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# The kinetic anation reactions of some rhodium cyclam complexes.

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## UMI®

THE KINETIC ANATION REACTIONS

OF SOME RHODIUM CYCLAM

COMPLEXES


BY

PATRICK J. DUNN


A Thesis

Submitted to the Faculty of Graduate Studies through the

Department of Chemistry in Partial Fulfillment of the

Requirements for the Degree of Master of

Science at the University of

Windsor


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# ABSTRACT

The replacement of water from an aquo complex by an anion is the reverse of an acid hydrolysis reaction and is called an "Anation" reaction.

A series of complexes of the type trans-$[Rh(cyclam)X(OH_2)]^{+2}$ were prepared for purposes of kinetic anation studies (cyclam representing 1,4,8,11-tetraazacyclotetradecane and X representing the halogens $Cl^-$, $Br^-$ and $I^-$). The experimental technique employed for kinetic studies was a spectrophotometric approach following the reaction:

$$trans-[Rh(cyclam)X(OH_2)]^{+2} + Y^- \rightleftharpoons trans-[Rh(cyclam)XY]^+ + OH_2$$
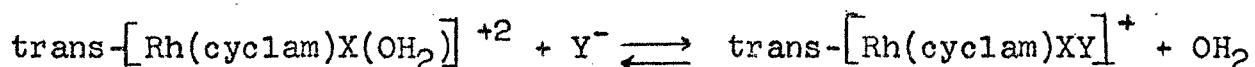
where Y represents the incoming species, being any one of the halides $Cl^-$, $Br^-$ or $I^-$.

A pooled variance method has been used for determining the standard error on the temperature dependent data. The kinetic results yielded enthalpy and entropy data and this data is compared directly with that of other transition metals, as well as other rhodium complexes. The results are correlated with respect to the kinetic trans effect, entering and leaving group effects, and mechanism involved.

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# I. INTRODUCTION

Substitution reactions of octahedral transition metals have been the subject of extensive investigation within the last few years and the subject of various reviews[1].

Three types of substitution reactions are observed in octahedral complexes in aqueous solution:

(i) Acid hydrolysis: replacement of a ligand by water (aquation);

(ii) Base hydrolysis: replacement of a ligand by a hydroxide ion;

(iii) Anation: replacement of a coordinated water by an anion (the reverse of an acid hydrolysis reaction).

Anation reactions are of particular interest since these studies yield direct nucleophilicity comparisons for the substituting ligand and provide a more direct approach at postulating a mechanism than does the acid hydrolysis reaction. For example, the anation reactions study $X-(OH_2)$, which has been proposed as the intermediate for the acid hydrolysis reaction mechanism[1d].

Reaction mechanisms for anation fall into two extremes boundaries. A dissociative mechanism ($S_N1$) leading to a five coordinate intermediate or activated complexes involves metal-ligand bond breaking. An associative mechanism ($S_N2$) leading to a seven coordinate activated complex involves bond making

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between substrate and reagent. Direct detection of the
reaction intermediate for anation could, if possible to isolate,
elucidate the extremes involved within a particular reaction.
However, a correlation of the reaction rates, involving specific
steric, electronic and charge effects as well as the nature of
the entering and leaving group can be helpful in inferring
the mechanism of a particular reaction.

## Factors Affecting Mechanism

Structural and electronic properties of substrates as well
as the nature of solvent and reagent greatly affect a particular
reaction.

Steric effects, such as increased congestion at the reaction
site cause the rate of a unimolecular reaction to increase,
while decreasing the rate of a bimolecular reaction. A
symmetrical environment would limit congestion, the steric
environment being the same for the trans reaction sites. A
strain free isomer which would be unsymmetrical with respect
to the metal ligand plane would enhance the reaction rate. It
is noted in the literature for the cobalt complexes with ligands
similar to cyclam, a more sterically congested reactant is some
twenty-five times more reactive than a symmetrical complex
(teta > tetb > cyclam [2], where teta and tetb are two
diastereoisomers of hexamethylated cyclam). The ligand
cyclam, a macrocyclic quadridentate ligand is very rigid and
insensitive to stereoisomerization, and due to its ease of formation
and inert behaviour, serves as a convenient ligand for kinetic

investigations.

Increasing the positive charge of a complex hinders dissociation of the metal-X bond, thus decreasing the rate of the dissociative reaction. The charge effect is less important in a bimolecular reaction. Here an increased positive charge promotes partial bond formation with the entering group, and retarding the metal-X bond breakage. Therefore, in a bimolecular reaction, the charge effect is dependent upon the contribution of the transition state.

The effect of leaving groups is important in a unimolecular reaction but less important in a bimolecular reaction. However, entering groups greatly affect a bimolecular reaction, thus not affecting a unimolecular reaction.

A positive inductive effect, leaving increased negative charge near the metal atom promotes an $S_N1$ reaction, but this inductive effect is not very large in these "metal amine" type complexes [3].

Non-labile ligands with $\pi$ donating capability may assist in the breakage of the Rh-OH$_2$ bond, thus stabilizing the five-coordinate intermediate. However, the cyclam ligand, studied here, has little if any $\pi$ donating capability. The ligands in the complex, Cl$^-$, Br$^-$ or I$^-$(particularly), have $\pi$ accepting capability and would cause a reduction of the electron density at the Rh metal centre. This would enhance bimolecular attack of entering group. But, since orienting ligands are directly attached to the central metal experiencing substitution, it was suggested that $\pi$ accepting ligands also promote a dissociative

reaction. The removal of a leaving group, water, would strengthen the remaining $5\sigma$ bonds. Consequently, this increases the $\pi$ interaction through closer ligand-metal distance. A ligand of stronger $\pi$ accepting capability would have a stronger demand to increase its $\sigma$ interaction, and thus facilitate a dissociative mechanism[4].

A correlation between the crystal field stabilization energies (CFSE) and the observed activation energies for octahedral cobalt (III) (low spin $d^6$) systems has been made[5]. Their calculations indicate a unimolecular reaction with a square-pyramidal intermediate, and a bimolecular reaction with a penta-gonal-bipyramidal intermediate are equally probable. However, steric effects favour the former reaction path.

The rate of reaction and mechanism is influenced by the nephelauxetic effect. Ligands lower in the nephelauxetic series give rise to smaller reductions in electron-repulsion parameters of the central metal ion. These metal complexes have a demand to expel leaving groups, thus gaining greater delocalization of the 4d electrons in the vacant orbital of rhodium. This tendency of reducing the ground state electronic repulsion in the transition state would promote a unimolecular reaction retarding a bimolecular reaction[6].

The chelation effect[7] also plays a role in reaction mechanisms. Increasing chelation down the amine series reduces the rate of acid hydrolysis, having the same effect on the reverse anation reaction:

$$\text{cyclam} < \text{en} < NH_3.$$
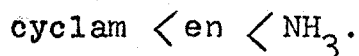
This reduction rate, parallel to the increasing order of the amine ligand in the nephelauxetic series, is fully consistent with a unimolecular reaction [8].

In all octahedral rhodium (III) complexes, the lack of a low lying vacant orbital for the formation of an extra $\sigma$ bond required for an associative mechanism, and steric congestion arising from six ligands around the central metal ion do not encourage bimolecular reactions.

One of the more interesting features of anation reactions, subject to kinetic studies, is the activation by non-reactive groups. For trans isomers, the ligands opposite to the $H_2O$ being replaced would be expected to exhibit a "trans" effect. This trans effect in metal complexes is used to describe the influence of a coordinated group upon the replacement of a ligand opposite to it. Extensive studies have resulted in placing the common ligands in an appropriate order with regard to their tendency to labilize a trans group.[1] This effect has been explained by use of an electrostatic approach (i.e., $\sigma$ bond effect upon weakened ground state), as well as the $\Pi$ electron withdrawal of the transition state by the trans labilizing ligand.

Kinetic and thermodynamic data, most useful in demonstrating this effect, correlates the order of decreasing trans effect with the following ligands:

$$I > Br > Cl.$$
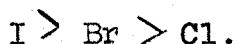
This order has been verified by numerous transition metal substitution reactions [9], and is further verified by these anation studies.

A dissociative activation process may be expected for the complexes in aqueous solution. The anation reactions which will be followed can be represented by the following equation:

$$\text{trans-}\left[\text{Rh(cyclam)X(OH}_2)\right]^{+2} + Y^- \longrightarrow \text{trans-}\left[\text{Rh(cyclam)XY}\right]^{+} + H_2O$$
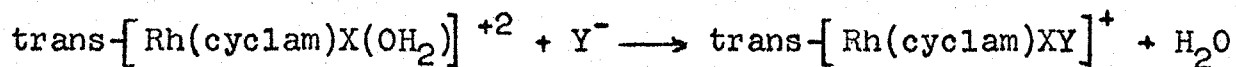
and the general anation rate of this reaction is given by the following expression [10]:

$$\text{Rate} = \frac{a\left[Y^{m-}\right]\left[RH_2O^{n+}\right]}{1+b\left[Y^{m-}\right]}$$

where a and b are suitable parameters. For this expression, the Rate $= k_{obs}\left[RH_2O^{n+}\right]$. It is from the slope and intercept of the straight plot of $1/k_{obs}$ against $1/\left[Y^{m-}\right]$, that a and b can be evaluated.

The rate law is consistent with a unimolecular dissociation of the aquo complex, which is then followed by a competition between the solvent water and the entering anion for a five-coordinate intermediate:

$$R(H_2O)^{n+} \xrightarrow[\text{slow}]{k_1} R^{n+} + H_2O$$

$$R^{n+} + H_2O \xrightarrow[\text{fast}]{k_{-1}} RH_2O^{n+}$$

$$R^{n+} + Y^{m-} \xrightarrow[\text{fast}]{k_2} RY^{(n-m)+}$$
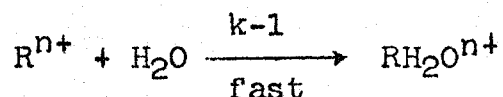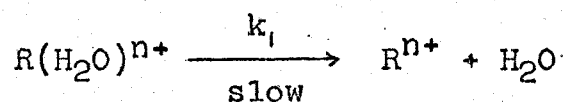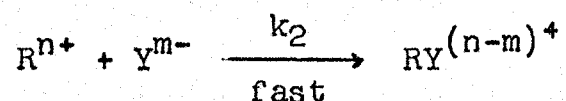
The corresponding rate law becomes:

$$\text{Rate} = \frac{k_1 k_2 \left[Y^{m-}\right]\left[R(H_2O)^{n+}\right]}{k_{-1}\left[H_2O\right] + k_2\left[Y^{m-}\right]}$$

where: $\quad k_2\, Y \quad k_{-1}\, H_2O,$

$$a = \frac{k_1 k_2}{k_{-1}\left[H_2O\right]} \quad \text{and} \quad b = \frac{k_2}{k_{-1}\left[H_2O\right]} \quad.$$

The rate of anation is then independent of the nature and concentration of Y, the incoming species and equals the rate of water exchange. For this bond-breaking reaction, one would expect positive values of $\Delta S^{\ddagger}$, $\Delta H^{\ddagger}$ measuring the difference in enthalpy between the reactants and the transition state.

