

to be a measurable increase in the Ni-N bond cleavage rate constant.²⁵

Species 5 in Figure 7 has the same groups dissociating from nickel as species 1, but k_{56} must be much larger than k_{12} . This has to be the case because the limiting rate becomes $k_{12}[\text{NiY}^{-2}]$ at high copper (neglecting path 1,4,5) but the over-all rate also equals $k_{56}[5]$.

$$\text{rate} = k_{12}[\text{NiY}^{-2}] = k_{56}[5]$$

Since $[5] \ll [\text{NiY}^{-2}]$, then obviously $k_{56} \gg k_{12}$.

The experimental value of k_{12} corresponds closely to the calculated value based on the stabilities of species 1 and 2 and the rate constant for water substitution. If k_{56} is estimated in the same manner it would be slightly less than k_{12} , but this neglects electrostatic repulsion between copper and nickel which must be sufficiently large to make $k_{56} \gg k_{12}$. Such a repulsion along Ni-N-C-C-N-Cu would serve to weaken the Ni-N bond resulting in faster cleavage of this segment. Of course, the repulsion would weaken the Cu-N bond as well. Indeed the stability of the intermediate species 5 must be less than that calculated from the stabilities of the segments, otherwise species 5 would be observable at high copper concentrations and it is not. The term for the electrostatic repulsion between the two metal iminodiacetate segments in 5 must be greater than 10^2 .

Predictions for Other EDTA-Exchange Reactions. It is only fair to ask under what conditions the simple rate expression in eq. 2 will hold for other EDTA-

(25) G. A. Melson and R. G. Wilkins, *J. Chem. Soc.*, 2662 (1963).

exchange reactions. An evaluation of the constants in a stepwise mechanism for the EDTA exchange with other metals indicates that deviations from eq. 2 as the concentration of M' is increased up to 1 M should be expected if $K_{M'IDA}/K_{MIDA} > 1$ and if $k_{M'}^{-\text{H}_2\text{O}}/k_{M}^{-\text{H}_2\text{O}} > 1$. This situation occurs for a number of cases with Cu(II) reactions because copper forms a very stable iminodiacetate complex ($\log K = 10.6$) and also has rapid water substitution. Thus the reactions of Cu^{+2} and MgY^{-2} , Cu^{+2} and CoY^{-2} , Cu^{+2} and CdY^{-2} , and Cu^{+2} and AlY^{-} could all show the same type of deviations found for Cu^{+2} and NiY^{-2} . There are other combinations such as Zn^{+2} and MgY^{-2} which would be predicted to act similarly. Many of the reactions with copper have been studied, but because they are fairly rapid the copper concentration has been around $10^{-4} M$ and hence has been too low to cause the shift to step 1,2.

On the other hand, the reaction of Zn^{+2} and NiY^{-2} would not be expected to deviate from eq. 2, and this was the case up to at least 0.4 M Zn^{+2} at pH 5.

The position of the rate-determining step in multidentate ligand exchange reactions can, in general, be expected to shift with concentrations of metal ions and hydrogen ion. This can lead to complex changes in reaction order and makes extrapolation of reaction rate data from one concentration level to another dangerous unless the full mechanism is considered.

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Some Exchange and Substitution Reactions of Hexachlororhodium(III) and Pentachloroaquorhodium(III) Ions in Aqueous Acid Solutions

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This paper reports an extension of previous studies in this laboratory of the chemistry of rhodium(III) complexes. The present work comprises an investigation of the kinetics of the equilibration $\text{RhCl}_6^{-3} + \text{H}_2\text{O} \rightleftharpoons \text{RhCl}_5\text{H}_2\text{O}^{-2} + \text{Cl}^-$ (1) utilizing spectrophotometric and isotopic tracer techniques. The reaction was studied in perchloric-hydrochloric acid media of constant ionic strength. The aquation of RhCl_6^{-3} and the anation of $\text{RhCl}_5\text{H}_2\text{O}^{-2}$ were examined independently by spectrophotometry. It was shown that either process is described by the rate law

$$-d(\text{RhCl}_6^{-3})/dt = k_1(\text{RhCl}_6^{-3}) - k_2(\text{RhCl}_5\text{H}_2\text{O}^{-2})(\text{Cl}^-)$$

Values of k_1 and k_2 were obtained at several temperatures by both aquation and anation procedure, and excellent agreement was obtained between the two sets of data. At 25°, $k_1 = 0.11 \text{ min.}^{-1}$ and $k_2 = 0.013 M^{-1} \text{ min.}^{-1}$.

