F_2PS_2H, $(F_2PS_2)_2$, and, as red crystals, tris(difluorodithiophosphinato)vanadium(III).[3a]

(e) **Titanium Tetrachloride.**—Titanium tetrachloride (0.2104 g, 1.11 mmol) and F_2PS_2H (0.5413 g, 4.04 mmol) were mixed and allowed to react as described above. The mixture slowly darkened to a red-orange solution. After standing (1 day) the mixture was fractionated to afford HCl (0.049 g, 1.34 mmol), excess F_2PS_2H (0.3859 g; consumed, 0.1554 g, 1.16 mmol) and an orange liquid, probably trichloro(difluorodithiophosphinato)-titanium(IV), of very low volatility. Repeating the reaction over 7 weeks or at 70° (1 day) afforded similar results. The liquid was sufficiently volatile to enable small amounts to be transferred (~2 days, 25° (10^{-4} mm)) to a break-seal for mass spectrometric or to an nmr tube for ^{19}F nmr characterization of the product.

(f) **Niobium or Tantalum Metal.**—Niobium metal did not react (25–70°, 100 days) with F_2PS_2H. Tantalum metal did not react at room temperature with F_2PS_2H but at 70° (140 days) catalyzed the decomposition of F_2PS_2H to P_2S_5 and a mixture of volatile products including SPF_3.

Summary and Conclusion

Unlike the reactions of F_2PS_2H with VCl_4 discussed herein and VCl_3,[3a] $OVCl_3$,[3a] O_2CrCl_2,[7] $MoCl_5$,[7] $MoCl_4$,[7] or $OMoCl_4$,[7] total replacement of chlorine was not achieved for $TiCl_4$, $NbCl_4$, $NbCl_5$, or $TaCl_5$, and the major products were complexes of the metals in their original valence states.

The major products in the reactions of HS_2PF_2 with $NbCl_5$ or $TaCl_5$ were the complexes $Cl_3M(S_2PF_2)_2$ (M = Nb, Ta), and in each case at least 2 mol of F_2PS_2H was consumed, and 2 mol of HCl or slightly more was evolved. The failure of the acid to reduce the oxidation states of the central metal atoms (except vanadium) illustrates the stability of the oxidation states 5+ (Nb, Ta) and 4+ (Ti) for these metals. The oxidation state 3+ is an important one for vanadium, and its resistance to oxidation to the 4+ state is greater than that of titanium. Thus the formation of the complex $V(S_2PF_2)_3$, with the highly favored six-coordination about vanadium, was most facile. The replacement of only one chlorine about titanium is surprising, when two chlorines are easily replaced by ligands such as acetylacetonate, but six-coordination about titanium could be satisfied by formation of a stable chlorine-bridged polynuclear complex which then does not suffer further replacement. It is of interest to note that, if the niobium and tantalum complexes are indeed nonionic, and the $F_2PS_2^-$ ligand is bidentate as suggested by the infrared and ^{19}F nmr spectra of the complexes, then these metals are in a seven-coordinate enviornment. Though uncommon, such an environment is known for these metals.[18,19]

Acknowledgment.—We thank the National Research Council of Canada for financial support of this work.

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Linear Free Energy Relationships in the Mercury(II)-Catalyzed Aquation of Halopentaaquochromium(III) Complexes[1a]

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The kinetics of the mercury(II)-catalyzed aquations of the halopentaaquochromium(III) complexes have been determined at 0.500 *M* ionic strength. The general form of the rate law is $-d \ln [Cr(H_2O)_5X^{2+}]/dt = (k_0 + k_{-1}[H^+]^{-1})[Hg^{2+}]$. The values of k_0 (M^{-1} sec^{-1}) at 25.0° are $<2 \times 10^{-7}$, 0.0347, 288, and *ca.* 6×10^7 for X = F, Cl, Br, and I and of k_{-1} (sec^{-1}) are 0.0312 and 210 for X = Cl and Br. Values of k_0 were also determined for the reactions of $Cr(H_2O)_5I^{2+}$ with $HgCl^+$ and $HgCl_2$ to be 9.10×10^7 and 518 M^{-1} sec^{-1} at 25.0°. Activation parameters were determined for most of these reactions. A linear free energy relationship was established for the Hg^{2+}-catalyzed reactions and had a slope of 0.90 ± 0.02, indicating substantial breaking of the Cr–X bond and making of the Hg–X bond in the transition state, in agreement with results of chemical competition studies.

