Polarographic and Coulometric Studies of cis-Dioxalatodiaquochromate(III)

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In a previous paper,[1] the present authors reported on the polarographic behavior of various oxalato complexes of chromium(III) in acidic or neutral aqueous solutions. As for dioxalatodiaquochromate(III), no reduction wave was observed, in acidic solutions, at less negative potentials than the potential of the reduction of hydrogen ions, while a reduction wave was obtained in neutral solutions. In this paper, an extensive study of the reduction of *cis*-dioxalatodiaquochromate(III) in neutral aqueous solutions at the mercury electrode is presented. The mechanism of the reduction process is discussed on the basis of the experimental results obtained by direct current and alternating current polarography, the measurements of Kalousek polarograms and current-time curves, and the controlled potential electrolysis.

Experimental

Materials.—*cis*-Potassium dioxalatodiaquochromate(III) was prepared according to the method of Werner.[2] It was identified as a cis-form, and its chromium and oxalate contents were determined by the procedure given by Palmer.[3]

Found: Cr, 15.18; ox, 53.5. Calcd. for $K[Cr(ox)_2(H_2O)_2]2H_2O$: Cr, 15.33; ox, 51.89%. *cis*-Potassium dioxalatodiaquochromate(III) is stable for a few months in the solid state and for a few hours in solutions, unless it is exposed to light. All the other chemicals used were of a guaranteed reagent grade.

Polarography. — Current-voltage curves were recorded with a pen-recording polarograph, a Yanagimoto Galvarecorder Model PR-2 with an automatic potential scanner. A Yanagimoto Y-GR 2 Galvarecorder was used for recording alternating current (a. c.) polarograms. Kalousek polarograms were recorded with the same circuit as has previously been described.[4] The current-time ($i-t$) curves during the life of a mercury drop were recorded with a Rikadenki ER-J1 recorder equipped with an RLDC-201 preamplifier.

Measurements were made at 25.00 ± 0.05°C unless otherwise stated. The characteristics of the dropping mercury electrode employed in this study are given in Table I. The cell equipment used was the same as has been reported on previously.[5] The potentials were referred to a saturated calomel electrode(SCE). The dissolved oxygen in the solution was removed by bubbling pure nitrogen gas through the solution. The current-potential curves presented in this paper are corrected for the residual current and for the ohmic (iR) drop across the electrolysis cell.

TABLE I. CHARACTERISTICS OF THE DROPPING MERCURY ELECTRODE

	Height of mercury reservoir cm.	Rate of flow of mercury, m mg./sec.	Drop time, t_d sec.
Electrode A*	50	1.499	3.32
Electrode B**	45	1.862	3.25

* Measured in a dearated 1.0 M KNO_3 solution containing 0.005% gelatin.

** Measured in a dearated 1.0 M KCl solution containing 0.005% gelatin.

Coulometry.—Controlled potential electrolysis[6] was carried out with a Yanagimoto automatic potentiostat, Model VE-3. The working electrode was a mercury-pool electrode whose surface area was approximately 20 cm^2. The anode was a platinum spiral electrode which was connected with the electrolytic solution through a salt bridge of potassium chloride. The electrolytic current was recorded with a Yanagimoto pen-recording Galvarecorder, Model GR-103. The electrical circuit of the equipment and the electrolysis cell used were the same as have been described previously by Tanaka et al.[7] The electrolytic solution was stirred by means of a magnetic stirrer and by bubbling pure nitrogen gas through the solution.

Results

The reduction wave of *cis*-dioxalatodiaquochromate(III) in potassium oxalate solutions changed considerably with time and was

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1) N. Tanaka, E. Itabashi and E. Kyuno, This Bulletin, **36**, 917 (1963).

2) A. Werner, W. J. Bowis, A. Hoblik, H. Schwarz and H. Surker, *Ann.*, **406**, 261 (1914).

3) W. G. Palmer, "Experimental Inorganic Chemistry," Cambridge University Press, Cambridge (1954), p. 387.

