

Kinetics and Mechanism of the Anation by Chloride, Bromide, Iodide, Nitrite, Azide and Thiocyanate Ions of the Aquopentachlororhodate(III) Anion

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The reaction $RhCl_5(H_2O)^{2-} + X^- \longrightarrow RhCl_5X^{3-} + H_2O$ has been studied and the pseudo first-order rate constant for the reaction was shown to have the form

$$k_{obs} = \frac{k_1[X^-] + k_2k_4/k_3}{k_2/k_3 + [X^-]},$$

a rate law that suggests the formation of the $RhCl_5^{2-}$ intermediate by a rate constant $k_1 = 2.9 \times 10^{-2} \text{ sec}^{-1}$ at 35°C and constant ionic strength. k_2/k_3 represents the efficiency with which the water captures the intermediate in competition with the nucleophile and has the values between 61.0 M and 7.0 M in the order $Br^- \gg I^- > SCN^- > NO_2^- > N_3^-$. k_4 represents the rate of generation of the intermediate from the acido complex $RhCl_5X^{3-}$. Values for the overall equilibrium

constant are obtained from the relation $K = \frac{k_1k_3}{k_2k_4} M^{-1}$. The results are discussed in terms of a limiting $S_N1(lim)$ -type reaction and compared to previously published results in Rh^{III} and Co^{III} systems.

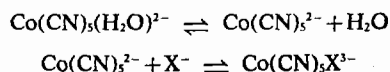
Introduction

Several studies of the replacement of co-ordinated water in rhodium(III) systems have been reported. The recent paper by Swaminathan and Harris¹ on the chloride anation of hexaaquorhodium(III) in aqueous acid medium, together with earlier work on ligand water exchange² have presented compelling evidence in support of a dissociative rate determining reaction as the most likely path facilitating the replacement of water by a nucleophile. It would thus appear that rhodium(III) parallels its congener cobalt(III) in reacting by an I_a mechanism in the sense defined by Langford and Gray³ but with an ion-pair formation preceding the dissociative interchange reaction.

The results of the experiments reported^{4,5} on the hydrolysis of hexachlororhodate(III) and the chloride ligand exchange with the latter complex as well as the hydrolysis of pentachlororhodate(III) gave no in-

dication of the type of rate determining reaction. Chloride anation studies of pentachlororhodate(III) and tetrachlororhodate(III) showed a first-order dependence upon chloride ion concentration. Similar observations were made on the iridium(III) systems studied by Garner and his co-workers.^{6,7,8} With no ion-pair pre-equilibrium likely to account for chloride ion concentration dependence, it was therefore decided to investigate more thoroughly the anation reaction in the aquopentachlororhodate(III).

This paper reports the results of experiments in which the nucleophile was changed from chloride to one of several other reagents to replace the water in aquopentachlororhodate(III). The results can best be interpreted in terms of a limiting S_N1 mechanism similar to the now classical study reported by Haim and Wilmarth⁹⁻¹³ on the $Co(CN)_5(H_2O)^{2-}$ anation reactions in which $Co(CN)_5^{2-}$ was considered to be an intermediate generated in the following fashion:



Experimental Section

Reagents materials. K_3RhCl_6 and $K_2RhCl_5(H_2O)$ were prepared by the methods previously described^{4,5} from Rh-metal, KCl and Cl_2 gas. Recrystallized NaBr, NaCl, $NaNO_2$, NaI, NaSCN, NaN_3 and $NaClO_4$ were used. Doubly distilled water was used in all cases. The NaI solutions were always freshly made up to ensure that I_2 was absent.

Apparatus. A Cary model 15 recording spectrophotometer was used for absorbancy and spectral measurements. A repetitive scan accessory was used for measuring whole spectral changes during the kinetic runs.

(6) I. A. Poulsen and C. S. Garner, *J. Am. Chem. Soc.*, **84**, 2032 (1962).

