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Kinetics of Electron-transfer Reactions Involving Ethylenediaminetetraacetatochromate(II) Ions as Reductants. I. Reactions with Some Isothiocyanatoammine Complexes of Chromium(III)[*1]

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Kinetics of electron-transfer reactions of ethylenediaminetetraacetatochromate(II) ions with some isothiocyanatoammine complexes of chromium(III), $\mathrm{Cr(NCS)_n(NH_3)_{6-n}^{(3-n)+}}$ ($n=0$, 1, 4 and 6), have been studied. The former ions are present in the forms of both $\mathrm{Cr^{II}(H_2O)edta^{2-}}$ and $\mathrm{Cr^{II}(H_2O)Hedta^{-}}$, but the reaction of $\mathrm{Cr^{II}(H_2O)Hedta^{-}}$ with $\mathrm{Cr(NCS)_n(NH_3)_{6-n}^{(3-n)+}}$ is not significant in the pH range from 3.6 to 5.3. Second-order rate constants ($l\ \mathrm{mol^{-1}sec^{-1}}$) of the reactions between $\mathrm{Cr^{II}(H_2O)edta^{2-}}$ and $\mathrm{Cr(NCS)_n(NH_3)_{6-n}^{(3-n)+}}$ at ionic strength 1.0 and 25°C are $<10^{-2}$ for $\mathrm{Cr(NH_3)_6^{3+}}$, 0.2 for $\mathrm{CrNCS(NH_3)_5^{2+}}$, 2.3 for $\mathrm{Cr(NCS)_4(NH_3)_2^{-}}$, and 28.2 for $\mathrm{Cr(NCS)_6^{3-}}$.

The electron-transfer reactions between chromium(II) ions and various oxidants have been investigated extensively. For example, it is known that the reactions of chromium(II) ions with various cobalt(III) complexes proceed through inner-sphere mechanisms, except haxaammine and tris(ethylenediamine)cobalt(III) complex ions.[1,2] The reactions between chromium(II) ions and acidopentaamminechromium(III) also proceed through inner-sphere mechanisms.[3] On the other hand, the electron-transfer reactions of tris(bipyridine)chromium(II) ions with various cobalt(III) complexes proceed through outer-sphere mechanisms.[2,4] The striking change in these electron-transfer reactions is brought by the complex formation of chromium(II) ions with bipyridine. Therefore, it seems worth while to investigate the electron-transfer reactions involving various chromium(II) complexes as reductants.

Stability constants of chromium(II) and chromium(III) complexes with ethylenediaminetetraacetate (EDTA) have been determined by Pecsok *et al.*[5] Recently, the rate constants of the complex-forming reactions between chromium(II) ions and EDTA have been determined in this laboratory.[6,7] These results have facilitated to investigate the electron-transfer reactions between chromium(II)-EDTA and various oxidants.

In this paper, kinetics of electron-transfer reactions between chromium(II)-EDTA and some isothiocyanatoammine complexes of chromium(III) ions, $\mathrm{Cr(NCS)_n(NH_3)_{6-n}^{(3-n)+}}$ ($n=0$, 1, 4 and 6), are presented. Although Hunt and Earley[8] reported on the semiquantitative experiments of electron-transfer reactions between chromium(II) and hexaaquochromium(III) ions in the presence of number of ligands, rate laws of these reactions were not presented.

Experimental

Materials. Aquohydrogenethylenediaminetetraacetatochromium(III), [Cr(H$_2$O)Hedta], was prepared by the method of Hamm.[9] The crude material was purified by the following procedures: 24 g of [Cr(H$_2$O)Hedta] in 25 m*l* of water was dissolved with 10 g of sodium acetate trihydrate. After filtration, 20 m*l* of concentrated nitric acid was added. Crystals were obtained upon heating the solution on the water-bath. The crystals were washed with warm water, ethanol and ether. Infrared spectra of the compound gave two peaks at 1739 and 1639 cm^{-1} in the carbonyl region, which essentially agree with the results reported by Dwyer and Garvan.[10] The peak at 1739 cm^{-1} which could be assigned to the free carboxylic acid group was less intense than the other at 1639 cm^{-1}. The relative intensities of these peaks support EDTA in chromium(III)-EDTA complex functioning as a pentadentate ligand.

