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The Reduction of Some μ-Hydroxo-cobaltammines

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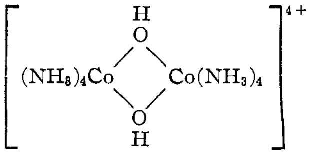

(hereafter called dimer) the rate law is $-\mathrm{d}\ \ln\ (\text{dimer})/\mathrm{d}t = a(\mathrm{H})^+/[1 + b(\mathrm{H}^+)]$. A mechanism is proposed in which the opening of one of the OH bridges is assisted by H^+, thereby forming $[[(NH_3)_4(H_2O)Co]_2OH]^{5+}$ as an intermediate. This intermediate then aquates at a rate which is inverse in (H^+). This mechanism is supported by the data on the reduction of the ion. When Cr^{2+} or Eu^{2+} react, the rate laws for reduction take the form $-\mathrm{d}\ \ln\ (\text{dimer})/\mathrm{d}t = a(\mathrm{H}^+) + k_r(\mathrm{M}^{2+})$, where a has the same value for the two reducing agents and is identical with the parameter a in the aquation reaction. This connection between the two processes is explained if Cr^{2+} and Eu^{2+} are assumed to scavenge the aquation intermediate efficiently. For V^{2+} the rate law for reduction of dimer has the form $-\mathrm{d}\ \ln\ (\text{dimer})/\mathrm{d}t = \{a(\mathrm{H}^+)/[1 + b(\mathrm{H}^+)]\} + k_r(\mathrm{V}^{2+})$. In this case we assume that V^{2+} does not interfere with the aquation reaction but does react rapidly with the product of the aquation reaction. The k_r terms correspond to direct attack by the reducing agents on the dimer, and, as expected, the values of k_r for the three reducing agents are different. Values of $\Delta H^{\ddagger}$ and $\Delta S^{\ddagger}$ for the various kinetic parameters referred to are reported, as well as for the reduction of $[((NH_3)_4Co(OH)_2)_3Co]^{6+}$ by Cr^{2+}.

Introduction

The reduction of mononuclear aquo or hydroxo ions has been studied rather intensively in the past 15 years, and considerable progress has been made in understanding the mechanism of the reactions. Much less has been done with the related species in the other extreme of complexity, namely, the solid hydroxides or oxides.[1] Polynuclear species bridged by O^{2-} or HO^- are intermediate in complexity between these extremes and can be expected to feature some of the characteristics of each. The methods applicable to the study of the mechanism of reduction of mononuclear species are equally applicable to solution species of higher complexity. An investigation of the more complex solution species is worthwhile in part because of the possible relevance of the results to the solid oxides or hydroxides, but in part also because this obvious extension of earlier studies seems to have merit in its own right. One aspect of special interest is the role which H^+ plays in the reduction process. In acidic solution H^+ is consumed in the net reduction process of the polynuclear ions, and the assistance, if any, which H^+ lends to the rate-determining act needs to be determined. A second aspect of interest is the influence which one metal ion oxidizing center exerts on another in the same molecule. Our results have contributed to the understanding of both aspects, but because only a single kind of oxidizing center has been explored, namely, Co(III), they do not provide a basis for generalizing to others, particularly in respect to the second aspect.

One of the two oxidizing agents studied, di-μ-hydroxooctaamminedicobalt(III), undergoes direct reaction with H^+ at a rate comparable to that of the reduction by Cr^{2+}, V^{2+}, or Eu^{2+}, at least when these are used at convenient concentrations. It was necessary, therefore, to study the aquation reaction

$$[(NH_3)_4Co(OH)_2Co(NH_3)_4]^{4+} + 2H^+ + 2H_2O = 2(NH_3)_4Co(OH_2)_2{}^{3+} \quad (1)$$

as a prelude to studying the reduction. In fact, the interrelationship of the acid-assisted aquation and the reduction process has contributed a great deal to the insight we have gained into these processes. The other oxidant, tris[di-μ-hydroxo-tetraamminecobalt(III)]cobalt(III) is much more resistant to aquation in the presence of H^+, and the reduction could be studied without interference from the aquation reaction. Lacking as they do the interplay between aquation and reduction, the kinetic results for this reagent seemed to be less interesting than for the former and were therefore not developed as extensively.

