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I. OVERVIEW OF THE METHODOLOGY OF TRANSITION METAL
SUBSTITUTION KINETICS. II. SPECTROPHOTOMETRIC INVESTIGATION
OF THE EXTENT OF ION-PAIRING BETWEEN
AQUOPENTAAMMINERHODIUM(III) AND CHLORIDE IN ACIDIC
AQUEOUS SOLUTION. III. THE SYNTHESIS OF TRANS-
DIAQUOBIS(ETHYLENEDIAMINE)IRIDIUM(III). IV. THE KINETICS OF
THE ANATION BY CHLORIDE OF TRANS-
DIAQUOBIS(ETHYLENEDIAMINE)RHODIUM(III) IN ACIDIC AQUEOUS
SOLUTION

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THE UNIVERSITY OF OKLAHOMA

GRADUATE COLLEGE

I. OVERVIEW OF THE METHODOLOGY OF TRANSITION
METAL SUBSTITUTION KINETICS

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ION-PAIRING BETWEEN AQUOPENTAAMMINERHODIUM(III) AND
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IV. THE KINETICS OF THE ANATION BY CHLORIDE OF
trans-DIAQUOBIS(ETHYLENEDIAMINE)RHODIUM(III)
IN ACIDIC AQUEOUS SOLUTION

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SUBMITTED TO THE GRADUATE FACULTY

in partial fulfillment of the requirements for the

degree of

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BY

ROBERT CARL PFAFF

Norman, Oklahoma

1980

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TABLE OF CONTENTS

	Page
LIST OF TABLES	vi
LIST OF FIGURES	viii
I. OVERVIEW OF THE METHODOLOGY OF TRANSITION METAL SUBSTITUTION REACTIONS	
Chapter	
1. THE TRADITIONAL APPROACH TO TRANSITION METAL KINETICS	1
2. A NOVEL APPROACH TO TRANSITION METAL KINETICS	4
3. DATA HANDLING TECHNIQUES	6
4. PURPOSE OF THE RESEARCH	10
REFERENCES	13
II. SPECTROPHOTOMETRIC INVESTIGATION OF THE EXTENT OF ION-PAIRING BETWEEN AQUOPENTAAMMINERHODIUM(III) AND CHLORIDE IN ACIDIC AQUEOUS SOLUTION	
Chapter	
1. INTRODUCTION	16
2. EXPERIMENTAL	22
3. RESULTS AND DISCUSSION	25
REFERENCES AND FOOTNOTES	31

III. THE SYNTHESIS OF trans-
DIAQUOBIS(ETHYLENEDIAMINE)IRIDIUM(III)

Chapter

1. INTRODUCTION	44
2. EXPERIMENTAL	46
3. RESULTS AND DISCUSSION	53
REFERENCES	56

IV. THE KINETICS OF THE ANATION BY CHLORIDE OF
trans-DIAQUOBIS(ETHYLENEDIAMINE)RHODIUM(III)
IN ACIDIC AQUEOUS SOLUTION

Chapter

1. INTRODUCTION	62
2. EXPERIMENTAL	66
3. RESULTS AND DISCUSSION	73
REFERENCES	87
APPENDICES	121

LIST OF TABLES

	Page
TABLE	
I-1. Rates of Anation Reactions of the Type <u>trans</u> -RhL ₄ X(H ₂ O) + Y → <u>trans</u> -RhL ₄ XY + H ₂ O at 50°C	14
II-1. Ion-pair Formation Constants Determined Spectrophotometrically for Some Complexes of Rhodium(III) with Common Anions	32
II-2. Ion-pairing Data for the Reaction Between Aquopentaamminerhodium(III) and Chloride at 15.0°C	33
II-3. Ion-pairing Data for the Reaction Between Aquopentaamminerhodium(III) and Chloride at 25.0°C	34
II-4. Ion-pairing Data for the Reaction Between Aquopentaamminerhodium(III) and Chloride at 25.0°C	35
II-5. Ion-pairing Data for the Reaction Between Aquopentaamminerhodium(III) and Chloride at 40.0°C	36
II-6. Spectral Ion-pairing Data Analysis at 15.0, 25.0, and 40.0°C and [H ⁺] = 0.01M	37
II-7. Spectral Ion-pairing Parameter Values Fit to Eqn. [23]	38
III-1. Compounds of Co ³⁺ , Rh ³⁺ , and Ir ³⁺ Synthesized by Base Hydrolysis	57
III-2. Compounds of Rh ³⁺ and Ir ³⁺ Synthesized by Photoaquation	58

IV-1. Assigned Mechanisms for Some Substitution Reactions of Rh(III)	89
IV-2. Kinetic Data on the Reaction $\text{trans-Rh(en)}_2(\text{H}_2\text{O})_2^{3+} + 2\text{Cl}^- \rightarrow$ $\text{trans-Rh(en)}_2\text{Cl}_2 + 2\text{H}_2\text{O}$ 90
IV-3. Potentiometric Data on the Reaction $\text{trans-Rh(en)}_2(\text{H}_2\text{O})_2^{3+} + 2\text{Cl}^- \rightarrow$ $\text{trans-Rh(en)}_2\text{Cl}_2 + 2\text{H}_2\text{O}$ 92
IV-4. pH Data on the Reaction $\text{trans-Rh(en)}_2(\text{H}_2\text{O})_2^{3+} + 2\text{Cl}^- \rightarrow$ $\text{trans-Rh(en)}_2\text{Cl}_2 + 2\text{H}_2\text{O}$ 93
IV-5. Parameters from the Fit of Kinetic Data at 50.0 and 65.0°C to the Dissociative Mechanism106
IV-6. Parameters from the Fit of Kinetic Data at 50.0 and 65.0°C to the Interchange Mechanism108
IV-7. Parameters from the Fit of Potentiometric Data at 25.0°C	. .109
IV-8. Parameters from the Fit of pH Data at 10, 20, and 30°C111
IV-9. Parameters from the Combination Fit of Data to the Dissociative Mechanism114
IV-10. Parameters from the Combination Fit of Data to the Interchange Mechanism117
IV-11. Parameters from the Combination Fit of Data to the Interdis Mechanism	118

LIST OF FIGURES

FIGURE	Page
I-1. Schematic Representation of the Systems Chosen for Study	15
II-1. Involvement of Ion-pairs in Substitution Mechanisms of Rhodium(III) Complexes	39
II-2. Ultraviolet-visible Spectra of Aquopentaamminerhodium(III) and Chloropentaamminerhodium(III) in Acidic Aqueous Solution	40
II-3. Fit of Ion-pairing Data by Method 1	41
II-4. Fit of Ion-pairing Data by Method 2	42
II-5. Fit of Ion-pairing Data by Method 5	43
III-1. Ultraviolet-visible Spectra of <u>trans</u> -dichlorobis(ethylenediamine) iridium(III) in Acidic Aqueous Solution	59
III-2. Spectra During the Thermal Aquation of <u>trans</u> -dichlorobis(ethylenediamine) iridium(III)	60
III-3. Spectrum of the Ion-exchange Eluents from the Thermal Aquation Experiments	61
IV-1. Ultraviolet-visible Spectra of <u>trans</u> -diaquobis(ethylenediamine)rhodium(III) and <u>trans</u> -dichlorobis(ethylene-diamine)rhodium(III) in Acidic Aqueous Solution	120

I. OVERVIEW OF THE METHODOLOGY OF TRANSITION
METAL SUBSTITUTION KINETICS

CHAPTER 1

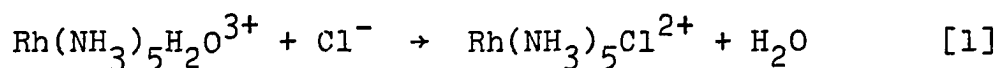
THE TRADITIONAL APPROACH TO
TRANSITION METAL KINETICS

The work presented herein represents part of an effort to develop a novel approach for the study of transition metal substitution kinetics. The traditional methodology incorporates assumptions which have been shown to be invalid and the novel approach seeks to alleviate these assumptions and the interpretational problems which result from them.

The traditional approach utilized attempts to maintain a high, constant ionic strength in all reaction mixtures by the addition of substitutionally inert salts, such as sodium perchlorate^{1,2}. This condition is employed in order to maintain constant values of the activity coefficients of the reactants. However, a great deal of evidence is available³ which indicates that activity coefficients vary with relative concentrations of two simple salts at constant ionic strengths above

approximately 0.3M. Therefore, the assumption that the activity coefficients are constant is not necessarily valid and, as a consequence, some of the kinetic behavior observed which has been interpreted in terms of a stoichiometric mechanism may, in fact, arise from activity coefficient variations.

In addition, pure equilibrium and rate constants cannot be extracted from data acquired in traditional experiments if the inert salt anion-pairs to the complex. Consider the reaction:



in which sodium perchlorate is added to maintain a high, constant ionic strength. If perchlorate, as well as chloride, ion-pairs to the complex ion, only a composite equilibrium constant is obtained¹:

$$K_{\text{obs}} = (K_{\text{Cl}} - K_{\text{ClO}_4}) / (1 + K_{\text{ClO}_4} \mu) \quad [2]$$

where K_{Cl} and K_{ClO_4} are the concentration quotients for the ion-pairing of chloride and perchlorate, respectively, to the metal complex ion and μ is the total ionic strength. Obviously, under constant ionic strength conditions, no useful information can be extracted from eqn. [2].

Under constant ionic strength conditions, the only kinetic parameter obtainable assuming an interchange stoichiometric mechanism for eqn. [1] is¹:

$$k_{\text{obs}} = k_1 K_{\text{Cl}} / (K_{\text{Cl}} - K_{\text{ClO}_4}) \quad [3]$$

where k_1 is the true rate constant for the interchange of the chloride ion-paired complex. It is clear that under these conditions, no useful information is obtained from eqn. [3]. This is not to say that the data collected are suspect, but rather that the data analysis techniques and the assumptions which underlie them should be critically examined.

CHAPTER 2

A NOVEL APPROACH TO TRANSITION METAL KINETICS

In the novel approach, no inert salt is added to the solutions and the ionic strength is determined solely by the reactant concentrations. This necessitates the calculation of the activity coefficients of the reactant ions as the activity coefficients in fact are not constant. The activity coefficients are calculated using⁴:

$$-\log\gamma_i = AZ_i^2[\sqrt{\mu}/(1+\sqrt{\mu})-b\mu] \quad [4]$$

where γ_i is the activity coefficient of the i^{th} ion, Z_i is the ionic charge, A is the Debye-Hückel temperature parameter, μ is the total ionic strength, and b is an empirically determined constant. This expression has been shown to give good results up to 0.3M ionic strength for 1:1 and some 2:1 electrolytes⁴ with $b=0.3$. Note that the method assumes that γ for an ion will depend only on its charge and the strength of the surrounding ionic medium.

The strength of the novel approach is its ability to

yield pure rate and equilibrium constants. However, this results in an increase in the number of parameters to be evaluated, compared to the constant ionic strength method. This makes it necessary to determine the fundamental thermodynamic constants by a variety of methods. With the variable ionic strength method, there are so many parameters that data fitting one kind of experiment would push the data to the limit of their ability to give well-defined parameter values. Therefore, several independent measurements of the parameters must be made in order to yield well-defined values with confidence.

CHAPTER 3

DATA HANDLING TECHNIQUES

Owing to the complexity of the kinetic and thermodynamic expressions used in this novel approach (see Sections II and IV), proper analysis of the data is crucial. In this work, extensive use has been made of a non-linear least-squares routine written at the University of Oklahoma⁵. As in most routines of this type, predicted values, $YC(i)$, of the dependent variables, $Y(i)$, are calculated using the mathematical expression to which the data are being fit, the M independent variables, $X(i,1)$ to $X(i,M)$, and the NP parameters, $B(1)$ to $B(NP)$ for each of the NO observations, such that:

$$YC(i) = f[X(i,1),X(i,2)\dots X(i,M),B(1),B(2)\dots B(NP)] \quad [5]$$

The routine seeks values of the parameters such that the function:

$$DEL = \sum_{i=1}^{NO} \{[Y(i)-YC(i)]*WEIGHT\}^2 \quad [6]$$

is minimized. The method used in the weighting is critical to

arriving at a rational solution to the fit. In this work, the Chi-Square method is used:

$$1/\text{WEIGHT}(i) = \sum_{j=1}^M [\partial \text{YC}(i) * \Delta X(i,j) / \partial X(i,j)] \quad [7]$$

where $\Delta X(i,j)$ is the estimated error in $X(i,j)$. Therefore, the i^{th} term of DEL is the statistical z-score of the i^{th} point squared:

$$z(i) = [\text{YC}(i) - Y(i)] / \Delta Y(i) \quad [8]$$

where $\Delta Y(i)$ is the expected standard deviation of $Y(i)$ based on errors in the independent variables. The overall quality of the fit is then obtained as the root mean standard deviation:

$$\text{RMSD} = \sqrt{[\text{DEL} / (\text{NO} - \text{NP})]} \quad [9]$$

where, again, NO is the number of observations and NP is the number of parameters being sought.

It is clear that, in the method of least-squares, the best-fit values of the parameters exhibit some uncertainty. In this work, the uncertainties in the parameter values are calculated as standard deviations; there are two major contributions to the standard deviations of the parameters. Owing to experimental errors, the best-fit parameter values may not describe every datum well and, as a result, the standard deviations of the parameters indirectly reflect the overall quality of the fit. The standard deviations also reflect the extent

to which the parameters are covariant, i.e., the extent to which a change in one parameter value affects the other parameter values. This contribution to the parameter standard deviations arises from the expression being fit and the standard deviations of parameters which are strongly covariant are large compared to those which are not strongly covariant. Therefore, fits must be discussed in terms of the definition of the parameters, i.e., the magnitude of the standard deviations in comparison to the parameter values.

The approach used in data analysis is to fit the data to all reasonable models of the reaction and then evaluate the fits statistically in order to deduce, if possible, the correct model. Each experimental technique possesses an inherent precision, e.g., pH meters commonly give values of $\text{pH} \pm 0.01$, and, therefore, the criterion for a good fit is an RMSD consistent with the inherent precision of the technique, 0.01. It is common, however, to obtain "good" fits for several models. In this situation, it is necessary to review related work in order to gain inferential data. It is considerably more straightforward to eliminate a model from consideration. If the inherent precision of the technique is taken to be the critical standard deviation of the model then, by the normal distribution curve, 95.45% of all experiments should yield RMSD values in the range:

$$\text{RMSD} \leq 2 * \text{SD}_{\text{crit}}$$

[10]

Models which yield an RMSD greater than $2*SD_{crit}$ are then eliminated as not describing the experimental data well.

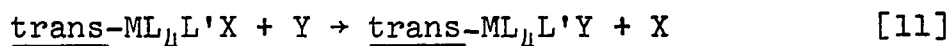
A final aspect is to investigate the definition of the parameters generated by this unique approach. If the parameters are too highly covariant to be well defined in the fits, they are of little value for scientific argument. However, the simultaneous computer fitting of data for several techniques should give well defined parameters.

In the present work, the data are analyzed according to models which incorporate various assumptions, e.g., absence of ion-pairing, presence of ion-pairing, etc. Each technique is modeled separately and then the techniques are combined and modeled using the same assumptions. In this manner, the quality of each technique can be evaluated and then, since all of the techniques measure separate facets of the same reaction, the data can be combined to allow each model to be evaluated. The specific models used are developed in Sections II and IV, as there are slight differences between the expressions for the two reactions.

CHAPTER 4

PURPOSE OF THE RESEARCH

The kinetics trans- effect has been the subject of considerable investigation by transition metal kineticists. It is clear from this work that the identity of the inert ligand, L', which is trans- to the labile ligand, X, in:



has a profound effect on the rate of substitution. Table I-1 shows rate data for some anation reactions of the type given in eqn. [11] from which comparisons are made as to the relative trans-effectiveness of the ligands. Comparison of analogous reactions in which the inert trans- ligand, L', is changed, reveals that the trans- effect order is $\text{OH}^- > \text{Br}^- > \text{Cl}^- > \text{H}_2\text{O}$, i.e., an OH^- trans- to the leaving group promotes a faster reaction (larger k) than an H_2O trans- to the leaving group.

The novel approach for the study of the kinetics of transition metal anation reactions offers an opportunity to refine the concept of the kinetic trans- effect. The data in Table I-1 also show that there are exceptions to the trans-

effectiveness order. It is not clear whether the exceptions are due to ionic strength effects or whether they are "real". If they are, indeed, due to ionic strength effects, one must immediately question the validity of such orderings. The novel approach gives pure rate constants and thermodynamic equilibrium constants which lend themselves easily to comparison as they are all infinite dilution values.

In addition, it has been convincingly shown that bond breaking between the metal and the leaving group is the kinetically important mode in reactions of cobalt(III)¹². For analogous reactions of rhodium(III), one would expect more associative behavior due to the larger size of rhodium(III). Although this is possibly true for reactions of the aquopentammine complexes, trans-Rh(en)₂(OH)(H₂O)²⁺ reacts more "dissociatively" than does its cobalt(III) analog¹.

Although the novel approach is theoretically sound, it is necessary to establish its experimental validity. Consequently, a course of research was initiated to establish the validity of the novel approach, as well as to clarify the nature of the kinetic trans- effect and investigate the roles of the attacking anion and the metal ion center. A schematic representation of the systems to be studied is shown in Figure I-1. This series of eighteen reactions will provide ample data to achieve each of the goals of the project. The work presented in this document covers the initial phase of this ambitious project. Clearly, a detailed study of eighteen reac-

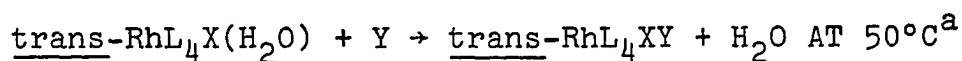
tions would occupy more time and effort than was available. Other phases of this project are, then, left for future research

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TABLE I-1

RATES OF ANATION REACTIONS OF THE TYPE



#	Reaction			$10^5 k_{21}^{\text{b}}$ $\text{M}^{-1}\text{s}^{-1}$	μ, M	$\text{Cl}^-:\text{Br}^-$ Rate Ratio	trans- Effect Ratio ^c	Relative eq. # ^c	Ref.
	L	X	Y						
1	H ₂ O	H ₂ O	Cl ⁻	0.016	2.5	1.2	1		6,7
2	H ₂ O	H ₂ O	Br ⁻	0.013	2.0		1		7
3	H ₂ O	OH ⁻	Cl ⁻	59	2.5	1.2	3700	1	6,7
4	H ₂ O	OH ⁻	Br ⁻	44	2.0		3400	2	7
5	H ₂ O	Cl ⁻	Cl ⁻	2.9	2.0		180	1	8
6	H ₂ O	Br ⁻	Br ⁻	5.5	2.0		420	2	7
7	1/2en	H ₂ O	Cl ⁻	0.13	1.0	.39	1		1
8	1/2en	H ₂ O	Br ⁻	0.33	0.2		1		1,9
9	1/2en	OH ⁻	Cl ⁻	640	1.0	.43	4900	7	1
10	1/2en	OH ⁻	Br ⁻	1500	0.2		4500	8	1,9
11	1/2en	Cl ⁻	Cl ⁻	72	0.2	1.2	560	7	10
12	1/2en	Cl ⁻	Br ⁻	62	0.2		190	8	10
13	1/2en	Br ⁻	Cl ⁻	680	0.2	1.3	5200	7	10
14	1/2en	Br ⁻	Br ⁻	530	0.2		1600	8	10
15	NH ₃	NH ₃	Cl ⁻	20.1	0.2	1.4			11
16	NH ₃	NH ₃	Br ⁻	14.4	0.2				11

Notes:

- Taken, with some modification, from ref. 7.
- Limiting second-order rate constants.
- Relative to the corresponding anation of the parent aquo complex.

FIGURE I-1
 SCHEMATIC REPRESENTATION OF THE SYSTEMS
 CHOSEN FOR STUDY

	Br^-	Br^-
	Cl^-	Cl^-
$\text{Co}(\text{NH}_3)_5\text{H}_2\text{O}^{3+}$	<u>trans</u> - $\text{Co}(\text{en})_2(\text{H}_2\text{O})_2^{3+}$	<u>trans</u> - $\text{Co}(\text{en})_2(\text{OH})(\text{H}_2\text{O})^{2+}$
$\text{Rh}(\text{NH}_3)_5\text{H}_2\text{O}^{3+}$	<u>trans</u> - $\text{Rh}(\text{en})_2(\text{H}_2\text{O})_2^{3+}$	<u>trans</u> - $\text{Rh}(\text{en})_2(\text{OH})(\text{H}_2\text{O})^{2+}$
$\text{Ir}(\text{NH}_3)_5\text{H}_2\text{O}^{3+}$	<u>trans</u> - $\text{Ir}(\text{en})_2(\text{H}_2\text{O})_2^{3+}$	<u>trans</u> - $\text{Ir}(\text{en})_2(\text{OH})(\text{H}_2\text{O})^{2+}$

15

II. SPECTROPHOTOMETRIC INVESTIGATION OF THE EXTENT OF ION-PAIRING BETWEEN AQUOPENTAAMMINERHODIUM(III) AND CHLORIDE IN ACIDIC AQUEOUS SOLUTION

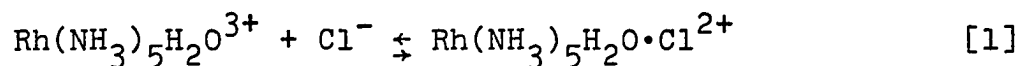
CHAPTER 1

INTRODUCTION

The concept of ion-pairing was first introduced by Werner¹ over sixty-five years ago. Since that time, a large amount of data has been reported² which clearly shows the importance of ion-pairing in transition metal substitution reactions. In this context, an ion-pair consists of a transition metal complex cation and an anion held in close proximity by electrostatic forces. The structure of the ion-pair is unknown; however, it is generally accepted² that inner-sphere ligands serve as binding sites and, in the case of protonated ligands, hydrogen bonding to the anion may be an importance source of stability.

Ion-pairing is an equilibrium process³ and, as such, an equilibrium constant expression can be written. Consider the ion-pair formation between aquopentaamminerhodium(III) and

chloride:



where $\text{Rh}(\text{NH}_3)_5\text{H}_2\text{O}\cdot\text{Cl}^{2+}$ is the resultant ion-pair. The equilibrium expression for the process (shown without charges for ease of presentation as are all subsequent expressions) is:

$$K_{\text{Cl}}^{\circ} = \frac{\{\text{Rh}(\text{NH}_3)_5\text{H}_2\text{O}\cdot\text{Cl}\}}{\{\text{Rh}(\text{NH}_3)_5\text{H}_2\text{O}\}\{\text{Cl}\}} \quad [2]$$

and, upon inclusion of the activity coefficients, the expression becomes:

$$K_{\text{Cl}}^{\circ} = \frac{[\text{Rh}(\text{NH}_3)_5\text{H}_2\text{O}\cdot\text{Cl}] \gamma_2}{[\text{Rh}(\text{NH}_3)_5\text{H}_2\text{O}][\text{Cl}]\gamma_3\gamma_1} \quad [3]$$

or:

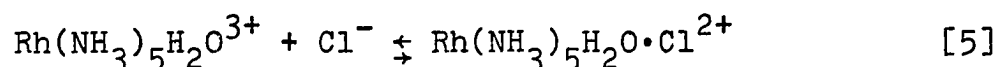
$$K_{\text{Cl}} = K_{\text{Cl}}^{\circ} \frac{\gamma_3\gamma_1}{\gamma_2} = \frac{[\text{Rh}(\text{NH}_3)_5\text{H}_2\text{O}\cdot\text{Cl}]}{[\text{Rh}(\text{NH}_3)_5\text{H}_2\text{O}][\text{Cl}]} \quad [4]$$

The possible involvement of ion-pairs in reaction mechanisms is illustrated in Figure II-1. The ion-pair can facilitate a ligand dissociation process or, owing to the short distance between the anion and the metal center, ion-pair formation can be the first step in an interchange process.

Direct measurement of the mechanistic involvement of ion-pairs is not possible; this information must be inferred from kinetic data. However, if ion-pair formation is to be considered as a possible reaction step, an independent

measure of the extent of ion-pair formation is extremely useful. Many methods have been successfully employed². These methods include polarography, conductivity, solubility studies, liquid-liquid extraction, ion-exchange studies, nuclear magnetic resonance, and potentiometry. However, in recent years, the spectrophotometric method has emerged as one of the primary methods for studying ion-pairing⁴⁻⁸.

The spectrophotometric method utilizes an increase in the extinction coefficients of the complex's charge-transfer bands⁹. This phenomenon results from an increase in electron density in the ligand serving as the binding site, thus increasing the spectroscopic transition probability and the band intensity. Specifically, for the reaction:



some measurable amount of each specie will be present in solution if the value of the equilibrium constant, K_{Cl} , is not extreme (so as to make either $[\text{Rh}(\text{NH}_3)_5\text{H}_2\text{O}]$ or $[\text{Rh}(\text{NH}_3)_5\text{H}_2\text{O}\cdot\text{Cl}]$ inconsequential compared to the total complex concentration). By Beer's law, then:

$$\text{Abs} = \epsilon_{\text{fc}}[\text{Rh}(\text{NH}_3)_5\text{H}_2\text{O}] + \epsilon_{\text{ip}}[\text{Rh}(\text{NH}_3)_5\text{H}_2\text{O}\cdot\text{Cl}] + \epsilon_{\text{Cl}}[\text{Cl}] \quad [6]$$

where Abs is the total absorbance and ϵ_{fc} , ϵ_{ip} , and ϵ_{Cl} are the extinction coefficients of the free complex, the ion-pair, and free chloride ion¹⁰, respectively. Under experimental conditions in which $[\text{Cl}]_{\text{total}} \gg [\text{Rh}(\text{NH}_3)_5\text{H}_2\text{O}]_{\text{total}}$, the absorb-

ance due to chloride can be treated as a simple correction factor, yielding:

$$\text{Abs} - \epsilon_{\text{Cl}}[\text{Cl}] = \epsilon_{\text{fc}}[\text{Rh}(\text{NH}_3)_5\text{H}_2\text{O}] + \epsilon_{\text{ip}}[\text{Rh}(\text{NH}_3)_5\text{H}_2\text{O}\cdot\text{Cl}] \quad [7]$$

Further:

$$[\text{M}]_t = [\text{Rh}(\text{NH}_3)_5\text{H}_2\text{O}] + [\text{Rh}(\text{NH}_3)_5\text{H}_2\text{O}\cdot\text{Cl}] = [\text{Rh}(\text{NH}_3)_5\text{H}_2\text{O}]_{\text{tot}} \quad [8]$$

where:

$$[\text{Rh}(\text{NH}_3)_5\text{H}_2\text{O}] = [\text{M}]_t / (1 + K_{\text{Cl}}[\text{Cl}]) \quad [9]$$

and:

$$[\text{Rh}(\text{NH}_3)_5\text{H}_2\text{O}\cdot\text{Cl}] = [\text{M}]_t K_{\text{Cl}}[\text{Cl}] / (1 + K_{\text{Cl}}[\text{Cl}]) \quad [10]$$

This, then, leads to:

$$(\text{Abs} - \epsilon_{\text{Cl}}[\text{Cl}]) / [\text{M}]_t = (\epsilon_{\text{fc}} + \epsilon_{\text{ip}} K_{\text{Cl}}[\text{Cl}]) / (1 + K_{\text{Cl}}[\text{Cl}]) \quad [11]$$

Noting that:

$$K_{\text{Cl}} = K_{\text{Cl}}^{\circ} \frac{\gamma_3 \gamma_1}{\gamma_2} \quad [12]$$

inclusion of the activity coefficients yields:

$$(\text{Abs} - \epsilon_{\text{Cl}}[\text{Cl}]) / [\text{M}]_t = \frac{(\epsilon_{\text{fc}} + \epsilon_{\text{ip}} K_{\text{Cl}}^{\circ} \frac{\gamma_3 \gamma_1}{\gamma_2} [\text{Cl}])}{(1 + K_{\text{Cl}}^{\circ} \frac{\gamma_3 \gamma_1}{\gamma_2} [\text{Cl}])} \quad [13]$$

and if:

$$A_{\text{corr}} = (\text{Abs} - \epsilon_{\text{Cl}}[\text{Cl}]) \quad [14]$$

then:

$$A_{\text{corr}}/[M]_t = \frac{(\epsilon_{fc} + \epsilon_{ip} K_{Cl}^o \frac{\gamma_3 \gamma_1}{\gamma_2} [Cl])}{(1 + K_{Cl}^o \frac{\gamma_3 \gamma_1}{\gamma_2} [Cl])} \quad [15]$$

which is in a form containing only experimental variables and empirical constants which can be determined through computer curve-fitting.

