acid concentration (5.3–10.6 *M*) and were corrected[3] to unit activity of water. As another significant comparison, the kinetic data for the aquation of $CrNO_3^{2+}$ can be cited. Swaddle[9] reported $k = 7.4 \times 10^{-5}$ sec^{-1} at 25° and $\mu = 1$ for this species ($\Delta H^{\ddagger} = 21.6 \pm 0.1$ kcal mol^{-1}).

Despite the somewhat indeterminate nature of the comparison between $CrClO_4^{2+}$ and $CrCF_3SO_3^{2+}$, it is certain that $CF_3SO_3^-$ is more nucleophilic toward Cr^{3+} than is ClO_4^-. It is still more certain that $CF_3SO_3^-$ is less nucleophilic toward Cr^{3+} than is NO_3^-. Even with NO_3^-, except at high concentrations, the extent of complexation of metal ions is small. The equilibrium constants for the association of Cr^{3+} with NO_3^-, $CF_3SO_3^-$, and ClO_4^- can be expected[4] to be inversely proportional to the rates of aquation, and on this basis a tenfold greater concentration of $CF_3SO_3^-$ than of NO_3^- is needed to produce the same degree of complex formation. The direct experiment done in a search for evidence of complex formation at 7.4 *M* CF_3SO_3H suggests that there is less than 10% conversion to a complex under these conditions. Thus it seems safe to conclude that when $CF_3SO_3^-$ is at ordinary concentration levels, say 2 *M* or less, the formation of a complex with Cr^{3+} is insignificant in extent. On this basis and on the basis of its other properties, the use of $CF_3SO_3^-$ as an indifferent anion appears to be very promising.

The decreasing lability with increased extent of complexation is unprecedented for Cr^{3+} as the central ion. Further work will need to be done in characterizing the complex species formed before this behavior is understood. The possibility that $CF_3SO_3^-$ can be a chelating ligand will need to be taken into account in considering the various alternatives. Almost as remarkable as the kinetic stability of the most highly complexed species is its spectrum (see Figure 2). The absorption properties displayed do, however, have precedent. Jones and Bjerrum[3] reported for the equilibrium spectrum of $Cr(H_2O)_6(ClO_4)_3$ in 13 *M* H_2SO_4 features which closely resemble those shown in Figure 2, there being peaks at 460 and 640 nm, and the long-wavelength band showing structure. In 13 *M* H_2SO_4, coordinated SO_4^{2-} is in all likelihood protonated; HSO_4^- and $CF_3SO_3^-$ are undoubtedly much alike in respect to their affinities for cations. The splitting of the long-wavelength band indicates a lowering of the symmetry about Cr(III).

A reasonable candidate for the complex formed at high acid is *trans*-$Cr(H_2O)_4(CF_3SO_3)_2^+$; if $CF_3SO_3^-$ has a weaker trans-labilizing effect than H_2O, the relative rates of aquation can be understood.[10]

Acknowledgment.—Financial support for this research by the Atomic Energy Commission, Grant No. AT 04 3 326, PA 7, is gratefully acknowledged.

[9] T. W. Swaddle, *J. Amer. Chem. Soc.*, **89**, 9338 (1967).

[10] This suggestion, made by one of the reviewers, seems to us to be more reasonable than our own earlier hypothesis which involved chelation by the ligand.

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Kinetics of the Aquation of Dichlorotetraaquochromium(III) Catalyzed by Monosubstituted Mercury(II) Complexes

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Received April 28, 1970

The kinetics of the aquation of *cis*-$Cr(H_2O)_4Cl_2^+$ catalyzed by $HgCl^+$ and of *trans*-$Cr(H_2O)_4Cl_2^+$ catalyzed by HgX^+ (X = Cl, Br, I, CN) have been examined at 15–35° and 0.50 *M* ionic strength. In each reaction, except for X = CN, the rate equation is of the form $-d \ln [Cr(H_2O)_4Cl_2^+]/dt = (k_0 + k_{-1}[H^+]^{-1})[HgX^+]$. Values of the activation parameters were determined for each term and were used in an attempt to elucidate energetic and structural features of the transition state. The reaction of *trans*-$Cr(H_2O)_4Cl_2^+$ with $HgCN^+$ follows the rate equation $-d \ln [Cr(H_2O)_4Cl_2^+]/dt = (a[H^+] + b)[HgCN^+]/(c + [H^+])$, which is interpreted in terms of several mechanisms which are consistent with this form of rate equation.