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The Arrhenius energies of activation are 25 and 17 kcal./mole, respectively. The reaction is essentially independent of acid concentration up to 4 M . In order to test whether the aquation path is the only one available for exchange of chloride by chloride, a direct study was made of the reaction $\text{RhCl}_6^{-3} + {}^{36}\text{Cl}^- \rightleftharpoons \text{RhCl}_5{}^{36}\text{Cl}^{-2} + \text{Cl}^-$. The kinetics of the isotopic exchange can be accounted for entirely by an aquation mechanism, according to reaction 1 and the succeeding aquation $\text{RhCl}_5\text{H}_2\text{O}^{-2} + \text{H}_2\text{O} \rightleftharpoons \text{RhCl}_4(\text{H}_2\text{O})_2^- + \text{Cl}^-$. Unfortunately, no conclusions can be drawn concerning the detailed mechanism of reaction 1. The forward process may involve a unimolecular dissociation of chloride ion as the rate-determining step, or bimolecular substitution of water for chloride. Since the reverse reaction seems to be a clear-cut bimolecular process (an ion-pairing mechanism is unlikely for ions of the same charge sign), it is quite possible that the aquation is also bimolecular in nature.

Previous studies in this laboratory have dealt with the kinetics of the oxalate exchange and acid-catalyzed aquation reactions^{2,3} of trisoxalatorhodium(III) complex anion, and of the water-exchange reaction⁴ of hexa-aquorhodium(III) cation. The present work comprises a kinetic and equilibrium examination of the process



in acidic aqueous solution, utilizing spectrophotometric and isotopic-exchange techniques. It is a logical extension of our own earlier work, in that it provides further understanding of the ligand substitution behavior of rhodium(III) complex ions in aqueous solution.

Several earlier investigators have reported upon the properties of chlororhodium(III) complexes in aqueous systems. Delépine⁵ was the first to recognize the probable occurrence of reaction 1, and Jørgensen⁶ has made some qualitative studies of the nature of the equilibration by spectrophotometry. Polarography has been applied by Cozzi and Pantani⁷ in an attempt to delineate the whole family of chlororhodium complexes and to evaluate the various equilibrium constants. A similar separative approach, utilizing ion-exchange columns, was recently utilized by Kleinberg and co-workers.⁸ None of these investigations has provided quantitative evidence concerning the kinetics of reaction 1. However, the closely-related hexachloroiridium(III)-pentachloro-aquo-iridium(III) equilibration has been subjected to detailed kinetic study by Poulsen and Garner,⁹ and the chlororhodium system will be seen to have closely parallel behavior in many respects.

Experimental Section

Potassium hexachlororhodium(III) was prepared¹⁰ in the solid state from pure metallic rhodium,¹¹ potassium chloride, and chlorine gas. About 80% conversion of rhodium metal to complex occurred in about 1 hr. Purification of the product was effected by leaching into concentrated (9 M) hydrochloric acid,¹² filtration, and recrystallization. Unreacted KCl in the material was avoided by always utilizing an excess of rhodium in the synthesis. The final product was examined analytically, determining rhodium by the usual reduction technique,⁴ chloride by the Mohr method, and potassium by a cation-exchange-pH-titration procedure.

Anal. Calcd. for K_3RhCl_6 : Rh, 23.7; Cl, 49.1; K, 27.1. Found: Rh, 23.7; Cl, 48.8; K, 27.2.

Spectrophotometric measurements confirmed the purity of the material.¹³

(2) D. Barton and G. M. Harris, *Inorg. Chem.*, **1**, 251 (1962).

(3) K. V. Krishnamurty, *ibid.*, **1**, 422 (1962).

