SYNTHETIC AND MECHANISTIC STUDIES
OF RUTHENIUM (III) COMPLEXES

by

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A thesis
submitted for the degree
of
MASTERS OF SCIENCE

Department of Chemistry,
School of General Studies,
Australian National University.

April, 1971.
With deep respect and affection,
this thesis is dedicated to my father,
the late Ronald Craig Wilson.
Except where due credit is given to the work of others, the work presented in this thesis is the candidate's own. 

David Wilson
ACKNOWLEDGEMENTS

I wish to thank Professor A. N. Hamblly and Professor I. G. Ross for making available the facilities of the Chemistry Department.

I wish also to thank my supervisor, Dr. J. A. Broomhead, for providing me with such an interesting research topic and for his helpful advice and guidance over the past two years.

I express my gratitude to the members of the technical staff of the Department for their expert assistance and valuable advice so cheerfully given.

I am very grateful to Mrs. M. Gaffey for the patience with which she has transformed a sometimes barely legible manuscript into this expertly typed document.

Finally I wish to place on record my thanks to my wife, not only for practical assistance in the preparation of diagrams and for proof reading, but for the constant encouragement she has given to me.
# Abbreviations

The following abbreviations are used consistently throughout the thesis:

<table>
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<tr>
<td>$A_0$</td>
<td>absorbance at commencement of reaction</td>
</tr>
<tr>
<td>$A_{eq}$</td>
<td>absorbance at equilibrium</td>
</tr>
<tr>
<td>$A_t$</td>
<td>absorbance at time, $t$</td>
</tr>
<tr>
<td>$A_\infty$</td>
<td>absorbance at end of reaction</td>
</tr>
<tr>
<td>$A - A$</td>
<td>bidentate diamine ligand</td>
</tr>
<tr>
<td>$\text{hpy}$</td>
<td>2,2' - bipyrindine</td>
</tr>
<tr>
<td>$\varepsilon$</td>
<td>extinction co-efficient</td>
</tr>
<tr>
<td>$E_a$</td>
<td>Arrhenius activation energy</td>
</tr>
<tr>
<td>$\text{en}$</td>
<td>ethylenediamine (1,2-diaminoethane)</td>
</tr>
<tr>
<td>$M$</td>
<td>molar (i.e. moles per litre)</td>
</tr>
<tr>
<td>$\text{MeSO}_3^-!$</td>
<td>methanesulphonate ion</td>
</tr>
<tr>
<td>$\text{mol}$</td>
<td>moles</td>
</tr>
<tr>
<td>$\mu$C</td>
<td>microcuries</td>
</tr>
<tr>
<td>$\text{OAc}^-$</td>
<td>acetate ion</td>
</tr>
<tr>
<td>$\text{ox}^2-$</td>
<td>oxalate ion</td>
</tr>
<tr>
<td>$R$</td>
<td>gas constant</td>
</tr>
<tr>
<td>$\Delta S_T^\neq$</td>
<td>entropy of activation at $T^\circ$ C.</td>
</tr>
<tr>
<td>$\text{TFS}^-$</td>
<td>toluene-p-sulphonate ion</td>
</tr>
<tr>
<td>$X^-$</td>
<td>anionic unidentate ligand</td>
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SUMMARY

Salts of the cis-[Ru Cl₂ en₂]⁺ and trans-[Ru Cl₂ en₂]⁺ ions have been prepared by a known sequence of reactions. Novel preparations of K₃[Ru ox₃]·4H₂O and [Ru ox₂ en][Ru ox₂ en].2H₂O from commercially available RuCl₃ have been investigated.

The acid and base hydrolyses of the trans-[Ru Cl₂ en₂]⁺ ion have been investigated by a combination of spectrophotometric and titrimetric techniques. A stopped-flow apparatus has been used to investigate the base hydrolysis of the cis-[Ru Cl₂ en₂]⁺ ion. Values of Eᵦ, log₁₀ΔA and ΔS⁺ have been determined for each of these reactions. Possible mechanisms are discussed in the light of the results and conclusions of previous workers.

By use of ³⁶Cl as a tracer, the reaction:

cis-[Ru Cl₂ en₂]⁺ + ethylene glycol → trans-[Ru Cl₂ en₂]⁺

190°C

has been shown to occur at least partly by an intramolecular mechanism.

* As defined on page 17
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CHAPTER 1

SYNTHESIS OF COMPOUNDS

INTRODUCTION

This thesis is concerned primarily with reactions of the cis- and trans- isomers of the dichlorobis(ethylenediamine)ruthenium(III) cation. It describes an extension of the work begun by L. Kane-Maguire (1) who first prepared and characterised salts of the isomers.

Complexes used in the present work were synthesised from ruthenium metal by methods closely following those of Kane-Maguire, and more direct syntheses using commercial ruthenium trichloride were investigated.

The hydrolysis of the cis- isomer in basic solution and the hydrolysis of the trans- isomer in both acidic and basic solutions have been studied in detail.

The isomerisation by which the cis- isomer is converted to the trans- has been studied by the use of radioactive chlorine-36 as a tracer.
MATERIALS

Ruthenium metal was obtained in powdered form from Goldsmith Brothers Division, National Lead Company, U.S.A. Ruthenium trichloride was obtained from both Johnson Matthey Chemicals Ltd., London and British Drug Houses Ltd., Poole, England. All other compounds of ruthenium were prepared by methods described below. Reagents were of "Laboratory Reagent" standard or higher, and were used as supplied by the manufacturers.

METHODS OF ANALYSIS

Microanalyses were performed by the Australian Microanalytical Service, C.S.I.R.O., Melbourne, or by the Microanalytical Service of the Research School of Chemistry, A.N.U., Canberra. Ultraviolet and visible absorption spectra were measured on a Cary 14H spectrophotometer, using a lightpath of 1 cm. unless otherwise stated. Infrared absorption spectra were obtained on a Unicam S.P. 200 G spectrophotometer. X-ray powder-diffraction patterns were obtained on a Philips 1051 diffractometer, using Ni-filtered Cu radiation.
SYNTHESIS OF RUTHENIUM COMPLEXES

The sequence of reactions by which cis- and trans-dichlorobis(ethylenediamine) ruthenium(III) chloride were made from ruthenium metal follows that described by Kane-Maguire, apart from minor variations.

Potassium μ-oxobis(pentachlororuthenate(IV)) 1-hydrate

Potassium hydroxide (9 g., 0.16 mole) was heated gently in a nickel crucible until effervescence had ceased, and then more strongly to a dull red heat. Finely-ground, dried potassium chlorate (2.3 g., 0.019 mole) was mixed intimately with ruthenium powder (1.5 g., 0.015 mole), and the mixture was gradually added to the melt over a period of 45 minutes. The crucible was heated less strongly for a further 30 minutes and allowed to cool. When cold, the crucible was washed out with 250 ml. of 5 M hydrochloric acid. The solution was boiled and filtered, and most of the undissolved solids were washed through the filter with hot, 5 M hydrochloric acid. The volume of filtrate was reduced on a steam bath to 100 ml., and a dark, purple product precipitated with cooling over several hours. The product was washed successively with ice water, ethanol and acetone. It was identified as $K_4\left[RuCl_5\right]_2O \cdot H_2O$ by its X-ray powder-diffraction pattern (2). Yield: 4.66 g., 84%. 

3.
X-ray Data for \( K_4\left[\text{RuCl}_5\right]_2\cdot O\cdot H_2O \)

Observed and published interplanar spacings (\(\AA\))

Ref. (2) : 8.51, 6.57, 5.02, 4.44, 4.27, 3.55, 3.25, 3.12,

Observed : 8.51, 6.56, 5.04, 4.44, 4.26, 3.56, 3.25, 3.12,

Ref. (2) : 3.08, 2.84, 2.73, 2.51, 2.48

Observed : 3.07, 2.84, 2.73, 2.51, 2.47

Potassium aquopentachlororuthenate(III)

\[
K_4\left[\text{RuCl}_5\right]_2\cdot O\cdot H_2O \quad (5\text{ g.})
\]

was added to 100 ml. of 1 M. HCl and heated on a steam bath. 30\% aqueous formaldehyde (7.7 ml.) was added, and heating was continued for 45 minutes, by which time all solid had dissolved. The solution was transferred to an evaporating basin and its volume was reduced to 20 ml. After cooling, acetone was added, with scratching, to precipitate the product, whose colour varied in different batches from dull orange to chocolate brown. Judged by their subsequent use in further syntheses all samples were equally pure, and variations in colour were probably due to particle size. Yield: 4.64 g., 93.0\%.

Potassium tris(oxalato)ruthenate (III) 4.5 hydrate.

Potassium oxalate monohydrate (15.7 g.) was dissolved in 100 ml. of cold water. \( K_2\left[\text{RuCl}_5\cdot H_2O\right] \) (10 g.) was added, and the solution was refluxed for 5 hours, during which time the colour changed from a reddish brown to a dark green. As soon as the solution had cooled, 100 ml. of methanol was added, with scratching, to precipitate a golden-yellow product. This was washed several
times with methanol and dried under vacuum. The X-ray powder-
diffraction pattern showed no sign of KCl, but indicated that
a small amount of (COOK)₂·H₂O may have been present. (Figure 1.1)
The solid changed colour over a period of weeks; the process
being accelerated by light. The dark product resembled earlier
batches of K₃[Ru ox₃]·4·5 H₂O in whose manufacture recovery
from solution had been effected after many hours of standing.
The powder-diffraction patterns of these samples were
substantially the same as that of the golden-yellow material,
but peaks were broader, indicating a less pure sample.
Yield: 14·3 g. 95%.

Oxalatohis(ethylenediamine)ruthenium(III)-bis (oxalato)
ethylene diamine ruthenate(III) dihydrate.

Potassium tris(oxalato)ruthenate(III) (10 g.) was
dissolved in 30 ml. of warm water and ethylenediammonium
oxalate (9.3 g.) was added. The solution was heated on a steam
bath for 20 minutes and a yellow precipitate formed. The
precipitate was filtered off and washed with cold water. On the
cooling of the filtrate, yellow crystals and white crystals
formed. The white crystals were removed by dissolving them in
a small volume of hot water, in which they are more soluble
than are the yellow, and filtering while hot. The process was
repeated until a mixture was obtained containing such a high
proportion of white crystals that further attempts at separation
were fruitless. Yield based on total Ru: 4.5 g., 67%.
Figure 1.1.

X-ray diffractometer pattern of $K_3\left[\text{Ruox}_3\right] \cdot \frac{1}{2}H_2O$, showing reflections corresponding to spacings from 2.2 to 10 Å. Arrows show peaks coinciding with, or corresponding to, the six strongest reflections listed for $K_2C_2O_4 \cdot H_2O$ (3). Numbers in parentheses are reported relative intensities for $K_2C_2O_4 \cdot H_2O$. It will be noted that the strongest reflection for $K_2C_2O_4 \cdot H_2O$ is at $d = 2.92$ Å, and the experimental peak at this position is very weak, indicating the presence of very little $K_2C_2O_4 \cdot H_2O$ in the sample.
cis-dichloro(ethylenediamine)ruthenium(III) chloride monohydrate

\[ \left [ \text{Ru ox en}_2 \right ] \left [ \text{Ru ox}_2 \text{ en} \right ] \cdot 2 \text{H}_2\text{O} \] (3 g.) was dissolved in 13 ml. of concentrated hydrochloric acid to give a red solution which was allowed to stand overnight at room temperature. A brown solid which separated was filtered off and washed with ethanol, and with acetone. The brown solid was dissolved in 27 ml. of boiling 1 M. hydrochloric acid and filtered. The orange solution was cooled and partly frozen by immersion of a glass rod cooled by liquid nitrogen. This produced a rapid precipitation of an orange solid. The solid was recrystallised from 1 M. hydrochloric acid to give crystalline, orange cis- \[ \left [ \text{RuCl}_2 \text{en}_2 \right ] \text{Cl.H}_2\text{O} \] which was identified by its ultraviolet absorption spectrum, and by its subsequent isomerisation to trans- \[ \left [ \text{RuCl}_2 \text{en}_2 \right ] \text{Cl.H}_2\text{O} \]

SPECTRUM

Broomhead & Kane-Maguire

\begin{align*}
\text{Measured on} & \quad \text{Cary 14H} \\
4 \times 10^{-4} \text{M. in} & \quad 1 \text{ M. HCl} \\
\text{Yield based on cationic Ru:} & \quad 1.45 \text{ g., 88%}.
\end{align*}

trans-dichloro(ethylenediamine)ruthenium(III) chloride hemihydrate

Ethylene glycol (25 ml.) was heated to its boiling point
in a large test tube. When the glycol had cooled to 60° C., cis-\([\text{RuCl}_2\text{en}_2] \text{Cl.H}_2\text{O}\) (0.5 g.) was added and the solution temperature was raised to boiling for one minute. The tube was then cooled by immersion in water, and the solution was poured through a Dowex 50 W-X cation-exchange column (acid form, bed volume 2 ml.). The column was washed with 10 ml. of water and then with 20 ml. of 2 M HCl. The volume of the acid solution was reduced by evaporation to 10 ml. Orange crystals of trans-\([\text{RuCl}_2\text{en}_2] \text{Cl.H}_2\text{O}\) precipitated on cooling. These were filtered off and washed with ethanol and with acetone. The compound was recrystallised from 1 M HCl, oven dried, and identified by its ultraviolet absorption spectrum.

Yield: 0.32 g., 64%.

**SPECTRUM**

<table>
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<th>Kane-Maguire (5)</th>
<th>342 (4080); 295sh. (745); 268sh. (810)</th>
</tr>
</thead>
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<tr>
<td>Measured on Cary 14 H</td>
<td>343 (4030); 295sh. (702); 268sh. (760)</td>
</tr>
</tbody>
</table>

* Fresh 4x10^-4 M. solution in 2x10^-2 M. MeSO_3 H

trans-dichloro(ethylenediamine)ruthenium(III) iodide hemihydrate.

To the mother liquors from the preparation and recrystallisation of trans-\([\text{RuCl}_2\text{en}_2] \text{Cl.H}_2\text{O}\), was added excess solid sodium iodide. A bright, red solid precipitated with cooling. This was washed with ice water, with ethanol, and with acetone. A broad absorption in the region of 3,300-4,000 cm^-1
in its infrared spectrum indicated the presence of some water in the complex. The ultraviolet absorption closely resembled that of the chloride salt. Microanalysis gave the following values:

\[
\begin{align*}
C, & \ 11.6\%; \ H, \ 4.0\%; \ N, \ 13.2\%; \ Cl, \ 17.4\%; \ I, \ 29.8\%.
\end{align*}
\]

\[
\begin{align*}
C_4H_{17}N_4O_5Cl_2Ru & \text{ requires } C, 11.2\%; \ H, 4.0\%; \ N, 13.1\%; \ Cl, 16.7\%; \ I, 29.6\%.
\end{align*}
\]

\[
\begin{align*}
\text{trans-dichloro}\text{-bis(ethylenediamine) ruthenium(III) methanesulphonate}
\end{align*}
\]

\[
\begin{align*}
\text{trans-} \left[ \text{RuCl}_2\text{en}_2 \right] \text{I.} 1/2\text{H}_2\text{O} \ (10 \text{ mg.}) & \text{ was dissolved in 5 ml. of cold, } 10^{-2} \text{ M. methanesulphonic acid and poured through a column of Dowex 50 W-X cation-exchange resin (acid form, bed volume 0.5 ml.). The column was washed with a further 5 ml. of } 10^{-2} \text{ M. methanesulphonic acid until washings gave no reaction with silver ions. The column was then eluted with 5 ml. of 1 M. methanesulphonic acid. The eluant was frozen and water was sublimed off under reduced pressure for 16 hours. The paste remaining was washed with ether to extract methanesulphonic acid until a bright, yellow solid formed. The solid was washed with ether and dried in air. The ultraviolet absorption spectrum of a solution of the solid was that of the trans-} \left[ \text{RuCl}_2\text{en}_2 \right]^+ \text{ cation.}
\end{align*}
\]
trans-chloro-aquohis(ethylenediamine)ruthenium(III) toluene-p-sulphonate monohydrate

Silver toluene-p-sulphonate (0.24 g., 0.0009 moles) was suspended in 21 ml. of water at 60°C., and trans-\([\text{RuCl}_2\text{en}_2\text{]}\) Cl.\(\frac{1}{2}\)H\(_2\)O (0.15 g., 0.00045 moles) was stirred in. The suspension was heated on a steam bath for nine minutes, after which time it was filtered to remove silver chloride. The silver chloride weighed 0.135 g. If two moles of chloride were removed from each mole of complex, the weight of silver chloride would be 0.128 g. The solution was immediately frozen by immersion in an acetone/dry ice mixture, and water was sublimed off over ten hours leaving a fluffy white powder which turned to a paste on warming to room temperature. The paste was washed with ether and then taken up in 3 ml. of water and immediately refrozen. The water was sublimed off as before. The remaining solid was washed with ether and dried in vacuum. Yield: 0.063 g., 32.3%. Microanalysis gave the following values: C, 34.09%; H, 4.85%; N, 8.49%; S, 9.7%; Cl, 7.25%. Calculated values for \(\text{RuCl. H}_2\text{O en}_2\text{TPS}_2\cdot\text{H}_2\text{O}\) are C, 34.0%; H, 5.4%; N, 8.8%; S, 10.1%; Cl, 5.6%. The main discrepancy is in the amount of chlorine. If it is assumed that all excess chloride is present as \([\text{RuCl}_2\text{en}_2\text{]}^+\), the chloride analysis alone indicates the presence of 17% \([\text{RuCl}_2\text{en}_2\text{]}\) TPS. Theoretical values for a mixture of \([\text{RuCl. H}_2\text{O en}_2\text{]}\) TPS\(_2\).H\(_2\)O in a weight-to-weight ratio 17:63 are C, 33.07%; H, 5.31%; Cl, 7.25%; S, 9.56%; N, 9.36%.
The spectrum was measured in $10^{-1}$ M. methanesulphonic acid in the region 220-400 nm., and the absorbance attributable to 17% of trans-$[\text{RuCl}_2\text{en}_2]^{2-}$ was subtracted from it. The spectrum so obtained bore similarity to the spectrum obtained after aquation of trans-$[\text{RuCl}_2\text{en}_2]^+$ to the extent that one mole of chloride was removed for each mole of complex as described in Chapter 3.

**Preparations from Commercial Ruthenium Trichloride**

Ruthenium trichloride is readily available in its water-soluble form. This substance appears to have present some ruthenium in a higher oxidation state, as when it is dissolved in water some effervescence occurs and a pungent gas is evolved. Both B.D.H. laboratory reagent (described as "RuCl$_3$ + H$_2$O") and the Johnson Matthey product (described as "RuCl$_3$.xH$_2$O") were used in attempts to prepare $K_3[\text{Ru ox}_3].4\frac{1}{2}H_2O$, and later $[\text{Ru ox en}_2][\text{Ru ox}_2\text{en}].2H_2O$, with similar results.

**Potassium tria(oxalato)ruthenate**

Ruthenium trichloride (1 g.) and potassium oxalate were dissolved in 50 ml. of water and 50 mg. of powdered charcoal was added. The solution was refluxed for 5$\frac{1}{2}$ hours and allowed to stand overnight. The colour of the solution remained inky black throughout. The charcoal was removed by filtration. Methanol (50 ml.) was added to the filtrate slowly, with scratching, and a black solid was deposited. This substance gave no X-ray powder
diffraction pattern indicating it was truly amorphous, and appeared to absorb evenly over the ultraviolet and visible region, suggesting that its "solution" was, in fact, colloidal. Addition of electrolytes failed to precipitate any solid. Cooling and addition of further methanol to the original solution gave a brown precipitate whose powder pattern was similar to aged samples of potassium tris(oxalato)ruthenate 4 hydrate prepared previously. The best yield obtained by this method was 1.4 g, or 63.1% based on Ru. This compares unfavourably with yields of 78.2% by the previous method. Judged by its appearance and powder pattern, the product prepared from RuCl₃ was less pure.

At present, while both Ru metal and RuCl₃ are available, the preparation from the metal is to be preferred.

