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Chronopotentiometry of Tris(ethylenediamine)chromium(III) Ions in Various Supporting Electrolyte Solutions

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The reduction of tris(ethylenediamine)chromium(III) ions at the dropping mercury electrode has been studied chronopotentiometrically in various supporting electrolyte solutions. The electrolysis at constant cathodic current in an acid solution gives a well-defined chronopotentiogram which corresponds to the one-electron reduction of chromium(III) to chromium(II). The anodic chronopotentiogram which is obtained by the current-reversal techniques is clearly separated from the cathodic one. Two cathodic steps are obtained in alkaline ethylenediamine solutions, and two anodic steps, at the current reversed. No chemical reaction involving hydrogen ions or ethylenediamine takes place prior to the electron transfer. The presence of very small amount of surface-active substances was found to improve the shape of chronopotentiograms. In the presence of EDTA, the one-electron cathodic chronopotentiogram splits into two steps.

In a previous paper,1) the present authors reported on the chromopotentiometric behavior of hexamminechromium(III) ions in acetate buffer solutions. Since only a little work has been reported on the electroreduction of tris(ethylenediamine)chromium(III) ions,2-4) it seems worthwhile to carry out the polarographic or chronopotentiometric study of this complex.

The present paper is concerned with the chronopotentiometry of tris(ethylenediamine)chromium(III) ions in various supporting electrolyte solutions. The observations in the cathodic chronopotentiometry and in the anodic chronopotentiometry by the current-reversal techniques will be presented, and the mechanism of the electrode processes will be discussed.

Experimental

Tris(ethylenediamine)chromium(III) chloride was

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1) N. Tanaka, A. Yamada and R. Tamamushi, This Bulletin., **37**, 1821 (1964).

2) N. Maki, Y. Shimura and R. Tsuchida, ibid., **31**, 413 (1958).

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

4) E. Fischerová and O. Fischer, *Chem. Zvesti*, **16**, 306 (1962).

prepared according to the method of Pfeiffer5); the chromium and nitrogen contents were determined by the usual methods.

Found: Cr, 12.79; N, 20.4. Calcd. for $[Cr(en)_3]Cl_3 \cdot 3^1/_2 H_2O$: Cr, 12.94; N, 20.9%.

As the complex is sensitive to light and not very stable in aqueous solutions6-9) precautions were taken when it was used. All other chemicals used were of analytical reagent grade. Redistilled water was used for the preparation of the solutions of desired concentrations. Polyoxyethylene laulyl ether (LEO), $C_{12}H_{25}O(C_2H_4O)_n$-OH (n=ca. 15), was used for a maximum suppressor. The contamination of the solution with surface-active substance was carefully avoided.

Chronopotentiometric measurements were carried out in general by following the procedure given in the previous paper.1) A dropping mercury electrode of a long drop time was used for the working electrode; it had an m value of 0.1164 mg./sec. and a drop time, t_d, of 61 sec., being measured in a deaerated solution containing 0.1 M acetate buffer and 0.9 M ammonium chloride at open circuit at 25 cm. of the mercury reservoir. The auxiliary electrode was a platinum wire, which was isolated in a compartment provided with a sintered glass disk. A saturated calomel electrode (SCE) was used for the reference electrode. Dissolved oxygen in the electrolytic solution was removed by bubbling purified nitrogen gas through the solution. All measurements were carried out at 25±0.1°C.

Results

In the polarographic measurements, tris(ethylenediamine)chromium(III) was found not to give a well-defined polarographic wave in neutral unbuffered solutions, but to give a well-defined wave in acetate buffer or acid solutions.10) Similar observations were made in the chronopotentiometric measurements. Typical examples are shown in Fig. 1.

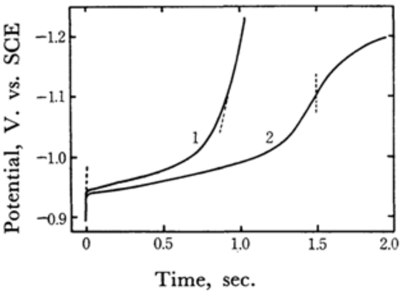

Fig. 1. Chronopotentiograms of 1 mM $[Cr(en)_3]Cl_3 \cdot 3^1/_2H_2O$ (1) in 0.9 M NH_4Cl+0.1 M acetate buffer (pH 4.6) and (2) in 1 M NH_4Cl at 25°C at current densities of (1) 0.231_4 and (2) 0.165_5 mamp.cm^{-2}. The measurements were started at 40 sec. after the beginning of the growth of mercury drop.