(7) J. C. Chang and C. S. Garner, *Inorg. Chem.*, **4**, 209 (1965).

(8) I. A. El-Awady, E. J. Bounsall, and C. S. Garner, *Inorg. Chem.*, **6**, 79 (1967).

(9) A. Haim and W. K. Wilmarth, *Inorg. Chem.*, **1**, 573 (1962).

(10) A. Haim and W. K. Wilmarth, *Inorg. Chem.*, **1**, 583 (1962).

(11) R. Grassi, A. Haim, and W. K. Wilmarth, *Inorg. Chem.*, **6**, 237 (1967).

(12) « Advances in Chemistry Series », No. 49, American Chemical Society, Washington, D. C. 1965, p. 31-54.

(13) Ref. 3 p. 87-88.

(1) K. Swaminathan and G. M. Harris, *J. Am. Chem. Soc.*, **88**, 4411 (1966).

(2) W. Plumb and G. M. Harris, *Inorg. Chem.*, **3**, 542 (1964).

(3) C. H. Langford and H. B. Gray, « Ligand Substitution Processes », W. A. Benjamin, Inc. Chapter 1.

(4) W. Robb and G. M. Harris, *J. Am. Chem. Soc.*, **87**, 4472 (1965).

(5) W. Robb and M. M. de V. Steyn, *Inorg. Chem.*, **6**, 616 (1967).

A Radiometer pH meter (Model 25 SE) was used for pH-measurements and titrations were done on an Auto Titrator TTT11, ABU1 and Titrigraph.

Kinetic studies. The solutions used for the kinetic studies were made *ca* 5 mM respect to the aquopentachlororhodium(III) complex, sufficient nucleophile added to give the desired concentration with sodium perchlorate added to bring the ionic strength up to 4.00 M. The reactant solutions were placed in 1 cm quartz cells housed in a thermostatted cell holder in the spectrophotometer. In experiments where the nucleophile concentration was low with resulting higher perchlorate concentrations, it was necessary to filter off any KClO_4 formed from $\text{K}_2\text{RhCl}_5(\text{H}_2\text{O})$. The wavelengths at which changes in optical density with time were followed were determined by the character of the absorption spectra of the reactant and product for each nucleophile employed. A region of suitably large difference in extinction coefficient was chosen. For $\text{X}^- = \text{Br}^-$ the reaction was followed at 555 m μ where the bromo complex exhibits a maximum¹⁵ ($\epsilon = 245$) whilst $\text{RhCl}_5(\text{H}_2\text{O})^{2-}$ shows only a weak absorbance ($\epsilon = 55$).⁵ In all other cases $\lambda_{\text{max}} = 507$ m μ with absorbancy index⁴ of 99 of $\text{RhCl}_5(\text{H}_2\text{O})^{2-}$ was chosen as a suitable region. Duplicate runs at 475 m μ for I^- , 300 m μ for N_3^- and 305 m μ for SCN^- , respectively, were made.

In all experiments care was taken to ensure that the nucleophile concentration was in such excess over that of the complex that pseudo first-order kinetics were assured.

Results

All experiments were carried out at 35°C and the ionic strength was maintained at 4.0 M with sodium perchlorate. The equilibrium reading for any particular run was taken after no further change in optical density was observed. The plots of $\ln(\text{OD}_\infty - \text{OD})$ versus time were always found to deviate from linearity as shown in Figure 1. Careful curve-stripping was carried out yielding the straight line plot for the fastest reaction (see Figure 1) and the half-times were taken from the latter. This technique has been satisfactorily applied in other studies¹⁶ where successive equilibrations were found to occur. The pseudo first-order rate constant, k_{obs} , was calculated from the relationship $k_{\text{obs}} = \frac{0.693}{t_{1/2}}$ the latter being derived from the relationship

$$\ln \frac{(\text{OD}_\infty - \text{OD})}{(\text{OD}_\infty - \text{OD}_0)} = k_{\text{obs}} t \quad (1)$$

with $t_{1/2} = t$ when $(\text{OD}_\infty - \text{OD}) = \frac{1}{2} (\text{OD}_\infty - \text{OD}_0)$.