Experimental Section

$[(NH_3)_4Co(OH)(OH_2)]SO_4$ was prepared by adding NH_4OH to a solution of diaquotetraamminecobalt(III) sulfate.[2] When the solution was at pH 8, alcohol was added in small portions and the precipitate which formed was separated, washed, and heated at 110° to constant weight. The salt[3] $[(NH_3)_4Co(OH)_2Co(NH_3)_4](SO_4)_2$ which formed was treated by the methods of Dubsky[4] and Werner[3] to convert it to the corresponding chloride. This was then dissolved in water, and sufficient $AgClO_4$ was added to precipitate all of the chloride. The AgCl was filtered off and the perchlorate precipitated by swamping with $NaClO_4$. The salt was then recrystallized twice from hot water. *Anal.* Calcd for $[(NH_3)_4Co(OH)_2Co(NH_3)_4](ClO_4)_4$: Co, 17.2; N, 16.3; Cl, 20.7; H, 3.8. Found: Co, 17.3; N, 16.5; Cl, 20.3; H, 3.7.

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[1] However, see B. Zabin and H. Taube, *Inorg. Chem.*, **3**, 963 (1964).

[2] G. Brauer, Ed., "Handbook of Preparative Inorganic Chemistry," Vol. II, 2nd ed, Academic Press Inc., New York, N. Y., 1965, p 1537.

[3] A. Werner, *Ber.*, **40**, 4434 (1907).

[4] J. V. Dubsky, *J. Prakt. Chem.*, **90**, 81 (1914).

Preparation of Tris[di-μ-hydroxo-tetraamminecobalt(III)]-cobalt(III) Perchlorate.—This compound was prepared by a modification of the procedure of Jorgensen.[5] Five grams of $[(NH_3)_4Co(OH_2)_2](ClO_4)_3$ was dissolved in 70 ml of 0.2 M NH_4OH. After 24 hr the solution was swamped with $NaClO_4$ to precipitate the tetrameric complex as purple-black crystals. The compound was recrystallized twice from water. In analysis, except for hydrogen, all of the elements determined gave values lower than expected, suggesting that the compound isolated was a hydrate. *Anal.* Calcd. for $[((NH_3)_4Co(OH)_2)_3Co](ClO_4)_6 \cdot 6H_2O$: Co, 18.7; N, 13.5; Cl, 17.1; H, 4.4. Found: Co, 19.1; N, 13.3; Cl, 17.5; H, 3.8.

Chromic and Chromous Perchlorate Solutions.—Chromic perchlorate solution was prepared as described by Nordmeyer[6a] and analyzed for total chromium. The concentration so determined was found to agree within 0.2% with the concentration calculated on the basis of potassium dichromate. Chromous perchlorate solution was prepared by addition of zinc amalgam to a previously deaerated portion of the stock solution of chromic perchlorate and was assumed to have the same concentration as the chromic solution. This assumption was supported by the lack of absorbance at 408 and 575 mμ in the spectrum of the reduced solution. Prior deaeration of the solution was found to be necessary to ensure rapid and complete reduction.

The acid concentration in the stock chromic perchlorate solution was determined as described by Nordmeyer[6a] and was assumed to remain unchanged after the reduction to chromous solution. Total perchlorate in the stock solution was calculated from the acid and chromic ion concentrations.

Vanadyl Perchlorate Solution.—Fisher reagent grade vanadyl sulfate was dissolved in water and the solution was filtered. The clear, deep blue filtrate was treated with barium perchlorate until a barely detectable excess of barium ion was present. The solution was digested on a steam bath for 3 hr and the supernatant liquid was decanted and filtered. The concentrations of vanadyl and perchlorate ions were determined as described elsewhere,[6b] and the acid concentration was calculated by difference.

Vanadous Perchlorate Solution.—These solutions were prepared by reduction of deaerated solutions of vanadyl perchlorate with amalgamated zinc. Since vanadous solutions are known to react slowly with perchlorate ion to produce chloride,[7] all solutions were used within 4 hr after the addition of the amalgamated zinc. The concentrations of the reduced solutions were assumed to be the same as those in the vanadyl solution with corrections for acid consumption during reduction. Spectrophotometric analysis confirmed the absence of vanadium(III) peaks in these solutions.

Europous Perchlorate Solution.—Europic oxide (99.9%) from Research Inorganic Corp. was dried at 110° and stored in a desiccator over Drierite. A weighed amount of this material was dissolved in an excess of perchloric acid by heating on a steam bath for a few minutes. The solution was cooled and diluted quantitatively. Deaerated samples of this solution were reduced with amalgamated zinc for at least 30 min. Such solutions were used within 4 hr of reduction owing to the production of chloride by the slow reaction of europous and perchlorate ions.[8]

The reducing power of europous perchlorate solutions made in this way was determined by allowing an excess of chloropentaamminecobalt(III) perchlorate to react with a measured volume of the solution and determining the amount of cobalt(II) produced. The reducing power was found to be equal within experimental error (less than 0.2%) to that calculated from the weight of europic oxide used. Acid concentration in the reduced solution was assumed to be equal to that of the europium(III) solution, which was in turn calculated from the amount of standard acid added and the amount of acid consumed by dissolution of the oxide.