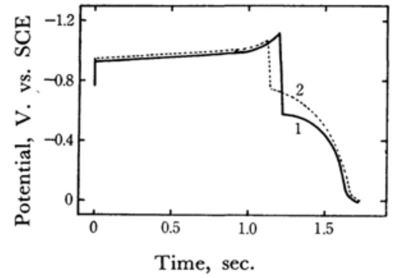

Fig. 2. Chronopotentiograms for the reduction and the subsequent reoxidation of 1 mM $[Cr(en)_3]Cl_3 \cdot 3^1/_2H_2O$ (1) in 0.9 M NHCl+0.1 M acetate buffer (pH 4.6) and (2) in 1 M NH_4Cl at 25°C. Current densities are (1) 0.181_7 mamp. cm^{-2} and (2) 0.186_0 mamp.cm^{-2}.

The characteristics of the potential-time curve for the reduction of tris(ethylenediamine)chromium(III) ions in neutral media were studied in a 1 M ammonium chroride solution. No linear relation was found between the concentration and the square root of the transition time. An example of the potential-time curves, which were obtained by the electrolysis at a constant cathodic current followed by the electrolysis at the constant anodic current of the same magnitude is given in Fig. 2. The values of τ_c/τ_a, $E^c_{t=0}$ and $E^a_{t=0}$ were determined to be 3.2, −0.94 V. vs. SCE and −0.75 V. vs. SCE respectively, where τ_c and $E^c_{t=0}$ mean the transition time and the potential at t=0 of the cathodic chronopotentiogram respectively, and τ_a and $E^a_{t=0}$, those of the anodic chronopotentiogram obtained by the current-reversal techniques respectively.

In acetate buffer solutions, well-defined chronopotentiograms were observed (see curve 1 in Figs. 1 and 2). The transition time (τ) was determined at various current densities (i) ranging from 0.179 to 0.508 mamp. cm^{-2}. The results showed that the product $i\tau^{1/2}$ was independent of the current density, indicating clearly that tris(ethylenediamine)chromium(III) ions are directly reduced at the electrode without any preceding chemical reaction prior to the electron-transfer process. The average value of $i\tau^{1/2}/C_O$, where C_O represents the concentration of the complex in the bulk of the solution, was obtained to be 0.211 mamp. sec$^{1/2}$ cm^{-2} mM^{-1}.

Measurements were also made at various concentrations of the complex. The results showed that the square root of the transition time was proportional to the concentration of the complex up to 1.5 mM, but at higher concentrations the transition time abnormally increased. The average value of $i\tau^{1/2}/C_O$ was obtained to be 0.211 mamp.

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5) P. Pfeiffer, P. Koch, G. Lando and A. Trieschman, *Ber.*, **37**, 4255 (1904).

6) S. Egashira, *J. Chem. Soc. Japan, Pure. Chem. Sect.* (*Nippon Kagaku Zasshi*), **79**, 301 (1958).

7) H. L. Schäfer and O. Kling, *Z. anorg. Chem.*, **287**, 296 (1956).

8) H. L. Schäfer and O. Kling, *J. Inorg. Nucl. Chem.*, **8**, 320 (1958).

9) H. L. Schäfer and O. Kling, *Z. Physik. Chem. N. F.*, **16**, 14 (1958).

10) N. Sato, B. S. thesis, Tohoku University (1962).

TABLE I. EFFECT OF IONIC STRENGTH ON THE CHRONOPOTENTIOGRAM OF 1mM $[Cr(en)_3]Cl_3 \cdot 3^1/_2\ H_2O$ OBTAINED AT CURRENT DENSITY OF 0.301_7 mamp. cm^{-2} IN SOLUTIONS CONTAINING 0.1 M ACETATE BUFFER

Ionic strength*	$E_{t=0}$ V. vs. SCE	τ sec.	$i\tau^{1/2}/C_O$ mamp. $sec^{1/2}\,cm^{-2}\,mM^{-1}$	Slope of log-plot mV.
0.1	−0.917	0.465	0.206	32
0.5	−0.929	0.475	0.208	47
1.0	−0.948	0.496	0.212	55
1.5	−0.962	0.502	0.214	59
2.0	−0.972	0.517	0.217	64

* Adjusted with NH_4Cl.

