The Reduction of Aquopentamminechromium(III) Ions at the Dropping Mercury Electrode

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The polarographic behavior of hexamminechromium(III) ions has been reported by several authors.[1-5] In the recent papers by Tanaka and his coworkers,[4,5] the characteristics of the electrode processes of hexamminechromium(III) ions in neutral and acid aqueous solutions have been extensively discussed. In contrast, the polarographic behavior of aquopentamminechromium(III) ions has not been investigated in detail, though the half-wave potential in an acetate buffer has been reported by Friend and Smith.[2]

The present paper is concerned with the reduction of aquopentamminechromium(III) ions at the dropping mercury electrode in aqueous solutions. The study was undertaken in order to find the effect of the substitution of a water molecule for ammonia in the hexamminechromium(III) ion on the reduction at the electrode. The observations in the direct current and the alternating current polarography, including the measurements of Kalousek polarograms and current-time curves, will be presented, and the mechanism of the electrode processes will be discussed.

Experimental

Aquopentamminechromium(III) nitrate was prepared according to the method proposed by Mori[6] and was converted then into chloride.[7] Aquopentamminechromium(III) perchlorate, $[Cr(H_2O)(NH_3)_5](ClO_4)_3$, was precipitated from the solution of the chloride. After recrystallization from water, the complex was identified by measuring its absorption spectra and by determining the chromium and nitrogen contents. Absorption bands were observed at 480 mμ and 365 mμ by the use of a Hitachi *Model EPU-2 spectrophotometer*. The complex was oxidized to chromate with hydrogen peroxide in an alkaline solution, and the chromate content was determined by the spectrophotometric method. Nitrogen was determined by the conventional method.[8]

Found: Cr, 11.38; N, 14.83. Calcd. for $[Cr(H_2O)(NH_3)_5](ClO_4)_3$: Cr, 11.47; N, 15.44%.

This complex is stable for a few months when it is preserved in a silica-gel desiccator in darkness, but for only two or three hours in an acid solution. Gelatin or polyoxyethylene lauryl ether (LEO) was used as a maximum suppressor. All other chemicals used were of a guaranteed reagent grade and were used without further purification.

Direct current (d. c.) polarograms were recorded by a Yanagimoto PB-4 pen-recording polarograph. A Yanagimoto Galvarecorder Y-GR 2 was used to record alternating current (a. c.) polarograms. Kalousek polarograms were recorded with the same

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1) N. Maki, Y. Shimura and R. Tsuchida, This Bulletin, **31**, 413 (1958).

2) J. A. Friend and P. W. Smith, *J. Phys. Chem.*, **63**, 314 (1959).

3) T. C. Ichniowski and A. F. Clifford, *J. Inorg. Nucl. Chem.*, **22**, 133 (1961).

4) N. Tanaka and G. Satô, *Nature*, **197**, 176 (1963).

5) N. Tanaka, K. Ebata and G. Satô, This Bulletin, **36**, 912 (1963).

6) M. Mori, *J. Chem. Soc. Japan, Pure Chem. Sec.* (*Nippon Kagaku Zassi*), **74**, 253 (1953).

7) J. H. S. King, *J. Chem. Soc.*, **127**, 2104 (1925).

8) T. Takagi and E. Hayashi, *J. Chem. Soc. Japan, Pure Chem. Sec.* (*Nippon Kagaku Zassi*), **78**, 445 (1957).

circuit as previously described.[9] Current-time (i-t) curves were recorded by using a Rikadenki ER-J 1 recorder with an RLDC-201 preamplifier. A brown-colored cell of a simple beaker type was used in all measurements. The dropping mercury electrode (DME) used had an m value of 1.76_6 mg./sec. and a drop time, t_d, of 4.90 sec./drop, when measured in an air-free 1.0 M potassium nitrate solution at 25°C and −0.5 V. vs. SCE at 50 cm. of the height of mercury reservoir. The potential of the DME was measured against a saturated calomel electrode (SCE), which was connected to the electrolytic solution through a Hume and Harris-type salt bridge. When a. c. polarograms were measured, a platinum wire electrode of a large surface area was inserted in the electrolytic solution as the third electrode; this electrode was terminated at the SCE through a 100 μF capacitor in order to minimize the impedance of the cell. A Hitachi model EHP-1 pH meter was used for the measurement of pH of the solution.

