
</tr>
<tr>
<td>30.5</td>
<td>1.040 1.001 2.041</td>
<td>1.028 1.023 2.051</td>
<td>1.034 1.012 2.046</td>
</tr>
<tr>
<td>37.5</td>
<td>0.929 1.074 2.003</td>
<td>0.928 1.074 2.002</td>
<td>0.928 1.074 2.002</td>
</tr>
<tr>
<td>47.0</td>
<td>0.837 1.183 2.020</td>
<td>0.828 1.197 2.025</td>
<td>0.832 1.190 2.022</td>
</tr>
<tr>
<td>64.5</td>
<td>0.660 1.320 1.980</td>
<td>0.550 1.516 2.066</td>
<td>0.605 1.418 2.023</td>
</tr>
<tr>
<td>75.5</td>
<td>0.540 1.408 1.948</td>
<td>0.507 1.466 1.973</td>
<td>0.524 1.437 1.961</td>
</tr>
</tbody>
</table>

Total average = $2.018 \times 10^{-3} \text{ M}$
Table XXXV

**ACID HYDROLYSIS OF Na[Co(HY)Br]**

Calculated Concentrations of Reactant and Product

Run 3

\[ [\text{NaClO}_4] = 0.05 \text{ M} \]
\[ [\text{HClO}_4] = 0.05 \text{ M} \]

Initial Concentration, \( a = 2.035 \times 10^{-3} \text{M} \)

\( T = 30^\circ \text{C} \)

<table>
<thead>
<tr>
<th>Time (hrs)</th>
<th>Calc'd conc. at 520 and 600m ( \mu ) Conc. x ( 10^3 ) moles/liter</th>
<th>Calc'd conc. at 540 and 600m ( \mu ) Conc. x ( 10^3 ) moles/liter</th>
<th>Average Concentrations Conc. x ( 10^3 ) moles/liter</th>
</tr>
</thead>
<tbody>
<tr>
<td></td>
<td>((\text{a-x}) \times \text{Total} )</td>
<td>((\text{a-x}) \times \text{Total} )</td>
<td>((\text{a-x}) \times \text{Total} )</td>
</tr>
<tr>
<td>3</td>
<td>1.745 0.174 1.919</td>
<td>1.730 0.247 1.977</td>
<td>1.738 0.211 1.949</td>
</tr>
<tr>
<td>6</td>
<td>1.618 0.348 1.966</td>
<td>1.588 0.399 1.987</td>
<td>1.603 0.373 1.976</td>
</tr>
<tr>
<td>9</td>
<td>1.489 0.508 1.997</td>
<td>1.480 0.522 2.002</td>
<td>1.484 0.516 2.000</td>
</tr>
<tr>
<td>12</td>
<td>1.361 0.653 2.014</td>
<td>1.364 0.639 2.003</td>
<td>1.363 0.646 2.009</td>
</tr>
<tr>
<td>15</td>
<td>1.266 0.718 1.984</td>
<td>1.255 0.733 1.988</td>
<td>1.260 0.726 1.986</td>
</tr>
<tr>
<td>21</td>
<td>1.103 0.885 1.988</td>
<td>1.083 0.922 2.005</td>
<td>1.093 0.903 1.996</td>
</tr>
<tr>
<td>24</td>
<td>1.044 0.958 2.002</td>
<td>1.044 0.958 2.002</td>
<td>1.044 0.958 2.002</td>
</tr>
<tr>
<td>29</td>
<td>0.952 1.030 1.982</td>
<td>0.942 1.045 1.987</td>
<td>0.947 1.038 1.985</td>
</tr>
<tr>
<td>35</td>
<td>0.878 1.110 1.988</td>
<td>0.857 1.154 2.011</td>
<td>0.868 1.132 2.000</td>
</tr>
<tr>
<td>48</td>
<td>0.764 1.248 2.012</td>
<td>0.749 1.270 2.019</td>
<td>0.756 1.259 2.015</td>
</tr>
<tr>
<td>60</td>
<td>0.672 1.328 2.000</td>
<td>0.653 1.357 2.010</td>
<td>0.662 1.342 2.004</td>
</tr>
<tr>
<td>75</td>
<td>0.570 1.400 1.970</td>
<td>0.539 1.451 1.990</td>
<td>0.554 1.425 1.979</td>
</tr>
</tbody>
</table>

Total average = \( 1.992 \times 10^{-3} \text{M} \)
Table XXXVI

ACID HYDROLYSIS OF Na\(\text{Co(HY)}\)Br

Calculated Concentrations of Reactant and Product

Run 4

\[\text{[NaClO}_4\text{]} = 0.05 \, \text{M}\]
\[\text{[HClO}_4\text{]} = 0.05 \, \text{M}\]

Initial Concentration, \(a = 2.042 \times 10^{-3} \, \text{M}\)

\(T = 30^\circ \text{C}\)

<table>
<thead>
<tr>
<th>Time (hrs)</th>
<th>Calc'd conc. at 520 and 600m(\mu) Conc(x) 10(^{+3}) moles/liter</th>
<th>Calc'd conc. at 540 and 600m(\mu) Conc(x) 10(^{+3}) moles/liter</th>
<th>Average Concentration Conc(x) 10(^{+3}) moles/liter</th>
</tr>
</thead>
<tbody>
<tr>
<td></td>
<td>(a-x) (x) Total</td>
<td>(a-x) (x) Total</td>
<td>(a-x) (x) Total</td>
</tr>
<tr>
<td>3</td>
<td>1.805 0.203 2.008</td>
<td>1.806 0.196 2.002</td>
<td>1.806 0.200 2.006</td>
</tr>
<tr>
<td>6</td>
<td>1.661 0.377 2.038</td>
<td>1.662 0.370 2.032</td>
<td>1.661 0.373 2.034</td>
</tr>
<tr>
<td>9</td>
<td>1.528 0.501 2.029</td>
<td>1.519 0.522 2.041</td>
<td>1.524 0.511 2.035</td>
</tr>
<tr>
<td>12</td>
<td>1.414 0.617 2.031</td>
<td>1.409 0.631 2.040</td>
<td>1.411 0.624 2.035</td>
</tr>
<tr>
<td>15</td>
<td>1.312 0.718 2.030</td>
<td>1.306 0.726 2.032</td>
<td>1.309 0.722 2.031</td>
</tr>
<tr>
<td>20</td>
<td>1.155 0.864 2.019</td>
<td>1.138 0.892 2.030</td>
<td>1.146 0.878 2.024</td>
</tr>
<tr>
<td>25</td>
<td>1.050 0.972 2.022</td>
<td>1.034 1.001 2.035</td>
<td>1.042 0.986 2.028</td>
</tr>
<tr>
<td>30.5</td>
<td>0.948 1.067 2.015</td>
<td>0.924 1.110 2.034</td>
<td>0.936 1.089 2.025</td>
</tr>
<tr>
<td>38</td>
<td>0.846 1.182 2.028</td>
<td>0.823 1.226 2.049</td>
<td>0.835 1.204 2.039</td>
</tr>
<tr>
<td>48</td>
<td>0.744 1.277 2.021</td>
<td>0.736 1.291 2.027</td>
<td>0.740 1.284 2.024</td>
</tr>
<tr>
<td>59</td>
<td>0.647 1.350 1.997</td>
<td>0.642 1.357 1.999</td>
<td>0.644 1.354 1.998</td>
</tr>
<tr>
<td>72</td>
<td>0.583 1.451 2.034</td>
<td>0.565 1.480 2.045</td>
<td>0.574 1.465 2.039</td>
</tr>
</tbody>
</table>

Total average = 2.026 \times 10^{-3} \, \text{M}
Table XXXVII
ACID HYDROLYSIS OF Na[Co(HY)Br]

Calculated Concentrations of Reactant and Product

Run 5

Initial Concentration, \( a = 2.122 \times 10^{-3} \) M

\( T = 30^\circ C \)

<table>
<thead>
<tr>
<th>Time (hrs)</th>
<th>Calc'd conc. at 520 and 600( \mu ) Conc. x ( 10^{+3} ) moles/liter</th>
<th>Calc'd conc. at 540 and 600( \mu ) Conc. x ( 10^{+3} ) moles/liter</th>
<th>Average Concentration Conc. x ( 10^{+3} ) moles/liter</th>
</tr>
</thead>
<tbody>
<tr>
<td>3</td>
<td>1.900 ( \times 10^{-1} ) 2.183 1.909 0.196 2.105</td>
<td>1.904 0.240 2.144</td>
<td>1.904 0.240 2.144</td>
</tr>
<tr>
<td>6</td>
<td>1.713 ( \times 10^{-1} ) 2.090 1.708 0.385 2.093</td>
<td>1.710 0.381 2.091</td>
<td>1.710 0.381 2.091</td>
</tr>
<tr>
<td>9</td>
<td>1.591 ( \times 10^{-1} ) 2.113 1.594 0.522 2.116</td>
<td>1.592 0.522 2.114</td>
<td>1.592 0.522 2.114</td>
</tr>
<tr>
<td>12</td>
<td>1.486 ( \times 10^{-1} ) 2.125 1.486 0.639 2.125</td>
<td>1.486 0.639 2.125</td>
<td>1.486 0.639 2.125</td>
</tr>
<tr>
<td>15</td>
<td>1.368 ( \times 10^{-1} ) 2.094 1.360 0.733 2.093</td>
<td>1.364 0.730 2.094</td>
<td>1.364 0.730 2.094</td>
</tr>
<tr>
<td>20</td>
<td>1.234 ( \times 10^{-1} ) 2.105 1.219 0.892 2.111</td>
<td>1.227 0.882 2.109</td>
<td>1.227 0.882 2.109</td>
</tr>
<tr>
<td>25</td>
<td>1.135 ( \times 10^{-1} ) 2.107 1.122 0.994 2.116</td>
<td>1.128 0.983 2.111</td>
<td>1.128 0.983 2.111</td>
</tr>
<tr>
<td>30.5</td>
<td>1.044 ( \times 10^{-1} ) 2.111 1.016 1.117 2.133</td>
<td>1.030 1.092 2.122</td>
<td>1.030 1.092 2.122</td>
</tr>
<tr>
<td>38</td>
<td>0.906 ( \times 10^{-1} ) 2.111 0.898 1.219 2.117</td>
<td>0.902 1.212 2.114</td>
<td>0.902 1.212 2.114</td>
</tr>
<tr>
<td>48</td>
<td>0.846 ( \times 10^{-1} ) 2.130 0.839 1.299 2.138</td>
<td>0.842 1.292 2.134</td>
<td>0.842 1.292 2.134</td>
</tr>
<tr>
<td>59</td>
<td>0.693 ( \times 10^{-1} ) 2.043 0.676 1.379 2.055</td>
<td>0.684 1.365 2.049</td>
<td>0.684 1.365 2.049</td>
</tr>
<tr>
<td>72</td>
<td>0.633 ( \times 10^{-1} ) 2.077 0.641 1.430 2.071</td>
<td>0.637 1.437 2.074</td>
<td>0.637 1.437 2.074</td>
</tr>
</tbody>
</table>

Total average = \( 2.107 \times 10^{-3} \) M
Table XXXVIII

ACID HYDROLYSIS OF Na[Co(HY)Br]

Calculated Concentrations of Reactant and Product

Run 6

[HClO₄] = 0.1 M

Initial Concentration, \( a = 2.020 \times 10^{-3} \text{M} \)

\( T = 30^\circ \text{C} \)

<table>
<thead>
<tr>
<th>Time (hrs)</th>
<th>( a-x )</th>
<th>Total (a-x)</th>
<th>X</th>
<th>Total</th>
<th>Calc'd Conc. at 520 and 600 m( \mu ) Conc. x ( 10^3 )</th>
<th>Calc'd Conc. at 540 and 600 m( \mu ) Conc. x ( 10^3 )</th>
<th>Average Concentration Conc. x ( 10^3 )</th>
</tr>
</thead>
<tbody>
<tr>
<td>3</td>
<td>1.788</td>
<td>0.196</td>
<td>1.984</td>
<td>1.785</td>
<td>0.203</td>
<td>1.988</td>
<td>1.786</td>
</tr>
<tr>
<td>6</td>
<td>1.627</td>
<td>0.370</td>
<td>1.997</td>
<td>1.643</td>
<td>0.341</td>
<td>1.984</td>
<td>1.635</td>
</tr>
<tr>
<td>9</td>
<td>1.515</td>
<td>0.479</td>
<td>1.994</td>
<td>1.514</td>
<td>0.486</td>
<td>2.000</td>
<td>1.514</td>
</tr>
<tr>
<td>12</td>
<td>1.403</td>
<td>0.595</td>
<td>1.998</td>
<td>1.398</td>
<td>0.602</td>
<td>2.000</td>
<td>1.400</td>
</tr>
<tr>
<td>15</td>
<td>1.320</td>
<td>0.682</td>
<td>2.002</td>
<td>1.310</td>
<td>0.697</td>
<td>2.007</td>
<td>1.315</td>
</tr>
<tr>
<td>20</td>
<td>1.169</td>
<td>0.820</td>
<td>1.989</td>
<td>1.158</td>
<td>0.842</td>
<td>2.000</td>
<td>1.163</td>
</tr>
<tr>
<td>25</td>
<td>1.081</td>
<td>0.914</td>
<td>1.995</td>
<td>1.064</td>
<td>0.943</td>
<td>2.007</td>
<td>1.073</td>
</tr>
<tr>
<td>30.5</td>
<td>0.979</td>
<td>1.016</td>
<td>1.995</td>
<td>0.958</td>
<td>1.052</td>
<td>2.010</td>
<td>0.968</td>
</tr>
<tr>
<td>38</td>
<td>0.878</td>
<td>1.096</td>
<td>1.974</td>
<td>0.842</td>
<td>1.161</td>
<td>2.003</td>
<td>0.860</td>
</tr>
<tr>
<td>48</td>
<td>0.800</td>
<td>1.212</td>
<td>2.012</td>
<td>0.782</td>
<td>1.241</td>
<td>2.023</td>
<td>0.791</td>
</tr>
<tr>
<td>59</td>
<td>0.672</td>
<td>1.284</td>
<td>1.956</td>
<td>0.662</td>
<td>1.299</td>
<td>1.961</td>
<td>0.667</td>
</tr>
<tr>
<td>72</td>
<td>0.649</td>
<td>1.343</td>
<td>1.992</td>
<td>0.622</td>
<td>1.393</td>
<td>2.015</td>
<td>0.635</td>
</tr>
</tbody>
</table>

Total average = 1.996 \times 10^{-3} \text{M}
Table XXXIX

ACID HYDROLYSIS OF Na[Co(HY)Br]

