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Kinetics, Mechanism, and Stereochemistry of Chloride Anation of Chloropentaaquorhodium(III) Complex Ion in Aqueous Solution. An Approach for Distinguishing between the Five-Coordinate-Intermediate and Ion-Pair-Interchange Mechanisms for Octahedral Complexes Containing at Least Two Water Ligands

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The rate of the chloride anation of $RhCl(H_2O)_5^{2+}$ has been studied as a function of (H^+), (Cl^-), and temperature. The data are found to be compatible with a five-coordinate-intermediate type of mechanism but not with an ion-pair-interchange mechanism. This discrimination of mechanism is made possible by the occurrence of simultaneous anation of acid and conjugate base forms of the parent complex. The cis and trans isomers of $RhCl_2(H_2O)_4^+$ have been isolated and their visible-ultraviolet spectra determined. The *trans*-$RhCl_2(H_2O)_4^+$ isomer is found to be the direct and only product of the anation of $RhCl(H_2O)_5^{2+}$. The previously observed near equivalence of OH^- and Cl^- as trans-labilizing substituents is confirmed in studies of the anation of $RhCl(H_2O)_4OH^+$.

Introduction

The kinetics of the aquation and chloride anation reactions of the chloroaquo complexes of rhodium(III), *viz.*

$$RhCl_n(H_2O)_{6-n}^{3-n} + Cl^- \rightleftarrows RhCl_{n+1}(H_2O)_{5-n}^{2-n} + H_2O$$

have been the subject of a number of studies by Harris, Robb, and coworkers, which to date have included the systems with $n = 0$,[2] $n = 4$,[3] and $n = 5$.[4,5] The present work, which concerns the chloride anation of the monochloro complex ($n = 1$), was undertaken in order to investigate further the apparent strong trans-labilizing effect of ligand chloride in these compounds. This effect is suggested by the fact that the only immediately observable product in the chloride anation[2] of $Rh(H_2O)_6^{3+}$ is *trans*-$RhCl_2(H_2O)_4^+$ and that the aquation[3] of $RhCl_5(H_2O)^{2-}$ apparently yields only *cis*-$RhCl_4(H_2O)_2^-$ as an initial product.[6] It is now demonstrated that the *trans*-$RhCl_2(H_2O)_4^+$ isomer is the sole direct product of the anation of $RhCl(H_2O)_5^{2+}$. This reaction proceeds at a rate more than an order of magnitude faster than the replacement of the first water ligand in $Rh(H_2O)_6^{3+}$, thus explaining the nonappearance of the monochloro species[2] as an intermediate in the chloride anation of $Rh(H_2O)_6^{3+}$.

The stereochemistry of the dichloro product arising from the anation of $RhCl(H_2O)_4OH^+$ has also been determined. These data indicate that chloride and hydroxide ligands are essentially equivalent as trans-labilizing substituents in these reactions, as has been suggested by earlier trans-effect studies of rhodium complexes.[7]

The interpretation of the kinetic data for the anation of the $RhCl(H_2O)_5^{2+}$ system and a reinterpretation of the analogous data[2] for the $Rh(H_2O)_6^{3+}$ system allow a choice to be made between the "five-coordinate-intermediate" and "ion-pair-interchange" types of mechanism. This discrimination is made possible by the fact that the acid and conjugate base forms of these complexes, which exist in equilibrium in aqueous solution, simultaneously undergo chloride anation and at different rates. The forms of the appropriate rate laws are such as to enable the otherwise impossible mechanistic distinction, as is shown by the detailed analysis in the Appendix. The data for the two cationic complexes under consideration appear to be compatible only with the five-coordinate-intermediate mechanism, as was previously suggested[5] for the anation of $RhCl_5(H_2O)^{2-}$ by various singly charged anions.

Experimental Section

Materials. Stock solutions of $HClO_4$, NaOH, and NaCl were prepared by dissolving reagent grade chemicals in doubly distilled water. $NaClO_4$ solutions were prepared by neutralizing 6 *M* $HClO_4$ with reagent grade Na_2CO_3. These solutions were rendered carbonate free by adjusting the pH to between 2 and 3 with $HClO_4$ and bubbling with N_2 for at least 1 hr. The pH was then adjusted to between 5 and 7 by the addition of carbonate-free NaOH.

Solid $Rh(H_2O)_6(ClO_4)_3$ was prepared from $RhCl_3 \cdot 3H_2O$ (Engelhardt Industries, Inc., Newark, N. J.) by a standard method.[8] The molar absorptivities of acid solutions of this preparation agreed with those reported earlier.[2] $RhCl(H_2O)_5(ClO_4)_2$ was prepared by heating a solution containing equimolar amounts of HCl and $Rh(H_2O)_6(ClO_4)_3$ at 90–95° for 48 hr. The solution was then placed on a column of Dowex 50W-X8 (H^+ form) 200–400 mesh resin and the $RhCl(H_2O)_5^{2+}$ was quantitatively eluted with 0.02 *M* $Th(ClO_4)_4$ (G. Frederick Smith and Co.), the pH of which was adjusted to between 1.1 and 1.4 with $HClO_4$. The aqueous solutions of $RhCl(H_2O)_5(ClO_4)_2$ and $HClO_4$ prepared in this manner were used without further purification in the experiments requiring $RhCl(H_2O)_5^{2+}$. These solutions had an average molar ratio of chloride to rhodium of 0.99 ± 0.03 and showed no spectral changes on standing at 5° for 2 months. The visible-ultraviolet spectrum shown in Figure 1 indicates molar absorptivities which are 16% larger than those reported previously[9] though the peak positions are identical.

Preparation and Identification of $RhCl_2(H_2O)_4^+$ Isomers. The anation product, $RhCl_2(H_2O)_4^+$, should exist in cis and trans forms but these have not previously been identified. When the monochloro species is heated at 70° for 60 hr with a 10–15-fold excess of HCl, the singly charged dichloro complex, which is the major product, is obtained by placing the product mixture on a column of Dowex 50W-X8 200–400 mesh resin in the acidic form and eluting with 0.15 *M* $HClO_4$. The $RhCl_2(H_2O)_4^+$ so obtained has absorption maxima at 450 and 350 nm, with a 450/350 peak absorbance ratio of 1.3 and an average chloride to rhodium molar ratio of 2.05 ± 0.06. This single-isomer species appears to be identical with that prepared by Kleinberg and coworkers.[9] A second dichloro preparation was obtained by heating a solution containing equimolar amounts of $RhCl(H_2O)_5^{2+}$ and HCl for 94 hr at 90–95°, separation from other products being achieved by ion-exchange chromatography as described above. This species has absorption maxima at 450 and 355 nm, with a 450/350 peak ratio of

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[1] Based on the Ph.D. dissertation of M. J. Pavelich, State University of New York at Buffalo, June 1970. Copy available from University Microfilms, Ann Arbor, Mich.

[2] K. Swaminathan and G. M. Harris, *J. Amer. Chem. Soc.*, 88, 4411 (1966).

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

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

[5] W. Robb, M. M. de V. Steyn, and H. Kruger, *Inorg. Chim. Acta*, 3, 383 (1969).

[6] K. L. Bridges and J. C. Chang, *Inorg. Chem.*, 6, 619 (1967).

[7] A. J. Poe and K. Shaw, *J. Chem. Soc. A*, 393 (1970).

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

[9] W. C. Wolsey, C. A. Reynolds, and J. Kleinberg, *Inorg. Chem.*, 2, 463 (1963).