(4) W. Plumb and G. M. Harris, *ibid.*, **3**, 542 (1964).

(5) M. Delépine, *Bull. soc. chim. Belges*, **36**, 108 (1927).

(6) K. Jørgensen, *Acta Chem. Scand.*, **10**, 500 (1956).

(7) D. Cozzi and M. Pantani, *J. Inorg. Nucl. Chem.*, **8**, 385 (1958).

(8) W. C. Wolsey, C. A. Reynolds, and J. Kleinberg, *Inorg. Chem.*, **2**, 467 (1963).

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

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

(11) Stated to be 99.99% pure by the suppliers, Fisher Scientific Co.

(12) If HCl is not present in excess, the rapid aquation of the hexachloro to the pentachloro-aquo complex occurs, as originally reported by Jørgensen.⁶

(13) Peaks were observed at 411 m μ (ϵ 83) and 518 m μ (ϵ 112) for the hexachloro salt, and at 402 m μ (ϵ 99) and 507 m μ (ϵ 99) for the penta-

potassium pentachloro-aquorhodium(III) was obtained by allowing a solution of the hexachlororhodium salt in dilute aqueous hydrochloric acid (~ 0.5 M) to stand for 0.5 hr., then adding ice-cold absolute ethanol. Potassium pentachloro-aquorhodium(III) precipitated immediately and was purified by repeating the dilute acid solution-ice-cold ethanol precipitation cycle.¹⁴ Analyses for rhodium and chloride were performed as before.

Anal. Calcd. for $\text{K}_2\text{RhCl}_5\cdot\text{H}_2\text{O}$: Rh, 27.2; Cl, 46.8. Found: Rh, 27.1; Cl, 46.9.

The spectrophotometric kinetic studies were carried out utilizing a Cary Model 15 spectrophotometer, making direct optical density vs. time plots of prepared samples maintained at the desired temperature in a specially constructed thermostated cell. The study of chloride-ion exchange rate with the chlororhodium species made use of hydrogen chloride-36.¹⁵ In a typical experiment, 10 ml. of an aqueous mixture of RhCl_6^{-3} and $\text{RhCl}_5\text{H}_2\text{O}^{-2}$ ions (total concentration, 0.015 M), 4 M in HCl, was thermostated at the desired temperature until equilibrium between the chlororhodium species was established (6-8 aquation half-times). The exchange reaction was then initiated by addition of a drop of the highly active hydrogen chloride-36 solution. Samples (1 ml.) were removed from the reaction mixture at suitable time intervals and immediately mixed with about 5 ml. of ice-cold ethanol. All the chlororhodium complex was thus precipitated quantitatively from the solution and collected by means of a demountable assembly in a geometrically reproducible form¹⁶ on weighed sintered glass disks. After drying and weighing, the samples were assayed for chlorine-36 content on a Nuclear-Chicago solid-sample counting apparatus. The fraction of exchange was evaluated in the usual way, and half-times of exchange were determined from conventional $\log(1 - F)$ vs. time plots.

Results and Discussion

A. Aquation-Anation Equilibration. Preliminary experiments showed that the aquation rate of hexachlororhodium(III) ion was independent of the initial concentration of the complex but was dependent on chloride concentration and possibly on ionic strength. A series of experiments was run at 25° in which the ionic strength was maintained constant (by use of perchloric acid or perchlorate salts) while the concentrations of chloride ion and of hydrogen ion were systematically varied (see Table I).

The data for any given run always conformed to simple first-order kinetics, in that straight-line plots of $\ln(D_t - D_\infty)$ vs. time were obtained,¹⁷ from the slopes of which the values for k_{obsd} were deduced in the conventional manner. The chloride ion dependence is satisfactorily accounted for in terms of a first-order-second-order equilibration with a mechanism as given in eq. 1. The rate expression for such a mechanism in

chloro-aquo. Kleinberg, *et al.*,⁸ reported corresponding values of 411 m μ (ϵ 94) and 518 m μ (ϵ 112), 402 m μ (ϵ 73) and 507 m μ (ϵ 73).

