22537-29-7; Mg^{2+}, 22537-22-0; Al^{3+}, 22537-23-1; Ca^{2+}, 14127-61-8; F^-, 16984-48-8; OH^-, 14280-30-9; NH_3, 7664-41-7; Cl^-, 16887-00-6; Br^-, 24959-67-9; I^-, 20461-54-5; $S{=}C(NH_2)_2$, 62-56-6; PPh_3, 603-35-0; CN^-, 57-12-5; $(C_6H_5)_2P(C_6H_4\text{-}SO_3^-)$, 65355-51-3; $As(C_6H_4\text{-}SO_3^-)_3$, 65355-50-2; $HO(CH_2)_2S(CH_2)_2OH$, 111-48-8; py, 110-86-1; CH_3COO^-, 71-50-1; SCN^-, 1111-68-8; glycine, 56-40-6; NTA, 139-13-9; EDDA, 5657-17-0; DTMA, 55682-22-9; HEDTRA, 150-39-0; EDTA, 60-00-4.

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Anation of Aquopentaamminerhodium(III) Cation by Chloride in Aqueous Solution. A Low, Variable Ionic Strength Approach for Studying Anation Reactions

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The high, constant ionic strength conditions conventionally employed in studying the kinetics of anation reactions yield data which have inherent interpretational shortcomings. Notably, pure rate and equilibrium constants cannot be extracted from such data. This paper reports the study of the Cl^- anation of $Rh(NH_3)_5H_2O^{3+}$ by a low, variable ionic strength approach which overcomes these shortcomings. The kinetics of the anation reaction were studied at 40–70 °C with $\mu \leq 0.3$ M, 0.01 $< [Cl^-] <$ 0.3 M, and $[H^+] = 0.01$ M. The ion pairing of the reactants was also studied spectrophotometrically at 15–40 °C and potentiometrically at 25 °C under similar concentration conditions. The data from these three types of experiments were fitted to various models using the Davies equation with an adjustable parameter b to correct for activity coefficient variations. The results confirm an interchange mechanism for the anation reaction. The zero ionic strength ion-pair association constant $K^\circ_{Cl^-}$ as well as the b parameter are temperature independent. The interchange rate k°_I has $\Delta H^\ddagger = 26.2$ kcal/mol and $\Delta S^\ddagger = 3.3$ cal/(deg mol). Experiments with significant amounts of ClO_4^- present show that it also pairs to the complex to such an extent that $K^\circ_{ClO_4^-} \approx K^\circ_{Cl^-}$. All three types of data can be fitted to a model having $K^\circ_{Cl^-} = 26.5 \pm 0.8$ M^{-1} and $b = 0.91 \pm 0.05$. Comparisons of k°_I values with rates of water exchange suggest that bond making is less important with this Rh(III) complex than with other presumably associatively activated metal complexes. Remaining ambiguities regarding the mechanism of the reaction are discussed.

Introduction

The conventional approach for studying the anation kinetics of octahedral transition-metal complexes in aqueous solution is to maintain the medium at a high constant ionic strength by the addition of substitutionally inert salts such as $NaClO_4$.[1,2] It has been pointed out, however, that data obtained under such conditions have two serious interpretational shortcomings when used to obtain mechanistic information.[1,3,4] This paper reports the study of the anation reaction

$$Rh(NH_3)_5H_2O^{3+} + Cl^- \rightarrow Rh(NH_3)_5Cl^{2+} + H_2O \qquad (1)$$

by a low, variable ionic strength approach which appears to overcome these problems to a substantial degree.

The high, constant ionic strength condition is usually employed in order to maintain a constant value for the activity coefficients of the reactants. However, it is almost certain that activity coefficients are not constant in such studies. There are abundant data on simple salt mixtures that show that the activity coefficients do vary as the relative amounts of two salts are varied at constant ionic strengths above about 0.3 M.[5] Thus the common practice of interpreting rate data from constant ionic strength studies of anation reactions solely in terms of a stoichiometric mechanism is seriously open to question. A part or all of the rate characteristics used to support a certain mechanism could be due simply to activity coefficient variations. Unfortunately, there are no reliable methods for estimating the magnitude of such variations for these anating systems.[3]

The second interpretational problelm is that pure rate and equilibrium constants cannot be extracted from such data if a component of the inert salt (i.e., ClO_4^-) ion pairs to the complex ion. As an example consider a reaction judged to proceed by an ion-pair interchange mechanism.[2] If ClO_4^- ion pairs to an extent comparable to that of the attacking anion X^-, kinetic and thermodynamic data can only yield the composite constants[1,3]

$$k_{calcd} = k_I K_X/(K_X - K_P)$$
$$K_{calcd} = (K_X - K_P)/(1 + K_P \mu)$$

(K_X and K_P are the concentration quotients for the ion pairing of X^- and ClO_4^-, respectively, to the complex, μ is the ionic strength and k_I is the rate constant for the interchange of the X^- ion-paired complex.) It can be seen that insight into the factors controlling reactivity cannot be gained from such parameters. Comparing k_{calcd} and/or K_{calcd} values for a series of systems is a fruitless exercise since one cannot determine

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which of the pure constants (k_I, K_X, or K_P) is causing the observed variation. There is a fair body of evidence which indicates that ClO_4^- does ion pair to cationic complexes to about the same extent as do other univalent anions.[4,6]

Burnett[4] attempted to overcome these problems by making reasoned assumptions as to the values of activity coefficients and ion-pairing constants; however, the mechanistic conclusions reached using these assumptions have been criticized.[7] The approach taken in the present work is to employ the conditions and the variety of measurements which will allow such parameters to be directly determined. The approach requires appreciable computer-assisted data fitting.

The general characteristics of the low, variable ionic strength approach are as follows: (1) Kinetic and thermodynamic studies are conducted on solutions where the only anion of substantial concentration is the reactive anion. No inert salts are added. (2) The total ionic strength of the solutions does not exceed 0.3 M. This limit allows one to employ eq 2 to

$$-\log \gamma_i = Z_i^2 A \left[\frac{\mu^{1/2}}{1 + \mu^{1/2}} - d\mu\right] \qquad (2)$$

determine activity coefficients. (In the equation γ_i represents the activity coefficient of the ith ion; Z_i, its charge; A, the Debye–Hückel temperature coefficient; μ, the ionic strength; and d, an empirically determined constant.) Davies[8] has shown that eq 2 with $d = 0.3$ successfully predicts activity coefficients for 1:1 and some 2:1 electrolytes up to $\mu = 0.3$ M. In the present work d is treated as an unknown, fitted parameter because of the complexity and high charge of the ions employed. (3) Fundamental constants for the system are determined by several independent means for comparative purposes. Adding d of eq 2 to the list of parameters to be fitted to a set of data should push most measurements to the limits of their ability to yield meaningful parameter values. For this reason, it is necessary to measure some constants for the system by several independent means in order to obtain a reliable definition of their values.