Another possible mechanism $S_N 2$, where bond-making is involved in the transition state, is evidenced by total dependence of the rate upon the concentration. As well in $S_N 2$ reactions there is a notable rate difference in changing the incoming group. Thermodynamic parameters, characteristic of this type of mechanism reveal small negative $\Delta S^{\ddagger}$ values, this representing more bond-association involved, less dissociation. The resulting seven-coordinate intermediate would have a pentagonal-bipyramidal shape or octahedral wedge.

However, another approach to the same reaction applies

to a rapid pre-equilibrium formation of an ion-pair between
cationic complex and entering anion [11]. This is then
followed by a unimolecular or bimolecular interchange between
leaving group and entering anion included in the ion-pair. This
has sometimes been referred to as an "Interchange mechanism":

$$RH_2O^{n+} + Y^{m-} \underset{}{\overset{\substack{fast \\ K}}{\rightleftharpoons}} \left[RH_2O^{n+}....Y^{m-}\right]$$

$$\left[RH_2O^{n+}....Y^{m-}\right] \underset{slow}{\overset{kY}{\longrightarrow}} RY^{(n-m)+} + H_2O.$$
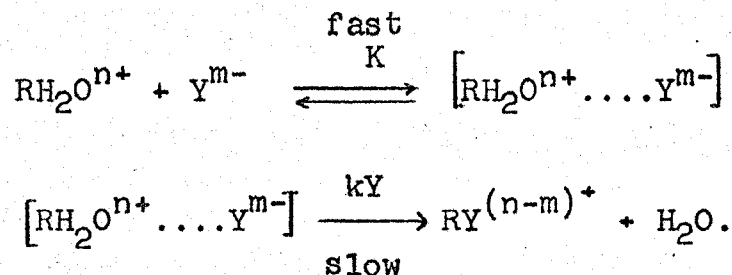
Here, K represents the ion-pair formation constant. The rate
law expressed for the above reactions becomes:

$$Rate = \frac{kYK\left[Y^{m-}\right]\left[RH_2O^{n+}\right]}{1-K\left[Y^{m-}\right]}$$

and $a = kYK$ and $b = K$.

In some cases such as the anation of cis-$\left[Co(en)_2NO_2(OH_2)\right]^{+2}$
by $N_3^-$ and $NCS^-$ [12], the anation of trans-$\left[Co(NH_3)_5(OH_2)\right]^{+3}$ by
$N_3^-$ [13], $H_2PO_4^-$ [14], $Cl^-$ [15] and $SO_4^{-2}$ [16], direct evidence
for ion pair formation has been obtained. In most other cases,
ion-association cannot be directly detected because of the rapid
anation reactions. Pioneer work was done on the anation reactions
of cobalt complexes of the type $\left[Co(NH_3)_5(OH_2)\right]^{+3}$ with several
different nucleophiles by Langford and Muir [17]. The conclusion
made from this work was that rate constants of the products are
only 20% of that of water exchange. This was presumably caused

by the nucleophile not being in a suitable position to enter into the inner sphere when the water ligand leaves, and thus another water molecule enters instead.

Analogous rhodium complexes show rate values ten times larger to those of the dissociative reaction of the cobalt (III) complexes [18]. This large increase is ascribed to an increase in the proportion of the ion-pairs which undergo interchange when the coordinated water molecule leaves. This is due to the anion in the outer sphere being closer to the water molecule it is to replace. As well, the presence of the anion in the outer sphere increases the rate at which the water molecule leaves. Nucleophilic assistance as well has been used to account for the above phenomenon [18].

It has been reported in the literature that the acid hydrolysis or aquation reaction of similar metal complexes (cobalt amine (cyclam) complexes) would not follow an $S_N2$ or $S_N2IP$ mechanism [19]. The results of kinetic studies do not unfortunately allow an unambiguous assignment of the detailed and intimate mechanism. Therefore, most postulations of mechanism lie somewhere between the extremes of the mechanisms shown in detail here.

## II. PREPARATION OF THE RHODIUM (III)

## HALOGENO-AQUO COMPLEXES

All of the complexes were prepared essentially by the method of E.J. Bounsall and S. Koprich[20].

The trans dibromo and diiodo cyclam complexes were prepared from the trans dichloro complex, with the aquo-halogeno complexes prepared from these dihalogenocomplexes. The general procedure followed for the monoaquo complexes involved the careful refluxing of the trans-$[Rh(cyclam)X_2]^{+1}$ in NaOH solution for the specified time (from 3 - 10 minutes) in order to obtain the monohydroxo intermediate. This intermediate was carefully acidified with $HClO_4$ and precipitated as the perchlorate salt (employing $NaClO_4$). Perchlorate has a very slight tendency to function as a donor ligand in complexes in aqueous solution and is also an excellent precipitating anion[21].

The intermediates for the above were carefully monitored on the ultraviolet-visible recording spectrophotometer in order to obtain the monohydroxo intermediate. If refluxing is continued longer than the limited time period, the dihydroxo and not the monohydroxo intermediate is obtained. After the recrystallization and vacuum drying, the complexes were verified by comparison with the published spectra of characterized complexes[22], using a Bausch and Lomb Spectronic 505 recording spectrophotometer. All the halogeno-aquo

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complexes prepared for kinetic purposes were analyzed by Spang Microanalytical Laboratories in Ann Arbor, Michigan.

RhCl$_3$.3H$_2$O (obtained from J. Bishop and Co. Platinum Works) was used as a source of Rh$^{+3}$ without further purification and reagent grade (Fisher Scientific Company, A.C.S.) sodium salts were used as anion sources. Reagent grade solvents and ion-exchanged distilled water were used throughout.

### 1,4,8,11-Tetraazacyclotetradecane (cyclam)

The open chain intermediate, 1,9-diamino-3,7-diazanonane, was prepared according to the procedure developed by Bounsall and Koprich[23].

(250 g, 1.2 moles, 126 ml) 1,3 dibromopropane was added dropwise to (360 g, 6.0 moles, 400 ml) ethylenediamine in 300 ml of ethanol (99% redistilled). Dropwise addition was necessary since the reaction was extremely exothermic. As well, the solution was cooled in an icebath during addition. The resultant yellow solution was heated under reflux for one hour. After cooling, (300 g, 5.3 moles) KOH was added and the reaction mixture was stirred for 30 minutes. The KBr and excess KOH was removed by filtration. After distilling of the excess ethanol (78.5°C) and ethylenediamine (116 - 117°C), the desired intermediate, a clear viscous liquid, 1,9-diamino-3,7-diazanonane (90 g, .56 moles, 47%) was separated by vacuum distillation (125 - 128°C, 3.5 mm Hg).

Following the procedure of Bounsall and Koprich[23], with slight modifications, cyclam was prepared.

(50 g, .25 moles) 1,3-dibromopropane and (40 g, .25 moles)

1,9-diamino-3,7-diazanonane were added to 4 litres of redis-
tilled absolute ethanol. The resultant solution turned from
colourless to yellow upon refluxing for 24 hours. After removing
3 litres of ethanol by distillation, the resultant solution
was cooled and (35 g, .62 moles) KOH was added, which again
precipitated the KBr and excess KOH. After removal by filtration,
the volume was reduced to 100 ml. This clear viscous yellow
solution, upon cooling for several hours, precipitated the white
product (3.5 g, 7%) which after being filtered and washed with
acetone was purified by vacuum sublimation ($120^\circ C$, 2 mm Hg).
The melting point of the product, 1,4,8,11-tetraazacyclotetra-
decane was 185 - $186^\circ C$ (sealed tube).

## Trans- $[Rh(cyclam)Cl_2]$Cl

(7.5 g, 28 mmoles) $RhCl_3 \cdot 3H_2O$ and (7.5 g, 37 mmoles) cyclam
were dissolved in 300 ml methanol and heated under reflux for
5 minutes during which the red mixture turned to a yellow
solution and precipitate. After careful filtration, the filtrate
was treated with 25 ml conc. HCl to precipitate the excess
cyclam as the tetrahydrochloride. Since the precipitate from
the filtrate used above was the corresponding cis-dichloro
salt, the HCl also precipitated any cis complex left in
solution. The remaining yellow solution, after being evaporated
to dryness yielded the desired product which was recrystallized
from 75 ml water and 25 ml conc. HCl, washed with acetone and
ether, and dried under vacuum for two hours (5.0 g, 43%).

## Trans-[Rh(cyclam)Br₂] Br

(500 mg, 1.22 moles) trans-[Rh(cyclam)Cl$_2$]Cl and (4.6 g, 44 mmoles) NaBr were dissolved in 50 ml water. After heating the yellow solution under reflux for 5 hours, it turned to an orange solution with orange precipitate. After cooling, the orange precipitate was filtered, and recrystallized by repeating the above procedure. The final product was washed in ethanol and ether and vacuum dried for two hours. The product yield was 200 mg (34%).

## Trans-[Rh(cyclam)I$_2$] I

Trans-[Rh(cyclam)I$_2$] I) trans-[Rh(cyclam)Cl$_2$] Cl and (3.2 g, 21 mmoles) NaI were added to 150 ml of H$_2$O and heated under reflux for 3 hours. In this time period, the solution colour changed from yellow to dark brown. The brown precipitate which was collected by filtration was recrystallized from 2 litres of water and 3.2 g NaI. Slow refluxing for several days of this solution aided in the purification of the complex. After slow evaporation to 200 ml, the brown product was filtered, washed with ethanol and ether, and dried under vacuum for two hours. The product yield was 550 mg (75%).

