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A Polarographic Investigation of the Reactions between Nitrate Ions and Chromium(II)-Cyclohexanediaminetetraacetate, Chromium(II)-Trimethylenediaminetetraacetate, and Chromium(II)-*N*-(2-Hydroxyethyl)ethylenediaminetriacetate Complexes

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Kinetic studies of the reactions between nitrate ions and Cr(II)-Y complexes, where Y represents cyclohexanediaminetetraacetic acid (CyDTA), trimethylenediaminetetraacetic acid (TRDTA), and *N*-(2-hydroxyethyl) ethylenediaminetriacetic acid (HEDTA), have been carried out. The reaction mechanisms of these complexes at the dropping mercury electrode were found to be expressed by the following equations:

$$\begin{array}{lll}
\mathrm{Cr(III)\text{-}Y} + \mathrm{e} & \longrightarrow & \mathrm{Cr(II)\text{-}Y} \\
\mathrm{Cr(II)\text{-}Y} + \mathrm{H^+} & \overset{K}{\rightleftharpoons} & \mathrm{Cr(II)\text{-}HY} \\
\mathrm{Cr(II)\text{-}Y} + \mathrm{NO_3^-} & \xrightarrow{k_1} & \mathrm{Cr(III)\text{-}Y} \\
\mathrm{Cr(II)\text{-}HY} + \mathrm{NO_3^-} & \xrightarrow{k_2} & \mathrm{Cr(III)\text{-}Y}
\end{array}$$

The formation constant, K, and the rate constants, k_1 and k_2, were determined in 0.1 M acetate buffer solutions of $\mu=0.5$ by procedures including a curve-fitting method; the results were $K=2.0\times10^4\ \mathrm{M^{-1}}$, $k_1=0.55\ \mathrm{M^{-1}\,s^{-1}}$ and $k_2=2.8\ \mathrm{M^{-1}\,s^{-1}}$ for Cr(II)-CyDTA, $K=2.4\times10^5\ \mathrm{M^{-1}}$, $k_1=1.0\times10^2\ \mathrm{M^{-1}\,s^{-1}}$, and $k_2<3\ \mathrm{M^{-1}\,s^{-1}}$ for Cr(II)-TRDTA and $k_1\sim2\times10^3\ \mathrm{M^{-1}\,s^{-1}}$ for Cr(II)-HEDTA.

It was reported in a previous paper[1] that chromium(II)-EDTA complexes which were formed by the electroreduction of ethylenediaminetetraacetatoaquochromate(III) ions were oxidized by nitrate ions at the surface of the electrode; a catalytic reaction took place in solutions containing both chromium(III)-EDTA and nitrate ions. The stoichiometry and the rate constant of the reaction were determined, and the reaction mechanisms were discussed.[1]

In this paper, the polarographic investigation of the reaction between nitrate ions and Cr(II)-Y at the dropping mercury electrode is presented, where Y represents CyDTA, TRDTA, and HEDTA. The stoichiometry and the mechanisms of the reaction are discussed, and the formation constant of the acid complex of Cr(II)-Y, and the second-order rate constants of the reactions between nitrate ions and Cr(II)-Y and Cr(II)-HY are presented.

Experimental

Sodium cyclohexandiaminetetraacetatochromate(III), Na[Crcydta]·4H_2O, sodium trimethylenediaminetetraacetatochromate(III), Na[Crtrdta]·4H_2O, and *N*-(2-hydroxyethyl)-ethylenediaminetriacetatochromium(III), [Cr(H_2O)hedta], were prepared according to Tanaka *et al.*,[2] Ogino *et al.*[3] and Bustin and Early[4] respectively. All the chemicals used were of a guaranteed grade.

Current-potential curves were obtained with a pen-recording polarograph, Yanagimoto Graphrecorder, with an automatic potential scanner. The dropping mercury electrode (DME) used in the measurement of the limiting current of $\mathrm{Crcydta^-}$ had a rate of mercury flow (m) of 1.86 mg $\mathrm{s^{-1}}$ and a drop time (t_d) of 5.00 s, as measured in an air-free solution containing a 0.1 M acetate buffer (pH 4.9) at −0.5 V *vs.* SCE and at a pressure of 50 cm of mercury. The DME used in the measurement of $\mathrm{Crtrdta^-}$ and Cr(H_2O)hedta had an m value of 1.34 mg $\mathrm{s^{-1}}$ and a t_d value of 4.75 s in an air-free solution containing a 0.1 M acetate buffer (pH 4.9) and 0.4 M sodium perchlorate at −1.34 V *vs.* SCE and at a pressure of 60 cm of mercury.