In the present work three types of measurements are made on the anating system: kinetic, spectrophotometric ion-pair, and potentiometric ion-pair measurements. If ion-pairing between the reactants exists to a measurable extent, each set of data should depend in some way both on the thermodynamic ion-pairing constant $K°_X$ and on a composite of d parameters for the accompanying activity ratio $\gamma_{3+}\gamma_{1-}/\gamma_{2+}$. Thus the feasibility of the low, variable ionic strength approach is to be judged by whether the three sets of data can be fitted to the same values of $K°_X$ and the composite d parameter and by whether these values are well defined.

The reaction symbolized in eq 1 was chosen for this investigation of the experimental approach because several studies[3,9,10] using conventional constant ionic strength conditions indicate that it has some useful features. The reaction appears to go cleanly to completion, and the rate is independent of proton concentrations at acidic pHs and is slow enough to allow ion pairing between the reactants to be studied without interference by product formation. Furthermore, the weight of the evidence to date does support an interchange mechanism[2] for the reaction.

Experimental Section

Materials. Deionized water with a specific resistance greater than 100 MΩ was used in all experiments. Stock solutions of HCl, NaCl, $HClO_4$, NaOH, and $AgClO_4$ were prepared and standardized as reported previously.[1] Solid $[Rh(NH_3)_5Cl]Cl_2$ was prepared by the published method.[11] Aqueous solutions of the complex show a spectrum having maxima or minima at 348, 308, 276, and 248 nm with molar absorptivities of 102, 75, 110, and 46 M^{-1} cm^{-1}, respectively. Solid $[Rh(NH_3)_5H_2O](ClO_4)_3$ was prepared from $Rh(NH_3)_5Cl^{2+}$ in a manner analogous to that used to prepare *trans*-$Rh(en)_2(H_2O)_2^{3+}$ from its dichloro precursor.[1] As judged by elemental analysis and UV spectra, the salt prepared in this manner requires at least two recrystallizations from water for purification. Anal. Calcd for $[Rh(NH_3)_5H_2O](ClO_4)_3$: N, 13.9; Cl, 21.2. Found: N, 13.7; Cl, 21.3. Acidic aqueous solutions of the complex show maxima or minima at 315, 284, 261, and 228 nm with molar absorptivities of 106, 70, 93, and 26 M^{-1} cm^{-1}, respectively. The spectra of $Rh(NH_3)_5H_2O^{3+}$ and $Rh(NH_3)_5Cl^{2+}$ show isobestic points at 332, 296, 265, and 241 nm with molar absorptivities of 89, 82, 92, and 49 M^{-1} cm^{-1}, respectively. Solid $[Co(NH_3)_6]Cl_3$ was prepared by the published method[12] and purified by recrystallization. The salt was analyzed for Cl^- content by potentiometric Ag^+ titrations. The results indicated that the salt had a 1.7 ± 0.3% impurity which was presumed to be waters of crystallization since repeated recrystallizations did not alter the result.

Spectral Ion-Pairing Measurements. These experiments monitored the effect of added Cl^- on the charge-transfer spectrum of $Rh(NH_3)_5H_2O^{3+}$. As the maximum in the charge-transfer spectrum occurs below 180 nm, these spectral measurements were conducted on the steep, high-wavelength slope of the band (at 208 nm). Working solutions were prepared using $[Rh(NH_3)_5H_2O](ClO_4)_3$ solid and stock solutions of HCl, NaCl, and/or $HClO_4$. Aliquots of these solutions were placed in a cuvette in the thermostated cell compartment of the spectrophotometer and their absorbances recorded. All working solutions had $[Rh(NH_3)_5H_2O^{3+}] \leq 0.002$ M and $[H^+] \geq 0.01$ M to keep the complex from dissociating a water proton.[9a] Solutions with complex salt and 0.01 M $HClO_4$ were used to establish the molar absorptivity of the free complex ion as 60 M^{-1} cm^{-1} at all temperatures. (Extrapolation of the complex plus Cl^- solution absorbances to $[Cl^-] = 0$ confirmed this number.) Solutions used to establish the ion pairing of Cl^- to the complex had $0.01 \leq [Cl^-] \leq 0.3$ M with no added $HClO_4$. The absorbances of these solutions had to be corrected for the absorbance of aqueous Cl^- which was appreciable under the conditions used. The absorbances of a series of HCl/NaCl solutions were measured just prior to the work with the complex solutions to establish a correction curve. The data gave good Beer's law plots yielding Cl^- extinction coefficients (in M^{-1} cm^{-1}) of 0.283 at 15 °C, 0.478 and 0.540 at 25 °C (two separate runs), and 1.047 at 40 °C. Apparently then, the absorbance of Cl^- is very temperature sensitive.

Potentiometric Ion-Pairing Measurements. The measuring system consisted of an Accumet 420 pH/ion meter operated in the expanded (0.1 mV) mode, a Fisher pH glass electrode, and an Orion solid-state Cl^- electrode. The glass electrode was connected to the normal sensing terminal of the meter while the Cl^- electrode was attached, through a shielding connection, to the reference terminal. Thus the system measured the HCl activity of a solution. The experimental procedure was as follows. A known amount of standardized HCl solution was placed in a thermostated cell, the electrodes were inserted, the stirred solution was allowed to thermally equilibrate, and the millivolt reading was recorded. The solution was then titrated with a second HCl solution, readings being recorded after each addition. These data establish a standard curve of millivolts vs. HCl activity. Amounts of the complex salt being studied were then added to the titrated HCl solution and millivolt readings recorded after each addition. These data were analyzed for the extent of ion pairing between the complex cation and Cl^-. The readings required 1–2 min to stabilize after each addition but then varied by no more than ±0.1 mV over the next 5 min. It required about 100 min to take five to eight standardization points and four to seven complex solution readings. To monitor the drift of the meter during this time period, millivolt readings were periodically taken of another thermostated HCl solution. Normal meter drift was about 0.2 mV every 30 min.