Oxalato(bis(ethylenediamine)ruthenium(III)) -

bis(oxalato)ethylenediamineruthenate(III) dihydrate

Ethylenediammonium oxalate (1.35 g.) was dissolved in 25 ml. of water on a steam bath. To the warm solution was added ruthenium trichloride (1 g.). The mixture was heated for half an hour, while sodium carbonate (0.59 g.) was added at such a rate as to keep its pH between 6 and 7. The solution was chilled on ice, filtered through sintered glass, and evaporated while cold to precipitate a yellow-green solid. This was recrystallised from water to give yellow crystals of $[\text{Ru ox }_2 \text{en}_2][\text{Ru ox}_2\text{en}] \cdot 2\text{H}_2\text{O}$ whose identity was confirmed by subsequent reaction to produce $^\text{cis-}\left[\text{RuCl}_2\text{en}_2\right] \text{Cl.H}_2\text{O}$. The yield by this method was 0.6 g. (30%)
which is less than the yield of 52.1% obtained by the sequence of reactions beginning with ruthenium metal.
DEFINITION OF RATE

In the present work, all reactions studied involve one and only one metal complex, C, as a reactant, and the "rate" will always be taken to mean the negative of the derivative of the molarity of that complex expressed as a function of time. All rates will, therefore, be positive and have units of moles per litre per unit time. This usage is consistent with that in relevant literature.

The rates of simple reactions can usually be expressed as a function of the concentrations of one or more of the reactants. In many cases the rate is proportional to the concentration of C.

\[ \frac{-d[C]}{dt} = k_1 [C] \]  

\begin{align*}
\text{i.e.} & \quad \frac{-d[C]}{dt} = k_1 [C] \\
\end{align*} \tag{1}

where \( k_1 \) is constant. Such reactions are known as "first order" reactions. The constant \( k_1 \) has dimensions \( \text{time}^{-1} \) and is known as the "first-order rate constant" for the reaction. Equation (1) may be integrated to express C in terms of t.
14.

viz.: \[ -k_1 \frac{d}{dt} [C] = [C]^{-1} \]

\[ -k_1 dt = \int [C]^{-1} d[C] \]

\[ -k_1 t = \ln[C] + \text{const.} \]

If \([C]_0\) is the value of \([C]\) when \(t=0\), then \[-k_1 t = \ln[C] - \ln[C]_0\]

i.e. \[ \ln\left(\frac{[C]}{[C]_0}\right) = -k_1 t \quad (2) \]

or \[ \log_{10}\left(\frac{[C]}{[C]_0}\right) = -2.303 k_1 t \quad (2a) \]

From (2), \([C] = [C]_0 \exp.(-k_1 t) \quad (3)\]

The "half-life", \(t_{1/2}\), of a first-order reaction is defined as the time taken for the concentration of a reactant (in this case \(C\)) to change by a factor of 0.5.

From equation (2), when \([C] = \frac{1}{2} [C]_0\),

\[ \ln \frac{1}{2} = -k_1 t_{1/2} \]

\[ t_{1/2} = -\ln 2 / k_1 = \ln 2 / k_1 \quad (4) \]

or \[ t_{1/2} = 2.303 \log_{10} 2 / k_1 \quad (4a) \]

The general second order reaction \(A + C \rightarrow \text{products}\)

has rate given by

\[ \frac{-d[C]}{dt} = k_2 [C][A] \quad (5) \]

Such an equation may be integrated by separating the variables and expressing the concentration side of the resulting equation as partial fractions (6).

The resulting equation is

\[ \frac{1}{([C]_0 - [A]_0)} \ln\left(\frac{[A]_0[C]/[C]_0[A]}{[C]}\right) = k_2 t \quad (6) \]
If equal molar quantities of two reactants \( A \) and \( C \) are consumed,

\[
[A]_0 - [A] = [C]_0 - [C].
\]

Equation (6) then reduces to

\[
\frac{1}{([C]_0 - [A]_0)} \ln \left( \frac{[A]_0 ([C]_0 - x)}{[C]_0 ([A]_0 - x)} \right) = k_2 t \tag{7}
\]

where \( x = [A]_0 - [A] = [C]_0 - [C] \).

**Pseudo first-order reactions.**

For the second-order reaction

\[
C + A \rightarrow \text{products},
\]

\[
\frac{-d[C]}{dt} = k_2[C][A] \tag{5}
\]

If \( A \) is present in sufficient excess \([A]\) will remain nearly constant as the reaction proceeds to completion.

Then

\[
\frac{-d[C]}{dt} = k_2[A]_0[C] \tag{6}
\]

or,

\[
\frac{-d[C]}{dt} = k_{\text{apparent}}[C] \tag{9}
\]

Because of the simpler form of the rate equation, it is common practice to study second order reactions with reactant \( A \) present in excess. The second order nature of the reaction may be confirmed by measuring the rate at a variety of concentrations of \( A \).
Unless \( \frac{[A]_0}{[C]_0} \) is very large, the plot of \( \log [C] \) against time for a pseudo first-order reaction will not be quite linear. Consider the reaction

\[ A + C \rightarrow \text{products}, \]

where the ratio \( \frac{[A]_0}{[C]_0} \) is 10. After one half-life,

\[ \frac{[C]_{1/2}}{[C]_0} = 0.5 \quad \text{where } [C]_{1/2} \text{ is the concentration of } C \text{ at } t_{1/2}. \]

From the stoichiometry,

\[ \frac{[A]_{1/2}}{[A]_0} = 0.95 \quad \text{where } [A]_{1/2} \text{ is the concentration of } A \text{ at } t_{1/2}. \]

The apparent first order rate constant is therefore 5% smaller at \( t_{1/2} \) than at \( t = 0 \). This error can, in principal, be made as small as desired by increasing the ratio of \( [A]_0 \) to \( [C]_0 \), but in practice a lower limit on \( [C]_0 \) is set by the sensitivity of the measuring technique used, and an upper limit on \( [A]_0 \) may be set by the maximum speed at which the reaction can be followed.

**The Dependence of Reaction Rate on Temperature**

It is well known that the rate of most chemical reactions increases with temperature. By analogy with the van't Hoff equation for temperature dependence of equilibrium constants (7), Arrhenius, in 1889, (8) suggested that the variation of rate constants with temperature might take the form

\[ \frac{d \ln k}{dT} = \frac{E_a}{RT^2} \quad (11) \]
where $T$ is temperature in degrees kelvin and $R$ is the gas constant. $E_a$ is the "activation energy", and represents the molar increase in potential energy of the molecule from the ground state to the transition state (Fig. 2.1)

From equation (11),

$$d \ln k = \frac{(E_a/RT^2)}{dT}$$

If $E_a$ is independent of temperature,

$$d \ln k = E_a (1/RT^2) dt$$

from which

$$\ln k = -\frac{E_a}{RT} + \ln A \quad (12)$$

where $\ln A$ is the constant of integration, or

$$\log_{10} k = -\frac{E_a}{(2.303RT)} + \log_{10} A \quad (12a)$$
From (12),
\[ k = A \exp\left(-\frac{E_a}{RT}\right) \]  
(13)
which is the form usually expressed as "the Arrhenius equation".

For most reactions, the rate constants follow closely the behaviour predicted by equation (13).
When \( E_a \) is small the coefficient shows variation with temperature (9).

The transition state theory (10) relates the rate constant to the free energy of activation, \( \Delta G^\pm \), by
\[ k_r = \left(\frac{kT}{h}\right) \exp\left(-\frac{\Delta G^\pm}{RT}\right) \]  
(14)
where \( k \) is the Boltzmann constant
\( k_r \) is the rate constant
and \( h \) is Planck's constant.

The enthalpy of activation, \( \Delta H^\pm \), is given by
\[ \Delta H^\pm = E_a - RT \]  
(15)

The entropy of activation, \( \Delta S^\pm \), is defined by
\[ \Delta S^\pm = \left(\frac{\Delta H^\pm - \Delta G^\pm}{T}\right) \]  
(16)
From equation (14),
\[ \ln \left(\frac{hk_r}{kT}\right) = -\frac{\Delta G^\pm}{RT} \]
or
\[ \log_{10}\left(\frac{hk_r}{kT}\right) = -\frac{\Delta G^\pm}{2.303RT} \]
so that

\[ \Delta G^\circ = -2.303 \text{ RT} \log_{10}(\frac{hk}{kT}) \]

then,

\[ \Delta S^\circ = \frac{E_a}{T-R} + 2.303R(\log_{10}h + \log_{10}k_r - \log_{10}k - \log_{10}T) \]

For the values:

\[ R = 1.987 \text{ cal.deg}^{-1}\text{mole}^{-1} \]
\[ k = 3.299 \times 10^{-25} \text{ cal deg}^{-1} \]
\[ h = 1.583 \times 10^{-34} \text{ cal.sec} \]

\[ \Delta S^\circ = \frac{E_a}{T} - 49.214 + 4.575(\log_{10}k_r - \log_{10}T) \]

Use of Optical Density to follow Reaction Kinetics

Consider a first-order reaction:

\[ \text{C + sundry reactants} \rightarrow \rightarrow \text{P + sundry products} \]

where C and P have different extinction coefficients at some wavelength, \( \lambda \), but all other species show no nett change in optical density at \( \lambda \) during the reaction.

At any time, \( t \),

\[ A_t = d( [C]_t \varepsilon_C + [P]_t \varepsilon_P ) \]

where \( \varepsilon_C \) and \( \varepsilon_P \) are the respective extinction coefficients of C and P at \( \lambda \), and \( d \) is the length of the light path through the solution.
From the stoichiometry,
\[ [P]_t = [C]_0 - [C]_t \]
where \([C]_0\) is the original concentration of C.

so

\[ A_t = d \left( [C]_t \varepsilon_C + [C]_0 \varepsilon_P - [C]_t \varepsilon_P \right) \]

\[ = d \left( [C]_t (\varepsilon_C - \varepsilon_P) + [C]_0 \varepsilon_P \right) \]

(20)

If the reaction proceeds to completion,

\[ A_\infty = [C]_0 \varepsilon_P d \]

From (20),

\[ A_t = d [C]_t (\varepsilon_C - \varepsilon_P) + A_\infty \]

\[ A_t - A_\infty = d [C]_t (\varepsilon_C - \varepsilon_P) \]

\[ [C]_t = \frac{(A_t - A_\infty)}{d(\varepsilon_C - \varepsilon_P)} \]

(21)

Dividing both sides by \([C]_0\),

\[ \frac{[C]_t}{[C]_0} = \frac{(A_t - A_\infty)}{d [C]_0 (\varepsilon_C - \varepsilon_P)} \]

but,

\[ d [C]_0 \varepsilon_C = A_0 \text{ and } d [C]_0 \varepsilon_P = A_\infty, \]

so

\[ \frac{[C]_t}{[C]_0} = \frac{(A_t - A_\infty)}{(A_0 - A_\infty)} \]

From equation (2a), page 14,

\[ \log_{10}\left( \frac{[C]_t}{[C]_0} \right) = -2.303 k_1 t \]

so

\[ \log_{10}\left( \frac{(A_t - A_\infty)}{(A_0 - A_\infty)} \right) = -2.303 k_1 t \]

or, for more convenient evaluation,

\[ 1 + \log_{10}\left( \frac{(A_t - A_\infty)}{(A_0 - A_\infty)} \right) = 1 - 2.303 k_1 t \]

(22)
Substitution reactions of octahedral metal complexes
may be subdivided into four classes, following the pattern
introduced by Ingold (11). These are nucleophilic, unimolecular
and bimolecular substitutions, $S_{N1}$ and $S_{N2}$; and electrophilic,
unimolecular and bimolecular substitutions, $S_{E1}$ and $S_{E2}$. The
present work is concerned only with nucleophilic substitutions.

As is true for substitutions at a saturated carbon
atom (12), there is no clear division between $S_{N1}$ and $S_{N2}$
mechanisms. A pure $S_{N1}$ is one in which a ligand is lost from
the complex to leave a definite, 5-coordinated intermediate
which then reacts with another ligand. A pure $S_{N2}$ reaction is
one in which a ligand becomes attached to the complex to form
a 7-coordinated species. Another ligand is then expelled. The
$S_{N1}$ situation is complicated by the role of the solvent. If the
dissociation is assisted by the incoming ligand, then to some
extent the incoming molecule is bonded to the complex before the
leaving group is lost. To that extent the substitution may be
considered to be bimolecular.

Current terminology (13) divides nucleophilic substitution
into four classes in which the pure $S_{N1}$ and $S_{N2}$ mechanisms referred
to above are known as $S_{N1} (\text{lim})$ and $S_{N2} (\text{lim})$ respectively, and the
intermediate cases are known as $S_{N1}$ or $S_{N2}$, depending on whether
bond-making is more important than bond-breaking in determining
the rate. The distinctions between these four classes are summarised in table 3.1 after Basolo and Pearson (13).

<table>
<thead>
<tr>
<th></th>
<th>$S_{N1}$ (lim)</th>
<th>$S_{N1}$</th>
<th>$S_{N2}$</th>
<th>$S_{N2}$ (lim)</th>
</tr>
</thead>
<tbody>
<tr>
<td>Degree of bond-breaking in rate step:</td>
<td></td>
<td></td>
<td></td>
<td></td>
</tr>
<tr>
<td>large</td>
<td>large</td>
<td>appreciable</td>
<td>none</td>
<td></td>
</tr>
<tr>
<td>Degree of bond-making in rate step:</td>
<td></td>
<td></td>
<td></td>
<td></td>
</tr>
<tr>
<td>none</td>
<td>none to small</td>
<td>appreciable</td>
<td>large</td>
<td></td>
</tr>
<tr>
<td>Evidence for intermediate of reduced C.N.:</td>
<td></td>
<td></td>
<td></td>
<td></td>
</tr>
<tr>
<td>definite</td>
<td>indefinite</td>
<td>none</td>
<td>none</td>
<td></td>
</tr>
<tr>
<td>Evidence for intermediate of expanded C.N.:</td>
<td></td>
<td></td>
<td></td>
<td></td>
</tr>
<tr>
<td>none</td>
<td>none</td>
<td>indefinite</td>
<td>definite</td>
<td></td>
</tr>
</tbody>
</table>

There is no single test which will assign a nucleophilic substitution to its correct class. Stereochemistry is one source of useful (though not unambiguous) information. The stereospecificity of an $S_{N1}$ reaction depends on the shape and symmetry of the intermediate. Generally, but not always, a high degree of stereospecificity indicates $S_{N2}$ character.

Good evidence for an $S_{N1}$ mechanism is a lack of dependence of the rate on the entering ligand, which is not involved in the rate-determining step.
The effect of other ligands may also give evidence of the molecularity of a nucleophilic substitution. Bulky ligands should impede the attack more in a six-coordinated stable complex than in a five-coordinated intermediate. A negative ligand which lowers the overall charge of the complex will facilitate dissociation, but lessen the likelihood of displacement. Basolo and Pearson (14) have summarised the expected effects of sizes and charges within a complex on the reaction rate for $S_N^1$ and $S_N^2$ reactions. Their data are presented in Table 3.2.

Table 3.2 Effect of sizes and charges on rates of $S_N^1$ and $S_N^2$ reactions.

<table>
<thead>
<tr>
<th></th>
<th>$S_N^1$ (lim)</th>
<th>$S_N^2$</th>
<th>$S_N^2$ (lim)</th>
</tr>
</thead>
<tbody>
<tr>
<td>Increased positive charge of central atom</td>
<td>decrease</td>
<td>opposing effects</td>
<td>increase</td>
</tr>
<tr>
<td>Increased size of central atom</td>
<td>increase</td>
<td>increase</td>
<td>increase</td>
</tr>
<tr>
<td>Increased negative charge of entering group</td>
<td>no effect</td>
<td>increase</td>
<td>increase</td>
</tr>
<tr>
<td>Increased size of entering group</td>
<td>no effect</td>
<td>decrease</td>
<td>decrease</td>
</tr>
<tr>
<td>Increased negative charge of leaving group</td>
<td>decrease</td>
<td>decrease</td>
<td>decrease</td>
</tr>
<tr>
<td>Increased size of leaving group</td>
<td>increase</td>
<td>opposing effects</td>
<td>decrease</td>
</tr>
<tr>
<td>Increased negative charge of other ligands</td>
<td>increase</td>
<td>opposing effects</td>
<td>decrease</td>
</tr>
<tr>
<td>Increased size of other ligands</td>
<td>increase</td>
<td>decrease</td>
<td>decrease</td>
</tr>
</tbody>
</table>
A single transition-state model which is applicable to $S_N^1$ (lim), $S_N^2$ (lim) and intermediate mechanisms was proposed in 1961 by N. S. Hush (15). The expected shape of a five-coordinated intermediate would be that of a square pyramid (Fig. 3.1 b) (16) as no gain in crystal field stabilisation could be expected from distortions to, say, a trigonal bipyramid (but see chapter 4). Hush calculated crystal field activation energies for hypothetical seven-coordinated intermediates with all bond lengths equal. A structure (Fig. 3.1 c) in which five ligands point towards vertices of an octahedron and the other two lie on either side of the remaining vertex was shown to have a C.F.A.E. lower than that for a pentagonal bipyramid (Fig. 3.1 a). In the transition state of a mechanism intermediate between $S_N^1$ (lim) and $S_N^2$ (lim), the length of the two non-octahedral bonds, $R^\pi$, would be greater than that of the remaining five, $R$. As the ratio $R^\pi/R$ increases, the structure limits to that of a square pyramid (Figs. 3.1 c, d, b).
The structure described by Hush has become known as an "octahedral wedge". Crystal field activation energies for high-spin and low-spin configurations $d^0 - d^{10}$ are summarised in table 3.4 after Basolo and Pearson (16) and Hush (15). Energy values are in terms of the octahedral splitting parameter, $Dq$, which is of the order of $1$ or $2 \times 10^3 \text{ cm}^{-1}$ for first row elements and somewhat greater for second and third row elements.
It must be remembered that the figures in Table 3.4 overlook the effects of the ligands themselves on the overall energies. Such effects have been found to be important in determining the mechanisms of substitutions. Comparisons from one metal to another may be made only if the differences in their Dq values are taken into account. The negative values of the C.F.A.E. for certain configurations indicate that an undistorted octahedron is unlikely to be the correct structure for the original complex and Dasolo and Pearson (18) suggest that these values are better considered zero.

**Table 3.4**

Crystal Field Activation Energies (in Dq)

for octahedron → structure specified.

<table>
<thead>
<tr>
<th>Configuration</th>
<th>Square Pyramid</th>
<th>Pentagonal Bipyramid</th>
<th>Octahedral Wedge</th>
</tr>
</thead>
<tbody>
<tr>
<td>d⁰</td>
<td>0</td>
<td>0</td>
<td>0</td>
</tr>
<tr>
<td>d¹</td>
<td>-0.57</td>
<td>-1.28</td>
<td>-2.08</td>
</tr>
<tr>
<td>d²</td>
<td>-1.14</td>
<td>-2.56</td>
<td>-0.68</td>
</tr>
<tr>
<td>d³</td>
<td>2.00</td>
<td>4.26</td>
<td>1.80</td>
</tr>
<tr>
<td>d⁴ high spin</td>
<td>-3.14</td>
<td>1.07</td>
<td>-2.79</td>
</tr>
<tr>
<td>d⁴ low spin</td>
<td>1.43</td>
<td>2.38</td>
<td>-0.26</td>
</tr>
<tr>
<td>d⁵ high spin</td>
<td>0</td>
<td>0</td>
<td>0</td>
</tr>
<tr>
<td>d⁵ low spin</td>
<td>0.86</td>
<td>1.70</td>
<td>1.14</td>
</tr>
<tr>
<td>d⁶ high spin</td>
<td>-0.57</td>
<td>-1.28</td>
<td>-2.08</td>
</tr>
<tr>
<td>d⁶ low spin</td>
<td>4.00</td>
<td>8.52</td>
<td>3.63</td>
</tr>
<tr>
<td>d⁷</td>
<td>-1.14</td>
<td>5.34</td>
<td>-0.98</td>
</tr>
<tr>
<td>d⁸</td>
<td>2.00</td>
<td>4.26</td>
<td>1.80</td>
</tr>
<tr>
<td>d⁹</td>
<td>-3.14</td>
<td>1.07</td>
<td>-2.79</td>
</tr>
<tr>
<td>d¹⁰</td>
<td>0</td>
<td>0</td>
<td>0</td>
</tr>
</tbody>
</table>
Acid Hydrolysis

"Acid hydrolysis" or "aquation" is the term used for nucleophilic substitution by water. The unqualified term "hydrolysis" may mean acid hydrolysis, base hydrolysis (see chapter 4), or the simultaneous occurrence of both reactions.