(OD_∞ , OD and OD_0 are the optical densities at times equilibrium, t and zero, respectively).

(14) G. H. Ayers and F. Young, *Anal. Chem.*, 24, 165 (1952).

(15) Unpublished results. Jorgenson, *Acta Chem. Scand.*, 10, 515 (1956) reports a value of $\epsilon = 190$.

(16) W. Robb, *Inorg. Chem.*, 6, 382 (1967).

Table I. Rate of reaction of $\text{RhCl}_5(\text{H}_2\text{O})^{2-}$ with Br^- . Ionic strength = 4.00

| Temp. °C | [Br ⁻] M | 10 ⁴ k _{obs} sec ⁻¹ |
|----------|----------------------|--|
| 30 | 0.50 | 2.63 |
| 30 | 1.00 | 4.67 |
| 30 | 2.00 | 7.35 |
| 30 | 3.00 | 8.95 |
| 30 | 4.00 | 10.68 |
| 35 | 0.60 | 6.80 |
| 35 | 0.80 | 7.70 |
| 35 | 1.00 | 9.15 |
| 35 | 2.00 | 14.71 |
| 35 | 3.00 | 21.43 |
| 35 | 4.00 | 24.62 |
| 40 | 0.50 | 11.83 |
| 40 | 1.00 | 18.67 |
| 40 | 2.00 | 29.67 |
| 40 | 3.00 | 38.50 |
| 40 | 4.00 | 50.67 |
| 45 | 0.50 | 21.17 |
| 45 | 1.00 | 32.17 |
| 45 | 1.50 | 43.83 |
| 45 | 2.00 | 65.00 |

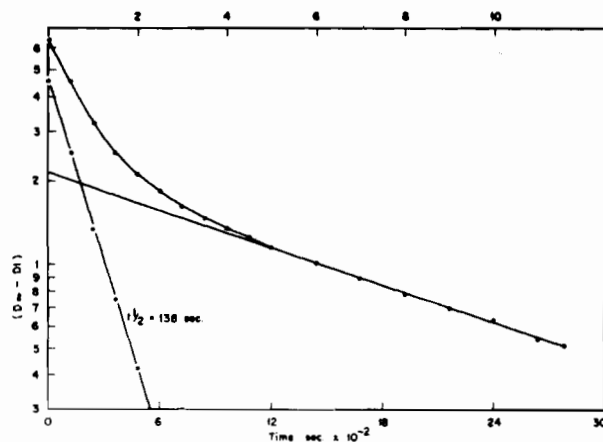


Figure 1. $[\text{SCN}^-] = 4.0$ M, $T = 35^\circ\text{C}$, $\lambda = 305$ m μ , $\mu = 4.0$ M

Table I gives the results of the reaction between $\text{RhCl}_5(\text{H}_2\text{O})^{2-}$ and Br^- . The concentration of $\text{RhCl}_5(\text{H}_2\text{O})^{2-}$ varied depending on the choice of a suitable optical density increment because preliminary experiments showed that the pseudo rate constant, k_{obs} , was quite independent of the concentration of complex. In this case a temperature dependence study was carried out, and the results are listed accordingly. Only the values given in column 3 taken at 35°C were used to calculate the specific rates constants given in Table VII of the discussion section. The reproducibility of the k_{obs} values was found to be better than 5% in all cases.