The potential of DME was referred to the saturated calomel electrode (SCE). The temperature of the electrolytic solution was maintained at 25±0.2 °C by means of a thermostated bath. Dissolved oxygen in the electrolytic solution was removed by bubbling pure nitrogen gas through the solution. Extra pure nitrogen gas (99.999%) was used in determining the stoichiometric ratio of the Cr(II) complexes to the nitrate ion of the reaction. No maximum suppressor was used in the cases of $\mathrm{Crcydta^-}$ and Cr(H_2O)hedta. As the reduction wave of $\mathrm{Crtrydta^-}$ gave a maximum, 2 μM LEO was added in determining the limiting current of $\mathrm{Crtrdta^-}$.

The measurements were made in 0.1 M acetate buffer solutions. The ionic strength was adjusted to 0.5 with sodium perchlorate, unless otherwise stated. The stoichiometry of the reactions of the Cr(II) complex with the nitrate ion was determined by the method reported in a previous paper.[1]

The controlled potential electrolysis was carried out with a Yanagimoto Controlled Potential Electrolyser. The working electrode was a mercury pool, while the auxiliary electrode was a platinum wire which was connected to the electrolytic solution through a sodium chloride agar bridge. The potential of the working electrode was referred to the SCE. Nitrogen gas was bubbled through the solution continuously to provide stirring and to remove atmospheric oxygen.

Results

Polarograms of $\mathrm{Crcydta^-}$, $\mathrm{Crtrdta^-}$, and Cr(H_2O)hedta Obtained at Various Concentrations of Nitrate Ions. The polarographic waves of $\mathrm{Crcydta^-}$, $\mathrm{Crtrdta^-}$, and Cr(H_2O)hedta obtained in acetate buffer solutions were of a one-electron diffusion-controlled reduction. Upon the addition of nitrate ions to these solutions, the limiting currents of these waves increased in height. Figure 1 shows as examples the reduction waves of $\mathrm{Crcydta^-}$ in the absence and in the presence of nitrate ions. Current $\bar{I}_c$ in Fig. 1 was found to be independent of the

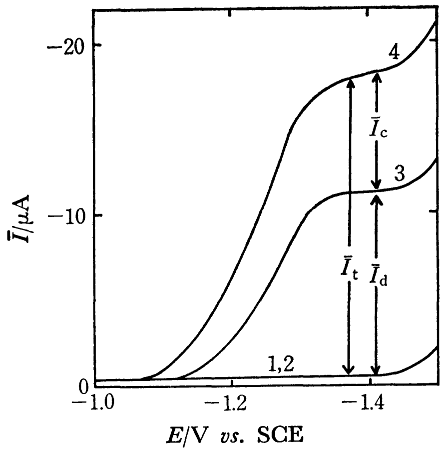

Fig. 1. Polarograms obtained with the solutions containing (1) 0.1M acetate buffer (pH 4.9), (2) (1)+ 0.25 M $NaNO_3$ (3) (1)+4 mM Crcydta$^-$ and (4) (3) +0.17 M $NaNO_3$.

height of mercury, indicating that $\bar{I}_c$ was kinetic in nature; that is, it was a catalytic current.

Apparent Rate Constants of the Reactions between Nitrate Ions and Cr(II)-CyDTA, Cr(II)-TRDTA, and Cr(II)-HEDTA. Let us consider the electrode processes given by the equations,

$$\mathrm{O} + ne \longrightarrow \mathrm{R} \qquad (1)$$

$$\mathrm{R} + \mathrm{Z} \xrightarrow{k} \mathrm{O} \qquad (2)$$

where O, R, and Z represent, respectively, the oxidant, the reductant, and the substance which is neither reduced nor oxidized at the potential at which O is reduced. The rate constant, k, of the chemical reaction given by Eq. (2) is calculated by means of Eqs. (3) to (7):[5–7]

$$\Psi(\chi_1) = \frac{\bar{I}_t + 2.37\times10^4\, nm^{1/3}t_d{}^{1/2}DC_o}{\bar{I}_d + 2.37\times10^4\, nm^{1/3}t_d{}^{1/2}DC_o} \qquad (3)$$

$$= (7/6)\chi_1{}^{-7/6}\left[2\int_0^{\chi_1}\chi^{2/3}f(\beta)\mathrm{d}\chi + \int_0^{\chi_1}\chi^{1/6}\exp(-\chi)\mathrm{d}\chi\right] \qquad (4)$$

