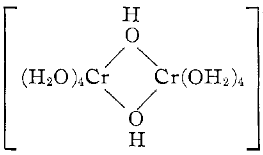
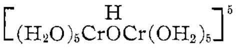
a somewhat weaker than first-order dependence of rate on (H^+).

A rather thorough study of equilibria and aquation kinetics for

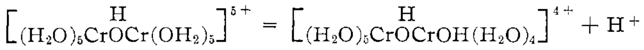


has been made[16] and in this system the intermediate



$$\left[(H_2O)_5Cr\overset{H}{O}Cr(OH_2)_5\right]^{5+}$$

which is analogous to the protonated cobalt(III) intermediate has been characterized. The result from this work which is especially germane to ours is the value of the equilibrium constant for



$$\left[(H_2O)_5Cr\overset{H}{O}Cr(OH_2)_5\right]^{5+} = \left[(H_2O)_5Cr\overset{H}{O}CrOH(H_2O)_4\right]^{4+} + H^+ \quad (7)$$

which is reported as 0.024. This probably can serve at least as a rough value of K for the dimeric cobalt system. The Cr(III) system differs from the Co(III) system in two important respects. The reaction analogous to (2) in the forward direction is independent of H^+, whereas for the cobalt dimer it is first order in H^+. The intermediate in the Cr(III) systems grows to higher concentrations than appears to be the case in our system. The reasons for the differences in the two systems are by no means clear to us.

There is little that is definite which can be said about the reactions involving direct attack by the reducing agents on the dimer. The similarity of the activation parameters for the reduction of the dimer and the tetramer by Cr^{2+} ($\Delta H^{\ddagger} = 8.3$ and 9.1 kcal, respectively; $\Delta S^{\ddagger} = -43$ and -39 eu, respectively) suggests similar modes of attack in the two cases. In the absence of oxygen tracer work it is idle to speculate on whether Cr^{2+} attacks a bridging oxygen or whether reduction takes place by an outer-sphere mechanism. It should be recognized, however, that refined and detailed tracer work will be needed to settle this important aspect of the mechanism because the isotopic consequences of the reactions of the intermediate species must be taken into account.

The nonlinearity of the plot of log (k_r/T) *vs.* $1/T$ for V^{2+} may indicate a change in mechanism for this reductant as the temperature increases. One possibility is that at low temperature an outer-sphere mechanism obtains, and at higher temperature, an inner-sphere mechanism. The activation energy in the limit in which substitution on $V(H_2O)_6{}^{2+}$ becomes rate determining is expected to be ~12 kcal/mole,[17] and this is consistent with the lower limit on $\Delta H_r^{\ddagger}$ for V^{2+} of 9 kcal/mole in the high-temperature region covered by our data.

Acknowledgment.—Financial support for this research by the Atomic Energy Commission, Contract No. At(04-3-326), is gratefully acknowledged.

(16) G. Thompson, Ph.D. Dissertation, University of California, Berkeley, Calif., 1964.

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The Rates of Some Mercury(II)-Catalyzed Aquations of Chloroaminecobalt(III) Complexes

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A kinetic study of the Hg(II)-catalyzed aquation of various Co(III) complexes of the types *cis*- and *trans*-CoA_4XCl^{n+} (where A = NH_3 or 0.5en) has been carried out. The rate constants for various X have been evaluated at 25° and an ionic strength of 1.0. For A = 0.5en and X = *cis*- and *trans*-NH_3, *cis*-pyridine, *cis*- and *trans*-H_2O, *cis*- and *trans*-NO_2^-, *trans*-N_3^-, and *trans*-Cl^- and for $Co(NH_3)_5Cl^{2+}$, the rate laws are second order. The kinetic behavior found in the reaction of *cis*-$Co(en)_2Cl_2{}^+$ with Hg(II) deviates from second-order behavior. The rate constants obtained are compared with rate constants for the Fe(II) reduction and the spontaneous aquation of the same complexes. It is concluded that a free energy correlation between transition states generated in the Fe(II) reduction and the Hg(II)-catalyzed aquation does not exist but that the energies of the transition states for the spontaneous and catalyzed aquations are related.

This investigation of the $Hg_{aq}{}^{2+}$-catalyzed aquation of various Co(III) complexes was undertaken for two purposes: to test further the model that the transition state of an inner-sphere electron-transfer reaction and the transition state of a $Hg_{aq}{}^{2+}$-catalyzed aquation are related[1] and to obtain information that will aid in the interpretation of the nature of the transition state in the acid hydrolysis of cobalt(III)-amine complexes.[2a]

Several $Fe_{aq}{}^{2+}$ reductions of Co(III) complexes have

(1) J. H. Espenson and S. R. Hubbard, *Inorg. Chem.*, **5**, 686 (1966), and references therein.

(2) C. H. Langford and H. B. Gray, "Ligand Substitution Processes," W. A. Benjamin, Inc., New York, N. Y., 1965: (a) pp 55–90; (b) pp 69–73.

been studied by Benson and Haim.[3] While it is not certain that these reactions proceed by the inner-sphere mechanism, the authors assumed that this was the mechanism. This series of Co(III) complexes (the majority of them with Cl^- as the assumed bridging group) can also be used in a study of the $\mathrm{Hg_{aq}}^{2+}$-catalyzed aquation, and the results of these two studies can then be compared to determine the suitability of a model that relates the free energy of activation in the two systems. The questions are: As the nonbridging group is varied, do the rates of reaction of the $\mathrm{Fe_{aq}}^{2+}$ reductions and $\mathrm{Hg_{aq}}^{2+}$-catalyzed aquations parallel one another? Are the transition states sufficiently related to be of predictive value?

