that scheme IV is correct—though, from the fair constancy of $Q_{x,y}$ values found for many individual species in the numerous schemes tested, it can be said that the numbers in Table VI are usefully accurate if the species to which they correspond do indeed exist. If scheme IV is correct, the ΔF and ΔH values may be good to a few tenths of a kcal.; the ΔC_p values are probably no better than ±20 cal./deg.

These approximate thermochemical values suggest a constancy of $\Delta H/y$ and $\Delta S/y$ for the polymeric species.

	$ThOH^{3+}$	$Th(OH)_2^{2+}$	$Th_2(OH)_2^{6+}$	$Th_4(OH)_8^{8+}$	$Th_6(OH)_{15}^{9+}$
$\Delta H/y$	5.9	7.0	7.4	7.22	7.23
$\Delta S/y$	0.9	5.5	14.2	13.3	13.0

These are the average enthalpies and entropies for the reaction shown in Table VI per OH^- ion bound or H^+ ion produced. From the previous study of uranium(VI) hydrolysis,[10] the corresponding values

	UO_2OH^+	$(UO_2)_2(OH)_2^{2+}$	$(UO_2)_3(OH)_5^+$
$\Delta H/y$	11	5.0	5.0
$\Delta S/y$	11	3	2

show roughly the same correlation. The entropy increases associated with thorium hydrolysis are seen to be much greater, owing presumably to the higher charge on the unhydrolyzed ion. The following polymerization reactions

	ΔH	ΔS
$4Th(OH)_2^{2+} \rightleftharpoons Th_4(OH)_8^{8+}$	2.0	63
$6Th(OH)_2^{2+} + 3H_2O \rightleftharpoons Th_6(OH)_{15}^{9+} + 3H^+$	25	130

evidently are favored far more by the accompanying entropy increase than they are hindered by the enthalpy increase. In the latter case, ~22 and 40, respectively, should be subtracted from ΔH and ΔS to correct for the three protons liberated.

CONTRIBUTION FROM THE INSTITUTE FOR ATOMIC RESEARCH AND
DEPARTMENT OF CHEMISTRY, IOWA STATE UNIVERSITY, AMES, IOWA

Aquation of Chloropentaaquochromium(III) Ion Catalyzed by Mercury(II) Complexes[1]

BY JAMES H. ESPENSON AND JAMES P. BIRK

Received October 22, 1964

The aquo and chloro complexes of mercury(II) ion accelerate release of chloride ion from the primary coordination sphere of monochloropentaaquochromium(III) ion. For each mercury(II) species which enhances this aquation, the observed rates follow the equation $-d \ln [CrCl^{2+}]/dt = (k_0 + k_{-1}[H^+]^{-1})[Hg(II)]$. The values of these rate constants for Hg^{2+} and $HgCl^+$ together with the activation parameters ΔH^* and ΔS^* for each reaction pathway were determined in media of constant unit ionic strength and constant perchlorate ion concentration. The mercury(II) species Hg^{2+} and $HgCl^+$ exert rate effects much larger than those of $HgCl_2$ and $HgCl_3^-$. A correlation is made of reaction rate with stability of the metal–chloride bond being formed; presumably chloride ion bridged transition states are involved here. Comparisons are presented between the activation parameters for the reaction $Hg^{2+} + CrCl^{2+}$ and the electron-transfer reaction $Cr^{2+} + CrCl^{2+}$; the higher rate of the latter reaction is due almost entirely to its lower ΔH^*.

Introduction

Metal ions possessing affinity for halide ions increase the rate of aquation of halo complexes. The aquation rates of haloamminecobalt(III) ions are accelerated by mercury(II), silver(I), and thallium(III) ions.[2] The rates of aquation of dichlorotetraaquochromium(III) and chloropentaaquochromium(III) ions are increased by silver(I) ion.[3]

We report here on a study of the aquation of chloropentaaquochromium(III) ion enhanced by mercury(II) species. These effects are quite dramatic. At 25° and 1 M H^+, for example, the half-life for aquation of chlorochromium(III) ion is *ca.* 570 hr. In the presence of 0.10 M Hg^{2+} the half-life under the same conditions is 87 sec.; with 0.10 M $HgCl^+$, it is 46 sec. The reactions taking place are[4]

$$CrCl^{2+} + HgCl_n^{2-n} = Cr^{3+} + HgCl_{n+1}^{1-n} \qquad (1)$$

The relatively rapid reactions of aquomercury(II) ion and monochloromercury(II) ion have been studied in detail. The reactions involving the dichloro and trichloro complexes of mercury(II) are much slower; these slight enhancements of the aquation rate are not far beyond those reasonably attributable to medium effects.

Experimental

Reagents.—Chlorochromium(III) ion was prepared by reaction of chromium(II) ion and chlorine[5]; the complex was separated and purified by cation exchange on Dowex 50W-X8 resin. Chloride ion and chlorine were washed from the resin with 0.01 F

---

[1] Contribution No. 1578. Work was performed in the Ames Laboratory of the U. S. Atomic Energy Commission.