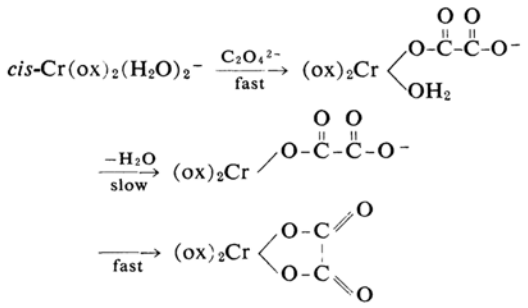
4) N. Tanaka, R. Tamamushi and M. Kodama, This Bulletin, **33**, 14 (1960).

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

6) J. J. Lingane, "Electroanalytical Chemistry," Interscience Publishers, Inc., New York (1958), pp. 450-481.

7) N. Tanaka, T. Nozoe, T. Takamura and S. Kitahara, This Bulletin, **31**, 827 (1958).

affected by the concentration of potassium oxalate. According to Hamm and Perkins,[8] this is due to the reaction of *cis*-dioxalatodiaquochromate(III) with oxalate ions to form trioxalatochromate(III) :



cis-Dioxalatodiaquochromate(III) gives an ill-defined current-potential curve in potassium nitrate solutions, while a well-defined and reproducible reduction wave is observed in potassium chloride or potassium sulfate solutions (see Fig. 1). Therefore, most of the measurements were carried out in potassium chloride solutions.

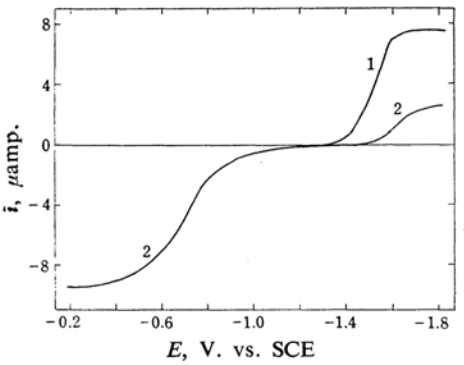


Fig. 1. A direct current polarogram (1) and a Kalousek polarogram (2) of 1.0 mM *cis*-$[Cr(ox)_2(H_2O)_2]^-$ in 0.3 M KCl solutions containing 0.005% gelatin. (Electrode A). For (2), the constant potential was applied at −1.80 V. vs. SCE.

In potassium chloride solutions, the limiting current was proportional to the concentration of the complex up to 2 mM and also to the square root of the effective height of the mercury reservoir. No well-defined wave was obtained in the absence of gelatin. The shape of the reduction wave was affected considerably by the concentration of gelatin. The reduction wave shifted to more negative potentials and its limiting current decreased with an increase in gelatin concentration (Table II).

8) R. E. Hamm and R. H. Perkins, *J. Am. Chem. Soc.*, **77**, 2083 (1955).

Table II. Effect of gelatin on the polarogram of 1.0 mM *cis*-$[Cr(ox)_2(H_2O)_2]^-$ in 0.3 M KCl solutions (electrode B)

Concn. of gelatin %	t_d sec.	$\bar{i}_d$ μamp.	$E_{1/2}$ V. vs. SCE
0	3.25	8.50±0.05	—*
0.001	3.25	8.42	−1.505
0.002	3.24	8.27	−1.509
0.005	3.23	7.89	−1.522
0.01	3.19	7.35	−1.542
0.02	3.15	6.04±0.05	−1.60

* Not determined because of maximum.

Measurements were also made in potassium chloride and potassium sulfate solutions of various ionic strengths. The results obtained are presented in Table III. The effect of the temperature on the reduction wave is shown in Table IV; the temperature coefficient of the limiting current was found to be 1.8%/degree in the range of 0 to 35°C. On the a. c. polarogram a peak was observed at a little more negative potential than the half-wave potential of the corresponding d. c. polarogram. One of the typical Kalousek polarograms of *cis*-dioxalatodiaquochromate(III) in a 0.3 M potassium chloride solution containing 0.005%

Table III. Effect of ionic strength and supporting electrolyte on the polarogram of 1.0 mM *cis*-$[Cr(ox)_2(H_2O)_2]^-$ in solutions containing 0.005% gelatin (electrode A)

