CONTRIBUTION FROM THE DEPARTMENT OF CHEMISTRY AND THE LABORATORY FOR RESEARCH ON THE STRUCTURE OF MATTER,
UNIVERSITY OF PENNSYLVANIA, PHILADELPHIA, PENNSYLVANIA 19104

Kinetics of the Aquation of the Isomeric Dichlorotetraaquochromium(III) Ions Catalyzed by Mercury(II) Ion

BY JAMES P. BIRK

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The kinetics of the mercury(II)-catalyzed aquations of *trans*- and *cis*-dichlorotetraaquochromium(III) ions have been studied over a range of Hg^{2+} and H^+ concentrations, at 15–35° and ionic strength 0.50 M. The aquation of the *trans* complex follows the rate equation $-\mathrm{d}\ln[trans\text{-}Cr(H_2O)_4Cl_2^+]/\mathrm{d}t = (k_0 + k_{-1}[H^+]^{-1})[Hg^{2+}]$, with $k_0 = 30.7\ M^{-1}\ sec^{-1}$ and $k_{-1} = 0.941\ sec^{-1}$ at 25°. The associated activation parameters are $\Delta H_0^{\ddagger} = 13.5 \pm 0.4$ kcal/mol, $\Delta S_0^{\ddagger} = -6.3 \pm 1.4$ eu, $\Delta H_{-1}^{\ddagger} = 19.0 \pm 0.6$ kcal/mol, and $\Delta S_{-1}^{\ddagger} = 5.1 \pm 2.1$ eu. Aquation of the *cis* complex follows the rate equation $-\mathrm{d}\ln[cis\text{-}Cr(H_2O)_4Cl_2^+]/\mathrm{d}t = (k_0 + k_{-1}[H^+]^{-1})[Hg^{2+}]^2/(1 + K_1[Hg^{2+}] + K_1K_2[Hg^{2+}]^2)$, where $k_0K_1^{-1} = 31.0\ M^{-1}\ sec^{-1}$, $k_{-1}K_1^{-1} = 5.29\ sec^{-1}$, $K_1 = (1.35 \pm 0.43) \times 10^3\ M^{-1}$, and $K_1K_2 = (1.76 \pm 0.40) \times 10^4\ M^{-2}$ ($K_2 = 13.0\ M^{-1}$) at 25°. This equation is consistent with the formation of two binuclear complexes, $Cr(H_2O)_4Cl_2Hg^{3+}$ and $Cr(H_2O)_4Cl_2Hg_2^{5+}$. Activation parameters for the terms $k_0K_1^{-1}$ and $k_{-1}K_1^{-1}$ are $\Delta H_0^{\ddagger} = 14.4 \pm 0.9$ kcal/mol, $\Delta S_0^{\ddagger} = -3.4 \pm 3.0$ eu, $\Delta H_{-1}^{\ddagger} = 20.4 \pm 0.5$ kcal/mol, and $\Delta S_{-1}^{\ddagger} = 13.3 \pm 1.6$ eu.

Introduction

Previous kinetic studies of Hg^{2+}-catalyzed aquations of chromium(III) complexes have been limited to $CrCl^{2+}$,[1,2] $Cr(NH_3)_5Cl^{2+}$,[3] $CrCN^{2+}$,[4] $CrBr^{2+}$,[5] and CrI^{2+}.[5] A related study is that of the Ag^+-catalyzed aquations of $CrCl_2^+$ and $CrCl^{2+}$.[6] The reactions of Hg^{2+} with *trans*- and *cis*-$CrCl_2^+$ (eq 1), to be described

$$CrCl_2^+ + Hg^{2+} = CrCl^{2+} + HgCl^+ \qquad (1)$$

here, are of interest for several reasons. It has been postulated that the activated complex for Hg^{2+}-catalyzed aquations, *e.g.*, $\{ClCrCl\cdots Hg^{3+}\}^{\ddagger}$, may resemble the activated complex for the corresponding electron-transfer reactions with Cr^{2+}, *e.g.*, $\{ClCrCl\cdots Cr^{3+}\}^{\ddagger}$.[1,3,7] Since the Cr^{2+}-catalyzed aquations of *trans*- and *cis*-$CrCl_2^+$ to $CrCl^{2+}$ have been studied,[8] these systems provide a further test of these postulates.

