Chronopotentiometry of Hexamminechromium(III) Ions in Acetate Buffer Solutions

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The reduction of hexamminechromium (III) ions at the dropping mercury electrode has been studied by several investigators under a fairly wide range of conditions.[1-6] Its characteristics in aqueous solutions, both neutral and acid, have been extensively discussed in two recent papers from this Laboratory.[2,6] The first paper demonstrated the role of hydrogen ions on the polarographic reduction of hexamminechromium (III), while the second was concerned with the study of the nature of the one-electron reduction wave of the complex in neutral and acid aqueous solutions.

The present chronopotentiometric investigation was undertaken to support the validity of some of the conclusions reported previously,[6] and to obtain a further insight into the mechanism of the electroreduction of hexamminechromium (III) ions.

Experimental

Hexamminechromium (III) chloride was prepared according to the method of Mori;[7] the chromium and nitrogen contents were determined by the usual methods.

Found: Cr, 19.79; N, 31.6. 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,[8] precautions were taken when it was used. All other chemicals were of analytical reagent grade. Redistilled water was used to prepare the solutions of desired concentrations. The contamination of the solutions with surface-active substances was carefully avoided.

A modified apparatus of the constant current supply described in the literature[9] was used for all measurements. A dropping mercury electrode of a long drop time (about 60 sec.) was used for a cathode. A mercury pool electrode with a large surface area served as an anode, which was connected to the cathode compartment of the cell through a salt bridge of low resistance. The characteristics of the dropping mercury electrode used in this study are given in Table I. A potential-time curve was obtained in a small fraction of a drop life, so that the surface area of the mercury drop did not change appreciably during the measurement.[10,11] Potentials of the dropping mercury electrode (working electrode) were measured against a saturated calomel electrode (SCE). The potential difference between the reference and the working electrode was fed through a direct-current preamplifier to a Toshiba oscilloscope, Model ST-1747A. The alternating voltage of audiofrequency from an oscillator, Yokogawa OV-21A, was supplied for the beam modulation. The transition time was

TABLE I. CHARACTERISTICS OF THE DROPPING MERCURY ELECTRODE

Mercury height h cm.	Rate of flow of mercury, m mg. sec,$^{-1}$	Drop time t_d sec.
25	0.116_4	61
70	0.341_6	22

Measured in a deaerated solution containing 0.1 M acetate buffer and 0.9 M NH_4Cl at open circuit.

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

[2] N. Tanaka and G. Satô, *Nature*, 197, 176 (1963).

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

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

[5] A. A. Vlček, "Progress in Inorganic Chemistry," Vol. 5, Interscience Publishers, Inc., New York, N. Y. (1963), p. 362.

[6] N. Tanaka, K. Ebata and G. Satô, This Bulletin, 36, 912 (1963).

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

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

[9] T. Murayama, *Sci. Repts. Tohoku Univ., Ser. I*, 45, 84 (1961).

[10] L. Gierst and A. Juliard, Int. Comm. Electrochem. Therm. Kin., Proceedings of the 2nd Meeting, Tamburini, Milan, 1950, pp. 117 and 229.

[11] L. Gierst and A. Juliard, *J. Phys. Chem.*, 57, 701 (1953).

determined by the method of Kuwana.[12] Dissolved oxygen in the electrolytic solution was removed by bubbling purified nitrogen gas through the solution. All measurements were made at 25±0.1°C.

Results

When a hanging mercury drop electrode was used for a working electrode, no reproducible chronopotentiogram was observed. At a dropping mercury electrode, however, reproducible chronopotentiograms were obtained. Figure 1 shows a typical example of a cathodic chronopotentiogram of hexamminechromium(III) ions obtained in an acetate buffer solution.

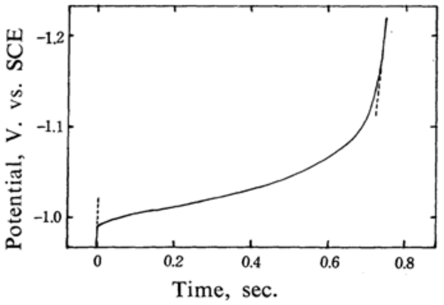

Fig. 1. Chronopotentiogram of 5 mM [Cr$(NH_3)_6]Cl_3$ in 0.1 M acetate buffer + 0.9 M NH_4Cl (pH 4.6) at 25°C. Current density, 1.44_8 mamp. cm^{-2}; surface area of the electrode, 2.93 mm^2. The measurement was started at 55 sec. after the beginning of the growth of a mercury drop.