All the measurements were carried out in a thermostat of 25±0.1°C, unless otherwise stated, and the dissolved oxygen in the electrolytic solution was removed by bubbling pure nitrogen gas through the solution. The d. c. and Kalousek polarograms given in this paper were corrected for the residual current and the iR drop across the cell. The half-wave potentials were determined from the plots of log $\bar{i}(\bar{i}_d-\bar{i})$ versus potential.

Results

In the preliminary experiments, aquopentamminechromium(III) was found not to give a well-defined polarographic wave in neutral unbuffered solutions, but to give a well-defined wave in acetate buffers or acid solutions. Typical examples are shown in Fig. 1. In this paper, therefore, only the results obtained in acid solutions are presented.

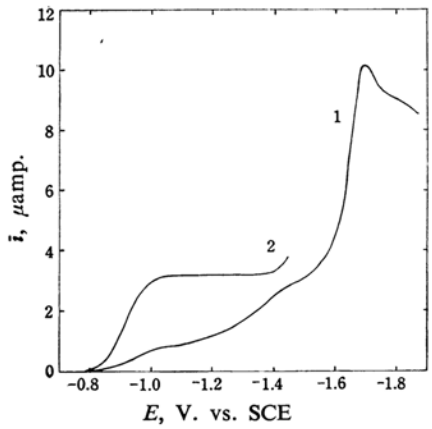

Fig. 1. Polarograms of 1.0 mM $[Cr(H_2O)(NH_3)_5](ClO_4)_3$: (1) in 1.0 M NaCl+0.005% gelatin; (2) in 0.1 M acetate buffer+0.9 M NaCl+0.005% gelatin (pH 4.46).

9) N. Tanaka, R. Tamamushi and M. Kodama, This Bulletin, 33, 14 (1960).

TABLE I. LIMITING CURRENTS OF 1.0 mM $[Cr(H_2O)(NH_3)_5](ClO_4)_3$ AT VARIED HEIGHTS OF THE MERCURY RESERVOIR IN SOLUTIONS CONTAINING 0.9 M NaCl, 0.1 M ACETATE BUFFER AND 0.005% GELATIN

$h_{corr.}$, cm.*	$\bar{i}_l$, μ amp.	$\bar{i}_l/\sqrt{h_{corr.}}$
48.4	3.14	0.452
58.4	3.47	0.454
68.4	3.78	0.457

* Height of mercury reservoir corrected for the back pressure.

The current-potential curves were obtained at various concentrations of aquopentamminechromium(III) ions in 0.1 M acetic acid-sodium acetate buffers containing 0.9 M ammonium chloride and 0.005% gelatin. The limiting current, $\bar{i}_l$, was proportional to the concentration and the value of $\bar{i}_l/C$ was found to be 3.18 μ amp./mM in the concentration range from 0.2 to 2.0 mM. The half-wave potentials were found to be independent of the concentration of the complex. Table I gives the limiting currents measured at different heights of the mercury reservoir. These results clearly indicate that the limiting current is diffusion-controlled. A comparison of the diffusion coefficient of aquopentamminechromium(III) as calculated by the Ilkovič equation and those of hexamminechromium(III)[5] and hexacyanochromate(III)[10] suggests that the wave is of a one-electron reduction. The limiting currents were also measured at various temperatures, and the activation energy for the process controlling the limiting current was calculated according to the method proposed by Vlček[11] to be 5.0 kcal./mol.

Table II presents the diffusion currents, half-wave potentials and slopes of the log-plots which were obtained at 1.0 mM of the complex.