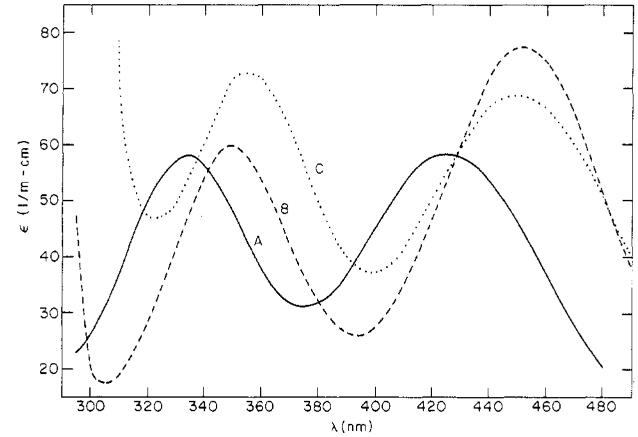

Figure 1. Visible-ultraviolet absorption spectra: A, $RhCl(H_2O)_5^{2+}$; B, *trans*-$RhCl_2(H_2O)_4^+$; C, *cis*-$RhCl_2(H_2O)_4^+$.

close to unity, and the average chloride to rhodium ratio for several preparations was 2.03 ± 0.11. Neither type of $RhCl_2(H_2O)_4^+$ shows any spectral change when stored for 1 month at 5° in aqueous solution. It was found that mixtures of the two isomers could be completely separated by ion-exchange chromatography by a method similar to that used in their initial preparations and that the first fractions always had a 450/350 peak ratio of 1.30 and the later fractions, 0.95. (See Figure 1 for complete spectra of the separated components.) This order of elution suggests that the former is the isomer of lower dielectric constant and is thus the trans species, while the latter is the cis. Analogous reasoning has been applied in the separation and identification of the cis and trans forms of $RhCl_4(H_2O)_2^-$, where a similar variation of ratio of absorbance maxima is observed.[6]

Methods of Analysis. Two methods were used for the quantitative determination of rhodium. In the spectrophotometric method, solutions of rhodium complex were treated with HCl and $SnCl_2$ essentially as outlined by Ayres, *et al.*[10] It was found that the 475-nm molar absorptivity of 4000 l. cm^{-1} mol^{-1} was only valid when (ClO_4^-) in the test solution was less than 0.45 *M*. At higher (ClO_4^-) the Rh-Sn absorption is decreased and broadened. The second procedure for rhodium determination was the gravimetric method outlined by Plumb.[11]

The chloride content of the rhodium complexes was determined by decomposing the complexes with Mg turnings and $HClO_4$, filtering out the rhodium metal, and titrating the filtrate with a solution of $Hg(NO_3)_2$ with sodium nitroprusside as indicator.[12] The $HClO_4$ and NaOH solutions were standardized against analytical grade hydrazine sulfate. The $NaClO_4$ and NaCl solutions were analyzed by washing aliquots of them onto columns of Dowex 50W-X8 (H^+ form) 50-100 mesh resin. The displaced acid was eluted from the columns and titrated against NaOH. This ion-exchange method was also used to determine the $HClO_4$ content of the stock $RhCl(H_2O)_5^{2+}$ solutions. It was assumed that each $RhCl(H_2O)_5^{2+}$ displaced two protons from the resin.

pH Titrations. A thermostated sample cell, controlled to ±0.1° and containing the glass electrode of a Beckman Research Model pH meter, was connected by an agar salt bridge, 4.0 *M* in NH_4NO_3, to an ambient-temperature solution of saturated KCl into which dipped the calomel electrode. The apparatus was calibrated by $HClO_4$ titrations. Thus the pH readings gave hydrogen ion concentrations rather than hydrogen ion activities at the required ionic strength. Immediately after a calibration, a solution containing the desired amounts of stock $RhCl(H_2O)_5^{2+}$, sodium salt (perchlorate or chloride), and water was placed in the thermostated sample cell, temperature equilibrium was established, and titration was carried out with a NaOH solution made up to the proper ionic strength with sodium salt. Where NaCl was used as the background salt, the complex was rapidly titrated to near the half-neutralization point and the pH was read. Point by point titration in NaCl would have been complicated by anation of the $RhCl(H_2O)_5^{2+}$.

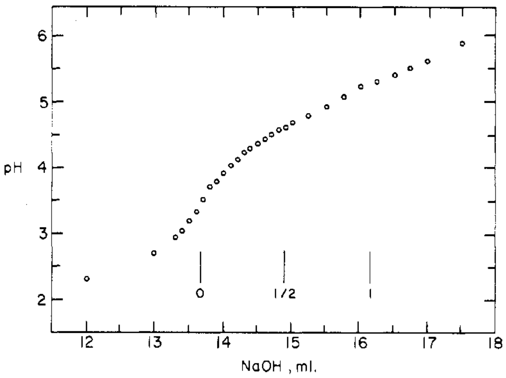

Figure 2. $RhCl(H_2O)_5^{2+}$ titration curve, with $T = 35°$, $I = 2.0\,M$ ($NaClO_4$), (complex) = 0.008 *M*. Ratios of moles of OH^- to moles of complex are indicated.

Table I. Acid-Base Hydrolysis Constants of $RhCl(H_2O)_5^{2+}$ Ion at 2.0 *M* Ionic Strength[a]

Temp, °C	Salt	−log *P*	Temp, °C	Salt	−log *P*
25.0	$NaClO_4$	4.87	45.0	NaCl	4.5
25.0	$NaClO_4$	4.86	50.0	$NaClO_4$	(4.34)[b]
29.7	$NaClO_4$	4.74	55.0	$NaClO_4$	(4.25)[b]
34.5	$NaClO_4$	4.65	65.0	$NaClO_4$	(4.08)[b]
44.5	$NaClO_4$	4.43	75.0	$NaClO_4$	(3.91)[b]
45.0	$NaClO_4$	4.48			

[a] (Complex) = 0.008 *M*. [b] Calculated by means of experimental temperature parameters given in text.

The $RhCl(H_2O)_5^{2+}$ titration curve at 35° and for an ionic strength of 2.0 *M* with $NaClO_4$ is shown in Figure 2. When the ratio of moles of OH^- added to moles of rhodium complex reached a value near 1, the solution developed cloudiness. Upon further titration a yellow precipitate appeared. Above a mole ratio of 1.5 steady pH readings could not be obtained. The precipitate rapidly disappeared when the solution was back-titrated with $HClO_4$. However, a spectral analysis of the back-titrated solutions revealed that an amount (15-30%) of the $RhCl(H_2O)_5^{2+}$ had been converted to $Rh(H_2O)_6^{3+}$. Solutions titrated to about the one-fourth neutralization point (pH ≃4.2) of the complex, where no precipitation occurred, showed no decomposition of $RhCl(H_2O)_5^{2+}$ over comparatively long times. Thus it is concluded that the rupture of the Rh-Cl bond observed at high pH is related to the precipitation reaction and is not due to simple aquation of $RhCl(H_2O)_4OH^+$.

The overall acid-base hydrolysis constant is given by (see Appendix for definition of terms)

$$P = \frac{T_B}{T_A}(H^+) = K_h \frac{1 + K'(Cl^-)}{1 + K(Cl^-)} \qquad (1)$$

It is seen that in absence of Cl^-, $P = K_h$. The hydrolysis constant can be evaluated for each point on the titration curve since the initial amounts of $HClO_4$, the total amount of rhodium complex, the amount of NaOH added, and the final concentration of H^+ are all known. The titration points in the region $0 < OH^-/Rh < {}^1/_3$ give a constant value for K_h. Above about the half-neutralization point the calculated value for K_h steadily increases with OH^-/Rh. This increase is attributed to an interference by the precipitation reaction mentioned above. Thus values for K_h are recorded only for the points in the region $0 < OH^-/Rh < {}^1/_3$. Furthermore, the kinetic studies described below were done only in the region $OH^-/Rh < {}^1/_5$.

The data for pK_h (−log *P* in $NaClO_4$ medium) as a function of temperature are given in Table I. These values are assigned an uncertainty of ±0.02 log unit, the average deviation of pK_h calculated from at least ten titration points. A nonweighted least-squares treatment[13] of a plot of pK_h *vs.* $1/T$ with $I = 2.0\,M$ ($NaClO_4$) gives $\Delta H° = 8.8 \pm 0.5$ kcal/mol and $\Delta S° = 7.5 \pm 1.6$ cal/mol deg. The values, at various temperatures, of pK_h derived from this plot for use in analyzing the kinetic data are included in Table I.

The value of −log *P* obtained at 45° in NaCl medium is assigned an uncertainty of ±0.1 log unit since this value was calculated from only one titration point.

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(10) G. H. Ayres, B. L. Tuffly, and J. S. Forrester, *Anal. Chem.*, 27, 1742 (1955).

(11) (a) W. Plumb and G. M. Harris, *Inorg. Chem.*, 3, 542 (1964); (b) W. Plumb, Ph.D. Dissertation, State University of New York at Buffalo, 1961.

(12) I. M. Kolthoff and E. B. Sandell, "Textbook of Quantitative Inorganic Analysis," Macmillan, New York, N. Y., 1952, p 548.

(13) W. J. Youder, "Statistical Methods for Chemists," Wiley, New York, N. Y., 1951, Chapter 5.

Kinetics. A solution containing the desired amounts of $RhCl(H_2O)_5(ClO_4)_2$, $HClO_4$ or NaOH, $NaClO_4$, and doubly distilled water was made up volumetrically at room temperature. The solution was heated at the reaction temperature for 10 min and the required amount of NaCl solution was added to initiate the reaction. The concentration of Cl^- was always at least 10 times greater than that of the rhodium complex. At given times, aliquots of the reaction mixture were extracted, cooled in an ice bath, and analyzed by one of two methods.