The effect of the aging of the electrode has been reported by several authors.[9,11,13] Therefore, some preliminary measurements were made with hexamminechromium(III) ions at the slowly dropping mercury electrode. The results given in Table II clearly indicate that no appreciable effect of the aging was observed under the present experimental conditions.

TABLE II. EFFECTS OF THE AGING OF THE SLOWLY DROPPING MFRCURY ELECTRODE ON THE CHRONOPOTENTIOGRAM OF 1 mM $[Cr(NH_3)_6]Cl_3$ OBTAINED IN 0.9 M NH_4Cl + 0.1 M ACETATE BUFFER

θ* sec.	$E_{\tau/4}$ V. vs. SCE	τ sec.	i, mamp.·cm^{-2}	$i\tau^{1/2}$ mamp.·sec$^{1/2}$ cm^{-2}
15	-1.03_3	0.140	0.693	0.259
30	-1.03_4	0.139	0.696	0.259
55	-1.03_4	0.140	0.693	0.259

* Time elapsed since the beginning of the growth of a mercury drop.

The values of $i\tau^{1/2}$, where i is the current density at the polarizable electrode and τ the transition time, were determined at various current densities for the reduction of hexamminechromium(III) ions at a dropping mercury electrode, with the results given in Table III, which shows that the product $i\tau^{1/2}$ is independent of the current density. This clearly indicates that hexamminechromium(III) ions are directly reduced at the electrode without any preceding chemical reactions prior to the electron-transfer process, being in a satisfactory agreement with the previous conclusion obtained in the polarographic study of the same complex.[6]

Measurements were also made at various concentrations of the complex. The results are presented in Table IV. The average value of $i\sqrt{\tau}/C_O^\circ$ obtained from some hundred runs, where C_O° represents the bulk concentration of the complex, was 0.256 mamp. sec$^{1/2}$ cm^{-2}·mM^{-1}. It may be assumed that a theoretical equation derived for a linear diffusion process is applied to the present system without introducing any significant error. According

TABLE III. TRANSITION TIMES FOR THE REDUCTION OF 2 mM $[Cr(NH_3)_6]Cl_3$ AT VARIOUS CURRENT DENSITIES

i mamp.cm^{-2}	τ sec.	$i\tau^{1/2}$, mamp.sec$^{1/2}$cm^{-2}
In 0.1 M acetate buffer + 0.9 M NH_4Cl		
0.443	1.37_0	0.518
0.574	0.801	0.514
0.745	0.475	0.513
0.972	0.282	0.515
1.25_9	0.169	0.518
1.63_9	0.100_2	0.519
2.28_4	0.0515	0.518
2.96_1	0.0302	0.515
4.16_8	0.0153	0.516
In 0.1 M acetate buffer + 0.9 M KCl		
0.476_2	1.15_7	0.512
1.39_0	0.133_2	0.507

TABLE IV. $i\tau^{1/2}/C_O^\circ$ FOR THE REDUCTION OF $[Cr(NH_3)_6]Cl_3$

C_O° mM	i mamp. cm^{-2}	τ sec.	$i\tau^{1/2}/C_O^\circ$ mamp.·sec$^{1/2}$cm^{-2}mM^{-1}
In 0.1 M acetate buffer + 0.9 M NH_4Cl (pH 4.6)			
5.00	1.44_8	0.736	0.249
2.85	1.08_2	0.441	0.252
2.15	1.44_4	0.146_3	0.257
2.00	2.28_4	0.0515	0.259
1.60	0.892	0.211_7	0.256
1.00	0.696	0.139	0.259
0.89	0.499	0.215_6	0.260
In 0.1 M acetate buffer + 0.9 M KCl (pH 4.6)			
2.00	0.476_2	1.15_7	0.256
2.00	1.39_0	0.133_2	0.254

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[12] C. D. Russell and J. M. Peterson, *J. Electroanal. Chem.*, **5**, 467 (1963).