As was discussed in Section I, the activity coefficients which appear in eqn. [15] are calculated using the Davies equation¹¹:

$$-\log \gamma_1 = AZ_1^2 (\sqrt{\mu}/(1+\sqrt{\mu}) - b\mu) \quad [16]$$

Rather than calculating individual values of the activity coefficients, it is computationally easier, in this case, to combine them and calculate a composite value. Define:

$$G = \frac{\gamma_3 \gamma_1}{\gamma_2} \quad [17]$$

Then:

$$-\log G = -\log \gamma_3 - \log \gamma_1 + \log \gamma_2 \quad [18]$$

By substituting eqn. [16] for each of the individual activity coefficients, the expression:

$$-\log G = 6A(\sqrt{\mu}/(1+\sqrt{\mu}) - (9b_3 - 4b_2 + b_1)\mu/6) \quad [19]$$

is obtained where b_1 , b_2 , and b_3 are the individual empirical constants of the 1+, 2+, and 3+ ions, respectively. Defining:

$$d = (9b_3 - 4b_2 + b_1)/6 \quad [20]$$

then:

$$-\log G = 6A(\sqrt{\mu}/(1+\sqrt{\mu}) - d\mu). \quad [21]$$

Substituting G for $\gamma_3\gamma_1/\gamma_2$ in eqn. [15] then yields:

$$A_{\text{corr}}/[M]_t = \frac{(\epsilon_{fc} + \epsilon_{ip} K_{Cl}^o G[Cl])}{(1 + K_{Cl}^o G[Cl])} \quad [22]$$

which contains the fewest parameters possible for the data analysis.

Results of the spectrophotometric ion-pairing studies on some compounds of rhodium(III) are shown in Table II-1. Although these data were obtained by the high, constant ionic strength method and are, therefore, suspect in the mind of the author, it is apparent that the values of the concentration quotients for the ammine complexes of rhodium(III) are in the range $10^{-2} < K_{ip} < 10^0$ and that, more importantly, the values of K_{ip} appear to be temperature independent and it suggests that, in the present work, the value of K_{Cl} (K_{ip} for chloride ion) should be such that both $\text{Rh}(\text{NH}_3)_5\text{H}_2\text{O}^{3+}$ and $\text{Rh}(\text{NH}_3)_5\text{H}_2\text{O} \cdot \text{Cl}^{2+}$ are present in measurable concentrations.

In this work, kinetic, spectrophotometric ion-pair, and potentiometric ion-pair measurements were made. The specific details of the spectrophotometric measurements are given here while the details of the kinetic measurements and the potentiometric ion-pairing measurements are available elsewhere⁷.

CHAPTER 2

EXPERIMENTAL

In the ion-pairing studies, water which was distilled and then deionized (specific resistance $>100\text{M}\Omega$) was used. All chemicals used were reagent grade quality. A stock solution of HCl was made from concentrated hydrochloric acid and standardized by titration with secondary standard NaOH. A stock solution of NaCl was made using a weighed amount of sodium chloride which had been heated for twelve hours at 120°C and 100mmHg .

Solid $[\text{Rh}(\text{NH}_3)_5\text{Cl}]\text{Cl}_2$ was prepared as described elsewhere¹². Aquopentaamminerhodium(III) perchlorate was prepared by the following method. Solid $[\text{Rh}(\text{NH}_3)_5\text{Cl}]\text{Cl}_2$ (1.0g, 3.4mmol) was combined with NaOH (0.41g, 10mmol) in H_2O (30ml) in a 50ml flask. The mixture was gently warmed until all solid had dissolved and then refluxed for 25 minutes. During the first five minutes of refluxing, the color changed from golden yellow to light yellow. After cooling to room temperature, the solution was acidified with concentrated HClO_4 and AgNO_3

(1.8g, 11mmol) was added to precipitate the liberated chloride ion. The solution was filtered to remove AgCl and the supernatant was made basic with solid NaOH to precipitate any excess silver as Ag₂O. The solution was filtered, acidified with HClO₄ and the volume was reduced to 20ml on a steam bath. Yellow crystals formed at room temperature overnight. The [Rh(NH₃)₅H₂O](ClO₄)₃ was then recrystallized twice from minimum H₂O with two drops of concentrated HClO₄. The yield was typically 70% (1.2g) based on the initial rhodium content.

The ultraviolet-visible spectra of acidic aqueous solutions of Rh(NH₃)₅H₂O³⁺ and Rh(NH₃)₅Cl²⁺ are given in Figure II-2. Rh(NH₃)₅H₂O³⁺ showed maxima at 315 and 261nm with molar absorptivities of 106 and 93M⁻¹cm⁻¹, respectively. Rh(NH₃)₅Cl²⁺ showed maxima at 348 and 276nm with molar absorptivities of 102 and 110M⁻¹cm⁻¹, respectively. All spectral measurements were made on a Cary 118C ultraviolet-visible spectrophotometer.

Complex solutions for the ion-pairing studies were made from the stock HCl and NaCl solutions and from solid [Rh(NH₃)₅H₂O](ClO₄)₃. Portions of these solutions were placed in a quartz cuvette in the thermostated cell holder of the spectrophotometer. After thermal equilibration was reached, as judged by the stabilization of the absorbance reading, the absorbance at 208nm was recorded. In all complex solutions, [Rh(NH₃)₅H₂O] < 0.002M and [H⁺] > 0.001M was maintained in order to prevent the dissociation of a proton from the coordinated

water¹³. In addition, $0.01 < [\text{Cl}^-] < 0.3\text{M}$ while the only source of ClO_4^- was the dissolved complex salt.

Preliminary results showed that solutions of NaCl and/or HCl exhibited significant absorbance at 208nm. Therefore, in addition to the complex solutions, standard solutions of known chloride concentration were made and their absorbances at 208nm were measured. The standard solutions were made such that their hydrogen ion concentration equalled that of the complex solutions and the range of chloride concentrations encompassed those of the complex solutions. This technique was employed rather than increasing the wavelength to a point where chloride absorbance was negligible because to do so would have moved the wavelength beyond the charge-transfer band.

Such experiments were run at 15.0°C, 25.0°C (two trials), and 40.0°C. The data collected are given in Table II-2 through Table II-5.

In order to establish the molar absorptivity of $\text{Rh}(\text{NH}_3)_5\text{H}_2\text{O}^{3+}$ at 208nm, solutions of $[\text{Rh}(\text{NH}_3)_5\text{H}_2\text{O}](\text{ClO}_4)_3$ in 0.01M HClO_4 were prepared and their spectra taken at various temperatures. No temperature dependence of ϵ_{fc} was seen and the value of ϵ_{fc} was calculated to be $60\text{M}^{-1}\text{cm}^{-1}$.

CHAPTER 3

RESULTS AND DISCUSSION

The data obtained in the four experiments were analyzed by computer, using the strategy discussed in Section I, solving for the parameters in¹⁴:

$$A_{\text{corr}} = \frac{(\epsilon_{fc} + \epsilon_{ip} K_{Cl}^o G[Cl])[M]_t}{(1 + K_{Cl}^o G[Cl])} \quad [23]$$

The results of these analyses are given in Table II-6 and Table II-7. In all analyses, the value of ϵ_{fc} was taken to be $60M^{-1}cm^{-1}$ (see Experimental).

In the data fits, several assumptions were tested. In Method 1, (see Figure II-3), values of $\epsilon_{ip} K_{Cl}^o$, K_{Cl}^o , and d (from the activity coefficient term) were calculated for each experiment. The best-fit parameter values are given in the first four lines of Table II-7. cursory examination of the Method 1 fits shows the parameter values to be poorly defined although the RMSD's appear reasonable. It must be noted that, since the absorbance measurements were made on the steep slope of the high-wavelength side of the charge-transfer band

and a significant correction was made for the absorbance of free Cl^- , a high RMSD is not unexpected. The Method 1 fits do, however, suggest that K_{Cl}° and d are temperature independent.

In Method 2 (see Figure II-4), K_{Cl}° was assumed to be very small, giving the condition: $K_{\text{Cl}}^{\circ}G[\text{Cl}] \ll 1$. Values of $\epsilon_{\text{ip}}K_{\text{Cl}}^{\circ}$ and d were then calculated for each experiment. The parameter values in Table II-7 for the Method 2 fits show much improved definition as compared to the Method 1 figures although the RMSD's are not significantly different. The data again suggest that the value of d is temperature independent.

In Method 3 (see Table II-7), the data were fit assuming all parameters to be temperature independent. The RMSD (0.054 absorbance units) was judged to be unreasonably high, based on its being greater than two times the experimentally inherent error limit of 0.010 absorbance unit. Thus the assumption that all of the parameters are temperature independent is invalidated.

In Method 4 (see Table II-7), the four spectral data sets were analyzed assuming that the temperature dependence resided in only one of the parameters, the other two being taken to be temperature independent. The RMSD's are acceptable in magnitude but are not significantly different from one another to determine which parameter is temperature dependent.

In Method 5 (see Figure II-5 and Table II-7), all data sets were analyzed simultaneously to give temperature independent values of K_{Cl}° and d and temperature dependent

values of $\epsilon_{ip} K_{Cl}^{\circ}$. Potentiometric ion-pairing data and kinetic data were included in the analysis⁷.

The parameter values given in Table II-7 do not easily lend themselves to interpretation. In Methods 1 and 4, the parameter values are poorly defined, although, as expected, the RMSD's of the fits are acceptable. This lack of definition can be attributed to overfitting of the data with the number of parameters being sought, i.e., the high covariance here results from fitting for more parameters than are necessary to obtain a reasonable fit. As has been discussed, Method 3 indicates that at least one of the parameters is temperature dependent. Method 2 shows much improved definition as resulting from using fewer parameters, i.e., the data are not being overfitted. In fact, Method 2 was invalidated by potentiometric ion-pairing measurements which demand a significantly large K_{Cl}° value⁷.

It is apparent that the spectral data of themselves do not give much insight into ion-pairing. What is needed is to fit together ion-pairing measurements from several independent techniques. Only in this situation can systematic errors of each method be minimized and the various parameters sought be well-defined. In the different methods, the computational relationships among the parameters vary due to the different forms of the equations being fit. Therefore, the covariance aspect of the relationships is decreased and the definition improved. Method 5 represents this approach.

The spectrophotometric ion-pairing, potentiometric ion-pairing, and kinetic data on the $\text{Rh}(\text{NH}_3)_5\text{H}_2\text{O}^{3+} + \text{Cl}^-$ system were simultaneously fit to the same values of K_{Cl}° and d^7 . The potentiometric relationship is described by:

$$[\text{FC}] = \frac{[\text{M}]_t}{1 + \frac{K_{\text{Cl}}^\circ G[\text{Cl}]_t}{(1+K_{\text{Cl}}^\circ G[\text{FC}])} + \frac{K_{\text{ClO}_4}^\circ G[\text{ClO}_4]_t}{(1+K_{\text{ClO}_4}^\circ G[\text{FC}])}} \quad [24]$$

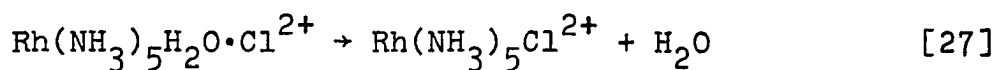
and:

$$[\text{IPC}] = \frac{K_{\text{Cl}}^\circ G[\text{Cl}]_t [\text{FC}]}{(1+K_{\text{Cl}}^\circ G[\text{FC}])} \quad [25]$$

Here, $[\text{Cl}]_t$ is the nominal chloride ion concentration, $[\text{ClO}_4]_t$ is the nominal perchlorate ion concentration, $[\text{FC}]$ is the free aquo complex concentration, and $[\text{IPC}]$ is the chloride ion-paired aquo complex concentration. The fitting process requires successive iteration through the two equations until concentration values stabilize. The kinetic relationship is described by:

$$k_{\text{obs}} = \frac{(k_i^\circ K_{\text{Cl}}^\circ G[\text{Cl}])}{(1+K_{\text{Cl}}^\circ G[\text{Cl}])} \quad [26]$$

where k_{obs} is the pseudo-first order rate constant for the formation of $\text{Rh}(\text{NH}_3)_5\text{Cl}^{2+}$ and k_i° is the rate constant for the kinetically important interchange step:



Utilizing this approach, the data yield well defined parameters and acceptable RMSD's, even though with the inclusion k_1^o and $K_{ClO_4}^o$, the number of parameters is increased.

In order to confirm that the interchange mechanism is indeed in force, other mechanisms must be considered. The rate law for the dissociative mechanism is computationally equivalent to eqn. [26]¹⁵. However, the fact that ion-pairing is required in order to explain the spectrophotometric and potentiometric data and the fact that the kinetic data does yield a K_{Cl}^o value identical to that obtainable in other techniques argues against the dissociative mechanism. The associative mechanism is described by¹⁵:

$$k_{obs} = k_2^o G[Cl] \quad [28]$$

In this case, plots of $G[Cl]$ vs. k_{obs} for the kinetic data would yield a straight line if the associative mechanism were in force. Although the kinetic data alone can be fit to eqn. [28], inclusion of the ion-pairing studies in the fits forces the data to deviate from linearity, such as is expected for the interchange mechanism.

Based on these results, the interchange mechanism has been assigned in the current work⁷. This conclusion is supported by previous work on this system^{5,6,13}. Further, the data give ratios of the interchange rate to the water exchange rate (k_1^o/k_{ex}) in the range 0.21 to 0.26 at the various temperatures. This would suggest that the reaction is dissociative-

ly activated (I_d mechanism), although values obtained by varying the anion would provide much more compelling evidence for the mode of activation since the value of k_i^o/k_{ex} should be insensitive to the identity of the anion if the reaction is, indeed, dissociatively activated. In addition, the low, variable ionic strength method has been shown to be viable as judged by its ability to yield well defined individual constants for the processes involved, rather than the composite constants yielded by conventional, constant ionic strength methods.

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TABLE II-1
 ION-PAIR FORMATION CONSTANTS DETERMINED
 SPECTROPHOTOMETRICALLY FOR SOME COMPLEXES
 OF RHODIUM(III) WITH COMMON ANAIONS

Complex	Anion	T, °C	μ , M	K_{ip}^*	Ref.
$\text{Rh}(\text{NH}_3)_5\text{H}_2\text{O}^{3+}$	Cl^-	65	1.5	.181(33)	1
		65	4.0	.18	2
		35	1.5	.094(40)	1
		25	4.0	.16	2
	Br^-	65	4.0	.08	2
		35	1.5	.059(35)	1
		25	4.0	.10	2
	HC_2O_4^-	$\text{C}_2\text{O}_4^{2-}$	51	1.0	2.02
51			1.0	7.99	3
$\text{Rh}(\text{en})_2(\text{H}_2\text{O})_2^{3+}$	Br^-	70	1.5	.519(51)	1
$\text{Rh}(\text{en})_2\text{Br}(\text{H}_2\text{O})^{2+}$	Cl^-	45	1.5	.647(66)	1

*The apparent concentration quotient. See eqn. [4], page 17. Numbers in parentheses are the errors in the least significant figures.

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TABLE II-2
 ION-PAIRING DATA FOR THE REACTION BETWEEN
 AQUOPENTAAMMINERHODIUM(III) AND CHLORIDE AT 15.0°C

Standard Solutions

[HCl]	[NaCl]	[Cl ⁻]	A ₂₀₈
.0120	0	.0120	.031
	.0720	.0840	.042
	.1440	.1560	.064
	.2160	.2280	.090
	.2880	.3000	.109

Working Solutions

[Rh] _t ^a	[H ⁺]	[Cl ⁻]	μ	A ₂₀₈	A _{corr}
9.89x10 ⁻⁴	.0120	.0120	.0179	.106	.080
		.0440	.0499	.127	.092
		.0760	.0819	.161	.116
		.1080	.1139	.175	.121
		.1400	.1459	.206	.143
		.1720	.1779	.217	.145
		.2040	.2099	.239	.158
		.2360	.2419	.261	.171
		.2680	.2739	.281	.182
		.3002	.3061	.302	.194

$${}^a[\text{Rh}]_t = [\text{Rh}(\text{NH}_3)_5\text{H}_2\text{O}^{3+}] + [\text{Rh}(\text{NH}_3)_5\text{H}_2\text{O}\cdot\text{Cl}^{2+}]$$

TABLE II-3
 ION-PAIRING DATA FOR THE REACTION BETWEEN
 AQUOPENTAAMMINERHODIUM(III) AND CHLORIDE AT 25.0°C

Standard Solutions

[HCl]	[NaCl]	[Cl ⁻]	A ₂₀₈
.0120	0	.0120	.028
	.0720	.0840	.048
	.1440	.1560	.093
	.2160	.2280	.128
	.2880	.3000	.160

Working Solutions

[Rh] _t ^a	[H ⁺]	[Cl ⁻]	μ	A ₂₀₈	A _{corr}
9.89x10 ⁻⁴	.0120	.0120	.0179	.103	.080
		.0440	.0499	.157	.119
		.0760	.0819	.203	.150
		.1080	.1139	.228	.160
		.1400	.1459	.272	.188
		.1720	.1779	.293	.194
		.2040	.2099	.329	.215
		.2360	.2419	.365	.235
		.2680	.2739	.394	.249
		.3002	.3061	.423	.263

$${}^a[\text{Rh}]_t = [\text{Rh}(\text{NH}_3)_5\text{H}_2\text{O}^{3+}] + [\text{Rh}(\text{NH}_3)_5\text{H}_2\text{O}\cdot\text{Cl}^{2+}]$$

TABLE II-4
 ION-PAIRING DATA FOR THE REACTION BETWEEN
 AQUOPENTAAMMINERHODIUM(III) AND CHLORIDE AT 25.0°C

Standard Solutions

[HCl]	[NaCl]	[Cl ⁻]	A ₂₀₈
.0150	0	.0150	.011
	.0800	.0950	.056
	.1600	.1750	.096
	.2000	.2150	.137
	.2800	.2950	.163

Working Solutions

[Rh] _t ^a	[H ⁺]	[Cl ⁻]	μ	A ₂₀₈	A _{corr}
2.02x10 ⁻³	.0150	.0150	.0271	.191	.180
		.0550	.0671	.316	.283
		.1350	.1471	.460	.384
		.1550	.1671	.489	.402
		.1750	.1871	.502	.404
		.1950	.2071	.533	.425
		.2150	.2271	.578	.459
		.2350	.2471	.571	.441
		.2550	.2671	.627	.486
		.2950	.3071	.677	.515

$${}^a[\text{Rh}]_t = [\text{Rh}(\text{NH}_3)_5\text{H}_2\text{O}^{3+}] + [\text{Rh}(\text{NH}_3)_5\text{H}_2\text{O}\cdot\text{Cl}^{2+}]$$

TABLE II-5
 ION-PAIRING DATA FOR THE REACTION BETWEEN
 AQUOPENTAAMMINERHODIUM(III) AND CHLORIDE AT 40.0°C

Standard Solutions

[HCl]	[NaCl]	[Cl ⁻]	A ₂₀₈
.0150	0	.0150	.022
	.0800	.0950	.106
	.1600	.1750	.195
	.2000	.2150	.252
	.2800	.2950	.317

Working Solutions

[Rh] _t ^a	[H ⁺]	[Cl ⁻]	μ	A ₂₀₈	A _{corr}
2.02x10 ⁻³	.0150	.0150	.0271	.244	.221
		.0550	.0671	.403	.338
		.1350	.1471	.604	.455
		.1550	.1671	.662	.491
		.1750	.1871	.693	.501
		.1950	.2071	.741	.528
		.2150	.2271	.809	.575
		.2350	.2471	.843	.588
		.2950	.3071	1.007	.688

$${}^a[\text{Rh}]_t = [\text{Rh}(\text{NH}_3)_5\text{H}_2\text{O}^{3+}] + [\text{Rh}(\text{NH}_3)_5\text{H}_2\text{O}\cdot\text{Cl}^{2+}]$$

TABLE II-6

SPECTRAL ION-PAIRING DATA ANALYSIS AT

15.0, 25.0, and 40.0°C AND $[H^+] = 0.01M$

Temp. °C	$[M]_t$ M	$[Cl^-]$ M	Absorbance (corrected for Cl^-) ^a					
			Exp.	Meth. 1	Meth. 2	Meth. 5		
15.0	9.89×10^{-4}	.0120	.080	.075	.075	.079		
		.0440	.092	.097	.097	.105		
		.0760	.116	.112	.113	.121		
		.1080	.121	.125	.125	.133		
		.1400	.143	.137	.137	.144		
		.1720	.145	.148	.148	.153		
		.2040	.158	.159	.159	.161		
		.2360	.171	.171	.170	.168		
		.2680	.182	.182	.182	.174		
		.3000	.194	.194	.194	.180		
		25.0 (Exp 1)	9.89×10^{-4}	.0120	.080	.085	.084	.090
				.0440	.119	.120	.121	.130
.0760	.150			.144	.145	.155		
.1080	.160			.164	.165	.174		
.1400	.188			.183	.182	.191		
.1720	.194			.200	.199	.206		
.2040	.215			.217	.215	.219		
.2360	.238			.233	.232	.230		
.2680	.249			.249	.249	.240		
.3000	.263			.264	.266	.248		
25.0 (Exp 2)	2.02×10^{-3}			.0150	.180	.186	.185	.189
				.0550	.283	.279	.278	.279
		.1350	.384	.377	.377	.381		
		.1550	.402	.396	.396	.400		
		.1750	.404	.414	.414	.418		
		.1950	.425	.431	.431	.435		
		.2150	.459	.447	.447	.450		
		.2350	.441	.463	.463	.463		
		.2550	.486	.479	.479	.476		
		.2950	.515	.510	.509	.497		
		40.0	2.02×10^{-3}	.0150	.221	.205	.202	.213
				.0550	.338	.323	.321	.334
.1350	.455			.459	.459	.474		
.1550	.491			.488	.488	.501		
.1750	.501			.515	.515	.526		
.1950	.528			.542	.542	.549		
.2150	.575			.568	.568	.570		
.2350	.588			.595	.595	.589		
.2950	.688			.675	.676	.637		

^aIn all methods, $\epsilon_{fc} = 60M^{-1}cm^{-1}$. In Methods 1 and 2, each data set is fitted separately. In Method 5, all data sets are fit together. In Method 2, $K_{Cl}^o G[Cl] \ll 1$. In Method 5, K_{Cl}^o is temperature independent; kinetic and potentiometric data are included.

TABLE II-7
SPECTRAL ION-PAIRING PARAMETER VALUES

FIT TO EQN. [23]

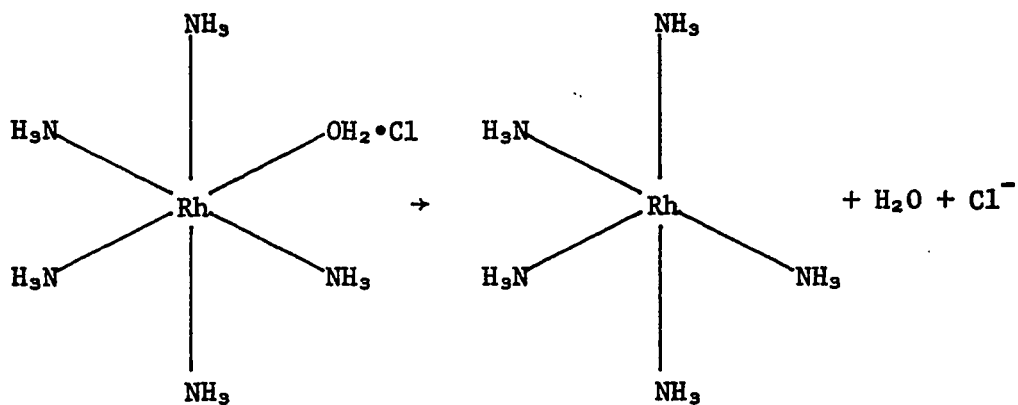
Method ^a	Data Set	K_{Cl}^0 M^{-1}	d	$10^{-3} \epsilon_{ip} K_{Cl}^0$ $M^{-2} cm^{-1}$	SD Abs Units
1	15.0°C	7±19	0.5±0.6	3.3±1.3	0.004
1	25.0°C(#1)	14±5	0.7±0.3	5.6±0.3	0.005
1	25.0°C(#2)	2±19	0.2±0.2	5.8±2.3	0.012
1	40.0°C	8±43	0.4±0.8	8.0±3.9	0.014
2	15.0°C	--- ^b	0.3±0.03	2.8±0.1	0.004
2	25.0°C(#1)	--- ^b	0.3±0.02	4.7±0.2	0.005
2	25.0°C(#2)	--- ^b	0.2±0.03	5.6±0.3	0.011
2	40.0°C	--- ^b	0.2±0.03	7.1±0.3	0.013
3	all ^c	20±7	1.3±0.7	5.9±0.5	0.054
4	all ^c	9±2	0.4±0.4	varied ^d	0.010
4	all ^c	16±2	varied ^e	6.9±0.5	0.016
4	all ^c	varied ^f	0.3±0.1	1.1±0.9 ^g	0.013
5	all ^h	26.5±0.8	0.91±0.05	varied ⁱ	0.060 ^j

Notes:

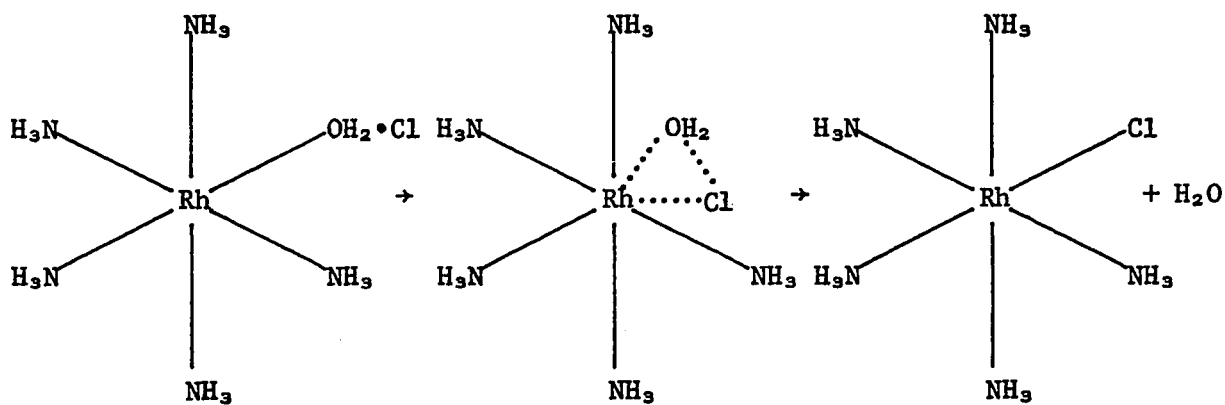
^aSee Results section for discussion of methods. ^b K_{Cl}^0 arbitrarily set to zero ($K_{Cl}^0 G[Cl] < 1$). ^cIncludes only the four spectral data sets. ^d $10^{-3} \epsilon_{ip} K_{Cl}^0 = 3.9, 6.0, 8.3(\pm 1.6)$ at 15.0, 25.0, 40.0°C, respectively. ^ed = 0.1, 0.5, 1.0(±0.1) at 15.0, 25.0, 40.0°C, respectively. ^f $K_{Cl}^0 = 3.4, 4.4, 7.8$ at 15.0, 25.0, 40.0°C, respectively. ^gValue is $10^{-3} \epsilon_{ip}, M^{-1} cm^{-1}$. ^hIncludes data from other experiments, see ref. 7. ⁱ $10^{-3} \epsilon_{ip} K_{Cl}^0 = 5480 \pm 230, 7660 \pm 220, 9880 \pm 210$ at 15.0, 25.0, 40.0°C, respectively. ^jSD is normalized across all data sets where the best-fit SD of each experiment is normalized to 0.050.