An average standardization run had [HCl] going from 0.006 to 0.027 M giving readings that varied over about 45 mV. Standard curves of E vs. $\log \gamma_1^2[H^+][Cl^-]$ were constructed from the known HCl concentration and γ_1 values computed from eq 2 taking $d = 0.3$ and $\mu = [HCl]$. These plots formed good straight lines with slopes (i.e., 60.0 mV at 25 °C) in good agreement with Nernst values. The average deviation of the standardization data points from the best fit straight line was less than 1% in HCl activty units (0.1–0.2 mV). The ion pairing of Cl^- to $Rh(NH_3)_5H_2O^{3+}$ was studied by adding solid $[Rh(NH_3)_5H_2O](ClO_4)_3$ to the HCl solution in such amounts that the complex cation and Cl^- were of comparable concentrations. This procedure introduces a great deal of ClO_4^- into the solution which complicates the data analysis since ion pairing of the complex to both anions must be considered. Attempts to circumvent the problem by preparing $[Rh(NH_3)_5H_2O]Cl_3$ in either the solid or solution phase proved fruitless. The chloride salt is extremely soluble and crystallization of it could not be achieved with any reproducibility. Pale yellow crystals that did form converted within hours at room temperature to the darker yellow $[Rh(NH_3)_5Cl]Cl_2$ compound. Experiments were run to replace ClO_4^- with Cl^- by passing acidic solutions of $[Rh(NH_3)_5H_2O](ClO_4)_3$ through a column of AG1-X4 resin in the Cl^- form. The potentiometric behavior of the resulting solutions was inconsistent with their analytical results. Presumably some resin material was being released into the solutions and was affecting the H^+ activity.

Experiments using $[Co(NH_3)_6]Cl_3$ as the complex salt were run to test the reliability of this potentiometric procedure. Four separate experiments totaling 16 different complex solutions with concentrations ranging from 0.011 to 0.044 M were run. The decrease in HCl activity of these solutions from that expected for completely dissociated ions was attributed to ion pairing between $Co(NH_3)_6^{3+}$ and Cl^-. Analysis of the data (see Results for details) gave the thermodynamic ion-pair association constant as 36 ± 9 M^{-1} and the composite activity coefficient parameter (b of eq 7) as 1.1 ± 0.2. The $K°_X$ value is in good agreement with those obtained[13] from conductance measurements, 31 and 35 M^{-1}.

Kinetic Measurements. The rate of formation of the $Rh(NH_3)_5Cl^{2+}$ complex was studied using the batch technique described previously.[1] All rate data were collected on solutions having $[H^+] = 0.01$ M with the $[Cl^-]$ varying from 0.01 to 0.30 M. Where $[Cl^-] \gtrsim 0.1$ M, $[Rh(NH_3)_5H_2O](ClO_4)_3$ was added to a concentration of about 1.7×10^{-3} M; where $[Cl^-] \lesssim 0.1$ M, the complex was added to a concentration of 3.5×10^{-4} M. Thus only the complex concentration will be appreciably altered and ion pairing by ClO_4^- will be insignificant in each run. The progress of the reaction was monitored spectrally, 5-cm cells being used when the complex concentration was 3.5×10^{-4} M. Under all conditions of the study the reaction solutions exhibited the isosbestic points expected for a conversion of $Rh(NH_3)_5H_2O^{3+}$ to $Rh(NH_3)_5Cl^{2+}$. Pseudo-first-order rate constants k_{obsd} for the disappearance of the aquo complex were obtained from the slope of $\ln(A_\infty - A_t)$ vs. time plots. A_∞ is the calculated absorbance of the solution at 348 nm for the case where all of the aquo complex has been converted to the chloro form, and A_t is the actual absorbance of the solution at 348 nm at time t. These plots showed first-order behavior over at least 2 half-times of the reaction under all conditions studied. The completeness of the reaction at low Cl^- concentrations (0.01–0.02 M) was confirmed. The spectra of reaction mixtures eventually attain an A_∞ that is 98% of that expected, indicating a 95% reaction completion. Solutions with $[Rh(NH_3)_5H_2O^{3+}] = 0.005$ M and $[Cl^-] = 0.015$ M were monitored by Cl^- titration. The results indicate that eventually 97% of the aquo complex is converted to chloro complex.

All spectral data in this study were obtained using a Cary 118C visible–ultraviolet spectrophotometer. Temperature control in the experiments was ±0.05 °C. The kinetic results indicate that no significant formation of $Rh(NH_3)_5Cl^{2+}$ would occur during the times involved in obtaining the potentiometric and spectral ion-pairing data.

Results

Data gathered from the three types of measurements on the interaction of $Rh(NH_3)_5H_2O^{3+}$ with Cl^- in aqueous solution are presented and discussed below. The symbolism employed has $ML_5 = Rh(NH_3)_5$, $X = Cl^-$, $P = ClO_4^-$, and the various species have been symbolized without charge to further simplify the presentation. Each set of data are computer fitted[1] to various models, most of which include the outer-sphere ion pairing of the reactants

$$ML_5H_2O + X \rightleftharpoons ML_5H_2O{\cdot}X \tag{3}$$

Such ion pairing will be assumed to be rapidly established and governed at all times by the equilibrium expression

$$K°_X \left[\frac{\gamma_3\gamma_1}{\gamma_2}\right] = \frac{[ML_5H_2O{\cdot}X]}{[ML_5H_2O][X]} \tag{4}$$

where the activity coefficient term is evaluated using the Davies equation, eq 2. Thus it is assumed that the activity of a species (even a kinetic transition-state complex) depends only on the magnitude of its charge and on the ionic strength of the solution. In several experiments the ion pairing of the complex cation to ClO_4^- is investigated by competition-type techniques. The symbol $K°_P$ represents the thermodynamic constant for this association, i.e., as defined by replacing X in eq 3 and 4 by P. The predominant activity function encountered in the fitting models is that shown in eq 4; thus the following definitions are employed to simplify the data analyses and its presentation:

Table I. Representative Set of Potentiometric Data at 25 °C

$[HX_t]$, M	$[M_t]$, M	$\gamma_1^2[X]$[a] Exptl	Calcn 1	Calcn 2	Calcn 3
0.019 14	0.006 93	0.0120	0.0125	0.0119	0.0121
0.019 14	0.014 36	0.0108	0.0116	0.0107	0.0109
0.019 14	0.022 28	0.0100	0.0110	0.0100	0.0101
0.026 87	0.006 80	0.0162	0.0173	0.0166	0.0168
0.026 87	0.014 06	0.0152	0.0161	0.0151	0.0152
0.026 87	0.021 34	0.0140	0.0154	0.0141	0.0142
0.034 99	0.003 25	0.0231	0.0233	0.0228	0.0230
0.034 99	0.012 00	0.0198	0.0211	0.0200	0.0202
0.034 99	0.021 08	0.0186	0.0200	0.0184	0.0185

[a] Calculations made using the following parameter values: calculation 1, $K°_X = K°_P = 0$; calculation 2, $K°_X = 73$ M^{-1}, $K°_P = 96$ M^{-1}, $b = 0.3$; calculation 3, $K°_X = K°_P = 26.5$ M^{-1}, $b = 0.9$.

$$G = \gamma_3\gamma_1/\gamma_2 \tag{5}$$

$$-\log G = 6A\left[\frac{\mu^{1/2}}{1 + \mu^{1/2}} - b\mu\right] \tag{6}$$

In eq 6 A and μ have the meanings assigned to them in eq 2, while b, a fitted parameter, is a composite of the Davies parameters d for the variously charged species:

$$b = [9d_3 + d_1 - 4d_2]/6 \tag{7}$$

Potentiometric Ion-Pairing Data. The activity of hydrochloric acid was measured potentiometrically at 25 °C in 17 solutions containing HX and $[ML_5H_2O](ClO_4)_3$. Data on a representative set of these solutions are given in Table I. The first column gives the total concentration of hydrochloric acid added to the solution; the second column, the total concentration of aquo complex salt. The remaining columns report experimental and calculated values of the activity function $\gamma_1^2[X]$, the result of dividing the measured HX activity by the known $[H^+]$.

