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Kinetics, Mechanism, and Stereochemistry of the Aquation and Chloride Anation Reactions of *fac*- and *mer*-Trichlorotriaquorhodium(III) Complexes in Acidic Aqueous Solution. A complete Reaction Scheme for Complex Ions of the General Formula $[\text{RhCl}_n(\text{OH}_2)_{6-n}]^{3-n}$

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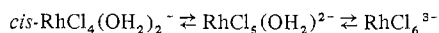
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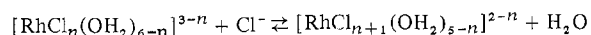
Improved procedures for preparing the title compounds are outlined, and their reactions in strongly acidic aqueous solution in the presence of varied concentrations of chloride are described. The *fac* isomer readily undergoes equilibration in the temperature range 35–55° resulting in a mixture of the parent compound and the three anation products *cis*- $\text{RhCl}_4(\text{OH}_2)_2^-$, $\text{RhCl}_5(\text{OH}_2)^{2-}$, and RhCl_6^{3-} only. The *mer* analog under similar conditions establishes a pseudoequilibrium with the aquation product *cis*- $\text{RhCl}_2(\text{OH}_2)_4^+$ and the anation product *trans*- $\text{RhCl}_4(\text{OH}_2)_2^-$. The latter, at higher temperatures and high chloride concentration, is converted irreversibly to $\text{RhCl}_5(\text{OH}_2)^{2-}$. A review of all relevant rate constant data for complexes of the type $[\text{RhCl}_n(\text{OH}_2)_{6-n}]^{3-n}$ is presented. These data are found to be consistent with a dissociative mechanism involving a square-pyramidal transition state, for both anations and aquations. The kinetic trans effect of ligand chloride is shown to be preeminent in determining the relative rate and steric course of each reaction. The results of this investigation enable a better understanding of some of the previously observed catalytic properties of chloroaquorhodium(III) complexes.

Introduction

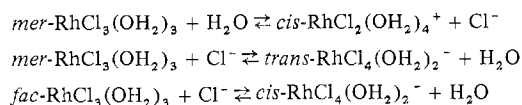
Kinetic studies of ligand substitution reactions of the chloroaquorhodium(III) complexes have so far encompassed the chloride anation of the hexaaquo² and chloropentaaquo³ species, both of which reactions are essentially unidirectional, and the aquation–anation equilibrations in the systems^{4–6}



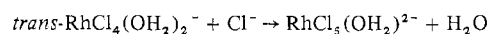
However, no rate data have been published relative to the complex $\text{RhCl}_3(\text{OH}_2)_3$, though its *fac* (1,2,3 or *cis*) and *mer* (1,2,6 or *trans*) isomers have been prepared and identified.⁷ A primary aim of the present work was to fill in the remaining blanks with respect to the rates and equilibria in the reaction sequence symbolized by



It turns out that in strongly acid solution the only significant processes in addition to those already mentioned above are three equilibrations



together with the slow unidirectional process



Our data on these systems provide further confirmation of the previously observed^{2,3} strong kinetic trans effect of the chloride ligand on reactions of chloroaquorhodium(III) complexes and enable an improved understanding of the well-known catalytic

properties of anionic chlororhodium(III) species in the hydration of acetylenes⁸ and in the activation of molecular hydrogen.⁹

Experimental Section

The following complexes were prepared in crystalline form* by established methods: $\text{Rh}(\text{OH}_2)_6(\text{ClO}_4)_3$,¹⁰ $\text{K}_2\text{RhCl}_5(\text{OH}_2)$,⁵ and K_3RhCl_6 .⁵ The complex ions $\text{RhCl}(\text{OH}_2)_5^{2+}$ and *cis*- and *trans*- $\text{RhCl}_2(\text{OH}_2)_4^+$ were separated by ion-exchange chromatography using previously published methods.³ However, separation of the isomers *fac*- and *mer*- $\text{RhCl}_3(\text{OH}_2)_3$ by the method of Wolsey, Reynolds, and Kleinberg⁷ could not be duplicated effectively so their technique was modified as follows.

The initial mixture of isomers is prepared in either of two ways. Refluxing a solution of $\text{Rh}(\text{OH}_2)_6(\text{ClO}_4)_3$ in 0.5 M HCl for 6–8 hr gives predominantly the *mer* isomer, whereas refluxing K_3RhCl_6 for 15 min in dilute perchloric acid gives mainly the *fac* isomer. Either solution is then passed through an 80–90-cm ion-exchange column containing a mixed-bed resin composed of equivalent amounts of anion resin in the chloride form, Bio-Rad 1-X8 (200–400 mesh), and protonated cation resin, Bio-Rad 50W-X8 (200–400 mesh). The temperature of the column is maintained at approximately 2° by passing ice-cold water through a water jacket surrounding the column. The neutral trichloro isomers are eluted with a weak perchloric acid solution (pH 3.5). Two distinct bands are obtained, and the initial ~4-cm portions of both bands and the "tail" of the second band are discarded. As with earlier work,⁷ the first band was assigned to the *mer* isomer and the second to the *fac*. This assignment, based on the difference in dipole moments of the two isomers, is supported by similar ion-exchange studies of analogous iridium(III)¹¹ and ruthenium(III)–chloroaquo¹² complexes and numerous other studies.¹³ The wavelengths of the maxima in the absorption spectra of both isomers agree exactly with those reported by Kleinberg et al.⁷ However, the molar extinction coefficients are somewhat different. For *mer*- $\text{RhCl}_3(\text{OH}_2)_3$ at 471 nm, ϵ is 85.2 (77.1), and at 370 nm, ϵ is 71.6