The trans diiodo complex was also prepared by refluxing for several weeks a solution of the cis dichloro salt in basic solution with sodium iodide. The solution was then acidified with hydriodic acid, evaporated, filtered and washed according to the above procedure. It was found that a purer trans-diiodo product could be obtained by this substitution and isomerization of the cis dichloro complex.

## Trans-$[Rh(cyclam)Cl(OH_2)](ClO_4)_2$

(500 mg, 1.21 mmoles) trans-$[Rh(cyclam)Cl_2]Cl$ was dissolved in a 25 ml water solution made basic by addition of (1 pellet, ~2.5 mmoles) NaOH. The resultant clear yellow solution was refluxed for 4 minutes, at which time the spectra revealed the correct Cl(OH) intermediate peak. The solution was cooled on ice and acidified by dropwise addition of concentrated $HClO_4$. The addition of (10 g, 72 mmoles) $NaClO_4$ precipitated the desired yellow product which was washed with ethanol and ether and dried under vacuum for two hours. The product yield was 200 mg (29%).

Anal. Calculated for $Rh(C_{10}H_{24}N_4)Cl(H_2O)(ClO_4)_2$: C, 21.62; H, 4.72; N, 10.08; Cl, 19.14. Found: C, 21.58; H, 4.92; N, 9.55 ; Cl, 18.87.

## Trans-$[Rh(cyclam)Br(OH_2)](ClO_4)_2$

(150 mg, .276 mmoles) trans-$[Rh(cyclam)Br_2]Br$ was refluxed in a 15 ml water solution made basic by addition of (1 pellet, ~ 2.5 mmoles) NaOH. After 3 ½ minutes of refluxing, yielding the Br(OH) intermediate, the solution was rapidly cooled, and acidified by dropwise addition of concentrated $HClO_4$. Immediately following this acidification, (10 g, 72 mmoles) $NaClO_4$ was added to precipitate the pale yellow-orange complex which was filtered, washed with 1:1 ethanol-ether and vacuum dried for two hours. The product yield was 94 mg (59%).

Anal. Calculated for $Rh(C_{10}H_{24}N_4)Br(H_2O)(ClO_4)_2$:

C, 20.01; H, 4.37; N, 9.34; Br, 13.32; Cl, 11.82. Found: C, 19.79; H, 4.35; N, 9.11; Br, 13.54; Cl, 11.69.

## Trans-$[Rh(cyclam)I(OH_2)](ClO_4)_2$
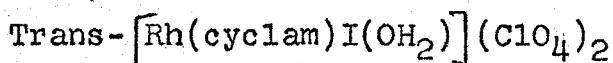
(293 mg, .427 mmoles) trans-$[Rh(cyclam)I_2]$I and (1 pellet, ~2.5 mmoles) NaOH was added to 25 ml water. The resultant brown solution turned to yellow-orange upon refluxing for 12 minutes, the spectra indicating total disappearance of reactant diiodo peak. After cooling, the solution in an icebath, the dropwise addition of concentrated $HClO_4$ turned the solution red. (10 g, 72 mmoles) $NaClO_4$ was added to precipitate the red complex which was washed with 1:1 ethanol-ether and vacuum dried for 2 hours. The product yield was 60 mg (22%).

Anal. Calculated for $[Rh(C_{10}H_{24}N_4)I(OH_2)](ClO_4)_2$: C, 18.56; H, 4.05; N, 8.65; I, 19.61; Cl, 10.96. Found: C, 18.42; H, 4.14; N, 8.49; I, 19.42; Cl, 11.08.

The orange filtrate remaining from the iodo-aquo complex was refrigerated for several months, after which time an orange product precipitated out of solution. This product proved to be simply the unreacted diiodo salt. Several initial attempts at making the above complex using dilute $HClO_4$ for acidification made precipitation difficult and lengthy, and after 3 weeks a black residue was obtained which proved to be reduced $Rh^o$ metal. The use of conc. $HClO_4$ as the acidifying agent resulted in the precipitation of the aquo species before any $Rh^o$ was found. Below is listed a table of the wavelengths and extinction coefficients of the electronic spectra for the above-mentioned complexes, and are identical with those found previously[22].

TABLE I

The Electronic Spectra of trans-$[Rh(cyclam)XY]^{n+}$ (Maxima)

| Complex | $\lambda(mu)$ | $\epsilon(l.\ cm^{-1}\ mole^{-1})$ |
|---|---|---|
| $Cl_2^+$ | 406, 310sh*, 242sh 204 | 78, 80, 3300, 37100 |
| $Br_2^+$ | 429, 285, 235 | 97.3, 2520, 34600 |
| $I_2^+$ | 515sh, 466, 353 275, 226 | 64, 204, 13100, 34500 22800 |
| $Cl(OH_2)^{+2}$ | 385, 296sh, 224sh | 55, 101, 4420 |
| $Br(OH_2)^{+2}$ | 468, 403, 310sh 204 | 37, 63, 106, 25600 |
| $I(OH_2)^{+2}$ | 494, 341sh, 301sh 271, 230 | 222, 763, 1290, 2240 24400 |

*sh = shoulder

# III. KINETIC STUDIES

The anation reactions were studied by monitoring the halogen substitutions spectrophotometrically at a specific wavelength; the wavelengths were chosen to obtain an optimum large difference between product-reactant absorbance intensities, and in a high extinction coefficient area in order to avoid precipitation of the less soluble disubstituted product using large amounts of complex. The maximum complex concentration was in the range of $10^{-4}$ to $10^{-5}$ molar thus avoiding product precipitation.

The charge transfer peaks of the products formed were employed to follow the course of the reaction with wavelengths between 200 - 275 $cm^{-1}$ and extinctions coefficients above 30000 $cm^{-1}$/mole. Table II contains the detailed information on wavelengths used for each set of anation reactions.

The reactant solutions were prepared using certified (Fisher Scientific, A.C.S.) sodium chloride, bromide and iodide. The analysis maximum limits of halide contamination for the above sodium salts were not sufficiently high to interfere. The halide anating concentration used in this study ranged from .003 M to 0.950 M. This concentration of the substituting anion always ensured 100% reaction, the least concentrated molar percentage of reacting anion being in excess of 100 times the molar complex amount. The overall ionic strength ($\mu$) was adjusted to 1.00 M using reagent grade

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## TABLE II

### Charge Transfer Spectral Peaks of Anation Products

| Reactant | Anating Anion | Product (complex) | (mu) (product) | $(1 \ cm^{-1} \ mole^{-1})$ |
|---|---|---|---|---|
| trans $Cl(OH_2)^{+2}$ | $Cl^-$ | trans $(Cl_2)^+$ | 204 | 37100 |
| trans $Br(OH_2)^{+2}$ | $Br^-$ | trans $(Br_2)^+$ | 235 | 34600 |
| trans $I(OH_2)^{+2}$ | $I^-$ | trans $(I_2)^+$ | 275 | 34500 |
| trans $Br(OH_2)^{+2}$ | $Cl^-$ | trans $(ClBr)^+$ | 221 | 32700 |
| trans $I(OH_2)^{+2}$ | $Cl^-$ | trans $(ClI)^+$ | 245 | 31300 |
| trans $I(OH_2)^{+2}$ | $Br^-$ | trans $(BrI)^+$ | 256 | 33900 |

(G.F. Smith) anhydrous sodium perchlorate. The hydrated form of $NaClO_4$ was found to have sufficiently high halide impurity so as to change the anating ion concentration (particularly at low concentrations). In the analyzed grade anhydrous $NaClO_4$, the combined chloride and chlorate maximum limit was .01%. The exact amount of halide contamination was determined using an ion selective electrode. The results of this study showed $<$ 1ppm chloride was present, which had no effect on the anation rates.

These reaction solutions were all prepared in $10^{-5}$ M $HClO_4$ since it was found that at this acidity no possibility of base hydrolysis could occur[24]. The NaI solutions were prepared fresh daily to ensure the absence of $I_2$ and $I_3^-$. The reaction medium (NaX, $NaClO_4$, $HClO_4$) was prepared in 100 ml volumetric flasks, 50 ml being used for the reaction with complex, the remaining solution used for blank readings.

An accurately weighed sample (six-figure accuracy) of the appropriate complex was transferred to an appropriate volumetric flask and dissolved and made up to the mark with $10^{-5}$ M $HClO_4$. A 5 ml aliquot was then pipetted into a 50 ml volumetric flask and both the reaction media and the complex were preheated to the desired anation temperature, before being mixed. Thermostated oil baths (Sargent) which could be regulated to $\pm 0.01^\circ$C were used for heating the solutions.

Volumetric flasks were used most appropriately for the kinetic solutions since they could easily be clamped into the oil bath, and glass-stoppered tops prevented evaporation

especially for the high temperature kinetics and aliquot samples could conveniently be removed.

There was no rate difference between aluminum foil-wrapped and unwrapped determinations; thus, the anation reactions were not sensitive to photolysis in these studies.

The reactions were studied over a wide temperature range from $30^{\circ}C$ - $90^{\circ}C$ with each specific set being studied over a $20^{\circ}$ temperature range for the purpose of determining activation parameters. The temperature range was chosen such that 2 - 3 half-lives could be conveniently studied. For the lowest temperature iodide anations, a time period of 3 - 8 hours was necessary to achieve one half-life. Any lengthier period would have resulted in $I_3^-$ formation and spectral and mechanistic interference.

For the first determination in a series, the ultraviolet spectrum was monitored on a recording spectrophotometer in order to observe isosbestic points (Figure 1). The subsequent determinations in a series where monitored at one specific wavelength on an Hitachi Perkin Elmer (Coleman 139 Model) Spectrophotometer.

There were 12 - 15 different concentration determinations monitored at the upper and lower temperature level. Six determinations were made at the middle temperature to demonstrate linearity of the activation enthalpy plots. At the middle temperature, the concentrations of anating species overlapped with those used at higher and lower temperatures.