Investigations of the acid hydrolysis of cobalt(III)–amine complexes continue to be a topic of interest. The central problems to which the investigations have been directed are: (1) the presence of intermediates of lower coordination number that exist long enough to be selective in their reactivity; (2) the amount of assistance that the entering group (water in dilute aqueous solutions) gives in reaching the transition state; and (3) an explanation of the stereochemistry of the acid hydrolysis of $\mathrm{Co(en)_2XY}^{n+}$ complexes. With regard to the first point, studies on the induced aquation of pentaamminecobalt(III) complexes in the presence of ligands that will capture the intermediate have led to the conclusion that an intermediate exists,[4–6] but a similar study on the spontaneous aquation has not given any support to the presence of the intermediate.[7] Similarly, investigations of the spontaneous and induced aquation of complexes of the type $\mathrm{Co(en)_2XY}^{n+}$ have shown two different stereochemistries.[8] Both of these types of investigations seem to support the hypothesis that there is a difference between the spontaneous and induced aquations; but they both are studies that investigate an effect that need not be operative in the transition state. Langford has offered a linear free energy correlation that suggests bond rupture is large and that bond making with the incoming water molecule is slight.[9] In this paper, we compare the rates of spontaneous aquations with those induced by $\mathrm{Hg_{aq}}^{2+}$ ion in an attempt to

$$\mathrm{CoA_4XCl}^{n+} + \mathrm{Hg_{aq}}^{2+} = \mathrm{CoA_4XH_2O}^{(n+1)+} + \mathrm{HgCl}^{+}$$

determine if there is any evidence for an energetic difference in the amount of bond formation with the incoming ligand in the transition state for the spontaneous and induced aquations.

The discussion of the second point centers around one of the early conclusions to come out of studies on the aquation of Co(III) complexes. This was that which accounted for the high rate of reactivity of $\mathrm{Co(en)_2OHCl}^+$ and $\mathrm{Co(en)_2NO_2Cl}^+$ as being due to SN1 and SN2 processes, respectively,[10] the increased rates resulting from electron-donating and -withdrawing properties of the ligands. This view has recently been questioned on the basis of experiments in nonaqueous solvents.[2b,11] Our comparison of the rates of the spontaneous and $\mathrm{Hg_{aq}}^{2+}$-induced reactions should give a test of this hypothesis without the necessity of interpreting nonaqueous kinetic data. Insofar as the $\mathrm{Hg_{aq}}^{2+}$-induced reactions do not require the formation of a bond to the incoming water molecule (and the observed products and stereochemical consequences of the induced aquations with several leaving groups seem to imply that this is true[4–6]), those reactions in which the water molecule plays a minor role in formation of the activated complex should parallel the induced reactions; whereas, in those spontaneous aquations in which bond formation is important, there should be no parallel between the rates of reactions.

Experimental Section

Preparation of the Complexes.—The complexes used in this study were all prepared by the literature procedures, or slight modifications thereof. Reference to the pertinent literature is given as follows: *cis*-$\mathrm{[Co(en)_2NO_2Cl]Cl}$ and *trans*-$\mathrm{[Co(en)_2NO_2Cl]NO_3}$,[12a] *cis*-$\mathrm{[Co(en)_2pyCl](ClO_4)_2}$,[13] *cis*-$\mathrm{[Co(en)_2H_2OCl]SO_4 \cdot 1.5H_2O}$,[12b] *trans*-$\mathrm{[Co(en)_2H_2OCl]SO_4}$,[14,15] *trans*-$\mathrm{[Co(en)_2Cl_2]ClO_4}$ and *cis*-$\mathrm{[Co(en)_2Cl_2]Cl \cdot H_2O}$,[16] *cis*-$\mathrm{[Co(en)_2NH_3Cl]Cl_2}$,[12c] *trans*-$\mathrm{[Co(en)_2NH_3Cl]ClClO_4}$,[12d] and *trans*-$\mathrm{[Co(en)_2N_3Cl]ClO_4}$;[17] $\mathrm{[Co(NH_3)_5Cl](ClO_4)_2}$ was prepared from $\mathrm{[Co(NH_3)_5CO_3]NO_3}$.[18]

The purity of the complexes was generally determined by spectroscopic techniques. The exceptions were *cis*- and *trans*-$\mathrm{Co(en)_2NO_2Cl}^+$, where the values of the extinction coefficients for both isomers and their respective aquated products determined were lower than the literature values[10a] by a factor of about 0.9.[19] Analyses of these compounds were thus obtained. *Anal.* Calcd for *cis*-$\mathrm{[Co(en)_2NO_2Cl]Cl}$: Co, 19.91; N, 23.65; C, 16.23; H, 5.44. Found: Co, 19.70; N, 23.22; C, 15.87; H, 5.88. Calcd for *trans*-$\mathrm{[Co(en)_2NO_2Cl]NO_3}$: Co, 18.27; N, 26.05; C, 14.89; H, 5.00. Found: Co, 18.32; N, 26.20; C, 15.23; H, 5.12. In addition, our results for the spontaneous aquation of the *trans* isomer at 25.0° agree with the extrapolated results of Asperger and Ingold.[10a] The results of the spectroscopic analyses of the remaining complexes are listed in Table I.[3,20–23]

Mercuric Ion Solutions.—Solutions of $\mathrm{Hg_{aq}}^{2+}$ were prepared by dissolving either HgO or $\mathrm{Hg(NO_3)_2}$ in perchloric acid solutions and reprecipitating HgO by adding sodium carbonate. This procedure was repeated three times and the final solution of $\mathrm{Hg(ClO_4)_2}$ was prepared by adding excess $\mathrm{HClO_4}$. The Hg(II) content was analyzed by precipitating $\mathrm{[Cu(en)_2]HgI_4}$ as de-

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(3) P. Benson and A. Haim, *J. Am. Chem. Soc.*, **87**, 3826 (1965).

(4) A. Haim and H. Taube, *Inorg. Chem.*, **2**, 1199 (1963).

(5) G. E. Dolbear and H. Taube, *ibid.*, **6**, 60 (1967).

(6) D. A. Buckingham, I. I. Olsen, A. M. Sargeson, and H. Satrapa, *ibid.*, **6**, 1027 (1967).