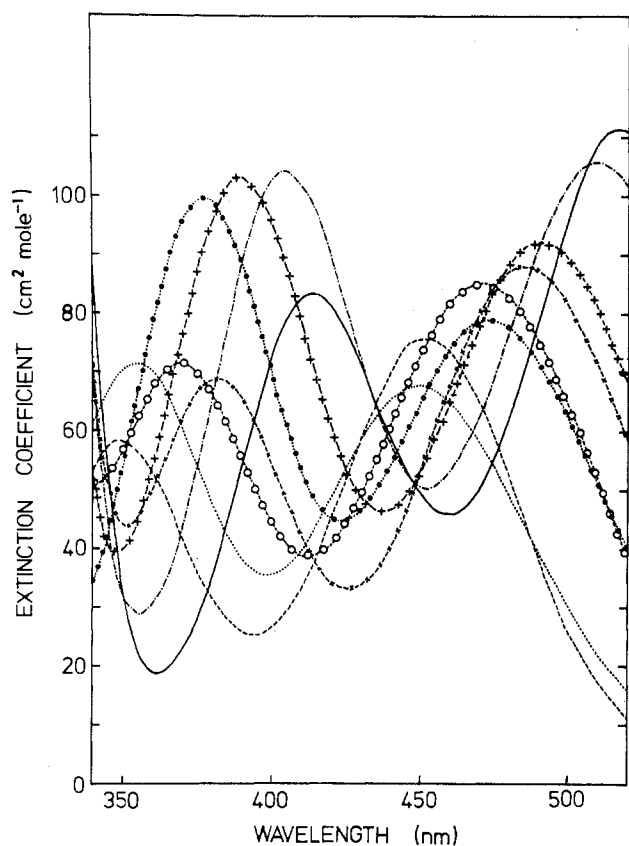


Figure 1. Visible absorption spectra of the chloro-aqua-rhodium(III) complexes: \cdots , $cis\text{-RhCl}_2(\text{OH}_2)_4^+$; $---$, $trans\text{-RhCl}_2(\text{OH}_2)_4^+$; $\bullet\cdots\bullet$, $fac\text{-RhCl}_3(\text{OH}_2)_3$; $\circ\cdots\circ$, $mer\text{-RhCl}_3(\text{OH}_2)_3$; $-\cdots-$, $cis\text{-RhCl}_4(\text{OH}_2)_2^-$; $\times\cdots\times$, $trans\text{-RhCl}_4(\text{OH}_2)_2^-$; $-\cdots-$, $\text{RhCl}_5(\text{OH}_2)_2^{2-}$.

(71.6), while for $fac\text{-RhCl}_3(\text{OH}_2)_3$ at 474 nm, ϵ is 78.4 (68.3), and at 376 nm, ϵ is 99.6 (93.5) $\text{cm}^2 \text{mol}^{-1}$. (The molar extinction coefficients given in parentheses are those of Wolsey et al.⁷)

Analysis¹⁴ of solutions of $mer\text{-RhCl}_3(\text{OH}_2)_3$ gave an average Rh:Cl ratio of 3.03, while for solutions of the fac isomer the ratio was 3.10. A slight excess of chloride ions may be expected due to elution of some chloride from the column by perchlorate ions. Separation of the cis - and $trans\text{-RhCl}_4(\text{OH}_2)_2^-$ ions was initially carried out by the method of Bridges and Chang¹⁵ and the spectra of the resulting solutions agreed to within 10% of their data. However, subsequent experiments on the chloride anation of cis - and $trans\text{-RhCl}_3(\text{OH}_2)_3$ showed serious discrepancies between the observed and calculated extinction coefficients during these runs. Apparently the presence of a large excess of nitrate required in the ion-exchange process results in some nitrate substitution. Garner and coworkers¹¹ have shown that nitrate ion is quite an effective nucleophile in reactions of the less reactive iridium(III)-chloro-aqua complexes. In view of these findings the $cis\text{-RhCl}_4(\text{OH}_2)_2^-$ was eluted from an anion column, Bio-Rad 1-X8 (200-400 mesh), maintained at 2°, in the chloride form using a 0.3 M HClO_4 solution. For the $trans$ isomer a similar column was used, but the eluent was 0.3 M HCl . Chloride analysis was not possible in these cases due to the presence of the excess of chloride ions.

The spectrum of each rhodium complex was measured in acid solution ($[\text{H}^+] \geq 1 \text{ M}$) using either a Cary 15 or Beckman DU spectrophotometer (fitted with a Gilford digital readout), and these are shown in Figure 1. Kinetic measurements were generally made "in situ" using a channeled metal cell block through which water was circulated from an external thermostat. For reaction temperatures $>85^\circ$, aliquots in sealed tubes were placed in an oil thermostat and a sampling method was used. The temperature was always controlled to within $\pm 0.1^\circ$.