Introduction

The aquation of cobalt(III) complexes appears to proceed *via* formation of a five-coordinate intermediate with "good" leaving groups (generated by reactions such as $Co(NH_3)_5X^{2+} + Hg^{2+}$ (X = Cl, Br, I)[2] and $Co(NH_3)_5N_3^{2+} + HNO_2$[3]). With relatively "poor" leaving groups, the mechanism is still dissociative[4] but apparently does not involve the formation of an intermediate.[5] In the case of the unassisted aquation of acidopentaamminecobalt(III) complexes, Langford[6] has shown that the free energy of activation $\Delta G^{\ddagger}$ for the forward reaction is linearly related to the standard free energy change $\Delta G°$ for the overall reaction

$$Co(NH_3)_5X^{2+} + H_2O = Co(NH_3)_5OH_2^{3+} + X^- \quad (1)$$

A plot of the log of the first-order rate constants *vs.* the log of the corresponding equilibrium constants (X = F, H_2PO_4, Cl, Br, I, NO_3) is fully linear with a slope of 1.0.[6] For the analogous reactions of iridium(III) complexes, the slope of the linear free energy relationship (LFER) is 0.9.[7] Both studies suggest that the role of the departing ligand in the transition state

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(1) (a) Taken in part from the M.S. thesis of C. M. I., 1971. (b) National Science Foundation Trainee, 1969–1971.

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for the aquation reaction is strongly similar to its role in the product as a solvated ion, even though the processes are not purely dissociative.[5]

Swaddle and Guastalla[8] investigated the LFER for the acid-independent path in the unassisted aquations of the halopentaaquochromium(III) complexes and found a slope of 0.56 at 25° and 0.59 at 50°. They concluded that the transition state of the aquation reaction resembles the products only to a moderate degree. Previous kinetic results on the reaction of $Cr(H_2O)_5Cl^{2+}$ with Hg^{2+} indicated that $HgCl^+$ is probably a "good" leaving group,[9] and indeed, when this reaction is carried out in NO_3^- or methanol–water solutions, the products contain $Cr(H_2O)_5NO_3^{2+}$[10] or $Cr(H_2O)_5CH_3OH^{3+}$[11] in amounts greater than could be accounted for by substitution on $Cr(H_2O)_6^{3+}$, suggesting the presence of a five-coordinate intermediate formed in a dissociative process.

In the present work we wish to develop the LFER for the mercury(II)-assisted aquations of the halopentaaquochromium(III) complexes (eq 2), so that the use of

$$Cr(H_2O)_5X^{2+} + Hg^{2+} + H_2O = Cr(H_2O)_6^{3+} + HgX^+ \quad (2)$$

the LFER as an indication of the degree of dissociation in the transition state can be tested on a system for which there is strong evidence for a completely dissociative mechanism.

Experimental Section

Preparation of Reagents.—Chloropentaaquochromium(III) perchlorate solutions were prepared by dissolving reagent grade chromium(III) chloride in 0.1 *M* perchloric acid, purging with nitrogen, and adding a small amount of chromium(II) perchlorate. After shaking with air, the solution was adsorbed on a column of Dowex 50W-X8 50–100 mesh cation-exchange resin and the monochloro complex was eluted with 2 *M* perchloric acid. The solution was stored at low temperature to prevent decomposition. The bromo and fluoro complexes were prepared from the analogous chromium(III) halides in the same manner except that a jacketed column held at 0° was used for the bromo complex and a column of 20–50 mesh Dowex resin was used for the fluoro complex. The iodo complex was prepared by adding chromium(II) to a solution of iodine prepared by reaction of iodic acid with sodium iodide in 0.1 *M* perchloric acid that had been purged with nitrogen. The solution was filtered and transferred to an ice water cooled column of resin and the monoiodo complex was eluted with 1.0 *M* perchloric acid. The purity of the solutions was checked spectrally using a Cary 14 recording spectrophotometer. Small amounts of hexaaquochromium(III) were found in both the fluoro and iodo complex solutions and the exact amount of each complex was determined from the spectra and the total chromium concentration determined by oxidation with alkaline peroxide and spectrophotometric analysis of the Cr(VI) produced.[12] Solutions of mercury(II), barium(II), and chromium(II) perchlorates,[9] lithium chloride,[13] and perchloric acid[9] were prepared as described previously. Lithium perchlorate solution was prepared by neutralizing a weighed amount of the hydroxide with perchloric acid and the final solution was analyzed by ion exchange. Care had to be taken to obtain solutions reasonably free of CO_2, or $BaCO_3$ would precipitate from reaction solutions. Distilled water was used in all solutions.

Kinetics.—Kinetics experiments were carried out with a Durrum stopped-flow spectrophotometer or with a Cary 14 recording spectrophotometer using an expanded-scale slide wire. Measurements were made at 670 nm for the fluoro complex, 440 nm for the chloro and bromo complexes, and 400 nm for the iodo complex. For the first three complexes, experiments covered the concentration ranges (0.5–1.0) × 10^{-3} *M* CrX^{2+}, (0.5–5.0) × 10^{-2} *M* Hg^{2+}, and 0.02–0.35 *M* H^+. The concentration of dipositive ions was held constant at 5.0 × 10^{-2} *M* by addition of barium perchlorate and ionic strength 0.500 *M* was maintained with lithium perchlorate.