(7) R. G. Pearson and J. W. Moore, *ibid.*, **3**, 1334 (1964); but see also H. Taube in Advances in Chemistry Series, No. 49, American Chemical Society, Washington, D. C., 1965, p 49, and ref 5.

(8) See, for instance, D. A. Loeliger and H. Taube, *Inorg. Chem.*, **5**, 1376 (1966).

(9) C. H. Langford, *ibid.*, **4**, 265 (1965).

(10) (a) S. Asperger and C. K. Ingold, *J. Chem. Soc.*, 2862 (1956); (b) F. Basolo and R. G. Pearson, "Mechanisms of Inorganic Reactions," 2nd ed, John Wiley and Sons, Inc., New York, N. Y., 1967, pp 170–177.

(11) M. L. Tobe, *Record Chem. Progr.* (Kresge-Hooker Sci. Lib.), **27**, 79 (1966).

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(13) C. Bifano and R. G. Linck, *J. Am. Chem. Soc.*, **89**, 3945 (1967).

(14) J. Meisenheimer, *Ann.*, **438**, 255 (1924).

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(17) P. J. Staples and M. L. Tobe, *J. Chem. Soc.*, 4812 (1960).

(18) F. Basolo and R. K. Murmann, *Inorg. Syn.*, **4**, 171 (1953).

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(20) M. E. Baldwin, S. C. Chan, and M. L. Tobe, *ibid.*, 4637 (1961).

(21) M. Linhard and M. Weigel, *Z. Anorg. Allgem. Chem.*, **271**, 101 (1952).

(22) M. L. Tobe, *J. Chem. Soc.*, 3776 (1959).

(23) D. A. Buckingham, I. I. Olsen, and A. M. Sargeson, *J. Am. Chem. Soc.*, **88**, 5443 (1966).

TABLE I

SPECTROSCOPIC ANALYSIS OF COMPLEXES

Complex	Found λ, Å	Found ε	Literature λ, Å	Literature ε	Ref
cis-$Co(en)_2H_2OCl^{2+}$	5185	89.3	5160	85.5	3
			5250	89.2	20
trans-$Co(en)_2H_2OCl^{2+}$	5890	30.1	5870	29.0	3
	5250	13.6	5250	13.2	20
	4700	22.7	4700	23.3	20
cis-$Co(en)_2Cl_2^+$	5350	91.5	5350	95.5	3
	5250	88.9	5250	89.2	20
trans-$Co(en)_2Cl_2^+$	6200	40.9	6150	43.2	3
			6200	41	21
cis-$Co(en)_2NH_3Cl^{2+}$	5220	69.4	5230	70.5	3
trans-$Co(en)_2NH_3Cl^{2+}$	5070	45.2	5070	43.2	22
	5270	49.9	5260	50.8	3
trans-$Co(en)_2N_3Cl^{2+}$	5730	244	5750	254	3
$Co(NH_3)_5Cl^{2+}$	5300	49.8	5300	50.1	23

TABLE II

SUMMARY OF KINETIC DATA FOR SOME Hg^{2+}-CATALYZED AQUATIONS OF COMPLEXES OF Co(III) AT 25° AND IONIC STRENGTH OF 1.0

Complex	10^3[Co(III)], *M*	10^2[Hg(II)], *M*	[H$^+$], *M*	No. of expts	*k*, M^{-1} sec^{-1}
trans-$Co(en)_2NH_3Cl^{2+}$	0.98–1.88	3.07–9.22	0.22–0.94	9	$(4.64 \pm 0.33) \times 10^{-3}$
cis-$Co(en)_2NH_3Cl^{2+}$	0.75–1.39	1.17–6.77	0.14–0.97	6	$(1.45 \pm 0.02) \times 10^{-2}$
cis-$Co(en)_2pyCl^{2+}$	0.55–1.23	1.55–7.07	0.24–0.97	10	$(1.51 \pm 0.08) \times 10^{-2}$
$Co(NH_3)_5Cl^{2+}$	0.71–1.13	1.26–9.44	0.72–0.91	7	$(1.16 \pm 0.08) \times 10^{-1}$
cis-$Co(en)_2H_2OCl^{2+}$	0.37–0.60	2.88–9.43	0.21–0.94	6	$(4.15 \pm 0.21) \times 10^{-2}$
trans-$Co(en)_2H_2OCl^{2+}$	0.34–1.04	4.72–18.9	0.37–0.84	5	$(1.32 \pm 0.04) \times 10^{-2}$
	10^4[Co(III)], *M*	10^4[Hg(II)], *M*			
trans-$Co(en)_2Cl_2^+$	0.20–0.88	12.8–84.8	1.00	9	3.81 ± 0.18
trans-$Co(en)_2N_3Cl^+$	0.12	1.69–16.2	1.00	7	18.7 ± 1.6
cis-$Co(en)_2NO_2Cl^+$	0.10–0.44	1.37–8.12	1.00	8	78.1 ± 4.3
trans-$Co(en)_2NO_2Cl^+$	0.20	2.41–30.8	1.00	9	77.0 ± 1.5

scribed by Vogel.[24] The solutions were Hg(I) free as determined by addition of Cl^-. Total anion concentration was determined by ion-exchange techniques.

Kinetics.—The rate of the reaction was followed spectrophotometrically with a Cary Model 14 spectrophotometer. All experiments were done at 25.0° and with a constant ionic strength of 1.0 using $NaClO_4$ prepared from Na_2CO_3 and reagent grade $HClO_4$. Doubly distilled water was used for the solutions. For the slower reactions, all of the reagents except the Hg_{aq}^{2+} solution were mixed and thermostated, and then a thermostated solution of the latter was added; the solution was mixed, poured into a thermostated cell, and placed in the thermostated compartment of the Cary. For the rapid reactions, small volumes of Hg_{aq}^{2+} solution were injected into a thermostated cell filled with all of the other components with a precalibrated μl pipet, mixed thoroughly, and placed in the Cary. Mixing times for this rapid procedure were as little as 5 sec.

Results

All reactions were carried out under pseudo-first-order conditions.