Table II gives the results for the reaction of $\text{RhCl}_5(\text{H}_2\text{O})^{2-}$ with I^- . The measurements were found to be quite reproducible provided fresh solutions were made up for each run. Table III gives the results of the reaction of $\text{RhCl}_5(\text{H}_2\text{O})^{2-}$ with NO_2^- . Table VI shows the results for the slower reaction taking place between $\text{RhCl}_5(\text{H}_2\text{O})^{2-}$ and NO_2^- which is presumed to be $\text{RhCl}_5(\text{NO}_2)^{3-} + \text{NO}_2^- \rightarrow$. Table IV lists the results when N_3^- was used as a nucleophile. No variations in hydrogen ion concentration were made

Table II. Rate constants for the reaction of $\text{RhCl}_5(\text{H}_2\text{O})^{2-}$ with I^- . Ionic strength = 4.00. Temperature = 35°C

| $[\text{I}^-]$ M | $10^4 k_{\text{obs}}$ sec ⁻¹ |
|---------------------|--|
| 0.25 | 1.7 |
| 0.50 | 3.0 |
| 0.75 | 4.6 |
| 1.00 | 6.2 |
| 1.50 | 9.1 |
| 1.75 | 10.6 |
| 2.00 | 11.6 |
| 2.50 | 14.7 |

Table III. Rate constants for the reaction of $\text{RhCl}_5(\text{H}_2\text{O})^{2-}$ with NO_2^- . Ionic strength = 4.00. Temperature = 35°C

| $[\text{NO}_2^-]$ M | $10^3 k_{\text{obs}}$ sec ⁻¹ |
|------------------------|--|
| 0.25 | 2.74 |
| 0.50 | 3.26 |
| 0.75 | 3.75 |
| 1.00 | 4.20 |
| 1.50 | 5.06 |
| 2.00 | 5.85 |
| 2.50 | 6.57 |
| 3.50 | 7.25 |
| 4.00 | 8.40 |

Table IV. Rate constants for the reaction of $\text{RhCl}_5(\text{H}_2\text{O})^{2-}$ with N_3^- . Ionic strength = 4.00. Temperature = 35°C

| $[\text{N}_3^-]$ M | $10^4 k_{\text{obs}}$ sec ⁻¹ |
|-----------------------|--|
| 0.25 | 11.5 |
| 0.50 | 27.5 |
| 1.00 | 54.2 |
| 1.50 | 90.0 |
| 2.00 | 102.5 |
| 2.50 | 122.5 |
| 3.00 | 126.0 |
| 4.00 | 130.0 |

Table V. Rate constants for the reaction of $\text{RhCl}_5(\text{H}_2\text{O})^{2-}$ with SCN^- . Ionic strength = 4.00. Temperature = 35°C.

| $[\text{SCN}^-]$ M | $10^4 k_{\text{obs}}$ sec ⁻¹ |
|-----------------------|--|
| 0.25 | 3.8 |
| 0.50 | 10.3 |
| 1.00 | 19.5 |
| 1.50 | 23.0 |
| 2.00 | 29.5 |
| 2.50 | 37.0 |
| 3.00 | 43.0 |
| 4.00 | 51.0 |

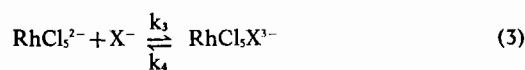
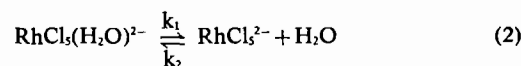
to study the acid catalysis of the aquation of the acido-complex. Finally, the results of the anation by SCN^- are given in Table V. In all Tables the last column gives the calculated value for the pseudo first-order rate constants utilizing the values for the rate constants given in Table VII in the discussion.