In aqueous solutions, acid hydrolysis is one of the most commonly encountered reactions. Indeed, if $S_N^1$-type dissociation takes place, the vast excess of water relative to any other potential ligand will make acid hydrolysis the most common reaction. Of course, the relative thermodynamic stabilities of the aquo complex and complexes formed by other nucleophiles might be such that the aquo complex is not isolated. Such behaviour alone cannot be considered proof for an $S_N^1$ mechanism however. Garrick (19) first found only slight dependence of the rate of aquation of $[\text{CoCl}(\text{NH}_3)_5]^{2+}$ on the concentration of a number of anions. Ette and Johnson (20) first found that the rate of exchange of radioactive chloride was the same as that for aquation of cis-$[\text{CoCl}_2\text{en}_2]^{+}$, indicating that the reaction took place via an aquo complex. Studies of nucleophilic substitution and isotopic exchange have been made for acido-amine complexes of cobalt (21), chromium (22,23), rhodium (24, 25, 26, 27), and iridium (28); and all these reactions appear to proceed via aquo complexes.

The results of Broomhead, Basolo and Pearson (29), and Broomhead and Kane-Maguire (30) show that $[\text{RuCl}(\text{NH}_3)_5]^{2+}$, and several complexes of the type $[\text{Ru}X_2(\AA)_2]^{+}$ undergo all their
nucleophilic substitutions in acid solution via an aquo complex.

Data for the acid hydrolysis of a number of complexes of the type \([\text{M}^{III}\text{Cl}_2\text{en}_2]^+\) are summarised in table 3.5.

**TABLE 3.5**

<table>
<thead>
<tr>
<th>Metal</th>
<th>Isomer</th>
<th>(10^5 k \text{ (sec}^{-1})</th>
<th>Temp. (°C)</th>
<th>Ref</th>
</tr>
</thead>
<tbody>
<tr>
<td>Co</td>
<td>cis</td>
<td>24.0</td>
<td>25</td>
<td>30</td>
</tr>
<tr>
<td>Co</td>
<td>trans</td>
<td>3.5</td>
<td>25</td>
<td>30</td>
</tr>
<tr>
<td>Cr</td>
<td>cis</td>
<td>33.0</td>
<td>25</td>
<td>23</td>
</tr>
<tr>
<td>Rh</td>
<td>cis</td>
<td>51</td>
<td>80</td>
<td>24</td>
</tr>
<tr>
<td>Rh</td>
<td>trans</td>
<td>2.7</td>
<td>80</td>
<td>24</td>
</tr>
<tr>
<td>Ir</td>
<td>trans</td>
<td>7*</td>
<td>130</td>
<td>27</td>
</tr>
<tr>
<td>Ru</td>
<td>cis</td>
<td>3.8</td>
<td>24.9</td>
<td>29</td>
</tr>
</tbody>
</table>

* anation rates for various nucleophiles

**EXPERIMENTAL**

The acid hydrolysis of the trans-[RuCl\(_2\)en\(_2\)]^+ ion was followed mainly by a spectrophotometric method. Results were confirmed by titration of the chloride ion in a reaction mixture at varying stages of reaction. Of the several methods available for volumetric determination of chloride ion, only two are suitable for use in strongly acidic solutions (31). These are titration by mercuric ion using nitroprusside ion as indicator (32),
and the indirect method of Volhard. The former is described in chapter 4. The latter was used in the present section of the work.

**Spectrophotometric Method**

The spectrum of the \( \text{trans-} [\text{RuCl}_2\text{en}_2]^+ \) ion (Fig. 3.2) was obtained from fresh, \( 3 \times 10^{-4} \) M. solutions of its recrystallised, oven-dried chloride salt in both \( 10^{-1} \) M. methanesulphonic acid and \( 10^{-1} \) M. hydrochloric acid. The spectrum of the \( \text{trans-} [\text{RuCl}_2\text{H}_2\text{Oen}_2]^+ \) cation was obtained from a solution in \( 10^{-1} \) M. methanesulphonic acid of the toluene-\( p \)-sulphonate salt the preparation is described in chapter 1.

A sample of the \( \text{trans-} [\text{RuCl}(\text{H}_2\text{O})\text{en}_2]^{+}\text{TPS}_2\cdot\text{H}_2\text{O} \) preparation is described in chapter 1 and a sample of \( \text{trans-} [\text{RuCl}_2\text{en}_2]^{+}\text{Cl}_2\cdot\text{H}_2\text{O} \) were subjected to identical treatment by chromatography. The solvent was composed of equal volumes of perchloric acid and tertiary butanol. A 28 cm. strip of Whatman number 1 paper (4 cm. wide) were used. The sample of \( \text{trans-} [\text{RuCl}(\text{H}_2\text{O})\text{en}_2]^{+}\text{TPS}_2\cdot\text{H}_2\text{O} \) separated into two components, the major of which had an Rf value of 0.46, and the minor of which had an Rf value of 0.01, corresponding to that of \( \text{trans-} [\text{RuCl}_2\text{en}_2]^{+}\text{Cl}_2\cdot\text{H}_2\text{O} \).

Microanalysis of the sample was consistent with the presence of 17\% \( \text{trans-} [\text{RuCl}_2\text{en}_2]^{+}\text{TPS}_2\cdot\text{H}_2\text{O} \).
Figure 3.2. Ultraviolet absorption spectrum of $3 \times 10^{-4} \text{M} \text{trans-} \left[ \text{RuCl}_2 \text{en}_2 \right] \text{Cl}_2 \cdot \text{H}_2 \text{O}$ in 0.1 M hydrochloric acid or 0.1 M methanesulphonic acid.
A correction was applied to the observed spectrum to compensate for this. The corrected spectrum is shown in figure 3.3.

All spectrophotometrically-followed acid hydrolyses were performed in situ in the thermostatted (±0.05°C) cell compartment of a Cary 14H spectrophotometer.

Weighed samples of approximately 0.2 mg. of trans-[RuCl₂en₂]⁺Cl·½H₂O or approximately 0.2 mg. of trans-[RuCl₂en₂]TF₅S·½H₂O were added to 3 ml of solvent in a 1 cm cell. The solvent consisted of dilute methanesulphonic acid (of known concentration) and sometimes contained sodium methanesulphonate to adjust its ionic strength. The solvent in the cell was already at the required temperature.

From within 15 seconds of mixing, until it reached a steady value, the absorbance of the solution at 343 nm was recorded continuously. For faster runs, allowance was made for the time between mixing and observation in subsequent calculations.

Because of weighing errors with sub-milligram samples, and because of the adherence of small amounts of complex to the weighing paper, it was found more satisfactory to calculate the concentration of complex from the extrapolated absorbance at zero time than from weight and volume measurements.

**EXTENT OF REACTION**

Under the conditions studied, the reaction

\[
\text{trans-} \left[ \text{RuCl}_2\text{en}_2 \right]^+ + \text{H}_2\text{O} \rightarrow \text{trans-} \left[ \text{RuCl.H}_2\text{Oen}_2 \right]^{2+} + \text{Cl}^-
\]

was not possible to weigh the complex directly into the cell, since the cell and solvent had to be thermostatted.
Figure 3.3. Corrected U.V. absorption Spectrum of 

trans-[RuCl₂H₂O.C₂H₄]TPS₂
Figure 3.4.
First-order plots of the acid hydrolysis of the trans-\([\text{RuCl}_2\text{en}_2]^+\) ion at various initial \([\text{Cl}^-]\) values.
does not proceed to completion. A plot of \(1 + \log_{10}\left(\frac{A_t - A_{\infty}}{A_0 - A_{\infty}}\right)\)

(see chapter 2) against time gives a straight line for small \(t\) but deviates considerably at larger values of \(t\), and reaches a constant value. This suggests that an equilibrium is established.

The extent of reaction was altered by performing the reaction under identical conditions of temperature (60.1 °C), acid strength (0.10 M) and ionic strength (0.1 M), varying only the initial chloride concentration. Plots of \(1 + \log_{10}\left(\frac{A_t - A_{\infty}}{A_0 - A_{\infty}}\right)\) against time for such a series of reactions are shown together in figure 3.4.

All plots start with the same slope but deviations become significant sooner for those reactions having a higher concentration of chloride ion. The reaction for which the initial chloride concentration was zero is linear for two half lives. From the final optical density of each reaction, an equilibrium constant was calculated in the following manner. It was assumed that no significant concentration of the

\[
\text{trans-} \left[\text{Ru(H}_2\text{O)}_2\text{en}_2\right]^{3+}
\]

ion had been formed.

For the equation :-

\[
\text{trans-} \left[\text{RuCl}_2\text{en}_2\right]^{+} + \text{H}_2\text{O} \rightleftharpoons \text{trans-} \left[\text{RuClH}_2\text{en}_2\right]^{2+} + \text{Cl}^-
\]

let \(X\) represent \(\text{trans-} \left[\text{RuCl}_2\text{en}_2\right]^{+}\); and

let \(Y\) represent \(\text{trans-} \left[\text{RuClH}_2\text{en}_2\right]^{2+}\)

Initially, \(A_0 = \varepsilon_x [X]_o t\) where \(t\) is solution thickness

At equilibrium \(A_{eq} = \varepsilon_x [X]_t + \varepsilon_y [Y]_t\)

From stoichiometry

\[
[X] = [X]_o - [Y]
\]

and \([\text{Cl}^-] = [\text{Cl}^-]_o + [Y]\)
From (1) and (2), \( A_{eq} \):

\[
A_{eq} = \mathcal{E}_x [X]_t - \mathcal{E}_x [Y]_t + \mathcal{E}_y [Y]_t
= A_o - \mathcal{E}_x [Y]_t + \mathcal{E}_y [Y]_t
= A_o + (\mathcal{E}_y - \mathcal{E}_x) [Y]_t
\]

\[
A_o - A_{eq} = (\mathcal{E}_x - \mathcal{E}_y) [Y]_t
\]

\[
[Y] = \frac{(A_o - A_{eq})}{(\mathcal{E}_x - \mathcal{E}_y) t}
\]

Equilibrium constants calculated from equations (2), (3) and (4) are listed in Table 3.6. Although the uncertainties are large, especially for the highest and lowest values of the initial chloride ion concentration, all six constants agree within their own limits of uncertainty.

**Table 3.6**

Experimental Equilibrium Constants for

\[
\text{trans-}[\text{RuCl}_2\text{en}_2]^+ + H_2O \rightarrow \text{trans-}[\text{RuCl}_2\text{H}_2\text{Oen}_2]^{2+} + \text{Cl}^-
\]

at 60.1°C.

<table>
<thead>
<tr>
<th>Initial Chloride Concentration (Moles/litre)</th>
<th>( \frac{[\text{trans-}[\text{RuCl}_2\text{H}_2\text{Oen}_2]^{2+}] [\text{Cl}^-]}{[\text{trans-}[\text{RuCl}_2\text{en}_2]^+] \text{(Moles/litre)}} )</th>
</tr>
</thead>
<tbody>
<tr>
<td>0</td>
<td>0.15 ± 0.15</td>
</tr>
<tr>
<td>( 4.00 \times 10^{-4} )</td>
<td>0.27 ± 0.06</td>
</tr>
<tr>
<td>( 1.00 \times 10^{-3} )</td>
<td>0.35 ± 0.03</td>
</tr>
<tr>
<td>( 1.23 \times 10^{-3} )</td>
<td>0.28 ± 0.03</td>
</tr>
<tr>
<td>( 1.02 \times 10^{-2} )</td>
<td>0.31 ± 0.03</td>
</tr>
<tr>
<td>( 1.00 \times 10^{-1} )</td>
<td>0.43 ± 0.16</td>
</tr>
<tr>
<td>Mean:</td>
<td>0.30 ± 0.05</td>
</tr>
</tbody>
</table>
Figure 3.5 First-order plot from spectrophotometric data for acid hydrolysis of the trans-\([\text{RuCl}_2\text{en}_2]^{+}\) ion. (From TABLE 3.7)

Table 3.7 shows the variation of optical density with time for a kinetic run in which the \([\alpha]_5^\circ\) A simple programme in "FOCAL" language (see Appendix ) was used to calculate the functions in columns 3 and 4.
TABLE 3.7

<table>
<thead>
<tr>
<th>t (min)</th>
<th>A</th>
<th>( \frac{A_t - A_\infty}{A_0 - A_\infty} )</th>
<th>( 1 + \log_{10}\left( \frac{A_t - A_\infty}{A_0 - A_\infty} \right) )</th>
</tr>
</thead>
<tbody>
<tr>
<td>0</td>
<td>0.640</td>
<td>1.000</td>
<td>1.000</td>
</tr>
<tr>
<td>8</td>
<td>0.596</td>
<td>0.904</td>
<td>0.956</td>
</tr>
<tr>
<td>16</td>
<td>0.557</td>
<td>0.816</td>
<td>0.913</td>
</tr>
<tr>
<td>24</td>
<td>0.522</td>
<td>0.741</td>
<td>0.870</td>
</tr>
<tr>
<td>32</td>
<td>0.490</td>
<td>0.671</td>
<td>0.827</td>
</tr>
<tr>
<td>40</td>
<td>0.461</td>
<td>0.608</td>
<td>0.784</td>
</tr>
<tr>
<td>48</td>
<td>0.433</td>
<td>0.546</td>
<td>0.737</td>
</tr>
<tr>
<td>56</td>
<td>0.412</td>
<td>0.500</td>
<td>0.699</td>
</tr>
<tr>
<td>64</td>
<td>0.391</td>
<td>0.454</td>
<td>0.657</td>
</tr>
<tr>
<td>72</td>
<td>0.371</td>
<td>0.411</td>
<td>0.613</td>
</tr>
<tr>
<td>80</td>
<td>0.356</td>
<td>0.387</td>
<td>0.577</td>
</tr>
<tr>
<td>88</td>
<td>0.341</td>
<td>0.345</td>
<td>0.538</td>
</tr>
<tr>
<td>96</td>
<td>0.328</td>
<td>0.316</td>
<td>0.500</td>
</tr>
<tr>
<td>104</td>
<td>0.315</td>
<td>0.288</td>
<td>0.459</td>
</tr>
<tr>
<td>112</td>
<td>0.297</td>
<td>0.248</td>
<td>0.395</td>
</tr>
<tr>
<td>120</td>
<td>0.288</td>
<td>0.229</td>
<td>0.359</td>
</tr>
<tr>
<td>128</td>
<td>0.280</td>
<td>0.211</td>
<td>0.324</td>
</tr>
</tbody>
</table>
The plot of $1 + \log_{10}\left(\frac{A_t - A_\infty}{A_0 - A_\infty}\right)$ appears in figure 3.5.

From the slope of the line, a first-order rate constant of $2.03 \times 10^{-4} \text{ sec}^{-1}$ was calculated as described in chapter 2.

**Dependence of Rate on Acid Concentration**

Data for the aquation of the trans- $\text{[RuCl}_2\text{en}_2]$\textsuperscript{+} ion at an ionic strength of 1.0M. are shown in Table 3.8.

**Table 3.8**

<table>
<thead>
<tr>
<th>Molarity of MeSO\textsubscript{3}H</th>
<th>$k_1$ (sec\textsuperscript{-1})</th>
</tr>
</thead>
<tbody>
<tr>
<td>1.00</td>
<td>$5.05 \times 10^{-4}$</td>
</tr>
<tr>
<td>1.00 $\times 10^{-1}$</td>
<td>$5.37 \times 10^{-4}$</td>
</tr>
<tr>
<td>1.00 $\times 10^{-2}$</td>
<td>$6.07 \times 10^{-4}$</td>
</tr>
</tbody>
</table>

A slight increase is observed over a hundredfold decrease in acid concentration. This may be due to a small amount of base hydrolysis (see Chapter 4).

**Temperature Dependence**

The rate constants for aquation of the trans- $\text{[RuCl}_2\text{en}_2]$\textsuperscript{+} ion at ionic strength and acid concentration of $10^{-1}$M at a variety of temperatures are shown in Table 3.9.
TABLE 3.9

<table>
<thead>
<tr>
<th>temperature °C</th>
<th>$10^4 x k_1$ (sec$^{-1}$)</th>
</tr>
</thead>
<tbody>
<tr>
<td>39.9</td>
<td>0.239</td>
</tr>
<tr>
<td>50.1</td>
<td>0.75</td>
</tr>
<tr>
<td>59.3</td>
<td>1.97</td>
</tr>
<tr>
<td>68.9</td>
<td>5.05</td>
</tr>
<tr>
<td>68.9</td>
<td>4.74</td>
</tr>
<tr>
<td>78.7</td>
<td>10.99</td>
</tr>
</tbody>
</table>

A plot of $\log_{10} k$ against the reciprocal of absolute temperature is shown in figure 3.6. The following Arrhenius parameters (see Chapter 2) were calculated from this data by a simple "FOCAL" programme (see Appendix).

\[
\log_{10} A = 10.63
\]

\[
E_a = 21.8 \text{ Kcal/mole}
\]

\[
\Delta S^{\mp} = -10.4 \text{ cal deg}^{-1} \text{ mol}^{-1}
\]
Figure 3.6 Temperature dependence of the acid hydrolysis of the trans-\([\text{RuCl}_2\text{en}_2]^{+}\) ion.
Titrmetric Study of the Reaction:

\[
\text{trans-} \left[ \text{RuCl}_2\text{en}_2 \right]^+ + \text{H}_2\text{O} \rightarrow \text{trans-} \left[ \text{RuCl(H}_2\text{O})\text{en}_2 \right]^{2+} + \text{Cl}^- \]

The acid hydrolysis of the trans-[RuCl₂en₂]⁺ ion was studied by measuring the concentration of chloride ion at various stages of reaction by the method of Volhard (22).

Six standard sodium chloride solutions from \(1 \times 10^{-3} M\) to \(6 \times 10^{-3} M\) were prepared. 3 ml. samples of these were passed through an ion exchange column and the entire procedure described below was followed to produce a graph of thiocyanate titre volume against chloride concentration. The figures obtained are shown in table 3-10, and the calibration graph is shown in figure 3.7.

Use of this graph obviated the need to make individual corrections to each experimental titre.

60 ml. of \(10^{-1} M\) methane sulphonic acid in a stoppered erlenmeyer flask was immersed in a thermostat bath at \(61.8 \pm 0.1^\circ C\). Approximately 40 mg. of trans-[RuCl₂en₂Cl₂H₂O] was shaken in, and a sample of approximately 4 ml. was immediately transferred by means of a safety pipette to a test tube in an ice bath.
Figure 3.7

Calibration curve for Volhard titrations.

ml. of NH$_4$NCS solution.