FIGURE II-1

INVOLVEMENT OF ION-PAIRS IN SUBSTITUTION MECHANISMS OF
RHODIUM(III) COMPLEXES



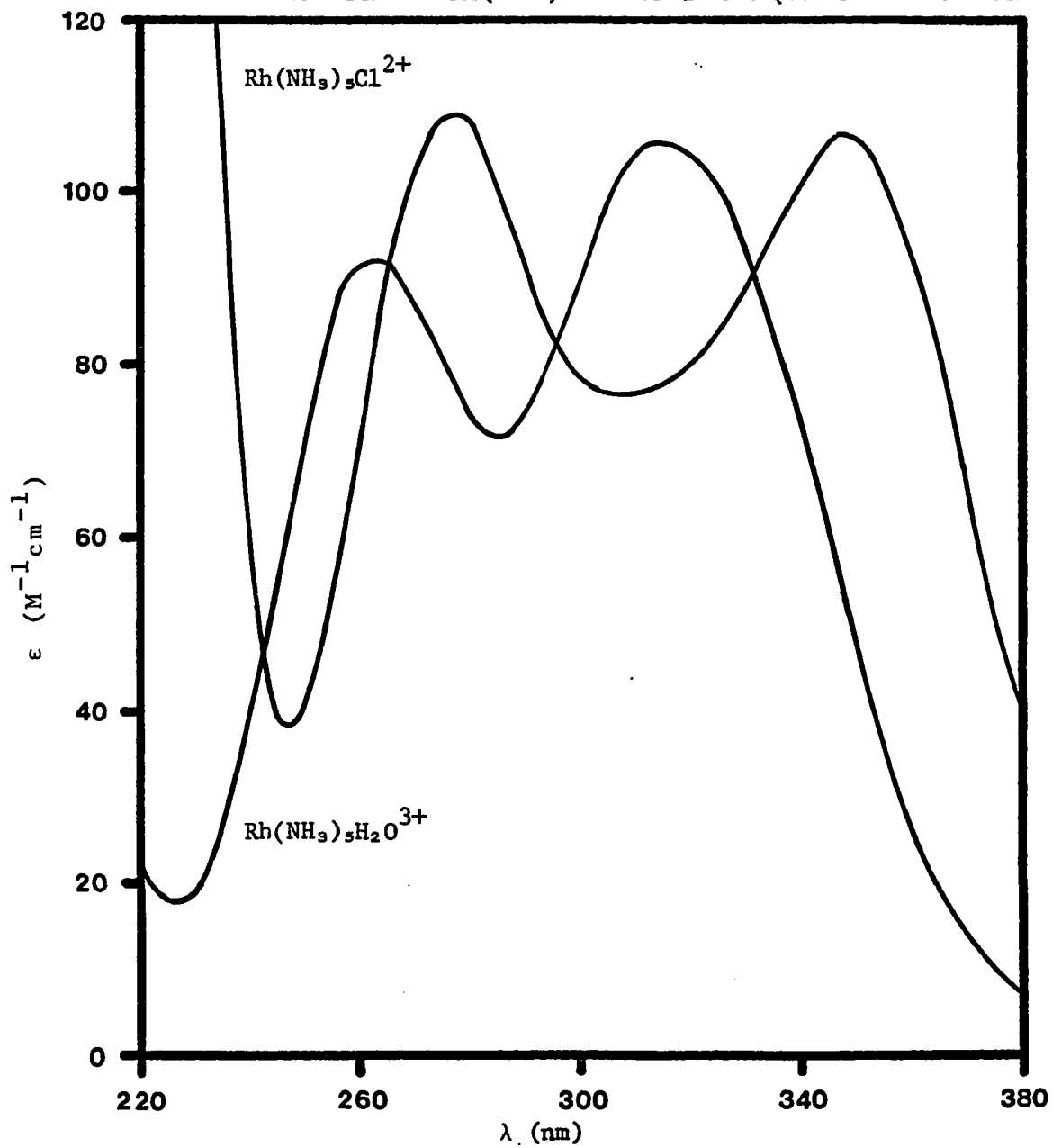
a) Ion-pairing Leading to Dissociation



b) Ion-pairing Leading to Interchange

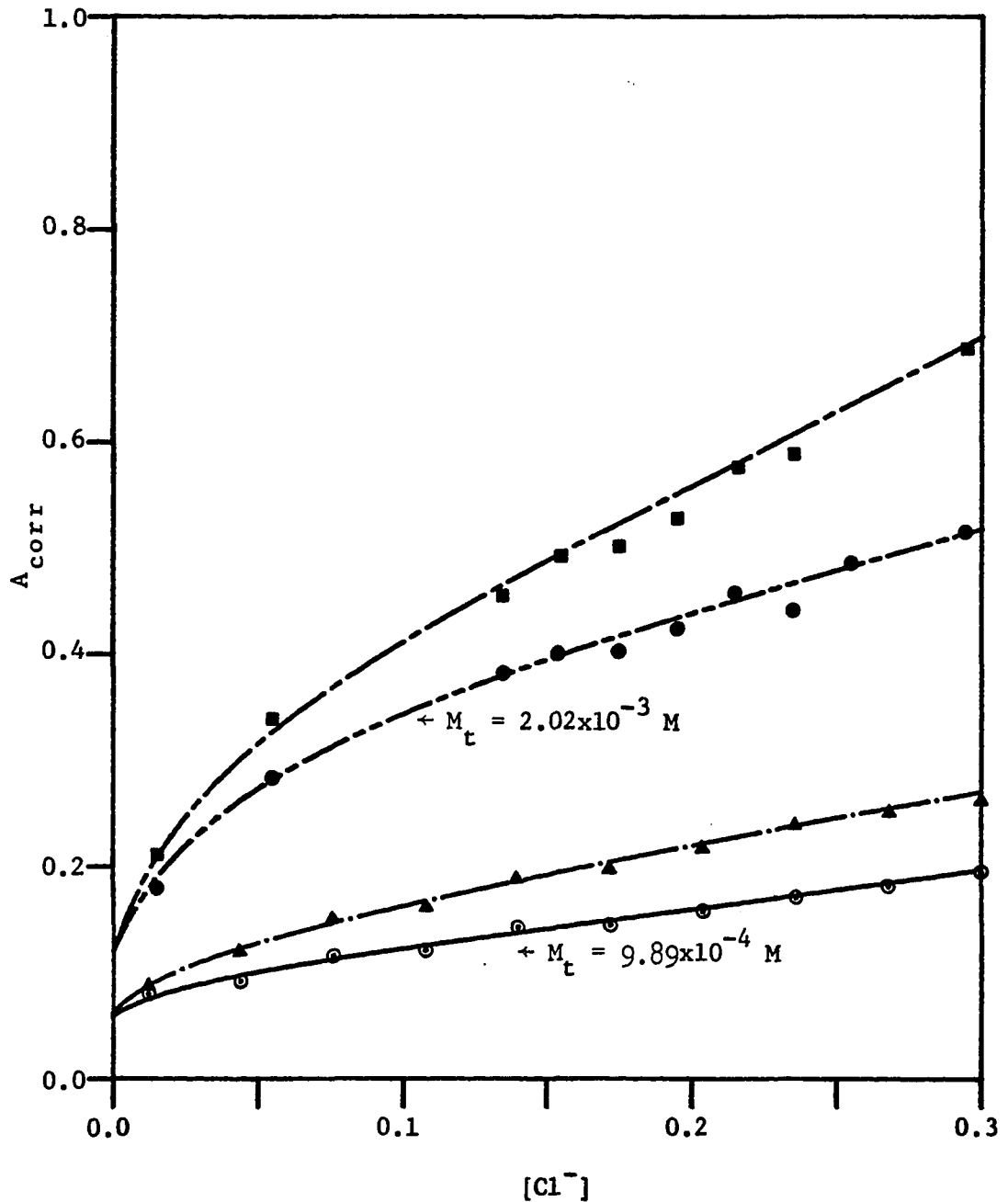
FIGURE II-2

ULTRAVIOLET-VISIBLE SPECTRA OF AQUOPENTAAMMINERHODIUM(III) AND
CHLOROPENTAAMMINERHODIUM(III) IN ACIDIC AQUEOUS SOLUTION



$[\text{H}^+] = 0.01 \text{ M}$, Total Ionic Strength = 0.02 M

FIGURE II-3
FIT OF ION-PAIRING DATA BY METHOD 1



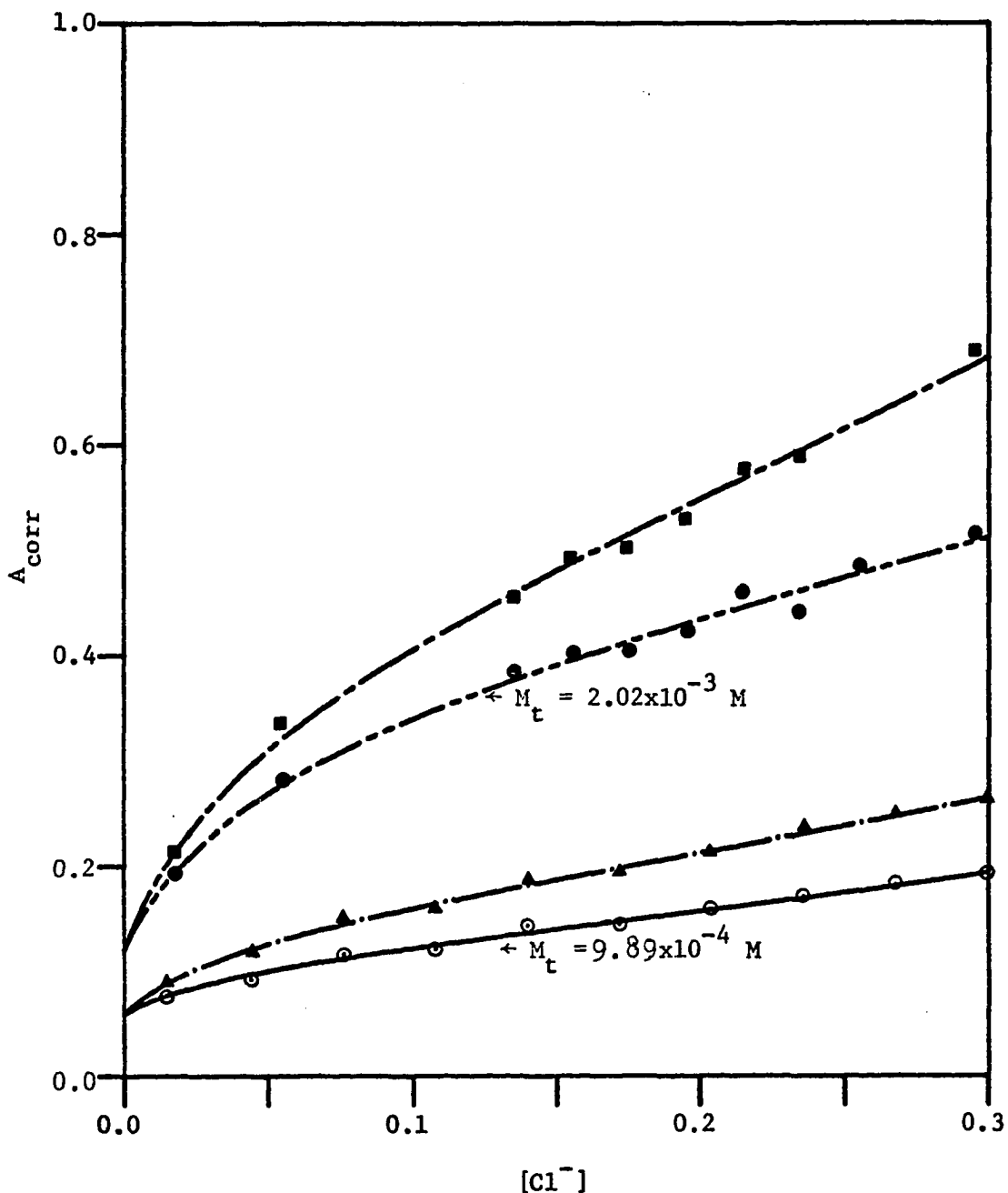
Method 1 fits individual values of K_{Cl}^o , d , and $\epsilon_{ip} K_{Cl}^o$ for each data set to the expression:

$$A_{corr} = \frac{(60 + \epsilon_{ip} K_{Cl}^o G[Cl])}{(1 + K_{Cl}^o G[Cl])} \cdot M_t$$

● $15.0^\circ C$, ▲ $25.0^\circ C$ (trial 1), ● $25.0^\circ C$ (trial 2), ■ $40.0^\circ C$

FIGURE II-4

FIT OF ION-PAIRING DATA BY METHOD 2



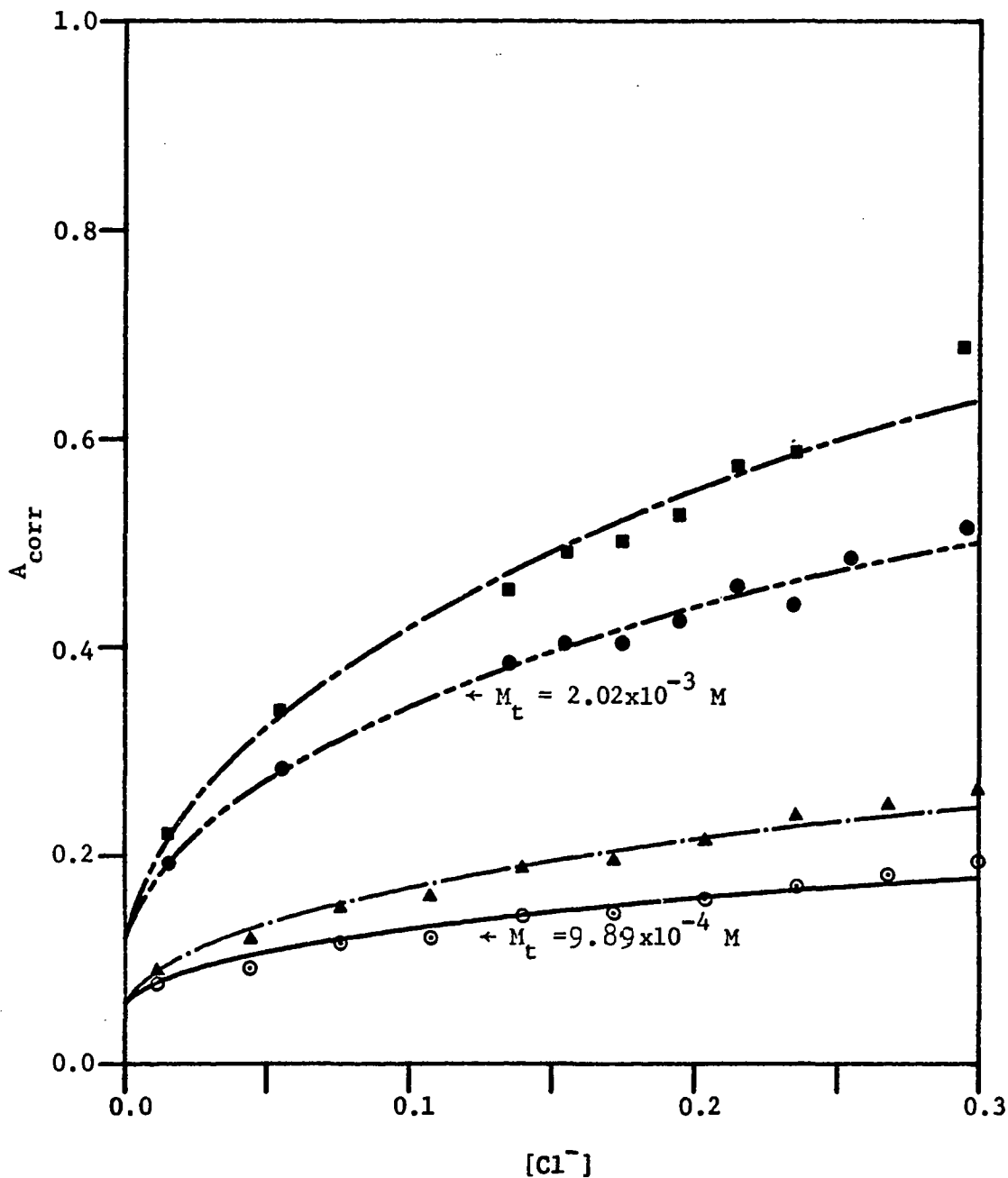
Method 2 fits values of $\epsilon_{ip} K_{Cl}^0$ for each data set to the expression:

$$A_{corr} = (60 + \epsilon_{ip} K_{Cl}^0 G[Cl]) \cdot M_t$$

○ 15.0°C, ▲ 25.0°C(trial 1), ● 25.0°C(trial 2), ■ 40.0°C

FIGURE II-5

FIT OF ION-PAIRING DATA BY METHOD 5



Method 5 fits values of $\epsilon_{ip} K_{Cl}^{\circ}$ for each data set to the expression:

$$A_{corr} = \frac{(60 + \epsilon_{ip} K_{Cl}^{\circ} G[Cl])}{(1 + K_{Cl}^{\circ} G[Cl])} \cdot M_t$$

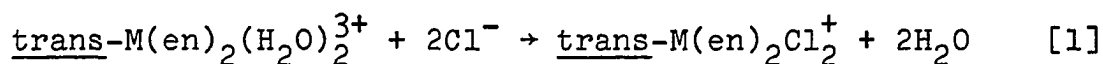
○ 15.0°C, ▲ 25.0°C(trial 1), ● 25.0°C(trial 2), ■ 40.0°C

III. THE SYNTHESIS OF
trans-DIAQUOBIS(ETHYLENEDIAMINE)IRIDIUM(III)

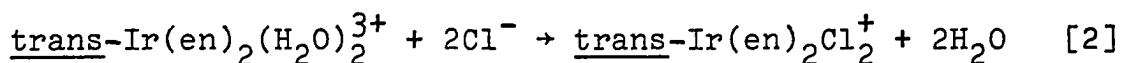
CHAPTER 1

INTRODUCTION

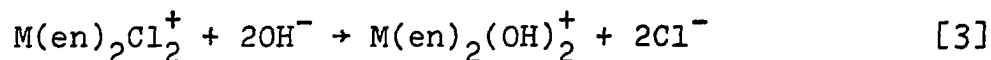
As part of the long-term project, the reaction:



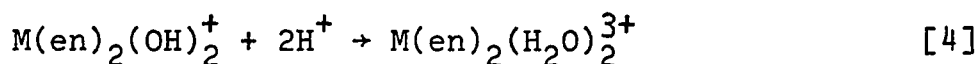
where $\text{M} = \text{Co}^{3+}$, Rh^{3+} , and Ir^{3+} were to be studied. In attempting to study the iridium reaction:



it was first necessary to synthesize the starting compound, a synthesis which has yet to appear in the literature. Two methods have been used to synthesize other compounds of this type. The first is base hydrolysis, which has traditionally been the approach of choice:



followed by:



Data on compounds of the types $M(en)_2(H_2O)_2^{3+}$ and $M(NH_3)_5H_2O^{3+}$ ($M = Co^{3+}$, Rh^{3+} , and Ir^{3+}) are given in Table III-1. It is clear from these data that, for the aquopentaamminemetal(III) complexes, the required temperature, basicity, and reaction time increases in the order $Co < Rh < Ir$. The trans-diaquobis(ethylenediamine)metal(III) complexes of cobalt and rhodium show a parallel trend. Thus it would be expected that trans-diaquobis(ethylenediamine)iridium(III) could be synthesized in a manner analogous to $Ir(NH_3)_5H_2O^{3+}$.

The alternative approach in these syntheses is photochemical aquation:

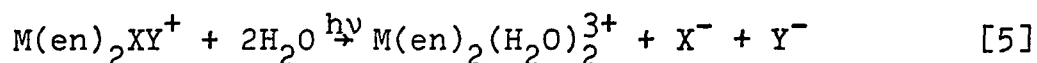


Table III-2 gives relevant data on rhodium(III) and iridium(III) compounds which have been synthesized photochemically. From these results, it is seen that photoaquation of $Rh(NH_3)_5Cl^{2+}$ and $Ir(NH_3)_5Cl^{2+}$ leads to the corresponding aquopentaammine complexes; however, the photoaquation of the trans-tetraammine and the trans-bis(ethylenediamine) complexes leads to substitution of only one chloride. Although this suggests that photoaquation of the second chloride is difficult, the approach should be investigated as a possible synthetic route.

CHAPTER 2

EXPERIMENTAL

Materials

All chemicals, with the exception of ethylenediamine dihydrochloride, were reagent grade and used without further purification. Doubly distilled water was used throughout. Ethylenediamine dihydrochloride was synthesized by the literature method⁹. A solution of neat ethylenediamine (10ml, 9.0g, 0.15mol) in absolute ethanol (20ml) was added dropwise to a solution of concentrated hydrochloric acid (30ml, 0.36mol) in absolute ethanol (50ml) until neutrality. The white ethylenediamine dihydrochloride was insoluble in ethanol. The product was washed with absolute ethanol and dried over CaCl_2 in vacuo.

Trans-dichlorobis(ethylenediamine)iridium(III) perchlorate was synthesized by the literature method¹⁰. Potassium hexachloroiridate(IV) (0.58g, 1.2mmol) was dissolved in hot H_2O (3ml). Sodium oxalate (0.08g, 0.60mmol) was added slowly. When the liberation of CO_2 subsided, the solution was brought

to a boil to complete the liberation. Ethylenediamine dihydrochloride (0.58g, 4.4mmol) and $\text{NaH}_2\text{PO}_2 \cdot \text{H}_2\text{O}$ (0.01g, 0.09mmol) were added. A green-brown precipitate formed. The solution was cooled to room temperature, concentrated HCl (0.5ml, 6.0mmol) was added, and the solution was filtered and the precipitate washed with cold water (0.5ml). The precipitate was dissolved in water (3ml) and neat ethylenediamine (0.2ml, 0.2g, 3.0mmol) was added. The solution was boiled for five minutes during which time the solution cleared and lightened to a golden-brown. Additional neat ethylenediamine (0.2ml, 0.2g, 3.0mmol) was added and the solution boiled for fifty minutes. Concentrated HCl was added to neutrality and the solution was boiled for an additional ten minutes. The solution was cooled and concentrated perchloric acid (1ml, 11mmol) was added. The trans- $[\text{Ir}(\text{en})_2\text{Cl}_2]\text{ClO}_4$ was allowed to precipitate at room temperature overnight.

Purification of the trans- $[\text{Ir}(\text{en})_2\text{Cl}_2]\text{ClO}_4$ was achieved by ion-exchange chromatography. The crude solid was dissolved in water (5ml) and introduced to a cation-exchange column (BioRad Ag50W-X8 resin) in the H^+ form. A bright yellow band was formed in the top 0.5cm of the column. The column was washed with water until the eluent was of neutral pH. The complex was eluted as a bright yellow band with 0.5M HCl (HClO_4 caused precipitation of the complex on the column). The volume of the fraction containing the complex was reduced to 5ml and concentrated HClO_4 (2ml, 21mmol) was added. The

purified product was allowed to precipitate overnight. The yield was typically 35% (0.1g, 0.2mmol) of trans-Ir(en)₂Cl₂]ClO₄. The ultraviolet-visible spectrum of trans-[Ir(en)₂Cl₂]ClO₄ is shown in Figure III-1. Maxima appear at 425, 345, and 373 (sh) nm with molar absorptivities of 11.8, 51.0, and 41.0M⁻¹cm⁻¹, respectively, which are in good agreement with the literature values¹⁰.

Recovery of Iridium from Wastes

During the course of this work, the recovery of spent iridium complexes was also investigated owing to the extreme expense of iridium. Much work has been done on this in other laboratories⁹⁻¹¹ which was found to apply to the present problem. A solution of hot aqueous KBrO₃ (10%) was added to a strongly acidic solution of the iridium waste compounds until Br₂ was no longer evolved. Potassium hydroxide (5M) was then added until the solution was just basic. The color of the solution turned to a deep blue and a colloidal precipitate of Ir(OH)₄ or IrO₂(H₂O)₂ was formed. The precipitate was removed from solution by filtration and the solid was brought to reflux in basic solution and refiltered.

The IrO₂(H₂O)₂ was converted to iridium metal by heating in a hydrogen atmosphere at 600-625°C for one hour. From the iridium metal, K₂IrCl₆, potassium hexachloroiridate(IV), was synthesized. Iridium metal (0.34g, 1.77mmol) was intimately mixed with KCl (0.80g, 10.7mmol) in a mortar. This mixture was placed in a Vycor tube and heated in a tube furnace at

600-625°C for one hour in a moist chlorine stream. The red-black mass was dissolved in hot water (50ml) and filtered to remove unreacted iridium metal. The solution was boiled for ten minutes with aqua regia (10ml) to complete the oxidation to Ir⁴⁺. Potassium hexachloroiridate(IV) was precipitated by adding saturated aqueous KCl and refrigerating overnight. The yield, based on iridium, was 80%.

Base Hydrolysis

Two approaches to base hydrolysis were used. In the first method, the reaction was carried out in a sealed Pyrex reactor comprised of a cylindrical body (100mm x 20mm ID) with a Teflon needle valve assembly mounted at one end. Trans-dichlorobis(ethylenediamine)iridium(III) perchlorate (0.1g, 0.2mmol) and sodium hydroxide (0.04g, 1.00mmol) were dissolved in water (20ml), placed in the reactor, and heated for three hours at 140°C in a thermostated oil bath. During this time, the yellow color of the solution lightened somewhat. The solution was cooled and introduced to a cation-exchange column (BioRad Ag50-X8 resin) in the H⁺ form. The complex formed a yellow band at the top of the column and the free chloride ion produced in the reaction was washed from the column with de-ionized water. The wash solutions from many of the experiments were tested for chloride ion content by potentiometry using a chloride specific vs. calomel electrode pair which had been previously standardized with a series of solutions of known chloride ion concentration.

Several cations, including H^+ , Mg^{2+} , Na^+ , and Th^{4+} , were used in an effort to elute the complex from the column. In addition, sodium hydroxide was used since the hydroxide should play an active role by neutralizing the resin-bound protons and converting the $Ir(en)_2(H_2O)_2^{3+}$ to $Ir(en)_2(OH)_2^+$. The decreased charge in the latter should make elution more rapid. In all cases, there was no conclusive evidence that the complex was, indeed, eluted (see Results and Discussion).

In the second method, the reaction was carried out under reflux conditions at atmospheric pressure. Trans-dichlorobis(ethylenediamine)iridium(III) perchlorate (0.108g, 0.224mmol) was dissolved in aqueous sodium hydroxide (0.016M, 29ml) and brought to reflux in a conventional reflux apparatus. Ultraviolet-visible spectra of the reaction mixture were recorded periodically which showed a slow but obvious reaction (see Figure III-2). The reflux was continued for fifty-two hours, at which time the spectrum of the solution appeared to be that of trans- $Ir(en)_2Cl(H_2O)^{2+}$ ¹⁰. From this mixture, a small (0.015g, 0.031mmol) amount of the starting material was recovered by reducing the volume to 10ml and adding concentrated $HClO_4$ (1ml, 11mmol). After filtering, the supernatant was introduced to a cation-exchange column (BioRad Ag50-X8 resin) in the H^+ form. Free chloride ion was washed from the column with deionized water and the wash was analyzed for chloride as described above. Sodium hydroxide (1M) was used to elute the product. Ultraviolet spectra were recorded of each

15ml fraction. The movement of the Na^+ front was easily seen as it substantially darkened the resin. All fractions from just prior to the Na^+ front elution showed identical spectra, one of which is shown in Figure III-3. The fractions were combined and the volume reduced to 10ml. Attempts were made to precipitate the product by slowly acidifying the solution with concentrated HClO_4 . This was done since it is not known if the compound would precipitate in the dihydroxy-, diaquo-, or aquohydroxy- form as does its rhodium(III) analog³. No product was isolated.

Photoaquation

Photoaquation of the trans- $\text{Ir}(\text{en})_2\text{Cl}_2^+$ was attempted at 254nm and 350nm. In the former case, trans- $[\text{Ir}(\text{en})_2\text{Cl}_2]\text{ClO}_4$ (0.112g, 0.231mmol) was dissolved in aqueous sodium hydroxide (0.033M, 15ml). The solution was placed in a water-jacketed quartz tube and irradiated in an apparatus consisting of eight GE 15 watt germicidal lamps (90% of emitted light at 254nm) in a circular arrangement. As this procedure was being investigated in terms of its synthetic utility, the irradiation was not quantitatively measured. Periodic ultraviolet spectra suggested the formation of trans- $\text{Ir}(\text{en})_2\text{Cl}(\text{H}_2\text{O})^{2+}$ although isobestic points were not observed¹⁰. A slight amount of the starting material was the only complex isolated. Attempts to precipitate the product at various pH's were unsuccessful.

Photoaquation was also attempted at 350nm using a commercial GE 275 watt sunlamp. Again, as this was done only

to evaluate the applicability of the approach, the wideband radiation centering at 350nm was deemed acceptable. Trans-dichlorobis(ethylenediamine)iridium(III) perchlorate (0.136g, 0.282mmol) was dissolved in aqueous sodium phosphate (0.25M, 25ml) and the solution was placed in a water cooled Pyrex vessel at 15°C. The sodium phosphate was used as a pH buffer (pH ~ 11). The lamp was placed 30cm from the vessel and the irradiation was continued for four hours. Periodic ultraviolet spectra were recorded which were similar to those of the 254nm photolysis. At the conclusion of the irradiation, a portion of the solution was mixed with NaCl (0.1g, 1.7mmol) and placed on a steam bath for three hours. A spectrum of this solution showed no changes indicating no regeneration of trans-dichlorobis(ethylenediamine)iridium(III).

CHAPTER 3

RESULTS AND DISCUSSION

In the absence of isolatable products, it is difficult to understand the chemistry involved in this work. The data, indeed, indicate that the reactions were not entirely successful. The potentiometric determinations of the chloride ion content in the base hydrolysis experiments show that a significant amount of chloride ion was produced in these reactions, typically 50% to 75% of the total available chloride. The spectra recorded in the photoaquation and in the refluxing base hydrolysis experiment indicate the formation of trans- $\text{Ir}(\text{en})_2\text{Cl}(\text{H}_2\text{O})^{2+}$ ¹². However, it would be expected that the addition of NaCl to an aqueous solution of trans- $\text{Ir}(\text{en})_2\text{Cl}(\text{H}_2\text{O})^{2+}$ would regenerate trans- $\text{Ir}(\text{en})_2\text{Cl}_2^+$ and this was shown not to be the case. Alternatively, the regeneration may be slow enough that no reaction was observable in the three hour time span of the experiment. However, in the analogous rhodium(III) reactions, the regeneration (anation) is faster than the hydrolysis at 50°C by a factor of about

500, depending on reactant concentrations¹². The rate constant for the aquation of trans-Ir(en)₂Cl₂⁺ at 105°C has been determined to be 5.9x10⁻⁶sec⁻¹¹³ and, therefore, the aquation reaction at 90-100°C should be readily observable. More work is required before the nonregeneration is understood.