[2] J. N. Brønsted and R. Livingston, *J. Am. Chem. Soc.*, **49**, 435 (1927); (b) F. A. Posey and H. Taube, *ibid.*, **79**, 255 (1957); (c) A. M. Sargeson, *Australian J. Chem.*, **17**, 385 (1964).

[3] P. J. Elving and B. Zemel, *J. Am. Chem. Soc.*, **79**, 5855 (1957).

[4] In general, water in the coordination sphere will be omitted from chemical formulas.

[5] H. Taube and H. Myers, *J. Am. Chem. Soc.*, **76**, 2103 (1954).

perchloric acid and the monochloro complex was eluted with 1 *F* perchloric acid. Chlorochromium(III) ion was analyzed spectrophotometrically after oxidation with peroxide in alkaline solution.[6] Perchloric acid was titrated directly with sodium hydroxide solution, after complexing chromium(III) with excess oxalate ion.[7] Chromium(II) perchlorate solutions were produced by electrolytic reduction of chromium(III) perchlorate at a mercury cathode. Chromium(III) perchlorate was the twice-recrystallized product from reduction of potassium dichromate with formic acid in perchloric acid solution.

Stock solutions of mercury(II) perchlorate were prepared by dissolving reagent grade mercury(II) oxide in a slight excess of perchloric acid. Any undissolved mercury(II) oxide was removed by filtration. These solutions were analyzed by at least two of the following three methods: (1) The concentration of mercury(II) was determined as one-half the difference between the total cation concentration and the hydrogen ion concentration. (Total cation concentration was found by titration with sodium hydroxide of the acid released from a cation-exchange column; hydrogen ion concentration was determined by direct titration with sodium hydroxide after complexing mercury(II) with excess sodium bromide.) (2) Mercury(II) was determined by a standard Volhard titration with thiocyanate ion to an iron(III) thiocyanate end point. (3) Mercury(II) was reduced to the metal with tin(II) chloride solution; after drying over an aspirator with acetone, the mercury was weighed, with a correction made for volatility.[8]

Monochloromercury(II) perchlorate solutions were prepared from equimolar quantities of lithium chloride and mercury(II) perchlorate solutions. The lithium chloride solution used in this preparation was prepared from the reagent grade solid and was analyzed both by ion exchange and by a Mohr titration with silver nitrate. These solutions contain appreciable concentrations of Hg^{2+} and $HgCl_2$; concentrations of $HgCl^+$ were calculated from the appropriate equilibrium quotients,[9] as described below.

Mercury(II) chloride solutions were prepared from the reagent grade solid and were analyzed by two methods: (1) Excess standard sodium hydroxide solution was added to precipitate mercury(II) oxide, which was reduced to the metal by warming with hydrogen peroxide. The excess sodium hydroxide was titrated with perchloric acid.[10] (2) Mercury(II) chloride was titrated with sodium hydroxide to a bromocresol purple end point after chloride ion was precipitated as silver chloride.[11]

Lithium perchlorate was prepared by the dissolution of lithium carbonate in perchloric acid and was recrystallized twice from conductivity water. Stock solutions were analyzed by ion exchange.

Water used in all solutions was triply distilled from alkaline permanganate in a Barnstead still. All other chemicals were reagent grade and were used without further purification.

Kinetics Experiments.—Solutions complete but for chlorochromium(III) ion were prepared in rubber-capped cylindrical 5-cm. spectrophotometer cells. These solutions and the stock solution of chlorochromium(III) ion were brought to constant temperature in a water bath for at least 30 min. prior to reaction. Chlorochromium(III) ion was introduced through the rubber cap of the cell with a hypodermic syringe calibrated to deliver. The solution was mixed and immediately placed in the water-filled cell compartment of a Cary Model 14 recording spectrophotometer. During the course of the reaction, the solution was maintained at the desired temperature by pumping thermostated water through the jacket of the cell compartment; this arrangement has been described in detail in an earlier publication.[12]

The reactions were followed spectrophotometrically to at least 95% completion by the decrease in absorbance due to chlorochromium(III) ion at the maxima, 4280 or 6070 Å. The molar absorbancy indices (M^{-1} cm.$^{-1}$) at these two wave lengths are 20.7 and 16.4, respectively, for chlorochromium(III) ion and 13.0 and 10.8, respectively, for aquochromium(III) ion. Most of the experiments reported here were carried out at 4280 Å.; preliminary experiments agreed at both wave lengths.

The concentration of mercury(II) species was 10–20 times that of chlorochromium(III) ion in all runs, approximating pseudo-first-order conditions. The Guggenheim method[13] was used to treat the spectrophotometric data so that the exact values of the absorbancy indices did not enter the calculations. Plots of log $[A_t - A_{t+\tau}]$ (the absorbance at time t minus the absorbance at time $t + \tau$, where τ is a constant time interval of about three half-lives) *vs.* time are linear, with slopes related to the apparent first-order rate constants for the reaction. Figure 1 shows typical plots for reactions of both Hg^{2+} and of $HgCl^+$. The slopes of these lines were determined by the method of averages.

