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Kinetics of Electron-Transfer Reactions Involving Ethylenediaminetetraacetatochromate(II) Ions as Reductants. II. Reactions with Some Acidopentaamminechromium(III) Complexes[*1]

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The rate of the electron-transfer reactions between ethylenediaminetetraacetatochromate(II) and some acidopentaamminechromium(III), $CrX(NH_3)_5^{2+}$, has been measured at ionic strength 1.0 ($NaClO_4$). The rate constants ($l\ mol^{-1}sec^{-1}$) for $X=F^-$, Cl^-, Br^- and OH^- are 2.07 at 25°C, 2×10^3 at 25°C, $>2\times10^3$ at 15°C and 2.4×10^2 at 25°C, respectively. These reactions produce ethylenediaminetetraacetatochromate(III) ions which do not contain an anion X. The mechanisms of these reactions are discussed.

It is known that the electron-transfer reactions of chromium(II) ions with halogenopentaamminechromium(III) complexes proceed through inner-sphere mechanisms,[1] in which halide ions originally coordinated to chromium(III) complexes act as bridging ligands. It is also known that the order of the efficiency of the bridging groups in the reactions between chromium(II) ions and acidopentaaquo- and hexaaquochromium(III) complexes is $Br^- > Cl^- > OH^- > F^- > NCS^- > H_2O$.[2,3]

In order to know the effect of the complex formation of chromium(II) ions with ethylenediaminetetraacetate (EDTA) on the electron-transfer reactions and to elucidate the mechanism of the reactions, the kinetics of the electron-transfer reactions between chromium(II)-EDTA and acidopentaamminechromium(III) complexes are dealt with in this paper. The results are compared with those reported in the previous papers.[1-5]

Experimental

A starting material for the preparation of all acidopentaamminechromium(III) complexes used was $[CrH_2O(NH_3)_5](NO_3)_3$, which was prepared by the method of Mori,[6] and from which $[CrH_2O(NH_3)_5](ClO_4)_3$ was obtained by the procedures reported by King.[7] $[CrF(NH_3)_5](ClO_4)_2$ was prepared by the method of Linhard and Weigel[8] from $[CrH_2O(NH_3)_5](ClO_4)_3$. $[CrCl(NH_3)_5]Cl_2$ was obtained by the method reported previously.[9] Its conversion to the perchlorate was carried out by the method of Ogard and Taube[1] with the aid of Dowex 50W-X8 cation exchange resin. $[CrBr(NH_3)_5]Br_2$ was prepared by the procedures reported in literature.[1] This compound was converted to the perchlorate by the recrystallization from aqueous perchloric acid solution. The results of the analysis of the chromium(III) compounds are given in Table 1.

Chromium(II) perchlorate solutions were prepared by the reduction of hexaaquochromium(III) perchlorate with zinc amalgam. Ionic strength of the solution was adjusted to 1.0 with sodium perchlorate. The pH of the solutions was adjusted by using acetate buffer solutions. In most cases, the temperature of kinetic measurement was 25°C and, in some cases, was varied between 5°C and 35°C to determine the kinetic parameters.

Other analytical and kinetic procedures were similar to those reported previously.[4]

Results and Discussion

Kinetics of the Reactions of Chromium(II)-EDTA with $CrF(NH_3)_5^{2+}$, $CrCl(NH_3)_5^{2+}$ and $CrBr(NH_3)_5^{2+}$. Figure 1 shows a typical example of the spectral change of the $CrF(NH_3)_5^{2+}$ in the presence of excess EDTA upon the addition of chromium(II) perchlorate solution (spectra A to D).[*2] The reaction seemed to be complete

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[*1] Presented at the 10th International Conference on Coordination Chemistry, Nikko, Japan, September, 1967.

1) A. E. Ogard and H. Taube, *J. Am. Chem. Soc.*, **80**, 1084 (1958).

2) D. L. Ball and E. L. King, *ibid.*, **80**, 1091 (1958).

3) N. Sutin, *Ann. Rev. Nucl. Sci.*, **56**, 285 (1962).