[13] T. Nagai, *J. Chem. Soc. Japan, Pure Chem. Sec.* (*Nippon Kagaku Zasshi*) **81**, 93 (1960).

to Sand[14] the value of $i\sqrt{\tau}/C_O^\circ$ for a linear diffusion is given by:

$$\frac{i\sqrt{\tau}}{C_O^\circ}=\frac{\sqrt{\pi}}{2}\,nF\sqrt{D_O}=85.51\,n\sqrt{D_O} \qquad (1)$$

where F is the Faraday; C_O°, the bulk concentration expressed in mM; D_O, the diffusion coefficient expressed in $cm^2\,sec^{-1}$ and n the number of electrons involved in the electroreduction. Introducing one for n and $0.85\times 10^{-5}\,cm^2\,sec^{-1}$ for D_O, which was determined polarographically, the theoretical value of $i\sqrt{\tau}/C_O^\circ$ is calculated to be 0.250 mamp.·$sec^{1/2}\,cm^{-2}\,mM^{-1}$. This value is in a good agreement with the experimental one.

The potential at $t=\tau/4\,(E_{\tau/4})$ and the potential at $t=0$ $(E_{t=0})$ were dependent on the current density and the concentration of the complex; these potentials change linearly with log i and log C_O° as are shown in Figs. 2 and 3.

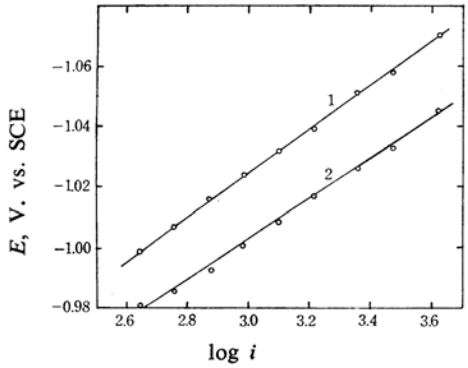

Fig. 2. Relations of (1) $E_{\tau/4}$ with log i and (2) $E_{t=0}$ with log i of 2 mM $[Cr(NH_3)_6]Cl_3$ obtained in 0.1 M acetate buffer + 0.9 M NH_4Cl (pH 4.6). Ohmic drop is corrected.

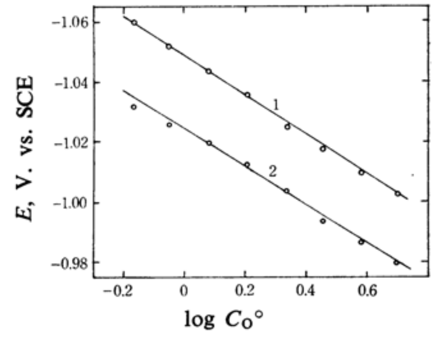

Fig. 3. Relations of (1) $E_{\tau/4}$ with log C_O° and (2) $E_{t=0}$ with log C_O° obtained at various concentrations of $[Cr(NH_3)_6]Cl_3$ in 0.1 M acetate buffer + 0.9 M NH_4Cl (pH4.6) at current density of 1.08_2 mamp. cm^{-2}.

Figure 4 shows the plots of the logarithmic functions of time against the electrode potential.[15] A plot of log $\{(\sqrt{\tau}-\sqrt{t})/\sqrt{t}\}$ versus E yields no straight line, but that of log $(\sqrt{\tau}-\sqrt{t})$ versus E yields a straight line with a reciprocal slope of 76 mV.

An example of the potential-time curves obtained by the electrolysis at a constant cathodic current followed by the anodic oxidation at the constant anodic current of

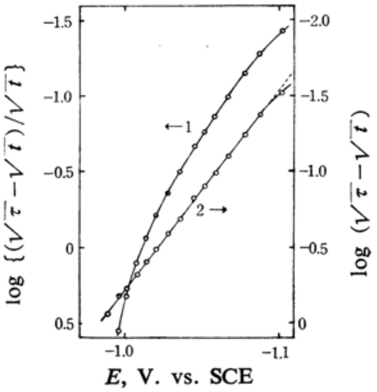

Fig. 4. Relations of (1) log $\{(\sqrt{\tau}-\sqrt{t})/\sqrt{t}\}$ vs. E and (2) log $(\sqrt{\tau}-\sqrt{t})$ vs. E obtained with 5 mM $[Cr(NH_3)_6]Cl_3$ in 0.1 M acetate buffer + 0.9 M NH_4Cl (pH 4.6).