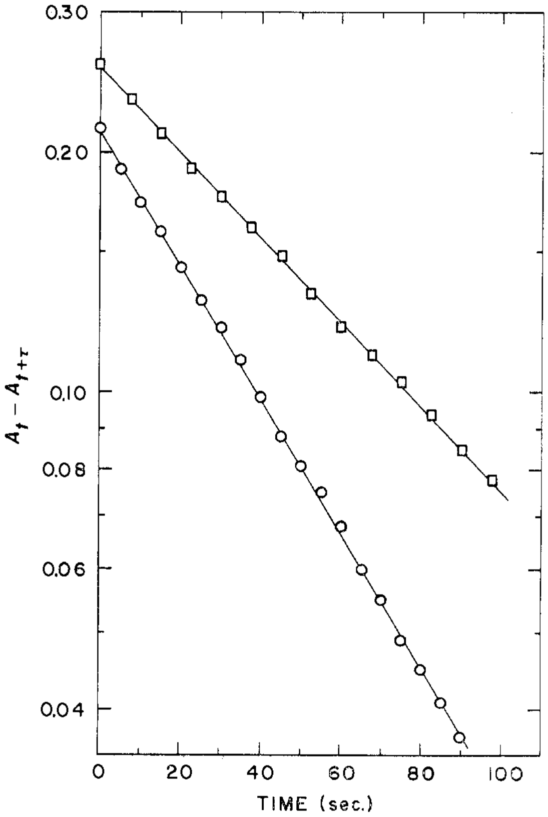

Figure 1.—Typical kinetic plots illustrating first-order dependence upon $[CrCl^{2+}]$: 8×10^{-3} *M* $CrCl^{2+}$ at t_0, 1.00 *M* ionic strength, 25.0°; □, 0.045 *M* $HgCl^+$, 0.028 *M* Hg^{2+}, 0.028 *M* $HgCl_2$, 0.502 *M* H^+; ○, 0.100 *M* Hg^{2+}, 0.200 *M* H^+ (medium iii). A = absorbance at 4280 Å. in a 5-cm. cell; zero time = first measured point.

Results

For each mercury(II) species, Hg^{2+}, $HgCl^+$, and $HgCl_2$, all the rate data follow a mixed second-order rate law

$$-d[CrCl^{2+}]/dt = k_{obsd}[CrCl^{2+}][Hg(II)] \qquad (2)$$

The reaction with aquomercury(II) ion may involve some important medium effects. Some studies have shown that the rates of a reaction between polyvalent ions of the same charge sign correlate better with the

---

[6] G. W. Haupt, *J. Res. Natl. Bur., Std.*, **48**, 414 (1952).

[7] E. L. King and J. A. Neptune, *J. Am. Chem. Soc.*, **77**, 3187 (1955).

[8] H. H. Willard and A. W. Boldyreff, *ibid.*, **52**, 569 (1930).

[9] L. G. Sillén, *Acta Chem. Scand.*, **3**, 539 (1949).

[10] E. Rupp, K. Müller, and P. Maiss, *Pharm. Zentralhalle*, **67**, 529 (1926).

[11] J. F. Coetzee, *J. Chem. Soc.*, 2098 (1951).

[12] J. H. Espenson, *J. Am. Chem. Soc.*, **86**, 5101 (1964).

[13] E. A. Guggenheim, *Phil. Mag.*, [7] **2**, 538 (1926).

concentration of oppositely charged ions than with ionic strength. For a reaction very similar to the present one, namely the reaction of $Co(NH_3)_5Br^{2+}$ and Hg^{2+}, Olson and Simonson[14] observed that constant ionic strength does not, in itself, ensure consistent rate constants. In their experiments, lithium, barium, and lanthanum perchlorates, each at the same total ionic strength, exhibited markedly different specific rates. These three electrolytes, on the other hand, in sets of experiments where each contributed equal concentrations of perchlorate ion, yielded rate constants in good agreement.

We carried out a series of experiments in triplicate in which either constant ionic strength or constant perchlorate ion concentration was maintained by either lithium perchlorate or barium perchlorate. The results are given in Table I. Despite the greater average deviations in the runs at constant perchlorate ion, there is better agreement between k_{obsd} in these media than between those in constant ionic strength. These effects were checked in a further series of kinetic experiments in three media: (i) Lithium perchlorate replaced both mercury(II) and hydrogen ions, to hold ionic strength at 1.00 M. (ii) Barium perchlorate replaced both mercury(II) and hydrogen ions, to hold ionic strength at 1.00 M. (iii) Barium perchlorate replaced mercury(II) ion, and lithium perchlorate replaced hydrogen ion; the total concentration of dipositive ions was maintained at 0.158 M and lithium perchlorate was added to hold ionic strength at 1.00 M. Rate constants determined at one or more temperatures for each of the media described above are given in Table II.

