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Reversible Iodometric Oxidation of Cobalt(II) in Ammoniacal Solutions

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At high ammonia concentrations cobalt(II) reacts stoichiometrically with triiodide to form iodopentamminecobalt(III). The reaction is reversible and mass action constants were obtained for the equation $2Co(NH_3)_5H_2O^{++} + I_3^- \rightleftarrows 2Co(NH_3)_5I^{++} + I^- + 2H_2O$. The rates of aquation and hydrolysis of iodopentamminecobalt(III) and the rates of reaction of the iodo complex and aquopentamminecobalt(III) with iodide were measured at 25°. A value of -0.33 volt was calculated for the half-reaction $Co(NH_3)_5H_2O^{++} \rightarrow Co(NH_3)_5H_2O^{+++} + e$.

Equilibrium studies between cobalt(II) and cobalt(III) complexes have been confined to potential measurements at a platinum electrode in the ammonia and ethylenediamine systems.[1] Earlier experiments show that in acid solutions iodopentamminecobalt(III) reacts with iodide to form iodine and cobalt(II),[2] while in ammoniacal solutions iodine and cobalt(II) react to form iodopentamminecobalt(III).[3,4] It appeared to be worthwhile, therefore, to investigate the equilibrium corresponding to the over-all reaction

$$2Co^{++} + 10NH_3 + I_3^- = 2Co(NH_3)_5I^{++} + I^- \qquad (1)$$

In the course of this study the conditions for the stoichiometric formation of iodopentamminecobalt(III) were determined and the formation of this complex from aquopentamminecobalt(III) was investigated. Other studies included the rates of aquation (acid hydrolysis) and hydrolysis of the iodo complex and the reduction of the complex by iodide. All measurements were made at 25° at 1 *M* total ionic strength.

Several sets of experiments confirmed earlier observations[5–7] that the homogeneous interconversion of the various cobalt(III) ammines is slow in ammoniacal solutions under ambient conditions. Accordingly these reactions were ignored in the present study. The uptake of oxygen by ammoniacal solutions of cobalt(II) and the photodecomposition[8] of $Co(NH_3)_5I^{++}$ were avoided by working in a nitrogen atmosphere in semi-darkness. Finally complications due to the hydrolysis of iodine were prevented by using solutions which were 1 *M* in ammonium ion and contained a large excess of iodide ion.

Experimental

Reagents.—Iodopentamminecobalt(III) perchlorate was prepared from the chloride[3] by triturating the latter with cold, concentrated perchloric acid in an ice-bath. The crude perchlorate was filtered, washed with alcohol, and air dried, and then the process was repeated twice. Finally, the salt was recrystallized by dissolving it rapidly in 0.1 *M* acetic acid at 35–40°, filtering, and allowing the filtrate to fall into ice-cold perchloric acid. After standing two hr., the crystals were filtered, washed with ice-cold 2 *M* perchloric acid, and then with alcohol and ether. *Anal.* Calcd.: Co, 12.54; I, 27.01. Found: Co, 12.59; I, 26.82.

Other $Co(NH_3)_5I^{++}$ salts were prepared by methods previously described.[3] Attempts to prepare iodoaquotetrammine-cobalt(III) iodide by heating the diaquo iodide at 70° until the loss in weight corresponded to the removal of one mole of water were unsuccessful.

Stock solutions of cobalt(II) were prepared from anhydrous $CoSO_4$. All other solutions were prepared from N.B.S. or C.P. A.C.S. reagent grade chemicals. Just prior to their use solutions of NH_4I were freed of iodine by titrating with either thiosulfate or arsenic(III) spectrophotometrically at 288 mμ.

Analytical.—Iodopentamminecobalt(III) and triiodide were determined spectrophotometrically using a Beckman DU Spectrophotometer with a thermostated cell compartment.

The observed absorption spectrum for the iodo complex was essentially identical with that reported by Linhard and Weigel.[8] It has a maximum at 288 mμ ($\beta = 17{,}400$ mole^{-1} cm.$^{-1}$), which coincides with the maximum in the ultraviolet region for triiodide.[9] A value of 35,800 mole^{-1} cm.$^{-1}$ was found for the molar extinction coefficient of triiodide in 1 *M* NH_4I at 288 mμ. This is somewhat lower than the value of 40,000 mole^{-1} cm.$^{-1}$ reported previously[9]

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[1] J. Bjerrum, "Metal Ammine Formation in Aqueous Solution," P. Haase and Son, Copenhagen, 1941, pp. 223, 242.