Second-Order Systems.—The majority of the reactions investigated followed straightforward second-order kinetics. The rate law found was

$$\frac{d[HgCl^+]}{dt} = k[Co(III)][Hg_{aq}^{2+}]$$

and in no case was any dependence on the acidity noted. However, as might be expected for a reaction between two positive ions, the reactions did show a significant dependence on the ionic strength of the medium. This dependence was not pursued in this work, but its magnitude shows up clearly in some of the comparisons with previously determined rate constants given below. The results of this investigation at unit ionic strength are given in Table II.

Literature values for comparison with some of the values determined here are as follows: For $Co(NH_3)_5Cl^{2+}$, Posey and Taube[25] report a value of 5.7×10^{-2} l. mole^{-1} sec^{-1} at ionic strength of 0.3 and a temperature of 25°. Loeliger and Taube[15] report values for *cis*- and *trans*-$[Co(en)_2H_2OCl]^{2+}$ at 23° of 5.2×10^{-2} l. mole^{-1} sec^{-1} (ionic strength 1.55) and 2.9×10^{-2} l. mole^{-1} sec^{-1} (ionic strength 2.8), respectively. Their qualitative observations on the rate of catalyzed aquation of *trans*-$[Co(en)_2N_3Cl]^+$ are also in agreement with the value reported here.

Complex Systems.—The results of the kinetic study of *cis*-$[Co(en)_2Cl_2]^+$ did not follow the simple kinetics found for the rest of the systems. Upon variation of the concentration of Hg_{aq}^{2+}, the apparent second-order rate constant changed: as the Hg_{aq}^{2+} concentration was increased, the second-order rate constant decreased. This phenomenon is illustrated with some of the data for *cis*-$[Co(en)_2Cl_2]^+$ in Table III.

TABLE III

SUMMARY OF DATA OF Hg_{aq}^{2+}-CATALYZED AQUATION OF *cis*-$Co(en)_2Cl_2^+$ [a]

Run	10^4[Hg^{2+}], *M*	k_{obsd}/[Hg^{2+}], M^{-1} sec^{-1}
34	1.02	208
35	1.02	191
17	1.99	170
24	3.86	150
47	5.35	161
27	5.97	147
31	11.6	102
38	11.6	117
39	21.2	107
40	56.4	45
48	101	30
44	216	23

[a] At 25.0°, ionic strength 1.0, and [Co(III)] = $(0.5\text{–}1) \times 10^{-5}$ *M*.

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(24) A. I. Vogel, "Quantitative Inorganic Analysis," John Wiley and Sons, Inc., New York, N. Y., 1961, p 488.

(25) F. A. Posey and H. Taube, *J. Am. Chem. Soc.*, **79**, 255 (1957).

The most likely explanation of this behavior is that there is a prior equilibrium that is being saturated as the concentration of Hg_{aq}^{2+} is increased. For a kinetic scheme in which there is a prior equilibrium between Hg_{aq}^{2+} and *cis*-$[Co(en)_2Cl_2]^+$, with either first-order decomposition of this complex

$$cis\text{-}[Co(en)_2Cl_2]^+ + Hg_{aq}^{2+} \overset{K}{\rightleftharpoons} [Co(en)_2Cl_2Hg]^{3+}$$

$$[Co(en)_2ClHg]^{3+} \xrightarrow{k_1} [Co(en)_2H_2OCl]^{2+} + HgCl^+ \qquad (1)$$

or second-order reaction of Hg_{aq}^{2+} with the remaining, uncomplexed *cis*-$[Co(en)_2Cl_2]^+$

$$cis\text{-}[Co(en)_2Cl_2]^+ + Hg_{aq}^{2+} \xrightarrow{k_2} cis\text{-}[Co(en)_2H_2OCl]^{2+} + HgCl^+ \qquad (2)$$

the observed pseudo-first-order rate constant is related to the mechanistically derived rate constants by the relationship

$$k_{obsd} = \frac{k_1K[Hg_{aq}^{2+}]}{1 + K[Hg_{aq}^{2+}]} \qquad (I)$$

or

$$k_{obsd} = \frac{k_2[Hg_{aq}^{2+}]}{1 + K[Hg_{aq}^{2+}]} \qquad (II)$$

Both mechanisms predict that a plot of the reciprocal of the observed pseudo-first-order rate contant *vs.* the reciprocal of the concentration of Hg_{aq}^{2+} should yield a straight line, the intercept and slope of which give the two parameters of the mechanisms. The data indicating this straight-line relationship for a variation in $[Hg_{aq}^{2+}]$ of about 200 are shown in Figure 1. The data are not very precise—compare runs 34 and 35 and 31 and 38 in Table III—because the reaction is quite rapid and the only suitable wavelength for observation, about 2600 Å, has a large value for the absorbance at the end of the reaction. Nevertheless, the results in Table III clearly indicate that the reaction is not second order, and the linearity of the plot in Figure 1 is sufficient to establish the relationship between the reciprocal of the pseudo-first-order rate constant and the inverse of the $[Hg_{aq}^{2+}]$. The rate constants extracted from this analysis are: intercept = 3.2 sec; slope = 4.9×10^{-3} M sec. Either mechanism 1 or 2 gives a value of 650 M^{-1} for K.

In addition, experiments designed to indicate the absorbance at zero time confirm that there is a prior complex formation. In a typical experiment, the value of the absorbance at 2640 Å, extrapolated to zero time, was 1.482. Of this absorbance, that due to the excess Hg_{aq}^{2+} was 0.108; therefore, the absorbance due to all Co(III) species at "zero" time was 1.374. The value of the absorbance due to a solution of *cis*-$[Co(en)_2Cl_2]^+$, without Hg^{2+} present and corrected for the slight spontaneous aquation, was 1.212. The difference, an increase in absorbance of about 0.16 absorbance unit in the presence of Hg^{2+}, is outside the experimental error.