Lithium perchlorate was used to maintain the concentration of ClO_4^- at 1.0 M for all runs.[9] It was usually prepared from Baker and Adamson lithium carbonate and concentrated perchloric acid as described by Nordmeyer.[6a] On occasion it was found to contain an impurity which oxidized Cr^{2+}. Repeated low-yield crystallization in such cases reduced the oxidizing component to allowable levels, *i.e.*, less than 5×10^{-5} M.

Methods of Measurement.—All kinetic runs were followed by means of a Cary Model 14 or 15 recording spectrophotometer. Temperature control was maintained by thermostated Forma-Temp circulating baths. Kinetic data were obtained by following the change in absorbance of the solutions at 528 and 504 mμ for the dimeric and tetrameric complexes, respectively, and were treated as described elsewhere.[10] In the redox reactions, a considerable excess of reducing agent and of H^+ was used, and the plots of ln $(A_t - A_\infty)$ *vs.* time were almost invariably straight lines. The data on the aquation of $[(NH_3)_4Co(OH)_2Co(NH_3)_4]^{4+}$ show an induction period with the apparent first-order specific rate increasing to a constant value after about 5% of the reaction was over. All runs were done at a constant perchlorate ion concentration of 1.00 M.

Results

Spectra.—The main spectral features of the complexes studied in acidic solution are shown in Table I.

TABLE I

SUMMARY OF THE ABSORPTION CHARACTERISTICS OF THE Co(III) COMPLEXES

Compound	λ_{max}, mμ	ϵ, l./mole cm
$[(NH_3)_4Co(OH)_2Co(NH_3)_4](ClO_4)_4$	286	2.48×10^3
	528	187
$[((NH_3)_4Co(OH)_2)_3Co](ClO_4)_6$	311	4.95×10^3
	504	212
	627	126

The values of ϵ for the tetrameric complex have been calculated on the assumption that the compound isolated was a hexahydrate (molecular weight 1247).

Aquation of the Complexes.—No observable change in the spectrum of the tetrameric species (hereafter often referred to as tetramer) is observed over periods of time longer than the reductions and under similar conditions, and being satisfied that aquation of the tetramer does not affect the reduction data, we made no effort to study this very slow reaction.

The kinetic data on the aquation of di-μ-hydroxo-octaamminedicobalt(III) (hereafter designated dimer) which are described below refer to reaction after the induction period is over. The specific rate increases with (H^+) but the increase is not simply linear in (H^+). The variation of rate with (H^+) can be represented by the equation

$$k_{aq} = \frac{a(H^+)}{1 + b(H^+)}$$

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[5] S. M. Jorgensen, *Z. Anorg. Allgem. Chem.*, **16**, 184 (1898).

[6] (a) F. Nordmeyer, Ph.D. Thesis, Stanford University, 1967; (b) L. Meites, Ed., "Handbook of Analytical Chemistry," McGraw-Hill Book Co., Inc., New York, N. Y., 1963, pp 3-73; J. P. Hunt, Ph.D. Thesis, University of Chicago, 1950.

[7] W. R. King, Jr., and C. S. Garner, *J. Phys. Chem.*, **58**, 29 (1954).

[8] D. J. Meier and C. S. Garner, *ibid.*, **56**, 853 (1952). Some doubt exists about this reduction; see also A. Adin and A. G. Sykes, *J. Chem. Soc., A*, 1230 (1966).

[9] In some of the experiments the concentration of 2:1 electrolyte ($Cr(ClO_4)_2 + Zn(ClO_4)_2$) is as high as ~0.2 M, and this electrolyte makes a major contribution to the ionic strength. In dealing with reactants and activated complexes having large positive charges in concentrated electrolyte, the concentration of the counterion appears to be a better index of electrolyte effects than is the ionic strength.

[10] A. A. Frost and R. G. Pearson, "Kinetics and Mechanism," 2nd ed, John Wiley and Sons, Inc., New York, N. Y., 1961, Chapter 2.

as shown by the data in Figure 1 in which $1/k_{aq}$ is plotted against $1/(H^+)$. The values of the parameters a and b are summarized in Table II.