The Hg^{2+}-catalyzed aquations of *trans*- and *cis*-$Co(en)_2Cl_2^+$ (en = ethylenediamine) were found to involve the formation of appreciable amounts of a binuclear complex, $Co(en)_2Cl_2Hg^{3+}$, with the *cis*, but not the *trans* complex.[9] Since the *cis* complex provides a configuration in which Hg^{2+} can simultaneously bond to two chlorides, a particularly stable situation,[10,11] such behavior is not too surprising. If this explanation is indeed correct, similar effects should be observed with the two isomers of $CrCl_2^+$. Finally, the kinetics of these processes are of interest in the interpretation of competition experiments designed to test for the possible occurrence of five-coordinate intermediates as immediate products in Hg^{2+}-catalyzed aquations.[5]

Experimental Section

Solutions of *trans*-$CrCl_2^+$ were prepared by dissolving Baker Analyzed chromium(III) chloride, $[Cr(H_2O)_4Cl_2]Cl\cdot 2H_2O$, in 0.01 M $HClO_4$, followed by absorption on Dowex 50W-X8 cation-exchange resin, washing with 0.01 M $HClO_4$, and elution with 0.20 M $HClO_4$. Solutions were analyzed either by measurement of the visible spectrum[12] or by oxidation with alkaline peroxide and measurement of the absorbance at 372 nm.[13] The two methods agreed to within 1%. Solutions of *cis*-$CrCl_2^+$ were prepared by the method of King.[12] Approximately 10-g samples of $[Cr(H_2O)_4Cl_2]Cl\cdot 2H_2O$ were sealed in 20 × 150 mm tubes and heated in an oven for 1 hr at 180°. The tubes were broken open while hot into *ca.* 300 ml of cold 10^{-3} M $HClO_4$ and the resulting solution was absorbed on a 13 mm × 8 ft jacketed column of Dowex 50W-X8, 50–100 mesh resin in the H^+ form, maintained at 2° by circulating ice water through the jacket. *Caution!* The sealed tubes are under considerable pressure when hot, so appropriate safety equipment and precautions should be used to avoid possible injury from flying glass while breaking the tubes. The column was loaded nearly to capacity and the contents were washed with 10^{-3} M $HClO_4$; then the dichlorochromium(III) species were slowly (during 18 hr) eluted with 0.10 M $HClO_4$. The relative absorbances at 450 and 635 nm, D_{450}/D_{635}, were used as a criterion of the isomeric content.[12] Only samples with a ratio of $D_{450}/D_{635} > 1.40$ were kept (~25% of the eluted material) and all experiments reported here were carried out with a sample having a ratio of 1.49. Solutions were stored at −78°. The extinction coefficients of the *cis* isomer at 450 and 635 nm were determined to be 28.7 and 19.3 $M^{-1}\ cm^{-1}$, in good agreement with King's values[12] of 28.8 and 19.6 $M^{-1}\ cm^{-1}$. Spectra were measured with a Cary 14 recording spectrophotometer.

Solutions of mercury(II) perchlorate,[1] barium perchlorate,[1] and lithium perchlorate[14] were prepared and analyzed as previously described. Perchloric acid solutions were dilutions of Baker Analyzed 70% $HClO_4$, which was not further purified. Distilled water was used in all solutions.

Kinetic experiments were carried out with a Durrum stopped-flow spectrophotometer. Measurements were made primarily at 635 nm for the *trans* isomer and at 450 nm for the *cis* isomer, but several measurements at other wavelengths in the visible region were in good agreement. Chromium(III) solutions were pre-

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[1] J. H. Espenson and J. P. Birk, *Inorg. Chem.*, **4**, 527 (1965).

[2] In general, coordinated water molecules will not be shown in chemical formulas.

[3] J. H. Espenson and S. R. Hubbard, *Inorg. Chem.*, **5**, 686 (1966).

[4] J. P. Birk and J. H. Espenson, *ibid.*, **7**, 991 (1968).

[5] J. P. Birk, unpublished experiments.

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

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[11] L. G. Sillén, *Acta Chem. Scand.*, **3**, 539 (1949), and references cited therein.

[12] E. L. King, M. J. M. Woods, and H. S. Gates, *J. Am. Chem. Soc.*, **80**, 5015 (1958).