Initial experiments with the iodo complex at room temperature indicated that at a CrI^{2+} concentration which would give an observable absorbance change (1.0 × 10^{-5} *M*) and a Hg^{2+} concentration high enough to ensure pseudo-first-order conditions (1.0 × 10^{-4} *M*), the half-life for the reaction was less than 1 msec even at 0.50 *M* H^+. The reaction was slowed to an observable rate by reducing the concentration of the active forms of the catalyst by complexation of Hg(II) by Cl^-. It has been shown previously that Hg^{2+} and $HgCl^+$ have similar catalytic activity, while the higher complexes are relatively inactive.[9,13–15] Thus, addition of Cl^- reduces the concentration of active catalysts while holding their concentrations nearly constant throughout the reaction as long as pseudo-first-order conditions in total Hg(II) are maintained. Iodide ion was not used because of the low solubility of HgI_2. The exact amount of each mercury complex and of the available free chloride in solution was calculated[13] for each total mercury concentration employed, (0.75–5.0) × 10^{-3} *M*, using literature values[16–18] of the equilibrium constants for the four complexation reactions and their variation with temperature. The values of K_1, K_2, K_3, and K_4 used were 8.9 × 10^6, 4.2 × 10^6, and 12.0 at 15°; 5.5 × 10^6, 3.0 × 10^6, 7.1, and 10.0 at 25°; 2.0 × 10^6, 4.2 × 10^6, 5.5, and 9.4 at 35°.

Absorbance–time data for all experiments were plotted by the Guggenheim method[19] and were generally linear for at least 90% reaction.

Results

Reaction of CrF^{2+}.—No evidence of mercury(II) catalysis was found for the aquation of the fluoro complex in solutions of 0.05 *M* Hg^{2+} and 0.1 *M* H^+ over the temperature range 45–65°. Assuming that a contribution from a catalytic reaction at least equal to that of the spontaneous reaction could have been detected and extrapolating literature data[20] for this aquation to 25° and 0.1 *M* H^+, an upper limit for the catalytic rate constant k_{CrF} (eq 3 below) can be set at $<2 \times 10^{-7}$ M^{-1} sec^{-1}. This limit is consistent with the value predicted from the LFER developed below.

Reaction of $CrCl^{2+}$ and $CrBr^{2+}$.—Linearity of the Guggenheim plots and variation of mercury(II) concentration over a tenfold range verified the expected first-order dependence on Cr(III) and Hg(II) concentrations according to the rate equation

$$-\mathrm{d} \ln\, [Cr(H_2O)_5X^{2+}]/\mathrm{d}t = k_{CrX}[Hg^{2+}] \quad (3)$$

Conformance to this rate equation is shown in Figure 1. Variation of the acid concentration at constant [Hg(II)] (see Table I) yielded the following equation for the second-order rate constant

$$k_{CrX} = k_0 + k_{-1}[H^+]^{-1} \quad (4)$$

Data taken at 15, 25, and 35° were each fit to this equation using a nonlinear least-squares computer program.[21] The computed values of k_0 and k_{-1} reproduce the data with an average deviation of 1.3%

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[21] The programs used are based on reports from Los Alamos Scientific Laboratory, LA-2367 + addenda, and were modified to operate on the IBM 360/75 computer.

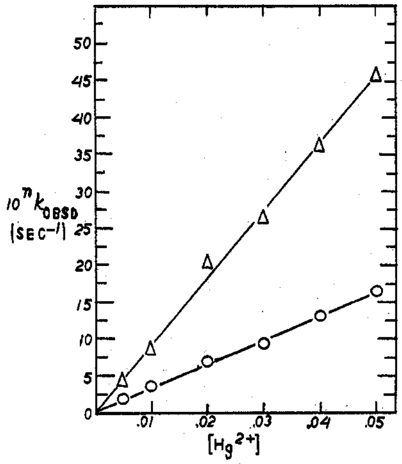

Figure 1.—Plot of k_{obsd} *vs.* $[Hg^{2+}]$ at 25° and 0.10 M H^+: ○, $CrCl^{2+}$, $n = 3$; Δ, $CrBr^{2+}$, $n = 0$.