[2] R. G. Yalman, *J. Am. Chem. Soc.*, **75**, 1842 (1953).

[3] R. G. Yalman, *ibid.*, **77**, 3219 (1955).

[4] R. G. Yalman, *Anal. Chem.*, **28**, 91 (1956).

[5] A. B. Lamb and A. T. Larson, *J. Am. Chem. Soc.*, **42**, 2024 (1920).

[6] A. Benrath, *Z. anorg. u. allgem. Chem.*, **177**, 286 (1929); A. Benrath and H. Pitzler, *ibid.*, **194**, 363 (1930).

[7] Reference 1, p. 260 ff.

[8] M. Linhard and M. Weigel, *Z. anorg. u. allgem. Chem.*, **266**, 49 (1951).

[9] A. D. Awtrey and R. E. Connick, *J. Am. Chem. Soc.*, **73** 1842 (1951).

but it is in good agreement with that reported by Chia[10] who observed that the molar extinction coefficient of I_3^- at 289 mμ decreases linearly with increasing iodide concentration.

Mixtures of aquocobalt(III) ammines were analyzed by the procedure outlined by Bjerrum.[11] No attempt was made to distinguish between tetraaquo, triaquo and diaquocobalt(III) ammines.

Stoichiometric Studies.—The products of the reaction between ammoniacal solutions of cobalt(II) and I_3^- were determined by adding 0.1 M NH_4I_3 to ammoniacal solutions containing 5×10^{-3} M $CoSO_4$ and 1 M NH_4ClO_4. The ammonia concentration varied from 0.03 to 2 M. The rate of addition of NH_4I_3 was adjusted so that $[Co(NH_3)_5I]I_2$ did not precipitate. Under these conditions there was no evidence for the formation of hexamminecobalt(III), and hydroxopentammine Co(III) was the only complex detected in solutions containing more than 0.155 M NH_3.

On the other hand when $[Co(NH_3)_5I]I_2$ precipitated, small amounts of hexamminecobalt(III) iodide also were formed. The amount of the latter increased with time, the rate of agitation, and the total amount of precipitate present. Similar results were observed with other iodopentamminecobalt(III) salts. The relationship between the rates of conversion of the iodo complexes to the corresponding hexamine salts and their solubilities[6] was not determined.

Rate Studies.—All solutions contained 2.5×10^{-5} M cobalt(III) and their ionic strength was adjusted to one molal by the addition of ammonium perchlorate. The base hydrolysis of iodopentamminecobalt(III) was determined in buffered ammoniacal solutions; all other experiments were performed in 0.001 M perchloric acid. The rates of aquation, base hydrolysis, and the reduction of iodopentamminecobalt(III) by iodide were determined from optical density measurements on chilled aliquots containing sodium thiosulfate or arsenic(III). The rate of reaction of aquopentamminecobalt(III) with iodide was determined by observing the rate of triiodide formation at 288 mμ in solutions containing 1 M NH_4I.

Equilibrium Studies.—The equilibrium studies were performed under homogeneous conditions using new, unscratched glassware. In each experiment the initial mixture contained 5×10^{-5} M $[Co(NH_3)_5I](ClO_4)_2$ and 0.1 M NH_4I. Ionic strength was adjusted to one molal by the additional NH_4ClO_4. The concentration of NH_3 varied from 0.0551 to 0.525 M. After 15–20 min. a sample of the reaction mixture was analyzed spectrophotometrically at 288 mμ for I_3^- and $Co(NH_3)_5I^{++}$. Simultaneously a 5-ml. sample was delivered into an ice-cold flask containing 0.500 ml. of 0.01 M arsenic(III) and measured at 1°.

From time to time additional sets of samples were analyzed. Due to the hydrolysis of $Co(NH_3)_5I^{++}$ the optical densities of the reaction mixtures slowly decreased. At the end of 3–6 days there was no evidence for unreacted I_3^- or $Co(NH_3)_5I^{++}$ and the optical density of each solution was very nearly equal to that of 5×10^{-5} M $Co(NH_3)_5OH^{++}$.