Introduction

As part of a continuing study[1-4] of the mechanism of aquation of chromium(III) complexes catalyzed by metal ions, in particular Hg(II), the aquations of *cis*- and *trans*-$CrCl_2^+$ catalyzed by HgX^+ (X = Cl, Br, I, CN) have been examined. In a previous study[3] of the reaction between $CrCl_2^+$[5] and Hg^{2+}, evidence was found for binuclear complex formation with the cis but not with the trans isomer. It was suggested that a binuclear complex would be formed only when it is possible to achieve a double-bridged configuration. The reaction between *cis*-$CrCl_2^+$ and $HgCl^+$ was examined to test further this proposal. Since the coordination of a third chloride to mercury(II) is not a particularly favorable process,[6,7] it would be expected that a bi-

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

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

[3] J. P. Birk, *ibid.*, **9**, 735 (1970).

[4] J. P. Birk and C. M. Pasquale, submitted for publication.

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

[6] L. D. Hansen, R. M. Izatt, and J. J. Christensen, *Inorg. Chem.*, **2**, 1243 (1963).

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

nuclear complex would not be formed with $HgCl^+$ if a double-bridged configuration is a necessary requirement.

In a number of reactions, the relative rates of Hg^{2+} and $HgCl^+$ have been shown to be opposite to the relative rates predicted on the basis of the formation constants of the products $HgCl^+$ and $HgCl_2$.[1,8,9] It has been proposed[1] that the source of this effect lies in electrostatic effects since the two reactants are of different charge. The reactions of *trans*-$CrCl_2^+$ with a number of mercury(II) complexes have been examined here in an attempt to provide a more rigorous explanation of this apparent discrepancy.

Experimental Section

The preparation and analysis of most reagent solutions and the techniques used to determine the stoichiometry and kinetics have been described previously.[3] Solutions of lithium chloride, lithium bromide, sodium iodide, and sodium cyanide were prepared from analytical grade materials and were analyzed by ion-exchange titrations.

Solutions of monosubstituted mercury(II) complexes were prepared by mixing the appropriate ligand with mercury(II) perchlorate in ratios of ligand:Hg(II) ≤ 1.0. In solutions containing iodide, much lower ratios were imposed by solubility limitations. It is known that the attainment of equilibrium in mercury(II) cyanide solutions is slow,[10] and poor reproducibility of rate constants in the *trans*-$CrCl_2^+$ + HgI^+ reaction suggested the same might be true of mercury(II) iodide solutions, so these solutions were prepared 15–20 hr before use. The concentrations of monosubstituted complexes, HgX^+, were calculated from the total concentrations of Hg(II) and X^-, after correcting for the disproportionation reaction[1]

$$2HgX^+ \rightleftharpoons Hg^{2+} + HgX_2 \qquad (1)$$

The appropriate first and second association constants necessary to calculate the disproportionation equilibrium constants were obtained from the literature.[6,7,10,11] Because of the disproportionation reactions, the observed pseudo-first-order rate constants had to be corrected for the contribution from the reaction with Hg^{2+}, as described previously,[1] using rate constants for that reaction from a previous study.[3]

Kinetics experiments were carried out with a Durrum stopped-flow spectrophotometer, primarily at 635 or 450 nm. The handling of materials and treatment of data have been described in an earlier study.[3] The Guggenheim method[12] was used to treat the absorbance–time data, since further aquation of $CrCl^{2+}$, although significantly slower, was sufficiently rapid especially at low $[H^+]$ to cause some interference.

Results

The primary product of the reactions of $CrCl_2^+$ with HgX^+ (X = Cl, Br, I, CN) was determined spectrally to be $CrCl^{2+}$ (eq 2), which aquates further in a subsequent slower step.

$$CrCl_2^+ + HgX^+ = CrCl^{2+} + HgXCl \qquad (2)$$

The kinetics of the reactions of HgX^+ with $CrCl_2^+$ were determined at 0.50 M ionic strength maintained with lithium perchlorate at 15.0, 25.0, and 35.0° over the initial concentration ranges $(0.5\text{–}1.0) \times 10^{-3}\ M$ $CrCl_2^+$, $6 \times 10^{-3}\text{–}5 \times 10^{-1}\ M$ H^+, and HgX^+ and total Hg(II) concentrations as indicated in Table I. The data followed excellent pseudo-first-order kinetics for >90% reaction, indicating a first-order dependence on $[CrCl_2^+]$. After correcting for the contribution to the rate from the reaction with Hg^{2+}, the data reasonably well follow the rate equation