4) H. Ogino and N. Tanaka, This Bulletin, **41**, 1622 (1968).

5) A. Anderson and N. A. Bonner, *J. Am. Chem. Soc.*, **76**, 3826 (1954).

6) M. Mori, *Nippon Kagaku Zassi (J. Chem. Soc. Japan, Pure Chem. Sect.)*, **74**, 253 (1953).

7) H. J. S. King, *J. Chem. Soc.*, **127**, 2100 (1925).

8) M. Linhard and M. Weigel, *Z. Anorg. Allg. Chem.*, **278**, 24 (1955).

9) N. Tanaka, M. Kamada, J. Fujita and E. Kyuno, This Bulletin, **37**, 222 (1964).

[*2] 0.16 mM $[Cr^{III}(H_2O)deta]_{t=0}$ given in Fig. 1 comes from chromium(III) ions which are present as impurity in the chromium(II) perchlorate solution and may be $Cr(H_2O)_6^{3+}$ and/or $[CrOH(H_2O)_4]_2^{4+}$. It was found that, when chromium(II) solution contaminated by chromium(III) ions was injected into excess EDTA solution, the same amount of $Cr^{III}(H_2O)edta^-$ as that of chromium(III) ions in the original solution was formed within the time of mixing.[4]

TABLE 1. ANALYSES OF THE CHROMIUM(III) COMPLEXES

Complex	Cr, %		N, %	
	Found	Calcd	Found	Calcd
$[CrH_2O(NH_3)_5](ClO_4)_3$	11.49	11.46	15.62	15.44
$[CrF(NH_3)_5](ClO_4)_2$	14.34	14.64	20.08	19.72
$[CrCl(NH_3)_5](ClO_4)_2$	13.66	14.00	19.10	18.85
$[CrBr(NH_3)_5](ClO_4)_2$	11.93	12.50	16.75	16.84

TABLE 2. RATE CONSTANTS OF THE REACTIONS BETWEEN CHROMIUM(II)-EDTA AND $CrF(NH_3)_5^{2+}$ AT $\mu=1.0$ ($NaClO_4$) AND 25°C

pH	$[CrF(NH_3)_5^{2+}]_{t=0}$ mM	$[Cr^{II}(H_2O)edta^{2-}]$ mM	k $l\,mol^{-1}\,sec^{-1}$
4.98	3.11	5.73	2.03
4.96	3.52	2.78	2.07
4.73	3.46	5.73	2.03
4.21	2.87	2.78	2.00
4.19	2.06	20.2	1.85
3.98	2.40	20.2	1.73
3.72	1.66	20.2	1.71
3.53	2.13	20.2	2.14

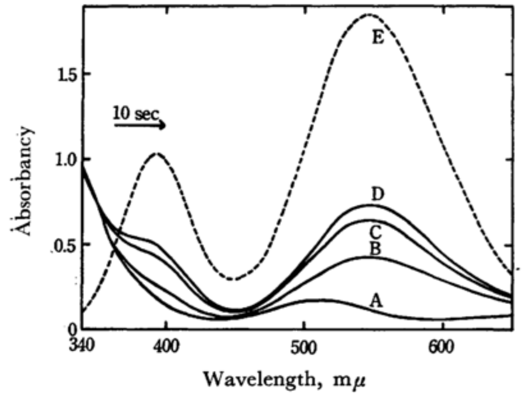

Fig. 1. Spectral change of the $CrF(NH_3)_5^{2+}$ solution in the presence of EDTA upon the addition of chromium(II) ions in sodium acetate-sodium perchlorate media: $[CrF(NH_3)_5^{2+}]_{t=0}=3.18$ mM, $[Cr(II)]_{t=0}=5.73$ mM, $[Cr^{III}(H_2O)edta^-]_{t=0}=0.16$ mM (see footnote), $[EDTA]_{t=0}=20$ mM, $\mu=1.0$, pH 4.99, 25°C, scanning speed=3.40 mμ/sec and cell length=1 cm. (A) Spectrum at $t=0$ over the whole range of wave length. (B) 10 sec (C) 130 sec and (D) 660 sec after the addition of chromium(II). Times given are for start of scan at 340 mμ. (E) Spectrum of the solution exposed to air after the measurement of spectrum D.