Table VI. Rate constants for the reaction of $\text{RhCl}_5(\text{NO}_2)^{3-}$ with NO_2^- . Ionic strength = 4.00. Temperature = 35°C.

| $[\text{NO}_2^-]$ M | $10^4 k_{\text{obs}}$ sec ⁻¹ |
|------------------------|--|
| 0.25 | 3.0 |
| | 3.0 |
| 0.50 | 6.0 |
| | 5.8 |
| 0.75 | 7.5 |
| | 8.2 |
| 1.00 | 9.7 |
| | 10.1 |
| 1.50 | 12.5 |
| | 12.3 |
| 2.00 | 15.2 |
| | 15.6 |
| 2.50 | 16.5 |
| | 16.5 |
| 3.00 | 18.7 |
| | 18.9 |
| 3.50 | 20.3 |
| | 20.3 |
| 4.00 | 21.4 |
| | 20.4 |

Discussion

The results of the experiments reported here can best be accommodated by the following set of equations:



RhCl_5^{2-} is postulated as an intermediate species generated from $\text{RhCl}_5(\text{H}_2\text{O})^{2-}$ or $\text{RhCl}_5\text{X}^{3-}$ with characteristic rate constants k_1 or k_4 . The ratio of rate constants k_2/k_3 would then be a measure of the efficiency of H_2O compared to X^- in competing for the intermediate. Making the usual steady-state assumption regarding the concentration of RhCl_5^{2-} , the differential equation relating the rate of change of $[\text{RhCl}_5(\text{H}_2\text{O})^{2-}]$ with time to the various rate constants¹⁷ can be summarily integrated to the form.¹⁸

$$k_{\text{obs}} = \frac{k_1[\text{X}^-] + k_2 k_4 / k_3}{k_2 / k_3 + [\text{X}^-]} \quad (4)$$

This is the now familiar expression utilized by Haim *et al.*¹¹ in the $\text{Co}(\text{CN})_5(\text{H}_2\text{O})^{2-}$ anation studies. The values for the rate constant were obtained from

plots of $\frac{1}{k_{\text{obs}} - k_4}$ vs. $\frac{1}{[\text{X}^-]}$ in all cases where it

was possible to estimate k_4 , the intercept obtained from a plot of k_{obs} vs. $[\text{X}^-]$. The equation:

$$\frac{1}{(k_{\text{obs}} - k_4)} = \frac{1}{(k_1 - k_4)} + \frac{k_2/k_3}{(k_1 - k_4)} \frac{1}{[\text{X}^-]} \quad (5)$$

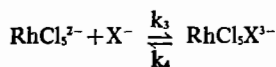
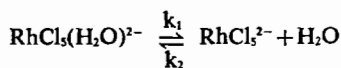
(17) F. Basolo and R. G. Pearson, « Mechanisms of Inorganic Reaction 2nd Ed. John Wiley and Sons, Inc., p. 204 and p. 193-194.

(18) Note that the rate constant k_2 has incorporated in it the concentration of water in the usual fashion.

is derived from equation (4) above, hence, k_1 can be obtained from the intercept and k_2/k_3 from the ratio of slope to intercept. When $X^- = N_3^-$ the value of k_4 was immeasurably small and hence the intercept of a plot of $\frac{1}{k_{obs}}$ vs $\frac{1}{[X^-]}$ was taken to be $\frac{1}{k_1}$.

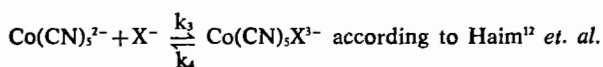
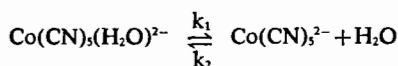
k_2/k_3 and k_4 were refined by using them as input values in a non-linear least squares programme on the IBM 360 system of the C.S.I.R. Table VII contains a summary of all of the rate constants. Included are the value for X^- from a previous study.⁴ For the sake of this discussion the data of Haim *et al.*¹² are also given in the Table.

