Reduction of Hexamminechromium(III) Ions at the Dropping Mercury Electrode

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(Received February 20, 1963)

It has been found that hexamminechromium(III) ions give no well-defined polarographic wave in unbuffered neutral solutions[1], but that, in acetate buffer solutions, they give a two-step wave, the first a well-defined one-electron reduction wave and the second a two-electron reduction wave[2,3]. The previous paper[2] also demonstrated that the first well-defined wave appears only when the solution contains sufficient hydrogen ions to neutralize the six ammonia molecules that the reduced chromium(II) species liberates.

Friend and Smith[3] observed the half-wave potential of the first wave at -0.83 to -0.84 V. versus a saturated calomel electrode and presumed a reduction mechanism similar to that of hexamminecobalt(III) ions, i. e., an irreversible electron transfer followed by hydrolysis of the divalent species.

Recently, Ichniowski and Clifford[4] investigated the polarographic behavior of hexamminechromium(III) in Divers' liquids and reported the half-wave potential to be -0.972 V. versus the mercury pool anode. From their experimental results, including the slope of the log-plot, they concluded that the electrode process is a reversible one. These results apparently contradict those obtained by Friend and Smith, but comparison of the two seems unreasonable because of the different solvents and reference electrodes used.

In this paper, extensive studies of the nature of the one-electron reduction wave of hexamminechromium(III) ions in aqueous solutions, both neutral and acid, are presented.

Experimental

Hexamminechromium(III) chloride was prepared according to the method of Mori[5]; the chromium and nitrogen contents were determined by the usual methods.

Found: Cr, 19.74%; N, 31.5%. Calcd. for $[Cr(NH_3)_6]Cl_3$: Cr, 19.96%; N, 32.2%.

As the complex is sensitive to light and not very stable in an aqueous solution[6], precautions were taken when it was used. All other chemicals used were of guaranteed reagent grade.

Direct current (d. c.) polarograms were recorded with a Yanagimoto Model PB-4 pen-recording polarograph. A Yanagimoto Y-GR 2 Galvarecorder with an automatic voltage scanner was used for recording alternating current (a. c.) polarograms. The Kalousek circuit used was the same as that

TABLE I. CHARACTERISTICS OF THE DROPPING MERCURY ELECTRODES AT -0.5 V. VS. SCE AND AT 55 cm. OF THE MERCURY HEIGHT

	Rate of flow of mercury, m mg./sec.	Drop time t_d, sec.
Electrode A*	1.92	4.72
Electrode B**	2.11	4.22

* Measured in deaerated solution containing 0.4 M NH_4Cl, 0.5 M KCl, 0.1 M acetate buffer and 0.005% gelatin.

** Measured in deaerated solution containing 1 M NH_4Cl and 0.005% gelatin.

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

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[6] D. Jørgensen and J. Bjerrum, *Acta Chem. Scand.*, 12, 1047 (1958).

described by Tanaka, Tamamushi and Takahashi[7]. The current-time curves were measured with an apparatus similar to that reported by Tamamushi, Momiyama and Tanaka[8].

The characteristics of the dropping mercury electrodes employed in this study are given in Table I. A saturated calomel electrode (SCE) with a large surface area served as the reference electrode. All measurements were carried out at 25°C unless otherwise stated. All the polarograms presented in this paper have been corrected for the residual current. The half-wave potentials and the log-plots are given after the correction for the *iR*-drop across the electrolysis cell.

Results

The current-potential curves of hexammine-chromium(III) ions, in both neutral and acid media, are given in Fig. 1. The nature of the wave in neutral media was investigated in a 0.1 M potassium chloride solution. Polarograms

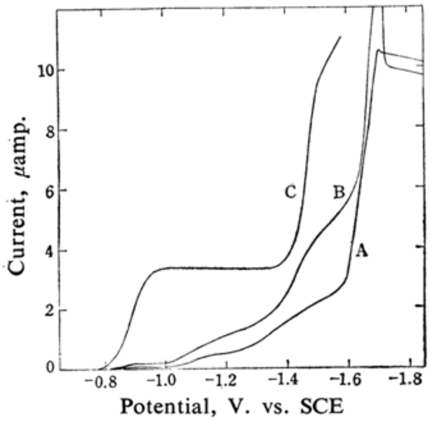

Fig. 1. Polarograms of 1 mM $[Cr(NH_3)_6]Cl_3$, in 0.1 M KCl (A), 0.1 M $NaClO_4$ (B) and in 0.1 M acetate buffer of pH 4.7 (C), in the presence of 0.005% gelatin.