(14) An alternative procedure has recently been suggested by S. N. Anderson and F. Basolo, *Inorg. Syn.*, **7**, 214 (1963). This was not attempted in the present study.

(15) Obtained in the form of a 4 M aqueous solution from Oak Ridge National Laboratory, Oak Ridge, Tenn.

(16) Details of the apparatus are given by W. Robb, Ph.D. Thesis, University of Melbourne, 1963.

(17) D_t = optical density at any given time, D_∞ = optical density at equilibrium.

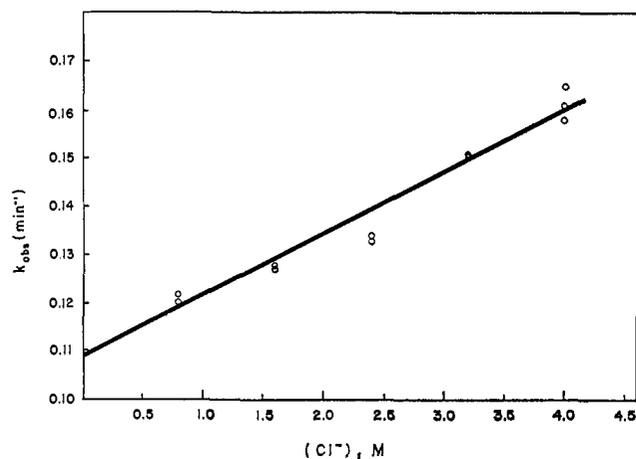


Figure 1.—Dependence of rate of RhCl_6^{3-} – $\text{RhCl}_5\text{H}_2\text{O}^{2-}$ equilibration on chloride ion concentration (25° , $\mu = 4.0\text{ M}$, $(\text{H}^+) = 4.0\text{ M}$).

the presence of excess added chloride, which makes the reverse process pseudo first order, is¹⁸

$$\ln \frac{a}{a-x} = \ln \frac{D_0 - D_\infty}{D_t - D_\infty} = (k_1 + k_2b)t \quad (2)$$

where a = initial concentration of hexachlororhodium(III) complex, $a - x$ = concentration at time t , and b = chloride ion concentration (essentially constant). k_1 and

Table I. Aquation–Anation Equilibration of K_3RhCl_6 at 25° and $\mu = 4\text{ M}$

| Run no. | Rh(III), $M \times 10^3$ | HCl, M | HClO_4 , M | LiCl, M | k_{obsd} , min.^{-1} |
|---------|-----------------------------|-------------|--------------------------|-------------------|---|
| 1 | 5.0 | 4.00 | 0.00 | ... | 0.158 |
| 2 | 2.5 | 4.00 | 0.00 | ... | 0.165 |
| 3 | 1.0 | 4.00 | 0.00 | ... | 0.161 |
| 4 | 5.0 | 3.20 | 0.80 | ... | 0.151 |
| 5 | 2.5 | 3.20 | 0.80 | ... | 0.151 |
| 6 | 3.6 | 2.40 | 1.60 | ... | 0.138 |
| 7 | 2.0 | 2.40 | 1.60 | ... | 0.139 |
| 8 | 5.0 | 1.60 | 2.40 | ... | 0.128 |
| 9 | 2.5 | 1.60 | 2.40 | ... | 0.128 |
| 10 | 2.5 | 1.60 | 2.40 | ... | 0.127 |
| 11 | 4.3 | 0.80 | 3.20 | ... | 0.120 |
| 12 | 2.5 | 0.80 | 3.20 | ... | 0.122 |
| 13 | 1.0 | 0.00 | 4.00 | ... | 0.115 ^b |
| 14 | 5.0 | 0.00 | ... | 4.00 | 0.165 |
| 15 | 2.5 | 0.00 | ... | 4.00 | 0.165 |
| 16 | 5.0 | 0.80 | ... | 3.20 | 0.170 |
| 17 | 2.5 | 0.80 | ... | 3.20 | 0.170 |
| 18 | 5.0 | 1.60 | ... | 2.40 | 0.158 |
| 19 | 2.5 | 1.60 | ... | 2.40 | 0.158 |
| 20 | 5.0 | 0.00 | ... | 4.00 ^a | 0.067 |
| 21 | 2.5 | 0.00 | ... | 4.00 ^a | 0.067 |

^a NaCl used instead of LiCl. ^b Value is for k_1 ; see text.

k_2 are the rate constants for the aquation and anation reactions,¹⁹ respectively, and obviously $k_{\text{obsd}} = k_1 +$

(18) A. A. Frost and R. G. Pearson, "Kinetics and Mechanism," John Wiley and Sons, Inc., New York, N. Y., 1961, p. 186.