TABLE I

PSEUDO-FIRST-ORDER RATE CONSTANTS FOR REACTION OF $CrCl^{2+}$ AND Hg^{2+} AT VARYING IONIC STRENGTHS AND PERCHLORATE ION CONCENTRATIONS[a]

	Salt added			
	$Ba(ClO_4)_2$	$LiClO_4$	$Ba(ClO_4)_2$	$LiClO_4$
Concn. of salt, F	0.125	0.375	0.242	0.484
Ionic strength, M	1.00	1.00	1.35	1.11
Total $[ClO_4^-]$, M	0.766	0.892	1.00	1.00
k_{obsd}, M^{-1} sec $^{-1}$	0.125	0.133	0.137	0.135
	0.128	0.130	0.148	0.140
	0.130	0.135	0.134	0.141
Av. k_{obsd}	0.128	0.133	0.141	0.139

[a] Reaction solutions were 0.008 M $CrCl^{2+}$, 0.1055 M Hg^{2+}, 0.300 M H^+; 25.0°.

Since hydrogen ion exerts a specific effect upon the observed second-order rate constant it is difficult to compare results applying to different media. In view of the results of Olson and Simonson,[14] and since ionic medium iii allows both constant anion concentration and constant ionic strength, it appears that these rate constants present the preferable choice.

In all cases plots of k_{obsd} *vs.* $[H^+]^{-1}$ were linear; Figure 2 presents these data graphically. These data are consistent with the rate equation

$$-d[CrCl^{2+}]/dt = (k_0 + k_{-1}[H^+]^{-1})[Hg^{2+}][CrCl^{2+}] \quad (3)$$

TABLE II

OBSERVED SECOND-ORDER RATE CONSTANTS[a] ($-[Hg^{2+}]^{-1}$ d ln $[CrCl^{2+}]/dt$, M^{-1} SEC.$^{-1}$), AS FUNCTIONS OF IONIC MEDIUM AND ACID CONCENTRATION

	Ionic medium[b]		
$[H^+]$, M	i	ii	iii[d]
Temperature 15°			
0.150	...	0.0656	0.0625 (0.0668)
0.200	...	0.0555	0.0534 (0.0542)
0.250	...	...	0.0471 (0.0466)
0.300	...	0.0374	0.0415 (0.0416)
0.400	...	0.0337	0.0335 (0.0353)
0.500	...	0.0290	0.0321 (0.0315)
0.600	...	0.0287	...
Temperature 25°			
0.125	0.296	...	...
0.150	0.251	...	0.246 (0.225)
0.200	0.203	0.187	0.193 (0.180)
0.250	0.173	...	0.154 (0.154)
0.300[c]	0.140	0.135	0.140 (0.136)
0.350	0.127	...	...
0.400	0.120	0.116	0.122 (0.114)
0.500	0.101	0.0935	0.102 (0.101)
0.600	0.0925	0.0885	...
Temperature 35°			
0.150	...	0.666	0.695 (0.703)
0.200	...	0.514	0.547 (0.560)
0.250	...	...	0.471 (0.474)
0.300	...	0.391	0.400 (0.417)
0.400	...	0.325	0.335 (0.345)
0.500	...	0.281	0.299 (0.302)
0.600	...	0.270	...

[a] Most runs reported here had mercury(II) concentrations of 0.100 M; but they include some runs with mercury(II) variation from 0.075 to 0.20 M. [b] The ionic media used in these experiments are defined in the body of the text. [c] In medium i, at 25.0° and 0.300 M H^+, k_{obsd} exhibits a distinct trend decreasing from 0.143 at 0.075 M Hg^{2+} to 0.132 at 0.200 M Hg^{2+}. [d] Values in parentheses were calculated from the activation parameters given in Table V. The average deviation of recalculated and observed rate constants is 3.1% (medium iii).

The reaction with $HgCl^+$ was studied under conditions where the initial concentration of chlorochromium(III) ion was relatively small and approximately the same in all runs at a constant 1.00 M ionic strength ($LiClO_4$). The presence of appreciable concentrations of Hg^{2+} in solutions of $HgCl^+$ must be taken into account in deriving rate constants for the species $HgCl^+$, since Hg^{2+} exhibits significant rate effects. The principal equilibrium in solutions containing 1:1 mole ratios of mercury(II) and chloride ions is

$$2HgCl^+ = Hg^{2+} + HgCl_2 \quad (4)$$

This equilibrium has been the subject of several studies. Sillén and Ingfeldt[15] reported the equilibrium quotient for reaction 4, Q_4, is 0.56 at 25.0° in a solution of 0.50 M ionic strength ($NaClO_4$); Marcus[16] also found Q_4 = 0.56 under the same conditions. Pechanski[17] determined this value to be 0.40 at 17.0° and 1.00 M ionic strength ($NaClO_4$), which is much closer to the conditions employed in this kinetic study. In a medium of 0.50 M ionic strength ($HClO_4$), Gallagher and King[18] found

---

[14] A. R. Olson and T. R. Simonson, *J. Chem. Phys.*, **17**, 1167 (1949).

[15] L. G. Sillén and G. Ingfeldt, *Svensk Kem. Tidskr.*, **58**, 61 (1946).

[16] Y. Marcus, *Acta Chem. Scand.*, **11**, 599 (1957).

[17] D. Pechanski, *J. chim. phys.*, **50**, 640 (1953).

[18] P. K. Gallagher and E. L. King, *J. Am. Chem. Soc.*, **82**, 3510 (1960).

