

71-19,512

RAASCH, Lou Reinhart, 1944-
STATIONARY ELECTRODE POLAROGRAPHY OF SOME
COBALT (III) AMINE COMPLEXES.

The University of Nebraska, Ph.D., 1971
Chemistry, analytical

University Microfilms, A XEROX Company, Ann Arbor, Michigan

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STATIONARY ELECTRODE POLAROGRAPHY
OF SOME COBALT(III) AMINE COMPLEXES

by

Lou R. Raasch

A THESIS

Presented to the Faculty of
The Graduate College in the University of Nebraska
In Partial Fulfillment of Requirements
For the Degree of Doctor of Philosophy
Department of Chemistry

Under the Supervision of Professor Robert C. Larson

Lincoln, Nebraska

August, 1970

TITLE

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Lou R. Raasch

APPROVED

DATE

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| <u>Robert C. Larson</u> | <u>August 6, 1970</u> |
| <u>James D. Carr</u> | <u>August 6, 1970</u> |
| <u>Henry F. Holtzclaw, Jr.</u> | <u>August 6, 1970</u> |
| <u>James H. Looker</u> | <u>August 6, 1970</u> |
| <u>Allen R. Edison</u> | <u>August 6, 1970</u> |
| <u> </u> | <u> </u> |
| <u> </u> | <u> </u> |

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Introduction:

Brdicka,¹ in 1933, used the polarographic reduction of hexaamminecobalt(III) chloride as a means of determining the presence of proteins. Although he was not primarily concerned with the investigation of the reduction of hexaamminecobalt(III) ion, he did present some qualitative measurements of the reduction potential. The polarographic half-wave potential was between -0.2 and -0.3 v. vs. S.C.E. in ammonia/ammonium chloride solution for the one-electron reduction of this species.

Willis, Friend and Mellor² studied various amine complexes of cobalt(III) in several supporting electrolytes. These authors found that the corresponding cobalt(II) complexes are unstable and decompose to yield aquated cobalt(II) ion in solution. Hence, the potential for the second reduction step, cobalt(II)/cobalt(0), occurs at the same potential for all the compounds they studied. As seen in Table I, the reduction potentials for the first reduction wave of each species vary over a range of about 0.4 volts. Thus, they concluded that the first reduction step was characteristic of that particular compound, but the second reduction step, at -1.2 v. vs. S.C.E.,

TABLE I
HALF-WAVE POTENTIALS FOR VARIOUS COBALT(III) AMINE COMPLEXES
IN 0.10 N POTASSIUM SULFATE AND SODIUM ACETATE SOLUTIONS.²

| Complex | $E_{1/2}$ v. vs. S.C.E. |
|---|----------------------------|
| $[\text{Co}(\text{NH}_3)_6]^{3+}$ | -0.437 |
| $[\text{Co}(\text{NH}_3)_5\text{NO}_2]^{++}$ | -0.264 |
| cis- $[\text{Co}(\text{NH}_3)_4(\text{NO}_2)_2]^+$ | -0.043 |
| trans- $[\text{Co}(\text{NH}_3)_4(\text{NO}_2)_2]^+$ | -0.207 |
| $[\text{Co}(\text{NH}_3)_3(\text{NO}_2)_3]$ | -0.026 |
| $[\text{Co}(\text{NH}_3)_2(\text{NO}_2)_4]^-$ | -0.070 |
| $[\text{Co}(\text{NH}_3)_5\text{OH}]^{++}$ | -0.473 |
| cis- and trans- $[\text{Co}(\text{NH}_3)_4\text{Cl}_2]^+$ | -0.415 |
| $[\text{Co}(\text{NH}_3)_3(\text{H}_2\text{O})_3]^{3+}$ | -0.249 |
| $[\text{Co}(\text{NH}_3)_5\text{H}_2\text{O}]^{3+}$ | -0.474 |

was due to the reduction of a species which could be formed from the product of the first reduction step, no matter which cobalt(III) amine complex was reduced. This could only be aquated cobalt(II) ion.