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

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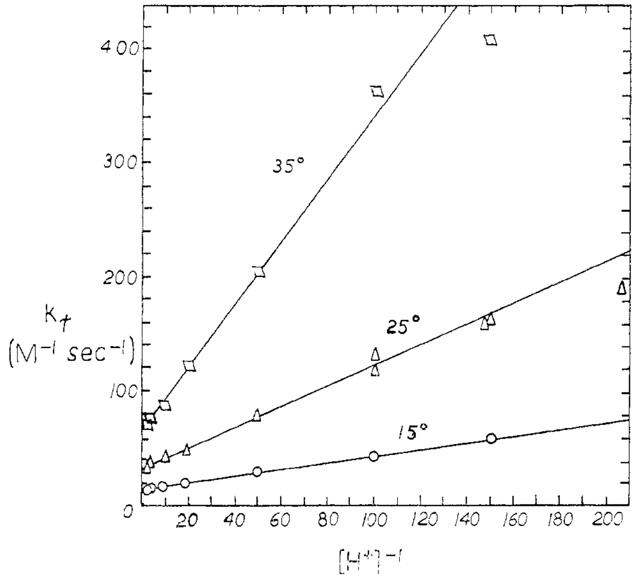

Figure 1.—Plots of k_t *vs.* $[H^+]^{-1}$ for the reaction of Hg^{2+} with *trans*-$CrCl_2^+$, showing conformity to eq 3. Lines were calculated from the parameters in Table II.

pared just before use by adding small volumes of a cold $CrCl_2^+$ stock solution to a solution containing all other materials previously brought to the appropriate temperature. The mercury(II) concentration was always maintained at 10–50 times that of $CrCl_2^+$, giving pseudo-first-order conditions. The Guggenheim method[15] was generally used to treat the data, since there was some interference from the Hg^{2+}-catalyzed aquation of $CrCl^{2+}$, especially at low $[H^+]$. Guggenheim plots were linear for at least 90% reaction. Five or six repetitive measurements were made on each reaction mixture, giving pseudo-first-order rate constants reproducible to ±1–2%. The reproducibility of completely independent duplicate measurements was generally of the order of ±2%. Considering all but two data points, which were poorly reproducible, the average deviations between duplicate experiments were in the range of 0.3–4.4%.

Results

The primary chromium product of the Hg^{2+}-catalyzed aquation of *trans*- and *cis*-$CrCl_2^+$ was in each case determined spectrally to be $CrCl^{2+}$, which aquates further in a second slower step. The reaction of the *cis* complex was particularly examined for the possible production of some Cr^{3+} without prior formation of $CrCl^{2+}$. Extrapolation of absorbance changes to the time of mixing indicated that very little if any Cr^{3+} was formed directly. The kinetics of these reactions were determined at 0.50 *M* ionic strength maintained with lithium perchlorate (and with barium perchlorate in some experiments) at 15.0, 25.0, and 35.0°, over the initial concentration ranges: 5×10^{-3}–5×10^{-2} *M* Hg^{2+}, 5×10^{-4}–1×10^{-3} *M* $CrCl_2^+$, and 5×10^{-3}–5×10^{-1} *M* H^+. Excellent linearity of pseudo-first-order plots indicated a first-order dependence on the total concentration of $CrCl_2^+$. The dependence of the rate on $[Hg^{2+}]$ is shown in Table I.

TABLE I

RATE CONSTANTS FOR THE REACTION OF Hg^{2+} WITH $CrCl_2^+$ AT 0.100 *M* H^+ AND 0.50 *M* IONIC STRENGTH

$10^2[Hg^{2+}]$, *M*	$10^2[Ba^{2+}]$, *M*	k,[a] M^{-1} sec^{-1}: *trans*-$CrCl_2^+$ 25.0°	*cis*-$CrCl_2^+$ 35.0°	*cis*-$CrCl_2^+$ 25.0°	*cis*-$CrCl_2^+$ 15.0°
0.496	0.00	41.9 ± 1.5	152 ± 3	67.8 ± 1.0	26.9
0.496	4.49	34.9	159 ± 7	66.4 ± 1.7	26.5
1.00	0.00	39.3 ± 0.1	179 ± 2	65.2 ± 0.4	25.9
1.00	4.00	38.0	167 ± 1	66.8 ± 1.0	24.3
2.01	0.00	37.3 ± 1.7	198 ± 5	62.1 ± 1.7	25.5
2.01	3.00	35.5	185 ± 2	62.6	24.5
3.01	0.00	36.0	201 ± 27	58.5 ± 2.5	...
3.01	2.00	33.9	201 ± 29	58.4	...
3.50	0.00	36.1	...	55.0	...
4.01	0.00	...	176 ± 2	52.5	21.5
4.01	1.00	...	177 ± 2	52.7	22.2
5.02	0.00	36.8 ± 0.6	162 ± 5	47.1 ± 0.3	20.7