The values of $\gamma_1^2[X]$ in the fourth column were calculated assuming that no ion pairing occurred in solution (e.g., assuming $[X] = [HX_t]$, $\mu = [HX_t] + 6[M_t]$, $d = 0.3$ for γ_1). It can be seen that these calculated values are consistently higher than the experimental values. The average deviation between the two sets is better than 6%. Since the standardization data (see Experimental Section) indicate that the system should give activity measurements to a reproducibility of 1%, this simple, insignificant ion-pair model must be rejected. (In this test model and in subsequent work the statistical F test[14] was used to judge the models.) Thus the potentiometric data demand that some complicating effect such as ion pairing be invoked.

The potentiometric data were computer fitted to a model which assumed measurable ion pairing to the complex by both chloride and perchlorate. It was assumed that formation of ion pairs caused a decrease in μ, [X], and [P]. Because $[HX_t]$ and $[M_t]$ are of the same order of magnitude in these experiments, determining $\gamma_1^2[X]$ (calculated) for each data point requires an iterative-type calculation. The calculation that appears to give the quickest and smoothest convergence is the following double-iterative method. Trial values of $K°_X$, $K°_P$,

Table II. Charge-Transfer Absorbance Data at 25 °C[a]

[X], M	Absorbance[b] Exptl	Calcn 1	Calcn 2	Calcn 3
0.0120	0.080	0.085	0.084	0.090
0.0440	0.119	0.120	0.121	0.130
0.0760	0.150	0.144	0.145	0.155
0.108	0.160	0.164	0.165	0.174
0.140	0.188	0.183	0.183	0.191
0.172	0.194	0.200	0.199	0.206
0.204	0.215	0.217	0.215	0.219
0.236	0.238	0.233	0.232	0.230
0.268	0.249	0.249	0.249	0.240
0.300	0.263	0.264	0.266	0.248

[a] Set 1, λ 208 nm, $[ML_5H_2O] = 0.0009\,93$ M, $[H^+] = 0.01$ M. [b] Calculations made using the following parameter values: calculation 1, $K^\circ_X = 13.8$ M^{-1}, $b = 0.7$, $\epsilon_{IP}K^\circ_X = 5640$ cm^{-1} M^{-2}; calculation 2, $K^\circ_X = 0$, $b = 0.3$, $\epsilon_{IP}K^\circ_X = 4650$ cm^{-1} M^{-2}; calculation 3, $K^\circ_X = 26.5$ M^{-1}, $b = 0.9$, $\epsilon_{IP}K^\circ_X = 7700$ cm^{-1} M^{-2}.

Table III. Various Fits of Spectral Data to Eq 10

Fit no.	Data fitted	K°_X, M^{-1}	b	$10^{-3}\epsilon_{IP}K^\circ_X$, cm^{-1} M^{-2}	SD, absorb unit
1	15 °C	7 ± 19	0.5 ± 0.6	3.3 ± 1.3	0.004
2	25 °C (1)	14 ± 5	0.7 ± 0.3	5.6 ± 0.3	0.005
3	25 °C (2)	2 ± 19	0.2 ± 0.2	5.8 ± 2.3	0.012
4	40 °C	8 ± 43	0.4 ± 0.8	8.0 ± 3.9	0.014
5	All	20 ± 7	1.3 ± 0.7	5.9 ± 2.5	0.054
6	All	16 ± 2	Varied[a,b]	6.9 ± 0.5	0.016
7	All	Varied[a,c]	0.3 ± 0.1	1.1 ± 0.9[a,e]	0.013
8	All	9 ± 2	0.4 ± 0.4	Varied[a,d]	0.010

[a] Values of varied parameters are at 15, 25, and 40 °C, respectively. [b] $b = 0.1, 0.5, 1.0$ (±0.1). [c] $K^\circ_X = 3.4, 4.9, 7.8$ ($\Delta H^\circ = 1.5 \pm 0.2$ kcal/mol, $\Delta S^\circ = 5.8 \pm 1.2$ cal/(mol deg)). [d] $10^{-3}\epsilon_{IP}K^\circ_X = 3.9, 6.0, 8.3$ (±1.6). [e] Value reported is for $10^{-3}\epsilon_{IP}$ cm^{-1} M^{-1}.

and b were assumed by the fitting program. In the first calculation G was calculated by taking $\mu = [HX_t] + 6[M_t]$. The concentration of free aquo complex, [R], was calculated by iterating through the equation

$$[R] = \frac{[M_t]}{1 + \left[\dfrac{K^\circ_X G[X_t]}{1 + K^\circ_X G[R]}\right] + \left[\dfrac{K^\circ_P G[P_t]}{1 + K^\circ_P G[R]}\right]} \tag{8}$$

taking [R] on the right-hand side equal to $[M_t]$ on the first pass. ($[X_t]$ and $[P_t]$ are the total concentrations of chloride and perchlorate, respectively.) The [R] was then used to calculate the concentration of other species in solution using equations such as

$$[ML_5H_2O\cdot X] = K^\circ_X G[X_t][R]/(1 + K^\circ_X G[R]) \tag{9}$$

A new value for μ was then calculated and the iteration through eq 8 begun again. This was continued until successive values of μ agreed to within 0.01%. The values of μ and [X] so generated were then used to calculate $\gamma_1{}^2[X]$ ($d = 0.3$ for eq 2).

Computer fitting gave as best fit values of the potentiometric parameters $K^\circ_X = 73 \pm 38$ M^{-1}, $K^\circ_P = 96 \pm 88$ M^{-1}, and $b = 0.3 \pm 0.4$. Values of $\gamma_1{}^2[X]$ calculated with these parameters are given in the fifth column of Table I. It can be seen that the agreement between calculated and experimental values is much better in this case, all 17 data points giving a reasonable standard deviation of ±1%. Unfortunately, the large standard deviations of the parameters indicate that the data are being overfitted by having three adjustable parameters. Thus the potentiometric data, by themselves, establish that measurable ion pairing is occurring in the system but do not yield well-defined values for the parameters.