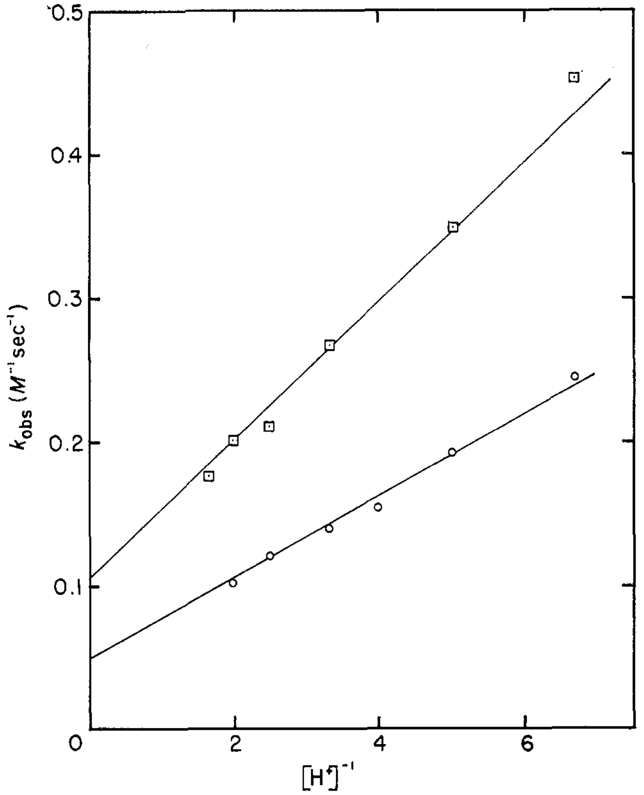

Figure 2.—Typical plots of k_{obsd} *vs.* $[H^+]^{-1}$ illustrating conformity of data to eq. 3 and 4: □, $HgCl^+$ at 25.0°; O, Hg^{2+} at 25.0°.

$\Delta H° = +1.0$ kcal. mole^{-1} for reaction 4. Assuming this latter value is independent of the change from 0.50 to 1.00 M ionic strength, which is equivalent to assuming the effect of this change in medium on Q_4 resides entirely in the entropy term, the corrected Q_4 is 0.38 at 25.0° and 1.00 M ionic strength. (This result is opposite in direction to the change in Q_4 predicted from the Debye–Hückel limiting law, but it appears a safer assumption than does the validity of the limiting law at these ionic strengths.) With the further assumption that substitution of $LiClO_4$ for $NaClO_4$ is without effect on Q_4, the fractions of mercury(II) existing as $HgCl^+$ are 0.440, 0.447, and 0.451 at 15.0, 25.0, and 35.0°, respectively. The known rates of reaction of Hg^{2+} and $CrCl^{2+}$ and the relative concentrations of Hg^{2+} are used to find the rate constants for $HgCl^+$; the relation is

$$k_{HgCl^+} = (-d\ln[CrCl^{2+}]/dt - k_{Hg^{2+}}[Hg^{2+}])/[HgCl^+] \quad (5)$$

Values of $k_{Hg^{2+}}$ used in evaluating k_{HgCl^+} are derived from those in Table I (medium i, 1.00 M ionic strength with $LiClO_4$); the relation $k_{Hg^{2+}}$ (25.0°, medium i) = $0.0375 + 0.324/[H^+]$ was corrected to other temperatures assuming the values for each path calculated for ΔH^* in medium iii. Table III summarizes the experimental results and the rate constants for reaction of $HgCl^+$ and $CrCl^{2+}$. The apparent second-order rate constant exhibits a functional dependence upon hydrogen ion concentration like that of Hg^{2+}, and a relation analogous to eq. 3 applies also to $HgCl^+$.

Table III

Second-Order Rate Constants (M^{-1} sec.$^{-1}$) for Reaction of $HgCl^+$ and $CrCl^{2+}$ [a]

Temp., °C.	$[H^+]$, M	$-[Hg(II)]^{-1} \times d\ln[CrCl^{2+}]/dt$	$-[HgCl^+]^{-1} d\ln[CrCl^{2+}]dt$	
			Obsd.[b]	Calcd.[c]
15.0	0.150	0.0809	0.136	0.138
	0.200	0.0649	0.110	0.114
	0.300	0.0513	0.089	0.0895
	0.400	0.0440	0.077	0.0773
	0.500	0.0408	0.073	0.0699
	0.600	0.0366	0.065	0.0650
25.0	0.150	0.273	0.454	0.418
	0.200	0.211	0.349	0.340
	0.300	0.160	0.268	0.261
	0.400	0.128	0.212	0.222
	0.500	0.119	0.203	0.199
	0.600	0.104	0.177	0.183
35.0	0.150	0.739	1.15	1.19
	0.200	0.593	0.93	0.954
	0.300	0.462	0.75	0.720
	0.400	0.359	0.575	0.603
	0.500	0.333	0.548	0.533
	0.600	0.298	0.493	0.486

[a] 1.00 M ionic strength maintained with $LiClO_4$. [b] Evaluated from the measured rate constants and those in Table II, according to eq. 5, as described in the text. [c] Calculated from the activation parameters in Table V.