$10^3 \times [Cl^-]$, (moles/litre)
TABLE 3-10

Data for Figure 3.7

<table>
<thead>
<tr>
<th>Chloride concentration</th>
<th>Measured volumes (ml.)</th>
<th>Average volume (ml.)</th>
</tr>
</thead>
<tbody>
<tr>
<td>1.00 x 10^{-3} M</td>
<td>18.38, 18.18</td>
<td>18.28</td>
</tr>
<tr>
<td>2.00</td>
<td>15.46, 15.36</td>
<td>15.42</td>
</tr>
<tr>
<td>3.00</td>
<td>13.02, 12.44</td>
<td>12.73</td>
</tr>
<tr>
<td>4.00</td>
<td>9.01, 8.92</td>
<td>8.96</td>
</tr>
<tr>
<td>5.00</td>
<td>5.92, 5.86</td>
<td>5.89</td>
</tr>
<tr>
<td>6.00</td>
<td>2.88, 2.92, 2.88</td>
<td>2.89</td>
</tr>
</tbody>
</table>

3 ml of this was passed through a Dowex 50 W-X acid form cation exchange column (bed volume 1 ml), and the anions were washed through with 5 ml water into a 100 ml erlenmeyer flask. To this was added 20 ml of 1.00 x 10^{-3} M AgNO₃, 0.2 M nitric acid, 5 drops of nitrobenzene, ten drops of saturated ferric alum solution in dilute HNO₃. The flask was shaken vigorously and placed in a dark cupboard for one hour to permit coagulation of the silver chloride formed. The contents of the flask were then titrated against 10^{-3} M NH₄SCN until the first perceptible, permanent colour was observed. The titration was performed in a three-sided white box and viewed by diffuse daylight. The molarity of chloride ion in the original solution was obtained from figure 3.7. The above procedure was repeated at varying intervals for the next three days. The data obtained are presented in Table 3.11.
From the stoichiometry of the reaction:

\[
\text{trans-}[\text{RuCl}_2\text{en}_2]^+ + \text{Cl}^- + \text{H}_2\text{O} \rightarrow \text{trans-}[\text{RuCl}.\text{H}_2\text{O}\text{en}_2]^{++} + 2\text{Cl}^- 
\]

and the assumption (valid in the early part of the run) that the contribution of the secondary aquation to the chloride concentration was negligible, the concentration, \(C_t\), of the trans-[RuCl_2en_2]^+ ion at various times (up to two hours) was calculated. The initial concentration, \(C_0\), was taken as that at \(t = 15\) seconds. A graph of \(1 + \log_{10}(C_t/C_0)\) was constructed (figure 3.8). From the slope, a first-order rate constant of \(3.4 \times 10^{-4} \text{ sec}^{-1}\) was calculated. This is higher than a value of \(2.4 \times 10^{-1} \text{ sec}^{-1}\) at \(61.8^\circ\), calculated from the spectrophotometric temperature dependence data (figure 3.6), possibly because of the contribution of the secondary hydrolysis.

**TABLE 3-11**

<table>
<thead>
<tr>
<th>Time (min)</th>
<th>Vol. of thiocyanate solution (ml)</th>
<th>(10^3 \times [\text{Cl}^-])</th>
</tr>
</thead>
<tbody>
<tr>
<td>0.25</td>
<td>13.56</td>
<td>2.58</td>
</tr>
<tr>
<td>15.0</td>
<td>12.58</td>
<td>2.91</td>
</tr>
<tr>
<td>30.0</td>
<td>11.92</td>
<td>3.15</td>
</tr>
<tr>
<td>45.0</td>
<td>10.62</td>
<td>3.45</td>
</tr>
<tr>
<td>60.0</td>
<td>10.48</td>
<td>3.57</td>
</tr>
<tr>
<td>90.0</td>
<td>9.83</td>
<td>3.77</td>
</tr>
<tr>
<td>121.25</td>
<td>9.40</td>
<td>3.93</td>
</tr>
<tr>
<td>180</td>
<td>9.28</td>
<td>3.98</td>
</tr>
<tr>
<td>300</td>
<td>8.70</td>
<td>4.15</td>
</tr>
<tr>
<td>435</td>
<td>8.18</td>
<td>4.26</td>
</tr>
<tr>
<td>1140</td>
<td>7.76</td>
<td>4.47</td>
</tr>
<tr>
<td>1860</td>
<td>5.36</td>
<td>5.28</td>
</tr>
<tr>
<td>2640</td>
<td>5.24</td>
<td>5.23</td>
</tr>
<tr>
<td>4440</td>
<td>4.40</td>
<td>5.55</td>
</tr>
</tbody>
</table>
Figure 3.8

First-order plot from volumetric data for the acid hydrolysis of the trans- [RuCl₂en₂]⁺ ion.
The base hydrolysis of octahedral complexes of the type \([\text{M}^{III}_n\text{A}_m\text{X}^+_\text{p}]\) (where M is a transition metal, A represents ammonia or a mono- or polydentate amine ligand, and X represents an anionic monodentate) have been most extensively studied for complexes of cobalt. In the past decade, however, results have been published for several other metals.

That the base hydrolysis of the cobalt acido-penta-ammines is extremely fast compared with other substitution reactions of cobalt complexes was recognised before 1937 (33). The reaction follows a second-order rate constant for the chloro complex at 25°C as 0.85 litre/mole^1 sec^1, which is 5 x 10^5 times as great as the first-order rate constant for aquation at the same temperature. The base hydrolysis of cis- and trans- \([\text{CoCl}_2\text{en}_2]^+\), and cis- and trans- \([\text{Co(OH)Clen}_2]^+\) were studied in 1956 by Pearson, Meeker and Basolo (34), and in 1962 by Chan and Tobe (35). These reactions follow a similar rate law, the rate constants for cis- and trans- \([\text{CoCl}_2\text{en}_2]^+\) being both about 10^7 times as great as the rate for aquation of the respective ions. The substitution took place with isomerisation and racemisation. Table 4.1 shows the isomeric composition of the products of base hydrolysis the loss of one chloride ligand from the ion in the first column.

† Water is approximately 55.5 molar in dilute aqueous solutions.
**TABLE 4.1**

<table>
<thead>
<tr>
<th>Reacting ion</th>
<th>Products formed</th>
</tr>
</thead>
<tbody>
<tr>
<td>trans- $[\text{CoCl}_2\text{en}_2]^+$</td>
<td>5% cis, 95% trans</td>
</tr>
<tr>
<td>trans- $[\text{Co(OH)Cl}_2\text{en}_2]^+$</td>
<td>94% cis, 6% trans</td>
</tr>
<tr>
<td>1-cis- $[\text{CoCl}_2\text{en}_2]^+$</td>
<td>21% 1-cis- (config. retained)</td>
</tr>
<tr>
<td>1-cis- $[\text{Co(OH)Cl}_2\text{en}_2]^+$</td>
<td>61% 1-cis- (config. retained)</td>
</tr>
</tbody>
</table>

The corresponding chromium complexes were studied in 1958 by Pearson, Munson, and Basolo (36). The rates of substitution by hydroxide in cis- and trans- $[\text{CrCl}_2\text{en}_2]^+$ were found to be much slower than those for the corresponding cobalt complexes, although the respective rates of aquation are similar.

The base hydrolyses of the cis- and trans- $[\text{RhCl}_2\text{en}_2]^+$ ions were investigated in 1963 by Johnson, Basolo and Pearson (24). The reactions took place with no appreciable isomerisation, and were slower by a factor of 1000 than those of the corresponding chromium complexes. Rate constants were of the same order of magnitude for base hydrolyses as for aquations.

The trans- $[\text{IrCl}_2\text{en}_2]^+$ cation was found by Rauer and Basolo (28) to react with hydroxide ion without loss of configuration. The rate for base hydrolysis was slower again than
that for the corresponding rhodium complex, and nearly identical to that for substitution by other nucleophiles studied.

The base hydrolysis of \( \text{cis-} [\text{Ru(OH)}\text{Clen}_2]^+ \) was studied by L. Kane-Maguire (50) who reported that the base hydrolysis of \( \text{cis-} [\text{RuCl}_2\text{en}_2]^+ \) was too fast even at 0°, using \( 10^{-4} \) hydroxide, to be measured by methods available to him. The \( \text{cis-} [\text{Ru(OH)}\text{Clen}_2]^+ \) reacted slightly faster than the corresponding cobalt complex, and there was found to be no optical or geometrical isomerisation during the course of the reaction. The base hydrolysis of \( [\text{Ru(NH}_3)_5\text{Cl}]^{2+} \) was studied by Broomhead, Basolo and Pearson (29), and by L. Kane-Maguire (50). The rate there was an order of magnitude faster than that for the corresponding \( [\text{Co(NH}_3)_5\text{Cl}]^{2+} \).

Rate constants for the base hydrolysis of a number of chloro-amine complexes at 25° are summarised in Table 4-2 with figures for the ratios of the rates of acid and base hydrolysis of the same complex where available. In some cases, the rate constants at 25° have been extrapolated from published activation energies and rate constants at higher temperatures.
Values of $k_{\text{OH}}$ for base hydrolysis of various complexes at 25° (litre.mol.$^{-1}$ sec.$^{-1}$)

Figures in square brackets are ratios $k_{\text{OH}}/k_{\text{H}_2\text{O}}$ (M$^{-1}$).

(a) 25.4°C; (b) extrapolated; (c) first-order constant (see text); (d) 55°;
(e) 80°; (f) this work; (g) low hydroxide concentrations only - see below.

<table>
<thead>
<tr>
<th></th>
<th>$\text{cis-} [\text{MC}_2\text{en}_2]^+$</th>
<th>$\text{trans-} [\text{MC}_2\text{en}_2]^+$</th>
<th>$[\text{MC}1(\text{NH}_3)_5]^{2+}$</th>
</tr>
</thead>
<tbody>
<tr>
<td>Co</td>
<td>$7.1 \times 10^2$, (35) $[3 \times 10^6]$</td>
<td>$3.16 \times 10^2$, (35) $[9 \times 10^7]$ (13)</td>
<td>$0.85$, (37) $[5 \times 10^5]$</td>
</tr>
<tr>
<td>Cr</td>
<td>$3.5 \times 10^{-4}$, (36) $[8 \times 10^1]$</td>
<td>$3.9 \times 10^{-5}$, (36) $[1 \times 10^3]$</td>
<td>$4 \times 10^{-4}$ (38)</td>
</tr>
<tr>
<td>Rh</td>
<td>$2 \times 10^{-3}$, (24) $[2 \times 10^3]$</td>
<td>$8 \times 10^{-8}$ b, c, (24) $&lt;10$ e</td>
<td></td>
</tr>
<tr>
<td>Ir</td>
<td>$3 \times 10^5$, g $[8 \times 10^5]$</td>
<td>$1.6 \times 10^{-8}$ b, c, (28) $[1]$</td>
<td>$4.9$, (29) $[10^6]$</td>
</tr>
<tr>
<td>Ru</td>
<td>$3 \times 10^5$, f $[8 \times 10^5]$</td>
<td>$2.4 \times 10^{-1}$ f $[6.3 \times 10^3]$</td>
<td></td>
</tr>
</tbody>
</table>

TABLE 4-2.
Mechanisms

A common feature of the base hydrolyses of acido-amine complexes of cobalt, chromium, ruthenium, and to some extent rhodium is that they show overall second-order kinetics; the rate being proportional to the concentrations of both hydroxide ion and reacting complex. The most obvious interpretation is a simple $S_N^2$ reaction (39). To explain the enhanced reactivity of the cobalt complexes to hydroxide ion, a "Grotthus Chain" mechanism has been proposed (35). This envisages transfer of protons from water molecule to water molecule as shown in figure 4.1.

The net result is the appearance of a hydroxide ion in the vicinity of the complex at the expense of a hydroxide ion elsewhere in solution, giving an apparently high mobility of hydroxide ions in aqueous solution. One would, however, expect other basic anions to show enhanced reactivity, and this is not the case in systems studied (19), (40).

Another mechanism which would give overall second-order kinetics is that proposed in 1937 by Carrick (33), and now known

Figure 4.1.
as the conjugate base mechanism. The first step involves loss of a proton from an ammonia or amine ligand to the hydroxide in solution.

\[ \text{e.g. } [\text{Co(NH}_3\text{_}5\text{Cl}]^{2+} + \text{OH}^- \rightleftharpoons [\text{Co(NH}_3\text{_}4\text{NH}_2\text{Cl}]^{+} + \text{H}_2\text{O}. \]

If this equilibrium lies well to the left, the concentration of the amido species at any time will be proportional to the concentrations of the penta-ammine complex and hydroxide ion. The amido species may now react by either a dissociative (S\text{N}_1), or displacement (S\text{N}_2) mechanism to replace the chloride ion with water.

\[ [\text{Co(NH}_3\text{_}4\text{NH}_2\text{Cl}]^{+} + \text{H}_2\text{O} \rightleftharpoons [\text{Co(NH}_3\text{_}4\text{NH}_2\text{H}_2\text{O}]^{2+} + \text{Cl}^- \]

The high reactivity of the amido species may be attributable to \( \Pi \)-bonding into the metal's \( e_g \) orbitals from the nitrogen's p orbitals in the trigonal bipyramidal intermediate. A proton is then immediately transferred from the water ligand to the amido ligand.

\[ [\text{Co(NH}_3\text{_}4\text{NH}_2\text{H}_2\text{O}]^{2+} \rightarrow [\text{Co(NH}_3\text{_}5\text{OH}]^{2+} \]

Under these conditions the rate is controlled by the second step, in which the concentration of the reacting species is determined by the concentrations of original complex and base. Depending on whether step 2 is unimolecular or bimolecular, the overall mechanism is known as S\text{N}_1 C.B. or S\text{N}_2 C.B.

A third mechanism which accounts for the second-order kinetics and the specific reactivity of the cobalt and ruthenium complexes towards hydroxide ion is the unimolecular "ion-pair" mechanism (35), (41). A hydroxide ion is attracted to the complex
by a "Grotthus chain" mechanism to form an ion-pair. The lifetime of the ion-pair is considerably longer than the time these two species would be together in the course of ordinary collision. The ion-pair then undergoes a unimolecular process of internal rearrangement. The result is an ion-pair in which the hydroxide ion is in the inner coordination sphere and the leaving group is more loosely held. This species dissociates. Since the rearrangement within the ion-pair controls the rate, and the concentration of the ion-pair is proportional to the concentrations of hydroxide ion and reacting complex, the overall process obeys a second-order rate law.

For the \([\text{Co}X(N\text{H}_3)_5]^{2+}\) ion, (where \(X = \text{Cl}, \text{Br} \text{ or } \text{NO}_3\)), the base hydrolysis appears to be unimolecular. Green and Tauhe (42) have shown by experiments in \(^{18}O\)-enriched water that the ratio of \(^{18}O\) to \(^{16}O\) in the base-hydrolysis product is independent of the leaving group \(X\) for \(X = \text{Cl}, \text{Br}, \text{NO}_3\). This indicates that the three reactions proceed via a common intermediate. Of the three mechanisms discussed above, only the \(S_N\) C.B. mechanism fulfils this condition. A difference in the ratio of \(^{18}O\) to \(^{16}O\) in the case of \([\text{Co}F(N\text{H}_3)_5]^{2+}\) suggests that its base hydrolysis is bimolecular, probably \(S_N\) C.B. Buckingham, Olsen and Sargeson (43) have confirmed the preceding results by showing that when base hydrolysis of \([\text{Co}X(N\text{H}_3)_5]^{2+}\) takes place in the presence of high concentrations of other anions, the ligands \(\text{NO}_2^-, \text{SCN}^-, \text{OAc}^-, \text{and } \text{N}_3^-\) were found to enter the complex in place of \(\text{OH}^-\). In the case of azide, up to 10% of the product contained the azide ligand.
Most evidence, then, supports the belief that the base hydrolysis of penta-amine cobalt complexes takes place via conjugate base mechanisms, either $S_N^1$ C.B., or $S_N^2$ C.B., depending on the leaving group. It is a reasonable assumption that the chelated amine complexes which show a similar reactivity also react via conjugate base mechanisms. Caglioti and Illuminati (44) reported that while the rate of base hydrolysis of $\text{cis-}[\text{Co(OAc)}_2\text{en}_2]^{2+}$ was dependent on hydroxide concentration, the second-order rate constant at $25^\circ$ being $5 \times 10^{-2}$ litre-mole$^{-1}$ sec.$^{-1}$, the corresponding his (2,2′ pyridine) complex, which has no potential acidic protons, showed only slight variation in rate over a range of 5 pH units, and a rate constant about half a million times smaller. This, and other data of Caglioti and Illuminati are presented in Table 4.3.
<table>
<thead>
<tr>
<th>Complex Ion</th>
<th>pH</th>
<th>pH</th>
</tr>
</thead>
<tbody>
<tr>
<td>$\text{cis-} \quad [\text{Co(OAc)}_2\text{en}_2]^+$</td>
<td>3</td>
<td>$k_1^' = 3.4 \times 10^{-5} (35^\circ)$</td>
</tr>
<tr>
<td>$\text{cis-} \quad [\text{Co(OAc)}\text{(OH)}\text{en}_2]^+$</td>
<td>6-8</td>
<td>$k_2^' = 2.4 \times 10^{-2} (25^\circ)$</td>
</tr>
<tr>
<td>$\text{trans-} \quad [\text{Co(OAc)}_2\text{en}_2]^+$</td>
<td>7-8</td>
<td>$k_2^&quot; = 1.1 \times 10^{-3} (25^\circ)$</td>
</tr>
<tr>
<td>$\text{trans-} \quad [\text{Co(OAc)}\text{(OH)}\text{en}_2]^+$</td>
<td>11-12</td>
<td>$k_2^&quot; = 8 \times 10^{-4} (35^\circ)$</td>
</tr>
<tr>
<td>$\text{cis-} \quad [\text{Co(OAc)}_2\text{bipy}_2]^+$</td>
<td></td>
<td></td>
</tr>
<tr>
<td>$\text{cis-} \quad [\text{Co(OAc)}\text{(OH)}\text{bipy}_2]^+$</td>
<td></td>
<td></td>
</tr>
<tr>
<td>$\text{cis-} \quad [\text{Co(OAc)}\text{(H}_2\text{O)}\text{bipy}_2]^2+$</td>
<td></td>
<td>$k_1'' = 10^{-7} (35^\circ)$</td>
</tr>
</tbody>
</table>

**TABLE 4 - 3.**

Data of Cagliotti and Illuminati (44)

**Kinetic Data for the Hydrolysis of Some Complex Ions of the series**

$[\text{CoX}_2(AA)_2]^+ \rightarrow [\text{CoXY}(AA)_2]^{n+}$ at diverse initial pH values. First-order rate constants ($k_1'$ and $k_2'$) in sec$^{-1}$; second-order rate constants ($k_2''$ and $k_2'''$) in litre mole$^{-1}$ sec$^{-1}$. Ionic strengths for the first-order reactions are in the range $10^{-3}$ to $10^{-2}$. 
Table 4.2 shows that the rate constants for base hydrolysis of cis- and trans- $[\text{CrCl}_2\text{en}_2]^+$, while several magnitudes less than those for the corresponding cobalt complexes, are greater than those for acid hydrolysis. The acidities of corresponding cobalt and chromium complexes, where measurable, are similar (36), so the chromium complexes would be expected to form conjugate bases in aqueous hydroxide solution. It is argued (36), (13) that the lesser reactivity of the chromium (III) complexes is due to the fact that the \(\pi\)-bonding electrons from the nitrogen's p orbitals into chromium's \(e_g\) orbitals are less repelled by the half-filled \(t_{2g}\) orbitals. There is, as a result, less tendency to distort into trigonal bipyramidal geometry. The smaller electron affinity of Cr\(^{3+}\) compared to Co\(^{3+}\) (35.5 ev cf 29.5 ev) (45) would make such \(\pi\)-bonding less favourable in the case of chromium.

The base hydrolysis of cis- $[\text{RhCl}_2\text{en}_2]^+$ shows first-order dependence on hydroxide concentration at pH 12.7 and 25\(^\circ\), but becomes independent at lower pH. The base hydrolysies of trans- $[\text{RhCl}_2\text{en}_2]^+$ (24) and trans- $[\text{IrCl}_2\text{en}_2]^+$ (28) have no dependence on hydroxide concentration, and are as slow as the anation reactions of the respective complexes. This behaviour would be explained if the acidities of the amine protons were considerably lower for the rhodium and iridium complexes than for those of cobalt, but no figures are obtainable to date.
The base-catalysed deuterium exchange rates for the cis- and trans-rhodium complexes are $4.5 \times 10^5 \text{litre} \cdot \text{mole}^{-1} \cdot \text{sec}^{-1}$ and $2.4 \times 10^5 \text{litre} \cdot \text{mole}^{-1} \cdot \text{sec}^{-1}$ respectively at $58.6^\circ$ compared with a value of $1.5 \times 10^5 \text{litre} \cdot \text{mole}^{-1} \cdot \text{sec}^{-1}$ for $\left[\text{CoCl} \left(\text{NH}_3\right)_5\right]^{2+}$ at $25^\circ$ (46). Without any knowledge of the lifetimes of the amido complexes, however, one cannot make inferences about the relative acidities. Johnson and her co-workers (24) argue plausibly that since the metal has little effect on the pKa values for $\left[M\left(\text{NH}_3\right)_5\cdot \text{H}_2\text{O}\right]^{3+} \leftrightarrow \left[M\left(\text{NH}_3\right)_5\text{OH}\right]^{2+} (M = \text{Co or Rh})$ it is unlikely that the acidities of the amine protons in the cis- and trans- $\left[M\text{Cl}_2\text{en}_2\right]^+$ complexes differ greatly for the two metals. Assuming that the lowered reactivity of the rhodium and iridium complexes is not due to lowered acidity, one must seek an explanation in terms of the reactivity of the amido complex.