All chemicals were of reagent grade and were used without further purification. The reactions were carried out at an ionic strength of 3.0 M and at a hydrogen ion concentration of 2.0 M, using appropriate mixtures of NaCl or NaClO_4 and HCl or HClO_4 .¹⁶ Under the adopted experimental conditions, first-order kinetics are obeyed over

Table I. Acid Dissociation Constants of Some Chloro-aqua-rhodium(III) Complexes at 25°

Complex	I, M	pK_a^a	Ref
$\text{Rh}(\text{OH}_2)_6^{3+}$	2.5 ^b	3.40	2
$\text{RhCl}(\text{OH}_2)_5^{2+}$	2.0 ^b	4.86 ± 0.01	3
$cis\text{-RhCl}_2(\text{OH}_2)_4^+$	~ 0	5.69 ± 0.03	This work
$trans\text{-RhCl}_2(\text{OH}_2)_4^+$	~ 0	6.0 ± 0.1	This work
$fac\text{-RhCl}_3(\text{OH}_2)_3$	~ 0	7.31 ± 0.03	This work
$mer\text{-RhCl}_3(\text{OH}_2)_3$	~ 0	6.96 ± 0.04	This work
	3.0 ^c	6.51 ± 0.04	This work
$trans\text{-IrCl}_4(\text{OH}_2)_2^-$	~ 0	8.4	20
	~ 0	10.1 ^d	20

^a Values given are for the dissociation of the first proton. ^b Ionic strength adjusted with NaClO_4 . ^c Ionic strength adjusted with NaCl . ^d Value for the dissociation of the second proton.

Table II. Chloride Anation of $mer\text{-RhCl}_3(\text{OH}_2)_3$ at 35.0°

$[\text{Cl}^-], M$	$10^5 k_{34}^t, M^{-1} \text{sec}^{-1}$	$[\text{Cl}^-], M$	$10^5 k_{34}^t, M^{-1} \text{sec}^{-1}$
0.642	5.99	2.49	5.98
1.03	5.81	2.50	5.60
1.28	6.04	2.75	5.89
1.50	5.32	3.00	5.73
1.64	5.77	3.25 ^a	6.05
1.80	5.39	3.50 ^a	5.70
2.0	5.74	3.00 ^b	20.8
		3.00 ^c	39.8

^a Only two runs at ionic strength >3.0 . ^b At 43.8°. ^c At 48.5°.

several half-lives of reaction. Unless otherwise stated, plots of $\log(\epsilon_\infty - \epsilon)$ vs. time were made by taking the molar extinction coefficient at "infinite time", ϵ_∞ , as that of the pure product measured independently.¹⁷

A Beckman Research model pH meter was used to monitor the pH during titrations of the chloro-aqua complexes. The pH meter was calibrated against standard HCl of $[\text{H}^+] > 10^{-3} \text{ M}$ rather than against commercial buffers. Thus the acid dissociation constants, K_a , are directly related to concentrations of hydrogen ion rather than activities. In each titration, corrections³ were made for the varying amounts of "free acid" in solution resulting from the ion-exchange process. The measured pK_a values are given in Table I.¹⁸

Results

At 35° and with chloride concentration in excess of 0.6 M, the anation of $mer\text{-RhCl}_3(\text{OH}_2)_3$ to produce $trans\text{-RhCl}_4(\text{OH}_2)_2^-$ goes essentially to completion, enabling a study of this reaction independently of the reverse aquation process. The results of such a study, made by observing the change in absorbance at 515 nm, are recorded in Table II. The second-order rate constants are derived from the observed pseudo-first-order constants by the relation $k_{34}^t = k_{\text{obsd}}/[\text{Cl}^-]$, using the strictly linear first 2 half-times of the experimental plots. Beyond 2 half-times, anation of the tetrachloro species to pentachloro causes some deviation from linearity in the plot, although (as will be shown below) this anation occurs at a rate only $1/300$ th as great as that of the trichloro predecessor. As observed throughout this investigation, there was no evidence of "direct" isomerization—i.e., that involving an internal redistribution of ligands. The figures in Table II show that there is no deviation from simple second-order kinetics over the entire range of chloride concentration and that a small increase in the ionic strength beyond 3.0 M has no discernible effect on the rate constant, as would be expected for bimolecular reaction between charged and uncharged species.

In order to evaluate the rate of aquation of $trans\text{-RhCl}_4(\text{OH}_2)_2^-$ to give the mer -trichloro species, the anation of the latter was studied at 50° and with chloride concentration in the range 0.339-1.03 M. Under these conditions the trichloro \rightleftharpoons tetrachloro reaction becomes an anation-aquation equilibrium analogous to that observed for the pentachloro-hexachloro system.⁵ For the $\log(\epsilon_\infty - \epsilon)$ vs. time plots, one therefore uses the experimentally determined equilibrium value

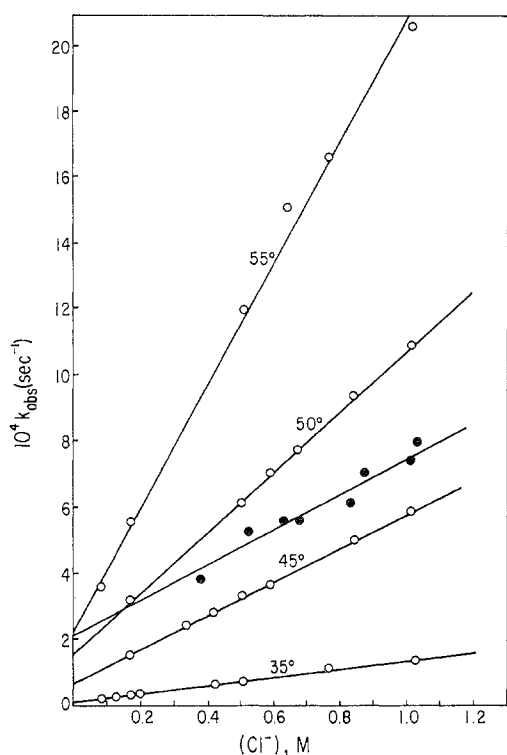


Figure 2. Open circles: dependence of the rate of the *fac*- $\text{RhCl}_3(\text{OH}_2)_3$ to *cis*- $\text{RhCl}_4(\text{OH}_2)_2^-$ "equilibration" on chloride concentration at 35, 45, 50, and 55°. Closed circles: corresponding plot for the *mer*- $\text{RhCl}_3(\text{OH}_2)_3$ to *trans*- $\text{RhCl}_4(\text{OH}_2)_2^-$ equilibration at 50°.