$$-\mathrm{d}\ln[CrCl_2^+]/\mathrm{d}t = k_X[HgX^+] \qquad (3)$$

TABLE I

RATE CONSTANTS FOR THE REACTION OF HgX^+ WITH $CrCl_2^+$ AT 25°, 0.100 M H^+, AND 0.50 M IONIC STRENGTH

$10^3[HgX^+]$,[a] M	$10^3[Hg(II)]$,[b] M	k_X,[c] $M^{-1}\ sec^{-1}$
	cis-$CrCl_2^+$ + $HgCl^+$	
1.63	10.0	94
3.17	10.0	104
4.04	10.0	109
8.08	20.1	105
20.2	50.0	99
	Av	102 ± 5
	trans-$CrCl_2^+$ + $HgCl^+$	
1.63	10.0	92.6
2.00	4.96	85.7
3.17	10.0	83.8
4.04	10.0	96.7, 81.6
8.08	20.1	82.9
20.2	50.0	84.5
	Av	86.8 ± 4.5
	trans-$CrCl_2^+$ + $HgBr^+$	
2.72	4.96	50.2
3.99	10.0	56.2
5.50	10.0	50.1, 55.9
11.0	20.1	53.7
	Av	53.2 ± 2.5
	trans-$CrCl_2^+$ + HgI^+	
1.50	10.0	21 ± 8
2.98	10.0	21 ± 5
4.98	20.1	22 ± 10
	Av	21 ± 8
	trans-$CrCl_2^+$ + $HgCN^+$	
3.43	4.96	43.6
4.62	10.0	42.9
6.93	10.0	48.3, 47.4
12.6	20.1	41.9
13.9	20.1	49.3
	Av	45.6 ± 2.8

[a] Corrected for disproportionation of HgX^+ to Hg^{2+} and HgX_2. [b] Total concentration of Hg(II) in all forms. [c] Corrected for reaction of Hg^{2+} with $CrCl_2^+$, as described in ref 1.

It was assumed in each case that HgX_2 provided no contribution to the overall rate, an assumption which is justified by the data given in Table I and by results of a previous study.[1] The precision of rate constants for the HgI^+ reaction was low, probably due to the fact that the Hg^{2+} concentrations were quite appreciable in these experiments because of low solubility of HgI_2, and the calculated values of k_I were thus the result of relatively small differences between two numbers.

The variation in values of k_X as a function of $[H^+]$ is shown in Table II (trans isomer; X = Cl, Br, I) and Table III (cis isomer; X = Cl). The data in each case show no systematic deviations from the rate equation

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

Values of k_0, k_{-1}, and the activation parameters associated with these rate constants are given in Table IV.

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(11) G. Anderegg, *Helv. Chim. Acta*, **40**, 1022 (1957).

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

TABLE II

VALUES OF THE RATE CONSTANTS FOR THE REACTION OF HgX^+ WITH *trans*-$CrCl_2^+$ AT VARIOUS $[H^+]$

$10^2[H^+]$, M	k_X, M^{-1} sec^{-1} X = Cl 15°	X = Cl 25°	X = Cl 35°	X = Br 15°	X = Br 25°	X = Br 35°	X = I 15°	X = I 25°	X = I 35°
49.7	...	...	...	...	51.6	...	...	...	...
48.9	27.8	78.3	145	...	...	...	...	...	...
47.4	...	...	...	...	...	80.6	...	21.4	29.6
29.0	29.7	79.9	141	...	...	...	...	...	...
28.0	...	...	...	...	49.1	85.2	...	...	...
27.5	...	...	...	...	...	...	...	16.4	31.6
10.0	34.6	81.6	163	23.6	50.1	89.2	...	20.7	55.9
5.16	37.3	95.4	208	...	59.9	93.1	...	27.6	...
5.01	...	...	...	23.3	64.6	...	7.89	...	...
2.00	50.9	126	327	27.8	87.2	179	8.17	49.1	155
1.50	52.1	...	...	30.2	99.4	183	8.08	...	...
1.20	...	...	...	...	115	...	...	...	...
1.00	76.6	172	598	...	...	...	...	75.1	...
0.803	86.5	...	...	...	...	...	...	...	...
0.669	...	227	...	...	180	420	...	125	...
0.602	...	...	...	47.7	186	452	24.9	...	601

TABLE III

VALUES OF THE RATE CONSTANTS FOR THE REACTION OF $HgCl^+$ WITH *cis*-$CrCl_2^+$ AT VARIOUS $[H^+]$

$10^2[H^+]$, M	$k_{Cl, cis}$, M^{-1} sec^{-1} 15°	25°	35°
48.6	28.2	...	138
28.7	...	79.7	...
25.9	...	83.3	...
25.1	28.7	...	146
10.0	41.6	102	235
5.20	67.6	...	490
5.00	...	156	...
2.03	140	284	1010
1.19	174	535	1420
1.01	232	555	1780

TABLE IV

VALUES OF RATE AND ACTIVATION PARAMETERS FOR THE REACTION OF HgX^+ WITH $CrCl_2^+$

		$\Delta H^{\ddagger}$, kcal/mol	$\Delta S^{\ddagger}$, eu	k^a 15°	25°	35°
cis-$CrCl_2^+$						
X = Cl	k_0 path	11.9 ± 1.3	−10.8 ± 4.4	24.1	50.0	99.3
	k_{-1} path	18.1 ± 0.9	5.7 ± 3.2	1.91	5.71	15.9
trans-$CrCl_2^+$						
X = Cl	k_0 path	13.0 ± 0.7	−6.6 ± 2.4	30.2	66.8	140
	k_{-1} path	19.1 ± 1.4	5.9 ± 4.9	0.392	1.25	3.65
X = Br	k_0 path	10.7 ± 1.3	−15.2 ± 4.3	21.4	41.4	77.0
	k_{-1} path	20.0 ± 1.9	7.8 ± 6.3	0.213	0.713	2.20
X = I	k_0 path	13.2 ± 4.2	−9.4 ± 14.0	4.59	10.9	23.2
	k_{-1} path	29.9 ± 3.5	41 ± 12	0.104	0.588	3.14