$$f(\beta) = \int_0^1 \frac{\beta\exp(-\beta^2\chi_1)}{\{1-(1-\beta^2)^{7/3}\}^{1/2}}\mathrm{d}\beta \qquad (5)$$

$$\chi_1 = \alpha k C_Z t_d \qquad (6)$$

where D is the diffusion coefficient and where C_0 and C_Z are the concentrations of O and Z respectively, Z being present in a large excess of O. α is the stoichiometric ratio of R to Z of Reaction (2). In this study, the Cr(III)-Y, Cr(II)-Y, and nitrate ions correspond to O, R, and Z respectively, and α was determined to be 8 from separate experiments. When $\chi_1 > 10$,

$$\Psi(\chi_1) = 0.812\chi_1{}^{1/2} + 1.92\chi_1{}^{-7/6} \qquad (7)$$

The rate constants which were obtained by means of Eq. (7) for the reactions between nitrate ions and Cr(II)-CyDTA, Cr(II)-TRDTA, and Cr(II)-HEDTA under various conditions are given in Tables 1 and 2 and Figs. 2 and 3, in which k_{app} corresponds to k in Eq. (6). The values of k_{app} thus obtained were found to be independent of [Cr(III)-Y] and [NO_3^-].

The catalytic currents of Crcydta$^-$ obtained at the given concentration of nitrate ions and the apparent rate constants calculated thereform increased with the increase in the concentration of hydrogen ions, as is shown in Table 1. However, they did not change upon the addition of the free ligand CyDTA, as long as the other conditions were the same. These results seem to indicate that the acid complex of Cr(II)-CyDTA, Cr(II)-HY, is formed, but not aquochromium(II); the latter reacts with nitrate ions very slowly.[8] In the case of Crtrdta$^-$, the catalytic current and the apparent rate constants calculated therefrom were found to decrease with the increase in the concentration of hydrogen ions, as is shown in Table 2. This tendency is opposite to that obtained with Crcydta$^-$. The height of the catalytic current did not change upon the addition of the free ligand TRDTA, just as in the

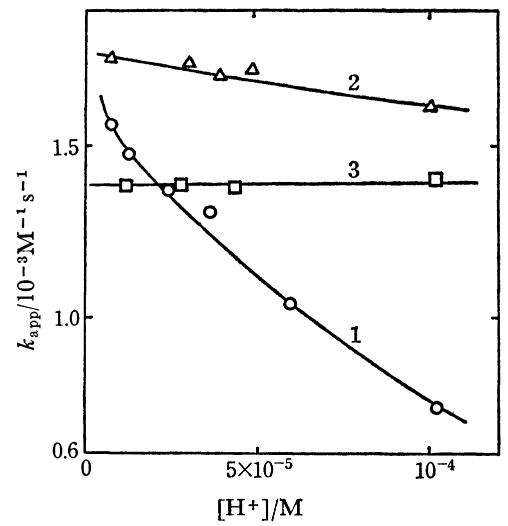

Fig. 2. Apparent rate constants of the reaction between nitrate ions and Cr(II)-HEDTA obtained at various concentrations of hydrogen ions with the solutions containing (1) 0.22 mM Cr(H_2O)hedta+1.2 mM $NaNO_3$ (μ=0.5), (2) (1)+1 mM HEDTA and (3) (1)+4 mM HEDTA.

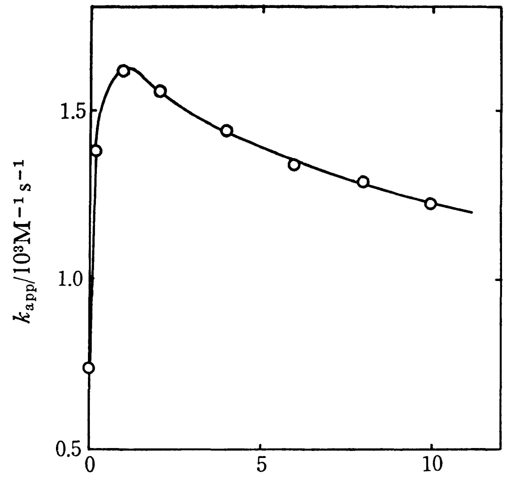

Fig. 3. Apparent rate constants of the reaction between nitrate ions and Cr(II)-HEDTA obtained at various concentrations of HEDTA.