TABLE II. EFFECTS OF pH AND SUPPORTING ELECTROLYTE ON THE POLAROGRAM OF 1 mM $[Cr(H_2O)(NH_3)_5](ClO_4)_3$ IN SOLUTIONS CONTAINING 0.1 M ACETATE BUFFER AND 0.005% GELATIN

Supporting electrolyte added	pH	$\bar{i}_d$ μ amp.	$E_{1/2}$ V. vs. SCE	Slope of log-plot mV.
0.9 M NaCl	3.46	2.99	−0.924	71
	3.78	3.06	−0.922	72
	4.46	3.17	−0.916	72
	5.58	3.14	−0.929	72
0.5 M NaCl + 0.4 M NH_4Cl	3.77	3.07	−0.925	71
0.9 M NH_4Cl	3.81	3.16	−0.934	72

10) D. N. Hume and I. M. Kolthoff, *J. Am Chem. Soc.*, 65, 1897 (1943).
11) A. A. Vlček, *Collection Czech. Chem. Commun.*, 24, 3538 (1959).

in 0.1 M acetate buffer solutions of various pH's containing either ammonium chloride or sodium chloride or both in a 0.9 M concentration. No appreciable change was observed in the half-wave potentials with the change of pH of the solution. On the other hand, the half-wave potentials were found to shift to more negative potentials with the increasing concentration of supporting electrolytes. Two examples are given in Table III.

TABLE III. EFFECT OF IONIC STRENGTH ON THE POLAROGRAM OF 1.0 mM $[Cr(H_2O)(NH_3)_5](ClO_4)_3$ IN SOLUTIONS CONTAINING 0.1 M ACETATE BUFFEE AND 0.005% GELATIN

Ionic strength	i_d μ amp.	$E_{1/2}$ V. vs. SCE	Slope of log-plot mV.
(A) Adjusted with NaCl.			
0.5	3.17	−0.906	67
1.0	3.12	−0.929	72
1.5	3.04	−0.939	72
2.0	2.85	−0.942	75
(B) Adjusted with NH_4Cl.			
0.5	3.14	−0.898	65
1.0	3.16	−0.934	72
1.5	3.12	−0.944	75
2.0	3.11	−0.950	72

Polarograms of 1.0 mM aquopentamminechromium(III) were recorded at various concentrations of gelatin and LEO in 0.1 M acetate buffers containing 0.9 M ammonium chloride; examples are given in Table IV. The increase in the concentration of gealtin shifts the half-wave potential to more negative potentials. Current-time curves during the life of a mercury drop, which were recorded at −0.94 V. vs. SCE under the same conditions as in Table IV, are reproduced in Fig. 2. In this measurement, the first mercury drop after the initiation of electrolysis was used.[12] The *i-t* curve obtained in the presence of 2×10^{-6} M LEO is nearly the same as that obtained without a maximum suppressor, whereas the presence of gelatin decreases the current to a great extent. Current-time curves were also recorded at various potentials and at various concentrations of gelatin and LEO. The results showed that the addition of 2×10^{-6} M LEO gives satisfactory *i-t* curves. In the absence of a maximum suppressor, however, no satisfactory *i-t* curves were obtained at −1.2 V. vs. SCE.

TABLE IV. EFFECT OF SURFACE ACTIVE SUBSTANCE ON THE POLAROGRAM OF 1.0 M $[Cr(H_2O)(NH_3)_5](ClO_4)_3$ IN SOLUTIONS CONTAINING 0.1 M ACETATE BUFFER AND 0.9 M NH_4Cl

Surface active substance	i_d μ amp.	$E_{1/2}$ V. vs. SCE	Slope of log-plot mV.
None	3.21	−0.911	72
Gelatin, 0.005%	3.21	−0.934	72
Gelatin, 0.01%	3.10	−0.979	75
LEO, 2×10^{-6} M	3.18	−0.918	71

12) J. Kůta and I. Smoler, *Collection Czech. Chem. Commun.*, **24**, 2208 (1959).