Figure 1

Spectral Changes during the Reaction

$trans\text{-}[Rh(cyclam)I(OH_2)]^{+2} + Br^-$
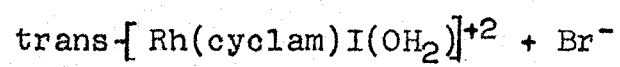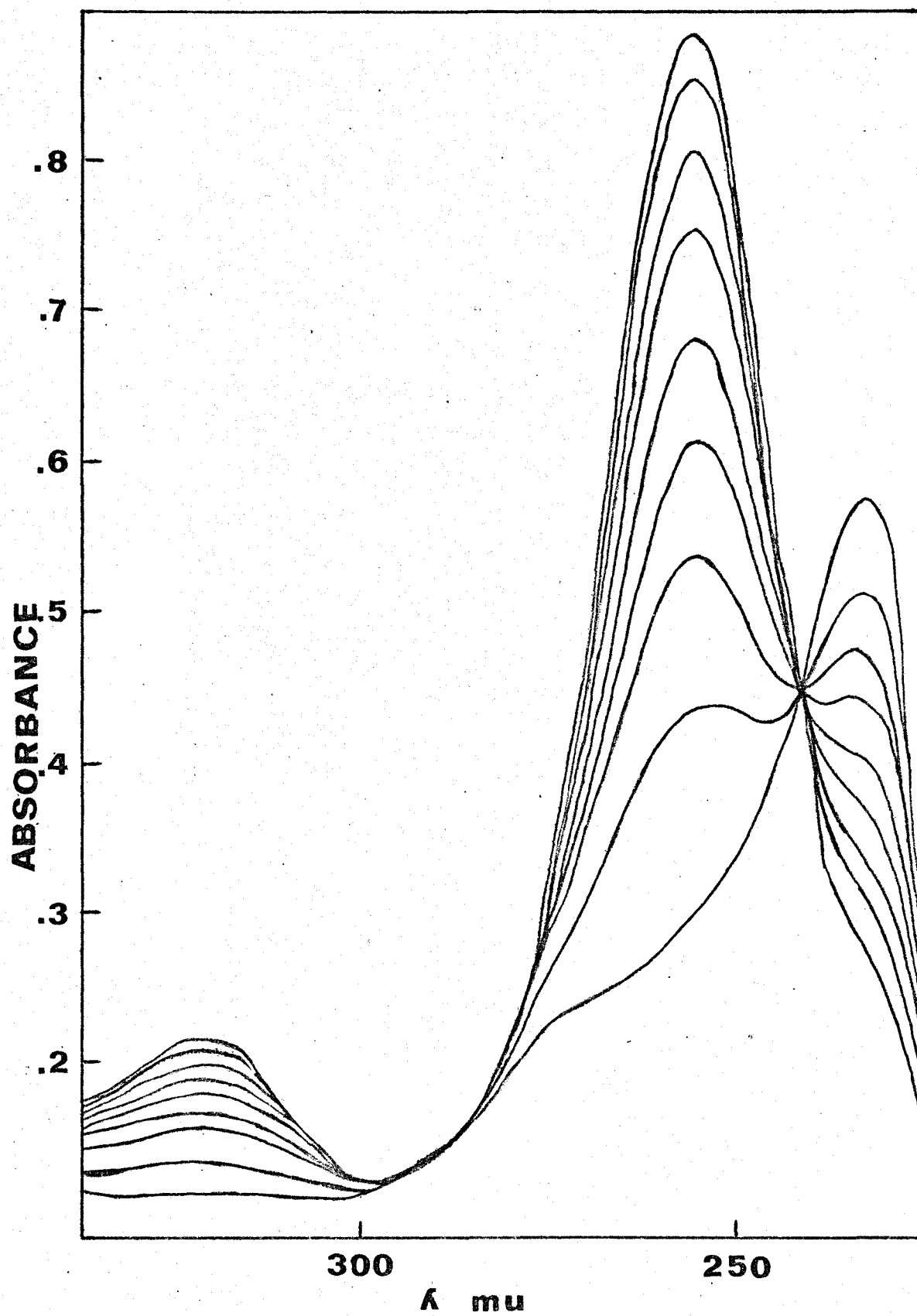
Figure 1

The rate constants were determined graphically (Figure II) by following the increase of the absorbance peak of the product, and these are     expressed in the following rate equation:

$$\text{Product Increase:} \quad k = \frac{2.303}{t} \log \frac{A_\infty - A_O}{A_\infty - A_T}$$

where $A_O$ is the initial absorbance reading or optical density, $A_\infty$ is the calculated value of 100% reactant completion or 100% product formation and $A_T$, the absorbance readings at suitable (t) time intervals. 5 ml aliquots were withdrawn at specific time intervals and measured specifically. In all cases, the $A_\infty$ values used were those calculated using product species known extinction coefficients.

In several of the runs, especially in the chloride substitutions which were the most rapid, there was very good agreement of experimental and calculated $A_\infty$ values. However, it was observed that the slower reactions which were monitored for more than 1 $\frac{1}{2}$ half-lives showed a leveling-off of the rate plot usually after the second half-life. This was especially noticeable in the iodide substitutions, even after one half-life. This point is further elaborated upon in the discussion. However, there appeared to be excellent linearity in the plot for at least the first half-life.

The pseudo-first order rate constants were obtained from the slope of the linear plot of $\log \frac{A_\infty - A_O}{A_\infty - A_T}$ vs. time. The measurements were found to be quite reproducible provided fresh

24

Figure 2

Graphical Determination of $k_{50}$ for Reaction

trans-$[\text{Rh}(\text{cyclam})\text{I}(\text{OH}_2)]^{+2} + \text{Cl}^-$

Figure 2
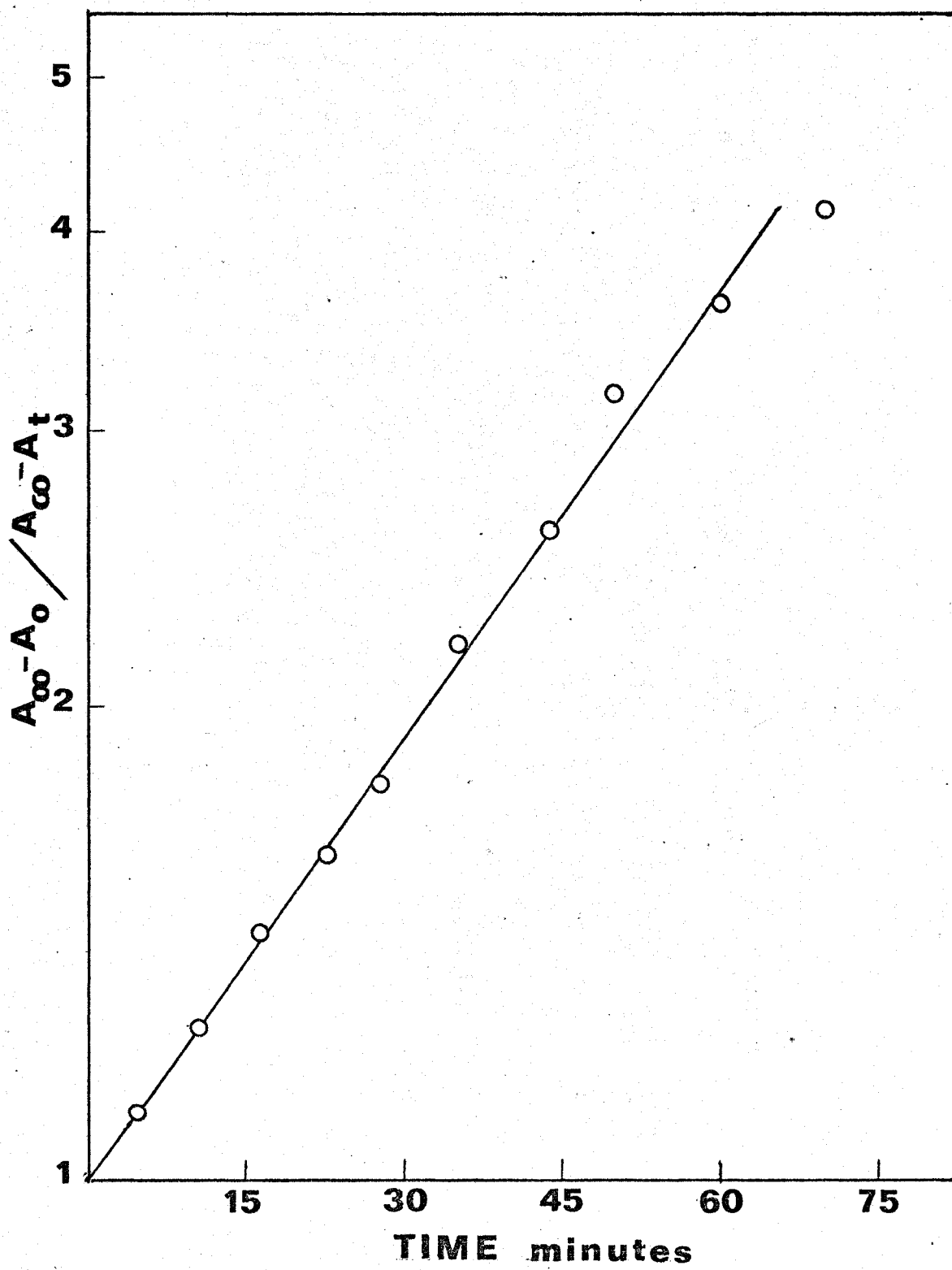
solutions were made up for each run.

From the rate constant data, the activation parameters can be calculated using the following transition state theory relationship:

$$k = \frac{kT}{h} \cdot e^{\Delta S^{\ddagger}/R} \cdot e^{-\Delta H^{\ddagger}/RT}$$

where R, the gas constant is 1.987 cal mole$^{-1}$ deg$^{-1}$, k, the Boltzmann constant is 1.381 x 10$^{-16}$ erg deg$^{-1}$ and h, Planck's constant, is 6.624 x 10$^{-27}$ erg sec.

For a reaction in solution in the liquid state, the activation enthalpy is different from the Arrhenius activation energy:

$$\Delta H^{\ddagger} = E_a - RT$$

the difference being approximately .6 k cal mole$^{-1}$ over the temperature range employed.