whithin 660 sec, since no change was observed in the spectrum after the measurement of spectrum D. The spectral change shown in Fig. 1 can be interpreted reasonably by the overall reaction,

$$CrX(NH_3)_5^{2+} + H_j edta^{(4-j)-} + H_2O \rightarrow Cr^{III}(H_2O)edta^- + X^- + 5NH_3 + jH^+ \quad (1)$$

where X should read F in this case. Equation (1) is generalized by writing $CrX(NH_3)_5^{2+}$ instead of $CrF(NH_3)_5^{2+}$. This equation is essentially identical with the overall reaction between chromium(II) ions and $Cr(NCS)_n(NH_3)_{6-n}^{(3-n)+}$ ions in the presence of EDTA.[4] Spectrum E was obtained when the solution was exposed to air after the completion of the reaction. The spectral change from D to E corresponds to the oxidation of $Cr^{II}(H_2O)edta^{2-}$ present in the solution to $Cr^{III}(H_2O)edta^-$ and reveals that the concentration of $Cr^{II}(H_2O)edta^{2-}$ remains constant during the reaction.

By considering the results mentioned above and those reported previously,[4] the mechanism of reaction (1) can be expressed by the following equations:

$$Cr^{2+} + H_j edta^{(4-j)-} + H_2O \rightleftharpoons Cr^{II}(H_2O)edta^{2-} + jH^+ \quad (2)$$

$$Cr^{II}(H_2O)edta^{2-} + CrX(NH_3)_5^{2+} \xrightarrow{k} Cr^{III}(H_2O)edta^- + Cr^{2+} + X^- + 5NH_3 \quad (3)$$

where reaction (3) is a rate-determining step because of the rapidity of the complex-forming reaction (2).[10,11] The rate law of the reaction (1) is given by the equation,

$$-\frac{d[CrX(NH_3)_5^{2+}]}{dt} = \frac{d[Cr^{III}(H_2O)edta^-]}{dt} = k[Cr^{II}(H_2O)edta^{2-}][CrX(NH_3)_5^{2+}] \quad (4)$$

Table 2 gives the results which were obtained on

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[10] K. Ogino(née Ebata) and N. Tanaka, This Bulletin, **39**, 2672 (1966).

[11] N. Tanaka and A. Yamada, *Rev. Polarog. (Kyoto)*, **14**, 234 (1967).

the rate of the reaction between $\mathrm{Cr^{II}(H_2O)edta^{2-}}$ and $\mathrm{CrF(NH_3)_5^{2+}}$ at 25°C. These data show that the reaction is strictly of second-order. The pH dependence of the rate was analyzed by the method reported previously,4) in which the formation of $\mathrm{Cr^{II}(H_2O)Hedta^-}$ was considered. The rate constant of the reaction,

$$\mathrm{Cr^{II}(H_2O)edta^{2-} + CrF(NH_3)_5^{2+} \rightarrow}$$
$$\mathrm{Cr^{III}(H_2O)edta^- + Cr^{2+} + F^- + 5\,NH_3} \quad (5)$$

was obtained to be 2.07 $l\,\mathrm{mol^{-1}sec^{-1}}$ and the rate constant of the reaction,

$$\mathrm{Cr^{II}(H_2O)Hedta^- + CrF(NH_3)_5^{2+} \rightarrow}$$
$$\mathrm{Cr^{III}(H_2O)Hedta + Cr^{2+} + F^- + 5\,NH_3} \quad (6)$$

was found to be less than 1 $l\,\mathrm{mole^{-1}sec^{-1}}$.