Rh$^{\text{III}}$ and Ir$^{\text{III}}$, like Co$^{\text{III}}$ have low spin d$^6$ configuration. Either the e$_g$ orbitals of the heavier metals are the wrong size to accept $\pi$ electrons from nitrogen or, in spite of such $\pi$-bonding, there is little tendency for the complex to distort to a trigonal bipyramidal shape. In all three cases studied for rhodium and iridium there is complete retention of configuration. It is believed, with conjugate base mechanisms unavailable, hydroxide substitution takes place via aquation as

\[ \text{This argument does not extend to ruthenium. pKa for } \left[\text{RuH}_2\text{O}\left(\text{NH}_3\right)_5\right]^{3+} \text{ is } 4.2 \text{ at } 25^\circ(29), \text{ cf. } \left[\text{CoH}_2\text{O}\left(\text{NH}_3\right)_5\right]^{3+}, 5.7; \text{ and } \left[\text{RhH}_2\text{O}\left(\text{NH}_3\right)_5\right]^{3+}, 5.9. \] (24)
described in Chapter 3.

Prior to this work, the kinetics of base hydrolysis of two ruthenium complexes had been studied; \([\text{RuCl(NH}_3)_5]^2+\) (29), (1), and cis- \([\text{RuOHClen}_2]^+\) (50). Both followed a second-order rate law and were faster than their cobalt analogues. Broomhead, Basolo and Pearson (29) calculated crystal field activation energies for five and seven-coordinate transition states for Cr\(^{3+}\), Co\(^{3+}\), Ru\(^{3+}\) and Rh\(^{3+}\). In the case of Ru\(^{3+}\), the C.F.A.E. for a trigonal bipyramidal transition state is nearly eight times as great as that for a seven-coordinate octahedral wedge, and the \(\pi\)-bonding tendency (as measured by the electron affinity) which offsets the C.F.A.E. in the trigonal bipyramid, is some 12\% smaller than for cobalt. It was concluded that ruthenium complexes were more likely to react via an \(S_n^2\) C.F. mechanism. The work of L. Kane-Maguire, who observed that base hydrolysis of cis- \([\text{RuCl}_2\text{en}_2]^+\) and cis- \([\text{RuOHClen}_2]^+\) takes place without racemisation, supports this view.

**THE BASE HYDROLYSIS OF THE trans-DICHLORODIETHYLENEDIAMINE RUTHENIUM (III) CATION**

The base hydrolysis of the trans- \([\text{RuCl}_2\text{en}_2]^+\) ion was studied principally by a spectrophotometric method but titrimetric techniques were used as a check on results obtained.

**Spectrophotometric Method**

The spectrophotometric method was similar to that described in Chapter 3 for acid hydrolysis.
The spectrum of the $\text{trans- } [\text{Ru(OH)}\text{Cl}_2\text{en}_2]^{+}$ ion was obtained in two ways:

(a) A drop of 40% W/V sodium hydroxide solution was added to a solution of $\text{trans- } [\text{Ru(H}_2\text{O)}\text{Cl}_2\text{en}_2]^{2+}$ in 0.1 M. methane sulphonate acid and the spectrum of the product was immediately recorded.

(b) A 1.5 x 10^{-3} M. solution of $\text{trans- } [\text{RuCl}_2\text{en}_2]\text{Cl} \cdot \frac{1}{2}\text{H}_2\text{O}$ was made in 5 x 10^{-2} M. sodium hydroxide solution in an ice bath. The spectrum of the resulting solution was observed at regular intervals in 2 mm cells. A spectrum similar to that obtained by method (a) appeared in about 30 minutes and further change was considerably slower. A sample of the solution was acidified with nitric acid and titrated with mercuric nitrate, using sodium nitro-prusside as indicator. The chloride concentration was found to be 2.9 x 10^{-3} M ± 5%. Thus, in addition to the chloride originally present as anion, a further mole of chloride was liberated for every mole of complex originally present.

The spectrum of the $\text{trans- } [\text{Ru(OH)}\text{Cl}_2\text{en}_2]^{+}$ ion was obtained from the same solution after the total free chloride concentration had reached 4.2 x 10^{-3} ± 5%. This spectrum was stable for three hours at 0.2 ± 0.1°C. in 5 x 10^{-2} M hydroxide, and after 24 hours had changed only at its minimum which had increased in intensity.
The three spectra are reproduced in figure 4.2. Lower temperatures were used for the base hydrolysis than for the acid hydrolysis, and the optical density was observed at 342 nm, \( \lambda_{\text{max}} \) for \( \text{trans-} \left[ \text{RuCl}_2\text{en}_2 \right]^+ \). Sodium hydroxide, with sodium methane sulphanate as an ionic strength adjuster was used as solvent. Otherwise, the technique described in Chapter 3 was followed. The data for a typical run are listed in Table 4-4.

<table>
<thead>
<tr>
<th>t(min)</th>
<th>( A_t )</th>
<th>( \frac{A_t - A_{\infty}}{A_0 - A_{\infty}} )</th>
<th>( 1 + \log_{10} \left( \frac{A_t - A_{\infty}}{A_0 - A_{\infty}} \right) )</th>
</tr>
</thead>
<tbody>
<tr>
<td>00</td>
<td>0.769</td>
<td>1.000</td>
<td>1.000</td>
</tr>
<tr>
<td>04</td>
<td>0.697</td>
<td>0.691</td>
<td>0.950</td>
</tr>
<tr>
<td>08</td>
<td>0.631</td>
<td>0.791</td>
<td>0.898</td>
</tr>
<tr>
<td>12</td>
<td>0.580</td>
<td>0.713</td>
<td>0.853</td>
</tr>
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<td>0.812</td>
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<td>20</td>
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<td>0.589</td>
<td>0.770</td>
</tr>
<tr>
<td>24</td>
<td>0.468</td>
<td>0.543</td>
<td>0.735</td>
</tr>
<tr>
<td>28</td>
<td>0.439</td>
<td>0.499</td>
<td>0.698</td>
</tr>
<tr>
<td>32</td>
<td>0.413</td>
<td>0.460</td>
<td>0.663</td>
</tr>
<tr>
<td>36</td>
<td>0.391</td>
<td>0.426</td>
<td>0.630</td>
</tr>
<tr>
<td>40</td>
<td>0.371</td>
<td>0.396</td>
<td>0.598</td>
</tr>
<tr>
<td>44</td>
<td>0.353</td>
<td>0.369</td>
<td>0.567</td>
</tr>
<tr>
<td>48</td>
<td>0.340</td>
<td>0.349</td>
<td>0.543</td>
</tr>
<tr>
<td>56</td>
<td>0.314</td>
<td>0.310</td>
<td>0.491</td>
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<tr>
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<td>0.303</td>
<td>0.293</td>
<td>0.467</td>
</tr>
<tr>
<td>64</td>
<td>0.295</td>
<td>0.281</td>
<td>0.448</td>
</tr>
<tr>
<td>68</td>
<td>0.288</td>
<td>0.270</td>
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<td>72</td>
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<td>0.263</td>
<td>0.419</td>
</tr>
<tr>
<td>76</td>
<td>0.276</td>
<td>0.252</td>
<td>0.401</td>
</tr>
<tr>
<td>80</td>
<td>0.272</td>
<td>0.246</td>
<td>0.391</td>
</tr>
</tbody>
</table>
Figure 4.2

Ultraviolet Absorption Spectra
A $1.57 \times 10^{-4}$ M solution of trans- $\text{[RuCl}_2\text{en}_2\text{]}^+$ in $4.00 \times 10^{-3}$ M sodium hydroxide with sufficient sodium methanesulphonate added to make the ionic strength equal to $0.10$ M was observed at $25.5^\circ$C.

The function $1 + \log_{10}\left(\frac{(A_t - A_\infty)}{(A_0 - A_\infty)}\right)$ (see Chapter 2) was plotted against time for a period of 80 minutes (figure 4.3). From the initial slope of this curve, an apparent first-order rate constant of $9.45 \times 10^{-4}$ sec$^{-1}$ was obtained. From figure 4.3 it can be seen that little deviation from the straight line was observed over the first half-life. The deviations were greater with the reactions run at lower temperatures, indicating that secondary hydrolysis (which is presumed to be responsible for the deviations) has a smaller energy of activation.

In all cases, initial slopes were used to determine rate constants from such first-order plots. Rate constants for a sequence of reactions are listed in Table 4 - 5.
First-order plot for base hydrolysis of the trans- \([\text{RuCl}_2\text{en}_2]^+\) ion, showing deviations beyond one half-life.

Temperature = 25.5°C.
A plot of observed rate constants $k_1$ against hydroxide concentration for all data at 20.05°C is shown in figure 4.4. The linear relationship $k_1 \propto [\text{OH}^-]$ shows that the reaction is second-order with a second-order rate constant of $1.32 \times 10^{-1}$ litre mole$^{-1}$ sec$^{-1}$. It can be seen from pairs of points representing the same hydroxide concentration at different ionic strengths that there is no significant dependence on ionic strength.
Figure 4.4. Dependence of the base hydrolysis of the trans- $\text{[RuCl}_2\text{CN}_2\text{]}^+$ ion on $[\text{OH}^-]$. 

$10^4 \times k_{\text{obs.}}$ vs. $10^3 \times \text{Molarity of hydroxide}$

- $\mu = 10^{-1} \text{M}$
- $\mu \approx [\text{OH}^-]$
Figure 4.5. Temperature dependence of the base hydrolysis of the trans- $[\text{RuCl}_2\text{en}_2]^+$ ion.

over variation by a factor of 50.

A plot of $\log_{10}k_{OH}$ against $10^3/T$ (equation (12a) of Chapter 2) gave the following values:

\[
E_a = 19.9 \text{ kcal. mole}^{-1}
\]
\[
\log A = 13.9
\]

From equation (18) of Chapter 2,
\[
\Delta S_{25}^\neq = +7.9 \text{ cal. deg}^{-1} \text{ mole}^{-1}.
\]
Attempted Use of Specific Chloride Ion Electrode

An Orion model 94-17 specific chloride-ion electrode was used in attempt to follow the base hydrolysis of the trans- $\left[ \text{RuCl}_2\text{en}_2 \right]^+$ by the rate of liberation of chloride ions. Figure 4.6 shows the apparatus employed.

The salt bridge was used to prevent contamination of the unknown solution by chloride ions from the reference electrode (47). The extra junction so introduced made direct correlation of potential with concentration impossible. With temperature held constant, reproducible linear dependence on the logarithm of concentration by meter deflection was found over the range of $4 \times 10^{-4} \text{ M}$ to $1.7 \times 10^{-3} \text{ M}$.
solution of chloride ion in 0.1 molar sodium hydroxide (figure 4.7).

When sufficient trans-[RuCl₂en₂]Cl·½H₂O to make a 4 x 10⁻³ M solution was added, the meter registered, within seconds, a reading indicative of a chloride concentration greater than 2 x 10⁻² M. Since this is stoichiometrically impossible, it must be concluded that the presence of the ruthenium complex interfered in some way with the working of the electrode. When the experiment was repeated with fresh solution a similar result was obtained. The method was, therefore, abandoned.
Reaction followed by Titration

Mercurimetric titration was used to follow the rate of chloride liberation in a reacting solution.

Attempts to use diphenylcarbazone as indicator gave erratic results below pH2. Sodium nitroprusside gave a reproducible (± 5%) endpoint under controlled light conditions. "Blank" titre corrections were necessary to allow for the solubility of mercuric nitroprusside and the partial dissociation of mercuric chloride.

Concentrations of complex and hydroxide were selected to provide a pseudo first-order reaction with a sufficiently high concentration to allow titration of the chloride ions released. The reaction was performed close to 0°C to allow time for the titrations to be performed.

90 ml of a solution of $2.004 \times 10^{-3}$ M trans-$\left[ \text{RuCl}_2\text{en}_2 \right] \text{Cl.H}_2\text{O}$ in $1.01 \times 10^{-2}$ M methanesulphonic acid was cooled in an ice bath. 5 ml of 1.00 M sodium hydroxide, at the same temperature was pipetted in and thoroughly mixed. Each sample was withdrawn through a chilled pipette, and run immediately into a 25 ml flask containing 6.4 ml of 6N nitric acid to arrest the base hydrolysis. It was then poured through a 1 ml column of Dowex 50 W-X cation-exchange resin (acid form) to remove all complex cations. The column was washed with at least 5 ml of water and the eluent was brought up to 10 ml. 5 drops of 10% sodium nitroprusside were added and the sample was titrated against $4.2 \times 10^{-3}$ M $\text{Hg(NO}_3\text{)}_2$. 
"Blank" titrations were performed with 10 ml samples of mercuric chloride solution from $2 \times 10^{-3}$ M to $9 \times 10^{-3}$ M. No steady variation of blank volume with concentration was observed, the contribution of the mercuric chloride dissociation being apparently very slight, and an average "blank volume" of 0.54 ml was used for all corrections.

The concentration of complex at the time of mixing was calculated from the concentration before mixing, assuming volumes to be additive. The expected concentration of chloride at infinite time was calculated as three times this quantity.

Initially, all chloride liberated must come from trans- $[\text{RuCl}_2\text{en}_2]^+$. The increase in the corrected titre volume is, therefore, proportional to the decrease in the concentration of the trans- $[\text{RuCl}_2\text{en}_2]^+$ ion for as long as the contribution from the secondary hydrolysis remains small.

Initially, the concentration of trans- $[\text{RuCl}_2\text{en}_2]^+$ is equal to that of the free chloride ion. At any time, "$t$", (until the secondary hydrolysis becomes significant), the concentration, "$C_t$" of the dichloro complex is given by $C_t = 2C_0 - \text{Cl}^-$, where $C_0$ is the initial concentration of complex. Since corrected titre volume is directly proportional to chloride concentration, the concentration of dichloro-complex at time "$t$" is equal to $2V_0 - V_t$, in arbitrary units, where $V_0$ is the initial corrected titre volume, and $V_t$ is the titre volume at time "$t$". The dimensionless expression $(2V_0 - V_t)/V_0$ gives the concentration of dichloro complex.
Figure 4.8. First-order plot for primary base hydrolysis of the trans- $[\text{RuCl}_2\text{en}_2]^+$ ion from volumetric data.

at time "t" as a fraction of initial concentration. If the reaction is pseudo first-order, a plot of $\log_{10}\left(\frac{2V_o - V_t}{V_o}\right)$ against time, figure 4.8, should give a straight line of slope $-2.303 k_1$ (where $k_1$ is the apparent first-order rate constant for the primary hydrolysis) until the contribution from secondary hydrolysis becomes significant.

If the first hydrolysis is sufficiently fast compared to the second, the latter may be studied when the former is effectively complete. A similar argument to that above shows that when the concentration of trans- $[\text{RuCl}_2\text{en}_2]^+$ is negligible,
the expression \[(3V_0 - V_t)/V_0\] is a measure of the concentration of trans- \([\text{Ru(OH)Cl en}_2]\)^+ as a fraction of total complex concentration, and, if the reaction is pseudo first-order, a plot of \(\log_{10} \left(\frac{(3V_0 - V_t)/V_0}{(3V_0 - V_t)/V_0}\right)\) against time (figure 4.9) in this region should give a straight line of slope \(-2.303 k_2\), (where \(k_2\) is the first-order rate constant for the secondary hydrolysis).

**Results**

Titration data are summarised in Table 4.6.
### Table 4 - 6

<table>
<thead>
<tr>
<th>Time (minutes)</th>
<th>titre (ml) measured</th>
<th>titre (ml) corrected</th>
<th>$\frac{2V_o - V_t}{V_o}$</th>
<th>$\frac{3V_o - V_t}{V_o}$</th>
</tr>
</thead>
<tbody>
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<td>0</td>
<td>2.60 *</td>
<td></td>
<td>1.00 ± 0.04</td>
<td></td>
</tr>
<tr>
<td>1.2</td>
<td>3.09</td>
<td>2.55</td>
<td>1.02 ± 0.13</td>
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</tr>
<tr>
<td>1.5</td>
<td>3.18</td>
<td>2.64</td>
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<td></td>
</tr>
<tr>
<td>16.2</td>
<td>4.30</td>
<td>3.76</td>
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<tr>
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<tr>
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<td>5.17</td>
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<tr>
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<td>6.09</td>
<td>5.55</td>
<td>negative</td>
<td>0.86 ± 0.09</td>
</tr>
<tr>
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<td>6.04</td>
<td>5.48</td>
<td>&quot;</td>
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</tr>
<tr>
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<td>6.14</td>
<td>&quot;</td>
<td>0.64 ± 0.09</td>
</tr>
<tr>
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<td>&quot;</td>
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</tr>
<tr>
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<td>6.41</td>
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</tr>
<tr>
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<td>7.79</td>
<td>7.25</td>
<td>&quot;</td>
<td>0.21 ± 0.09</td>
</tr>
<tr>
<td>2475</td>
<td>7.85</td>
<td>7.31</td>
<td>&quot;</td>
<td>0.19 ± 0.09</td>
</tr>
<tr>
<td>∞</td>
<td>7.80 *</td>
<td>&quot;</td>
<td>0 *</td>
<td></td>
</tr>
</tbody>
</table>

* Calculated from known concentration of complex.

**Errors**

The main source of error is in the titration itself. Results
were found to be reproducible to within 0.2 ml which is ± 5%. The error in the blank titration value is comparatively small, being the average of ten readings. The error in the parameter $2V_0 - V_t$ is then $2\sqrt{2}/10$ ml $\approx 0.3$ ml, and the error in $3V_0 - V_t$ is $\sqrt{13}/10$ ml $\approx 0.4$ ml. Thus, the percentage errors for small values of these parameters are magnified, and make such values useless for plotting rate constants. It is on this basis that the errors in Table 4 - 6 are calculated.

From figure 4.8, the value of the apparent first-order rate constant for the first stage is $(6.7 \pm 2) \times 10^{-4}$, giving a second-order rate constant of $(1.5 \pm 0.4) \times 10^{-2}$, which is consistent with the value of $1.02 \times 10^{-2}$ gained by extrapolation of the Arrhenius plot from the more extensive spectrophotometric data (figure A-3). The fact that the figure from the present work is higher is not surprising, as even in the first half life to chloride evolution the contribution from the secondary base hydrolysis should be noticeable.

The value for the apparent first-order rate constant for the secondary hydrolysis (figure 4.9) is $4 \times 10^{-5}$ sec$^{-1}$, and the second-order rate constant is $1 \times 10^{-3}$.

In summary, the results of the titrimetric study of the base hydrolysis of the trans-$\left[\text{RuCl}_2\text{en}_2\right]^+$ ion confirm those already obtained from spectrophotometry but insufficient points were obtained for each reaction to provide independent evidence that the reactions are pseudo first-order.

* See Addendum
Further use was made of the volumetric data to show that the primary and secondary base hydrolyses of the trans- \( \text{[RuCl}_2\text{en}_2]^+ \) ion are both pseudo first-order reactions under the conditions studied. The combined titration data for the two reactions were fitted to a complex rate equation for consecutive first-order reactions.

Use of Heathkit model EC-1 Analogue Computer to determine Rate Constants.