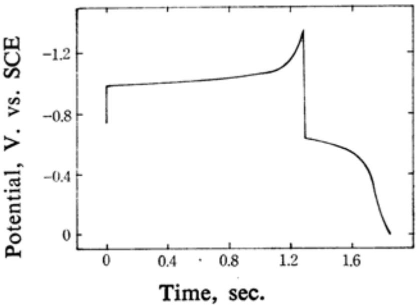

Fig. 5. Chronopotentiogram for the reduction and subsequent reoxidation of 2 mM $[Cr(NH_3)_6]Cl_3$ in 0.1 M acetate buffer + 0.9 M NH_4Cl (pH 4.6) at current density of 0.470_6 mamp. cm^{-2}.

TABLE V. TRANSITION TIMES FOR THE REOXIDATION PROCESS OF 2 mM $[Cr(NH_3)_6]Cl_3$ RECORDED IN 0.1 M ACETATE BUFFER + 0.9 M KCl AT CURRENT DENSITY OF 0.461_0 mamp. cm^{-2}

τ_c sec.	τ_a sec.	τ_c/τ_a	$E^c_{t=0}$* V. vs. SCE	$E^a_{t=0}$** V. vs. SCE
1.10	0.36_7	3.0_0	−0.98	−0.63
0.99_3	0.33_3	2.9_5		
0.86_6	0.28_3	3.0_6		

* Potential of the cathodic wave at time zero.
** Potential of the anodic wave at time zero.

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[14] H. J. S. Sand, *Phil. Mag.*, 1, 45 (1901).

[15] W. H. Reinmuth, *Anal. Chem.*, 32, 1514 (1960).

the same magnitude with the opposite sign is given in Fig. 5. The cathodic and the anodic potential-time curves are separated by approximately 0.35 V. The ratio τ_c/τ_a determined with 2 mM hexamminechromium(III) ions in an acetate buffer solution is presented in Table V, where τ_c is the transition time for the cathodic process and τ_a, that for the following anodic process. The ratio of τ_c/τ_a fluctuates around 3, the theoretical value that is expected when the reduced species is soluble and the current densities at the forward and the reverse process are equal in magnitude.16)

Discussion

The mechanism of electroreduction of the heamminechromium(III) ions in acid buffer solutions has been reported as follows;6)

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

$$[Cr(NH_3)_6]^{2+} + n\,H_3O^+ \rightarrow [Cr(H_2O)_n(NH_3)_{6-n}]^{2+} + n\,NH_4^+ \qquad (3)$$

It may be concluded from the d. c. polarographic and the chronopotentiometric investigations that hexamminechromium(III) ions are directly reduced at the dropping mercury electrode without any preceding chemical reaction prior to the electron-transfer process. The Kalousek polarograms6) and the current-reversal chronopotentiograms indicate that the overall process of the reduction of hexamminechromium(III) to chromium(II) proceeds irreversibly at the dropping mercury electrode:

$$[Cr(NH_3)_6]^{3+} + e + n\,H_3O^+ \rightarrow [Cr(H_2O)_n(NH_3)_{6-n}]^{2+} + n\,NH_4^+ \qquad (4)$$

Two mechanisms may be considered. One is that, although the electron-transfer process given by Eq. 2 proceeds reversibly, the net electrode process appears to be irreversible on account of the extreme rapidity of the following chemical reactions, while the other is that the electron-transfer process itself proceeds irreversibly.

The characteristics of the chronopotentiogram for the first17-19) and the second20,21) mechanism have already been analyzed theoretically, which are given in Table VI.15)

In the reduction of hexamminechromium(III), the plot of log $(\sqrt{\tau}-\sqrt{t})$ vs. E yields a straight line, whose slope is somewhat greater than 59 mV., a theoretical value expected for a reversible one-electron reduction at 25°C. This suggests the possibility of the electron-transfer process itself being irreversible. According to the results of theoretical analysis given in Table VI, the slope of the plot should be equal to the constant $\boldsymbol{RT}/\alpha n\boldsymbol{F}$ independently of the concentration of the hexamminechromium(III) and the current density i. However, as is seen in Table VII, the slopes of the plots obtained experimentally vary with the transition time, and increase with increasing current density at the same concentration of the complex. This fact can not be explained satisfactorily by the mechanism which assumes the totally irreversible electron-transfer process.