Laitinen, Bailar, Holtzclaw and Quagliano³ have shown that capillary active substances such as gelatin or octyl alcohol cause shifts of the half-wave potential of the first wave to more negative values for the polarographic reduction of hexaamminecobalt(III) ion. Supporting electrolytes of good complexing ability shift the first wave to more negative potentials and decrease the diffusion rate. In 0.10 M potassium nitrate, the half-wave potential was reported to be -0.244 v. vs. S.C.E., while in 0.10 M potassium chloride it was -0.255 v. vs. S.C.E. In more strongly complexing media, such as potassium tartrate, potassium citrate, potassium sulfate, and potassium acetate, half-wave potentials of -0.305, -0.270, -0.465, and -0.362 v. vs. S.C.E. were observed, respectively, for the reduction of hexaamminecobalt(III) ion in those media. The authors postulated that there exists some super complex or ion pair in the complexing medium which causes the negative shift in half-wave potential and the decrease in diffusion rate.

The half-wave potential reported by Laitinen, et al, agrees with that observed by Brdicka, while it is more positive than that observed by Willis, Friend and Mellor. The differing supporting electrolytes and their complexing abilities are the main cause of these variances in the observed half-wave potentials for the reduction of the cobalt(III) amine complexes. The data reported by Laitinen, Bailar, Holtzclaw and Quagliano shows that the more non-complexing supporting electrolytes gave the more positive half-wave potentials, thus indicating less formation of such a "super complex" and, in any case, minimizing the effects which might be caused by a complexing supporting electrolyte.

Laitinen, Frank, and Kivalo⁴ studied the reduction of hexaamminecobalt(III) ion in 0.10 M sodium perchlorate supporting electrolyte. Two waves were observed, one at -0.250 v. vs. S.C.E. corresponding to the one-electron cobalt(III)/cobalt(II) reduction, and a second wave at -1.230 v. vs. S.C.E. for the cobalt(II)/cobalt(0) two electron reduction. At concentrations above two millimolar, maxima were observed on the first wave. These authors also found that ammonia was liberated upon the reduction of the hexaamminecobalt(III) ion.

This information agrees with the data for the reduction of hexaamminecobalt(III) ion in potassium nitrate, which is also a non-complexing supporting electrolyte. The evidence that ammonia is produced in the reduction of hexaamminecobalt(III) ion supports the hypothesis that cobalt(II) complexes are unstable and are able to dissociate into free ligands and aquated cobalt(II) ion in solution.

The ammonia liberated in the electrode reaction can react with water to produce hydroxide ions. Since the typical concentration of an electroactive species to be investigated polarographically is 10^{-3} M, the maximum concentration of ammonia which could be released from an ammonia containing complex would be 6×10^{-3} M. Under actual experimental conditions, only a very small fraction of the total electroactive species is ever reduced, and that only at the electrode surface. Therefore, the 6×10^{-3} M concentration of ammonia is a limiting value which can only be approached at the electrode surface. The amount of ammonia released will not change the bulk solution pH, but a 10^{-3} or 6×10^{-3} M concentration of ammonia at the electrode surface will be able to influence the conditions at the electrode surface. This may produce a marked

effect upon a process occurring at the electrode.

While the simplest system, from the information provided by Willis, et al,² or Laitinen, et al,³ would appear to be one in which there is only a non-complexing supporting electrolyte, the system is actually extremely complicated by the variation of pH at the electrode surface with the extent of the electrode reaction freeing ammonia. The pH at the electrode surface may be fixed by buffering the solution. This will eliminate the uncertainty in knowing the pH at the electrode surface, but it does, however, again present the problem of what the effects of the complexing ability of the buffering supporting electrolyte may be. Thus, the most useful supporting electrolytes for investigating the reduction mechanisms of cobalt amine complexes are those which are capable of buffering the solution, yet are very weak complexing agents.

