KINETICS AND PHOTOEFFECTS OF OXIDATION AND REDUCTION OF HEXAAMMINECOBALT COMPLEX IN ALKALINE MEDIA

KOTARO OGURA and YOICHI FUKUSHIMA

Department of Applied Chemistry, Yamaguchi University, Ubc, Yamaguchi-Ken 755, Japan

(Received 14 March 1980)

Abstract—Cyclic voltammograms of hexaamminecobalt complex have been measured in high pH solutions. The spectroscopic result suggested that hydroxoamminecobalt complex adsorbed on the electrode surface during cathodic polarization, and this species grew to form cobalt hydroxide after a long time of electrolysis. In the anodic process, the reaction orders for pH and NH₃ were both |1|. Based on these results, the reaction mechanism has been discussed.

The effect of light on the electrode process has been studied by irradiating with ultraviolet light of the 254 nm mercury resonance line. It has been indicated that the hydroxoammine complex is decomposed to cobalt hydroxide and free ligand under light.

INTRODUCTION

It has been known that the oxidation of aquo cobalt(II) ion to trivalent state is very unfavorable as can be understood from the standard potential E_0 = 1.84 V(*nhe*) of $[Co(H_2O)_6]^{3+}/[Co(H_2O)_6]^{2+}$. However, Co(II) ion is readily oxidized in the presence of a variety of complexing ligands, especially nitrogen donor; *eg*, for the redox couple of hexaamminecobalt complex $E_0 = 0.1$ V(*nhe*). This is attributed to the formation of a stable complex of trivalent cobalt with NH₃.

Metal complexes including cobalt [1-13] have been studied polarographically by many investigators, although only a few works on the oxidation of metal complexes have been reported; eg, for Fe(II)-diimine complexes [14-16]. Almost all of the polarographic interests are focussed on the fact that such complexes can be reduced giving stable species with the same formulas but with charges of only +1,0 or even -1. It is known that lower valence state of cobalt can be stabilized by coordinating ligands such as aromatic diimines. Unlike these ligands, the coordination of saturated amines with cobalt leads to the stabilization of higher valence state of metal. Higher valent cobalt is also stabilized in basic media: $E_0 = 0.17 V(nhe)$ of $CoO(OH)(s)-Co(OH)_2(s)[17]$. Hence the stabilization of lower or higher valence state of cobalt is strongly dependent on the nature of ligand and the solvent used.

In the present paper, the kinetics and photoeffect of oxidation and reduction of hexaamminecobalt complex have been studied in alkaline solution, and the mechanism of the processes discussed.

EXPERIMENTAL

Hexaamminecobalt(III) chloride was prepared by the following procedure. 240 g of $CoCl_2$, $6H_2O$ and 160 g of NH_4Cl were dissolved into 0.2 dm³ of water, and 4 g of charcoal and 0.5 dm³ of NH_4OH were added to the solution. This solution was aerated by bubbling air until the color of the solution was changed from red to yellowish brown, and crystals of hexaamminecobalt(III) chloride were precipitated. After this the crystals and the charcoal were collected, and the precipitate was transfered into 1.5 dm^3 of water containing 20 cm³ of concentrated hydrochloric acid. The separation of $[\text{Co}(\text{NH}_3)_6]\text{Cl}_3$ and charcoal was accomplished by filtration from hot solution. 0.4 dm³ of concentrated HCl was added to this filtrate, and a yellowish orange crystal was precipitated. This crystal was collected and washed with 60 % and 95 % ethanol solution, and the product was then dried at 80 ~ 100°C.

The stock solution of $[Co(NH_3)_6]^{3+}$ was prepared by dissolving 4 mM hexaamminecobalt chloride in 0.15 M sodium sulfate, and the pH was changed by adding sodium hydroxide solution. All solutions were deaerated with purified nitrogen gas before use.

Kinetic measurements were performed electrochemically by the cyclic voltammetric method. The equipments used were described previously[18]. The test electrode was a platinum wire of 0.17 cm^2 area. The electrode was washed in chromic acid mixture for 1 min and then with distilled water before each run. The counter electrode was a smooth platinum plate. A saturated calomel electrode was used as the reference electrode. All potentials are reported with respect to SCE. The temperature of these experiments was 22 $\pm 0.2^{\circ}$ C.