(19) Preliminary experiments have shown that the rate of the second aquation step, $\text{RhCl}_5\text{H}_2\text{O}^{2-} + \text{H}_2\text{O} \rightarrow \text{RhCl}_4(\text{H}_2\text{O})_2^- + \text{Cl}^-$, is not more than 10% as great as the one under discussion. Its contribution to the optical density data could therefore be ignored, especially since even the equilibrium concentration of tetrachlorodiaquo complex is probably quite low under high free chloride concentration conditions.⁸ Garner and co-workers^{9,20} find similar relations to hold in the corresponding iridium(III) system.

k_2b . It was possible to evaluate k_1 and k_2 separately by plotting k_{obsd} vs. b for all the chloride-variable runs, as shown in Figure 1. The intercept gives a value for k_1 of 0.11 min.^{-1} and the slope of k_2 of $0.012\text{ M}^{-1}\text{ min.}^{-1}$. Run no. 13, made in absence of chloride ion so that the reverse process was initially negligible,²¹ confirms this interpretation in that in this case $k_1 = 0.115\text{ min.}^{-1}$, in good agreement with the graphically determined value.

Several other runs were made in which Na^+ or Li^+ was substituted for all or part of the H^+ normally present (see runs 14 to 21). It is seen that Li^+ substitution has little or no effect, but a considerable deceleration occurs when Na^+ is used. Obviously, the process is not acid catalyzed in the usual sense, but it is apparently quite sensitive to the size of the cations present in the solution. Possibly, an ion-pairing phenomenon is involved, but not enough data are at present available to warrant further discussion of this question at this time.

The equilibration concept of the reaction was confirmed by several experiments in which the starting material was the pentachloro-aquorhodium(III) complex. The rate of the net addition of chloride to form the hexachloro salt was followed spectrophotometrically, again as a function of chloride ion concentration. Equation 2 served to analyze the data as before, and rate constants were obtained which agreed well with the previous results (see Table II). A temperature-dependence

Table II. Temperature Dependence of the Rates of Aquation of RhCl_6^{3-} and Anation of $\text{RhCl}_5\text{H}_2\text{O}^{2-}$ Ions in 4 M Acidic Solution

| | 15° | 20° | 25° |
|---|------------|------------|--------------------|
| A. Starting material: K_3RhCl_6 (0.005 M) | | | |
| k_1 , min.^{-1} | 0.028 | 0.059 | 0.11 |
| k_2 , $\text{M}^{-1}\text{ min.}^{-1}$ | 0.0041 | 0.0076 | 0.012 |
| B. Starting material: K_2RhCl_5 (0.005 M) | | | |
| k_1 , min.^{-1} | 0.024 | 0.067 | 0.10 |
| k_2 , $\text{M}^{-1}\text{ min.}^{-1}$ | 0.0060 | 0.010 | 0.016 |
| C. Mean values | | | |
| k_1 , min.^{-1} | 0.026 | 0.063 | 0.11 ^a |
| k_2 , $\text{M}^{-1}\text{ min.}^{-1}$ | 0.0050 | 0.0088 | 0.013 ^a |
| $K = k_1/k_2$, M | 5.2 | 7.1 | 8.5 |

^a Weighted means, having regard for the number of runs made by each procedure.

study of the rate was carried out in which series of chloride-varied runs were made at various temperatures, using both hexachloro and pentachloro-aquo complex as starting materials. Values of k_1 and k_2 were obtained at various temperatures by the graphical procedure already mentioned. The results, including those at 25° on the hexachloro complex already discussed, are given in Table II.