TABLE I

VALUES OF THE RATE CONSTANTS FOR THE REACTION OF Hg^{2+} WITH CrX^{2+} AT VARIOUS $[H^+]$

$10^2[H^+]$, M	k_{CrX}, M^{-1} sec^{-1}: X = Cl, 15°	X = Cl, 25°	X = Cl, 35°	X = Br, 15°	X = Br, 25°	X = Br, 35°
35.0	0.0318	0.124	0.369	327	894	1980
30.0	0.0356	0.138	0.413		963	
25.0	0.0395	0.161	0.469	385	1130	2590
20.0	0.0467	0.189	0.561	439	1360	3150
15.0	0.0636	0.241	0.721	542	1720	
10.0	0.0866	0.347	1.05	673		5680
6.7	0.128	0.501	1.45	975	3460	
5.0	0.174	0.666			4390	
2.0		1.58				

for $CrCl^{2+}$ and 1.0% for $CrBr^{2+}$. The values of k_0 and k_{-1} obtained at each temperature were then fit to the absolute rate theory expression to obtain the activation parameters for both reactions. Values of the rate and activation parameters are given in Table II. The activation parameters reproduce the values of k_0 and k_{-1} with average deviations of 6 and 4% for $CrCl^{2+}$ and 4 and 7% for $CrBr^{2+}$.

TABLE II

VALUES OF THE RATE AND ACTIVATION PARAMETERS FOR THE REACTION OF Hg^{2+} WITH CrX^{2+}

Compd		$\Delta H^{\ddagger}$, kcal/mol	$\Delta S^{\ddagger}$, eu	k^a: 15°	25°	35°
$CrCl^{2+}$	k_0 path	22.0 ± 1.2	8.5 ± 2.9	0.00818	0.0347	0.106
	k_{-1} path	20.9 ± 0.9	4.5 ± 3.2	0.00805	0.0312	0.0918
$CrBr^{2+}$	k_0 path	6.7 ± 0.8	−24.9 ± 2.7	173	288	397
	k_{-1} path	20.0 ± 1.5	19.0 ± 5.1	53.5	210	552

[a] Units of k_0 and k_{-1} are M^{-1} sec^{-1} and sec^{-1}, respectively.

Values of these parameters have been determined previously[9] for the $CrCl^{2+}$ reaction in a different ionic medium (0.158 M 2+ ions, 1.00 M ionic strength). Considering the difference in medium, the agreement is quite good—*e.g.*, values of k_0 and k_{-1} at 25° in the previous study were 0.0478 M^{-1} sec^{-1} and 0.0266 sec^{-1}.

Reaction of CrI^{2+}.—For the reaction of the iodo complex with mercury(II) in the presence of added chloride ion, the dependence on total mercury(II) concentration is not simple when the free chloride ion concentration is below 1.5×10^{-2} M. At this chloride concentration the [Hg(II)] dependence is simple first order, but deviation from this dependence increases as $[Cl^-]$ is decreased (Figure 2). The data did not fit any simple rate equation well but are consistent with a dependence of the form

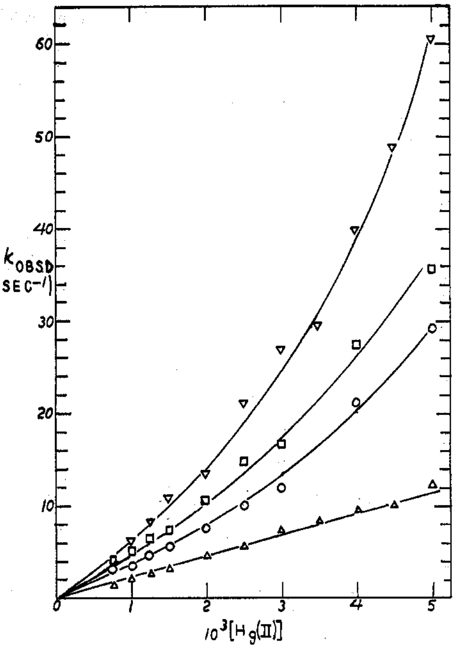

Figure 2.—Observed rate constant *vs.* [Hg(II)] for the reaction of Hg(II) with CrI^{2+} at 25° and 0.50 M H^+: Δ, 1.5×10^{-2} M Cl^-; ○, 8.5×10^{-3} M Cl^-; □, 6.3×10^{-3} M Cl^-; ▽, 5.0×10^{-3} M Cl^-.

$$-\mathrm{d}\ln\,[Cr(H_2O)_5I^{2+}]/\mathrm{d}t = a[Hg(II)] + b[Hg(II)]^2 + c[Hg(II)]^3 \quad (5)$$

Attempts to determine the chloride dependence of the last two terms were not successful. We do not understand the origin of the additional terms but behavior of this type has been observed previously in the Ag^+-catalyzed aquation of $Co(NH_3)_5I^{2+}$.[22] If the value of a in eq 5 is set equal to the limiting slope of the Hg(II) dependence illustrated in Figure 2 and the observed rate constant is assumed to be a composite of the individual constants for reaction with each form of mercury present, the relationship can be expressed as

$$a = k_{obsd}/[Hg(II)] = k_{Hg}[Hg^{2+}]/[Hg(II)] + k_{HgCl}[HgCl^+]/[Hg(II)] + k_{HgCl_2}[HgCl_2]/[Hg(II)] + k_{HgCl_3}[HgCl_3^-]/[Hg(II)] + k_{HgCl_4}[HgCl_4^{2-}]/[Hg(II)] \quad (6)$$