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Complexes, $[Cr(NH_3)_6]Cl_3$,[11] $[CrNCS(NH_3)_5](SCN)_2$,[12] and $K_3[Cr(NCS)_6]\cdot 4H_2O$,[13] were prepared by the procedures described in literatures. $[CrNCS(NH_3)_5](SCN)_2$ was converted to perchlorate by recrystallization from aqueous perchloric acid. The solution of $(NH_4)_3[Cr(NCS)_6]\cdot 4H_2O$ was obtained by passing the solution of $K_3[Cr(NCS)_6]\cdot 4H_2O$ through Dowex 50W-X8 cation exchange resins in the ammonium form. Then, the solution was evaporated to dryness. The compound $(NH_4)_3[Cr(NCS)_6]\cdot 4H_2O$ thus obtained was purified by recrystallization from 95% ethanol. $NH_4[Cr(NCS)_4(NH_3)_2]\cdot 2/3\ H_2O$ of reagent grade was purchased from Nakarai Chemicals, Ltd.

The results of the chemical analysis of the chromium(III) complexes used in this paper are given in Table 1.

TABLE 1. ANALYSIS OF THE CHROMIUM(III) COMPLEXES

Complex	Cr, %		N, %	
	Found	Calcd	Found	Calcd
$[Cr(H_2O)Hedta]$	14.22	14.47	7.80	7.80
$[Cr(NH_3)_6]Cl_3$	19.92	19.96	31.95	32.26
$[CrNCS(NH_3)_5](ClO_4)_2$	13.31	13.19	21.56	21.32
$NH_4[Cr(NCS)_4(NH_3)_2]\cdot 2/3H_2O$	14.28	14.92	28.25	28.14
$(NH_4)_3[Cr(NCS)_6]\cdot 4H_2O$	9.71	9.87	23.78	23.94

The acidic solution of hexaaquochromium(III) perchlorate was prepared by the reduction of sodium dichromate in perchloric acid with hydrogen peroxide. Solutions of chromium(II) perchlorate were obtained by the reduction of hexaaquochromium(III) perchlorate with zinc amalgam. Chromium(II) chloride solutions were prepared by dissolving chromium metal into hydrochloric acid.

All other chemicals used were of reagent grade.

Procedures. As chromium(II) solutions were air-sensitive, the experiments were carried out in an oxygen-free nitrogen atmosphere. A trace of oxygen was removed from nitrogen gas by passing the gas through a series of acidic chromium(II) solutions.

Total chromium concentration in a given solution was determined spectrophotometrically as CrO_4^{2-} after oxidation with alkaline peroxide.[14]

Chromium(II)-EDTA solutions were prepared by injecting chromium(II) solutions into excess EDTA solutions. The following two methods were used for the determination of the concentration of chromium(II)-EDTA: In the first method, the concentration of chromium(II)-EDTA was taken as equal to that of a known amount of chromium(II) ions. Chromium(II) content was determined by the method reported in the literature.[15] Chromium(II) solutions contained chromium(III) ions as impurity. The chromium(III) ions in the original solution may be $Cr(H_2O)_6^{3+}$ and/or $[CrOH(H_2O)_4]_2^{4+}$, the latter of which is known to be a product upon the air-oxidation of chromium(II) ions.[16,17] The contamination of chromium(III) ions was greater in the more dilute chromium(II) solutions. It was found spectrophotometrically that, when a chromium(II) solution which was contaminated by chromium(III) ions was injected into an excess EDTA solution, the same amount of chromium(III)-EDTA as that of chromium(III) in the original solution was formed within the time of mixing. The absorption spectra of chromium(II)-EDTA and chromium(III)-EDTA complexes which were obtained in this work are as mentioned later (see Fig. 1). In the second method, the following procedure was used: Absorbancy of the chromium(II)-EDTA solution containing chromium(III)-EDTA was measured at a proper wave length. The concentrations of both chromium(II)-EDTA and chromium(III)-EDTA were calculated from the total chromium concentration, the value of absorbancy and the extinction coefficients of both chromium(II)-EDTA and chromium(III)-EDTA. In most cases, this procedure was used, because this was simpler than the first one.

The determination of hydrogen ion concentrations in chromium(II) solutions and acidic hexaaquochromium(III) perchlorate solutions was carried out by the method reported in the literatures.[18,19] Concentrations of zinc(II) ions in the chromium(II) perchlorate solutions were determined polarographically.