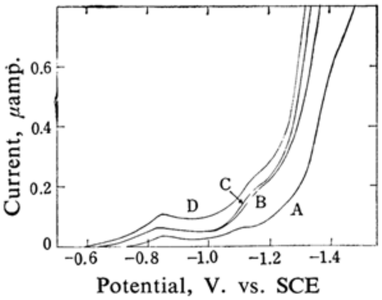

Fig. 2. Polarograms of 0.25 mM (A), 0.5 mM (B), 1 mM (C) and 5 mM (D) of $[Cr(NH_3)_6]\cdot Cl_3$ in 0.1 M KCl.

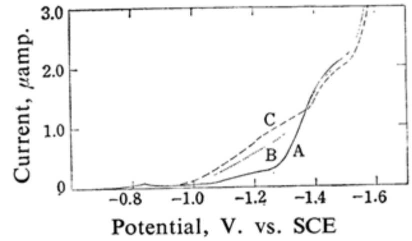

Fig. 3. Polarograms of 1 mM $[Cr(NH_3)_6]Cl_3$ in 0.1 M KCl in the absence (A) and in the presence of 0.001% (B) and 0.005% (C) of gelatin.

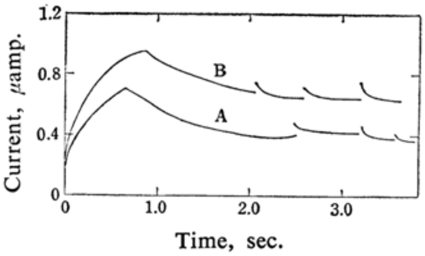

Fig. 4. Current-time curves during the life of a mercury drop measured at −1.25 V. (A) and −1.30 V. (B) in 0.1 M KCl.

TABLE II. EFFECT OF THE HEIGHT OF MERCURY RESERVOIR ON THE LIMITING CURRENT OF 0.5 mM $[Cr(NH_3)_6]Cl_3$

Supporting electrolyte: 0.1 M acetate buffer $+0.4$ M $NH_4Cl+0.5$ M $KCl+0.005\%$ gelatin (pH 4.9)

Electrode: A

h_{corr}* cm.	$\bar{i}_{-1.2}$**$/\sqrt{h_{corr}}$ μ amp. $cm^{-1/2}$
63.4	0.260
53.4	0.256
48.4	0.254
43.4	0.254
38.4	0.252

* Height of mercury reservoir corrected for the back pressure

** Current at −1.2 V. vs. SCE.

TABLE III. EFFECT OF GELATIN ON THE POLAROGRAM OF 1 mM $[Cr(NH_3)_6]Cl_3$ IN ACID MEDIA

Concn. of gelatin %	$\bar{i}_d$, μ amp.	$E_{1/2}$ V. vs. SCE	Slope of log-plot mV.
A. In 0.1 M acetate buffer $+0.9$ M NH_4Cl (pH 4.8) (Electrode B)			
0.002	3.57	-0.96_2	66
0.005	3.57	-0.97_8	65
0.01	3.54	-1.01_6	73
B. In 0.012 N $HCl+0.984$ M NH_4Cl (Electrode A)			
0.001	3.51	-0.96_2	68
0.005	3.51	-0.98_3	68
0.01	3.47	−1.04	79

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[7] N. Tanaka, R. Tamamushi and A. Takahashi, *Collection Czech. Chem. Commun.*, **25**, 3016 (1960).

