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Kinetic and thermodynamic studies of some rhodium cyclam complexes.

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KINETIC AND THERMODYNAMIC STUDIES
OF
SOME RHODIUM CYCLAM COMPLEXES

By

HENRY HSIAO-LIANG CHUNG

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ABSTRACT

The base hydrolysis of trans- $Rh(cyclam)XY^+$ (cyclam= 1,4,8,11-tetraazacyclotetradecane; X and Y = Cl^-, Br^- and I^-) has been studied in aqueous solution over a range of hydroxide concentration at various temperatures. All of the reactions proceed with complete retention of configuration, and no trans to cis isomerization is found in this study. The kinetics are done at a constant ionic strength with excess of hydroxide ion (smallest ratio=200/1) so that pseudo first order rate constants are obtained for all the determinations. Up to 2.00 M, there is a direct first-order dependence upon the hydroxide concentration. The results of the rate constants and the activation parameters are interpreted in terms of an S_N1CB mechanism. The kinetic trans effect of these complexes increases along the series on a rate basis Cl^-, Br^-, I^-, but based on enthalpies of activation $I^- > Br^- = Cl^-$. These Rh(III) complexes exhibit kinetic class (b) character on the ΔH^* basis. The behaviour of these complexes is compared with that of the cyclam complexes of Co (III) and Cr(III) and the corresponding Rh(III) complexes of tetraammine and bis(ethylenediamine).

Equilibrium studies involving halide interchange in the trans- $Rh(cyclam)XY^+$ systems have been studied at different temperatures to permit calculation of the ΔH values. The solutions are adjusted to 1×10^{-5} M acid concen-

tration for the complexes in order to prevent base hydrolysis. The halide concentration in each solution is greater than 2.5 x 10^{-3} M, so that no acid hydrolysis occur. The ionic strengths for the equilibrium constants, K_1 and K_2, are different thereby preventing the interference of the triiodide formation. The thermodynamic class (b) character is found for these complexes in terms of both equilibrium constants and Δ H values and Rh(III) is compared with other metals of class (b) character. The relative enthalpies of bonding of these complexes are in the order di-iodo > iodobromo > iodochloro > dibromo > bromochloro > dichloro. The thermodynamic trans effect is in the order $I^- > Br^- = Cl^-$ on the basis of the Δ H values and the equilibrium constants.

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I. INTRODUCTION

1. Base hydrolysis reactions

Kinetic substitution reactions in octahedral six-coordinate transition metal complexes have been the subject of extensive investigations and reviews (1). These studies have provided abundant information on new geometries, coordination numbers, electron configurations, and mechanistic processes. Although differences in behavior are found, and indeed are to be expected, it is surprising how limited is the range of behavior encountered. As a rule, octahedral complexes undergo acid hydrolysis and substitution reactions with other ligands at similar rates and are not sensitive to the nature and concentration of the incoming group. Only first order kinetics is observed.

In marked contrast, one nucleophile, hydroxide ion, exhibits distinctly different behaviour and the term base hydrolysis has been assigned to these reactions. This substitution by hydroxide takes place at rates that are many orders of magnitude faster than other substitution reactions of the complexes. The reactions are second order overall, first order in each of the complex and the hydroxide concentration.

For the substitution reactions, involving nucleophiles other than OH^-, a solvent molecule has usually been postulated to be involved,with (in aqueous solution) the aquo complex the product of the initial slow step irrespective of the mechanism involved. Thus acid hydrolysis is the slow step and precedes substitution by the other incoming nucleophiles and accounts for reaction with H_2O and all other nucleophiles having the same rate. Psuedo first order kinetics is expected as found and no direct mechanistic conclusion can be drawn from the kinetics alone. In certain cases, a dissociative mechanism (S_N1) was assigned where there was direct kinetic (2) or stereochemical evidence for an intermediate of lower coordination number (3), but in most situations such a species does not live long enough to equilibrate with its environment. The aquo complex formed as the intermediate is then anated in a fast reaction by the incoming nucleophile to form the final product. Not surprisingly, these anation studies (replacement of H_2O by another nucleophile) on aquo complexes have revealed dependence upon the nature and concentration of the incoming ligand (4).

The mechanism of base hydrolysis of octahedral complexes has been the subject of much discussion. Four different mechanisms have been proposed to explain the rapid base hydrolysis.

The first mechanism, proposed on the basis of the kinetic form by Ingold and co-workers (5), is a simple S_N2 (substitution, nucleophilic, bimolecular) reaction between the incoming hydroxide ion and the metal complexes, where both the leaving group and the entering group are partially bonded in the octahedral complex of the rate determining step.

$$R_4XMY^{n+} + OH^- \xrightarrow{\text{slow}} \left[R_4XM\genfrac{}{}{0pt}{}{Y}{OH} \right]^{(n-1)+} \xrightarrow{\text{fast}} R_4XMOH^{n+} + Y^-$$

This mechanism was further elaborated by Chan and Tobe (6) who suggested that the unique high reactivity of the hydroxide ion towards the trans- and cis- $Co(en)_2Cl_2{}^+$, $Co(en)_2ClBr{}^+$, $Co(en)_2(OH)Cl{}^+$ and $Co(en)_2(OH)Br{}^+$ complexes in aqueous solution could be explained in terms of its mobility through the solvent shell of the complex ions (1d). Any other anionic reagent would require some desolvation in order to enable the reagents to come into contact, but the hydroxide ion can pass through the solvent shell by a Grotthus proton-transfer mechanism and appear in a position suitable for substitution without occurrence of desolvation. The hydroxide ion will have a similar mobility around the complex ion, although the Grotthus chain may also include the amine protons and those on the co-ordinated hydroxide group. The mobility of the hydroxide ion about the complex may be visualised as a "sticky" collision whereby the reagents are kept together longer than is usual, even in solution, and are able to change their relative orientations.

In very early work (1939), Lamb (7) found that the addition of sodium hydroxide to solution of chloro-and bromopentamminerhodium(III) complexes resulted in the rapid conversion of these substances to their corresponding hydroxopentammines and the reaction was first order in

OH^- concentration. At that time he also postulated the simple S_N2 mechanism.

The second mechanism, commonly known as S_N1CB (substitution, nucleophilic, unimolecular, conjugate base), was first suggested by Garrick (8) based on the work of James, Spoor and Briscoe (9) who found that the hexammine-cobalt(III) cation exchanged hydrogen with deuterium oxide. Since this complex is known to be very stable with regard to loss of ammonia, it was proposed that the exchange is accomplished by the following ionization:

$$Co(NH_3)_6{}^{+3} + D_2O \rightleftharpoons Co(NH_3)_5NH_2{}^{+2} + HD_2O^+$$

This view is substantiated by the fact that the rate of exchange varies inversely as the hydrogen-ion concentration. Furthermore, salts of complex ions of the type $Pt(NH_3)_4NH_2Cl^{+2}$ and $Pt(NH_3)_5NH_2{}^{+3}$ have indeed been isolated (10). Garrick suggested that the role of hydroxide ion was essentially catalytic and that it served to generate a dissociatively reactive entity by removing a proton from the complex. The suggested reaction path may be outlined as follows:

$$\begin{tikzcd}
Co(NH_3)_5Cl^{+2} \arrow[d, shift right, "OH^-"'] & & \\
Co(NH_3)_4NH_2Cl^{+1} + H_2O \arrow[u, shift right, "H^+"'] \arrow[r, "slow"] & Co(NH_3)_4NH_2H_2O^{+2} \arrow[d] & + Cl^- \\
& Co(NH_3)_5OH^{+2} &
\end{tikzcd}$$

With such a reaction mechanism the rate of hydrolysis would be of the first order in hydroxide ion concentration, as this controls the amount of the amido reactive intermediate, $Co(NH_3)_4NH_2Cl^{+1}$, available for reaction.

This mechanism was strongly supported and elaborated on by Basolo and Pearson (11). They suggested that this mechanism involved a rapid acid-base deprotonation of the amine-proton of the complex. This was then followed by a rate determining dissociative aquation of the amido-conjugate base. This mechanism could be illustrated as follows.

$$R_4XMY^{n+} + OH^- \underset{k_{-1}}{\overset{k_1}{\rightleftharpoons}} R_3(R\text{-}H)XMY^{(n-1)+} + H_2O \quad \text{(fast)}$$

$$R_3(R\text{-}H)XMY^{(n-1)+} \xrightarrow{k_{cb}} R_3(R\text{-}H)XM^{n+} + Y^- \quad \text{(slow)}$$

$$R_3(R\text{-}H)XM^{n+} + H_2O \longrightarrow R_3(R\text{-}H)XM(H_2O)^{n+} \quad \text{(fast)}$$

$$R_3(R\text{-}H)XM(H_2O)^{n+} \longrightarrow R_4XMOH^{n+} \quad \text{(fast)}$$

This mechanism was initially supported by the fact that the characteristic second order kinetic form of the base hydrolysis reaction was only observed when the complex contained ligands with a potentially acidic proton such as H_2O, NH_3, ethylenediamine, and other amines.

For this mechanism, if one assumes that the first step involving proton transfer is truly an equilibrium and fast compared to the dissociation, then the kinetic expression is obtained as follows.

$$-\frac{d\,[R_4XMY^{n+}]_t}{dt} = \frac{K \cdot k_{cb}\,[R_4XMY^{n+}]_t\,[OH^-]}{1 + K\,[OH^-]}$$

where $[R_4XMY^{n+}]_t$ represents the total concentrations of the complex and its conjugate base and K ($K = k_1/k_2$) represents the conjugate base formation constant.

For cobalt(III)-amine complexes, where the pK_a for amine protons is usually greater than 15, it could be shown that under most experimental conditions $1 \gg K[OH^-]$, and

$$\text{Rate} = k_{cb} \cdot K[OH^-][\text{complex}]$$

or

$$\text{Rate} = \frac{k_{cb} \cdot K_a}{K_w} \cdot [OH^-][\text{complex}]$$

where K_a represents the acid dissociation constant of the amine complex.

The S_N1CB mechanism is supported by a variety of indirect arguments and direct evidences. This mechanism consists of two major steps. These are the initial formation of a reactive amido complex and the unimolecular aquation of this amido complex. The first and simplest is the behavior of complexes containing an acidic proton. The formation of an amido conjugate base requires the presence of an amine proton in the complexes. It was found that complexes without these acidic protons, such as trans- $Co(py)_4Cl_2{}^+$ and trans- $Co(tep)_2Cl_2{}^+$ (12), and trans- $Co(bip)_2(NO_2)_2{}^+$ and trans- $Co((C_2H_5)_2P \cdot CH_2 \cdot CH_2 \cdot P(C_2H_5)_2)_2Cl_2{}^+$ (13), are insensitive to base hydrolysis. These results coupled with the generality of base catalysis in the complexes containing protons strongly suggest requirement of an acidic proton for rapid base hydrolysis.

The second important group of studies concerns the nature of the entering group. The simple S_N2 mechanism requires that the hydroxide ion be the entering group, whereas the conjugate base mechanism allows a water molecule, or even another anion, to function as the entering group. Hydroxide is only required in the first deprotonation step. In aqueous solution it is difficult to distinguish hydroxide entry from water entry because of facile proton transfer. It is not surprising that the first competition studies were carried out in a non-aqueous medium. Pearson, Schmidtke and Basolo (14) studied the following reaction in dimethylsulfoxide. They found that the trans- $Co(en)_2(NO_2)Cl^+ + NO_2^- \longrightarrow$ trans- $Co(en)_2(NO_2)_2^+ + Cl^-$ rate was first order, independent of entering nitrite concentration. On the introduction of small amounts of hydroxide, the rate of chloride release was greatly accelerated but the product remained trans- $Co(en)_2(NO_2)_2^+$. Since it was shown that $Co(en)_2(NO_2)OH^+$ was not labile under the reaction conditions, it followed that the initial entering group was either the nitrite ion or a molecule of dimethylsulfoxide, not hydroxide. Similar behavior has been demonstrated for the analogous Rh(III) complexes (15).

An experiment was devised by Green and Taube (16) to show that hydroxide need not be the entering group in the aqueous base-catalyzed reaction. If the reaction is run in water enriched in ^{18}O, and hydroxide functions as the entering group, the $^{16}O/^{18}O$ ratio of hydroxide ion should correspond to the $^{16}O/^{18}O$ ratio in the hydrolysis product, barring relatively small kinetic-isotope effects. The $^{16}O/^{18}O$ ratio in hydroxide is 1.040 times the ratio in water, according to results for the equilibrium

$$H_2{}^{16}O + {}^{18}OH^- = H_2{}^{18}O + {}^{16}OH^-.$$

The kinetic-isotope effect is expected to favour ^{16}O so that the factor 1.040 probably represents a minimum if hydroxide is the entering group, and 1.000 should represent a minimum if water is the entering group. The increase in the $^{16}O/^{18}O$ ratio of the hydroxo product (compared to the solvent) was 1.0056 for base hydrolysis of $Co(NH_3)_5Cl^{2+}$, 1.0056 for base hydrolysis of $Co(NH_3)_5Br^{2+}$, 1.0056 for base hydrolysis of $Co(NH_3)_5NO_3{}^{2+}$, and 0.9975 for base hydrolysis of $Co(NH_3)_5F^{2+}$. The result favors water entry in all four cases. The common value for the chloro, bromo, and nitrato complexes suggests that a common intermediate reacts with water in these cases, as would be the case if the dissociative step of the amido complex were actually a two step dissociative process.

If the dissociative constant of the amido group, k_{cb}, is increased and becomes comparable to the rate of formation of the amido conjugate base, two phenomena would be expected.

First, the product would exchange one amine proton more than the unreacted substrate and second, the system would be subject to general base catalysis. These predictions were supported by the work of Poon and Tobe (17). They found that the base hydrolysis of trans- $Co(D_4\text{-cyclam})Cl_2{}^+$ in protium solvent indicated that the product had exchanged 20% more of its deuterium than the unreacted substrate in the same experiment, and the exchange was too slow for the reactant to account for the extra exchange in the product. This extra exchange which amounts to one amine proton, must take place as the reaction proceeds and is fully consistent with a conjugate base mechanism. The same observation was reproducible using trans- $Co(D_4\text{-cyclam})Br_2{}^+$.

A third mechanism was suggested by Chan and Leh (18). They studied the replacement of coordinated chloride in the chloropentamminecobalt(III) cation in aqueous solution over a wide range of alkali concentrations. The rate constant plots were non-linear in hydroxide concentration, and the authors claimed that this kinetic dependence could only be explained on the basis of the ion-pair mechanism, according to which the reaction between the cobalt(III) cation and the hydroxide ion proceed by a pre-equilibrium formation of an "intimate" ion-pair between the two ions, followed by a rate determining rearrangement within the ion-pair. They extended the above investigations to other similar complexes, where it was shown that, when four ammonia groups in the chloropentamminecobalt(III) cation were changed to two ethylenediamine ligands, and thereafter to one triethylenetetramine ligand, the non-linearity in the dependence of observed first order rate constants on hydroxide concentration becomes less and less noticeable. This observation, they claimed, constitutes evidence against the conjugate-base mechanism for the base hydrolysis of octahedral cobalt(III) complexes in aqueous solutions, since the conjugate base would be formed to the same extent in each. Therefore, they proposed this ion-pair mechanism, the difference in first order OH^- dependence between the different amines being simply a difference in the extent of ion-pairing. This mechanism involved a rapid pre-equilibrium formation of an ion-pair between the complex and the hydroxide ion which was then followed by a rate-determining unimolecular (S_N1IP) or bimolecular (S_N2IP) rearrangement between the leaving group and the hydroxide ion:

$$R_4XMY^{n+} + OH^- \overset{K_{IP}}{\rightleftharpoons} R_4XMY^{n+}\cdot OH^-$$

$$R_4XMY^{n+}\cdot OH^- \xrightarrow{k} R_4XMOH^{n+}\text{-}Y^-$$

where K_{IP} represents the ion-pair association constant and k the rearrangement rate constant within the ion-pair. The derived rate law however, is identical to that predicted by the S_N1CB mechanism:

$$-\frac{d[R_4XMY^{n+}]}{dt} = \frac{kK_{IP}[R_4XMY^{n+}][OH^-]}{1 + K_{IP}[OH^-]}$$

and for a small equilibrium amount of the ion-pair, the above equation becomes

$$-\frac{d[R_4XMY^{n+}]}{dt} = kK_{IP}[OH^-][\text{complex}]$$

Recently, Chan and Lau (19) have suggested that the ion-pair and the conjugate base mechanisms are similar and differ only in the extent to which the proton is transferred from the complex to the base. The base hydrolysis of the cis-chloroaniline-bis(ethylenediamine) cobalt(III) cation is very much more rapid than that of the corresponding chloroalkylamine complexes, and proceeds by the conjugate-base mechanism. Here, the conjugate-base is formed by proton removal from the aniline ligand and the dissociation constant of its conjugate-acid is about 10^{-11}. On the other hand, the base hydrolysis of the sterically similar chloropyridinebis(ethylenediamine)cobalt(III) cation with no acidic proton is likewise significantly faster than that of the corresponding chloroalkylamine complexes. Since the pyridine ligand neither provides acidic protons by itself, nor acts as an acid-strengthening group as a whole for other protons, the acid dissociation constant of the chloropyridinebis-(ethylenediamine)cobalt(III) cation can at most be only 10^{-17} (i.e., a weaker acid than solvent water.) For these reasons, the base hydrolysis of this divalent ion is believed to take place by an ion-pair mechanism. They then proposed a rationalization for these two mechanisms. Before any reaction can take place, the hydroxide ion must approach the complex, the equilibrium distance of closest approach

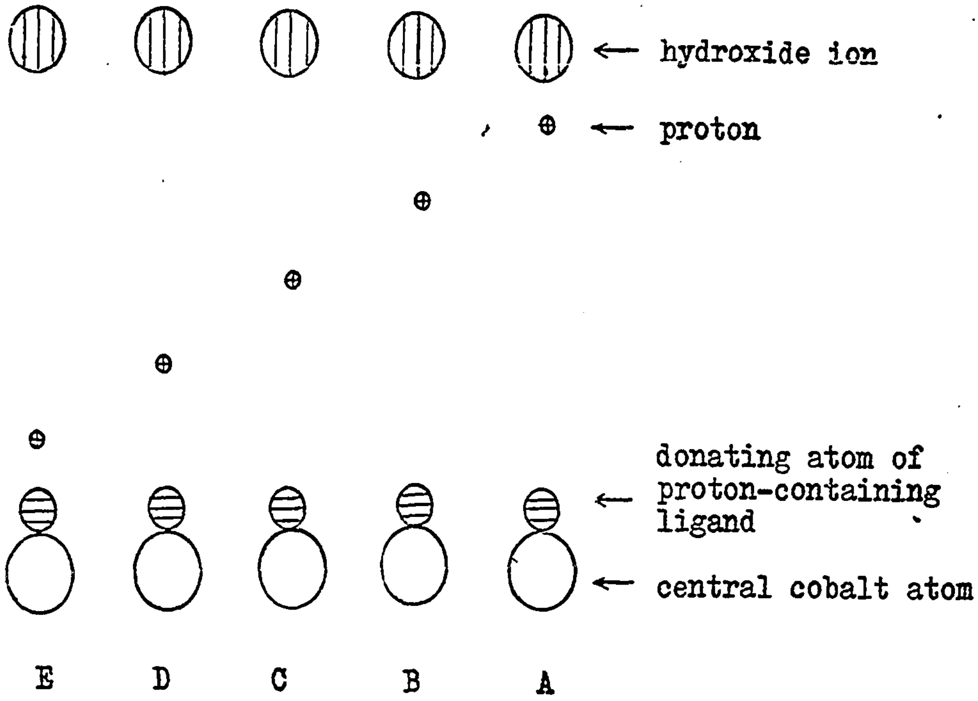


Figure 1 Schematic representation of the conjugate-base/ion-pair mechanistic spectrum.

therefore, attains a constant value, independent of the hydroxide concentration.

This evidence was found by Takemoto and Jones (20). They determined the rate of disappearance of the hexamminecobalt(III) ion in sodium hydroxide solutions over the hydroxide concentration range of 0.122 M to 2.1 M at 61.8°C. Above a hydroxide ion concentration of 0.50 M the rate was essentially independent of hydroxide concentration and reached a limiting value of about 2.8×10^{-4} sec^{-1}. It was impossible from the rate data to distinguish between an S_N1CB or S_N1IP as the reaction mechanism.

The fourth redox mechanism, providing an explanation of why the Co(III) complexes are particularly sensitive to base hydrolysis, was suggested by Gillard (21) based on observations from preparative work.

He assigns to hydroxide ion the role of reducing agent. It is proposed that an electron is transferred from the hydroxide to the cobalt(III) and that the hydroxyl radical remains trapped in the vicinity of the labile complex species while the complex rearranges its environment to a more stable form. The reduction of cobalt(III) to the labile cobalt(II) by the reducing hydroxide ion is the rate determining step. The intermediate is the ion-pair. Thus, for a Co(III) complex:

$$Co^{III}(NH_3)_5Cl^{+2} + OH^- \rightleftharpoons Co^{III}(NH_3)_5Cl^{+2}\cdot OH^- \quad \text{(fast)}$$

$$Co^{III}(NH_3)_5Cl^{+2}\cdot OH^- \longrightarrow Co^{II}(NH_3)_5Cl^{+}\cdot OH \quad \text{(slow)}$$

$$Co^{II}(NH_3)_5Cl^{+}\cdot OH \longrightarrow Co^{II}(NH_3)_5{}^{+2}\cdot OH + Cl^- \quad \text{(fast)}$$

$$Co^{II}(NH_3)_5{}^{+2}\cdot OH \longrightarrow Co^{III}(NH_3)_5OH^{+2} \quad \text{(fast)}$$

The base hydrolysis of octahedral cobalt(III)-ammine and -amine complexes has been extensively studied and reviewed (22). It has long been well known that cobalt(III)-ammine and -amine complexes react very rapidly with hydroxide ion according to second order kinetics, first order with respect to both the complex and the hydroxide ion concentration. Extensive agreement has been reached that the mechanism is S_N1CB with the five-coordinated intermediate product of the slow step assuming trigonal bipyramidal geometry. This is in keeping with the observation that base hydrolysis is accompanied by stereochemical change and that cis and trans isomers do not differ enormously in their reactivity (Figure 2) and in a trigonal bipyramid

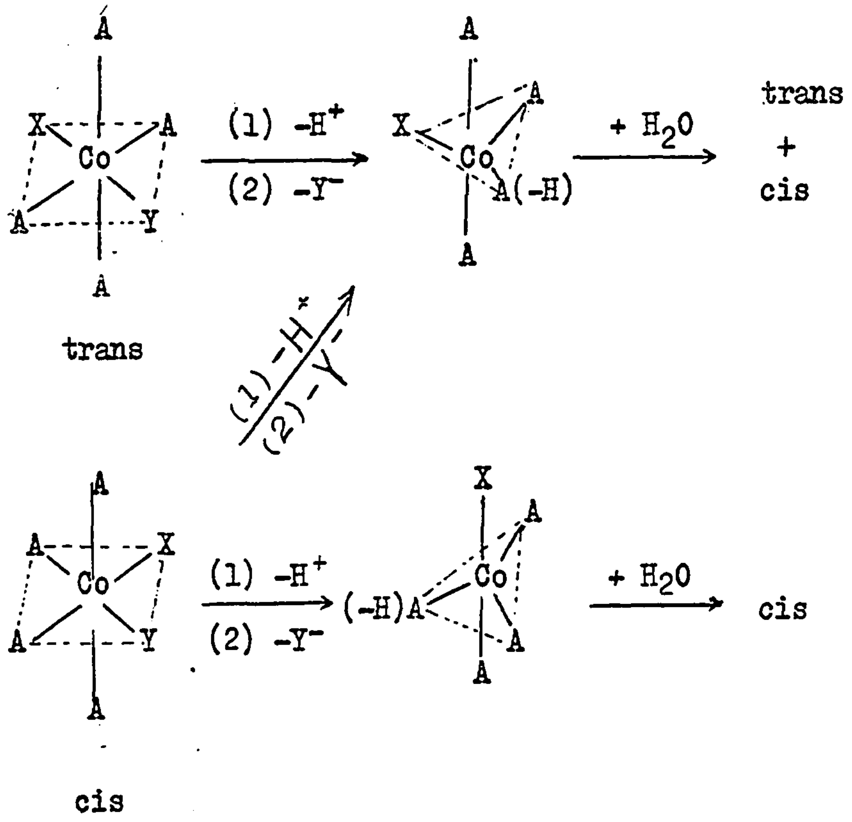


Figure 2 Mechanism of reaction proposed for base hydrolysis of trans- and cis-A_4XCoY^{n+}.

and at much longer distances from the metal ion than the five inert ligands (Figure 3).

The trans-dihalogenobis(ethylenediamine)rhodium(III) complexes reacting completely independent of hydroxide ion concentration was found by Bounsall (24).

Recently, Bounsall and Koprich (25) have successfully synthesized some trans-diacido(cyclam)rhodium(III) complexes (cyclam represents 1,4,8,11-tetraazacyclotetradecane). They found that substitution reactions took place with strict retention of configuration and were independent of the nature and concentration of the incoming ligand. One striking feature was that these complexes were sensitive to base hydrolysis. This observation was unexpected in view

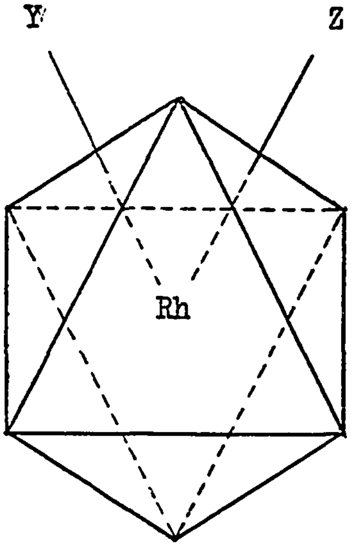


Figure 3 Seven-coordinated transition state for Rh(III) complexes; Y and Z are leaving and entering groups respectively.

of the other Rh(III)-ammine and -amine complexes, insensitivity to OH^-, mentioned above, but identical to that found for Co(III), Cr(III), and Ru(III) . Thus, in view of this anomaly, it became important to study the base hydrolysis of these Rh(III)-cyclam complexes with a view to elucidating the mechanism and comparing with Co(III) complexes.

The only base hydrolysis data for the analogous cyclam complexes is for trans- $Co(cyclam)Cl_2{}^+$ (26). The authors reported that the base hydrolysis of trans-isomer was a fast, two stage reaction and had been studied in buffer solutions. In the pH region 6.2 to 7.4 the first stage, which had a first-order rate dependence on hydroxide concentration, was rate-determining but at higher pH the second stage, whose rate was independent of pH , became distinguishable and eventually rate-determining. This stage was identified as the aquation of trans- $Co(cyclam)Cl(OH)^+$ and the assignment confirmed by studies on the independently prepared hydroxochloro-cation. All the reactions proceeded with complete retention of configuration. The base hydrolysis of trans- $Co(cyclam)Cl_2{}^+$ was some twenty times faster than that of the unusually reactive trans- $Co(en)_2Cl_2{}^+$ complex. Since the rate of the acid hydrolysis of the trans-dichloro-cyclam complex was less than that of the ethylenediamine complex, the ratio of the rate constants of base hydrolysis to acid hydrolysis was considerably greater than that for the ethylenediamine analogue. The authors claimed that there was insufficient information to say whether this sensitivity to base hydrolysis was a consequence of the presence of the cyclic amine or was simply a consequence of the presence of a secondary amine ligand.

In further studies by Poon and Tobe (17), it was reported that the base hydrolysis of the trans- $Co(cyclam)Cl_2^+$ complex indicated considerably more proton exchange in the product than in the substrate. They claimed that this extra exchange did not take place subsequent to the act of base hydrolysis and therefore must have been a consequence of the base hydrolysis itself; this evidence appeared to offer reasonable proof of the deprotonated conjugate base mechanism.