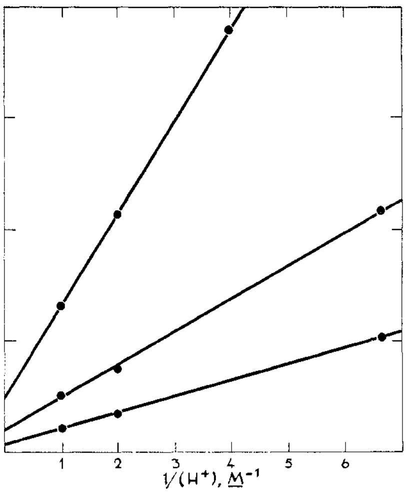


Figure 1.—Plot of $1/k_{aq}$ *vs.* $1/(H^+)$ for aquation of the dihydroxo-bridged dimer at 43.1 (lower), 34.5 (middle), and 25.0° (upper). $(ClO_4^-) = 1.00$ *M*; $(Co_2^{4+}) = \sim 4 \times 10^{-4}$ *M*.

TABLE II

VALUES OF CONSTANTS FOR AQUATION OF THE DIMER

Temp, °C	10^3a, M^{-1} sec^{-1}	b, M^{-1}
25.0	1.2 ± 0.1	0.57 ± 0.05
34.5	3.3 ± 0.5	0.53 ± 0.1
43.1	6.8 ± 0.5	0.34 ± 0.07

The Reduction of the Tetramer.—Only the reduction of tetramer by Cr^{2+} was studied. The products of the reaction are Co^{2+}, $Cr(H_2O)_6^{3+}$, and NH_4^+ and there was no evidence for the accumulation of an intermediate. The reaction in an excess of Cr^{2+} is strictly first order in (tetramer); the data summarized in Figure 2 show that the rate is first order in (Cr^{2+}) and independent of (H^+). (Note that k_{obsd} is defined as $-d \ln (\text{tetramer})/dt$.) Intermediates of lower complexity undoubtedly are formed by the attack of Cr^{2+} on the tetramer, but they apparently react more rapidly with Cr^{2+} than does the tetramer. The specific rates at 25.0, 35.0, and 45.2° $[(H^+) = 0.30$ *M* and $(Cr^{2+}) = 0.074$ *M*$]$ are $(3.2 \pm 0.1) \times 10^{-3}$, $(6.1 \pm 0.2) \times 10^{-3}$, and $(10.7 \pm 0.1) \times 10^{-3}$ M^{-1} sec^{-1}. These yield for the parameters $\Delta H^{\ddagger}$ and $\Delta S^{\ddagger}$ the values 9.1 ± 0.5 kcal/mole and -39 ± 2 eu, respectively.

The Reduction of the Dimer.—The final product with each of the reducing agents Cr^{2+}, Eu^{2+}, and V^{2+} acting on dimer is Co^{2+}. Runs with reducing agent in excess show that the reaction is strictly first order in the oxidizing complex, and in following the course of the reaction in a given experiment we found no evidence for the accumulation of intermediates in any of the systems. In Figure 3 are shown data which illustrate the variation of k_{obsd} ($\equiv -d \ln (\text{dimer})/dt$) with the concentration of the reductants Cr^{2+} and Eu^{2+} and with (H^+). It is clear from these data and those summarized in Table III that the rate law for these reductants has the form

$$k_{obsd} = k'_{aq}(H^+) + k_r(\text{reductant})$$

It is further to be noted that k'_{aq} for Cr^{2+} as reducing agent is identical with the corresponding coefficient for Eu^{2+} and is equal to the parameter a for the aquation reaction. Figure 3 also shows the relation of k'_{aq} to k_{aq}. The relation between these parameters will be considered later.

Representative data for V^{2+} as reducing agent are shown in Figure 4 and the complete data are summarized in Table III. In this system also there is a two-term rate law; the second term is similar in form to that for Cr^{2+} or Eu^{2+} as reducing agent, but the first differs in the way it depends on (H^+). The lines in Figure 4 have been drawn to extrapolate to the value of k_{aq} at $(V^{2+}) = 0$, and this treatment gives a satisfactory representation of the data except that at the lowest concentrations of (V^{2+}) the points often fall below the lines thus drawn—see also the comparison of k_{obsd} and k_{calcd} in Table III. A deviation of this kind is quite in order because at low concentration of