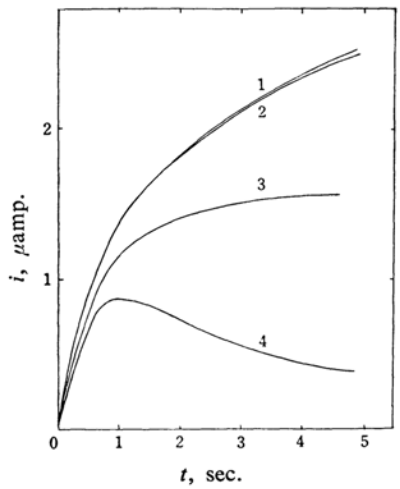

Fig. 2. Current-time curves of 1.0 mM $[Cr(H_2O)(NH_3)_5](ClO_4)_3$ measured at −0.94 V. vs. SCE in solutions containing 0.1 M acetate buffer and 0.9 M NH_4Cl in the absence (curve 1) and in the presence of 2×10^{-6} M LEO (curve 2), 0.005% gelatin (curve 3) and 0.01 % gelatin (curve 4).

Kalousek and a. c. polarograms were recorded to examine the polarographic reversibility of the reduction of the complex. A typical example of the Kalousek polarograms, which was obtained in a solution containing 0.1 M

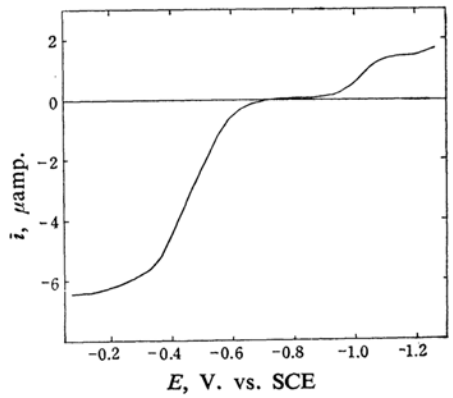

Fig. 3. Kalousek polarogram of 1.0 mM $[Cr(H_2O)(NH_3)_5](ClO_4)_3$ obtained at exchange frequency of 5 cycles/sec. in a solution containing 0.1 M acetate buffer, 0.9 M NH_4Cl and 0.005% gelatin. The potential is set up at −1.2 V. vs. SCE.

acetate auffer, 0.9 M ammonium chloride and 0.005% gelatin, is reproduced in Fig. 3.

Discussion

Aquopentamminechromium(III) gives no well-defined wave in neutral unbuffered solutions because it contains basic ligands and, when reduced, it forms an insoluble film on the surface of the electrode, as has already been reported in the case of the polarographic reduction of hexamminechromium(III).[4,5] In an acid solution, the ammonia molecules that the reduced chromium(II) species liberates are neutralized by hydrogen ions diffusing from the bulk of the solution; consequently, the formation of such an insoluble film is prevented.[4,5] The limiting current of the wave in acid media is diffusion-controlled in every respect; the value of 5.0 kcal./mol. obtained seems appropriate for the activation energy of the diffusion.

The fact that the half-wave potential was almost independent of the hydrogen ion concentration of the solution suggests that the hydrogen ions are not involved in the chemical reaction, if any, preceding the electron transfer (see Table II). Table III shows that the shift of the half-wave potential is due not to an increase in ammonium ion concentration but to an increase in total ionic concentration. It is suggested that no chemical reaction involving ammonium ions takes place prior to the electron transfer.

The reduction of aquopentamminechromium-(III) to chromium(II) species in an acid solution appears to be irreversible in the polarographic sense. A straight log-plot with a reciprocal slope of approximately 70 mV., which is somewhat greater than that expected for a reversible one-electron reduction wave, suggests the irreversible nature of the wave (see Tables II, III and IV). The value of $i_p/(n\bar{i}_d\sqrt{t_d})$, where i_p means the peak current of the a.c. polarogram, $\bar{i}_d$, the average diffusion current of the corresponding d.c. polarogram, and n, the number of electrons involved in the electrode process, represents the degree of polarographic reversibility of the electrode reaction.[13] In Table V, $i_p/(n\bar{i}_d\sqrt{t_d})$ values for the aquopentamminechromium(III) ion and other simple and complex ions are presented. The aquopentamminechromium (III) gives smaller values than that for nickel(II) in a potassium chloride solution, suggesting the complete irreversibility of the reduction of the complex. The irreversibility is supported also by the shape of the Kalousek polarogram (Fig. 3). The increase in exchange frequencies of the on-and-off switch from 5 cycl./sec. to 30 cycl./sec. showed no feature of reversibility.