The limiting slopes and the relative concentrations of the mercury complexes at each free chloride concentration were fit to this equation with a nonlinear least-squares computer program. The most satisfactory fit was obtained with k_{Hg}, k_{HgCl_3}, and k_{HgCl_4} set equal to zero. Allowing k_{Hg}, k_{HgCl_3}, or both to vary did not improve the fit appreciably and gave a value for k_{Hg} greater than that for a diffusion-controlled reaction. Even assuming a diffusion-controlled rate, the Hg^{2+}-catalyzed path never contributes more than 0.1% to the overall rate at the concentrations accessible to us, excluding an accurate determination of k_{Hg} by this method. Thus any value of k_{Hg} at the diffusion-controlled limit or lower would be consistent with this data treatment, which also gives rise to a standard deviation of k_{Hg}

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TABLE III

RATE CONSTANTS AND RELATIVE MERCURY COMPLEX CONCENTRATIONS FOR THE REACTION OF CrI^{2+} WITH Hg(II) AT 0.50 M H^+

$10^3[Cl^-]$, M	$10^{-3}k_{obsd}/[Hg(II)]$, M^{-1} sec^{-1} 15°	25°	35°	$10^{10}[Hg^{2+}]/[Hg(II)]^a$	$10^5[HgCl^+]/[Hg(II)]^a$	$10[HgCl_2]/[Hg(II)]^a$
15.0	1.05	2.34	5.53 ± 0.16	2.39	1.97	8.91
12.0	1.37	2.64	6.83 ± 0.53	3.82	2.52	9.13
10.0	1.44	3.22	8.66 ± 0.10	5.47	3.04	9.27
8.50	2.07	3.88	9.53 ± 1.13	7.83	3.66	9.39
6.30	2.31	5.10	12.74 ± 0.58	14.5	5.02	9.55
5.60	2.49	5.60		18.4	5.68	9.60
5.00	2.55	6.40		23.2	6.39	9.64

[a] Relative mercury complex concentrations are given for 25°. The ratios at other temperatures can be calculated readily from the equilibrium constants given in the text.

TABLE IV

VALUES OF THE RATE CONSTANTS AND ACTIVATION PARAMETERS FOR THE REACTION OF CrI^{2+} WITH $HgCl^+$ AND $HgCl_2$

	$\Delta H^{\ddagger}$, kcal/mol	$\Delta S^{\ddagger}$, eu	k_{HgCl_m}, M^{-1} sec^{-1} 15°	25°	35°
$HgCl^+$	15.3 ± 5.0	29.6 ± 16.6	5.26×10^7	9.10×10^7	32.4×10^7
$HgCl_2$	9.34 ± 0.94	−14.7 ± 3.1	3.16×10^2	5.18×10^2	9.76×10^2

over an order of magnitude larger than its value. For these reasons, it was necessary to use an alternate method, described below, to estimate the value of k_{Hg}. The values of the limiting slopes at 0.50 M H^+ and the relative concentrations of the mercury complexes at 25° used in eq 6 can be found in Table III. The data at 15, 25, and 35° are reproduced by the computed values of k_{HgCl} and k_{HgCl_2} (Table IV) with an average deviation of 6.0, 2.0, and 6.4%, respectively. The rate parameters for reaction with each mercury complex were fit to the absolute rate theory expression, and the activation parameters derived in this way (Table IV) reproduced k_{HgCl} and k_{HgCl_2} with an average deviation of 19.7 and 4.0%, respectively. Variation of acid concentration at constant free chloride indicated the same dependence as found for the other chromium complexes (eq 4) and showed that the rate constants obtained at 0.50 M H^+ are sufficiently small to be an excellent approximation to the acid-independent term k_0. The variation of acid dependence with chloride concentration was not investigated because of the large number of parameters involved.