Table VII. Rate constant for the reactions



| Nucleophile X^- | $10^3 k_1$ sec ⁻¹ | k_2/k_3 M | $10^3 k_4$ sec ⁻¹ | $K = \frac{k_1 k_3}{k_2 k_4} M^{-1}$ |
|------------------------------|---------------------------------|----------------|---------------------------------|--------------------------------------|
| Cl ⁻ | 2.5 | 47.0 | 80.0 | 0.08 |
| Br ⁻ | 3.3 | 61.0 | 3.8 | 1.25 |
| I ⁻ | 3.3 | 55.0 | 0.2 | 3.00 |
| SCN ⁻ | 2.1 | 12.7 | 2.5 | 9.1 |
| NO ₂ ⁻ | 2.3 | 9.4 | 22.0 | 1.1 |
| N ₃ ⁻ | 4.1 | 7.0 | small | large |
| | mean=2.9 | | | Using mean value for k_4 |

All measurements made at 35°C.



| | | | |
|-----------------------------|------|-----------------------|------|
| Cl ⁻ | 9.2 | | 0.36 |
| Br ⁻ | 8.83 | 1.68×10^{-3} | 0.99 |
| I ⁻ | 4.73 | 74×10^{-3} | 42 |
| SCN ⁻ | .147 | 2.71×10^{-3} | 1460 |
| N ₃ ⁻ | 1.68 | 5.5×10^{-3} | 1530 |

All measurements made at 40°C

The first major point of difference between the $\text{RhCl}_5(\text{H}_2\text{O})^{2-}$ anation reactions and those of $\text{Co}(\text{CN})_5(\text{H}_2\text{O})^{2-}$ arises from the fact that not only can a nucleophile X^- replace the water, but it can replace the chloride ligands as well. It has already been intimated in the preceding section that this is in fact the case. Whilst great care was taken to ensure that only the first reaction was measured, an attempt shall be made to rationalise any doubts that may have arisen as to whether the results given in Table VII do in fact describe the reactions 2 and 3. By far the most compelling evidence must be the consistency

observed in the k_1 values *i.e.* averaging 2.9×10^{-2} sec⁻¹ that it is in fact the water that is displaced and not one of the chloride ligands.

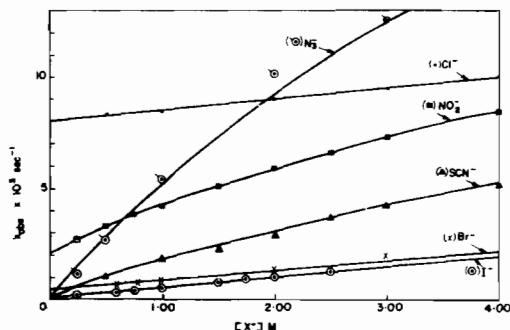


Figure 2. Calcd. line using values in Table I $T = 35^\circ\text{C}$
 $\mu = 4.00 \text{ M}$.

Furthermore, it is an indisputable fact that the product of chloride anation of $\text{RhCl}_5(\text{H}_2\text{O})^{2-}$ is RhCl_6^{3-} and radioactive chloride exchange experiments reported earlier⁴ show that no major amount of direct exchange takes place between RhCl_6^{3-} and $^{36}\text{Cl}^-$ or for that matter between $\text{RhCl}_5(\text{H}_2\text{O})^{2-}$ and $^{36}\text{Cl}^-$ but that a solvolysis path exists accounting for almost all of the exchange. Sound arguments leading up to a prediction that water would be replaced in preference to one of the chloride ligands in the initial reaction emerge from the very thorough studies on substitution reaction in rhodium(III) complexes reported by Poë¹⁹ *et al.* in which it was shown that the HSAB²⁰ principle, as formulated by Pearson, can be used to great advantage. Certainly H_2O can be considered to be a harder base than any of the anating reagents used in this study. An incoming nucleophile would therefore preferentially replaced the water rather than one of the chloride ligands in an initial reaction. Some rather convincing data were taken from the experiments in which $X^- = \text{NO}_2^-$, where the second reaction was measured as well. It is not unreasonable to ascribe it to a reaction say: $\text{RhCl}_5(\text{NO}_2)^{3-} + \text{NO}_2^- \rightleftharpoons \text{RhCl}_4(\text{NO}_2)_2^{3-} + \text{Cl}^-$, ignoring any intimate detail *e.g.* hydrolyses, then, as shown in Table VIII the corresponding k_1 value obtained is a little more than one tenth of the value for k_1 in equation (4), Table VII.