Calculated Concentrations of Reactant and Product

Run 7

$[\text{NaNO}_2] = 0.1 \text{ M}$

Initial Concentration, $a = 4.181 \times 10^{-3} \text{ M}$

$T = 30^\circ \text{C}$

<table>
<thead>
<tr>
<th>Time (hrs)</th>
<th>Calc'd conc. at 520 and 600 m $\mu$ Conc. x 10$^{-3}$</th>
<th>Calc'd conc. at 540 and 600 m $\mu$ Conc. x 10$^{-3}$</th>
<th>Average Concentration Conc. x 10$^{-3}$</th>
<th>Total average = $4.248 \times 10^{-3} \text{ M}$</th>
</tr>
</thead>
<tbody>
<tr>
<td>3.5</td>
<td>3.868 0.406 4.274</td>
<td>3.858 0.421 4.279</td>
<td>3.863 0.414 4.277</td>
<td></td>
</tr>
<tr>
<td>6.5</td>
<td>3.497 0.740 4.237</td>
<td>3.483 0.769 4.252</td>
<td>3.490 0.755 4.245</td>
<td></td>
</tr>
<tr>
<td>9.5</td>
<td>3.279 0.987 4.266</td>
<td>3.274 0.994 4.268</td>
<td>3.276 0.991 4.267</td>
<td></td>
</tr>
<tr>
<td>12.5</td>
<td>3.035 1.234 4.269</td>
<td>3.031 1.241 4.272</td>
<td>3.033 1.238 4.271</td>
<td></td>
</tr>
<tr>
<td>15.5</td>
<td>2.831 1.430 4.261</td>
<td>2.824 1.444 4.268</td>
<td>2.827 1.437 4.264</td>
<td></td>
</tr>
<tr>
<td>18.5</td>
<td>2.615 1.596 4.211</td>
<td>2.584 1.647 4.231</td>
<td>2.599 1.621 4.220</td>
<td></td>
</tr>
<tr>
<td>21.5</td>
<td>2.501 1.749 4.250</td>
<td>2.479 1.785 4.264</td>
<td>2.490 1.766 4.256</td>
<td></td>
</tr>
<tr>
<td>28.5</td>
<td>2.191 2.003 4.194</td>
<td>2.139 2.097 4.236</td>
<td>2.165 2.050 4.215</td>
<td></td>
</tr>
<tr>
<td>33.5</td>
<td>1.992 2.242 4.234</td>
<td>1.961 2.293 4.254</td>
<td>1.976 2.268 4.244</td>
<td></td>
</tr>
<tr>
<td>38.5</td>
<td>1.906 2.344 4.250</td>
<td>1.885 2.380 4.265</td>
<td>1.895 2.362 4.257</td>
<td></td>
</tr>
<tr>
<td>44.5</td>
<td>1.756 2.467 4.223</td>
<td>1.717 2.533 4.250</td>
<td>1.736 2.500 4.236</td>
<td></td>
</tr>
<tr>
<td>50.5</td>
<td>1.650 2.576 4.226</td>
<td>1.642 2.591 4.233</td>
<td>1.646 2.584 4.230</td>
<td></td>
</tr>
</tbody>
</table>

Total average = $4.248 \times 10^{-3} \text{ M}$
Table XL

ACID HYDROLYSIS OF Na[Co(HY)Br]

Calculated Concentrations of Reactant and Product

Run 8
\[ \text{[NaNO}_3\text{]} = 0.1 \text{ M} \]
Initial Concentration, \( a = 3.970 \times 10^{-3} \text{M} \)
\( T = 30^\circ \text{C} \)

<table>
<thead>
<tr>
<th>Time (hrs)</th>
<th>Calc'd conc. at 520 and 600 μ</th>
<th>Calc'd conc. at 540 and 600 μ</th>
<th>Average Concentration</th>
</tr>
</thead>
<tbody>
<tr>
<td></td>
<td>Conc. x 10⁺³ moles/liter</td>
<td>Conc. x 10⁺³ moles/liter</td>
<td>Conc. x 10⁺³ moles/liter</td>
</tr>
<tr>
<td></td>
<td>(a-x) x Total</td>
<td>(a-x) x Total</td>
<td>(a-x) x Total</td>
</tr>
<tr>
<td>2</td>
<td>3.620 0.232 3.852</td>
<td>3.625 0.225 3.850</td>
<td>3.622 0.229 3.851</td>
</tr>
<tr>
<td>4</td>
<td>3.478 0.414 3.892</td>
<td>3.480 0.406 3.886</td>
<td>3.479 0.410 3.889</td>
</tr>
<tr>
<td>6</td>
<td>3.231 0.624 3.855</td>
<td>3.229 0.624 3.853</td>
<td>3.230 0.634 3.854</td>
</tr>
<tr>
<td>8</td>
<td>2.986 0.820 3.806</td>
<td>2.962 0.864 3.826</td>
<td>2.976 0.844 3.820</td>
</tr>
<tr>
<td>10</td>
<td>2.920 0.994 3.914</td>
<td>2.920 0.994 3.914</td>
<td>2.920 0.994 3.914</td>
</tr>
<tr>
<td>12</td>
<td>2.649 1.219 3.868</td>
<td>2.622 1.263 3.885</td>
<td>2.635 1.241 3.876</td>
</tr>
<tr>
<td>16</td>
<td>2.401 1.466 3.867</td>
<td>2.400 1.466 3.866</td>
<td>2.401 1.466 3.867</td>
</tr>
<tr>
<td>23</td>
<td>2.123 1.756 3.879</td>
<td>2.103 1.792 3.895</td>
<td>2.113 1.774 3.887</td>
</tr>
<tr>
<td>29</td>
<td>1.897 1.988 3.885</td>
<td>1.887 2.010 3.897</td>
<td>1.892 2.004 3.896</td>
</tr>
<tr>
<td>35</td>
<td>1.718 2.148 3.866</td>
<td>1.678 2.221 3.899</td>
<td>1.698 2.185 3.883</td>
</tr>
<tr>
<td>46</td>
<td>1.466 2.351 3.817</td>
<td>1.415 2.438 3.853</td>
<td>1.440 2.395 3.835</td>
</tr>
<tr>
<td>59</td>
<td>1.246 2.576 3.822</td>
<td>1.191 2.670 3.861</td>
<td>1.218 2.623 3.841</td>
</tr>
<tr>
<td>71</td>
<td>1.114 2.707 3.821</td>
<td>1.078 2.772 3.850</td>
<td>1.096 2.740 3.836</td>
</tr>
</tbody>
</table>

Total average = 3.865 x 10⁻³ M
### Table XLI

**ACID HYDROLYSIS OF Na[Co(HY)Br]**

Calculated Concentrations of Reactant and Product

#### Run 9

| [NaNO₂] | 0.1 M
| Initial Concentration, a = 1.124 \times 10^{-3} M
| T = 30°C

<table>
<thead>
<tr>
<th>Time (hrs.)</th>
<th>Calc'd conc. at 520 and 600 m(\mu) Conc. x (10^3) moles/liter</th>
<th>Calc'd conc. at 540 and 600 m(\mu) Conc. x (10^3) moles/liter</th>
<th>Average Concentration Conc. x (10^3) moles/liter</th>
</tr>
</thead>
<tbody>
<tr>
<td>2</td>
<td>1.070 0.036 1.106</td>
<td>1.068 0.036 1.104</td>
<td>1.069 0.036 1.105</td>
</tr>
<tr>
<td>4</td>
<td>0.999 0.094 1.093</td>
<td>1.001 0.087 1.088</td>
<td>1.000 0.091 1.091</td>
</tr>
<tr>
<td>6</td>
<td>0.944 0.145 1.089</td>
<td>0.940 0.152 1.092</td>
<td>0.942 0.149 1.091</td>
</tr>
<tr>
<td>8</td>
<td>0.889 0.196 1.085</td>
<td>0.895 0.181 1.076</td>
<td>0.892 0.189 1.081</td>
</tr>
<tr>
<td>10</td>
<td>0.852 0.347 1.099</td>
<td>0.846 0.254 1.100</td>
<td>0.849 0.251 1.100</td>
</tr>
<tr>
<td>12</td>
<td>0.784 0.326 1.110</td>
<td>0.782 0.326 1.108</td>
<td>0.783 0.326 1.109</td>
</tr>
<tr>
<td>16</td>
<td>0.730 0.399 1.129</td>
<td>0.726 0.406 1.132</td>
<td>0.728 0.403 1.131</td>
</tr>
<tr>
<td>23</td>
<td>0.640 0.479 1.119</td>
<td>0.630 0.501 1.131</td>
<td>0.635 0.490 1.125</td>
</tr>
<tr>
<td>29</td>
<td>0.578 0.537 1.115</td>
<td>0.571 0.552 1.123</td>
<td>0.574 0.544 1.118</td>
</tr>
<tr>
<td>35</td>
<td>0.520 0.588 1.108</td>
<td>0.512 0.602 1.114</td>
<td>0.516 0.595 1.111</td>
</tr>
<tr>
<td>46</td>
<td>0.446 0.660 1.106</td>
<td>0.436 0.675 1.111</td>
<td>0.441 0.668 1.109</td>
</tr>
<tr>
<td>59</td>
<td>0.389 0.718 1.107</td>
<td>0.383 0.733 1.116</td>
<td>0.386 0.726 1.112</td>
</tr>
<tr>
<td>71</td>
<td>0.347 0.747 1.094</td>
<td>0.326 0.784 1.110</td>
<td>0.336 0.766 1.102</td>
</tr>
</tbody>
</table>

**Total average = 1.106 \times 10^{-3} M**
Table XLII

ACID HYDROLYSIS OF Na[Co(HY)Br]

Calculated Concentrations of Reactant and Product

Run 10

$[\text{NaNO}_3]= 0.1 \text{ M}$

Initial Concentration, $a = 1.062 \times 10^{-3}\text{M}$

$T = 30^\circ\text{C}$

<table>
<thead>
<tr>
<th>Time (hrs)</th>
<th>Calc'd. conc. at 520 and 600 nm</th>
<th>Average Concentration</th>
</tr>
</thead>
<tbody>
<tr>
<td></td>
<td>Conc. $\times 10^{-3}$/ moles/liter</td>
<td>Conc. $\times 10^{-3}$/ moles/liter</td>
</tr>
<tr>
<td></td>
<td>(a-x) x Total</td>
<td>(a-x) x Total</td>
</tr>
<tr>
<td>2</td>
<td>1.022 0.080 1.102</td>
<td>1.037 0.051 1.088</td>
</tr>
<tr>
<td>4</td>
<td>0.976 0.116 1.092</td>
<td>0.983 0.102 1.085</td>
</tr>
<tr>
<td>6</td>
<td>0.931 0.167 1.098</td>
<td>0.936 0.160 1.096</td>
</tr>
<tr>
<td>8</td>
<td>0.876 0.218 1.094</td>
<td>0.877 0.218 1.095</td>
</tr>
<tr>
<td>10</td>
<td>0.838 0.261 1.099</td>
<td>0.839 0.261 1.100</td>
</tr>
<tr>
<td>12</td>
<td>0.768 0.334 1.102</td>
<td>0.770 0.327 1.097</td>
</tr>
<tr>
<td>16</td>
<td>0.708 0.377 1.085</td>
<td>0.706 0.384 1.090</td>
</tr>
<tr>
<td>23</td>
<td>0.614 0.464 1.078</td>
<td>0.603 0.479 1.082</td>
</tr>
<tr>
<td>29</td>
<td>0.552 0.515 1.067</td>
<td>0.548 0.522 1.070</td>
</tr>
<tr>
<td>35</td>
<td>0.496 0.573 1.069</td>
<td>0.487 0.588 1.075</td>
</tr>
<tr>
<td>46</td>
<td>0.429 0.631 1.060</td>
<td>0.418 0.646 1.064</td>
</tr>
<tr>
<td>59</td>
<td>0.368 0.689 1.057</td>
<td>0.364 0.697 1.061</td>
</tr>
<tr>
<td>71</td>
<td>0.328 0.726 1.054</td>
<td>0.320 0.740 1.060</td>
</tr>
</tbody>
</table>

Total average = $1.082 \times 10^{-3}\text{M}$
Table XLIII
ACID HYDROLYSIS OF Na[Co(HY)Br]

Calculated Concentrations of Reactant and Product

Run 11
[NaBr] = 0.1 M
Initial Concentration, $a = 2.033 \times 10^{-3} M$
$T = 30^\circ C$

<table>
<thead>
<tr>
<th>Time (hrs)</th>
<th>Calc'd conc. at 520 and 600 m$\mu$ moles/liter</th>
<th>Calc'd conc. at 540 and 600 m$\mu$ moles/liter</th>
<th>Average Concentration moles/liter</th>
</tr>
</thead>
<tbody>
<tr>
<td></td>
<td>$(a-x)$ x Total</td>
<td>$(a-x)$ x Total</td>
<td>$(a-x)$ x Total</td>
</tr>
<tr>
<td>3</td>
<td>1.090 0.167 2.076</td>
<td>1.908 0.174 2.082</td>
<td>1.908 0.171 2.079</td>
</tr>
<tr>
<td>6</td>
<td>1.777 0.283 2.060</td>
<td>1.759 0.312 2.071</td>
<td>1.768 0.298 2.066</td>
</tr>
<tr>
<td>9</td>
<td>1.648 0.428 2.076</td>
<td>1.645 0.429 2.074</td>
<td>1.646 0.429 2.075</td>
</tr>
<tr>
<td>12</td>
<td>1.527 0.537 2.064</td>
<td>1.522 0.544 2.066</td>
<td>1.524 0.541 2.065</td>
</tr>
<tr>
<td>15</td>
<td>1.428 0.631 2.059</td>
<td>1.429 0.631 2.060</td>
<td>1.428 0.631 2.059</td>
</tr>
<tr>
<td>21</td>
<td>1.238 0.806 2.044</td>
<td>1.213 0.849 2.062</td>
<td>1.225 0.828 2.053</td>
</tr>
<tr>
<td>24</td>
<td>1.180 0.878 2.058</td>
<td>1.172 0.892 2.064</td>
<td>1.176 0.875 2.051</td>
</tr>
<tr>
<td>29</td>
<td>1.068 0.982 2.050</td>
<td>1.058 1.001 2.059</td>
<td>1.063 0.992 2.055</td>
</tr>
<tr>
<td>35</td>
<td>0.972 1.103 2.075</td>
<td>0.957 1.132 2.089</td>
<td>0.964 1.118 2.082</td>
</tr>
<tr>
<td>48</td>
<td>0.824 1.248 2.072</td>
<td>0.818 1.263 2.081</td>
<td>0.821 1.256 2.077</td>
</tr>
<tr>
<td>60</td>
<td>0.698 1.321 2.019</td>
<td>0.683 1.350 2.033</td>
<td>0.690 1.336 2.026</td>
</tr>
<tr>
<td>75</td>
<td>0.593 1.408 2.001</td>
<td>0.572 1.451 2.023</td>
<td>0.582 1.430 2.012</td>
</tr>
</tbody>
</table>

Total average = $2.058 \times 10^{-3} M$
Table XLIV

ACID HYDROLYSIS OF Na[Co(HY)Br]