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

The activation parameters for each system were determined by fitting all data for that system simultaneously to the absolute rate theory expression, using a nonlinear least-squares computer program[13] in which the data points were weighted as k_X^{-2}. The activation parameters reproduce the values of k_X in Tables II and III with average deviations of 7, 11, and 19%, respectively, for X = Cl, Br, and I (trans isomer), and 8% for X = Cl with the cis isomer.

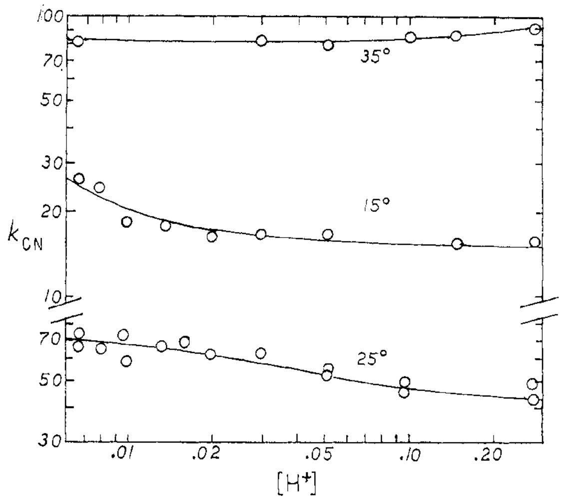

Figure 1.—Plot of k_{CN} *vs.* $[H^+]$ on a log–log scale for the reaction between *trans*-$CrCl_2^+$ and $HgCN^+$.

The $[H^+]$ dependence of the $HgCN^+$ reaction with *trans*-$CrCl_2^+$ proved to be more complex than for the other reactions. A plot of log k_{CN} *vs.* log $[H^+]$, as shown in Figure 1, exhibits different behavior at the three temperatures. The most complex behavior is observed at 25° and is consistent with a rate equation of the form of eq 4, but with the $HgCN^+$ concentration corrected either for extensive hydrolysis of $HgCN^+$ to Hg(CN)(OH) or for extensive protonation of $HgCN^+$ to $HgCNH^{2+}$

$$k_{CN} = (a + b[H^+]^{-1})[H^+]/(c + [H^+]) \qquad (5)$$

Possible interpretations of this form of rate equation are considered below. Data at the other temperatures are consistent with the limiting forms of this equation—at 15°, the data are consistent with the limiting form having $[H^+] \gg c$

$$k_{CN} = a + b[H^+]^{-1} \qquad (6)$$

while at 35°, the limiting form with $c \gg [H^+]$ is

$$k_{CN} = bc^{-1} + ac^{-1}[H^+] \qquad (7)$$

Values of the parameters which could be extracted from the data at each temperature using nonlinear least-squares computer programs[13] are given in Table V.

TABLE V

RATE PARAMETERS FOR THE REACTION OF $HgCN^+$ WITH *trans*-$CrCl_2^+$

Quantity^a	Value 15°	25°	35°
a, M^{-1} sec^{-1}	14.5 ± 0.6	38.3 ± 5.1	
b, sec^{-1}	0.061 ± 0.010	2.3 ± 1.6	
c, M		0.030 ± 0.024	
ac^{-1}, M^{-2} sec^{-1}			36.3 ± 9.0
bc^{-1}, M^{-1} sec^{-1}			79.5 ± 1.2

[a] Parameters are defined in eq 5–7.

The lines drawn through the data in Figure 1 were calculated from these parameters, which reproduce the data with an average deviation of 5%.

Discussion

In the reaction of Hg^{2+} with $CrCl_2^+$,[3] evidence was found for the formation of a binuclear complex $CrCl_2Hg^{3+}$, with the cis but not the trans complex. The rate behavior of this system was consistent with the

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

complex being kinetically stable and it was suggested that the complex existed in a double-bridged configuration since mercury(II) forms particularly stable disubstituted complexes, HgX_2.[6,7] These postulates are reinforced by the results of the study of $HgCl^+$ + *cis*-$CrCl_2^+$, where no evidence was found for the formation of a binuclear complex. Since the third association constants for formation of mercury(II) halide complexes are quite small compared to the second association constants,[6,7] it is reasonable that a binuclear complex would not be formed in this system if such a binuclear complex would necessarily involve double bridging.