Similar experiments were made on the systems containing $\mathrm{CrCl(NH_3)_5^{2+}}$ and $\mathrm{CrBr(NH_3)_5^{2+}}$ ions. It was found spectrophotometrically that a product of the reaction of $\mathrm{Cr^{II}(H_2O)edta^{2-}}$ with $\mathrm{CrCl(NH_3)_5^{2+}}$ or $\mathrm{CrBr(NH_3)_5^{2+}}$ was not $\mathrm{Cr^{III}Xedta^{2-}}$ but $\mathrm{Cr^{III}(H_2O)edta^-}$. The reaction between $\mathrm{Cr^{II}(H_2O)edta^{2-}}$ and $\mathrm{CrBr(NH_3)_5^{2+}}$ was so rapid that the rate constant could not be determined.

Kinetics of the Reaction of Chromium(II)-EDTA with $\mathrm{CrH_2O(NH_3)_5^{3+}}$. In the reaction between chromium(II)-EDTA and $\mathrm{CrH_2O(NH_3)_5^{3+}}$, the observed second-order rate constants were considerably dependent on pH as shown in Fig. 2. In the pH range investigated, $\mathrm{CrH_2O(NH_3)_5^{3+}}$ ions are appreciably hydrolyzed, because the hydrolysis constant expressed by

$$K_h = \frac{[\mathrm{CrOH(NH_3)_5^{2+}}][\mathrm{H^+}]}{[\mathrm{CrH_2O(NH_3)_5{}^{3+}}]} \quad (7)$$

is 6.7×10^{-6} moll^{-1} at ionic strength 1.0 ($\mathrm{NaClO_4}$) and 25°C.12) Hence, it is reasonable to assume that the reaction in question proceeds through the following two simultaneous reaction paths:

$$\mathrm{Cr^{II}(H_2O)edta^{2-} + CrH_2O(NH_3)_5^{3+}} \xrightarrow{k_1}$$
$$\mathrm{Cr^{III}(H_2O)edta^- + Cr^{2+} + H_2O + 5NH_3} \quad (8)$$

$$\mathrm{Cr^{II}(H_2O)edta^{2-} + CrOH(NH_3)_5^{2+}} \xrightarrow{k_2}$$
$$\mathrm{Cr^{III}(H_2O)edta^- + Cr^{2+} + OH^- + 5NH_3} \quad (9)$$

By considering these reactions, the following equation can be obtained for the observed rate constant, k.

$$k = \frac{k_1 + k_2K_h/[\mathrm{H^+}]}{1 + K_h/[\mathrm{H^+}]} \times \frac{1}{1 + K^{\mathrm{H}}[\mathrm{H^+}]} \quad (10)$$

$$\text{where} \quad K^{\mathrm{H}} = \frac{[\mathrm{Cr^{II}(H_2O)Hedta^-}]}{[\mathrm{Cr^{II}(H_2O)edta^{2-}}][\mathrm{H^+}]} \quad (11)$$

and the value of K^{H} has been determined to be $10^{3.00}$.13)

This equation is rewritten as,

$$k\alpha' = k_1 + k_2K_h/[\mathrm{H^+}] \quad (12)$$

$$\text{where} \quad \alpha' = (1 + K_h/[\mathrm{H^+}])(1 + K^{\mathrm{H}}[\mathrm{H^+}]) \quad (13)$$

If the values of left-hand side of Eq. (12) are plotted against reciprocal hydrogen ion concentrations, linear plots will be obtained. Figure 3 shows the plots of $k\alpha'$ *vs.* reciprocal hydrogen ion concentrations. The best values of intercept and slope were calculated by least square method, with the aid of the data in Fig. 3. The relation,

$$k\alpha' = (0\pm1) + (1.62\pm0.03)\times10^{-3}/[\mathrm{H^+}] \quad (14)$$

was obtained. Uncertainties in Eq. (14) represent standard deviations. The value of intercept is practically zero. This means that the reaction proceeds through the sole path represented by Eq. (9). The rate constant of the reaction is 2.4×10^2 $l\,\mathrm{mol^{-1}sec^{-1}}$ and the value of k_1 is less than 1 $l\,\mathrm{mol^{-1}sec^{-1}}$.