Recently, Campi, Ferguson and Tobe (27) have studied the base hydrolysis of trans- and cis- $Cr(cyclam)Cl_2^+$ complexes. They reported that a typical second order rate law was observed. The rates were very much less than those of the corresponding cobalt (III) complexes and the greater reactivity of the cyclic amine complexes, compared to those with ethylenediamine, was found in all cases. The reactions proceeded with complete retention of configuration.

Unpublished results of Fitzgerald on studies of trans- and cis- $Rh(cyclam)Cl_2^+$ complexes have been mentioned (22c). It therefore is of interest to study the base hydrolysis of the cyclam-rhodium complexes to compare with the cyclam complexes of cobalt(III) and chromium(III), and the rhodium(III) complexes of the tetraammine and bis(ethylenediamine).

2. The trans effect

The term " trans effect " in metal complexes was first recognized by Werner (28) and elaborated by Chernyaev (29) to describe the influence of a coordinated group upon the replacement of a ligand opposite to it, as evidenced by the ease of preparation of four-coordinate square planar Pt(II) complexes. Extensive observations since then have made it possible to place the common ligands in an approximate order of their tendency to labilize a trans group. A conference on the trans effect held in Russia in 1952 defined the principle in the following way (30): " In compounds with square or octahedral structure with a central complex-forming cation, the rate of substitution of an atom or molecule linked to the central atom is determined by the nature of the substituent at the opposite end of the diagonal. Thus the stability of the bond between this (central) atom and any substituent is little affected by the character of the neighboring atoms or molecules, but is greatly influenced by those more distant, in the trans position, on the diagonal of the square." This is a remarkably clear definition when it is realized that it was formulated by a committee. In a comprehensive review (31) on the trans effect in metal complexes the kinetic trans effect has been more neatly defined as " the effect of a coordinated group upon the rate of substitution reactions of ligands opposite to it ". Metal complexes in which the rate influence of the opposite, or trans groups,is definitely greater than the influence of adjacent, or cis groups, will be considered in their reactions to show a trans effect. Similarly, metal complexes in which the rate influence of cis groups is greater than the influence of trans groups will show a "cis effect". The cis effect for certain ligands in octahedral Co(III) complexes is large, while in square planar Pt(II) complexes, is small.

Most of the work on the trans effect has been on the square planar Pt(II) complexes and the substitution reactions of these systems are highly stereospecific. Historically Pt(II) kinetics have dominated kinetic trans effect studies.

To explain the phenomena of the trans effect, several theories (32) have been evolved which were classified essentially into two main categories. They are the electrostatic-polarization theory and the π - bonding theory. These two theories can be unified in terms of the molecular orbital theory of bonding in these systems. The polarization theory stresses the importance of the ground state contribution to the rates of reaction, whereas the π-bonding theory is primarily concerned with the transition state. A high rate of reaction can be due either to an unusual instability in the ground state of the reactant complex or to an unusual stability in the transition state or both factors. Since reaction rates are related to differences in activation energies between reactants and activated complexes, the best criteria of the trans influence of various ligand would be energies of activation. The use of simple rate data can lead to wrong conclusions when testing theories of energetics, since the relative rate constants depend on the temperatures studied, whereas the energies of activation are not dependent on the temperatures. In the Pt(II) cases where activation energies have been measured, high rates of reaction were generally found to parallel low energies of activation.

The polarization theory: The simple electrostatic approach, modified for polarization and covalent σ-bonding effects(33) places the emphasis on the weakening in the ground state of the bond to the trans ligand. This would lead to a high rate of reaction if the transition state involves a breaking, or partial breaking of the bond. A pictorial representation of the polarization trans-effect theory is shown in Figure 4.

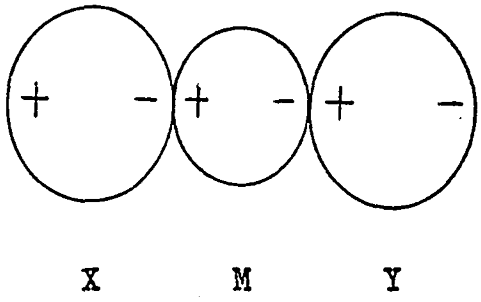


Figure 4 Distribution of charge in induced dipoles on the X-M-Y axis.

On the basis of this theory the large trans effect of X is due to its causing a weakening of the M-Y bond. This theory offers an explanation on the basis of charge distribution. Thus, the primary positive charge on the metal induces a dipole in the ligand X and Y. If X and Y are identical, then there is a symmetrical distribution of the induced dipoles and the resultant dipole is zero. However, if the ligand X is more polarizable than Y, there is no longer a mutual compensation of the induced dipole, and the dipole in X induces a dipole in the metal atom (particularly if M is polarizable). The orientation of this induced dipole in the metal is such as to repel negative charge in ligand Y. Hence the attraction of Y for M is reduced and the bond is lengthened and weakened. The virtue of this theory is that it explains the parallelism between the magnitude of trans influence of X and its polarizability, e.g., $H^- \sim I^- > Cl^-$.

Since this is an electrostatic theory, it immediately arouses some objections. For example, the induced dipole on M should depend on the net charge of X more strongly than on the induced moment. Also it will be greater if the M-X bond distance is small. This leads to the wrong prediction that Cl^- will have a larger trans effect than I^-. This objection can be removed if the effect of covalent bonding in these systems is considered. It is probable that ligands of high polarizability will be involved in increased covalent bonding through M to X. Initially the trans effect due to the M-X covalency was explained on the basis

This makes it easier for a solvent molecule (or other nucleophile) to attach itself to cobalt and to initiate an S_N2 cis displacement of the chloride ion if the chloro group is trans to the nitro group. There should be a small effect also for a nitro group at the cis position. Thus, the electron-withdrawing groups cause rate increases by promoting an S_N2 mechanism, or at least by increasing the amount of bond making in the transition state.

On the other hand, an electron donor ligand such as OH^- and Br^- places more negative charge on the metal, thereby increasing the ease of dissociation of other groups. An S_N1 mechanism is facilitated in which bond breaking is important and bond making is minimized.

The molecular orbital theory for σ and π-trans effects:

A simplified molecular orbital energy level diagram for octahedral metal complexes is shown in Figure 6. The most stable orbitals are σ bonding. The π-bonding molecular orbitals are next in order of stability. Then come the antibonding partners of these σ- and π-bonding molecular orbitals.

By making use of this type of bonding scheme, it is possible to account for the large trans effect for strong σ-bonding ligands X such as H^- and CH_3^-. Since the trans ligand X and the leaving group Y in trans-R_4XMY must share the same $_x$ orbital in the overall molecular orbitals, it follows

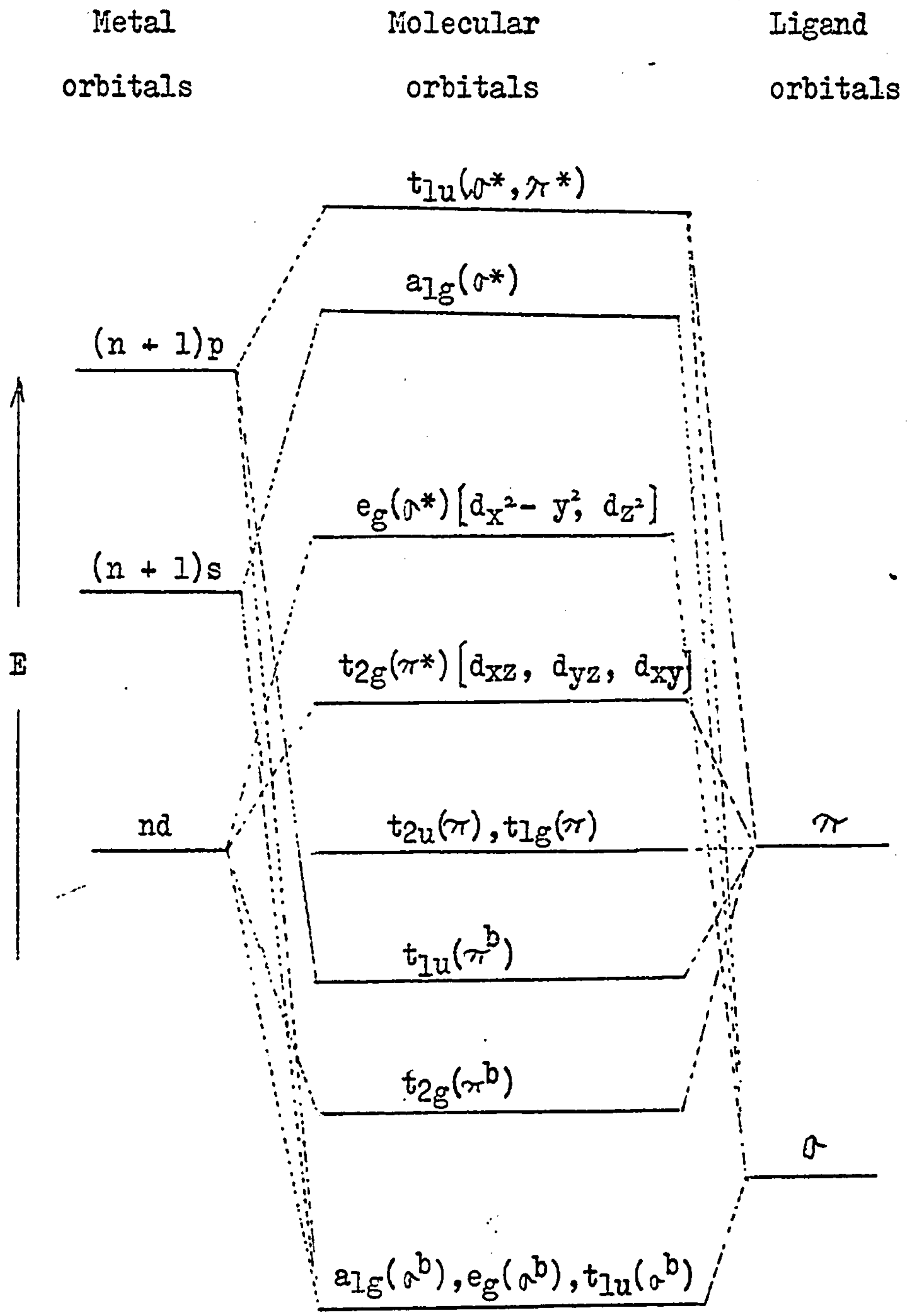


Figure 6 Molecular orbital energy level diagram for octahedral metal complexes.

that a strong σ-bonding ligand X will take on the large share of the bonding σ_x molecular orbital considering the x-axis as the reaction coordinate, leaving a much smaller share for Y(Figure 7).

(a) (b)

Figure 7 The σ bonding of X-M-Y, using the σ_x molecular orbital. (a) The σ-bond strengths of X and Y are about equal. (b) The σ bond strength of X is much great than that of Y.

This means that the M-Y bond is weakened, as was also predicted by the polarization theory. Regardless of the mechanism of substitution, such a result is expected to lead to an increased rate of replacement of Y.

It may perhaps be visualized more easily if one simply realizes that a good σ-covalent ligand, such as H^-, will place a great deal of negative charge in the P_x orbital of the metal. This in turn will repel the electrons of any ligand in the trans position which must also use the same P_x orbital.

For ligands such as C_2H_4, CO, and CN^- that form strong π bonds and are good trans activators, the effect has been explained in terms of the π-bonding theory described earlier. It accounts for overall stablization through the increased use of the π molecular orbitals in the activated complex, but mainly by the equatorial ligands which include the trans activator resulting in a trans effect. Thus, the transition state is greatly stabilized if X is capable of bonding to the π orbitals. This delocalizes electronic charge to the ligands and lowers the energy of the system. Since there are more filled π orbitals in the transition state than in the ground state, the transition state is stabilized to a great extent. Thus, the net effect of a good π-acceptor ligand X is to lower the activation energy for reaction.

It appears that ligands which are good trans activators fall in one of three categories: (1) strong σ-bonding, such as H^- and CH_3^-; (2) strong π-bonding, such as C_2H_4 and CO; and (3) moderate σ- and π-bonding, such as I^- and $SC(NH_2)_2$. Ligands such as NH_3 and OH^- that are weak (covalent) σ and π bonding are low in the trans-effect series.

Techniques, other than kinetic, to aid in the establishment of trans effect sequences have includes acid strengths (35), infrared spectral shifts (36), X-ray (37), and dipole moment studies (38).

The trans effect for the square planar Pt(II) data is by far the most extensive and gives the order (39): CO, CN^-, $C_2H_4 > PR_3$; $H^- > CH_3^-$, $C_6H_5^-$, NO_2^-, I^-, $SCN^- > Br^-$, $Cl^- > Py$, NH_3, OH^-, H_2O. Although Pt(II) complexes are the best known and most extensively investigated square planar complexes, other d^8 systems also form stable complexes of this type. However these stable complexes of Ni(II), Pd(II), Au(III), Rh(I), and Ir(I) are generally fairly labile. This means that isomeric structures are more common than for Pt(II) and that stereospecific reactions, if they occur, may go unnoticed because an unstable isomeric product may readily rearrange to yield either the more stable or the less soluble isomer.

This has been shown to be the case for the reaction of $Pd(NO_2)_4{}^{2-}$ with ammonia (40). Assuming a trans effect order of $NO_2^- > NH_3$, similar to the order Pt(II), the reaction product is expected to be the cis isomer. Instead the trans form is isolated leading one to believe that NH_3 has a greater trans effect than NO_2. However when the reaction is carried out at lower temperatures appreciable amounts of cis-$Pd(NH_3)_2(NO_2)_2$ form. It is therefore suggested that the initial reaction product is the cis-isomer in accord with a greater trans effect of NO_2^- compared to NH_3. This is then followed by rearrangement to the less soluble trans product.

The most thoroughly trans effect studied for octahedral complexes are those of Co(III) and Pt(IV).

For octahedral Pt(IV) complexes, a different order from that of Pt(II) was found. A tentative order of decreasing trans effect which is based on products isolated (41) as well as rate data (42), is $I^- > Br^- > Cl^- > NO_2^- > SCN^- \simeq OH^- > NH_3$. However, the substitution reactions of Pt(IV) are catalyzed by light, simple electron reducing agents (43) and Pt(II).

An order of trans effect for octahedral Co(III) complexes, based on rate data for the acid hydrolysis of trans-$Co(en)_2XCl^+$(44) is $OH^- > NO_2^- > N_3^- > CN^- > Br^- > Cl^- > NH_3 > NCS^-$. This is changed to $NO_2^- > CN^- > N_3^- > NH_3 > Br^- > Cl^- > OH^- > NCS^-$, based on activation energies. However, two different mechanisms appear to be involved depending on the π-donor or acceptor properties of the trans ligand. Moreover, for Co(III) it is well established that cis substituents affect the rates of reaction to an equal or greater degree than trans substituents.

The rates of replacement of Cl^- from some trans-$Rh(en)_2XCl^+$ complexes have been measured by Bott, Bounsall and Poe (45). The trans effect of X increases along the series Cl^-, Br^-, I^- whether it is measured in terms of rate constants or enthalpies of activation. The enthalpies of activation decrease by about 2 kcal./mole when X changes from chloride to bromide, or from bromide to iodide.

The kinetic results for the acid hydrolysis of the trans-Rh(cyclam)XCl^+ complexes have been reported (46) and the kinetic trans effect, increasing in the order of Cl^-, Br^-, I^-, was found in terms of both rates and enthalpies of activation.

The trans effect, as defined, is a measure of the trans labilizing ability of a given ligand relative to that for other ligands. Activation by a trans group can have, as well as a labilizing kinetic effect, a destabilizing thermodynamic effect. It is apparent that trans activation may, in the ground state, result in a decrease in the M-Y bond strength opposite. If thermodynamic data is obtained as a function of changes in trans directing ligands, the effect may be called "thermodynamic trans effect", quite distinguishable from the "kinetic trans effect", and of course there is no requirement that the kinetic and thermodynamic effects for a series of ligands, be in the same direction.

Equilibrium constants for reactions of Pt(II) complexes in solution have been reviewed by Basolo and Pearson (31). They reported that the affinities of various ligands for Pt(II) decreased in the order $CN^- \sim OH^- > NH_3 > SCN^- \sim I^- > Br^- > Cl^- \gg F^- \sim H_2O$. Except for the position of NH_3 and OH^- the order paralleled that of the kinetic trans effect order.

The thermodynamic trans effect of octahedral complexes in trans-$Rh(en)_2XCl^+$ decreased along I^-, Br^-, Cl^- (47), identical with the kinetic trans effect order (45).

Equilibrium measurements on the whole series of the trans-dihalogeno(cyclam)rhodium(III) complexes were taken to reveal the thermodynamic trans effect order and could be compared with the kinetic trans effect order determined from the substitution reactions previously studied and the base hydrolysis results in this work.

3. Thermodynamic Stabilities of Complexes

Since Sidgwick (48) in 1941 summarized the few available data on the relative affinities of the common ligands for various acceptor molecules and ions, the experimental material has increased enormously accompanied by revised and extended correlations (49). Two regular features have been reported by Ahrland, Chatt and Davies (50): (i) There is, in general, a very great difference between the coordinating affinities of the first and the second element from each of the three groups of ligand atoms in the Periodic Table, i.e., between N and P, O and S, and F and Cl. (ii) There are two classes of acceptor: (a) those which form their most atable complexes with the first ligand atom of each group, i.e., with N, O, and F, and (b) those which form their most stable complexes with the second or a subsequent member of each group. Thus, for class (a) acceptors the order of stability is as follows:

$$F^- \gg Cl^- > Br^- > I^-$$

$$O \gg S > Se > Te$$

$$N \gg P > As > Sb > Bi$$

Whereas for class (b) the order of stability is:

$$F^- < Cl^- < Br^- < I^-$$

$$O \ll S \sim Se \sim Te$$

$$N \ll P > As > Sb > Bi.$$

The class (a) and (b) classification of metal ions has been extended by Pearson (51) to include a large number of ligands in aqueous solution with the water molecule, or with OH^-, the product of its deprotonation. For none of the class (a) cations, whatever the size or charge, is it possible to establish with certainty an association with Cl^-, Br^-, I^-, S, N, or C.

Apart from coulombic forces, there must be other types of interaction. These will be referred to as "nonelectrovalent" forces and the term will include everything not due to classical electrostatic action. Nonelectrovalent behavior is encountered for class (b) metal ions and in its purest form for noble-metal cations of low charge. In the rough picture of bond formation by the sharing of an electron pair between the central atom and the ligand, it is significant that the stability of the complex is found to increase both with the tendency of the cation to take up electrons (i.e., with increasing ionization potential of the metal involved), and with the tendency of the ligand atom to give up electrons (i.e., with decreasing electronegativity of the nonmetal). The nonelectrovalent interaction between ligands with class (b) cations of low charge changes gradually to electrovalent interaction with increasing charge.

(2) The π-bonding theory. The important feature of class (b) metals in the view of Ahrland, Chatt and Davies (50)is considered to be the presence of loosely held outer d-orbital electrons which can form π bonds by donation to

suitable ligands. Such ligands would be those in which empty d orbitals are available on the coordinating atom, such as P, As, S, and I. Unsaturated ligands such as CO and isonitriles would be able to accept metal electrons by the use of empty, but not too unstable, molecular orbitals. Class (a) metals would have tightly held outer electrons, but also there would be empty orbitals available, not too high in energy, on the metal ion. Basic atoms such as O and F particularly could form π bonds in the opposite sense, by donating electrons from the ligand to the empty orbitals of the metal. With class (b) acceptors, there would be a repulsive interaction between the sets of filled orbitals on metal and on O and F ligands.

(3) The polarization theory. Williams (53) suggested that the high polarising power of b-subgroup cations, relative to their size and charge, accounts for the observed orders of stability of the halide complexes and for the stability of metal dithizone complexes.

It is well known that the bond energies of the F-F, O-O, N-N single bonds are markedly smaller than those of the corresponding elements in the next row of the periodic table. Pitzer (54) has recognized that the London (dispersion) attractive forces between these nonbonding electrons make an important contribution to the bond energy for the elements below the first octet. (Even for bonded atoms it may be argued that the electron correlations responsible for London forces will operate for the non-bonding electrons.)

London correlation occurs because of the electrostatic repulsion of electrons for each other. Such London forces depend on the product of the polarizabilities of the interacting groups and vary inversely with the sixth power of the distance between them. They are large when both groups are highly polarizable and have short distance. The evidence is that inclusion of the London term greatly reduces the anomaly in the series F_2, Cl_2, etc.

Drago and Wenz (55) have compared the relative acidities of ICl, Br_2 and SO_2 by evaluating the heats of formation of the adducts formed with N,N-dimethylacetamide. The relative order of acidity, including iodine is: $ICl > I_2 > SO_2 > Br_2$. They concluded that polarizability must be a very important factor contributing to acidity but not the dipole moment of the acids.

Pearson (51) has claimed that the common features which bring out class (a) behavior are small size and high positive oxidation state. Class (b) behavior is associated with a low or zero oxidation state and/or with large size. Both metals and non-metals can be either (a) or (b) type acids and bases depending on their charge and size. Since the features which promote class (a) behavior are those which lead to low polarizability, and those which create type (b) behavior lead to high polarizability, class (a) acids are called hard acids and class (b) acids soft acids. Class (a) acids prefer to bind to hard or nonpolarizable bases. Class (b) acids prefer to bind to soft or polarizable bases. Since class (a) acids are themselves hard and since class (b) acids are soft, a simple rule is : hard acids bind strongly to hard bases and soft acids bind strongly to soft bases. He has then suggested that polarizability is simply a convenient property to use as this classification. It may well be that other properties which are roughly proportional to polarizability are more responsible for the typical behavior of the two classes of acids. For example, a low ionization potential is usually linked to a high polarizability, and a high ionization potential to a low polarizability. Hence, ionization potential or the related electronegativity might be the important property. Unsaturation, with the possibility of acceptor bonding in the acid-base complex, and ease of reduction, favoring strong electron transfer to the acid, are also associated with high polarizability.

Bounsall and Poë (47) have obtained the temperature dependence of the equilibrium constants for the stepwise replacement by iodide of the chloro in trans- $Rh(en)_2Cl_2{}^+$, and of the bromo in trans- $Rh(en)_2Br_2{}^+$. From their data and the equilibrium constant data for the successive replacement of chloro in trans- $Rh(en)_2Cl_2{}^+$ by bromide (56), the relative enthalpies of bonding of the dihalogeno-complexes are in the order di-iodo > iodobromo > iodochloro > dibromo > bromochloro > dichloro. These complexes exhibit the class (b) character and the thermodynamic trans effect is qualitatively consistent with a polarization theory.

(4) The solvation theory. Parker (57) has stressed the effects of protic and dipolar aprotic solvents on solutes. Anions are much less solvated in dipolar aprotic than in protic solvents such as water. In protic solvents, anions are solvated by ion-dipole interactions, on which is superimposed a strong hydrogen bonding which is greatest for small anions. Thus solvation by protic solvents decreases strongly in the series of anions OH^-, $F^- \gg Cl^- > Br^- > N_3^- > I^- > SCN^-$. In dipolar aprotic solvents, anions are solvated by ion-dipole interaction, on which is superimposed an interaction due to the mutual polarisability of the anion and the solvent molecule, which is greatest for large anions. Solvation of anions by dipolar aprotic solvents thus decreases slightly, in the reverse order to that given above for protic solvents.

Poë and Vaidya (58) have used the few available results for the heats of replacement of one halogen in a complex by another to estimate the relative strengths of the bonds after allowance for hydration effects. Even in those complexes for which the stability order is $Cl^- < Br^- < I^-$ [class (b)] the bond strengths are in the order $Cl^- > Br^- > I^-$. Although for similar systems the degree of class (b) behavior can be associated with a narrowing of the bond strength differences, they suggested that this narrowing of the bond strength differences cannot be due to $d\pi$ back-bonding effects, nor is it due to polarization, caused by increased effective charge on the metal ion. They postulated that the metal ion size is the major factor in determining the relative bond-strengths in similar systems and thus, indirectly, the degree of class (b) character, larger ions exhibiting more class (b) character then smaller ones. Thus solvation tends to destroy class (a) character and enhance class (b) behaviour.

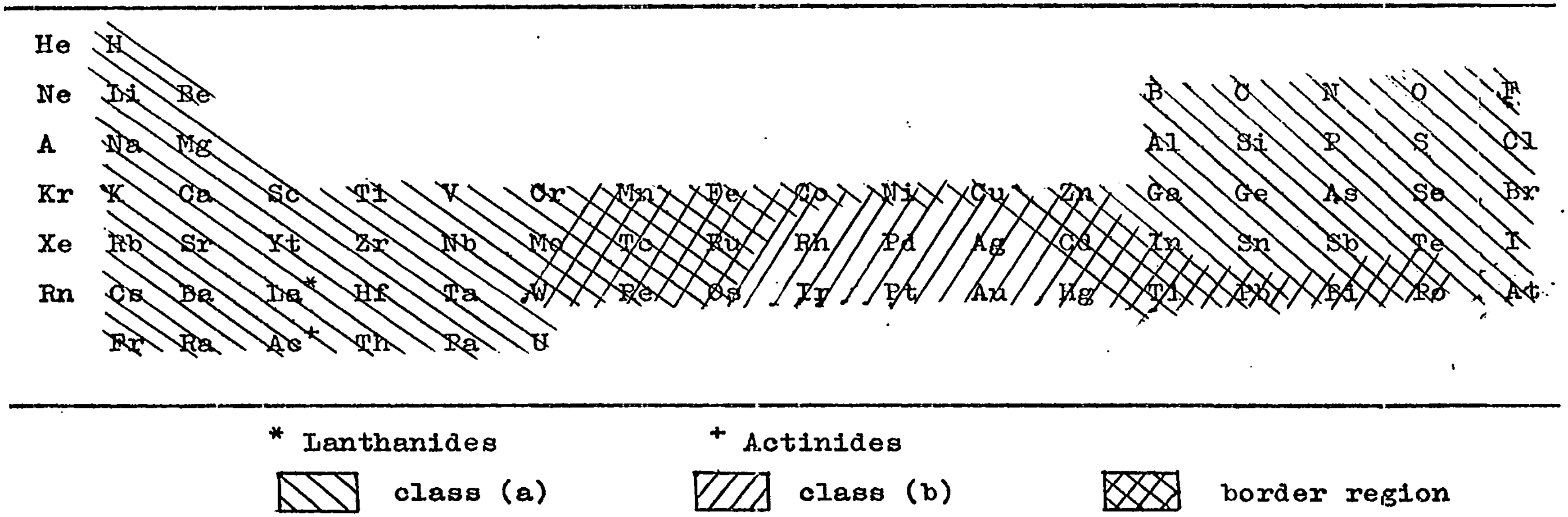
Most metals in their common valency states belong to class (a) as does the hydrogen ion, and therefore the affinities of ligands for class (a) acceptors tend to run roughly parallel to their basicities, except when steric and other factors, such as solvation and chelation intervene.

Metals of greatest class (b) character are those at the end of the transition metal series. Class (b) character also increases on descending a group so that elements of highest class (b) character are found in a triangle in the periodic table with a base which extends from iridium to mercury and with an apex at copper (Figure 8). Included clearly are the metals Cu(I), Rh(I),Pd(II),Ag(I),Pt(II), and Hg(II).

The class (a) or class (b) character of many acceptors is so well defined that they can be classified beyond any doubt even from purely qualitative observations of the stabilities of their complexes, but this is not the case in the border region. On the contrary the boundary is somewhat diffuse, mainly because the various oxidation states of the border elements have different characters. The border almost certainly runs between copper and zinc,

Figure 8

Classification of acceptor atoms in their normal valent states



and between cadmium and indium. Thallium, lead, bismuth, and tellurium are all bordline elements, and according to their complex halides (59) just on the side of class (b). Copper (I) is in class (b), but cobalt (II), nickel (II), and copper (II) are on the border, having a weak class (a) character towards halide ions (60), and a weak class (b) character toward group VI (61) and perhaps group V ligand atoms. But even when the oxidation state is specified the boundary still remains slightly diffuse, depending on its detail on the specific group of ligand atoms under consideration. The transition between classes (a) and (b) within the periodic table is thus a more or less gradual one, where a tentative classification of the acceptor atoms in their normal valency states is given. The border region around the core of pronounced class (b) acceptors is fairly extensive. In this region, exact quantitative determinations are necessary to determine the character of a certain acceptor towards a given group of ligand atoms.