Ionic strength of the solution was adjusted to be 1.0 with sodium perchlorate or sodium chloride. The pH of the solutions was regulated by using acetate buffer which was prepared from acetic acid and primary standard sodium carbonate. A Hitachi F-5 pH meter with accuracy of ±0.01 pH unit was used for the measurement of the pH of the solutions.

The reaction vessels were quartz spectrophotometer cells of 1 cm in length of light path. Kinetic runs were made by recording the change of absorbancy at a given wave length as a function of time, using a Hitachi EPS-3 pen-recording spectrophotometer. In most of kinetic runs, the solutions containing a given amount of chromium(III) complex ions, EDTA, acetate buffer and indifferent salt were added to the cell which was then sealed with a serum cap. After the solution was purged with nitrogen gas for at least ten minutes, chromium(II) solution was added by a calibrated syringe. The mixing of the solutions was performed by passage of a rapid stream of nitrogen gas. In some experiments, the chromium(II) solution was added to the deoxygenated solution containing EDTA, acetate buffer and indifferent salt in a serum capped cell by a syringe and then the solution of chromium(III) complex ions was added as the last reagent by a syringe. In both manners, the first absorbancy reading was obtained within 5 sec.

Temperature of optical cells was controlled to be 25.0±0.1°C by circulating water through cell holder. The deoxygenated solution of chromium(II) or chromium(III) ions in a syringe was also equilibrated at 25°C in the thermostated-bath before mixing.

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Results and Discussion

Absorption Spectra of Chromium(II)-EDTA and Chromium(III)-EDTA Complexes. A pentadentate structure of EDTA in chromium(II)-EDTA complex has been proposed by Pecsok *et al.*[5] Therefore, the formula $\mathrm{Cr^{II}(H_2O)edta^{2-}}$ will be used in this paper for chromium(II)-EDTA complex.

Schwarzenbach and Biedermann[20] showed that chromium(III)-EDTA complex contains one water molecule in the first coordination sphere. And, Hoard *et al.*[21] reported that in an intermediate pH range from 5 to 9, both $\mathrm{Cr^{III}(H_2O)edta^-}$ and $\mathrm{Cr^{III}(OH)edta^{2-}}$ are probably converted, though perhaps slowly, into the hexadentate $\mathrm{Cr^{III}edta^-}$. In addition, they isolated the hexadentate complex in the solid state. In the present paper, the formula $\mathrm{Cr^{III}(H_2O)edta^-}$ is assigned tentatively to chromium(III)-EDTA complex in the solution by the following observations: (a) Infrared spectra of chromium(III)-EDTA complex in solid state supported a pentadentate structure of EDTA as mentioned in the experimental section. (b) Visible and ultraviolet spectra of $\mathrm{[Cr(H_2O)Hedta]}$ dissolved in distilled water were essentially identical with those in acetate buffer solution. (c) In this work, the pH of the solutions was restricted within the range from 3.6 to 5.3 by using acetate buffer solutions. No spectral changes in visible and ultraviolet regions were observed by the change of the pH of the solutions.

The spectra of $\mathrm{Cr^{II}(H_2O)edta^{2-}}$ and $\mathrm{Cr^{III}(H_2O)edta^-}$ at ionic strength 1.0 ($\mathrm{NaClO_4}$) in acetate buffer solutions are given in Fig. 1. The concentration of acetate in the buffer was varied from 0.24 to 0.75 M. For comparison, the spectrum of chromium(II) ions in perchloric acid is also given in Fig. 1. The molar extinction coefficients of maximum absorption of $\mathrm{Cr^{III}(H_2O)edta^-}$ at 393 mμ and 545 mμ were 112 and 206, respectively, which essentially agree with the results reported by Hamm.[9]

The shape of spectrum of $\mathrm{Cr^{II}(H_2O)edta^{2-}}$ resembles that of $\mathrm{Cr^{2+}}$ ions, so that the color of a $\mathrm{Cr^{II}(H_2O)edta^{2-}}$ solution is sky blue similar to that of a chromium(II) solution. The molar extinction coefficients of maximum absorptions of $\mathrm{Cr^{II}(H_2O)edta^{2-}}$ at 715 and 1060 mμ were 18 and 10, respectively. The extinction coefficient of $\mathrm{Cr^{II}(H_2O)edta^{2-}}$ is the same with that of $\mathrm{Cr^{III}(H_2O)edta^-}$ at 365 and 673 mμ, respectively, as indicated with arrows in Fig. 1.

