Ionic Charge Effect on the Reduction Potential of Inert-type Metal Complex

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It has been found that there is a relation between the half-wave potentials of polarographic reduction waves and the frequencies of the maxima of the absorption spectra of inert-type metal complexes. In the polarographic study of cobalt(III), chromium(III) and rhodium(III) complexes, Vlček[1] pointed out that the half-wave potentials of the reduction waves of $[MXY_5]$-type complexes were shifted to more positive values with an increasing difference in the position of ligands X and Y in the spectrochemical series, and that the plot of $E_{1/2}$ against $\Delta\nu$ gave a straight line. Maki, Shimura and Tsuchida[2], who studied the polarographic reductions of a number of cobalt(III) complexes, reached the same conclusion.

In the course of our studies of the electrode processes of chromium(III) complexes, we found that the repulsion and attraction between the electrode and the reducible species plays an important role in determining the reduction potential of the species. In contrast with oxalatocobalt(III) complexes[2], the reduction potentials of oxalatochromium(III) complexes were shifted to more negative potentials with an increasing number of oxalates coordinated. In this paper, the study of the polarographic reduction of various oxalatochromium(III) complexes is presented, and the relation of the reduction potential and the ionic charge is discussed.

Experimental

Current-potential curves were obtained with a pen-recording polarograph, Yanagimoto Galvarecorder Model AP-1, with an automatic potential scanner. The dropping mercury electrode used had an *m* value of 1.499 mg./sec. and a drop time, t_d, of 3.32 sec. as measured in an air-free 1 M potassium nitrate solution at -1.70 V. vs. SCE at 50 cm. of the mercury reservoir. The cell equipment used in this study was the same as has been reported

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[1] A. A. Vlček, *Discussions Faraday Soc.*, 26, 164 (1958).

[2] N. Maki, Y. Shimura and R. Tsuchida, This Bulletin, 30, 909 (1957).

previously[3]. Potentials were referred to the saturated calomel electrode (SCE). The current-potential curves presented in this paper are corrected for the residual current and the *iR* drop across the electrolysis cell. All measurements were carried out in a thermostat of 25±0.1°C unless otherwise stated.

$K_3[Cr(ox)_3]\cdot 3H_2O$[4] (ox=oxalate), *cis*-$K[Cr(ox)_2(H_2O)_2]\cdot 2H_2O$[5], *trans*-$K[Cr(ox)_2(H_2O)_2]\cdot 3H_2O$[5], *cis*-$(NH_4)_2[Cr(OH)(ox)_2(H_2O)]\cdot H_2O$[5], and *cis*-$K[Cr(ox)_2(NH_3)_2]\cdot H_2O$[5] were prepared with the procedures given in the literature. $K[Cr(ox)_2en]\cdot KI$ (en=ethylenediamine), $[Cr(ox)(NH_3)_4]I$, and $[Cr(ox)(en)_2]I$ were prepared with newly-devised procedures[6]. The analysis of these compounds gave the following results:

$K[Cr(ox)_2en]\cdot KI$
Calcd.: Cr, 10.52; N, 5.69; C, 14.57%
Found: Cr, 10.49; N, 6.01; C, 15.10%
$[Cr(ox)(NH_3)_4]I$
Calcd.: Cr, 16.83; N, 18.13; C, 7.76%
Found: Cr, 16.59; N, 18.20; C, 7.72%
$[Cr(ox)(en)_2]I$
Calcd.: Cr, 13.34; N, 14.47; C, 18.60%
Found: Cr, 13.88; N, 14.61; C, 18.72%

Results and Discussion

Current-potential curves of the oxalatochromium(III) complexes were obtained in various supporting electrolyte solutions. In acid solutions or acetate buffers only the monooxalato complexes gave a polarographic wave; this is considered to be due to the reduction from chromium(III) to chromium(II). One of the current-potential curves of monooxalatobis(ethylenediamine)chromium(III) is reproduced in Fig. 1. Di- and trioxalato complexes of chromium(III) gave no reduction wave at less negative potentials than the potential of the reduction of hydrogen ions. This is in agreement with the findings of Hamm and Davis[7], who reported that dioxalatodiaquochromate(III) gave no wave in the solution with an ionic strength of 0.3 containing potassium nitrate, nitric acid, 0.1 F potassim oxalate, and 0.005% gelatin.