Calculations and Results

Reaction Rates.—In each experiment the changes in optical density followed first order kinetics. The rate law for the base hydrolysis of iodopentamminecobalt(III) is

$$k_{obs.} = k_a + k_r\,[OH^-] \qquad (2)$$

where k_a and k_h are the rate constants for the aquation and base hydrolysis of the iodo complex, respectively. The rate law for the disappearance of the iodo complex in acidic solutions containing iodide is

$$k_{obs.} = k_a + k_r[I^-] \qquad (3)$$

The results of measurements at 25, 35, and 45° are summarized in Table I. Good agreement was found between the values of k_a determined from the aquation of iodopentamminecobalt(III) in 0.001 M perchloric acid and those calculated from equations 2 and 3. The ratio of $k_h:k_a$ and the values of ΔH^* and ΔS^* for the aquation and base hydrolysis of the iodo complex are of the expected order of magnitude.[12]

TABLE I

RATES OF REACTION OF IODOPENTAMMINECOBALT(III)[a]

25°, $\mu = 1.0$

Reaction	k	ΔH^*, kcal./mole	ΔS^*, e.u.
Aquation	$8.3 \pm 0.2 \times 10^{-6}$ sec.$^{-1}$	19	−16
	$6.7 \pm .5 \times 10^{-6}$ sec.$^{-1}$ from equation 2		
	$8.0 \pm .5 \times 10^{-6}$ sec.$^{-1}$ from equation 3		
Base hydrolysis	$3.7 \pm .2$ M^{-1} sec.$^{-1}$ M^{-1}	21	19
Reduction	$4.3 \pm .2$ M^{-1} sec.$^{-1}$ M^{-1}	14	−19

[a] Quadruplicate experiments.

When iodide ion is added to acidic solutions of $Co(NH_3)_5H_2O^{+++}$, the over-all reaction is the formation of iodine and cobalt(II). No difference could be detected in the rate of disappearance of aquopentamminecobalt(III) in 0.01 M cobalt(III) solutions and the rate of formation of triiodide in 10^{-5} M cobalt(III) solutions. In both sets of experiments the rate law is second order with respect to iodide.[2] Reaction rates were determined at 25, 35, and 45°. At 25° the second order rate constant, k_t, is 1.0×10^{-6} sec.$^{-1}$ M^{-1}; $\Delta H^* = 23$ kcal./mole and $\Delta S^* = -8$ e.u.

Equilibrium Studies.—The mass action constant for equation 1 is given by

$$K' = [CoI(III)]^2[I^-]/[Co(II)]^2[I_3^-][NH_3]^{10} \qquad (1a)$$

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[10] Y. Chia, Thesis, University of California, Berkeley, 1958. The author wishes to thank Professor Robert E. Connick for making this thesis available.

[11] Reference 1, p. 265.

[12] A. W. Adamson and F. Basolo, *Acta Chem. Scand.*, **9**, 1261 (1955).

The triiodide concentration can be calculated from

$$[I_3^-] = (D_1 - D_2)/\beta_{I_3^-} \quad (4)$$

where $\beta_{I_3}^-$ is the molar absorption coefficient of triiodide, D_1 is the optical density of the equilibrium mixture and D_2 is the optical density of the corresponding chilled aliquot containing arsenic(III). D_2 is related to the various cobalt species by

$$D_2 = \beta_1[\mathrm{CoI(III)}] + \beta_2[\mathrm{CoOH(III)}] + \beta_3\Sigma[\mathrm{Co(II)}] \quad (5)$$

where [CoI(III)] and [CoOH(III)] are the molar concentrations of iodo and hydroxopentamminecobalt(III), respectively, β_1 and β_2 are their respective molar absorption coefficients, Σ[Co(II)] is the total concentration of cobalt(II), and β_3 is the molar absorption coefficient of ammoniacal solutions of cobalt(II). From the initial experimental conditions, *viz.*, all of the cobalt added in the form of the iodo complex and no triiodide present, and the stoichiometry of equation 1