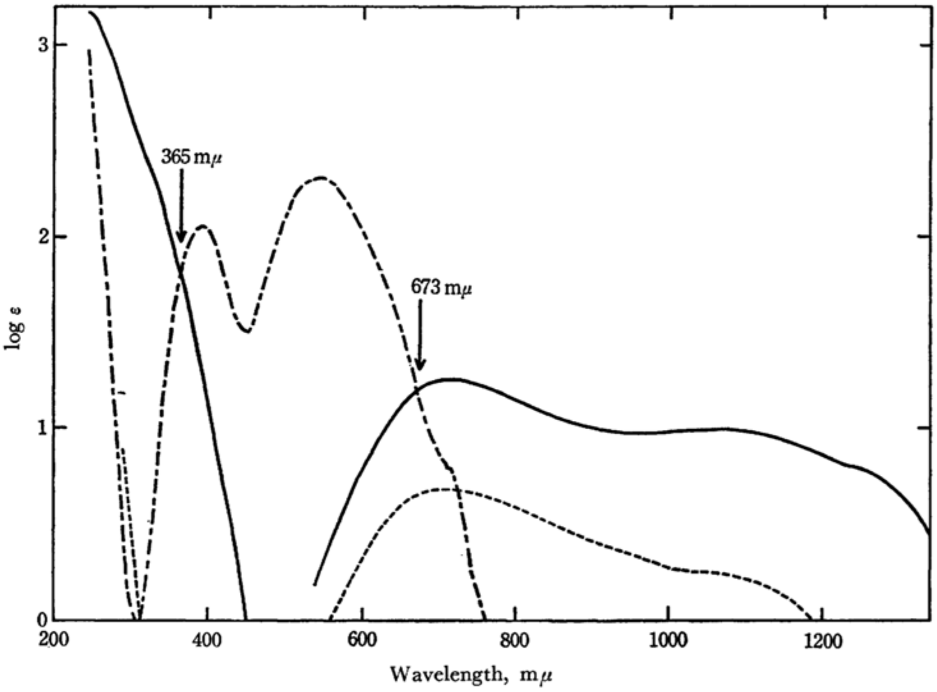

Fig. 1. Absorption spectra of $\mathrm{Cr^{II}(H_2O)edta^{2-}}$ in sodium acetate-sodium perchlorate media (——), $\mathrm{Cr^{III}(H_2O)edta^-}$ in sodium acetate-sodium perchlorate media (-·-·-) and $\mathrm{Cr^{2+}}$ in $\mathrm{HClO_4}$ (----).

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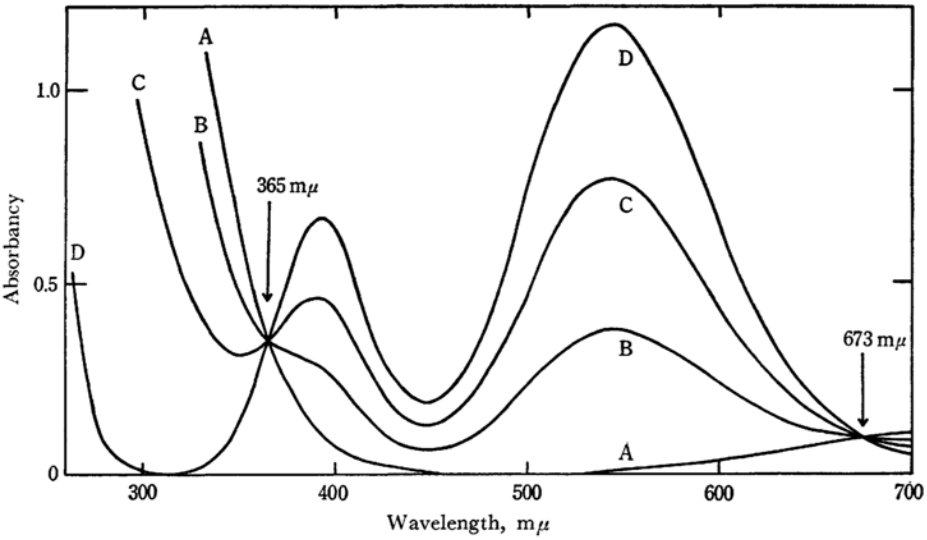