[a] Uncertainties quoted are the average deviations when several determinations were carried out at the same concentrations; $k = [Hg^{2+}]^{-1}(-d \ln[CrCl_2^+]/dt)$.

Reaction with *trans*-$CrCl_2^+$.—The reaction of Hg^{2+} with *trans*-$CrCl_2^+$ shows an apparent decrease in second-order rate constant, calculated assuming eq 2 to describe the $[Hg^{2+}]$ dependence.

$$-d \ln [trans\text{-}CrCl_2^+]/dt = k_t[Hg^{2+}] \tag{2}$$

The observed decrease in k_t with increasing $[Hg^{2+}]$ could be expected to arise either from a medium effect or from the formation of appreciable amounts of a binuclear complex, $CrCl_2Hg^{3+}$. When Ba^{2+} is added to maintain the total concentration of dipositive ions at 0.05 *M*, the value of k_t remains much more constant and exhibits no apparent trend. Thus within the experimental accuracy it would appear that the effect can be entirely attributed to a medium effect, although the formation of low concentrations of a binuclear complex cannot be ruled out. Similar effects of the ionic medium on the rate constant were observed in the reaction between Hg^{2+} and $CrCl^{2+}$ and have been discussed in detail previously.[1]

As might be expected from previous studies,[1,3] the $[H^+]$ dependence of k_t can be fairly well described by

$$k_t = k_0 + k_{-1}[H^+]^{-1} \tag{3}$$

Conformity of data to this equation is shown in Figure 1. The k_{-1} path can reasonably be attributed to hydrolysis of $CrCl_2^+$ (eq 4),[1,3] followed by reaction with Hg^{2+} (eq 5 and 6). The negative deviations

$$CrCl_2^+ + H_2O \overset{K_a << 1}{\rightleftharpoons} CrCl_2(OH) + H^+ \tag{4}$$

$$CrCl_2(OH) + Hg^{2+} \xrightarrow{k_{-1}'} CrCl(OH)^+ + HgCl^+ \tag{5}$$

$$CrCl(OH)^+ + H^+ = CrCl^{2+} + H_2O \tag{6}$$

from eq 3 observed at very low $[H^+]$ are probably due to hydrolysis of Hg^{2+} and further hydrolysis of chromium(III). If the concentration of Hg^{2+} is corrected for hydrolysis,[16,17] the deviations are lessened but not entirely removed, so it seems unlikely that there is significant reaction involving $HgOH^+$ unless its reactivity is very similar to that of Hg^{2+}, and appreciable hydrolysis of Cr(III) species, possibly including the binuclear complex, is a likely cause of the remainder of the deviations. These explanations are somewhat tenuous, however, and other factors

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(16) S. Hietanen and L. G. Sillén, *Acta Chem. Scand.*, **6**, 747 (1952).

(17) L. Ciavatta and M. Grimaldi, *J. Inorg. Nucl. Chem.*, **30**, 563 (1968).

TABLE II

RATE AND ACTIVATION PARAMETERS FOR THE REACTION OF Hg^{2+} WITH *trans*-$CrCl_2^+$

	Value	
Quantity	k_0,[a] M^{-1} sec^{-1}	k_{-1},[a] sec^{-1}
$\Delta H^{\ddagger}$, kcal/mol	13.5 ± 0.4	19.0 ± 0.6
$\Delta S^{\ddagger}$, eu	-6.3 ± 1.4	5.1 ± 2.1
k at 35°	66.5	2.76
at 25°	30.7	0.941
at 15°	13.4	0.299

[a] These parameters are described by eq 3.

might be involved—*e.g.*, the hydrolysis constants of Hg^{2+} could be in error, or medium effects may be involved.