Halogeno-complexes may be defined as being kinetically of class (a) if they become kinetically less stable as the leaving group in substitution reactions changes from chloride to iodide, as evidenced by a rate constant increase along the series or, better still, a ΔH^* decrease occurs. Kinetic class (b) behaviour results if the kinetic stability increases along this series, as indicated by rate constant decreases as the leaving group changes from chloride to iodide, or an increase in ΔH^* occurs.

The trans- $Rh(en)_2XY^+$ complexes ($Y = I^-$, Br^- and Cl^-) have been found (45) kinetically of class (b) on both relative rate data at 50°C and on the ΔH^* values. Kinetic class (b) character has been observed in a few other systems (62).

Further studies of the interchange of halogen in the trans- $Rh(cyclam)XY^+$ complexes were investigated here to compare with the dihalogeno-bis(ethylendiamine)rhodium(III) system and further determine class (a) or class (b) behaviour for Rh(III), especially important since Ir(III) has been assigned to class (a) on the basis of equilibrium data (63) on the hydrolysis of $Ir(NH_3)_5X^{2+}$.

II. Preparation of Complexes

1. Materials

1,3-Dibromopropane was obtained from Eastman Kodak Co. and anhydrous ethylenediamine was obtained from Fisher Scientific Co. These two reagents were used to prepare 1,4,8,11-tetraazacyclotetradecane (cyclam).

Hydrated rhodium trichloride ($RhCl_3 \cdot 3H_2O$) was obtained from J. Matthey Bishop, Inc. and was used as a source of Rh(III) metal for the preparation of trans-dichloro(cyclam)rhodium (III) chloride, which was the starting material for all the other trans-dihalogeno(cyclam)-rhodium(III) halides or perchlorates.

Deuterium oxide, minimun isotopic purity which contained 99.7 atom % D, was obtained from Merck, Sharp & Dohme of Canada Ltd. and was used to prepare the trans-dihalogeno(D_4-cyclam)rhodium(III) halides (D_4-cyclam = N,N',N'',N'''-tetradeuterio-cyclam).

Reagent grade chemicals and solvents were used throughout.

2. Instruments

The electronic spectra and optical densities were recorded over a wavelength range of 200 to 500 mμ using a Bausch and Lomb Spectronic 505 recording spectrophotometer.

A ^1H n.m.r. spectrum was obtained to identify cyclam using a JNM-C-60 HL high resolution nuclear magnetic resonance instrument.

A Beckman IR 12 infrared spectrophotometer was used to identify the D_4-cyclam-rhodium compounds.

The micro-analysis of the compounds, prepared in these studies, was obtained from Spang Microanalytical Laboratory.

3. Preparations

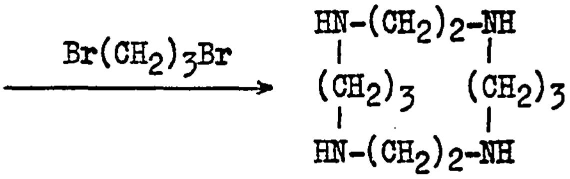
1,4,8,11-Tetraazacyclotetradecane (cyclam) and trans-dihalogeno(cyclam)rhodium (III) halides or perchlorates were prepared according to the procedure developed by Bounsall and Koprich (25)with slight variations.
The compounds were identified by electronic spectra and microanalysis.

(i) Preparation of Cyclam

Cyclam was prepared by the reaction of 1,3-dibromopropane and 1,9-diamino-3,7-diazanonane, the latter prepared initially by the reaction of ethylenediamine with the same dibromopropane all according to the following equation, using ethanol as the reaction media:

$$2\ NH_2(CH_2)_2NH_2 + Br(CH_2)_3Br \longrightarrow NH_2(CH_2)_2NH(CH_2)_3NH(CH_2)_2NH_2$$

1,9-diamino-3,7-diazanonane



$$\xrightarrow{Br(CH_2)_3Br} \begin{array}{ccc} HN-(CH_2)_2-NH \\ | \qquad\qquad\quad | \\ (CH_2)_3 \qquad (CH_2)_3 \\ | \qquad\qquad\quad | \\ HN-(CH_2)_2-NH \end{array}$$

cyclam

1,9-Diamino-3,7-diazanonane

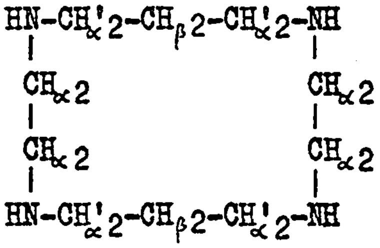
1,3-Dibromopropane (250 g, 1.20 moles, 126 ml) was added dropwise to ethylenediamine (360 g, 6.0 moles, 400 ml) in 300 ml ethanol in an ice-water bath, during which the solution turned yellow. The addition was dropwise because the reaction was extremely exothermic. The resultant solution was heated under reflux for one hour. Potassium hydroxide (300 g, 5.3 moles) was added and the hot solution stirred for 30 minutes to precipitate the bromide. The KBr and excess KOH were removed by filtration. The ethanol (b.p. 78°C) and excess ethylenediamine (b.p. 118°C) were removed by distillation. The 1,9-diamino-3,7-diazanonane was then separated by vacuum distillation (128°C, 2.4 mm Hg) as clear viscous liquid (86 g, 0.54 moles, 43% yield).

1,4,8,11-tetraazacyclotetradecane (cyclam)

1,3-Dibromopropane (50 g, 0.25 moles) and 1,9-diamino-3,7-diazanonane (43 g, 0.27 moles) were added to four liters of absolute ethanol, and heated under reflux for 24 hours, during which the solution turned from colorless to yellow. Three liters of ethanol were removed by distillation. Potassium hydroxide (35 g, 0.63 moles) was added to the solution. The solution was cooled and the potassium bromide were removed by filtration. The volume of the solution was reduced to 100 ml, during which the excess potassium hydroxide was removed by decantation. The yellow viscous solution was cooled overnight to precipitate the white product, which was filtered, washed with acetone, and purified by vacuum sublimation (130°C, 4 mm Hg). The product was 3.1 grams (16 mmoles , 5.8% yield).

Calculated for $C_{10}H_{24}N_4$: C,59.95; H,12.08; N,27.97. Found: C,59.93; H, 12.14; N,27.93%.

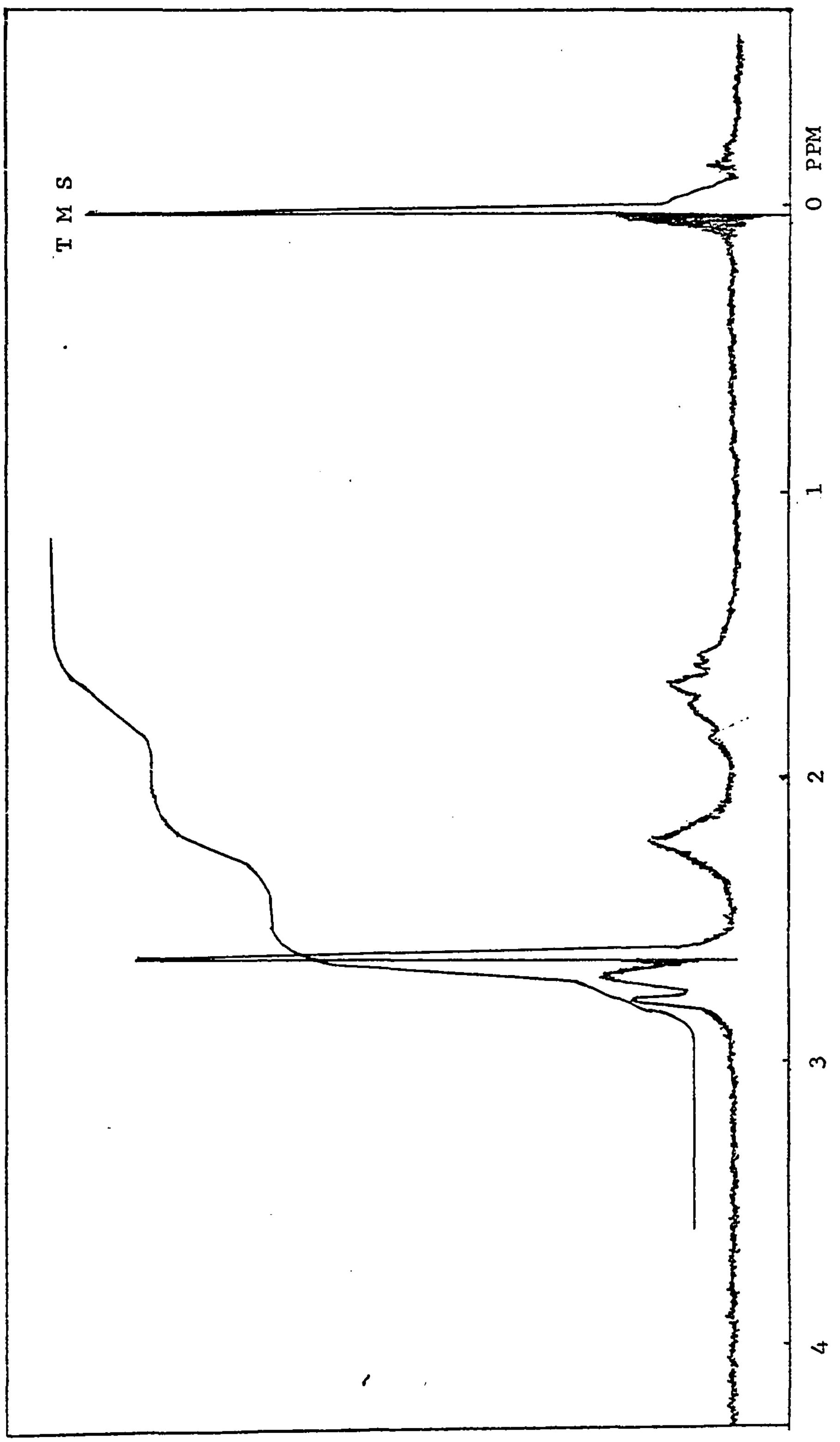
The proton n.m.r. spectrum of the cyclam compound is shown in Figure 9. It revealed what appeared to be a quintet at 1.73 ppm down-field from internal TMS [tetramethylsilane, $(CH_3)_4Si$] , a broad singlet at 2.23 ppm and a complex multiplet center at 2.74 ppm. The integration of the spectrum from left to right gave peak area ratios of 4:1:1. The spectrum indicates that there are four different types of proton in the cyclam molecule, identified below as H, H_α, H_α' and H_β.



The quintet appearing at 1.73 ppm could be attributed to the H_β protons of which there are four. The broad singlet at 2.23 ppm is characteristic of protons attached to nitrogen atoms in amines. The multiplet center at 2.74 ppm down-field from TMS can be analysed to consist of a triplet (2.78 ppm) and a singlet (2.70 ppm) of equal

Figure 9

The ^{1}H n. m. r. spectrum of 1,4,8,11-tetraazacyclotetradecane


T M S
0 PPM
1
2
3
4

areas. These are the α-protons to the amino group in the cyclam molecule. The eight H_α protons are all equivalent and have no immediate neighbours. They therefore appear as a sharp singlet at 2.70 ppm. The eight H_α' protons are also equivalent but are coupled with the H_β- protons. They appear as a triplet at 2.78 ppm.

(ii) Preparation of trans-dihalogeno(cyclam)rhodium halides or perchlorates

The sensitive base hydrolysis of the trans-dihalogeno-(cyclam)rhodium(III) complexes provided an excellent pathway in these preparations.

The trans-Rh(cyclam)X_2^+ ($X = Br^-$ and I^-) complexes were prepared from the trans-Rh(cyclam)Cl_2^+ complex by heating in hydroxide to produce the dihydroxo complex in solution, and acidified to produce the diaquo complex. The desired anions were then added and heated for certain times in order to obtain the dihalogeno complexes which were precipitated.

The trans-Rh(cyclam)X(OH)$^+$ complexes ($X=Cl^-$, Br^- and I^-) were prepared by heating the trans-Rh(cyclam)X_2^+ complexes in hydroxide solution for certain times in order to obtain the monohydroxo complexes and then were precipitated.

The mixed dihalogeno complexes of the type trans-Rh(cyclam)XY^+ were prepared by producing the trans-Rh(cyclam)X(OH)$^+$ in hydroxide solution, followed by acidification to produce the monoaquo complexes and the desired anion was added and heated for certain times in order to obtain the appropriate complex which was then precipitated.

trans-[Rh(cyclam)Cl_2]Cl

$RhCl_3 \cdot 3H_2O$ (6.0 g, 22 mmoles) and cyclam (6.0 g, 30 mmoles) were dissolved in 300 ml methanol and heated under reflux for 5 minutes, during which the red mixture turned to a yellow solution with a yellow precipitate. The reaction mixture was cooled and filtered. The yellow precipitate was cis-[Rh(cyclam)Cl_2]Cl. The filtrate was treated with 25 ml concentrated HCl to precipitate the excess cyclam as the yellow tetrahydrochloride, and any cis-isomer left in the reaction solution. After filtration, the solution was evaporated to dryness. The yellow residue was recrystallized from 75 ml water and 25 ml conc. HCl, washed with acetone and ethyl ether, and dried under vacuum for 2 hours. The product was 3.7 gram (9.0 mmoles, 41% yield).

Anal. calculated for [Rh($C_{10}H_{24}N_4$)Cl_2]Cl: C,29.32; H,5.91; N,13.68; Cl,25.97. Found: C,28.98; H,5.90; N,13.58; Cl,25.82%.

trans-[Rh(cyclam)Br_2]Br

trans-[Rh(cyclam)Cl_2]Cl (992 mg, 2.38 mmoles) was dissolved in 25 ml water. Sodium hydroxide (5.0 g, 125 mmoles) was added to the solution. The solution was heated under reflux for one hour, during which the color of the solution changed from yellow to pale yellow, and was then slightly acidified with HBr (15 ml of 48% solution, 130 mmoles). The color of the solution changed to orange. Sodium bromide (6.0 g, 58 mmoles) was added to the solution and the solution was then heated under reflux for one hour, during which an orange precipitate formed. The precipitate was filtered, washed with ethanol and ethyl ether, and dried under vacuum for 2 hours. The product was 1.014 g (1.87 mmoles, 78% yield).

Anal. Calculated for $[Rh(C_{10}H_{24}N_4)Br_2]Br$: C, 22.12; H,4.46; N,10.32; Br, 44.15%. Found: C,22.24; H,4.40; N,10.39; Br, 44.06%.

trans-$[Rh(cyclam)I_2]I$

trans-$[Rh(cyclam)Cl_2]Cl$ (1.693 g, 4.14 mmoles) and NaI (10.0 g, 67 mmoles) were dissolved in 3 liters of water. Sodium hydroxide (1 pellet, ~2.5 mmoles) was added to the solution to adjust the solution slightly basic. The solution was heated under reflux for 2 days, during which the color of the solution changed from pale yellow to brown. The solution was acidified by adding 10 drops of HI (47% of solution, ~ 3 mmoles) and was then slowly evaporated to 200 ml. The brown precipitate was filtered and then recrystallized from 3 liters of water and sodium iodide (10 g, 67 mmoles) by heating under reflux for 2 days. The volume of the solution was reduced by evaporation to 200 ml. The product was filtered, washed with ethanol and ethyl ether, and dried under vacuum for

2 hours. The product was 2.10 g (3.08 mmoles, 75% yield).

Anal. calculated for [Rh($C_{10}H_{24}N_4$)I_2]I: C,17.56; H, 3.54; N,8.19; I,55.66%. Found: C,17.56; H,3.38; N,8.18; I,55.70%.

trans-[Rh(cyclam)Cl(OH)](ClO_4)

trans-[Rh(cyclam)Cl_2]Cl (304 mg, 0.743 mmoles) and NaOH (1 pellet, ~2.5 mmoles) were dissolved in 20 ml water and heated under reflux for 3 minutes. Sodium perchlorate ($NaClO_4 \cdot H_2O$, 5.0 g, 36 mmoles) was added to precipitate the white complex. The precipitate was filtered, washed with ethanol and ethyl ether, and dried under vacuum for 2 hours. The product was 147 mg (0.323 mmoles, 44% yield).

Anal. calculated for [Rh($C_{10}H_{24}N_4$)Cl(OH)](ClO_4): C, 26.39; H,5.54; N, 12.31; Cl, 15.58%. Found: C,26.41; H,5.45; N,12.11; Cl, 15.65%.

trans-[Rh(cyclam)Br(OH)](ClO_4)

trans-[Rh(cyclam)Br_2]Br (200 mg, 0.368 mmoles) was dissolved in 15 ml H_2O. One pellet of NaOH (~2.5 mmoles) was added to the solution. The solution was heated under reflux for 5 minutes, during which the solution turned pale yellow. $NaClO_4 \cdot H_2O$ (5.0 g, 36 mmoles) was added to the solution and was stirred to dissolve. The solution was cooled with ice, during which a light orange precipitate formed. The precipitate was filtered, washed with ethanol and ethyl ether, and dried under vacuum for 2 hours. The product was 101 mg (0.202 mmoles, 55% yield).

Anal. calculated for $[Rh(C_{10}H_{24}N_4)Br(OH)](ClO_4)$: C,24.04; H,5.05; N, 11.21; Cl,7.10; Br,15.99%. Found: C,24.04; H,4.99; N,11.04; Cl,7.30; Br,15.81%.

trans-$[Rh(cyclam)I(OH)](ClO_4)$

trans-$[Rh(cyclam)I_2]I$ (251 mg, 0.367 mmoles) and NaOH (1 pellet,~2.5 mmoles) were added to 25 ml water and heated under reflux for 10 minutes. The solution was filtered and then heated under reflux for an additional 2 minutes. $NaClO_4 \cdot H_2O$ (5.0 g, 36 mmoles) was added to precipitate the orange complex. The precipitate was filtered, washed with ethanol and ethyl ether, and dried under vacuum for 2 hours. The product was 78 mg(0.142 mmoles, 39% yield).

Anal. calculated for $[Rh(C_{10}H_{24}N_4)I(OH)](ClO_4)$: C,21.97; H,4.61; N,10.25; I,23.22; Cl,6.49%. Found: C,22.09; H,4.53; N,10.11; I,23.26; Cl, 6.39%.

trans-$[Rh(cyclam)ClBr](ClO_4)$

trans-$[Rh(cyclam)Cl_2]Cl$ (216 mg, 0.528 mmoles) and NaOH (1 pellet,~2.5 mmoles) were dissolved in 25 ml of water and heated under reflux for 5 minutes, during which the solution turned paler yellow. Concentrated HBr (10 ml,48%, 87 mmoles) and $HClO_4$ (10 ml, 70% of solution, 11 mmoles) were added and the solution was heated at 55°C for 20 hours, during which a yellow precipitate formed. The precipitate was filtered and recrystallized from 125 ml of water and 1 ml $HClO_4$ (70% of solution, 11 mmoles). The light orange precipitate was filtered, washed with ethanol and ethyl ether, and dried under vacuum for 2 hours. The product was 210 mg (0.405 mmoles, 77% yield).

Anal. calculated for $[Rh(C_{10}H_{24}N_4)ClBr](ClO_4)$: C, 23.19; H, 4.67; N, 10.82; Cl, 13.69; Br, 15.42%. Found: C, 23.29; H, 4.69; N, 10.77; Cl, 13.57; Br, 15.51%.

trans-$[Rh(cyclam)ClI](ClO_4)$

trans-$[Rh(cyclam)I_2]I$ (200 mg, 0.293 mmoles) and NaOH (1 pellet, ~ 2.5 mmoles) were dissolved in 50 ml water and heated under reflux for 15 minutes. 5 ml of conc. HCl (60 mmoles) were added and the solution was refluxed for 15 minutes. $NaClO_4 \cdot H_2O$ (10 g, 72 mmoles) was added to the solution. The solution was cooled and an orange precipitate formed. The precipitate was filtered, washed with ethanol and ethyl ether, and dried under vacuum for 2 hours. The product was 105 mg (0.186 mmoles, 64% yield).

Anal. calculated for $[Rh(C_{10}H_{24}N_4)ClI](ClO_4)$: C, 21.26; H, 4.28; N,9.82, Cl,12.55; I, 22.46%. Found: C,21.00; H,4.11; N,9.66; Cl,12.72; I,22.27%.

trans- $[Rh(cyclam)BrI](ClO_4)$

trans-$[Rh(cyclam)I_2]I$ (303 mg, 0.444 mmoles) and NaOH (1 pellet, ~ 2.5 mmoles) were dissolved in 50 ml water and heated under reflux for 15 minutes. If any undissolved diiodo compound remained, it was removed by filtering the light brown solution. Conc. HBr (4 ml of 48% solution, 35 mmoles) was added to the solution and the solution was refluxed for 15 minutes. $NaClO_4 \cdot H_2O$ (10 g, 72 mmoles) was added to precipitate the complex. The solution was cooled and the orange precipitate was filtered, washed with ethanol and ethyl ether, and dried under vacuum for 2 hours. The product was 153 mg (0.252 mmoles, 57% yield).

Anal. calculated for $[Rh(C_{10}H_{24}N_4)BrI](ClO_4)$: C, 19.71; H,3.97; N,9.19; Br,13.11; I,20.82; Cl,5.81%. Found: C,19.97; H,4.03; N,9.37; Br,13.40; I,21.01; Cl,6.02%.

The electronic spectra of the above complexes are recorded in Table 1 and Figures 10, 11and 12.

Table 1

The electronic spectra of trans-Rh(cyclam)XY$^+$ complexes

complex X	Y	λ (mμ)	ε ($l \cdot cm^{-1} \cdot mole^{-1}$)
I	I	466,353,275,226	201,13300,35200,21600
I	Br	497,459,321,256	148,152,6130,33400
I	Cl	493,445*,308,245	226,134,3600,31500
Br	Br	429,285,235	98,2520,35200
Br	Cl	418,312*,260*,221	91,95,2010,31200
Cl	Cl	406,310*,242*,204	78,82,3340,38100
I	OH	443,393,275,230	156,162,5310,25400
Br	OH	373,277*	116,392
Cl	OH	363,276	103,182

* shoulder

Figure 10

The charge transfer spectra of some trans-$[Rh(cyclam)X_2]^+$ complexes.

—— trans-$[Rh(cyclam)I_2]^+$

---- trans-$[Rh(cyclam)Br_2]^+$

—.— trans-$[Rh(cyclam)Cl_2]^+$

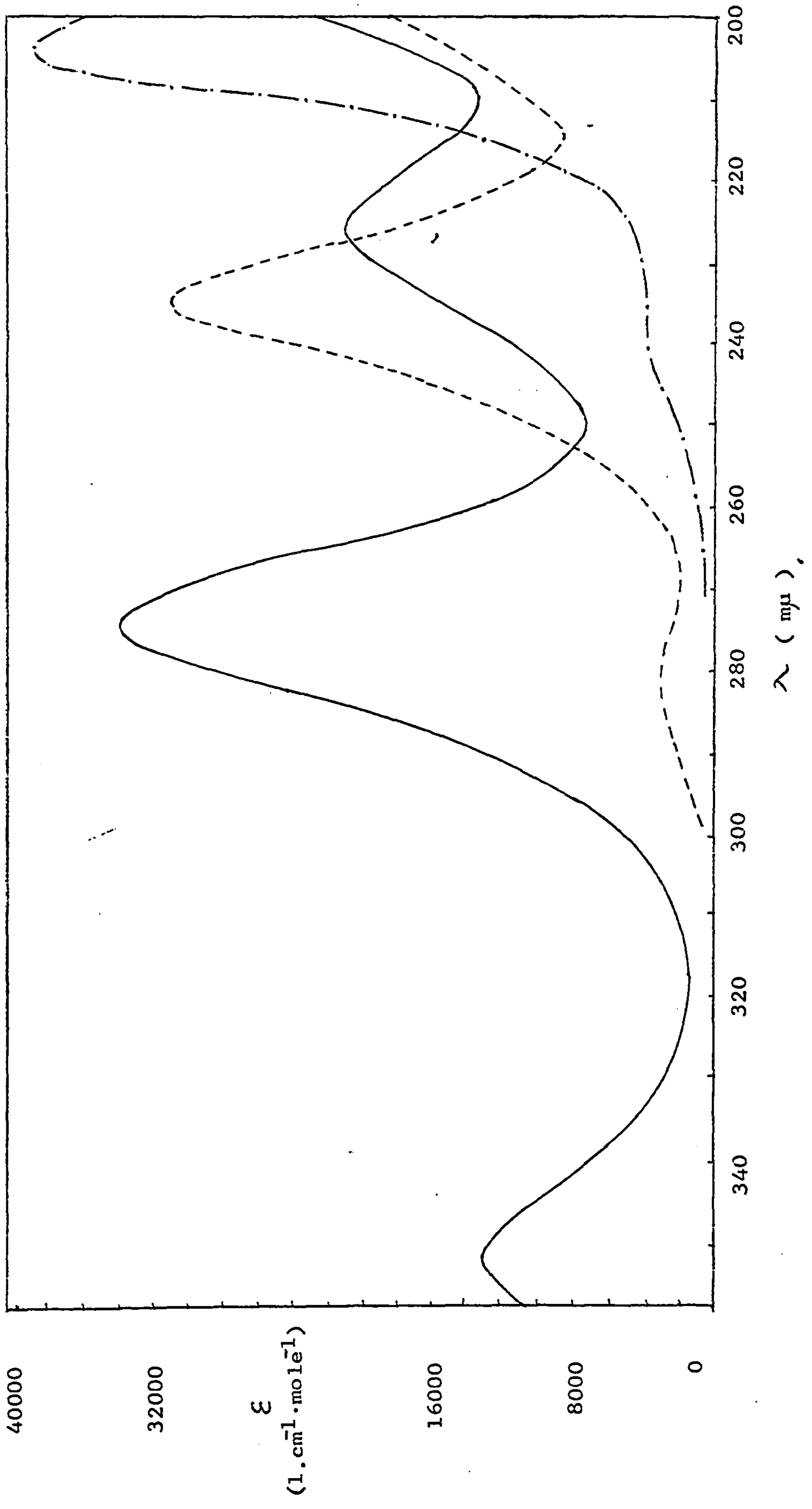

40000
32000
ε
(1.cm^{-1}.mole^{-1})
16000
8000
0
200
220
240
260
280
300
320
340
λ (mμ),

Figure 11

The charge transfer spectra of some trans-[Rh(cyclam)XY]$^+$ complexes.