Spectral Ion-Pairing Data. Studies of the effect of chloride on the absorbance in the charge-transfer region of the aquo complex spectrum were conducted at 15, 25 (two separate experiments), and 40 °C. The data for one of the 25 °C experiments are shown in Table II. The experimental absorbances given in the second column have been corrected for the background absorbance of aqueous Cl^- (see Experimental Section). The usual assumption was made in analyzing the data: that the X ion-paired form of the complex has a higher molar absorptivity than the free complex and that the increase in absorbance with [X] is due to the mass-action shifting of the equilibrium in eq 3 to the right.

The absorbance vs. [X] data were first analyzed according to eq 10, where Abs is the corrected absorbance of the solution; $[M_t]$, its total concentration of complex; ϵ_M, the molar absorptivity of the free complex; and ϵ_{IP}, the molar absorptivity of the X ion-paired complex. ϵ_M was taken as 60 cm^{-1} M^{-1} (see Experimental Section). ϵ_{IP}, K°_X, and b of the G term were determined by computer fitting the data to eq 10 assuming that each absorbance reading had a constant absolute uncertainty. The best fit values of the parameters are $K^\circ_X = 13.8 \pm 4.9$ M^{-1}, $b = 0.68 \pm 0.27$, and $\epsilon_{IP}K^\circ_X = 5640 \pm 330$ cm^{-1} M^{-2}. The absorbance values in the third column of Table II were calculated from eq 10 using these values. It can be seen that the fit is reasonable giving a standard deviation of ±0.005 absorbance unit for the data points.

$$Abs/[M_t] = (\epsilon_M + \epsilon_{IP}K^\circ_X G[X])/(1 + K^\circ_X G[X]) \tag{10}$$

These data were also fitted to a model which assumes that ion pairs exist but to such a small extent that K°_X cannot be measured. The equation used was eq 10 with a denominator of 1.0. Mathematically the assumption was that $K^\circ_X G[X] << 1$. The best fit values obtained were $b = 0.28 \pm 0.02$ and $\epsilon_{IP}K^\circ_X = 4650 \pm 170$ cm^{-1} M^{-2}. The absorbance values in the fourth column of Table II were calculated using these parameters. It can be seen that a reasonable fit is again obtained since the standard deviation is ±0.005. Thus these data, by themselves, cannot eliminate the possibility that K°_X is too small to be measured. The problem is that the data are being overfitted with the number of parameters used. (The absorbance values in the last column of Table II were calculated using parameters from a combination fit of all data collected and will be discussed later.)

Table III lists the parameters generated by various fits of the spectral data to eq 10. Fit numbers 1–4 give the results of fitting the individual sets of data collected. The standard deviations of the fits, given in the last column, range from ±0.004 to ±0.014. For comparative purposes it will be assumed that a reasonable standard deviation is ±0.012 absorbance unit. This high value can be rationalized since the absorbance values were obtained on the steep slope of the charge-transfer band and required the subtraction of a substantial Cl^- absorbance. It can be seen from the middle columns of the table that fits 1–4 do not give parameters that are at all well defined. Fits 5–8 have all of the spectral data simultaneously computer fitted to eq 10 using various assumptions. The only useful piece of information comes from fit 5 which has an unacceptably high SD = ±0.054. Thus the assumption in fit 5, that all the parameters are independent of temperature, must be rejected. In fits 6–8 it was assumed that the temperature dependence resided in b, K°_X, and ϵ_{IP}, respectively. It is seen that the SD values for each fit are acceptably close to the expected ±0.012. Thus the temperature-dependent parameter cannot be determined, and, even if an arbitrary choice were made, the parameter values cannot be well defined. Regarding the latter point, the parameter standard deviations listed in Table III are underestimates of the true variability of the parameters. This is due to the

Table IV. Kinetic Data at 40 °C[a]

[X], M	μ, M	$10^6 k_{\mathrm{obsd}}$,[c] s^{-1} Exptl	Calcn 1	Calcn 2	Calcn 3
0.0100	0.0121	1.94[b]	1.86	1.85	2.00
0.0200	0.0221	2.89[b]	2.97	3.02	3.14
0.0300	0.0321	3.55	3.82	3.92	4.00
0.0400	0.0420	4.38	4.53	4.67	4.71
0.0701	0.0804	6.71	6.24	6.07	6.32
0.0800	0.0820	6.60	6.78	6.87	6.83
0.110	0.120	8.38	8.21	7.87	8.12
0.130	0.140	9.18	9.08	8.67	8.89
0.170	0.181	10.3	10.6	10.2	10.3
0.190	0.200	11.3	11.3	10.9	10.9
0.210	0.220	11.9	12.0	11.6	11.4
0.230	0.240	12.7	12.5	12.3	11.9
0.250	0.260	13.0	13.1	13.0	12.4
0.270	0.280	13.6	13.6	13.7	12.8
0.290	0.300	14.0	14.0	14.4	13.2
0.300	0.310	14.3[b]	14.2	14.8	13.4

[a] $[H^+] = 0.0100$ M, $[M_t] = 3.4 \times 10^{-4}$ or 1.7×10^{-3} M (see μ value). [b] Represents average of multiple determinations. [c] Calculations made using the following equations and parameters: calculation 1, eq 12, $k^\circ_I K^\circ_X = 3.92 \times 10^{-4}\ M^{-1}\ s^{-1}$, $b = 0.98$, $K^\circ_X = 22.7\ M^{-1}$; calculation 2, eq 13, $k^\circ_2 = 3.71 \times 10^{-4}\ M^{-1}\ s^{-1}$, $b = 0.26$; calculation 3, eq 12, $k^\circ_I K^\circ_X = 4.31 \times 10^{-4}\ M^{-1}\ s^{-1}$, $b = 0.91$, $K^\circ_X = 26.5\ M^{-1}$.

coupling of the various parameter values in the fit. For example, fit 8 shows a standard deviation for K°_X which would lead one to expect its value to lie between 5 and 13 M^{-1} (2 × SD of K°_X). However absorbance SD's less than ±0.015 (i.e., acceptable fits) can be obtained with $K^\circ_X = -24\ M^{-1}$ and with $K^\circ_X = 20\ M^{-1}$ if appropriate values of b and the ϵ_{IP} are chosen.