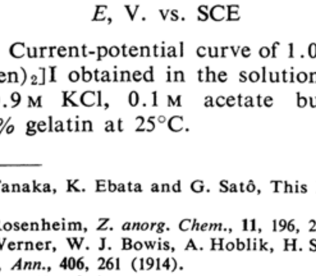

Fig. 1. Current-potential curve of 1.0 mM $[Cr(ox)(en)_2]I$ obtained in the solution containing 0.9 M KCl, 0.1 M acetate buffer and 0.005% gelatin at 25°C.

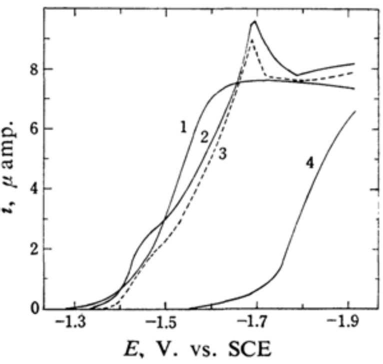

Fig. 2. Current-potential curves of 1.0 mM dioxalatochromate(III) complexes obtained in 0.3 M KCl solutions containing 0.005% gelatin at 25°C: 1, *cis*-$[Cr(ox)_2(H_2O)_2]^-$; 2, *cis*-$[Cr(ox)_2(NH_3)_2]^-$; 3, $[Cr(ox)_2(en)]^-$; 4, *cis*-$[Cr(OH)(ox)_2(H_2O)]^{2-}$.

The reduction waves of dioxalatochromate(III) complexes, therefore, were measured in neutral solutions. The examples shown in Fig. 2 were obtained with 1.0 mM of the complexes in solutions containing 0.3 M potassium chloride and 0.005% gelatin. Dioxalatodiaquochromate(III) gives a well-defined wave, as is shown in Fig. 2.

All attempts to obtain a polarographic wave of trioxalatochromate(III) ions were unsuccessful. No wave was obtained, even in a 0.1 M tetramethylammonium bromide solution. This leads to the conclusion that trioxalatochromate(III) is not reducible at the dropping mercury electrode in the possible range of potential.

Table I gives the potentials at $\bar{i}=\bar{i}_l/10$ (denoted as $\bar{i}_l/10$-potential) on the polarographic waves of mono- and dioxalato complexes. The use of half-wave potentials was avoided because of the irregular polarograms observed with most of the dioxalato complexes. Table I indicates that the monooxalato complexes give the $\bar{i}_l/10$-potential at approximately $-1.05\sim-1.1$ V., the dioxalato complexes of univalent anions, at approximately $-1.4\sim-1.45$ V., and the dioxalato complexes of divalent anions, at -1.67 V.

In oxalatocobalt(III) complexes, the half-wave potential shifts to more positive potentials with an increasing number of oxalates coordinated[2]; this shift is considered to agree

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

[4] A. Rosenheim, *Z. anorg. Chem.*, **11**, 196, 225 (1892).

[5] A. Werner, W. J. Bowis, A. Hoblik, H. Schwarz and H. Surber, *Ann.*, **406**, 261 (1914).

[6] The details of the syntheses of these compounds will be published elsewhere.

[7] R. E. Hamm and R. E. Davis, *J. Am. Chem. Soc.*, **75**, 3085 (1953).