The acid dependence of the reactions of *cis*- and *trans*-$CrCl_2^+$ with HgX^+ (X = Cl, Br, I) is typical of that observed in other Cr(III)–Hg(II) reactions.[1,3] A mechanism consistent with this rate behavior is

$$CrCl_2^+ + HgX^+ \xrightarrow{k_0} HgXCl + \text{(five-coordinate species?)} \qquad (8)$$

$$\text{five-coordinate species} + H_2O \overset{\text{fast}}{=} CrCl^{2+} \qquad (9)$$

$$CrCl_2^+ + H_2O \overset{K_a <<1}{\rightleftharpoons} Cr(OH)Cl_2 + H^+ \qquad (10)$$

$$Cr(OH)Cl_2 + HgX^+ \xrightarrow{k_{-1}} HgXCl + \text{(five-coordinate species?)} \qquad (11)$$

$$\text{five-coordinate species} + H_2O \overset{\text{fast}}{=} Cr(OH)Cl^+ \qquad (12)$$

$$Cr(OH)Cl^+ + H^+ \overset{\text{fast}}{=} CrCl^{2+} + H_2O \qquad (13)$$

That hydrolysis of Cr(III) and not of Hg(II) is the cause of the acid dependence is suggested by the absence of an acid-dependent path in the reaction of Hg^{2+} with $Cr(NH_3)_5Cl^{2+}$.[8] The probable formation of five-coordinate intermediates in these systems is indicated by results of competition experiments.[14,15]

The acid dependence of the reaction between *trans*-$CrCl_2^+$ and $HgCN^+$ can be accommodated by an analogous mechanism if extensive hydrolysis of $HgCN^+$ (eq 14) is postulated

$$HgCN^+ + H_2O \overset{K}{\rightleftharpoons} Hg(OH)CN + H^+ \qquad (14)$$

$$CrCl_2^+ + HgCN^+ \xrightarrow{k_0} CrCl^{2+} + Hg(CN)Cl \qquad (15)$$

$$Cr(OH)Cl_2^+ + HgCN \xrightarrow{k'_{-1}} Cr(OH)Cl^+ + Hg(CN)Cl \qquad (16)$$

$$k_{CN} = (k_0 + k'_{-1}K_a[H^+]^{-1})[H^+]/(K + [H^+]) \qquad (17)$$

A third path involving $CrCl_2^+$ and Hg(OH)CN could be postulated but is improbable in view of the low catalytic activity of disubstituted Hg(II) complexes.[1] This mechanism requires a hydrolysis constant of $HgCN^+$, $K = 0.03\ M$, which is considerably larger than that of other Hg(II) complexes. Contrary to the behavior of most polyprotic acids, the hydrolysis constant of Hg^{2+} ($1.4 \times 10^{-4}\ M$[16]) is lower than that of $HgOH^+$ ($4.6 \times 10^{-3}\ M$[16]) and of $HgCl^+$ ($8.9 \times 10^{-4}\ M$[16]). Thus it would not be unreasonable for the hydrolysis constant of $HgCN^+$ to be larger than that of Hg^{2+} although the magnitude of the difference leaves this interpretation open to question. An estimate of the hydrolysis constant of $HgCN^+$ may be obtained from a combination of the formation constants of Hg(OH)CN[17] and $HgCN^+$,[11] which gives $K = 7 \times 10^{-4}\ M$. Unfortunately the formation constants were determined at two different temperatures and ionic strengths, neither corresponding to the conditions of this study, but the discrepancy is probably too large to be due entirely to the difference in conditions.

An alternative mechanism can be proposed which involves extensive protonation of $HgCN^+$ (eq 18)

$$HgCN^+ + H^+ \overset{K_H}{\rightleftharpoons} HgCNH^{2+} \qquad (18)$$

$$CrCl_2^+ + HgCN^+ \xrightarrow{k_0} CrCl^{2+} + Hg(CN)Cl \qquad (19)$$

$$CrCl_2^+ + HgCNH^{2+} \xrightarrow{k} CrCl^{2+} + Hg(CN)Cl + H^+ \qquad (20)$$

$$Cr(OH)Cl_2 + HgCNH^{2+} \xrightarrow{k'} CrCl^{2+} + Hg(CN)Cl + H_2O \qquad (21)$$

$$k_{CN} = ((k_0 + k'K_aK_H) + kK_H[H^+])/(1 + K_H[H^+]) \qquad (22)$$

A path involving $Cr(OH)Cl_2$ and $HgCN^+$ has no corresponding term appearing in the rate law and is thus negligible within the accuracy of the experiments. This mechanism would require a value of $K_H = 33\ M^{-1}$ at 25°. No data are available on the protonation of $HgCN^+$ and apparently the only protonation constants determined for cationic cyanide complexes are for the chromium(III) complexes $Cr(CN)_2^+$ ($K_H = 0.21\ M^{-1}$),[18] $CrCN^{2+}$ ($0.19\ M^{-1}$),[19] and $CrNC^{2+}$ ($0.9\ M^{-1}$).[20] These numbers are 30–150 times smaller than the proposed value of K_H for $HgCN^+$, and although it is difficult to predict the effect of a change in the central metal ion, this number does appear to be excessively large, considering the fact that no evidence was found for protonation of various cyanomercury(II) complexes on addition of acid to $Hg(CN)_4^{2-}$ solutions.[21,22] Even though this interpretation cannot be absolutely ruled out, the observed magnitude of K_H does cast reasonable doubt on the validity of this mechanism.