(a) The Spectral Method (for Runs in the Range $0 < pH \leqslant 1.6$). The aliquot was warmed to room temperature and its absorbance at 450 nm was taken with a Beckman DU spectrophotometer equipped with a Gilford Model 220 linear absorbance readout. k_{obsd}, the pseudo-first-order rate constant for the disappearance of $RhCl(H_2O)_5{}^{2+}$, was taken as the negative slope of the conventional ln $(A_\infty - A_t)$ *vs.* time plot. (A_t is the absorbance of the reaction mixture at time t; A_∞ is the calculated absorbance of the solution for the condition where all the $RhCl(H_2O)_5{}^{2+}$ has been converted to *trans*-$RhCl_2(H_2O)_4{}^+$. A consistent experimental value for A_∞ could not be obtained, probably because of the slow subsequent anation of the first-formed product.)

(b) The Column Method (for Runs in the Range $0.2 \leqslant pH \leqslant 3.8$). With this method, the rate was monitored for only the first 10–15% of the reaction. A 4.0 ml amount of sample, mixed with 0.5 ml of 0.5 *M* $HClO_4$, was placed on a 22 cm high, 1-cm diameter column of Dowex 50W-X8 (H^+ form) 200–400 mesh resin. The column was eluted with 40 ml of 0.5 *M* $HClO_4$. This eluted material was treated with HCl and $SnCl_2$ to determine its rhodium content.[10] Under these conditions only the complexes with charge $\leqslant 1+$ are eluted. k_{obsd} was taken as the slope of the ln$[(Rh)_T - (Rh)_P]$ *vs.* time plot. ($(Rh)_T$ is the total concentration of rhodium in the reaction mixture; $(Rh)_P$ is the concentration of all product species in the reaction mixture at time t.) No buffer system could be found for the region $2 < pH < 4$ which did not react with $RhCl(H_2O)_5{}^{2+}$. The desired pH for the reaction mixtures was therefore obtained simply by the addition of the requisite amounts of $HClO_4$ or NaOH. For runs with pH <1.7, the acidity was calculated from the amount of $HClO_4$ or NaOH added to the acidified stock solution of Rh(III) complex. For runs at lower acidity, the pH was measured directly during the experiment using the pH measurement setup described above.

Results

Chloride Anation of the Monochlororhodium(III) Complex.

A study was first made of the pH dependence of the rate of anation with constant chloride concentration (0.553 *M*) at 65° and fixed ionic strength (2.0 *M*, $NaClO_4$ + NaCl). For runs at pH <1.7, linear plots were obtained over at least 1 half-time of reaction. For pH >1.7, the plots were linear for the first 10–15% of reaction during which period the pH is relatively constant in spite of the lack of buffering. The first-order dependence of the rate on monochlororhodium concentration was confirmed by some runs in which the initial amount of complex was varied. Consistent rate data are obtainable from these 10–15% straight-line portions of the reaction. The results are presented in Figure 3, where k_{obsd} is the pseudo-first-order rate constant for disappearance of monochloro complex in both its acidic and basic forms to produce *trans*- and/or *cis*-dichloro product. At a given chloride ion concentration, k_{obsd} should vary with (H^+) independently of the detailed nature of the anation mechanism, as shown by eq A17 in the Appendix, *viz.*

$$k_{obsd} = [F_A(H^+) + F_BP]/[(H^+) + P] \qquad (2)$$

In this F_A and F_B are composites of rate constants, equilibrium constants, and anion concentrations, as illustrated by eq A16 and A25 of the Appendix, but have the dimensions of pseudo-first-order rate constants. From the data in Table I, it can be seen that within experimental error P does not vary with (Cl^-) at 45° and constant ionic strength of 2.0 *M*. Assuming that this constancy holds at other temperatures, one concludes that $P = K_h$, the latter being the known measured hydrolysis constant of the complex in 2.0 *M* perchlorate medium.[14] The solid line of Figure 3 is plotted according to eq 2, using $P = 8.4 \times 10^{-5}$ *M*, the extrapolated value given in Table I for K_h at 65°. F_A was taken to be $(9.0 \pm 0.6) \times 10^{-5}$ sec^{-1}, the average k_{obsd} for runs with pH <1.7, where (H^+) greatly exceeds K_h and k_{obsd} appears to have its constant minimum value. F_B was calculated from the runs with pH >1.7, and its average value of $(315 \pm 40) \times 10^{-5}$ sec^{-1} was used in plotting the curve.

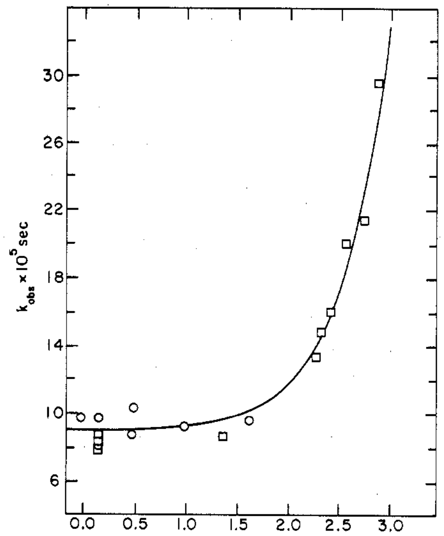

Figure 3. Dependence of k_{obsd} on pH, with $T = 65°$, (NaCl) = 0.553 *M*, $I = 2.0$ *M* ($NaClO_4$), and (complex) = 0.006–0.012 *M*: ○ = spectral method; □, column method.

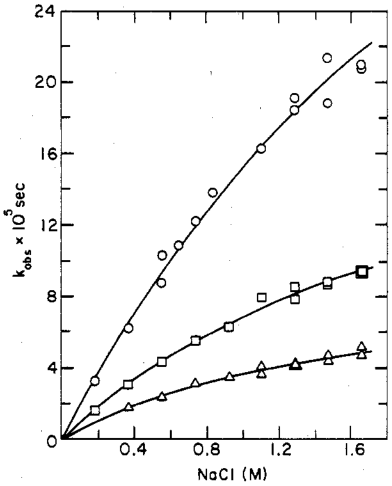

Figure 4. Dependence of k_{obsd} on concentration of chloride, with $(H^+) = 0.33$ *M*, $I = 2.0$ *M* with ($NaClO_4$), and (complex) = 0.006 *M*: ○, 65°; □, 60°; △, 55°.

Attention was next focused on the dependence of the rate of anation on the chloride ion concentration at various acidities. With $(H^+) = 0.33$ *M*, where the terms in P of eq 2 are negligible and $k_{obsd} = F_A$ (see above), data were obtained at 55, 60, and 65° ($I = 2.0$ *M*) and are presented in Figure 4. The two mechanisms for anation of aquo complexes lead to mathematically identical expressions for k_{obsd} at acidities high enough such that the conjugate base form of the complex contributes negligibly to the process (see eq A21 and A26 of the Appendix). Accepting for the moment the "five-

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[14] Equation A8 of the Appendix suggests that P should vary with (Cl^-) used in making up the constant ionic strength solution. However, if P is essentially independent of the $(Cl^-)/(ClO_4^-)$ ratio, then K and K' must be either very small or approximately equal, so that $P = K_h$.

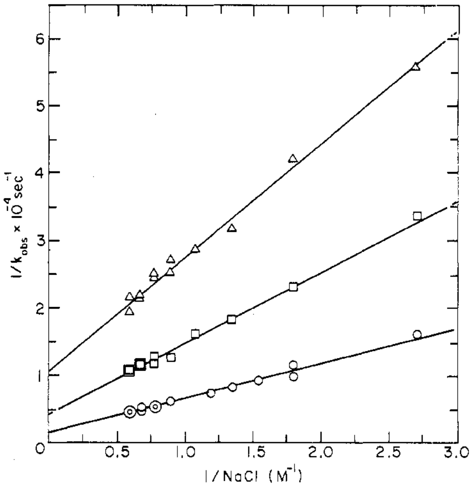

Figure 5. Reciprocal plot of k_{obsd} *vs.* (Cl^-) data, with (H^+) = 0.33 M, I = 2.0 M ($NaClO_4$), and (complex) = 0.006 M: ○, 65°; □, 60°; △, 55°.

coordinate-intermediate" terminology, eq A21 applies under high acid conditions, whence

$$\frac{1}{k_{obsd}} = \frac{1}{F_A} = \frac{1}{k_1} + \frac{1}{k_1(k_3/k_2)(Cl^-)} \tag{3}$$

The data, when plotted in this double reciprocal fashion, do in fact yield good straight lines, as shown in Figure 5. Values for k_1, k_3/k_2, and their standard deviations were evaluated from the intercept and slope of the plots by a weighted least-squares treatment[15] and are recorded in Table II. Also given in Table II are conventional transition-state theory parameters for the variations of k_1 and k_3/k_2 with temperature, as evaluated by nonweighted least-squares treatment.[13]

Data were next collected concerning the variation of k_{obsd} with chloride ion concentration at low acidities. Substituting the known values of P (assumed equal to K_h), (H^+), and F_A as determined by eq 3 into eq 2, F_B can be calculated for each run. The data for 45, 50, and 55° at I = 2.0 M ($NaClO_4$ + NaCl) are presented in Figure 6. Again adopting the "five-coordinate-intermediate" terminology, one derives from eq A22 the relation

$$\frac{1}{k'_{obsd}} = \frac{1}{F_B} = \frac{1}{k'_1} + \frac{1}{k'_1(k'_3/k'_2)(Cl^-)} \tag{4}$$

Double reciprocal plots of the data in this form yield reasonably straight lines as shown in Figure 7 and enable evaluation of k'_1, k'_3/k'_2, and their standard deviations by weighted least-squares treatment.[15] The values so obtained are given in Table II together with temperature parameters determined as described earlier.

