Kinetics and Mechanism of the Reaction of Chloride Ion with Hexaaquorhodium(III) Ion in Acidic Aqueous Solution

K. Swaminathan and G. M. Harris[1]

Contribution from the Department of Chemistry, State University of New York at Buffalo, Buffalo, New York 14214. Received May 20, 1966

Abstract: The rate studies were carried out spectrophotometrically at a constant ionic strength of 2.5, using reaction mixtures such that the hydrogen ion concentration was varied between 0.133 and 2.152 *M* and chloride between 0.100 and 0.962 *M*. The data are satisfactorily interpreted by means of a rate-determining dissociative reaction, involving ligand water elimination from the aquorhodium(III) cation paired with a chloride anion and followed by rapid chloride addition. A strong inverse hydrogen ion concentration dependence results from the acid–base equilibrium, $Rh(H_2O)_6^{+3} \rightleftarrows Rh(H_2O)_5OH^{+2} + H^+$, and the fact that the conjugate base cation is about 6000 times more reactive than the fully protonated cation. The acid dissociation constant for the above reaction as well as the two ion-pair equilibrium constants and the two rate constants have been determined at 75, 80, and 85°. The overall rate of chloride addition is identical within experimental error with that of water exchange under comparable conditions, supporting the dissociative mechanism concept. The species $Rh(H_2O)_5Cl^{+2}$ does not appear in the kinetic studies, owing to the very rapid addition of a second chloride ion (in the presence of the excess of the latter) to yield $Rh(H_2O)_4Cl_2^+$ as the sole product. This result is discussed in terms of the possibility of the *trans* effect of the first chloride ligand.

In previous work in this laboratory, quantitative kinetic evidence was obtained concerning the water-for-chloride substitution reaction of hexachlororhodium(III) ion, and the chloride-for-water reaction of pentachloroaquorhodium(III) ion.[2] It appeared logical to carry out a complementary investigation at the other extremity of the chloroaquorhodium(III) series of complexes, *viz.*, to study the chloride-for-water substitution of hexaaquorhodium(III) ion, particularly as pertinent kinetic data are already available for the ligand water exchange process of this latter complex ion.[3] None of the earlier work on the Rh_{aq}^{III}–Cl^- system has been concerned with the kinetic aspects of the chloride addition process. Lederer mentions[4] the use of paper electrophoresis and ion-exchange chromatography to separate cationic, neutral, and anionic chlororhodium species, obtained by reacting HCl with $Rh(OH)_3$. Kleinberg and co-workers,[5] in their study of the aqueous Rh(III)–chloride equilibrium system, found that all species of the general type $[Rh(H_2O)_{6-n}Cl_n]^{3-n}$ could be obtained by heating hexaaquorhodium(III) perchlorate with hydrochloric acid. The extent of chloride substitution was a function of the concentration of the hydrochloric acid and of the time of boiling of the solutions, but no quantitative kinetic relations were established. In the present paper, a detailed rate study is reported concerning the reaction of chloride ion with $Rh(H_2O)^{+3}$ as a function of several variables, and the mechanism of the process is deduced. This very slow anation of an aquo cation appears to offer a clear-cut example of a ligand water dissociation-controlled reaction, as is commonly accepted to be the mechanism for corresponding reactions in a number of much more labile systems.[6] A significant feature of the study is that the species $Rh(H_2O)_5Cl^{+2}$ is not observable in the kinetic study, owing to the greatly increased rate of Cl^- substitution in $Rh(H_2O)_5Cl^{+2}$ as compared to $Rh(H_2O)_6^{+3}$. This effect is reasonably attributable to the *trans*-labilizing influence of the first chloride ligand on the remaining ligand water.

Experimental Section

Hexaaquorhodium(III) perchlorate was prepared according to the method of Ayres and Forrester.[7] A stock solution, 0.73 *M* in perchloric acid, was prepared for the kinetic studies and analyzed for rhodium as the metal[8] and for perchlorate as the nitron salt.[9] Dry and acid-free hexaaquorhodium(III) perchlorate was obtained for the hydrolysis equilibrium experiments by drying a sample of the crystalline salt under vacuum at 100° for 10 hr. Sodium chloride and hydrochloric acid solutions were standardized gravimetrically as silver chloride.