TABLE 1. TOTAL CURRENTS OF Crcydta$^-$ AND APPARENT RATE CONSTANTS OF THE REACTION BETWEEN Crcydta$^-$ AND NITRATE IONS MEASURED IN THE SOLUTIONS CONTAINING 0.8 mM Crcydta$^-$ AND 0.16 M $NaNO_3$

$[H^+]/10^{-5}$ M	$-\bar{I}_t/\mu A$	$k_{app}/M^{-1}\,s^{-1}$
0.166	3.79	0.623
1.26	4.44	0.972
1.90	4.77	1.18
3.31	5.20	1.46
3.62	5.29	1.53
5.50	5.63	1.77
7.25	5.76	1.87

TABLE 2. TOTAL CURRENTS OF Crtrdta$^-$ AND APPARENT RATE CONSTANTS OF THE REACTION BETWEEN Crtrdta$^-$ AND NITRATE IONS MEASURED IN THE SOLUTIONS CONTAINING 0.32 mM Crtrdta$^-$ AND 7.2 mM $NaNO_3$

$[H^+]$ 10^{-5} M	$-I_t$ μA	Potential measured V *vs.* SCE	k_{app} $M^{-1}\,s^{-1}$
0.151	3.08	−1.46	76.1
0.438	2.70	−1.43	50.5
1.35	1.95	−1.40	24.0
2.04	1.69	−1.39	16.5
3.08	1.34	−1.38	9.97

case of Crcydta$^-$. From the measurements of the half-wave potentials of Crtrdta$^-$ at various concentrations of hydrogen ions, it was found that Cr(II)–TRDTA formed the acid complex, CrHtrdta$^-$.[9] This suggests that no appreciable amount of aquochromium(II) exists in the solution, while the acid complex, CrHtrdta$^-$, does.

The apparent rate constant of the reaction between nitrate ions and $Cr(H_2O)$hedta$^-$ decreased with the increase in the hydrogen-ion concentration (see Curve 1 in Fig. 2). This pH-dependency of the apparent rate constant became smaller upon the addition of free HEDTA (Curve 2 in Fig. 2). When 4 mM of free HEDTA was present in the solution, the apparent rate constants were found to be almost independent of the hydrogen-ion concentration (Curve 3 in Fig. 2). The apparent rate constants which were obtained at the same concentration of hydrogen ion increased with an increase in the concentration of free HEDTA, but gave a maximum value at a certain concentration of free HEDTA and then decreased, as is shown in Fig. 3. The increase in the apparent rate constant at lower concentrations of free HEDTA may be explained by considering that aquochromium(II) is formed in the absence of free HEDTA, while the formation of aquochromium(II) is prevented by the addition of HEDTA. On the other hand, the decrease in the apparent rate constant with an increase in the concentration of free HEDTA is not completely understood; it may, however, be due to the reaction between free HEDTA and the reduction intermediates of nitrate ions.

Discussion

It is considered that the mechanisms of the catalytic electrode reactions of Cr(III)–Y taking place in the presence of nitrate ions may be indicated as follows:

$$\mathrm{Cr(III)\text{-}Y} + e \longrightarrow \mathrm{Cr(II)\text{-}Y} \qquad (8)$$

$$\mathrm{Cr(II)\text{-}Y} + H^+ \overset{K}{\rightleftharpoons} \mathrm{Cr(II)\text{-}HY} \qquad (9)$$

$$\mathrm{Cr(II)\text{-}Y} + NO_3^- \xrightarrow{k_1} \mathrm{Cr(III)\text{-}Y} \qquad (10)$$

$$\mathrm{Cr(II)\text{-}HY} + NO_3^- \xrightarrow{k_2} \mathrm{Cr(III)\text{-}Y} \qquad (11)$$

where K is the formation constant of the acid complex and k_1 and k_2 are the second-order rate constants of the reactions given by Eqs. (10) and (11) respectively. When Y is CyDTA or TRDTA, the electrode reactions are considered to proceed by the mechanisms given by Eqs. (8) to (11). When Y is HEDTA, the reaction seems to proceed by the mechanisms given by Eqs. (8) to (10) or by Eqs. (8) to (11), unless free HEDTA exceeds a certain amount. In the latter case, Reaction (10) proceeds as fast as Reaction (11).

If the reaction proceeds according to Eqs. (8) to (11), the apparent rate constant is given by the following equations:

$$-\frac{d[\mathrm{Cr(II)}]_t}{dt} = 8k_{app}[\mathrm{Cr(II)}]_t[NO_3^-] \qquad (12)$$

$$K = \frac{[\mathrm{Cr(II)\text{-}HY}]}{[\mathrm{Cr(II)\text{-}Y}][H^+]} \qquad (13)$$

$$[\mathrm{Cr(II)}]_t = [\mathrm{Cr(II)\text{-}Y}] + [\mathrm{Cr(II)\text{-}HY}] \qquad (14)$$

$$k_{app} = \frac{k_1 + k_2K[H^+]}{1 + K[H^+]} \qquad (15)$$

With the apparent rate constants and the hydrogen-ion concentrations, the formation constant, K, and the rate constants, k_1 and k_2, were obtained by the curve-fitting method; they are given in Table 3.