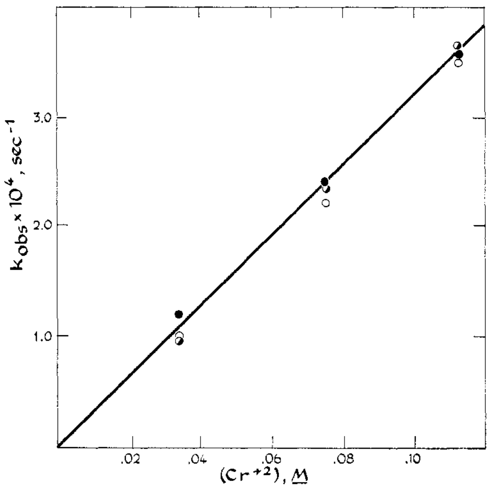


Figure 2.—Plot of k_{obsd} *vs.* chromous ion concentration for the reactions of tetramer and chromous ions. Tetramer $\sim 2 \times 10^{-4}$ *M*; $(ClO_4^-) = 1.0$ *M*: ●, 0.15 *M* H^+; ◑, 0.30 *M* H^+; ○, 0.45 *M* H^+.

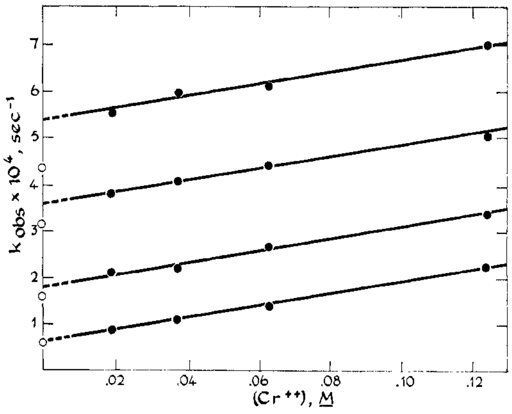


Figure 3.—Pattern of kinetic behavior for reaction of the dihydroxo-bridged dimer with chromous ion at $(H^+) = 0.05$ (lowest), 0.15, 0.30, and 0.45 *M* (highest) at 25°. Points on the vertical axis represent k_{obsd} for aquation of dimer at the various acidities. The data for Eu^{2+} extrapolate to the same intercepts, but the slopes of the lines are different.

Table III

The Rate of Reduction of Dimer by Cr^{2+}, Eu^{2+}, and V^{2+} as Function of the Temperature and the Concentration of Reductant and of Hydrogen Ion[a]

(H^+)	10^2 (reductant)	10^4 k_{obsd}, sec^{-1}	10^4 k_{calcd}, sec^{-1}
	Cr^{2+} at 25°		
0.050	0.0186	0.92	0.93
0.050	0.0372	1.26	1.25
0.050	0.0620	1.63	1.69
0.050	0.124	2.79	2.75
0.150	0.0186	2.29	2.14
0.150	0.0372	2.46	2.46
0.150	0.0620	2.94	2.90
0.150	0.124	3.98	3.98
0.300	0.0186	4.02	3.96
0.300	0.0372	4.31	4.30
0.300	0.0620	4.73	4.74
0.300	0.124	5.5	5.8
0.450	0.0186	5.5	5.8
0.450	0.0372	6.1	6.1
0.450	0.0620	6.4	6.6
0.450	0.124	7.5	7.6
	Cr^{2+} at 34.8°		
0.050	0.0371	2.31	2.49
0.050	0.0743	3.59	3.57
0.050	0.111	4.59	4.60
0.150	0.0371	5.5	5.3
0.150	0.0743	6.6	6.4
0.150	0.111	7.7	7.4
	Cr^{2+} at 45.0°		
0.050	0.0371	5.4	5.2
0.050	0.0743	7.2	6.9
0.050	0.111	9.0	8.4
0.15	0.0371	11.5	12.2
0.15	0.0743	13.5	13.9
0.15	0.111	14.6	15.4
	Eu^{2+} at 25°		
0.15	0.0034	2.81	2.89
0.15	0.0100	5.1	5.3
0.15	0.0200	8.8	8.8
0.45	0.0034	6.7	6.5
0.45	0.0100	9.0	8.9
0.45	0.0200	12.6	12.4
	Eu^{2+} at 34.6°		
0.15	0.0034	6.0	6.3
0.15	0.0100	9.5	10.0
0.45	0.0034	13.3	14.9
0.45	0.0100	17.0	18.7
0.45	0.0200	22.7	24.4
	Eu^{2+} at 43.1°		
0.15	0.0034	13.3	13.0
0.15	0.0100	17.4	17.7
0.15	0.0200	23.4	25.2
0.45	0.0100	40.8	38.4
0.45	0.0200	47.6	45.8
	V^{2+} at 25°		
0.15	0.0025	3.74	4.25
0.15	0.0050	6.2	6.8
0.15	0.0075	9.2	9.4
0.45	0.0025	6.9	6.9
0.45	0.0050	9.3	9.4
0.45	0.0075	12.5	12.0
	V^{2+} at 34.6°		
0.15	0.0025	7.4	7.7
0.15	0.0050	10.7	11.0
0.15	0.0075	14.0	13.2
0.45	0.0025	15.4	15.4
0.45	0.0050	18.8	18.7
0.45	0.0075	22.2	21.9
	V^{2+} at 44.4°		
0.15	0.0025	13.8	15.3
0.15	0.0050	20.4	20.7
0.15	0.0075	25.4	26.0
0.45	0.0025	30.5	33.3
0.45	0.0050	38.5	38.7
0.45	0.0100	50.1	49.3