Calculated Concentrations of Reactant and Product

Run 12

$[\text{NaBr}]= 0.1 \text{ M}$

Initial Concentration, $a = 2.004 \times 10^{-3} \text{M}$

$T = 30^\circ \text{C}$

<table>
<thead>
<tr>
<th>Time (hrs)</th>
<th>Calc'd. conc. at 520 and 600 m$\mu$ moles/liter</th>
<th>Calc'd. conc. at 540 and 600 m$\mu$ moles/liter</th>
<th>Average Concentration moles/liter</th>
</tr>
</thead>
<tbody>
<tr>
<td>3</td>
<td>1.926 x 10^{-3} 0.087 2.013</td>
<td>1.878 x 10^{-3} 0.174 2.052</td>
<td>1.902 x 10^{-3} 0.131 2.033</td>
</tr>
<tr>
<td>6</td>
<td>1.743 x 10^{-3} 0.319 2.062</td>
<td>1.756 x 10^{-3} 0.298 2.054</td>
<td>1.749 x 10^{-3} 0.309 2.058</td>
</tr>
<tr>
<td>9</td>
<td>1.634 x 10^{-3} 0.428 2.062</td>
<td>1.631 x 10^{-3} 0.435 2.066</td>
<td>1.632 x 10^{-3} 0.432 2.064</td>
</tr>
<tr>
<td>12</td>
<td>1.470 x 10^{-3} 0.537 2.007</td>
<td>1.467 x 10^{-3} 0.544 2.011</td>
<td>1.468 x 10^{-3} 0.541 2.009</td>
</tr>
<tr>
<td>15</td>
<td>1.382 x 10^{-3} 0.639 2.021</td>
<td>1.389 x 10^{-3} 0.624 2.013</td>
<td>1.386 x 10^{-3} 0.632 2.018</td>
</tr>
<tr>
<td>21</td>
<td>1.208 x 10^{-3} 0.798 2.006</td>
<td>1.188 x 10^{-3} 0.827 2.015</td>
<td>1.198 x 10^{-3} 0.813 2.011</td>
</tr>
<tr>
<td>24</td>
<td>1.154 x 10^{-3} 0.856 2.010</td>
<td>1.141 x 10^{-3} 0.878 2.019</td>
<td>1.147 x 10^{-3} 0.867 2.014</td>
</tr>
<tr>
<td>29</td>
<td>1.063 x 10^{-3} 0.936 1.999</td>
<td>1.046 x 10^{-3} 0.965 2.011</td>
<td>1.054 x 10^{-3} 0.951 2.005</td>
</tr>
<tr>
<td>35</td>
<td>0.949 x 10^{-3} 1.052 2.001</td>
<td>0.929 x 10^{-3} 1.081 2.010</td>
<td>0.939 x 10^{-3} 1.067 2.006</td>
</tr>
<tr>
<td>48</td>
<td>0.761 x 10^{-3} 1.205 1.966</td>
<td>0.747 x 10^{-3} 1.233 1.980</td>
<td>0.754 x 10^{-3} 1.219 1.973</td>
</tr>
<tr>
<td>60</td>
<td>0.678 x 10^{-3} 1.299 1.977</td>
<td>0.656 x 10^{-3} 1.342 1.998</td>
<td>0.667 x 10^{-3} 1.321 1.988</td>
</tr>
<tr>
<td>75</td>
<td>0.601 x 10^{-3} 1.379 1.980</td>
<td>0.572 x 10^{-3} 1.430 2.002</td>
<td>0.584 x 10^{-3} 1.405 1.989</td>
</tr>
</tbody>
</table>

Total average = $2.013 \times 10^{-3} \text{M}$
### Table XLV

**ACID HYDROLYSIS OF Na[Co(HY)Br]**

<table>
<thead>
<tr>
<th>Run 13</th>
<th>[<strong>NaNO₃</strong>] = 0.1 M</th>
<th>Initial concentration, a = 2.044 x 10⁻³ M</th>
<th>T = 30°C</th>
</tr>
</thead>
</table>

<table>
<thead>
<tr>
<th>Time (hrs)</th>
<th>Calc'd conc at 520 and 600m μ Conc x 10⁻³ moles/liter</th>
<th>Calc'd conc at 540 and 600m μ Conc x 10⁻³ moles/liter</th>
<th>Average Concentration Conc x 10⁻³ moles/liter</th>
</tr>
</thead>
<tbody>
<tr>
<td>3</td>
<td>1.913 0.188 2.101</td>
<td>1.918 0.181 2.099</td>
<td>1.916 0.184 2.100</td>
</tr>
<tr>
<td>6</td>
<td>1.796 0.317 2.113</td>
<td>1.798 0.319 2.117</td>
<td>1.797 0.318 2.115</td>
</tr>
<tr>
<td>10</td>
<td>1.606 0.479 2.085</td>
<td>1.607 0.472 2.079</td>
<td>1.606 0.476 2.082</td>
</tr>
<tr>
<td>15</td>
<td>1.428 0.639 2.067</td>
<td>1.425 0.645 2.070</td>
<td>1.426 0.642 2.068</td>
</tr>
<tr>
<td>18</td>
<td>1.331 0.748 2.079</td>
<td>1.323 0.761 2.084</td>
<td>1.327 0.754 2.081</td>
</tr>
<tr>
<td>21</td>
<td>1.262 0.812 2.074</td>
<td>1.256 0.820 2.076</td>
<td>1.259 0.816 2.075</td>
</tr>
<tr>
<td>26</td>
<td>1.175 0.885 2.060</td>
<td>1.144 0.936 2.080</td>
<td>1.160 0.910 2.070</td>
</tr>
<tr>
<td>30.5</td>
<td>1.053 1.016 2.069</td>
<td>1.033 1.052 2.095</td>
<td>1.043 1.034 2.077</td>
</tr>
<tr>
<td>37.5</td>
<td>0.969 1.096 2.065</td>
<td>0.960 1.110 2.070</td>
<td>0.964 1.098 2.062</td>
</tr>
<tr>
<td>47</td>
<td>0.866 1.234 2.100</td>
<td>0.849 1.262 2.111</td>
<td>0.858 1.248 2.106</td>
</tr>
<tr>
<td>64.5</td>
<td>0.697 1.371 2.068</td>
<td>0.674 1.408 2.082</td>
<td>0.686 1.388 2.074</td>
</tr>
<tr>
<td>75.5</td>
<td>0.624 1.444 2.068</td>
<td>0.602 1.480 2.082</td>
<td>0.614 1.462 2.076</td>
</tr>
</tbody>
</table>

Total average = 2.082 x 10⁻³ M
Table XLVI

ACID HYDROLYSIS OF Na[Co(HY)Br]

Calculated Concentrations of Reactant and Product

Run 14

[NaNO₂] = 0.1 M

Initial Concentration, a = 2.026 x 10⁻³ M

T = 30°C

<table>
<thead>
<tr>
<th>Time (hrs)</th>
<th>Calc'd conc. at 520 and 600μm</th>
<th>Calc'd conc. at 540 and 600μm</th>
<th>Average Concentration</th>
</tr>
</thead>
<tbody>
<tr>
<td></td>
<td>Conc x 10⁻³ moles/liter (a-x) x Total</td>
<td>Conc x 10⁻³ moles/liter (a-x) x Total</td>
<td>Conc x 10⁻³ moles/liter (a-x) x Total</td>
</tr>
<tr>
<td>3</td>
<td>1.950 0.065 2.015</td>
<td>1.900 0.145 2.045</td>
<td>1.925 0.105 2.030</td>
</tr>
<tr>
<td>6</td>
<td>1.778 0.298 2.076</td>
<td>1.783 0.283 2.066</td>
<td>1.780 0.290 2.070</td>
</tr>
<tr>
<td>10</td>
<td>1.586 0.464 2.050</td>
<td>1.586 0.464 2.050</td>
<td>1.586 0.464 2.050</td>
</tr>
<tr>
<td>15</td>
<td>1.398 0.639 2.037</td>
<td>1.398 0.639 2.033</td>
<td>1.396 0.639 2.035</td>
</tr>
<tr>
<td>18</td>
<td>1.302 0.747 2.049</td>
<td>1.301 0.747 2.048</td>
<td>1.302 0.747 2.049</td>
</tr>
<tr>
<td>21</td>
<td>1.239 0.834 2.073</td>
<td>1.250 0.820 2.070</td>
<td>1.244 0.827 2.071</td>
</tr>
<tr>
<td>26</td>
<td>1.149 0.929 2.078</td>
<td>1.135 0.950 2.085</td>
<td>1.142 0.940 2.082</td>
</tr>
<tr>
<td>30.5</td>
<td>1.047 1.001 2.048</td>
<td>1.023 1.044 2.067</td>
<td>1.035 1.023 2.058</td>
</tr>
<tr>
<td>37.5</td>
<td>0.976 1.088 2.064</td>
<td>0.954 1.124 2.078</td>
<td>0.965 1.106 2.071</td>
</tr>
<tr>
<td>47</td>
<td>0.866 1.219 2.085</td>
<td>0.847 1.255 2.102</td>
<td>0.856 1.237 2.093</td>
</tr>
<tr>
<td>64.5</td>
<td>0.704 1.343 2.047</td>
<td>0.713 1.328 2.041</td>
<td>0.708 1.335 2.043</td>
</tr>
<tr>
<td>75.5</td>
<td>0.622 1.408 2.030</td>
<td>0.597 1.465 2.062</td>
<td>0.609 1.436 2.045</td>
</tr>
</tbody>
</table>

Total average = 2.058 x 10⁻³ M
Table XLVII

ACID HYDROLYSIS OF Na[Co(HY)Br]

Calculated Concentrations of Reactant and Product

Run 15
Distilled Water
Initial Concentration, \( a = 2.117 \times 10^{-3} \text{M} \)
\( T = 30^\circ C \)

<table>
<thead>
<tr>
<th>Time (hrs)</th>
<th>Calc'd conc. at 520 and 600 m( \mu ) Conc. x ( 10^+3 ) moles/liter</th>
<th>Calc'd conc. at 540 and 600 m( \mu ) Conc. x ( 10^+3 ) moles/liter</th>
<th>Average Concentration Conc. x ( 10^+3 ) moles/liter</th>
</tr>
</thead>
<tbody>
<tr>
<td>3</td>
<td>( (a-x) = 1.990 \times 10^{-3} )</td>
<td>( (a-x) = 1.976 \times 10^{-3} )</td>
<td>( (a-x) = 2.128 \times 10^{-3} )</td>
</tr>
<tr>
<td>6</td>
<td>( (a-x) = 1.848 \times 10^{-3} )</td>
<td>( (a-x) = 1.817 \times 10^{-3} )</td>
<td>( (a-x) = 2.109 \times 10^{-3} )</td>
</tr>
<tr>
<td>13</td>
<td>( (a-x) = 1.540 \times 10^{-3} )</td>
<td>( (a-x) = 1.527 \times 10^{-3} )</td>
<td>( (a-x) = 2.113 \times 10^{-3} )</td>
</tr>
<tr>
<td>16</td>
<td>( (a-x) = 1.457 \times 10^{-3} )</td>
<td>( (a-x) = 1.451 \times 10^{-3} )</td>
<td>( (a-x) = 2.132 \times 10^{-3} )</td>
</tr>
<tr>
<td>20</td>
<td>( (a-x) = 1.327 \times 10^{-3} )</td>
<td>( (a-x) = 1.312 \times 10^{-3} )</td>
<td>( (a-x) = 2.125 \times 10^{-3} )</td>
</tr>
<tr>
<td>24</td>
<td>( (a-x) = 1.257 \times 10^{-3} )</td>
<td>( (a-x) = 1.247 \times 10^{-3} )</td>
<td>( (a-x) = 2.135 \times 10^{-3} )</td>
</tr>
<tr>
<td>31</td>
<td>( (a-x) = 1.143 \times 10^{-3} )</td>
<td>( (a-x) = 1.127 \times 10^{-3} )</td>
<td>( (a-x) = 2.166 \times 10^{-3} )</td>
</tr>
<tr>
<td>38</td>
<td>( (a-x) = 1.016 \times 10^{-3} )</td>
<td>( (a-x) = 1.003 \times 10^{-3} )</td>
<td>( (a-x) = 2.134 \times 10^{-3} )</td>
</tr>
<tr>
<td>45</td>
<td>( (a-x) = 0.939 \times 10^{-3} )</td>
<td>( (a-x) = 0.903 \times 10^{-3} )</td>
<td>( (a-x) = 2.129 \times 10^{-3} )</td>
</tr>
<tr>
<td>53</td>
<td>( (a-x) = 0.810 \times 10^{-3} )</td>
<td>( (a-x) = 0.777 \times 10^{-3} )</td>
<td>( (a-x) = 2.102 \times 10^{-3} )</td>
</tr>
<tr>
<td>63</td>
<td>( (a-x) = 0.730 \times 10^{-3} )</td>
<td>( (a-x) = 0.702 \times 10^{-3} )</td>
<td>( (a-x) = 2.109 \times 10^{-3} )</td>
</tr>
<tr>
<td>74.25</td>
<td>( (a-x) = 0.682 \times 10^{-3} )</td>
<td>( (a-x) = 0.662 \times 10^{-3} )</td>
<td>( (a-x) = 2.119 \times 10^{-3} )</td>
</tr>
</tbody>
</table>

Total average = \( 2.132 \times 10^{-3} \text{M} \)
XLVIII TABLE

ACID HYDROLYSIS OF Na[Co(HY)Br]

Calculated Concentrations of Reactant and Product
Run 16
Distilled Water
Initial Concentration, a = 2.011 x 10^{-3} M
T = 30°C

<table>
<thead>
<tr>
<th>Time (hrs)</th>
<th>Calc'd. conc. at 520 and 600 m /μ conc. x 10^3 moles/liter</th>
<th>Calc'd. cond. at 540 and 600 m /μ conc. x 10^3 moles/liter</th>
<th>Average Concentration conc. x 10^3 moles/liter</th>
</tr>
</thead>
<tbody>
<tr>
<td></td>
<td>(a-x) x Total</td>
<td>(a-x) x Total</td>
<td>(a-x) x Total</td>
</tr>
<tr>
<td>6</td>
<td>1.763 0.247 2.010</td>
<td>1.761 0.254 2.015</td>
<td>1.762 0.350 2.012</td>
</tr>
<tr>
<td>13</td>
<td>1.475 0.544 2.019</td>
<td>1.475 0.544 2.019</td>
<td>1.475 0.544 2.019</td>
</tr>
<tr>
<td>16</td>
<td>1.383 0.653 2.036</td>
<td>1.396 0.631 2.027</td>
<td>1.390 0.642 2.032</td>
</tr>
<tr>
<td>20</td>
<td>1.275 0.740 2.015</td>
<td>1.266 0.755 2.021</td>
<td>1.270 0.748 2.018</td>
</tr>
<tr>
<td>24</td>
<td>1.190 0.849 2.039</td>
<td>1.192 0.842 2.034</td>
<td>1.191 0.846 2.037</td>
</tr>
<tr>
<td>31</td>
<td>1.049 0.958 2.007</td>
<td>1.038 0.972 2.010</td>
<td>1.044 0.965 2.009</td>
</tr>
<tr>
<td>38</td>
<td>0.952 1.052 2.004</td>
<td>0.943 1.067 2.010</td>
<td>0.948 1.059 2.007</td>
</tr>
<tr>
<td>45</td>
<td>0.865 1.139 2.004</td>
<td>0.846 1.168 2.014</td>
<td>0.856 1.153 2.009</td>
</tr>
<tr>
<td>53</td>
<td>0.754 1.241 1.995</td>
<td>0.747 1.255 2.002</td>
<td>0.750 1.248 1.998</td>
</tr>
<tr>
<td>63</td>
<td>0.693 1.321 2.014</td>
<td>0.695 1.313 2.008</td>
<td>0.694 1.317 2.011</td>
</tr>
<tr>
<td>74.25</td>
<td>0.646 1.364 2.010</td>
<td>0.626 1.400 2.026</td>
<td>0.636 1.382 2.018</td>
</tr>
</tbody>
</table>

Total average = 2.016 x 10^{-3} M
Table XLIX

ACID HYDROLYSIS OF Na[Co(HY)Br]

Calculated Concentration of Reactant and Product

Run 17

\[ \text{[NaNO}_2\text{]} = 0.1 \text{ M} \]
\[ \text{[NaCo}^2\text{]} = 0.886 \times 10^{-3} \text{ M} \]

Initial Concentration, \( a = 1.643 \times 10^{-3} \text{ M} \)

\( T = 30^\circ \text{C} \)