Recently, Gellings22) studied the characteristics of the current-potential curves for the electrode process of kinetic nature, where he proposed a method by which the potential can be expressed as a function of the current by the application of Lagrange's theorem. This method was applied in this study to a general treatment for the chronopotentiometric potential-time curve for the process represented by the following scheme:

TABLE VI. DIAGNOSTIC CRITERIA FOR KINETIC SCHEMES

No.	Kinetic schem	Linear ln-plot	Slope of ln-plot	$\dfrac{\partial E_{\tau/4}}{\partial \ln i}$	$\dfrac{\partial E_{\tau/4}}{\partial \ln C_O^\circ}$	$\dfrac{\tau_a}{\tau_c}$
1	$O\rightleftharpoons R\rightarrow Y$	$\sqrt{\tau}-\sqrt{t}$	$\boldsymbol{RT}/n\boldsymbol{F}$	$-\boldsymbol{RT}/n\boldsymbol{F}$	$\boldsymbol{RT}/n\boldsymbol{F}$	0 or 1/3
2	$O\rightarrow R$	$\sqrt{\tau}-\sqrt{t}$	$\boldsymbol{RT}/\alpha n\boldsymbol{F}$	$-\boldsymbol{RT}/\alpha n\boldsymbol{F}$	$\boldsymbol{RT}/\alpha n\boldsymbol{F}$	1/3 or 0

Potential relations for kinetic schemes

1 $$E=E_e^\circ+\frac{\boldsymbol{RT}}{n\boldsymbol{F}}\ln(\sqrt{\tau}-\sqrt{t})+\frac{\boldsymbol{RT}}{2n\boldsymbol{F}}\ln\frac{\sigma_f{}^*}{\pi}$$

2 $$E=E_e^\circ+\frac{\boldsymbol{RT}}{\alpha n\boldsymbol{F}}\ln(\sqrt{\tau}-\sqrt{t})+\frac{\boldsymbol{RT}}{\alpha n\boldsymbol{F}}\ln\frac{2k_s{}^{**}}{\sqrt{\pi D}}$$

* σ_f: Rate constant for a following chemical reaction.

** k_s: Rate constant for electron-transfer at $E=E_e^\circ$.

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16) A. C. Testa and W. H. Reinmuth, *Anal. Chem.*, 32, 1512 (1960).

17) P. Delahay, C. C. Mattax and T. Berzins, *J. Am. Chem. Soc.*, 76, 5319 (1954).

18) W. K. Snead and A. E. Remick, ibid., 79, 6121 (1957).

19) W. H. Reinmuth and A. C. Testa, *Anal. Chem.*, 32, 1518 (1960).

20) P. Delahay and T. Berzins, *J. Am. Chem. Soc.*, 75, 2486 (1953).

21) P. Delahay and G. Mamantov, *Anal. Chem.*, 27, 478 (1955).

22) P. J. Gellings, *Z. Elektrochem.*, 66, 477, 481 (1962).

TABLE VII. KINETIC PARAMETERS OF HEXAMMINECHROMIUM(III) OBTAINED FROM THE CHRONOPOTENTIOMETRIC MEASUREMENTS

C_O° mM	i, mamp.· cm^{-2}	τ sec.	$E_{t=0}$* V. vs. SCE	log-plot slope, mV.
2.00	1.63_9	0.100_0	-1.01_7	85
2.85	1.08_2	0.439	-0.99_1	80
5.00	1.44_8	0.736	-0.98_4	76
2.00	0.44_3	1.36_9	-0.98_0	73

* Corrected for ohmic drop across the electrolytic cell.

$$\mathrm{O}+n\mathrm{e} \rightleftharpoons \mathrm{R} \tag{5}$$

$$\mathrm{R} \underset{\sigma_b}{\overset{\sigma_f}{\rightleftharpoons}} \mathrm{Y} \quad (\sigma_f/\sigma_b \gg 1) \tag{6}$$

where O is a reducible substance, R its reduction product, Y a substance which is neither reduced nor oxidized at the potentials where the reduction of O occurs and σ_f and σ_b are the rate constants of the following chemical reaction.