Plots of the mean rate constants according to conventional Arrhenius procedure (see Figure 2) yield values of the activation energies of 25 and 17 kcal./mole for aquation and anation, respectively. The enthalpy of reaction 1 is thus $\Delta H = 8\text{ kcal./mole}$. Little is known of the thermodynamics of water substitution for

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

(21) For this run, the reverse reaction is not pseudo first order, so the data were treated according to first-order–second-order equilibration kinetics (see ref. 18).

halide in stable halo complexes of the transition metals other than that provided by Schug and King²² on chloroaquochromium(III) complexes. Their data indicate values of $\Delta H = -7$ and -5 kcal./mole for $\text{Cr}(\text{H}_2\text{O})_5\text{Cl}^{+2}$ and $\text{Cr}(\text{H}_2\text{O})_4\text{Cl}_2^+$ aquation processes. These ΔH values are opposite in sign from the value quoted above for RhCl_6^{-3} . This is somewhat unexpected, since the ionic charge is reversed from the Cr(III) cases. However, the stabilities of chlororhodium complexes are notably much greater than those of the corresponding chlorochromium species.²³ It is also significant that the heat of the reaction $\text{IrCl}_5(\text{H}_2\text{O}) + \text{H}_2\text{O} \rightarrow \text{Cl}^- + \text{IrCl}_4(\text{H}_2\text{O})_2$ has a zero or small positive value.²⁰

An attempt was made to confirm directly the magnitude of the equilibrium constant $K = (\text{RhCl}_5\text{H}_2\text{O}^{-2}) \cdot (\text{Cl}^-) / (\text{RhCl}_6^{-3})$, the values for which, as determined from the rate constant ratios, are included in Table II. Equilibrium mixtures of the chlororhodium species were prepared by allowing K_3RhCl_6 dissolved in 3 M aqueous HCl to stand for a period of several half-times of aquation-anation equilibration at 25°. The spectrum in the 500-m μ region was then examined, and the known absorption coefficients¹³ of the hexachloro and pentachloroaquo species were used to calculate the ratio of the two salts present. The results of several experiments lead to a mean value of about 3 M. We are unable to explain fully the discrepancy between our equilibrium and our kinetically derived data, except to acknowledge that the former are subject to considerably more experimental error than are the rate constant ratio results.²⁵ We adopt our kinetic data as more reliable and by means of the best-fit plot of $\log K$ and $\log k_1$ vs. $1/T$ (see Figure 2) evaluate K and k_1 values for use in the chloride-exchange data interpretation, as indicated in Table III.

Table III. Chloride Ion Exchange in Equilibrated Aqueous RhCl_6^{-3} - $\text{RhCl}_5\text{H}_2\text{O}^{-2}$ Solution^a

| Temp., °C. | $t_{1/2}$, min. | k_{ex} , min. ⁻¹ | K , ^b M | k_1 , ^b min. ⁻¹ | k_3 , min. ⁻¹ |
|------------|------------------|--------------------------------------|----------------------|---|----------------------------|
| 25 | 75.5 | 0.15 | 8.7 | 0.12 | 0.01 |
| 30 | 47.0 | 0.29 | 11.0 | 0.24 | 0.02 |
| 35 | 27.5 | 0.58 | 13.7 | 0.47 | 0.03 |

^a (Chlororhodium) = 0.015 M, (HCl) = 4.0 M, $\mu = 4$ M. ^b Calculated as explained in section B.

B. Chloride-Exchange Reaction. In view of the apparently bimolecular substitution reaction of Cl^-

(22) K. Schug and E. L. King, *J. Am. Chem. Soc.*, **80**, 1089 (1958).

(23) For example, the formation constant⁸ of $\text{Rh}(\text{H}_2\text{O})_5\text{Cl}^{+2}$ in aqueous solution at 120° is greater than 10^8 , while that for $\text{Cr}(\text{H}_2\text{O})_5\text{Cl}^{+2}$ is close to unity under similar conditions.²⁴

(24) H. S. Gates and E. L. King, *J. Am. Chem. Soc.*, **80**, 5011 (1958).