The activation parameters for the two paths described by eq 3 were calculated by fitting all data simultaneously to the absolute rate theory expression, using a nonlinear least-squares computer program[18] in which each data point was weighted as k_t^{-2}. The activation and rate parameters are summarized in Table II. These parameters refer specifically to a medium containing 0.01 M dipositive ions at an ionic strength of 0.50 M. Data at very low [H^+] which showed significant deviations from eq 3 (Figure 1) were omitted from these calculations. The activation parameters reproduce the values of the rate constants included in the calculations with an average deviation of 3.4%.

Reaction with ***cis*****-$CrCl_2^+$.**—The reaction of Hg^{2+} with *cis*-$CrCl_2^+$ also exhibits trends in the second-order rate constant (Table I) calculated assuming a simple mixed-second-order rate equation. In this case, however, addition of Ba^{2+} to maintain the concentration of dipositive ions at 0.05 M has little effect on the value of the rate constant. The differences between the rate constants in the presence or absence of Ba^{2+} show no trend with [Hg^{2+}] and can be attributed to experimental scatter. Since Ba^{2+} has no effect on the value of the rate constant, the change in rate constant with increasing [Hg^{2+}] cannot be due to a medium effect. Similar effects have been observed in the reaction between Hg^{2+} and *cis*-$Co(en)_2Cl_2^+$ and were explained by the formation of a binuclear complex.[9] An analogous complex formation reaction (eq 7) can be invoked here, leading to the rate

$$cis\text{-}CrCl_2^+ + Hg^{2+} \overset{K_1}{\rightleftharpoons} cis\text{-}CrCl_2Hg^{3+} \qquad (7)$$

equation

$$-\mathrm{d} \ln [cis\text{-}CrCl_2^+]/\mathrm{d}t = k[Hg^{2+}]/(1 + K_1[Hg^{2+}]) \qquad (8)$$

Interpretation of the rate effects in terms of complex formation is supported by measurement of the absorbance change in the reaction as a function of [Hg^{2+}]. In a typical set of experiments at 25°, the absorbance changes at 450 nm for the *cis* isomer (in arbitrary units, with the various adjustments on the stopped-flow apparatus held constant) were 64, 59, 55, 51, 49, and 49 for $10^2[Hg^{2+}]$ = 0.496, 1.00, 2.01, 3.01, 4.01, and 5.02 M. For the *trans* isomer on the other hand, the absorbance change under identical conditions, but at 635 nm, was 45 ± 1 (in different arbitrary units) throughout the same concentration range. Thus it is clear that the apparent change in rate constant with increasing [Hg^{2+}] cannot arise from the same source for the two isomers.

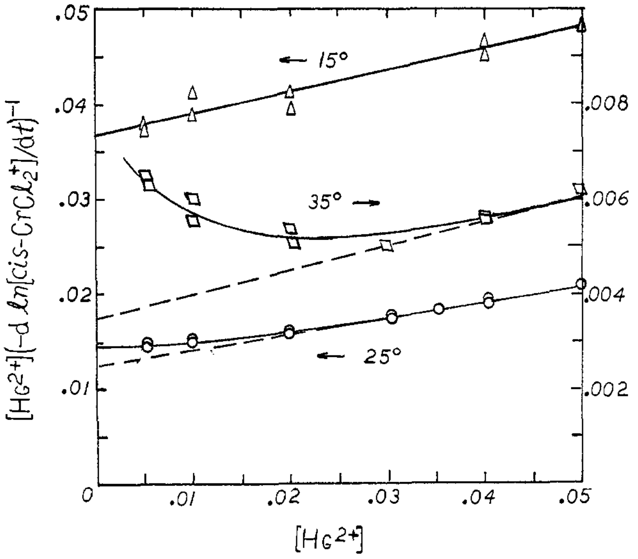

Figure 2.—Plots of $[Hg^{2+}](-\mathrm{d} \ln [cis\text{-}CrCl_2^+]/\mathrm{d}t)^{-1}$ *vs.* [Hg^{2+}] for the reaction of Hg^{2+} with *cis*-$CrCl_2^+$, showing conformity to eq 10 and 11. Solid lines were calculated from eq 10 and the parameters in Table III. Dashed lines indicate behavior that would be expected if eq 8 were obeyed.