Discussion

For a series of reactions which proceed by the same mechanism, there should be a correlation between the change in $\Delta G^{\ddagger}$ and the change in $\Delta G°$, which are proportional to the log of the rate constants for the forward reactions and the log of the equilibrium constants for the overall reactions, respectively. The equilibrium constants listed in Table V are for the anation reactions[8,16]

$$Cr^{3+} + X^- \rightleftharpoons CrX^{2+} \quad (K_{CrX}) \qquad (7)$$

$$Hg^{2+} + X^- \rightleftharpoons HgX^+ \quad (K_{HgX}) \qquad (8)$$

and the overall reaction

$$CrX^{2+} + Hg^{2+} \rightleftharpoons Cr^{3+} + HgX^+ \quad (K = K_{HgX}/K_{CrX}) \qquad (9)$$

Literature values of K_{CrX} were extrapolated to 0.50 M ionic strength using the relationship derived by Swaddle and Gaustalla[8] for the ionic strength dependence of the formation reaction (eq 7) of CrI^{2+}

$$\log K_{CrX} = d + 2.35I^{1/3} + eI \qquad (10)$$

Calculation of the constants in eq 10 for $CrCl^{2+}$ was based on the experimental equilibrium constants at two other ionic strengths.[8] The values of d and e for $CrBr^{2+}$ were assumed to be the averages of those for the chloride and iodide complexes since an equilibrium constant was available at only one ionic strength for $CrBr^{2+}$. The probable validity of this procedure is indicated by excellent agreement between the known value of K_{CrBr} and that calculated by this procedure. The values of d and e used are −0.347 and −2.963 for $CrCl^{2+}$, −0.266 and −5.065 for $CrBr^{2+}$, and −0.17 and −7.22[8] for CrI^{2+}.

TABLE V

RATE CONSTANTS AND EQUILIBRIUM CONSTANTS AT 25° AND 0.50 M IONIC STRENGTH

X	Log k_0	Log K_{HgX}	Log K_{CrX}	Log K	Log k_{an}[a]
F	<−6.7	1.03	−4.33	−3.30	
Cl	−1.46	6.74	−1.27	8.01	−9.47
Br	2.46	9.05	−3.33	12.38	−9.92
I	7.79	12.87	−5.44	18.31	−10.52
−NCS[b]	−4.07	9.08[c]	2.14	6.94	−11.01

[a] k_{an} is the second-order rate constant for the acid-independent path in the formation of CrX^{2+} from Cr^{3+} and HgX^+ ($k_{an} = k_0/K$). [b] J. N. Armor and A. Haim, *J. Amer. Chem. Soc.*, **93**, 867 (1971). [c] Ionic strength is 1.0 M; L. Ciavatta and M. Grimaldi, *Inorg. Chim. Acta*, **4**, 312 (1970).

The value of k_0 for the reaction of CrI^{2+} with Hg^{2+} was estimated from the rate constant for the reaction with $HgCl^+$ using an average value of the ratio k_{Hg}/k_{HgCl} observed in other systems. This ratio ranged from 0.4 to 1.1 for a wide variety of mono- and dichlorochromium(III) complexes[9,13,14,23,24] with an average value of 0.68 ± 0.18. Additional confirmation of this value is given by the fact that the k_{Hg}/k_{HgCl} ratio for *cis*-$Co(en)_2Cl_2^+$,[15] the k_{Hg}/k_{HgNO_3} ratio for $CrCl^{2+}$ and $CrBr^{2+}$,[10] and the k_{Hg}/k_{HgX} ratio for $CrCl_2^+$ (where X = Cl, Br, and I)[13] all fall within this range.

The plot of log k_0 (eq 4) *vs.* log K (eq 9) for the chloride, bromide, and iodide complexes (Figure 3) yields a good linear relationship with a slope of 0.90 ± 0.02. Following the arguments of Leffler and Grunwald[25] this slope suggests that the transition state of the acid-independent path of the assisted aquation resembles the products of the overall reaction to a large degree, *i.e.*,

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90%. Such a conclusion lends support to the proposal of an essentially dissociative mechanism for the assisted aquation of the halochromium(III) complexes with the possible formation of a short-lived five-coordinate intermediate. Further evidence for such a mechanism is found in the results of competition studies in which the Hg(II)-assisted aquations were carried out in the presence of added nitrate ion[10] or methanol.[11] Though the competition ratio in the first case was not independent of nitrate ion concentration, an analysis of the data assuming two parallel paths and a different ratio for each path found both ratios to be constant throughout the series of chromium complexes despite the tremendous differences in rates. In the second case, experiments involved seven different induced solvolysis reactions of halo- or azidochromium(III) complexes with catalysis by Tl^{3+}, Hg^{2+}, Ag^{+}, or HNO_2, and the average number of bound methanol molecules per chromium(III) ion, $\bar{n}$, was constant within the experimental error of ±4%. Assuming a pentaaquochromium(III) ion intermediate, the ratio of the rate constants for reaction with water or methanol was determined from the dependence of $\bar{n}$ upon solvent concentration and was found to be 1.8. This kinetic discrimination of the proposed intermediate was contrasted with an equilibrium discrimination of 9 which was calculated as a statistically corrected equilibrium quotient for replacement of one water molecule in hexaaquochromium(III) ion by methanol. The fact that the kinetic discrimination factor was closer to unity was thought to be consistent with the presumed high reactivity of the intermediate.