It was subsequently found that the cation-exchange resin (BioRad Ag50-X8) decomposed somewhat when exposed to base. Ultraviolet spectra of the eluent obtained by washing the column with aqueous NaOH (1M) were recorded and these spectra were identical to that in Figure III-3. Therefore, it is likely that the spectra obtained of the base hydrolysis column eluents were primarily due to column decomposition products rather than the complex. It is probable, however, that the trans-Ir(en)₂Cl(H₂O)²⁺ was synthesized in these experiments as indicated by the spectra of the reaction mixtures. This suggests that the complex undergoes some kind of transformation while bound to the ion-exchange resin. The nature of this transformation is unclear; it is possible that the complex forms a new organometallic compound with the resin (sulfito functionality on a polystyrene backbone). It is also possible that the complex undergoes some process such as polymerization in solution. It has been suggested that the trans-Rh(en)₂(OH)(H₂O)²⁺ undergoes polymerization in solution³ and so this must be considered possible for trans-Ir(en)₂(OH)(H₂O)²⁺. In addition, this resin (BioRad Ag50-X8) has been shown to have catalytic activity in reactions of aquo complexes of

cobalt(III)¹⁴. The fate of the iridium complex is, then, unknown but it is probably left resin-bound throughout the attempts to elute it.

In retrospect, there is another approach which may provide a means of synthesizing trans-Ir(en)₂(H₂O)₂³⁺. The complex cis-Ir(en)₂(H₂O)₂³⁺ has been characterized¹⁵. In addition, it has been found that some complexes of the type cis-Ir(en)₂XYⁿ⁺ undergo cis- to trans- isomerization when photolyzed¹⁶. In view of this, cis-Ir(en)₂(H₂O)₂³⁺ or cis-Ir(en)₂(OH)₂⁺ may undergo photoisomerization to trans-Ir(en)₂(H₂O)₂³⁺ or trans-Ir(en)₂(OH)₂⁺, respectively. As this work was based on preliminary results in this laboratory, the existence of the cis- isomer was not seen in the literature and, as the focus of this project was on the direct synthesis of trans-diaquobis(ethylenediamine)iridium(III), the Soviet work continued to go unnoticed.

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TABLE III-1
 COMPOUNDS OF Co^{3+} , Rh^{3+} , and Ir^{3+}
 SYNTHESIZED BY BASE HYDROLYSIS

Compound	Conditions	Ref.
$\text{Co}(\text{NH}_3)_5\text{H}_2\text{O}^{3+}$	$\text{Co}(\text{NH}_3)_5\text{CO}_3\text{Cl}$ (2g) in 1:1 $\text{HNO}_3:\text{H}_2\text{O}$ for 20 min. at 20°C	2
$\text{Rh}(\text{NH}_3)_5\text{H}_2\text{O}^{3+}$	$\text{Rh}(\text{NH}_3)_5\text{Cl}_3$ (3g) in 90ml 0.11M NaOH at reflux for 15 min.	3
$\text{Ir}(\text{NH}_3)_5\text{H}_2\text{O}^{3+}$	$\text{Ir}(\text{NH}_3)_5\text{Cl}_3$ (3g) in 100ml 1.0M NaOH at reflux for 8 hours	4
<u>trans</u> - $\text{Co}(\text{en})_2(\text{H}_2\text{O})_2^{3+}$	<u>trans</u> - $\text{Co}(\text{en})_2\text{Cl}_3$ (2g) with 2 equiv. Ag_2O at 0°C in water	5
<u>trans</u> - $\text{Rh}(\text{en})_2(\text{H}_2\text{O})_2^{3+}$	<u>trans</u> - $\text{Rh}(\text{en})_2\text{Cl}_3$ (3g) in 90ml 0.17M NaOH at reflux for 20 min.	3

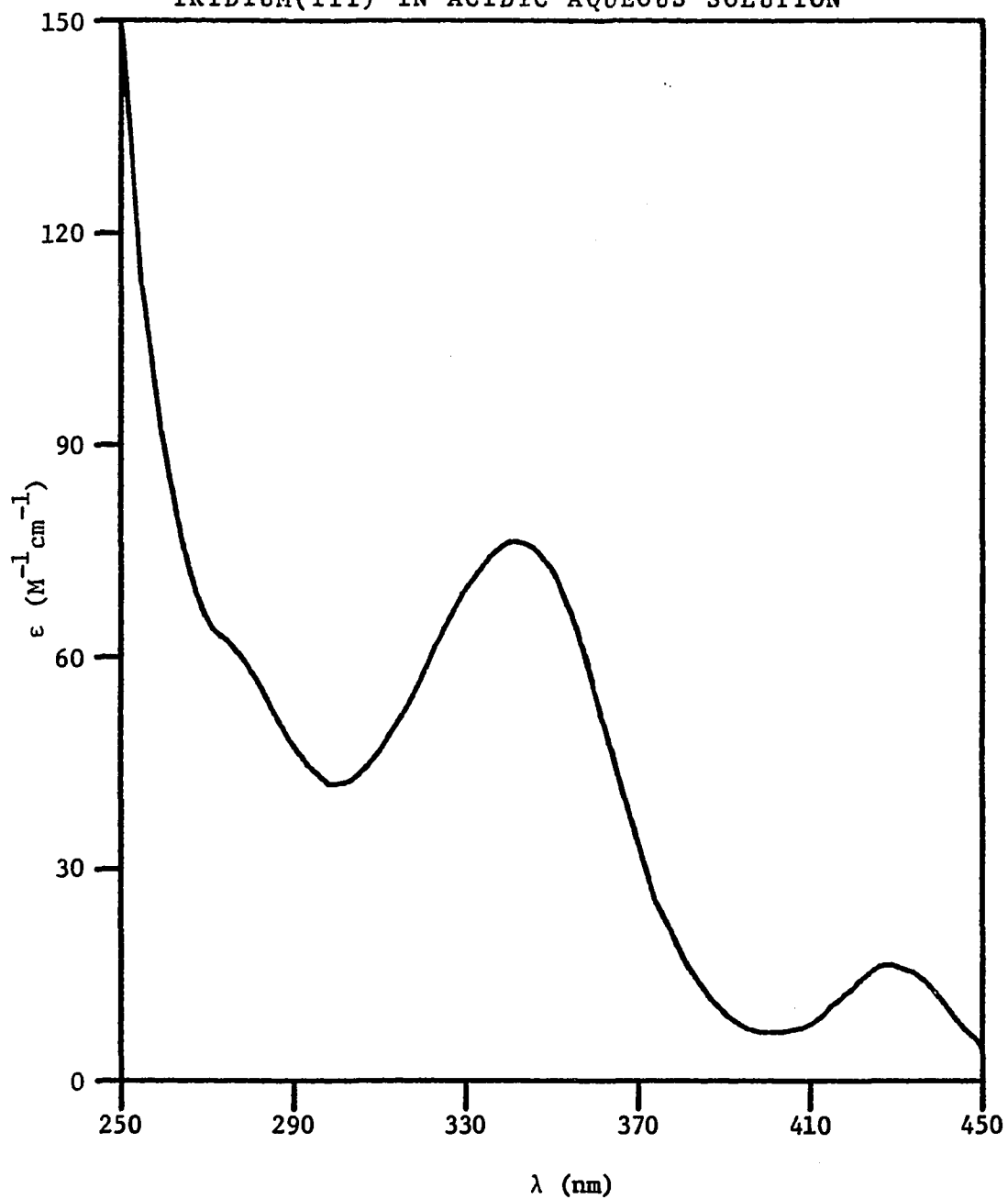
TABLE III-2
 COMPOUNDS OF Rh³⁺ and Ir³⁺
 SYNTHESIZED BY PHOTOAQUATION

Compound	Precursor	λ , nm	Type	Φ	Ref
Rh(NH ₃) ₅ H ₂ O ³⁺	Rh(NH ₃) ₅ Cl ²⁺	358	LF	.13	6
Ir(NH ₃) ₅ H ₂ O ³⁺	Ir(NH ₃) ₅ Cl ²⁺	313	LF	.13	7
		254	CT	.15	7
<u>trans</u> -Rh(NH ₃) ₄ H ₂ OCl ²⁺	<u>trans</u> -Rh(NH ₃) ₄ Cl ₂ ⁺	407	LF	.13	6
<u>trans</u> -Rh(en) ₂ Cl(H ₂ O) ²⁺	<u>trans</u> -Rh(en) ₂ Cl ₂ ⁺	407	LF	.057	6
<u>trans</u> -Ir(en) ₂ Cl(H ₂ O) ²⁺	<u>trans</u> -Ir(en) ₂ Cl ₂ ⁺	350	LF	.13	8
		254	CT	.086	8

FIGURE III-1

ULTRAVIOLET-VISIBLE SPECTRUM OF *trans*-DICHLOROBIS(ETHYLENEDIAMINE)

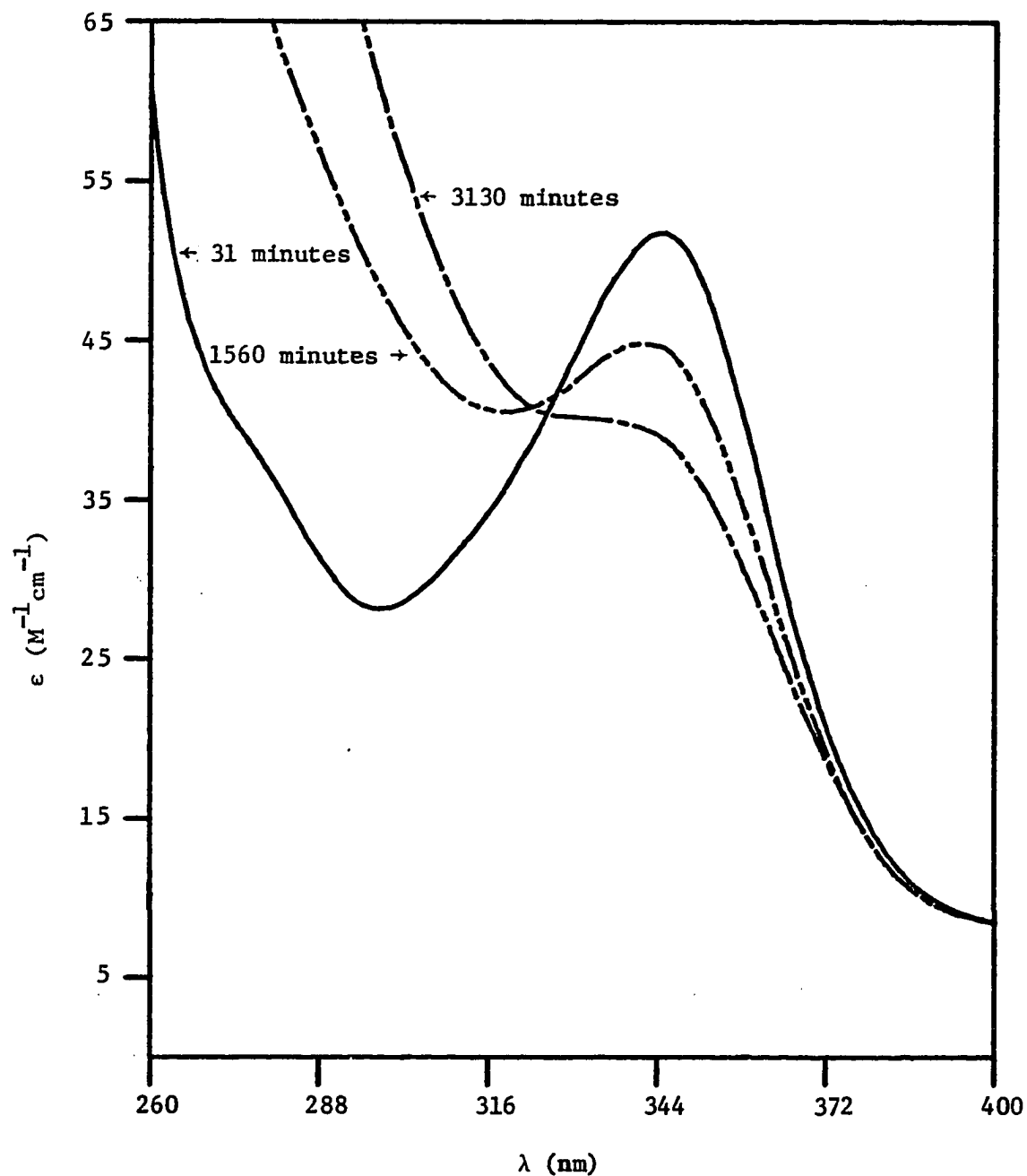
IRIDIUM(III) IN ACIDIC AQUEOUS SOLUTION



$[H^+] = 0.01 M$, Total Ionic Strength = 0.02 M

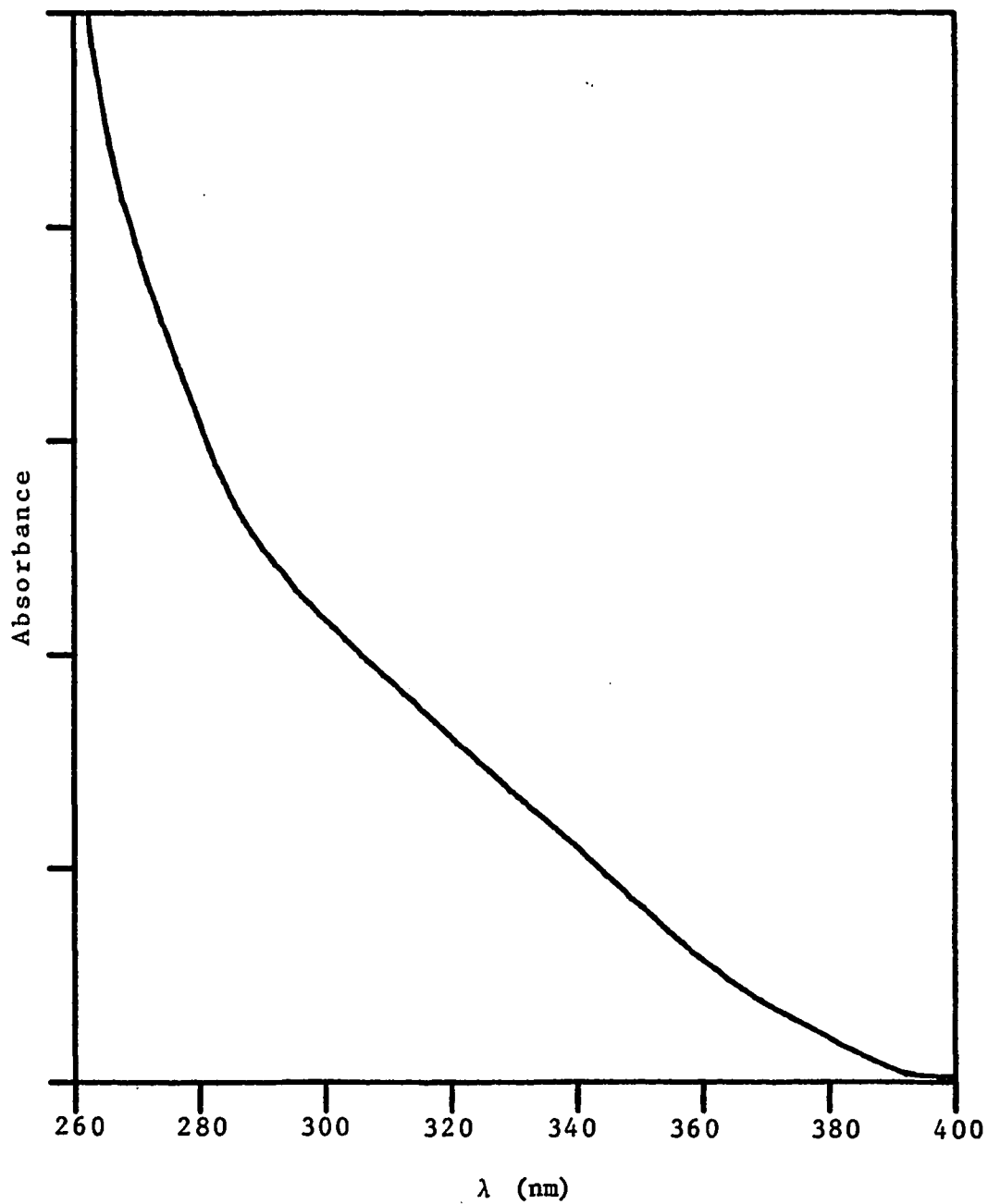
FIGURE III-2

SPECTRA DURING THE THERMAL AQUATION OF
trans-DICHLOROBIS(ETHYLENEDIAMINE)IRIDIUM(III)



$[OH^-] = 1.6 \times 10^{-2} M$, Total Complex Concentration = $7.7 \times 10^{-3} M$

FIGURE III-3
SPECTRUM OF THE ION-EXCHANGE ELUENTS FROM
THE THERMAL AQUATION EXPERIMENTS



Note:

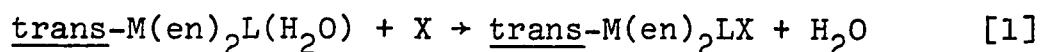
As the spectrum is of an eluent of unknown composition, the concentration is unknown.

IV. THE KINETICS OF THE ANATION BY CHLORIDE OF
trans-DIAQUOBIS(ETHYLENEDIAMINE)RHODIUM(III)
IN ACIDIC AQUEOUS SOLUTION

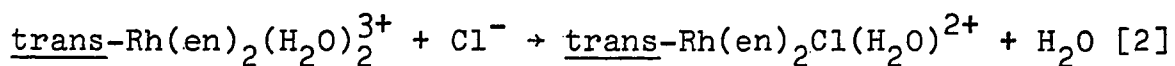
CHAPTER 1

INTRODUCTION

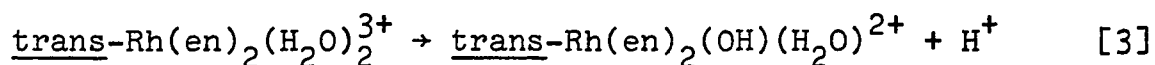
Reactions of the type:



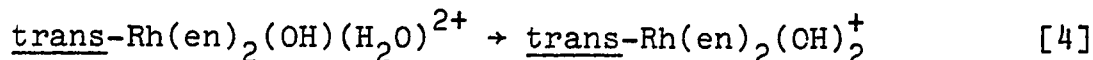
were chosen for study because they permit the evaluation of the trans-effectiveness of the trans- ligand, L, and the nucleophilicity of the attacking anion, X, while minimizing the need to consider the role of stereochemical changes in the mechanism. The kinetics and mechanism of one such reaction:



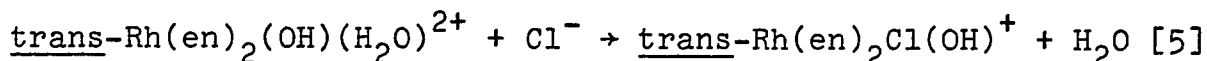
is reported here. In addition, the coordinated waters in the reactant complex are found to be acidic¹:



and:



Consequently, in moderately acidic solutions, two simultaneous reactions are observed, eqn. [2] and:



The reaction has also been shown^{1,2} to proceed to completion giving only the desired product. This situation renders the reaction ideal for comparing the relative trans-effectiveness of H₂O and OH⁻. Another attractive feature of this reaction is that it has been studied previously by the traditional approach^{1,2} so that the results of the traditional and novel approaches can be compared.

Results of previous studies relevant to this work are summarized in Table IV-1 (also see Table I-1). These data clearly show that, although the reactions of aquopentaammine-rhodium(III) are possibly more associative in nature than the cobalt(III) analog, the reactions of trans-diaquobis(ethylenediamine)rhodium(III) and pentaquochlororhodium(III) are more dissociative in nature than trans-diaquobis(ethylenediamine)cobalt(III). The reasons for this difference are unclear. Comparison of cobalt(III) and rhodium(III) suggests that the reactions of rhodium(III) are more sensitive to the identities of the inert ligands than are the reactions of the analogous cobalt(III) complexes. The mechanisms of the rhodium(III) com-

plexes in Table IV-1 can be discussed in terms of the inert ligands. In the aquopentaammine complex, the inert ligands contain no unshared electron pairs, while the pentaquochloro and the trans-diaquobis(ethylenediamine) complexes have water and/or hydroxide at the inert axial position whose oxygen atoms have unshared electron pairs. Five-coordinated species, such as are required by the dissociative (D) mechanism¹⁰, could be stabilized by electron donation to the metal by coordinated hydroxide and, to a lesser extent, by coordinated water. This is consistent with the observation that, for the bis(ethylenediamine)rhodium(III) complexes reacting with chloride, the basic aquohydroxy- form of the diaquo- complex accounts for more than 95% of the measured rate, even in moderately acidic solutions¹. The previous assignment of a dissociative mechanism may, then, only describe the mechanism followed by the aquohydroxy- form; the mechanism followed by the acidic diaquo- form may be dissociative or an interchange (I) mechanism, as the aquopentaammine- complex follows, but has remained undetermined due to the overwhelming contribution to the overall rate by the aquohydroxy- form.

As was discussed in Section II, ion-pair formation between the complex cation and the attacking anion may be kinetically important, as in the reaction of aquopentaammine-rhodium(III) with chloride⁵, but its importance in other reactions may be small. Previous work on the trans-diaquobis-(ethylenediamine)rhodium(III) system indicates that, although

the complex does form ion-pairs⁷, the mechanisms of these reactions are dissociative in nature, rendering the kinetic importance of ion-pair formation unclear¹.

Therefore, it is expected that for the reaction of trans-diaquobis(ethylenediamine)rhodium(III) and/or trans-aquoxybis(ethylenediamine)rhodium(III) with chloride the dissociative mechanism will be observed. In addition, the extent of ion-pair formation should be small but measurable. The experimental techniques employed in this work investigate the kinetic behavior of the system as well as its many possible equilibria. Batch kinetics, potentiometric ion-pairing, spectrophotometric ion-pairing, and pH measurements assure a broad base of data which should yield well defined parameters and a detailed description of the reaction.

CHAPTER 2

EXPERIMENTAL

Materials

All compounds used in this work were reagent grade and used without further purification except where noted to the contrary. Doubly distilled water was used throughout. Stock solutions of sodium hydroxide were made from saturated aqueous NaOH and standardized by titration into aqueous solutions of potassium hydrogen phthalate (KHP). Solutions of HCl and HClO₄ were made from the concentrated acids and standardized by titration with secondary standard NaOH. Solutions of NaOH, HCl, and HClO₄ with background concentrations of NaCl or NaClO₄ were also made using weighed amounts of the sodium salts and the acid or base concentration standardized as described above. Ethylenediamine dihydrochloride was made as described in Section II.

The rhodium starting material was hydrated rhodium(III) chloride (RhCl₃·3H₂O, Alfa). Trans-dichlorobis(ethylenediamine)rhodium(III) perchlorate was prepared by the literature

method¹¹. Hydrated rhodium(III) chloride (1.000g, 3.800mmol) and ethylenediamine dihydrochloride (1.010g, 7.588mmol) were dissolved in aqueous KOH (0.152M, 50ml, 7.600mmol) and brought to reflux. After the solution cleared, additional aqueous KOH (0.152M, 50ml, 7.600mmol) was added dropwise over twenty minutes. Following the final addition, two pellets of solid KOH were added. The light yellow solution was filtered through a medium fritted-glass crucible with Filter-aid to remove the small amount of insoluble gray material formed during the reaction. The volume of the supernatant was then reduced to 50ml on a steam bath. Concentrated nitric acid (20ml) was added and the yellow trans-[Rh(en)₂Cl₂]NO₃ was allowed to precipitate at room temperature over four hours. The solution was filtered and the solid trans-[Rh(en)₂Cl₂]NO₃ was dissolved in minimum hot water. Concentrated perchloric acid (2ml) was added and trans-[Rh(en)₂Cl₂]ClO₄ was allowed to precipitate at room temperature overnight. The typical yield was 40% based on rhodium.

Trans-aquoxybis(ethylenediamine)rhodium(III) perchlorate was made by the method given below¹. Trans-dichlorobis(ethylenediamine)rhodium(III) perchlorate (1.000g, 2.541mmol) was dissolved in aqueous NaOH (0.102M, 50ml, 5.100mmol) and the solution was refluxed for twenty minutes. The yellow color of the solution lightened within the first five minutes. The solution was cooled and concentrated perchloric acid was added until the solution was acidic. Silver

nitrate (0.91g, 5.35mmol) was added to precipitate the liberated chloride. Completeness of precipitation was tested by mixing equal volumes of the solution and aqueous silver nitrate (0.10M). No reaction confirmed that precipitation was complete; a precipitate showed that the precipitation of chloride from the reaction mixture was incomplete and additional silver nitrate was added to the reaction mixture until it tested complete. The solution was filtered through Filter-aid to remove the solid AgCl. Solid NaOH was then added to the supernatant to precipitate excess silver. The solution was filtered through Filter-aid to remove the Ag₂O formed. Concentrated perchloric acid was added to the supernatant until it had a pH of about 6. The volume of the solution was reduced to 20ml on a steam bath and then refrigerated overnight to precipitate the trans-[Rh(en)₂(OH)(H₂O)](ClO₄)₂. The typical yield was 20% based on the starting complex. Generally, one recrystallization from minimum hot water was required to purify the complex. After use, the diaquo- complex invariably reverted to the dichloro- precursor and regeneration of trans-[Rh(en)₂(OH)(H₂O)](ClO₄)₂ was done routinely.

Batch Kinetics

Batch kinetic experiments¹ were performed at 50.0 and 65.0°C. In these experiments, reaction mixtures were prepared at room temperature using measured volumes of the stock HCl and NaCl solutions, water, and solid trans-aquo-hydroxybis-(ethylenediamine)rhodium(III) perchlorate. The mixtures were

then placed in a bath thermostated to $\pm 0.02^\circ\text{C}$ and allowed to equilibrate thermally for 20-30 minutes. Aliquots were periodically drawn, quenched in ice, and stored at $2-3^\circ\text{C}$ until the conclusion of the experiment. The aliquots were then warmed to room temperature and ultraviolet-visible spectra were recorded using a Cary 118C spectrophotometer. The ultraviolet-visible spectra of trans-dichlorobis(ethylenediamine)rhodium(III) and trans-diaquobis(ethylenediamine)rhodium(III) are given in Figure IV-1. The only observed product of the reaction was the dichloro- complex because of the much higher rate of reaction of the first-formed chloro-aquo- complex^{1,13}. Therefore, all kinetic data was given by mixtures of these two spectra. The spectrum of trans-diaquobis(ethylenediamine)rhodium(III) shows maxima at 351 and 274 nm with molar absorptivities of 61.6 and $138.1\text{M}^{-1}\text{cm}^{-1}$, respectively. The spectrum of trans-dichlorobis(ethylenediamine)rhodium(III) shows maxima at 407 and 287nm with molar absorptivities of 82.5 and $126.4\text{M}^{-1}\text{cm}^{-1}$, respectively. Four isobestic points are observed (379, 324, 288, 271nm). In most trials, however, only the absorbances at 407nm were recorded. Rate data were collected on solutions where $0.0006 < [\text{Rh}(\text{en})_2(\text{H}_2\text{O})_2] < 0.003\text{M}$, $0.001 < [\text{H}^+] < 0.2\text{M}$, and $0.01 < [\text{Cl}^-] < 0.3\text{M}$. No inert salt was added to maintain constant ionic strength. In all cases, $[\text{Rh}(\text{en})_2(\text{H}_2\text{O})_2] \ll [\text{Cl}^-]$ so that pseudo-first order kinetics were observed. Maintaining pseudo-first order conditions greatly simplified the rate expressions (see Results

and Discussion). The pseudo-first order rate constant, k_{obs} , was determined for each trial from a plot of $\ln(A_{\infty} - A_t)$ vs. time, where A_{∞} is the calculated absorbance at 407nm for trans-dichlorobis(ethylenediamine)rhodium(III) (complete reaction) and A_t is the actual absorbance at 407nm of the reaction mixture at time t . The plots were linear under all conditions through at least two half-lives.

Potentiometry

Potentiometric ion-pairing measurements were made at 25.0°C. The apparatus consisted of a Corning 112 pH/mv meter readable to 0.1mv, a Fisher glass electrode connected to the meter input terminal, and an Orion solid-state chloride specific electrode connected through a shielded connection to the reference terminal. In this configuration, the apparatus measured HCl activity. The procedure was as follows. Water (40ml) was placed in a thermostated vessel and allowed to equilibrate thermally for at least ten minutes. The electrodes were inserted and the water was then titrated with an HCl solution of known concentration and the millivolt reading recorded after each addition. This process was continued until the HCl concentration in the solution was $\sim 5 \times 10^{-3}$ M. The data allowed the construction of a standardization plot of millivolt reading vs. HCl activity. To this solution, small amounts of solid trans- $[\text{Rh}(\text{en})_2(\text{OH})(\text{H}_2\text{O})](\text{ClO}_4)_2$, typically ~ 0.025 g (~ 0.055 mmol), were added and the millivolt readings recorded after each addition. A decrease in the millivolt

reading following each addition was interpreted as showing the uptake of H^+ and/or Cl^- by the complex through the action of an acid-base equilibrium and an ion-pairing equilibrium, respectively. The reading required 1-2 minutes to stabilize but then remained stable for at least ten minutes. In a typical trial, six to eight standard additions were used, followed by four complex additions. The total time required for each trial was approximately 100 minutes. Spectra of the solutions at the end of each trial showed no evidence of substitution by chloride.

pH Titrations

The acid-base behavior of trans-diaquobis(ethylenediamine)rhodium(III) was first investigated at 50°C to be consistent with the kinetics experiments. However, this was abandoned as the ultraviolet-visible spectra of the solutions after titration showed significant decomposition of the complex. Therefore, pH titrations were carried out at 10.0, 20.0, and 30.0°C at which temperatures no decomposition or substitution by chloride was observed spectrally over the course of the titration. The apparatus consisted of a Corning 112 pH/mv meter readable to 0.001 pH unit, a Fisher glass electrode, and a Fisher calomel reference electrode. The experimental procedure was as follows. Aqueous sodium chloride (0.010M, 40.0ml) was placed in a thermostated vessel and allowed to equilibrate thermally for at least fifteen minutes. This solution was titrated with an HCl solution of known concentration and a back-

ground NaCl concentration of 0.010M in order to construct a standardization curve of pH reading vs. $p(\text{activity}_H)$. The background NaCl concentration was used to keep the chloride ion concentration approximately constant over the course of the titration. The solid complex ($\sim 0.05\text{g}$, $\sim 0.11\text{mmol}$) was then added and allowed to dissolve (10-15 minutes). The resulting solution was then back-titrated with an NaOH solution of known concentration and a background NaCl concentration of 0.010M. Typically, the pH reading stabilized within one minute after each addition and then remained stable for several minutes. pH drift was only observed at pH readings above approximately 5.00. This procedure was repeated using solutions with background NaCl concentrations of 0.050, 0.100, 0.200, and 0.250M. Two titrations were performed at each background concentration at each temperature. In addition, the procedure was repeated at 20.0 and 30.0°C using HClO_4 and NaClO_4 as the acid and the background salt, respectively. In these trials, the NaClO_4 concentrations used were 0.010 and 0.200M.