Just as a point of interest, the rate constant for dissociation of water²¹ from $\text{RhCl}_4(\text{H}_2\text{O})_2^-$ is computed to be 4.2×10^{-3} sec⁻¹ which compares favourably with the value of 3.6×10^{-3} sec⁻¹ for the reaction of NO_2^- with $\text{RhCl}_5(\text{NO}_2)^-$ mentioned above, Table VIII. This could be an indication that an hydrolysis step precedes the substitution of chloride by NO_2^- as follows:

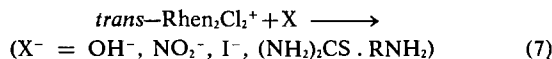


(19) (a) H. L. Bott, E. J. Bounsell, and A. J. Poë, *J. Chem. Soc. (A)*, (1966) pp. 78, 1275 and b) *ibid.*, (1967), 206.

(20) R. G. Pearson and J. Songstad, *J. Am. Chem. Soc.*, 89, 158 (1967) and previous references therein.

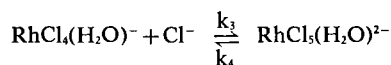
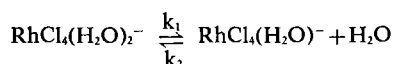
(21) Taking the data from ref. 5 and treating according to procedure of Haim and Wilmath, ref. 12.

in which the $\text{RhCl}_4(\text{H}_2\text{O})(\text{NO}_2)^{2-}$ species dissociates the water at a rate comparable to that for $\text{RhCl}_4(\text{H}_2\text{O})_2^-$. This point finds suitable support if reference is made to the findings of Johnson, Basolo and Pearson²² in their study of the reaction of:



where all nucleophiles replaced the chloride at the same rate indicating the operation of a solvolysis intermediate path. Furthermore, it was noted that when RhCl_6^{3-} was taken as the starting material for substitution by the nucleophiles used in the present study, an hydrolysis reaction was observed in each case, thus concurring with the findings of Pearson *et al.* mentioned above.

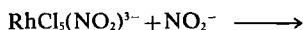
Table VIII. Rate constants for reaction^{5,21}



at 35°C, $\mu = 4.00 \text{ M}$ $[\text{H}^+] = 4.000 \text{ M}$

$k_1 = 4.2 \times 10^{-3} \text{ sec}^{-1}$ $k_2/k_3 = 3.48 \text{ M}$ $k_4 = 1.6 \times 10^{-4} \text{ sec}^{-1}$

Rate constants^a for the reaction



Data taken from Table VI and treated according to equation 5. $T = 35^\circ\text{C}$, $\mu = 4.00$, $\text{pH} = 6.8$.

$k_1 = 3.6 \times 10^{-3} \text{ sec}^{-1}$ $k_2/k_3 = 2.6 \text{ M}$ $k_4 \approx 0$

^a Values obtained by non-linear least-squares analysis on IBM 360.⁵

It would be instructive now to compare and contrast the rate constants for reactions 2 and 3 with those reported by Haim *et al.* on the $\text{Co}(\text{CN})_5(\text{H}_2\text{O})^{2-}$ system. Firstly it can be seen from the values given in Table VII that k_1 is more than an order of magnitude greater for the $\text{RhCl}_5(\text{H}_2\text{O})^{2-}$ than it is for $\text{Co}(\text{CN})_5(\text{H}_2\text{O})^{2-}$ not even taking into account the difference in temperatures. This would imply that the metal-oxygen bond seems stronger for cobalt than it is for rhodium. A comparison of the relative $\text{p}K_a$ values for the acids would be an indication of this, but our attempts to measure the $\text{p}K_a$ for $\text{RhCl}_5(\text{H}_2\text{O})^{2-}$ met with failure because the hydroxide precipitates²³ from solution at $\text{pH} = 8.5$ during titrimetric procedures and for similar reasons it is not possible to use a spectrophotometric method.