Several experiments were performed with stoichiometric concentration of chloride ion equal to that of Hg(II). In this medium, the predominant form of Hg(II) is $HgCl^+$, although the concentrations of Hg_{aq}^{2+} and $HgCl_2$ are both significant. Using an equilibrium constant for the reaction

$$Hg_{aq}^{2+} + HgCl_2 = 2HgCl^+$$

of 2.5,[26] the pseudo-first-order rate constants were corrected for the amount of reaction proceeding through the path

$$\frac{-d[Co(en)_2Cl_2^+]}{dt} = \frac{k[Hg_{aq}^{2+}]}{1 + k'[Hg_{aq}^{2+}]}[Co(en)_2Cl_2^+]$$

and the remaining rate term was set equal to

$$\frac{-d[Co(en)_2Cl_2^+]}{dt} = k_3[HgCl^+][Co(en)_2Cl_2^+]$$

This assumption has the effect of setting the rate of reaction of $HgCl_2$ with *cis*-$[Co(en)_2Cl_2]^+$ as zero, a not unwarranted assumption,[1,26] and of neglecting complex formation between $HgCl^+$ and *cis*-$[Co(en)_2Cl_2]^+$. This latter assumption is justified on the basis of the small magnitude of β_3 for the Hg(II)–Cl^- system, the fact that no other complex studied here showed this prior equilibrium (and thus it apparently takes two *cis*-Cl^-'s per Co(III) to generate a stable complex), and the consistent results obtained by this treatment. Over a concentration range of 1.9×10^{-4} to 9.9×10^{-4} M for Hg(II), the second-order rate constant for the reaction of $HgCl^+$ with *cis*-$[Co(en)_2Cl_2]^+$ had a value of 241 ± 35 M^{-1} sec^{-1} and showed no trend with total mercury concentration, *i.e.*, $HgCl^+$ concentration.

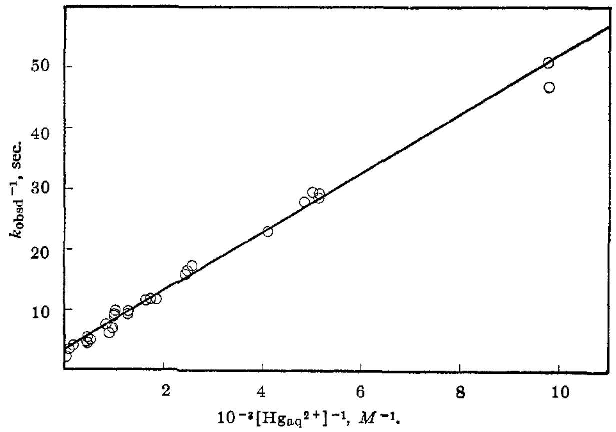

Figure 1.—Determination of the rate parameters for the reaction of Hg_{aq}^{2+} with *cis*-$Co(en)_2Cl_2^+$, at 25.0° and ionic strength 1.0.

Discussion

Considerable study has now been devoted to complexes of the type $Co(en)_2XCl^{n+}$. In Table IV are listed some of the pertinent data for this discussion: the rates of the mercury-catalyzed aquation as determined here, along with the stereochemical consequences of this catalyzed aquation;[15,27-29] the rate and stereochemistry of the spontaneous aqua-

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[26] See the discussions by J. H. Espenson and J. P. Birk, *Inorg. Chem.*, **4**, 527 (1965), and in ref 1.

[27] D. A. Buckingham, I. I. Olsen, and A. M. Sargeson, *Australian J. Chem.*, **20**, 597 (1967).

[28] A. M. Sargeson, *ibid.*, **17**, 385 (1964).

[29] M. N. Hughes and M. L. Tobe, *J. Chem. Soc.*, 1204 (1965).

TABLE IV

SUMMARY OF RATE CONSTANTS FOR VARIOUS REACTIONS OF $Co(en)_2ACl^{n+}$ COMPLEXES

Complex	$k_{Hg^{2+}}$,[a] M^{-1} sec^{-1}	Product, % *cis*	Ref	k_{aq}, sec^{-1}	Conditions	Product, % *cis*	Ref	$k_{Fe^{2+}}$,[b] M^{-1} sec^{-1}
trans-$Co(en)_2NH_3Cl^{2+}$	4.6×10^{-3}	...		3.4×10^{-7} [c]	0.1 *N* $HClO_4$	0	22	6.6×10^{-5}
cis-$Co(en)_2NH_3Cl^{2+}$	1.4×10^{-2}	...		3.6×10^{-7} [c]		100	30, 31	1.8×10^{-5}
cis-$Co(en)_2pyCl^{2+}$	1.5×10^{-2}	...		$(4.4–5.4) \times 10^{-7}$ [d]	...	...	32	7.9×10^{-4} [f]
trans-$Co(en)_2H_2OCl^{2+}$	1.3×10^{-2}	40	15	2.5×10^{-6}	HNO_3	0–50	33	2.4×10^{-1}
cis-$Co(en)_2H_2OCl^{2+}$	4.2×10^{-2}	100	15	1.6×10^{-6}	HNO_3	90–100	33	4.6×10^{-4}
$Co(NH_3)_5Cl^{2+}$	1.2×10^{-1}	100[e]	27	1.95×10^{-6}	...	100[e]	27, 34	1.35×10^{-3} [g]
trans-$Co(en)_2Cl_2^+$	3.8	28		3.53×10^{-5}	10^{-2} HNO_3	35	20, 36	3.2×10^{-2}
cis-$Co(en)_2Cl_2^+$	~300	100	28	2.44×10^{-4}	10^{-2} HNO_3	100	20, 37	1.6×10^{-3}
trans-$Co(en)_2NO_2Cl^+$	78	0	29	9.7×10^{-4}	$<10^{-2}$ H^+	0	10a	...
cis-$Co(en)_2NO_2Cl^+$	77	100	*a*	1.1×10^{-4}	$<10^{-2}$ H^+	100	10a	...
trans-$Co(en)_2N_3Cl^+$	19	0	15	2.2×10^{-4}	$<10^{-2}$ H^+	20	38	6.2×10^{-2}