The instantaneous current at constatnt potential during the life of a mercury drop is given as a function of time,

$$i = k\,t^{x} \qquad (1)$$

where k is a constant. The plot of log i against log t, therefore, should give a straight line with a slope of the value of x. In the case of the reduction of aquopentamminechromium(III), a straight line was obtained only when LEO was added as a maximum suppressor in a concentration of 2×10^{-6} M. The addition of gelatin was found to cause the

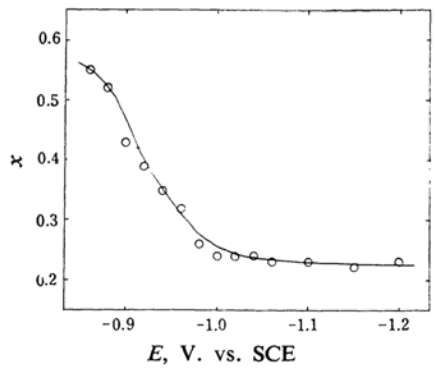

Fig. 4. The values of x in Eq. 1 at varied potentials, measured with 1.0 mM $[Cr(H_2O)(NH_3)_5](ClO_4)_3$ in a solution containing 0.1 M acetate buffer, 0.9 M NH_4Cl and 2×10^{-6} M LEO.

TABLE V. VALUES OF $i_p/n\bar{i}_d\sqrt{t_d}$

Oxidant	Supporting electrolyte*	$i_p/(n\bar{i}_d\sqrt{t_d})$ ʊ amp^{-1}sec$^{-1/2}$
1.0 mM $[Cr(H_2O)(NH_3)_5](ClO_4)_3$	0.9 M NaCl+0.1 M acetate buffer	3.9
1.0 mM $[Cr(H_2O)(NH_3)_5](ClO_4)_3$	0.9 M NH_4Cl+0.1 M acetate buffer	2.8
1.0 mM $[Cr(NH_3)_6]Cl_3$	0.9 M NH_4Cl+0.1 M acetate buffer	9.2
0.5 mM $Cd(NO_3)_2$	1.0 M KNO_3	202
0.5 mM $Zn(NO_3)_2$	1.0 M $NaClO_4$	57.6
0.5 mM $Ni(NO_3)_2$	0.1 M KCl	7.2

* All solutions contain 0.005% gelatin.

13) M. Senda, M. Senda and I. Tachi, *J. Electrochem. Soc. Japan (Denki Kagaku)*, 27, 83 (1959).

shape of the current-time curve to deteriorate and to give no linear plot of log i vs. log t. The values of x at various potentials, therefore, were determined in the presence of 2×10^{-6} M LEO. The plot of x vs. potential, as shown in Fig 4, varies from 0.55 to 0.23 with increasing negative potentials, suggesting that the electrode process is kinetic in nature at the foot of the wave, but diffusion-controlled at the limiting current plateau.