The rate data were evaluated statistically using a method of pooled variance for populations of different means but with common variance[25]. Assuming the variance of rate constants to be independent of temperature, the percent standard deviation for the temperature is:

$$\%r = \sqrt{\frac{\sum_T S_T}{N-3}}$$

where N is the total number of runs at all three temperatures

and $S_T$ is expressed by the relationship

$$S_T = \sum_i \frac{(k_i - \bar{k})^2}{\bar{k}} \ \%$$

where $k_i$ is the rate constant at temperature T, and $\bar{k}$ is average rate constant at temperature T.

The percent standard deviation for the rate constant at a given temperature is given by:

$$\%\sigma_{kT} = \frac{\%\sigma}{n}$$

where $\%\sigma$ is that for the three temperatures, and n is the number of runs at that particular temperature.

Since the transition state theory is employed for reaction rates, and the assumption that the activation enthalpy is constant over a small temperature range, the rate constants are considered in pairs, as seen below:

$$\Delta H_{12}^{\ddagger} = 4.576 \ \frac{T_1 T_2}{T_1 - T_2} \ \log \frac{k_1 T_2}{k_2 T_1}$$

$\Delta H_{12}$ being the activation enthalpy at temperatures $T_1$ and $T_2$, and $k_1$ and $k_2$ are then corresponding rate constants. Therefore, over the three temperature ranges studied, values of $\Delta H_{12}^{\ddagger}$, $\Delta H_{13}^{\ddagger}$, $\Delta H_{23}^{\ddagger}$ are obtained.

The standard deviation of $\Delta H_{12}^{\ddagger}$, calculated assuming exact values for temperature, i.e., $\pm 0.01^{\circ}C$, is expressed by:

$$\delta(\Delta H_{12}^{\ddagger}) = \pm 4.576 \frac{T_1 T_2}{T_1 - T_2} \left( \delta^2 \log k_1 + \delta^2 \log k_2 \right)^{\frac{1}{2}}$$

where $\delta_{\log k}$ is approximately $\log (1 - \sigma_k / 100)$ and $\sigma_k$ is expressed as a percentage.

The enthalpy of activation is found, employing a weighted average of enthalpies found by pairing the temperatures:

$$\Delta H^{\ddagger} = \frac{W_{12} H_{12}^{\ddagger} + W_{23} H_{23}^{\ddagger} + W_{13} H_{13}^{\ddagger}}{W_{12} + W_{23} + W_{13}}$$

and

$$T(\Delta H^{\ddagger}) = 1/(W_{12} + W_{13} + W_{23})^{\frac{1}{2}}$$

where $W_{12} = 1/\delta^2 (\Delta H_{12}^{\ddagger})$.

The entropy of activation calculations were made by substituting the average enthalpy value determined as above into the following equation:

$$\Delta S^{\ddagger} = 4.576 \log \frac{k}{T} + \frac{\Delta H^{\ddagger}}{T} - 47.23 \ (\text{cal deg}^{-1} \text{mole}^{-1})$$

and

$$\delta(\Delta S^{\ddagger}) = \pm \left[ 4.576 \delta^2_{\log k} + \sigma(\frac{\Delta H^{\ddagger}}{T})^2 \right]^{\frac{1}{2}}$$

The agreement of $\Delta H_{12}^{\ddagger}$, $\Delta H_{13}^{\ddagger}$, and $\Delta H_{23}^{\ddagger}$ corresponds to the linearity of the activation enthalpy plot. By employing the transition state theory rate expression, the value of $\Delta H^{\ddagger}$ is calculated from the slope of the plot of $1/T$ vs. $1/K$, Y intercept dependent on $\Delta S^{\ddagger}$. Therefore, if $\Delta H^{\ddagger}$ and $\Delta S^{\ddagger}$ are reasonably constant for a particular reaction series, the plots do not

cross, and log k then gives an unambiguous indication of reactivity order. However, when there is a variation in the $\Delta H^{\ddagger}$ and $\Delta S^{\ddagger}$ values, the plots can cross giving contradictory results. It is for this reason that the $\Delta H$ values are stressed over the kinetic rate data. As seen in Figure III, (the activation enthalpy plots of trans-$[Rh(cyclam)I(OH_2)]^{+2}$ + $Cl^-$, $Br^-$, $I^-$), there is no cross over of results, thus the data can be interpreted directly from the graph.

The kinetic results of the halogen anation substitutions are given in Table III to Table VIII. The last column in the table indicates the absolute first order rate constant.

The average anation rates for these reactions are summarized in Table IX.

These rates represent the spectrophotometric approach for anation reactions, and not included in the study was the iodide anation of trans-$[Rh(cyclam)Br(OH_2)]^{+2}$ nor the bromide or iodide anation of trans-$[Rh(cyclam)Cl(OH_2)]^{+2}$. These reaction rates could not be determined spectrophotmetrically due to the strong absorption peaks of NaBr and NaI which completely masked out the change transfer peaks of the products.

Figure 3

Activation Enthalpy Plots of the Anation Reactions:

A. trans-$[Rh(cyclam)I(OH_2)]^{+2} + Cl^-$

B. trans-$[Rh(cyclam)I(OH_2)]^{+2} + Br^-$

C. trans-$[Rh(cyclam)I(OH_2)]^{+2} + I^-$
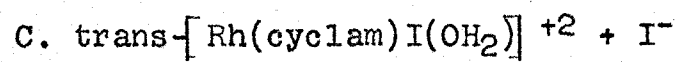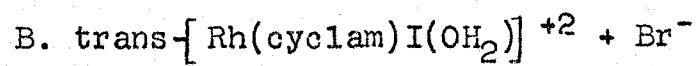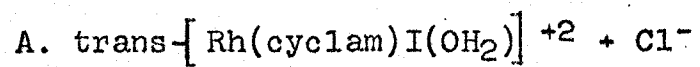
Figure 3
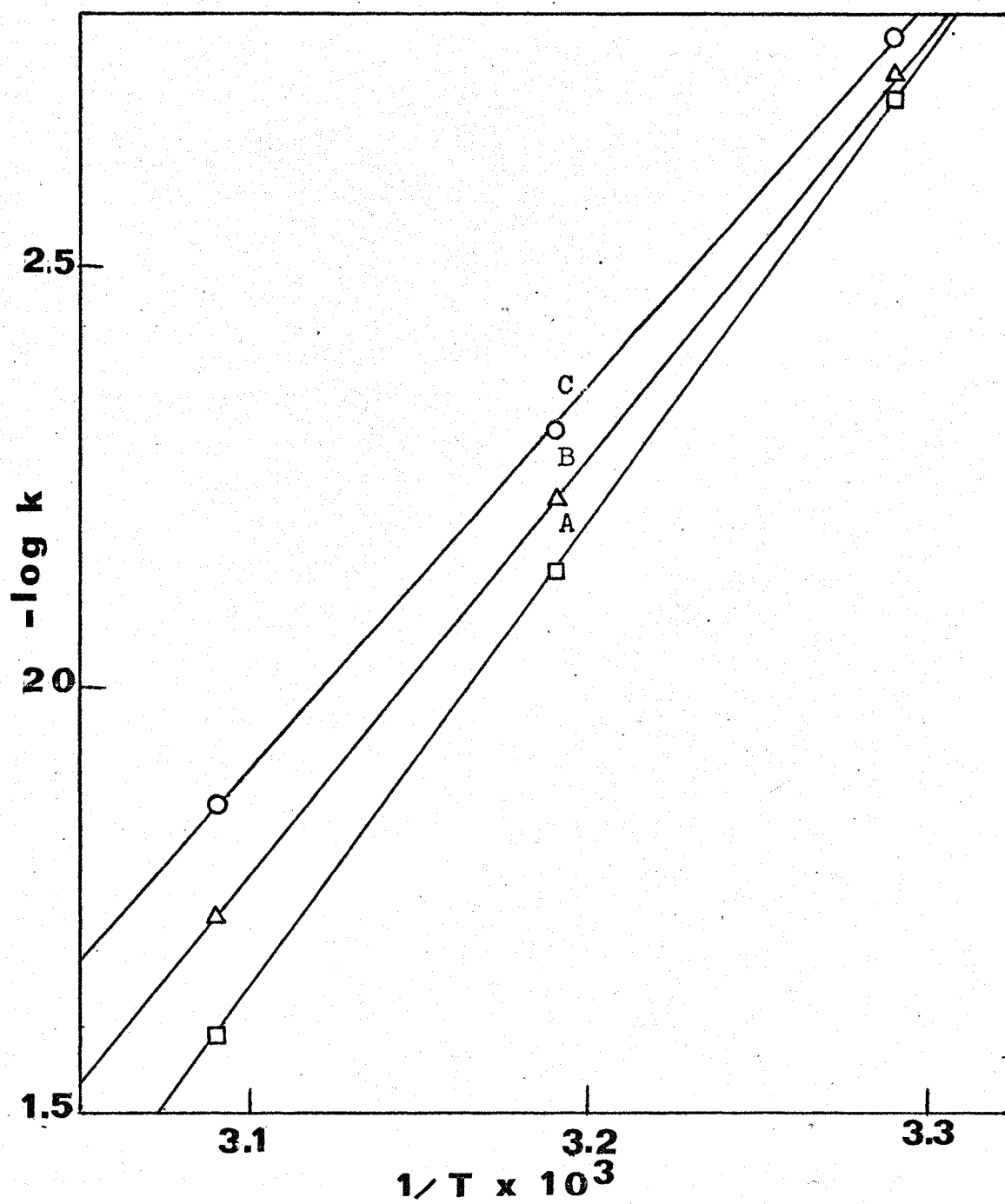
## TABLE III

Substitution Rates of $trans\text{-}[Rh(cyclam)I(OH_2)]^{+2} + Cl^-$

| $T^\circ C$ | $[Cl^-]$ | $[NaClO_4]$ | $10^{-5}k,\ (sec^{-1})$ | $10^{-2}k\ (sec^{-1})/[Cl^-]$ |
|---|---|---|---|---|
| 50 | .003 | .997 | 8.31 | 2.77 |
| | .004 | .996 | 10.32 | 2.58 |
| | .005 | .995 | 12.90 | 2.58 |
| | .006 | .994 | 16.08 | 2.68 |
| | .007 | .993 | 17.92 | 2.56 |
| | .0075 | .9925 | 19.95 | 2.66 |
| | .008 | .992 | 21.12 | 2.64 |
| | .010 | .990 | 24.60 | 2.46 |
| | .015 | .985 | 36.75 | 2.45 |
| | .0175 | .9825 | 46.55 | 2.66 |
| | .020 | .980 | 48.40 | 2.42 |
| | .025 | .975 | 56.00 | 2.24 |
| | .030 | .970 | 73.50 | 2.45 |
| 40 | .008 | .992 | .600 | .750 |
| | .015 | .985 | 1.073 | .715 |
| | .020 | .980 | 1.472 | .736 |
| | .025 | .975 | 1.835 | .734 |
| | .030 | .970 | 2.175 | .725 |
| | .040 | .960 | 2.828 | .707 |