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TABLE IV. EFFECT OF IONIC STRENGTH AND SUPPORTING ELECTROLYTE ON THE POLAROGRAM OF HEXAMMINECHROMIUM(III) IN SOLUTIONS CONTAINING 0.01 N ACID AND 0.005% GELATIN

Ionic strength	NH_4ClO_4			NH_4Cl			$(NH_4)_2SO_4$			$BaCl_2$		
	I*	$E_{1/2}$, V. vs. SCE	Slope** mV.	I*,	$E_{1/2}$, V. vs. SCE	Slope** mV.	I*	$E_{1/2}$, V. vs. SCE	Slope** mV.	I*	$E_{1/2}$, V. vs. SCE	Slope** mV.
0.01				1.81	−0.81							
0.02				1.83	-0.81_5							
0.05				1.85	−0.84		1.62	−0.86				
0.1	1.83	-0.88_3	59 (51)	1.82	-0.87_0	61 (52)	1.62 (1.62_5)	-0.88_5	59 (53)	1.78 (1.79)	-0.88_3	62 (57)
0.2	1.84	-0.91_5	64 (51)	1.82	-0.91_6	61 (53)	1.60 (1.61)	-0.91_7	59	1.78 (1.79_5)	-0.90_7	63
0.4				1.82	-0.94_5	65	1.59 (1.62)	-0.95_4	61			
1.0				1.81 (1.80)	-0.98_3	68	1.56 (1.62)	-0.98_5	62	1.74 (1.80)	-0.96_2	68 (64)

The concentration of the complex was 1 mM when $\mu \geq 0.1$. When $\mu < 0.1$ smaller concentrations were used to prevent the migration current.

* Diffusion current constant. The value in parentheses is that corrected for the viscosity according to Eq. 5.

** Slope of log-plot. The value in parentheses is that of the upper part of the plot corresponding to the part of the wave at more negative potentials.

obtained at various concentrations of the complex are shown in Fig. 2. No linear relation was found between the concentration and the current. The plots of log h (mercury height) versus log $\bar{i}$ (average current) gave straight lines whose slopes were close to unity at −1.1 V. and −1.2 V. vs. SCE. In Fig. 3, the effect of gelatin on the current-potential curve of hexamminechromium(III) ions in a 0.1 M potassium chloride solution is shown. The current-time curves during the life of a mercury drop were measured at various potentials; those measured at −1.25 V. and −1.30 V. are reproduced in Fig. 4.

In acetic acid-sodium acetate buffer solutions, well-developed waves were observed (see C in Fig. 1). The limiting current was proportional to the concentration of the complex up to 5 mM and to the square root of the height of the mercury reservoir as seen in Table II. No well-defined wave was obtained in the absence of gelatin, while in the presence of gelatin the shape of the wave was affected considerably by the concentration of gelatin. Table III indicates a parallel shift of the wave toward negative potentials observed at lower gelatin concentrations. Diffusion current constants, half-wave potentials, and slopes of the log-plots obtained in various supporting electrolytes and at varied ionic strength are given in Table IV. Measurements were also made at various concentrations of ammonium and

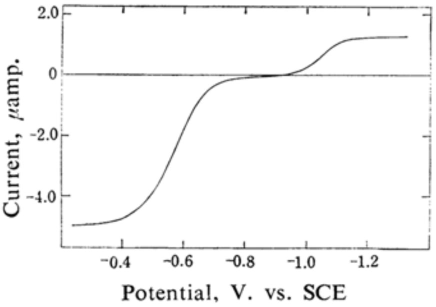

Fig. 5. A Kalousek polarogram of 0.7 mM $[Cr(NH_3)_6]Cl_3$ in 0.1 M acetate buffer +0.9 M NH_4Cl+0.002% gelatin (pH 4.7). The constant potential was set at −1.30 V. vs. SCE.