Ionic strength	$\bar{i}_d$ μamp.	$E_{1/2}$ V. vs. SCE	Slope of log-plot, mV. Before $E_{1/2}$	After $E_{1/2}$
(A) KCl				
0.08	6.87	-1.54_5	90	90
0.1	7.18	-1.53_4	95	85
0.3	7.33	-1.52_2	103	82
0.6	7.35	-1.51_6	127	80
1.0	7.35	-1.50_9	157	79
(B) K_2SO_4				
0.1	6.15	-1.55_0	88	88
0.3	6.59	-1.52_8	97	86
0.6	6.96	-1.52_2	97	83
1.0	6.99	-1.51_0	105	81

Table IV. Effect of temperature on the polarogram of 1.0 mM *cis*-$[Cr(ox)_2(H_2O)_2]^-$ in 0.3 M KCl solutions containing 0.005% gelatin (electrode A)

Temp. °C	$\bar{i}_d$ μamp.	$E_{1/2}$ V. vs. SCE	Slope of log-plot, mV. Before $E_{1/2}$	After $E_{1/2}$
0.3	4.87	-1.57_0	130	78
5.0	5.37	-1.55_0	123	79
15.0	6.43	-1.54_1	110	80
25.0	7.33	-1.52_2	103	82
34.9	8.21	-1.51_0	95	85

gelatin is reproduced in Fig. 1, where the anodic wave is apparently separated from the cathodic wave. The current-time curves during the life of a mercury drop were recorded at various potentials and at various concentrations of gelatin. Some of the curves are shown in Fig. 2.

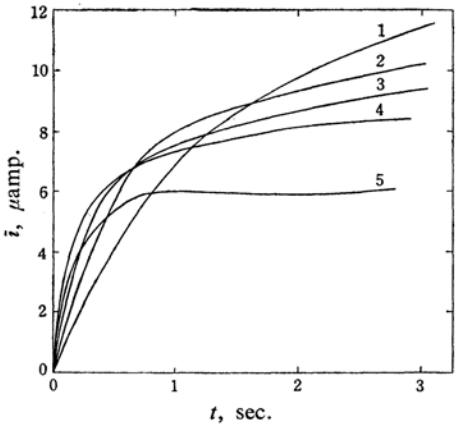


Fig. 2. Current-time curves of 1.0 mM *cis*-$[Cr(ox)_2(H_2O)_2]^-$ measured at −1.75 V. vs. SCE in 0.3 M KCl solutions containing various concentrations of gelatin: (1) 0%; (2) 0.001%; (3) 0.005%; (4) 0.01%; (5) 0.02% gelatin present. (Electrode B).

The number of electrons which are involved in the overall electrode reaction of *cis*-dioxalatodiaquochromate(III) was determined coulometrically by controlled potential electrolysis. The electricity Q (coulombs) required in the controlled potential electrolysis was determined by integrating the recorded current-time curves, with correction being made for the contribution of the residual current. The number of electrons, n, can be calculated from the relation

$$n=\frac{Q}{FN}\times\frac{(\bar{i}_l)_2}{(\bar{i}_l)_1-(\bar{i}_l)_2}$$

where N is the initial amount of *cis*-dioxalatodiaquochromate(III) present in the solution expressed in mole; F, the faraday, and $(\bar{i}_l)_1$ and $(\bar{i}_l)_2$, the limiting currents of the polarograms before and after the electrolysis respectively. The current-voltage curves after the electrolysis were different from those before the electrolysis, as Fig. 3 shows. This seemed due to the increase in the pH of the solution during the course of electrolysis. In the determination of $(\bar{i}_l)_2$, the pH of the solution after the electrolysis was adjusted with hydrochloric acid to be equal to that of the initial solution. The controlled potential electrolysis of *cis*-dioxalatodiaquochromate(III) was also complicated by the evolution of hydrogen gas at the cathode which was observed when the

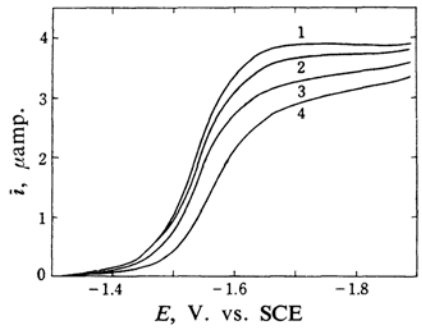


Fig. 3. Current-voltage curves of *cis*-$[Cr(ox)_2(H_2O)_2]^-$ in 0.3 M KCl solutions containing 0.005% gelatin before (1) and after (2-4) the controlled potential electrolysis. (Electrode B). The concentration of the complex and the pH of the initial solution were 0.50 mM and 5.29, respectively. The electrolysis periods and pH of the resulted solutions are: 2, 100 sec. (pH 5.49); 3, 180 sec. (pH 5.50); 4, 300 sec. (pH 5.82).