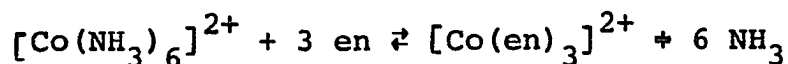
In another paper, Laitinen and Kivalo⁵ studied the effects of complexing agents upon the polarographic reduction of hexaamminecobalt(III) ion. By comparing the half-wave potentials with equilibrium potential measurements, it was concluded that the first step in the reduction process is the electron transfer to form hexaamminecobalt(II) ion. Bjerrum⁶ has shown

by potentiometric titration that the oxidation-reduction reaction of the hexaamminecobalt(III)/hexaamminecobalt(II) system is reversible. However, his titrations were made in solutions containing an excess of ammonia and an ammonium salt. This means that his determinations were done under conditions such that the hexaamminecobalt(II) ion is stabilized. Polarographically, the reduction of hexaamminecobalt(III) ion is irreversible in most media. Laitinen and Kivalo attribute this to a slow kinetic step, the transformation of the hexaamminecobalt(II) ion from the initial d^2sp^3 hybridization structure to the stable sp^3d^2 form of the hexaamminecobalt(II) complex.

In the presence of ethylenediamine, the reduction of hexaamminecobalt(III) ion occurs at the reversible reduction potential of tris(ethylenediamine)cobalt(III) ion, although that ion is not present in the original solution. In concentrated chloride solution, however, the second step of the reduction process was observed to be shifted 0.4 v. to a more positive potential because of the formation of a chloro complex of cobalt(II) by rapid exchange of ligands by the hexaamminecobalt(II) ion. In concentrated hydroxide medium, the potential was also shifted, but in this case, to a more negative

potential.

In exploring the reduction mechanism of hexaamminecobalt(III) ion in ethylenediamine solutions, Laitinen and Kivalo⁵ first ascertained that the hexaamminecobalt(III) complex was stable in ethylenediamine containing solutions by observing the polarographic reduction of the complex at its normal potential when such solutions were acidified. The polarographic half-wave reduction potential obtained in a solution 0.10 M in potassium nitrate and 0.10 M in ethylenediamine was -0.465 v. vs. S.C.E., which is very close to the half-wave potential for the reduction of tris-(ethylenediamine)cobalt(III) ion in this medium. Since the hexaamminecobalt(III) ion does not decompose in this solution, it must still be present, and hence, be reduced at its normal potential. The differences must then be due to some process which occurs after the reduction of the hexaamminecobalt(III) ion to the hexaamminecobalt(II) ion. Since the complexes of cobalt(II) are much more labile than the corresponding cobalt(III) complexes,⁷ there then exists at the electrode surface, an equilibrium with the complexing agent in solution:



Since the ethylenediamine is present in a large excess and the cobalt(II) ethylenediamine complex is more stable than the hexaamminecobalt(II) complex, any hexaamminecobalt(II) ion which is formed as a reduction product immediately reacts to form tris(ethylenediamine)cobalt(II) ion. Since it is still near the electrode surface, it is also oxidized to tris(ethylenediamine)cobalt(III) ion and no net current flow is observed. The polarographic reduction wave observed is that for the tris(ethylenediamine)cobalt(III) ion at its usual reduction potential.

Brdicka⁸ had also studied the reduction of the chloro complex of divalent cobalt. The half-wave potential for the reduction of cobalt(II) ion in 5 M calcium chloride of -0.822 v. vs. S.C.E., compared to a half-wave potential of -0.876 v. vs. S.C.E. for the second reduction wave of hexaamminecobalt(III) ion in the same supporting electrolyte, indicates that the reduction product from the first wave must undergo ligand exchange (at least partially) to form the chloro complex of cobalt(II). Laitinen and Kivalo have shown that a similar effect is observed for the reduction of hexaamminecobalt(III) ion in concentrated hydroxide solutions. In 10 M sodium hydroxide, cobalt(II)

ion gave a half-wave potential of -1.54 v. vs. S.C.E. and hexaamminecobalt(III) ion gave two waves with half-wave potentials of -0.35 v. and -1.54 v. vs. S.C.E., thus providing a simile to the reaction mechanism of the chloro case.

Laitinen and Grieb,⁹ investigating the reduction of tris(ethylenediamine)cobalt(III) ion, found that the conditions necessary for a reversible reduction are that an excess of ethylenediamine be present. Using sodium perchlorate as the supporting electrolyte, a half-wave potential of -0.4414 v. vs. S.C.E. was obtained. As this value was relatively constant over a range of perchlorate concentrations varying from 0.10 to 4.0 M, it was used to calculate a "standard" half-wave potential. They also estimated the magnitudes of the equilibrium constants for the dissociation reactions of ion-pairs formed by tris(ethylenediamine)-cobalt(III) ion with certain anions such as chloride, sulfate, and nitrate. The order of their stabilities is: sulfate greater than chloride greater than nitrate.