Table III. Reaction Rate Parameters for Chloro-aquorhodium(III) Complex Ions^e

Reactant	ΔH^\ddagger , kcal/mol	ΔS^\ddagger , eu
A. Anation Reactions		
$\text{Rh}(\text{OH}_2)_6^{3+}$	32.8 ± 2.4^a	13 ± 7^a
$\text{RhCl}(\text{OH}_2)_5^{2+}$	28.7 ± 1.2^b	9 ± 4^b
<i>cis</i> - $\text{RhCl}_2(\text{OH}_2)_4^+$	26.9 ± 0.2	8 ± 1
<i>trans</i> - $\text{RhCl}_2(\text{OH}_2)_4^+$	34.2 ± 0.8	13 ± 2
<i>fac</i> - $\text{RhCl}_3(\text{OH}_2)_3$	26.2 ± 0.3	9 ± 1
<i>mer</i> - $\text{RhCl}_3(\text{OH}_2)_3$	28.0 ± 0.5	13 ± 2
<i>cis</i> - $\text{RhCl}_4(\text{OH}_2)_2^-$	21.4 ± 1.5^c	3 ± 5^c
<i>trans</i> - $\text{RhCl}_4(\text{OH}_2)_2^-$	31.6 ± 0.5	36 ± 2
$\text{RhCl}_5(\text{OH}_2)^{2-}$	16.4 ± 1.7^d	-22 ± 5^d
B. Aquation Reactions		
<i>mer</i> - $\text{RhCl}_3(\text{OH}_2)_3$	32.8 ± 0.7	-19 ± 2
<i>cis</i> - $\text{RhCl}_4(\text{OH}_2)_2^-$	30.9 ± 1.5	19 ± 5
$\text{RhCl}_5(\text{OH}_2)^{2-}$	25.1 ± 1.2^c	6 ± 4^c
RhCl_6^{3-}	24.2 ± 4.9^d	10 ± 17^d

^a Reference 2. ^b Reference 3. ^c Reference 4. ^d Reference 5. ^e The rate data from each of the references were recalculated using the least-squares procedure to obtain the various rate parameters given and their standard deviations.

of ϵ_∞ , and the observed rate constants fulfill the relationship $k_{\text{obsd}} = k^{43} + k^{34}[\text{Cl}^-]$. A plot was thus made of k_{obsd} vs. $[\text{Cl}^-]$ (see Figure 2), which yielded from the intercept $k^{43} = 2.1 \times 10^{-4} \text{ sec}^{-1}$ and from the slope $k^{34} = 5.2 \times 10^{-4} \text{ sec}^{-1}$ at 50°. The latter value is satisfactorily consistent with the extrapolated value calculated from the data obtained by the other procedure at 35.0, 43.8, and 48.5° and a chloride concentration of 3.0 M, viz., $4.9 \times 10^{-4} \text{ sec}^{-1}$ (see Table II). The data at all four temperatures were used in evaluating the activation parameters which are presented in Table III. However, due to the uncertainties in the mode of determination of k^{43} , a temperature variation study of this constant was not attempted at this time.

In the temperature range 35–55° and $0.082 M < [\text{Cl}^-] <$

Table IV. Rate Constant Data for Various Reactions of Chloro-aquorhodium(III) Complexes

A. <i>fac</i> - $\text{RhCl}_3(\text{OH}_2)_3 + \text{Cl}^- \rightleftharpoons \text{cis-RhCl}_4(\text{OH}_2)_2^- + \text{H}_2\text{O}$					
Temp, °C	35	45	50	55	
$10^4 k^{c34}$, $M^{-1} \text{ sec}^{-1}$	1.24 ± 0.02	5.11 ± 0.04	9.3 ± 0.2	18.2 ± 0.7	
$10^5 k^{c43}$, sec^{-1}	1.15 ± 0.13	6.7 ± 0.2	14.7 ± 1.3	25 ± 4	
B. <i>trans</i> - $\text{RhCl}_4(\text{OH}_2)_2^- + \text{Cl}^- \rightarrow \text{RhCl}_5(\text{OH}_2)^{2-} + \text{H}_2\text{O}$					
Temp, °C	72.8	81.3	90.9	97.7	
$10^5 k^{45}$, $M^{-1} \text{ sec}^{-1}$	0.49	1.51	5.58	11.1	
C. <i>trans</i> - $\text{RhCl}_2(\text{OH}_2)_4^+ + \text{Cl}^- \rightarrow \text{mer-RhCl}_3(\text{OH}_2)_3 + \text{H}_2\text{O}$					
Temp, °C	72.7	81.3	90.9	97.7	
$10^6 k^{23}$, $M^{-1} \text{ sec}^{-1}$	1.34	4.13	17.9	36.6	
D. <i>cis</i> - $\text{RhCl}_2(\text{OH}_2)_4^+ + \text{Cl}^- \rightleftharpoons \text{mer-RhCl}_3(\text{OH}_2)_3 + \text{H}_2\text{O}$					
Temp, °C	51.3	52.3	61.0	68.9	72.2
$10^4 k^{\text{ct}}$, $M^{-1} \text{ sec}^{-1}$	2.34	2.59	7.55	21.9	28.9
Temp, °C	55.1	60.0	64.3	70.0	
$10^5 k^{\text{ct}}$, sec^{-1}	1.23	2.47	5.10	11.0	

^a Result obtained with $1.5 M < [\text{Cl}^-] < 3.0 M$ (see text).