For consecutive reactions of the first order

\[
\begin{align*}
A & \xrightarrow{k_1} B \\
B & \xrightarrow{k_2} C
\end{align*}
\]

The concentrations of the three species at any time \( t \) are given by (48)

\[
\begin{align*}
A &= A_0 e^{-k_1 t} \\
B &= \frac{A_0 k_1}{k_2 - k_1} (e^{-k_1 t} - e^{-k_2 t}) \\
C &= A_0 \left[ 1 + \frac{1}{k_1 - k_2} (k_2 e^{-k_2 t} - k_1 e^{-k_2 t}) \right]
\end{align*}
\]

From the stoichiometry of the base hydrolyses of trans- \( \text{[RuCl}_2\text{en}_2]^+ \) and trans- \( \text{[Ru(OH)Cl}_2\text{en}_2]^+ \); if \( A \) represents trans- \( \text{[RuCl}_2\text{en}_2]^+ \), \( B \) represents trans- \( \text{[Ru(OH)Cl}_2\text{en}_2]^+ \), and \( C \) represents \( \text{[Ru(OH)Cl}_2\text{en}_2]^+ \), the concentration of liberated chloride at time \( t \) is given by

\[
[C_l] = B + 2C = A_0 \left[ 2 - 2e^{-k_1 t} - \left( \frac{k_1}{k_2 - k_1} \right) (e^{-k_1 t} - e^{-k_2 t}) \right]
\]

Since \( [C_l]_\infty = 2A_0 \),

\[
\frac{[C_l]}{[C_l]_\infty} = 1 - e^{-k_1 t} - \frac{k_1}{2(k_2 - k_1)} (e^{-k_1 t} - e^{-k_2 t})
\]
Figure 4-10 shows the circuit which was used on a Heathkit model EC-1 electronic analogue computer (49) to simulate for given values representing $A_0$, $k_1$ and $k_2$, the time dependence of $A$, $B$, $C$ and $B+2C$, here representing the chloride concentration.

The output of amplifier 4 was plotted against time on a VOM 5 recorder, and with $k_1$ set at the maximum possible and $k_2 = 0$, the initial condition $A_0$ was set so that the concentration or potential scale matched that used in plotting experimental data.

The computer was run repeatedly and $k_1$ and $k_2$ were varied until the simulated concentration-time curve matched, as nearly as possible, the experimental data (figure 4,11). The output of amplifier 8 was then examined without alteration of the settings. This showed the first-order decay of $A$, and a measurement of the half-life gave the
Figure 4.11. Computer simulation of Chloride evolution by two-stage base hydrolysis of \[ \text{trans-} \ [\text{RuCl}_2\text{en}_2]^{+} \]

\[
\frac{[\text{Cl}]}{[\text{Cl}]_{\infty}} = 1 - \exp(-6.7 \times 10^{-4} \cdot t) - \left(\frac{k_1}{2(k_2-k_1)}\right)\exp(6.7 \times 10^{-4} \cdot t - 4.1 \times 10^{-5} \cdot t)
\]
value of $k_1$ set by the variable resistor $R$, in terms of the time scale determined by the chart speed. The variable resistor $R_2$ was substituted for $R_1$ without alteration of its setting, and examination of the output of amplifier 8 gave the value of $k_2$.

The values obtained for $k_1$ and $k_2$ were $6.7 \times 10^{-4} \text{ sec}^{-1}$ and $4.1 \times 10^{-5} \text{ sec}^{-1}$ respectively. These values agree well with those obtained from the initial rate ($k_1$) and the rate after five half-lives of the primary hydrolysis ($k_2$).

**BASE HYDROLYSIS OF THE cis-DICHLORODIS(ETHYLENE-DIAMINE)RUTHENIUM(III) CATION**

As mentioned above, Kane-Maguire (5) reported that the reaction

\[
\text{cis-} \left[ \text{RuCl}_2\text{en}_2 \right]^+ + \text{OH}^- \rightarrow \text{cis-} \left[ \text{Ru(OH)Cl en}_2 \right]^+ + \text{Cl}^- 
\]

takes place with full retention of geometrical and optical configuration. The rate was found to be extremely fast, even in $10^{-4}$ M. sodium hydroxide, and was not studied kinetically. This reaction has now been investigated using a stopped-flow apparatus.

The equipment is shown diagramatically in figure 4.14. A brass block (A) is kept at constant temperature by the circulation of water from a thermostat (not shown). Embedded in the block are two cylindrical, perspex storage chambers (B1 and B2) and two polythene syringes (C1 and C2). The rubber plungers of the syringes are operated by brass rods which are coupled at their tops and operated together by a lever (D). Below the brass block is a
perspex block with tubes connecting P1, P2, Cl, and C2 as shown. Polytetrafluoroethylene stopcocks (E1 and E2) are placed between the respective syringes and storage chambers and a T-shaped stopcock (F) is placed between the two syringes. Below the stopcock (F) a flexible silicone rubber tube leads to a 1 cm silica cell (G) through which liquids may flow before being discharged from the system. The apparatus sits above the cell compartment of a Cary 14 spectrophotometer so that the cell (G) rests in the thermostatted cell-holder of that instrument. A rubber stopper (H) with two tubes, one of which may be closed by a pinchcock is fitted to the chamber (B2).

Because of the extreme reactivity of \( \text{cis-}[\text{RuCl}_2\text{en}_2]^+ \) towards hydroxide ion, it was found necessary to work in solutions having a hydroxide concentration of \( 2.35 \times 10^{-4} \) M. Consequently special precautions were found necessary to ensure that the hydroxide solutions were kept at the required concentrations. Dilute solutions of barium hydroxide were prepared from a standardised solution of reagent grade barium hydroxide which was kept under an atmosphere of nitrogen. All water used had previously been boiled and stored under nitrogen to remove carbon dioxide and mixing was performed in a carbon dioxide-free atmosphere in a glove-box. Dilute solutions were transferred to the storage chamber (B2) of the mixing apparatus by means of a polythene syringe. Nitrogen was bled through the chamber before and as the solutions were introduced. The
Figure 4.14

Diagramatic view of stopped-flow apparatus.
pinchcock was then closed to maintain a slight positive pressure of nitrogen over the solutions. In this way, uptake of carbon dioxide from the air was prevented.

In order to observe the reaction under pseudo first-order conditions, solutions of cis- \([\text{RuCl}_2\text{en}_2\text{Cl}_2\text{H}_2\text{O}]\) were generally of the order of \(10^{-5}\) molar. Also, a special slidewire measuring in the range 0 to 0.2 absorbance units was employed.

Fresh solutions of barium hydroxide with barium methane sulphonate to adjust ionic strength were stored in chamber (B2). cis- \([\text{RuCl}_2\text{en}_2\text{Cl}_2\text{H}_2\text{O}]\), dissolved in carbon dioxide-free barium methane sulphonate solution at the same ionic strength and temperature, was placed in chamber (B1).

After temperature equilibration, stopcocks (E1 and E2) were opened and the separate solutions were drawn into their respective syringes. The stopcocks (E1 and E2) were closed, the stopcock (F) was turned so as to connect all three passages and the syringes were immediately operated to expel approximately half their contents down the common passage and into the cell (G). Immediately the movement of the syringes was stopped, the stopcock (F) was closed. The change of optical density with time at least 355 nm was recorded for at least half-lives. The stopcock (F) was then opened and the remainder of the solutions were mixed in the same way. Thus, for each determination, two sets of data showing optical density against time were obtained. Occasionally, differences larger than could be explained by the inherent errors
Figure 4.15. First-order plot for base hydrolysis of the cis-\([\text{RuCl}_2\text{en}_2]^+\) ion.

of measurement were found between the two sets of data. In such cases the entire determination was repeated, and consistent sets of data were obtained. These generally agreed with one of the former pair. A possible explanation for these occasional discrepancies is that a bubble of air or nitrogen had passed through one of the tubes, resulting in unequal volumes of the two solutions being mixed.

Experimental data for a typical kinetic run are given in Table 4-8. Here, a 3.02 \(\times\) \(10^{-5}\) M. solution of cis-\([\text{RuCl}_2\text{en}_2]^+\) complex has reacted with hydroxide ion in a 7.05 \(\times\) \(10^{-4}\) N. \(\text{Ba(OH)}_2\) solution. The ionic strength was 1.0\(\times\)\(10^{-1}\) M., and the temperature was 15.2 ± 0.1° C. The function \(1 + \log_{10}\left(\frac{(A_t - A_\infty)}{(A_o - A_\infty)}\right)\)
(see Chapter 2) was computed at ten points and the first-order plot is shown in Figure 4.15.

At an ionic strength of 0.1 M and a temperature of $15.1 \pm 0.1^\circ C$, the rate constants listed in column 2 of Table 4-7 were found.

<table>
<thead>
<tr>
<th>$10^4 [\text{OH}^-]$</th>
<th>Original $k$ observed $x 10^3$ (sec$^{-1}$)</th>
<th>Later values of $k$ observed $x 10^3$ (See text)(sec$^{-1}$)</th>
<th>Values of $k$ observed $x 10^5$ after washing (sec$^{-1}$)</th>
</tr>
</thead>
<tbody>
<tr>
<td>2.32</td>
<td>2.7, 2.7</td>
<td></td>
<td>3.0, 2.8</td>
</tr>
<tr>
<td>3.52</td>
<td>3.9, 4.0</td>
<td></td>
<td>5.7, 5.6</td>
</tr>
<tr>
<td>4.70</td>
<td>6.2, 6.1</td>
<td></td>
<td>5.2, 5.3</td>
</tr>
<tr>
<td>7.05</td>
<td>9.7, 10.0</td>
<td>39.7, 36.6</td>
<td>9.9, 9.6</td>
</tr>
<tr>
<td>9.40</td>
<td>14.1,13.0,13.4,13.4</td>
<td>53.7, 52.5</td>
<td></td>
</tr>
<tr>
<td>14.10</td>
<td>40.5,39.9,34.4,40.0</td>
<td>73.8, 77.0</td>
<td></td>
</tr>
<tr>
<td>18.8</td>
<td>106,108</td>
<td></td>
<td></td>
</tr>
</tbody>
</table>

Observed rate constants at varying hydroxide concentrations. See text for explanation of circumstances under which different values were obtained.
Figure 4.15. Hydroxide dependence of the observed rate constant for the base hydrolysis of the cis-\([RuCl_2en_2]^+\) ion.

\[ T = 15.1^\circ C, \quad \mu = 0.1 \text{ M.} \]
TABLE 4-8.

<table>
<thead>
<tr>
<th>Time (sec.)</th>
<th>Absorbance</th>
<th>$1 + \log_{10}\left(\frac{A_t - A_\infty}{A_0 - A_\infty}\right)$</th>
</tr>
</thead>
<tbody>
<tr>
<td>0</td>
<td>0.0220</td>
<td>1.000</td>
</tr>
<tr>
<td>10</td>
<td>0.0200</td>
<td>0.950</td>
</tr>
<tr>
<td>20</td>
<td>0.0180</td>
<td>0.894</td>
</tr>
<tr>
<td>30</td>
<td>0.0165</td>
<td>0.847</td>
</tr>
<tr>
<td>40</td>
<td>0.0154</td>
<td>0.803</td>
</tr>
<tr>
<td>50</td>
<td>0.0143</td>
<td>0.762</td>
</tr>
<tr>
<td>60</td>
<td>0.0132</td>
<td>0.720</td>
</tr>
<tr>
<td>70</td>
<td>0.0123</td>
<td>0.677</td>
</tr>
<tr>
<td>80</td>
<td>0.0115</td>
<td>0.636</td>
</tr>
<tr>
<td>90</td>
<td>0.0108</td>
<td>0.596</td>
</tr>
</tbody>
</table>

$A_\infty = .0035$

From Figure 4.15, the apparent first-order rate constant is $1.0 \times 10^{-4}$ sec$^{-1} \pm 10\%$

The data of the first two columns of Table 4-7 are shown graphically in Figure 4.16. The observed first-order rate constants increase in direct proportion to the hydroxide concentration up to $7.05 \times 10^{-4}$ M. Above this concentration they are not reproducible but are, in all determinations, considerably greater than would be expected from extrapolation of the data from runs at lower hydroxide concentration.
Figure 4.17. Dependence of rate constant on hydroxide concentration for the base hydrolysis of the cis- \([\text{RuCl}_2\text{en}_2]^+\) ion.

\[ T = 13.4^\circ, \quad \mu = 10^{-3} \text{ M}. \]
It was found that on repetition of some of the runs after several weeks, significantly higher values of the rate constants were obtained. These results are listed in column 3 of Table 4 - 7. The entire system was washed by passing 1 M. hydrochloric acid through it at least five times, rinsed with distilled water at least ten times, and allowed to stand for a week filled with distilled water. The cell was further washed with concentrated hydrochloric acid followed by water before being subjected to the same treatment as the rest of the system. The results listed in column 4 of Table 4 - 7 were obtained. Although the rate constants were reduced, they did not reproduce the original values of the rate constant for concentration 9.40 x 10^{-4} M. and above. A possible explanation for the behaviour described is that an alternative mechanism exists and becomes more important at higher hydroxide concentrations. Traces of material left in the system appear to assist this alternative mechanism. However, an attempt to promote such catalysis by introduction of some aged solution of reaction products was ineffective.

Figure 4.16 shows that the dependence of the rate on hydroxide concentrations up to 7 x 10^{-4} M. can be approximated by an overall second-order rate law. From Figure 4.16, the second-order rate constant at 15.1^\circ C and an ionic strength of 0.1 M is 12.5 litre mole^{-1} sec^{-1} ± 10%.

At an ionic strength of 10^{-3} M. and a temperature of
Figure 4-17a. Logarithmic plot of the data of Table 4-9. The curvature of the line shows that the relationship between hydroxide concentration and observed rate cannot be accounted for by an equation of the form $k_{obs} = x [OH^-]^y$, where $x$ and $y$ are constant.
13.4 ± 0.1° all rates were faster than under the conditions described above, and the dependence on hydroxide concentration was of an order higher than one over the range 2.35 - 9.40 x 10⁻⁴ M. The data are summarised in table 4.9 and shown graphically in Figure 4.17.

<table>
<thead>
<tr>
<th>10⁴ [OH⁻]</th>
<th>10³ k_{obs.}</th>
</tr>
</thead>
<tbody>
<tr>
<td>2.35</td>
<td>4.4, 4.6</td>
</tr>
<tr>
<td>4.70</td>
<td>11.2, 11.7</td>
</tr>
<tr>
<td>7.05</td>
<td>30.7, 31.3</td>
</tr>
<tr>
<td>9.40</td>
<td>78.5, 84.4</td>
</tr>
</tbody>
</table>

Hydroxide dependence of the observed rate constant for the base hydrolysis of the cis- [RuCl₂en₂]⁺ ion.

\[ T = 13.4° \text{ C} \]
\[ \mu = 10⁻³ \text{ M} \]

**Temperature Dependence**

The reaction rate was measured at a variety of temperatures. The ionic strength was 0.1 M and the hydroxide concentration was 2.35 x 10⁻⁴ M. Second-order rate constants are given in Table 4 -10. Figure 4.18 shows a plot of \( \log_{10}k_2 \) against \( 10^3/T \).
From a least-squares analysis of the data the following parameters were calculated:

\[ \log_{10} A = 13.7 \pm 0.5 \quad \Delta S^\ddagger = 2 \pm 2 \text{ e.u.} \]

\[ E_a = 16.7 \pm 0.6 \text{ kcal/mol} \]

In summary, the base hydrolysis of the \( \text{cis-}[\text{RuCl}_2\text{en}_2]^+ \) ion may be approximated by a second-order rate law only at a high ionic...
TABLE 4-10.

<table>
<thead>
<tr>
<th>Temp. (°C)</th>
<th>$10^3 \cdot k_1$ (sec$^{-1}$)</th>
<th>$k_2$ (litre. mole$^{-1}$ sec$^{-1}$)</th>
</tr>
</thead>
<tbody>
<tr>
<td>13.5</td>
<td>2.04</td>
<td>8.55</td>
</tr>
<tr>
<td>15.2</td>
<td>2.72</td>
<td>11.6</td>
</tr>
<tr>
<td>17.5</td>
<td>2.98</td>
<td>12.8</td>
</tr>
<tr>
<td>19.7</td>
<td>4.32</td>
<td>18.4</td>
</tr>
<tr>
<td>23.1</td>
<td>6.41</td>
<td>27.3</td>
</tr>
<tr>
<td>29.7</td>
<td>10.8</td>
<td>45.8</td>
</tr>
<tr>
<td>34.1</td>
<td>14.1</td>
<td>59.7</td>
</tr>
<tr>
<td>35.6</td>
<td>16.4</td>
<td>69.7</td>
</tr>
<tr>
<td>38.0</td>
<td>24.0</td>
<td>102.2</td>
</tr>
</tbody>
</table>

strength (such as $10^{-1}$ M.) and at hydroxide concentrations below $10^{-3}$ M. At higher concentrations, rate constants were not reproducible, but indicated a higher-than-second-order dependence on the hydroxide concentration. The second-order rate constant for the reaction at an ionic strength of $10^{-1}$ M. and for hydroxide concentrations up to $7.05 \times 10^{-4}$ M. is given by $k_2 = (5 \times 10^{13}) \exp (1.67 \times 10^4 / RT)$. 
Use of $^{36}\text{Cl}$ to study the Isomerisation:

$$\text{cis-[RuCl}_2\text{en}_2]^{+} \xrightarrow{\text{ethylene glycol at 190}} \text{trans-[RuCl}_2\text{en}_2]^{+}$$

The trans-dichlorotris(ethylenediamine)ruthenium(III) cation may be made from the corresponding cis isomer by heating at the boil for one minute in ethylene glycol as stated in Chapter 1. As yet, no mechanism for this reaction has been postulated.

The first, and most extensively studied such isomerisation is that between cis- and trans- $[\text{CoCl}_2\text{en}_2]^{+}$. In aqueous solution the isomerisation takes place with aquation and re-association (20). In methanol, the mechanism is also thought to be dissociative (57).

An intramolecular mechanism is believed to be responsible for the isomerisation of the ion trans- $[\text{Co(en)}_2\text{H}_2\text{O}(\text{NH}_3)]^{+3}$ to its cis isomer. There, a metal-ethylenediamine bond is broken. The five-coordinated intermediate so formed gives either the cis or the trans isomer on reformation of the bond.

Another intramolecular mechanism is the trigonal twist (Figure 5.1) proposed by Bailar (54) for racemisation and isomerisation reactions.
In either of the above intramolecular mechanisms, exchange of ligands does not take place. Separate exchange reactions by either isomer may still occur. Thus, while the absence of exchange is indicative of an intramolecular isomerisation, the observation of exchange is ambiguous.

EXPERIMENTAL

Materials

Chlorine-36 was obtained from the Australian Atomic Energy Commission as $^36\text{Cl}$ in 2 M. hydrochloric acid with a specific activity of $2.5 \mu\text{Ci} / \text{mg. Cl} \pm 2\%$. Standard $\beta$-sources of $^{210}\text{Po}/^{210}\text{Bi}$ were obtained from the Radiochemical Centre, Amersham, U.K. Counting was performed in a lead castle using a "Twentieth Century Electronics type E93H" Geiger tube and an "Ekco N53CF" scaler. Cation exchange resin was Dowex 50W-X,
acid form. Inactive hydrochloric acid was made by diluting May and Baker "P" grade hydrochloric acid with distilled water.

\[ {\text{Cl}}_{\text{labelling of cis-}} \left[ \text{RuCl}_2\text{en}_2 \right] \text{Cl}_0 \]

The finely-powdered, inactive cis isomer (50 mg.) was dissolved in cold, 2 M. HCl (5 \times 10^{-1} \mu C/mg. Cl \pm 20\%) and acetone was immediately added. The solid which precipitated was collected on a millipore glass-fibre filter pad, washed with acetone, dried, and weighed. The yield was 42.4 mg (84\%). No attempt was made to recover the complex which remained in solution.

Emission of \( \beta \)-radiation from the sample was counted for eleven periods totalling 6,000 seconds. During nine periods interspersed with the above, background counts were recorded for 4,500 seconds. Regular checks against a standard source of \( ^{210} \text{Pr} / ^{210} \text{Bi} \) showed a counter efficiency of 10.5\% (\pm 0.1\%).