Mercury(II) chloride and trichloromercury(II) ion accelerate aquation only slightly, if at all. The rate of aquation increases with these species in solution, but the small equilibrium concentration of monochloromercury(II) ion contributes a substantial fraction of this effect.

Since the pathways involving $HgCl^+$ proceed at high specific rates, their contributions to the reaction rate remain important even in solutions with as little as 0.0003% of the formal mercury(II) concentration in the form of $HgCl^+$. For this reason, the concentration of $HgCl^+$ must be known accurately before an assessment can be made of whether $HgCl_2$ provides an appreciable reaction path. We can estimate $[HgCl^+]$ most reliably in solutions containing relatively high concentrations of Cl^- and $HgCl_2$, so that chloride ion released by the chromium(III) complex as reaction proceeds cannot affect $[HgCl^+]$ appreciably. Such solutions have the disadvantage that they then contain significant concentrations of $HgCl_3^-$, which may also affect the reaction rate. In addition, the spontaneous aquation of $CrCl^{2+}$ proceeds at a rate comparable to that observed in these experiments. If all three chloromercury(II) complexes may act as catalysts, chlorochromium(III) ion disappears at an over-all rate given by

$$-d\ln[CrCl^{2+}]/dt = k_{aq} + k_1[HgCl^+] + k_2[HgCl_2] + k_3[HgCl_3^-]$$

Provided the $HgCl_3^-$ term is negligible, when $[HgCl^+]$ is replaced by $[HgCl_2][Cl^-]^{-1}Q_2^{-1}$

$$-d\ln[CrCl^{2+}]/dt = k_{aq} + (k_1Q_2^{-1}[Cl^-]^{-1} + k_2)[HgCl_2] \quad (6)$$

From the work of Sillén[9,15] and of Marcus,[16] Q_2 is 3.0×10^6 M^{-1} at 0.50 M ionic strength. Correcting this value to the present 1.0 M ionic strength according to an

TABLE IV

AQUATION OF $CrCl^{2+}$ IN SOLUTIONS CONTAINING[a] $HgCl_2$ AND $HgCl_3^-$

$[Cl^-]$[b]	0.064	0.032	0.078
$[HgCl_2]$[b]	0.064	0.064	0.032
$[HgCl_3^-]$[b]	0.036	0.018	0.022
$[HgCl^+]$[c] × 10^7	3.3	6.7	1.4
$-d \ln [CrCl^{2+}]/dt$, sec.$^{-1}$ × 10^7	7.3	10.2	6.0
$k_1[HgCl_2]/Q_2[Cl^-]$, sec.$^{-1}$ × 10^7	0.87	1.75	0.36
k_{aq},[d] sec.$^{-1}$ × 10^7	4.0	4.0	4.0
k_2, M^{-1} sec.$^{-1}$ × 10^6	3.8	6.9	5.4

[a] 0.008 M $CrCl^{2+}$, 0.300 F $HClO_4$, 1.00 M ionic strength with $LiClO_4$, 25.0°. [b] Calculated using $Q_3 = 8.92\ M^{-1}$ (ref. 16). No correction was made for change of ionic strength from 0.50 to 1.00 M. [c] Calculated using $Q_2 = 2.7 \times 10^6\ M^{-1}$ and k_1 from Table III. [d] Ref. 18.

TABLE V

ACTIVATION PARAMETERS AND RATE CONSTANTS FOR REACTIONS OF $CrCl^{2+}$ WITH Hg(II) SPECIES

	Hg^{2+} reaction[a]	$HgCl^+$ reaction[b]
ΔH_0^*, kcal. mole^{-1} [c]	17.7 ± 1.7	15.5 ± 1.0
ΔS_0^*, cal. mole^{-1} deg.$^{-1}$	-5.3 ± 5.7	-10.9 ± 3.4
k_0 (25.0°), M^{-1} sec.$^{-1}$	0.0478	0.105
ΔH_{-1}^*, kcal. mole^{-1}	20.9 ± 0.9	19.3 ± 0.7
ΔS_{-1}^*, cal. mole^{-1} deg.$^{-1}$	4.3 ± 3.0	0.2 ± 2.5
k_{-1} (25.0°), sec.$^{-1}$	0.0266	0.0470

[a] In Li^+–Ba^{2+} medium (iii). [b] In $LiClO_4$–$HClO_4$ solution of ionic strength 1.00 M. [c] Deviations are standard deviations.

extended Debye–Hückel equation[19] yields $Q_2 = 2.7 \times 10^6\ M^{-1}$. Values of k_2 in eq. 6 were calculated from this value of Q_2, the value of k_1 appropriate to this hydrogen ion concentration (Table III), and k_{aq} from the work of Swaddle and King.[20] Table IV presents the results of these computations for three experiments in which the reaction was followed to only ~30% completion, calculated on the assumption that the reaction follows pseudo-first-order rate behavior. If we further assume that only $HgCl_2$, and not $HgCl_3^-$, for instance, is responsible for the residual rate, then the mean value of k_2 is $5 \pm 2 \times 10^{-6}\ M^{-1}$ sec.$^{-1}$. The identification of this path with the term $k_2[HgCl_2]$ ignores changes in activity coefficients at constant ionic strength and denies that the nonelectrolyte $HgCl_2$ may exert effects on ion activities; this term represents these medium effects along with specific rate effects, the presence of which has not been demonstrated unequivocally.