^b $[\text{Cl}^-] = 3.0 M$. ^c $[\text{Cl}^-] = 0.5 M$. ^d $[\text{Cl}^-] = 0.5 M$. ^e $[\text{Cl}^-]_0 = 0.0$.

1.021 M, the anation of *fac*- $\text{RhCl}_3(\text{OH}_2)_3$ results in an equilibrium mixture of the parent compound together with *cis*- $\text{RhCl}_4(\text{OH}_2)_2^-$, $\text{RhCl}_5(\text{OH}_2)^{2-}$, and RhCl_6^{3-} . The reaction was thus studied as an equilibration, making the absorbance measurements at 397 nm, one of the isobestic points for the tetrachloro-pentachloro product mixture. Again, the observed ϵ_∞ value was employed in plotting the absorbance data, and the observed pseudo-first-order rate constants were plotted as a function of $[\text{Cl}^-]$ at the various temperatures as shown in Figure 2. The derived values for the anation and aquation rate constants according to the relation $k_{\text{obsd}} = k^{c43} + k^{c34}[\text{Cl}^-]$ are given in Table IVA and the corresponding temperature parameters are presented in Table III. A number of runs were also conducted at 50° with chloride concentrations in the range 1.5–3.0 M. Under these conditions, the reaction is effectively unidirectional (less than 1% of the trichloro species remains at equilibrium). Since the product consists almost wholly of pentachloro and hexachloro species, the absorbance measurements were made at 506 nm, an isobestic point for the product mixture. The anation rate constant is derived from the simplified expression $k^{c34} = k_{\text{obsd}}/[\text{Cl}^-]$, and the values obtained at a number of chloride concentrations are shown.

$[\text{Cl}^-], M$	1.50	1.80	2.00	2.40	2.75	3.00	3.00
$10^4 k^{c34}, M^{-1} \text{ sec}^{-1}$	9.76	9.31	9.83	9.40	8.78	9.26	8.92

The average of these values is included in Table IVA and is seen to be in excellent agreement with the value obtained at 50° by the equilibration procedure at lower chloride concentrations.

The anation of *trans*- $\text{RhCl}_4(\text{OH}_2)_2^-$ was studied at 506 nm, an isobestic point for the pentachloro and hexachloro species. The *mer*-trichloro complex was used as the source of the reactant, since under the conditions of these runs (72.8–97.7° and $[\text{Cl}^-] = 3.0 M$) the *mer*-trichloro is converted to *trans*-tetrachloro complex in less than 2 min. The results are given in Table IVB and the temperature variation parameters in Table III. The anation of *trans*- $\text{RhCl}_2(\text{OH}_2)_4^+$ was followed at 375 nm, an isobestic point for *mer*-trichloro and *trans*-tetrachloro complexes. The chloride concentration was 0.5 M, and the temperature parameters and rate constants obtained are given in Tables III and IVC, respectively.

The anation-aquation equilibration between *cis*- $\text{RhCl}_2(\text{OH}_2)_4^+$ and *mer*- $\text{RhCl}_3(\text{OH}_2)_3$ goes practically entirely in the direction of anation in the presence of 0.5 M chloride, and this process was followed at 472 nm. The reverse reaction, the aquation of *mer*- $\text{RhCl}_3(\text{OH}_2)_3$, was followed in the absence of added chloride at 490 nm, the only product being the

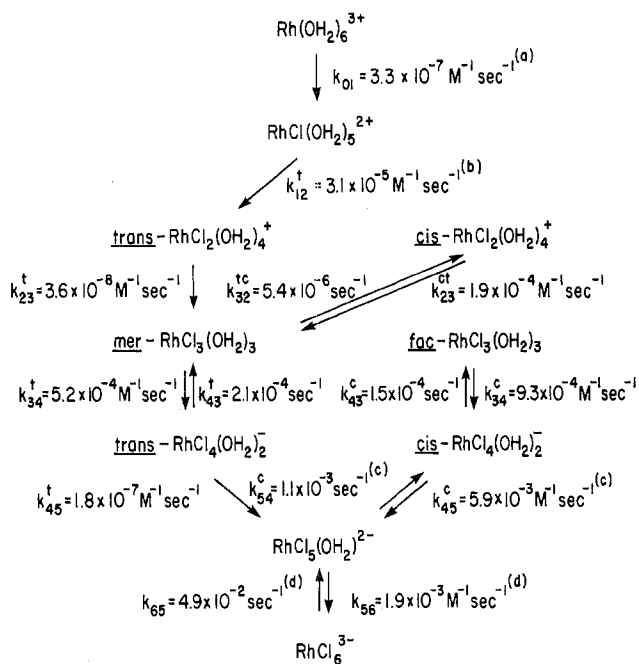


Figure 3. Reaction scheme for the chloroaquorhodium(III) system at 50°: (a) ref 2; (b) ref 3; (c) ref 4; (d) ref 5.