$$A = [\mathrm{CoI(III)}] + [\mathrm{CoOH(III)}] + \Sigma[\mathrm{Co(II)}]$$

and

$$[\mathrm{Co(II)}] = 2[I_3^-] = 2(D_1 - D_2)/\beta_{I_3^-}$$

where A is the initial concentration of iodopentamminecobalt(III). Using these relationships [CoOH(III)] and Σ[Co(II)] can be eliminated from equation 5. Then, upon rearranging, the equilibrium concentration of iodopentamminecobalt(III) is given by

$$[\mathrm{CoI(III)}] = \{D_2 - \beta_2 A + 2(D_1 - D_2)(\beta_2 - \beta_3)/\beta_{I_3^-}\}/(\beta_1 - \beta_2) \quad (6)$$

The results of equilibrium measurements at various ammonia concentrations are summarized in Table II. It is apparent from the marked variation in K' with $[NH_3]$ that the equilibrium reaction does not correspond to equation 1. This together with the previous observation that only pentamminecobalt(III) complexes could be observed in solutions containing more than 0.155 M ammonia indicates that the equilibrium reaction is

$$2\mathrm{Co(NH_3)_5H_2O^{++}} + I_3^- \longrightarrow 2\mathrm{Co(NH_3)_5I^{++}} + I^- \quad (7)$$

and

$$K = [\mathrm{Co(NH_3)_5I^{++}}]^2[I^-]/[\mathrm{Co(NH_3)_5H_2O^{++}}]^2[I_3^-] \quad (7a)$$

TABLE II

SUMMARY OF EQUILIBRIUM CONSTANTS FOR THE FORMATION OF IODOPENTAMMINECOBALT(III)[a]

25°, μ = 1.0, 0.100 M iodide

5×10^{-5} M iodopentamminecobalt(III)

$[NH_3]$	K'	α	K
0.0551	6.95×10^{14}	0.00565	55×10^5
.105	1.15×10^{13}	.0296	21
.131	1.30×10^{12}	.0468	8.7
.234	2.35×10^{11}	.131	6.5[b]
.262	7.40×10^{9}	.154	4.7[b]
.390	3.35×10^{8}	.250	4.3[b]
.511	4.50×10^{7}	.314	5.3[b]
.525	3.40×10^{7}	.326	4.9[b]
			av. $5.1 \pm 0.6 \times 10^5$

[a] Each value of K' is an average of five or more sets of measurements having an average deviation of three per cent. [b] Used in computing average.

From equations 1a and 7a

$$K = K'[NH_3]^{10}/\alpha^2$$

where $\alpha = [\mathrm{Co(NH_3)_5H_2O^{++}}]/\Sigma[\mathrm{Co(II)}]$. Values of α given in the third column were calculated from the consecutive constants for the formation of cobalt(II) ammines at 25° in 1 M ammonium nitrate.[13] Consistent values of K were obtained for solutions containing more than 0.234 M ammonia and a plot of K *vs.* $[NH_3]$ showed that the rapid increase in K commenced at ammonia concentrations less than 0.15 M. The marked increase in K at low ammonia concentrations is consistent with the rapid decrease in α with decreasing $[NH_3]$ and the earlier observation that at low ammonia concentrations other cobalt(III) ammines are formed.

Discussion

The oxidation–reduction potential of the reaction

$$\mathrm{Co(NH_3)_5H_2O^{++}} \longrightarrow \mathrm{Co(NH_3)_5H_2O^{+++}} + e \quad (8)$$

in 1 M NH_4NO_3 at 25° can be calculated from published data to be −0.370 volt. This potential was calculated from

$$E = 0.0591\{\beta_6(\mathrm{III}) - \beta_5(\mathrm{II})\} + E_{\mathrm{II,III}} \quad (8a)$$

where β_6(II) and β_5(III) are the respective logarithms of the mass action constants for the formation of $\mathrm{Co(NH_3)_5H_2O^{++}}$ and $\mathrm{Co(NH_3)_5H_2O^{+++}}$ from their aqueous ions and $E_{\mathrm{II,III}}$ is the oxidation–reduction potential of the aqueous ions. From Bjerrum's data[11] a value of 5.56 was obtained for β_5(II). From the data[14] for β_6(III) and k_6(III), the logarithm of the formation constant of hexammine cobalt(III) from the pentammine complex, the heats of formation of $\mathrm{Co(NH_3)_6^{+++}}$ and $\mathrm{Co\text{-}(NH_3)_5H_2O^{+++}}$ from the pentammine[15] and tetrammine,[15] respectively, and assuming that

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(13) Reference 1, p. 188.