Activation Parameters.—Activation parameters for the reaction with aquomercury(II) ion in Li^+–Ba^{2+} medium (iii) and the reaction with monochloromercury(II) ion in Li^+ medium were calculated from the absolute rate equations assuming that ΔS^* and ΔH^* are not functions of temperature over the range investigated. This calculation of activation parameters for the two simultaneous pathways in each reaction utilized simultaneously data at each $[H^+]$ and temperature, fitting the data with a nonlinear least-squares computer program.[21] Table V summarizes the results of these computations in terms of the activation parameters and the true rate constants k_0 and k_{-1}.

Discussion

The effectiveness of a given metal complex in removing chloride ion from the coordination sphere of chromium(III) correlates, at least approximately, with the stability of the chloro complex formed as a product. The data are limited, however, to the mercury(II) reactions studied here and to that of silver ion studied by Elving and Zemel.[3,22]

The accelerating effect of aquomercury(II) ion on the aquation of halopentaamminecobalt(III) complexes is considered by Basolo and Pearson[23] to take place *via* a mechanism in which one metal ion and its coordination sphere displaces another metal ion and its coordination sphere from about the halide ion. This involves a halide-bridged transition state

$$(H_2O)_nHg\cdots X\cdots Co(NH_3)_5$$

Posey and Taube[2b] postulated, on the basis of isotope rate effects, that affinity of mercury(II) for halide, rather than bond making between cobalt and the incoming water in the transition state, is the important feature of cobalt–halogen bond breaking. Mercury(II) aids bond breaking through bond formation, *i.e.*, mercury(II) essentially pulls halide ion from the coordination sphere of cobalt.

A similar chloride-bridged transition state seems likely for the reaction paths under consideration here. The form of the rate law requires the presence of the two metal ions in the transition state. The crude correlation of reaction rate and stability of the metal ion–chloride bond being formed adds some support to this argument.

Provided the rate law term $k_0[Hg^{2+}][CrCl^{2+}]$ has associated with it a mechanism involving chloride ion bridging in the transition state, this transition state resembles that for the electron-transfer reaction of chromium(II) ion and chlorochromium(III) ion studied by Ball and King.[24] These transitions states are

$$\{(H_2O)_5CrCl\cdots Hg^{4+*}\} \text{ and } \{(H_2O)_5CrCl\cdots Cr^{4+}\}^*$$

As Ogard and Taube[25] suggested in connection with analogous reactions of halopentaammine complexes, a comparison of ΔH^* and ΔS^* for these two transition states is of some interest. Unfortunately, measurements on the rapid Cr^{2+}–$CrCl^{2+}$ exchange reaction were carried out at but a single temperature, so that the

---

(19) Ionic strength correction was of the form $\log Q/K^0 = -\Delta(Z^2)\cdot[A\sqrt{I}/(1 + \sqrt{I}) - 0.1I]$.

(20) T. W. Swaddle and E. L. King, *Inorg. Chem.*, **4**, 532 (1965).

(21) The computer program using the individual data points for evaluation of activation parameters in the multi-term rate equation was written by R. H. Moore at Los Alamos Scientific Laboratory (L. A. 2367 + Addenda). As the computation was carried out here, a weighting of $1/k^2$ for each term was used.

(22) The rate constants for $HgCl^+$ and Hg^{2+} differ by a factor of ~2; their stability quotients differ by a factor of 2 in the opposite direction. The trend in rates these ions exhibit is opposite to that claimed here. These small variations, ~4-fold over-all, may be due to electrostatic effects on the reaction rates of ions of different charge types; the trends in reactivity for substances of widely differing stability appear approximately correct.

(23) F. Basolo and R. G. Pearson, "Mechanisms of Inorganic Reactions," John Wiley and Sons, New York, N. Y., 1958, p. 153.

(24) D. L. Ball and E. L. King, *J. Am. Chem. Soc.*, **80**, 1091 (1958).

(25) A. E. Ogard and H. Taube, *ibid.*, **80**, 1084 (1958).

activation parameters are not available. If we choose $Cr(NH_3)_5Cl^{2+} + Cr^{2+}$ as a model reaction, it is possible to estimate values for the desired comparison. The reaction $Cr(NH_3)_5Cl^{2+} + Cr^{2+}$ has $\Delta H^* = 11$ kcal. mole^{-1} and $\Delta S^* = -23$ e.u.; its rate at 0° is *ca.* 700-fold lower than that of $Cr(OH_2)_5Cl^{2+} + Cr^{2+}$. If we assume that the rate factor resides exclusively in the entropy term,[26] ΔS^* for $Cr(OH_2)_5Cl^{2+} + Cr^{2+}$ becomes -10 e.u. Since the values of ΔS^* for $CrCl^{2+} + Cr^{2+}$ and $CrCl^{2+} + Hg^{2+}$ are essentially the same (-10 and -5 e.u.), the 5-kcal. difference in activation enthalpy provides the factor of $\sim 10^3$ by which the rate of $CrCl^{2+} + Cr^{2+}$ exceeds that of $CrCl^{2+} + Hg^{2+}$. It is also of interest to note that the $CrCl^{2+} + Cr^{2+}$ exchange reaction, with $\Delta G° = 0$, has a higher rate than does $CrCl^{2+} + Hg^{2+}$, with a substantially negative value of $\Delta G°_{298} = -7.6$ kcal. The electron-transfer aspect of the $CrCl^{2+} + Cr^{2+}$ reaction is the distinguishing factor between these two systems. The lack of correlation of the two systems with regard to k and $\Delta G°$ suggests that the transition states may not be as similar as we have suggested. The bridging in the substitution reaction may be of a different sort than in the electron-transfer case, or a chlorine atom transfer may be the central feature of the latter process.