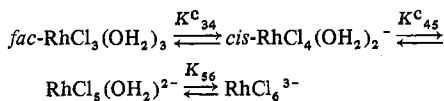
cis-dichloro complex as proven by the development of three clearly defined isobestic points (361, 410, and 445 nm) during the course of the reaction (refer to Figure 1). The anation and aquation rate constants obtained in these runs are recorded in Table IVD and the temperature parameters in Table III.

Discussion

To provide a complete picture of the kinetics and equilibrium data for the chloroaquorhodium system, all the known anation and aquation rate constants (including those previously published) have been extrapolated or interpolated to 50° and are presented in Figure 3. Omitted arrows indicate inobservable reaction paths since their rate constants under the specified conditions are too small to be distinguishable within the 3% experimental uncertainty. The most outstanding feature of these reactions is that their steric course is dictated solely by the trans effect of the chloride ligands on each reactant species. For example, RhCl6³⁻ undergoes stepwise aquation only by the release of chloride trans to another chloride in a short chain of reactions which produces only cis compounds and which ends with the extremely stable complex fac-RhCl₃(OH₂)₃. (The latter shows no tendency to lose additional chloride even when refluxed for several hours.) The steric course of the reverse chain of anations starting with the fac-trichloro complex is likewise determined by the trans effect of the ligand chlorides in labilizing the water ligand replaced by chloride and results in the chain of cis equilibrations illustrated in the figure. Similarly, commencing with the Rh(OH₂)₆³⁺ cation, only anations trans to a chloride ligand occur readily and result (with one exception) in a completely trans series of products. The apparent exception is the mer-RhCl₃(OH₂)₃ to cis-RhCl₂(OH₂)₄⁺ interconversion which is nevertheless also governed by the chloride ligand trans effect. Unlike the cis series mentioned above, most of the trans conversions are unidirectional so that complete thermal equilibration is impossible, although a pseudoequilibrium can be established between trans-tetrachloro, mer-trichloro, and cis-dichloro species because of the very slow (and irreversible) anation of the trans-tetrachloro complex to give the pentachloro complex. These limitations apply, of course, only to strongly acidic solutions such as employed in this work, where only negligible amounts of hydroxo species are present. Otherwise,

a greatly modified steric course pattern is to be expected since hydroxide and chloride ligands have almost identical trans effects, as previously shown³ in the study of chloride anation of RhCl(OH₂)₅²⁺ ion.

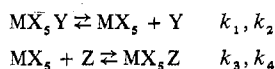
Clearly this type of reaction scheme, with its rigid stereospecificity and its combination of reversible and irreversible steps, makes determination of a consistent set of formation constants for the whole series impossible. It is not surprising therefore that earlier attempts to make such determinations^{7,19} diverge widely, nor do they provide data in agreement with ours for the short true equilibrium series



For this we obtain (at 50°, I = 3.0 M) K^c₃₄ = 6.3, K^c₄₅ = 5.3, and K^s₆ = 0.039, respectively. The scheme also explains the much greater difficulty experienced in preparing the cis-dichloro complex in acidic solutions of Rh(OH₂)₆³⁺ and chloride as compared to the trans isomer.³ It is seen that for the former, a roundabout path is required involving the mer-trichloro ⇌ cis-dichloro equilibration. Also, it is now understandable that nothing but cis products have been observed in studies of chloroaquorhodium(III) complexes where the starting material is the hexachloro species.^{4,15}

It should be noted that the strong trans-labilizing effect of chloride ligand is observed in other chloroaquo transition metal complexes. For example, the reactions of the chloroaquorhenium(III) complexes are largely influenced by this effect though it was not completely dominant. Thus, the aquation of mer-RuCl₃(OH₂)₃ leads to 90% cis- and 10% trans-dichloro product.¹² Similarly, it appears from the published spectral data²⁰ that the sole product of the aquation of IrCl₅(OH₂)₂²⁻ is the cis-tetrachloro isomer. By contrast, the anation of CrCl(OH₂)₅²⁺ by chloride exhibits absolutely no trans-orienting influence though the corresponding iodide does so.²¹ Further, it has been found²² that cis-CrCl₂(OH₂)₄⁺ aquates approximately twice as fast as does its trans analog. It is obvious that the chloride ligand trans effect in chloroaquo complexes is very dependent on the nature of the central metal ion.

We turn now to consideration of the mechanism of the chloroaquorhodium(III) reactions. The interpretation of the data concerning anation by chloride of the hexaaquo and chloropentaaquo cations is complicated by the inevitability of ion pairing of such species with the entering anion, but the evidence tends to favor a clearly dissociative ("five-coordinate intermediate") mechanism.³ Further support of this view comes from a study²³ of the anation of Rh(OH₂)₆³⁺ by bromide ion, which yields a rate constant for the bromide entry which is very little different from that for replacement by chloride under the same conditions. At the other end of the series, chloride exchange with RhCl₆³⁻ and RhCl₅(OH₂)₂²⁻ was found⁵ to occur solely by the aquation path to the exclusion of direct exchange by an associative mechanism. Also, data obtained in the study of the anation of RhCl₅(OH₂)₂²⁻ by a series of nucleophiles⁶ was best interpreted in terms of the conventional dissociative mechanism according to the pattern^{24a} (Y ≡ H₂O, Z ≡ Cl⁻)



The corresponding rate constant expression is given by

$$k_{obsd} = \frac{k_1 k_3 (Z) + k_2 k_4 (Y)}{k_2 (Y) + k_3 (Z)} \quad (1)$$

with k₁ having a constant value independent of the entering nucleophile Z and k₂/k₃ being representative of the substi-