The spectral characteristics of the chloro complexes $RhCl^{+2}$, $RhCl_2^+$, and $RhCl_3$ were determined on samples of the species obtained by the ion-exchange procedure developed by Kleinberg, *et al.*[5] Two solutions for ion-exchange separation were prepared: the first by reacting a 1:1 Rh(III):Cl^- solution for 45 hr at 80°, and the second by reacting a 1:3 solution for 90 hr at the same temperature. The rhodium content of the three separated complexes was determined spectrophotometrically,[10] and their spectra were recorded on a Cary Model 15 spectrophotometer. No significant differences between our data and that of Kleinberg, *et al.*,[5] were noted except for some small discrepancies in the magnitudes of the molar absorptivity values. Our absorptivity figures as used in the kinetics experiments were

	323 mμ	395 mμ	450 mμ
$Rh(H_2O)_6^{+3}$	32.5	57.9	16.6
$Rh(H_2O)_4Cl_2^+$	57.5	25.7	64.7

The rate studies were performed at a constant ionic strength of 2.5, using reaction mixtures containing the requisite amounts of rhodium(III) perchlorate, perchloric or hydrochloric acid, and

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[1] To whom requests for reprints should be addressed.

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

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

[4] M. Lederer, Proceedings of the Moscow Conference on Analytical Chemistry, 1957 (quoted in *J. Chromatog.*, **1**, 279 (1958)).

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

[6] M. Eigen and R. G. Wilkins, Advances in Chemistry Series, No. 49, American Chemical Society, Washington, D. C., 1965, p 55.

[7] G. H. Ayres and J. S. Forrester, *J. Inorg. Nucl. Chem.*, **3**, 365 (1957).

[8] W. C. Hillebrand, G. E. Lundell, H. A. Bright, and J. J. Hoffman, "Applied Inorganic Analysis," John Wiley and Sons, Inc., New York, N. Y., 1953, p 380.

[9] O. Loebich, *Z. Anal. Chem.*, **68**, 34 (1926).

[10] S. S. Berman and R. Ironside, *Can. J. Chem.*, **36**, 1151 (1958).

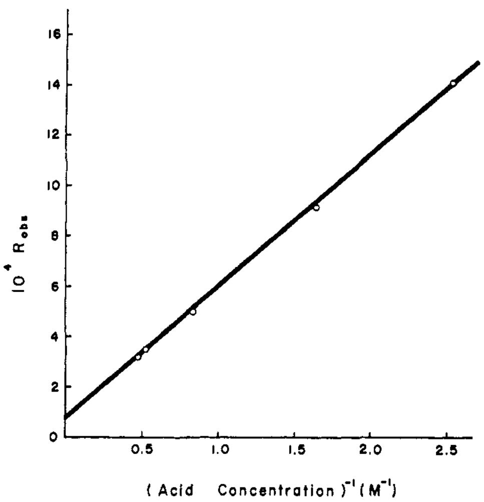

Figure 1. Rate of anation of $Rh(H_2O)_6^{+3}$ ion by Cl^- ion as a function of acidity: 80°, $(Rh^{III}) = 9.32 \times 10^{-3}$ *M*, $(Cl^-) = 0.199$ *M*.

sodium perchlorate or chloride. Aliquots of the thermostated reaction mixture were withdrawn at suitable time intervals, and chilled immediately to room temperature; the absorbances were measured at 352, 395, and 450 mμ on a Beckman DU spectrophotometer. The concentrations of $Rh(H_2O)_6^{+3}$ and $RhCl_2^+$ in the various solutions were calculated from the sets of simultaneous total absorbance equations by means of a computer program.[11]

The acid dissociation (hydrolysis) constant of the hexaaquorhodium(III) ion was determined by pH measurements on the acid-free salt solution in a similar manner to that previously described.[3] Determinations were made in a thermostated cell utilizing a Beckman research model pH meter, standardized at each temperature against potassium hydrogen phthalate.[12] The values obtained for the pK_a of reaction 4 (see below) were 3.40,[13] 3.20, and 3.08 at 25, 45, and 60°, respectively. This corresponds to a heat of reaction of 4.3 kcal/mole. The data were extrapolated to yield equilibrium-constant values at 75, 80, and 85° as recorded in Table I.

Results and Discussion

Series of experiments were run to determine the effects of changes in hydrogen ion and chloride ion concentration on the reaction rate, as well as its temperature variation. Some data on the acid dependence at 80° are presented in Figure 1. It is seen that the same strong inverse relationship between rate and (H^+) occurs as was observed for the water exchange, with, again, a residual acid-independent rate as indicated by the nonzero intercept. The variation of the rate with (Cl^-) is close to first order at low values of (Cl^-) only, showing a steady fall-off from this order at higher values. Data which illustrate this fact are presented in Figures 2 and 3.