When $|i/i_0|$ is less than 2, where i_0 means the exchange current density for the electrochemical reaction given by Eq. 5, i. e., in the case of a reversible electron-transfer, Eq. 7 holds:

$$\psi=\ln\frac{g}{h}+\sum_{n=1}^{\infty} B_n \frac{f^n}{g^{n\beta}h^{n\alpha}} \tag{7}$$

$$\text{with} \quad \psi=\frac{n\boldsymbol{F}}{\boldsymbol{RT}}(E-E_e^\circ),\ f=i/i_0,\ g=C_O/C_O^\circ,$$

$$h=C_R/C_O^\circ \ \text{and}\ B_n=\frac{(-1)^n\Gamma(n\alpha)}{n!\Gamma(n\alpha-n+1)}$$

for which the condition for convergence is:

$$|f\alpha^\alpha\beta^\beta/(g^\beta h^\alpha)|<1$$

In the case of a large current density ($|i/i_0|>2$), i. e., in the case of an irreversible electron-transfer, Eq. 8 is satisfied:

$$-\alpha\psi=\ln\frac{f}{g}+\sum_{n=1}^{\infty} A_n \frac{h^n g^{n\beta/\alpha}}{f^{n(1+\beta/\alpha)}} \tag{8}$$

$$\text{with} \quad A_n=\frac{\Gamma\left(n-\dfrac{n}{\alpha}\right)}{n!\Gamma\left(1-\dfrac{n}{\alpha}\right)}$$

for which the condition for convergence is:

$$|h^\alpha g^\beta/(\alpha^\alpha\beta^\beta f)|<1$$

In Eqs. 7 and 8, α and β represent the transfer coefficients for the cathodic and the anodic process respectively ($\alpha+\beta=1$), C_O and C_R the concentrations of O and R at the electrode surface respectively, C_O° represents the concentration of O in the bulk of the solution, E the potential of cathode at time t, E_e the formal standard potential of the electroactive couple, A_n and B_n are the coefficients in power series$^{22)}$ and Γ is the gamma function. According to Delahay et al.$^{17)}$ the concentrations of O and R at the electrode surface are given as:

$$C_O(0,t)=C_O^\circ-\frac{2i\sqrt{t}}{n\boldsymbol{F}\sqrt{\pi}\sqrt{D_O}} \tag{9}$$

$$C_R(0,t)=\frac{i}{n\boldsymbol{F}\sqrt{D}}\left(\frac{2\sqrt{t}}{\sqrt{\pi}K}+\frac{\mathrm{erf}\sqrt{\sigma_f t}}{\sqrt{\sigma_f}}\right)$$

where K is the equilibrium constant for the reaction given by Eq. 6 ($K\gg1$), D the common value of D_R and D_Y which are assumed to be the same, and erf means the error function. Introducing Eq. 9 into Eqs. 7 and 8, Eqs. 10 and 11 are obtained for a reversible and an irreversible electron-transfer process respectively. In Eqs. 10 and 11, k_s represents the rate constant for the electron-transfer process at $E=E_e^\circ$.

In Eq. 10 the potential at $t=0$ ($E_{t=0}$) becomes definite only when $\sqrt{\sigma_f t}>2$, otherwise

$$\begin{aligned}E=E_e^\circ&+\frac{\boldsymbol{RT}}{n\boldsymbol{F}}\ln\frac{1-\sqrt{t/\tau}}{\dfrac{i}{n\boldsymbol{F}C_O^\circ\sqrt{D}}\left(\dfrac{2\sqrt{t}}{\sqrt{\pi}K}+\dfrac{\mathrm{erf}\sqrt{\sigma_f t}}{\sqrt{\sigma_f}}\right)}\\&+\frac{\boldsymbol{RT}}{n\boldsymbol{F}}\sum_{n=1}^{\infty}B_n\frac{(i/i_0)^n}{(1-\sqrt{t/\tau})^{n\beta}\left[\sqrt{D_O/D}\left(\dfrac{1}{K}\sqrt{t/\tau}+\dfrac{\sqrt{\pi}}{2}\ \dfrac{\mathrm{erf}\sqrt{\sigma_f t}}{\sqrt{\sigma_f\tau}}\right)\right]^{n\alpha}}\end{aligned} \tag{10}$$