Anation Kinetic Data. The rate of formation of $Rh(NH_3)_5Cl^{2+}$ from $Rh(NH_3)_5H_2O^{3+}$ and chloride was studied at temperatures from 40 to 70 °C, with $0.01 \leq [X] \leq 0.3$ M and with $[H^+] = 0.01$ M. The experiments were run with $[M_t] << [X_t]$ so that pseudo-first-order conditions were obtained. The data collected at 40 °C are given in Table IV with the third column giving the experimentally determined values of k_{obsd}, the pseudo-first-order rate constant for the disappearance of the aquo complex. Numbers in the fourth column represent the best fit of the data to the ion-pair interchange model. In this model it is assumed that the only species capable of forming product is the X ion-paired complex.

$$ML_5H_2O \cdot X \rightarrow ML_5X + H_2O \quad k_I \tag{11}$$

This generates the kinetic equation

$$k_{obsd} = (k^\circ_I K^\circ_X G[X])/(1 + K^\circ_X G[X]) \tag{12}$$

The fit of the data to this equation is quite good as can be seen by comparing the two columns, the standard deviation of the experimental data being ±4%. The best fit values of the various parameters with their standard deviations are given in the first line of Table V.

The form of eq 12 fits not only an interchange (I) mechanism but also a dissociative (D) mechanism.[2] Unfortunately these kinetic data are so flexible that they also give a reasonable fit to a simple bimolecular-attack model, the associative (A) mechanism.[2] Numbers in the fifth column of Table IV show the fit of the data to eq 13. The fit is reasonable,

$$k_{obsd} = k^\circ_2 G[X] \tag{13}$$

giving a standard deviation of ±5.5% for the data points with $k^\circ_2 = (3.71 \pm 0.08) \times 10^{-4}\ M^{-1}\ s^{-1}$ and with the G terms calculated using $b = 0.26 \pm 0.02$. (Note that an I mechanism with an immeasurably small K°_X value causes eq 12 to reduce to the form of eq 13.)

Table V. Various Fits of Kinetic Data to Eq 12

Fit. no.	Data fitted	K°_X, M	b	$10^4 k^\circ_I K^\circ_X$, $M^{-1}\ s^{-1}$	SD, %
1	40 °C	22.7 ± 1.6	0.98 ± 0.12	3.92 ± 0.08	3.9
2	50 °C	23.0 ± 1.8	0.88 ± 0.10	15.4 ± 0.3	2.2
3	60 °C	−3.5 ± 4.3	0.14 ± 0.04	57.4 ± 1.7	4.5
4	70 °C	22.6 ± 5.7	0.64 ± 0.17	198 ± 5	5.2
5	All	23.8 ± 2.1	0.76 ± 0.10	Varied[a]	5.7

[a] $k^\circ_I K^\circ_X \times 10^4$ M s at 40, 50, 60, and 70 °C, respectively, is 4.33, 16.5, 58.3, and 191 from fitted parameters; $\Delta H^\ddagger/R = 13\,240 \pm 64$ K; $\Delta S^\ddagger/R + \ln K^\circ_X + \ln (k/h) = 28.78 \pm 0.20$.

Table V also gives the parameters for the fit to eq 12 of the other sets of kinetic data collected. The SD values for the individual fits vary from ±2.2 to ±5.2%. Thus in subsequent model testing an SD of ±5% will be taken as the expected value for these data. Inspection of the results in Table V shows that the apparent discontinuity of the 60 °C values of K°_X and b is simply a peculiarity of the fitting. Thus with fit 5 where all of the kinetic data are simultaneously fitted to eq 12, an acceptable SD value of ±5.7% is obtained. Again, one must not be misled by parameter standard deviations generated in such multiparameter fits. Due to coupling of SD's, the kinetic data, by themselves, do not yield well-defined parameter values. For example, all of the kinetic data can be collectively fitted to eq 13 ($K^\circ_X = 0$) with a reasonable SD in k_{obsd} of ±5.9% given the proper choice of b, $\Delta H^\ddagger$, and $\Delta S^\ddagger$ values.

Combination Data Fits. Up to this point the data from the three sets of experiments have been analyzed separately. The only substantive information obtained is that the potentiometric data require that K°_X be measurably large. In an attempt to overcome the problems of overfitting inherent in the individual data sets, all of the potentiometric, spectral, and kinetic data were collectively fitted. In these fits the calculation of the standard deviations of the data points had to be normalized so as not to overweight one set of data. The expected SD values, in fractions, are 0.050 for kinetic, 0.010 for potentiometric, and 0.012 for spectral data. Thus the SD values were normalized by multiplying the potentiometric deviations by 5 and the spectral deviations by 4. The potentiometric data were analyzed in these fits using the assumption that $K^\circ_p = K^\circ_X$. Data supportive of this assumption are given below.

As regards appropriate models for the combination fits, the potentiometric data exclude any immeasurably small K°_X model and the kinetic data require that k°_I be temperature dependent while the spectral data require that either K°_X, b, or ϵ_{IP} be temperature dependent. Thus each of the three models fitted using the ion-pairing equations (eq 8, 9, 10, 12) had k°_I as temperature dependent but differed as to whether K°_X, b, or ϵ_{IP} was allowed to be temperature dependent.

Both the K°_X and b temperature-dependent models fail to give adequate fits. They give, respectively, overall normalized SD values of ±0.102 and ±0.086 as compared to the expected value of ±0.050. Thus these models are rejected. The ϵ_{IP} temperature-dependent model does, however, give a reasonable fit to all data with an overall normalized SD value of ±0.060. Table VI lists the parameters generated by this model; the top set are parameters directly fitted by the model while the bottom set are other parameters of interest. The last nine rows of the table give the nonnormalized SD values for each set of data for this fit. It can be seen that the SD for each set (except for the 40 °C spectral data) is within the 99% F test value[13] of its expected value. The bad fit of the 40 °C spectral data is the result of one point only. When this point is excluded, a reasonable SD value of ±0.014 is obtained. The last columns of Tables I, II, and IV show the appropriate quantities calculated using the parameters in Table VI.