[a] This work; 25° and μ 1.0. [b] Reference 3; 25° and $\Sigma[ClO_4^-] = 1.0$. [c] Extrapolated to 25°. [d] Guesses based on data at 35.0° extrapolated to 25.0° with activation parameters for *cis*- and *trans*-$[Co(en)_3NH_3Cl]^{2+}$. [e] This refers to the percentage retention of configuration; it is assumed that $Co(NH_3)_5Cl^{2+}$ gives the same product of spontaneous aquation as does $Co(NH_3)_5Br^{2+}$. [f] Reference 13. [g] Reference 39; μ 1.0.

tions;[20,22,27,30–38] and the kinetic results of the Fe^{2+} reduction of the complexes.[3,13,39] These data have been taken directly from the sources indicated; a few extrapolations have been necessary in order to reduce all of the data to 25.0°. Some of these extrapolations are made on data taken from two sources and thus are probably limited in accuracy.

The rate of the Hg_{aq}^{2+}-catalyzed aquation of *cis*-$[Co(en)_2Cl_2]^+$ has been estimated from the data on the $HgCl^+$-catalyzed aquation. This procedure is justified by an inspection of the data in the literature regarding the relative rates of aquation by Hg_{aq}^{2+} and $HgCl^+$ on Cr(III) complexes. Espenson and co-workers find that the relative efficiencies of these two ions, $k_{HgCl^+}/k_{Hg^{2+}}$, are 2.2,[26] 1.1,[1] and 1.7[26] for $Cr(H_2O)_5Cl^{2+}$, $Cr(NH_3)_5Cl^{2+}$, and $Cr(H_2O)_4(OH)Cl^+$, respectively, providing the inverse H^+ path in the catalyzed aquation of $Cr(H_2O)_5Cl^{2+}$ signifies the reaction of the Hg(II) compounds with $Cr(H_2O)_4(OH)Cl^+$. Thus it is reasonable to assign a value of about 250–350 M^{-1} sec^{-1} for the reaction of Hg_{aq}^{2+} with $[Co(en)_2Cl_2]^+$ in the absence of complex formation between the two ions. It is interesting to note that if mechanism 2 (above) is operative, the calculated second-order rate constant for the reaction between Hg_{aq}^{2+} and *cis*-$[Co(en)_2Cl_2]^+$ is 200 M^{-1} sec^{-1}. On the basis of this relationship between the estimated value and the observed slope of the line in Figure 1, we favor mechanism 2, although it is clear that there is no direct evidence on this point.

It is not too surprising that complex formation between Hg_{aq}^{2+} and the Co(III) complex occurred: Loeliger and Taube[15] have postulated similar complex formation to account for the observed spectral changes upon mixing Hg_{aq}^{2+} and *cis*-$[Co(en)_2(N_3)_2]^+$, although in their case the complex is kinetically stable. If one compares these results with those of electron-transfer reactions of Cr(II), there is a profound difference. King and co-workers have established that the reaction of Cr^{2+} with *cis*-$[Cr(H_2O)_4F_2]^+$ proceeds by a monobridged path,[40] although the reaction of Cr_{aq}^{2+} with *cis*-$[Cr(H_2O)_4(N_3)_2]^+$ proceeds by a dibridged path.[41] While it does not follow from our experiments that the complex between Hg_{aq}^{2+} and *cis*-$[Co(en)_2Cl_2]^+$ involves both chlorines, the absence of an observable equilibrium with any of the other Co(III) complexes strongly suggests that both chlorines are involved. Similar arguments apply to the observations of Loeliger and Taube.[15] If these arguments are true, the formation of the dibridged intermediate is possible in both the *cis*-Cl_2 and *cis*-$(N_3)_2$ systems with Hg_{aq}^{2+}. On the other hand, Cr_{aq}^{2+} does not find the dibridged path advantageous in the reaction with *cis*-$[Cr(H_2O)_4F_2]^+$. This difference in the nature of the reactivities of Hg_{aq}^{2+} and Cr_{aq}^{2+} is consistent with the conclusions reached by comparing the catalyzed aquations with Fe_{aq}^{2+} reductions.

Many workers have put forth the idea that there is some resemblance between an Hg_{aq}^{2+}-catalyzed aquation of a Co(III) complex and the corresponding inner-sphere reduction.[1,25] Although it is not established that the ferrous ion reductions of Co(III) complexes of the type listed in Table IV proceed by the inner-sphere mechanism, there are arguments that indicate that they do. Benson and Haim summarized some of these,[3] and since then other experiments lend credibility to their assignment of the inner-sphere mechanism. Experiments on systems in which the Fe_{aq}^{2+} reduction of the Co(III) complex is sufficiently rapid to generate finite amounts of the intermediate Fe(III)–inner-sphere product[42] support this mechanism in the previous work.[3] Candlin and Halpern have also presented arguments in favor of the inner-sphere mechanism for the Fe_{aq}^{2+}

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(41) R. Snellgrove and E. L. King, *ibid.*, **84**, 4609 (1962).

(42) A. Haim and N. Sutin, *ibid.*, **88**, 5343 (1966).

reduction of some cobalt(III)–amine complexes.[43] If it is accepted that the reductions with Fe_{aq}^{2+} are by the inner-sphere mechanism, then it is clear from Table IV that there is not a good correlation between the rates of the Hg_{aq}^{2+}-catalyzed aquations and the Fe_{aq}^{2+} reductions. While the slower reductions are generally matched by slower catalyzed aquations (and spontaneous aquations, as pointed out by Benson and Haim[3]), there are complexes where the dissimilarity is striking: *trans*-$[Co(en)_2H_2OCl]^{2+}$ is aquated at a low rate by Hg_{aq}^{2+}, but the reduction by Fe_{aq}^{2+} is very rapid; the order of reactivity of *cis*- and *trans*-$[Co(en)_2NH_3Cl]^{2+}$ is reversed in the two systems; and the relative values for the two systems upon variation of the *cis* ligand do not correspond.