A third type of mechanism consistent with a rate law of the observed form (eq 5) can be obtained by considering the sum of terms in the denominator to arise from the occurrence of a steady-state intermediate of simplest empirical formula, $Hg(CN)Cr(OH)Cl_2^+$. Unfortunately, the rate equation indicates only the compositions of the activated complexes,[23] so all possible ways of forming the activated complexes must be considered as legitimate mechanisms. Using electrical analogs to reaction rates [23,24] as a guide, four indistinguishable mechanisms can be proposed: mechanism I

$$HgCN^+ + CrCl_2^+ \xrightarrow{k_1} Hg(CN)Cl + CrCl^{2+} \qquad (23)$$

$$HgCN^+ + CrCl_2^+ + H_2O \underset{k_3}{\overset{k_2}{\rightleftharpoons}} Hg(CN)Cr(OH)Cl_2^+ + H^+ \qquad (24)$$

$$Hg(CN)Cr(OH)Cl_2^+ \xrightarrow{k_4} Hg(CN)Cl + Cr(OH)Cl^+ \qquad (25)$$

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[24] T. W. Newton and F. B. Baker, *Advan. Chem. Ser.*, **No. 71**, 268 (1967).

mechanism II

$$\mathrm{HgCN^+ + CrCl_2^+ \xrightarrow{k_1} Hg(CN)Cl + CrCl^{2+}} \tag{26}$$

$$\mathrm{CrCl_2^+ + H_2O \underset{rapid}{\overset{Q<<1}{\rightleftharpoons}} Cr(OH)Cl_2 + H^+} \tag{27}$$

$$\mathrm{HgCN^+ + Cr(OH)Cl_2 \underset{k_6}{\overset{k_5}{\rightleftharpoons}} Hg(CN)Cr(OH)Cl_2^+} \tag{28}$$

$$\mathrm{Hg(CN)Cr(OH)Cl_2^+ + H^+ \xrightarrow{k_7} Hg(CN)Cl + CrCl^{2+} + H_2O} \tag{29}$$

mechanism III

$$\mathrm{HgCN^+ + CrCl_2^+ + H_2O \underset{k_3}{\overset{k_2}{\rightleftharpoons}} Hg(CN)Cr(OH)Cl_2^+ + H^+} \tag{30}$$

$$\mathrm{Hg(CN)Cr(OH)Cl_2^+ + H^+ \xrightarrow{k_7} Hg(CN)Cl + CrCl^{2+} + H_2O} \tag{31}$$

$$\mathrm{Hg(CN)Cr(OH)Cl_2^+ \xrightarrow{k_4} Hg(CN)Cl + Cr(OH)Cl^+} \tag{32}$$

mechanism IV

$$\mathrm{CrCl_2^+ + H_2O \underset{rapid}{\overset{Q<<1}{\rightleftharpoons}} Cr(OH)Cl_2 + H^+} \tag{33}$$

$$\mathrm{HgCN^+ + Cr(OH)Cl_2 \underset{k_6}{\overset{k_5}{\rightleftharpoons}} Hg(CN)Cr(OH)Cl_2^+} \tag{34}$$

$$\mathrm{HgCN^+ + CrCl_2^+ + H_2O \underset{k_3}{\overset{k_2}{\rightleftharpoons}} Hg(CN)Cr(OH)Cl_2^+ + H^+} \tag{35}$$

$$\mathrm{Hg(CN)Cr(OH)Cl_2^+ + H^+ \xrightarrow{k_7} Hg(CN)Cl + CrCl^{2+} + H_2O} \tag{36}$$

The relation between the observed parameters in eq 5 and those derived for the above mechanisms is given in Table VI. A further ambiguity arises in mechanisms II and IV in that eq 27 and 33 could be replaced by a deprotonation of $\mathrm{HgCN^+}$ (eq 14, but with $K \ll 1$). Since in these mechanisms *c* is a composite rate constant, the magnitude of *c* cannot be used to rule out any of these mechanisms.