The photoeffect was studied by irradiating with ultraviolet light of the 254 nm mercury resonance line during the electrochemical measurements. The source for this light was a Hamamatsu TV L937–04 lowpressure mercury lamp. The photolysis was carried out in the main electrolytic cell having a flat circular quartz window to admit ultraviolet light, and the cell was water-jacketed to maintain a constant temperature.

The absorption spectrum of the complex was measured by a double-beam spectrophotometer (Shimazu UV-200) using 1 cm quartz cell. A Hitachi-Horiba M5 pH meter was used for pH measurements.

RESULTS

In Figure 1, the cyclic voltammograms of hexaamminecobalt(III) complexes are shown at 100 mV/s



Fig. 1. Cyclic voltammograms of hexaamminecobalt(III) complex at 100 mV/s in the solutions of various pH's.

in alkaline solutions. The electrode was first polarized from the immersion potential to the cathodic side, and the cathodic sweep was reversed at -0.7 V. The potential sweep was again reversed at +0.7 V. It is seen from this figure that at pH 12.5 two cathodic peaks are at $-0.52 V(E_{pc1})$ and $0.1 V(E_{pc2})$ on the cathodic sweep, and a distinct peak is at $0.11 V(E_{pa})$ on the anodic sweep. The peaks at E_{pa} and E_{pc2} become gradually less apparent with decreasing pH, although the peak at E_{pc1} is almost independent of pH.

The pH-dependence of E_{pa} and i_{pa} is exhibited in Fig. 2. E_{pa} is independent of pH in the weak alkaline solutions, but it is linearly related with the slope of -0.065 V/pH at pH values > 10.2. Similar pHdependence was also observed for i_{pa} . The log of i_{pa} is plotted vs pH in Fig. 2. $\log i_{pa}$ is proportional to pH with the slope of 0.96 $\log i/\text{pH}$ at pH's above 11.2. The peak at E_{pc2} was obscure at pH values < 11.0, and a distinct pH-dependence was not valid for this peak.

The effects of the ammonium ion concentration on the cyclic voltammograms are depicted in Fig. 3. The first cathodic peak is not significantly affected by the addition of ammonium ion, though E_{pc1} shifts slightly to the cathodic side; however, the anodic peak and second cathodic peak were dependent fairly on the addition of ammonium sulfate. It is seen from this figure that these peaks shift to the noble side, and the magnitudes of the anodic and cathodic current decrease with increasing the concentration of ammonium ion.

In Fig. 4, the log of the anodic peak current is plotted against the log of the ammonium concentration, and the linear relationship holds between them with the slope of -0.97.

In Fig. 5, the cyclic voltammograms at various scan rates are displayed. The anodic current peak was linearly related with the square root of scan rate \sqrt{v} , and the result is shown in Fig. 6. This indicates that the anodic processes at the electrode are diffusioncontrolled.

The electrolysis of hexaamminecobalt(III) solution using two platinum plates as the electrodes has been carried out at -0.6 V for 3 h. The solution in the cathode compartment, and the species deposited on the cathodic electrode were collected to measure absorption spectra. The collection of the deposited species was performed by immersing the electrode into



Fig. 2. Relationships between E_{pa} and $\log i_{pa}$ vs pH. Potential scan rate: 100 mV/s.



Fig. 3. Cyclic voltammograms of hexaamminecobalt(III) complex at 100 mV/s and pH 12.5 in the presence of various concentrations of ammonium sulfate.



Fig. 4. Relationship between $\log i_{pa} vs \log C_{NH_4^+}$.

rum of the solution in the cathode compartment was

sulfuric acid solution of pH 0.8. Absorption spectra of this solution as well as $CoCl_2$ and $Co(NH_3)_6Cl_3$ alth solutions of pH 0.8 have been taken, and the results are shown in Fig. 7. The absorption spectrum of $CoCl_2$ whi solution has the characteristic bands at 195 and 510 nm, and that of $[Co(NH_3)_6]Cl_3$ solution has the bands at 210, 315 and 465 nm. The absorption spect-



Fig. 5. Cyclic voltammograms of hexaamminecobalt(III) complex at pH 11.5 and various scan rates.