Fig. 2. Spectral change of $Cr^{II}(H_2O)edta^{2-}$ solution in sodium acetate-sodium perchlorate media of ionic strength 1.0: (A) 5.89 mM $Cr^{II}(H_2O)edta^{2-}$; (B and C) Partly oxidized with air; and (D) Completely oxidized with air. The concentration of acetate is 0.24 M.

Figure 2 shows the spectral change of $Cr^{II}(H_2O)edta^{2-}$ solution which occurred when air was bubbled through the solution. Two isosbestic points were observed at 365 and 673 mμ by the addition of appropriate amounts of oxygen. The spectrum obtained after the solution was saturated with air is shown by curve D in Fig. 2. This spectrum is in a satisfactory agreement with that of 5.89 mM $Cr^{III}(H_2O)edta^-$. These observations revealed that there was no indication of the formation of intermediates such as dimeric species. Therefore, the spectral change in Fig. 2 can be expressed reasonably with the following equation:

$$2Cr^{II}(H_2O)edta^{2-} + \frac{1}{2}O_2 + 2H^+ \rightarrow 2Cr^{III}(H_2O)edta^- + H_2O \qquad (1)$$

Kinetics of the Electron-transfer Reactions between $Cr^{II}(H_2O)edta^{2-}$ and $Cr(NCS)_n(NH_3)_{6-n}^{(3-n)+}$. Figure 3 gives a typical example of the spectral change of the $Cr(NCS)_6^{3-}$ solution containing excess EDTA upon the addition of chromium(II) perchlorate solution (spectra A to D). The same spectral change was observed, when a $Cr(NCS)_6^{3-}$ solution was injected into a chromium(II) solution containing excess EDTA. The reaction seemed to be complete within 600 sec, since no change was observed in the spectrum after the measurement of spectrum D in Fig. 3. The shape of spectrum D is in a satisfactory agreement with that of $Cr^{III}(H_2O)edta^-$. Therefore, the overall reaction is expressed reasonably as follows:

$$Cr(NCS)_6^{3-} + H_jedta^{(4-j)-} + H_2O \rightarrow Cr^{III}(H_2O)edta^- + 6NCS^- + jH^+ \qquad (2)$$

In Fig. 3, there are three isosbestic points at 380, 404 and 466 mμ. This is also consistent with Eq. (2). The rate of reaction (2) observed in the absence of chromium(II) ions was much slower than the rate of the reaction observed in the presence of chromium(II) ions. It was also found that the rate of the reaction between chromium(II) ions and $Cr(NCS)_6^{3-}$ complexes in sodium chloride-hydrochloric acid media was extremely slow.*2

After the completion of the reaction, the solution was exposed to air, the spectrum of which is shown by curve E in Fig. 3. This spectrum also coincides with that of $Cr^{III}(H_2O)edta^-$. The concentration of $Cr^{III}(H_2O)edta^-$ which corresponds to the difference in absorbancy in the spectra D and E was found to be equal to the concentration of chromium(II) ions which was initially added. That is, the concentration of chromium(II)-EDTA remained constant during the reaction. As shown in Fig. 1, the absorption of $Cr^{II}(H_2O)edta^{2-}$ is negligible over the range of wave length in Fig. 3 under the experimental condition.

By considering these results, the following mechanism can be deduced for reaction (2):

$$Cr^{2+} + H_jedta^{(4-j)-} + H_2O \rightleftharpoons Cr^{II}(H_2O)edta^{2-} + jH^+ \qquad (3)$$

$$Cr^{II}(H_2O)edta^{2-} + Cr(NCS)_6^{3-} \xrightarrow{k} Cr^{III}(H_2O)edta^- + Cr^{2+} + 6NCS^- \qquad (4)$$

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*2 The reaction between chromium(II) ions and $Cr(NCS)_6^{3-}$ complexes may be the chromium(II)-catalyzed dissociation reaction of $Cr(NCS)_6^{3-}$ complexes, but, no systematic investigation either on the stoichiometry or on the kinetics of the reaction has been made.