Table V. Catalysis of the Hydration of Acetylene by Chloroaquorhodium(III) Complex Ions

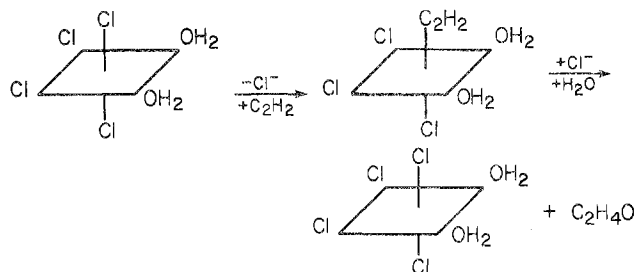
$[\text{Cl}^-], M$	Rate of C_2H_2 uptake, ^a $M \text{ sec}^{-1} \times 10^5$	$[\text{RhCl}_6^{3-}],^b \%$	$[\text{RhCl}_5(\text{OH}_2)^{2-}],^b \%$	$[\text{cis-RhCl}_4(\text{OH}_2)_2]^{-},^b \%$	$[\text{fac-RhCl}_3(\text{OH}_2)_3],^b \%$
3.5	0.38	12	84	5	0
0.2	6.12	0	37	35	28
0.08	4.62	0	13	29	58
0.04	3.42	0	4	19	76
0.025	0	0	1	11	88

^a Taken from ref 28. (Temperature is 60° ; $I = [\text{H}^+] = 6.0 M$; $[\text{C}_2\text{H}_2] \cong 2 \times 10^{-2} M$.) ^b Calculated from our equilibrium constant data at 50° , $I = 3.0 M$.

tutional efficiency of Z relative to the potentially replaceable ligand Y. A definitive argument in favor of this type of mechanism is provided by a recent measurement²⁵ of the volume of activation for the aquation ($Y \equiv \text{Cl}^-$, $Z \equiv \text{H}_2\text{O}$) of RhCl_6^{3-} for which a value of $\Delta V^\ddagger = +23.4 \text{ ml/mol}$ is obtained at 25° . This is to be compared with the figure²⁵ $\Delta V^\ddagger = +22.7 \text{ ml/mol}$ relative to the aquation of $\text{Co}(\text{CN})_5\text{Cl}^{3-}$, the classic example of a purely dissociative mechanism according to the preceding scheme.^{24a} In the present work, the observed rate constants for anation were consistently found to be cleanly second order (see Table II and Figure 2) in contrast to the requirement of eq 1 above. Obviously, the anations of complexes such as either geometrical isomer of the trichloro or tetrachloro species provide examples of not infrequently observed systems^{24b} in which $k_2(Y) \gg k_3(Z)$.

The activation parameters listed in Table III and given in Figure 3 provide an additional basis for discussion of both the trans effect and the mechanism of the various reactions under consideration. One notes that for the anation reactions where no trans chloride is available to labilize the water ligand undergoing replacement—namely, k_{01} , k_{23} , and k_{45} —the rate constants are all within a factor of 10 of one another, showing that there is no major dependence on the charge of the reactant ion. Furthermore, these rates are slower by a factor of at least 100 than any of the other anation rates recorded. As seen in Table III, this factor is almost entirely attributable to higher enthalpies of activation for the three slow anations. These have ΔH^\ddagger values in the range 32–34 kcal/mol, as compared to an average value of about 26 kcal/mol for the other anations (exclusive of that for $\text{RhCl}_5(\text{OH}_2)^{2-}$, which is much lower due to special circumstances to be discussed below). This is in agreement with the concept that the trans effect results from a weakening of the trans σ bond,^{24c} thus lowering the magnitude of ΔH^\ddagger without changing the geometry of the transition state nor resulting in any stereochemical rearrangement during the course of the substitution. The total weight of the evidence presented so far leaves little doubt that the transition state has a square-pyramidal configuration. For this configuration, one might predict that as more chloride ions are coordinated to the central metal ion, considerable distortion of the regular structure results from the increasing electrostatic repulsion. This effect is possibly manifested in the extreme case of $\text{RhCl}_5(\text{OH}_2)^{2-}$, for which ΔS^\ddagger is highly negative (–22 eu) and ΔH^\ddagger is significantly lower than for any of the other steps. The normal situation in these reactions is for ΔS^\ddagger to be positive as a result of decreases in the solvation energy as the transition state is formed. This is noted, for example, in the reverse of the reaction just mentioned, the aquation of RhCl_6^{3-} , where the highly symmetrical triply negative reactant is undergoing conversion to a somewhat distorted doubly negative ion and a small singly negative ion. A similar situation is found in the aquation of *cis*- $\text{RhCl}_4(\text{OH}_2)_2^-$, where a large negative ion undergoes conversion to a large uncharged species and a small negative ion and ΔS^\ddagger is strongly positive. By contrast, the aquation of *mer*- $\text{RhCl}_3(\text{OH}_2)_3$, a reaction in which an uncharged reactant is converted into ionic products, has a highly negative ΔS^\ddagger consistent with a greatly increased solvation energy.