Fig. 6. Relationship between i_{pa} and \sqrt{v} .

quite similar to that of $[Co(NH_3)_6]Cl_3$ solution, although the former absorbance was slightly smaller than the latter. On the other hand, the solution in which the deposited species was dissolved has the absorption bands at the same wave length as $CoCl_2$ solution does as seen from Fig. 7. Furthermore, the absorption band at 195 nm shifted toward 210 nm (the wave length characteristic for $[Co(NH_3)_6]^{3+}$) with



Fig. 7. Absorption spectra of 4 mM CoCl₂ (pH 0.8):-----, 0.04 mM Co(NH₃)₆Cl₃ (pH 0.8):----, and the species deposited on the electrode surface (dissolved into solution of pH 0.8):----.



Fig. 8. Cyclic voltammograms of hexaamminecobalt(III) complex at pH 11.9 and scan rate 100 mV/s in dark and under light of 254 nm.

decreasing the electrolysis time. These facts suggests that the species deposited on the electrode surface changed from cobalt hydroxide to hydroxoamminecobalt complex with decreasing the electrolysis time.

In Fig. 8, the cyclic voltammograms of hexaamminecobalt complex at pH 11.9 and scan rate 100 mV/s are shown in dark and under light of 254 nm. As seen from this figure, each potential peak except E_{pc1} is not significantly affected by the irradiation of light. However, the current decreases always, and the first cathodic wave oscillates irregularly under irradiation of light.

The species deposited at -0.6 V for a certain time was dissolved anodically, and i_{pa} is plotted against the deposition time in dark as well as under light of 254 nm in Fig. 9. i_{pa} first increases with the deposition time, and



Fig. 9. Relationship between i_{pe} and the deposition time at -0.6 V in dark and under light of 254 nm. pH: 12.5.

then reaches to a certain value in dark. Similar relation is obtained under light of 254 nm, but the magnitude of the current is smaller by about 15 per cent under light than in dark.

The photo-anodic current i_{pa}^* which was obtained by subtracting i_{pa} in dark from i_{pa} under light of 254 nm is exhibited in Fig. 10. It is seen that the anodic current is always smaller under light than in dark; this trend is especially conspicuous at pH values > 11.5.

DISCUSSION

The spectroscopic result implied that in the cathodic polarization hydroxoammine complex first absorbed on the electrode surface, and then this species grew to form cobalt hydroxide in a long time of electrolysis. Hence, in the cyclic voltammetric experiment, $[CoOH(NH_3)_5]_{ads}$ was assumed to adsorb on the electrode.

As seen from Figs. 1 and 3, the current at E_{pe1} is not significantly affected by pH and the concentration of added ammonium ion. This may mean that OH⁻ and NH₃ are not involved in the rate determining step. Probable cathodic processes are represented by the following steps, and step [ii] is assumed to be rate-determining.

$$[i] [Co(NH_3)_6]^{3+} + OH^- \rightleftharpoons [CoOH(NH_3)_5]^{2+} + NH_3$$

$$[ii] [CoOH(NH_3)_5]^{2+} + 2e \rightarrow [CoOH(NH_3)_5]_{ads}$$

From Fig. 2, the pH dependence of E_{pa} and $\log i_{pa}$ at higher pH are expressed by (1) and (2).

$$(\partial E_{pa}/\partial pH)_{C_{NH_{a}^{+}}} = -0.065 \text{ V/pH}$$
(1)

$$(\partial \log i_{pa}/\partial pH)_{CNH^+} = 0.96 \tag{2}$$

The following equation holds from Fig. 4.

$$(\partial \log i_{pa}/\partial \log C_{NH_{a}^{+}})\mathbf{p}\mathbf{H} = -0.97 \qquad (3)$$



Fig. 10. Anodic potocurrent (i_{pa}^*) vs pH.

The concentration of NH_3 in solution should be proportional to that of added ammonium ion, and hence (2) and (3) point out that the reaction orders for pH and NH_3 are approximately 1 and -1, respectively.

From these experimental facts, the following mechanism is proposed for the anodic process occurring at E_{pa} .