<table>
<thead>
<tr>
<th>Time (hrs)</th>
<th>Calc'd conc at 520 and 600μμ</th>
<th>Calc'd conc at 540 and 600μμ</th>
<th>Average Concentration</th>
</tr>
</thead>
<tbody>
<tr>
<td></td>
<td>Conc. x 10^{-3}/moles/liter</td>
<td>Conc. x 10^{-3}/moles/liter</td>
<td>Conc. x 10^{-3}/moles/liter</td>
</tr>
<tr>
<td>3</td>
<td>1.584 0.123 1.707</td>
<td>1.580 0.131 1.711</td>
<td>1.582 0.127 1.709</td>
</tr>
<tr>
<td>6</td>
<td>1.464 0.247 1.711</td>
<td>1.404 0.348 1.752</td>
<td>1.434 0.298 1.732</td>
</tr>
<tr>
<td>9</td>
<td>1.360 0.356 1.716</td>
<td>1.259 0.537 1.796</td>
<td>1.309 0.446 1.756</td>
</tr>
<tr>
<td>12</td>
<td>1.158 0.537 1.695</td>
<td>1.090 0.653 1.743</td>
<td>1.124 0.595 1.719</td>
</tr>
<tr>
<td>17</td>
<td>1.021 0.660 1.681</td>
<td>0.947 0.784 1.731</td>
<td>0.984 0.724 1.708</td>
</tr>
<tr>
<td>22</td>
<td>0.954 0.740 1.694</td>
<td>0.889 0.856 1.745</td>
<td>0.921 0.798 1.719</td>
</tr>
<tr>
<td>28</td>
<td>0.867 0.813 1.680</td>
<td>0.814 0.907 1.721</td>
<td>0.840 0.860 1.700</td>
</tr>
<tr>
<td>34</td>
<td>0.788 0.892 1.680</td>
<td>0.732 0.994 1.726</td>
<td>0.760 0.943 1.703</td>
</tr>
<tr>
<td>42</td>
<td>0.711 0.988 1.691</td>
<td>0.669 1.050 1.719</td>
<td>0.690 1.015 1.705</td>
</tr>
<tr>
<td>54</td>
<td>0.601 1.081 1.682</td>
<td>0.568 1.139 1.707</td>
<td>0.584 1.110 1.694</td>
</tr>
<tr>
<td>64</td>
<td>0.543 1.110 1.653</td>
<td>0.499 1.190 1.689</td>
<td>0.521 1.145 1.666</td>
</tr>
</tbody>
</table>

Total average = \( 1.711 \times 10^{-3} \text{ M} \)
Table L

ACID HYDROLYSIS OF Na[Co(HY)Br]

Calculated Concentrations of Reactant and Product

Run 18

\[ [\text{NaNO}_2] = 0.1 \text{ M} \]
\[ [\text{NaCoY}] = 1.133 \times 10^{-3} \text{ M} \]

Initial Concentration, \( a = 1.503 \times 10^{-3} \text{ M} \)

\( T = 30^\circ \text{C} \)

<table>
<thead>
<tr>
<th>Time (hrs.)</th>
<th>Calc'd conc. at 520 and 600 m(\mu) Conc. x 10^3</th>
<th>Calc'd conc. at 540 and 600 m(\mu) Conc. x 10^3</th>
<th>Average Concentration Conc. x 10^3</th>
</tr>
</thead>
<tbody>
<tr>
<td></td>
<td>( (a-x) \times ) Total</td>
<td>( (a-x) \times ) Total</td>
<td>( (a-x) \times ) Total</td>
</tr>
<tr>
<td>3</td>
<td>1.467 0.102 1.569</td>
<td>1.465 0.102 1.567</td>
<td>1.466 0.102 1.568</td>
</tr>
<tr>
<td>6</td>
<td>1.323 0.218 1.541</td>
<td>1.307 0.247 1.554</td>
<td>1.315 0.232 1.547</td>
</tr>
<tr>
<td>9</td>
<td>1.258 0.312 1.570</td>
<td>1.249 0.326 1.575</td>
<td>1.253 0.319 1.572</td>
</tr>
<tr>
<td>12</td>
<td>1.063 0.508 1.571</td>
<td>1.066 0.508 1.574</td>
<td>1.064 0.508 1.572</td>
</tr>
<tr>
<td>17</td>
<td>0.949 0.617 1.566</td>
<td>0.954 0.602 1.556</td>
<td>0.951 0.610 1.561</td>
</tr>
<tr>
<td>22</td>
<td>0.888 0.689 1.577</td>
<td>0.889 0.689 1.578</td>
<td>0.888 0.689 1.577</td>
</tr>
<tr>
<td>28</td>
<td>0.787 0.769 1.556</td>
<td>0.796 0.755 1.551</td>
<td>0.791 0.762 1.553</td>
</tr>
<tr>
<td>34</td>
<td>0.740 0.820 1.560</td>
<td>0.745 0.813 1.558</td>
<td>0.742 0.817 1.559</td>
</tr>
<tr>
<td>42</td>
<td>0.684 0.900 1.584</td>
<td>0.667 0.929 1.596</td>
<td>0.675 0.915 1.590</td>
</tr>
<tr>
<td>54</td>
<td>0.573 0.936 1.509</td>
<td>0.551 0.972 1.523</td>
<td>0.562 0.954 1.516</td>
</tr>
<tr>
<td>64</td>
<td>0.509 1.023 1.532</td>
<td>0.503 1.060 1.563</td>
<td>0.506 1.042 1.548</td>
</tr>
</tbody>
</table>

Total average = 1.560x 10^{-3} \text{ M}
Table LI

ACID HYDROLYSIS OF Na[Co(HY)Br]

Calculated Concentrations of Reactant and Product

Run 19

$\text{HClO}_4 = 1.0 \text{ M}$

Initial Concentration, $a = 1.997 \times 10^{-3}$M

$T = 30^\circ \text{C}$

<table>
<thead>
<tr>
<th>Time (hrs)</th>
<th>Calc'd conc at 520 and 600m$\mu$ conc. x $10^{+3}$ moles/liter</th>
<th>Calc'd conc at 540 and 600m$\mu$ conc. x $10^{+3}$ moles/liter</th>
<th>Average Concentration conc. x $10^{+3}$ moles/liter</th>
</tr>
</thead>
<tbody>
<tr>
<td></td>
<td>(a-x) x Total</td>
<td>(a-x) x Total</td>
<td>(a-x) x Total</td>
</tr>
<tr>
<td>3</td>
<td>1.820 0.210 2.030</td>
<td>1.819 0.210 2.029</td>
<td>1.820 0.210 2.030</td>
</tr>
<tr>
<td>6</td>
<td>1.639 0.374 2.013</td>
<td>1.621 0.405 2.026</td>
<td>1.630 0.390 2.020</td>
</tr>
<tr>
<td>9</td>
<td>1.510 0.483 1.993</td>
<td>1.480 0.530 2.020</td>
<td>1.495 0.507 2.002</td>
</tr>
<tr>
<td>12</td>
<td>1.376 0.600 1.976</td>
<td>1.354 0.639 1.993</td>
<td>1.365 0.620 1.985</td>
</tr>
<tr>
<td>15</td>
<td>1.260 0.701 1.961</td>
<td>1.230 0.755 1.985</td>
<td>1.245 0.728 1.973</td>
</tr>
<tr>
<td>21</td>
<td>1.085 0.857 1.942</td>
<td>1.051 0.911 1.962</td>
<td>1.068 0.884 1.952</td>
</tr>
<tr>
<td>24</td>
<td>1.044 0.896 1.940</td>
<td>0.998 0.974 1.972</td>
<td>1.021 0.935 1.956</td>
</tr>
<tr>
<td>30</td>
<td>0.967 0.958 1.925</td>
<td>0.924 1.036 1.960</td>
<td>0.945 0.997 1.942</td>
</tr>
<tr>
<td>38</td>
<td>0.837 1.059 1.896</td>
<td>0.792 1.137 1.929</td>
<td>0.814 1.103 1.917</td>
</tr>
<tr>
<td>48</td>
<td>0.743 1.144 1.887</td>
<td>0.692 1.238 1.930</td>
<td>0.717 1.191 1.908</td>
</tr>
<tr>
<td>59</td>
<td>0.681 1.215 1.896</td>
<td>0.629 1.308 1.937</td>
<td>0.655 1.262 1.917</td>
</tr>
<tr>
<td>74</td>
<td>0.608 1.324 1.932</td>
<td>0.577 1.379 1.956</td>
<td>0.592 1.352 1.944</td>
</tr>
</tbody>
</table>

Total average $= 1.962 \times 10^{-3}$M

218
Table LII

ACID HYDROLYSIS OF Na[Co(HY)Br]

Calculated Concentrations of Reactant and Product

Run 20

\[ [\text{HClO}_4] = 1.0 \text{ M} \]

Initial Concentration, \( a = 2.017 \times 10^{-3} \text{M} \)

\( T = 30^\circ \text{C} \)

<table>
<thead>
<tr>
<th>Time (hrs)</th>
<th>Calc'd conc at 520 and 600m</th>
<th>Calc'd conc at 540 and 600m</th>
<th>Average Concentration</th>
</tr>
</thead>
<tbody>
<tr>
<td></td>
<td>500 m ( \text{m} )</td>
<td>540 m ( \text{m} )</td>
<td>Conc. ( x 10^+3 )</td>
</tr>
<tr>
<td></td>
<td>Conc. ( x 10^+3 ) moles/liter</td>
<td>Conc. ( x 10^+3 ) moles/liter</td>
<td>Conc. ( x 10^+3 ) moles/liter</td>
</tr>
<tr>
<td>3</td>
<td>1.845 0.202 2.047</td>
<td>1.852 0.187 2.039</td>
<td>1.848 0.195 2.043</td>
</tr>
<tr>
<td>6</td>
<td>1.698 0.343 2.041</td>
<td>1.685 0.366 2.051</td>
<td>1.691 0.355 2.046</td>
</tr>
<tr>
<td>13</td>
<td>1.356 0.693 2.049</td>
<td>1.325 0.740 2.065</td>
<td>1.340 0.717 2.057</td>
</tr>
<tr>
<td>16</td>
<td>1.254 0.810 2.064</td>
<td>1.237 0.841 2.078</td>
<td>1.245 0.826 2.071</td>
</tr>
<tr>
<td>20</td>
<td>1.152 0.864 2.016</td>
<td>1.102 0.950 2.052</td>
<td>1.127 0.903 2.030</td>
</tr>
<tr>
<td>24</td>
<td>1.058 0.958 2.016</td>
<td>1.010 1.044 2.054</td>
<td>1.034 1.001 2.035</td>
</tr>
<tr>
<td>31</td>
<td>0.959 1.059 2.018</td>
<td>0.898 1.168 2.066</td>
<td>0.928 1.114 2.042</td>
</tr>
<tr>
<td>38</td>
<td>0.871 1.121 1.992</td>
<td>0.816 1.223 2.039</td>
<td>0.843 1.172 2.015</td>
</tr>
<tr>
<td>45</td>
<td>0.787 1.199 1.986</td>
<td>0.726 1.308 2.034</td>
<td>0.756 1.254 2.010</td>
</tr>
<tr>
<td>53</td>
<td>0.693 1.301 1.994</td>
<td>0.648 1.386 2.034</td>
<td>0.670 1.344 2.014</td>
</tr>
<tr>
<td>63</td>
<td>0.580 1.347 1.997</td>
<td>0.598 1.441 2.039</td>
<td>0.624 1.394 2.018</td>
</tr>
<tr>
<td>74.25</td>
<td>0.598 1.433 2.031</td>
<td>0.553 1.510 2.063</td>
<td>0.576 1.472 2.048</td>
</tr>
</tbody>
</table>

Total average = 2.036 \( x 10^{-3} \text{M} \)

219
Table LIII
ACID HYDROLYSIS OF Na[Co(HY)Br]

Calculated Concentrations of Reactant and Product
Run 21
$[\text{NaNO}_3] = 0.1 \text{ M}$
Initial Concentration, $a = 2.173 \times 10^{-3} \text{ M}$
$T = 40^\circ \text{C}$

<table>
<thead>
<tr>
<th>Time (hrs)</th>
<th>Calc'd Conc. at 520 and 600$\mu$m (a-x) x Total</th>
<th>Calc'd Conc. at 540 and 600$\mu$m (a-x) x Total</th>
<th>Average Conc. (a-x) x Total</th>
</tr>
</thead>
<tbody>
<tr>
<td>1.50</td>
<td>1.902 0.239 2.141</td>
<td>1.906 0.232 2.138</td>
<td>1.904 0.236 2.140</td>
</tr>
<tr>
<td>3.00</td>
<td>1.706 0.501 2.207</td>
<td>1.714 0.486 2.200</td>
<td>1.710 0.494 2.204</td>
</tr>
<tr>
<td>4.50</td>
<td>1.509 0.682 2.191</td>
<td>1.502 0.697 2.199</td>
<td>1.505 0.690 2.195</td>
</tr>
<tr>
<td>6.50</td>
<td>1.307 0.827 2.134</td>
<td>1.305 0.827 2.132</td>
<td>1.306 0.827 2.133</td>
</tr>
<tr>
<td>7.50</td>
<td>1.207 0.929 2.136</td>
<td>1.187 0.958 2.145</td>
<td>1.197 0.944 2.141</td>
</tr>
<tr>
<td>9.00</td>
<td>1.119 1.023 2.142</td>
<td>1.102 1.052 2.154</td>
<td>1.111 1.038 2.149</td>
</tr>
<tr>
<td>10.50</td>
<td>1.028 1.110 2.138</td>
<td>1.014 1.132 2.146</td>
<td>1.021 1.121 2.142</td>
</tr>
</tbody>
</table>

Total average = $2.158 \times 10^{-3} \text{ M}$
Table LIV

ACID HYDROLYSIS OF Na[Co(HY)Br]

Calculated Concentrations of Reactant and Product

Run 22

\[ \text{[NaNO}_3\text{]} = 0.1 \text{ M} \]

Initial Concentration, \( a = 2.221 \times 10^{-3} \text{M} \)

\( T = 40^\circ \text{C} \)

<table>
<thead>
<tr>
<th>Time (hrs)</th>
<th>Calc'd Conc. at 520 and 600 m( \mu ) Conc. ( \times 10^3 ) moles/liter</th>
<th>Calc'd Conc. at 540 and 600 m( \mu ) Conc. ( \times 10^3 ) moles/liter</th>
<th>Average Concentration Conc. ( \times 10^3 ) moles/liter</th>
</tr>
</thead>
<tbody>
<tr>
<td>1.50</td>
<td>1.928 0.312 2.240</td>
<td>1.933 0.305 2.238</td>
<td>1.930 0.309 2.239</td>
</tr>
<tr>
<td>3.00</td>
<td>1.731 0.544 2.275</td>
<td>1.745 0.530 2.275</td>
<td>1.738 0.537 2.275</td>
</tr>
<tr>
<td>4.50</td>
<td>1.519 0.718 2.237</td>
<td>1.517 0.718 2.235</td>
<td>1.518 0.718 2.236</td>
</tr>
<tr>
<td>6.00</td>
<td>1.339 0.864 2.203</td>
<td>1.331 0.878 2.209</td>
<td>1.335 0.871 2.206</td>
</tr>
<tr>
<td>7.50</td>
<td>1.245 0.965 2.210</td>
<td>1.237 0.980 2.217</td>
<td>1.241 0.973 2.214</td>
</tr>
<tr>
<td>9.00</td>
<td>1.157 1.060 2.217</td>
<td>1.141 1.089 2.230</td>
<td>1.149 1.075 2.224</td>
</tr>
<tr>
<td>10.50</td>
<td>1.081 1.146 2.227</td>
<td>1.067 1.168 2.235</td>
<td>1.074 1.157 2.231</td>
</tr>
</tbody>
</table>

Total average = \( 2.232 \times 10^{-3} \text{M} \)
Table LV

ACID HYDROLYSIS OF Na[Co(HY)Br]