A satisfactory interpretation of all the observed data is provided by the following reaction mechanism.

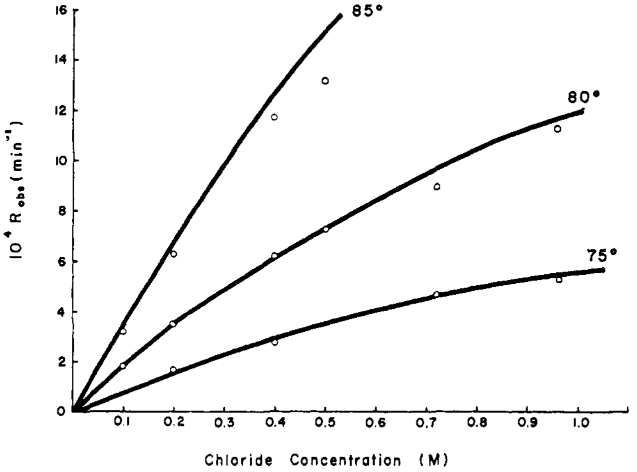

Figure 2. Rate of anation of $Rh(H_2O)_6^{+3}$ ion by Cl^- ion as a function of temperature and (Cl^-): $(Rh^{III}) = 9.32 \times 10^{-3}$ *M*, (acid) = 1.914 *M*.

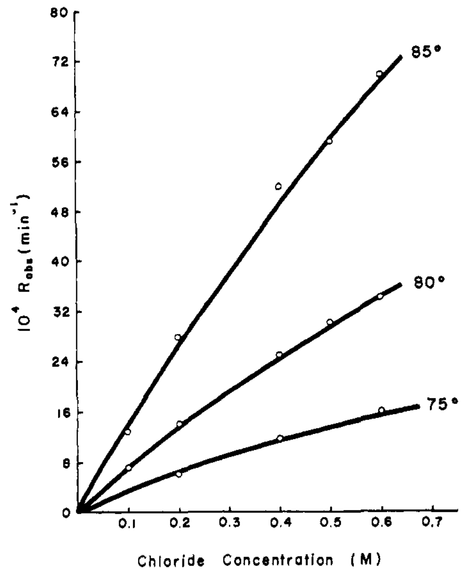

Figure 3. Rate of anation of $Rh(H_2O)_6^{+3}$ ion by Cl^- ion as a function of temperature and (Cl^-): $(Rh^{III}) = 9.32 \times 10^{-3}$ *M*, (acid) = 0.393 *M*.

$$Rh(H_2O)_6^{+3} \rightleftharpoons Rh(H_2O)_5OH^{+2} + H^+ \quad K_a \tag{1}$$

$$Rh(H_2O)_6^{+3} + Cl^- \rightleftharpoons Rh(H_2O)_6^{+3}\cdot Cl^- \quad K_1 \tag{2}$$

$$Rh(H_2O)_5OH^{+2} + Cl^- \rightleftharpoons Rh(H_2O)_5OH^{+2}\cdot Cl^- \quad K_2 \tag{3}$$

$$Rh(H_2O)_6^{+3}\cdot Cl^- \longrightarrow Rh(H_2O)_5Cl^{+2} + H_2O \quad k_1 \tag{4}$$

$$Rh(H_2O)_5OH^{+2}\cdot Cl^- \longrightarrow Rh(H_2O)_4OHCl^+ + H_2O \quad k_2 \tag{5}$$

$$Rh(H_2O)_5Cl^{+2} + Cl^- \longrightarrow Rh(H_2O)_4Cl_2^+ + H_2O \quad \text{fast} \tag{6}$$

$$Rh(H_2O)_4OHCl^+ + Cl^- \longrightarrow Rh(H_2O)_3OHCl_2 + H_2O \quad \text{fast} \tag{7}$$

Reactions 1, 2, and 3 represent continuously maintained equilibria, the first being of the usual acid–base type, and the other two ion-pairing processes. The rate-determining reactions are (4) and (5). The exact nature of (6) and (7) is as yet uninvestigated, except to determine that they exist and are very much more rapid than (4) and (5), respectively.[15] The usual kinetic

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[11] The spectrophotometric data showed no evidence for the existence of appreciable amounts of $RhCl^{+2}$ at any stage of the reaction, though after several half-times of $RhCl_2^+$ formation, there were indications of the appearance of small amounts of $RhCl_3$. The pseudo-first-order rate constants were evaluated from the conventional plots of log $(Rh(H_2O)_6^{+3})$ *vs.* time utilizing the completely linear initial portion of the curves, which extended over an interval of at least one half-time of reaction.