——— trans-[Rh(cyclam)IBr]$^+$

----- trans-[Rh(cyclam)ICl]$^+$

—·— trans-[Rh(cyclam)BrCl]$^+$

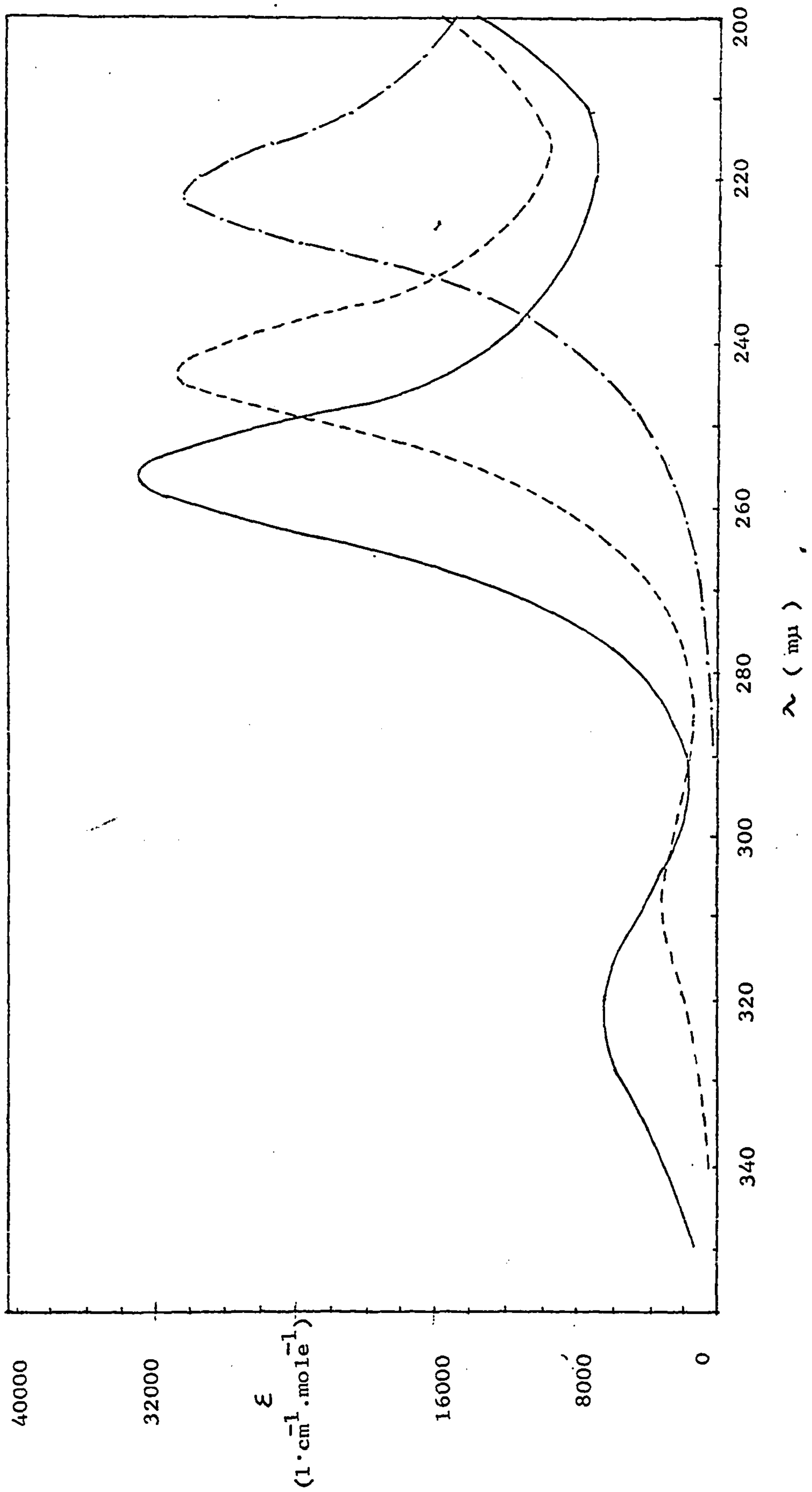

40000
32000
16000
8000
0
ε
(l·cm^{-1}.mole^{-1})
200
220
240
260
280
300
320
340
λ (mμ)

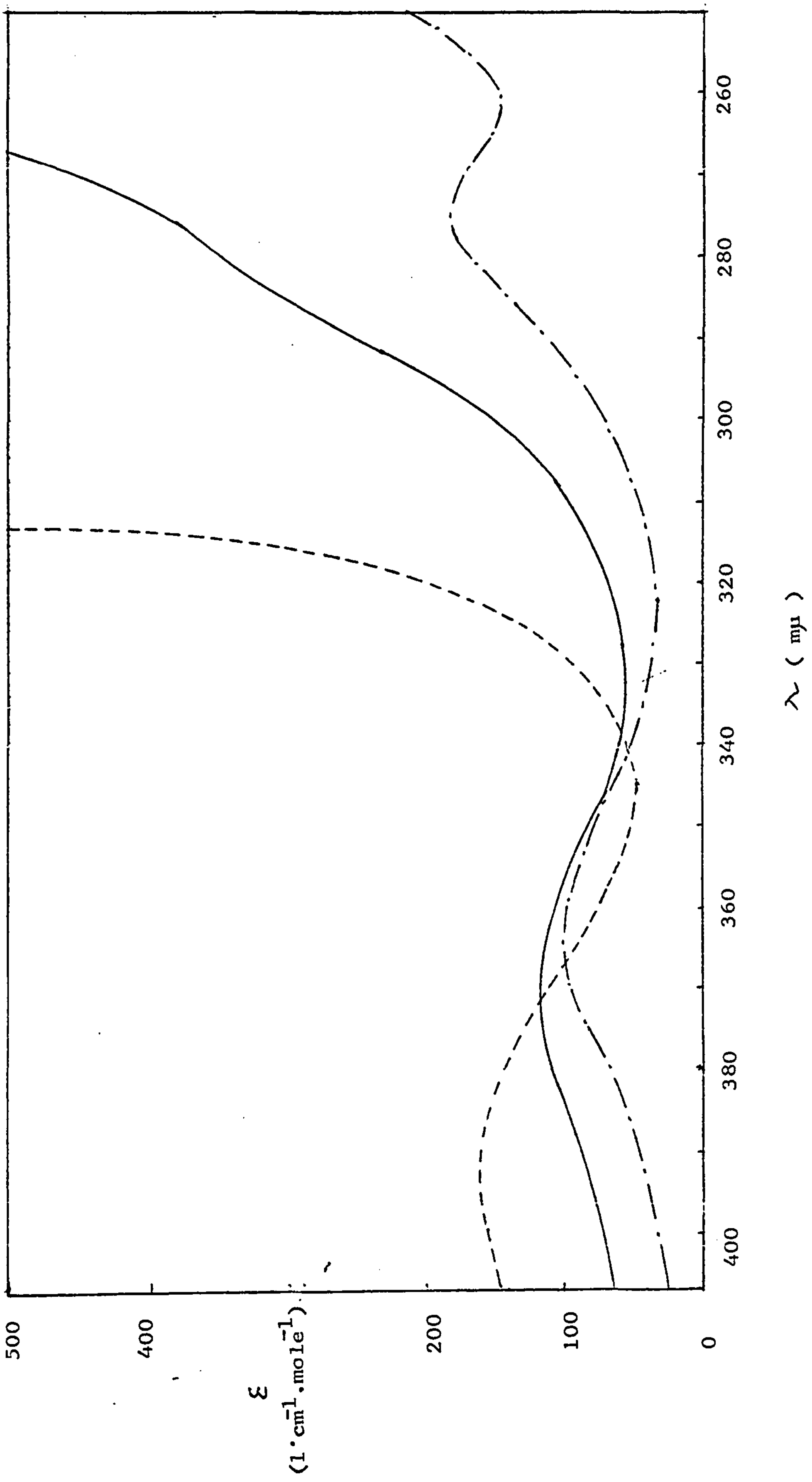
Figure 12

The electronic spectra of some trans-[Rh(cyclam)X(OH)]$^+$ complexes.

----- trans-[Rh(cyclam)I(OH)]$^+$

—— trans-[Rh(cyclam)Br(OH)]$^+$

—·— trans-[Rh(cyclam)Cl(OH)]$^+$


260
280
300
320
340
360
380
400
λ (mμ)
500
400
200
100
0
ε
(l·cm^{-1}.mole^{-1})

(iii) Preparation of trans-dihalogeno(D_4-cyclam)rhodium(III) halides (D_4-cyclam = N,N',N'',N'''-tetradeuteriocyclam)

The trans-[Rh(D_4-cyclam)X_2]X was prepared by dissolving the corresponding trans-[Rh(cyclam)X_2]X in hydroxide solution using D_2O as a solvent.

trans-[Rh(D_4-cyclam)Cl_2]Cl

trans-[Rh(cyclam)Cl_2]Cl (115 mg, 0.282 mmoles) was dissolved in 10 ml D_2O. NaOH (1 pellet, ~2.5 mmoles) was added. The yellow solution was heated under reflux for 2 hours and was then slightly acidified with 6 drops of conc. HCl (~ 4 mmoles) and was heated again for 2 hours. The solution was allowed to cool and precipitate. The yellow precipitate was filtered, washed with ethyl ether and dried under vacuum for 2 hours. The product was 93 mg (0.225 mmoles, 79% yield).

The IR spectrum of the deuterio-substituted cyclam complex of the trans-[Rh(D_4-cyclam)Cl_2]$^+$ showed a deuterium enrichment of approximately 95% (see relative peak heights of N-H and N-D stretching regions, Figure 13). The electronic spectrum of the complex indicated that it remained as the trans-dichloro species after deuteration.

trans-[Rh(D_4-cyclam)I_2]I

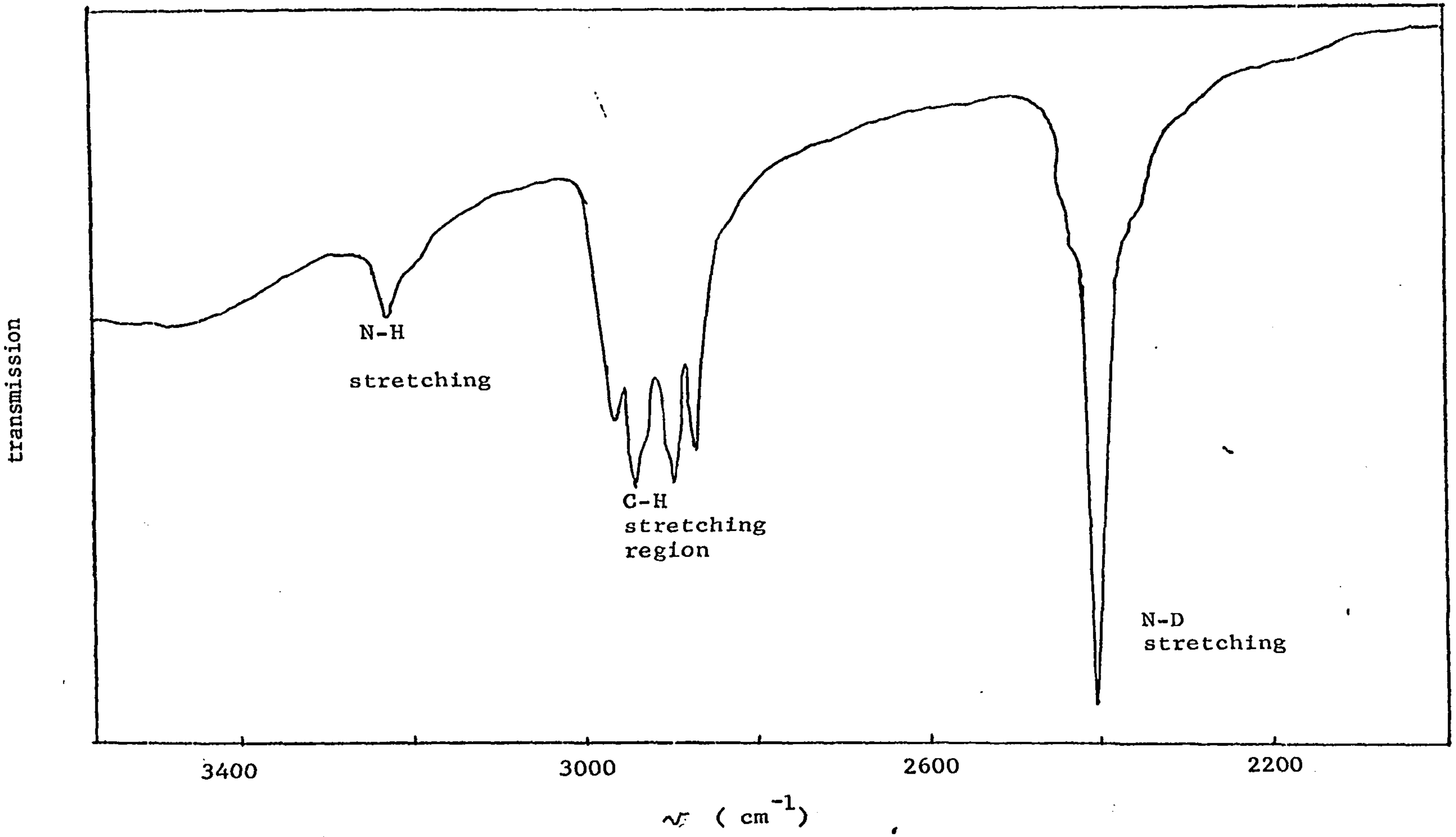
trans-[Rh(cyclam)I_2]I (120 mg, 0.175 mmoles) was dissolved in 10 ml of D_2O. NaOH (1 pellet, ~2.5 mmoles) was added to the solution. The brown solution was heated

Figure 13

The infrared spectrum of the trans-[Rh(D_4-cyclam)I_2]$^+$ complex.

Figure 13

The infrared spectrum of the trans-[Rh(D_4-cyclam)I_2]$^+$ complex.


transmission
N-H
stretching
C-H
stretching
region
N-D
stretching
3400
3000
2600
2200
ν̃ (cm^{-1})

under reflux for 1 hour, slightly acidified with 13 drops of HI (47% of solution, ~4 mmoles), and heated again for 2 hours, during which a brown precipitate formed.

The precipitate was filtered, washed with ethyl ether, and dried under vacuum for 2 hours. The product was 87 mg (0.126 mmoles, 72% yield).

The IR spectrum of the deuterio- substituted cyclam complex of the trans- $Rh(D_4\text{-cyclam})I_2^+$ showed a deuterium enrichment of approximately 90%. The electronic spectrum of the complex indicated that it remained as the trans-diiodo species after deuteration.

III. Kinetic Studies

1. Results

The kinetic studies of the base hydrolysis of the trans-Rh(cyclam)X_2^+ and trans- Rh(cyclam)XY^+ complexes were carried out spectrophotometrically. A Mettler microgrammatic balance was used to weigh the compounds accurately to the sixth decimal of a gram. The thermostatic oil baths, equipped with Sargent heat & circulator and thermonitor, were capable of holding temperature constant to ± 0.01° C. For all kinetic runs, water, previously distilled and ion-exchanged, was rendered carbon dioxide free by boiling, and then cooled, and stored under an atmosphere of nitrogen. Stock solution of sodium hydroxide was standardized with potassium hydrogen phthalate using phenolphthalein as indicator before each run.

An accurately weighed quantity of the compound and the appropriate concentration of NaOH solution were prepared separately in equal volumes of water. Sufficient $NaNO_3$ was added to the NaOH solution before dilution to ensure a final ionic strength of 0.30 M in the reaction mixture. ($NaClO_4$ could not be used due to the insufficient solubility in this media of the complexes under investigation.) The two solutions were previously brought to reaction temperature in a thermostated oil bath and then mixed in a volumetric flask and stoppered tightly. The flask was not wrapped in aluminum foil, since no differences due to photo-catalysis were observed between results from wrapped and unwrapped flasks.

The final concentrations of the complexes varied from $3\text{x}10^{-5}$ M for the diiodo to $3\text{x}10^{-4}$ M for the dibromo complexes, with the lowest ratio of $[OH^-]$ to [complex] throughout being 200 to 1, and therefore quite sufficient to ensure psuedo-first order kinetics. At appropriate time intervals, aliquots were withdrawn and quenched in cold water to room temperature. The reaction mixtures were analyzed immediately at a wavelength for which the difference between the absorbance intensities of the reactant and product was large, usually that of a charge transfer peak with an extinction coefficient over 2,500 $\text{l.cm}^{-1}.\text{mole}^{-1}$.

The reactions were studied over a wide temperature range from 25 to 85°C. Each complex was studied at three temperatures over a 30 degree range to permit calculation of the activation parameters and with six different concentrations of alkali employed. The reaction rate was followed for at least one half-life and usually for between two and three half-lives. The rate of disappearance of the complex always followed the first order kinetic law, and the pseudo first order rate constants for the reactions were determined graphically from the relationship:

$$k_{obd} = \frac{2.30}{t} \log \frac{a}{a - x} = \frac{2.30}{t} \log \frac{A_0 - A_\infty}{A_t - A_\infty}$$

where t is the time in seconds, A_0 is the absorbance of the initial reading, A_t is the absorbance at time t, and A_α is the absorbance calculated from the known extinction coefficient of the product being formed. Isosbestic points were obtained in some systems in the wavelength range studied. For the bromoiodo system, the isosbestic points were at 298 mμ and 390 mμ. A typical plot is shown in Figure 14. Good first order rate plots were obtained throughout. A typical plot is showed in Figure 15. Second order rate constants were calculated from the following expression:

$$k = \frac{k_{obs}}{[OH^-]}$$

Excellent straight line plots of k_{obs} vs $[OH^-]$ were obtained throughout, over the range of OH^- concentrations used. A typical plot is given in Figure 16.

No evidence of trans to cis isomerization was found in these studies. The electronic spectra of the final solutions were examined and it was found that these spectra were virtually the same as those of the corresponding trans-monohydroxo-halogeno complexes. Thus the first step base hydrolysis of these complexes in these studies was complete and stereoretentive. This fact was found in the preparative work and the substitution and anation studies (64).

The activation parameters were calculated from the transition state theory expression for the thermodynamic treatment of reaction rates (65).

$$k = \frac{KT}{h} . e^{\Delta S^*/R} . e^{-\Delta H^*/RT}$$

Figure 14

Reaction spectrum of trans-[Rh(cyclam)IBr]$^+$ with 0.30 M OH$^-$ at 40°C forming trans-[Rh(cyclam)I(OH)]$^+$.
(time intervals = 30 minutes)

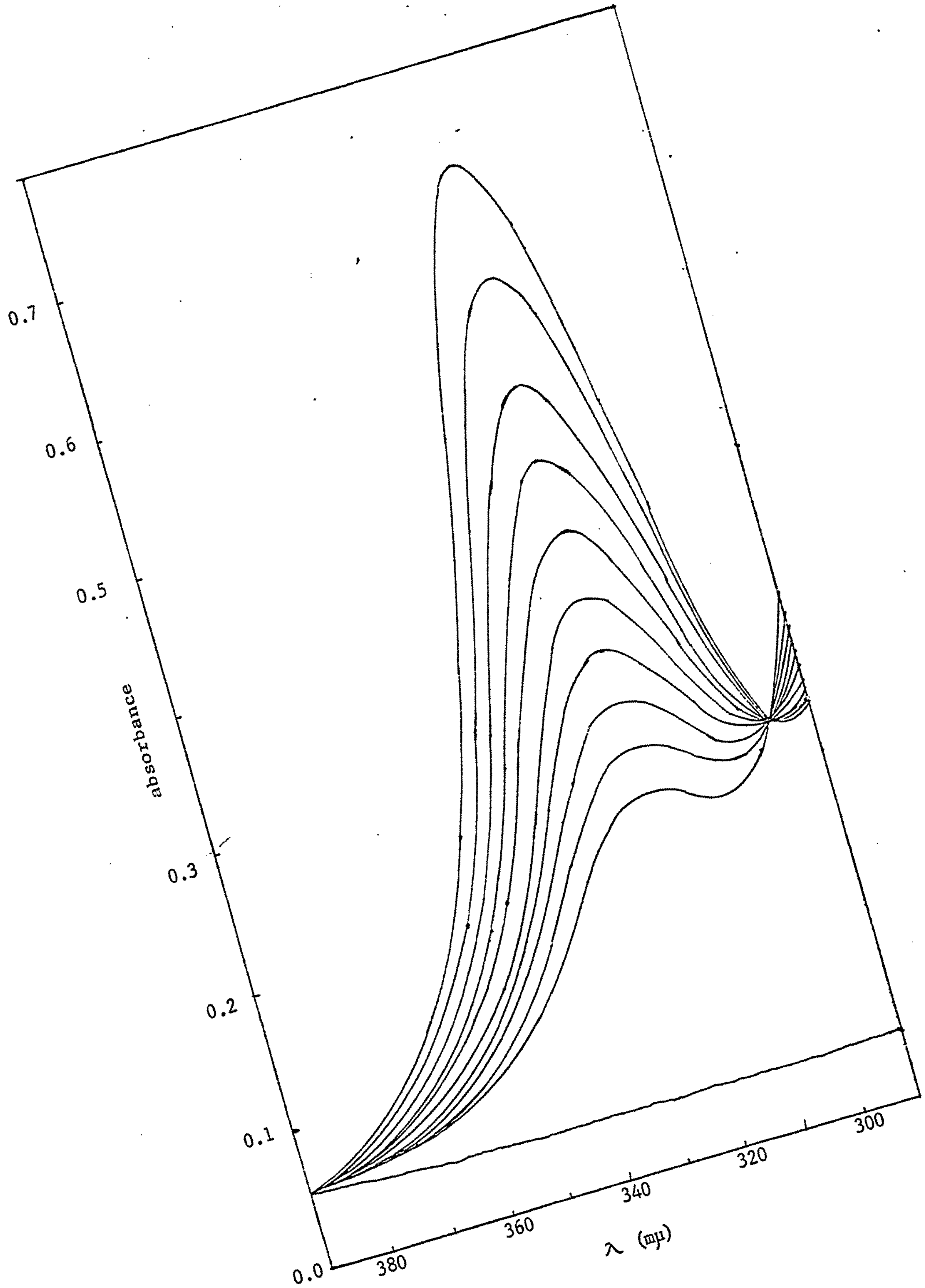

0.7
0.6
0.5
absorbance
0.3
0.2
0.1
0.0
380
360
340
320
300
λ (mμ)

Figure 15

A typical pseudo first order rate plot for the reaction of trans-$[\mathrm{Rh(cyclam)Br_2}]^+$ with $\mathrm{OH^-}$ at 55°C (ionic strength = 0.30 M)

● $\mathrm{OH^-}$ = 0.30 M
△ $\mathrm{OH^-}$ = 0.25 M
▣ $\mathrm{OH^-}$ = 0.20 M
○ $\mathrm{OH^-}$ = 0.15 M
▲ $\mathrm{OH^-}$ = 0.10 M
□ $\mathrm{OH^-}$ = 0.05 M

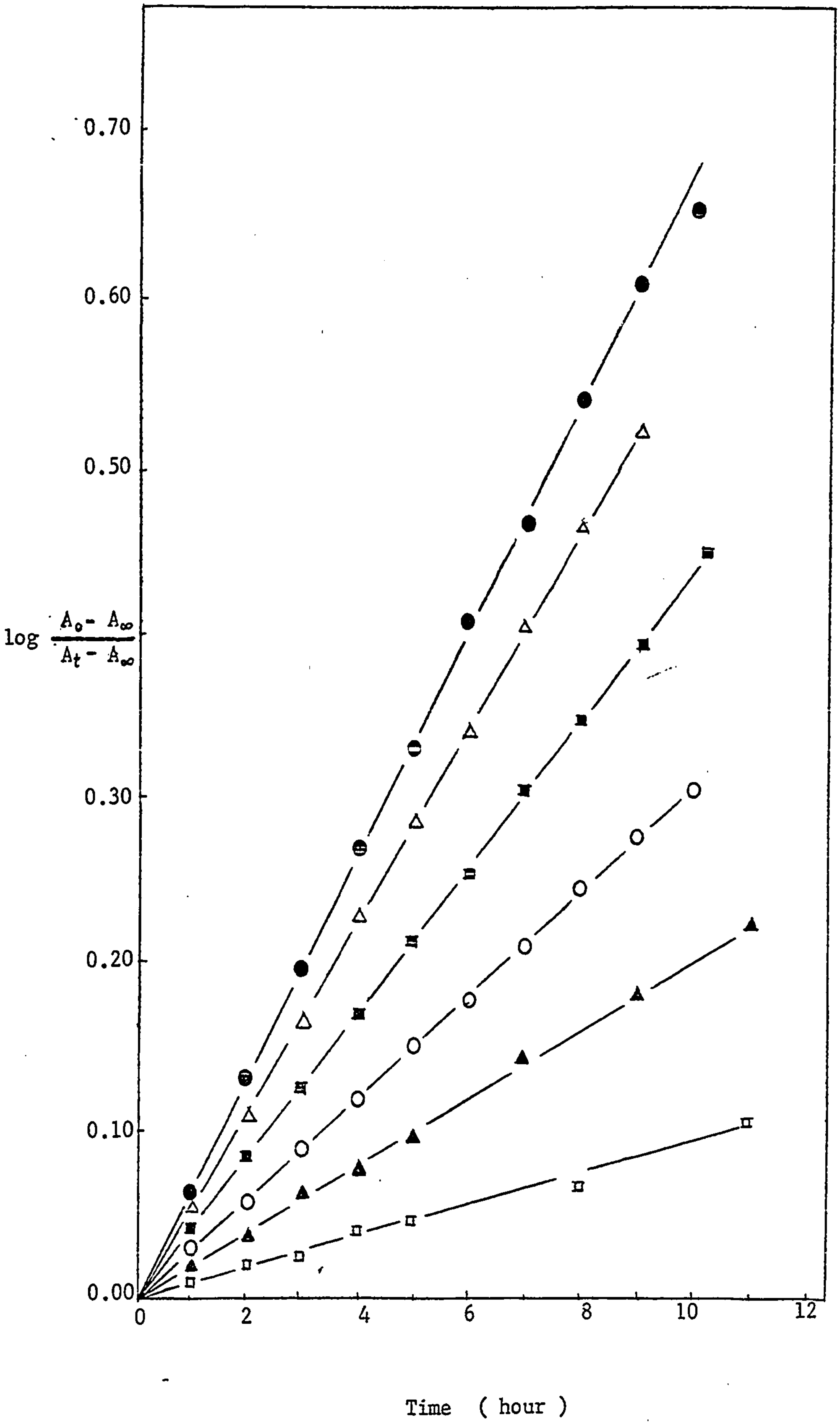
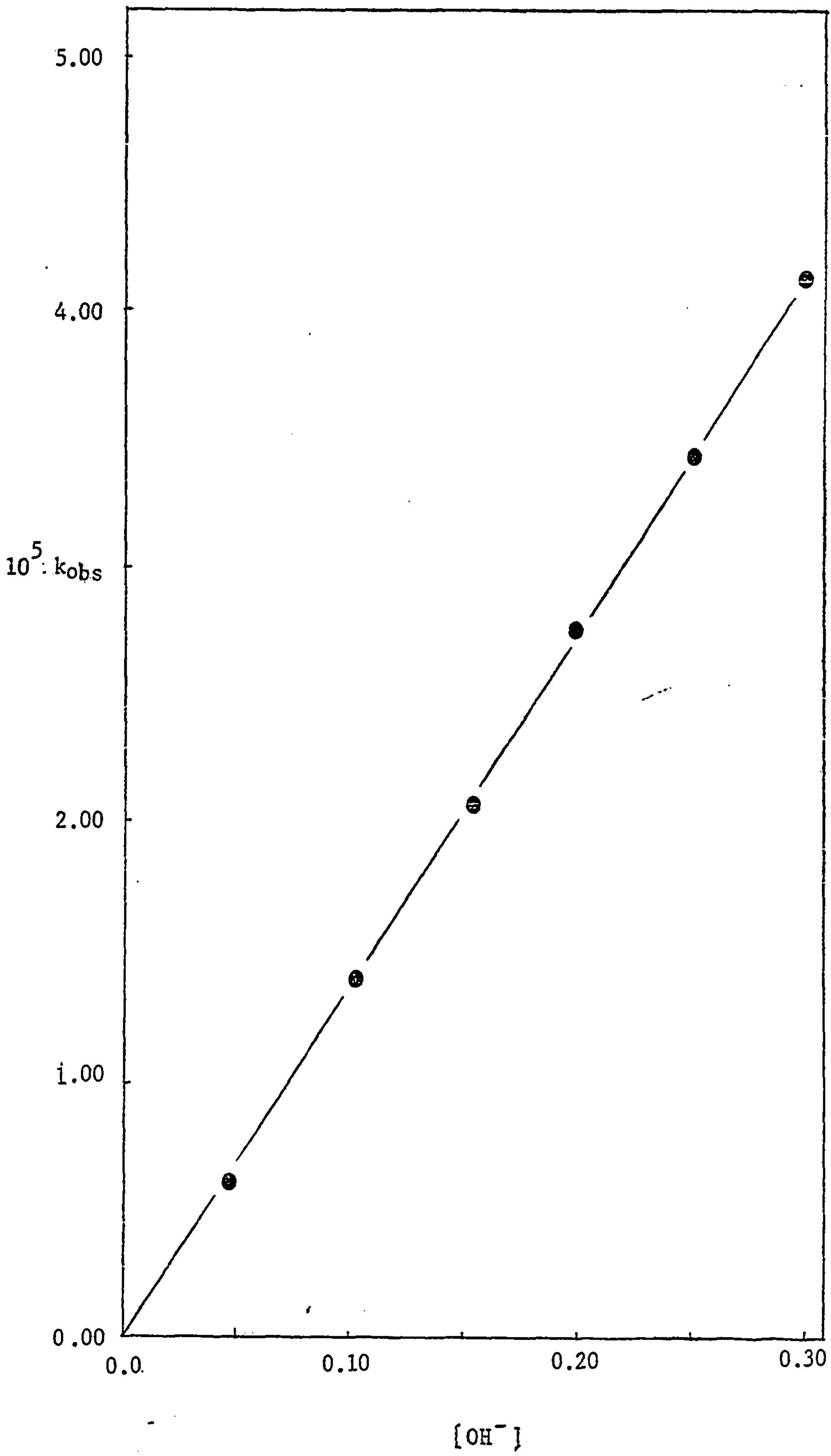

log $\frac{A_0 - A_\infty}{A_t - A_\infty}$
0.00
0.10
0.20
0.30
0.50
0.60
0.70
0
2
4
6
8
10
12
Time (hour)

Figure 16

A typical second order rate constant plot of k_{obs} for trans-[Rh(cyclam)Br_2]$^+$ with OH^- at 55°C (an ionic strength of 0.30 M)


5.00
4.00
$10^5 \cdot k_{obs}$
2.00
1.00
0.00
0.0
0.10
0.20
0.30
$[OH^-]$

where R (gas constant) is 1.987 cal·mole^{-1}·deg^{-1}, K (Boltz-

where R (gas constant) is 1.987 cal·mole^{-1}·deg^{-1}, K (Boltz-

mann constant) is 1.381 x 10^{-16} erg·deg^{-1}, and h (Planck constant) is 6.624 x 10^{-27} erg·sec.

activation enthalpy is less than the Arrhenius activation energy by RT or ~ 0.6 kcal·mole^{-1} in the range of temperatures employed.

$$\Delta H^* = E_a - RT$$

The rate data were evaluated statistically using the method of pooled variances (66). In this treatment the rate constants are assumed to be random variables which have the same standard deviations (expressed as a percentage of the constant) irrespective of the temperature. This is a reasonable assumption on theoretical grounds and also when the standard deviations of groups of constants obtained at different temperatures are compared. The standard deviation of an individual value for a constant is then calculated from all the values of the constants. Therefore, the percent standard deviation for the three temperatures is

$$\% \sigma = \left(\frac{\sum_T S_T}{N - 3} \right)^{\frac{1}{2}}$$

where N is the total number of the runs at all 3 temperatures, and

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

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

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

$$\% \sigma_{k_T} = \frac{\% \sigma}{\sqrt{n}}$$

where $\% \sigma$ is that for the 3 temperatures and n is the number of runs at the particular temperature being considered. Since the values of $\bar{k}$ are different at different temperatures, the pooled varience technique requires the use of percentages.