Thus the collective data of this study can be fitted to only one simple model having substantial ion pairing, K°_X and b

Table VI. Parameters from the Combination Fit of All Data to the $k°_I$, ϵ_{IP} Temperature Dependent Model

Parameter	Value	Unit
SD (overall)	0.060	Normalized[a]
$K°_X$	26.5 ± 0.8	M^{-1}
b	0.91 ± 0.05	
$\epsilon_{IP}K°_X$ (15 °C)	5480 ± 230	cm^{-1} M^{-2}
$\epsilon_{IP}K°_X$ (25 °C)	7660 ± 220	cm^{-1} M^{-2}
$\epsilon_{IP}K°_X$ (40 °C)	9880 ± 210	cm^{-1} M^{-2}
$\Delta H^{\ddagger}/R$	13220 ± 63	K
$\Delta S^{\ddagger}$ intercept[b]	28.7 ± 0.2	
$\Delta H^{\ddagger}$	26.2	kcal/mol
$\Delta S^{\ddagger}$	3.3	cal/(mol deg)
$k°_I$ (40 °C)	1.63	10^{-5} s^{-1}
$k°_I$ (50 °C)	6.19	10^{-5} s^{-1}
$k°_I$ (60 °C)	21.7	10^{-5} s^{-1}
$k°_I$ (70 °C)	71.1	10^{-5} s^{-1}
SD (P) 17[c]	1.4	%
SD (S–15) 10	0.008	Absorb unit
SD (S–25–1) 10	0.010	Absorb unit
SD (S–25–2) 10	0.012	Absorb unit
SD (S–40) 9	0.021 (0.014)[d]	Absorb unit
SD (K–40) 20	6.2	%
SD (K–50) 10	3.5	%
SD (K–60) 31	5.8	%
SD (K–70) 25	5.7	%

[a] Standard deviations normalized to expected best value of ±0.050; see text. [b] $\Delta S^{\ddagger}$ intercept = $\Delta S^{\ddagger}/R + \ln (k/h) + \ln K°_X$. [c] SD calculated for each data set (nonnormalized). Terms inside parentheses indicate data set considered; e.g. (S–25–1) is spectral data, 25 °C, set no. 1. Number outside parentheses is the number of data points. [d] The value of 0.014 was obtained by dropping the highest absorbance point from consideration.

Table VII. Effect of Perchlorate on the Anation Kinetics at 40 °C[a]

		10^6k_{obsd}, s^{-1}		
[X], M	[P], M	Exptl	Calcd ($K°_P = K°_X$)	Calcd ($K°_P = 0$)
0.100	0.100	5.80	5.56	8.48
0.100	0.200	4.92	4.44	9.80
0.200	0.100	9.31	8.88	12.2

[a] $[M_t]$ = 0.001 835 M, $[H^+]$ = [X] + [P]; calculated values from eq 14 using parameters in Table VI.

Table VIII. Effect of Perchlorate on the Charge-Transfer Spectrum[a]

			Absorbance		
Temp, °C	[X], M	[P], M	Exptl	Calcd ($K°_P = K°_X$)	Calcd ($K°_P = 0$)
25	0.100	0.200	0.267	0.247	0.401
25	0.100	0.101	0.275	0.281	0.365
25	0.200	0.101	0.379	0.373	0.469
40	0.100	0.200	0.323	0.293	0.502
40	0.100	0.101	0.337	0.337	0.450
40	0.200	0.101	0.480	0.466	0.596

[a] $[M_t]$ = 0.002 019 M, $[H^+]$ = [P], λ 208 nm; calculated values from eq 15 using parameters in Table VI.

temperature independent, and $k°_I$ and ϵ_{IP} temperature dependent. Also in this fit a reasonable definition of the parameters is achieved. Fits of the data to the model using various fixed b values reveal that adequate fits can only be achieved within the limits $b = 0.7$, $K°_X = 23$ M^{-1} and $b = 1.2$, $K°_X = 28$ M^{-1} with appropriate adjustments in the other parameters. Further inspection reveals the reason for this tightening of parameter values. In all fits b and $K°_X$ are positively correlated; that is, they must adjust in the same direction to maintain an adequate fit. With the spectral and kinetic data the SD's rise sharply at high b and $K°_X$ values while with the potentiometric data SD increases sharply at low values. Thus when the sets are combined, the overlap of these oppositely rising SD functions creates a deep, sharply defined SD well. In short the potentiometric data are essential, at least in this case, for establishing a tight definition of the b and $K°_X$ parameters.

Perchlorate Ion Pairing. In order to obtain information on the extent of ion pairing of the aquo complex by perchlorate anion, kinetic and charge-transfer spectral experiments were run with significant amounts of this anion present. The results are presented in Tables VII and VIII. The third to the last column in each table gives the experimentally determined quantities while the last column gives the calculated values assuming no perchlorate ion pairing, $K°_P = 0$. The latter were calculated with eq 12 and 10, respectively, using the parameter values given in Table VI. These calculations show that the experimental values are too low to be explained simply in terms of the increase in ionic strength accompanying the addition of perchlorate.

To account for perchlorate ion pairing in the experiments the following equations were used: for the kinetic data

$$k_{obsd} = k°_I K°_X G[X]/(1 + K°_X G[X] + K°_P G[P]) \qquad (14)$$

which assumes an I mechanism with $ML_5H_2O{\cdot}P$ unreactive; for the spectral data

$$Abs/[M_t] = (\epsilon_M + \epsilon_M K°_P G[P] + \epsilon_{IP} K°_X G[X])/(1 + K°_P G[P] + K°_X G[X]) \qquad (15)$$

which assumes that $ML_5H_2O{\cdot}P$ has a molar absorptivity identical with that of the free complex. This is supported by data on solutions having $0.01 \leq [P] \leq 0.2$ M and [X] = 0. Values of $Abs/[M_t]$ varied erratically between 60 and 80 cm^{-1} M^{-1}. The values in the second to the last columns of Tables VII and VIII were calculated from eq 14 and 15, respectively, using the parameter values in Table VI and taking $K°_P = K°_X$. It can be seen that these calculated values agree fairly well with those determined experimentally. Thus both the kinetic and spectral data demand the near-equivalence of $K°_X$ and $K°_P$.

Discussion

The purpose of this work was to investigate the utility of the low, variable ionic strength approach for studying anation reactions. The results led the authors to conclude that the approach is viable. Further, the approach is preferable to the conventional high, constant ionic approach especially since pure rate and equilibrium constants can be extracted from the data.

The viability of the low, variable ionic strength approach was to be judged by comparing the results on $K°_X$ and b from the three different types of experiments. As expected, introducing b as an adjustable parameter did cause each separate set of data to be overfitted allowing little information to be obtained. However, the three sets of data can be fitted to identical values of $K°_X$ and b and the combination fit does allow all parameters to be defined within reasonable bounds of uncertainty (Table VI). Thus the experimental approach is a viable one. In this regard it should be noted that the $K°_X$ value and the $K°_P \approx K°_X$ result are compatible with the results obtained from conductance experiments on other +3, −1 systems under conditions of low, variable ionic strength.[4,6,13] Furthermore, all previous studies[3,9b,10b] are compatible with assigning an associative interchange (I_a) mechanism[2] to $Rh(NH_3)_5H_2O^{3+}$ substitution reactions. The success of the combination fit (Table VI) using eq 12 confirms the I stoichiometric mechanism in the present work.