TABLE III (concluded)

| T°C | $[Cl^-]$ | $[NaClO_4]$ | $10^{-5}k$, $(sec^{-1})$ | $10^{-2}k$ $(sec^{-1})/[Cl^-]$ |
|---|---|---|---|---|
| 30 | .020 | .980 | .400 | .200 |
| | .025 | .975 | .530 | .212 |
| | .030 | .970 | .600 | .200 |
| | .035 | .965 | .689 | .197 |
| | .040 | .960 | .792 | .198 |
| | .045 | .955 | .936 | .208 |
| | .050 | .950 | 1.050 | .210 |
| | .055 | .945 | 1.144 | .208 |
| | .060 | .940 | 1.320 | .220 |
| | .065 | .935 | 1.430 | .220 |
| | .070 | .930 | 1.386 | .198 |
| | .080 | .920 | 1.536 | .192 |

TABLE IV

Substitution Rates of trans-$\left[\text{Rh(cyclam)I(OH}_2)\right]^{+2}$ + Br$^-$

| T°C | [Br$^-$] | [NaClO$_4$] | $10^{-5}k$ (sec$^{-1}$) | $10^{-2}k$ (sec$^{-1}$)/[Br$^-$] |
|---|---|---|---|---|
| 50 | .004 | .996 | 8.00 | 2.00 |
| | .005 | .995 | 9.45 | 1.89 |
| | .006 | .994 | 11.28 | 1.88 |
| | .007 | .993 | 13.86 | 1.98 |
| | .008 | .992 | 15.84 | 1.98 |
| | .009 | .991 | 19.53 | 2.17 |
| | .010 | .990 | 17.90 | 1.79 |
| | .015 | .985 | 27.30 | 1.82 |
| | .020 | .980 | 35.00 | 1.75 |
| | .030 | .970 | 51.30 | 1.71 |
| | .035 | .965 | 60.50 | 1.73 |
| | .040 | .960 | 63.60 | 1.59 |
| 40 | .006 | .994 | .408 | .680 |
| | .007 | .993 | .476 | .680 |
| | .020 | .980 | 1.360 | .680 |
| | .025 | .975 | 1.675 | .670 |
| | .040 | .960 | 2.680 | .670 |
| | .045 | .955 | 30.38 | .675 |

TABLE IV (concluded)

| $T^{o}C$ | $[Br^-]$ | $[NaClO_4]$ | $10^{-5}k$ (sec$^{-1}$) | $10^{-2}k$ (sec$^{-1}$)/$[Br^-]$ |
|---|---|---|---|---|
| 30 | .020 | .980 | .374 | .187 |
|    | .025 | .975 | .445 | .178 |
|    | .030 | .970 | .549 | .183 |
|    | .035 | .965 | .613 | .175 |
|    | .040 | .960 | .772 | .193 |
|    | .045 | .955 | .837 | .186 |
|    | .050 | .950 | .950 | .190 |
|    | .055 | .945 | 1.018 | .185 |
|    | .060 | .940 | 1.122 | .187 |
|    | .065 | .935 | 1.222 | .188 |
|    | .070 | .930 | 1.351 | .193 |
|    | .085 | .915 | 1.709 | .201 |

## TABLE V

Substitution Rates of trans-$[Rh(cyclam)I(OH_2)]^{+2}$ + $I^-$

| $T^\circ C$ | $[I^-]$ | $[NaClO_4]$ | $10^{-5}k$ (sec$^{-1}$) | $10^{-2}1$ (sec$^{-1}$)/$[I^-]$ |
|---|---|---|---|---|
| 50 | .003 | .997 | 4.11 | 1.37 |
| | .004 | .996 | 5.28 | 1.32 |
| | .006 | .994 | 7.86 | 1.31 |
| | .007 | .993 | 9.45 | 1.35 |
| | .009 | .991 | 11.88 | 1.32 |
| | .010 | .990 | 14.00 | 1.40 |
| | .020 | .980 | 26.60 | 1.33 |
| | .025 | .975 | 34.00 | 1.36 |
| | .030 | .970 | 41.10 | 1.37 |
| | .035 | .965 | 48.65 | 1.39 |
| | .040 | .960 | 53.20 | 1.33 |
| | .045 | .955 | 58.95 | 1.31 |
| 40 | .008 | .992 | .388 | .485 |
| | .009 | .991 | .437 | .485 |
| | .025 | .975 | 1.223 | .489 |
| | .030 | .970 | 1.491 | .497 |
| | .045 | .955 | 2.219 | .493 |
| | .055 | .945 | 2.723 | .495 |

TABLE V (concluded)

| $T^{\circ}C$ | $[I^-]$ | $[NaClO_4]$ | $10^{-5}k \ (sec^{-1})$ | $10^{-2}k \ (sec^{-1})/[I^-]$ |
|---|---|---|---|---|
| 30 | .040 | .960 | .664 | .166 |
|  | .045 | .955 | .702 | .156 |
|  | .050 | .950 | .800 | .160 |
|  | .055 | .945 | .886 | .161 |
|  | .060 | .940 | .924 | .154 |
|  | .065 | .935 | 1.053 | .162 |
|  | .070 | .930 | 1.155 | .165 |
|  | .075 | .925 | 1.230 | .164 |
|  | .080 | .920 | 1.288 | .161 |
|  | .085 | .915 | 1.403 | .165 |
|  | .090 | .910 | 1.503 | .167 |
|  | .095 | .905 | 1.625 | .171 |

TABLE VI

Substitution Rates of trans-$\left[Rh(cyclam)Br(OH_2)\right]^{+2}$ + $Cl^-$

| T°C | $\left[Cl^-\right]$ | $\left[NaClO_4\right]$ | $10^{-7}k$ (sec$^{-1}$) | $10^{-4}k$ (sec$^{-1}$)/$\left[Cl^-\right]$ |
|---|---|---|---|---|
| 70 | .044 | .956 | 3.62 | 8.22 |
| | .046 | .954 | 3.84 | 8.35 |
| | .048 | .952 | 3.86 | 8.05 |
| | .050 | .950 | 4.35 | 8.70 |
| | .054 | .946 | 4.42 | 8.20 |
| | .058 | .942 | 4.99 | 8.61 |
| | .066 | .934 | 5.58 | 8.46 |
| | .070 | .930 | 5.84 | 8.35 |
| | .074 | .926 | 6.20 | 8.38 |
| | .080 | .920 | 6.55 | 8.19 |
| | .230 | .770 | 19.30 | 8.39 |
| | .400 | .600 | 20.40 | 8.19 |
| | .400 | .600 | 34.90 | 8.71 |
| 60 | .100 | .900 | .286 | .286 |
| | .105 | .895 | .302 | .288 |
| | .110 | .890 | .326 | .296 |
| | .120 | .880 | .348 | .290 |
| | .125 | .875 | .375 | .300 |
| | .400 | .600 | 1.080 | .271 |

TABLE VI (concluded)

| $T^{\circ}C$ | $[Cl^-]$ | $[NaClO_4]$ | $10^{-7}k$ $(sec^{-1})$ | $10^{-4}k$ $(sec^{-1})/[Cl^-]$ |
|---|---|---|---|---|
| 60 | .600 | .400 | 1.745 | .291 |
| 50 | .600 | .400 | .361 | .602 |
| | .620 | .380 | .382 | .616 |
| | .640 | .360 | .401 | .626 |
| | .660 | .340 | .403 | .610 |
| | .720 | .280 | .428 | .595 |
| | .740 | .260 | .443 | .598 |
| | .760 | .240 | .432 | .569 |
| | .800 | .200 | .452 | .565 |
| | .800 | .200 | .452 | .565 |

TABLE VII

Substitution Rates of trans-$\left[ Rh(cyclam)Br(OH_2) \right]^{+2}$ + Br$^-$

| $T^\circ C$ | $[Br^-]$ | $[NaClO_4]$ | $10^{-7}k \ (sec^{-1})$ | $10^{-4}k \ (sec^{-1})/[Br^-]$ |
|---|---|---|---|---|
| 70 | .050 | .950 | 3.62 | 7.23 |
|  | .052 | .948 | 3.66 | 7.03 |
|  | .056 | .946 | 3.77 | 6.73 |
|  | .060 | .940 | 3.87 | 6.45 |
|  | .064 | .936 | 4.32 | 6.75 |
|  | .068 | .932 | 4.66 | 6.85 |
|  | .072 | .928 | 5.13 | 7.12 |
|  | .076 | .924 | 5.48 | 7.21 |
|  | .080 | .920 | 5.20 | 6.50 |
|  | .084 | .916 | 5.38 | 6.40 |
|  | .170 | .830 | 10.93 | 6.45 |
|  | .200 | .800 | 13.10 | 6.55 |
|  | .200 | .800 | 12.90 | 6.45 |
| 60 | .175 | .825 | .376 | 2.15 |
|  | .180 | .820 | .405 | 2.25 |
|  | .185 | .815 | .440 | 2.38 |
|  | .190 | .810 | .429 | 2.26 |
|  | .195 | .805 | .439 | 2.25 |
|  | .200 | .800 | .474 | 2.37 |

## TABLE VII (concluded)

| $T^{o}C$ | $[Br^-]$ | $[NaClO_4]$ | $10^{-7}k$ (sec$^{-1}$) | $10^{-4}k$ (sec$^{-1}$)/$[Br^-]$ |
|---|---|---|---|---|
| 60 | .700 | .300 | 1.576 | 2.25 |
|    | .700 | .300 | 1.462 | 2.09 |
| 50 | .700 | .300 | .340 | .485 |
|    | .720 | .280 | .353 | .490 |
|    | .740 | .260 | .365 | .493 |
|    | .760 | .240 | .369 | .486 |
|    | .780 | .220 | .373 | .478 |
|    | .820 | .180 | .397 | .484 |
|    | .840 | .160 | .416 | .495 |
|    | .860 | .140 | .433 | .504 |
|    | .880 | .120 | .432 | .491 |
|    | .900 | .100 | .446 | .495 |
|    | .920 | .080 | .459 | .499 |
|    | 1.00 | .00 | .413 | .413 |
|    | 1.00 | .00 | .450 | .450 |