Calculated Concentrations of Reactant and Product

Run 23

\[ [\text{NaNO}_3] = 0.1 \text{ M} \]

Initial Concentration, \( a = 1.899 \times 10^{-3} \text{M} \)

\( T = 50^\circ \text{C} \)

<table>
<thead>
<tr>
<th>Time (hrs)</th>
<th>Calc'd. conc. at 520 and 600(\mu) Conc. x (10^3) moles/liter</th>
<th>Calc'd. conc. at 540 and 600(\mu) Conc. x (10^3) moles/liter</th>
<th>Average Conc. x (10^3) moles/liter</th>
</tr>
</thead>
<tbody>
<tr>
<td>1</td>
<td>1.429 0.428 1.857</td>
<td>1.421 0.443 1.864</td>
<td>1.425 0.436 1.861</td>
</tr>
<tr>
<td>2</td>
<td>1.182 0.675 1.857</td>
<td>1.175 0.689 1.864</td>
<td>1.178 0.682 1.860</td>
</tr>
<tr>
<td>2.5</td>
<td>1.103 0.776 1.879</td>
<td>1.095 0.791 1.886</td>
<td>1.099 0.784 1.883</td>
</tr>
<tr>
<td>3.0</td>
<td>1.012 0.842 1.854</td>
<td>0.989 0.885 1.874</td>
<td>1.001 0.866 1.867</td>
</tr>
<tr>
<td>3.5</td>
<td>0.956 0.922 1.878</td>
<td>0.935 0.958 1.893</td>
<td>0.945 0.940 1.885</td>
</tr>
<tr>
<td>4.5</td>
<td>0.762 1.096 1.858</td>
<td>0.748 1.125 1.873</td>
<td>0.755 1.111 1.866</td>
</tr>
<tr>
<td>5.5</td>
<td>0.721 1.139 1.860</td>
<td>0.691 1.190 1.881</td>
<td>0.706 1.160 1.866</td>
</tr>
<tr>
<td>9.75</td>
<td>0.555 1.350 1.905</td>
<td>0.537 1.379 1.916</td>
<td>0.546 1.366 1.912</td>
</tr>
</tbody>
</table>

Total average = 1.870 x \(10^{-3}\)M
Table LVI

ACID HYDROLYSIS OF Na[Co(HY)Br]

Calculated Concentrations of Reactant and Product

Run 24

[NaNO₂] = 0.1 M
Initial Concentration, a = 1.860 x 10⁻³ M
T = 50°C

<table>
<thead>
<tr>
<th>Time (hrs)</th>
<th>Calc'd conc. at 520 and 600 μm</th>
<th>Calc'd conc. at 540 and 600 μm</th>
<th>Average Concentration</th>
</tr>
</thead>
<tbody>
<tr>
<td></td>
<td>Conc. x 10⁻³ moles/liter</td>
<td>Conc. x 10⁻³ moles/liter</td>
<td>Conc. x 10⁻³ moles/liter</td>
</tr>
<tr>
<td>1</td>
<td>1.460 0.421 1.881</td>
<td>1.455 0.428 1.883</td>
<td>0.425 0.425 1.882</td>
</tr>
<tr>
<td>2</td>
<td>1.189 0.668 1.857</td>
<td>1.178 0.689 1.867</td>
<td>1.188 0.679 1.867</td>
</tr>
<tr>
<td>2.5</td>
<td>1.122 0.754 1.876</td>
<td>1.106 0.783 1.889</td>
<td>1.114 0.769 1.883</td>
</tr>
<tr>
<td>3.0</td>
<td>1.015 0.871 1.886</td>
<td>1.008 0.878 1.886</td>
<td>1.011 0.875 1.886</td>
</tr>
<tr>
<td>3.5</td>
<td>0.961 0.929 1.890</td>
<td>0.946 0.951 1.897</td>
<td>0.953 0.940 1.893</td>
</tr>
<tr>
<td>4.5</td>
<td>0.769 1.067 1.836</td>
<td>0.735 1.132 1.867</td>
<td>0.752 1.100 1.852</td>
</tr>
<tr>
<td>5.5</td>
<td>0.727 1.118 1.845</td>
<td>0.703 1.161 1.864</td>
<td>0.715 1.142 1.857</td>
</tr>
<tr>
<td>9.75</td>
<td>0.546 1.328 1.874</td>
<td>0.526 1.357 1.883</td>
<td>0.535 1.343 1.878</td>
</tr>
</tbody>
</table>

Total average = 1.874 x 10⁻³ M

223
Table LVII

ACID HYDROLYSIS OF Na[Co(HY)Cl]

Calculated Concentrations of Reactant and Product

Run 25

\[ \text{[NaNO}_3\text{]} = 0.1 \text{ M} \]

Initial Concentration, \( a = 2.245 \times 10^{-3} \text{ M} \)

\[ T = 30^\circ \text{C} \]

<table>
<thead>
<tr>
<th>Time (hrs)</th>
<th>((a-x)) (x) Total</th>
<th>Calc'd Conc. at 520 and 600(\mu)</th>
<th>Conc. (x 10^3)</th>
<th>Calc'd Conc. at 540 and 600(\mu)</th>
<th>Conc. (x 10^3)</th>
<th>Average Concentration</th>
<th>Conc. (x 10^3)</th>
</tr>
</thead>
<tbody>
<tr>
<td>3</td>
<td>2.204 0.038 2.242</td>
<td>2.201 0.046 2.247</td>
<td>2.202 0.042 2.242</td>
<td></td>
<td></td>
<td></td>
<td></td>
</tr>
<tr>
<td>5.0</td>
<td>2.141 0.093 2.234</td>
<td>2.136 0.100 2.236</td>
<td>2.138 0.097 2.235</td>
<td></td>
<td></td>
<td></td>
<td></td>
</tr>
<tr>
<td>7.5</td>
<td>2.095 0.139 2.234</td>
<td>2.091 0.147 2.238</td>
<td>2.093 0.143 2.236</td>
<td></td>
<td></td>
<td></td>
<td></td>
</tr>
<tr>
<td>10.0</td>
<td>2.057 0.185 2.242</td>
<td>2.055 0.185 2.240</td>
<td>2.056 0.185 2.241</td>
<td></td>
<td></td>
<td></td>
<td></td>
</tr>
<tr>
<td>13.0</td>
<td>2.024 0.208 2.232</td>
<td>2.022 0.216 2.238</td>
<td>2.023 0.212 2.235</td>
<td></td>
<td></td>
<td></td>
<td></td>
</tr>
<tr>
<td>17.0</td>
<td>1.960 0.262 2.222</td>
<td>1.955 0.278 2.233</td>
<td>1.957 0.269 2.226</td>
<td></td>
<td></td>
<td></td>
<td></td>
</tr>
<tr>
<td>24.0</td>
<td>1.838 0.378 2.216</td>
<td>1.828 0.394 2.222</td>
<td>1.833 0.386 2.219</td>
<td></td>
<td></td>
<td></td>
<td></td>
</tr>
<tr>
<td>29.0</td>
<td>1.756 0.463 2.219</td>
<td>1.752 0.471 2.223</td>
<td>1.754 0.467 2.221</td>
<td></td>
<td></td>
<td></td>
<td></td>
</tr>
<tr>
<td>34.0</td>
<td>1.675 0.540 2.215</td>
<td>1.674 0.540 2.214</td>
<td>1.674 0.540 2.214</td>
<td></td>
<td></td>
<td></td>
<td></td>
</tr>
<tr>
<td>39.0</td>
<td>1.639 0.586 2.225</td>
<td>1.610 0.634 2.244</td>
<td>1.624 0.610 2.234</td>
<td></td>
<td></td>
<td></td>
<td></td>
</tr>
<tr>
<td>50.5</td>
<td>1.454 0.763 2.217</td>
<td>1.453 0.763 2.216</td>
<td>1.453 0.763 2.216</td>
<td></td>
<td></td>
<td></td>
<td></td>
</tr>
</tbody>
</table>

Total average = \(2.239 \times 10^{-3}\text{M}\)
### Table LVIII

**ACID HYDROLYSIS OF Na[(Co(HY)Cl)]**

**Calculated Concentrations of Reactant and Product**

**Run 26**

\[
\text{[NaNO}_3\text{]} = 0.1 \text{ M}
\]

Initial Concentration, \( a = 2.363 \times 10^{-3} \text{M} \)

**T - 30°C**

<table>
<thead>
<tr>
<th>Time (hrs.)</th>
<th>Calc'd conc. at 520 and 600 m ( \mu )</th>
<th>Calc'd conc. at 540 and 600 m ( \mu )</th>
<th>Average Concentration</th>
</tr>
</thead>
<tbody>
<tr>
<td></td>
<td>Conc. ( \times 10^{-3} ) moles/liter</td>
<td>Conc. ( \times 10^{-3} ) moles/liter</td>
<td>Conc. ( \times 10^{-3} ) moles/liter</td>
</tr>
<tr>
<td></td>
<td>(a-x) x Total</td>
<td>(a-x) x Total</td>
<td>(a-x) x Total</td>
</tr>
<tr>
<td>3</td>
<td>2.307 0.058 2.365</td>
<td>2.306 0.058 2.364</td>
<td>2.307 0.058 2.365</td>
</tr>
<tr>
<td>5.0</td>
<td>2.269 0.131 2.400</td>
<td>2.265 0.139 2.404</td>
<td>2.267 0.135 2.402</td>
</tr>
<tr>
<td>7.5</td>
<td>2.231 0.154 2.385</td>
<td>2.227 0.162 2.389</td>
<td>2.229 0.158 2.387</td>
</tr>
<tr>
<td>10.0</td>
<td>2.182 0.208 2.390</td>
<td>2.184 0.201 2.385</td>
<td>2.183 0.204 2.387</td>
</tr>
<tr>
<td>13.0</td>
<td>2.140 0.239 2.379</td>
<td>2.136 0.247 2.383</td>
<td>2.138 0.243 2.381</td>
</tr>
<tr>
<td>17.0</td>
<td>2.073 0.293 2.366</td>
<td>2.073 0.293 2.366</td>
<td>2.073 0.293 2.366</td>
</tr>
<tr>
<td>24.0</td>
<td>1.930 0.424 2.354</td>
<td>1.927 0.424 2.351</td>
<td>1.928 0.424 2.352</td>
</tr>
<tr>
<td>29.0</td>
<td>1.866 0.502 2.368</td>
<td>1.864 0.502 2.366</td>
<td>1.865 0.502 2.367</td>
</tr>
<tr>
<td>34.0</td>
<td>1.781 0.563 2.344</td>
<td>1.770 0.579 2.349</td>
<td>1.776 0.571 2.347</td>
</tr>
<tr>
<td>39.0</td>
<td>1.690 0.664 2.354</td>
<td>1.682 0.679 2.361</td>
<td>1.686 0.672 2.358</td>
</tr>
<tr>
<td>50.5</td>
<td>1.510 0.872 2.382</td>
<td>1.508 0.872 2.380</td>
<td>1.509 0.872 2.381</td>
</tr>
</tbody>
</table>

Total average = \( 2.372 \times 10^{-3} \text{M} \)

---

225
Table IX

ACID HYDROLYSIS OF Na[Co(HY)Cl]

Calculated Concentrations of Reactant and Product

Run 27

\[ \text{[NaNO}_3\] = 0.1 \text{ M} \]

Initial Concentration, \( a = 1.809 \times 10^{-3}\text{M} \)

\( T = 40^\circ\text{C} \)

<table>
<thead>
<tr>
<th>Time (hrs)</th>
<th>(a-x) x Total</th>
<th>Calc'd conc at 520 and 600m( \mu ) Conc. x ( 10^3)</th>
<th>Calcd. conc at 540 and 600m( \mu ) Conc. x ( 10^3)</th>
<th>Average Concentration Conc. x ( 10^3)</th>
</tr>
</thead>
<tbody>
<tr>
<td>1.25</td>
<td>1.788 0.044 1.832</td>
<td>1.791 0.022 1.813</td>
<td>1.790 0.033 1.823</td>
<td></td>
</tr>
<tr>
<td>2.75</td>
<td>1.664 0.108 1.772</td>
<td>1.664 0.108 1.772</td>
<td>1.664 0.108 1.772</td>
<td></td>
</tr>
<tr>
<td>4.25</td>
<td>1.618 0.162 1.780</td>
<td>1.618 0.162 1.780</td>
<td>1.618 0.162 1.780</td>
<td></td>
</tr>
<tr>
<td>5.75</td>
<td>1.558 0.239 1.797</td>
<td>1.561 0.231 1.792</td>
<td>1.560 0.235 1.795</td>
<td></td>
</tr>
<tr>
<td>7.25</td>
<td>1.507 0.309 1.816</td>
<td>1.516 0.293 1.809</td>
<td>1.512 0.301 1.813</td>
<td></td>
</tr>
<tr>
<td>9.25</td>
<td>1.451 0.378 1.829</td>
<td>1.450 0.378 1.828</td>
<td>1.450 0.378 1.828</td>
<td></td>
</tr>
<tr>
<td>11.25</td>
<td>1.360 0.447 1.807</td>
<td>1.353 0.463 1.816</td>
<td>1.356 0.455 1.811</td>
<td></td>
</tr>
<tr>
<td>13.25</td>
<td>1.269 0.532 1.801</td>
<td>1.264 0.540 1.804</td>
<td>1.266 0.536 1.802</td>
<td></td>
</tr>
<tr>
<td>15.25</td>
<td>1.200 0.586 1.786</td>
<td>1.204 0.579 1.783</td>
<td>1.202 0.582 1.784</td>
<td></td>
</tr>
<tr>
<td>27.25</td>
<td>0.889 0.879 1.768</td>
<td>0.866 0.918 1.784</td>
<td>0.877 0.899 1.776</td>
<td></td>
</tr>
<tr>
<td>39.75</td>
<td>0.578 1.204 1.782</td>
<td>0.585 1.188 1.773</td>
<td>0.581 1.196 1.777</td>
<td></td>
</tr>
</tbody>
</table>

Total average = \( 1.797 \times 10^{-3}\text{M} \)

226
Table LX
ACID HYDROLYSIS OF Na[Co(HY)Cl]

Calculated Concentrations of Reactant and Product

Run 28
Initial Concentration, \( a = 2.199 \times 10^{-3} \text{M} \)
\( T = 40^\circ C \)
\( [\text{NaNO}_3] = 0.1 \text{ M} \)

<table>
<thead>
<tr>
<th>Time (hrs)</th>
<th>Calc'd conc at 520 and 600 ( \mu ) moles/liter ( \times 10^{-3} )</th>
<th>Calc'd conc at 540 and 600 ( \mu ) moles/liter ( \times 10^{-3} )</th>
<th>Average Concentration ( \times 10^{-3} ) moles/liter</th>
</tr>
</thead>
<tbody>
<tr>
<td>4.25</td>
<td>1.948 0.239 2.187</td>
<td>1.957 0.224 2.181</td>
<td>1.952 0.232 2.184</td>
</tr>
<tr>
<td>5.75</td>
<td>1.880 0.309 2.189</td>
<td>1.891 0.293 2.184</td>
<td>1.885 0.301 2.186</td>
</tr>
<tr>
<td>7.25</td>
<td>1.820 0.386 2.206</td>
<td>1.828 0.370 2.198</td>
<td>1.824 0.378 2.202</td>
</tr>
<tr>
<td>9.25</td>
<td>1.716 0.494 2.210</td>
<td>1.718 0.494 2.212</td>
<td>1.717 0.494 2.211</td>
</tr>
<tr>
<td>11.25</td>
<td>1.604 0.617 2.221</td>
<td>1.610 0.602 2.212</td>
<td>1.607 0.610 2.217</td>
</tr>
<tr>
<td>13.25</td>
<td>1.535 0.671 2.206</td>
<td>1.538 0.663 2.201</td>
<td>1.536 0.667 2.203</td>
</tr>
<tr>
<td>15.25</td>
<td>1.458 0.748 2.206</td>
<td>1.455 0.756 2.211</td>
<td>1.456 0.752 2.208</td>
</tr>
<tr>
<td>27.25</td>
<td>1.032 1.157 2.189</td>
<td>1.016 1.180 2.196</td>
<td>1.024 1.169 2.193</td>
</tr>
<tr>
<td>39.75</td>
<td>0.777 1.497 2.274</td>
<td>0.780 1.497 2.277</td>
<td>0.778 1.497 2.275</td>
</tr>
</tbody>
</table>