Plots of $[Hg^{2+}](-\mathrm{d} \ln [cis\text{-}CrCl_2^+]/\mathrm{d}t)^{-1}$ *vs.* [Hg^{2+}] at 0.100 M H^+ are given in Figure 2 and should be linear if eq 8 accurately describes the data. Reasonably good linearity is observed at 15°, but systematic deviations are noted at 25° and more significantly at 35°. The nature of these deviations suggests a more complex rate equation (eq 10) consistent with the formation of a second binuclear complex

$$cis\text{-}CrCl_2Hg^{3+} + Hg^{2+} \overset{K_2}{\rightleftharpoons} cis\text{-}CrCl_2Hg_2^{5+} \qquad (9)$$

$$-\mathrm{d} \ln [cis\text{-}CrCl_2^+]/\mathrm{d}t = k_c[Hg^{2+}]^2/(1 + K_1[Hg^{2+}] + K_1K_2[Hg^{2+}]^2) \qquad (10)$$

A plot of log ($-\mathrm{d}$ ln [*cis*-$CrCl_2^+$]/dt) *vs.* log [Hg^{2+}] indicates that the apparent order in [Hg^{2+}] decreases between the limits of 2 and 0 with increasing [Hg^{2+}], consistent with eq 10. The apparent simpler behavior at 15° can then be attributed to the limiting form of eq 10 which arises if most of the $CrCl_2^+$ is in the form of $CrCl_2Hg^{3+}$ ($K_1[Hg^{2+}] \gg 1$)

$$-\mathrm{d} \ln [cis\text{-}CrCl_2^+]/\mathrm{d}t = k_cK_1^{-1}[Hg^{2+}]/(1 + K_2[Hg^{2+}]) \qquad (11)$$

The only parameters which could be determined at all three temperatures were $k_cK_1^{-1}$ and K_2. Because $K_1[Hg^{2+}] \gg 1$ at 15°, the limiting form of the rate equation (eq 11) must be used at this temperature. Attempts to fit the 15° data to eq 10 yielded a wide range of values of k_c, K_1, and K_1K_2 which were obviously not consistent with values at the higher tem-

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

TABLE III

RATE, EQUILIBRIUM, AND ACTIVATION PARAMETERS FOR THE REACTION OF Hg^{2+} AND *cis*-$CrCl_2^+$

Quantity	Value				
	$k_0K_1^{-1}$, M^{-1} sec^{-1}	$k_{-1}K_1^{-1}$, sec^{-1}	K_1, M^{-1}	K_1K_2, M^{-2}	K_2, M^{-1}
$\Delta H^{\ddagger}$ or $\Delta H°$, kcal/mol	14.4 ± 0.9	20.4 ± 0.5	-26.1	*a*	*a*
$\Delta S^{\ddagger}$ or $\Delta S°$, eu	-3.4 ± 3.0	13.3 ± 1.6	-73	*a*	*a*
k^b or K at 35°	70.4	16.8	$(3.23 \pm 1.14) \times 10^2$	$(2.74 \pm 0.56) \times 10^3$	8.5
at 25°	31.0	5.29	$(1.35 \pm 0.43) \times 10^3$	$(1.76 \pm 0.40) \times 10^4$	13.0
at 15°	12.9	1.54	$(6.22 \times 10^3)^c$	$(3.80 \times 10^4)^c$	6.13 ± 0.84

[a] Values are temperature dependent. [b] Calculated from the activation parameters. [c] Extrapolated from the higher temperatures.