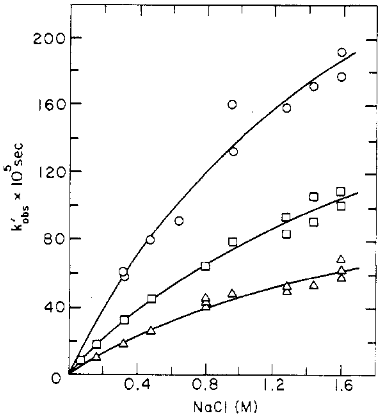

Figure 6. Dependence of k'_{obsd} (see text) on (Cl^-), with I = 2.0 M ($NaClO_4$) and (complex) = 0.012 M: ○, 55°; □, 50°; △, 45°.

Table II. Anation of $RhCl(H_2O)_5^{2+}$ Ion by Cl^- Ion[a]

A. Kinetic Parameters

Temp, °C	$10^5 k_1$, sec^{-1}	k_3/k_2, M^{-1}	$10^4 k'_1$, sec^{-1}	k'_3/k'_2, M^{-1}
75	(360)[b]	(0.155)[b]	(290)[b]	(0.49)[b]
65	64.5 ± 8.4	0.307 ± 0.040	(110)[b]	(0.49)[b]
60	23.3 ± 1.8	0.412 ± 0.035	(68)[b]	(0.49)[b]
55	9.4 ± 0.7	0.631 ± 0.053	41 ± 6	0.513 ± 0.085
50	(3.1)[b]	(0.92)[b]	25 ± 2	0.459 ± 0.045
45	(1.1)[b]	(1.36)[b]	14 ± 2	0.487 ± 0.076

B. Temperature Parameters

Kinetic parameter	$\Delta H^{\ddagger}$, kcal/mol	$\Delta S^{\ddagger}$, cal/deg mol	$\Delta(\Delta H^{\ddagger})$, kcal/mol	$\Delta(\Delta S^{\ddagger})$, cal/deg mol
k_1	41.8 ± 2.0	50.1 ± 6.1		
k_3/k_2			−15.9 ± 1.6	−49.4 ± 4.8
k'_1	21.7 ± 0.9	−3.5 ± 2.7		
k'_3/k'_2			1.0 ± 2.1	1.8 ± 6.4

[a] Ionic strength 2.0 M. [b] Calculated by means of temperature parameters in part B.

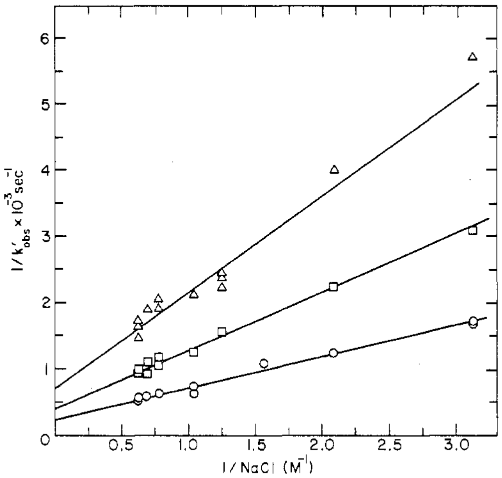

Figure 7. Reciprocal plot of k'_{obsd} (see text) *vs.* (Cl^-) data, with I = 2.0 M ($NaClO_4$) and (complex) = 0.012 M: ○, 55°; □, 50°; △, 45°.

Stereochemistry of Reaction Products. The relative amounts of *cis*- and *trans*-dichloro products obtained by anation of the monochlororhodium(III) complex are dependent on the acidity. Several lines of evidence show that the immediate and exclusive product of $RhCl(H_2O)_5^{2+}$ anation is the trans species. First, in runs at 65° and pH <1.7 (see Figure 3) the spectra of the reaction mixtures show an isosbestic point at 380 nm for at least 1 half-time of reaction at various hydrogen and chloride ion concentrations. Figure 1 suggests that the only two species which can be present under such circumstances are the $RhCl(H_2O)_5^{2+}$ and *trans*-$RhCl_2(H_2O)_4^+$ complexes. More extensive spectral confirmation of this conclusion was obtained as follows. A run was made at 65° with (H^+) = 0.333 M, (Cl^-) = 0.738 M, and I = 2.0 M by measurement of the absorbance at 360, 370, 380, 390, 410, and 450 nm, respectively. At 380 nm, the absorbance was constant at 0.193 ± 0.001. At each of the other wavelengths, using for A_∞ the known absorbance of *trans*-$RhCl_2(H_2O)_4^+$, straight-line plots were obtained which yielded a constant value for k_{obsd} within the limits (10.8 ± 0.8) × 10^{-5} sec^{-1}. For one of the partially reacted samples, the absorb-

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[15] G. N. Wilkinson, *Biochem. J.*, 80, 324 (1961).

ances at 350, 360, 370, 390, 400, 410, and 450 nm were used to determine its composition and resulted in identical analysis within the limits 56 ± 2% $RhCl(H_2O)_5^{2+}$ and 44 ± 2% *trans*-$RhCl_2(H_2O)_4^+$. Finally, a 60% cis-40% trans solution of dichloro complex was heated in 0.3 M $HClO_4$ at 65° for times longer than the half-times for monochloro complex anation under the conditions just described. No spectral change was observable in the cis-trans mixture during such periods, proving that cis-trans interconversion is very much slower than anation in these systems, if it occurs at all.

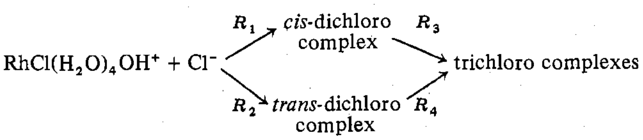
The spectra of reacting mixtures at 65° and pH >1.7 exhibit no isosbestic points. Qualitative analysis using ion-exchange chromatography and spectroscopy[16] revealed that the products consisted of *cis*- and *trans*-$RhCl_2(H_2O)_4^+$, $Rh(Cl)_3(H_2O)_3$, and, in some cases, $RhCl_4(H_2O)_2^-$. It can be assumed that the trichloro and tetrachloro complexes are formed by the subsequent anation of the initial dichlororhodium(III) product.

A quantitative study was made of the product distribution in reactions run at high pH, $T = 45°$, and $I = 2.0$ M, with results as given in Table III. At a given time the entire reaction mixture was quenched in an ice bath and the extent of reaction was determined by the standard column method. A similar, acidified aliquot was placed on a Dowex column and eluted with water. This effluent was treated with $SnCl_2$[10] to determine the trichloro plus tetrachloro composition of the product. The remainder of the reaction mixture was acidified and its $RhCl_2(H_2O)_4^{2+}$ fraction was isolated chromatographically. The relative amounts of cis and trans isomers were determined from spectrophotometric measurements at several different wavelengths. The last column indicates the percentage of *trans*-dichloro product which arose from the anation of the acidic form of the complex, $RhCl(H_2O)_5^{2+}$. This was calculated from the expression

$$\% \text{ of product from } RhCl(H_2O)_5^{2+} = \frac{100F_A(H^+)}{F_A(H^+) + F_BK_h} \quad (5)$$

where F_A and F_B are calculated from the known k's (see Table II) and (Cl^-) by substitution into eq 3 and 4. The value used for (H^+) was the median value measured during the run.