TABLE V. EFFECT OF AMMONIUM ION ON THE POLAROGRAM OF 1mM $[Cr(NH_3)_6]Cl_3$, IN 0.1 M ACETATE BUFFER+0.005% GELATIN (pH 4.9) AT IONIC STRENGTH 1.0 (KCl)

Concn. of NH_4Cl, M	$E_{1/2}$ V. vs. SCE	Slope of log-plot, mV.
0	-0.97_0	67
0.10	-0.97_0	70
0.40	-0.96_8	66
0.90	-0.97_0	67

TABLE VI. EFFECT OF pH ON THE POLAROGRAM OF 1 mM $[Cr(NH_3)_6]Cl_3$ IN 0.4 M NH_4Cl+ 0.005% GELATIN AT IONIC STRENGTH 1.0 (KCl)

pH or acid concn.	$E_{1/2}$ V. vs. SCE	Slope of log-plot, mV.
pH 5.45*	-0.97_2	64
pH 4.83*	-0.97_7	65
pH 4.51*	-0.97_7	65
pH 3.91*	-0.98_1	64
[HCl]=0.012 N	-0.98_3	68
[HCl]=0.024 N	-0.98_7	67

* pH was adjusted with the acetate buffer of 0.1 M in acetate.

TABLE VII. EFFECT OF TEMPERATURE ON THE POLAROGRAM OF 1 mM $[Cr(NH_3)_6]Cl_3$ IN 0.1 M ACETATE BUFFER + 0.9 M NH_4Cl + 0.005% GELATIN (pH 4.56)*

Temp. °C	i_d μ amp.	$E_{1/2}$, V. vs. SCE	Slope of log-plot, mV.	$2.303\frac{RT}{nF}$ mV.
0.5	2.45	-1.02_0	61	54.3
15.0	3.15	-0.99_5	65	57.2
25.0	3.59	-0.97_8	67	59.2
35.0	4.10	-0.96_4	71	61.2

* Electrode B was used.

hydrogen ions at a constant ionic strength of 1.0. The results are presented in Tables V and VI. In Table VII, the results obtained at various temperatures are given.

On the a. c. polarogram, a peak was observed at a little more negative potential than the half-wave potential on the corresponding d. c. polarogram. One of the typical Kalousek polarograms of hexamminechromium(III) ions in an acetate buffer solution is reproduced in Fig. 5, where the anodic wave is clearly separated from the cathodic one.

Discussion

In Unbuffered Neutral Solutions.—In a 0.1 M potassium chloride solution, no well-defined wave of hexamminechromium(III) was observed. Upon the addition of hydrochloric acid, a wave began to appear at −0.89 V.; it attained its full development just when the ratio of the flux of hydrogen ions diffusing toward the electrode to that of the complex ions was equal to six. Further addition of the acid made no essential change in the shape of the developed wave[2]. Hydrogen ions seem to play an essential role in the reduction of hexamminechromium(III) to its divalent state. However, as will be mentioned later, hydrogen ions are considered not to be involved in any chemical reaction prior to the electron transfer; they act rather as a neutralizing agent on the ammonia which the divalent chromium species liberates. In an unbuffered neutral solution, the liberated ammonia will make the solution layer near the electrode surface alkaline; it will also cause the divalent chromium species to precipitate as an insoluble film on the surface of the electrode.

This explanation is supported by the following observations. In a 0.1 M potassium chloride solution, the current in the potential region between −0.6 V. and −1.3 V. was almost independent of the concentration of the complex ions (Fig. 2), and the currents at −1.1 V. and −1.2 V. were nearly proportional to the height of the mercury reservoir. The addition of gelatin increased the current between −1.0 V. and −1.35 V., as can be clearly seen in Fig. 3. In addition, further confirmation was obtained by measuring the current-time curve during the life of a mercury drop. Not only did the instantaneous current reach its highest value in the early life of the drop and then decrease with time, but also several sudden breaks were observed in the current (Fig. 4).

It is, therefore, expected that any reagent that can prevent divalent chromium from precipitating will make the one-electron reduction wave of hexamminechromium(III) appear. Figure 6 shows that the wave of hexamminechromium(III) is nearly complete when 1 mM of disodium dihydrogen ethylenediaminetetraacetate (EDTA) was added to a neutral solution of the complex; the divalent chromium is kept in the solution as its EDTA complex.