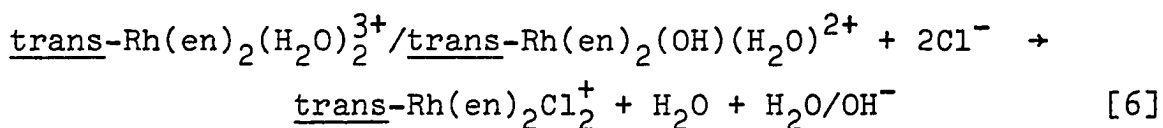
Spectral Ion-pairing

Spectrophotometric ion-pairing studies were attempted using the method discussed in Section II. Preliminary results¹² showed, however, no change in absorbance as chloride concentration was changed. No conclusion could be drawn as to whether ion-pairing was not occurring or whether the molar absorptivities of the free complex and the ion-paired complex are the same.

CHAPTER 3

RESULTS AND DISCUSSION

In order to establish the mechanism of the reaction:



it is necessary to consider a variety of mechanisms. As previously discussed, the substitution of the second coordinated water is fast compared to the first and so the two steps can not be kinetically separated. This is supported by the absence of any observable intermediate in the ultraviolet-visible spectra of kinetic samples. The rate laws for the dissociative (D), interchange (I), and bimolecular-attack (B) mechanisms are derived in Appendices IV-1 through IV-3. In addition, another mechanism, referred to here as the interdis mechanism, is considered. The interdis mechanism assumes the interchange mechanism for the acidic diaquo- form of the complex and the dissociative mechanism for the basic aquohydroxy- form of the complex. The rationale behind the interdis mechanism is discussed in the Introduction to this project (see page 64).

Batch Kinetics

The final forms of the rate laws are discussed below. In all of the mechanisms, only substitution by the first chloride is considered kinetically important^{1,13}. In each rate law, the nomenclature used follows from the derivation given in the appropriate appendix. The dissociative mechanism (see Appendix IV-1) assumes that both the acidic diaquo- and the basic aquohydroxy- forms of the complex react to form five-coordinated species by dissociating a bound water ligand as a prerequisite step to their reaction with chloride. The rate law for the dissociative mechanism is then found to be:

$$k_{\text{obs}} = \frac{k_a^{\circ} k_1^{\circ} G_a [H][Cl] + k_b^{\circ} k_3^{\circ} K_h^{\circ} G_b G_h [Cl]}{k_a^{\circ} G_a [Cl] + k_2^{\circ} [H_2O] \quad k_b^{\circ} G_b [Cl] + k_4^{\circ} [H_2O]} \quad [7]$$

$(K_h^{\circ} G_h + [H])$

where k_a° , k_1° , and k_2° are kinetic parameters of the acid "pathway", k_b° , k_3° , and k_4° are kinetic parameters of the base "pathway", K_h° is the acid dissociation constant of the complex, and the "G" terms are activity coefficient terms.

The interchange mechanism (see Appendix IV-2) assumes that both the acid and base forms of the complex form ion-pairs with chloride and that the kinetically important step involves the interchange of ion-paired chloride and coordinated water. The rate law for the interchange mechanism is then found to be:

$$k_{\text{obs}} = \frac{k_a^\circ K_a^\circ G_a [H][Cl] + k_b^\circ K_b^\circ K_h^\circ G_b G_h [Cl]}{[H](1+K_a^\circ G_a [Cl]) + K_h^\circ G_h (1+K_b^\circ G_b [Cl])} \quad [8]$$

where K_a° and K_b° are the equilibrium constants for the ion-pairing of chloride with the acid and base forms of the complex, respectively.

The bimolecular-attack mechanism (see Appendix IV-3) assumes that both the acid and the base forms of the complex react in one-step processes to coordinate chloride and eliminate water. The rate law for the bimolecular-attack mechanism is:

$$k_{\text{obs}} = \frac{k_a^\circ G_a [H][Cl] + k_b^\circ K_h^\circ G_b G_h [Cl]}{(K_h^\circ G_h + [H])} \quad [9]$$

The interdis mechanism is a combination of the interchange and the dissociative mechanisms and so is not explicitly derived in an appendix. To reiterate, the interdis mechanism assumes an interchange mechanism for the anation of the acid form of the complex and the dissociative mechanism for the anation of the base form of the complex. This rate law is given by:

$$k_{\text{obs}} = \frac{k_a^\circ K_a^\circ G_a [H][Cl] + \frac{k_b^\circ k_3^\circ K_h^\circ G_b G_h [Cl]}{k_b^\circ G_b [Cl] + k_4^\circ [H_2O]}}{[H](1+K_a^\circ G_a [Cl]) + K_h^\circ G_h (1+K_b^\circ G_b [Cl])} \quad [10]$$

It should be noted that the mechanisms given in eqn. [7] through eqn. [10] are general forms and that it is possible that one or more reaction step does not occur. In this event,

the rate laws simplify greatly. Results of the data analyses of kinetic data to the dissociative mechanism are given in Table IV-5. In all data fits, the value of the Debye-Hückel activity coefficient factor for the 1+ ion, b_1 , is taken to be 0.30, which has been shown to be applicable for 1:1 electrolytes¹⁵. The most obvious feature of this data is the apparent absence of reactivity in the acid pathway, i.e., the acid form of the complex appears to be nonreactive. The Debye-Hückel activity coefficient factor for the 2+ ion, b_2 , is also set to zero (see page 20) since all efforts to resolve values of b_2 proved fruitless. The acid pathway kinetic parameters were also undetectable. Table IV-5 describes the limiting dissociative rate expression for the base pathway. It is clear from these fits that covariance poses a significant problem to obtaining good definition of the parameters. Fit no. 1, in which all of the kinetic parameters are allowed to vary, yields parameter values which are poorly defined although the RMSD is acceptable (corresponding to an error of 7×10^{-6} for $k_{\text{obs}} = 10^{-5}$). Fit no. 2 partially compensates for this by converting the equation from the form:

$$\frac{K_1 X}{K_2 + K_3 X} \quad [11]$$

such as is used in Fit no. 1, to the form:

$$\frac{K_4 X}{1 + K_5 X} \quad [12]$$

which is mathematically equivalent but simpler ($K_4 = K_1/K_2$ and $K_5 = K_3/K_2$). The parameters in Fit no. 2 are better defined and the RMSD also improves. Fit no. 3 represents further simplification of the rate law where it is assumed that the value of the denominator in eqn. [12] remains essentially constant, i.e., $1 \gg K_5 X$. Fit no. 3 indicates that this is an oversimplification as the RMSD (1.14×10^{-10}) increases sharply compared to Fit no. 2 (6.17×10^{-11}).

Results of the data fits of kinetic data to the interchange mechanism are given in Table IV-6. Again, all attempts to fit values of b_2 were fruitless. In Fit no. 1, an attempt was made to fit parameters of the acid pathway. This resulted in poor definition of the parameters. In addition, Fit no. 1 yielded values for the acid pathway which were comparable in magnitude to those for the base pathway which contradicts the results previously reported on this reaction. Fit no. 2 eliminates the acid pathway and although the definition of the parameters improves markedly, the RMSD remains virtually unchanged (Fit no. 1: 1.14×10^{-10} , Fit no. 2: 1.13×10^{-10}). Fit no. 3 introduces chloride ion-pairing and gives an improvement in both definition and the RMSD (5.20×10^{-11} , corresponding to an error of 5×10^{-6} at $k_{\text{obs}} = 10^{-5}$).

With the elimination of the acid pathway from consideration, the dissociative mechanism and the interdis mechanism become virtually identical except for the inclusion of ion-pairing in the interdis mechanism. Owing to the high

covariance among parameters in the interdis mechanism, there were no successful fits when ion-pairing was allowed. However, if ion-pairing is not allowed ($K_a^o = K_b^o = 0$) and the acid pathway is inoperative, the interdis mechanism and the dissociative mechanism are identical.

The bimolecular-attack mechanism is mathematically equivalent to the interchange mechanism if ion-pairing is not allowed. This is not to suggest that the two mechanisms are identical, but rather that, if $1 \gg K_a^o G_a [Cl]$ and $1 \gg K_b^o G_b [Cl]$ in the interchange mechanism, the two become mathematically indistinguishable.

Potentiometry

Fits of the potentiometric data to the functions:

$$[H^+] = \frac{K_h^o G_h A_t (1 + K_b^o G_b [Cl] + K_{bp}^o G_b [ClO_4])}{B_t (1 + K_a^o G_a [Cl] + K_{ap}^o G_a [ClO_4])} \quad [13]$$

$$[Cl] = [Cl]_o - \frac{K_a^o G_a A_t [Cl]}{(1 + K_a^o G_a [Cl] + K_{ap}^o G_a [ClO_4])} - \frac{K_b^o G_b B_t [Cl]}{(1 + K_b^o G_b [Cl] + K_{bp}^o G_b [ClO_4])} \quad [14]$$

and:

$$Y(i) = [H^+][Cl^-]\gamma_1^2 \quad [15]$$

are given in Table IV-7. In the equations, K_{ap}^o and K_{bp}^o are the equilibrium constants for ion-pair formation of perchlorate with the acid and base forms of the complex, respectively, and A_t and B_t are the total concentrations of the acid and

base forms of the complex, including free complex and ion-paired species, respectively (see page 28). Fits no. 2 and 5 clearly show the difficulty in fitting a value of b_2 . The two fits are identical except for the fitted value of b_2 in Fit no. 5. Inclusion of b_2 serves no computational purpose as it does not significantly affect the RMSD (Fit no. 2: 1.26%, Fit no. 5: 1.28%), while destroying the definition of the parameters. The inclusion of perchlorate ion-pairing (Fits no. 3 and 4) also does not significantly affect the RMSD (Fit no. 3: 1.28%, Fit no. 4: 1.65%). However, the presence of chloride ion-pairing is indicated although it is not necessary to arrive at a satisfactory fit (Fit no. 1 (no ion-pairing): 1.84%, Fit no. 2 (chloride ion-pairing): 1.26%).

pH Titrations

Fits of the pH data to the expression:

$$[H^+] = \frac{K_h^\circ G_h A_t (1 + K_b^\circ G_b [Cl] + K_{bp}^\circ G_b [ClO_4])}{B_t (1 + K_a^\circ G_a [Cl] + K_{ap}^\circ G_a [ClO_4])} \quad [16]$$

are given in Table IV-8. These fits indicate that the pH titrations are of limited value in the present work. Fits no. 8 and 9 utilized all of the data. The two fits differ only in that Fit no. 9 allows ion-pairing between chloride and the base form of the complex. The unacceptably high RMSD (0.148 pH unit) yielded by both fits clearly illustrates the problem pervading the data. No successful fits were obtained when

values of b_2 or K_a° were being allowed to vary. In an effort to determine the cause of the high RMSD's when all points were considered, the data were separated by temperature. Fits no. 1 through 6 give the results of these analyses. Clearly, none of the RMSD values yielded are acceptable. The pH technique should yield an inherent accuracy of ± 0.01 pH unit. The "best" of these fits is given by Fit no. 2 (0.07 pH unit) which must be eliminated on statistical grounds (see pages 8 and 9). It is necessary, therefore, to eliminate all of these fits from consideration as they describe the data poorly. Fit no. 7 represents the fit of the data from the perchlorate titrations to eqn. [16]. Although these data offer an improved fit, they are statistically unacceptable (RMSD = 0.039 pH unit).

The data were also separated by the background salt concentration. No successful fits were obtained from these groups, although it would be expected that grouping the data by background salt concentration (and, hence, approximately by ionic strength) would simplify the data analyses.

In view of the fits of the pH data, it should be concluded that the pH titration technique is not well suited to this reaction. The reasons for this are unclear. The form of eqn. [16] indicates that K_a° and K_b° may be difficult to resolve if they are the same order of magnitude, especially if a narrow range of chloride ion concentrations is used. The resolution of K_a° and K_b° can also be complicated if either is small, i.e., $1 \gg K_a^\circ G_a [Cl]$ or $1 \gg K_b^\circ G_b [Cl]$. In this case the RMSD would

not be sensitive to changes in the values of K_a° or K_b° and the data analysis program would be unable to determine rational values. It is also possible that a chemical reaction, other than the equilibria being studied, proceeded during the course of the titration. It was noted that there was spectral evidence of decomposition during the 50°C titrations and, although there was no spectral evidence of decomposition at 10, 20, or 30°C, such decomposition could proceed to an extent which is not spectrally observable. The instability of trans-Rh(en)₂(OH)(H₂O)²⁺ in neutral solution^{1,9} has been reported and it is likely that this instability extends to slightly acidic solutions where the base form of the complex is still present in equilibrium with the acid form of the complex. The decomposition product has not been characterized but a metal complex polymer has been suggested¹.

Combination Data Fits

As stated previously (see page 9), the most useful information should be derived from simultaneous fitting of all of the experimental data. The data fits of each experimental technique determine their quality and applicability to the project. In addition, the individual data fits also can show what reaction steps must necessarily be considered or eliminated. In the present case, it is clear that values of the Debye-Hückel parameter, b_2 , cannot be determined and that values reported for b_3 are a combination of the true b_2 and b_3 ($b_3 \text{ obs} = b_3 - 4/9b_2$). It is also clear that the pH titra-

tion data are not reliable and they are therefore eliminated from the combination data fits. The kinetic data fits indicate that the acid pathway should not be considered. It is not clear whether the acid pathway is inoperative or whether the rate of the acid pathway reaction is so small in comparison to the base pathway as to make it indeterminable at the hydrogen ion concentrations used.

In the combination fits, the values of DEL (see pages 6 and 7) are normalized so that the kinetic data and the potentiometric data are weighted equally. To achieve this, the weights applied to each data point are adjusted so that DEL for the "best" potentiometric fit is 1.000 and DEL for the "best" kinetic fit is 1.000. The adjustment is performed by further weighting of each point by $1/\sqrt{\text{"best" DEL}}$, where the "best" DEL is that of the best individual technique fit:

$$\text{DEL}_{\text{comb}} = 1 = \frac{\text{NO}}{\sum_{i=1}^{\text{NO}} \{[Y(i)-Y_C(i)] * \text{WEIGHT} / \sqrt{\text{"best" DEL}}\}^2} \quad [17]$$

Therefore, in a combination fit of the potentiometric data and the kinetic data, the expected DEL_{comb} is 2.000 (1.000 + 1.000). RMSD is then found in the normal manner (see eqn. [9] on page 7).

In the combination fits, the criterion for a "good" fit is then one in which DEL_{comb} approaches 2.000. With 100 data points, the target RMSD (SD_{crit} , see pages 7 and 8) is 0.14 - 0.15, depending on the number of parameters being allowed to float (see eqn. [9] on page 7).

The combination fits of the kinetic and the potentiometric data to the dissociative mechanism are given in Table IV-9. Fit no. 1 demonstrates the poor fit obtained when the acid pathway is considered. The definition of b_3 and the acid pathway kinetic parameters is especially poor and the RMSD is rather high. The simplified dissociative mechanism being tested in Fits no. 2 through 5 assumes no contribution from the acid pathway:

$$k_{\text{obs}} = \frac{k_b^{\circ} k_3^{\circ} K_h^{\circ} G_b^{\circ} G_h^{\circ} [\text{Cl}]}{(k_b^{\circ} G_b^{\circ} [\text{Cl}] + k_4^{\circ} [\text{H}_2\text{O}])(K_h^{\circ} G_h^{\circ} + [\text{H}])} \quad [18]$$

A comparison of Fits no. 2 and 3 indicates chloride ion-pairing as Fit no. 3 yields better definition of the parameters and a slightly lower RMSD (Fit no. 2 (no ion-pairing): 0.241, Fit no. 3 (chloride ion-pairing): 0.215). Fit no. 4, in which all of the base pathway kinetic parameters are allowed to vary, represents overfitting of the data and yields very poor definition although the RMSD improves somewhat. Fit no. 5 is a simplification of Fit no. 4 (see page 76, eqns. [11] and [12]). Fit no. 5 results in improved definition and although the RMSD is the lowest of the dissociative fits (0.194), it is still high (DEL = 3.50). It should be noted that in these fits to the dissociative mechanism, ion-pairing has not been considered in the kinetic expression.

Table IV-10 gives the results of the successful data fits of the kinetic and the potentiometric data to the inter-

change mechanism. Fit no. 1 assumes no ion-pairing and is, therefore, computationally equivalent to the bimolecular-attack mechanism. Only Fit no. 2 approached a "good" fit (RMSD = 0.165) and, again, seems to indicate the presence of chloride ion-pairing. Fit no. 3 is an example of overfitting and yielded poor definition of the acid pathway kinetic parameters.

The results of the successful data fits of the kinetic and the potentiometric data to the interdis mechanism are given in Table IV-11. Fit no. 3 represents extreme overfitting based on the poor definition of the parameters and the extremely high RMSD (0.946). Fit no. 2 fits values of the acid pathway kinetic parameters although, again, the definition is poor. Fit no. 1, however, assumes no acid pathway reaction and the simplified base pathway. Here, the definition of the parameters is good and the RMSD is acceptable (RMSD = 0.148 = 1.01*SD_{crit}, DEL = 2.34). The rate law followed by Fit no. 1 is:

$$k_{\text{obs}} = \frac{k_b^{\circ} k_3^{\circ} K_a^{\circ} G_b G_h [Cl]}{k_4^{\circ} ([H](1+K_a^{\circ} G_a [Cl]) + K_h^{\circ} G_h (1+K_b^{\circ} G_b [Cl])) [H_2O]} \quad [19]$$

Although the superiority of Fit no. 1 is not as striking as one would wish, it must be concluded that the reaction given by eqn. [6] proceeds by a dissociative mechanism along the base pathway. In addition, the participation of the acid pathway is small enough under the conditions used

to be considered inconsequential, if the acid pathway is operative at all. No evidence was found for perchlorate ion-pairing with the acid or base form of the complex but ion-pairing of chloride with both the acid and base forms of the complex was found. The existence of ion-pairing in conjunction with a dissociative mechanism is not unexpected as the attacking chloride ions must be in close proximity to the available coordination site at the time of dissociation in order to be inserted. The magnitude of the ion-pairing constants is a factor of 10 higher than those of other rhodium(III) complexes (see Table II-1). This apparent discrepancy can be explained in terms of the activity coefficients and the fact that under constant ionic strength conditions the apparent ion-pairing constant is a composite value (see page 2, eqn. [2]). The apparent ion-pairing constant for the base form of the complex, K_b , is given by $K_b = K_b^{\circ} G_b$, where G_b is the activity coefficient term. At ionic strengths of 1.0M and above, the activity coefficient term can easily account for the ten-fold discrepancy.

The activation parameters derived from this work are found as follows. A plot of $\ln(k_b^{\circ} k_3^{\circ} K_h^{\circ} / T)$ vs. $1/T$ gives a line where the slope = $-15710^{\circ}K = -\Delta H^{\ddagger} / R - \Delta H^{\circ}(K_h) / R$ and the intercept = $32.59 = \Delta S^{\circ}(K_h) / R + \Delta S^{\ddagger} / R + \ln(k/h) + \ln K_a^{\circ} - \ln K_b^{\circ} - \ln[H^{\ddagger}]$ for the base pathway as a whole. This treatment gives values of $\Delta H^{\ddagger} = 48.8 \text{ kJ/mole}$ and $\Delta S^{\ddagger} = -183 \text{ J/mole-}^{\circ}K$. These values agree well with those found previously for this and

similar reactions^{1,13}.

This study again affirms the applicability of the novel approach although limitations arose which were not apparent in the simpler study. The dissociative mechanism has been established more equivocally than is possible from traditional experiments. Furthermore, the data strongly support that the dissociation is accompanied by significant ion-pairing. This latter conclusion is unavailable from traditional studies. Finally, values of the pure ion-pairing constants are obtained which also are unavailable from traditional studies. The limitations which arise come from the complexity of the system and the constraints of the novel approach. The ionic strength requirement limited the range of hydrogen ion concentrations available and, therefore, no information was obtained on the acid pathway. This would seem to preclude the study of the kinetic trans- effect of water since most diaquo- complexes show this large disparity of the rates for the diaquo- and hydroxoquo- forms of the complex. This same limitation prevented a large enough variation in the chloride ion concentration to allow resolution of k_p^0 and k_4^0 .

As a final thought, it is remarkable that even with the failure of two of my four experimental techniques, the novel approach still exceeds the traditional approach in its ability to provide more information which is of higher reliability.

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KEY TO TABLES

In the Tables, the following units and nomenclature are used:

- a. All concentrations are in units of molarity.
- b. All pseudo-first order rate constants are in units of sec^{-1} .
- c. All temperatures are in $^{\circ}\text{C}$.
- d. Rh_t refers to the total nominal concentration of the complex cation.
- e. b_1 , b_2 , and b_3 are the Debye-Hückel activity coefficient parameters for the 1+, 2+, and 3+ ions, respectively, in units of M^{-1} . See page 4.
- f. Values in parentheses are standard deviations of the parameters.
- g. Values of ΔH° are in kJ/mole ; values of ΔS° are in $\text{J/mole-}^{\circ}\text{K}$. In all cases, these values refer to the acid dissociation constant (K_h).
- h. K_{ap}° and K_{bp}° are the equilibrium constants for the ion-pairing of perchlorate with the acid and base forms of the complex, respectively, in units of M^{-1} .

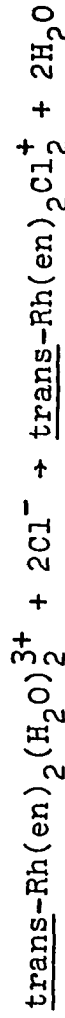
TABLE IV-1
 ASSIGNED MECHANISMS FOR SOME
 SUBSTITUTION REACTIONS OF RH(III)

Complex	Assigned Mechanism*	Ref.
$\text{Co}(\text{NH}_3)_5\text{H}_2\text{O}^{3+}$	I_d	3
<u>trans</u> - $\text{Co}(\text{en})_2(\text{OH})(\text{H}_2\text{O})^{2+}$	I	4
$\text{Rh}(\text{NH}_3)_5\text{H}_2\text{O}^{3+}$	I_a	6-8
	I_d	5
$\text{Rh}(\text{H}_2\text{O})_5\text{Cl}^{2+} / \text{Rh}(\text{H}_2\text{O})_4(\text{OH})\text{Cl}^+$	D	9
<u>trans</u> - $\text{Rh}(\text{en})_2(\text{H}_2\text{O})_2^{3+} / \text{Rh}(\text{en})_2(\text{OH})(\text{H}_2\text{O})^{2+}$	D	1

* Rate data is not given since the variety of mechanisms and conditions make direct comparison difficult. See text. Taken with some modification from ref. 1.

TABLE IV-2

KINETIC DATA ON THE REACTION



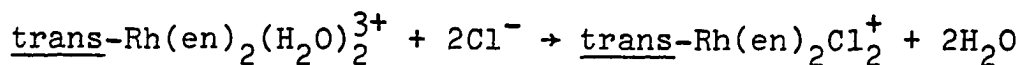
Temp, °C	k_{obs}	$[\text{H}^+]$	$[\text{Cl}^-]$	Rh_t
50	1.88E-05	0.010	0.0500	9.95E-04
	2.37E-05	0.010	0.1000	9.95E-04
	2.89E-05	0.010	0.1500	9.95E-04
	3.12E-05	0.010	0.2000	9.95E-04
	2.88E-05	0.010	0.2000	9.96E-04
	2.96E-05	0.010	0.2300	9.96E-04
	3.10E-05	0.010	0.2600	9.96E-04
	3.13E-05	0.010	0.2900	9.96E-04
	3.29E-05	0.010	0.1500	3.03E-03
	3.61E-05	0.010	0.2020	3.03E-03
	3.79E-05	0.010	0.2380	3.03E-03
	4.03E-05	0.010	0.2900	3.03E-03
	3.31E-05	0.010	0.1500	3.03E-03
	3.62E-05	0.010	0.1900	3.03E-03
	3.74E-05	0.010	0.2300	3.03E-03
	3.75E-05	0.010	0.2700	3.03E-03
	3.99E-05	0.010	0.3000	3.03E-03
	3.13E-05	0.010	0.1000	2.97E-03
	3.40E-05	0.010	0.1280	2.97E-03
	3.55E-05	0.010	0.1520	2.97E-03
	3.66E-05	0.010	0.1760	2.97E-03
	3.85E-05	0.010	0.2000	2.97E-03
	2.11E-05	0.010	0.0500	2.80E-03
	2.47E-05	0.010	0.0700	2.80E-03
	2.75E-05	0.010	0.0900	2.80E-03
	2.99E-05	0.010	0.1100	2.80E-03
	3.26E-05	0.010	0.1300	2.80E-03
	5.60E-06	0.050	0.0898	2.68E-03
	6.19E-06	0.050	0.1298	2.68E-03
	6.63E-06	0.050	0.1698	2.68E-03
	6.92E-06	0.050	0.2098	2.68E-03
	7.21E-06	0.050	0.2498	2.68E-03
	2.71E-06	0.100	0.0995	2.07E-03
	2.75E-06	0.100	0.1395	2.07E-03
	2.96E-06	0.100	0.1795	2.07E-03
	3.17E-06	0.100	0.2195	2.07E-03
	3.25E-06	0.100	0.2595	2.07E-03
	4.74E-06	0.070	0.2704	2.07E-03
	4.14E-06	0.080	0.2401	2.07E-03
	3.48E-06	0.090	0.2098	2.07E-03
	3.16E-06	0.100	0.1795	2.07E-03
	2.65E-06	0.109	0.1493	2.07E-03
	1.81E-06	0.203	0.2530	2.82E-03
	1.59E-06	0.241	0.2814	2.82E-03

TABLE IV-2 (Continued)

	1.40E-06	0.280	0.2918	2.82E-03
	5.58E-06	0.049	0.1492	2.82E-03
	6.15E-06	0.049	0.2012	2.82E-03
	6.67E-06	0.049	0.2492	2.82E-03
	3.80E-05	0.001	0.0104	6.28E-04
	5.38E-05	0.001	0.0204	6.28E-04
	6.93E-05	0.001	0.0305	6.28E-04
	7.07E-05	0.001	0.0404	6.28E-04
	7.94E-05	0.001	0.0504	6.28E-04
65	4.64E-05	0.050	0.1003	2.52E-03
	5.11E-05	0.050	0.1503	2.52E-03
	5.38E-05	0.050	0.2004	2.52E-03
	5.50E-05	0.050	0.2504	2.52E-03
	5.59E-05	0.050	0.3004	2.52E-03
	3.89E-05	0.050	0.0503	2.35E-03
	2.51E-05	0.101	0.1007	2.35E-03
	1.94E-05	0.151	0.1510	2.35E-03
	1.63E-05	0.201	0.2013	2.35E-03
	1.43E-05	0.252	0.2516	2.35E-03
	1.84E-05	0.151	0.1510	1.58E-03
	1.96E-05	0.151	0.1760	1.58E-03
	2.06E-05	0.151	0.2010	1.58E-03
	2.06E-05	0.151	0.2260	1.58E-03
	2.07E-05	0.151	0.2510	1.58E-03

TABLE IV-3

POTENTIOMETRIC DATA ON THE REACTION

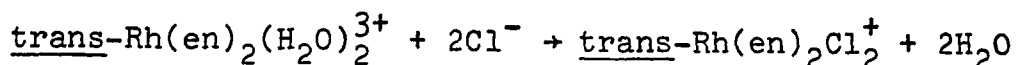


AT 25°C

$[\text{H}^+][\text{Cl}^-]\gamma_1^2$	$[\text{HCl}]$	Rh_t
2.65E-05	6.54E-03	1.34E-03
1.96E-05	6.54E-03	2.55E-03
1.39E-05	6.54E-03	3.74E-03
8.83E-06	6.54E-03	4.90E-03
8.16E-05	1.09E-02	1.10E-03
7.27E-05	1.09E-02	1.93E-03
6.25E-05	1.09E-02	2.96E-03
5.10E-05	1.09E-02	4.30E-03
2.61E-04	1.93E-02	9.72E-04
2.38E-04	1.93E-02	2.11E-03
2.21E-04	1.93E-02	2.99E-03
2.00E-04	1.93E-02	4.14E-03
2.24E-05	5.83E-03	1.10E-03
1.65E-05	5.83E-03	2.28E-03
1.27E-05	5.83E-03	3.10E-03
8.42E-06	5.83E-03	4.18E-03
1.72E-04	1.56E-02	9.39E-04
1.54E-04	1.56E-02	2.05E-03
1.39E-04	1.56E-02	3.04E-03
1.16E-04	1.56E-02	4.73E-03
2.82E-03	6.73E-02	1.19E-03
2.75E-03	6.73E-02	2.15E-03
2.65E-03	6.73E-02	3.47E-03
2.58E-03	6.73E-02	4.50E-03
2.22E-05	5.89E-03	1.18E-03
1.65E-05	5.89E-03	2.30E-03
6.57E-06	5.89E-03	4.71E-03
3.70E-06	5.89E-03	5.74E-03
2.62E-06	2.42E-03	1.22E-03
4.61E-07	2.42E-03	3.34E-03
2.65E-07	2.42E-03	4.28E-03
1.54E-07	2.42E-03	5.61E-03