[a] $(ClO_4^-) = 1$ *M*; (dimer) $\simeq$ (3–4) $\times 10^{-4}$ *M*.

reducing agent, the rate of reduction must in actual fact decrease and become zero as the concentration of reductant becomes zero. The extrapolation to a finite intercept corresponds to the assumption that intermediates resulting, for example, from the attack of H^+ on the dimer do not accumulate. This condition must fail as the concentration of reductant becomes small enough and we see evidence of this in the data for V^{2+}.

In Table IV the parameters k_r for the three reducing agents are summarized as well as k'_{aq} for Cr^{2+} and Eu^{2+}. The values of k_{calcd} shown in the last column of Table III are obtained using these parameters; in the case where V^{2+} is the reductant the first term of the rate law is the value of k_{aq} appropriate to the particular temperature and acidity. The comparison of k_{calcd} with k_{obsd} provides a test of the rate laws proposed for the three reducing agents acting on the dimer. Except for the deviation referred to in the case of V^{2+}, the rate laws account for the data within the limits of error of the measurements.

The values of $\Delta H^{\ddagger}$ and $\Delta S^{\ddagger}$ corresponding to the several parameters are also entered in Table IV. In one case only, that of k_r for V^{2+}, is there serious deviation from linearity in the plot of log (k/T) against $1/T$, and a value of $\Delta H^{\ddagger}$ for V^{2+} has not therefore been entered in Table IV. The value of $\Delta H^{\ddagger}$ corresponding to the low-temperature interval is 4 kcal/mole; that for the higher temperature interval is 9 kcal/mole.

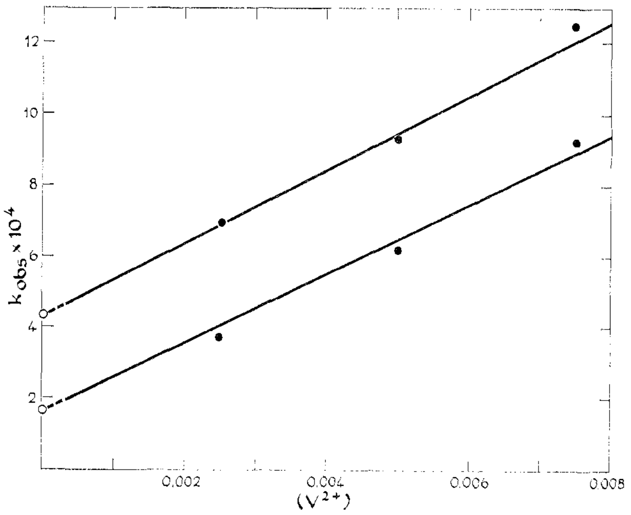


Figure 4.—The variation of k_{obsd} with (V^{2+}) at 25° and $\mu = 1.00$: upper line, data at 0.45 *M* H^+; lower, at 0.15 *M* H^+. The points on the vertical areas are the values of k_{aq} at the two acidities.