The actual distribution of dichlororhodium(III) isomers produced in the anations of $RhCl(H_2O)_4OH^+$ cannot be ascertained at this time since the relative rates of anation of *cis*- and *trans*-dichloro species to give higher chlororhodium(III) complexes is not yet known. The *trans*-dichloro species may be highly reactive at these pH's. However, limits can be put on the distribution by considering the scheme



If $R_3 \gg R_4$, the data of Table III suggest that the R_1/R_2 ratio is about 90/10 on the average, while if $R_4 \gg R_3$, the R_1/R_2 ratio becomes 40/60. Undoubtedly, the actual distribution lies between these extremes such that R_1 and R_2 do not differ by a factor of more than 2 or 3. The possibility that rapid interconversion of the isomers contributes to the establishment of the cis/trans distribution ratio can be eliminated, since a solution of *trans*-dichlororhodium(III) complex heated under the same conditions specified for the second run in Table III (except that Cl^- was absent) showed no spectral change. A solution containing 55% cis and 45% trans treated in the same way also showed no spectral change.

Table III. High-pH Product Distribution[a]

(NaCl), M	pH (median value)[b]	Extent of reaction, %	Distribution of total product, % $RhCl_{>2}$	*cis*-$RhCl_2$	*trans*-$RhCl_2$	% of trans product from $RhCl(H_2O)_5^{2+}$
1.600	3.7	29	42	37 ± 9	21 ± 9	7
1.600	3.8	51	51	37 ± 5	12 ± 5	5
0.800	3.6	45	40	44 ± 4	16 ± 4	10

[a] $I = 2.0$ M, $T = 45°$, (complex) = 0.012 M. [b] Variable over range of approximately ±0.1 pH unit during experiment.

Discussion

The rate data presented above have been interpreted in terms of the "five-coordinate-intermediate" (FCI) mechanism using eq 6 as the rate law. The complete rate law for the FCI

$$k_{obsd} = \left[\frac{k_1(k_3/k_2)(Cl^-)(H^+)}{1 + (k_3/k_2)(Cl^-)} + \frac{k'_1(k'_3/k'_2)(Cl^-)K_h}{1 + (k'_3/k'_2)(Cl^-)}\right]\frac{1}{(H^+) + K_h} \quad (6)$$

mechanism is derived in the Appendix and is given by eq A17-A19. Equation 6 was obtained by assuming that only the first-power terms in eq A18 and A19 contribute and by assuming that $P = K_h$. The latter assumption is supported by the 45° data in Table I, which shows that P is essentially unaffected by substituting NaCl for $NaClO_4$ as the salt used to establish the ionic strength. The most probable explanation for this is that ClO_4^- and Cl^- ion-pair to the complexes to quite similar degrees, a concept which is supported by the observation that the constant for ClO_4^- ion-pairing to $Co(NH_3)_5Cl^{2+}$ is quite similar to that for Cl^- ion-pairing.[17] In these circumstances, $K_Y \approx K_Z$ and $K'_Y \approx K'_Z$ so that $K \approx K' \approx 0$ and $P \approx K_h$ (see eq A8). The linear plots of Figures 5 and 7 illustrate that the first-power term assumption for eq A18 and A19 is correct. Two possible explanations of this are outlined in the Appendix, *viz.*, that ion-pairing is negligible or that ion-pairing does not affect the measurable kinetic parameters (see eq A21). The truth may lie in a combination of these conditions or in some other set of conditions not considered here. It follows therefore that the kinetic values listed in Table II may not necessarily denote the simple parameters indicated (*i.e.*, k_1, k_3/k_2, k'_1, and k'_3/k'_2) but may refer to more complicated expressions for A, E, A', and E' as defined in eq A18 and A19. However, the data obviously are fitted well by the FCI rate law utilized.

In contrast, the data are not well-fitted by the alternative possibility, the "ion-pair-interchange" (IPI) mechanism.[18] The IPI rate law is also derived in the Appendix and is given by eq A29. In attempting to fit the data to this rate law, K_h values are taken from Table I while k_{in} and K are assigned the values shown in Table II for k_1 and k_3/k_2, respectively. Algebraic rearrangement of eq A29 gives

$$\frac{1}{k_{obsd}} = \frac{D}{k'_{in}K'} + \frac{1}{k'_{in}} \quad (7)$$

where

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(16) The procedure of ref 9 was used for the $RhCl_3(H_2O)_3$ and $RhCl_4(H_2O)_2^-$ separation and identification.

(17) D. W. Archer, D. A. East, and C. B. Monk, *J. Chem. Soc. A*, 720 (1965).

(18) Background material on the FCI and IPI mechanisms is given in: (a) A. Haim, R. J. Gassi, and W. K. Wilmarth, *Advan. Chem. Ser.*, No. 49, 31 (1965); (b) F. Basolo and R. G. Pearson, "Mechanisms of Inorganic Reactions," 2nd ed, Wiley, New York, N. Y., 1967, p 193 ff.

$$D = \frac{k_{\text{obsd}}[(\text{H}^+) + K(\text{Cl}^-)(\text{H}^+) + K_{\text{h}}] - k_{\text{in}}K(\text{Cl}^-)(\text{H}^+)}{k_{\text{obsd}}K_{\text{h}}(\text{Cl}^-)}$$

Since all the terms in D are known, a plot of the high-pH kinetic data (see Figures 6 and 7) in the form $1/k_{\text{obsd}}$ *vs.* D should yield values of k'_{in} and K'. The 45° data are plotted in this fashion in Figure 8, where it is seen that the two "squared" points do not conform to the pattern of the remainder of the data. The hydrogen ion concentration in these two runs was 5×10^{-4} M whereas that for the other runs was close to 2×10^{-4} M. Thus it seems that the IPI rate law is not consistent with the (H^+) dependence of the reaction. Ignoring the two squared points, a weighted least-squares treatment[15] of the remaining data yields the solid line shown in Figure 8. The intercept is $(-5.7 \pm 2.5) \times 10^3$ sec and the slope is $(1.43 \pm 0.06) \times 10^3$ M sec, indicating a best fit value of $K' = -4 \pm 2$ M^{-1}. This constant is defined in the Appendix (see eq A8) as

$$K' = \frac{K'_{\text{Y}} - K'_{\text{Z}}}{1 + K'_{\text{Z}}I}$$

so it can be negative if $K'_{\text{Z}} > K'_{\text{Y}}$. However, with $I = 2.0$ M, the smallest K' can reasonably be is $-\frac{1}{2}$ M^{-1} (*i.e.*, for $K_{\text{Y}} \rightarrow 0$, $K_{\text{Z}} \rightarrow \infty$). The best fit value of -4 M^{-1} requires that K'_{Z} be negative, which is impossible. Even if the data are pushed to their extreme by taking $K' = 0$ (the 90% confidence limit of -4 ± 2 M^{-1}), a good fit to the IPI mechanism still cannot be obtained. At 45° and $(\text{Cl}^-) = 2.0$ M, the kinetic parameters predict a value for $-\log P$ of 5.0 [*viz.*, $-\log K_{\text{h}} = 4.45$, $K' = 0$, K $(=k_3/k_2) = 1.3$ M^{-1} substituted into eq A8]. The experimentally determined value of $-\log P$ in 2.0 M Cl^- is 4.5 ± 0.1 (Table I).

Summarizing, it is seen that the attempt to fit the 45° data to the IPI mechanism yields three inconsistencies: the (H^+) dependence of the reaction is not properly described, a negative value is obtained for one of the ion-pairing constants, and the kinetic and pH titration values for P do not agree. Our conclusion is therefore that the "ion-pair-interchange" mechanism is not operating in these anation reactions.