[12] V. Gold, "pH Measurements," Methuen and Co., Ltd., London, 1956, p 118.

[13] In reasonable agreement with previously reported figures for this constant at this temperature.[3,14]

[14] G. S. Ayres and J. S. Forrester, *J. Phys. Chem.*, **63**, 1979 (1959).

[15] Preliminary data suggest a factor such that $k_6/k_4 = 45$ at 75° with $(H^+) \sim 2$ *M* and $(Cl^-) = 0.4$ *M*.

analysis of this mechanism (under conditions where $K_a \ll (H^+)$, as is true here) leads to a rate law such that the observed first-order rate constant under specified conditions is given by

$$k_{\mathrm{obsd}} = \frac{k_1K_1(\mathrm{Cl}^-)}{1 + K_1(\mathrm{Cl}^-)} + \frac{k_2K_2K_a(\mathrm{Cl}^-)}{[1 + K_2(\mathrm{Cl}^-)](\mathrm{H}^+)}$$

A set of "best fit" values[16a] for the constants k_1, k_2, K_1, and K_2, together with the predetermined extrapolated constants K_a at the specified temperatures, are recorded in Table I. These have been used to calculate the full curves of Figures 1, 2, and 3, and have been plotted semilogarithmically in the conventional manner to evaluate the following activation energies and heats of reaction (all given in units of kcal/mole):[16b] $\Delta H_1 = -8, \Delta H_2 = -11, E_1 = 37, E_2 = 39$.

Table I. Rate Parameters for the Reaction of Chloride Ion with Hexaaquorhodium(III) Ion

Temp, °C	10^4k_1, min^{-1}	k_2, min^{-1}	K_1, M^{-1}	K_2, M^{-1}	10^3K_a, M	$10^{-3}\cdot k_2/k_1$
75	3.3	1.9	0.9	0.6	1.1	5.8
80	6.3	4.5	0.8	0.5	1.2	7.1
85	15.0	10.0	0.7	0.4	1.3	6.7

Some quite significant conclusions may be drawn from these experiments. Firstly, the rate of water exchange with the hexaaquorhodium(III) cation[3] in 2.12 M $HClO_4$ at 80° and ionic strength 12 has a value of $k_{\mathrm{obsd}} = 10^{-2}\ \mathrm{min}^{-1}$. Data on the ionic strength effect in this earlier study[3] enable an estimate such that at $I = 2.5$, k_{obsd} should be about 0.25 as great as at $I = 12$, or $k_{\mathrm{obsd}} = 2.5 \times 10^{-3}\ \mathrm{min}^{-1}$. If it is assumed that k_1 and k_2 of the present work are comparable with k_1 and k_2 of the water-exchange study, one estimates[17] a value for k_{obsd} (water exchange) using the k_1 and k_2 values of Table I at 80° of $2.9 \times 10^{-3}\ \mathrm{min}^{-1}$. This close agreement between the k_{obsd} values lends strong support to the concept that the rate-determining processes in the chloride addition reactions (eq 4 and 5 above) are in fact the previously proposed[3] water dissociation reactions

$$Rh(H_2O)_6^{+3} \longrightarrow Rh(H_2O)_5^{+3} + H_2O$$

$$Rh(H_2O)_5OH^{+2} \longrightarrow Rh(H_2O)_4OH^{+2} + H_2O$$

One also must conclude that the ion-pairing phenomenon in the chloride addition reaction has about the same influence on the lability of the coordinated water molecules as does perchlorate ion–aquo complex ion pairing in the water-exchange process. The difference in the latter case is that ClO_4^- ion cannot effectively compete with water to refill the vacant ligand position, while chloride ion can and does. Actually, the ionic radii of the solvated anions are not very greatly different[18] so they would be expected to have similar ion-pairing capabilities. The temperature variation data for chloride addition and water exchange are not strictly comparable, since the heat of the ion-pairing reaction cannot be identified in the latter process. However, one notes that the net activation energy for either chloride addition reaction is close to 30 kcal/mole ($\Delta H_1 + E_1 = 29$ and $\Delta H_2 + E_2 = 28$) and not experimentally distinguishable from the value of 33 kcal/mole reported for the water exchange. It is clear, moreover, that the large difference in reactivity of the species $Rh(H_2O)_6^{+3}$ and $Rh(H_2O)_5OH^{+2}$ is not the result of energy difference in the activated states from which ligand water is eliminated.