Table IV

Kinetic Parameters for the Reduction of Dimer as Function of Temperature

Reductant	Temp, °C	$10^4k'_{aq}$	10^3k_r
Cr^{2+}	25.0	12.2[a]	1.73[b]
	34.8	28.0	2.91
	43.0	70	...
	45.0	...	4.44
Eu^{2+}	25.0	12.0[c]	35[d]
	34.6	28.8	57
	43.1	69	74
V^{2+}	25.0	*e*	102[f]
	34.6	*e*	129
	44.4	*e*	213

[a] $\Delta H^{\ddagger} = 16.3 \pm 1$ kcal/mole; $\Delta S^{\ddagger} = -17 \pm 3$ eu. [b] $\Delta H^{\ddagger} = 8.3 \pm 1$ kcal/mole; $\Delta S^{\ddagger} = -43 \pm 3$ eu. [c] $\Delta H^{\ddagger}$ and $\Delta S^{\ddagger}$ as for Cr^{2+}. [d] $\Delta H^{\ddagger} = 6.8 \pm 1$ kcal/mole; $\Delta S^{\ddagger} = -42 \pm 3$ eu. [e] $k_{aq} \times 10^4$ at 0.15 *M* H^+ and at 25.0, 34.6, and 44.4° is 1.7 ± 0.1, 4.5 ± 0.2, and 10.0 ± 0.5; at 0.45 *M* H^+ and the same three temperatures it is 4.3 ± 0.2, 12.2 ± 0.3, and 28 ± 1 sec^{-1}. [f] $\Delta H^{\ddagger}$ not constant over the temperature interval.

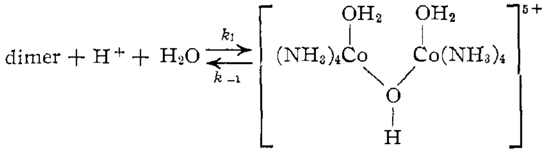
The final product of the aquation of the dimer is the ion $(NH_3)_4Co(OH_2)_2^{3+}$. It is necessary for the interpretation of the reduction data to have some knowledge of the rate at which this ion, if it were formed, is reduced. The reduction of $(NH_3)_4Co(OH_2)_2^{3+}$ by Cr^{2+} is known[11] to be so rapid that an appreciable concentration will not accumulate even at the lowest concentration of Cr^{2+} used. To check on the rate of reduction by Eu^{2+} and V^{2+}, carbonatotetraamminecobalt(III) perchlorate was dissolved in 0.15 *M* $HClO_4$. The reaction of the carbonato complex with acid is rapid and yields the diaquo ion. Solutions of Eu^{2+} and V^{2+} were added to separate portions of the diaquo solution, and values of

(11) K. D. Kopple and R. R. Miller, *Proc. Chem. Soc.*, 306 (1963).

0.4 and 5 M^{-1} sec^{-1} were estimated for the rate constants of the two reduction processes at 25°.

Discussion

We propose for the mechanism of aquation of the dimer



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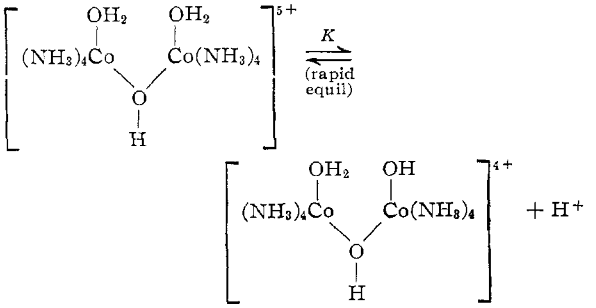

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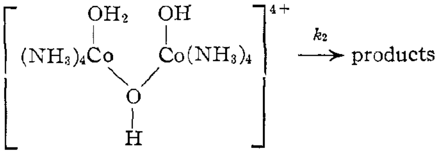


(4)

This mechanism leads to the steady-state rate law

$$\frac{-\mathrm{d}\ \ln(\text{dimer})}{\mathrm{d}t} = \frac{k_1(\mathrm{H}^+)}{1 + (k_{-1}/k_2K)(\mathrm{H}^+)} \tag{5}$$

This has the form of the observed rate law with $a = k_1$ and $b = k_{-1}/k_2K$. An alternative formulation, namely, that the dimer be substantially protonated and the activated complex for aquation have the same composition, would also account for the kinetics, but it can be dismissed because there is no evidence from a spectrophotometric examination of the dimer in acidic solution for appreciable protonation and because this formulation does not offer an explanation of the reduction kinetics. The mechanism proposed for aquation needs only a simple, reasonable elaboration to account for the reduction kinetics and for the connection between the reduction and aquation kinetics, namely, that $k'_{\mathrm{aq}} = a$.