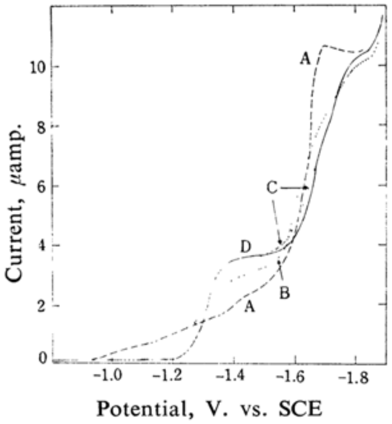

Fig. 6. Polarograms of 1 mM $[Cr(NH_3)_6]Cl_3$ in solutions containing 1 M KCl and 0.005% gelatin without (A) and with 0.52 mM (B), 1.04 mM (C) and 1.56 mM (D) of EDTA. The residual current is not corrected.

That a well-defined one-electron reduction wave does not appear in neutral solutions, though it does in acid media, is a general characteristic of those chromium(III) complexes that have one or more basic ligands, unless the corresponding divalent complexes are stable enough to be maintained in the solution. In fact, the following complex ions gave the one-electron reduction wave in acetate buffer solutions (with 0.005% gelatin added), but not in neutral solutions: $[Cr(H_2O)(NH_3)_5]^{3+}$, $[Cr(en)_3]^{3+}$ (en = ethylenediamine), *trans*-$[Cr(NCS)_2(NH_3)_4]^+$, *trans*-$[Cr(NCS)_2(pn)_2]^+$ (pn = propylenediamine), $[Cr(ox)(en)_2]^+$ (ox = oxalate), and *trans*-$[Cr(NCS)_4(NH_3)_2]^-$. On the other hand, a well-defined reduction wave of chromium(III) to chromium(II) is observed in potassium chloride or sodium chloride solutions for hexathiocyanatochromate(III), tris(dipyridyl)chromium(III)[9] and ethylenediaminetetraacetatochromate(III).

In Acid Media.—Every experimental result indicates that the limiting current of the wave in an acetate buffer solution is controlled by diffusion. Assuming the limiting current to correspond to one-electron reduction, the diffusion coefficient of hexamminechromium(III) ions was calculated to be $0.85\times10^{-5}\,\mathrm{cm^2\,sec^{-1}}$ at 25°C in an air-free solution containing a 0.1 M acetate buffer, 0.9 M ammonium chloride, and 0.005% gelatin. This value appears to be appropriate for this type of ion[10]. From the change in the limiting current with a change in temperature, the activation energy of diffusion was calculated to be 5.0 kcal./mol.

In most cases, the log-plots gave straight lines whose slopes were 60 to 70 mV. (see Tables IV, V and VI). The values are close to 59 mV. which is to be expected in a reversible one-electron reduction at 25°C. However, as is shown in Fig. 5, the shape of the Kalousek polarogram was that of an irreversible wave, and the peak of an a. c. polarogram was much lower than that expected for a reversible wave. It has been pointed out by Senda, Senda and Tachi[11] that the value of $i_p/(n\,\bar{\imath}_d\sqrt{t_d})$ represents the degree of polarographic reversibility, where i_p is the peak current in the a. c. polarogram, $\bar{\imath}_d$, the diffusion current (average) in the corresponding d. c. polarogram, n, the number of electrons involved in the electrode process, and t_d, the drop time. The value for the reduction wave of hexamminechromium(III) ion in acetate buffer solutions was calculated to be 0.009 k℧amp^{-1} sec$^{-1/2}$, which is as small as that for a typical irreversible reduction wave of hydrated nickel(II) ions[12].

The above-mentioned observations can be explained by assuming that the electron transfer between hexamminechromium(III) and the divalent chromium is irreversible with the transfer coefficient close to, or by some chance appearing to be, unity. However, there is the alternative explanation of these observations. The electron transfer process is assumed to proceed reversibly, and the divalent chromium species produced on the surface of the electrode to undergo hydrolysis:

$$[\mathrm{Cr(NH_3)_6}]^{3+}+\mathrm{e}\rightleftarrows[\mathrm{Cr(NH_3)_6}]^{2+} \tag{1}$$

$$[\mathrm{Cr(NH_3)_6}]^{2+}+n\,\mathrm{H_2O}\rightleftarrows[\mathrm{Cr(H_2O)}_n\mathrm{(NH_3)}_{6-n}]^{2+}+n\,\mathrm{NH_3} \tag{2}$$