(25) The "equilibrium" system undoubtedly contains a small amount of $\text{RhCl}_4(\text{H}_2\text{O})_2^-$ ion, either in *cis* or *trans* forms or both. Insufficient data on this species preclude any attempt to correct for this factor in the spectrophotometric equilibrium constant determination. Previously reported K values for the hexachloro-pentachloroaquo system were obtained under quite different conditions so are not strictly comparable. Cozzi and Pantani's data⁷ suggest a K value of about 2 at room temperature and $\mu \sim 1$ M, while Kleinberg, *et al.*,⁸ obtained a value of about 3 at 120° and $\mu \sim 6$ M. More significantly, Poulsen and Garner's results⁹ show that K for the corresponding iridium(III) system at 50° increases from 3 to 9 as μ is decreased from 3.7 to 2.2 M, while Connick²⁸ quotes a value of 10 at 25° and $\mu = 5$ M for the ruthenium(III) case.

(26) R. E. Connick, "Advances in the Chemistry of the Coordination Compounds," S. Kirschner, Ed., The Macmillan Co., New York, N. Y., 1961, p. 15.

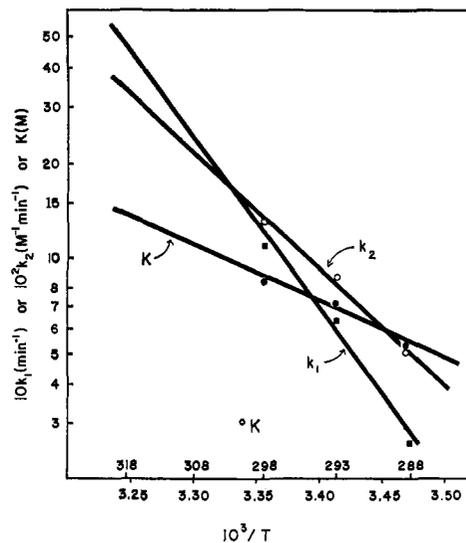


Figure 2. Temperature dependence of rate and equilibrium constants in RhCl_6^{-3} - $\text{RhCl}_5\text{H}_2\text{O}^{-2}$ system ($\mu = 4.0$ M, $(\text{H}^+) = 4.0$ M).

for H_2O in the anation process just discussed,²⁷ it is of interest to know whether chloride for chloride substitution occurs directly in either of the chlororhodium(III) species under consideration. The results of the chloride-exchange experiments are given in Table III, under the varied conditions specified (all half-times given are the mean of duplicate runs).

The analysis of the data shown in Table III was performed by assuming that exchange occurred by aquation entirely, not only by reaction 1 but by the next succeeding process



The concentration of the tetrachloro species is undoubtedly low, so the rate of exchange is given by

$$R = k_1(\text{RhCl}_6^{-3}) + k_3(\text{RhCl}_5\text{H}_2\text{O}^{-2}) \quad (4)$$

where k_3 is the forward rate constant of reaction 3.

The equilibrium relation between RhCl_6^{-3} and $\text{RhCl}_5\text{H}_2\text{O}^{-2}$ holds, such that the concentrations of the two species are given by $a - x_\infty$ and x_∞ , where $a =$ total rhodium(III) concentration, and $(\text{Cl}^-) = b$ (effectively constant since $b \gg a$).

The exchange rate is then²⁸

$$k_{\text{ex}} = k_1 + k_3 \frac{K}{b} = \frac{0.693}{t_{1/2}} \left(\frac{6b + 5K}{b} \right) \quad (5)$$

Utilizing the previously obtained best-fit values of K and the corresponding k_1 values, figures were obtained for k_3 as shown.²⁹

(27) It is assumed that ion pairing is absent or negligible between Cl^- and $\text{RhCl}_5\text{H}_2\text{O}^{-2}$ because of electrostatic repulsion.

(28) In this system, the McKay equation becomes

$$R = \frac{0.693}{t_{1/2}} \frac{[6(a - x_\infty) + 5x_\infty]b}{[6(a - x_\infty) + 5x_\infty + b]}$$

Since $b \gg a$ and $K = bx_\infty / (a - x_\infty)$, this relation can be simplified and combined with eq. 4 to yield (5).