TABLE I. POTENTIALS AT $\bar{i}=\bar{i}_l/10$ OF THE CURRENT-POTENTIAL CURVES OF VARIOUS OXALATOCHROMIUM(III) COMPLEXES (AT 25°C)

Complex ion	Supporting electrolyte	Potential at $\bar{i}=\bar{i}_l/10$ V. vs. SCE
$[Cr(ox)_3]^{3-}$	0.1 M $(CH_3)_4NBr$	—
cis-$[Cr(OH)(ox)_2(H_2O)]^{2-}$	0.3 M KCl	−1.67
cis-$[Cr(ox)_2(H_2O)_2]^-$	0.3 M KCl	−1.44
cis-$[Cr(ox)_2(H_2O)_2]^-$	0.3 M KCl	−1.44*
trans-$[Cr(ox)_2(H_2O)_2]^-$	0.3 M KCl	−1.43*
cis-$[Cr(ox)_2(NH_3)_2]^-$	0.3 M KCl	−1.43
$[Cr(ox)_2(en)]^-$	0.3 M KCl	−1.41
$[Cr(ox)(NH_3)_4]^+$	0.9 M KCl+0.1 M acetate buffer	−1.10
$[Cr(ox)(en)_2]^+$	0.9 M KCl+0.1 M acetate buffer	−1.06

* Measured at 0°C.

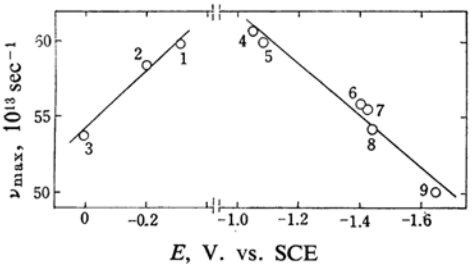

Fig. 3. Relation between the reduction potentials and the frequencies of the first absorption band of oxalatocobalt(III) and oxalatochromium(III) complexes: 1, $[Co(ox)(en)_2]^+$; 2, $[Co(ox)(NH_3)_4]^+$; 3, $[Co(ox)_2(NH_3)_2]^-$; 4, $[Cr(ox)(en)_2]^+$; 5, $[Cr(ox)(NH_3)_4]^+$; 6, $[Cr(ox)_2(en)]^-$; 7, *cis*-$[Cr(ox)_2(NH_3)_2]^-$; 8, *cis*-$[Cr(ox)_2(H_2O)_2]^-$; 9, *cis*-$[Cr(OH)(ox)_2(H_2O)]^{2-}$.

with the order of the spectrochemical series. In Fig. 3, the half-wave potentials of oxalatocobalt(III) complexes and the $\bar{i}_l/10$-potentials of oxalatochromium(III) complexes are plotted against the frequencies of the absorption band of the cobalt(III)[8] and chromium(III) complexes respectively. The absorption spectra of all the chromium(III) complexes were measured in this laboratory[9] except for that of the hydroxodioxalatoaquochromate(III) complex, which was obtained by Grant and Hamm[10].

It is interesting to note that, in the cobalt(III) and chromium(III) complexes, the absorption bands shift in the same direction with an increasing number of oxalates coordinated, whereas the reduction potentials shift in the opposite directions. The oxalatocobalt(III) complexes are reduced at the positively-charged electrode, whereas the oxalatochromium(III) complexes are reduced at the negatively-charged electrode. This indicates that the electrostatic effect between the reacting species and the electrode is one of the important factors in determining the reduction potential. In the case of chromium(III) complexes, the difference in repulsion between the reacting species and the electrode seems to cancel out the difference in ease with which one electron enters into the reacting chromium(III) species. These observations definitely suggest that the relationship between the reduction potential and the structure of the metal complex can be discussed only when the difference in the electrostatic interaction between the reacting species and the electrode can be disregarded or after an appropriate correction is made for the difference.

Summary

Current-potential curves of various oxalato complexes of chromium(III) were obtained at the dropping mercury electrode in acid or neutral aqueous solutions. The reduction potentials that were defined as potentials at $\bar{i}=\bar{i}_l/10$ were found to shift to more negative potentials with an increasing number of oxalates coordinated. The ionic charge effect on the reduction potentials was discussed in connection with the electrostatic interaction between the reacting species and the electrode.

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[8] Y. Shimura and R. Tsuchida, This Bulletin, **28**, 572 (1955).

[9] The details will be published elsewhere.

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