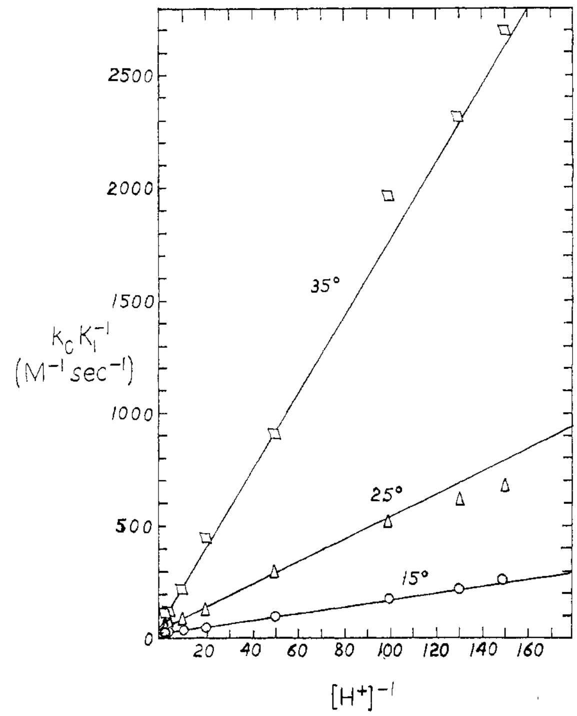

Figure 3.—Plots of $k_cK_1^{-1}$ *vs.* $[H^+]^{-1}$ for the reaction of Hg^{2+} with *cis*-$CrCl_2^+$, showing conformity to eq 12. Lines were calculated from parameters in Table III.

peratures but which gave the same value of $k_cK_1^{-1}$ and K_2 as obtained from eq 11. A value of $K_1 = 6.22 \times 10^3\ M^{-1}$ could be determined for 15° by extrapolation from the higher temperatures. This value is consistent with the data obeying the limiting rate equation (eq 11) since $(K_1[Hg^{2+}] + K_1K_2[Hg^{2+}]^2)$ contributes 96.8–99.7% of the value of the denominator in eq 10 over the range of $[Hg^{2+}]$ studied.

The parameter $k_cK_1^{-1}$ shows a dependence on $[H^+]$ given by

$$k_cK_1^{-1} = k_0K_1^{-1} + k_{-1}K_1^{-1}[H^+]^{-1} \qquad (12)$$

Conformity of data to this equation is shown in Figure 3. Deviations at very low $[H^+]$ have already been discussed for the *trans* complex. Values of the rate, equilibrium, and activation parameters, determined with nonlinear least-squares computer programs,[18] are given in Table III. These parameters reproduce the values of $k_cK_1^{-1}$ with an average deviation of 4.8%.

Three possible interpretations can be placed on the rate parameter k_c

$$2Hg^{2+} + cis\text{-}CrCl_2^+ \xrightarrow{k_c} CrCl^{2+} + HgCl^+ + Hg^{2+} \qquad (13)$$

$$Hg^{2+} + cis\text{-}CrCl_2Hg^{3+} \xrightarrow{k_c'} CrCl^{2+} + HgCl^+ + Hg^{2+} \qquad (14)$$

$$cis\text{-}CrCl_2Hg_2^{5+} \xrightarrow{k_c''} CrCl^{2+} + HgCl^+ + Hg^{2+} \qquad (15)$$

where $k_c' = k_cK_1^{-1}$ and $k_c'' = k_cK_1^{-1}K_2^{-1}$. Since both k_c and K_1 decrease, while K_2 increases and then decreases slightly with increasing temperature and it is unlikely that a simple rate constant will decrease with increasing temperature (*i.e.*, have a negative $\Delta H^{\ddagger}$), the first possible interpretation (eq 13) can be eliminated. However, either of the other two interpretations is consistent with the available data and these remain kinetically indistinguishable. The path having an inverse $[H^+]$ dependence probably arises from slight hydrolysis of the reactive form of Cr(III).

Discussion

It has been postulated several times[1,3,7] that the activated complexes for mercury(II)-catalyzed aquations of metal halide complexes should bear some resemblance to those for the analogous electron-transfer reactions of the metal halides with chromium(II) ion, since both systems appear to involve the formation of halide-bridged binuclear species either as intermediates or as activated complexes. If these activated complexes do indeed closely resemble one another, similar values of the entropy of activation might be expected for the two processes. A comparison can be made between the $\Delta S^{\ddagger}$ for the Hg^{2+}- (acid-independent path) and Cr^{2+}-catalyzed aquations of *trans*-$CrCl_2^+$. For the Hg^{2+} reaction, $\Delta S^{\ddagger} = -6.3$ eu while for the Cr^{2+} reaction, the value is -30.2 eu.[8] These results are similar to those observed in previous comparisons of electron transfer and Hg^{2+}-catalyzed substitution reactions[3,9]—there does not appear to be any simple correspondence between the activation processes for the two types of reaction. It might at least naively be expected that the structural changes occurring on Cr(III) during formation of the activated complex would be of opposite effect in the two systems—a loosening of the nonbridging ligands (giving a more positive $\Delta S^{\ddagger}$) in the Cr^{2+} reaction in order to equalize energies for electron transfer and a tightening of coordination to nonbridging ligands (giving a more negative $\Delta S^{\ddagger}$) as the Cl^- bridge in the Hg^{2+} reaction becomes less strongly bonded to Cr(III) and thus has less effect in diffusing the electrostatic attraction of Cr(III) for the other ligands. The opposite effects would be observed on Cr^{2+} and Hg^{2+}—Cr^{2+} must coordinate more strongly to its ligands to equalize energies for electron transfer, while Hg^{2+} on coordination to Cl^- would relax its hold on its other ligands. Since the structural changes on Cr(III) would provide contributions to $\Delta S^{\ddagger}$ opposite to the differences observed, apparently the structural changes on Cr^{2+} and on Hg^{2+} play a dominant and differing role in determining the magnitude of $\Delta S^{\ddagger}$. It would appear then that any resemblance between the activated complexes for the two types of reaction is fairly superficial.