The rapidity of reactions 6 and 7 relative to 4 and 5 deserves further comment. It is obvious that the placement of the first chloride ion within the chloroaquo complex ion inner coordination sphere has a strong labilizing influence on the remaining ligand water molecules, greatly accelerating the second step in the anation process, though not necessarily the third.[15] It is tempting to ascribe this behavior to the *trans* effect[19] of the ligand chloride opposite to water, leading to the entities *trans*-$Rh(H_2O)_4Cl_2^+$ or *trans*-$Rh(H_2O)_3OHCl_2$ as the major dichloro species. We have as yet no unequivocal proof that this is so, though the spectrum of the product seems to be consistent with the *trans* assignment.[20] One notes, moreover, that the rate of Cl^- addition to $RhCl_5H_2O^{-2}$ is at least an order of magnitude greater than that for addition[21] to $RhCl_4(H_2O)_2^-$, again perhaps explainable in *trans*-effect terms.[22]

It must be noted that the value of the k_2/k_1 ratio in the present study (about 6000 at 75°) does not agree well with the same ratio reported in the water-exchange study[3] despite the already noted agreement in the overall k_{obsd} values under comparable conditions. A redetermination of the ratio for the water-exchange process, employing the same inverse plot procedure used in the present work (see Figure 1), leads to a value of about 1200 for data[24] at 64.4°. Since the temperature dependence of the rate-constant ratio is small (see last column of Table I) the discrepancy does not arise from the temperature differential. Actually, the analyses of the acidity-dependence data on which these ratios are based are subject to large errors since the method is not very sensitive nor the data very complete (especially in the water-exchange work). Furthermore, no evidence is available concering the effect of ionic

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(16) (a) Obtained by a combination of trial-and-error computation and curve-fitting as illustrated in the figures. The error limits are of the order of magnitude ±10% for each of the constants. (b) The indicated error limits are approximately ±2 kcal/mole.

(17) Since the acid concentration is high relative to K_a, $k_{\mathrm{obsd}} = k_1 + k_2K_a/(H^+)$.

(18) C. B. Monk, "Electrolytic Dissociation," Academic Press Inc., New York, N. Y., 1961, p 271.

(19) R. W. Parry and R. N. Kelly in "The Chemistry of Co-ordination Compounds," J. C. Bailar, Jr., Ed., Reinhold Publishing Corp., New York, N. Y., 1956, p 147.

(20) The data of Kleinberg, *et al.*,[5] on the separated *cis* and *trans* forms of $Rh(H_2O)_3Cl_3$ suggest that much higher values for the absorptivity of the $Rh(H_2O)_4Cl_2^+$ species should be found than are calculated from our results, if it were indeed in the *cis* form.

(21) Preliminary results reported by W. Robb, private communication.

(22) It is of interest that our observation of a *trans*-labilizing influence on ligand water by chloride in $Rh(H_2O)_5Cl^{+2}$ is in direct contrast with the recently reported[23] absence of such an effect in $Cr(H_2O)_5Cl^{+2}$, though strong in $Cr(H_2O)_5I^{+2}$. We can offer no explanation of this fact except to record it as another example of the many differences in the chemistry of d^3 chromium(III) and d^6 rhodium(III).

(23) P. Moore, F. Basolo, and R. O. Pearson, *Inorg. Chem.*, 5, 223 (1966).

(24) See ref 3, Figure 2.

strength variation on this ratio, which might be far from negligible.

The magnitudes of the ion-pairing equilibrium constants reported in this paper as K_1 and K_2 are quite reasonable for ions of the type concerned. Extrapolating from the data given in Table I, one estimates K_1 and K_2 at 25° to be approximately 10 and 5, respectively. A typical value for a 3:1 ion pair at this temperature is provided by work[25] on the $Cr(H_2O)_6^{+3}$–Cl^- system, where $K_1 = 13$. K_2, which refers to a 2:1 pair, should of course be smaller, as is found.

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[25] C. Postmus and E. L. King, *J. Phys. Chem.*, 59, 1208 (1955).