TABLE IV-4

pH DATA ON THE REACTION



Temp, °C	$-\log a_{\text{H}}$	$[\text{Cl}^-]$	$[\text{ClO}_4^-]$	Rh_t	$[\text{H}^+]_0$
10	3.933	1.21E-02	6.04E-03	3.02E-03	2.11E-03
	3.969	1.21E-02	6.02E-03	3.01E-03	2.04E-03
	4.032	1.21E-02	6.00E-03	3.00E-03	1.91E-03
	4.103	1.21E-02	5.97E-03	2.98E-03	1.78E-03
	4.126	1.21E-02	5.96E-03	2.98E-03	1.73E-03
	4.164	1.21E-02	5.94E-03	2.97E-03	1.66E-03
	4.192	1.21E-02	5.93E-03	2.97E-03	1.60E-03
	4.221	1.21E-02	5.92E-03	2.96E-03	1.53E-03
	4.277	1.21E-02	5.90E-03	2.95E-03	1.42E-03
	4.307	1.21E-02	5.89E-03	2.94E-03	1.38E-03
	4.338	1.20E-02	5.88E-03	2.94E-03	1.32E-03
	4.368	1.20E-02	5.86E-03	2.93E-03	1.25E-03
	4.416	1.20E-02	5.85E-03	2.92E-03	1.19E-03
	4.514	1.20E-02	5.81E-03	2.91E-03	1.00E-03
	4.586	1.20E-02	5.79E-03	2.90E-03	9.10E-04
	4.644	1.20E-02	5.77E-03	2.89E-03	8.14E-04
	4.685	1.20E-02	5.76E-03	2.88E-03	7.54E-04
	4.728	1.20E-02	5.75E-03	2.87E-03	6.89E-04
	4.775	1.20E-02	5.73E-03	2.87E-03	6.31E-04
	4.882	1.20E-02	5.71E-03	2.86E-03	5.11E-04
	4.976	1.20E-02	5.70E-03	2.85E-03	4.47E-04
	5.209	1.20E-02	5.66E-03	2.83E-03	2.70E-04
	5.450	1.20E-02	5.64E-03	2.82E-03	1.52E-04
	4.327	1.22E-02	1.01E-02	5.05E-03	2.16E-03
	4.353	1.21E-02	1.01E-02	5.03E-03	2.07E-03
	4.369	1.21E-02	1.00E-02	5.02E-03	2.02E-03
	4.391	1.21E-02	1.00E-02	5.01E-03	1.95E-03
	4.413	1.21E-02	1.00E-02	5.00E-03	1.88E-03
	4.455	1.21E-02	9.96E-03	4.98E-03	1.76E-03
	4.502	1.21E-02	9.91E-03	4.96E-03	1.62E-03
	4.548	1.21E-02	9.87E-03	4.93E-03	1.50E-03
	4.576	1.21E-02	9.84E-03	4.92E-03	1.43E-03
	4.599	1.21E-02	9.82E-03	4.91E-03	1.37E-03
	4.650	1.21E-02	9.78E-03	4.89E-03	1.24E-03

TABLE IV-4 (Continued)

4.678	1.21E-02	9.76E-03	4.88E-03	1.18E-03
4.711	1.21E-02	9.74E-03	4.87E-03	1.11E-03
4.771	1.21E-02	9.69E-03	4.85E-03	9.89E-04
4.836	1.21E-02	9.65E-03	4.83E-03	8.68E-04
4.913	1.21E-02	9.61E-03	4.80E-03	7.42E-04
5.001	1.20E-02	9.57E-03	4.78E-03	6.17E-04
5.097	1.20E-02	9.53E-03	4.76E-03	4.99E-04
5.268	1.20E-02	9.47E-03	4.73E-03	3.32E-04
5.357	1.20E-02	9.45E-03	4.72E-03	2.64E-04
5.430	1.20E-02	9.42E-03	4.71E-03	2.02E-04
5.646	1.20E-02	9.39E-03	4.69E-03	8.53E-05
4.351	5.26E-02	9.46E-03	4.73E-03	2.58E-03
4.372	5.26E-02	9.44E-03	4.72E-03	2.52E-03
4.393	5.26E-02	9.42E-03	4.71E-03	2.45E-03
4.413	5.26E-02	9.39E-03	4.70E-03	2.39E-03
4.454	5.26E-02	9.35E-03	4.68E-03	2.27E-03
4.496	5.25E-02	9.31E-03	4.66E-03	2.15E-03
4.559	5.25E-02	9.25E-03	4.63E-03	1.97E-03
4.602	5.25E-02	9.21E-03	4.61E-03	1.85E-03
4.643	5.25E-02	9.17E-03	4.59E-03	1.74E-03
4.690	5.25E-02	9.13E-03	4.57E-03	1.62E-03
4.738	5.25E-02	9.09E-03	4.55E-03	1.50E-03
4.785	5.25E-02	9.05E-03	4.53E-03	1.38E-03
4.836	5.25E-02	9.01E-03	4.51E-03	1.27E-03
4.888	5.24E-02	8.98E-03	4.49E-03	1.16E-03
4.945	5.24E-02	8.94E-03	4.47E-03	1.05E-03
5.004	5.24E-02	8.90E-03	4.45E-03	9.35E-04
5.068	5.24E-02	8.86E-03	4.43E-03	8.27E-04
5.179	5.24E-02	8.81E-03	4.40E-03	6.64E-04
5.268	5.24E-02	8.77E-03	4.39E-03	5.49E-04
5.400	5.24E-02	8.72E-03	4.36E-03	4.10E-04
4.226	5.26E-02	8.40E-03	4.20E-03	2.62E-03
4.274	5.26E-02	8.37E-03	4.18E-03	2.50E-03
4.321	5.26E-02	8.33E-03	4.17E-03	2.37E-03
4.368	5.26E-02	8.29E-03	4.15E-03	2.25E-03
4.414	5.26E-02	8.26E-03	4.13E-03	2.13E-03
4.462	5.26E-02	8.22E-03	4.11E-03	2.01E-03
4.509	5.26E-02	8.19E-03	4.09E-03	1.89E-03
4.555	5.25E-02	8.15E-03	4.08E-03	1.78E-03
4.606	5.25E-02	8.11E-03	4.06E-03	1.65E-03
4.653	5.25E-02	8.08E-03	4.04E-03	1.54E-03
4.705	5.25E-02	8.05E-03	4.02E-03	1.43E-03
4.758	5.25E-02	8.01E-03	4.01E-03	1.31E-03
4.814	5.25E-02	7.98E-03	3.99E-03	1.20E-03
4.892	5.25E-02	7.93E-03	3.97E-03	1.05E-03
4.931	5.25E-02	7.91E-03	3.96E-03	9.76E-04
5.014	5.25E-02	7.87E-03	3.93E-03	8.38E-04
5.066	5.24E-02	7.84E-03	3.92E-03	7.56E-04
5.243	5.24E-02	7.78E-03	3.89E-03	5.35E-04
5.358	5.24E-02	7.74E-03	3.87E-03	4.19E-04

TABLE IV-4 (Continued)

3.099	1.04E-01	6.80E-03	3.40E-03	4.00E-03
3.131	1.04E-01	6.78E-03	3.39E-03	3.91E-03
3.165	1.04E-01	6.76E-03	3.38E-03	3.82E-03
3.218	1.04E-01	6.73E-03	3.36E-03	3.69E-03
3.315	1.04E-01	6.68E-03	3.34E-03	3.48E-03
3.383	1.04E-01	6.65E-03	3.32E-03	3.35E-03
3.454	1.04E-01	6.62E-03	3.31E-03	3.22E-03
3.534	1.04E-01	6.59E-03	3.30E-03	3.09E-03
3.612	1.04E-01	6.56E-03	3.28E-03	2.97E-03
3.691	1.04E-01	6.54E-03	3.27E-03	2.85E-03
3.772	1.04E-01	6.51E-03	3.25E-03	2.72E-03
3.850	1.04E-01	6.48E-03	3.24E-03	2.60E-03
3.921	1.04E-01	6.45E-03	3.23E-03	2.48E-03
3.993	1.04E-01	6.42E-03	3.21E-03	2.36E-03
4.060	1.04E-01	6.40E-03	3.20E-03	2.24E-03
4.151	1.04E-01	6.36E-03	3.18E-03	2.07E-03
4.238	1.04E-01	6.32E-03	3.16E-03	1.91E-03
4.288	1.04E-01	6.30E-03	3.15E-03	1.81E-03
4.351	1.04E-01	6.27E-03	3.14E-03	1.69E-03
4.413	1.04E-01	6.24E-03	3.12E-03	1.57E-03
4.465	1.04E-01	6.22E-03	3.11E-03	1.47E-03
4.517	1.04E-01	6.20E-03	3.10E-03	1.37E-03
4.571	1.04E-01	6.17E-03	3.09E-03	1.27E-03
4.627	1.04E-01	6.15E-03	3.08E-03	1.16E-03
4.671	1.04E-01	6.13E-03	3.07E-03	1.08E-03
2.957	1.04E-01	5.65E-03	2.83E-03	3.89E-03
2.989	1.04E-01	5.63E-03	2.81E-03	3.76E-03
3.031	1.04E-01	5.60E-03	2.80E-03	3.63E-03
3.078	1.04E-01	5.58E-03	2.79E-03	3.48E-03
3.122	1.04E-01	5.55E-03	2.78E-03	3.36E-03
3.172	1.04E-01	5.53E-03	2.76E-03	3.23E-03
3.225	1.04E-01	5.51E-03	2.75E-03	3.11E-03
3.288	1.04E-01	5.48E-03	2.74E-03	2.98E-03
3.389	1.04E-01	5.45E-03	2.72E-03	2.80E-03
3.431	1.04E-01	5.43E-03	2.72E-03	2.73E-03
3.510	1.04E-01	5.41E-03	2.71E-03	2.61E-03
3.639	1.04E-01	5.38E-03	2.69E-03	2.43E-03
3.818	1.04E-01	5.33E-03	2.67E-03	2.19E-03
3.976	1.04E-01	5.29E-03	2.64E-03	1.96E-03
4.178	1.04E-01	5.23E-03	2.62E-03	1.68E-03
4.241	1.04E-01	5.21E-03	2.61E-03	1.59E-03
4.318	1.04E-01	5.19E-03	2.60E-03	1.47E-03
4.397	1.04E-01	5.17E-03	2.58E-03	1.34E-03
4.460	1.04E-01	5.15E-03	2.57E-03	1.24E-03
4.543	1.04E-01	5.12E-03	2.56E-03	1.11E-03
2.996	2.04E-01	4.92E-03	2.46E-03	3.52E-03
3.036	2.04E-01	4.90E-03	2.45E-03	3.40E-03
3.078	2.03E-01	4.87E-03	2.44E-03	3.27E-03
3.099	2.03E-01	4.86E-03	2.43E-03	3.21E-03
3.124	2.03E-01	4.85E-03	2.43E-03	3.15E-03

TABLE IV-4 (Continued)

3.147	2.03E-01	4.84E-03	2.42E-03	3.09E-03
3.177	2.03E-01	4.83E-03	2.41E-03	3.02E-03
3.228	2.03E-01	4.81E-03	2.40E-03	2.90E-03
3.260	2.03E-01	4.80E-03	2.40E-03	2.84E-03
3.289	2.03E-01	4.79E-03	2.39E-03	2.78E-03
3.323	2.03E-01	4.78E-03	2.39E-03	2.72E-03
3.395	2.03E-01	4.76E-03	2.38E-03	2.60E-03
3.433	2.03E-01	4.75E-03	2.37E-03	2.55E-03
3.473	2.03E-01	4.74E-03	2.37E-03	2.49E-03
3.556	2.03E-01	4.72E-03	2.36E-03	2.38E-03
3.608	2.03E-01	4.70E-03	2.35E-03	2.32E-03
3.705	2.03E-01	4.68E-03	2.34E-03	2.20E-03
3.759	2.03E-01	4.67E-03	2.34E-03	2.14E-03
3.850	2.03E-01	4.66E-03	2.33E-03	2.04E-03
3.904	2.03E-01	4.64E-03	2.32E-03	1.98E-03
3.957	2.03E-01	4.63E-03	2.32E-03	1.91E-03
4.021	2.03E-01	4.62E-03	2.31E-03	1.84E-03
4.087	2.03E-01	4.61E-03	2.30E-03	1.76E-03
4.170	2.03E-01	4.59E-03	2.29E-03	1.65E-03
4.253	2.03E-01	4.57E-03	2.28E-03	1.54E-03
4.308	2.03E-01	4.55E-03	2.28E-03	1.46E-03
4.375	2.03E-01	4.54E-03	2.27E-03	1.37E-03
4.460	2.03E-01	4.52E-03	2.26E-03	1.26E-03
4.543	2.03E-01	4.50E-03	2.25E-03	1.14E-03
4.721	2.03E-01	4.45E-03	2.23E-03	9.02E-04
3.069	2.03E-01	5.14E-03	2.57E-03	3.43E-03
3.112	2.03E-01	5.12E-03	2.56E-03	3.31E-03
3.164	2.03E-01	5.09E-03	2.55E-03	3.18E-03
3.217	2.03E-01	5.07E-03	2.53E-03	3.06E-03
3.277	2.03E-01	5.05E-03	2.52E-03	2.94E-03
3.346	2.03E-01	5.02E-03	2.51E-03	2.81E-03
3.419	2.03E-01	5.00E-03	2.50E-03	2.70E-03
3.500	2.03E-01	4.98E-03	2.49E-03	2.58E-03
3.592	2.03E-01	4.96E-03	2.48E-03	2.46E-03
3.692	2.03E-01	4.93E-03	2.47E-03	2.34E-03
3.835	2.03E-01	4.90E-03	2.45E-03	2.18E-03
3.937	2.03E-01	4.88E-03	2.44E-03	2.06E-03
4.031	2.03E-01	4.86E-03	2.43E-03	1.95E-03
4.123	2.03E-01	4.84E-03	2.42E-03	1.83E-03
4.216	2.03E-01	4.82E-03	2.41E-03	1.71E-03
4.248	2.03E-01	4.81E-03	2.40E-03	1.67E-03
4.277	2.03E-01	4.80E-03	2.40E-03	1.61E-03
4.378	2.03E-01	4.78E-03	2.39E-03	1.49E-03
4.448	2.03E-01	4.76E-03	2.38E-03	1.38E-03
4.512	2.03E-01	4.74E-03	2.37E-03	1.29E-03
4.561	2.03E-01	4.73E-03	2.36E-03	1.22E-03
4.611	2.03E-01	4.71E-03	2.36E-03	1.15E-03
4.661	2.03E-01	4.70E-03	2.35E-03	1.08E-03
4.714	2.03E-01	4.69E-03	2.34E-03	1.01E-03
4.767	2.03E-01	4.65E-03	2.32E-03	8.00E-04

TABLE IV-4 (Continued)

4.823	2.03E-01	4.66E-03	2.33E-03	8.67E-04
4.882	2.03E-01	4.65E-03	2.32E-03	7.95E-04
4.944	2.03E-01	4.63E-03	2.32E-03	7.18E-04
5.013	2.03E-01	4.62E-03	2.31E-03	6.44E-04
3.353	2.53E-01	5.60E-03	2.80E-03	3.08E-03
3.425	2.53E-01	5.58E-03	2.79E-03	2.97E-03
3.529	2.53E-01	5.55E-03	2.77E-03	2.82E-03
3.606	2.53E-01	5.53E-03	2.76E-03	2.72E-03
3.704	2.53E-01	5.50E-03	2.75E-03	2.59E-03
3.802	2.53E-01	5.48E-03	2.74E-03	2.48E-03
3.905	2.53E-01	5.45E-03	2.73E-03	2.35E-03
3.998	2.53E-01	5.43E-03	2.71E-03	2.23E-03
4.090	2.53E-01	5.40E-03	2.70E-03	2.11E-03
4.171	2.53E-01	5.38E-03	2.69E-03	2.00E-03
4.249	2.53E-01	5.36E-03	2.68E-03	1.88E-03
4.325	2.53E-01	5.33E-03	2.67E-03	1.77E-03
4.401	2.53E-01	5.31E-03	2.66E-03	1.66E-03
4.471	2.53E-01	5.29E-03	2.64E-03	1.54E-03
4.538	2.53E-01	5.27E-03	2.63E-03	1.43E-03
4.611	2.53E-01	5.24E-03	2.62E-03	1.32E-03
4.682	2.53E-01	5.22E-03	2.61E-03	1.21E-03
4.764	2.53E-01	5.19E-03	2.60E-03	1.09E-03
4.828	2.53E-01	5.18E-03	2.59E-03	9.92E-04
4.897	2.53E-01	5.16E-03	2.58E-03	8.93E-04
4.935	2.53E-01	5.15E-03	2.57E-03	8.47E-04
4.973	2.53E-01	5.14E-03	2.57E-03	7.96E-04
5.013	2.53E-01	5.13E-03	2.56E-03	7.48E-04
5.060	2.53E-01	5.12E-03	2.56E-03	6.95E-04
5.107	2.53E-01	5.10E-03	2.55E-03	6.39E-04
5.157	2.53E-01	5.09E-03	2.55E-03	5.91E-04
5.208	2.53E-01	5.08E-03	2.54E-03	5.41E-04
5.262	2.53E-01	5.07E-03	2.54E-03	4.90E-04
5.321	2.53E-01	5.06E-03	2.53E-03	4.40E-04
5.352	2.53E-01	5.06E-03	2.53E-03	4.15E-04
3.620	2.53E-01	5.40E-03	2.70E-03	2.68E-03
3.724	2.53E-01	5.38E-03	2.69E-03	2.55E-03
3.877	2.53E-01	5.34E-03	2.67E-03	2.37E-03
4.036	2.53E-01	5.30E-03	2.65E-03	2.19E-03
4.137	2.53E-01	5.28E-03	2.64E-03	2.07E-03
4.278	2.53E-01	5.24E-03	2.62E-03	1.88E-03
4.401	2.53E-01	5.21E-03	2.60E-03	1.71E-03
4.518	2.53E-01	5.17E-03	2.59E-03	1.53E-03
4.560	2.53E-01	5.16E-03	2.58E-03	1.47E-03
4.632	2.53E-01	5.14E-03	2.57E-03	1.36E-03
4.711	2.53E-01	5.12E-03	2.56E-03	1.24E-03
4.790	2.53E-01	5.09E-03	2.55E-03	1.13E-03
4.828	2.53E-01	5.32E-03	2.66E-03	2.24E-03
4.907	2.53E-01	5.06E-03	2.53E-03	9.63E-04
4.988	2.53E-01	5.04E-03	2.52E-03	8.55E-04
5.077	2.52E-01	5.02E-03	2.51E-03	7.44E-04

TABLE IV-4 (Continued)

	5.113	2.52E-01	5.01E-03	2.50E-03	6.89E-04
	5.177	2.52E-01	5.00E-03	2.50E-03	6.35E-04
	5.223	2.52E-01	4.98E-03	2.49E-03	5.81E-04
	5.323	2.52E-01	4.97E-03	2.48E-03	4.97E-04
	5.409	2.52E-01	4.95E-03	2.48E-03	4.25E-04
	5.539	2.52E-01	4.94E-03	2.47E-03	3.33E-04
	5.660	2.52E-01	4.92E-03	2.46E-03	2.63E-04
	5.802	2.52E-01	4.91E-03	2.45E-03	1.92E-04
20	3.893	1.26E-02	8.36E-03	4.18E-03	2.57E-03
	3.919	1.26E-02	8.34E-03	4.17E-03	2.49E-03
	3.940	1.26E-02	8.33E-03	4.16E-03	2.43E-03
	3.961	1.26E-02	8.31E-03	4.15E-03	2.37E-03
	3.986	1.26E-02	8.29E-03	4.14E-03	2.30E-03
	4.011	1.26E-02	8.27E-03	4.14E-03	2.23E-03
	4.033	1.26E-02	8.25E-03	4.13E-03	2.17E-03
	4.057	1.26E-02	8.23E-03	4.12E-03	2.11E-03
	4.082	1.26E-02	8.22E-03	4.11E-03	2.04E-03
	4.107	1.26E-02	8.20E-03	4.10E-03	1.97E-03
	4.129	1.26E-02	8.18E-03	4.09E-03	1.91E-03
	4.155	1.26E-02	8.16E-03	4.08E-03	1.85E-03
	4.178	1.26E-02	8.15E-03	4.07E-03	1.79E-03
	3.516	1.26E-02	5.86E-03	2.93E-03	2.60E-03
	3.534	1.26E-02	5.86E-03	2.93E-03	2.56E-03
	3.569	1.26E-02	5.84E-03	2.92E-03	2.49E-03
	3.603	1.26E-02	5.83E-03	2.91E-03	2.43E-03
	3.637	1.26E-02	5.82E-03	2.91E-03	2.36E-03
	3.671	1.26E-02	5.80E-03	2.90E-03	2.29E-03
	3.700	1.26E-02	5.79E-03	2.90E-03	2.23E-03
	3.735	1.26E-02	5.78E-03	2.89E-03	2.17E-03
	3.769	1.26E-02	5.77E-03	2.88E-03	2.10E-03
	3.833	1.26E-02	5.74E-03	2.87E-03	1.98E-03
	3.868	1.26E-02	5.73E-03	2.86E-03	1.91E-03
	3.902	1.26E-02	5.72E-03	2.86E-03	1.84E-03
	3.964	1.26E-02	5.69E-03	2.85E-03	1.72E-03
	4.031	1.25E-02	5.67E-03	2.83E-03	1.60E-03
	4.164	1.25E-02	5.62E-03	2.81E-03	1.35E-03
	4.233	1.25E-02	5.59E-03	2.80E-03	1.23E-03
	4.307	1.25E-02	5.57E-03	2.79E-03	1.11E-03
	4.384	1.25E-02	5.55E-03	2.77E-03	9.82E-04
	4.465	1.25E-02	5.52E-03	2.76E-03	8.62E-04
	4.550	1.25E-02	5.50E-03	2.75E-03	7.47E-04
	3.782	5.25E-02	5.84E-03	2.92E-03	2.48E-03
	3.801	5.25E-02	5.83E-03	2.92E-03	2.45E-03
	3.840	5.25E-02	5.82E-03	2.91E-03	2.39E-03
	3.877	5.25E-02	5.81E-03	2.90E-03	2.32E-03
	3.914	5.25E-02	5.80E-03	2.90E-03	2.27E-03
	3.951	5.25E-02	5.78E-03	2.89E-03	2.21E-03
	3.991	5.25E-02	5.77E-03	2.88E-03	2.14E-03
	4.025	5.25E-02	5.76E-03	2.88E-03	2.08E-03
	4.062	5.25E-02	5.75E-03	2.87E-03	2.02E-03

TABLE IV-4 (Continued)

4.097	5.25E-02	5.73E-03	2.87E-03	1.97E-03
4.136	5.25E-02	5.72E-03	2.86E-03	1.90E-03
4.203	5.25E-02	5.70E-03	2.85E-03	1.79E-03
4.274	5.24E-02	5.67E-03	2.84E-03	1.67E-03
4.345	5.24E-02	5.65E-03	2.82E-03	1.55E-03
3.948	5.26E-02	6.91E-03	3.46E-03	2.62E-03
3.974	5.26E-02	6.90E-03	3.45E-03	2.58E-03
4.002	5.26E-02	6.89E-03	3.44E-03	2.52E-03
4.037	5.26E-02	6.87E-03	3.43E-03	2.46E-03
4.070	5.26E-02	6.85E-03	3.43E-03	2.40E-03
4.102	5.26E-02	6.84E-03	3.42E-03	2.34E-03
4.133	5.26E-02	6.82E-03	3.41E-03	2.28E-03
4.164	5.26E-02	6.81E-03	3.40E-03	2.22E-03
4.195	5.26E-02	6.80E-03	3.40E-03	2.16E-03
4.227	5.26E-02	6.78E-03	3.39E-03	2.10E-03
4.258	5.26E-02	6.77E-03	3.38E-03	2.04E-03
4.320	5.26E-02	6.74E-03	3.37E-03	1.92E-03
4.381	5.26E-02	6.71E-03	3.35E-03	1.80E-03
3.682	1.03E-01	7.00E-03	3.50E-03	3.04E-03
3.744	1.03E-01	6.97E-03	3.48E-03	2.92E-03
3.801	1.03E-01	6.94E-03	3.47E-03	2.80E-03
3.838	1.03E-01	6.92E-03	3.46E-03	2.73E-03
3.873	1.03E-01	6.90E-03	3.45E-03	2.65E-03
3.910	1.03E-01	6.88E-03	3.44E-03	2.57E-03
3.977	1.03E-01	6.85E-03	3.42E-03	2.43E-03
4.021	1.03E-01	6.82E-03	3.41E-03	2.33E-03
4.070	1.03E-01	6.80E-03	3.40E-03	2.22E-03
4.117	1.03E-01	6.77E-03	3.39E-03	2.12E-03
4.217	1.03E-01	6.72E-03	3.36E-03	1.89E-03
4.294	1.03E-01	6.68E-03	3.34E-03	1.72E-03
3.032	1.04E-01	6.67E-03	3.33E-03	4.22E-03
3.045	1.04E-01	6.66E-03	3.33E-03	4.18E-03
3.061	1.04E-01	6.65E-03	3.32E-03	4.13E-03
3.083	1.04E-01	6.63E-03	3.32E-03	4.05E-03
3.092	1.04E-01	6.63E-03	3.31E-03	4.03E-03
3.105	1.04E-01	6.62E-03	3.31E-03	3.99E-03
3.129	1.04E-01	6.60E-03	3.30E-03	3.92E-03
3.150	1.04E-01	6.59E-03	3.30E-03	3.86E-03
3.177	1.04E-01	6.57E-03	3.29E-03	3.79E-03
3.227	1.04E-01	6.55E-03	3.27E-03	3.67E-03
3.282	1.04E-01	6.52E-03	3.26E-03	3.54E-03
3.311	1.04E-01	6.50E-03	3.25E-03	3.48E-03
3.370	1.04E-01	6.48E-03	3.24E-03	3.35E-03
3.437	1.04E-01	6.45E-03	3.22E-03	3.22E-03
3.499	1.04E-01	6.42E-03	3.21E-03	3.10E-03
3.567	1.04E-01	6.39E-03	3.20E-03	2.97E-03
3.631	1.04E-01	6.37E-03	3.18E-03	2.86E-03
3.699	1.04E-01	6.34E-03	3.17E-03	2.73E-03
3.763	1.04E-01	6.31E-03	3.16E-03	2.61E-03
3.826	1.04E-01	6.29E-03	3.14E-03	2.49E-03

TABLE IV-4 (Continued)