(14) Reference 1, pp. 251, 281.

the heats of formation of other cobalt(III) amines are the same as that for the pentammine,[16] a value of 30.30 was estimated for β_5(III). In calculating β_6(III) Bjerrum[17] extrapolated the original data of Noyes and Deahl[18] for the potential of the aqueous cobalt ions to 1 M HNO_3 at 30°. The same procedure was used here to obtain a value of −1.830 volts for $E_{II,III}$ in 1 M HNO_3 at 25°. This value was used in the above calculation.

The oxidation–reduction potential for equation 8 can be calculated in 1 M NH_4ClO_4 at 25° from

$$E = 0.0591(\log K^{1/2} - \log Q) + E_{I^-,I_3^-} \quad (8b)$$

where K is the mass action constant for equation 7 and E_{I^-,I_3^-} is the potential of the iodide–triiodide couple. The latter was assumed to be equal to −0.5465, the value of the standard potential corrected for activity coefficients in 1 M KI. Q is the mass action constant for the equilibrium

$$Co(NH_3)_5H_2O^{+++} + I^- \underset{k_a}{\overset{k_f}{\leftarrow}} Co(NH_3)_5I^{++} + H_2O \quad (9)$$

$$Q = [Co(NH_3)_5I^{++}]/[Co(NH_3)_5H_2O^{+++}][I^-] = k_f/k_a \quad (9a)$$

At 25° the second order rate constant for the disappearance of iodopentamminecobalt(III) in NH_4I solutions is 4.3 sec.$^{-1}$ M^{-1} while that for the disappearance of aquopentamminecobalt(III) is 1×10^{-6} sec.$^{-1}$ M^{-1}. It seems likely that the rate determining step in the latter reaction is either equation 9 or the displacement of the water molecule in an outer-sphere complex, $CO(NH_3)_5H_2O,I^{++}$. If the rate determining step is equation 9, then Q can be calculated from the ratio of the forward and reverse rate constants (9a). This mechanism is supported in part by the fact that values of Q calculated in this way agree favorably with similar mass action constants for the formation of chloro-[19,20] and bromopentamminecobalt(III)[20] (Table III) determined under equilibrium conditions.

TABLE III

EQUILIBRIUM CONSTANTS OF ACIDOPENTAMMINE-COBALT(III) COMPLEXES

45°		μ, 1 M
Complex	K	Method
Chloro	1.25	Observed spectrophotometrically
Bromo	0.48	Observed spectrophotometrically
Iodo	.21	Calculated, equation 9a

When the value of Q calculated at 25° by means of equation 9a is used in equation 8b, a value of −0.33 volt is obtained for the pentammine couple. This value is 40 millivolts more positive than that calculated by means of equation 8a. In view of the experimental diffculties, the assumptions made, and the dependence of the final calculations on a large number of experimental observations, no significance can be attached to this difference. Rather the data indicate that the different experimental procedures give comparable results.

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(15) K. B. Yatsimirskii and L. L. Pankova, *Zhur. Obshchei Khim.*, **19**, 617 (1949).

(16) This assumption was tested by comparing the value of 34.54 for β_6(III) in 1 M NH_4NO_3 at 25° obtained from the data of Bjerrum[13] and Yatsimirskii and Pankova[15] with that of 34.51 calculated from the data of Lamb and Larson.[5]

(17) Reference 1, p. 233.

(18) A. A. Noyes and T. J. Deahl, *J. Am. Chem. Soc.*, **59**, 1337 (1937).

(19) B. Adell, *Z. anorg. u. allgem. Chem.*, **246**, 303 (1941).

(20) R. G. Yalman, unpublished observations. Experiments are now underway to determine the formation of outer-sphere complexes of aquopentamminecobalt(III) with Cl^-, Br^-, and I^-.