The validity of the LFER for these reactions may depend on whether the k_0 values used here are truly simple rate constants. It is possible that a prior equilibrium forming a mercury(II)–chromium(III) binuclear complex with $K_{\text{bin}} << 1$ could exist and that this binuclear complex could then aquate with rate constant k_{aq} to give the observed products.

$$CrX^{2+} + Hg^{2+} \overset{K_{\text{bin}}}{\rightleftharpoons} CrXHg^{4+} \overset{K_{\text{aq}}}{\rightleftharpoons} Cr^{3+} + HgX^{+} \quad (11)$$

If such a situation existed, then $k_0 = k_{\text{aq}}K_{\text{bin}}$ and $K = K_{\text{aq}}K_{\text{bin}}$. If K_{bin} made a significant contribution to k_0 and K and if it varied consistently over the series of reactions, the linearity of the free energy plot could be due to swamping of any true correlation. Examination of equilibrium constants for formation of a variety of binuclear complexes involving mercury(II) and chromium(III)[23,24,26–28] or cobalt(III)[15,29] mono- and dihalo (or pseudohalo) complexes reveals no simple relationship with the formation constants for the corresponding mercury–halide (or pseudohalide) complexes.[16,30–32] Addition of the data (Table V) for the $CrNCS^{2+}$–Hg^{2+} reaction (X = NCS in eq 11), which has been shown to contain a prior equilibrium step,[26] to the plot in Figure 3 shows that this reaction does not fit the LFER. The values of K_{bin} and $k_{\text{aq}}K_{\text{bin}}$ observed by Armor and Haim[26] are 1.66×10^{4} M^{-1} and 8.5×10^{-5} M^{-1} sec^{-1}. In order to fit the LFER either $k_{\text{aq}}K_{\text{bin}}$ or K for the overall reaction must change by a factor of *ca.* 50. If our reactions proceeded by an analogous mechanism, it would be expected that the $CrNCS^{2+}$ data would fit the relationship better, especially since the unassisted aquation of this complex fits Swaddle's[8] LFER very well. For these reasons we believe that the slope of the LFER is a valid indication of the degree of dissociation of the Cr–X bond in the transition state of the assisted aquation. While it would be desirable to test these conclusions further by considering as well the reactions of Hg^{2+} with $CrCN^{2+}$ [27] and with CrN_3^{2+},[33] for which kinetic data are available, unfortunately all the required equilibrium data are not available.

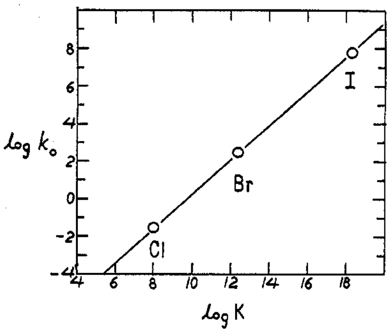

Figure 3.—Linear free energy relationship for the reaction of CrX^{2+} and Hg^{2+}.

Espenson[34] has used another approach to the investigation of this mechanism by examining the anation reactions of chromium(III) as represented by the forward reaction of the equilibrium in eq 7. The acid-independent rate constants fall in a range of (0.08–73) $\times 10^{-8}$ M^{-1} sec^{-1} for a wide variety of anionic and neutral ligands. The narrow width of this range was proposed as evidence for a common rate-determining feature of these complexation reactions which is probably ligand-assisted loss of coordinated water. The fact that the range for Cr(III) anations is wider than that for the analogous Fe^{3+} (2.6–127 M^{-1} sec^{-1})[35] and $Co(NH_3)_5OH_2^{3+}$ (1.5×10^{-9} to 1.0×10^{-7} M^{-1} sec^{-1})[4] reactions is consistent with the results of LFER investigations which indicate a greater role for the leaving ligand in the aquation of CrX^{2+} (slope 0.56)[8] than in the aquation of $Co(NH_3)_5X^{2+}$ (slope 1.0),[6] supporting the proposal that this greater ligand dependence indicates that bond making does play a role in the mechanism for the Cr(III) reactions.

Gibson and Carlyle[36] have extended the Fe(III) data to include the mercury(II)-assisted aquation of monochloroiron(III). The anation rate constants for Fe^{3+} reacting with $HgCl_2$ and $HgCl_3^{-}$ are 5 and 104 M^{-1} sec^{-1}, respectively (assuming only 20% of the measured rate constants corresponds to the acid-independent path in 0.45 M H^{+}). Thus the mercury complex anations probably fall within the same range as the unassisted reactions, suggesting similar mechanisms.