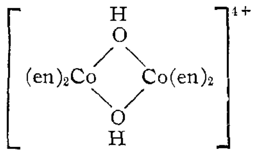
To account for the k_r term in the rate law, we write for each reducing agent a step in which it attacks the dimer directly

$$\mathrm{M}^{2+} + \text{dimer} \longrightarrow \text{products} \tag{6}$$

The ion $(NH_3)_4Co(OH_2)_2^{3+}$ is presumably a product of this reaction, as it is of the aquation, and it has been shown to react rapidly with the reducing agents. To explain the fact that $k'_{\mathrm{aq}} = a$, we assume that Cr^{2+} and Eu^{2+} react so rapidly with the intermediate of the aquation reaction that reaction 2 does not appreciably reverse. For V^{2+} we assume that the reaction with the intermediate is much slower, so that the aquation reaction takes its normal course though V^{2+} is present, and the reducing agent then reacts rapidly with the final product of the aquation reaction.

On the basis of the mechanism advanced, the intermediate species as formulated in eq 2–4 are reasonable in the light of observations we have made and on other grounds as well. Loss of protons from coordinated water (or NH_3) is known to labilize metal ions for substitution at another position, and thus the fact that the deprotonated intermediates rather than the protonated form aquates finds a natural explanation. The difference in reactivity toward the intermediate of Cr^{2+} and Eu^{2+} on the one hand and of V^{2+} on the other also is reasonable in the light of other experience. The group Co–OH of the deprotonated intermediate is an excellent site for attack by Cr^{2+}, which is known[12] to react with $(NH_3)_5CoOH^{2+}$ 10^6–10^7 times more rapidly than with $(NH_3)_5CoOH_2^{3+}$. A similar comparison is not possible for Eu^{2+} but it is known[13] that Eu^{2+} reacts *ca.* 10^5 times more rapidly with $(NH_3)_5CoF^{2+}$ than with $(NH_3)_5CoOH_2^{3+}$. For Cr^{2+} this rate ratio is $>10^6$, indicating that an F^-/H_2O rate ratio is little different from an OH^-/H_2O rate ratio and thus a much greater reactivity of Eu^{2+} through a coordinated OH^- compared to H_2O is expected. For V^{2+}, on the other hand, not much rate improvement upon deprotonation of the intermediate is expected. In marked contrast to the behavior with Cr^{2+}, the rate term corresponding to the reduction by V^{2+} of $(NH_3)_5CoOH_2^{3+}$ by way of $(NH_3)_5CoOH^{2+}$ has not been detected.[14] Furthermore, the rate of reduction by V^{2+} of $(NH_3)_5CoF^{2+}$ is *ca.* 5 times greater[13] than of $(NH_3)_5CoOH_2^{3+}$. Thus V^{2+} is not in a position to take advantage of a higher reactivity for the deprotonated form compared to the protonated one, and the rate of attack on the protonated intermediate is therefore not expected to be much faster than on the original dimer. On this basis it is not surprising that V^{2+} does not interfere with the normal aquation process.

The aquation in acid of the ion



which is similar to ours, has been studied,[15] and the rate law

$$\frac{-\mathrm{d}\ln(\text{complex})}{\mathrm{d}t} = k'(\mathrm{H}^+) + k''$$

is reported. Except for the experiment at 0.1 *M*, all of the experiments were done at low acid, $\leq 5 \times 10^{-2}$ *M*. It is to be noted that at low acid our rate law reduces to $k_1(\mathrm{H}^+)$. Our value of 12×10^{-4} M^{-1} sec^{-1} for k_1 at 25° in 1 *M* $LiClO_4$ agrees as well as can be expected with the value of k', which is 5×10^{-4} M^{-1} at 25° in 1 *M* $NaNO_3$. The k'' path made a very small contribution to the reaction in Rasmussen and Bjerrum's work. Our rate law in the limit of low (H^+) and the rate law they advocate agree in indicating

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[12] R. K. Murmann, H. Taube, and E. A. Posey, *J. Am. Chem. Soc.*, **79**, 262 (1957).

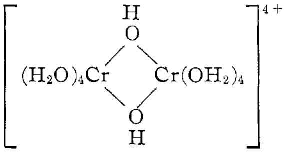
[13] J. P. Candlin, J. Halpern, and D. L. Trimm, *ibid.*, **86**, 1019 (1964).

[14] A. M. Zwickel and H. Taube, *ibid.*, **83**, 793 (1961).

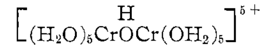
[15] S. E. Rasmussen and J. Bjerrum, *Acta Chem. Scand.*, **9**, 735 (1955).

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

A rather thorough study of equilibria and aquation kinetics for

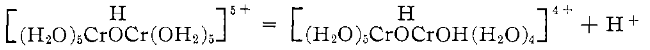


has been made[16] and in this system the intermediate



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

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



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

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.

[17] H. J. Price and H. Taube, *Inorg. Chem.*, **7**, 1 (1968).

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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.