Therefore, if we ask if the change in the difference in free energy between the ground and transition states is similar in the Hg(II)-catalyzed aquation and the Fe_{aq}^{2+} reduction as the nonbridging ligands are varied (as would be expected if, for instance, the Co–Cl bond motion were dominant in the comparison of the two systems), it appears that the answer is no. From the data presented here the rates of the Hg_{aq}^{2+}-catalyzed aquations bear no simple relationship to those of inner-sphere electron-transfer reactions. This is, perhaps, not a result that should be too surprising. To have this correlation requires that the various free energy terms that make up the free energy of activation be related. It appears from the available data that solvation effects are important in both types of reactions,[44,45] but they differ in that the Co(III) center demands tighter coordination of the second coordination sphere waters in the aquation reactions, whereas the incipient Co(II) ion demands a relaxation of solvation before the electron can be transferred. The effect of the variable nonbridging ligand would presumably be different in these two cases. Similar arguments apply to the first coordination sphere rearrangements and to the electronic effects of the variable ligand. The result of this varying response is that the change in the free energies of activation with a change in nonbridging ligand is not linearly related in the two processes. While it may be possible to correlate entropies of activation[1] or volumes of activation,[43] the justification for these procedures needs testing.

We now turn to a comparison of the data for the mercury-catalyzed aquation with those for the spontaneous aquation. Figure 2 is a plot of the log of the rate constant for the spontaneous aquation, k_{Cl}, *vs.* the log of the rate constant for the mercury-catalyzed aquation, $k_{Hg^{2+}}$. For a rigorous discussion of the data, we should compare k_{Cl} with the first-order rate constant for aquation where the leaving group is $HgCl^+$

$$Hg^{2+} + Co(en)_2XCl^{n+} \overset{K_I}{\rightleftharpoons} Co(en)_2XClHg^{(n+2)+}$$

$$Co(en)_2XClHg^{(n+2)+} \xrightarrow{k'} Co(en)_2XH_2O^{(n+1)+} + HgCl^+$$

$$k_{Hg^{2+}} = k'K_I$$

Unfortunately, there is no indication of the magnitude of the affinity of mercury for chloride bound to a cobalt(III).[46] If we presume that this affinity does not change much as the "directing group" is varied,[47] then the plot shown in Figure 2 can be discussed.

Figure 2 shows a fair correlation between the two sets of rate constants. Certainly if the points for X = *trans*-NO_2^-, *trans*-N_3^-, and *trans*-H_2O are not included, the correlation is very good. What this correlation implies is that the response of the two leaving groups to a change in the variable group is parallel. Therefore, there is not a "duality of mechanisms" as X is changed, unless that duality also pertains to $HgCl^+$ as a leaving group.

It can be argued that the very fact that the *trans*-NO_2^- complex does not fit the plot indicates that the mechanism of this aquation depends upon whether Cl^- or $HgCl^+$ is the leaving group. While this is certainly true, the issue to which we wish to direct ourselves is this: Is the spontaneous aquation of *trans*-$Co(en)_2NO_2Cl^+$ predominantly SN2 in nature compared to that of *trans*-$Co(en)_2Cl_2^+$? According to the general interpretation, as put forward graphically,[48] the rate for the SN1 path for spontaneous aquation of *trans*-$Co(en)_2NO_2Cl^+$ is about 10^{-15} sec^{-1}. It is clear that the point for the mercury-catalyzed aquation falls nowhere near the value corresponding to this spontaneous aquation rate. There are still rationalizations that will allow one to continue to argue that the spontaneous aquation of *trans*-$Co(en)_2NO_2Cl^+$ involves an SN2 path. There is, for instance, no proof that the mercury-catalyzed aquation goes through predominantly unimolecular dissociation once the $HgCl^+$ group is formed. One could argue that there is a powerful bond-making role for water in this transition state just as in the transition state for the spontaneous aquation. However, against this role for water in the catalyzed aquations is the steric bulk of the mercury ion and its coordination sphere, and the results that have thus far been obtained on induced aquations—both $N_2 + N_2O$ and HgX^+ leaving groups give the same stereochemical results, indicating a common intermediate and thus one with little bond making with incoming solvent molecules.[15,49]

The reasons for the deviations of the *trans*-NO_2^-, *trans*-N_3^-, and *trans*-H_2O complexes from the straight line in Figure 2 can be explained on any of a number of models, among which the correct model is not easily ascertained. Among these models are: (1) variation in values of K_I in the preequilibrium step when the variable group is *trans*-NO_2, *trans*-N_3, and *trans*-H_2O;

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[43] J. P. Candlin and J. Halpern, *Inorg. Chem.*, **4**, 1086 (1965).

[44] T.-L. Ni and C. S. Garner, *ibid.*, **6**, 1071 (1967).

[45] See the review by R. A. Marcus, *Ann. Rev. Phys. Chem.*, **15**, 155 (1964).

[46] A study of this problem is currently being undertaken with NCS^--substituted Co(III) complexes.

[47] The acidity of *cis*- and *trans*-$Co(en)_2AH_2O^{n+}$ as A is varied is within a factor of 10 of the mean value; see C. J. Hawkins, A. M. Sargeson, and G. H. Searle, *Australian J. Chem.*, **17**, 598 (1964), and M. L. Tobe, *Sci. Progr.* (London), **48**, 483 (1960).

[48] F. Basolo and R. G. Pearson, "Mechanisms of Inorganic Reactions," 2nd ed, John Wiley and Sons, Inc., New York, N. Y., 1967, p 172.