Calculations using results of the mercury(II)-assisted aquation of $CrCl^{2+}$[9] yield values for the rate

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constants for anation of Cr(III) by $HgCl^+$, $HgCl_2$, and $HgCl_3^-$ of 9.6×10^{-10}, 3.8×10^{-9}, and 7.9×10^{-8} M^{-1} sec^{-1}, respectively. These rate constants are within the Cr(III) range found by Espenson[34] despite the difference in charge involved in the first two reactions. The present study and the data of Armor and Haim[26] on $CrNCS^{2+}$ yield a range of rate constants for anation of Cr^{3+} by HgX^+ of only $(0.98–34) \times 10^{-11}$ M^{-1} sec^{-1} (Table V) and a value for anation by HgClI of 7.2×10^{-11} M^{-1} sec^{-1}. This range is narrower than that found by Espenson for the unassisted Cr(III) anations and is comparable to the range found for the Fe(III) anations. Since the LFER for the assisted Cr(III) aquations indicates that this transition state resembles the products of the reaction more than does that for the unassisted reactions, it is reasonable that the anation rates should show a smaller dependence on the entering ligand. The fact that the rate constants for the HgX^+ anations are lower than those found for X^- anations is probably due in part to a difference in ionic strength (0.50 instead of 1.0 M) and charge type as well as the difference in the role played by the incoming ligand in the transition state.

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Hydrolysis Kinetics of the *trans*-Dichloro- and *trans*-Dibromobis(1,3-diaminopropane)chromium(III) Cations in Acidic Aqueous Solution

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The synthesis of *trans*-$[Cr(tmd)_2Cl_2]Br$, *trans*-$[Cr(tmd)_2(OH_2)(OH)](ClO_4)_2$, and *trans*-$[Cr(tmd)_2Br_2]X$ (X = Br, ClO_4) is described, and the cations *trans*-$Cr(tmd)_2Cl_2^+$, *trans*-$Cr(tmd)_2(OH_2)Cl^{2+}$, *trans*-$Cr(tmd)_2(OH_2)Br^{2+}$, *trans*-$Cr(tmd)_2(OH_2)_2^{3+}$, *cis*-$Cr(tmd)_2(OH_2)_2^{3+}$, and $Cr(tmd)(OH_2)_4^{3+}$ have been isolated and characterized in solution. At 25.0°, the first-order rate constants and kinetic parameters for the primary hydrolysis of *trans*-$Cr(tmd)_2X_2^+$ (X = Cl, Br) (corresponding to the formation of *trans*-$Cr(tmd)_2(OH_2)X^{2+}$) are 10^5k (sec^{-1}) = 2.08 ± 0.06 (0.1 F HNO_3), 36.2 ± 1.3 (0.3 F HNO_3); E_a (kcal mol^{-1}) = 24.5 ± 0.3, 22.9 ± 0.3; log [PZ (sec^{-1})] = 13.26, 13.34; $\Delta S°_{298}$ (cal deg^{-1} mol^{-1}) = $+0.1 \pm 0.5$, $+0.5 \pm 0.5$, respectively. The secondary hydrolysis of these cations is complicated by isomerization and concurrent Cr–N bond rupture. The first-order halide release rate constants and kinetic parameters for *trans*-$Cr(tmd)_2(OH_2)X^{2+}$ (X = Cl, Br) in 1.0 F HNO_3 at 45.0° are 10^5k (sec^{-1}) = 2.88 ± 0.06, 13.6 ± 0.8; E_a (kcal mol^{-1}) = 21.7 ± 0.5, 24.2 ± 0.5; log [PZ (sec^{-1})] = 10.39, 12.73, respectively.

Introduction

In the past several years, much effort has been focused on the kinetic and mechanistic behavior of octahedral transition metal complexes.[2] In particular, the diacidobis(ethylenediamine)cobalt(III) and, to a lesser extent, the analogous chromium(III) complexes[3] have received considerable attention. More recently, kinetic studies have been concentrated on multidentate[4–6] and macrocyclic[7] polyamine systems. Of considerable interest is the effect of an increase in the ring size on the reaction rate, although only a few such comparative studies have been made. *trans*-$Co(tmd)_2X_2^+$ (X = Cl, Br)[8] is one such system that has recently been investigated.[9]

As part of a program to investigate the mode of acid hydrolysis of some analogous Co(III) and Cr(III) complexes,[10–14] we have studied the rates of halide release from *trans*-$Cr(tmd)_2X_2^+$ (X = Cl, Br). The rate constants and kinetic parameters allow a comparison with similar data (where available) for the *trans*-$M(AA)_2X_2^+$ (M = Co, Cr; AA = en, pn, tmd; X = Cl, Br) systems.

A preliminary report on the rate of the primary hydrolysis of *trans*-$Cr(tmd)_2Cl_2^+$ at 35.0° has been published.[15]

Experimental Section

The amine, 1,3-diaminopropane, was obtained from Aldrich Chemical Co. and used without further purification. All other chemicals were reagent grade quality. The ion-exchange material used was Zeo-Karb 225, SRC-6 cation-exchange resin in

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