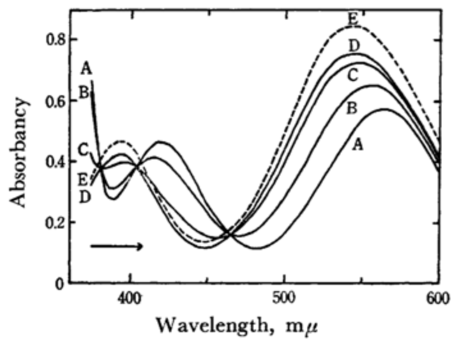

Fig. 3. Spectral change of the $Cr(NCS)_6^{3-}$ solution containing EDTA in sodium acetate-sodium perchlorate media upon the addition of chromium(II) ions: $[Cr(NCS)_6^{3-}]_{t=0}=3.56$ mM, $[Cr(II)]_{t=0}=0.47_2$ mM, $[EDTA]_{t=0}=12.5$ mM, 25°C, $\mu=1.0$, pH 3.71, Scanning speed=3.42 mμ/sec. (A) Spectrum at $t=0$ over the range of all wave length. (B) 10 sec (C) 120 sec and (D) 600 sec after the addition of chromium(II). Times given are for start of scan at 374 mμ. (E) Spectrum of the solution which was exposed to air after spectrum D was measured.

where reaction (4) is the electron-transfer reaction between $Cr^{II}(H_2O)edta^{2-}$ and $Cr(NCS)_6^{3-}$. In this mechanism, reaction (4) is a rate-determining step because the complex-forming reaction (reaction 3) of chromium(II) ions is considered to be very fast.[6,7] The rate law for reaction (2) is expressed as

$$-\frac{d[Cr(NCS)_6^{3-}]}{dt} = \frac{d[Cr^{III}(H_2O)edta^{-}]}{dt}$$
$$= k[Cr^{II}(H_2O)edta^{2-}][Cr(NCS)_6^{3-}] \qquad (5)$$

Since the concentration of $Cr^{II}(H_2O)edta^{2-}$ remains constant during the reaction, the integration of Eq. (5) leads to

$$\ln|D_t - D_\infty| =$$
$$-k[Cr^{II}(H_2O)edta^{2-}]t + \ln|D_0 - D_\infty| \qquad (6)$$

where D_0, D_t and D_∞ are absorbancies at time 0, t and infinite, respectively.

An example of the kinetic run of the reaction between chromium(II)-EDTA and $Cr(NCS)_6^{3-}$ ions is shown in Fig. 4. Excellent first-order plots were obtained as expected from Eq. (6).

Table 2 gives the results obtained on the rate of the reaction between chromium(II)-EDTA and $Cr(NCS)_6^{3-}$ ions. The rate constants were independent of the initial concentrations of both

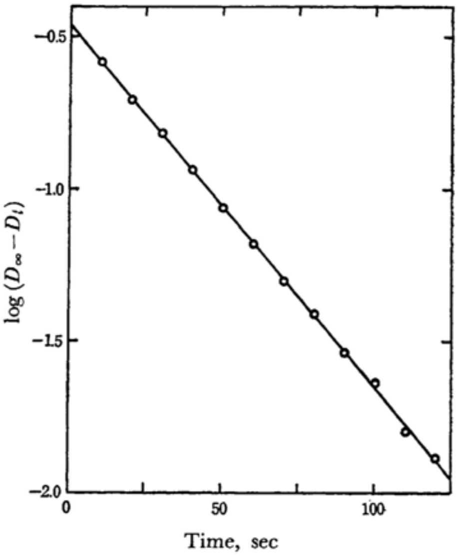

Fig. 4. A typical kinetic run of the reaction between $Cr^{II}(H_2O)edta^{2-}$ and $Cr(NCS)_6^{3-}$ in the presence of EDTA at 510 mμ: $[Cr^{II}(H_2O)edta^{2-}]=0.994$ mM, $[Cr(NCS)_6^{3-}]_{t=0}=3.47$ mM, $[EDTA]_{t=0}=12.5$ mM, pH 5.25.