Concurrently with the above study, Kivalo¹⁰ examined the polarographic behavior of tris(ethylenediamine)cobalt(III) ion in the absence of excess complexing agent. The polarographic reduction under these conditions is irreversible. The product of

the first reduction wave, the divalent complex, is unstable and dissociates to lower amine complexes. The dissociation of the reduced species influences the shape of the wave and also the half-wave potential. Bjerrum⁶ has shown that the tris(ethylenediamine)-cobalt(III)/tris(ethylenediamine)cobalt(II) couple is potentiometrically reversible, thus the irreversibility must be due to the chemical reaction following the electron transfer.

Using radioactive tracer techniques, Lewis, Coryell, and Irvine¹¹ found a high rate of electron exchange between the two tris(ethylenediamine)cobalt complexes. This implies a large natural exchange current, a property which should provide polarographic reversibility.¹² Kivalo¹⁰ has found that the irreversibility of the polarographic reduction in the absence of excess ethylenediamine is due to the chemical deactivation by dissociation of the reduction product.

Some other interesting facets of the reduction of cobalt complexes have been observed by Holtzclaw and Sheetz.¹³ These authors noted that there occur two waves for the one-electron reduction of some bis(ethylenediamine)cobalt(III) complexes. The second wave had nearly the same polarographic half-wave potential for all the compounds exhibiting two waves

for the first reduction step. It was thought that such a species could only arise from the aquation of the parent compound.

Maki, Shimura, and Tsuchida¹⁴ observed two waves for the polarographic reduction of dibromo- and dichloro-bis(ethylenediamine)cobalt(III) ions and also assumed that the second wave was due to an aquated species. In light of the ligand exchange reaction in the reduction of hexaamminecobalt(III) ion in ethylenediamine solution reported by Laitinen and Kivalo,⁵ a better mechanism for the occurrence of two waves for the first reduction step has been proposed.

Mason and White¹⁵ observed two waves for the one-electron reduction of dinitrobis(ethylenediamine)cobalt(III) ion. The first wave was attributed to the dinitro-species, while the second wave was attributed to the reduction of tris(ethylenediamine)cobalt(III) ion. The tris(ethylenediamine)cobalt(III) ion is produced at the electrode surface by a mechanism similar to that proposed by Laitinen and Kivalo for the reduction of hexaamminecobalt(III) ion in excess ethylenediamine. This type of mechanism was studied in more detail by Larson, Henney and Holtzclaw,¹⁶ who found multiple polarographic waves for the one-electron reduction of aquated bis(ethylenediamine)cobalt(III) ions.

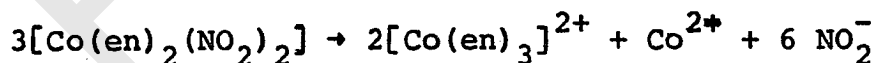
The reduction of a cobalt(III) complex will be, as the first reduction product, a cobalt(II) complex that is labile and can exchange ligands. A complex such as the dinitrobis(ethylenediamine)cobalt(III) ion, when reduced, would produce a mixture of cobalt(II) ions, nitrite ions, and ethylenediamine. The cobalt(II) ions and ethylenediamine would react to produce an equilibrium amount of tris(ethylenediamine)cobalt(II) ion at the electrode surface. As it is formed, it would be oxidized to tris(ethylenediamine)cobalt(III) ion; thus removing it from the equilibrium and causing the equilibrium to provide more of the cobalt(II) complex to be oxidized.