Total average = 2.207 \( \times 10^{-3} \text{M} \)
**Table LXI**

**ACID HYDROLYSIS OF Na\[Co(HY)Cl\]**

Calculated Concentrations of Reactant and Product

Run 29

\[\text{[NaNO}_2\text{]} = 0.1 \text{ M}\]

Initial Concentration, \( a = 1.814 \times 10^{-3} \text{M} \)

\( T = 50^\circ\text{C} \)

<table>
<thead>
<tr>
<th>Time (hrs)</th>
<th>Calc'd conc. at 520 and 600 m(\lambda) / moles/liter</th>
<th>Calc'd conc. at 540 and 600 m(\lambda) / moles/liter</th>
<th>Average Concentration / moles/liter</th>
</tr>
</thead>
<tbody>
<tr>
<td></td>
<td>(a-x) x Total</td>
<td>(a-x) x Total</td>
<td>(a-x) x Total</td>
</tr>
<tr>
<td>1.0</td>
<td>1.780 0.123 1.903</td>
<td>1.809 0.069 1.878</td>
<td>1.794 0.096 1.890</td>
</tr>
<tr>
<td>1.5</td>
<td>1.712 0.185 1.897</td>
<td>1.740 0.139 1.879</td>
<td>1.726 0.162 1.888</td>
</tr>
<tr>
<td>2.0</td>
<td>1.655 0.231 1.886</td>
<td>1.668 0.208 1.876</td>
<td>1.661 0.220 1.881</td>
</tr>
<tr>
<td>2.5</td>
<td>1.556 0.347 1.903</td>
<td>1.573 0.316 1.889</td>
<td>1.504 0.332 1.896</td>
</tr>
<tr>
<td>3.0</td>
<td>1.482 0.386 1.868</td>
<td>1.488 0.370 1.858</td>
<td>1.485 0.378 1.863</td>
</tr>
<tr>
<td>4.0</td>
<td>1.399 0.494 1.893</td>
<td>1.410 0.471 1.881</td>
<td>1.404 0.483 1.887</td>
</tr>
<tr>
<td>6.0</td>
<td>1.105 0.764 1.869</td>
<td>1.118 0.741 1.859</td>
<td>1.111 0.753 1.864</td>
</tr>
<tr>
<td>8.0</td>
<td>0.948 0.903 1.851</td>
<td>0.959 0.880 1.839</td>
<td>0.953 0.892 1.845</td>
</tr>
<tr>
<td>11.0</td>
<td>0.777 1.064 1.841</td>
<td>0.777 1.064 1.841</td>
<td>0.777 1.064 1.841</td>
</tr>
<tr>
<td>20.0</td>
<td>0.368 1.489 1.857</td>
<td>0.360 1.505 1.865</td>
<td>0.364 1.496 1.860</td>
</tr>
<tr>
<td>27.5</td>
<td>0.253 1.628 1.881</td>
<td>0.257 1.620 1.877</td>
<td>0.255 1.624 1.879</td>
</tr>
</tbody>
</table>

Total average = 1.873 \( \times 10^{-3} \text{M} \)

228
Table LXII
ACID HYDROLYSIS OF Na[Co(HY)Cl]

Calculated Concentrations of Reactant and Product
Run 30
\[ \text{[NaNO}_3\text{]} = 0.1 \text{ M} \]
Initial Concentration, \( a = 2.033 \times 10^{-3} \text{M} \)
\( T = 50^\circ\text{C} \)

<table>
<thead>
<tr>
<th>Time (hrs)</th>
<th>Calc'd conc. at 520 and 600(\mu) Conc. (x) (10^3)/moles/liter</th>
<th>Calc'd conc. at 540 and 600(\mu) Conc. (x) (10^3)/moles/liter</th>
<th>Average Concentration Conc. (x) (10^3)/moles/liter</th>
</tr>
</thead>
<tbody>
<tr>
<td>0.5</td>
<td>(2.012) (0.046) (2.058)</td>
<td>(2.017) (0.038) (2.055)</td>
<td>(2.014) (0.042) (2.056)</td>
</tr>
<tr>
<td>1.0</td>
<td>(1.942) (0.116) (2.058)</td>
<td>(1.951) (0.100) (2.051)</td>
<td>(1.946) (0.108) (2.054)</td>
</tr>
<tr>
<td>1.5</td>
<td>(1.884) (0.185) (2.069)</td>
<td>(1.894) (0.162) (2.056)</td>
<td>(1.889) (0.174) (2.063)</td>
</tr>
<tr>
<td>2.5</td>
<td>(1.685) (0.386) (2.071)</td>
<td>(1.702) (0.355) (2.057)</td>
<td>(1.693) (0.371) (2.064)</td>
</tr>
<tr>
<td>3.5</td>
<td>(1.565) (0.502) (2.067)</td>
<td>(1.576) (0.486) (2.062)</td>
<td>(1.570) (0.494) (2.064)</td>
</tr>
<tr>
<td>5.5</td>
<td>(1.370) (0.694) (2.064)</td>
<td>(1.375) (0.687) (2.062)</td>
<td>(1.372) (0.691) (2.063)</td>
</tr>
<tr>
<td>7.5</td>
<td>(1.060) (0.964) (2.024)</td>
<td>(1.058) (0.964) (2.022)</td>
<td>(1.059) (0.964) (2.023)</td>
</tr>
<tr>
<td>9.5</td>
<td>(0.897) (1.134) (2.031)</td>
<td>(0.904) (1.126) (2.030)</td>
<td>(0.900) (1.130) (2.030)</td>
</tr>
<tr>
<td>11.5</td>
<td>(0.802) (1.242) (2.044)</td>
<td>(0.800) (1.242) (2.042)</td>
<td>(0.801) (1.242) (2.043)</td>
</tr>
<tr>
<td>22.5</td>
<td>(0.267) (1.780) (2.047)</td>
<td>(0.253) (1.806) (2.059)</td>
<td>(0.260) (1.793) (2.053)</td>
</tr>
</tbody>
</table>

Total average, \(= 2.051 \times 10^{-3} \text{M} \)
Table LXIII

ACID HYDROLYSIS OF Na[Co(YOH)Cl]

Calculated Concentration of Reactant and Product

Run 31

\[ [\text{NaNO}_2] = 0.1 \text{ M} \]

Initial Concentration, \( a = 2.050 \times 10^{-3} \text{M} \)

\( T = 30^\circ \text{C} \)

<table>
<thead>
<tr>
<th>Time (hr s)</th>
<th>Calc'd conc. at 520 and 600 m( \mu ) Conc. x (10^3) moles/liter</th>
<th>Calc'd conc. at 540 and 600 m( \mu ) Conc. x (10^3) moles/liter</th>
<th>Average Concentrations Conc. x (10^3) moles/liter</th>
</tr>
</thead>
<tbody>
<tr>
<td>3</td>
<td>( 2.022 \times 10^{-3} )</td>
<td>( 2.014 \times 10^{-3} )</td>
<td>( 2.018 \times 10^{-3} )</td>
</tr>
<tr>
<td>6</td>
<td>( 1.914 \times 10^{-3} )</td>
<td>( 1.932 \times 10^{-3} )</td>
<td>( 1.923 \times 10^{-3} )</td>
</tr>
<tr>
<td>9</td>
<td>( 1.836 \times 10^{-3} )</td>
<td>( 1.871 \times 10^{-3} )</td>
<td>( 1.854 \times 10^{-3} )</td>
</tr>
<tr>
<td>12</td>
<td>( 1.768 \times 10^{-3} )</td>
<td>( 1.740 \times 10^{-3} )</td>
<td>( 1.754 \times 10^{-3} )</td>
</tr>
<tr>
<td>22</td>
<td>( 1.600 \times 10^{-3} )</td>
<td>( 1.613 \times 10^{-3} )</td>
<td>( 1.607 \times 10^{-3} )</td>
</tr>
<tr>
<td>27</td>
<td>( 1.503 \times 10^{-3} )</td>
<td>( 1.470 \times 10^{-3} )</td>
<td>( 1.486 \times 10^{-3} )</td>
</tr>
<tr>
<td>32</td>
<td>( 1.432 \times 10^{-3} )</td>
<td>( 1.397 \times 10^{-3} )</td>
<td>( 1.414 \times 10^{-3} )</td>
</tr>
<tr>
<td>37</td>
<td>( 1.372 \times 10^{-3} )</td>
<td>( 1.312 \times 10^{-3} )</td>
<td>( 1.342 \times 10^{-3} )</td>
</tr>
<tr>
<td>46.5</td>
<td>( 1.217 \times 10^{-3} )</td>
<td>( 1.156 \times 10^{-3} )</td>
<td>( 1.186 \times 10^{-3} )</td>
</tr>
<tr>
<td>56.5</td>
<td>( 1.084 \times 10^{-3} )</td>
<td>( 1.030 \times 10^{-3} )</td>
<td>( 1.057 \times 10^{-3} )</td>
</tr>
</tbody>
</table>

Total average = \( 2.002 \times 10^{-3} \text{M} \)
Table LXIV

ACID HYDROLYSIS OF Na[Co(YOH)Cl]

Calculated Concentrations of Reactant and Product

Run 32
[NaNO₂] = 0.1 M

Initial Concentration, a = 2.335 x 10⁻³ M

T = 30°C

<table>
<thead>
<tr>
<th>Time (hrs.)</th>
<th>Calc'd Conc at 520 and 600 μm</th>
<th>Average Concentration</th>
</tr>
</thead>
<tbody>
<tr>
<td></td>
<td>Conc. x 10⁻³ moles/liter</td>
<td>Calc'd Conc at 540 and 600 μm</td>
</tr>
<tr>
<td></td>
<td>(a-x) x Total</td>
<td>(a-x) x Total</td>
</tr>
<tr>
<td>3</td>
<td>2.304 0.054 2.358</td>
<td>2.296 0.062 2.358</td>
</tr>
<tr>
<td>6</td>
<td>2.191 0.179 2.370</td>
<td>2.195 0.171 2.366</td>
</tr>
<tr>
<td>9</td>
<td>2.111 0.280 2.391</td>
<td>2.096 0.303 2.399</td>
</tr>
<tr>
<td>12</td>
<td>2.085 0.311 2.396</td>
<td>2.061 0.342 2.403</td>
</tr>
<tr>
<td>22</td>
<td>1.894 0.514 2.408</td>
<td>1.869 0.545 2.414</td>
</tr>
<tr>
<td>27</td>
<td>1.718 0.584 2.302</td>
<td>1.685 0.630 2.315</td>
</tr>
<tr>
<td>32</td>
<td>1.631 0.669 2.300</td>
<td>1.595 0.716 2.311</td>
</tr>
<tr>
<td>37</td>
<td>1.565 0.732 2.297</td>
<td>1.516 0.802 2.318</td>
</tr>
<tr>
<td>46.5</td>
<td>1.394 0.879 2.273</td>
<td>1.373 0.910 2.283</td>
</tr>
<tr>
<td>56.5</td>
<td>1.279 0.949 2.228</td>
<td>1.174 1.097 2.271</td>
</tr>
</tbody>
</table>

Total average = 2.438 x 10⁻³ M
Table LXV

ACID HYDROLYSIS OF Na[Co(YOH)Cl]

Calculated Concentrations of Reactant and Product

Run 33
[NaNO₃] = 0.1 M
Initial Concentration, a = 2.214 x 10⁻³ M
T = 40°C

<table>
<thead>
<tr>
<th>Time (hrs)</th>
<th>Calc'd conc. at 520 and 600 m u</th>
<th>Calc'd conc. at 540 and 600 m u</th>
<th>Average Concentration</th>
</tr>
</thead>
<tbody>
<tr>
<td></td>
<td>Conc. x 10⁻³ moles/liter</td>
<td>Total (a-x)</td>
<td>Conc. x 10⁻³ moles/liter</td>
</tr>
<tr>
<td>2</td>
<td>2.085 0.148 2.233</td>
<td>2.128 0.086 2.214</td>
<td>2.106 0.117 2.223</td>
</tr>
<tr>
<td>4</td>
<td>1.959 0.249 2.208</td>
<td>1.925 0.303 2.228</td>
<td>1.937 0.276 2.213</td>
</tr>
<tr>
<td>6</td>
<td>1.809 0.381 2.190</td>
<td>1.788 0.412 2.200</td>
<td>1.798 0.397 2.195</td>
</tr>
<tr>
<td>8.5</td>
<td>1.615 0.568 2.183</td>
<td>1.616 0.568 2.184</td>
<td>1.616 0.568 2.184</td>
</tr>
<tr>
<td>12.00</td>
<td>1.456 0.685 2.141</td>
<td>1.400 0.763 2.163</td>
<td>1.428 0.724 2.152</td>
</tr>
<tr>
<td>21.00</td>
<td>1.016 1.089 2.105</td>
<td>0.937 1.198 2.135</td>
<td>0.976 1.144 2.120</td>
</tr>
<tr>
<td>26.00</td>
<td>0.959 1.144 2.103</td>
<td>0.881 1.253 2.134</td>
<td>0.920 1.199 2.119</td>
</tr>
<tr>
<td>32.5</td>
<td>0.863 1.253 2.116</td>
<td>0.773 1.377 2.150</td>
<td>0.818 1.315 2.133</td>
</tr>
</tbody>
</table>

Total average = 2.167 x 10⁻³ M

232
Table LXVI

ACID HYDROLYSIS OF Na[Co(YOH)Cl]

Calculated Concentrations of Reactant and Product

Run 34

\[ [\text{NaNO}_2] = 0.1 \text{ M} \]

Initial Concentration, \( a = 1.694 \times 10^{-3} \text{M} \)

\( T = 40^\circ \text{C} \)

<table>
<thead>
<tr>
<th>Time (hrs)</th>
<th>Calc'd conc. at 520 and 600( \mu ) Conc. ( x 10^3 ) moles/liter</th>
<th>Calc'd conc. at 540 and 600( \mu ) Conc. ( x 10^3 ) moles/liter</th>
<th>Average Concentration Conc. ( x 10^3 ) moles/liter</th>
</tr>
</thead>
<tbody>
<tr>
<td>2</td>
<td>1.607 0.086 1.693</td>
<td>1.614 0.078 1.692</td>
<td>1.610 0.082 1.692</td>
</tr>
<tr>
<td>4</td>
<td>1.481 0.202 1.683</td>
<td>1.479 0.202 1.681</td>
<td>1.480 0.202 1.682</td>
</tr>
<tr>
<td>6</td>
<td>1.389 0.288 1.677</td>
<td>1.372 0.311 1.683</td>
<td>1.380 0.300 1.680</td>
</tr>
<tr>
<td>8.5</td>
<td>1.241 0.467 1.708</td>
<td>1.217 0.498 1.715</td>
<td>1.229 0.482 1.711</td>
</tr>
<tr>
<td>10.0</td>
<td>1.072 0.591 1.663</td>
<td>1.054 0.615 1.669</td>
<td>1.063 0.603 1.666</td>
</tr>
<tr>
<td>20.0</td>
<td>0.788 0.872 1.660</td>
<td>0.739 0.941 1.680</td>
<td>0.763 0.907 1.670</td>
</tr>
<tr>
<td>25.3</td>
<td>0.721 0.918 1.639</td>
<td>0.668 0.988 1.656</td>
<td>0.693 0.953 1.646</td>
</tr>
<tr>
<td>31.8</td>
<td>0.662 0.988 1.650</td>
<td>0.600 1.074 1.674</td>
<td>0.631 1.031 1.662</td>
</tr>
</tbody>
</table>