The results obtained from the d. c., the a. c. and the Kalousek polarograms and the current-time curves indicate that the reduction of aquopentamminechromium(III) to chromium-(II) proceeds irreversibly at the dropping mercury electrode and that its overall electrode process in an acid solution may be written as follows:

$$Cr(H_2O)(NH_3)_5^{3+} + e \rightarrow Cr(H_2O)(NH_3)_5^{2+} \quad (2)$$

$$Cr(H_2O)(NH_3)_5^{2+} + n\,H_2O + n\,H^+ \rightarrow Cr(H_2O)_{n+1}(NH_3)_{5-n}^{2+} + n\,NH_4^+ \quad (3)$$

When the electrode reaction is totally irreversible, the following equation holds:[14]

$$\ln\frac{\bar{i}_d-\bar{i}}{\bar{i}} = \ln\{1.13(\Lambda\sqrt{t_d})^{-1}\}+\frac{\alpha nF}{RT}(E-E_{1/2}^{r})$$

$$\Lambda=\frac{k_s f_O^{\beta} f_R^{\alpha}}{(D_O^{\beta}D_R^{\alpha})^{1/2}} \qquad (\alpha+\beta=1) \quad (4)$$

where $E_{1/2}^{r}$ indicates the reversible half-wave potential, k_s, the standard rate constant, α, the transfer coefficient, and f_O and f_R, the activity coefficients of oxidized and reduced forms respectively. If f_O and f_R are assumed to be unity and D_O and D_R, equal to D, Eq. 4 can be simplified. When $\bar{i}$ equals $\bar{i}_d/2$, the equation,

$$\log k_f^{\circ} = \log 1.13 - \frac{1}{2}\log t_d + \frac{1}{2}\log D + \frac{2.303RT}{\alpha nF}E_{1/2} \quad (5)$$

is obtained, where k_f° indicates the forward rate constant at 0 V. In this paper, a saturated calomel electrode at the observed temperature was used for the reference.

The diffusion coefficients were obtained from the limiting currents with the aid of the Ilkovič equation. The values of log k_f° were determined at various temperatures, as Table VI shows. With these values, the heat of activation of the electrode process, $\Delta H^{\neq}_{E=0}$, was calculated to be 40.2 kcal./mol., being referred to the SCE.[15]

Table VI. Log k_f°'s of the reduction of $[Cr(H_2O)(NH_3)_5]^{3+}$ at various temperatures in solutions containing 0.1 M acetate buffer, 0.9 M NH_4Cl and 2×10^{-6} M LEO

Temp. °C	$E_{1/2}$ V. vs. SCE	α	$D^{1/2}\times10^3$ cm. $sec^{-1/2}$	t_d sec.	log k_f°
0.4	−0.972	0.89	1.89	4.40	−18.9
10.0	−0.951	0.88	2.19	4.34	−17.8
17.0	−0.935	0.85	2.46	4.23	−16.6
25.0	−0.918	0.83	2.83	4.12	−15.7
35.0	−0.893	0.83	3.25	4.02	−14.8

Although all experimental results support the irreversible electrode process of reaction 2 and although this irreversibilty seems to be attributed to the electronic rearrangement of aquopentamminechromium(III) from t_{2g}^3 to $e_g t_{2g}^2$,[16] there seems to be another possible mechanism. As has been reported in the case of hexamminechromium(III) ions,[5] reaction 2 may proceed reversibly in the polarographic sense, followed by the rapid aquation of the reduced species, aquopentamminechromium(II) ions. This mechanism would also explain the observations in the a. c. and the Kalousek polarograms. At the present moment, however, it seems not to be possible to decide by which mechanism the electrode reaction proceeds at the dropping mercury electrode.

Summary

The reduction of aquopentamminechromium-(III) ions at the dropping mercury electrode has been studied in acid solutions by means of the measurement of the direct current, the alternating current and the Kalousek polarograms and the current-time curves. The d. c. polarogram gives a well-defined wave corresponding to the one-electron reduction of chromium(III) to chromium(II). All polarograms, including the Kalousek ones, indicate the irreversibility of the reduction of aquopentamminechromium(III) ions. The heterogeneous rate constants at 0 V. vs. SCE at various temperatures have been presented, and the possible mechanisms for the electrode process have been discussed.

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14) H. Matsuda, *Z. Elektrochem.*, **61**, 489 (1957); **62**, 977 (1958).
15) R. Tamamushi, *Review of Polarography*, **10**, 1 (1962).
16) A. A. Vlček, *Discussions Faraday Soc.*, **26**, 164 (1958).