It should be noted that in our study[2] of chloride anation of the $\text{Rh(H}_2\text{O)}_6{}^{3+}$ ion we interpreted the data in terms of the IPI mechanism. However, in deriving the rate equation used in that work, we failed to take into account the fact that the overall hydrolysis constant, P, has a (Cl^-)-dependent term. Thus we obtained an equation of the same form as (A27) (with $(\text{H}^+) \gg P$) rather than of the same form as eq A31. In fact, the data of ref 2 cannot be adequately fitted with $K_1 = K_2$, as required by the IPI mechanism. We therefore alter our previous conclusion in favor of the FCI mechanism for the $\text{Rh(H}_2\text{O)}_6{}^{3+}$ anation by chloride, in keeping with the data given in Table I of ref 2 (with $K_1 \equiv k_3/k_2$ and $K_2 \equiv k'_3/k'_2$) and consistent with the interpretation of the present study. Incidentally, we are now able to calculate directly the rate constant for the entry of the second chloride under the conditions of the earlier study, where only the entry of the first chloride was measurable. At 75°, $(\text{Cl}^-) = 1.0$ M, $I = 2.0$ M, and $(\text{H}^+) = 0.393$ M, for example, the total rate constant for anation of the hexaaquo species by chloride is 3.6×10^{-5} sec^{-1} (calculated from data in Table I of ref 2) while for the entry of the second chloride, the rate constant is about 5×10^{-4} sec^{-1} as determined from the extrapolated values for the hydrolysis constant given in our Table I and the rate parameters given in Table II. Obviously, with the second step in the anation proceeding at a rate some 13 times greater than the first, only the latter will be measurable in the kinetic study, as was previously concluded.[2]

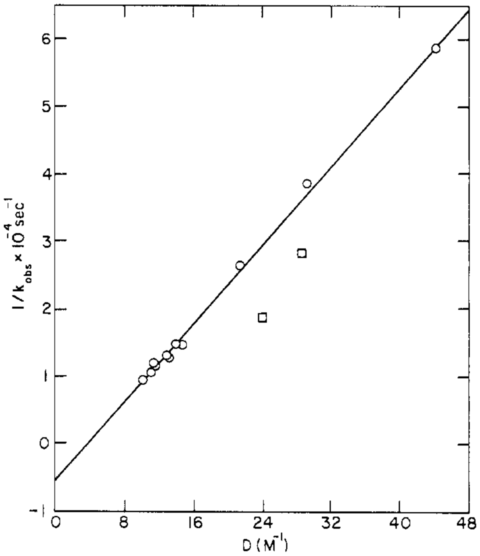

Figure 8. $1/k_{\text{obsd}}$ *vs.* D (see text) at 45° with $I = 2.0$ M (NaClO_4) and (complex) = 0.012 M.

In another earlier paper[5] a study was made of the anation of the anion $\text{RhCl}_5(\text{H}_2\text{O})^{2-}$ by several singly charged anions. These data were interpreted in terms of the FCI mechanism. It seemed unlikely that the curvature in the k_{obsd} *vs.* (anion) plots could be due to ion-pairing between the negatively charged reactants. Our present study shows that even with the cationic complexes where ion-pairing undoubtedly occurs, the FCI mechanism fits the available data much more satisfactorily than does the IPI mechanism. One may conclude therefore that all the anation reactions of the chloroaquorhodium(III) species proceed through five-coordinate intermediates which are stable enough to distinguish between reactants, though there are still some unexplained complications in this type of system.[19]

The fact that *trans*-$\text{RhCl}_2(\text{H}_2\text{O})_4{}^+$ is the only direct product of the anation of $\text{RhCl(H}_2\text{O)}_5{}^{2+}$ indicates that the chloride ligand is exerting a strong labilizing effect on the H_2O ligand in the trans position. Furthermore, this stereochemistry would indicate that the five-coordinate intermediate has a square-pyramidal geometry. The trans-labilizing ability of chloride is also seen in the aquation of $\text{RhCl}_5(\text{H}_2\text{O})^{2-}$, where the major reaction product is *cis*-$\text{RhCl}_4(\text{H}_2\text{O})_2{}^-$.[3,6] Thus it seems that the chloride trans effect also operates through the entire series of chloroaquorhodium(III) species. Chloride anation beginning with $\text{Rh(H}_2\text{O)}_6{}^{3+}$ should successively yield *trans*-$\text{RhCl}_2(\text{H}_2\text{O})_4{}^+$, *trans*-$\text{RhCl}_3(\text{H}_2\text{O})_3$, and *trans*-$\text{RhCl}_4(\text{H}_2\text{O})_2{}^-$, while aquation beginning with $\text{RhCl}_6{}^{3-}$ should yield only cis isomers of the species mentioned.

A direct way to compare the trans-labilizing abilities of hydroxide and chloride is possible by measuring the relative amounts of *cis*- and *trans*-$\text{RhCl}_2(\text{H}_2\text{O})_4{}^+$ produced by the anation of $\text{RhCl(H}_2\text{O)}_4\text{OH}^+$. The assumption would have to be made that the reactive form of $\text{RhCl(H}_2\text{O)}_4\text{OH}^+$ has a cis configuration.[20] Then, with a FCI mechanism and equal chlo-

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(19) H. L. Bott, A. J. Poe, and K. Shaw, *J. Chem. Soc. A*, 1745 (1970).

(20) The probability that only *cis*-$\text{RhCl(H}_2\text{O)}_4\text{OH}^+$ is reactive was not considered in the rate law derivations since it does not alter the mechanistic arguments presented above. To allow for such a factor in the IPI mechanism, k'_{in} in eq A29 would have to be multiplied by that fraction of $[\text{RhCl(H}_2\text{O)}_4\text{OH}]\text{Cl}$ which has a cis configuration, and in the FCI mechanism each dissociation rate constant in F_{B} would be multiplied by a similar fraction.

ride and hydroxide trans effects, one would expect a 1:1 ratio of isomers in the product. As already pointed out, the $RhCl(H_2O)_4OH^+$ product distribution cannot be unambiguously determined until the relative anation rates of *cis*- and *trans*-$RhCl_2(H_2O)_4^+$ at high pH's are known. However, the data in Table III do substantiate the idea of very similar trans-labilizing effects for chloride and hydroxide. The trans effect order $Cl^- \approx OH^- \gg H_2O$ has also been observed by Poe and coworkers for the amine complexes of rhodium(III).[7]

Registry No. $Rh(H_2O)_6{}^{3+}$, 16920-31-3; $RhCl(H_2O)_5{}^{2+}$, 15696-62-5; *cis*-$RhCl(H_2O)_4OH^+$, 37498-45-6; *cis*-$RhCl_2(H_2O)_4^+$, 37498-46-7; *trans*-$RhCl_2(H_2O)_4^+$, 37498-47-8; chlorine, 7782-50-5.

Acknowledgment. Support of this research by means of grants from the National Science Foundation to the State University of New York at Buffalo (Grants GP-6708 and GP-106451) is gratefully acknowledged.

Appendix

Let us symbolize an octahedral complex cation with at least two aquo ligands by the formula $ML_4(H_2O)_2{}^{n+}$. (In the present study M = Rh, $L_4 = (H_3O)_3Cl$, and $n = 2$.) In a system containing reactive anions Y (*e.g.*, Cl^-) and inert anions Z (*e.g.*, ClO_4^-) in large excess (such that (Y) + (Z) = I, the ionic strength, and I is constant), the following continuously and simultaneously maintained equilibria must be considered (complex ion charge designations are eliminated for convenience)

$$ML_4(H_2O)_2 \rightleftarrows ML_4(H_2O)(OH) + H^+ \qquad Q \quad (A1)$$

$$ML_4(H_2O)_2 + Y \rightleftarrows ML_4(H_2O)_2{\cdot}Y \qquad K_Y \quad (A2)$$

$$ML_4(H_2O)_2 + Z \rightleftarrows ML_4(H_2O)_2{\cdot}Z \qquad K_Z \quad (A3)$$

$$ML_4(H_2O)(OH) + Y \rightleftarrows ML_4(H_2O)(OH){\cdot}Y \qquad K'_Y \quad (A4)$$

$$ML_4(H_2O)(OH) + Z \rightleftarrows ML_4(H_2O)(OH){\cdot}Z \qquad K'_Z \quad (A5)$$

The overall acid-base hydrolysis constant, which is evaluated in this work by pH titration of the complex ion solution, is given by

$$P = (H^+)\frac{(ML_4(H_2O)(OH)) + (ML_4(H_2O)(OH){\cdot}Y) + (ML_4(H_2O)(OH){\cdot}Z)}{(ML_4(H_2O)_2) + (ML_4(H_2O)_2{\cdot}Y) + (ML_4(H_2O)_2{\cdot}Z)}$$

In terms of total acidic and basic forms of the complex ion, T_A and T_B, this may be written

$$P = (H^+)T_B/T_A \qquad (A6)$$

and in terms of the various equilibrium constants of eq A1-A5, eq A6 becomes

$$P = \frac{1 + K'_Y(Y) + K'_Z(Z)}{1 + K_Y(Y) + K_Z(Z)}Q \qquad (A7)$$

Defining[19] new constants $K = (K_Y - K_Z)/(1 + K_Z I)$ and $K' = (K'_Y - K'_Z)/(1 + K'_Z I)$, one can rewrite (A7) in the form

$$P = K_h\frac{1 + K'(Y)}{1 + K(Y)} \qquad (A8)$$

where

$$K_h = Q\frac{1 + K'_Z I}{1 + K_Z I}$$

and is constant at a given ionic strength since Q, K'_Z, and K_Z are constant under this condition. K_h is the overall hydrolysis constant in pure inert anion medium ((Y) = 0, (Z) = I).