Total average = \( 1.676 \times 10^{-3} \text{M} \)
Table LXVII
ACID HYDROLYSIS OF Na[Co(YOH)Cl]

Calculated Concentrations of Reactant and Product
Run 35
\[ \text{Initial Concentration, } a = 2.030 \times 10^{-3} \text{M} \]
\[ T = 50^\circ \text{C} \]

<table>
<thead>
<tr>
<th>Time (hrs)</th>
<th>Calc'd. conc. at Conc. x $10^+3$</th>
<th>Calc'd. conc. at Conc. x $10^+3$</th>
<th>Average Concentration Conc. x $10^+3$</th>
</tr>
</thead>
<tbody>
<tr>
<td>0.5</td>
<td>1.990 $\times$ 10^+3 0.016</td>
<td>2.014 $\times$ 10^+3 0.016</td>
<td>2.002 $\times$ 10^+3 0.016</td>
</tr>
<tr>
<td>1.0</td>
<td>1.874 $\times$ 10^+3 0.140</td>
<td>1.902 $\times$ 10^+3 0.101</td>
<td>1.888 $\times$ 10^+3 0.120</td>
</tr>
<tr>
<td>1.5</td>
<td>1.794 $\times$ 10^+3 0.210</td>
<td>1.768 $\times$ 10^+3 0.249</td>
<td>1.781 $\times$ 10^+3 0.230</td>
</tr>
<tr>
<td>2.5</td>
<td>1.548 $\times$ 10^+3 0.444</td>
<td>1.549 $\times$ 10^+3 0.444</td>
<td>1.548 $\times$ 10^+3 0.444</td>
</tr>
<tr>
<td>3.5</td>
<td>1.402 $\times$ 10^+3 0.591</td>
<td>1.426 $\times$ 10^+3 0.560</td>
<td>1.416 $\times$ 10^+3 0.576</td>
</tr>
<tr>
<td>5.5</td>
<td>1.204 $\times$ 10^+3 0.755</td>
<td>1.169 $\times$ 10^+3 0.809</td>
<td>1.186 $\times$ 10^+3 0.782</td>
</tr>
<tr>
<td>7.5</td>
<td>0.932 $\times$ 10^+3 1.004</td>
<td>0.874 $\times$ 10^+3 1.089</td>
<td>0.903 $\times$ 10^+3 1.047</td>
</tr>
<tr>
<td>9.5</td>
<td>0.821 $\times$ 10^+3 1.105</td>
<td>0.757 $\times$ 10^+3 1.191</td>
<td>0.789 $\times$ 10^+3 1.148</td>
</tr>
<tr>
<td>11.5</td>
<td>0.758 $\times$ 10^+3 1.167</td>
<td>0.702 $\times$ 10^+3 1.245</td>
<td>0.725 $\times$ 10^+3 1.211</td>
</tr>
<tr>
<td>22.5</td>
<td>0.531 $\times$ 10^+3 1.362</td>
<td>0.434 $\times$ 10^+3 1.494</td>
<td>0.482 $\times$ 10^+3 1.428</td>
</tr>
</tbody>
</table>

Total average = $1.972 \times 10^{-3}$
Table LXVIII
ACID HYDROLYSIS OF Na[Co(YOH)Cl]

Calculated Concentrations of Reactant and Product

Run 36

\[ \text{NaNO}_3 \] = 0.1 M

Initial Concentration, \( a = 1.997 \times 10^{-3} \text{M} \)
\( T = 50^\circ \text{C} \)

<table>
<thead>
<tr>
<th>Time (hrs)</th>
<th>Calc'd. conc. at 520 and 600 m ( \mu ) Conc. x 10(^+3) moles/liter</th>
<th>Calc'd. conc. at 540 and 600 m ( \mu ) Conc. x 10(^+3) moles/liter</th>
<th>Average Concentration Conc. x 10(^+3) moles/liter</th>
</tr>
</thead>
<tbody>
<tr>
<td>0.5</td>
<td>1.930 0.054 1.984</td>
<td>1.943 0.031 1.974</td>
<td>1.936 0.043 1.979</td>
</tr>
<tr>
<td>1</td>
<td>1.823 0.156 1.979</td>
<td>1.861 0.101 1.962</td>
<td>1.842 0.126 1.968</td>
</tr>
<tr>
<td>1.5</td>
<td>1.745 0.233 1.978</td>
<td>1.747 0.226 1.973</td>
<td>1.746 0.230 1.976</td>
</tr>
<tr>
<td>2.5</td>
<td>1.482 0.476 1.958</td>
<td>1.480 0.475 1.955</td>
<td>1.481 0.476 1.957</td>
</tr>
<tr>
<td>3.5</td>
<td>1.362 0.591 1.953</td>
<td>1.374 0.576 1.950</td>
<td>1.368 0.584 1.952</td>
</tr>
<tr>
<td>5.5</td>
<td>1.153 0.778 1.931</td>
<td>1.124 0.817 1.941</td>
<td>1.138 0.798 1.936</td>
</tr>
<tr>
<td>7.5</td>
<td>0.911 1.012 1.923</td>
<td>0.854 1.089 1.943</td>
<td>0.882 1.051 1.933</td>
</tr>
<tr>
<td>9.5</td>
<td>0.800 1.113 1.913</td>
<td>0.725 1.214 1.939</td>
<td>0.762 1.165 1.927</td>
</tr>
<tr>
<td>11.5</td>
<td>0.749 1.175 1.924</td>
<td>0.661 1.300 1.961</td>
<td>0.705 1.238 1.943</td>
</tr>
<tr>
<td>22.5</td>
<td>0.495 1.393 1.888</td>
<td>0.413 1.510 1.923</td>
<td>0.454 1.452 1.906</td>
</tr>
</tbody>
</table>

Total average = 1.947 x 10\(^{-3}\)M
Table LXIX

ACID HYDROLYSIS OF Na\([\text{Co(YOH)Br}]\)

Calculated Concentrations of Reactant and Product

Run 37

\[ [\text{NaNO}_2] = 0.1 \text{ M} \]

Initial Concentration, \(a = 3.261 \text{ M} \)

\(T = 30^\circ\text{C}\)

<table>
<thead>
<tr>
<th>Time (hrs)</th>
<th>(a-x) (x) Total</th>
<th>Calc'd conc. at 520 and 600m(\mu) conc. (x) (10^{-3}) moles/liter</th>
<th>Calc'd conc. at 540 and 600m(\mu) conc. (x) (10^{-3}) moles/liter</th>
<th>Average Concentration conc. (x) (10^{-3}) moles/liter</th>
</tr>
</thead>
<tbody>
<tr>
<td>3</td>
<td>2.726 0.404 3.130</td>
<td>2.709 0.435 3.144</td>
<td>2.717 0.420 3.137</td>
<td></td>
</tr>
<tr>
<td>6</td>
<td>2.383 0.745 3.128</td>
<td>2.319 0.862 3.181</td>
<td>2.351 0.804 3.156</td>
<td></td>
</tr>
<tr>
<td>9.00</td>
<td>2.064 1.064 3.128</td>
<td>1.974 1.227 3.201</td>
<td>2.019 1.148 3.164</td>
<td></td>
</tr>
<tr>
<td>12.00</td>
<td>1.804 1.312 3.116</td>
<td>1.721 1.537 3.158</td>
<td>1.762 1.425 3.187</td>
<td></td>
</tr>
<tr>
<td>22</td>
<td>1.261 1.849 3.110</td>
<td>1.149 2.049 3.198</td>
<td>1.205 1.949 3.154</td>
<td></td>
</tr>
<tr>
<td>27</td>
<td>1.158 2.197 3.355</td>
<td>0.964 2.296 3.260</td>
<td>1.061 2.246 3.307</td>
<td></td>
</tr>
<tr>
<td>32</td>
<td>1.005 2.337 3.342</td>
<td>0.819 2.671 3.490</td>
<td>0.912 3.504 3.416</td>
<td></td>
</tr>
<tr>
<td>37</td>
<td>0.868 2.484 3.352</td>
<td>0.703 2.780 3.483</td>
<td>0.786 2.632 3.418</td>
<td></td>
</tr>
<tr>
<td>46.5</td>
<td>0.745 2.578 3.323</td>
<td>0.585 2.865 3.450</td>
<td>0.665 2.721 3.386</td>
<td></td>
</tr>
<tr>
<td>56.5</td>
<td>0.683 2.640 3.323</td>
<td>0.481 2.989 3.470</td>
<td>0.582 2.814 3.396</td>
<td></td>
</tr>
</tbody>
</table>

Total average = \(3.265 \times 10^{-3}\)M
### Table LXX

**ACID HYDROLYSIS OF Na[Co(YOH)Br]**

Calculated Concentrations of Reactant and Product

**Run 38**

\[ \text{[NaNO}_2\text{]} = 0.1 \text{ M} \]

**Initial Concentration, } a = 1.870 \times 10^{-3} \text{ M} \]

**T = 30°C**

<table>
<thead>
<tr>
<th>Time (hrs)</th>
<th>Calc'd. conc. at 520 and 600mμ</th>
<th>Calc'd. conc. at 540 and 600mμ</th>
<th>Average Concentration</th>
</tr>
</thead>
<tbody>
<tr>
<td></td>
<td>Conc. x 10^3/ moles/liter</td>
<td>Conc. x 10^3/ moles/liter</td>
<td>Conc. x 10^3/ moles/liter</td>
</tr>
<tr>
<td>3</td>
<td>1.630 0.241 1.871</td>
<td>1.628 0.241 1.869</td>
<td>1.629 0.241 1.870</td>
</tr>
<tr>
<td>5</td>
<td>1.500 0.380 1.880</td>
<td>1.476 0.419 1.895</td>
<td>1.488 0.395 1.883</td>
</tr>
<tr>
<td>7.5</td>
<td>1.303 0.543 1.846</td>
<td>1.273 0.598 1.871</td>
<td>1.288 0.570 1.858</td>
</tr>
<tr>
<td>10.00</td>
<td>1.154 0.675 1.829</td>
<td>1.107 0.761 1.868</td>
<td>1.173 0.718 1.891</td>
</tr>
<tr>
<td>13.00</td>
<td>1.026 0.792 1.818</td>
<td>0.955 0.924 1.879</td>
<td>0.990 0.858 1.848</td>
</tr>
<tr>
<td>16.00</td>
<td>0.870 0.963 1.833</td>
<td>0.807 1.079 1.886</td>
<td>0.839 1.021 1.860</td>
</tr>
<tr>
<td>23.00</td>
<td>0.705 1.156 1.861</td>
<td>0.614 1.320 1.934</td>
<td>0.660 1.238 1.898</td>
</tr>
<tr>
<td>28.00</td>
<td>0.592 1.296 1.888</td>
<td>0.505 1.452 1.957</td>
<td>0.548 1.374 1.922</td>
</tr>
<tr>
<td>33.00</td>
<td>0.495 1.281 1.776</td>
<td>0.398 1.444 1.842</td>
<td>0.446 1.362 1.808</td>
</tr>
<tr>
<td>38.00</td>
<td>0.449 1.366 1.815</td>
<td>0.363 1.522 1.885</td>
<td>0.406 1.444 1.850</td>
</tr>
<tr>
<td>49.50</td>
<td>0.428 1.359 1.787</td>
<td>0.297 1.592 1.889</td>
<td>0.362 1.476 1.838</td>
</tr>
</tbody>
</table>

**Total average** = 1.867 x 10^{-3} \text{ M}
Table LXXI

ACID HYDROLYSIS OF Na\[Co(YOH)Br]\]

Calculated Concentrations of Reactant and Product
Run 39

\[\text{[NaNO}_3\text{]} = 0.1 \text{ M}\]

Initial Concentration, \(a = 1.228 \times 10^{-3}\text{M}\)

\(T = 30^\circ\text{C}\)

<table>
<thead>
<tr>
<th>Time (hrs)</th>
<th>Calc'd. conc. at 520 and 600m (\mu) Conc. x (10^3) moles/liter</th>
<th>Calc'd. conc. at 540 and 600m (\mu) Conc. x (10^3) moles/liter</th>
<th>Average Concentration Conc. x (10^3) moles/liter</th>
</tr>
</thead>
<tbody>
<tr>
<td>1.25</td>
<td>1.014 0.241 1.255</td>
<td>1.047 0.186 1.233</td>
<td>1.029 0.213 1.242</td>
</tr>
<tr>
<td>2.75</td>
<td>0.812 0.411 1.223</td>
<td>0.772 0.481 1.253</td>
<td>0.792 0.446 1.238</td>
</tr>
<tr>
<td>4.25</td>
<td>0.651 0.543 1.194</td>
<td>0.616 0.606 1.222</td>
<td>0.634 0.574 1.208</td>
</tr>
<tr>
<td>5.75</td>
<td>0.536 0.644 1.180</td>
<td>0.499 0.706 1.205</td>
<td>0.518 0.675 1.193</td>
</tr>
<tr>
<td>7.25</td>
<td>0.429 0.761 1.190</td>
<td>0.370 0.838 1.208</td>
<td>0.400 0.800 1.200</td>
</tr>
<tr>
<td>9.25</td>
<td>0.381 0.792 1.173</td>
<td>0.318 0.901 1.219</td>
<td>0.350 0.846 1.196</td>
</tr>
<tr>
<td>11.25</td>
<td>0.317 0.838 1.155</td>
<td>0.247 0.963 1.210</td>
<td>0.282 0.900 1.182</td>
</tr>
<tr>
<td>13.25</td>
<td>0.289 0.901 1.190</td>
<td>0.216 0.994 1.210</td>
<td>0.252 0.948 1.200</td>
</tr>
<tr>
<td>15.25</td>
<td>0.270 0.885 1.155</td>
<td>0.198 1.017 1.215</td>
<td>0.234 0.951 1.185</td>
</tr>
<tr>
<td>27.25</td>
<td>0.211 0.970 1.181</td>
<td>0.158 1.064 1.222</td>
<td>0.184 1.017 1.201</td>
</tr>
<tr>
<td>39.75</td>
<td>0.195 0.994 1.189</td>
<td>0.126 1.118 1.244</td>
<td>0.160 1.056 1.216</td>
</tr>
</tbody>
</table>

Total average = \(1.206 \times 10^{-3}\text{M}\)
Table LXXII

ACID HYDROLYSIS OF Na[Co(YOH)Br]

Calculated Concentrations of Reactant and Product

Run 40

\[ [\text{NaNO}_3] = 0.1 \text{ M} \]

Initial Concentration, \( a = 1.819 \times 10^{-3} \text{M} \)

\( T = 30^\circ \text{C} \)