[iii]
$$[CoOH(NH_3)_5]_{ads} + OH^-$$

 $\approx [Co(OH)_2(NH_3)_4]^- + NH_3$

$$[iv] [Co(OH)_2(NH_3)_4]^- \rightarrow Co(OH)_2 + 4NH_3 + e$$

If we assume that step [iv] is rate-determining, the following equation applies:

$$i = kFa_1 \exp(-\alpha F\Delta\phi/RT) \tag{4}$$

where a_1 is the activity of $[Co(OH)_2(NH_3)_4]^-$, and the other symbols have their usual significance. Reaction [iii] is the reversible chemical reaction, and the equilibrium constant is represented by Eq. (5).

$$K = a_1 a_{\rm NH_3} / a_2 a_{\rm OH^{-1}} \tag{5}$$

where a_2 , $a_{\rm NH_3}$ and $a_{\rm OH^-}$ denote the activities of $[CoOH(\rm NH_3)_3]_{ads}$, NH₃ and OH⁻, respectively.

From (4) and (5),

$$i = kFKa_2a_{OH} - /a_{NH} \exp(-\alpha F\Delta\phi/RT)$$
 (6)

The reaction orders for pH and NH₃ calculated from (6) are both [1], and hence the above reaction mechanism rationalizes the present experimental results. According to Fig. 6, the anodic process is diffusion-controlled, and the diffusing species is probably $[Co(OH)_2(NH_3)_4]^-$. As shown in Fig. 1, a small current peak exists at peak E_{pc2} , may be due to the reverse process of reaction [iv].

As seen from Fig. 8, the first cathodic wave oscillates irregularly under irradiation of light, however, on the anodic sweep such behavior is not observed. So, it is possibly the cathodic process that suffered directly the effect of light, and as a result of this the anodic current would be decreased. The effect of irradiation of light on the anodic peak is not significant at lower pH than 11.5, but very large at higher pH as shown in Fig. 10. These results are consistent with the following mechanism.

$$\begin{bmatrix} v \end{bmatrix} \begin{bmatrix} CoOH(NH_3)_5 \end{bmatrix}^{2+} + OH^{-} \xrightarrow{hv} Co(OH)_2^{+} + 5NH_3$$

In this reaction, $[CoOH(NH_3)_5]^{2+}$ is consumed to form $Co(OH)_2^+$ under irradiation of light, and in reaction [ii] the formation of $[CoOH(NH_3)_5]_{ads}$ may be inhibited, which would result in the decrease of anodic current under light as observed in Fig. 8.

REFERENCES

- A. A. Vlček, Nature, Lond. 180, 573 (1957), Z. Elektrochem 61, 1014 (1958).
- G. M. Waind and B. Martin, J. inorg. nucl. Chem. 8, 551 (1958).
- R. Ripan, A. Farcas and O. Pirínger, Z. Anorg. Allg. Chem. 346, 211 (1966).
- K. Morinaga, K. Nakano, S. Saito and K. Nakamura, Bull. Chem. Soc. Japan 39, 357 (1966).
- 5. K. Morinaga, Review of Polarography (Japan), 14, 251 (1967).
- N. Tanaka and Y. Sato, Bull. Chem. Soc. Japan, 41, 2059 (1968).
- 7. N. Tanaka and Y. Sato, Electrochim. Acta, 13, 335 (1968).
- N. Maki, K. Yamamoto, H. Sunahara and S. Sakuraba, Bull. Chem. Soc., Japan, 42, 3159 (1969).
- 9. N. Maki, Bull. Chem. Soc. Japan, 42, 3617 (1969).
- H. Bartelt and H. Skilandat, J. Electroanal. Chem. 23, 407 (1969).
- 11. H. Bartelt, Electrochim. Acta, 16, 629 (1971).
- S. Sammatano and R. P. Bonomo, J. Electroanal. Chem., 46, 109 (1973).
- 13. N. Maki, ibid., 51, 353 (1974).
- K. Ogura, K. Nahara and M. Ueda, *Electrochim. Acta*, 21, 807 (1977).
- 15. K. Ogura, H. Urabe and T. Yosino, ibid., 22, 285 (1977).
- K. Ogura and K. Miyamoto, *ibid.*, 22, 1357 (1977), 23, 509 (1978).
- F. A. Cotton and G. Wilkinson, Advanced Inorganic Chemistry, John Wiley & Son, Inc., New York, 1966, p. 864.
- K. Ogura and K. Arinobu, J. Electroanal. Chem. 89, 175 (1978).