Acknowledgment.—We appreciate helpful discussions with Drs. E. L. King and T. W. Swaddle and are grateful to them for access to their unpublished data on the kinetics of aquation of chlorochromium(III) ion. We are grateful to Dr. T. W. Newton for supplying us with the Los Alamos computer programs and for the aid he has given us in adapting these programs for kinetic data to our computer facilities.

[26] Activation parameters for $Cr(NH_3)_5F^{2+} + Cr^{2+}$ are $\Delta H^* = 13.4$ kcal./mole and $\Delta S^* = -30$ e.u. (ref. 21); and for $Cr(OH_2)_5F^{2+} + Cr^{2+}$, 13.7 kcal. mole^{-1} and -20 e.u. (ref. 20).

CONTRIBUTION FROM THE DEPARTMENT OF CHEMISTRY,
UNIVERSITY OF COLORADO, BOULDER, COLORADO

The Rate of Aquation of Halopentaaquochromium(III) Ion in Acidic Aqueous Solution[1]

BY THOMAS W. SWADDLE AND EDWARD L. KING

Received December 22, 1964

The rates of aquation of fluorochromium(III) ion, chlorochromium(III) ion, and iodochromium(III) ion have been studied in acidic solution of unit ionic strength over a range of temperature. All observed reaction pathways are first order in chromium complex; the orders with respect to hydrogen ion for these pathways are +1 and 0 for fluorochromium(III) ion, and 0 and -1 for chlorochromium(III) ion and iodochromium(III) ion. Activation parameters were evaluated for each rate law term. For the rate law term $k_0[Cr(OH_2)_5F^{2+}]$, the value of ΔS^* is abnormally positive, which is interpreted to mean that the corresponding transition state yields hydrofluoric acid and hydroxochromium(III) ion, not fluoride ion and aquochromium(III) ion. Measurement of the equilibrium extent of aquation of fluorochromium(III) ion as a function of temperature allowed evaluation of ΔH and $\Delta S°$ for the reaction: $Cr(OH_2)_5F^{2+} + H^+ + H_2O = Cr(OH_2)_6^{3+} + HF$.

This paper presents studies of the rate of aquation of chloropentaaquochromium(III) ion and iodopentaaquochromium(III) ion

$$Cr(OH_2)_5X^{2+} + H_2O = Cr(OH_2)_6^{3+} + X^-$$

and of fluoropentaaquochromium(III) ion

$$Cr(OH_2)_5F^{2+} + H^+ + H_2O = Cr(OH_2)_6^{3+} + HF$$

in acidic aqueous solution with ionic strength $I = 1.00$ M over a range of temperature. With data from the analogous study involving bromopentaaquochromium(III) ion,[2] it is possible to compare for the four reactions the rate coefficients and activation parameters for corresponding terms of the rate law

$$-\frac{d \ln [Cr(OH_2)_5X^{2+}]}{dt} = \sum k_i[H^+]^i$$

which each reaction obeys (with the experimental acidity range disclosing $i = 0$ and -1 for $X^- = Cl^-$, Br^-, and I^-, and $i = 1$ and 0 for $X^- = F^-$).

Experimental Details

Reagents.—Reagent grade perchloric acid was used without further purification. Lithium perchlorate, used to maintain the ionic strength, was prepared from reagent grade lithium carbonate and perchloric acid; the salt was recrystallized several times from distilled and de-ionized water. Dowex 50W-X8 was used in the cation-exchange procedures.

Fluoropentaaquochromium(III) Ion.—An acidic solution containing fluorochromium(III) ion (as fluoropentaaquochromium(III) ion will be called) as the only chromium- and fluoride-containing species was prepared as follows. Equimolar amounts of chromium(III) perchlorate and potassium fluoride were brought together at relatively high concentrations (~ 2 M); the solution was boiled under reflux for 3 hr. and cooled to 0°, and the precipitated potassium perchlorate was removed. Fifteenfold dilution of this solution with water followed by cation-exchange separation allowed isolation of fluorochromium(III) ion from a small amount of difluorochromium(III) ion, which was eluted with 0.1 M perchloric acid, and larger amounts of

---

[1] This work was supported by the United States Atomic Energy Commission, Contract AT (11-1)-1286.

[2] F. A. Guthrie and E. L. King, *Inorg. Chem.*, **3**, 916 (1964).