TABLE VI

RELATION BETWEEN EMPIRICAL[a] AND DERIVED[b] RATE PARAMETERS

Mechanism[b]	*a*	*b*	*c*
I	k_1	$(k_1k_4 + k_2k_4)/k_3$	k_4/k_3
II	k_1	$(k_1k_6 + k_5k_7Q)/k_7$	k_6/k_7
III	$k_2k_7/(k_3 + k_7)$	$k_2k_4/(k_3 + k_7)$	$k_4/(k_3 + k_7)$
IV	$k_2k_7/(k_3 + k_7)$	$k_5k_7Q/(k_3 + k_7)$	$k_6/(k_3 + k_7)$

[a] Defined in eq 5. [b] Given in eq 23–36.

It has been noted in several studies that $\mathrm{HgCl^+}$ is at least as good a catalyst for aquation as is $\mathrm{Hg^{2+}}$, if not better.[1,8,9] These differences in rate are opposite to those which might be predicted on the basis of the formation constants of the reaction products $\mathrm{HgCl^+}$ and $\mathrm{HgCl_2}$ (5.50×10^6 and 3.02×10^6)[7] which are directly proportional to the overall equilibrium constants for the catalyzed aquation reactions. A possible cause of this discrepancy has been proposed to be electrostatic effects on the rates of reactions of ions of different charge.[1] It was hoped that the comparison of rates for Hg(II) complexes containing a variety of ligands would provide further information concerning this problem. In trying to develop a linear free energy relation to examine these effects quantitatively only the path independent of $[\mathrm{H^+}]$ was considered. It was necessary to obtain values of the equilibrium constants for the reaction

$$\mathrm{Hg^{II}X + Cl^- \overset{K_{Hg}}{\rightleftharpoons} Hg^{II}XCl} \tag{37}$$

which would be directly proportional to the equilibrium constants for the overall reaction (eq 2). Values of K_{Hg} and the associated ΔH and ΔS were obtained by combining published values[6,7,25–28] of the equilibrium constants or thermodynamic functions for the reactions

$$\mathrm{Hg^{II}X_2 + HgCl_2 \rightleftharpoons 2Hg^{II}XCl} \tag{38}$$

$$\mathrm{Hg^{2+} + 2Cl^- \rightleftharpoons HgCl_2} \tag{39}$$

$$\mathrm{Hg^{2+} + X \rightleftharpoons Hg^{II}X} \tag{40}$$

$$\mathrm{Hg^{II}X + X \rightleftharpoons Hg^{II}X_2} \tag{41}$$

Values of the rate and equilibrium parameters are summarized in Table VII. A linear relationship exists between log k_0 and log K_{Hg} for X = $\mathrm{H_2O}$, Br, and I, but the values for X = Cl deviate significantly from this relationship. It is possible that the discrepancy arises from the use of ΔG, rather than ΔH or ΔS, in the attempted correlation. If there is a deviation from such correlations, it would be most likely to occur for X = $\mathrm{H_2O}$ since this Hg(II) complex is of a different charge than the others. Examination of Table VII indicates that the value of $\Delta H_0^{\ddagger}$ is relatively constant and independent of ΔH for X = $\mathrm{H_2O}$, Cl, and I. The discrepancy for X = Br may be due to faulty data, possibly arising from incorrect values of the equilibrium constants used to calculate the distribution of the species in solutions of $\mathrm{Hg^{2+}}$ and $\mathrm{Br^-}$. Considering the remarkable constancy of the other values of $\Delta H_0^{\ddagger}$ and the fact that the equilibrium constants used to evaluate the data were interpolations of values determined at other temperatures by two different sets of workers,[6,7] this is not an unreasonable rationalization of the data. A constant value of $\Delta H_0^{\ddagger}$ for the various complexes probably indicates that the energy involved in breaking the Cr–Cl bond is considerably more important in determining the magnitude of $\Delta H_0^{\ddagger}$ than is the energy involved in making the Hg–Cl bond.

TABLE VII

THERMODYNAMIC PARAMETERS FOR THE REACTION OF *trans*-$\mathrm{CrCl_2^+}$ WITH $\mathrm{Hg^{II}X}$ AT 25°

			kcal/mol		eu	
X	Log k_0[a]	Log K_{Hg}[b]	$\Delta H_0^{\ddagger}$[a]	ΔH[b]	$\Delta S_0^{\ddagger}$[a]	ΔS[b]
$\mathrm{H_2O}$	1.49	6.74	13.5	5.5	−6.3	12.4
$\mathrm{Cl^-}$	1.82	6.48	13.0	7.3	−6.6	5.3
$\mathrm{Br^-}$	1.62	6.80	10.7	6.3	−15.2	7.3
$\mathrm{I^-}$	1.04	6.53	13.2	4.8	−9.4	6.4

[a] Parameters correspond to the rate term, $k_0[\mathrm{Hg^{II}X}][\mathrm{CrCl_2^+}]$.
[b] Parameters are for the reaction $\mathrm{Hg^{II}X + Cl^- \rightleftharpoons Hg^{II}XCl}$.