The ratio for k_2/k_3 measured in this study is consistently higher than those reported in the $\text{Co}(\text{CN})_5(\text{H}_2\text{O})^{2-}$ study indicating that the water competes much more effectively for the penta co-ordinated in-

termediate generated than any of the nucleophiles do when compared to the cobalt system. It may be noted that the order of decreasing k_2/k_3 is the same for the two systems with $\text{X}^- = \text{Cl}^-$ being anomalous for this study. The value of 47 M reported here was measured in 4 M hydrogen ion medium,⁴ all other measurements were made in 4 M Na^+ medium. As reported earlier,⁴ a large specific cation effect was observed and this could certainly account for the anomaly. However, the difference is of minor importance for the purpose of the study.

By far the biggest single difference between the two systems can be found in the relative values for k_4 , where the cobalt complexes react much slower than the rhodium complexes. The ratios of k_1/k_4 are also vastly different covering a range of 200 in rhodium *cf.* 40 in cobalt system. This fact, it will be appreciated, makes the estimation of k_1 values rather more subject to errors than would be the case experienced by Haim *et al.*

Some more points of difference are to be found in the values for $K = \frac{k_1 k_3}{k_2 k_4} \text{ M}^{-1}$ which can be

taken as a measure of the equilibrium constants between the aquo and acido complexes. The halogen complexes are in the expected order and so too are N_3^- and SCN^- compared to the values determined for $\text{Co}(\text{CN})_5\text{X}^{3-}$ ($\text{X}^- = \text{N}_3^-$ and SCN^-). In each instance the azide ion emerged as being the most reactive of all nucleophiles for study. The rather high K value for the iodo complex is a little surprising but it would require a good deal more experimentation to ascertain the real significance of this observation bearing in mind the extremely high I_3^- reactivity reported by Haim *et al.* Whilst care was taken to exclude I_2 from the study reported here, it is possible that it appears as a catalyst in the I^- reaction.

The overall reaction mechanism discussed in this paper also appears to knit quite well with the findings of Swaminathan and Harris¹ in their study of the chloride anation of the hexaaquorhodium(III) cation in which it was found that subsequent to the formation of an ion-pair the chloride enters the co-ordination sphere at a rate governed by the dissociation of a water molecule. The dissociation rate was equal to the rate of water exchange with the $\text{Rh}(\text{H}_2\text{O})_6^{3+}$ reported by Plumb and Harris.² A good deal more data are required to thoroughly test this mechanism using more amenable complex substrates. Even the carefully assembled results reported by Garner⁶⁻⁸ and his co-workers on the aquochloroiridate(III) systems seem to fit this kinetic pattern *i.e.* the first-order chloride-ion concentration dependence of their anation studies may be accounted for in this manner.

The kinetic pattern established by Butler, Basolo and Pearson²⁴ for the carbon monoxide insertion reaction of $\text{C}_5\text{H}_5\text{Mo}(\text{CO})_2\text{CH}_3$ with triphenylphosphine was the same as that presented in this paper, and it would appear that investigations along these lines would be fruitful to say the least. A recently completed study on the anation reactions of some bromorhodate(III) complexes²⁵ should verify this opinion.

(22) S. A. Johnson, F. Basolo, and R. G. Pearson, *J. Am. Chem. Soc.*, **85**, 1741 (1963).

(23) S. N. Anderson and F. Basolo, *Inorg. Syn.*, **7**, 214 (1963) used the formation of the hydroxide as a preliminary step in preparation of $\text{RhCl}_5 \cdot 3\text{H}_2\text{O}$ complex.

(24) I. S. Butler, F. Basolo, and R. G. Pearson, *Inorg. Chem.*, **6**, 2074 (1967).

(25) W. Robb and P. v. Z. Bekker, unpublished results.