TABLE VIII

Substitution Rates of trans-$\left[\text{Rh(cyclam)Cl(OH}_2)\right]^{+2}$ + Cl$^-$

| T°C | [Cl$^-$] | [NaClO$_4$] | $10^{-5}k$ (sec$^{-1}$) | $10^{-3}k$ (sec$^{-1}$)/[Cl$^-$] |
|---|---|---|---|---|
| 90 | .060 | .940 | 9.06 | 1.51 |
| | .064 | .936 | 9.28 | 1.45 |
| | .068 | .932 | 9.72 | 1.43 |
| | .072 | .928 | 10.30 | 1.43 |
| | .076 | .924 | 10.56 | 1.39 |
| | .080 | .920 | 10.80 | 1.35 |
| | .084 | .916 | 11.84 | 1.41 |
| | .088 | .912 | 12.67 | 1.44 |
| | .092 | .908 | 12.60 | 1.37 |
| | .096 | .904 | 13.63 | 1.39 |
| | .096 | .904 | 13.34 | 1.42 |
| | .200 | .800 | 28.00 | 1.40 |
| 80 | .200 | .800 | .822 | .411 |
| | .205 | .795 | .839 | .419 |
| | .210 | .790 | .920 | .438 |
| | .215 | .785 | .884 | .411 |
| | .220 | .780 | 1.012 | .460 |
| | .225 | .775 | 1.049 | .460 |

TABLE VIII (concluded)

| T°C | $[Cl^-]$ | $[NaClO_4]$ | $10^{-5}k$ (sec$^{-1}$) | $10^{-3}k$ (sec$^{-1}$)/$[Cl^-]$ |
|---|---|---|---|---|
| 70 | .20 | .800 | .253 | .127 |
| | .70 | .300 | .888 | .127 |
| | .72 | .280 | .936 | .130 |
| | .74 | .260 | .971 | .131 |
| | .76 | .240 | .974 | .128 |
| | .78 | .220 | .975 | .125 |
| | .80 | .200 | .945 | .118 |

TABLE IX

Average Anation Rates of trans-$\left[Rh(cyclam)X(OH_2)\right]^{+2} + Y^-$

| $T^oC$ | X | Y | $k\ (sec^{-1})/\left[Y^-\right]$ | $\sigma$ |
|--------|-----|-----|-------------------------------|----------|
| 30 | I | Cl | $2.05 \times 10^{-3}$ | .03 |
|    | I | Br | $1.87 \times 10^{-3}$ | .02 |
|    | I | I  | $1.63 \times 10^{-3}$ | .02 |
| 40 | I | Cl | $7.34 \times 10^{-3}$ | .03 |
|    | I | Br | $6.78 \times 10^{-3}$ | .02 |
|    | I | I  | $4.87 \times 10^{-3}$ | .01 |
| 50 | I | Cl | $2.58 \times 10^{-2}$ | .03 |
|    | I | Br | $1.87 \times 10^{-2}$ | .01 |
|    | I | I  | $1.35 \times 10^{-2}$ | .01 |
| 50 | Br | Cl | $5.97 \times 10^{-5}$ | .03 |
|    | Br | Br | $4.91 \times 10^{-5}$ | .01 |
| 60 | Br | Cl | $2.92 \times 10^{-4}$ | .01 |
|    | Br | Br | $2.28 \times 10^{-4}$ | .02 |
| 70 | Br | Cl | $8.35 \times 10^{-4}$ | .03 |
|    | Br | Br | $6.85 \times 10^{-4}$ | .03 |
| 70 | Cl | Cl | $1.26 \times 10^{-4}$ | .03 |

TABLE IX (concluded)

| $T^{\circ}C$ | X | Y | $k\ (sec^{-1})/[Y^-]$ | $\sigma$ |
|---|---|---|---|---|
| 80 | Cl | Cl | $4.34 \times 10^{-4}$ | .16 |
| 90 | Cl | Cl | $1.42 \times 10^{-3}$ | .09 |

# IV. DISCUSSION AND CONCLUSIONS

## a) The Trans Effect

As was mentioned previously in the introduction, both kinetic and thermodynamic data can be used to compare the trans effect of the halogen ligands quantitatively.

From Table IX, the rate constants at $50^\circ$C show that $Cl^-$ anation of the $I(OH_2)$ complex is some 430 times faster than $Br(OH_2)$ anation with $Cl^-$. At $70^\circ$C, it is noted that $Cl^-$ anation of the $Br(OH_2)$ is 6.6 times faster than the same anation of the $Cl(OH_2)$ complex. From this data, the kinetic trans effect would be $I > Br > Cl$.

Thermal data for the anation reactions is found in Table X, and Table XI demonstrates the enthalpy of activation results obtained using a weighted average of enthalpies by pairing of temperatures. The thermal data demonstrates the same trans effect order as above. There is a marked increase in $\Delta H^\ddagger$, 4.45 k cal mole$^{-1}$ in comparing the $Cl^-$ anation of $I(OH_2)$ with that of the $Br(OH_2)$ complex. However, in moving from the $Cl^-$ anation of $Br(OH_2)$ to $Cl(OH_2)$, $\Delta H^\ddagger$ is 1.08 k cal mole$^{-1}$. This is evidence that the trans effect of $I^-$ is much greater than either $Br^-$ or $Cl^-$, the $Br^-$ trans effect being slightly greater than the $Cl^-$. This order is also supported by the $\Delta S^\ddagger$ evidence which appears in Table X. Thus, the kinetic trans effect parallels the polarizability of these ions, and is the order expected, based on the polarization theory concept of trans bond weakening [26].
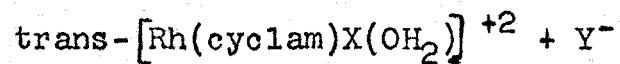
46

TABLE X

Thermal Parameters for the Anation Reaction

$$\text{trans-}\left[\text{Rh(cyclam)X(OH}_2)\right]^{+2} + Y$$
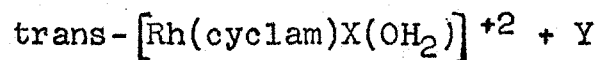
| X | Y$^-$ | $\Delta H^{\ddagger}$ k cal mole$^{-1}$ | $\Delta S^{\ddagger}$ cal deg$^{-1}$ mole$^{-1}$ |
|---|---|---|---|
| I | Cl | 23.97 ± .15 | 8.29 ± .28 |
| I | Br | 21.79 ± .21 | 1.00 ± .39 |
| I | I | 19.95 ± .09 | -5.42 ± .17 |
| Br | Cl | 28.42 ± .07 | 10.11 ± .13 |
| Br | Br | 28.35 ± .13 | 9.47 ± .22 |
| Cl | Cl | 29.55 ± .17 | 10.99 ± .28 |

## TABLE XI

Linearity of $\Delta H^{\ddagger}$ Plots for the Anation Reaction

trans-$[Rh(cyclam)X(OH_2)]^{+2} + Y^-$

| X | $Y^-$ | $\Delta H_{12}^{\ddagger}$ | $\Delta H_{23}^{\ddagger}$ | $\Delta H_{13}^{\ddagger}$ |
|---|---|---|---|---|
| I | Cl | 24.60 | 23.98 | 23.39 |
| I | Br | 19.81 | 21.77 | 23.62 |
| I | I | 19.83 | 19.95 | 20.06 |

The effect of changing the entering group can also be seen from the data of Table IX and Table X. For the $I(OH_2)$ complexes at $50^{\circ}C$ the $I^-$ anation is the slowest. The bromide and chloride anations are 1.15 and 1.26 times faster respectively than the corresponding $I^-$ anation. The kinetic order of entering groups would appear to be $Cl > Br > I$.

The $\Delta H^{\ddagger}$ data indicates, however, that the $I^-$ anation of the $I(OH_2)$ complex is easiest; the $\Delta H^{\ddagger}$ for $Br^-$ and $Cl^-$ anation requiring approximately 2.0 and 4.0 k cal mole$^{-1}$ more energy. Thus, the true nucleophilicity order of the entering group is $I > Br > Cl$, which is supported by literature evidence [9a].

b) Mechanism of Anation

The possibility of ion-pair participitation was investigated since it was thought to play a role in the mechanistic behaviour of the trans-$[Rh(cyclam)I(OH_2)]^{+2}$ complex intermediates.

The anation rate involving an ion-pair and a dissociative process is practically independent of the entering anion in which the five coordinate intermediate is so unstable that it recombines with any available ligand. There is no evidence from the kinetic and thermal data reported here that anation is independent of the entering anion. (See Table IX and Table X for the trans-$[Rh(cyclam)X(OH_2)]^{+2}$ complexes.)

Reaction kinetics can demonstrate ion-pairing. If ion-pairing is complete at the lowest concentrations used, the rates of anation or replacement of one anion by another will

be found to be independent of the concentration of the entering anion [27]. Also with ion-pairing, there is a noticeable decrease in observed rate constant with increased concentration of the substituent. Neither of the above situations were observed for the concentration Maxima and Minima (Table III - Table VIII) studied.

Spectroscopic evidence for ion-pairing is a shift in the near ultraviolet spectra of the complex and an immediate increase in the absorbancy upon addition of free halide [18]. A greater shift would be expected by $Br^-$ than $Cl^-$ since the former will more readily lose its charge, increasing its susceptibility to ion-pair. Iodide would show the greatest effect.