(29) An alternative interpretation assumes that second-order chloride exchange may occur according to the reactions



and



As yet, no direct aquation rate data for the penta-chloro complex are available from which to deduce accurate k_3 values. However, the values presented in Table III are quite reasonable.¹⁹ The activation energy for the process is of the order of magnitude of 20 kcal./mole. Comparable data on the reactions of the iridium(III) system,^{9,20} the similarities with which have already been mentioned, show that $k_1:k_2:k_3 = 20:10:1$ at 50° and $\mu \sim 4 M$. These reactions are about 1% as rapid as for the rhodium(III) species, largely attributable to a 10-kcal./mole higher activation energy for the iridium(III) compounds. Otherwise, the two series of complexes behave in a very analogous manner.

Apparently, the only chloride-exchange paths fully available to the chlororhodium species are the aquation processes, a not unreasonable finding in view of the great excess of H₂O over Cl⁻ ion as a substitutional reagent. But it is of interest that, on an equimolar basis, chloride-for-water substitution in the RhCl₅H₂O⁻² complex ion is considerably more facile than water-for-chloride in RhCl₆⁻³. The comparable second-order rate constants at 25° (allowing also for the statistical advantage of 6 in the latter reaction) are $k_2 = 0.013 M^{-1} \text{ min.}^{-1}$ and $k_1(\text{cor.}) = k_1/6 \times 50 = 0.0004 M^{-1} \text{ min.}^{-1}$. Both of these reactions are very much more rapid than either water exchange⁴ with Rh(H₂O)₆⁺³ or chloride substitution for water³⁰ in Rh(H₂O)₆⁺³. The latter two reactions have approximately equal rates, with half-times at 25° of the order of several

in addition to the aquation mechanism of reaction 1. The rate equation can then be shown to be

$$k_{\text{ex}} = k_1 + k_2b + k_7K = \frac{0.693}{t_{1/2}} \left(\frac{6b + 5K}{b} \right)$$

If it is assumed as a first approximation that $k_7 = \frac{5}{6}k_6$ (i.e., they only differ on a statistical basis), one obtains k_6 values of 0.001, 0.004, and 0.007 min.⁻¹ at the three temperatures utilized. These values require an unreasonably high activation energy to account for the temperature coefficient of k_6 . The "direct exchange" path is therefore excluded from consideration.

(30) K. Swaminathan and G. M. Harris, to be published.

months. Furthermore, the chloride concentration dependence of the Cl⁻-Rh(H₂O)₆⁺³ reaction falls off steadily from first order as the chloride ion concentration exceeds a few tenths molar, in good agreement with an ion-pair formation mechanism followed by rate-determining dissociation of the water molecule which is replaced by chloride. It is indeed interesting how the substitutional lability of the coordinated water in aquorhodium(III) complexes depends so drastically on the number of chloride ions simultaneously coordinated to the central metal ion. The rates range from rather high lability in RhCl₅H₂O⁻² to rather extreme stability in Rh(H₂O)₆⁺³. This phenomenon has been commented upon previously in connection with the ruthenium(III) series of complexes.²⁶ A qualitative explanation based on the crystal-field splitting influence of the chloride ion as compared to water molecule was offered, which is equally applicable to the rhodium(III) and iridium(III) cases. The only property of the systems which changes at all greatly in going down the Ru(III)-Rh(III)-Ir(III) series of complexes is the greatly decreasing rate of ligand substitution.

Unfortunately, it is impossible to draw conclusions concerning the detailed mechanism of the aquation process of reaction 1. It may involve unimolecular dissociation of chloride (as usually proposed for chlorocobaltic complexes³¹) as the rate-determining step, or bimolecular substitution of water for chloride. In the anation direction, reaction 1 appears to be a clear-cut bimolecular process. It is thus highly probable that aquation of RhCl₆⁻³ ion is also bimolecular in nature, with outer-sphere water as the attacking reagent.

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(31) See, for example, F. Basolo and R. G. Pearson, *Advan. Inorg. Chem. Radiochem.*, **3**, 1 (1961).