TABLE II. EFFECT OF SUPPORTING ELECTROLYTE ON THE CHRONOPOTENTIOGRAM OF 1 mM$[Cr(en)_3]Cl_3 \cdot 3^1/_2\ H_2O$ OBTAINED IN SOLUTIONS CONTAINING 0.1 M ACETATEBUFFER AT IONIC STRENGTH OF 1.0

Supporting electrolyte	$i\tau_c^{1/2}/C_O$ mamp. $sec^{1/2}\,cm^{-1}mM^{-1}$	τ_c/τ_a	$E^c_{t=0}$ V. vs. SCE	$E^a_{t=0}$ V. vs. SCE	Slope of log-plot, mV.
0.9M NH_4Cl	0.211	2.9_9	−0.94	−0.57	55
0.9M NaBr	0.205	3.0_2	−0.93	−0.62	65
0.9M KNO_3	0.204	varied*	−0.93	−0.53	not linear
0.3M en·2HCl	0.206	2.9_1	−0.96	−0.59	65
0.3M $(NH_4)_2SO_4$	0.182	3.0_3	−0.95	−0.48	not linear
0.3M $CaCl_2$	0.204	3.0_0	−0.91	−0.58	55

* See text and Table IV.

$sec^{1/2}\,cm^{-2}\,mM^{-1}$ in the range of the concentration up to 1.5 mM. According to Sand[11] the value of $i\tau^{1/2}/C_O$ is expressed as

$$i\tau^{1/2}/C_O=\frac{\pi^{1/2}}{2}n\boldsymbol{F}D_O{}^{1/2}=85.51nD_O{}^{1/2} \qquad (1)$$

where $\boldsymbol{F}$ is the Faraday, C_O the bulk concentration expressed in mM, D_O the diffusion coefficient expressed in $cm^2\,sec^{-1}$, i the current density expressed in mamp. cm^{-2} and n the number of electrons involved in the electrode reaction. The transition time constant $i\tau^{1/2}/C_O$ is correlated to the polarographic diffusion current constant I, which is given by the equation,

$$I = 607\,nD_O{}^{1/2} \qquad (2)$$

when the original form of the Ilkovic equation and the average current during the life of a mercury drop are employed. Hence, one obtains

$$i\tau^{1/2}/C_O = 0.1409\,I \qquad (3)$$

Introducing 1.47 μamp. $sec^{1/2}\,mg^{-2/3}\,mM^{-1}$ for I, which was determined by the polarographic measurement, the theoretical value of $i\tau^{1/2}/C_O$ was caluclated to be 0.207 mamp. $sec^{1/2}cm^{-2}mM^{-1}$. This value was in a satisfactory agreement with the experimental one.

The potential at $t=0$ ($E_{t=0}$) was found to be dependent on the current density and to change linearly with log i as shown in Fig. 3. Chronopotentiograms were obtained at various pH's in acetate buffer solutions, when the potential at $t=0$, the slope of the log-plot (log $(\tau^{1/2}-t^{1/2})$ vs. E) and the transition time constant were found to be independent of pH of the solution. The transition time constant, the potential at $t=0$ and the slope of the log-plot which were obtained at varied ionic strengths and in various supporting electrolyte solutions are given in Tables I and II, respectively. The effect of LEO on the chronopotentiogram of tris(ethylenediamine)-chromium(III) ions is shown in Table III. The transition time was not affected unless the concentration of LEO exceeded 5×10^{-4} M, whereas the potential at $t=0$ is affected by the addition of 5×10^{-6} M LEO.

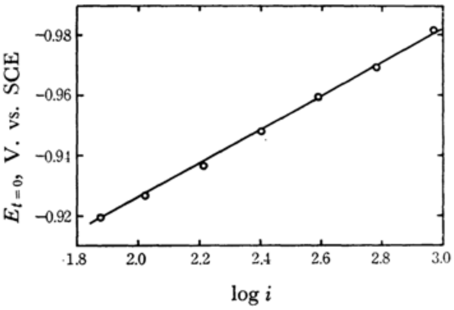

Fig. 3. Relation of $E_{t=0}$ with log i for the reduction of 1 mM $[Cr(en)_3]Cl_3 \cdot 3^1/_2H_2O$ in 0.9 M NH_4Cl+0.1 M acetate buffer. Ohmic drop is corrected.