Table 2. Rate constants of the reaction between chromium(II)-EDTA and $Cr(NCS)_6^{3-}$ at $\mu=1.0$ ($NaClO_4$) and 25°C

pH	$[Cr(NCS)_6^{3-}]_{t=0}$ mM	$[Cr^{II}(H_2O)edta^{2-}]$ mM	k $l\,mol^{-1}\,sec^{-1}$	Wavelength for measurement, mμ
5.25	3.47	0.994	27.6	510
4.93	2.86	1.06	29.5	510
4.92	3.37	1.03	29.3	510
4.87	2.78	2.78	28.4	510
4.81	2.96	5.73	27.7	510
4.80	0.949	1.06	28.8	510
4.74	3.93	1.06	30.0	545
4.73	5.62	1.06	29.0	422
4.60	3.23	0.964	27.2	510
4.48	3.03	0.457	29.2	510
4.28	3.01	0.964	27.8	422
4.17	2.92	2.78	26.7	510
4.11	3.33	5.78	24.5	510
4.00	3.24	0.964	25.3	510
3.81	3.48	0.964	24.6	510

chromium(II)-EDTA and $Cr(NCS)_6^{3-}$. Therefore, the reaction is strictly of second-order. Rate constants obtained at different wave length are in a good agreement. A rigorous treatment of the pH dependence of rates was made, because it is known that $Cr^{II}(H_2O)edta^{2-}$ forms protonated species, $Cr^{II}(H_2O)Hedta^-$, at lower pH's. If the presence of $Cr^{II}(H_2O)Hedta^-$ is considered, the electron-transfer reaction may proceed through the following two simultaneous reaction paths:

$$Cr^{II}(H_2O)edta^{2-} + Cr(NCS)_6^{3-} \xrightarrow{k_1} Cr^{III}(H_2O)edta^- + Cr^{2+} + 6NCS^- \qquad (7)$$

$$Cr^{II}(H_2O)Hedta^- + Cr(NCS)_6^{3-} \xrightarrow{k_2} Cr^{III}(H_2O)Hedta + Cr^{2+} + 6NCS^- \qquad (8)^{*3}$$

Then, the observed rate constant k can be expressed as

$$k = \frac{k_1/[H^+]+k_2K^H}{1/[H^+]+K^H} \qquad (9)$$

where

$$K^H = \frac{[Cr^{II}(H_2O)Hedta^-]}{[Cr^{II}(H_2O)edta^{2-}][H^+]} \qquad (10)$$

The value of K^H has been determined to be $10^{3.00}$ at ionic strength 0.1 and 20°C by Pecsok *et al.*5) Equation (9) is rewritten as

$$k\alpha = \frac{k_1}{[H^+]} + k_2K^H \qquad (11)$$

where

$$\alpha = \frac{1}{[H^+]} + K^H \qquad (12)$$

Figure 5 shows the plots of $k\alpha$ vs. reciprocal hydrogen ion concentrations in the reaction of chromium(II)-EDTA with $Cr(NCS)_6^{3-}$. The value of k_1 obtained from the slope is equal to 28.2 $l\ mol^{-1}\ sec^{-1}$. The value of the intercept is approximately zero. It could be deduced from standard deviations of the plots that k_2 is less than 50 $l\ mol^{-1} sec^{-1}$.

Similar kinetic behaviors were found for the reactions involving other chromium(III) complexes.

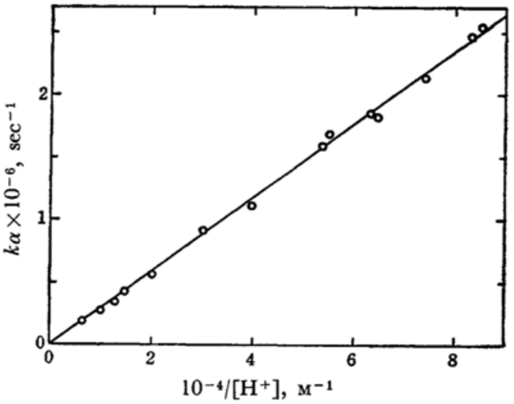

Fig. 5. The values of left hand side of Eq. (11) as a function of reciprocal hydrogen ion concentrations in the reaction between chromium(II)-EDTA and $Cr(NCS)_6^{3-}$.