3.887	1.04E-01	6.26E-03	3.13E-03	2.38E-03
3.937	1.04E-01	6.23E-03	3.12E-03	2.26E-03
4.094	1.04E-01	6.17E-03	3.08E-03	1.97E-03
3.048	2.04E-01	6.02E-03	3.01E-03	4.02E-03
3.076	2.04E-01	6.00E-03	3.00E-03	3.93E-03
3.101	2.04E-01	5.98E-03	2.99E-03	3.85E-03
3.120	2.04E-01	5.97E-03	2.99E-03	3.80E-03
3.140	2.04E-01	5.96E-03	2.98E-03	3.74E-03
3.162	2.04E-01	5.95E-03	2.97E-03	3.68E-03
3.208	2.04E-01	5.92E-03	2.96E-03	3.56E-03
3.257	2.04E-01	5.89E-03	2.95E-03	3.44E-03
3.312	2.04E-01	5.87E-03	2.93E-03	3.32E-03
3.372	2.04E-01	5.84E-03	2.92E-03	3.20E-03
3.435	2.04E-01	5.82E-03	2.91E-03	3.08E-03
3.503	2.04E-01	5.79E-03	2.90E-03	2.96E-03
3.571	2.04E-01	5.77E-03	2.88E-03	2.85E-03
3.637	2.04E-01	5.75E-03	2.87E-03	2.74E-03
3.722	2.04E-01	5.72E-03	2.86E-03	2.61E-03
3.782	2.04E-01	5.70E-03	2.85E-03	2.51E-03
3.854	2.04E-01	5.67E-03	2.84E-03	2.40E-03
3.926	2.04E-01	5.65E-03	2.82E-03	2.28E-03
3.991	2.04E-01	5.62E-03	2.81E-03	2.17E-03
4.115	2.04E-01	5.58E-03	2.79E-03	1.95E-03
4.228	2.04E-01	5.53E-03	2.77E-03	1.75E-03
4.397	2.04E-01	5.47E-03	2.73E-03	1.44E-03
4.508	2.04E-01	5.43E-03	2.71E-03	1.25E-03
2.948	2.04E-01	5.69E-03	2.84E-03	4.16E-03
2.960	2.04E-01	5.68E-03	2.84E-03	4.11E-03
2.975	2.04E-01	5.66E-03	2.83E-03	4.05E-03
2.988	2.04E-01	5.65E-03	2.83E-03	4.00E-03
3.008	2.04E-01	5.64E-03	2.82E-03	3.93E-03
3.028	2.04E-01	5.63E-03	2.81E-03	3.85E-03
3.042	2.04E-01	5.62E-03	2.81E-03	3.81E-03
3.060	2.04E-01	5.60E-03	2.80E-03	3.75E-03
3.079	2.04E-01	5.59E-03	2.80E-03	3.69E-03
3.108	2.04E-01	5.57E-03	2.79E-03	3.60E-03
3.164	2.04E-01	5.54E-03	2.77E-03	3.44E-03
3.211	2.04E-01	5.52E-03	2.76E-03	3.33E-03
3.290	2.04E-01	5.48E-03	2.74E-03	3.15E-03
3.377	2.04E-01	5.45E-03	2.72E-03	2.98E-03
3.442	2.04E-01	5.43E-03	2.71E-03	2.86E-03
3.548	2.04E-01	5.39E-03	2.70E-03	2.69E-03
3.709	2.04E-01	5.34E-03	2.67E-03	2.44E-03
3.970	2.04E-01	5.26E-03	2.63E-03	2.05E-03
4.086	2.04E-01	5.22E-03	2.61E-03	1.86E-03
4.173	2.04E-01	5.20E-03	2.60E-03	1.72E-03
4.348	2.04E-01	5.14E-03	2.57E-03	1.43E-03
4.364	2.04E-01	5.13E-03	2.57E-03	1.41E-03
4.380	2.04E-01	5.13E-03	2.56E-03	1.38E-03
4.396	2.04E-01	5.12E-03	2.56E-03	1.36E-03

TABLE IV-4 (Continued)

2.920	2.54E-01	5.23E-03	2.62E-03	4.11E-03
2.949	2.54E-01	5.21E-03	2.60E-03	3.99E-03
2.955	2.54E-01	5.20E-03	2.60E-03	3.97E-03
2.966	2.54E-01	5.20E-03	2.60E-03	3.92E-03
2.983	2.54E-01	5.18E-03	2.59E-03	3.86E-03
3.003	2.54E-01	5.17E-03	2.59E-03	3.79E-03
3.018	2.54E-01	5.16E-03	2.58E-03	3.73E-03
3.039	2.54E-01	5.15E-03	2.57E-03	3.66E-03
3.073	2.54E-01	5.13E-03	2.56E-03	3.55E-03
3.093	2.54E-01	5.12E-03	2.56E-03	3.49E-03
3.113	2.54E-01	5.11E-03	2.55E-03	3.43E-03
3.201	2.54E-01	5.06E-03	2.53E-03	3.20E-03
3.256	2.54E-01	5.04E-03	2.52E-03	3.07E-03
3.307	2.54E-01	5.02E-03	2.51E-03	2.96E-03
3.370	2.54E-01	5.00E-03	2.50E-03	2.84E-03
3.424	2.54E-01	4.98E-03	2.49E-03	2.72E-03
3.514	2.54E-01	4.95E-03	2.48E-03	2.60E-03
3.671	2.54E-01	4.91E-03	2.45E-03	2.35E-03
3.781	2.54E-01	4.88E-03	2.44E-03	2.22E-03
4.056	2.54E-01	4.81E-03	2.41E-03	1.83E-03
4.262	2.54E-01	4.76E-03	2.38E-03	1.52E-03
2.919	2.54E-01	5.38E-03	2.69E-03	4.14E-03
2.933	2.54E-01	5.37E-03	2.69E-03	4.08E-03
2.958	2.54E-01	5.35E-03	2.68E-03	3.98E-03
2.985	2.54E-01	5.33E-03	2.67E-03	3.88E-03
3.014	2.54E-01	5.32E-03	2.66E-03	3.78E-03
3.037	2.54E-01	5.30E-03	2.65E-03	3.70E-03
3.066	2.54E-01	5.28E-03	2.64E-03	3.61E-03
3.128	2.54E-01	5.25E-03	2.62E-03	3.42E-03
3.165	2.54E-01	5.23E-03	2.61E-03	3.33E-03
3.303	2.54E-01	5.17E-03	2.58E-03	3.01E-03
3.382	2.54E-01	5.14E-03	2.57E-03	2.86E-03
3.442	2.54E-01	5.12E-03	2.56E-03	2.75E-03
3.545	2.54E-01	5.09E-03	2.55E-03	2.59E-03
3.672	2.54E-01	5.06E-03	2.53E-03	2.40E-03
3.914	2.54E-01	4.99E-03	2.50E-03	2.06E-03
4.077	2.54E-01	4.95E-03	2.47E-03	1.83E-03
4.240	2.54E-01	4.90E-03	2.45E-03	1.59E-03
3.315	1.27E-02	5.41E-03	2.71E-03	2.62E-03
3.358	1.27E-02	5.39E-03	2.70E-03	2.52E-03
3.434	1.26E-02	5.37E-03	2.68E-03	2.36E-03
3.488	1.26E-02	5.34E-03	2.67E-03	2.25E-03
3.556	1.26E-02	5.32E-03	2.66E-03	2.11E-03
3.601	1.26E-02	5.30E-03	2.65E-03	2.02E-03
3.650	1.26E-02	5.29E-03	2.64E-03	1.92E-03
3.717	1.26E-02	5.26E-03	2.63E-03	1.80E-03
3.776	1.26E-02	5.24E-03	2.62E-03	1.68E-03
3.826	1.26E-02	5.23E-03	2.61E-03	1.59E-03
3.877	1.26E-02	5.21E-03	2.60E-03	1.50E-03
3.935	1.25E-02	5.19E-03	2.60E-03	1.39E-03

TABLE IV-4 (Continued)

3.988	1.25E-02	5.18E-03	2.59E-03	1.30E-03
3.999	1.25E-02	5.17E-03	2.59E-03	1.29E-03
4.029	1.25E-02	5.16E-03	2.58E-03	1.24E-03
4.063	1.25E-02	5.15E-03	2.58E-03	1.18E-03
3.351	1.26E-02	5.51E-03	2.75E-03	2.54E-03
3.425	1.26E-02	5.48E-03	2.74E-03	2.37E-03
3.477	1.26E-02	5.46E-03	2.73E-03	2.26E-03
3.534	1.26E-02	5.43E-03	2.72E-03	2.14E-03
3.590	1.26E-02	5.41E-03	2.71E-03	2.02E-03
3.648	1.26E-02	5.39E-03	2.70E-03	1.91E-03
3.702	1.26E-02	5.37E-03	2.69E-03	1.80E-03
3.762	1.26E-02	5.35E-03	2.68E-03	1.68E-03
3.817	1.25E-02	5.33E-03	2.67E-03	1.58E-03
3.865	1.25E-02	5.31E-03	2.66E-03	1.49E-03
3.924	1.25E-02	5.29E-03	2.65E-03	1.38E-03
3.976	1.25E-02	5.28E-03	2.64E-03	1.29E-03
4.036	1.25E-02	5.26E-03	2.63E-03	1.19E-03
4.092	1.25E-02	5.24E-03	2.62E-03	1.10E-03
4.138	1.25E-02	5.23E-03	2.61E-03	1.03E-03
4.166	1.25E-02	5.22E-03	2.61E-03	9.88E-04
4.205	1.25E-02	5.21E-03	2.61E-03	9.32E-04
4.256	1.25E-02	5.20E-03	2.60E-03	8.61E-04
3.409	5.27E-02	5.16E-03	2.58E-03	2.57E-03
3.502	5.26E-02	5.12E-03	2.56E-03	2.38E-03
3.611	5.26E-02	5.09E-03	2.54E-03	2.18E-03
3.723	5.26E-02	5.05E-03	2.52E-03	1.97E-03
3.839	5.26E-02	5.01E-03	2.50E-03	1.77E-03
3.905	5.26E-02	4.99E-03	2.49E-03	1.65E-03
3.973	5.26E-02	4.97E-03	2.48E-03	1.53E-03
4.059	5.25E-02	4.94E-03	2.47E-03	1.39E-03
4.116	5.25E-02	4.92E-03	2.46E-03	1.30E-03
4.161	5.25E-02	4.91E-03	2.45E-03	1.23E-03
4.227	5.25E-02	4.89E-03	2.45E-03	1.13E-03
4.238	5.25E-02	4.89E-03	2.44E-03	1.11E-03
4.282	5.25E-02	4.88E-03	2.44E-03	1.04E-03
4.347	5.25E-02	4.86E-03	2.43E-03	9.55E-04
3.266	5.26E-02	4.74E-03	2.37E-03	2.62E-03
3.280	5.26E-02	4.73E-03	2.37E-03	2.58E-03
3.329	5.26E-02	4.72E-03	2.36E-03	2.48E-03
3.392	5.26E-02	4.70E-03	2.35E-03	2.35E-03
3.449	5.26E-02	4.68E-03	2.34E-03	2.24E-03
3.505	5.26E-02	4.66E-03	2.33E-03	2.14E-03
3.607	5.26E-02	4.63E-03	2.31E-03	1.96E-03
3.653	5.26E-02	4.62E-03	2.31E-03	1.88E-03
3.711	5.26E-02	4.60E-03	2.30E-03	1.79E-03
3.833	5.25E-02	4.57E-03	2.28E-03	1.58E-03
3.921	5.25E-02	4.54E-03	2.27E-03	1.44E-03
3.982	5.25E-02	4.52E-03	2.26E-03	1.34E-03
4.061	5.25E-02	4.50E-03	2.25E-03	1.23E-03
2.851	1.04E-01	5.25E-03	2.62E-03	4.29E-03

TABLE IV-4 (Continued)

2.907	1.04E-01	5.20E-03	2.60E-03	4.02E-03
3.008	1.04E-01	5.13E-03	2.57E-03	3.63E-03
3.030	1.04E-01	5.12E-03	2.56E-03	3.55E-03
3.111	1.04E-01	5.08E-03	2.54E-03	3.30E-03
3.213	1.04E-01	5.03E-03	2.51E-03	3.02E-03
3.311	1.04E-01	4.99E-03	2.49E-03	2.79E-03
3.412	1.04E-01	4.95E-03	2.48E-03	2.58E-03
3.513	1.04E-01	4.92E-03	2.46E-03	2.39E-03
3.628	1.04E-01	4.88E-03	2.44E-03	2.18E-03
3.725	1.04E-01	4.85E-03	2.43E-03	2.01E-03
3.823	1.04E-01	4.82E-03	2.41E-03	1.83E-03
3.927	1.04E-01	4.79E-03	2.39E-03	1.65E-03
4.020	1.04E-01	4.74E-03	2.37E-03	1.39E-03
2.890	1.04E-01	5.55E-03	2.78E-03	4.20E-03
3.011	1.04E-01	5.46E-03	2.73E-03	3.70E-03
3.110	1.04E-01	5.40E-03	2.70E-03	3.37E-03
3.212	1.04E-01	5.35E-03	2.67E-03	3.10E-03
3.315	1.04E-01	5.30E-03	2.65E-03	2.85E-03
3.414	1.04E-01	5.26E-03	2.63E-03	2.63E-03
3.514	1.04E-01	5.22E-03	2.61E-03	2.43E-03
3.610	1.04E-01	5.19E-03	2.59E-03	2.24E-03
3.668	1.04E-01	5.17E-03	2.59E-03	2.14E-03
3.723	1.04E-01	5.15E-03	2.58E-03	2.04E-03
3.830	1.04E-01	5.12E-03	2.56E-03	1.84E-03
3.928	1.04E-01	5.08E-03	2.54E-03	1.67E-03
4.059	1.04E-01	5.04E-03	2.52E-03	1.44E-03
4.104	1.04E-01	5.03E-03	2.51E-03	1.36E-03
2.941	2.04E-01	5.49E-03	2.74E-03	4.08E-03
3.065	2.04E-01	5.40E-03	2.70E-03	3.62E-03
3.160	2.04E-01	5.34E-03	2.67E-03	3.33E-03
3.262	2.04E-01	5.29E-03	2.64E-03	3.07E-03
3.362	2.04E-01	5.25E-03	2.62E-03	2.85E-03
3.463	2.04E-01	5.21E-03	2.60E-03	2.65E-03
3.563	2.04E-01	5.17E-03	2.59E-03	2.47E-03
3.659	2.04E-01	5.14E-03	2.57E-03	2.30E-03
3.759	2.04E-01	5.11E-03	2.55E-03	2.13E-03
3.861	2.04E-01	5.07E-03	2.54E-03	1.96E-03
3.957	2.04E-01	5.04E-03	2.52E-03	1.80E-03
4.083	2.04E-01	5.00E-03	2.50E-03	1.58E-03
4.247	2.04E-01	4.95E-03	2.47E-03	1.32E-03
2.862	2.04E-01	4.90E-03	2.45E-03	4.13E-03
2.868	2.04E-01	4.90E-03	2.45E-03	4.10E-03
2.964	2.04E-01	4.83E-03	2.41E-03	3.69E-03
3.066	2.04E-01	4.76E-03	2.38E-03	3.32E-03
3.166	2.04E-01	4.71E-03	2.36E-03	3.03E-03
3.172	2.04E-01	4.71E-03	2.35E-03	3.01E-03
3.265	2.04E-01	4.67E-03	2.34E-03	2.79E-03
3.305	2.04E-01	4.65E-03	2.33E-03	2.70E-03
3.371	2.04E-01	4.63E-03	2.32E-03	2.57E-03
3.471	2.04E-01	4.60E-03	2.30E-03	2.38E-03

TABLE IV-4 (Continued)

3.586	2.04E-01	4.57E-03	2.28E-03	2.19E-03
3.702	2.04E-01	4.54E-03	2.27E-03	2.02E-03
3.840	2.04E-01	4.50E-03	2.25E-03	1.81E-03
3.998	2.04E-01	4.46E-03	2.23E-03	1.57E-03
2.979	2.54E-01	5.69E-03	2.84E-03	4.07E-03
3.015	2.54E-01	5.66E-03	2.83E-03	3.94E-03
3.097	2.54E-01	5.60E-03	2.80E-03	3.66E-03
3.197	2.54E-01	5.55E-03	2.77E-03	3.37E-03
3.295	2.54E-01	5.50E-03	2.75E-03	3.13E-03
3.389	2.54E-01	5.46E-03	2.73E-03	2.93E-03
3.489	2.54E-01	5.42E-03	2.71E-03	2.74E-03
3.583	2.54E-01	5.39E-03	2.69E-03	2.57E-03
3.686	2.54E-01	5.35E-03	2.68E-03	2.39E-03
3.779	2.54E-01	5.32E-03	2.66E-03	2.23E-03
3.884	2.54E-01	5.29E-03	2.64E-03	2.06E-03
3.980	2.54E-01	5.25E-03	2.63E-03	1.90E-03
4.092	2.54E-01	5.22E-03	2.61E-03	1.71E-03
4.223	2.54E-01	5.17E-03	2.59E-03	1.49E-03
3.028	2.54E-01	5.99E-03	3.00E-03	4.06E-03
3.079	2.54E-01	5.96E-03	2.98E-03	3.88E-03
3.178	2.54E-01	5.89E-03	2.95E-03	3.58E-03
3.281	2.54E-01	5.84E-03	2.92E-03	3.32E-03
3.378	2.54E-01	5.79E-03	2.90E-03	3.10E-03
3.477	2.54E-01	5.75E-03	2.88E-03	2.90E-03
3.577	2.54E-01	5.71E-03	2.86E-03	2.71E-03
3.679	2.54E-01	5.67E-03	2.84E-03	2.52E-03
3.777	2.54E-01	5.63E-03	2.82E-03	2.34E-03
3.907	2.54E-01	5.58E-03	2.79E-03	2.10E-03
4.003	2.54E-01	5.55E-03	2.77E-03	1.93E-03
4.094	2.54E-01	5.51E-03	2.76E-03	1.76E-03
4.322	2.54E-01	5.42E-03	2.71E-03	1.35E-03
20 4.400	0.00E+00	1.55E-02	2.69E-03	1.08E-03
4.412	0.00E+00	1.55E-02	2.69E-03	1.06E-03
4.425	0.00E+00	1.55E-02	2.68E-03	1.04E-03
4.496	0.00E+00	1.55E-02	2.65E-03	9.46E-04
4.531	0.00E+00	1.54E-02	2.64E-03	9.01E-04
4.591	0.00E+00	1.54E-02	2.62E-03	8.28E-04
4.651	0.00E+00	1.54E-02	2.60E-03	7.60E-04
4.456	0.00E+00	1.61E-02	2.99E-03	1.06E-03
4.489	0.00E+00	1.61E-02	2.97E-03	1.01E-03
4.542	0.00E+00	1.61E-02	2.95E-03	9.32E-04
4.567	0.00E+00	1.60E-02	2.93E-03	8.99E-04
3.598	0.00E+00	2.05E-01	2.60E-03	2.57E-03
3.668	0.00E+00	2.05E-01	2.59E-03	2.47E-03
3.685	0.00E+00	2.05E-01	2.59E-03	2.44E-03
3.790	0.00E+00	2.05E-01	2.57E-03	2.29E-03
3.888	0.00E+00	2.05E-01	2.55E-03	2.14E-03
3.901	0.00E+00	2.05E-01	2.55E-03	2.12E-03
3.966	0.00E+00	2.04E-01	2.54E-03	2.02E-03
4.082	0.00E+00	2.04E-01	2.52E-03	1.84E-03

TABLE IV-4 (Continued)

4.192	0.00E+00	2.04E-01	2.50E-03	1.66E-03
4.276	0.00E+00	2.04E-01	2.49E-03	1.53E-03
3.755	0.00E+00	2.06E-01	3.02E-03	2.72E-03
3.802	0.00E+00	2.06E-01	3.01E-03	2.64E-03
3.820	0.00E+00	2.06E-01	3.01E-03	2.61E-03
3.900	0.00E+00	2.06E-01	2.99E-03	2.47E-03
3.989	0.00E+00	2.06E-01	2.98E-03	2.32E-03
4.099	0.00E+00	2.05E-01	2.95E-03	2.12E-03
4.181	0.00E+00	2.05E-01	2.93E-03	1.97E-03
4.279	0.00E+00	2.05E-01	2.91E-03	1.78E-03
4.377	0.00E+00	2.05E-01	2.89E-03	1.59E-03
30 4.332	0.00E+00	1.53E-02	2.57E-03	1.04E-03
4.340	0.00E+00	1.53E-02	2.57E-03	1.03E-03
4.358	0.00E+00	1.53E-02	2.56E-03	1.01E-03
4.370	0.00E+00	1.53E-02	2.56E-03	9.96E-04
4.393	0.00E+00	1.53E-02	2.55E-03	9.67E-04
4.430	0.00E+00	1.52E-02	2.54E-03	9.23E-04
4.458	0.00E+00	1.52E-02	2.53E-03	8.91E-04
4.490	0.00E+00	1.52E-02	2.52E-03	8.57E-04
4.547	0.00E+00	1.52E-02	2.50E-03	7.95E-04
4.128	0.00E+00	1.45E-02	2.16E-03	1.06E-03
4.160	0.00E+00	1.45E-02	2.15E-03	1.02E-03
4.226	0.00E+00	1.44E-02	2.14E-03	9.45E-04
4.300	0.00E+00	1.44E-02	2.12E-03	8.63E-04
4.367	0.00E+00	1.44E-02	2.10E-03	7.93E-04
4.375	0.00E+00	1.44E-02	2.10E-03	7.83E-04
4.392	0.00E+00	1.43E-02	2.10E-03	7.69E-04
4.427	0.00E+00	1.43E-02	2.09E-03	7.34E-04
4.464	0.00E+00	1.43E-02	2.08E-03	6.99E-04
4.499	0.00E+00	1.43E-02	2.07E-03	6.67E-04
3.442	0.00E+00	2.05E-01	2.62E-03	2.73E-03
3.481	0.00E+00	2.05E-01	2.61E-03	2.66E-03
3.564	0.00E+00	2.05E-01	2.59E-03	2.51E-03
3.650	0.00E+00	2.05E-01	2.58E-03	2.36E-03
3.760	0.00E+00	2.05E-01	2.56E-03	2.17E-03
3.855	0.00E+00	2.04E-01	2.54E-03	2.01E-03
3.952	0.00E+00	2.04E-01	2.52E-03	1.84E-03
4.055	0.00E+00	2.04E-01	2.51E-03	1.67E-03
4.174	0.00E+00	2.04E-01	2.48E-03	1.46E-03
4.201	0.00E+00	2.04E-01	2.48E-03	1.42E-03
4.255	0.00E+00	2.04E-01	2.47E-03	1.33E-03
4.297	0.00E+00	2.04E-01	2.46E-03	1.26E-03
4.325	0.00E+00	2.03E-01	2.46E-03	1.21E-03
3.281	0.00E+00	2.05E-01	2.32E-03	2.77E-03
3.297	0.00E+00	2.05E-01	2.32E-03	2.73E-03
3.310	0.00E+00	2.05E-01	2.32E-03	2.70E-03
3.351	0.00E+00	2.05E-01	2.31E-03	2.62E-03
3.372	0.00E+00	2.05E-01	2.30E-03	2.57E-03
3.428	0.00E+00	2.04E-01	2.30E-03	2.47E-03
3.460	0.00E+00	2.04E-01	2.29E-03	2.41E-03

TABLE IV-5

PARAMETERS FROM THE FIT OF KINETIC DATA AT 50.0 AND 65.0°C
TO THE DISSOCIATIVE MECHANISM¹

Fit no.	1 ^f	2
b_1^e	0.3	0.3
b_2	0	0
b_3	0.272(0.074)	0.272(0.023)
$\Delta H^\circ g$	118(22)	118(20)
ΔS°	323(67)	323(63)
$k_a^\circ k_1^\circ(50^\circ)$	0	0
$k_a^\circ k_1^\circ(65^\circ)$	0	0
$k_a^\circ(50^\circ)$	0	0
$k_a^\circ(65^\circ)$	0	0
$k_2^\circ(50^\circ)$	1	1
$k_2^\circ(65^\circ)$	1	1
$k_b^\circ k_3^\circ k_h^\circ(50^\circ)$	$2.04 \times 10^{-4} (3.26 \times 10^{-4})$	$5.91 \times 10^{-5} (0.53 \times 10^{-5})$
$k_b^\circ k_3^\circ k_h^\circ(65^\circ)$	$1.30 \times 10^{-5} (0.53 \times 10^{-5})$	$6.15 \times 10^{-4} (1.07 \times 10^{-4})$
$k_b^\circ(50^\circ)$	$589 (9.4 \times 10^6)$	36.9(5.0)
$k_b^\circ(65^\circ)$	$14.4 (5.8 \times 10^4)$	39.2(11.3)
$k_4^\circ(50^\circ)$	15.9(2600)	1
$k_4^\circ(65^\circ)$	0.367(1500)	1
RMSD ^j	6.96×10^{-11}	6.17×10^{-11}

Notes:

i. See Appendix IV-1.

j. Each pointed is weighted by k_{obs} . See page 6, eqn. [6].

TABLE IV-5 (Continued)

Fit no.	3
b_1	0.3
b_2	0
b_3	0.091(0.024)
ΔH°	105(51)
ΔS°	281(157)
$k_a^{\circ}k_1^{\circ}(50^\circ)$	0
$k_a^{\circ}k_1^{\circ}(65^\circ)$	0
$k_a^{\circ}(50^\circ)$	0
$k_a^{\circ}(65^\circ)$	0
$k_2^{\circ}(50^\circ)$	1
$k_2^{\circ}(65^\circ)$	1
$k_b^{\circ}k_3^{\circ}K_h^{\circ}(50^\circ)$	$3.13 \times 10^{-5} (0.23 \times 10^{-5})$
$k_b^{\circ}k_3^{\circ}K_h^{\circ}(65^\circ)$	$3.25 \times 10^{-4} (0.54 \times 10^{-4})$
$k_b^{\circ}(50^\circ)$	0
$k_b^{\circ}(65^\circ)$	0
$k_4^{\circ}(50^\circ)$	1
$k_4^{\circ}(65^\circ)$	1
RMSD	1.14×10^{-10}

TABLE IV-6

PARAMETERS FROM THE FIT OF KINETIC DATA AT 50.0 AND 65.0°C
TO THE INTERCHANGE MECHANISM¹

Fit no.	1 ^f	2
b_1^e	0.3	0.3
b_2	0	0
b_3	0.0900(0.0291)	0.0917(0.0243)
$\Delta H^\circ g$	51.9(260)	99.8(54)
ΔS°	116(803)	266(169)
K_a°	0	0
K_b°	0	0
$k_a^\circ K_a^\circ(50^\circ)$	$1.31 \times 10^{-4} (2.06 \times 10^{-4})$	0
$k_a^\circ K_a^\circ(65^\circ)$	$1.31 \times 10^{-4} (2.21 \times 10^{-4})$	0
$k_b^\circ K_b^\circ K_h^\circ(50^\circ)$	$2.80 \times 10^{-5} (0.48 \times 10^{-5})$	$3.12 \times 10^{-5} (0.23 \times 10^{-5})$
$k_b^\circ K_b^\circ K_h^\circ(65^\circ)$	$2.80 \times 10^{-4} (1.10 \times 10^{-4})$	$3.21 \times 10^{-4} (0.53 \times 10^{-4})$
RMSD ^j	1.14×10^{-10}	1.13×10^{-10}

Fit no.	3
b_1	0.3
b_2	0
b_3	0.526(0.133)
ΔH°	113(52)
ΔS°	302(160)
K_a°	28.8(3.7)
K_b°	36.8(7.2)
$k_a^\circ K_a^\circ(50^\circ)$	0
$k_a^\circ K_a^\circ(65^\circ)$	0
$k_b^\circ K_b^\circ K_h^\circ(50^\circ)$	$3.27 \times 10^{-5} (0.52 \times 10^{-5})$
$k_b^\circ K_b^\circ K_h^\circ(65^\circ)$	$3.30 \times 10^{-4} (0.15 \times 10^{-4})$
RMSD	5.20×10^{-11}

Notes:

i. See Appendix IV-2.

j. Each pointed is weighted by k_{obs} . See page 6, eqn. [6].

TABLE IV-7

PARAMETERS FROM THE FIT OF POTENTIOMETRIC DATA AT 25.0°C

Fit no.	1 ^f	2
b ₁ ^e	0.3	0.3
b ₂	0	0
b ₃	0.673(0.253)	0.794(0.200)
K _h ^o	1.98x10 ⁻⁴ (0.12x10 ⁻⁴)	1.98x10 ⁻⁴ (0.09x10 ⁻⁴)
K _a ^o	0	13.8(2.8)
K _b ^o	0	74.7(16.2)
K _{ap} ^o	0	0
K _{bp} ^o	0	0
RMSD ^j (%)	1.84	1.26
Fit no.	3	4
b ₁	0.3	0.3
b ₂	0	0
b ₃	3.38(3.54)	0.447(2.06)
K _h ^o	1.94x10 ⁻⁴ (0.37x10 ⁻⁴)	1.79x10 ⁻⁴ (0.46x10 ⁻⁴)
K _a ^o	20.4(17.6)	12.1(8.1)
K _b ^o	9.26(74.8)	47.9(167)
K _{ap} ^o	90.0(122)	= K _a ^o
K _{bp} ^o	9.34x10 ⁻³ (107)	= K _b ^o
RMSD	1.28	1.65

Notes:

j. Each data point is weighted by $100/[H][Cl]y_i^2$, i.e., RMSD is a percent. See page 6, eqn. [6].

TABLE IV-7 (Continued)

Fit no.	5
b_1	0.3
b_2	$3.98 \times 10^{-6} (2.16)$
b_3	0.797(8.98)
K_h^o	$1.98 \times 10^{-4} (0.30 \times 10^{-4})$
K_a^o	13.8(3.4)
K_b^o	74.6(203)
K_{ap}^o	0
K_{bp}^o	0
RMSD	1.28

TABLE IV-8

PARAMETERS FROM THE FIT OF pH DATA AT 10, 20, AND 30°C

Fit no.	1 ^f	2
Data Sets	10°	20°
b ₁ ^e	0.3	0.3
b ₂	0	0
b ₃	0.0462(0.0980)	0.205(0.028)
ΔH° _g	9.88x10 ⁻⁵ (1.13x10 ⁻⁵)*	1.55x10 ⁻⁵ (0.05x10 ⁻⁵)*
ΔS°	-	-
K _a ^o	0	0
K _b ^o	0	0
K _{ap} ^o h	0	0
K _{bp} ^o	0	0
RMSD ^j (pH units)	0.199	0.070
Fit no.	3	4
Data Sets	30°	20°,30°
b ₁	0.3	0.3
b ₂	0	0
b ₃	0.307(0.030)	0.256(0.021)
ΔH°	1.81x10 ⁻⁴ (0.05x10 ⁻⁴)*	-0.01(0.005)
ΔS°	-	18500(1580)
K _a ^o	0	0
K _b ^o	0	0
K _{ap} ^o	0	0
K _{bp} ^o	0	0
RMSD	0.077	0.074

Notes:

j. The data is not weighted, i.e., RMSD is linear in pH.