When a small amount of disodium ethylenediaminetetraacetate (EDTA) is added to the solution, the one-electron cathodic chronopotentiogram of the tris(ethylenediamine)chromium(III) ions split into two steps. A typical example of the

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

TABLE III. EFFECT OF LEO ON THE CHRONOPOTENTIOGRAM OF 1 mM $[Cr(en)_3]Cl_3 \cdot 3^1/_2H_2O$ OBTAINED AT CURRENT DENSITY OF 0.214_7 mamp.sec$^{1/2}$ IN SOLUTIONS CONTAINING 0.9M NH_4Cl AND 0.1M ACETATE BUFFER

Concn. of LEO, M	τ sec.	$E_{t=0}$ V. vs. SCE	$i\tau^{1/2}/C_O$ map.sec$^{1/2}$ cm^{-2} mM^{-1}
0	0.980	−0.932	0.212
5×10^{-9}	0.978	−0.931	0.212
5×10^{-8}	0.978	−0.931	0.212
5×10^{-7}	0.982	−0.932	0.212
5×10^{-6}	0.979	−0.955	0.212
5×10^{-5}	0.980	−1.210	0.212
5×10^{-4}	0.960	−1.244	0.211

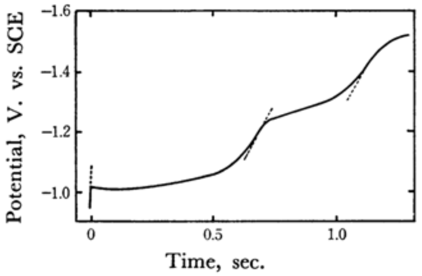

Fig. 4. Chronopotentiogram of 0.99 mM $[Cr(en)_3]Cl_3 \cdot 3^1/_2H_2O$ obtained in the presence of 0.203 mM EDTA at current density of 0.223_6 mamp. cm^{-2} in the solution (pH 4.6) containing 0.9 M NH_4Cl and 0.1 M acetate buffer.

chronopotentiogram is shown in Fig. 4.

Chronopotentiograms in alkaline ethylenediamine solutions were not so simple as in acid solutions. As shown in Fig. 5, two cathodic steps were observed in a solution containing 0.5 M ethylenediamine dihydrochloride and 1 M sodium hydroxide, and two anodic steps at the current reversed.

Discussion

Tris(ethylenediamine)chromium(III) ion gives no well-defined chronopotentiogram in neutral unbuffered solutions, because it contains basic ligands and, when reduced, it forms an insoluble film on the surface of the electrode, as has already been reported in the case of the polarographic reduction of some chromium(III) complexes.12−14) In an acid solution the ethylenediamine molecules which the reduced chromium(II) species liberate are neutralized by hydrogen ions diffusing from the bulk of the solution; consequently, the formation of an insoluble film is prevented. It may be concluded from the results obtained at various current densities and at various concentrations of the complex that tris(ethylenediamine)chromium(III) ions are directly reduced at the dropping mercury electrode without any preceding chemical reaction prior to the electron-transfer process. The anodic chronopotentiograms obtained by the current-reversal techniques indicate that the overall process of the reduction of tris(ethylenediamine)chromium(III) to chromium(II) species proceeds irreversibly at the dropping mercury electrode:

$$[Cr(en)_3]^{3+} + e + 2p\ H_3O^+ \rightarrow [Cr(H_2O)_{2p}(en)_{3-p}]^{2+} + p\ H_2en^{2+} \quad (4)$$

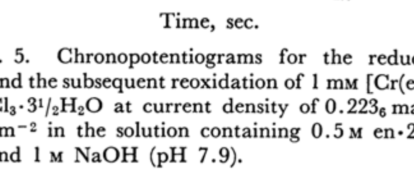

Fig. 5. Chronopotentiograms for the reduction and the subsequent reoxidation of 1 mM $[Cr(en)_3]Cl_3 \cdot 3^1/_2H_2O$ at current density of 0.223_6 mamp. cm^{-2} in the solution containing 0.5 M en·2HCl and 1 M NaOH (pH 7.9).