(for a reveversible electron-transfer)

$$\begin{aligned}E=E_e^\circ&+\frac{\alpha n\boldsymbol{F}}{\boldsymbol{RT}}\ln\frac{1-\sqrt{t/\tau}}{\dfrac{i}{n\boldsymbol{F}k_sC_O^\circ}}\\&-\frac{\boldsymbol{RT}}{\alpha n\boldsymbol{F}}\sum_{n=1}^{\infty}A_n\frac{(1-\sqrt{t/\tau})^{n\beta/\alpha}\left[\sqrt{D_O/D}\left(\dfrac{1}{K}\sqrt{t/\tau}+\dfrac{\sqrt{\pi}}{2}\ \dfrac{\mathrm{erf}\sqrt{\sigma_f t}}{\sqrt{\sigma_f\tau}}\right)\right]^n}{(i/i_0)^{n(1+\beta/\alpha)}}\end{aligned} \tag{11}$$

(for an irreversible electron-transfer)

becomes infinite, since the value of the error function virtually is equal to unity for an argument larger than 2. When $\sqrt{\sigma_f t} > 2$, the plot of E vs. log $(\sqrt{\tau} - \sqrt{t})$ should yield a straig lhtine whose slope is equal to $2.3\boldsymbol{RT}/\boldsymbol{nF}$. In Eq. 11, on the other hand, $E_{t=0}$ is independent of σ_f, because the additional term (the third term) of the equation becomes zero when t equals zero. Hence, $E_{t=0}$ vs. log i and $E_{t=0}$ vs. log $C_O°$ should yield straight lines whose slopes equal $-2.3\,\boldsymbol{RT}/\alpha n\boldsymbol{F}$ and $2.3\,\boldsymbol{RT}/\alpha n\boldsymbol{F}$ respectively. Finally, in both Eqs. 10 and 11, it is expected that the logarithmic term, log $(\sqrt{\tau} - \sqrt{t})$, varies with potential linearly or curvilinearly depending on the magnitude of the additional term of the equations. This explains the experimental results that the slope of the apparently linear log-plot varied with the transition time. (See Table VII).

The value of $E_{t=0}$ was found to change linearly with log i and with log $C_O°$. If Eq. 11 can be applied, the absolute value of the reciprocal slopes of $E_{t=0}$ vs. log i and $E_{t=0}$ vs. log $C_O°$ should be equal to the constant $2.3\boldsymbol{RT}/\alpha n\boldsymbol{F}$, because the additional term of Eq. 11 approaches zero at $t=0$. In the experiments, the reciprocal slopes of $E_{t=0}$ vs. log i and $E_{t=0}$ vs. log $C_O°$ were found to be -66 mV. and 65 mV. respectively at 25°C, as are seen in Figs. 2 and 3. Thus, every slope of log-plot was somewhat greater than 59 mV., a theoretical value expected for a reversible one-electron reduction at 25°C. As for the potential at $t=0$ ($E_{t=0}$), definite values were obtained, which also support the mechanism given by Eq. 11. Consequently, the irreversibility of the electron-transfer process itself is favorably inferred.

In view of the above-mentioned facts a reasonable conclusion that may be drawn from the available data is that hexamminechromium(III) ions are irreversibly reduced at the dropping mercury electrode without any preceding chemical reactions prior to the more or less irreversible electron-transfer process, followed by the rapid aquation of the reduced species.

Summary

The reduction of hexamminechromium(III) ions at the dropping mercury electrode has been studied chronopotentiometrically in acetate buffer solutions. The electrolysis at constant cathodic current gives a well-defined chronopotentiogram which corresponds to the one-electron reduction of chromium(III) to chromium(II), but the anodic chronopotentiogram which is obtained by the electrolysis at constant anodic current is clearly separated from the cathodic one.

A general treatment for a chronopotentiometric potential-time curve for the electrode process with the following chemical reaction has been developed by the application of Lagrange's theorem. The results indicate that hexamminechromium(III) ions are irreversibly reduced at the dropping mercury electrode without any preceding chemical reactions prior to the more or less irreversible electron-transfer process, followed by the rapid aquation of the reduced species.

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