* Value is that of K_h^o.

TABLE IV-8 (Continued)

Fit no.	5	6
Data Sets	20°	30°
b ₁	0.3	0.3
b ₂	0	0
b ₃	0.260(0.046)	0.190(0.035)
ΔH°	1.24x10 ⁻⁴ (0.04x10 ⁻⁴)*	1.87x10 ⁻⁴ (0.05x10 ⁻⁴)*
ΔS°	-	-
K _a ^o	0	0
K _b ^o	8.05(12.4)	17.5(20.7)
K _{ap} ^o	0	0
K _{bp} ^o	0	0
RMSD	0.082	0.072
Fit no.	7	8
Data Sets	C10 ₄ ⁻	ALL
b ₁	0.3	0.3
b ₂	0	0
b ₃	0.389(0.010)	0.134(0.018)
ΔH°	1.07x10 ⁻⁴ (0.02x10 ⁻⁴)(20°)*	33.9(1.6)
ΔS°	1.52x10 ⁻⁴ (0.03x10 ⁻⁴)(30°)*	43.2(5.4)
K _a ^o	0	0
K _b ^o	0	0
K _{ap} ^o	0	0
K _{bp} ^o	0	0
RMSD	0.039	0.148

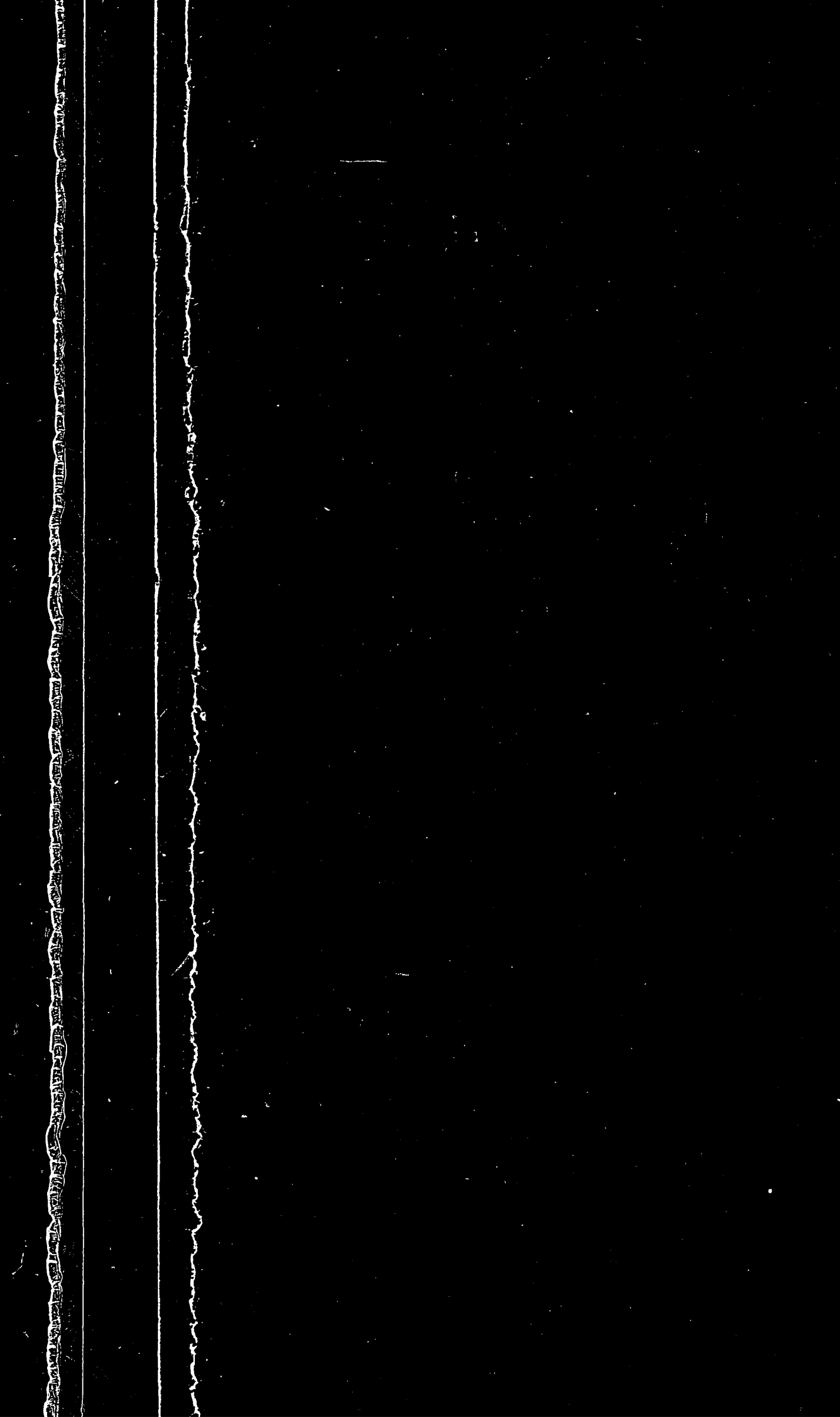


TABLE IV-8 (Continued)

Fit no.	9
Data Sets	ALL
b_1	0.3
b_2	0
b_3	0.052(0.030)
ΔH°	36.2(1.6)
ΔS°	50.9(5.7)
K_a°	0
K_b°	6.56(2.57)
K_{ap}°	0
K_{bp}°	0
RMSD	0.148

TABLE IV-9
PARAMETERS FROM THE COMBINATION FIT OF DATA
TO THE DISSOCIATIVE MECHANISMⁱ

Fit no.	1 ^f	2
b_1^e	0.3	0.3
b_2	0	0
b_3	0.0915(0.0235)	0.0986(0.0226)
$\Delta H^\circ g$	94.8(8.3)	101(3)
ΔS°	249(283)	269(9)
K_a°	0	0
K_b°	0	0
K_{ap}°	0	0
K_{bp}°	0	0
$k_a^\circ k_1^\circ(50^\circ)$	$1.85 \times 10^{-4} (2.10 \times 10^{-4})$	0
$k_a^\circ k_1^\circ(65^\circ)$	$8.05 \times 10^{-5} (15.0 \times 10^{-5})$	0
$k_b^\circ k_3^\circ k_h^\circ(50^\circ)$	$2.65 \times 10^{-5} (0.52 \times 10^{-5})$	$3.06 \times 10^{-5} (0.20 \times 10^{-5})$
$k_b^\circ k_3^\circ k_h^\circ(65^\circ)$	$3.00 \times 10^{-4} (0.28 \times 10^{-4})$	$3.10 \times 10^{-4} (0.22 \times 10^{-4})$
$k_b^\circ(50^\circ)$	0	0
$k_b^\circ(65^\circ)$	0	0
$k_4^\circ(50^\circ)$	1	1
$k_4^\circ(65^\circ)$	1	1
RMSD ^j	0.243	0.241

Notes:

- i. See Appendix IV-1. Fits include potentiometric and kinetic data.
- j. Normalized to the best-fit individual DEL's equal to 1.

TABLE IV-9 (Continued)

Fit no.	3	4
b_1	0.3	0.3
b_2	0	0
b_3	0.0965(0.0202)	0.285(0.033)
ΔH°	101(3)	109(3)
ΔS°	268(8)	294(12)
K_a°	14.2(4.5)	0
K_b°	81.6(21.1)	0
K_{ap}°	0	0
K_{bp}°	0	0
$k_a^\circ k_1^\circ(50^\circ)$	0	0
$k_a^\circ k_1^\circ(65^\circ)$	0	0
$k_b^\circ k_3^\circ K_h^\circ(50^\circ)$	$3.08 \times 10^{-5}(0.18 \times 10^{-5})$	$2.24 \times 10^{-4}(44800 \times 10^{-4})$
$k_b^\circ k_3^\circ K_h^\circ(65^\circ)$	$3.17 \times 10^{-4}(0.19 \times 10^{-4})$	$1.24 \times 10^{-4}(67700 \times 10^{-4})$
$k_b^\circ(50^\circ)$	0	146(2920000)
$k_b^\circ(65^\circ)$	0	8.93(48700)
$k_4^\circ(50^\circ)$	1	3.84(76800)
$k_4^\circ(65^\circ)$	1	0.201(10900)
RMSD	0.215	0.196

TABLE IV-9 (Continued)

Fit no.	5
b_1	0.3
b_2	0
b_3	0.285(0.033)
ΔH°	109(3)
ΔS°	294(12)
K_a°	0
K_b°	0
K_{ap}°	0
K_{bp}°	0
$k_a^\circ k_1^\circ(50^\circ)$	0
$k_a^\circ k_1^\circ(65^\circ)$	0
$k_b^\circ k_3^\circ K_h^\circ(50^\circ)$	$5.83 \times 10^{-5} (0.77 \times 10^{-5})$
$k_b^\circ k_3^\circ K_h^\circ(65^\circ)$	$6.18 \times 10^{-4} (1.31 \times 10^{-4})$
$k_b^\circ(50^\circ)$	38.1(7.7)
$k_b^\circ(65^\circ)$	44.5(19.1)
$k_4^\circ(50^\circ)$	1
$k_4^\circ(65^\circ)$	1
RMSD	0.194

TABLE IV-10
PARAMETERS FROM THE COMBINATION FIT OF DATA
TO THE INTERCHANGE MECHANISM¹

Fit no.	1 ^f	2
b ₁ ^e	0.3	0.3
b ₂	0	0
b ₃	0.0986(0.0226)	0.247(0.034)
ΔH ^o _g	101(2)	84.8(3.3)
ΔS ^o	269(9)	215(10)
K _a ^o	0	11.2(2.7)
K _b ^o	0	30.9(4.2)
k _a ^o K _a ^o (50°)	0	0
k _a ^o K _a ^o (65°)	0	0
k _b ^o K _b ^o K _h ^o (50°)	3.06x10 ⁻⁵ (0.20x10 ⁻⁵)	3.62x10 ⁻⁵ (0.21x10 ⁻⁵)
k _b ^o K _b ^o K _h ^o (65°)	3.16x10 ⁻⁴ (0.22x10 ⁻⁴)	3.28x10 ⁻⁴ (0.19x10 ⁻⁵)
RMSD ^j	0.241	0.165

Fit no.	3
b ₁	0.3
b ₂	0
b ₃	0.213(0.052)
ΔH ^o	97.3(8.3)
ΔS ^o	257(27)
K _a ^o	14.6(4.4)
K _b ^o	28.6(6.0)
k _a ^o K _a ^o (50°)	1.46x10 ⁻⁴ (3.04x10 ⁻⁴)
k _a ^o K _a ^o (65°)	7.74x10 ⁻⁶ (193x10 ⁻⁶)
k _b ^o K _b ^o K _h ^o (50°)	4.70x10 ⁻⁵ (0.92x10 ⁻⁵)
k _b ^o K _b ^o K _h ^o (65°)	4.06x10 ⁻⁴ (0.53x10 ⁻⁴)
RMSD	0.248

Notes:

- i. See Appendix IV-2. Fits include potentiometric and kinetic data.
- j. Normalized to the best-fit individual DEL's equal to 1.

TABLE IV-11
PARAMETERS FROM THE COMBINATION FIT OF DATA
TO THE INTERDIS MECHANISMⁱ

Fit no.	1 ^f	2
b_1^e	0.3	0.3
b_2	0	0
b_3	0.316(0.057)	0.467(0.164)
$\Delta H^\circ g$	81.8(2.8)	97.3(7)
ΔS°	205(9)	257(26)
K_a°	14.9(2.3)	25.9(3.0)
K_b°	73.0(9.3)	56.7(12.5)
$k_a^\circ K_a^\circ(50^\circ)$	0	$9.99 \times 10^{-6} (242 \times 10^{-6})$
$k_a^\circ K_a^\circ(65^\circ)$	0	$1.55 \times 10^{-4} (1.64 \times 10^{-4})$
$k_b^\circ k_3^\circ K_h^\circ(50^\circ)$	$3.55 \times 10^{-5} (0.20 \times 10^{-5})$	$4.67 \times 10^{-5} (0.89 \times 10^{-5})$
$k_b^\circ k_3^\circ K_h^\circ(65^\circ)$	$3.21 \times 10^{-4} (0.20 \times 10^{-4})$	$3.64 \times 10^{-4} (0.64 \times 10^{-4})$
$k_b^\circ(50^\circ)$	0	0
$k_b^\circ(65^\circ)$	0	0
$k_4^\circ(50^\circ)$	1	1
$k_4^\circ(65^\circ)$	1	1
RMSD ^j	0.148	0.223

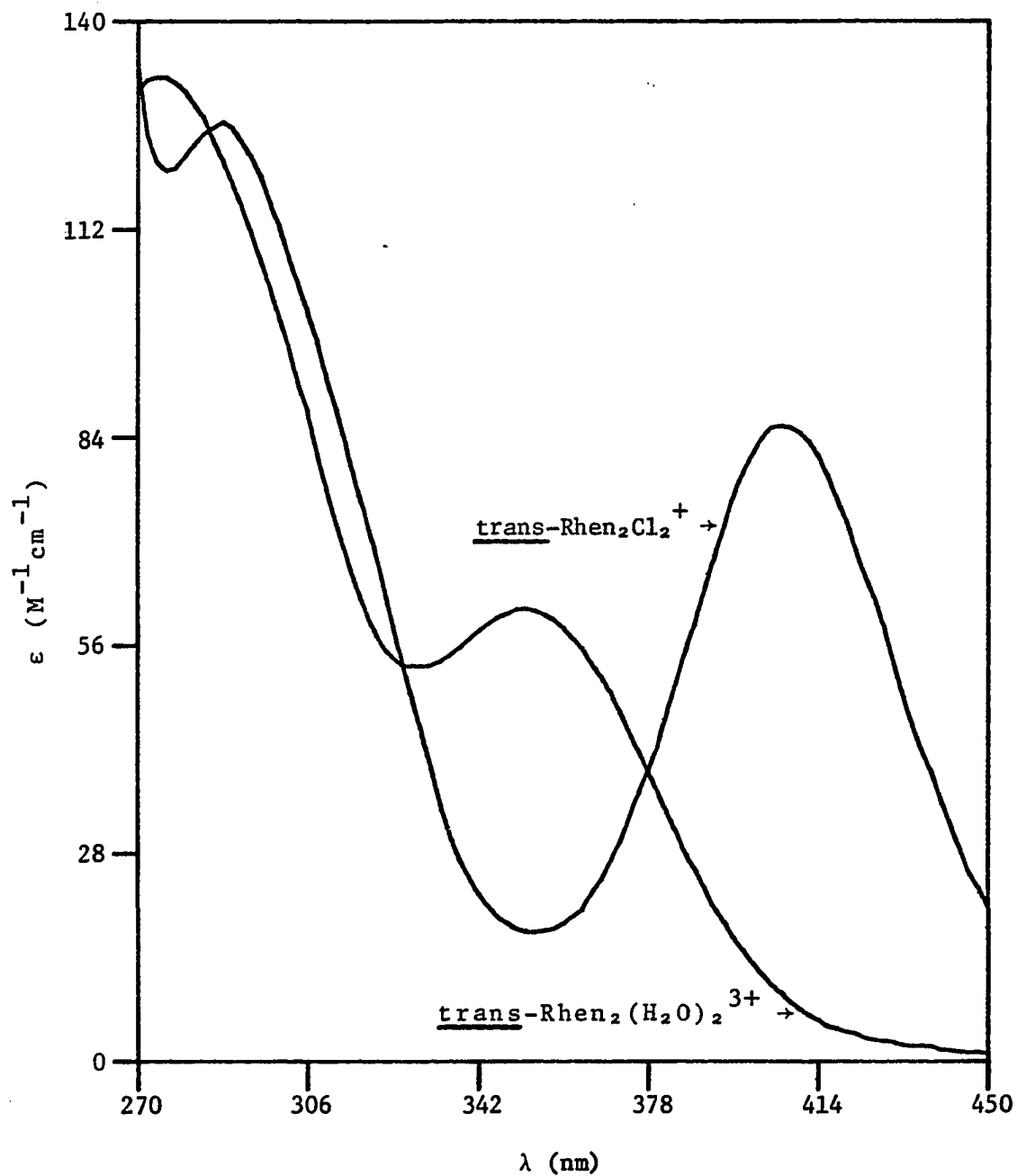
Notes:

- i. See text, pages 64 and 75, for details of the mechanism.
- j. Normalized to the best-fit individual DEL's equal to 1.

TABLE IV-11 (Continued)

Fit no.	3
b_1	0.3
b_2	0
b_3	0.841(0.703)
ΔH°	99.8(32.4)
ΔS°	264(108)
K_a°	16.5(21.0)
K_b°	42.0(42.0)
$k_a^\circ K_a^\circ(50^\circ)$	0
$k_a^\circ K_a^\circ(65^\circ)$	0
$k_b^\circ k_3^\circ K_h^\circ(50^\circ)$	$6.48 \times 10^{-5} (5.88 \times 10^{-5})$
$k_b^\circ k_3^\circ K_h^\circ(65^\circ)$	$6.58 \times 10^{-4} (43.9 \times 10^{-4})$
$k_b^\circ(50^\circ)$	29.5(51.0)
$k_b^\circ(65^\circ)$	206(1620)
$k_4^\circ(50^\circ)$	1
$k_4^\circ(65^\circ)$	1
RMSD	0.946

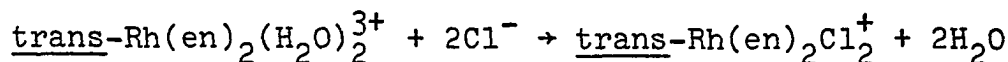
FIGURE IV-1
ULTRAVIOLET-VISIBLE SPECTRA OF trans-DIAQUOBIS(ETHYLENEDIAMINE)
RHODIUM(III) AND trans-DICHLOROBIS(ETHYLENEDIAMINE) RHODIUM(III)
IN ACIDIC AQUEOUS SOLUTION



$[\text{H}^+] = 0.10 \text{ M}$, Total Ionic Strength = 0.11 M

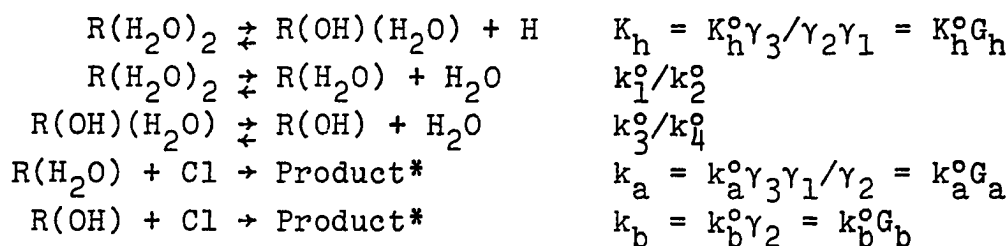
APPENDIX IV-1

THE DISSOCIATIVE MECHANISM FOR THE REACTION



NOTE: All charges have been dropped for ease of presentation.

Define: $\text{R} = \text{Rh(en)}_2$



$$d[\text{Product}]/dt = k_a[\text{R(H}_2\text{O)}][\text{Cl}] + k_b[\text{R(OH)}][\text{Cl}]$$

$$d[\text{R(H}_2\text{O)}]/dt = 0 = -k_a[\text{R(H}_2\text{O)}][\text{Cl}] + k_1[\text{R(H}_2\text{O)}_2] - k_2[\text{R(H}_2\text{O)}][\text{H}_2\text{O}]$$

$$[\text{R(H}_2\text{O)}] = \frac{k_1[\text{R(H}_2\text{O)}_2]}{k_a[\text{Cl}] + k_2[\text{H}_2\text{O}]}$$

$$d[\text{R(OH)}]/dt = 0 = -k_b[\text{R(OH)}][\text{Cl}] + k_3[\text{R(OH)(H}_2\text{O)}] - k_4[\text{R(OH)}][\text{H}_2\text{O}]$$

$$[\text{R(OH)}] = \frac{k_3[\text{R(OH)(H}_2\text{O)}]}{k_b[\text{Cl}] + k_4[\text{H}_2\text{O}]}$$

$$d[\text{Product}]/dt = \frac{k_a k_1[\text{R(H}_2\text{O)}_2][\text{Cl}] + k_b k_3[\text{R(OH)(H}_2\text{O)}][\text{Cl}]}{k_a[\text{Cl}] + k_2[\text{H}_2\text{O}]} \frac{1}{k_b[\text{Cl}] + k_4[\text{H}_2\text{O}]}$$

* The reaction with the second chloride is much faster than the first. Only the first substitution is kinetically important. See text.

APPENDIX IV-1 (Continued)

$$\text{Define: } Rh_t = [R(H_2O)_2] + [R(OH)(H_2O)]$$

$$K_h = \frac{[R(OH)(H_2O)][H]}{[R(H_2O)_2]}$$

$$K_h = \frac{(Rh_t - [R(H_2O)_2])[H]}{[R(H_2O)_2]}$$

$$[R(H_2O)_2] = \frac{Rh_t [H]}{K_h + [H]}$$

$$K_h = \frac{[R(OH)(H_2O)][H]}{Rh_t - [R(OH)(H_2O)]}$$

$$[R(OH)(H_2O)] = \frac{Rh_t K_h}{K_h + [H]}$$

$$\begin{aligned} d[\text{Product}]/dt &= \frac{k_a k_1 Rh_t [H][Cl]}{(K_h + [H])(k_a [Cl] + k_2 [H_2O])} \\ &+ \frac{k_b k_3 K_h Rh_t [Cl]}{(K_h + [H])(k_b [Cl] + k_4 [H_2O])} \end{aligned}$$

Under pseudo-first order conditions:

$$k_{\text{obs}} = d[\text{product}]/(Rh_t dt)$$

$$\begin{aligned} k_{\text{obs}} &= \frac{k_a k_1 [H][Cl]}{(K_h + [H])(k_a [Cl] + k_2 [H_2O])} \\ &+ \frac{k_b k_3 K_h [Cl]}{(K_h + [H])(k_b [Cl] + k_4 [H_2O])} \end{aligned}$$

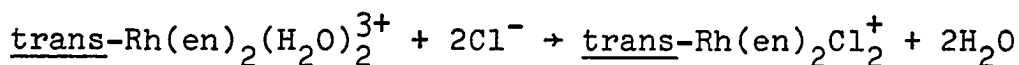
APPENDIX IV-1 (Continued)

Inserting Activity Coefficients:

$$k_{\text{obs}} = \frac{k_a^{\circ} k_1^{\circ} G_a [H][Cl]}{(K_h^{\circ} G_h + [H])(k_a^{\circ} G_a [Cl] + k_2^{\circ} [H_2O])} + \frac{k_b^{\circ} k_3^{\circ} K_h^{\circ} G_b G_h [Cl]}{(K_h^{\circ} G_h + [H])(k_b^{\circ} G_b [Cl] + k_4^{\circ} [H_2O])}$$

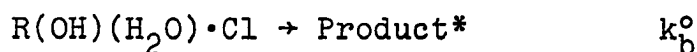
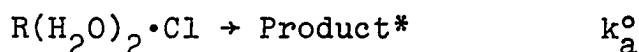
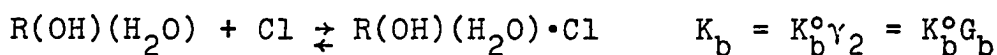
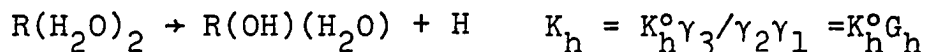
APPENDIX IV-2

THE INTERCHANGE MECHANISM FOR THE REACTION



NOTE: All charges have been dropped for ease of presentation.

Define: $\text{R} = \text{Rh(en)}_2$



$$d[\text{Product}]/dt = k_a[\text{R(H}_2\text{O)}_2 \cdot \text{Cl}] + k_b[\text{R(OH)(H}_2\text{O)} \cdot \text{Cl}]$$

$$[\text{R(H}_2\text{O)}_2 \cdot \text{Cl}] = K_a[\text{R(H}_2\text{O)}_2][\text{Cl}]$$

$$[\text{R(OH)(H}_2\text{O)} \cdot \text{Cl}] = K_b[\text{R(OH)(H}_2\text{O)}][\text{Cl}]$$

$$d[\text{Product}]/dt = k_a K_a [\text{R(H}_2\text{O)}_2][\text{Cl}] + k_b K_b [\text{R(OH)(H}_2\text{O)}][\text{Cl}]$$

$$[\text{A}]_t = [\text{R(H}_2\text{O)}_2] + [\text{R(H}_2\text{O)}_2 \cdot \text{Cl}]$$

$$[\text{R(H}_2\text{O)}_2] = \frac{[\text{A}]_t}{1 + K_a[\text{Cl}]}$$

$$[\text{B}]_t = [\text{R(OH)(H}_2\text{O)}] + [\text{R(OH)(H}_2\text{O)} \cdot \text{Cl}]$$

$$[\text{R(OH)(H}_2\text{O)}] = \frac{[\text{B}]_t}{1 + K_b[\text{Cl}]}$$

* The reaction with the second chloride is much faster than the first. Only the substitution of the first chloride is kinetically important. See text.

APPENDIX IV-2 (Continued)

$$d[\text{Product}]/dt = \frac{k_a K_a [A]_t [Cl]}{1 + K_a [Cl]} + \frac{k_b K_b [B]_t [Cl]}{1 + K_b [Cl]}$$

$$Q = \frac{[B]_t [H]}{[A]_t} = \frac{K_h (1 + K_b [Cl])}{(1 + K_a [Cl])}$$

$$Rh_t = [A]_t + [B]_t$$

$$[A]_t = \frac{Rh_t [H]}{Q + [H]} \quad ; \quad [B]_t = \frac{Rh_t Q}{Q + [H]}$$

$$d[\text{Product}]/dt = \frac{k_a K_a Rh_t [H] [Cl]}{(Q + [H])(1 + K_a [Cl])} + \frac{k_b K_b Q Rh_t [Cl]}{(Q + [H])(1 + K_b [Cl])}$$

Under pseudo-first order conditions:

$$k_{\text{obs}} = d[\text{Product}]/(Rh_t dt)$$

and substituting for Q:

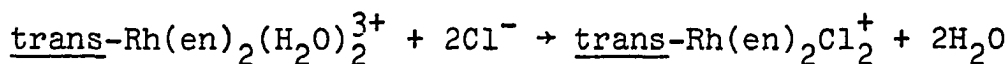
$$k_{\text{obs}} = \frac{k_a K_a [H] [Cl] + k_b K_b K_h [Cl]}{[H](1 + K_a [Cl]) + K_h (1 + K_b [Cl])}$$

Inserting Activity Coefficients:

$$k_{\text{obs}} = \frac{k_a^\circ K_a^\circ G_a [H] [Cl] + k_b^\circ K_b^\circ K_h^\circ G_b G_h [Cl]}{[H](1 + K_a^\circ G_a [Cl]) + K_h^\circ G_h (1 + K_b^\circ G_b [Cl])}$$

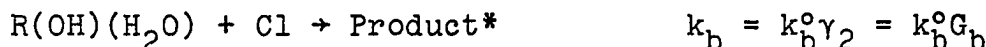
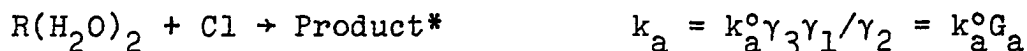
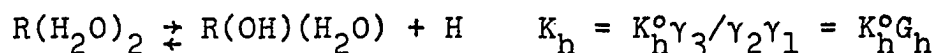
APPENDIX IV-3

THE BIMOLECULAR-ATTACK MECHANISM FOR THE REACTION



NOTE: All charges have been dropped for ease of presentation.

Define $R = \text{Rh(en)}_2$



$$d[\text{Product}]/dt = k_a [R(\text{H}_2\text{O})_2][\text{Cl}] + k_b [R(\text{OH})(\text{H}_2\text{O})][\text{Cl}]$$

$$K_h = \frac{[R(\text{OH})(\text{H}_2\text{O})][\text{H}]}{[R(\text{H}_2\text{O})_2]}$$

$$R_{h_t} = [R(\text{H}_2\text{O})_2] + [R(\text{OH})(\text{H}_2\text{O})]$$

$$[R(\text{H}_2\text{O})_2] = \frac{R_{h_t} [\text{H}]}{K_h + [\text{H}]} \quad ; \quad [R(\text{OH})(\text{H}_2\text{O})] = \frac{R_{h_t} K_h}{K_h + [\text{H}]}$$

$$d[\text{Product}]/dt = \frac{k_a R_{h_t} [\text{H}][\text{Cl}] + k_b K_h R_{h_t} [\text{Cl}]}{K_h + [\text{H}]}$$

Under pseudo-first order conditions:

$$k_{\text{obs}} = d[\text{Product}]/(R_{h_t} dt)$$

$$k_{\text{obs}} = \frac{k_a [\text{H}][\text{Cl}] + k_b K_h [\text{Cl}]}{K_h + [\text{H}]}$$

Inserting Activity Coefficients:

$$k_{\text{obs}} = \frac{k_a^\circ G_a [\text{H}][\text{Cl}] + k_b^\circ K_h^\circ G_h G_h [\text{Cl}]}{K_h^\circ G_h + [\text{H}]}$$

* The reaction with the second chloride is much faster than the first. Only the first substitution is kinetically important. See text.