In alkaline ethylenediamine solutions, the first cathodic and the first anodic chronopotentiogram appeared in approximately the same potential region. This observation agrees with the result which was obtained by Fischerovâ and Fischer4) in their oscillograph-polarographic study on the reduction of the same complex.

The potential of the cathodic chronopotentiogram is dependent on the ionic strength of the solution; the potential at $t=0$ ($E^c_{t=0}$) shifts to more negative potentials as the ionic strength increases (Table I). Such a shift is also observed in the reduction of other chromium(III) complexes.13−15)

A plot of $E_{t=0}$ versus log i yielded a straight line with a slope of 55 mV. The plot of $\log(\tau^{1/2}-t^{1/2})$ versus E in various supporting electrolyte solutions, however, did not always yield a straight line as given in Table II. This makes the theoretical analysis of the potential-time curve less feasible. According to the theoretical treatment of potential-time curves reported previously,1) the slope of these plots is equal to $2.3\,\boldsymbol{R}T/n\boldsymbol{F}$ for a reversible electron-transfer and $2.3\,\boldsymbol{R}T/\alpha n\boldsymbol{F}$ for an irreversible electron-transfer, where α represents the transfer coefficient and $\boldsymbol{R}$ the gas constant. At the moment, however, it seems impossible to decide, from the experimental results, by which process the reduction of tris(ethylenediamine)chromium(III) ions takes place, because of the insufficient knowledge on

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12) N. Tanaka and G. Satô, *Nature*, **197**, 176 (1963).

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

14) N. Tanaka, Y. Sato, R. Tamamushi and G. Satô, ibid., **36**, 1193 (1963).

15) N. Tanaka, E. Itabashi, R. Tamamushi and G. Satô, ibid., **37**, 226 (1964).

the reactivity of chromium(II) complexes.

The ratio of τ_c/τ_a fluctuates around 3, i. e., 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] The value of τ_c/τ_a in potassium nitrate solutions was found to increase as τ_c increased, as seen in Table IV. This suggests the interaction between the reduced chromium(II) complex and nitrate ions.

TABLE IV. TRANSITION TIME FOR THE REOXIDATION PROCESS OF 1 mM $[Cr(en)_3]Cl_3 \cdot 3^1/_2H_2O$ RECORDED AT CURRENT DENSITY OF 0.182_0 mamp.cm^{-2} IN 0.9 M KNO_3 + 0.1 M ACETATE BUFFER

τ_c sec.	τ_a sec.	τ_c/τ_a	$E^c_{t=0}$ V. vs. SCE	$E^a_{t=0}$ V. vs. SCE
1.2_8	0.30_0	4.2_7	−0.93	−0.53
1.0_8	0.28_0	3.8_6		
0.88_0	0.25_0	3.5_2		
0.68_0	0.25_0	3.4_0		

The transition time constant of tris(ethylene diamine)chromium(III) ions (0.211 mamp.sec$^{1/2}$ cm^{-2}mM^{-1}) obtained in the solution containing 0.1 M acetate buffer and 0.9 M ammonium chloride was smaller by 20 per cent than that of hexamminechromium(III) ions obtained under the same condition. The difference is considered to be due to a larger size of the ethylenediamine complex ion. The transition time constant obtained in the ammonium sulfate solution was found to be smaller by some 10 per cent than that obtained in other supporting electrolytes. This is considered as due to the ion-pair formation of tris(ethylenediamine)chromium(III) with sulfate ions, the details of which will be reported elsewhere.

It is known that the transition time decreases more or less markedly when a strongly adsorbable substance is present in the solution.[17-19] In the case of the reduction of tris(ethylendiamine)-chromium(III) ions, in contrast, the addition of a very low concentration of surface-active substances improved the shape of the potential-time curves (see Fig. 6). In the absence of surface-active substance, no satisfactory chronopotentiogram was obtained; a sudden change or a drift in potential occurred, immediately before the transition time is attained. Table III indicates that the addition of LEO up to 5×10^{-7} M in concentration gives satisfactory chronopotentiograms of tris(ethylenediamine)chromium(III) ions. A similar example of the improvement of a chronopotentiogram by the addition of a small amount of surface-active substance has been reported for the reduction of copper(II) ions in the presence of polyacrylamide.[19]