Holtzclaw and Sheetz found that the one-electron reduction wave was present as two waves for bis(ethylenediamine)cobalt(III) complexes, but not for the tetraamminecobalt(III) complexes. There are two factors in favor of the ethylenediamine complexes being more apt to follow the reaction scheme previously described. The stability of tris(ethylenediamine)-cobalt(II) ion is greater than the stability of the hexaamminecobalt(II) ion. Hence, there need not be very much free ethylenediamine present in order to form some tris(ethylenediamine)cobalt(II) ion which could be oxidized. Secondly, the electron transfer

rate for the tris(ethylenediamine)cobalt(III)/tris(ethylenediamine)cobalt(II) couple is greater than the electron transfer rate for the hexaamminecobalt(III)/hexaamminecobalt(II) couple. Holtzclaw and Sheetz did their work in 0.10 M potassium chloride solution and did not buffer the system, thus the ethylenediamine produced by the dissociation of the cobalt(II) ethylenediamine complex would be sufficient to change the pH at the electrode surface. There is some dependence upon pH as to the relative wave heights for the two parts of the one-electron reduction when they are observed.

Such a relationship was found by Mason and White¹⁵ in their study of the trans-dinitrobis(ethylenediamine)-cobalt(III) ion. If all the ethylenediamine available were used to form tris(ethylenediamine)cobalt(II) ion, the second wave would be 2/3 of the total wave height for the cobalt(III)/cobalt(II) reduction step.

This is suggested by the stoichiometry of the reaction:



This should be the case unless the monoethylenediamine-cobalt(II) complex is particularly stable or the formation of tris(ethylenediamine)cobalt(II) ion is rate limited.

Mason and White have found that the second wave,

attributed to the reduction of tris(ethylenediamine)-cobalt(III) ion has a limiting height of one-half of the total wave height. Thus, either its rate of formation is somehow limited, or the monoethylenediaminecobalt(III) complex is exceptionally stable.

Larson, Henney, and Holtzclaw¹⁶ have found that the aquated bis(ethylenediamine)cobalt(III) species may have as many as three waves for the one-electron reduction step. The aquated bis(ethylenediamine)-cobalt(III) ion may exist in three forms: diaquobis(ethylenediamine)cobalt(III) ion, aquohydroxobis(ethylenediamine)cobalt(III) ion, or dihydroxobis(ethylenediamine)cobalt(III) ion.

Since hydroxide ion is a stronger ligand than water, the hydroxide complexes are expected to have more negative reduction potentials than the aquo complexes. Larson, et al, have found that the first wave has a half-wave potential of +0.02 v. vs. S.C.E., and the second wave has a half-wave potential of -0.06 v. vs. S.C.E., while the third wave has a half-wave potential which varies from -0.40 v. in slightly acidic solution to -0.52 v. vs. S.C.E. in basic solution.

The first two waves are due to the diaquobis(ethylenediamine)cobalt(III) ion and to the slow

equilibrium between the diaquo- and aquohydroxo-bis(ethylenediamine)cobalt(III) complexes. The third wave is due to the aquohydroxobis(ethylenediamine)-cobalt(III) ion. Thus, if a complex is sufficiently labile in solution to form aquated complexes, like dichlorobis(ethylenediamine)cobalt(III) complexes, two waves can be produced by the aquated species. However, a non-labile complex such as the dinitro-bis(ethylenediamine)cobalt(III) ion cannot follow such a mechanism, and the production of tris(ethylenediamine)cobalt(II) ion is a more probable route.

Konrad and Vlcek¹⁷ found that the tris(ethylenediamine)cobalt(II) ion is polarographically active, and can be oxidized to the corresponding cobalt(III) complex. None of the lower cobalt(II) ethylenediamine complexes are electroactive with respect to oxidation to the corresponding cobalt(III) complex. The polarographic half-wave potential, corrected for the ratio of the diffusion coefficients of the reduced and oxidized forms, was identical with the potential measured at a platinum electrode. The value determined was -0.496 v. vs. C.E. or -0.465 v. vs. S.C.E. The anodic limiting current has kinetic character when the equilibrium is shifted towards the aquated cobalt(II) species.