$$\mathrm{NH_3+H^+}\rightleftarrows\mathrm{NH_4^+} \tag{3}$$

If the forward reaction of Reaction 2 is rapid and the backward reaction is extremely slow, the net electrode process will appear to be irreversible in the a. c. and the Kalousek polarogram. Similar mechanisms, viz., mechanisms involving a rapid electron transfer followed by a chemical reaction, have been reported for the oxidation of ascorbic acid[13] and for the reduction of manganese (II) complexes[14]. In these cases, the half-wave potential is dependent on the rate of the following reaction[14,15], as given by

$$E_{1/2}=E_{1/2}^\circ+\frac{\boldsymbol{RT}}{n\boldsymbol{F}}\ln 0.89\ (k\,t_d)^{1/2} \tag{4}$$

where $E_{1/2}^\circ$ is the half-wave potential with no following reaction and k, the first-order rate constant of the following reaction.

At the moment, it seems impossible to decide, from the experimental results, by which mechanism the reduction of hexamminechromium(III) ions takes place. This is mainly because of insufficient knowledge on the reactivity of chromium(II) complexes.

Table IV shows that in all electrolytes the half-wave potentials shift to more negative potentials with an increase in ionic strength. The shift is much greater than can be expected from the change in the activity coefficients of electroactive species with ionic strength.

The diffusion currents show a slight decrease with increasing ionic strength, but they become almost independent of the ionic strength in the range from 0.1 to 1.0 after the effect of viscosity is corrected for by the equation:

$$I_{corr}=\frac{I}{\sqrt{\eta_{rel}}} \tag{5}$$

where I is the diffusion current constant observed, I_{corr}, that corrected for the viscosity, and η_{rel}, the relative viscosity[16]. The diffusion current constants in ammonium sulfate, however, were found lower by some 10% than those in other electrolytes. This is considered as due to the formation of ion pairs between hexamminechromium(III) ions and anions.

As is seen in Table V, the half-wave potentials vary by no more than a few millivolts when ammonium chloride is replaced by potassium chloride, provided that pH and ionic strength are kept constant. Similarly, the half-wave potential is almost independent of the hydrogen ion concentration of the solution (Table VI). These results indicate definitely

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[14] J. Biernat and J. Koryta, *Collection Czech. Chem. Commun.*, **25**, 38 (1960).

[15] D. M. H. Kern, *J. Am. Chem. Soc.*, **75**, 2473 (1953).

[16] "Landolt-Börnstein, Physikalisch-Chemsiche Tabellen," Verlag von Julius Springer, Berlin (1923).

that there is no chemical reaction involving hydrogen ions, ammonium ions or ammonia preceding the electron transfer.

Summary

The reduction of hexamminechromium(III) ion at the dropping mercury electrode has been studied in neutral and acid aqueous solutions. Hexamminechromium(III) ion gives no well-defined d. c. polarographic wave in an unbuffered neutral solution, whereas in an acid solution it gives a well-defined two-step wave, the first wave corresponding to the reduction of chromium(III) to chromium(II) and the second, to that of chromium(II) to chromium(0).

The first wave of the d. c. polarogram obtained in an acid solution is diffusion-controlled and gives a slope of the log-plot close to that expected for a reversible wave. The a. c. and the Kalousek polarogram, however, are of the irreversible type. No chemical reaction involving hydrogen ions, ammonium ions or ammonia takes place preceding the electron transfer. Considering these results, the following mechanism is temporarily suggested for the reduction of hexamminechromium(III) ions at the dropping mercury electrode:

$$[Cr(NH_3)_6]^{3+} + e \rightleftharpoons [Cr(NH_3)_6]^{2+}$$

$$[Cr(NH_3)_6]^{2+} + n\,H_2O \longrightarrow [Cr(H_2O)_n(NH_3)_{6-n}]^{2+} + n\,NH_3$$

$$NH_3 + H^+ \rightleftharpoons NH_4^+$$

The authors wish to thank the Ministry of Education for the financial support granted for this research.

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