Finally, it is of interest to relate our findings concerning the composition of equilibrated chloroaquorhodium(III) systems to a number of observations in the literature concerning these species as catalysts. Unfortunately, much of the research on catalysis by “rhodium chloride” has employed the conventional commercial product $\text{RhCl}_3 \cdot 3\text{H}_2\text{O}$. This compound becomes of rather indefinite composition when dissolved in water since it undergoes a series of aquations and anations to yield a mixture of chloroaquorhodium(III) species.²⁶ There is also evidence of the presence of polymeric species in such systems.²⁷ However, one catalytic study in which particular attention was paid to the actual composition of the chloroaquorhodium(III) complex deals with the hydration of acetylene in strongly acidic solution.²⁸ The catalytic effect is appreciable for chloride concentrations in the range 0.04–3.5 M but is negligible beyond these limits in either direction, and there was no evidence for the presence of rhodium in lower oxidation states. In Table V, the concentrations of the relevant rhodium(III) complexes as calculated from our equilibrium data for suitably aged solutions (see above for values of K_{34} , K_{45} , and K_{56} at 50° and $I = 3.0 M$) are given at the chloride concentrations used in the catalysis study²⁸ and compared with the reported rates of acetylene uptake.²⁹ This comparison indicates that the pentachloro and *fac*-trichloro species are inactive but that there is a fair degree of parallelism between our estimates of the relative amount of *cis*-tetrachloro complex and the catalytic activity, allowing for undoubted discrepancies between our calculated product distribution and the true state of affairs in the catalysis experiments. This parallelism is contrary to James and Rempel's²⁸ conclusion that $\text{RhCl}_5(\text{OH}_2)^{2-}$ is the preeminently active species but is still consistent with their view that a π complex is formed between C_2H_2 and the Rh(III) center in such a way as to place a water ligand *cis* to the acetylene in the “active intermediate”. However, the expected “active intermediate” to be obtained by replacement of chloride by acetylene in $\text{RhCl}_5(\text{OH}_2)^{2-}$ or one ligand water by acetylene in $\text{RhCl}_4(\text{OH}_2)_2^-$ is apparently either not formed or is ineffective for acetylene hydration. The only effective path would seem to be that in which acetylene reversibly replaces chloride in $\text{RhCl}_4(\text{OH}_2)_2^-$ according to the scheme



An alternative reaction path involving replacement of water by acetylene in $\text{RhCl}_3(\text{OH}_2)_3$ obviously does not contribute, perhaps because negative charge on the rhodium complex is necessary for acetylene π -complex formation to occur.

It is interesting that the limitations involving aquo ligand stereochemistry mentioned above do not seem to play a part in the catalytic activation of molecular hydrogen as reported

in an earlier study by the same authors,³⁰ where it is found that RhCl_6^{3-} is more active than either the pentachloro or the tetrachloro congeners. However, the mechanism of this process appears to be quite different from that discussed above in that it requires direct replacement of chloride ligand by H^- derived from the heterolytic splitting of H_2 in the first step of the reaction, as proposed in previous studies of hydrogen activation by chlororhodium(III) complexes.^{31,32} It is of interest in this connection that the activation parameters for this kind of process are given as³¹ $\Delta H^\ddagger = 24.5$ kcal/mol, $\Delta S^\ddagger = 9$ eu, and (at 80°) $k = 0.63 M^{-1} \text{sec}^{-1}$, which agree rather well with the published parameters⁵ for the aquation of RhCl_6^{3-} . It should be mentioned in conclusion that some recent studies³³ indicate a close relationship between the catalyzed oxidation of ethylene by chloroaquorhodium(III) complexes in the presence of Fe(III) and the rates of aquation of Rh(III) species. However, since much of the work was carried out at low acidity, the situation is complicated by the presence of hydroxorhodium(III) complexes, nor were activation parameters determined. We therefore are unable to add anything further to the discussion of this system beyond the relationships already pointed out by the authors.

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Registry No. $\text{Rh(OH}_2)_6^{3+}$, 16920-31-3; $\text{RhCl(OH}_2)_5^{2+}$, 15696-62-5; *trans*- $\text{RhCl}_2(\text{OH}_2)_4^+$, 37498-47-8; *mer*- $\text{RhCl}_3(\text{OH}_2)_3$, 54630-78-3; *trans*- $\text{RhCl}_4(\text{OH}_2)_2^-$, 48019-53-0; $\text{RhCl}_5(\text{OH}_2)_2^-$, 15276-84-3; RhCl_6^{3-} , 21412-00-0; *cis*- $\text{RhCl}_4(\text{OH}_2)_2^-$, 54595-35-6; *fac*- $\text{RhCl}_3(\text{OH}_2)_3$, 54595-36-7; *cis*- $\text{RhCl}_2(\text{OH}_2)_4^+$, 37498-46-7; Cl^- , 16887-00-6; C_2H_2 , 74-86-2.

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- (17) The rate constants obtained are symbolized throughout this paper in the form $k_{r,mn}$. When r is given as a single letter, it refers to the geometry of both the reacting and product species ($r = c$ or t for *cis* (*fac*) or *trans* (*mer*)). In the two cases where isomerization occurs, $r = tc$ or ct , indicating *trans* \rightarrow *cis* or *cis* \rightarrow *trans* changes. The subscripts *mn* are numerals defining the number of Cl^- ions in reactant and product species, respectively.
- (18) It was impossible to titrate either *cis*- or *trans*- $\text{RhCl}_4(\text{OH}_2)_2^-$ due to the relatively rapid rate at which these ions undergo base hydrolysis. Attempts to titrate *mer*- $\text{RhCl}_3(\text{OH}_2)_3$ in $3 M \text{NaNO}_3$ were frustrated by a rapid spontaneous decrease in pH above pH 3. In $3 M \text{NaCl}$, this effect was not observed, again substantiating the relatively strong nucleophilicity of nitrate ion for complexes of this type (see ref 11).
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