Using the transition state theory expression for reaction rates,and assuming that the activation enthalpy is constant for the small temperature range used, the consideration of the rate constants in pairs gives the expression:

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

where ΔH_{12}^{*} is the activation enthalpy determined on the basis of the two temperatures T_1 and T_2, and k_1 and k_2 are the respective rate constants at these temperatures. Therefore, three temperatures give the three values ΔH^{*}_{12}, ΔH^{*}_{23}, and ΔH^{*}_{13}.

The standard deviation on ΔH^{*}_{12} was calculated assuming exact values for the temperature. This could be done since the temperatures were regulated to ± 0.01°C. The standard deviation of ΔH^{*}_{12} is accordingly:

$$\sigma_{\Delta H^*_{12}} = 4.576 \frac{T_1 \cdot T_2}{T_1 - T_2} \left[(\sigma_{\log k_1})^2 + (\sigma_{\log k_2})^2 \right]^{\frac{1}{2}} \mathrm{cal \cdot mole}$$

where $\sigma_{\log k}$ is approximately $\log\left(1+\frac{\sigma_k}{100}\right)$ and σ_k is expressed as a percentage.

When the rate constants were measured at three different temperatures, the best enthalpy value is taken as the weighted mean of the three values found from constants at the three pairs of temperatures as shown in the following equations.

$$\Delta H^* = \frac{W_{12}\Delta H^*_{12} + W_{23}\Delta H^*_{23} + W_{13}\Delta H^*_{13}}{W_{12} + W_{23} + W_{13}} \quad \mathrm{cal \cdot mole}^{-1}$$

and

$$\sigma_{(\Delta H^*)} = \frac{1}{W_{12} + W_{23} + W_{13}} \quad ,$$

where

$$W_{12} = \frac{1}{\sigma_{(H^*_{12})}^2} \quad .$$

In all these calculations, any errors, which are caused by uncertainties in the temperatures are ignored. This is justified since any difference in the temperature between two measurements of a constant will be reflected in the variations in the constants obtained which in turn is reflected by the values of the standard deviations. The uncertainty in ΔH^* caused by uncertainty in the values of $T_1 - T_2$ will be less than 1 or 2% which is considerably less than the deviations obtained by the above procedure.

The entropy of activation is found by substituting the determined value of the enthalpy of activation in the original transition state expression:

$$\Delta S^* = 4.576 \log \frac{k}{T} + \frac{\Delta H^*}{T} - 47.23 \qquad \text{cal}\cdot\text{deg}^{-1}\cdot\text{mole}^{-1}$$

and

$$\sigma_{(\Delta S^*)} = \pm\left[4.576\,\sigma_{(\log k)}^{2} + \frac{\sigma_{(\Delta H^*)}^{2}}{T}\right]^{\frac{1}{2}} \div \frac{\sigma_{(\Delta H^*)}}{T}$$

The agreement of ΔH^*_{12}, ΔH^*_{23}, and ΔH^*_{13} is an indiction of the linearity of the activation enthalpy plot. The enthalpies of activation could also be obtained from the slope of a plot of log(k/T) vs 1/T. The most linear plot was obtained for the base hydrolysis of the trans-dibromo complex, and the least linear, for the base hydrolysis of the trans-dichloro complex. The poorest log(k/T) vs 1/T plot is showed in Figure 17.

The kinetic results are collected in Tables 2, 3 and 4. The calculation was carried out by using IBM 360 Computer (Model 50).

Figure 17

The enthalpy of activation plot of
log(k/T) vs 1/T plot for base hydrolysis of
trans-[Rh(cyclam)Cl_2]$^+$ complex.

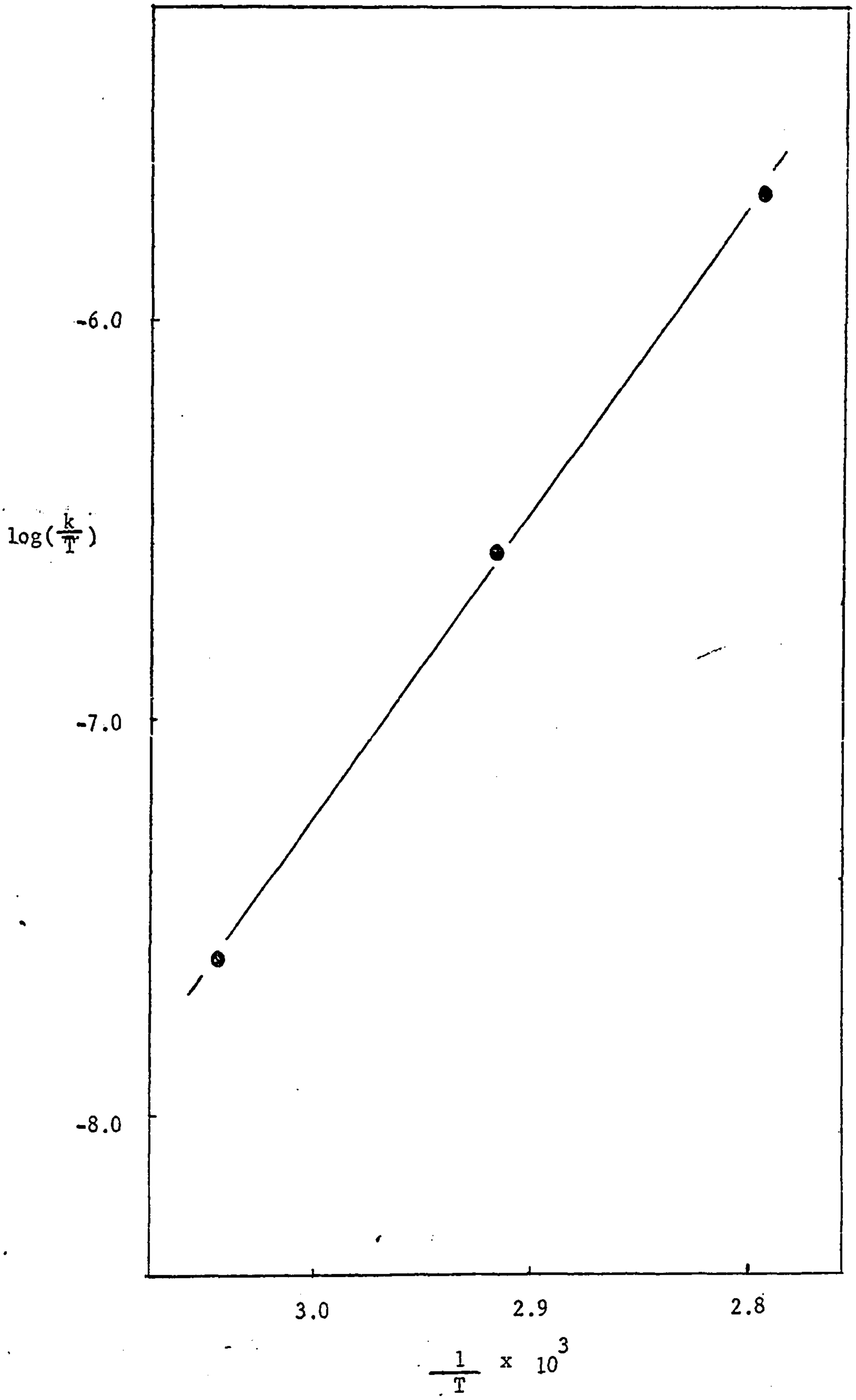

-6.0
-7.0
-8.0
log($\frac{k}{T}$)
3.0
2.9
2.8
$\frac{1}{T}$ x 10^3

Table 2

Pseudo first order rate constants, k_{obs}, and second order rate constants, k, for the base hydrolysis of the trans-[Rh(cyclam)XY]$^+$ complexes in aqueous solution at an ionic strength of 0.30 M.

Table 2 a

trans-$[Rh(cyclam)I_2]^+$ + OH^- → trans-$[Rh(cyclam)I(OH)]^+$ + I^-

T (°C)	OH^- (M)	$10^6 \cdot k_{obs}$ (sec^{-1})	$10^5 \cdot k$ ($sec^{-1} \cdot M^{-1}$)
25	0.30	10.5	3.51
	0.25	8.91	3.57
	0.20	7.50	3.75
	0.15	5.66	3.77
	0.10	3.61	3.61
	0.05	1.81	3.62
40	0.30	169	56.3
	0.25	147	58.8
	0.20	105	52.5
	0.15	80.0	53.3
	0.10	52.0	52.0
	0.05	30.0	60.0
55	0.30	2200	760
	0.25	1810	725
	0.20	1510	755
	0.15	1180	787
	0.10	748	748
	0.05	371	742

Table 2 b

trans- $[\mathrm{Rh(cyclam)IBr}]^+$ + $\mathrm{OH^-} \longrightarrow$ trans- $[\mathrm{Rh(cyclam)I(OH)}]^+$ + $\mathrm{Br^-}$

T (°C)	$\mathrm{OH^-}$ (M)	$10^6.k_{obs}$ ($\mathrm{sec^{-1}}$)	$10^5.k$ ($\mathrm{sec^{-1}.M^{-1}}$)
25	0.30	5.94	1.98
	0.25	4.96	1.98
	0.20	3.76	1.88
	0.15	2.85	1.90
	0.10	1.96	1.96
	0.05	0.985	1.97
40	0.30	75.3	25.1
	0.25	65.9	26.4
	0.20	52.5	26.3
	0.15	41.2	27.4
	0.10	25.1	25.1
	0.05	13.0	26.0
55	0.30	728	243
	0.25	622	249
	0.20	529	265
	0.15	369	245
	0.10	271	271
	0.05	265	265

Table 2 c

trans-[Rh(cyclam)ICl]$^+$ + OH$^-$ → trans-[Rh(cyclam)I(OH)]$^+$ + Cl$^-$

T (°C)	OH$^-$ (M)	$10^6 \cdot k_{obs}$ (sec^{-1})	$10^5 \cdot k$ (sec$^{-1} \cdot$M^{-1})
25	0.30	3.46	1.15
	0.25	3.17	1.26
	0.20	2.72	1.36
	0.15	1.98	1.32
	0.10	1.13	1.13
	0.05	0.52	1.04
40	0.30	37.0	12.4
	0.25	32.1	12.8
	0.20	23.8	11.9
	0.15	19.9	13.3
	0.10	15.5	15.5
	0.05	6.60	13.2
55	0.30	332	111
	0.25	295	118
	0.20	256	128
	0.15	193	129
	0.10	120	120
	0.05	60.3	121

Table 2 d

trans-$[Rh(cyclam)Br_2]^+ + OH^- \rightarrow$ trans-$[Rh(cyclam)Br(OH)]^+ + Br^-$

T (°C)	OH^- (M)	$10^6 \cdot k_{obs}$ (sec^{-1})	$10^5 \cdot k$ ($sec^{-1} \cdot M^{-1}$)
40	0.30	3.17	1.06
	0.25	2.56	1.02
	0.20	2.08	1.04
	0.15	1.40	0.933
	0.10	0.855	0.855
	0.05	0.424	0.848
55	0.30	43.8	14.6
	0.25	37.1	14.8
	0.20	28.5	14.3
	0.15	20.0	13.5
	0.10	13.6	13.3
	0.05	6.00	12.0
70	0.30	449	150
	0.25	378	151
	0.20	305	153
	0.15	231	154
	0.10	154	154
	0.05	73.9	148

Table 2 e

trans-[Rh(cyclam)BrCl]$^+$ + OH$^-$ → trans-[Rh(cyclam)Br(OH)]$^+$ + Cl$^-$

T (°C)	OH (M)	$10^6 \cdot k_{obs}$ (sec^{-1})	$10^5 \cdot k$ (sec$^{-1} \cdot$M^{-1})
55	0.30	10.7	3.56
	0.25	9.39	3.76
	0.20	7.50	3.75
	0.15	5.08	3.38
	0.10	3.52	3.52
	0.05	1.79	3.58
70	0.30	122	40.5
	0.25	104	41.7
	0.20	86.9	43.5
	0.15	63.3	42.2
	0.10	41.7	41.7
	0.05	21.7	40.9
85	0.30	1080	360
	0.25	915	366
	0.20	752	376
	0.15	534	356
	0.10	367	367
	0.05	181	362

Table 2 f

trans-$[Rh(cyclam)Cl_2]^+ + OH^- \rightarrow$ trans-$[Rh(cyclam)Cl(OH)]^+ + Cl^-$

T (°C)	OH^- (M)	$10^6 \cdot k_{obs}$ (sec^{-1})	$10^5 \cdot k$ ($sec^{-1} \cdot M^{-1}$)
55	0.30	2.28	0.759
	0.25	1.88	0.751
	0.20	1.51	0.754
	0.15	1.13	0.752
	0.10	0.732	0.732
	0.05	0.375	0.749
70	0.30	23.5	7.83
	0.25	20.0	7.99
	0.20	16.0	7.99
	0.15	11.9	7.91
	0.10	7.84	7.84
	0.05	3.92	7.84
85	0.30	227	75.7
	0.25	191	76.3
	0.20	150	75.1
	0.15	114	76.2
	0.10	74.9	74.9
	0.05	36.6	73.1

Table 3

Summary of second order rate constants for base hydrolysis of trans-[Rh(cyclam)XY]$^+$ complexes.

complex		T	$10^5 \cdot \bar{k}$
X	Y	(°C)	($sec^{-1} \cdot M^{-1}$)
I	I	25	3.64 ± 0.06
		40	55.5 ± 1.0
		55	753 ± 13
I	Br	25	1.95 ± 0.03
		40	26.1 ± 0.4
		55	256 ± 4
I	Cl	25	1.21 ± 0.5
		40	13.2 ± 0.5
		55	121 ± 4
Br	Br	40	0.958 ± 0.03
		55	13.8 ± 0.4
		70	152 ± 5
Br	Cl	55	3.59 ± 0.04
		70	41.8 ± 0.5
		85	365 ± 4
Cl	Cl	55	0.750 ± 0.004
		70	7.90 ± 0.04
		85	75.7 ± 0.4

Table 4

Activation parameters for base hydrolysis of trans-[Rh(cyclam)XY]$^{+}$ complexes

complex X	Y	ΔH^* (kcal·mole^{-1})	ΔS^* (cal·deg^{-1}·mole^{-1})	$10^5 \cdot \bar{k}_{55°C}$ (sec^{-1}·mole^{-1})
I	I	33.9 ± 0.1	34.9 ± 0.2	753 ± 13
I	Br	30.8 ± 0.2	23.2 ± 0.4	256 ± 4
I	Cl	29.2 ± 0.3	17.0 ± 0.5	121 ± 4
Br	Br	35.4 ± 0.2	31.5 ± 0.4	13.8 ± 0.4
Br	Cl	35.3 ± 0.1	28.5 ± 0.2	3.59 ± 0.04
Cl	Cl	35.3 ± 0.2	25.1 ± 0.7	0.750 ± 0.004

2 Discussion

The distinctive features of the base hydrolysis reactions of the cyclam complexes in comparison with other substitution reactions of Rh(III) complexes in addition to being first order in OH^- concentration, are the fast rates, the large enthalpies of activation, and the large positive entropies of activation which are found throughout the series of complexes studied.

The large enthalpies of activation for the cyclam complexes of transition metals are expected bacause of the destabilization of the transition state due to less efficient solvation with increasing chelation (67). In addition, the increased rigidity of the cyclam chelate resists rearrangement in the transition state.

An uncommon feature is the high relative rates paralleled by high enthalpies of activation, which are found in the series of trans-Rh(cyclam)IY^+($Y = I^-$, Br^- and Cl^-) and trans-Rh(cyclam)BrY^+ ($Y = Br^-$ and Cl^-) complexes. For trans-Rh(cyclam)IY^+complexes, the relative rates for Y are in the order $I^- > Br^- > Cl^-$, whereas the enthalpies of activation decrease from I^- through Br^- to Cl^-. The same orders of the relative rates and ΔH^* were found for trans-Rh(cyclam)BrY^+. This was a little unexpected, even though the relative rates are temperature dependent, and for a different range of temperatures the order of relative rates could be reversed.

The values of entropies of activation for the same series show a decrease in ΔS^* as Y changes along the series I^-, Br^- and Cl^-, which is expected since,as a leaving group, the Cl^- ion would be more easily solvated, the Br^- ion less solvated, and the I^- ion, least solvated. Hence, the smaller the Y^- ion, the smaller would be the expected ΔS^*. From the above consideration, as well one could expect the complex with chloro as the leaving group to react the fastest, the bromo the next slowest and the iodo the slowest, which is the order found and thus ΔS^* reinforces the relative rate order, and the reverse of the ΔH^* order. Although ΔH^* obviously makes the much larger contribution to the absolute value of the rate constant, calculations show that if the ΔS^* values were decreased by only 25%, a reversal of the relative rate order would occur, and thus the rates would parallel the ΔH^* order.

The rates and activation parameters for the base hydrolysis reactions of the trans-Rh(cyclam)XY^+ complexes can be used to compare the trans effects of the halogeno ligands quantitatively and to classify the complexes as kinetically class (a) or (b).

Kinetic trans effect

A trans effect order can be found for the group trans to the leaving group. For the trans-Rh(cyclam)XCl^+ complexes with Cl^- as the leaving group, the rate constants are 121, 3.59 and 0.750 x 10^{-5} $sec^{-1}.M^{-1}$ (in the ratio of 161:5:1) at 55°C for $X = I^-$, Br^- and Cl^- respectively, and the values of enthalpies of activation are 29.2, 35.3 and 35.3 kcal·mole^{-1} respectively. Thus, it is clear the trans effect in the trans-Rh(cyclam)XCl^{+} complexes is $I^{-} > Br^{-} > Cl^{-}$, in terms of rate constants. On the enthalpies of activation basis, the trans effect is $I^{-} > Br^{-} = Cl^{-}$, I^{-} being clearly 6.1 kcal·mole^{-1} greater than Br^{-} and Cl^{-}, which are identical. With Br^{-} as the leaving group, with $X = I^{-}$ and Br^{-}, these rate constants are in the ratio of 19:1 and I^{-} has a ΔH^{*} value 4.6 kcal·mole^{-1} lower than Br^{-}.

Br^{-} has always been found a better trans activator than Cl^{-} in all other studies on both octahedral and square planar complexes on the basis of relative rates (68). Of these, ΔH^{*} values were available from only two studies- the acid substitutions of $Rh(en)_2XY^{+}$ (45) and Rh(cyclam)XY^{+} (46) systems in which $Br^{-} > Cl^{-}$ by only 1.5 and 1.0 kcal·mole^{-1}, respectively.

Kinetic class (a) and (b) character

A systematic trend occurs in the ease of releasing Y^{-} from the trans-Rh(cyclam)IY^{+} complexes. At 55°C the rate constants for $Y = Cl^{-}$, Br^{-} and I^{-} are 121, 256, and 753 x 10^{-5} sec^{-1}·M^{-1} (the ratio is 1:2:3, allowing for statistical effects). Thus, on a relative rate constant basis the complexes appear kinetically more labile as Y changes from Cl^{-} to Br^{-} and to I^{-}, and therefore of class (a). However, the values of enthalpies of activation are 29.2, 30.8 and 33.9 kcal·mole^{-1} respectively and the complexes become kinetically more inert as Y changes from Cl^- to Br^- and to I^- by 1.6 and 3.1 kcal·mole^{-1} differences respectively and indicate class (b) behaviour. Since the relative rate constant effect is dependent upon the temperature chosen for comparison, the enthalpy of activation is much more reliable, and thus it can be concluded that the trans-Rh(cyclam)IY$^+$ complexes are kinetically of class (b). With Br^- in the trans position, and Br^- and Cl^- the leaving groups, the same effect is observed : Br^- is released two times as quickly as Cl^-, after allowing for statistical effects, but the ΔH^* of Br^- is greater than Cl^-, though very slightly (0.1 kcal·mole^{-1}).

The kinetic class (b) character of the Rh(III) in the trans-Rh(cyclam)IY$^+$ complexes agrees with the acid substitution results for the same complexes. Kinetic class (b) character of Rh(III) metal is common in some other Rh(III) systems, such as $Rh(NH_3)_5X^{2+}$(69) and $Rh(en)_2XY^+$ (45).

Mechanism

Comparison of the rates of the base hydrolysis observed in this study with the other substitution reactions (46) of the trans-Rh(cyclam)XY$^+$ complexes (Appendix 1) indicates that the rates of base hydrolysis are approximate 15 to 250 times faster at equivalent temperatures than those of the other substitution reactions and follow second order kinetics, first order with respect to the complex concentration and to the hydroxide ion concentration. Thus, an S_N1 mechanism can be ruled out on the kinetic form. For the other substitution reactions of the trans-Rh(cyclam)XY$^+$ complexes by Z in neutral or acidic aqueous media, the rates were found to be independent of the nature and concentration of the nucleophile, and no change of the rate was found over a five-fold increase in ionic strength (0.02 to 0.10 M). Since this difference in both the kinetic form and rates of the reactions can not be explained in terms of the same mechanism, postulated to be on the borderline between S_N1 and S_N2, obviously it is necessary to find a specific mechanism for the hydroxide ion, related to its unique role as the anion of the solvent.

For the trans-diiodo complex at 40°C, with the ionic strength adjusted to 3.00 M, there was a direct first order dependence on the hydroxide ion concentration up to 2.00 M. This concentration of OH^- is the limiting value found by Takemoto and Jones (20) for the reaction of $Co(NH_3)_6^{3+}$, and led them to discard S_N2 in favour of S_N1CB or S_N1IP. As no such limiting value was found here, a simple S_N2 mechanism cannot be discarded on the evidence alone. However, negative ΔS^* values would be expected for S_N2 reactions, whereas large positive ΔS^* values were found thoughout.

In organic and inorganic chemistry (70), it is usually found that reactions whose rates depend on "specific hydroxide ion catalysis" involve acid-base equilibria before reaction. The hydroxide ion produces an active intermediate which then reacts faster than the original substrate.

A dissociative conjugate base (S_N1CB) or ion-pair (S_N1IP) mechanism for base hydrolysis reactions would have a large positive entropy of activation (22c). This is because the activation complex is less solvated than the reactant. The formation of the transition state is accompanied by an increase in the disorder of the solvent as well as the reacting species which results in a positive entropy of activation (65). Thus, the high positive entropies of activation indicate a considerable loosening of bonds in the process of attaining the transition state. This suggests that formation of the transition state is accompanied by a net decrease in bonding in the rate determining step and is also the case in the base hydrolysis of the trans- Rh(cyclam)XY$^+$ complexes. Thus, the mechanism for the base hydrolysis of the trans- Rh(cyclam)XY$^+$ complexes is not likely of the S_N2CB or S_N2IP type, where a negative ΔS^* would be expected. Takemoto and Jones (20) have used the identical criterion (large positive ΔS^*) to distinguish between S_N1CB and S_N2CB, and also S_N1IP and S_N2IP mechanisms. The dissociative character of base hydrolysis has been postulated for Rh(III) by Panunzi and Basolo (15), although it had been suggested (2c) that Rh(III) complexes have a greater tendency to undergo S_N2 reactions than do corresponding Co(III) complexes.

It seems reasonably clear (3b) that the normal mechanism for the base hydrolysis of octahedral Co(III)-ammine and -amine complexes involves an S_N1CB mechanism in which the five coordinated intermediate takes on trigonal bipyramidal geometry (Figure 18a). This is due to the observation that base hydrolysis is often accompanied by stereochemical change and that cis and trans isomers do not differ enormously in their reactivity. This can be understood if the main labilizing effect occurs in the transition state since in a trigonal bipyramid the symmetry distinction between ligands that were originally trans or cis to the leaving group is lost. Since stereochemical change is not observed in Rh(III) as was the case in Co(III), it suggests strongly (2c) that any five-coordinated intermediate is square pyramidal (Figure 18b). The crystal field stabilization energy for the square pyramidal structure is greater in a low spin d^6 system than for the trigonal bipyramidal structure (71). Because of the greater crystal

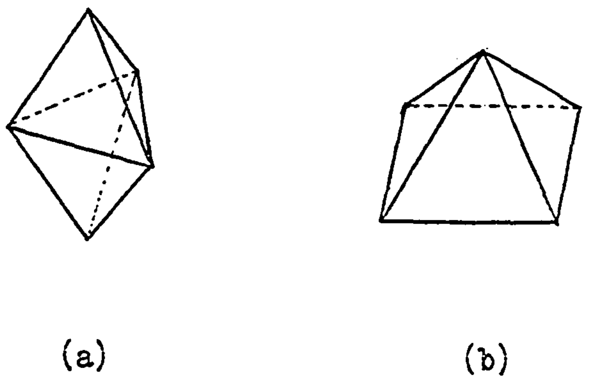


Figure 18 Geometrical structures of metal complexes
(a) trigonal bipyramidal (b) square pyramidal.

field strength of Rh(III) relative to Co(III), it is suggested (72) that the greater loss in crystal field stabilization energy would make it easier to produce a square pyramidal structure in the Rh(III) systems.