The value of k_2 is larger than k_1 in the cases of Cr(II)–EDTA and Cr(II)–CyDTA. This seems reasonable,

TABLE 3. RATE CONSTANTS OF THE REACTION BETWEEN Cr(II)Y (Y: CyDTA, TRDTA, AND HEDTA) AND NITRATE IONS, AND THE FORMATION CONSTANT OF Cr(II)-HY.

	Cr(II)-EDTA	Cr(II)-CyDTA	Cr(II)-TRDTA	Cr(II)-HEDTA
$k_1/M^{-1}\,s^{-1}$	$(6.2\pm0.1)\times10$	$(5.5\pm0.4)\times10^{-1}$	$(9.8\pm0.8)\times10$	2×10^3
$k_2/M^{-1}\,s^{-1}$	$(3.0\pm0.1)\times10^3$	2.81 ± 0.08	< 6	—
k_2/k_1	4.8×10	5.1	$< 6\times10^{-2}$	—
K/M^{-1}	$(2.5\pm0.1)\times10^3$	$(2.0\pm0.1)\times10^4$	$(2.4\pm0.3)\times10^5$	—
K/M^{-1}	$10^{3.00}$ [10]	—	10^5 [9]	—

Uncertainties represent standard deviations.

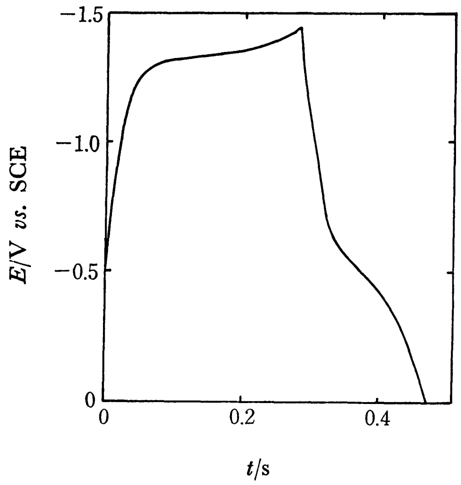

Fig. 4. Chronopotentiogram for the reduction and the subsequent reoxidation of 0.64 mM Crtrdta$^-$ obtained at current density of 5.19×10^{-4} A/cm^2 in the solution containing 0.1 M acetate buffer (pH 4.0) and 0.4 M NaClO$_4$.

because the electrostatic repulsion of acid complexes with nitrate ions is smaller than that of the normal complexes, Cr(II)-EDTA and Cr(II)-CyDTA. The k_2 value of Cr(II)-EDTA is of the same order as the k_1 value of Cr(II)-HEDTA; this is probably because the complexes are similar in both charge and structure. In the case of Cr(II)-TRDTA, on the other hand, k_2 is smaller than k_1. A current-reversal chronopotentiogram of Crtrdta$^-$ indicated an irreversible nature of the electrode reaction; it is shown in Fig. 4. This seems to suggest that the structure of the acid complex of Cr(II)-TRDTA changes rapidly to a structure similar to aquochromium(II), which can react with nitrate ions only slowly.

The magnitudes of the k_1 values of Cr(II)-CyDTA, Cr(II)-TRDTA, and Cr(II)-EDTA are in the following order:

Cr(II)-TRDTA > Cr(II)-EDTA > Cr(II)-CyDTA

The above order may be compared with the standard potentials of these complexes, which are −1.29,[9] −1.220,[11] and −1.198[12] V *vs.* SCE for Cr(III, II)-TRDTA, Cr(III, II)-EDTA, and Cr(III, II)-CyDTA respectively. The correlation between the rate constant and the standard potential is apparent. However, as Cr(III, II)-EDTA and Cr(III, II)-CyDTA have almost the same standard potentials, the difference in the k_1 values of Cr(II)-EDTA and Cr(II)-CyDTA may come from the difference in structure. The standard rate constants of the electrode reactions of Cr(H$_2$O)edta$^-$ and Crcydta$^-$ show a similar tendency; those of Cr(H$_2$O)edta$^-$ and Crcydta$^-$ are 0.21 cm s^{-1} [11] and 0.029 cm s^{-1} [12] respectively.

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