electrolysis was continued for a longer time. Under these conditions, a shorter period of electrolysis was more favorable for determining the quantity of electricity required for the reduction of *cis*-dioxalatodiaquochromate(III). Therefore, a procedure previously reported[7] was employed to determine the true value of n; the apparent n values obtained from the electrolyses of varied electrolysis periods were plotted against the electrolysis period to estimate the true value of n by the extrapolation of the plot to a zero time (Fig. 4). Fig. 4 indicates that the reduction process of *cis*-dioxalatodiaquochromate(III) at a mercury electrode in potassium chloride solutions is a three-electron process.

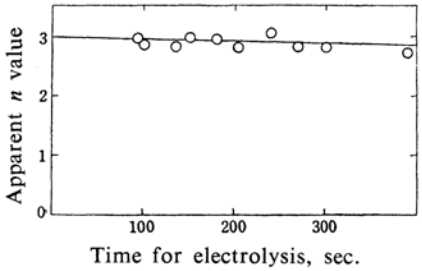


Fig. 4. Plot of apparent number of electrons involved in the reduction of *cis*-$[Cr(ox)_2(H_2O)_2]^-$ as a function of electrolysis period, being measured in 0.3 M KCl solutions containing 0.005% gelatin. The initial concentration of the complex was 0.50 mM. The controlled potential was −1.70 V. vs. SCE.

In order to examine the reduced species of *cis*-dioxalatodiaquochromate(III), current-voltage curves were measured, using a mercury

pool electrode with an area of approximately 1 cm^2 as a working electrode. An apparent anodic wave was observed when the working electrode was polarized at less negative potentials than −0.4 V. vs. SCE immediately after it had been polarized for 5 to 10 min. at the potentials where the reduction of the complex takes place. No anodic current, however, was observed at the DME inserted in the same solution. This result clearly indicated that the reduced substance was contained in the mercury of the electrode. The conventional chemical analysis of the mercury which had been used as the cathode in the electrolysis also showed the presence of chromium.

Discussion

The experimental results indicate that the limiting current of *cis*-dioxalatodiaquochromate(III) in 0.3 M potassium chloride solutions containing 0.005% gelatin is diffusion-controlled. The diffusion coefficient is calculated to be 6.0×10^{-6} cm^2 sec^{-1} at 25°C by using the Ilkovič equation under the assumption that the number of electrons is equal to three. This value seems reasonable when it is compared with those of analogous complex ions, such as hexamminechromium(III) (8.5×10^{-6} cm^2 sec^{-1})[5] and aqopentamminechromium(III) (8.0×10^{-6} cm^2 sec^{-1}).[9]

The alternating current and the Kalousek polarograms suggest that the reduction process of *cis*-dioxalatodiaquochromate(III) in neutral solutions is totally irreversible in the polarographic sense. The relation between $\log\{\bar{i}/(\bar{i}_d-\bar{i})\}$ and the electrode potential, E, however, does not give a straight line. This complication makes the theoretical analysis of the current-potential curve less feasible.

The decrease in the limiting current with the decrease in the ionic strength of potassium chloride solutions is due to the migration effect, because *cis*-dioxalatodiaquochromate(III) is an anion. The potentials of the reduction wave are also dependent on the ionic strength of the solution; the half-wave potential shifts to more negative potentials as the ionic strength decreases (Table III). This can be explained, at least qualitatively, by considering the effect of the diffuse double layer on the irreversible reduction process.