One now assumes that substitution of Y for ligand water is complete and takes place by a five-coordinate-intermediate mechanism which requires release of H_2O from the coordination sphere prior to attachment of Y. Reaction with Y occurs either in competition with water reentry or in unimolecular processes involving ion pairs. The various possible reactions occur in two parallel series (eq A9A-A15A and A9B-A15B), involving the acid and conjugate base forms of the complex ion.

$$ML_4(H_2O)_2 \underset{k_2}{\overset{k_1}{\rightleftarrows}} ML_4(H_2O) + H_2O \qquad (A9A)$$

$$ML_4(H_2O) + Y \xrightarrow{k_3} ML_4(H_2O)Y \qquad (A10A)$$

$$ML_4(H_2O)_2{\cdot}Y \underset{k_5}{\overset{k_4}{\rightleftarrows}} ML_4(H_2O){\cdot}Y + H_2O \qquad (A11A)$$

$$ML_4(H_2O){\cdot}Y + Y \xrightarrow{k_6} ML_4(H_2O)Y{\cdot}Y \qquad (A12A)$$

$$ML_4(H_2O){\cdot}Y \xrightarrow{k_7} ML_4(H_2O)Y \qquad (A13A)$$

$$ML_4(H_2O)_2{\cdot}Z \underset{k_9}{\overset{k_8}{\rightleftarrows}} ML_4(H_2O){\cdot}Z + H_2O \qquad (A14A)$$

$$ML_4(H_2O){\cdot}Z + Y \xrightarrow{k_{10}} ML_4(H_2O)Y{\cdot}Z \qquad (A15A)$$

$$ML_4(H_2O)(OH) \underset{k'_2}{\overset{k'_1}{\rightleftarrows}} ML_4(OH) + H_2O \qquad (A9B)$$

$$ML_4(OH) + Y \xrightarrow{k'_3} ML_4(OH)Y \qquad (A10B)$$

$$ML_4(H_2O)(OH){\cdot}Y \underset{k'_5}{\overset{k'_4}{\rightleftarrows}} ML_4(OH){\cdot}Y + H_2O \qquad (A11B)$$

$$ML_4(OH){\cdot}Y + Y \xrightarrow{k'_6} ML_4(OH)Y{\cdot}Y \qquad (A12B)$$

$$ML_4(OH){\cdot}Y \xrightarrow{k'_7} ML_4(OH)Y \qquad (A13B)$$

$$ML_4(H_2O)OH{\cdot}Z \underset{k'_9}{\overset{k'_8}{\rightleftarrows}} ML_4(OH){\cdot}Z + H_2O \qquad (A14B)$$

$$ML_4(OH){\cdot}Z + Y \xrightarrow{k'_{10}} ML_4(OH)Y{\cdot}Z \qquad (A15B)$$

The total rate of reaction of the acidic form is

$$-dT_A/dt = k_3(ML_4(H_2O))(Y) + k_6(ML_4(H_2O){\cdot}Y)(Y) + k_7(ML_4(H_2O){\cdot}Y) + k_{10}(ML_4(H_2O){\cdot}Z)(Y)$$

which, when one applies the stationary-state hypothesis with respect to the three five-coordinate intermediates produced in reactions A9A, A11A, and A14A, can be expressed in the form

$$-dT_A/dt = F_AT_A = \left\{\frac{k_1\dfrac{k_3}{k_2}(Y)}{1 + \dfrac{k_3}{k_2}(Y)} + \frac{\left[k_4\dfrac{k_6}{k_5 + k_7}(Y) + k_4\dfrac{k_7}{k_5 + k_7}\right]K_Y(Y)}{1 + \dfrac{k_6}{k_5 + k_7}(Y)} + \frac{k_8\dfrac{k_{10}}{k_9}(Y)K_Z(Z)}{1 + \dfrac{k_{10}}{k_9}(Y)}\right\}\frac{T_A}{1 + K_Y(Y) + K_Z(Z)} \qquad (A16)$$

One can derive an entirely parallel expression for $-dT_B/dt = F_BT_B$, using eq A9B-A15B, where the various k's and K's are the primed analogs of those in eq A16. The observed rate constant for the total process becomes, by use of eq A6 and the fact that $T = T_A + T_B$

$$k_{\text{obsd}} = -\frac{1}{T}\left(\frac{dT}{dt}\right) = [F_A(H^+) + F_BP]\frac{1}{(H^+) + P} \qquad (A17)$$

The factor F_A of eq A16 can be rearranged into the form

$$F_A = \frac{A(Y) + B(Y)^2 + C(Y)^3 + D(Y)^4}{1 + E(Y) + F(Y)^2 + G(Y)^3 + H(Y)^4} \qquad (A18)$$

with an entirely parallel form for F_B

$$F_B = \frac{A'(Y) + B'(Y)^2 + C'(Y)^3 + D'(Y)^4}{1 + E'(Y) + F'(Y)^2 + G'(Y)^3 + H'(Y)^4} \qquad (A19)$$

The constants A, A', B, B', etc., in these equations are complicated combinations of I, the constant ionic strength, and the various k's and K's. Obviously, with so many parameters available, eq A17 can be made to fit almost any set of rate data for this type of reaction.

Most of the anation data reported in the literature to date concern reactions in acid solution where $(H^+) \gg P$ and $F_A \cdot (H^+) \gg F_BP$. Then eq A17 reduces to $k_{\text{obsd}} = F_A \cdot$ Invariably, such data can be linearly fitted to double reciprocal plots of the type $1/k_{\text{obsd}}$ *vs.* $1/(Y)$, indicating that only the terms in eq A18 which are first power in (Y) contribute.

Therefore, the following approximation can be made

$$F_A \cong \frac{A(Y)}{1 + E(Y)} \qquad (A20)$$

This condition can be realized by at least two sets of simplifying assumptions.

(a) Ion-pairing contributes negligibly to the process, or $K_Y = K_Z = 0$. Then one has

$$F_A = \frac{k_1(k_3/k_2)(Y)}{1 + (k_3/k_2)(Y)} \qquad (A21)$$

This is the conventional five-coordinate-intermediate expression derived from eq A9A and A10A.

(b) Ion-pairing has no effect on the rate of water release from the complex nor does it affect the ratio of rate of reaction with Y to that with water ($k_1 = k_4 = k_8$, $k_3/k_2 = k_6/k_5 = k_{10}/k_9$). Furthermore reaction A13A contributes negligibly to the total process ($k_7 \approx 0$). These assumptions yield an equation identical with (A21).

If similar assumptions are applied to the reaction of the base complexes, the five-coordinate-intermediate rate law given by eq A17-A19 can be simplified to eq A22.

$$k_{\text{obsd}} = \left[\frac{k_1\frac{k_3}{k_2}(H^+)(Y)}{1 + \frac{k_3}{k_2}(Y)} + \frac{k'_1\frac{k'_3}{k'_2}P(Y)}{1 + \frac{k'_3}{k'_2}(Y)}\right]\frac{1}{(H^+) + P} \qquad (A22)$$

The alternative mechanism for interpreting octahedral complex anation data is the ion-pair-interchange mechanism where it is assumed that the only species in solution that can give rise to products are the Y-ion-paired species. Reaction occurs *via* the interchange of outer-sphere Y with inner-sphere water

$$ML_4(H_2O)_2\cdot Y \xrightarrow{k} ML_4(H_2O)Y + H_2O \qquad (A23A)$$

$$ML_4(H_2O)OH\cdot Y \xrightarrow{k'} ML_4(OH)Y + H_2O \qquad (A23B)$$

The rate of reaction for the acidic form is

$$-dT_A/dt = F_AT_A = k(ML_4(H_2O)_2\cdot Y) \qquad (A24)$$

When the equilibria in reactions A2 and A3 are considered, F_A is given by

$$F_A = \frac{kK_Y(Y)}{1 + K_Z(Z) + K_Y(Y)} \qquad (A25)$$

[Note that eq A16 reduces to (A25) if it is assumed that $k_3 = k_6 = k_{10} = 0$. Then k in eq A25 becomes $k_4k_7/(k_5 + k_7)$.] By introducing the variable K (see eq A8) and the apparent interchange rate constant[19]

$$k_{\text{in}} = k'\frac{K_Y}{K_Y - K_Z}$$

F_A can be arranged into the form

$$F_A = \frac{k_{\text{in}}K(Y)}{1 + K(Y)} \qquad (A26)$$

An analogous primed expression can be derived for F_B. The total rate law for the ion-pair-interchange mechanism is found by again substituting for F_A and F_B in eq A17, *i.e.*

$$k_{\text{obsd}} = \left[\frac{k_{\text{in}}K(Y)(H^+)}{1 + K(Y)} + \frac{k'_{\text{in}}K'(Y)P}{1 + K'(Y)}\right]\frac{1}{(H^+) + P} \qquad (A27)$$