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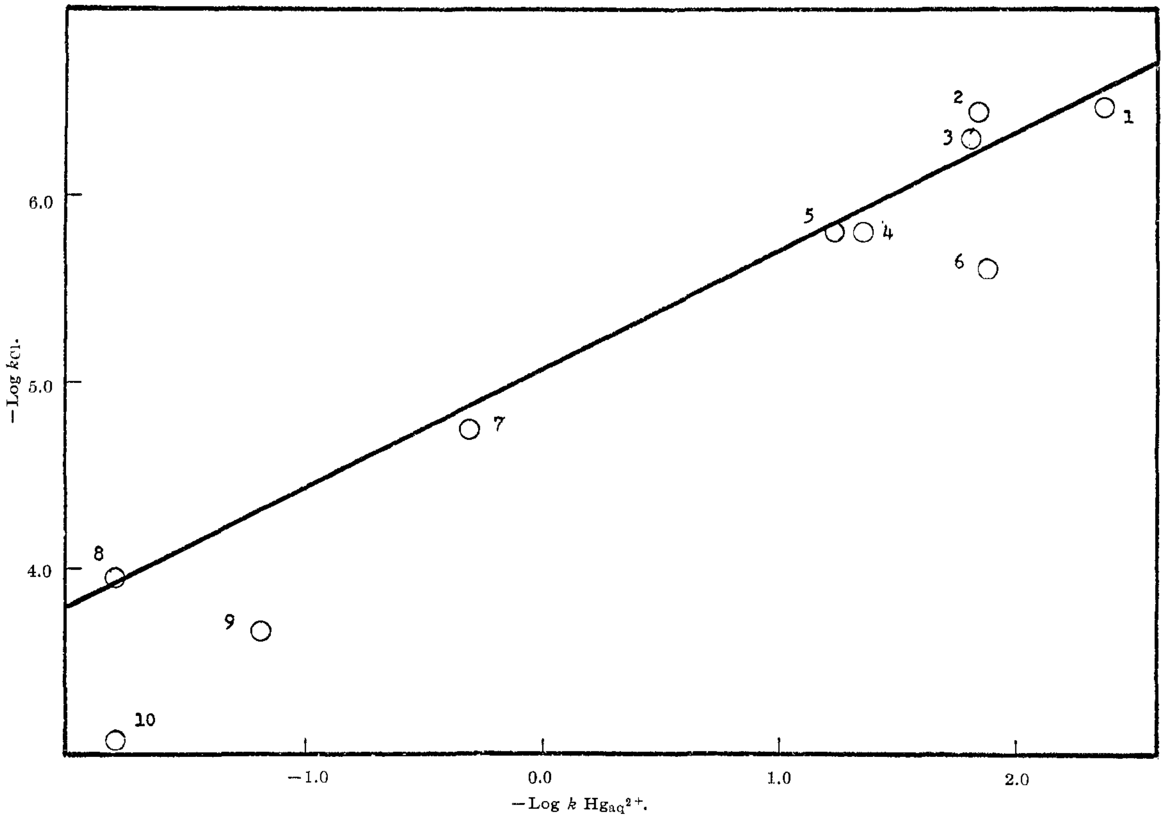

Figure 2.—The negative logarithm of the rate of spontaneous aquation as a function of the negative logarithm of the rate of Hg(II)-catalyzed aquation: (1) *trans*-$Co(en)_2NH_3Cl^{2+}$, (2) *cis*-$Co(en)_2NH_3Cl^{2+}$, (3) *cis*-$Co(en)_2pyCl^{2+}$, (4) *cis*-$Co(en)_2H_2OCl^{2+}$, (5) $Co(NH_3)_5Cl^{2+}$, (6) *trans*-$Co(en)_2H_2OCl^{2+}$, (7) *trans*-$Co(en)_2Cl_2^{+}$ (corrected for statistical difference), (8) *cis*-$Co(en)_2NO_2Cl^{+}$, (9) *trans*-$Co(en)_2N_3Cl^{+}$, (10) *trans*-$Co(en)_2NO_2Cl^{+}$.

(2) changes in the nature of the solvation requirements as the *trans* ligand is changed.

The slope of the line in Figure 2 can be compared to results of other workers. That slope

$$\frac{d \log k_{Cl}}{d \log k_{Hg^{2+}}}$$

is about 0.6, compared with a value of 1.04 for

$$\frac{d \log k_{Cl}}{d \log k_{Br}}$$

from a similar plot where the leaving groups are Cl^- and Br^-[50] and with a value much greater than 1 for

$$\frac{d \log k'_{Cl}}{d \log k'_{Hg^{2+}}}$$

with the few data reported in the Cr(III) system.[1,26] We interpret the difference between the value of 0.6 found in comparing the leaving groups Cl^- and $HgCl^+$ and the value of 1.0 found in comparing the leaving groups Cl^- and Br^- as caused by a greater dependence on the ability of the variable group to perform its rate-enhancing function in the $HgCl^+$ system; this follows directly from considerations that require some amount of solvent participation in the transition state for the spontaneous aquations,[7] but with little, if any, participation in the transition state where the leaving group is $HgCl^+$. We have, on the other hand, no explanation for the rate data that have been obtained in the Cr(III) system—there the Hg_{aq}^{2+}-catalyzed aquation is much less sensitive to the nature of the remaining ligands in the coordination sphere than is the spontaneous aquation.[1]

Finally, some remarks can be made about the stereochemical consequences of the spontaneous and induced aquations. This investigation has indicated that there is some similarity between the transition states for the aquation with Cl^- and $HgCl^+$ as leaving groups. Between those transition states and products there are the possibilities of intermediates. Our results do not demand that these intermediates be similar for the two leaving groups, unless the intermediates are energetically similar to the transition states. A similar product distribution for the two leaving groups would indicate that there are intermediates similar in nature, or that the intermediates are not very stable compared to their respective transition state (or, in the limit, that there are no intermediates). The question that cannot be answered with the data available at the moment is whether the products are similar. The data in Table IV indicate that there is a possibility for similar products, but the reactants that give large stereochemical rearrangement—*trans*-OH^-, *trans*-NCS^-—cannot be studied with Hg_{aq}^{2+} because of hydrolysis or other complexation reactions.

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[50] The pertinent data are listed by S. C. Chan and M. L. Tobe, *J. Chem. Soc.*, 5700 (1963).