Two further points should be made concerning the values reported in Table VI. The present study obtains $\Delta H^{\ddagger} = 26$ kcal/mol while a value of 25 kcal/mol was reported by previous studies. This difference does not represent a difference in raw data between the studies but rather reflects the use of the temperature-dependent Debye–Hückel term (A of eq 6) in the analysis of the present data. This is seen by the fact that k_{obsd} values obtained in the present study at $[\text{Cl}^-] = 0.2$ M are within experimental error of the values obtained by Poe[9a] under similar conditions: e.g., 40 °C, 5.9 vs. 5.6; 50 °C, 21 vs. 20; 70 °C, 230 vs. 220 (k_{obsd} in units of 10^{-5} s^{-1}). Secondly, the fact that ϵ_{IP} has a strong temperature dependence is unexpected since the charge-transfer transition should be temperature independent. However the absorbance of aqueous Cl^- at 208 nm was found to be temperature dependent. Thus ϵ_{IP} may reflect an effect of the complex on the absorbance of Cl^- as well as the expected effect of Cl^- on the charge-transfer transition of the complex.

Regarding the mechanistic utility of the variable ionic strength approach, the results may be viewed as follows. The spectral and potentiometric data are best interpreted in terms of ion pairing, and they would generate values and error limits for K°_{X} and b similar to those given in Table VI if the two sets were fitted without the kinetic data. The fact that the kinetic data when fitted to an I mechanism can generate these same K°_{X} and b values leads to the conclusion that the I mechanism is correct. This same type of logic is used with data collected using the high, constant ionic strength approach (i.e., comparing spectral and kinetic values of K_{calcd} of eq 17). Thus with either approach the evidence supporting a particular stoichiometric mechanism assignment is about equally compelling. An advantage of the variable ionic strength approach is that activity corrections are handled explicitly (with $b = 0.9$ in the present case) relieving some of the uncertainty on this account concerning stoichiometric mechanism assignment. The most striking advantage is that individual rate and equilibrium constants can be extracted from the variable ionic strength data because perchlorate ion pairing is not a factor. Thus if the I mechanism is correct for the $\text{Rh(NH}_3)_5\text{H}_2\text{O}^+ + \text{Cl}^-$ reaction, values of k°_{I}, K°_{X}, and K°_{P} can be directly obtained from the data presented here. The $K^\circ_{\text{P}} \approx K^\circ_{\text{X}}$ result of the present study confirms that such values cannot be obtained from constant ionic strength data.[1,3]

The latter advantage of the low, variable ionic strength approach for obtaining mechanistic insight is demonstrated by comparing the pure constants k°_{I} with the measured rates of water exchange.[10,15] Values of $k^\circ_{\text{I}}/k_{\text{EX}}$ vary from 0.21 to 0.26 at the various temperatures. Accepting the associative intimate mechanism assignment,[10b,16] this result implies that while Cl^- is probably a more powerful nucleophile than H_2O on a per entity basis, H_2O is the more successful nucleophile due to its occupying more outer coordination sphere sites of the complex. The result further implies that the nucleophilicity difference between Cl^- and H_2O is relatively small suggesting that bond making is less important in the Rh(III) reaction than it appears to be in some Cr^{3+} reactions.[17]

Although the data and mechanistic conclusions from the present and past studies of eq 1 agree, there remains at least one ambiguity regarding the mechanism of the system. The interpretation of high, constant ionic strength anation data[3,9b] appears to depend on the relationships

$$k_{\text{obsd}} = (k^\circ_{\text{I}} K^\circ_{\text{X}} G[\text{X}])/(1 + K^\circ_{\text{X}} G[\text{X}] + K^\circ_{\text{P}} G[\text{P}]) \qquad (16)$$

$$k_{\text{calcd}} = \frac{k^\circ_{\text{I}} K_{\text{X}}}{K_{\text{X}} - K_{\text{P}}} \qquad K_{\text{calcd}} = \frac{K_{\text{X}} - K_{\text{P}}}{1 + K_{\text{P}}\mu} \qquad (17)$$

where k_{calcd} and K_{calcd} are the apparent interchange and ion-pairing constants derived from the usual $1/k_{\text{obsd}}$ vs. $1/[\text{X}]$ plots. The fact that values of K_{calcd} are of the order of 0.1 M^{-1} is consistent with the near-equality of K°_{X} and K°_{P} found in the present study. However, the values found for k_{obsd} lead to ambiguities. If the I mechanism is correct for this reaction and if eq 16 is applicable at high ionic strength, then no value of k_{obsd} greater than k°_{I} should be observed.[3] The extrapolated value of k°_{I} from the present study at 65 °C is 4.2×10^{-4} s^{-1}. Both of the high ionic strength studies report higher k_{obsd} values (7×10^{-4} and 20×10^{-4} s^{-1}). These discrepancies between the two types of studies might be rationalized in terms of eq 16 not being applicable at high μ. Thus k°_{I} might be media dependent (a breakdown in the assumption of activity coefficients being dependent only on the charge of the species), or the reactive species at high μ might be an ion triplet[4] whose interchange rate is greater than k°_{I}. At present there is no substantial evidence for or against either possibility. An alternative explanation would have the reaction occur by essentially a concerted bimolecular encounter, i.e., eq 13. This is consistent with $\Delta V^\ddagger = -4$ cm^3/mol for water exchange[10b] and with the almost first-order dependence of the anation rate on [X] no matter what concentration ranges are being studied.[9] Such an explanation, however, would require that X ion-paired complexes not have a statistical advantage toward reaction, and it would have to excuse the similarity between kinetic ion-pairing parameters and those determined by other means as simply a mathematical peculiarity of the system. Neither of these ideas is attractive. Thus some important ambiguities exist concerning our understanding of the reactivity of $\text{Rh(NH}_3)_5\text{H}_2\text{O}^{3+}$. We are presently studying systematically different reaction systems using the low, variable ionic strength approach in the belief that patterns will emerge that will help eliminate such ambiguities in our understanding of octahedral complex substitution reactions.

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Registry No. $\text{Rh(NH}_3)_5\text{H}_2\text{O}^{3+}$, 15337-79-8; Cl^-, 16887-00-6; ClO_4^-, 14797-73-0.

Supplementary Material Available: Tables listing potentiometric data, charge-transfer spectral data, and kinetic data, respectively (6 pages). Ordering information is given on any current masthead page.

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(16) The authors wish to thank a referee for pointing out that $k^\circ_{\text{I}} < k_{\text{EX}}$ does not itself refute the I_a mechanism assignment. The $k^\circ_{\text{I}}/k_{\text{EX}}$ ratio would suggest the alternative I_d mechanism only if various anions yielded essentially the same ratio. As yet pure k_{I} values for other anions are unavailable.

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