Note that, as written, eq A27 is mathematically identical with eq A22 appearing to rule out a mechanistic distinction on the basis of *form* of the rate law alone. However, substituting for P the equality of eq A8, one can write for eq A22

$$k_{\text{obsd}} = \left[\frac{k_1\frac{k_3}{k_2}(Y)(H^+)}{1 + \frac{k_3}{k_2}(Y)} + \frac{k'_1\frac{k'_3}{k'_2}(Y)K_h}{1 + \frac{k'_3}{k'_2}(Y)} \times \frac{1 + K'(Y)}{1 + K(Y)}\right]\frac{1}{(H^+) + K_h\frac{1 + K'(Y)}{1 + K(Y)}} \qquad (A28)$$

while eq A27 becomes

$$k_{\text{obsd}} = \left[\frac{k_{\text{in}}K(Y)(H^+) + k'_{\text{in}}K'(Y)K_h}{1 + K(Y)}\right] \times \frac{1}{(H^+) + K_h\frac{1 + K'(Y)}{1 + K(Y)}} \qquad (A29)$$

One sees immediately the fundamental difference in the two rate laws. The five-coordinate intermediate law (eq A28) is less restrictive than the ion-pair-interchange law (eq A29). Equation A29 has two fewer adjustable parameters and it has a common denominator within the bracket. This latter restriction is most clearly evident when reactions of the acid and conjugate base forms both contribute substantially to the total rate under circumstances such that $(H^+) \gg P$. Then eq A28 and A29 become respectively

$$k_{\text{obsd}} = \frac{k_1\frac{k_3}{k_2}(Y)}{1 + \frac{k_3}{k_2}(Y)} + \left[\frac{k'_1\frac{k'_3}{k'_2}(Y)K_h}{1 + \frac{k'_3}{k'_2}(Y)}\right] \times \left(\frac{1 + K'(Y)}{1 + K(Y)}\right)\frac{1}{(H^+)} \qquad (A30)$$

$$k_{\mathrm{obsd}} = \frac{k_{\mathrm{in}}K(\mathrm{Y}) + k'_{\mathrm{in}}K'(\mathrm{Y})K_{\mathrm{h}}/(\mathrm{H}^+)}{1 + K(\mathrm{Y})} \qquad \text{(A31)}$$

It is obvious that the ratio of the slope to the intercept of $1/k_{\mathrm{obsd}}$ *vs.* $1/(\mathrm{Y})$ plots for the ion-pair-interchange mechanism (inverse of eq A31) is constant and independent of the acidity. However, such a simplified plot is not possible for the five-coordinate-intermediate mechanism except under the unlikely circumstance that $k_3/k_2 = K$ and $k'_3/k'_2 = K'$, when eq A30 and A31 become mathematically identical.

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Metal Ion Catalysis of *S*-Ethyl Thiooxalate Hydrolysis

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Kinetic studies of the base hydrolysis of ethyl thiooxalate, $^-\mathrm{O_2CCOSEt}$ ($\mathrm{EtSOx^-}$), to give $\mathrm{C_2O_4}^{2-}$ and EtSH have been carried out in the absence and presence of metal ions, $\mathrm{M^{2+}}$. With $\mathrm{Pb^{2+}}$, $\mathrm{Ni^{2+}}$, and $\mathrm{Mg^{2+}}$, the rate of ester hydrolysis follows the expression: rate = $k_3[\mathrm{EtSOx^-}][\mathrm{M^{2+}}][\mathrm{OH^-}]$. As previously suggested for the metal ion catalyzed hydrolysis of the analogous ethyl oxalate ($\mathrm{EtOx^-}$), the mechanism of the reaction is believed to involve rapid coordination of the ester by the metal ion followed by rate-determining $\mathrm{OH^-}$ attack on the ester. At 25° the values of k_3 (M^{-2} sec^{-1}) decrease with the metal ion as follows: $\mathrm{Pb^{2+}}$ (1.69×10^6) > $\mathrm{Ni^{2+}}$ (1.80×10^4) > $\mathrm{Mg^{2+}}$ (1.78×10^2). It was observed that each of these metal ions accelerated the rate of hydrolysis of both $\mathrm{EtOx^-}$ and $\mathrm{EtSOx^-}$ by essentially the same factor suggesting that the sulfur (or ether oxygen) is not coordinated to the metal ion in the $\mathrm{M(ester)^+}$ species undergoing $\mathrm{OH^-}$ attack.

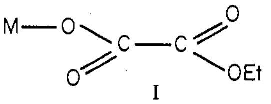
Introduction

In an earlier paper,[2] we discussed the metal ion catalyzed hydrolysis of ethyl oxalate, $^-\mathrm{O_2CCO_2Et}$ ($\mathrm{EtOx^-}$). The kinetic and equilibrium data for that reaction were interpreted in terms of the mechanism

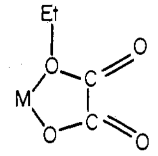
$$\mathrm{M^{2+} + EtOx^-} \overset{K_f}{\rightleftarrows} \mathrm{MEtOx^+} \qquad (1)$$

$$\mathrm{MEtOx^+ + OH^-} \xrightarrow{k} \mathrm{M(C_2O_4) + EtOH} \qquad (2)$$

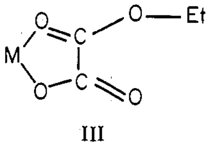
Initial coordination of the ester (eq 1) was rapid; this was followed by $\mathrm{OH^-}$ attack on the coordinated ester in the rate-determining step. An unresolved aspect of the reaction was the nature of $\mathrm{EtOx^-}$ coordination to the metal in the $\mathrm{MEtOx^+}$ intermediate. There were three possibilities



I



II



III

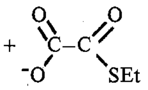
In all cases, electron withdrawal by the positive metal ion would be expected to facilitate $\mathrm{OH^-}$ attack at the ester carbonyl carbon atom, thereby enhancing the rate of hydrolysis.

Support for structure I derives from the known increase in rate on neutralizing the negative charge of the anionic carboxylate group. That is, base hydrolysis at 25° of one ester group in $\mathrm{EtO_2CCO_2Et}$ occurs at a rate (3960 M^{-1} sec^{-1} [3]) which is 5.8×10^3 times faster than that of $^-\mathrm{O_2CCO_2Et}$ (0.687 M^{-1} sec^{-1} [2]). By comparison, when bound to $\mathrm{Cu^{2+}}$ as $\mathrm{Cu(EtOx)^+}$, the ester hydrolyzed at a rate (1.4×10^5 M^{-1} sec^{-1} [2]) which was 2×10^5 times greater than that for free $\mathrm{EtOx^-}$. This increased rate is not so large that it could not be accounted for by a charge effect in a structure such as I. The rates with other metal ions were even less than observed for $\mathrm{Cu^{2+}}$ and could even more readily be explained in terms of structure I.

Support of structure II comes from an X-ray investigation[4] of the ester complex $\mathrm{Cu[N(CH_2CO_2)_2CH(}$*i*$\mathrm{\text{-}Pr)CO_2Et](H_2O)_2}$, which shows weak coordination of the C–O–Et oxygen atom to the Cu(II). This suggests that complex II may be the active form of the ester during hydrolysis.

Acid-catalyzed hydrolyses of esters have long been believed[5] to proceed *via* an intermediate in which the carbonyl oxygen of the ester was protonated. In the same manner metal ions acting as Lewis acids might also be expected to coordinate at that oxygen as shown in structure III.

It should be emphasized that while structures II or III may be the active form for $\mathrm{OH^-}$ attack, the known weak coordinating ability of ester groups[6] suggests that the predominant form of $\mathrm{MEtOx^+}$ in solution is structure I. The purpose of the present research was to establish the importance (or lack thereof) of structure II to $\mathrm{EtOx^-}$ hydrolysis. We have therefore examined the metal ion catalyzed hydrolysis of the analogous thio ester *S*-ethyl thiooxalate ($\mathrm{EtSOx^-}$)



$$\mathrm{M^{2+}} + {}^-\mathrm{O(O)C{-}C(O)SEt} + \mathrm{H_2O} \rightarrow \mathrm{M(C_2O_4) + EtSH + H^+} \qquad (3)$$

If structure II is the form of the ester undergoing $\mathrm{OH^-}$ attack, its concentration should change markedly as the ether oxygen is replaced by sulfur; this would in turn affect the rate of hydrolysis correspondingly. On the other hand,

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[1] Fellow of the Alfred P. Sloan Foundation, 1970–1972.

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