Isomerisation

\[ \text{cis-} \left[ \text{RuCl}_2\text{en}_2 \right] \text{Cl}^+ \cdot \text{H}_2\text{O} \] (42.4 mg) was dissolved in ethylene glycol (3 ml) by warming. The solution was heated to its boiling point for one minute, was cooled under a tap, and was poured on a Dowex 50W-X cation exchange column (acid form, bed volume 0.3 ml.). The column was then washed with 5 ml of water. Inactive 2 M. hydrochloric acid (3 ml.) was then forced through the column under pressure. The eluent so obtained was
quickly frozen by immersion in liquid nitrogen. Hydrochloric acid was sublimed off in an evacuated freeze-drying apparatus. This required four hours. The solid remaining was redissolved in 3 ml. of 2 M. hydrochloric acid. The solution was frozen and freeze-dried again. After eight hours, the solid remaining was taken up as a slurry in acetone and collected on a millipore pad as a disc of area 2.1 cm$^2$. The yield was 3.6 mg. (8.5%).

A lower rate of $\beta$-emission from the trans isomer made it necessary to count both the sample and the background for longer periods than had been necessary for the cis. The sample's activity was counted for a total of 375,765 seconds, the background for 180,000 seconds. Counter efficiency was kept at 15.1% ($\pm$ 0.15%).

**TREATMENT OF DATA**

Because $^{36}$Cl has a half-life of $3 \times 10^5$ years, corrections for decay of sample activity were not necessary.

**Corrections for Self-absorption**

Since $\beta$ radiation is significantly absorbed by matter, samples of finite thickness will absorb some of their own radiation, thereby giving an apparently low count rate. This does not matter if two samples of identical thickness and density are compared but, as in this experiment, when samples of different
thicknesses are compared, correction must be made for the greater self-absorption of the thicker sample. The ratio of self-absorption of two samples of active material is approximated from the external absorption coefficient of the radiation under consideration (53).

The absorption, by various thicknesses of aluminium, of $\beta$ radiation from a sample containing $^{36}$Cl was measured. A least-squares analysis showed that a plot of thickness ($t$ mg cm$^{-2}$) against the ratio, $c$, of the count rate at zero thickness to the count at thickness, $t$, is best approximated by $\log_{10}c = \log_{10} 1.10 - 0.00794t$. In all, 42,021 counts were recorded in the absorption measurement, giving an overall standard deviation of $\frac{100 \sqrt{\text{42,021}}}{42,021}$% that is, 0.49%.

The sample of the trans isomer had a thickness of $1.7 \pm 0.03$ mg cm$^{-2}$. If the same activity were contained in a sample of negligible thickness it would be increased by a factor of $1.03 \pm 0.02$. The sample of the cis isomer had a thickness of $20.29 \pm 0.03$ mg cm$^{-2}$. Its activity in a sample of negligible thickness would show a count rate increased by a factor of $1.41 \pm 0.02$. 
CALCULATIONS

Terminology

\[ R = \text{observed count rate} \]
\[ t = \text{time} \]
\[ S = R_t = \text{total number of counts received in time interval, } t. \]

Subscripts:
“cis” and “trans” refer to the particular samples of the respective isomers used in this experiment.
“b” refers to the background present when the cis sample was being counted.
“b’” refers to the background present when the trans sample was being counted.

Errors quoted are standard deviations based on the Poisson distribution.

i.e. \( X = \chi^2 \)
\[
\begin{align*}
S_{\text{cis}} + b &= 28,620 \pm 169 \text{ counts} \\
t_{\text{cis}} + b &= 6,000 \text{ seconds} \\
R_{\text{cis}} + b &= 4.77 \pm 0.012 \text{ counts per sec.} \\
S_b &= 1,055 \pm 32 \text{ counts} \\
t_b &= 4,500 \text{ seconds} \\
R_b &= 0.23 \pm 0.0071 \text{ counts per sec.} \\
R_{\text{cis}} &= 4.54 \pm \left(0.012^2 + 0.0071^2\right)^{\frac{1}{2}} \text{ counts per sec.} \\
&= 4.54 \pm 0.044 \text{ counts per sec.} \\
\text{Counter efficiency} &= 10.5 \pm 0.1\% \\
\end{align*}
\]

Rate of emission at surface
\[
= \frac{4.54}{0.105} \pm \left(0.01^2 + 0.01^2\right)^{\frac{1}{2}} \cdot \frac{4.54}{0.105}
= 43.2 \pm 0.86 \text{ counts per sec.}
\]

Actual rate of disintegration (allowing for self absorption)
\[
= 43.2 \times 1.41 \pm \left(0.02^2 + \left(\frac{0.2}{43.2}\right)^2\right)^{\frac{1}{2}} \times 43.2 \times 1.41
= 60.9 \pm 1.8 \text{ disintegrations/sec.}
\]

Molar rate of disintegration for \text{cis} isomer
\[
= (60.9 \pm 1.8) \times \frac{345.8}{0.0424} \text{ disintegrations per sec. per mole}
= (4.96 \pm 0.15) \times 10^5 \text{ disintegrations per sec. per mole.}
\]
$S_{\text{trans}} + b' = 167,386 \pm 409$ counts

$t_{\text{trans}} + b' = 375,765$ seconds

$R_{\text{trans}} + b' = 0.445 \pm 0.00109$ counts/sec.

$S_{b'} = 51,448 \pm 227$ counts

$t_{b'} = 180,000$ seconds

$R_{b'} = 0.286 \pm 0.00126$ counts/sec.

$R_{\text{trans}} = 0.159 \pm 0.00167$ counts/sec.

Counter efficiency $= 15.1 \pm 0.15\%$

Rate of emission at surface $= 1.05 \pm 0.02$ counts/sec.

Self-absorption correction factor $1.03 \pm 0.02$

Actual rate of disintegration

$= 1.08 \pm 0.3$ disintegrations/sec.

Molar rate of disintegration for trans isomer

$= (1.01 \pm 0.03) \times 10^5$ disintegrations per sec. per mole.
DISCUSSION

The results show that 20.4 ± 0.9% of the molar activity originally in the cis complex was in the recovered trans complex.

The first-order rate constant for aquation of \( \text{cis-} \left[ \text{RuCl}_2\text{en}_2 \right]^+ \) is \( 4 \times 10^{-5} \text{ sec}^{-1} \) at 24.9° (29). Chloride exchange in this complex proceeds via aquation in acid solution. During the labelling process, the cis complex was in solution for less than 90 seconds at 25° C. The most exchange which could have taken place at this stage is 0.4%, so at least 99.6% of the activity of the cis sample was in the anion.

If the only mechanism of isomerisation were dissociative, at least 33-1/3% of the original activity of the cis sample would have entered the cation of the trans. The figure would be higher (up to 66-2/3%) unless every intermediate formed gave the trans isomer and not the cis.

The percentage of the original molar activity found in the trans isomer was 20.4 ± 0.9%. Either a dissociative mechanism is not wholly responsible for the isomerisation or some activity was lost from the trans isomer on recovery. The rate of aquation of the trans- \( \left[ \text{RuCl}_2\text{en}_2 \right]^+ \) ion at 25° C. may be estimated by extrapolation of the data of table 3.9 of this thesis. It would be no greater than \( 3 \times 10^{-6} \text{ sec}^{-1} \).
The trans isomer was never in alkaline or neutral solution and spent less than 300 seconds in acid solution and on the column. The most chloride exchange which could be expected is 0.1%.

Conclusion

Less than the statistically-expected amount of radioactive chloride for a dissociative isomerisation was found in the trans complex. From the known rate of anation of the trans complex, the deficiency cannot be due to subsequent exchange during the recovery process.

The isomerisation:

\[
\text{trans-} \quad \left[\text{RuCl}_2\text{en}_2\right]^+ \quad \rightarrow \quad \text{cis-} \quad \left[\text{RuCl}_2\text{en}_2\right]^+ 
\]

performed as described, occurs at least partly by an intramolecular mechanism.
CHAPTER 6

DISCUSSION OF KINETIC RESULTS

Acid Hydrolysis of the trans-\([\text{RuCl}_2\text{en}_2]^+\) ion.

Apart from those of ruthenium (III), no hydrolysis reactions of \(d^5\) acido-amine complexes have been studied. Manganese (II) and iron (III) form labile, high-spin complexes and no acido-amine complexes of technecium (II) and rhenium (II) are known. Although bromopenta-amine osmium (III) bromide has been prepared (55), no information has been published concerning its hydrolysis reactions.

The reactions of the ruthenium complexes may be compared to those of the corresponding \(d^6\), low-spin cobalt and rhodium complexes.

Table 6.1 shows a collection of data obtained by various workers. Rate constants at 25°C for the rhodium complexes have been extrapolated from published constants at higher temperatures. Values of the entropy of activation, \(\Delta S^+\), at 25°C for cobalt and rhodium complexes have been calculated from published figures by equation (18) of Chapter 2.

It will be seen from Table 6.1 that the acid hydrolysis rates for the cis- complexes exceed the rates for the respective trans- complexes for all three metals. No single, satisfactory explanation has been found for this although several have been suggested. The "trans effect" theory (56) predicts that the trans isomer would react more rapidly than the cis because OCl⁻...
<table>
<thead>
<tr>
<th>Complex</th>
<th>$k_{25^\circ}$ (sec$^{-1}$)</th>
<th>$E_a$ (kcal)</th>
<th>$\Delta S^\ddagger_{25}$ (eu)</th>
</tr>
</thead>
<tbody>
<tr>
<td>cis- $[\text{CoCl}_2\text{en}_2]^+$</td>
<td>$24.0 \times 10^{-5}$</td>
<td>22.2</td>
<td>-3 *</td>
</tr>
<tr>
<td>trans- $[\text{CoCl}_2\text{en}_2]^+$</td>
<td>$3.5 \times 10^{-5}$</td>
<td>27.5</td>
<td>+11 *</td>
</tr>
<tr>
<td>trans- $[\text{CoCl}(\text{NH}_3)_5]^{2+}$</td>
<td>$0.17 \times 10^{-5}$</td>
<td>23</td>
<td>-9 *</td>
</tr>
<tr>
<td>cis- $[\text{RhCl}_2\text{en}_2]^+$</td>
<td>$29 \times 10^{-8}$</td>
<td>25</td>
<td>-7 *</td>
</tr>
<tr>
<td>trans- $[\text{RhCl}_2\text{en}_2]^+$</td>
<td>$3.2 \times 10^{-8}$</td>
<td>25.5</td>
<td>-9 *</td>
</tr>
<tr>
<td>trans- $[\text{RhCl}(\text{NH}_3)_5]^{2+}$</td>
<td>$16 \times 10^{-8}$</td>
<td>22.8</td>
<td>-15 *</td>
</tr>
<tr>
<td>cis- $[\text{RuCl}_2\text{en}_2]^+$</td>
<td>$38 \times 10^{-6}$</td>
<td>21.1</td>
<td>-10</td>
</tr>
<tr>
<td>trans- $[\text{RuCl}_2\text{en}_2]^+$</td>
<td>$4.4 \times 10^{-6}$</td>
<td>21.8</td>
<td>-10</td>
</tr>
<tr>
<td>trans- $[\text{RuCl}(\text{NH}_3)_5]^{2+}$</td>
<td>$0.7 \times 10^{-6}$</td>
<td>23</td>
<td>-11</td>
</tr>
</tbody>
</table>

**TABLE 6-1.**

Kinetic Data for primary Acid Hydrolysis of acido-amine Complexes of Cobalt, Rhodium and Ruthenium.

* Calculated from published data in reference cited

Ø Extrapolated from published rate constants at higher temperatures

Figures in parentheses are references to literature
is a better trans activator than NH$_3$. Basolo and Pearson (57) suggest that the presence of a halogen in the cis position might more greatly activate the cis-$[\text{CoCl}_2\text{en}_2]^+$ ion by $\pi$-bonding from ligand to metal. It has been suggested that electrostatic repulsions between neighbouring ionic ligands in cis-$[\text{CoCl}_2\text{en}_2]^+$ favour the breakup of this complex. However, the trans-$[\text{Co(NO}_2\text{)Clen}_2]^+$ ion reacts more rapidly than its cis isomer, so a purely electrostatic argument does not account for the behaviour. The ratios of the respective cis-$^\text{dichloro}$ and trans-$^\text{dichloro}$

rates are 6.8 for cobalt, 9.3 for rhodium, and 8.6 for ruthenium.

The activation energies for the rhodium complexes are higher than those for the cobalt and ruthenium complexes (with the exception of trans-$[\text{CoCl}_2\text{en}_2]^+$). This is reflected in the slower reaction rates, which are approximately $10^{-2}$ times those for corresponding ruthenium complexes. The anomalously high activation energy for the trans-$[\text{CoCl}_2\text{en}_2]^+$ ion is balanced by its more positive entropy of activation. The corresponding rhodium and ruthenium complexes do not show such behaviour.

The faster reaction rates of the cobalt complexes relative to those of ruthenium must be attributed mainly to a more positive entropy of activation, as the activation energies for the cobalt complexes are higher than those for the ruthenium complexes.
From Table 3-4, it can be seen that the crystal field activation energy (C.F.A.E.) in Dq for a $d^5$ low-spin complex is smaller than that for a $d^6$ low-spin complex. This suggests that the former should be more reactive. Even when allowance is made for the smaller value of Dq for first-row elements, an energetic argument based on C.F.A.E. would predict that cobalt should react more slowly than ruthenium.

Entropies of activation for the rhodium and ruthenium complexes are comparable. Activation energy is the controlling factor here, and the prediction based on C.F.A.E. agrees with experiment.

The weight of evidence for cobalt acido-amine complexes (58), (59) favours a substantially $S_N^1$ reaction although there is disagreement between authors as to the stereocchemistry of the five-coordinated intermediate.

The molecularity of the aquation of the rhodium complexes is still subject to debate. Chan (27), and Johnson, Basolo and Pearson (24) interpret their data in terms of a substantially $S_N^2$ reaction. Pöö, Shaw and Wendt (25) prefer to explain them by a dissociative mechanism with an ion-pair intermediate. In any case, the behaviour of the rhodium complexes is different from that of the cobalt complexes in that the incoming ligand is more involved in the intermediate species.
The work of L. Kane-Maguire (30) with a number of complexes of the type cis- \([\text{RuX}_2(A-A)_2]^+\) gave evidence that the acid hydrolysis of these complexes showed substantial \(S^2_2\) character.

The more-positive entropies of activation for the cobalt complexes support the view that their hydrolysis has more \(S^1\) character. A dissociative rate-controlling step would involve an increase in entropy. An associative rate-controlling step would involve a decrease.

The similarity in the relative rates of acid hydrolysis for cis- and trans- \([\text{MCI}_2\text{en}_2]^+\) and \([\text{MCI(NH}_3)_5]^2+\) for \(M = \text{Co and Ru}\) seems to be largely coincidental in view of the different values of \(E_a\) and \(\Delta S^\dagger\). Furthermore, the acid hydrolysis of the trans- \([\text{CoCl}_2\text{en}_2]^+\) ion is accompanied by the isomerisation of 35% of the ion to the cis form.

No such isomerisation occurs with either cis- or trans- \([\text{RuCl}_2\text{en}_2]^+\)

The hydrolyses of the rhodium complexes show more similarity to those of the ruthenium complexes. The cis- and trans- \([\text{RhCl}_2\text{en}_2]^+\) ions do not isomerise. The differences in the rates of hydrolysis are due primarily to the higher activation energy for rhodium (III), which has been accounted for by the C.F.A.E.

The data obtained, considered in the light of the reactions of the cis- \([\text{RuCl}_2\text{en}_2]^+\) and \([\text{RuCl(NH}_3)_5]^2+\) ions and
<table>
<thead>
<tr>
<th>Complex</th>
<th>( k_b ) (litre.mol.(^{-1}).sec(^{-1}))</th>
<th>( k_a ) (litre.mol.(^{-1}).sec(^{-1}))</th>
<th>( k_b/k_a )</th>
</tr>
</thead>
<tbody>
<tr>
<td>cis- ([\text{CoCl}_2\text{en}_2]^{+})</td>
<td>7.1 \times 10^2</td>
<td>4.3 \times 10^{-6}</td>
<td>1.6 \times 10^8</td>
</tr>
<tr>
<td>trans- ([\text{CoCl}_2\text{en}_2]^{+})</td>
<td>3.2 \times 10^{-3}</td>
<td>6.3 \times 10^{-7}</td>
<td>2.0 \times 10^9</td>
</tr>
<tr>
<td>([\text{CoCl(NH}_3)_5]^{2+})</td>
<td>8.5 \times 10^{-1}</td>
<td>3.1 \times 10^{-8}</td>
<td>2.7 \times 10^9</td>
</tr>
<tr>
<td>cis- ([\text{RhCl}_2\text{en}_2]^{+})</td>
<td>2 \times 10^{-3}</td>
<td>3.8 \times 10^{-8} \text{ (a)}</td>
<td>5.5 \times 10^4</td>
</tr>
<tr>
<td>trans- ([\text{RhCl}_2\text{en}_2]^{+})</td>
<td>8 \times 10^{-8} \text{ (a, b)}</td>
<td>3.2 \times 10^{-8} \text{ (a, b)}</td>
<td>2.5</td>
</tr>
<tr>
<td>([\text{RhCl(NH}_3)_5]^{2+})</td>
<td>4 \times 10^{-4}</td>
<td>1.3 \times 10^{-8} \text{ (a)}</td>
<td>3.1 \times 10^4</td>
</tr>
<tr>
<td>trans- ([\text{IrCl}_2\text{en}_2]^{+})</td>
<td>1.6 \times 10^{-8} \text{ (a, b)}</td>
<td>1.6 \times 10^{-8} \text{ (a, b)}</td>
<td>1</td>
</tr>
<tr>
<td>cis- ([\text{RuCl}_2\text{en}_2]^{+})</td>
<td>3 \times 10^{-1} \text{ (d)}</td>
<td>6.8 \times 10^{-7}</td>
<td>4.4 \times 10^7</td>
</tr>
<tr>
<td>trans- ([\text{RuCl}_2\text{en}_2]^{+})</td>
<td>2.4 \times 10^{-2}</td>
<td>7.9 \times 10^{-8}</td>
<td>3.0 \times 10^5</td>
</tr>
<tr>
<td>([\text{RuCl(NH}_3)_5]^{2+})</td>
<td>4.9</td>
<td>1.3 \times 10^{-8}</td>
<td>3.8 \times 10^8</td>
</tr>
</tbody>
</table>

(a) extrapolated; (b) first-order constant (see text); (c) this work; (d) low hydroxide concentrations (see text)
corresponding rhodium and cobalt complexes are consistent with the view that the acid hydrolysis of the \( \text{trans-} \left[ \text{RuCl}_2\text{en}_2 \right]^+ \) ion follows an \( S_n^2 \) mechanism.

**Base Hydrolysis of the cis- and trans- \( \left[ \text{RuCl}_2\text{en}_2 \right]^+ \) Ions.**

The results in Chapter 4 and those of other workers (50), (29), show that the base hydrolys is of all the acid-amine complexes of ruthenium (III) studied are faster by several powers of ten than their acid hydrolys es.

Second-order rate constants, \( k_b \), for several chloro-amine complexes of ruthenium, cobalt, rhodium and iridium are listed in the second column of Table 6.2. The figures in the third column are artificial, second-order rate constants for corresponding acid hydrolys es. They are calculated on the (unproven) assumption that water plays a first-order role in those reactions. Since the molarity of water in dilute, aqueous solutions is 55.5, \( k_a = k_1/55.5 \). The ratios \( k_b/k_a \) in column four are a measure of the specific reactivity of the complexes towards hydroxide ion. Second-order rate constants for the \( \text{trans-} \left[ \text{RhCl}_2\text{en}_2 \right]^+ \) and \( \text{trans-} \left[ \text{IrCl}_2\text{en}_2 \right]^+ \) ions have not been published. The figures given for these in columns 2 and 3 are first-order rate constants (in sec\(^{-1}\)) extrapolated to 25\(^\circ\). The corresponding figures in column 4 are ratios of first order rate constants.
No data are available for the cis- \([\text{IrCl}_2\text{en}_2]^{+}\) and \([\text{IrCl}(\text{NH}_3)_5]^{2+}\) ions.

Apart from the trans- \([\text{RhCl}_2\text{en}_2]^{+}\) and trans- \([\text{IrCl}_2\text{en}_2]^{+}\) ions, all the complexes show substantially enhanced reactivity towards hydroxide ion. The rhodium complexes show a smaller effect by a factor of about $10^4$.