The ultraviolet spectra for the anation of trans-[Rh(cyclam) I(OH_2)]$^{+2}$ are seen in Figure 4. Identical maxima are found at 229 $cm^{-1}$ for the complex with $10^{-5}$ M $HClO_4$ and 1.0 M $NaClO_4$. A shift in maxima to 230 $cm^{-1}$ is found for the same complex in .003 M $Cl^-$ and .003 M $Br^-$ ($\mu$ adjusted to 1.00 with $NaClO_4$). The bathochromic shift is understandable since the products, trans-[Rh(cyclam)ClI]$^+$ and trans-[Rh(cyclam)BrI]$^-$ have strong absorption peaks at 245 $cm^{-1}$ and 256 $cm^{-1}$ respectively. The slight shift in peak maxima is within experimental error and cannot be attributed to ion-pair formation. The iodide spectra could not be investigated, the $I^-$ having strong absorption in the 225 $cm^{-1}$ region. Since there is little supporting evidence from this data for ion-pair formation, an interchange mechanism postulated in the introduction seems unlikely.

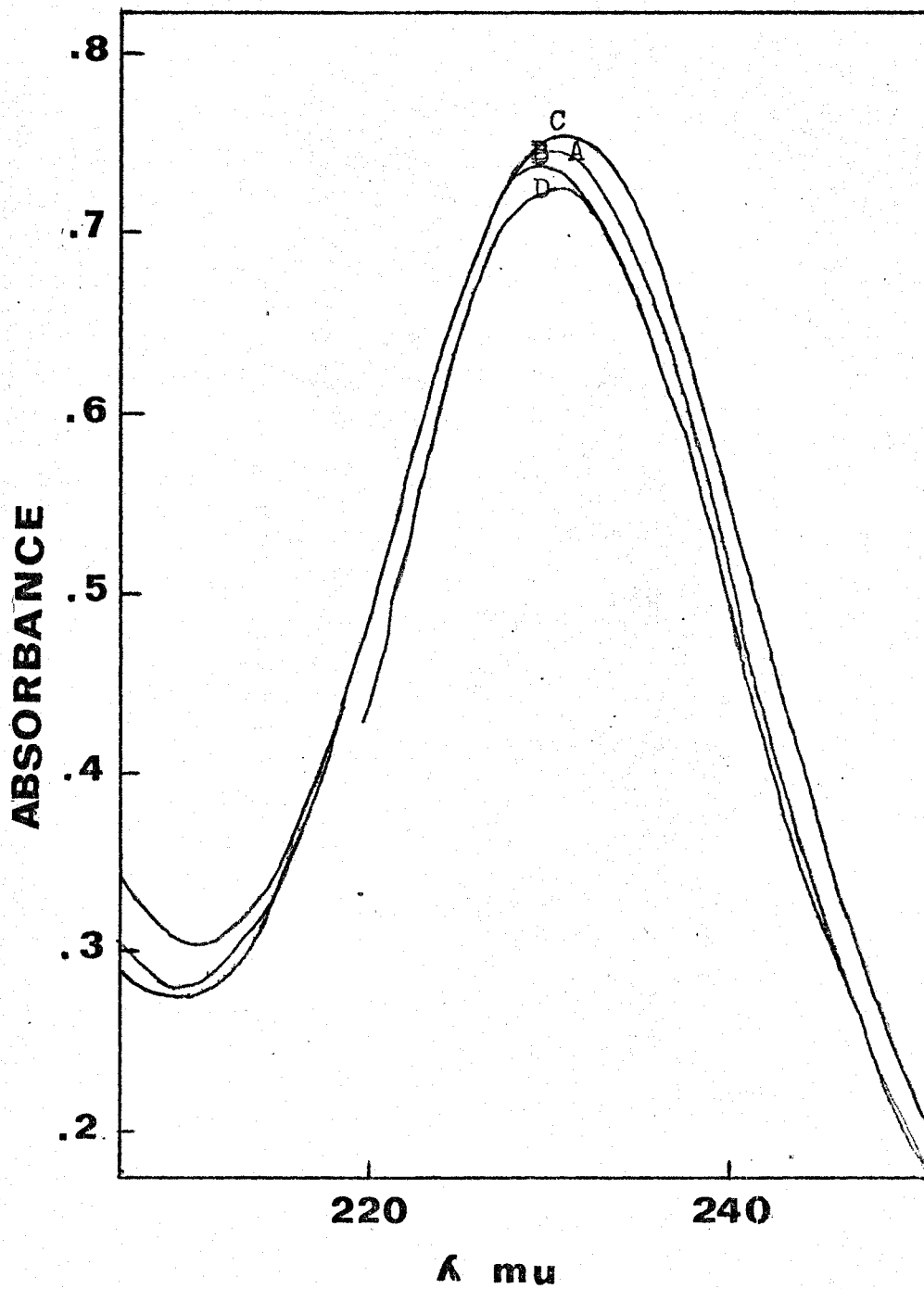The only prime evidence for the postulation of a completely

Figure 4

Charge Transfer Spectra* of :

A. trans $I(OH_2)$ + $10^{-5}$ $HClO_4$

B. trans $I(OH_2)$ + 1.00 M $NaClO_4$

C. trans $I(OH_2)$ + .003 M NaCl + .997 M $NaClO_4$

D. trans $I(OH_2)$ + .003 M NaBr + .997 M $NaClO_4$

* Spectra on a Beckman DK-1A recording spectrophotometer.

Figure 4

dissociative mechanism, i.e., unimolecular dissociation of the aquo complex followed by a competition between the solvent water and the entering anion for a five-coordinate intermediate, can be noted from the $\Delta S^{\ddagger}$ values in Table X.

All of the anation reactions except iodide anation of the $I(OH_2)$ complex yield positive $\Delta S^{\ddagger}$ values. This simply means that the entropy of transition state is greater than the entropy of the reactants [28]. This notable increase in entropy corresponds to a more ordered or less random molecular configuration. Since the iodide anation of the $I(OH_2)$ complex has negative $\Delta S^{\ddagger}$ it can be concluded that the Rhodium complex and the $I^-$ ion are more tightly bound together in the transition state causing considerable loss of freedom [28] and appreciably more bond making. Since the $I(OH_2)$ complex anation with $Br^-$ and $Cl^-$ have positive $\Delta S^{\ddagger}$, a more loosely bound intermediate prevails, and, as a result, more dissociation would appear possible. From this $\Delta S^{\ddagger}$ data, it can be concluded that the $Cl(OH_2) \gtrsim Br(OH_2) > I(OH_2)$ with regard to favouring a dissociative type of mechanism.

Indicative of a dissociative type of mechanism is small differences in the rate of the different incoming groups [29]. Rate variations can be noted in Table IX. If the differences can be considered negligible, these rate variations could indicate that dissociation is occurring. As well, these differences can be justified by the difference in the nucleophilicities of the incoming ligands. However, based on $\Delta H^{\ddagger}$ values, the fastest rate, $Cl^-$, has the lowest nucleophilicity, with iodide the best nucleophile.

The intermediate of the dissociative mechanism could be a trigonal-bipyramid or a square-pyramidal structure. But the trigonal-bipyramidal structure would require one nitrogen of the cyclam tetramine to be out of the trigonal plane; since cyclam is a stereoretentive ligand, it would favour a tetragonal form of the intermediate, and this form over the trigonal-bipyramid would not have any marked systematic effect on the rate of reaction [30]. The following represents the skeletal relationship of the square-pyramidal five-coordinate intermediate resulting from the release of water from trans-$[Rh(cyclam)Cl(OH_2)]^{+2}$ [31]:
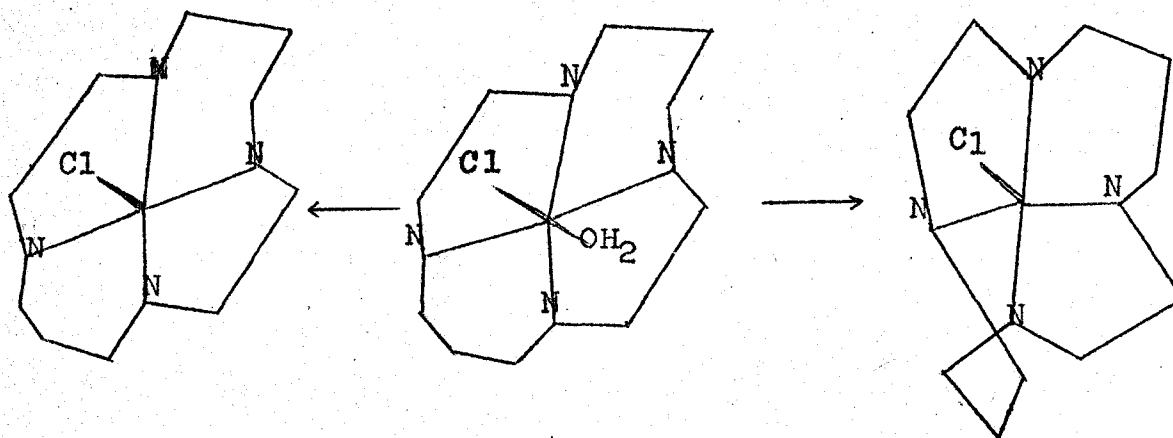


There was a noticeable leveling-off effect of the first order rate plots especially with the anation of the trans-$I(OH_2)$ with $I^-$ and less noticeably in the anation of trans-$Cl(OH_2)$ with $Cl^-$. From calculations, using aquation values of Koprich [32] it was determined that the leveling-off effect of the individual kinetic plots could not be accounted for by appreciable acid hydrolysis of the product. Only 3% of the product peak decrease could be explained by this reaction.

The evidence available to support an $S_N2$ type mechanism

includes the small dependence of these anation rates on the nature of the incoming group (Table IX), but largely the complete dependence on the concentration of the entering group. (The concentration range, (.003 - 1.00), studied herein, was limited by the time and temperature range over which the anations could be studied.) In addition, the $\Delta H^\dagger$ data (Table X) indicates a real dependence on the nature of the incoming group ($I^- \sim$ 2.0 k cal mole$^{-1}$ greater than $Br^-$, which is $\sim$ 2.0 k cal mole$^{-1}$ greater than $Cl^-$). The positive $\Delta S^\dagger$ values strongly support dissociation or bond-breaking, and does little to support association or bond-making, except for the $I^-$ anation of $I(OH_2)^{-2}$ which may be accounted for by the large $\Pi$ accepting ability of $I^-$.

Based on the results of the studies of these trans$\cdot$ $[Rh(cyclam)X(OH_2)]^{+2}$, there is no means of assigning unambiguously a specific mechanism. The mechanism lies somewhere between the two extremes of totally $S_N1$ or $S_N2$ and it would be incorrect to suppose that these reactions would have a unique mechanism.

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