TABLE 3. RATE CONSTANTS OF ELECTRON-TRANSFER REACTIONS BETWEEN $Cr^{II}(H_2O)edta^{2-}$ AND $Cr(NCS)_n(NH_3)_{6-n}^{(3-n)+}$ AT $\mu=1.0$ AND 25°C

Complex	Rate constant $l\ mol^{-1}$ sec^{-1}	Medium	Absorption maxima of ligand field bands $\tilde{\nu}\times10^{-3}$, cm^{-1}	
			1 st band	2 nd band
$Cr(NH_3)_6^{3+}$	$<10^{-2}$	NaCl	21.46	28.41
$CrNCS(NH_3)_5^{2+}$	0.2	NaCl	20.49	27.32
$Cr(NCS)_4(NH_3)_2^-$	2.3	$NaClO_4$	19.08	25.38
$Cr(NCS)_6^{3-}$	28.2	$NaClO_4$	17.67	23.70

Second-order rate constants of the reaction between $Cr^{II}(H_2O)edta^{2-}$ and $Cr(NCS)_n(NH_3)_{6-n}^{(3-n)+}$ are given in Table 3. Although $Cr(NH_3)_6^{3+}$ ions were found to react with chromium(II)-EDTA, only an upper limit of rate constant was obtained, because of extremely slow rate of the reaction. Since $Cr(NH_3)_6^{3+}$ complex has no electron-pair exposed, the mechanism of this electron-transfer reaction is probably of outer-sphere type.

The rate constants of $Cr(NCS)_n(NH_3)_{6-n}^{(3-n)+}$ shown in Table 3 increase with the number of thiocyanate anions coordinated, in spite of the increase of electrostatic repulsion between reactants. If these reactions occur *via* activated complexes which involve thiocyanate anions as a bridge between chromium(II)-EDTA and $Cr(NCS)_n(NH_3)_{6-n}^{(3-n)+}$, it may be expected that the rate of electron-transfer reactions increases with the number of groups coordinated to chromium(III) which are able to mediate an electron. However, the increase of the rate constants given in Table 3 is much larger than expected from the statistical factor mentioned above. This suggests a large contribution of the free energy change of the reactions in question.

King and Ball23) reported that the electron-transfer reaction of chromium(II) ions with $CrNCS(H_2O)_5^{2+}$ ions proceeds through an activated complex which involves a coordinated thiocyanate anion as a bridge between the chromium(II) and chromium(III). Haim and Sutin24) reported

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[*3] It should be noted that chromium(III)-EDTA ions are present in the forms of both $Cr^{III}(H_2O)edta^-$ and $Cr^{III}(H_2O)Hedta$ at lower pH's. The pK value for the reaction

$$Cr^{III}(H_2O)edta^- + H^+ \rightleftharpoons Cr^{III}(H_2O)Hedta$$

has been determined to be 3.19,20) or 2.27.22)

22) C. Furlani, G. Morpurgo and G. Sartori, *Z. anorg. u. allgem. Chem.*, **303**, 1 (1960).

23) D. L. King and E. L. Ball, *J. Am. Chem. Soc.*, **80**, 1091 (1958).

24) A. Haim and N. Sutin, *ibid.*, **88**, 434 (1966).

that chromium(II) ions react with $FeNCS^{2+}$ and various isothiocyanatocobalt(III) complexes to produce both $CrSCN^{2+}$ and $CrNCS^{2+}$. It was shown spectrophotometrically that the chromium(III)-EDTA of the products obtained in this work contained no thiocyanate anion in the first coordination sphere. This was also verified from the behavior of the product on the ion-exchange resins. However, this does not necessarily preclude inner-sphere mechanisms of the reactions investigated in this work. It is considered that the reactions of $Cr^{II}(H_2O)edta^{2-}$ with $CrNCS(NH_3)_5^{2+}$, $Cr(NCS)_4(NH_3)_2^-$ and $Cr(NCS)_6^{3-}$ proceed through an inner-sphere mechanism.[25]

The absorption maxima of the ligand field band of $Cr(NCS)_n(NH_3)_{6-n}^{(3-n)+}$ are also given in Table 3. It is of interest that there is a correlation between the rate constants and the wave numbers of the absorption maxima of $Cr(NCS)_n(NH_3)_{6-n}^{(3-n)+}$.

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[25] H. Ogino and N. Tanaka, This Bulletin, in press.