Experiments were done on the deuterium-hydrogen exchange reactions of trans- Rh(cyclam)Cl_2 $^+$ and trans- Rh(cyclam)I_2 $^+$. These two complexes were chosen, because they represent the two extremes in rates, the former being the slowest and the latter the fastest in the base hydrolysis series studied. An appropriate amount of trans-[Rh(D_4-cyclam)X_2]X was dissolved in water, and a solution of NaOH was added. The reaction mixture was heated at different times and temperatures, and the complex precipitated by addition of $NaClO_4$. The precipitate was filtered, washed with ethyl ether, and dried under vacuum, and analyzed by an IR spectrum. The infrared spectra showed that the deuterium of the amine group in the complexes exchanged with hydrogen in hydroxide solution. All the four amine deuterium atoms contained in the complex could be interchanged with hydrogen. The extent of exchange depended on the concentration of the hydroxide ion, the temperature of the reaction, and the time of the reaction. These hydrogen-deuterium exchanges were found to be faster than even the dissociative reaction step of the complex. But this was not the case in neutral and acidic solution, in which the hydrogen-deuterium exchanges were comparably very much less under the same conditions, indicating a conjugate base mechanism to be involved.

Thus a conjugate base mechanism in which the hydroxide ion is involved initially in a rapid acid base equilibrium in this study, is consistent with the work of James, Anderson and Briscoe in hexaamminecobalt(III) complex (9a) and with Poon and Tobe's base hydrolysis result of trans- $Co(D_4\text{-cyclam})X_2^+$ for the hydrogen-deuterium exchange evidence (17). The same experiment of Poon and Tobe's investigation of the ratio of hydrogen-deuterium exchange in the unreacted reactant and the product could not be done here, because the rate of proton exchange was much faster than the dissociative rate step. It was found that the four deuteria had changed to hydrogens before the rate determining step had proceeded to a significant degree, even if the concentration of hydroxide ion was 0.005 M, which was lower than the OH^- concentration in the base hydrolysis studied. Poon and Tobe found that the rates of the proton exchange were relatively slow, while the base hydrolysis was relatively very fast for trans-Co-(cyclam)Cl_2^+ and trans-Co(cyclam)Br_2^+, so the product exchanging one amine proton more than the reactant would be observed.

The behaviour of the dissociation of the proton from the original substrate could rule out the ion-pair mechanism for base hydrolysis of the trans-Rh(cyclam)XY^+ complexes.

The whole mechanism of base hydrolysis of these trans-Rh(cyclam)XY^+ complexes, following the S_N1CB mechanism, can be outlined as follows, with the second step being rate determing:

$$\text{trans- Rh(cyclam)XY}^{+} + \text{OH}^{-} \xrightleftharpoons[\text{fast}]{K} \text{trans- Rh(cyclam-H)XY} + \text{H}_2\text{O}$$

$$\text{trans- Rh(cyclam-H)XY} \xrightarrow[\text{slow}]{k_{cb}} \text{trans- Rh(cyclam-H)X}^{+} + \text{Y}^{-}$$

$$\text{trans- Rh(cyclam-H)X}^{+} + \text{H}_2\text{O} \xrightarrow{\text{fast}} \text{trans- Rh(cyclam-H)X(H}_2\text{O)}^{+}$$

$$\text{trans- Rh(cyclam-H)X(H}_2\text{O)}^{+} \xrightarrow{\text{fast}} \text{trans- Rh(cyclam)X(OH)}^{+}$$

The first step is the fast deprotonation of the amine group in the trans- Rh(cyclam)XY $^{+}$ to form its conjugate base. The second step is the rate-determining step of the dissociation of the leaving group. The third and the fourth steps are the very fast processes. The water molecule bonds to the Rh(III) in the trans- Rh(cyclam-H)X^{+} complex and the water proton rearranges to the amido group to form the hydroxo complex.

An energetic diagram of the reaction can be drawn as in Figure 19 .

Comparisons

The rates for base hydrolysis of dichloro complexes of Rh(III), Co(III) (26) and Cr(III) (27) are given in Table 5. For the cyclam complexes of all three metals no steric change was observed in the course of reactions. This is no surprise as the increased rigidity of the cyclam chelate resists rearrangement in the transition state.

The sensitivity to base hydrolysis of the analogous cyclam complexes on the rates are in the order Co(III)

Figure 19

Reaction profile for the base hydrolysis of trans-[Rh(cyclam)XY]$^+$

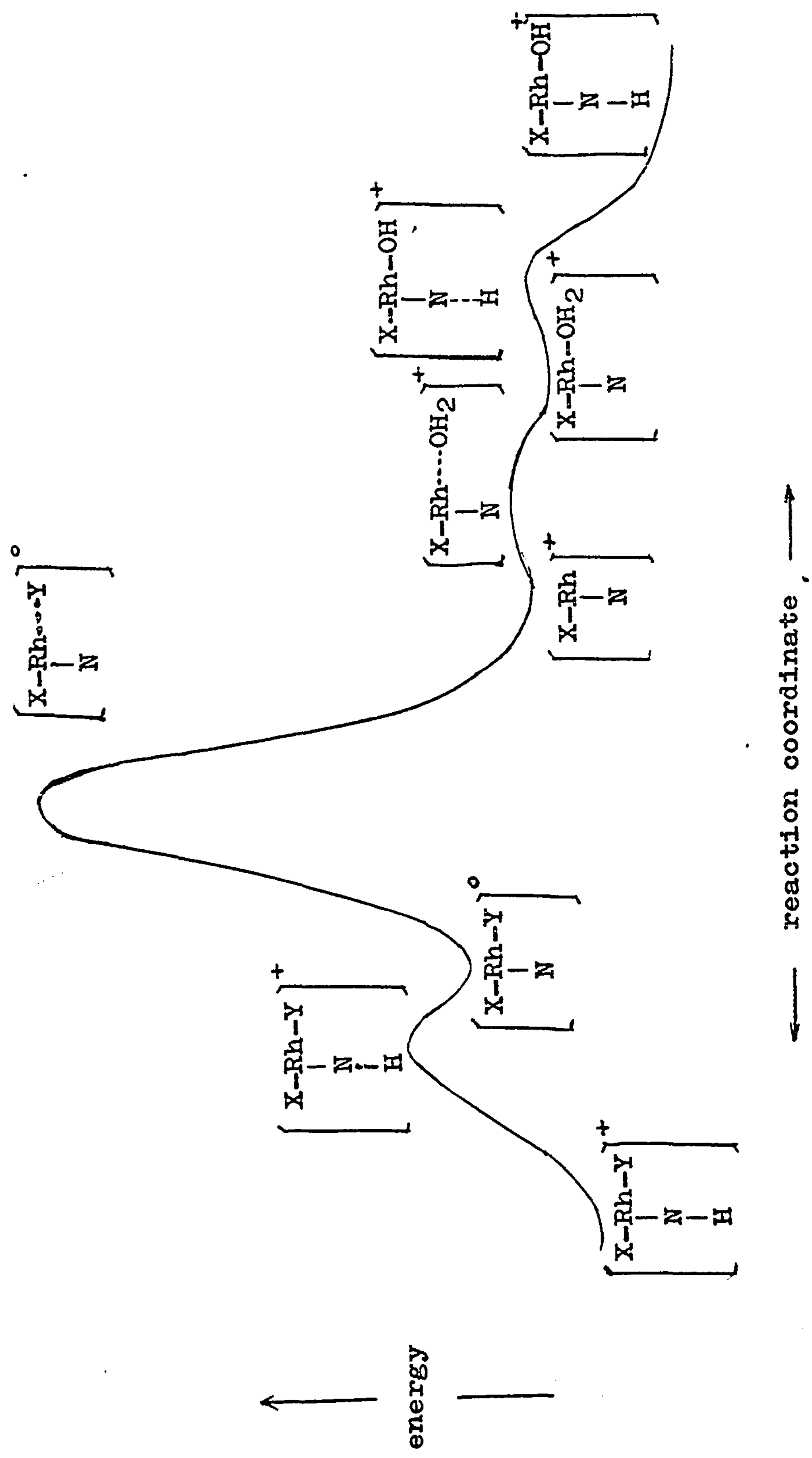

X-Rh-Y
N-H
X-Rh-Y
N-H
X-Rh-Y
N
X-Rh···Y
N
X-Rh
N
X-Rh···OH2
N
X-Rh-OH2
N
X-Rh-OH
N···H
X-Rh-OH
N-H
energy
reaction coordinate

Table 5

Second order rate constants ($sec^{-1} \cdot M^{-1}$) for the base hydrolysis of dichloro(cyclam) complexes of Co(III), Cr(III) and Rh(III) in aqueous solution (various ionic strengths) at 25°C.

complex	Co(III)	Cr(III)	Rh(III)
trans-M(cyclam)Cl_2^+	67,000 [a]	1.3 [b]	3.8×10^{-8} [c]

a Ref. 26   b Ref. 27   c This work (extrapolated)

$\gg$ Cr(III) $\gg$ Rh(III). Unfortunately, for Co(III) and Cr(III) there are no temperature dependent studies to yield ΔH^* values. The acid strengths are a measure of K_a and give the order Cr > Co > Rh for amine complexes, it can be expected to be in the same order for cyclam. The electron affinities are a measure of the tendency of the various metal ions to accept electrons from the amido group through σ or π-bonding. They give the reactivity order Co > Rh > Cr. The crystal field activation energies indicate how easy it is to form the necessary transition state for an S_N1CB mechanism and give the order Cr > Co > Rh (72) irrespective of the intermediate structure.

the low electron affinity, which causes the amido group to be ineffective. The comparison between Co and Cr electron affinities might be made equally well in terms of the ease of forming Co(II) in solution, and the difficulty of forming Cr(II). The lowest rate for Rh(III) is expected on the basis of a low acidity and a large crystal field activation energy, which counteracts a reasonably large electron affinity.

A greater reactivity of the cyclam complexes, compared with the tetraammine and bis (ethylenediamine) complexes (2c) of Rh(III), is found in this study.

For the S_N1CB mechanism, the rate is proportional to K, where K is the equilibrium constant of the substrate and its conjugate base. It is evident that the cyclam complexes have a tendency to form their conjugate bases, which then react faster than their original substrates, and are sensitive to base hydrolysis. But this is not the case in the tetraammine and the bis(ethylenediamine) complexes, which show no $[OH^-]$dependence at all. It is then assumed that the tetraamine and the bis(ethylenediamine) complexes of Rh(III) do not have a tendency to form their conjugate bases in hydroxide solution.

IV. Equilibrium Studies

1. Results

The equilibrium constants, K_1 and K_2 , of the trans-complexes for the reaction ,

$$\mathrm{Rh(cyclam)X_2^+} \underset{X}{\overset{\substack{K_1\\ Y}}{\rightleftharpoons}} \mathrm{Rh(cyclam)XY^+} \underset{X}{\overset{\substack{K_2\\ Y}}{\rightleftharpoons}} \mathrm{Rh(cyclam)Y_2^+}$$

where $X=Cl^-$ with $Y=Br^-$ and I^-, and where $X=Br^-$ with $Y=I^-$, were determined at three temperatures.

5 ml aliquots of the correct concentration of an aqueous stock solution of the appropriate trans-dihalgeno-complex were diluted to 50 ml in a volumetric flask with aqueous solutions containing :

(a) only the same halide as that in the complex

(b) only the substituting halide, different to that in the complex

(c) various ratios of the two halides, X^- and Y^-.

In addition the stock solution contained sufficient $HClO_4$, so that, upon dilution, the final acid concentration was 1.0×10^{-5} M in order to avoid base hydrolysis. The total ionic strength using halide was kept constant throughout, being 0.010 M and 0.10 M in the determination of K_2 and K_1 respectively. The ionic strength for K_2 determinations had to be less to eliminate interference by the formation of tri-iodide. (It was determined in acidic solution that the maximum limit of I^- could be 0.02 M.) The I_3^- spectrum has absorbance maxima (285 and 353 mμ) at almost the same wavelengths as the trans-diiodo-complex (275 and 353 mμ) with extinction coefficients of 390,000 vs. 35,200 and 26,400 vs 13,300 $l.cm^{-1}.mole^{-1}$, respectively.

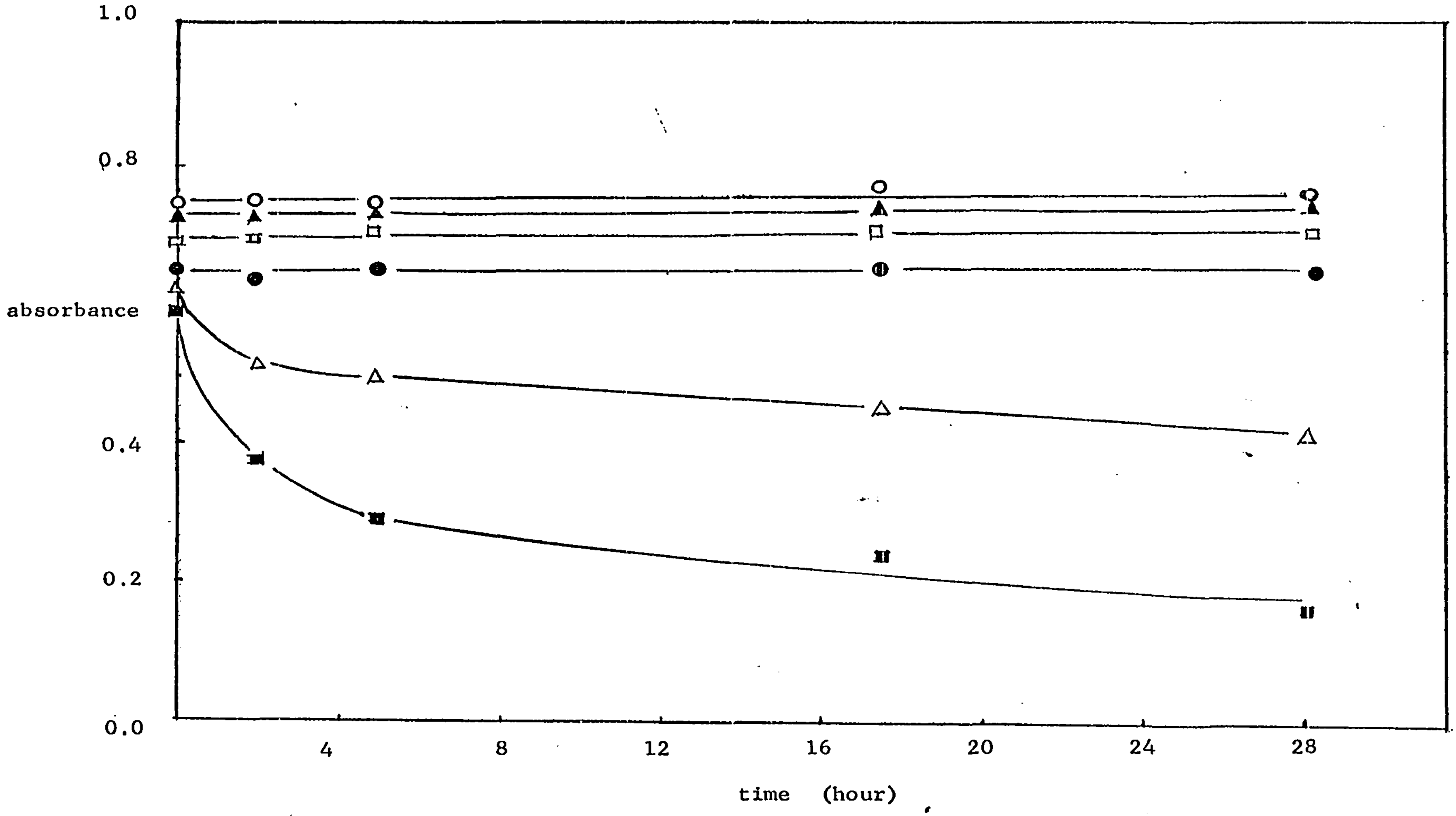
The lowest individual concentration of any halide used was 2.86×10^{-2} M. This concentration for all complexes was found to be well above the minimum concentration required (2.5×10^{-3} M) to prevent acid hydrolysis, which occured with the di-iodo complex, the results of which study is shown in Figure 20. The dibromo system tolerated a bromide concentration of as low as 3.0×10^{-4} M before acid hydrolysis occurred, and the dichloro system showed no hydrolysis even in water only, over a longer period than that employed in the equilibrium determinations.

The flasks were then thermostated (wrapping in aluminum foil was found unnecessary since no photocatalytic effect was observed) at the appropriate three temperatures, and periodic absorbance measurements taken on a Bausch & Lomb Spectronic 505 recording spectrophotometer at the wavelength where the difference in absorbances between reactants and products was large until equilibrium was attained (no change in absorbance over long periods). All samples were quenched in a cold water bath immediately on withdrawal from the flasks, and their absorbance spectra were measured immediately in 1-cm silica cells. Reference solutions were used which contained the same amounts of all reagents other than the complex. The reactions of the complexes are sufficiently slow that no readjustment of equilibrium

Figure 20

The effect of concentration of halide on acid hydrolysis of the reaction of trans-[Rh(cyclam)I_2]$^+$ with x M I^- in [H^+]=1 x 10^{-5} M at 85°C.

x = 0.0150	○
0.0100	▲
0.0050	□
0.0025	●
8×10^{-5}	△
0.0000	■


1.0
0.8
absorbance
0.4
0.2
0.0
4
8
12
16
20
24
28
time (hour)

occurred during the time of measurement of the spectra. No trans to cis isomerization was found in this study.

Determination of K_2

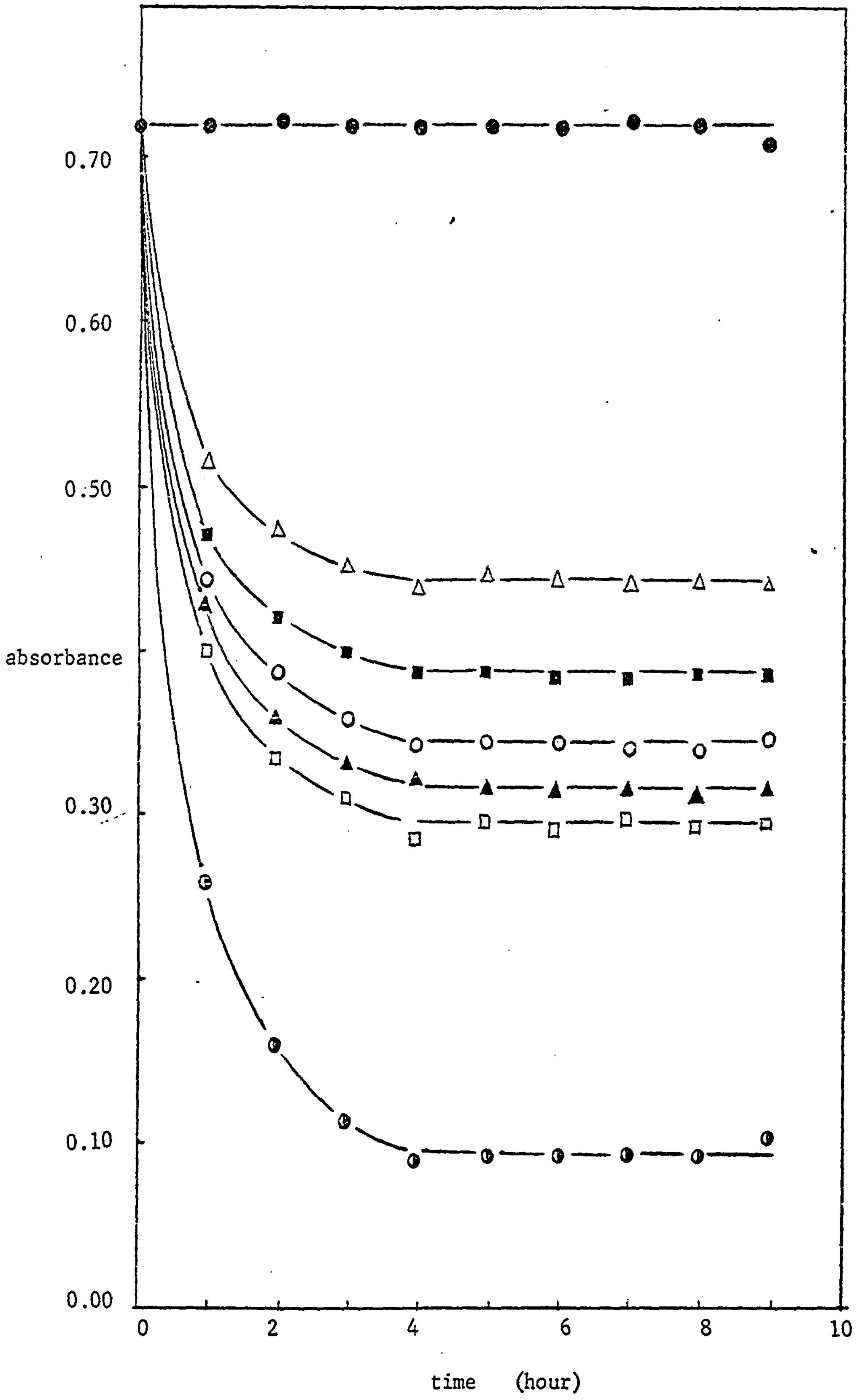
From experimental observation, it was evident that complexes of the chlorobromo, the bromoiodo and the chloroiodo, formed in solution from the reaction of the dibromo with Cl^-, and the diiodo with Br^- and Cl^- respectively, were stable at even 95°C for at least 5 days, 3 and 5 hours well beyond the time required to attain equilibrium without reacting further to form the dichloro, the dibromo and the dichloro respectively. A typical plot indicating this stability is shown in Figure 21. This behaviour could be expected from the kinetic substitution results (46) where a labilising effect of $I^- > Br^- > Cl^-$ was found. These results indicated that equilibrium between the dibromo and the chlorobromo; the diiodo and the bromoiodo; and the diiodo and the chloroiodo complexes would be attained well before any dichloro, dibromo, and dichloro complexes were formed respectively. Hence in determining K_2 at these temperatures only the bromochloro and the dibromo; the bromoiodo and diiodo; and the chloroiodo and diiodo species were involved and need be considered. Further evidence of this was the appearance of excellent isosbestic points for the systems.

The final concentrations of the complexes varied from

Figure 21

An absorbance vs time plot of the trans-[Rh(cyclam)ClI]$^+$-trans-[Rh(cyclam)I$_2$]$^+$ equilibrium in [H$^+$] = 1×10^{-5} M at 85°C with an ionic strength of 0.01 M. The absorbances were obtained at 353 mu, a maximum absorption of the trans-[Rh-(cyclam)I$_2$]$^+$ complex. The [Cl$^-$]/[I$^-$] ratios are

∞ , ◉
1.78 , □
1.48 , ▲
1.19 , ○
0.595, ■
0.398, △
0.000. ●


absorbance
0.00
0.10
0.20
0.30
0.50
0.60
0.70
0
2
4
6
8
10
time (hour)

3.0×10^{-4} M for the dibromo and 5.0×10^{-5} M for the diiodo in this determination. In each determination, the absorbance spectrum of each solution was recorded on the same chart paper, and good to excellent isosbestic points were apparent on the equilibrium trace. A typical set of spectra for the trans-diiodo-chloroiodo system, corresponding to a kinetic reaction of diiodo of about 8 half-lives, is shown in Figure 22. At the temperature employed, equilibrium was attained after 2½ hours and spectra remained constant for at least 4 hours thereafter.

The values of K_2 were calculated from each different $[X^-]/[Y^-]$ mixture using the following expression.

$$K_2 = \frac{[\mathrm{Rh(cyclam)}Y_2^+]}{[\mathrm{Rh(cyclam)}XY^+]} \cdot \frac{[X^-]}{[Y^-]} = \frac{A - A_1}{A_2 - A} \cdot \frac{[X^-]}{[Y^-]}$$

where A is the measured absorbance of the solution containing X and Y and A_1 and A_2 are the absorbances when all of the complex is present as the trans- $\mathrm{Rh(cyclam)}XY^+$ ($[Y^-]=0$) and the trans- $\mathrm{Rh(cyclam)}Y_2^+$ ($[X^-]=0$) respectively, all measured at the same appropriate wavelength. The wavelengths chosen for measurement were 285 and 353 mµ corresponding to the absorbance peaks of the trans-dibromo and the trans-diiodo complexes respectively. The results for the dibromo-bromochloro, the diiodo-bromoiodo, and the diiodo-chloroiodo systems are given in Tables 6., 7 and 8 respectively.

A value of K_2 at a particular temperature can also obtained from the slope of a plot of $(A-A_1).[X^-]/[Y^-]$

Table 6

The trans-[Rh(cyclam)ClBr]$^+$+Br$^- \overset{K_2}{\rightleftharpoons}$ trans-[Rh(cyclam)Br$_2$]$^+$+ Cl$^-$ equilibrium

λ = 285 mμ, μ = 0.01 M.

T (°C)	$\frac{[Cl^-]}{[Br^-]}$	A	$A - A_1$	$A_2 - A$	K_2
85	∞	0.220			
	1.83	0.420	0.200	0.402	0.910
	1.55	0.444	0.224	0.378	0.918
	1.26	0.478	0.258	0.344	0.945
	0.975	0.522	0.302	0.300	0.981
	0.686	0.570	0.350	0.252	0.953
	0.393	0.637	0.417	0.185	0.886
	0.000	0.822			
90	∞	0.220			
	1.83	0.410	0.190	0.410	0.848
	1.55	0.445	0.225	0.375	0.930
	1.26	0.472	0.252	0.348	0.912
	0.975	0.506	0.286	0.314	0.888
	0.686	0.565	0.345	0.255	0.928
	0.393	0.640	0.420	0.180	0.917
	0.000	0.820			
95	∞	0.218			
	0.879	0.518	0.300	0.299	0.882
	0.780	0.537	0.319	0.280	0.889
	0.686	0.550	0.332	0.267	0.853
	0.588	0.572	0.354	0.245	0.850
	0.490	0.605	0.387	0.212	0.894
	0.393	0.630	0.412	0.187	0.866
	0.000	0.817			

Table 7

The $trans\text{-}[Rh(cyclam)BrI]^{+} + I^{-} \overset{K_2}{\rightleftharpoons} trans\text{-}[Rh(cyclam)I_2]^{+} + Br^{-}$ equilibrium

$\lambda = 353$ mμ, $\mu = 0.01$ M.