<table>
<thead>
<tr>
<th>Time (hrs)</th>
<th>Calc'd conc at 520 and 600m ( \mu ) Conc. x 10^{-3}</th>
<th>Calc'd conc at 540 and 600m ( \mu ) Conc. x 10^{-3}</th>
<th>Average Concentration Conc. x 10^{-3}</th>
</tr>
</thead>
<tbody>
<tr>
<td>1.50</td>
<td>1.403 0.388 1.791</td>
<td>1.386 0.419 1.805</td>
<td>1.394 0.404 1.798</td>
</tr>
<tr>
<td>3.00</td>
<td>1.128 0.706 1.834</td>
<td>1.122 0.714 1.836</td>
<td>1.125 0.710 1.835</td>
</tr>
<tr>
<td>4.50</td>
<td>0.928 0.908 1.836</td>
<td>0.879 0.994 1.873</td>
<td>0.908 0.951 1.859</td>
</tr>
<tr>
<td>6.00</td>
<td>0.719 1.049 1.768</td>
<td>0.657 1.157 1.814</td>
<td>0.688 1.103 1.791</td>
</tr>
<tr>
<td>7.50</td>
<td>0.633 1.141 1.774</td>
<td>0.568 1.258 1.826</td>
<td>0.600 1.200 1.800</td>
</tr>
<tr>
<td>9.00</td>
<td>0.557 1.203 1.760</td>
<td>0.479 1.343 1.822</td>
<td>0.518 1.273 1.791</td>
</tr>
<tr>
<td>10.50</td>
<td>0.487 1.266 1.753</td>
<td>0.402 1.421 1.823</td>
<td>0.444 1.344 1.788</td>
</tr>
</tbody>
</table>

Total average = \( 1.807 \times 10^{-3} \text{M} \)
### Table LXXIII
ACID HYDROLYSIS OF Na[Co(YOH)Br]

Calculated Concentrations of Reactant and Product

**Run 41**

\[ [\text{NaNO}_3] = 0.1 \text{ M} \]

Initial Concentration, \( a = 1.709 \times 10^{-3} \text{M} \)

\( T = 50^\circ \text{C} \)

<table>
<thead>
<tr>
<th>Time (hrs)</th>
<th>Calc'd conc. at 520 and 600 m( \mu ) Conc. ( x 10^3 ) moles/liter ((a-x) x ) Total</th>
<th>Calc'd conc. at 540 and 600 m( \mu ) Conc. ( x 10^3 ) moles/liter ((a-x) x ) Total</th>
<th>Average Concentration ( x 10^3 ) moles/liter ((a-x) x ) Total</th>
</tr>
</thead>
<tbody>
<tr>
<td>0.5</td>
<td>1.286 0.419 1.705</td>
<td>1.262 0.458 1.720</td>
<td>1.274 0.439 1.713</td>
</tr>
<tr>
<td>1.0</td>
<td>1.054 0.637 1.691</td>
<td>0.988 0.753 1.741</td>
<td>1.021 0.695 1.716</td>
</tr>
<tr>
<td>1.5</td>
<td>0.884 0.807 1.691</td>
<td>0.830 0.900 1.730</td>
<td>0.887 0.854 1.711</td>
</tr>
<tr>
<td>2.0</td>
<td>0.749 0.947 1.696</td>
<td>0.693 1.048 1.741</td>
<td>0.721 0.998 1.719</td>
</tr>
<tr>
<td>2.5</td>
<td>0.587 1.102 1.689</td>
<td>0.518 1.227 1.745</td>
<td>0.552 1.164 1.716</td>
</tr>
<tr>
<td>3.0</td>
<td>0.518 1.126 1.644</td>
<td>0.436 1.273 1.709</td>
<td>0.477 1.200 1.677</td>
</tr>
<tr>
<td>4.0</td>
<td>0.481 1.203 1.684</td>
<td>0.401 1.343 1.744</td>
<td>0.441 1.273 1.714</td>
</tr>
<tr>
<td>6.0</td>
<td>0.338 1.366 1.704</td>
<td>0.257 1.514 1.771</td>
<td>0.298 1.440 1.738</td>
</tr>
<tr>
<td>8.0</td>
<td>0.373 1.312 1.685</td>
<td>0.280 1.483 1.763</td>
<td>0.326 1.397 1.723</td>
</tr>
<tr>
<td>11.0</td>
<td>0.294 1.421 1.715</td>
<td>0.205 1.576 1.781</td>
<td>0.250 1.498 1.748</td>
</tr>
<tr>
<td>20.0</td>
<td>0.299 1.428 1.727</td>
<td>0.211 1.576 1.787</td>
<td>0.255 1.502 1.757</td>
</tr>
</tbody>
</table>

**Total average** = \( 1.718 \times 10^{-3} \text{M} \)
Table LXXIV

ACID HYDROLYSIS OF Na[Co(YOH)Br]

Calculated Concentration of Reactant and Product

Run 42

[NaNO₃] = 0.1 M

Initial Concentration, a = 2.287 x 10⁻³M

T = 50°C

<table>
<thead>
<tr>
<th>Time (hrs)</th>
<th>Calc'd. conc. at 520 and 600 m/μ</th>
<th>Avg. Conc.</th>
<th>Calc'd. conc. at 540 and 600 m/μ</th>
<th>Avg. Conc.</th>
<th>Average Concentration</th>
</tr>
</thead>
<tbody>
<tr>
<td></td>
<td>Conc. x 10⁻³ moles/liter (a-x) x Total</td>
<td>Conc. x 10⁻³ moles/liter (a-x) x Total</td>
<td>Conc. x 10⁻³ moles/liter (a-x) x Total</td>
<td></td>
<td></td>
</tr>
<tr>
<td>0.5</td>
<td>1.748 0.543 2.291</td>
<td>1.724 0.582 2.306</td>
<td>1.736 0.563 2.299</td>
<td></td>
<td></td>
</tr>
<tr>
<td>1.0</td>
<td>1.432 0.862 2.294</td>
<td>1.400 0.924 2.324</td>
<td>1.416 0.893 2.309</td>
<td></td>
<td></td>
</tr>
<tr>
<td>1.5</td>
<td>1.192 1.087 2.279</td>
<td>1.134 1.196 2.330</td>
<td>1.163 1.142 2.305</td>
<td></td>
<td></td>
</tr>
<tr>
<td>2.0</td>
<td>1.030 1.258 2.288</td>
<td>0.950 1.398 2.348</td>
<td>0.990 1.328 2.318</td>
<td></td>
<td></td>
</tr>
<tr>
<td>2.5</td>
<td>0.797 1.483 2.280</td>
<td>0.730 1.599 2.329</td>
<td>0.764 1.541 2.305</td>
<td></td>
<td></td>
</tr>
<tr>
<td>3.0</td>
<td>0.737 1.584 2.321</td>
<td>0.643 1.747 2.390</td>
<td>0.690 1.666 2.356</td>
<td></td>
<td></td>
</tr>
<tr>
<td>4.0</td>
<td>0.677 1.669 2.346</td>
<td>0.586 1.832 2.418</td>
<td>0.632 1.750 2.382</td>
<td></td>
<td></td>
</tr>
<tr>
<td>6.0</td>
<td>0.547 1.778 2.325</td>
<td>0.454 1.949 2.403</td>
<td>0.500 1.864 2.364</td>
<td></td>
<td></td>
</tr>
<tr>
<td>8.0</td>
<td>0.514 1.739 2.253</td>
<td>0.404 1.933 2.337</td>
<td>0.459 1.836 2.295</td>
<td></td>
<td></td>
</tr>
<tr>
<td>11.0</td>
<td>0.454 1.793 2.247</td>
<td>0.342 1.995 2.337</td>
<td>0.398 1.894 2.292</td>
<td></td>
<td></td>
</tr>
<tr>
<td>20.0</td>
<td>0.435 1.832 2.267</td>
<td>0.330 2.019 2.349</td>
<td>0.382 1.926 2.308</td>
<td></td>
<td></td>
</tr>
</tbody>
</table>

Total average = 2.321 x 10⁻³M
Table LXXV

ACID HYDROLYSIS OF Na[Co(HY)Br]

Calculated Concentrations of Reactant and Product

Run 43

\[\text{[St(NO_3)_2]} = 0.1 \text{ M}\]

Initial Concentration, \(a = 2.130 \times 10^{-3}\) M

\(T = 30^\circ\text{C}\)

<table>
<thead>
<tr>
<th>Time (hrs)</th>
<th>Calc'd conc at 520 and 600m (\mu) Conc. (\times 10^{-3})/ moles/liter</th>
<th>Calc'd conc at 540 and 600m (\mu) Conc. (\times 10^{-3})/ moles/liter</th>
<th>Average Concentration Conc. (\times 10^{-3})/ moles/liter</th>
</tr>
</thead>
<tbody>
<tr>
<td>3</td>
<td>1.924 (0.247 \times 2.171) 1.934 (0.224 \times 2.158) 1.929 (0.236 \times 2.165)</td>
<td></td>
<td></td>
</tr>
<tr>
<td>6</td>
<td>1.692 (0.457 \times 2.149) 1.691 (0.457 \times 2.148) 1.692 (0.457 \times 2.149)</td>
<td></td>
<td></td>
</tr>
<tr>
<td>9</td>
<td>1.518 (0.616 \times 2.134) 1.523 (0.602 \times 2.125) 1.520 (0.609 \times 2.129)</td>
<td></td>
<td></td>
</tr>
<tr>
<td>12</td>
<td>1.398 (0.747 \times 2.145) 1.403 (0.740 \times 2.143) 1.400 (0.744 \times 2.144)</td>
<td></td>
<td></td>
</tr>
<tr>
<td>15</td>
<td>1.278 (0.864 \times 2.142) 1.272 (0.870 \times 2.142) 1.275 (0.867 \times 2.142)</td>
<td></td>
<td></td>
</tr>
<tr>
<td>21</td>
<td>1.042 (1.038 \times 2.080) 1.024 (1.074 \times 2.098) 1.033 (1.056 \times 2.089)</td>
<td></td>
<td></td>
</tr>
<tr>
<td>24</td>
<td>0.970 (1.103 \times 2.073) 0.955 (1.132 \times 2.087) 0.962 (1.118 \times 2.080)</td>
<td></td>
<td></td>
</tr>
<tr>
<td>30</td>
<td>0.858 (1.212 \times 2.070) 0.840 (1.248 \times 2.088) 0.849 (1.230 \times 2.079)</td>
<td></td>
<td></td>
</tr>
<tr>
<td>38</td>
<td>0.737 (1.321 \times 2.058) 0.699 (1.386 \times 2.085) 0.717 (1.354 \times 2.071)</td>
<td></td>
<td></td>
</tr>
<tr>
<td>48</td>
<td>0.606 (1.435 \times 2.041) 0.577 (1.480 \times 2.057) 0.591 (1.458 \times 2.049)</td>
<td></td>
<td></td>
</tr>
<tr>
<td>59</td>
<td>0.500 (1.546 \times 2.046) 0.490 (1.560 \times 2.050) 0.495 (1.553 \times 2.048)</td>
<td></td>
<td></td>
</tr>
<tr>
<td>74</td>
<td>0.411 (1.669 \times 2.080) 0.404 (1.684 \times 2.088) 0.408 (1.676 \times 2.084)</td>
<td></td>
<td></td>
</tr>
</tbody>
</table>

Total average = \(2.102 \times 10^{-3}\) M
Table LXXVI

ACID HYDROLYSIS OF Na[Co(HY)Br]

Calculated Concentrations of Reactant and Product

Run 44

$\left[\text{Sb(NO}_3\text{)}_5\right] = 0.1 \text{ M}$

Initial Concentration, $a = 2.004 \times 10^{-3} \text{ M}$

$T = 30^\circ\text{C}$

<table>
<thead>
<tr>
<th>Time (hrs)</th>
<th>Calc'd conc. at 520 and 600 m$\mu$ Conc. $\times 10^3$/ moles/liter</th>
<th>Calc'd conc. at 540 and 600 m$\mu$ Conc. $\times 10^3$/ moles/liter</th>
<th>Average Concentration Conc. $\times 10^3$/ moles/liter</th>
</tr>
</thead>
<tbody>
<tr>
<td>3</td>
<td>1.809 $\times 10^{-3}$ 2.019</td>
<td>1.802 $\times 10^{-3}$ 2.027</td>
<td>1.805 $\times 10^{-3}$ 2.018 2.023</td>
</tr>
<tr>
<td>6</td>
<td>1.592 $\times 10^{-3}$ 2.006</td>
<td>1.586 $\times 10^{-3}$ 2.007</td>
<td>1.589 $\times 10^{-3}$ 2.007 2.007</td>
</tr>
<tr>
<td>9</td>
<td>1.444 $\times 10^{-3}$ 2.003</td>
<td>1.444 $\times 10^{-3}$ 2.003</td>
<td>1.444 $\times 10^{-3}$ 2.003 2.003</td>
</tr>
<tr>
<td>12</td>
<td>1.297 $\times 10^{-3}$ 1.994</td>
<td>1.286 $\times 10^{-3}$ 2.004</td>
<td>1.291 $\times 10^{-3}$ 1.999 2.004</td>
</tr>
<tr>
<td>15</td>
<td>1.214 $\times 10^{-3}$ 2.012</td>
<td>1.211 $\times 10^{-3}$ 2.017</td>
<td>1.212 $\times 10^{-3}$ 2.012 2.014</td>
</tr>
<tr>
<td>21</td>
<td>0.990 $\times 10^{-3}$ 1.962</td>
<td>0.968 $\times 10^{-3}$ 1.977</td>
<td>0.979 $\times 10^{-3}$ 1.970 1.970</td>
</tr>
<tr>
<td>24</td>
<td>0.922 $\times 10^{-3}$ 1.967</td>
<td>0.909 $\times 10^{-3}$ 1.976</td>
<td>0.915 $\times 10^{-3}$ 1.971 1.971</td>
</tr>
<tr>
<td>30</td>
<td>0.808 $\times 10^{-3}$ 1.947</td>
<td>0.798 $\times 10^{-3}$ 1.959</td>
<td>0.803 $\times 10^{-3}$ 1.953 1.953</td>
</tr>
<tr>
<td>38</td>
<td>0.680 $\times 10^{-3}$ 1.935</td>
<td>0.656 $\times 10^{-3}$ 1.955</td>
<td>0.668 $\times 10^{-3}$ 1.945 1.945</td>
</tr>
<tr>
<td>48</td>
<td>0.565 $\times 10^{-3}$ 1.915</td>
<td>0.550 $\times 10^{-3}$ 1.929</td>
<td>0.557 $\times 10^{-3}$ 1.922 1.922</td>
</tr>
<tr>
<td>59</td>
<td>0.490 $\times 10^{-3}$ 1.912</td>
<td>0.455 $\times 10^{-3}$ 1.935</td>
<td>0.472 $\times 10^{-3}$ 1.923 1.923</td>
</tr>
<tr>
<td>74</td>
<td>0.422 $\times 10^{-3}$ 1.996</td>
<td>0.398 $\times 10^{-3}$ 2.016</td>
<td>0.410 $\times 10^{-3}$ 1.996 2.006</td>
</tr>
</tbody>
</table>

Total average $= 1.978 \times 10^{-3} \text{ M}$
I, Melvin Lee Morris, was born in Cincinnati, Ohio, March 27, 1929. I received my secondary school education in the Cleveland Heights, Ohio, public school system and my undergraduate training at The Ohio State University. I received my Bachelor of Science degree in 1951. I was drafted into the United States Army in 1952 and released from active duty in the latter part of 1953. I enrolled for graduate study at The Ohio State University in 1954 and received my Master of Science degree in Chemistry in 1955. In 1955 I was granted a teaching assistantship and in 1956 obtained a Development Fund Grant.