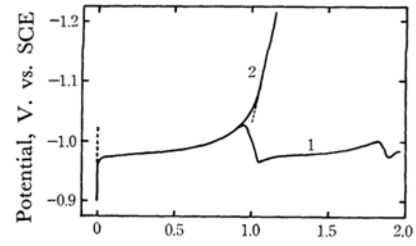

Fig. 6. Chronopotentiograms of 1 mM $[Cr(en)_3]Cl_3 \cdot 3^1/_2H_2O$ obtained at current density of 0.238_6 mamp.cm^{-2} in the solution containing 0.9 M KSCN and 0.1 M acetate buffer (1) in the absence and (2) in the presence of 5×10^{-9} M of LEO.

In the presence of EDTA, the cathodic chronopotentiogram of tris(ethylenediamine)chromium(III) ions splits into two steps; the potential of the first step is almost the same as that of the chronopotentiogram obtained in the absence of EDTA, while the potential of the second step corresponds to the oxidation-reduction potential of chromium(II)- and chromium(III)-EDTA complexes. The first step decreases in the transition time with the increase in the EDTA concentration, and it vanishes when the EDTA concentration exceeds a critical value. A plot of $\tau_1^{1/2}$ versus $[EDTA]/C_O$ yields a nearly straight line as is seen in Fig. 7, where τ_1 is the transition time of the first step, [EDTA] the concentration of EDTA and C_O the concentration of the complex. These phenomena were considered as being caused by the electrode process given as follows [20,21]:

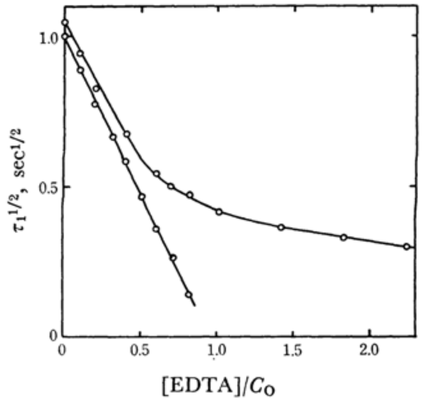

Fig. 7. Relation of $\tau_1^{1/2}$ with $[EDTA]/C_O$ obtained at various concentrations of $[Cr(en)_3]Cl_3 \cdot 3^1/_2H_2O$ in the solution containing (1) 0.1 M acetate buffer and 0.9 M NH_4Cl and (2) 0.1 M acetate buffer and 0.3 M $CaCl_2$. Current densities are (1) 0.211_6 mamp.cm^{-2} and (2) 0.195_7 mamp.cm^{-2}.

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

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

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

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

[20] N. Tanaka and K. Ebata, *J. Electroanal. Chem.*, **8**, 120 (1964).

[21] K. Ebata, *Sci. Repts. Tohoku Univ., Ser. I*, **47**, 191 (1964).

$$\begin{aligned} &[\mathrm{Cr(en)_3}]^{3+}+\mathrm{e} \rightarrow [\mathrm{Cr(en)_3}]^{2+} \\ &[\mathrm{Cr(en)_3}]^{2+}+\mathrm{EDTA} \rightleftharpoons \mathrm{Cr(II)\text{-}EDTA}+3\mathrm{en} \qquad (5) \\ &\mathrm{Cr(II)\text{-}EDTA} \rightarrow \mathrm{CrY(H_2O)^-}+\mathrm{e} \end{aligned}$$

where Y^{4-} represents a quadrivalent EDTA anion and Cr(II)-EDTA, either $[\mathrm{CrYH_2O}]^{2-}$ or $[\mathrm{Cr(HY)(H_2O)}]^-$ according to the pH of the solution.[22] As is seen in Fig. 7, when a large excess of calcium ions is present in the solution, the decrease in transition time of the first step is much smaller than that observed in the absence of calcium ions. This is considered to be due to the decrease in the activity of free EDTA anions because a large excess of calcium ions reacts with free EDTA anions to form stable calcium-EDTA complexes. The details will be reported elsewhere.

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

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[22] R. L. Pecsok, L. D. Shields and W. P. Schaeffer, *Inorg. Chem.*, **3**, 114 (1964).