T (°C)	$\frac{[Br^-]}{[I^-]}$	A	$A - A_1$	$A_2 - A$	K_2
85	∞	0.153			
	1.78	0.352	0.199	0.379	0.935
	1.48	0.376	0.223	0.355	0.930
	1.19	0.407	0.254	0.324	0.933
	0.893	---	---	---	---
	0.595	0.504	0.351	0.227	0.920
	0.398	0.560	0.407	0.171	0.947
	0.000	0.731			
90	∞	0.145			
	1.78	0.335	0.190	0.390	0.867
	1.48	0.355	0.210	0.370	0.840
	1.19	0.393	0.248	0.332	0.889
	0.893	0.435	0.290	0.290	0.893
	0.595	0.491	0.353	0.234	0.898
	0.398	0.547	0.402	0.178	0.899
	0.000	0.725			
95	∞	0.148			
	2.36	0.292	0.144	0.421	0.825
	2.06	0.314	0.166	0.399	0.857
	1.78	0.333	0.185	0.380	0.867
	1.48	0.350	0.202	0.363	0.824
	1.19	0.380	0.234	0.331	0.841
	0.893	0.424	0.276	0.289	0.853
	0.595	0.470	0.322	0.243	0.788
	0.000	0.713			

Table 8

The trans-[Rh(cyclam)ClI]$^+$ + I^- $\overset{K_2}{\rightleftharpoons}$ trans-[Rh(cyclam)I_2]$^+$ + Cl^- equilibrium

$\lambda = 353$ mμ, $\mu = 0.01$ M

T (°C)	$\frac{[Cl^-]}{[I^-]}$	A	$A - A_1$	$A_2 - A$	K_2
85	∞	0.051			
	1.28	0.295	0.244	0.425	0.735
	1.09	0.315	0.264	0.405	0.711
	0.893	0.344	0.293	0.376	0.696
	0.695	0.387	0.336	0.333	0.701
	0.496	0.443	0.392	0.277	0.702
	0.298	----	----	----	----
	0.000	0.720			
90	∞	0.052			
	1.28	0.272	0.220	0.433	0.650
	1.09	0.295	0.243	0.410	0.650
	0.893	0.322	0.270	0.383	0.630
	0.695	0.362	0.310	0.343	0.628
	0.496	0.420	0.368	0.285	0.640
	0.298	0.503	0.451	0.202	0.665
	0.000	0.705			
95	∞	0.050			
	1.48	0.233	0.183	0.472	0.574
	1.28	0.255	0.205	0.450	0.583
	1.09	0.280	0.230	0.425	0.590
	0.893	0.310	0.260	0.395	0.588
	0.695	0.345	0.295	0.360	0.570
	0.496	0.405	0.355	0.300	0.587
	0.298	0.485	0.435	0.220	0.589
	0.000	0.705			

against (A_2-A). Good straight lines were obtained and values agreed quite well with the average values obtained from calculations outlined above. A typical plot is given in Figure 23.

The relationship between the equilibrium constant, K, enthalpy, ΔH, and entropy, ΔS, is given by the following equation.

$$\ln K = \frac{\Delta S}{R} - \frac{\Delta H}{RT}$$

where R is the gas constant and T is the temperature in absolute units. The enthalpies, entropies and the standard deviations of the thermodynamic parameters are calculated by using a statistical method which is described in Chapter 3. The results are listed in Table 9.

Figure 22

Ultraviolet spectra of trans-[Rh(cyclam)ClI]$^+$-trans-[Rh(cyclam)I_2]$^+$ equilibrium mixtures at 90°C, $\mu = 0.01$ M. [Cl^-]/[I^-] ratios are

(a) ∞ ,
(b) 1.28 ,
(c) 1.09 ,
(d) 0.893,
(e) 0.695,
(f) 0.496,
(g) 0.298,
(h) 0.000,
(i) the base line.

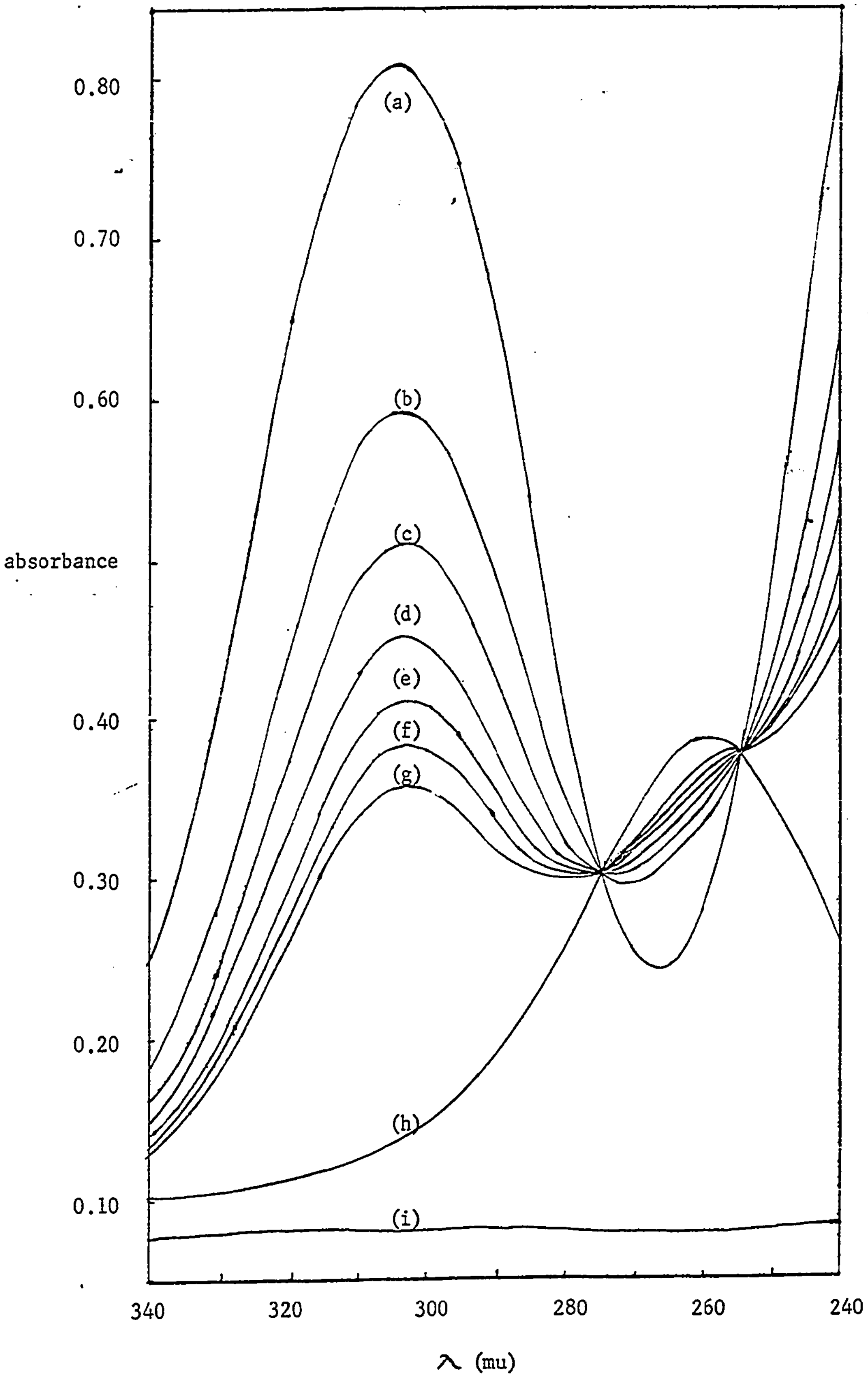

0.80
0.70
0.60
absorbance
0.40
0.30
0.20
0.10
(a)
(b)
(c)
(d)
(e)
(f)
(g)
(h)
(i)
340
320
300
280
260
240
λ (mu)

Figure 27

A plot of $(A - A_1)\cdot\frac{[Cl^-]}{[I^-]}$ vs $(A_2 - A)$ for the system of trans-$[Rh(cyclam)ClI]^+$ - trans-$[Rh(cyclam)I_2]^+$ at 95°C.

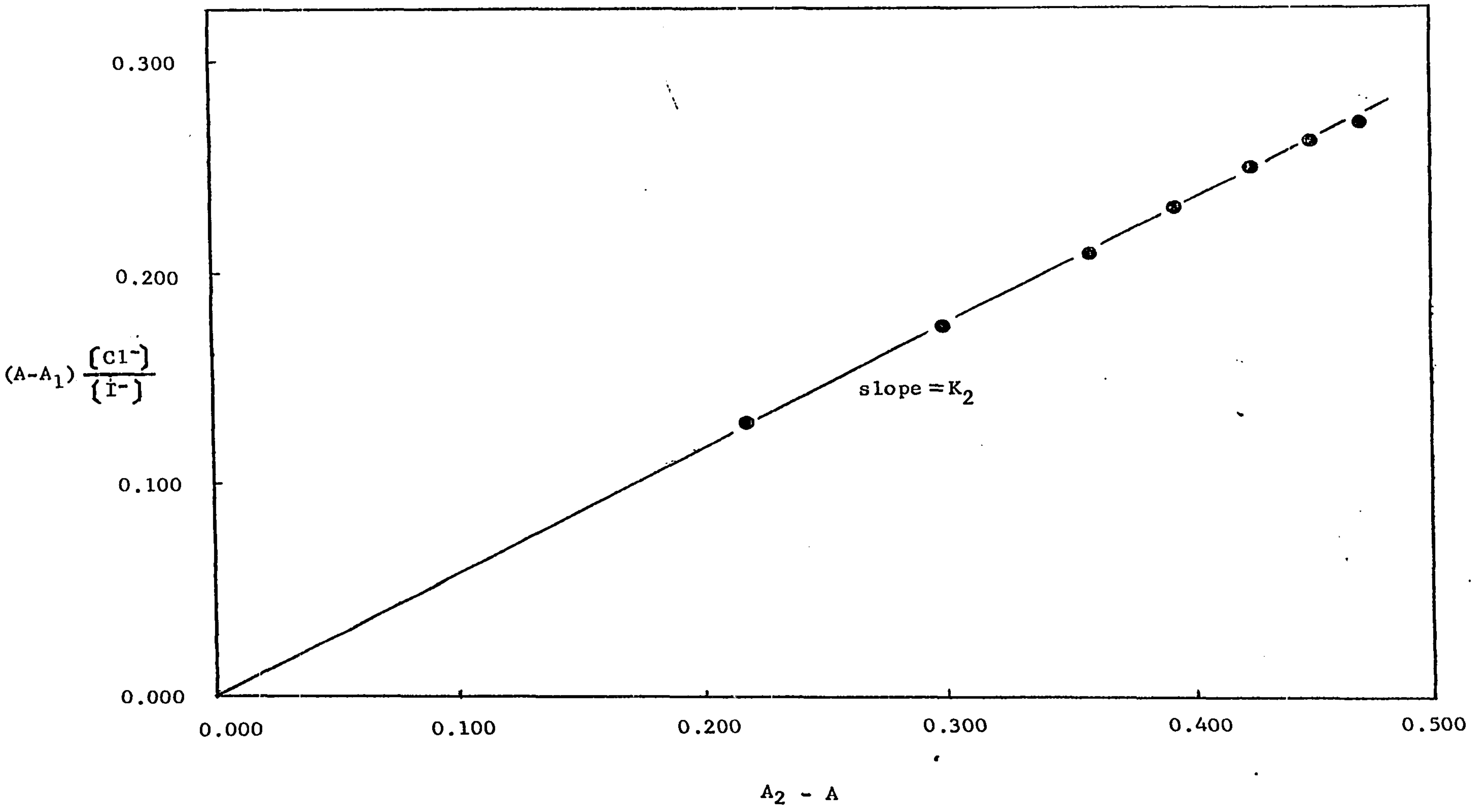

0.300
0.200
0.100
0.000
$(A-A_1)\frac{[Cl^-]}{[I^-]}$
slope = K_2
0.000
0.100
0.200
0.300
0.400
0.500
$A_2 - A$

Table 9

Summary of the equilibrium constants, K_2, and the thermodynamic parameters

---

$$\text{trans-[Rh(cyclam)ClBr]}^+ + \text{Br}^- \xrightleftharpoons{K_2} \text{trans-[Rh(cyclam)Br}_2]^+ + \text{Cl}^-$$

		Graphically
85°C	$K_2 = 0.932 \pm 0.034$	0.944
90°C	$K_2 = 0.904 \pm 0.031$	0.910
95°C	$K_2 = 0.872 \pm 0.019$	0.871

$\Delta H_2 = -1.80 \pm 1.11$ kcal·mole^{-1}

$\Delta S_2 = -5.17 \pm 3.06$ cal·deg^{-1}·mole^{-1}

$$\text{trans-[Rh(cyclam)BrI]}^+ + \text{I}^- \xrightleftharpoons{K_2} \text{trans-[Rh(cyclam)I}_2]^+ + \text{Br}^-$$

		Graphically
85°C	$K_2 = 0.933 \pm 0.010$	0.932
90°C	$K_2 = 0.881 \pm 0.023$	0.881
95°C	$K_2 = 0.836 \pm 0.027$	0.844

$\Delta H_2 = -2.88 \pm 0.39$ kcal·mole^{-1}

$\Delta S_2 = -8.17 \pm 1.08$ cal.deg^{-1}.mole^{-1}

$$\text{trans-[Rh(cyclam)ClI]}^+ + \text{I}^- \xrightleftharpoons{K_2} \text{trans-[Rh(cyclam)I}_2]^+ + \text{Cl}^-$$

		Graphically
85°C	$K_2 = 0.709 \pm 0.016$	0.708
90°C	$K_2 = 0.644 \pm 0.014$	0.640
95°C	$K_2 = 0.583 \pm 0.008$	0.583

$\Delta H_2 = -5.14 \pm 0.70$ kcal·mole^{-1}

$\Delta S_2 = -15.02 \pm 1.96$ cal.deg^{-1}.mole^{-1}

Determination of K_1

Solution of the dichloro-, dichloro-, and dibromo-complexes were mixed with solutions containing chloride and bromide; chloride and iodide; and bromide and iodide mixtures, respectively in various ratios (solutions of pure X and pure Y were inappropriate) and allowed to come to equilibrium at three different temperatures (85°, 70°and 55°C). Since, under these conditions, the mixed halogeno complexes formed react faster than the starting complexes, equilibrium became established among all three complexes (the dichloro, the chlorobromo, and the dibromo; and the dichloro, the chloroiodo and the diiodo; and the dibromo, the bromoiodo and the diiodo, respectively). Equilibria were attained after about 14 days for these three systems at 85°C, and about 45 days at 55°C.

Since these solutions contained all three species in equilibrium, values of K_1 could not be calculated directly from experimentally measured absorbance data, as could values of K_2. The following expression was developed for obtaining K_1 :

$$A = \varepsilon bc \qquad (1)$$

where A is the measured absorbance, ε is the molar extinction coefficient, b is the path-length of the optical cell in cm. (b = 1 in this work) and c is the molar concentration. Therefore at equilibrium, for the three species present,

$$A = \varepsilon_0[\mathrm{Rh(cyclam)X_2^+}] + \varepsilon_1[\mathrm{Rh(cyclam)XY^+}] + \varepsilon_2[\mathrm{Rh(cyclam)Y_2^+}]$$

where ε_0, ε_1 and ε_2 are the molar extinction coefficients of the X_2, XY and Y_2 complexes respectively, at the appropriate particular wavelength where measurements were taken. The above expression using the equilibrium relationships of K_1 and K_2 with the concentrations of the complexes and the free halides, becomes:

$$A = [\mathrm{Rh(cyclam)XY}^+]\left\{\frac{\varepsilon_c}{K_1}\cdot\frac{[X^-]}{[Y^-]} + \varepsilon_1 + K_2\cdot\varepsilon_2\frac{[Y^-]}{[X^-]}\right\} \qquad (2)$$

The total concentration of the complexes at equilibrium is :

$$[\mathrm{Cpx}] = [\mathrm{Rh(cyclam)X_2}^+] + [\mathrm{Rh(cyclam)XY}^+] + [\mathrm{Rh(cyclam)Y_2}^+]$$

Again, using the equilibrium relationships, the above equation becomes :

$$[\mathrm{Cpx}] = [\mathrm{Rh(cyclam)XY}^+]\left\{\frac{1}{K_1}\cdot\frac{[X^-]}{[Y^-]} + 1 + K_2\frac{[Y^-]}{[X^-]}\right\} \qquad (3)$$

Inserting equations (2) and (3) into equation (1), equation (4) can be obtained.

$$\varepsilon = \frac{A}{[\mathrm{Cpx}]} = \frac{\dfrac{\varepsilon_0}{K_1}\cdot\dfrac{[X^-]}{[Y^-]} + \varepsilon_1 + \varepsilon_2\cdot K_2\cdot\dfrac{[Y^-]}{[X^-]}}{\dfrac{1}{K_1}\cdot\dfrac{[X^-]}{[Y^-]} + 1 + K_2\cdot\dfrac{[Y^-]}{[X^-]}} \qquad (4)$$

where ε is the apparent extinction coefficients calculated from the measured absorbances, and known concentrations of starting complex measured at one wavelength, for the various solutions of different $[Y^-]/[X^-]$ ratios. By rearrangement of equation (4), K_1 can be obtained as follows:

$$K_1 = \frac{\varepsilon - \varepsilon_0}{(\varepsilon_1 - \varepsilon)\frac{[Y^-]}{[X^-]} + (\varepsilon_2 - \varepsilon)\cdot K_2 \cdot \frac{[Y^-]^2}{[X^-]^2}} \qquad (5) .$$

Equation (5) was therefore used in calculating K_1, using values of K_2 obtained by extrapolation from higher temperatures of the previously determined K_2 values by means of a plot of log K_2 against $1/T$, after corrections were made for the differences in ionic strength. A higher ionic strength (0.10 M) was used in the determination of K_1 than that used in the determination of K_2, because of the high $[X^-]/[Y^-]$ ratios needed to retain sufficient trans- $Rh(cyclam)X_2^+$ and trans- $Rh(cyclam)XY^+$ species (those involved in the K_1 expression) and because inconsistent results, no doubt due to acid hydrolysis, were obtained if $[Y^-]$ dropped below about 2×10^{-3} M. The highest concentration of I^- used was 8×10^{-3} M, not sufficiently high to result in tri-iodide interference. ε_0, ε_1 and ε_2 are the experimentally determined extinction coefficients for the appropriate complexes at the wavelength chosen for the measurement.

K_2 at the higher ionic strength was determined from the following equation:

$$K_{2(H)} \doteq K_{2(L)} \cdot \frac{\gamma_{X^-(L)}}{\gamma_{Y^-(L)}} \cdot \frac{\gamma_{Y^-(H)}}{\gamma_{X^-(H)}}$$

where the subscripts H and L refer to higher and lower ionic strength respectively. The values of the activity coefficients, γ, for NaX and NaY at ionic strengths 0.01 M and 0.10 M were experimental values at 25°C obtained from Robinson (73). The temperature-dependence of these ratios was assumed to be negligible since the individual activity coefficients change in the same way with temperature. No significant errors were introduced by any approximate nature of these corrections because the calculation of K_1 is not greatly affected by the value of K_2 and the corrections are small. For example, for the chloro-bromo system at 85°C, a ±13% error in K_2 would be required to introduce an error of only ±1% into the value obtained for K_1.

The results are given in Tables 10,11 and 12. The enthalpies, entropies and the standard deviations of the thermodynamic parameters are obtained as before (Table 13).

Table 10

The trans- Rh(cyclam)Cl_2^+ + $Br^- \overset{K_1}{\rightleftharpoons}$ trans- Rh(cyclam)$ClBr^+$ + Cl^- equilibrium

[complex]=5.41×10^{-4} M, λ=270 mμ(shoulder of dichloro complex),

μ = 0.10 M

ε_0=600; ε_1=1500; ε_2=2100 $cm^{-1}\cdot mole^{-1}$

K_2 = 1.17 at 55°C, 1.05 at 70°C, and 0.934 at 85°C.

T (°C)	$\frac{[Cl^-]}{[Br^-]}$	ε	$\varepsilon-\varepsilon_0$	$\varepsilon_1-\varepsilon$	$\varepsilon_2-\varepsilon$	K_1
55	17.0	767	167	733	1333	3.48
	16.0	782	182	718	1318	3.57
	15.0	795	195	705	1305	3.61
	14.0	795	195	705	1305	3.36
	13.0	800	200	700	1300	3.17
	12.0	802	202	698	1298	2.93
70	17.0	751	151	749	1349	3.08
	16.0	758	158	742	1342	3.04
	15.0	760	160	740	1340	2.90
	14.0	767	167	733	1333	2.83
	13.0	787	187	713	1313	2.97
	12.0	810	210	690	1290	3.13
85	17.0	726	126	774	1374	2.52
	16.0	739	139	761	1361	2.62
	15.0	743	143	757	1357	2.51
	14.0	754	154	746	1346	2.61
	13.0	767	167	733	1333	2.65
	12.0	775	175	725	1325	2.54

Table 11

The trans- $Rh(cyclam)Br_2{}^+ + I^- \overset{K_1}{\rightleftharpoons}$ trans- $Rh(cyclam)BrI^+ + Br^-$ equilibrium

[complex]=3.57×10^{-4} M, λ= 322mμ(peak maximum of bromoiodo complex), μ = 0.10 M.

ε_0=195; ε_1=5933; ε_2=2078 $cm^{-1} \cdot mole^{-1}$

K_2= 1.35 at 55°C, 1.15 at 70°C, and 0.936 at 85°C.

T (°C)	$\frac{[Br^-]}{[I^-]}$	ε	$\varepsilon - \varepsilon_0$	$\varepsilon_1 - \varepsilon$	$\varepsilon_2 - \varepsilon$	K_1
55	17.0	524	437	3037	1226	2.36
	16.0	541	454	3020	1209	2.32
	15.0	565	478	2996	1185	2.31
	14.0	595	508	2966	1155	2.31
	13.0	623	536	2938	1127	2.28
	12.0	651	564	2910	1099	2.22
70	17.0	506	419	3055	1244	2.26
	16.0	538	451	3023	1212	2.32
	15.0	542	455	3019	1208	2.20
	14.0	560	473	3001	1190	2.15
	13.0	582	495	2979	1168	2.10
	12.0	609	522	2952	1141	2.06
85	17.0	479	392	3082	1271	2.13
	16.0	496	409	3065	1254	2.09
	15.0	511	424	3050	1239	2.05
	14.0	542	455	3019	1208	2.07
	13.0	545	458	3016	1205	1.93
	12.0	593	506	2968	1157	2.00

Table 12

The trans- $Rh(cyclam)Cl_2^+ + I^- \overset{K_1}{\rightleftharpoons}$ trans- $Rh(cyclam)ClI^+ + Cl^-$ equilibrium

[complex] = 6.97×10^{-4} M, λ = 308 mμ(peak maximum of chloroiodo complex), μ = 0.10 M.

$\varepsilon_0 = 87$; $\varepsilon_1 = 3561$; $\varepsilon_2 = 1750$ $cm^{-1} \cdot mole^{-1}$.

K_2 = 1.38 at 55°C, 1.05 at 70°C, and 0.715 at 85°C.

T (°C)	$\frac{[Cl^-]}{[I^-]}$	ε	$\varepsilon-\varepsilon_0$	$\varepsilon_1-\varepsilon$	$\varepsilon_2-\varepsilon$	K_1
55	17.0	1448	1253	4485	630	4.69
	16.0	1532	1337	4401	546	4.81
	15.0	1635	1440	4298	443	4.97
	14.0	1691	1496	4242	387	4.89
	13.0	1750	1557	4183	328	4.78
	12.0	1815	1620	4118	263	4.68
70	17.0	1387	1192	4546	691	4.41
	16.0	1457	1262	4476	621	4.46
	15.0	1496	1301	4437	582	4.35
	14.0	1605	1410	4328	473	4.52
	13.0	1709	1514	4228	369	4.62
	12.0	1776	1581	4157	302	4.54
85	17.0	1324	1129	4609	754	4.41
	16.0	1400	1205	4533	678	4.21
	15.0	1470	1275	4463	608	4.24
	14.0	1565	1370	4368	513	4.35
	13.0	1588	1393	4345	490	4.13
	12.0	1689	1494	4244	389	4.18

Table 13

Summary of the equilibrium constants, K_1, and the thermodynamic parameters trans-$[\mathrm{Rh(cyclam)Cl_2}]^+ + \mathrm{Br^-} \overset{K_1}{\rightleftharpoons}$ trans-$[\mathrm{Rh(cyclam)ClBr}]^+ + \mathrm{Cl^-}$

55°C	$K_1 = 3.35 \pm 0.26$
70°C	$K_1 = 2.99 \pm 0.11$
85°C	$K_1 = 2.57 \pm 0.09$

$\Delta H_1 = -1.88 \pm 0.64$ kcal·mole^{-1}

$\Delta S_1 = -3.38 \pm 1.79$ cal·deg^{-1}·mole^{-1}

trans-$[\mathrm{Rh(cyclam)Br_2}]^+ + \mathrm{I^-} \overset{K_1}{\rightleftharpoons}$ trans-$[\mathrm{Rh(cyclam)BrI}]^+ + \mathrm{Br^-}$

55°C	$K_1 = 4.80 \pm 0.11$
70°C	$K_1 = 4.48 \pm 0.10$
85°C	$K_1 = 4.21 \pm 0.08$

$\Delta H_1 = -1.02 \pm 0.23$ kcal·mole^{-1}

$\Delta S_1 = -0.01 \pm 0.21$ cal·deg^{-1}.mole^{-1}

trans-$[\mathrm{Rh(cyclam)Cl_2}]^+ + \mathrm{I^-} \overset{K_1}{\rightleftharpoons}$ trans-$[\mathrm{Rh(cyclam)ClI}]^+ + \mathrm{Cl^-}$

55°C	$K_1 = 2.30 \pm 0.05$
70°C	$K_1 = 2.18 \pm 0.10$
85°C	$K_1 = 2.05 \pm 0.07$

$\Delta H_1 = -0.90 \pm 0.31$ kcal·mole^{-1}

$\Delta S_1 = -1.07 \pm 0.87$ cal·deg^{-1}·mole^{-1}

2. Discussion

Thermodynamic class (a) or (b) character

The class (a) or (b) character of the Rh(III) metal in the trans-dihalogeno(cyclam) complexes studied can be judged on an overall basis by the overall equilibrium constants, $K_1 \cdot K_2$, or the overall enthalpies, $\Delta H_1 + \Delta H_2$, for the systems (Table 14). Thus, at 55°C the equilibrium constant for replacement of both chloride ligands in trans-Rh(cyclam)Cl_2^+ by bromide is 3.91 and that for replacement of two bromide ligands by iodide is 6.50. There is a small but definite increase in stability from the dichloro- through the dibromo- to the di-iodo-complex and so the dihalogeno-(cyclam)-rhodium (III) system is slightly class (b). Although equilibrium constants and ΔG values are more readily available and thus frequently have to be accepted as measures of class (a) or (b) character, the possible temperature-dependence of the resulting classification, and the tendency to interpret the classification in terms of bond strengths, makes enthalpy changes a better basis when they have been measured. The enthalpy changes for the complete replacement of chloride by bromide, and of bromide by iodide, are -3.68 and -3.90 kcal·mole^{-1} respectively. Since two halide ligands are replaced by two different halides in each case, the ΔH per ligand exchange is therefore -1.84 and -1.95 kcal per ligand exchange. This exothermicity obviously indicates the stability increase from dichloro through the dibromo to the

Table 14

Overall equilibrium constants, K, and enthalpies, ΔH, of the trans-$[Rh(cyclam)X_2]^+$ – trans-$[Rh(cyclam)Y_2]^+$ systems

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$$\text{trans-}[\text{Rh(cyclam)Cl}_2]^+ \underset{\text{Cl}^-}{\overset{\text{Br}^-\ (K_1)}{\rightleftharpoons}} \text{trans-}[\text{Rh(cyclam)ClBr}]^+ \underset{\text{Cl}^-}{\overset{\text{Br}^-\ (K_2)}{\rightleftharpoons}} \text{trans-}[\text{Rh(cyclam)Br}_2]^+$$

$K = K_1 \cdot K_2 = 3.91$ at 55°C

$= 3.12$ at 70°C

$= 2.40$ at 85°C

$\Delta H = \Delta H_1 + \Delta H_2$

$= -3.68\ \text{kcal} \cdot \text{mole}^{-1}$

$$\text{trans-}[\text{Rh(cyclam)Br}_2]^+ \underset{\text{Br}^-}{\overset{\text{I}^-\ (K_1)}{\rightleftharpoons}} \text{trans-}[\text{Rh(cyclam)BrI}]^+ \underset{\text{Br}^-}{\overset{\text{I}^-\ (K_2)}{\rightleftharpoons}} \text{trans-}[\text{Rh(cyclam)I}_2]^+$$

$K = K_1 \cdot K_2 = 6.50$ at 55°C

$= 5.13$ at 70°C

$= 3.94$ at 85°C

$\Delta H = \Delta H_1 + \Delta H_2$

$= -3.90\ \text{kcal} \cdot \text{mole}^{-1}$

$$\text{trans-}[\text{Rh(cyclam)Cl}_2]^+ \underset{\text{Cl}^-}{\overset{\text{I}^-\ (K_1)}{\rightleftharpoons}} \text{trans-}[\text{Rh(cyclam)ClI}]^+ \underset{\text{Cl}^-}{\overset{\text{I}^-\ (K_2)}{\rightleftharpoons}} \text{trans-}[\text{Rh(cyclam)I}_2]^+$$

$K = K_1 \cdot K_2 = 3.17$ at 55°C

$= 2.28$ at 70°C

$= 1.47$ at 85°C

$\Delta H = \Delta H_1 + \Delta H_2$

$= -6.04\ \text{kcal} \cdot \text{mole}^{-1}$

---

diiodo, and the class (b) character is clearly revealed.