The formation of appreciable concentrations of a binuclear complex, *cis*-$ClCr_2Hg^{3+}$, has ample precedent. Similar complexes have been observed in the reaction of Hg^{2+} with *cis*-$Co(en)_2Cl_2^+$,[9] *cis*-$Co(en)_2(N_3)_2^+$,[19] $CrCN^{2+}$,[4] $Co(NH_3)_5CN^{2+}$,[20] and $CrNCS^{2+}$.[21] The occurrence of binuclear complexes in the case of *cis* but not *trans* isomers of dichloro complexes is not unreasonable since the *cis* complexes provide a configuration in which double-bridging can occur. In the reaction of Hg^{2+} with *cis*-$Co(en)_2Cl_2^+$,[9] although the reactive form (complexed or uncomplexed) of Co(III) could not be distinguished kinetically, indirect arguments have been advanced in favor of the uncomplexed form being the kinetically reactive species. This would then imply that a configuration involving double-bridging is particularly stable, and to accomplish aquation, a single-bridged configuration must be attained. Similar conclusions can be drawn for the reaction of Hg^{2+} with *cis*-$CrCl_2^+$. The rate equation (eq 10) can be interpreted in terms of two binuclear complexes, *cis*-$CrCl_2Hg^{3+}$ and *cis*-$CrCl_2Hg_2^{5+}$, and an activated complex of composition $\{CrCl_2Hg_2^{5+}\}^{\ddagger}$. In this case the form of the rate equation is consistent with three different mechanisms (eq 13–15). The reaction of uncomplexed *cis*-$CrCl_2^+$ with $2Hg^{2+}$ (eq 13) can be eliminated since the data would require a negative enthalpy of activation for such a process, an unlikely situation. Over much of the concentration range studied, $CrCl_2Hg^{3+}$ is the predominant form of Cr(III), but since the activated complex contains one more Hg^{2+}, this presumably double-bridged configuration cannot be a configuration of appreciable reactivity. In contrast to the *cis*-$Co(en)_2Cl_2^+$ system, however, the reactive single-bridged configuration is reached by coordination of a second Hg^{2+}, although whether this is accomplished by formation of the activated complex from $CrCl_2Hg^{2+} + Hg^{2+}$ (eq 14) or from $CrCl_2Hg_2^{5+}$ (eq 15) cannot be distinguished kinetically.

Since a limiting form (eq 11) of the rate equation (eq 10) was observed at 15°, and this limiting form would have been consistent with the formation of only one binuclear complex, $CrCl_2Hg^{3+}$, in the absence of further information, the question arises whether the rate equation observed[9] for the reaction of Hg^{2+} with *cis*-$Co(en)_2Cl_2^+$ is also such a limiting form (eq 11) or whether it is indeed the form expected for coordination of only one Hg^{2+} (eq 8). In either case, the value of one equilibrium constant (K_2 or K_1, respectively) can be determined. The value for complexation of *cis*-$Co(en)_2Cl_2^+$ was 650 M^{-1} at 25°,[9] reasonably similar to the value of $K_1 = 1350\ M^{-1}$ for *cis*-$CrCl_2^+$, but very dissimilar to $K_2 = 13\ M^{-1}$. Thus for some reason, the two systems appear to proceed by different mechanisms, although these mechanisms do have in common the feature that the double-bridged configuration must be destroyed to accomplish the aquation reaction.

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