They found that the slowest step in the formation of the tris(ethylenediamine)cobalt(II) ion is the attachment of the third ethylenediamine. In the reduction of tris(ethylenediamine)cobalt(III) ion, the electrode product is inactivated by a reaction involving hydrogen ions. It was found that the loss of the first ethylenediamine from tris(ethylenediamine)cobalt(II) ion was the rate determining step in its dissociation. A value of $5 \times 10^3 \text{ sec}^{-1}$ was obtained for the rate of loss of the first ethylenediamine from tris(ethylenediamine)cobalt(II) ion. The shift in half-wave potential with pH in the region about pH 6 to pH 7 was used to calculate the rate. If sulfate were present, the formation of the complex sulfatobis(ethylenediamine)-cobalt(II) provided a second reaction path for the formation of the electroactive cobalt(II) complex. Vlcek¹⁸ had previously reported that complexes of the monohalogenpentaamminecobalt(III) type are reduced with retention of their stoichiometric composition. This is also the case for the cobalt(III) ethylenediamine complexes.

The reduction of tris(ethylenediamine)cobalt(III) ion is reversible. In solutions where the reduced form is unstable, there is a chemical reaction following the electron transfer. This dissociation reaction

causes the reduction to appear as if it were irreversible.

Since the development of the theory necessary to apply linear potential scan voltammetry to the measurement of electrode kinetics and the rates of coupled chemical reactions in recent years,²²⁻⁴¹ we undertook to apply this technique to the study of the reduction mechanisms of various cobalt(III) amine complexes. The purpose of our study is to extend the range of conditions in which the mechanism of the reduction of tris(ethylenediamine)cobalt(III) ion is known. To begin, it was felt that the hexaamminecobalt(III) ion should also be studied. Several other cobalt(III) amine complexes were studied, but most of them appeared to be irreversible charge transfer processes; thus quantitative measurements of any coupled chemical reactions are not possible.

The necessary theoretical considerations necessary for the elucidation of the desired information from the experimental data are presented in the next section.

Theoretical Survey:

Tanaka and Tamamushi,¹⁹ in an effort to bring some uniformity to the reporting of kinetic parameters of electrode reactions surveyed the state of the art in 1964. A general electrode reaction, $O + n e^- \rightarrow R$, consists of 4 parts: (1) mass transport to the electrode, (2) the electron transfer at the electrode surface, $X + n e^- \rightarrow Y$, (3) the processes which accompany the electron transfer process, $O \rightarrow X$ and $Y \rightarrow R$, and finally (4) mass transport away from the electrode. The rate of electron transfer, psuedo first order, are represented by:

$$\text{Reduction:} \quad k_c = k_c^0 \exp(-\alpha n F E / RT) \quad (1A)$$

$$\text{Oxidation:} \quad k_a = k_a^0 \exp(\beta n F E / RT) \quad (1B)$$

where E is the electrode potential (European convention) measured against a suitable reference electrode.

α and β are the cathodic and anodic transfer coefficients. The k^0 's are the rate constants at a potential of 0.0 v. The other terms have their usual meanings. At the standard potential, E^0 , both k_c and k_a are equal to the standard rate constant, k_s .

Vlcek²⁰ has determined the rates of electron transfer for some cobalt amine complexes. He has also determined the cathodic transfer coefficients for these complexes. The electron exchange rate for

hexaamminecobalt(III) ion in 0.14 M perchloric acid and 1.26 M sodium perchlorate was reported as $k_c^0/D^{1/2}$ being 2.1×10^{-4} . The cathodic transfer coefficient was determined to be 0.67.

Recently, Bartelt and Skilandat²¹ determined the electrochemical-kinetic parameters of the tris-(ethylenediamine)cobalt(III)/tris(ethylenediamine)-cobalt(II) system. They found that α was equal to 0.76 ± 0.02 . The electron exchange parameters varied from 0.46×10^{-2} cm/sec. in 1 N sodium thiosulfate supporting electrolyte to 2.9×10^{-2} cm/sec. in 1 M sodium perchlorate supporting electrolyte (Table II). These authors found evidence for the formation of outer sphere complexes with some anions. There was also some evidence for hydrolysis, dependent on the ratio of the oxidized and reduced forms present, causing a partial coverage of the electrode surface, hence decreasing the exchange current. Again it was found that the lower cobalt(II) ethylenediamine complexes are not active in the electron transfer process. Their work, done on a platinum electrode, compares well with a value of 9×10^{-2} cm/sec. at 19°C obtained by Laitinen and Randlès²² with a mercury electrode.

The rates of electron transfer for both the hexaamminecobalt(III)/hexaamminecobalt(II) and the