The trans- \([\text{RuCl}_2\text{en}_2]^{+}\) ion shows less specific reactivity than either of the other two ruthenium complexes. For cobalt, by contrast, the trans- isomer shows ten times more preference for the hydroxide ion than does the cis. Previous workers (29), (50) have shown that the base hydrolyses of the \([\text{RuCl}(\text{NH}_3)_5]^{2+}\) and cis- \([\text{RuCl}_2\text{en}_2]^{+}\) ions can be best accounted for by an $S_{N2}$ C.B. mechanism. A bimolecular mechanism also seems likely for the rhodium and iridium complexes.

The $S_{N1}$ C.B. mechanism for cobalt is assisted by $\Pi$-bonding in the 5-coordinated amido intermediate. To date, nothing has been said regarding the relative positions of the amido group and the leaving group in an $S_{N2}$ C.B. mechanism. The following is suggested as an explanation of the rapidity of $S_{N2}$ C.B. substitutions. It also accounts for the faster rates of substitution exhibited by the cis- isomers.

In the following discussion, optical isomers are regarded as identical, as they are energetically equivalent.
The cis- and trans-isomers of the \([\text{RuCl}_2\text{en}_2]^{+}\) ion are depicted in Figure 6.1.

It will be seen that in the cis complex, a nitrogen donor atom may be in either of two non-equivalent environments. Two of them (labelled "t") are trans to chloride ligands. The remaining two (labelled "c") are trans to each other. In the trans complex, each nitrogen donor is trans to another nitrogen donor. Thus the cis complex (but not the trans) may form two distinct amido species. These will be referred to as the "t"
amido species or the "c" amido species depending on whether a "t" nitrogen or a "c" nitrogen has deprotonated.

It is suggested that the "t" amido species favours the S₉₂ C.B. mechanism. Since the trans isomers cannot form "t" amido species they are at a disadvantage and show slower reaction rates. The theory also predicts, as is observed, that rates for base hydrolysis of chloropenta-ammine complexes will be more comparable with those of the cis isomers than the trans.

Two explanations are available. The chloride ligand may exert a trans effect on the nitrogen donor atom trans to it. This would make the nitrogen more electronegative and its protons more acidic. The result would be a greater concentration of the amido species in solution, and consequently a faster rate.

Secondly, in a "t" amido species already formed, the amido group may exert a trans labilizing effect on the chloride ligand, making it more susceptible to attack. This would lower the activation energy and thereby promote the reaction. Either or both of these effects would tend to increase the rate.

Arrhenius activation energies for the cis and trans isomers of \([\text{RuCl}_2\text{en}_2]^+\) and \([\text{RhCl}_2\text{en}_2]^+\), and trans- \([\text{IrCl}_2\text{en}_2]^+\) are shown in Table 6.3.
TABLE 6.3

Arrhenius Activation Energies (kcal) for Selected Complexes.

<table>
<thead>
<tr>
<th>METAL</th>
<th>cis</th>
<th>trans</th>
<th>Reference</th>
</tr>
</thead>
<tbody>
<tr>
<td>Ru</td>
<td>16.7</td>
<td>19.9</td>
<td>this work</td>
</tr>
<tr>
<td>Rh</td>
<td>25</td>
<td>25.5</td>
<td>(6)</td>
</tr>
<tr>
<td>Ir</td>
<td>29.2</td>
<td>29.2 *</td>
<td>(16)</td>
</tr>
</tbody>
</table>

* $\Delta H^\ddagger$

For the ruthenium complexes, the activation energy is definitely higher for the trans-isomer. The effect is less pronounced, but still present, for the rhodium complexes.

Also noteworthy is the trend down the columns. This is as expected from the crystal field activation energies (Table 3.4), as $D_q$ is greater for Ir than for Rh.

Special mention should be made of the dependence of the rate constant for the base hydrolysis of the cis- $[\text{Ru Cl}_2\text{en}_2]^+$ ion on hydroxide concentration. The discussion above is based on the behaviour of the reaction at hydroxide concentrations up to $7 \times 10^{-4}$ M. The reason for the deviation from a second-order rate law above that concentration is not understood.
The logarithmic plot in figure 4-17a shows that the relationship cannot be expressed in the form

\[ k_{obs} = x [OH^-]^y \]

where \( x \) and \( y \) are constants.
Because the dependence is linear up to that point and deviates sharply above it, it seems probable that a second-order mechanism (such as $S_N^1 C.F.$) is primarily responsible in the more dilute solutions. A mechanism of higher order becomes predominant at higher concentrations of hydroxide.

The effect may be due to catalysis by other materials present, although no definite evidence for this has been found. Another possible explanation may lie in the formation of a diamido species by the loss of two protons. Although the loss of a second proton would involve charge separation, the resulting, anionic species should more readily lose chloride.

Until reproducible data have been obtained for the dependence of the rate on hydroxide concentrations above $7 \times 10^{-4} \text{ M}$, the behaviour cannot satisfactorily be explained.
APPENDIX

KINETIC PROGRAMMES IN "FOCAL" LANGUAGE

"Focal" is a keyboard-oriented user language for small digital computers. Details may be found in "Focal Programming Manual" published by Digital Equipment Corporation, Massachusetts, 1968.

The following two programmes were widely used.
Programme I enables rapid calculation of rate constants from spectro-photometric data. It tabulates values of
\[ 1 + \log_{10} \left( \frac{(A_t - A_\infty)}{(A_0 A_\infty)} \right) \] (see Chapter 2) and plots approximate values of the parameter against \( t \). The latter step is intended not for calculation purposes but enables a quick check that the data are consistent with a first-order rate law.

The programme then calculates, by a least-squares method, an approximate value of the first-order rate constant \( k \). Since, in a kinetic run, not all points are equally valid, the least-squares value of \( k \) should not be considered the "best" value. A better value may be obtained by plotting the data tabulated and measuring \( k \) from the slope of the line of visual "best fit".

The second programme was used to calculate \( E_a \) and \( \log_{10} A \) (as defined in Chapter 2) from a set of rate constants at varied temperatures. It tabulates values of \( 10^3/T \) and
\[ \log_{10} k, \] calculates values of \( E_a \) and \( \log A \) by the method of least squares, and gives the statistical uncertainties in these parameters. It then prints coordinates of two points defining the line of best fit, to enable a graph to be drawn as a visual check.

Listings of the two programmes and a sample of the printout from each are reproduced below.
Programme 1

C-F)CAL., 1968

01.01 I !!!!!!!
01.02 A "REF" N
01.03 A "N?" N
01.10 I "AYS. VALUES ?", !: F Z=1, V: A Y(Z)
01.20 I !: A "LVE INTERVAL" Y: F Z=1, V: S X(Z)=(Z-1)*YY
01.21 A "A INFINITY" Y: G 1.25
01.25 S L=([FLG](Y(Z)-YY)) / (2.30258)
01.30 F Z=1, N: S Y(Z)=([FLG](Y(Z)-YY)) / (2.30258-LD)
01.32 I " TIME SEC 1+L" !
01.33 F Z=1, N: 74.02, X(Z), 77.03," "1+Y(Z), !
01.50 I !!!!; F Z=1, V-1: D 1.60
01.60 I 74.02, X(Z), \*\*; D 7

02.00 S Y=0; S v=0; S 0=0; S r=0; S s=0; F Z=1, V: D 2.05
02.04 D 2.10; S h=(J+v-v*r)/(J+2-v*0); S a=(v-r*J)/v
02.25 F Z=1, N: S S=S+(x*(Z)+a-v(Z))*2
02.06 T 7, !!"SLOPE" S:00 2:2: 1:01
02.08 S a=0+x(Z)+2: S J=J+x(Z)
02.13 F Z=1, N: S v=a+y(Z); S R=R+x(Z)*Y(Z)
02.20 I !!,"APPARENT 1ST ORDER CONSTANT"-2.30258-3,"SEC-1"
Printout from Programme 1

REF: 0312.11
N?: 10
ABS. VALUES?
TIME INTERVAL: 10
A INFINITY: 110

<table>
<thead>
<tr>
<th>TIME SEC</th>
<th>1+LOG</th>
</tr>
</thead>
<tbody>
<tr>
<td>+ 0.00</td>
<td>+ 1.000</td>
</tr>
<tr>
<td>+ 10.00</td>
<td>+ 0.927</td>
</tr>
<tr>
<td>+ 20.00</td>
<td>+ 0.878</td>
</tr>
<tr>
<td>+ 30.00</td>
<td>+ 0.829</td>
</tr>
<tr>
<td>+ 40.00</td>
<td>+ 0.778</td>
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<tr>
<td>+ 50.00</td>
<td>+ 0.730</td>
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<tr>
<td>+ 60.00</td>
<td>+ 0.686</td>
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<tr>
<td>+ 70.00</td>
<td>+ 0.632</td>
</tr>
<tr>
<td>+ 80.00</td>
<td>+ 0.583</td>
</tr>
<tr>
<td>+ 90.00</td>
<td>+ 0.549</td>
</tr>
</tbody>
</table>

SLOPE = -0.49504E-02

APPARENT 1ST ORDER CONSTANT = +0.113987E-01SEC^-1
Programme 2

+C NEW Arrhenius with standard errors

01.21 ask "Number of points?" N
01.02 type ! "enter centigrade temperatures" !
01.03 FOR Z=1, N: ask 1(Z)
01.04 TYPE ! "enter rate constant" !
01.05 FOR Z=1, N: ask <(Z)
01.06 FOR Z=1, N: sei A(Z)=1<1(Z)+273.15>
01.07 FOR Z=1, N: sei Y(Z)=Log<<(Z)>/2.30268
01.19 I !!!!, "TCEN1. 1000X1<ELIV X LOG K", !
01.15 F Z=1, N: 0 1.25
01.16 GO TO 2.03
01.20 I Z6.03, t(Z), , , 75.33, 1000x(XZ), , , 7, X(Z), , , 75.33, Y(Z)
01.25 0 1.21 I !

02.03 S X=0; S Y=0; S AX=X; S XY=0
02.10 F Z=1, N: S X=X+X(Z): S Y=Y+Y(Z): S AX=AX+X(Z)+Z
02.11 F Z=1, N: S XY=XY+Y(Z)+Z: S AX=AX+X(Z)*Y(Z)
02.20 S A=(X+Y-N+AX)/((N-2)-N+AX): S A=(Y/N-N+AX)
02.30 S SE=Y+T/2-N-AX-AY/N; S SE=SQ1(SE/<<Y-2>)
02.40 S SA=SSE/SUM(AX-A+2/V)
02.50 S SA=SSE/SUM(AX-A+2/V)
02.60 I Z, !!!!, "SLPF", , , S Y, "SP, !!
02.70 I Z6.03, "LOG A", , , S Y, "SA, !!
02.80 I "CA"-4.75E-03*SA, , , S D, "A-5.75E-03*SA, "<CAL>
02.90 I !!!!, "POINTS DEFINING REL LINE!" !!!!, 1000X1, LOG K
02.42 F Z=1, N=1, N: I Z6.03, 1.1(A(Z)-1.0): , , 6+X(XZ)
02.43 I !!!!!
Printout from Programme 2

N=8

T CENTIGRADE
13.5 : 15.2 : 17.5 : 19.7 : 23.1 : 29.7 : 38.0 : 35.6

RATE CONSTS

<table>
<thead>
<tr>
<th>T CENT.</th>
<th>1000/T KELVIN</th>
<th>K</th>
<th>LOG K</th>
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<td>++ 13.50</td>
<td>++ 3.489</td>
<td>++ 0.855000E+01</td>
<td>++ 0.932</td>
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<td>++ 15.20</td>
<td>++ 3.468</td>
<td>++ 0.115700E+02</td>
<td>++ 1.063</td>
</tr>
<tr>
<td>++ 17.50</td>
<td>++ 3.441</td>
<td>++ 0.127500E+02</td>
<td>++ 1.106</td>
</tr>
<tr>
<td>++ 19.70</td>
<td>++ 3.415</td>
<td>++ 0.184000E+02</td>
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<td>++ 23.10</td>
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</tr>
<tr>
<td>++ 29.70</td>
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<td>++ 0.458300E+02</td>
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<td>++ 0.696800E+02</td>
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SLOPE=-0.371752E+04 S.D.=+0.148852E+03

LOG A=+ 13.934 S.D.=+ 0.502

EA=+ 17.008 S.D.=+ 0.681 KCal.

POINTS DEFINING BEST LINE

<table>
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<th>LOG K</th>
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</thead>
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<td>++ 0.965</td>
</tr>
<tr>
<td>++ 3.239</td>
<td>++ 1.894</td>
</tr>
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REFERENCES

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(58) ibid, Chapter 3.

ADDENDUM

In response to the examiners' comments, the spectrophotometric data for the base hydrolysis of the trans- \([\text{RuCl}_2\text{en}_2]^+\) ion have been re-calculated using \(A_\infty\) values calculated from the spectra of the trans- \([\text{RuCl}_2\text{en}_2]^+\) and trans- \([\text{RuOHCl}_2\text{en}_2]^+\) ions.

The extinction coefficient of the trans- \([\text{RuCl}_2\text{en}_2]^+\) ion at 342 nm is 4.030. The extinction coefficient of the trans- \([\text{RuOHCl}_2\text{en}_2]^+\) ion at the same wavelength is 580. Thus, the theoretical \(A_\infty\) value for the first stage reaction is given by \((\frac{4.030}{580})A_0\).

Table A-1 shows rate data for a kinetic run performed at a temperature of 25-50°C. The concentration of complex was \(1.56 \times 10^{-4}\) M. The concentration of hydroxide was \(4.00 \times 10^{-3}\). The ionic strength was 0.1. The value of \(A_\infty\) was calculated, as described above, to be 0.091.

The function \(\Delta t = \frac{A_t - A_\infty}{A_\infty - A_0}\) was plotted against time on semi-logarithmic graph paper (figure A-1). From the initial slope of this curve, an apparent first-order rate constant of \(1.00 \times 10^{-3}\) sec\(^{-1}\)
Figure A-1

First-order plot for base hydrolysis of the trans-$[\text{RuCl}_2\text{en}_2]^+$ ion, using theoretical $A_\infty$

$[\text{OH}^-] = 4 \times 10^{-3} \text{ M}, \text{ Temperature } = 25-60^\circ\text{C}$.
### TABLE A-1

<table>
<thead>
<tr>
<th>$k$ (min)</th>
<th>$A_t$</th>
<th>$\frac{A_t - A_\infty}{A_0 - A_\infty}$</th>
</tr>
</thead>
<tbody>
<tr>
<td>0</td>
<td>0.630</td>
<td>1</td>
</tr>
<tr>
<td>4</td>
<td>0.570</td>
<td>0.889</td>
</tr>
<tr>
<td>4</td>
<td>0.508</td>
<td>0.774</td>
</tr>
<tr>
<td>6</td>
<td>0.472</td>
<td>0.707</td>
</tr>
<tr>
<td>8</td>
<td>0.431</td>
<td>0.631</td>
</tr>
<tr>
<td>10</td>
<td>0.392</td>
<td>0.570</td>
</tr>
<tr>
<td>12</td>
<td>0.367</td>
<td>0.512</td>
</tr>
<tr>
<td>14</td>
<td>0.341</td>
<td>0.464</td>
</tr>
<tr>
<td>16</td>
<td>0.320</td>
<td>0.425</td>
</tr>
<tr>
<td>18</td>
<td>0.301</td>
<td>0.390</td>
</tr>
<tr>
<td>20</td>
<td>0.286</td>
<td>0.362</td>
</tr>
<tr>
<td>22</td>
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<td>0.340</td>
</tr>
<tr>
<td>24</td>
<td>0.262</td>
<td>0.317</td>
</tr>
<tr>
<td>26</td>
<td>0.253</td>
<td>0.301</td>
</tr>
</tbody>
</table>

was obtained.

Table A-2 shows rate constants at varying base concentrations, ionic strengths, and temperatures. All rate constants have been calculated using theoretical $A_\infty$ values.
<table>
<thead>
<tr>
<th>Complex Molarity</th>
<th>Hydroxide Molarity</th>
<th>Ionic Strength</th>
<th>Temperature (°C)</th>
<th>$k_1$ (sec$^{-1}$)</th>
<th>$k_2$ (litre mole$^{-1}$ sec$^{-1}$)</th>
</tr>
</thead>
<tbody>
<tr>
<td>1.74 x 10$^{-4}$</td>
<td>2.00 x 10$^{-3}$</td>
<td>2 x 10$^{-3}$</td>
<td>20.05</td>
<td>2.1 x 10$^{-4}$</td>
<td></td>
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<tr>
<td>2.02</td>
<td>3.00</td>
<td>3 x 10$^{-3}$</td>
<td>&quot;</td>
<td>3.4 x 10$^{-4}$</td>
<td></td>
</tr>
<tr>
<td>2.11</td>
<td>4.00</td>
<td>4 x 10$^{-3}$</td>
<td>&quot;</td>
<td>5.5 x 10$^{-4}$</td>
<td></td>
</tr>
<tr>
<td>2.33</td>
<td>5.00</td>
<td>5 x 10$^{-3}$</td>
<td>&quot;</td>
<td>6.8 x 10$^{-4}$</td>
<td></td>
</tr>
<tr>
<td>2.02</td>
<td>8.00</td>
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<td>&quot;</td>
<td>1.02 x 10$^{-3}$</td>
<td>1.35 x 10$^{-4}$</td>
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<tr>
<td>2.05</td>
<td>2.00</td>
<td>0.1</td>
<td>&quot;</td>
<td>2.0 x 10$^{-4}$</td>
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</tr>
<tr>
<td>1.91</td>
<td>4.00</td>
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<td>&quot;</td>
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<td></td>
</tr>
<tr>
<td>1.63</td>
<td>8.00</td>
<td>&quot;</td>
<td>&quot;</td>
<td>1.17 x 10$^{-3}$</td>
<td></td>
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<tr>
<td>1.81</td>
<td>6.00</td>
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<td>&quot;</td>
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<tr>
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<tr>
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<td>25.5</td>
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<td>2.50 x 10$^{-1}$</td>
</tr>
<tr>
<td>2.00</td>
<td>4.00</td>
<td>28.3</td>
<td>28.3</td>
<td>1.29 x 10$^{-3}$</td>
<td>3.22 x 10$^{-1}$</td>
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<tr>
<td>1.87</td>
<td>4.00</td>
<td>31.6</td>
<td>31.6</td>
<td>1.89 x 10$^{-3}$</td>
<td>4.72 x 10$^{-1}$</td>
</tr>
</tbody>
</table>

**Table A-2**

A plot of observed rate constants $k_1$ against hydroxide concentration for all data at 20.05 °C is shown in Figure A-2. The linear relationship $k_1$ $\propto$ [OH$^-$.] shows that the reaction is second order with a second-order rate constant of 1.35 x 10$^{-1}$ litre mole$^{-1}$ sec$^{-1}$. It can be seen from pairs of points representing the same hydroxide concentration at different ionic strengths that there is no significant dependence.
on ionic strength over variation by a factor of 50.

Figure A-2 Dependence of the base hydrolysis of the trans-\([\text{Ru Cl}_2\text{en}_2]^+\) ion on \([\text{OH}^-]\)
A plot of $\log_{10} k_{\text{on}}$ against $10^3/T$ (equation (12a) of Chapter 2) gave the following values:

$E_a = 19.1$ kcal. mole$^{-1}$

$\log_{10} A = 14.3$

From equation (18) of Chapter 2,

$\Delta S^{\pm}_{25} = +6.8$ cal. deg.$^{-1}$ mole$^{-1}$.

Figure A-3 Temperature dependence of the base hydrolysis of the trans-$[\text{RuCl}_2\text{en}_2]^+$ ion.
Conclusion

The values of the rate constants are slightly higher than those derived in Chapter 4. The activation energy is 4% smaller than that derived in Chapter 4, $\log_{10} A$ is 3% greater and $\Delta S^*$ is 15% smaller.

It is agreed that the parameters obtained by use of theoretical $A_{0x}$ values are more meaningful than those contained in Chapter 4. The differences in these parameters are sufficiently small not to affect the general conclusions drawn elsewhere in this thesis.