As has been mentioned above, the shape of the reduction wave of *cis*-dioxalatodiaquochromate(III) gradually changes during the course of the controlled potential electrolysis. This is considered due to the increase in the pH of the solution, and is supported by the observation of the change in the reduction wave with the change in the pH of the solution. Figure 5 shows the current-potential curves obtained in 0.3 M potassium chloride solutions containing 0.005% gelatin at three different pH's, the adjustments being made with sodium hydroxide. It has been known that there exist the following equilibria in the aqueous solution of *cis*-dioxalatodiaquochromate(III):[10]

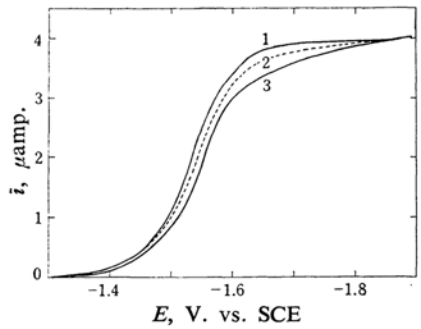


Fig. 5. Current-voltage curves of 0.5 mM *cis*-$[Cr(ox)_2(H_2O)_2]^-$ obtained in 0.3 M KCl solutions of various pH's containing 0.005% gelatin: 1, pH 5.3 (no NaOH added); 2, pH 5.6; 3, pH 5.9. (Electrode B).

$$cis\text{-}[Cr(ox)_2(H_2O)_2]^- \rightleftharpoons cis\text{-}[Cr(OH)(ox)_2(H_2O)]^{2-} + H^+ \quad (pK=6.4)$$

$$cis\text{-}[Cr(OH)(ox)_2(H_2O)]^{2-} \rightleftharpoons cis\text{-}[Cr(OH)_2(ox)_2]^{3-} + H^+ \quad (pK=8.8)$$

The polarographic reduction wave of *cis*-hydroxodioxalatoaquochromate(III) appears at a potential about 200 mV. more negative than that of *cis*-dioxalatodiaquochromate(III).[1] Therefore, the change in the reduction wave of *cis*-dioxalatodiaquochromate(III) in solutions of pH 5~6 is considered to be due to the contribution of *cis*-hydroxodioxalatoaquochromate(III), whose concentration increases with an increasing pH.

The polarographic reduction wave of *cis*-dioxalatodiaquochromate(III) in potassium chloride solutions resembles the hydrogen wave. However, the appearance of a large anodic wave on the Kalousek polarogram (Fig. 1) eliminates the possibility that the reduction wave of *cis*-dioxalatodiaquochromate(III) is due to the discharge of hydrogen ions; hydrogen ions in potassium chloride solutions were found to give no apparent anodic wave on the Kalousek polarogram. The results obtained by controlled potential electrolysis

9) N. Tanaka, Y. Sato, R. Tamamushi and G. Satô, This Bulletin, 36, 1059 (1963).

10) D. M. Grant and R. E. Hamm, *J. Am. Chem. Soc.*, 78, 3006 (1956).

and coulometric analysis suggest that *cis*-dioxalatodiaquochromate(III) is reduced at the mercury electrode to chromium(0), probably to chromium amalgam.

From these results, it can be concluded that the reduction process of *cis*-dioxalatodiaquochromate(III) at the DME in potassium chloride solutions proceeds irreversibly according to this overall reaction;

$$cis\text{-}[Cr(ox)_2(H_2O)_2]^- + 3\ e \rightarrow Cr(0) + 2\ ox^{2-} + 2\ H_2O$$

Summary

The current-voltage curves of *cis*-dioxalatodiaquochromate(III) have been recorded at the dropping mercury electrode in various supporting electrolyte solutions. A well-defined wave with a half-wave potential of -1.52_2 V. vs. SCE was obtained in 0.3 M potassium chloride solutions containing 0.005% gelatin. The limiting current in this case was proved to be diffusion-controlled from its dependence on the effective pressure of mercury on the dropping mercury electrode and from the characteristics of the current-time curve during the life of a mercury drop. The electrode reaction of the complex was found to be irreversible by a study of both the characteristics of the Kalousek polarogram and the relation of $\log\{\bar{i}/(\bar{i}_d-\bar{i})\}$ against E.

The number of electrons involved in the reduction was determined by the controlled-potential coulometric method. The coulometric investigation showed that *cis*-dioxalotodiaquochromate(III) is reduced to the metal at the dropping mercury electrode. This conclusion was also supported by the detection of chromium from the surface of the mercury pool electrode used in the controlled potential electrolysis. The value of the diffusion coefficient of *cis*-dioxalatodiaquochromate(III), calculated for a three-electron reduction, was also reasonable in comparison with those of other chromium(III) complexes.

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