It is difficult to assess the effect that such errors in

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$\Delta H_0^{\ddagger}$ would have on the value of $\Delta S_0^{\ddagger}$ for X = Br, but it is likely that the value of $\Delta S_0^{\ddagger}$ would be more positive than that given in Table VII. A reasonably linear correlation between $\Delta S_0^{\ddagger}$ and ΔS is obtained for X = Cl, Br, and I even if $\Delta S_0^{\ddagger}$ for X = Br is as much as 5 eu more positive than the value in Table VII, while $\Delta S_0^{\ddagger}$ for X = H_2O deviates significantly from this correlation. It should be noted that the uncertainty on the values of $\Delta S_0^{\ddagger}$ are sufficiently large to preclude any rigorous quantitative treatment of the correlation, but the value of $\Delta S_0^{\ddagger}$ for X = H_2O is definitely too positive compared to the values for the other X, implying an abnormally disordered transition state for X = H_2O. This is opposite to the deviation that would be expected were it caused by charge effects and increased electrostriction of solvent due to a more highly charged transition state with X = H_2O. A possible explanation for the positive deviation lies in the structure of the transition state. Solution X-ray studies have established that $HgCl_2$ exists in aqueous solution as *trans*-$Hg(H_2O)_4Cl_2$ in a distorted octahedral configuration.[29] Assuming that the transition states for the *trans*-$CrCl_2^+$–$Hg^{II}X$ reactions have a similar linear configuration about Hg(II), $\{Cl\text{–}Cr^{III}\text{–}Cl\text{---}Hg^{II}\text{–}X\}^{\ddagger}$, the steric requirements for formation of the transition state with X = Cl, Br, and I would be much more stringent than with X = H_2O, since in the former reactions only one H_2O coordinated to Hg(II) would be in a suitable position to be displaced by $CrCl_2^+$, while with X = H_2O, any of the six coordinated H_2O's could be displaced. The transition states for X = Cl, Br, and I would then have a higher degree of order than that with X = H_2O, leading to an excessively positive $\Delta S_0^{\ddagger}$ in the latter case.

Acknowledgment.—Partial support of this work by the Advanced Research Projects Agency and by the Petroleum Research Fund, administered by the American Chemical Society, is gratefully acknowledged.

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Water Exchange between Solvent and Aquomanganese(II) and Aquophenanthrolinemanganese(II) Complexes[1]

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Received June 11, 1970

Water-exchange rates with $Mn(H_2O)_6^{2+}$, $Mn(phen)(H_2O)_4^{2+}$, and $Mn(phen)_2(H_2O)_2^{2+}$ are reported. k_1 (per water molecule) values at 0° are 5.9×10^6, $(1.3 \pm 0.2) \times 10^7$, and $(3.1 \pm 0.3) \times 10^7$ sec^{-1}, respectively. $\Delta H^{\ddagger}$ values for all three species are in the range (9 ± 2) kcal mol^{-1}. Estimates of A/h are made, and electronic relaxation times from ^{17}O nmr and epr measurements are compared.

Introduction

In this laboratory, we have examined the effect of coordinated ligands on the lability of coordinated water molecules using ^{17}O nmr measurements. Attention was initially concentrated on various nickel(II) complexes and revealed an interesting difference between nonaromatic and aromatic nitrogen donors.[2,3] We are extending this work to manganese(II) and cobalt(II)[4] to see if a general pattern emerges.

There is very little information on substitution effects in manganese(II) complexes. Levanon and Luz[5] examined the effect of chloride ion on the proton line widths in methanol solutions of Mn^{2+} and estimated a rate of exchange for the monochloro complex. A small rate enhancement was observed. The manganese(II)–phenanthroline system was chosen for this study because of the relatively stable complexes formed and the existence of good equilibrium data.

Experimental Section

$MnCl_2 \cdot 4H_2O$ was used as the source of manganese(II) because the perchlorate salts of the phenanthroline complexes were found to be insoluble; purity was checked by EDTA titration. Hydrated 1,10-phenanthroline was dried by vacuum sublimation followed by double recrystallization from dry benzene, mp 117°, lit.[6] mp 117°. 1,10-Phenanthroline hydrochloride was prepared as the monohydrate by treating 1,10-phenanthroline with concentrated aqueous hydrochloric acid, evaporating to dryness, and purifying by repeated precipitation from aqueous solution with acetone. Equivalent weight found (by titration with base) was 236; that calculated for phen·HCl·H_2O was 234.5. *Anal.* Calcd for phen·HCl·H_2O: Cl, 15.1. Found: Cl, 15.1.

In order to avoid working with solutions of pH around 7 (which could cause uncertainties in the blank line width and hydrolysis

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[1] This research supported by USAEC Contract AT(45-1)-2221-T4 and this report is RLO-2221-T4-1.

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