Data from other systems, which exhibit class (b) behaviour, are given in Table 15 for comparison. The more negative the ΔH values, the more class (b) character the metal or complex is. Thus, the Hg(II) has the highest class (b) character in all the two systems. In the chloro-iodo systems, for which there is more available data, the class (b) character of the metals is in the order Hg(II) > Zn(II) > Pt(IV) > Rh(III). In the bromo-iodo systems, the class (b) character of Zn(II) and Rh(III) is in the reverse order of the chloro-iodo system, and likewise the Pt(IV) and Rh(III) in the chloro-bromo systems.

The equilibrium constants for the stepwise interchange of iodide ions with the halogens in $PtCl_6{}^{2-}$ or $PtBr_6{}^{2-}$ have been determined by Poe and Vaidya (74). Thus Pt(IV) is clearly a class (b) species when judged by the relative stability constants of its halogeno- complexes with $I^- > Br^- > Cl^-$. On the enthalpy basis, the relative stabilities of the halogeno-platinates are $PtCl_6{}^{2-} > PtBr_6{}^{2-} \ll PtI_6{}^{2-}$, and the classification is therefore not so clear. However, the authors claim that the very high relative stability of the iodide supports a predominantly class (b) classification.

The class (b) character is compared between the cyclam and bis(ethylenediamine) complexes of Rh(III). The ΔH values for stepwise interchanges of halides in the systems are given in Table 16. For Cl-Br interchange, the cyclam system for both replacement steps on a ΔH basis exhibits

Table 15

Thermodynamic data for halogeno-replacement reactions

system	ΔH (kcal/mole)	ΔH per ligand exchange
$[PtCl_6]^{2-}$ - $[PtBr_6]^{2-}$ [a]	+4	+0.67
$[Rh(en)_2Cl_2]^+$ - $[Rh(en)_2Br_2]^+$ [b]	0	0
$[Rh(cyclam)Cl_2]^+$ - $[Rh(cyclam)Br_2]^+$ [d]	-3.7	-1.9
$[ZnBr_4]^{2-}$ - $[ZnI_4]^{2-}$ [e]	-1.2	-0.30
$[HgBr_4]^{2-}$ - $[HgI_4]^{2-}$ [e]	-17	-4.2
$[Rh(en)_2Br_2]^+$ - $[Rh(en)_2I_2]^+$ [c]	-6.0	-3.0
$[Rh(cyclam)Br_2]^+$ - $[Rh(cyclam)I_2]^+$ [d]	-3.90	-1.95
$[PtCl_6]^{2-}$ - $[PtI_6]^{2-}$ [a]	-19	-3.3
$[ZnCl_4]^{2-}$ - $[ZnI_4]^{2-}$ [e]	-19.5	-4.9
$[HgCl_4]^{2-}$ - $[HgI_4]^{2-}$ [e]	-25	-6.1
$[Rh(en)_2Cl_2]^+$ - $[Rh(en)_2I_2]^+$ [c]	-5.3	-2.7
$[Rh(cyclam)Cl_2]^+$ - $[Rh(cyclam)I_2]^+$ [d]	-6.04	-3.02

All the Rh(III) complexes are trans-isomers.

[a] Ref. 74. [b] Ref. 56. [c] Ref. 47. [d] This work.

[e] Ref. 58.

Table 16

Thermodynamic data for stepwise halogeno-replacement reactions of $(en)_2$ and cyclam complexes of Rh(III).

system	Δ H per ligand exchange (kcal/mole)
$Rh(en)_2Cl_2^+$ - $Rh(en)_2ClBr^+$	0
$Rh(cyclam)Cl_2^+$ - $Rh(cyclam)ClBr^+$	-1.88
$Rh(en)_2ClBr^+$ - $Rh(en)_2Br_2^+$	0
$Rh(cyclam)ClBr^+$ - $Rh(cyclam)Br_2^+$	-1.80
$Rh(en)_2Br_2^+$ - $Rh(en)_2BrI^+$	-2.62
$Rh(cyclam)Br_2^+$ - $Rh(cyclam)BrI^+$	-1.02
$Rh(en)_2BrI^+$ - $Rh(en)_2I_2^+$	-3.38
$Rh(cyclam)BrI^+$ - $Rh(cyclam)I_2^+$	-2.88
$Rh(en)_2Cl_2^+$ - $Rh(en)_2ClI^+$	+0.9
$Rh(cyclam)Cl_2^+$ - $Rh(cyclam)ClI^+$	-0.90
$Rh(en)_2ClI^+$ - $Rh(en)_2I_2^+$	-6.18
$Rh(cyclam)ClI^+$ - $Rh(cyclam)I_2^+$	-5.14

All the complexes are trans-isomers.

much more class (b) character than is observed in the bis(ethylenediamine) system. For Br-I interchange, the cyclam system is slightly less class (b) behaviour than the bis(ethylenediamine) system in both replacement steps. For Cl-I interchange in the cyclam system, the first step replacement has more class (b) character, while the second step has less class (b) character than the bis(ethylenediamine) system, but on the overall basis the cyclam system has more class (b) behaviour than the bis(ethylenediamine) system.

Ahrland, Chatt, and Davies (50) have emphasised that any inferences as to class (a) or (b) character must be made on the basis of heats rather than free energies. If this is applied to the $Zn(hal)_4{}^{2-}$ complexes, it is found that zinc is a class (b) metal, in contrast to its previous classification as (a) on the basis of a positive ΔG value. The relative instability of $ZnI_4{}^{2-}$ arises because the favourable heat of formation is overcome by an unusually large and unfavourable entropy of formation. However, Poe and Vaidya (58) suggested that for halogeno-complexes, if an estimate of relative bond strengths is to be made from equilibrium data, not only must the relative heats of formation be considered but quantitative allowance must also be made for solvation effects. The overall heat of replacement of chloride, in a complex, by iodide is determined by the relative magnitude of the opposing effects of solvation and bond strengths. In aqueous solution the bond strength effect usually just overcomes the preferential hydration of the small halide ion and the chloro-complex is stronger than the iodo-complex, but when the bonding in the iodo-complex becomes relatively less weak, hydration effects become dominant, and the iodo-complex becomes the stronger.

The different enthalpies of bonding in the complexes which includes the enthalpies of bonding of the ligands to metal ion and of the solvent to the complex, can be calculated from equilibrium measurements and by using differences in the hydration enthalpy of the free halides, which were found (75) to be:

$$\Delta H_{hyd.}(Br^-) - \Delta H_{hyd.}(Cl^-) = 8.1 \text{ kcal/g. ion,}$$

$$\Delta H_{hyd.}(I^-) - \Delta H_{hyd.}(Br^-) = 10.4 \text{ kcal/g. ion, and}$$

$$\Delta H_{hyd.}(I^-) - \Delta H_{hyd.}(Cl^-) = 18.5 \text{ kcal/g. ion.}$$

From the chloro-iodo system

$$\text{trans- Rh(cyclam)ClI}^+ + I^- \longrightarrow \text{trans- Rh(cyclam)I}_2{}^+ + Cl^- \qquad \Delta H = -5.1 \text{ kcal.}$$

$$\text{trans- Rh(cyclam)ClI}^+_{aq.} \longrightarrow \text{trans- Rh(cyclam)I}_2{}^+_{aq.} \qquad \Delta H = 13.4 \text{ kcal.}$$

The ΔH of the last reaction as written indicates that trans- Rh(cyclam)$I_2{}^+_{aq.}$ is less stable than the trans- Rh(cyclam)-ClI$^+_{aq.}$ by 13.4 kcal. This is an approximate measure of the Rh-I and Rh-Cl bond strength differences in the two complexes. The solvation of the larger trans- Rh(cyclam)-$I_2{}^+$ ion will be less than the smaller trans- Rh(cyclam)ClI$^+$ ion. Similary, the values of the other systems can also be obtained. The values are shown in Table 17. If

Table 17

The ΔH° values of the trans-$[Rh(cyclam)XY]^{+}_{aq.}$ - trans-$[Rh(cyclam)XZ]^{+}_{aq.}$ systems

system	ΔH° (kcal/mole)
trans-$[Rh(cyclam)ICl]^{+}_{aq.} \rightarrow$ trans-$[Rh(cyclam)I_2]^{+}_{aq.}$	13.4 ± 0.7
trans-$[Rh(cyclam)IBr]^{+}_{aq.} \rightarrow$ trans-$[Rh(cyclam)I_2]^{+}_{aq.}$	7.5 ± 0.4
trans-$[Rh(cyclam)ClBr]^{+}_{aq.} \rightarrow$ trans-$[Rh(cyclam)Br_2]^{+}_{aq.}$	6.3 ± 1.1
trans-$[Rh(cyclam)Cl_2]^{+}_{aq.} \rightarrow$ trans-$[Rh(cyclam)ICl]^{+}_{aq.}$	17.6 ± 0.3
trans-$[Rh(cyclam)Cl_2]^{+}_{aq.} \rightarrow$ trans-$[Rh(cyclam)ClBr]^{+}_{aq.}$	6.2 ± 0.6
trans-$[Rh(cyclam)Br_2]^{+}_{aq.} \rightarrow$ trans-$[Rh(cyclam)BrI]^{+}_{aq.}$	9.4 ± 0.2

the highest value is taken arbitrarily as zero the enthalpies of these trans- Rh(cyclam)XY $^+$ complexes are shown in Table 18. Enthalpies of trans- Rh(cyclam)XY $^+$ are plotted against the enthalpies of trans- Rh(cyclam)ClY $^+$ in Figure 24, where X^- and Y^- are chloride, bromide, or iodide. The trends in these values reveal clearly the linear enthalpy relationships. The smaller the increase in enthalpy along the series $Y=Cl^-$, Br^-, I^- the greater is the class (b) character of the trans- Rh(cyclam)X $^{2+}$. The class (b) character of the Lewis acid trans- Rh(cyclam)X $^{2+}$ therefore increases steadily along the series $X=Cl^-$, Br^-, I^-. These enthalpy effects which are transmitted across the rhodium ion are quite appreciable, unlike the free energy effects which are very much smaller. This implies that the effects on the entropy are just counter-balanced by those on the enthalpy. Thus, it is found that the higher the enthalpy of the solvated complex ion the higher is the entropy. The systematic changes show that the "softness" of a Lewis acid can be a function not only of the ion to which the Lewis base becomes directly attached but also of the softness of other groups already attached to that ion. In this case an iodide makes the rhodium ion to which it is attached appreciably more soft than does the relatively hard chloride ion.

Thermodynamic trans effect

For the equilibrium reactions, the values of K_1/K_2

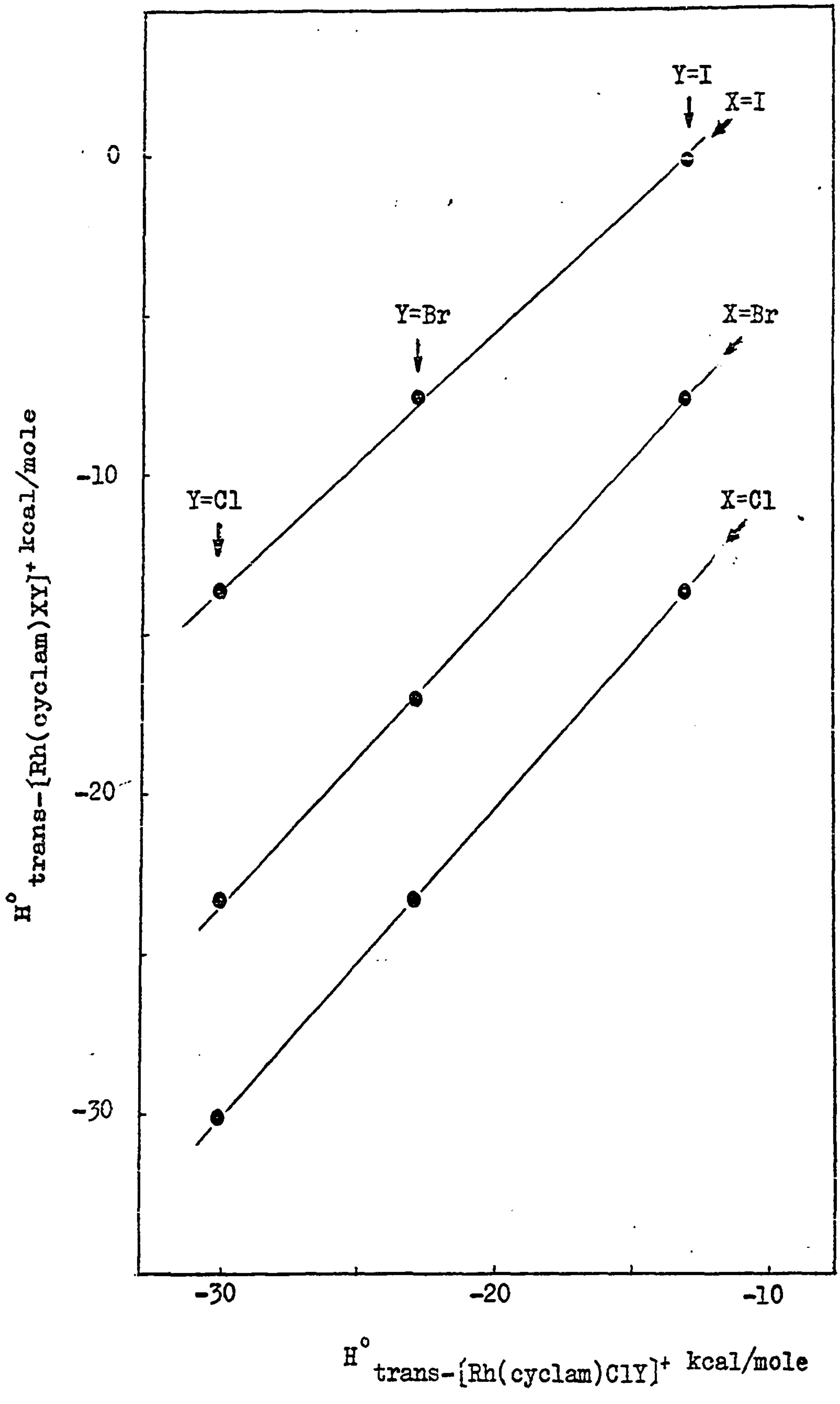
Table 18

The relative H^{o} values of the trans- Rh(cyclam)XY $^{+}$ complexes taking arbitrarily the trans—Rh(cyclam)I_2 $^{+}$ value as zero

complex	H^{o}(kcal/mole)
trans-[Rh(cyclam)I_2]$^{+}$	0
trans-[Rh(cyclam)IBr]$^{+}$	- 7.5 ± 0.4
trans-[Rh(cyclam)ICl]$^{+}$	-13.4 ± 0.7
trans-[Rh(cyclam)Br_2]$^{+}$	-16.9 ± 0.4
trans-[Rh(cyclam)BrCl]$^{+}$	-23.2 ± 1.2
trans-[Rh(cyclam)Cl_2]$^{+}$	-30.2 ± 1.1

Figure 24

Linear enthalpy relationships for the trans-[Rh(cyclam)XY]$^+$ complexes in aqueous solution. Enthalpies are measured relative to H^0(trans-[Rh(cyclam)I_2]$^+$) taken arbitrarily as zero. The gradients for the lines when X=Cl^-, Br^-, and I^- are in the ratios 1.00: 0.96: 0.81


Y=I
X=I
Y=Br
X=Br
Y=Cl
X=Cl
0
-10
-20
-30
-30
-20
-10
$H^{o}_{trans-[Rh(cyclam)XY]^+}$ kcal/mole
$H^{o}_{trans-[Rh(cyclam)ClY]^+}$ kcal/mole

would be expected to be 4, if statistical factors were the only ones involved (76). This arises because the release of the first X^- ligand is, in terms of complex ion concentration, numerically twice as probable as the release of the second. Any departure from this relationship is a measure of the different effect of X^- in the position trans to the reacting Y^-, and a measure of the thermodynamic trans effect. The value of K_1/K_2 for the equilibrium systems are shown in Table 19. All the values of K_1/K_2 are less than 4 except for the bromo-iodo system at 85°C. At 55°C, for the chloro-bromo, bromo-iodo and chloro-iodo systems, the ratios K_1/K_2 are 2.87, 3.55 and 1.67 respectively. The values are 72, 89 and 42% respectively of those expected from statistical considerations. Thus, the replacement of a Cl^- by a Br^- is thermodynamically easier if there is a Br^- rather than a Cl^- in the trans-position. Then the thermodynamic trans effect of Br^- is greater than Cl^-. Similarly, the thermodynamic trans effect of I^- is greater than Br^- and I^- is greater than Cl^-. Thus, the thermodynamic trans effect is $I^- > Br^- > Cl^-$.

On the basis of ΔH, the effect of changing the halide X^- on the trans- $Rh(cyclam)XY^+$ complexes is shown in Table 20. Where some of the equilibria were not studied directly, the values were obtained from suitable combinations of measured values. With the same leaving and incoming groups in the three sets of reactions, the complexes with the iodo in the trans- position to the same leaving groups

Table 19

The values of K_1/K_2 for the systems of
trans-$[Rh(cyclam)X_2]^+$ - trans-$[Rh(cyclam)XY]^+$ - trans-$[Rh(cyclam)Y_2]^+$
(ionic strength = 0.01 M)

$$\text{trans-}[\mathrm{Rh(cyclam)Cl_2}]^+ \xrightleftharpoons[\mathrm{Cl^-}]{\mathrm{Br^-}} \overset{(K_1)}{\text{trans}}\text{-}[\mathrm{Rh(cyclam)ClBr}]^+ \xrightleftharpoons[\mathrm{Cl^-}]{\mathrm{Br^-}} \overset{(K_2)}{\text{trans}}\text{-}[\mathrm{Rh(cyclam)Br_2}]^+$$

$$\begin{aligned} K_1/K_2 &= 2.87 \text{ at } 55^\circ\mathrm{C} \\ &= 2.86 \text{ at } 70^\circ\mathrm{C} \\ &= 2.75 \text{ at } 85^\circ\mathrm{C} \end{aligned}$$

$$\text{trans-}[\mathrm{Rh(cyclam)Br_2}]^+ \xrightleftharpoons[\mathrm{Br^-}]{\mathrm{I^-}} \overset{(K_1)}{\text{trans}}\text{-}[\mathrm{Rh(cyclam)BrI}]^+ \xrightleftharpoons[\mathrm{Br^-}]{\mathrm{I^-}} \overset{(K_2)}{\text{trans}}\text{-}[\mathrm{Rh(cyclam)I_2}]^+$$

$$\begin{aligned} K_1/K_2 &= 3.55 \text{ at } 55^\circ\mathrm{C} \\ &= 3.91 \text{ at } 70^\circ\mathrm{C} \\ &= 4.50 \text{ at } 85^\circ\mathrm{C} \end{aligned}$$

$$\text{trans-}[\mathrm{Rh(cyclam)Cl_2}]^+ \xrightleftharpoons[\mathrm{Cl^-}]{\mathrm{I^-}} \overset{(K_1)}{\text{trans}}\text{-}[\mathrm{Rh(cyclam)ClI}]^+ \xrightleftharpoons[\mathrm{Cl^-}]{\mathrm{I^-}} \overset{(K_2)}{\text{trans}}\text{-}[\mathrm{Rh(cyclam)I_2}]^+$$

$$\begin{aligned} K_1/K_2 &= 1.67 \text{ at } 55^\circ\mathrm{C} \\ &= 2.09 \text{ at } 70^\circ\mathrm{C} \\ &= 2.87 \text{ at } 85^\circ\mathrm{C} \end{aligned}$$

Table 20

Δ H values for the reactions of

$\text{trans-}[\mathrm{Rh(cyclam)XY}]^{+} + \mathrm{Z}^{-} \rightarrow \text{trans-}[\mathrm{Rh(cyclam)XZ}]^{+} + \mathrm{Y}^{-}$

X	Cl[a]	Br[a]	I[b]	Cl[b]	Br[a]	I[a]	Cl[a]	Br[b]	I[a]
Y	Cl	Cl	Cl	Br	Br	Br	Cl	Cl	Cl
Z	Br	Br	Br	I	I	I	I	I	I
ΔH (kcal/mole)	-1.9	-1.8	-2.3	+1.0	-1.0	-2.9	-0.9	+0.8	-5.1
std. dev. (kcal/mole)	0.6	1.1	0.8	0.7	0.2	0.4	0.3	1.3	0.7

[a] Direct measurement [b] Indirect estimate

are more stable than the bromo- and chloro- in the trans-position to the same leaving groups, as seen by the more negative ΔH values of the iodo-complexes than those of the bromo- and chloro-complexes. But the ΔH values of the bromo- and the chloro in the trans position in the three sets of the reactions are not clearly distinguishable, as one set indicates Br^- more stable than Cl^-, but two sets are reversed. However,for the two sets in which Cl^- appears greater than Br^-, both involve a value with Br^- in the trans position where the standard deviation is large and therefore this uncertainty gives rise to caution in making a final decision. In addition, considering the standard deviations for these two cases, one indicates a considerable overlap range and therefore the possibility of a reversal, but the other, does not, but in the system an estimated value was involved. However considering both the ΔH and equilibrium constant data (which quite clearly showed $I^- > Br^- \sim Cl^-$), the overall evidence would clearly indicate a thermodynamic trans effect order for the trans- $Rh(cyclam)XY^+$ complexes to be $I^- > Br^- \sim Cl^-$. Thus, this effect increases as the group in the trans position changes from chloro or bromo to iodo. This thermodynamic trans effect is paralleled by the kinetic trans effect observed in the same complexes (64). The labilising effect of the halides increases along the series Cl^-, Br^-,I^- and is presumably, at least in part, a consequence of weakening the trans- bond. Other evidence for weakening of the trans- bond is provided by the infrared absorption data shown in Table 21. It is clear that the replacement

Table 21

Rhodium halide stretching frequencies in trans-Rh(cyclam)XY$^+$.

complex X	complex Y	ν_{Rh-Cl} (cm^{-1})
Cl	Cl	289
Br	Cl	282
I	Cl	278

of chloride by bromide and iodide in the trans position to the chloride lowers the Rh-Cl stretching frequencies. The iodide has stronger effect than the bromide. Although there will be some coupling of the vibration of the two halides, these frequencies are a roughly tentative indication of the relative force constants of the individual bonds. Thus, the effect of the weakening of the trans-chloro bond in the trans- Rh(cyclam)XCl $^+$ complexes increases in the order Cl$^-$, Br$^-$ and I$^-$.

This trans effect is not consistant with the d back-bonding theory. This would predict that a Rh-Cl bond trans to an iodide would be weakened less than a Rh-I bond and the presence of one iodide in the complex should decrease the relative affinity for another (77). Johnson, Basolo, and Pearson (2c) have also argued, on the basis of kinetic evidence, that π -bonding is not important in rhodium (III) complexes. The data are qualitatively consistant with a polarisation theory involving greater electron transfer towards the rhodium, the greater the polarisability of the halide. This results in a decreased effective ionic charge on the rhodium and a consequent trans bond weakening which will be greater, the greater the strength of the bond affected.

V.CONCLUSION

The base hydrolysis reactions, equilibrium studies as well as the acid substitution and anation reactions of the trans- Rh(cyclam)XY $^+$ complexes have now all been studied. Thus, the reaction mechanisms, kinetic and thermodynamic trans effects and class (a) and (b) characters of these complexes are comprehensively understood.

Although it would extremely difficult, if not impossible to prepare the mixed dihalogeno cis compounds, the results of the base hydrolysis of the cis compound would be interesting. Preparation of complexes containing ligands which could exhibit linkage isomerism, such as SCN^- and particularly OCN^- would be of interest.

Appendix 1a

Substitution rate constants of the reaction:

trans-[Rh(cyclam)XY]$^+$ + Z$^-$ → trans-[Rh(cyclam)XZ]$^+$ + Y$^-$

X	Y	Z	T (°C)	10^6k (sec^{-1})
I	I	Cl	55	7.55
		Br		7.67
		Cl	70	51.4
		Br		51.0
		Cl	85	290
		Br		292
I	Br	I	55	7.93
		I	70	46.8
		I	85	232
I	Cl	I	55	8.36
		I	70	45.6
		I	85	212
Br	Br	I	75	0.737
		I	85	2.40
		I	95	7.44
Br	Cl	Br	75	0.480
		Br	85	1.42
		Br	95	4.10
Cl	Cl	I	75	0.756
		I	85	2.35
		I	95	6.94

Appendix 1a (continued)

X	Y	Z	T (°C)	10^6k (sec^{-1})
Br	I	Br	95	1.6
Cl	Br	Cl	95	0.30
Cl	I	Cl	95	No apparent reaction after 63 hours

Appendix 1b.

Activation parameters for acid hydrolysis of trans-$[Rh(cyclam)XY]^+$ complexes

complex X	Y	ΔH^* (kcal·mole^{-1})	ΔS^* (cal·deg^{-1}·mole^{-1})	$10^6k_{85°C}$ (sec^{-1})
I	I	27.7 ± 0.1	+2.29 ± 0.13	292 ± 2
I	Br	25.6 ± 0.1	-4.02 ± 0.21	232 ± 2
I	Cl	24.5 ± 0.1	-7.34 ± 0.13	212 ± 1
Br	Br	28.7 ± 0.2	-4.41 ± 0.46	2.40 ± 0.03
Br	Cl	26.6 ± 0.1	-11.4 ± 0.3	1.42 ± 0.01
Cl	Cl	27.6 ± 0.1	-7.61 ± 0.36	2.35 ± 0.02

Appendix 2a

Anation rate constants of the reaction:

$$\text{trans-}[Rh(cyclam)X(H_2O)]^{2+} + Z^- \rightarrow \text{trans-}[Rh(cyclam)XZ]^+ + H_2O$$

X	Z	T (°C)	10^4k ($sec^{-1}.M^{-1}$)
I	Cl	30	20.5
I	Br		18.7
I	I		16.3
I	Cl	40	73.4
I	Br		67.8
I	I		48.7
I	Cl	50	258
I	Br		187
I	I		135
Br	Cl	50	0.597
Br	Br		0.491
Br	Cl	60	2.92
Br	Br		2.28
Br	Cl	70	8.35
Br	Br		6.85
Cl	Cl	70	1.26
Cl	Cl	80	4.34
Cl	Cl	90	14.2

Appendix 2b

Activation parameters for the anation reactions of trans-$[Rh(cyclam)X(H_2O)]^{2+}$ complexes

X	Z	ΔH^* (kcal·mole^{-1})	ΔS^* (cal·deg^{-1}·mole^{-1})
I	Cl	24.0 ± 0.2	8.29 ± 0.28
I	Br	21.8 ± 0.2	1.00 ± 0.39
I	I	20.0 ± 0.1	-5.42 ± 0.17
Br	Cl	28.4 ± 0.7	10.11 ± 0.13
Br	Br	28.4 ± 0.1	9.47 ± 0.22
Cl	Cl	29.6 ± 0.2	10.99 ± 0.28

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