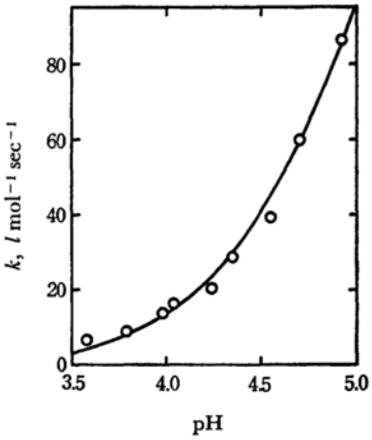

Fig. 2. The pH dependence of the observed second-order rate constant, k, for the reaction between chromium(II)-EDTA and $\mathrm{CrH_2O(NH_3)_5^{3+}}$ at 25°C and μ=1($\mathrm{NaClO_4}$).

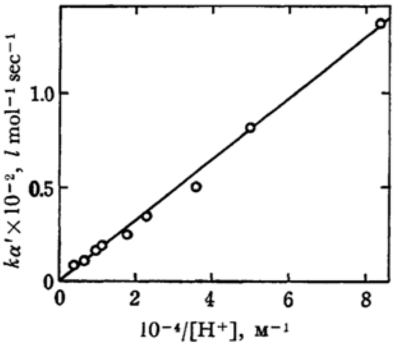

Fig. 3. The values of left-hand side of Eq. (12) as a function of reciprocal hydrogen ion concentration in the reaction between chromium(II)-EDTA and $\mathrm{CrH_2O(NH_3)_5^{3+}}$.

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12) H. Ogino, unpublished result.

13) R. L. Pecsok, L. D. Shields and W. P. Schefer, *Inorg. Chem.*, **3**, 114 (1964).

It should be noted that reactions other than Eqs. (8) and (9), such as

$$Cr^{II}(H_2O)Hedta^- + CrH_2O(NH_3)_5^{3+} \xrightarrow{k_3} Cr^{III}(H_2O)Hedta + Cr^{2+} + H_2O + 5NH_3 \quad (15)$$

and

$$Cr^{II}(H_2O)Hedta^- + CrOH(NH_3)_5^{2+} \xrightarrow{k_4} Cr^{III}(H_2O)edta^- + Cr^{2+} + H_2O + 5NH_3 \quad (16)$$

could have been considered. From the analysis of the data given in Fig. 2, it was found that there is no significant contribution of reaction (15) to the overall reaction under consideration. Reaction (16) cannot be distinguished from Eq. (8), since the interconversion of the acid and the base form of the reactants is rapid enough to maintain the equilibrium between them during the reaction. By considering both reactions (9) and (16), the following equation can be obtained instead of Eq. (12).

$$k\alpha' = k_4K^HK_h + k_2K_h/[H^+] \quad (17)$$

The value of intercept of the linear plots of $k\alpha'$ *vs.* reciprocal hydrogen ion concentrations corresponds to the value of $k_4K^HK_h$. The value which was estimated with the aid of the values of K^H [13] and K_h[12] was smaller than $2\times10^2\ l\ mol^{-1}sec^{-1}$.

Discussion on the Rate Constants of the Reactions between $Cr^{II}(H_2O)edta^{2-}$ and $CrX(NH_3)_5^{2+}$ Complexes. The second-order rate constants of the reaction between $Cr^{II}(H_2O)edta^{2-}$ and acido- and aquopentaamminechromium(III) complexes are given in Table 3. The kinetic parameters obtained in this study are given in Table 4 together with those of other related systems. A striking feature presented in Table 3 is a great variety of rate with the nature of the complexes.

TABLE 3. RATE CONSTANTS OF THE ELECTRON-TRANSFER REACTION BETWEEN $Cr^{II}(H_2O)edta^{2-}$ AND ACIDO- AND AQUOPENTAAMMINECHROMIUM(III) COMPLEXES AT $\mu=1.0$ ($NaClO_4$) AND 25°C

Complex	k $l\ mol^{-1}\ sec^{-1}$
$Cr(NH_3)_6^{3+}$	$<10^{-2}$ [a]
$CrH_2O(NH_3)_5^{3+}$	<1
$CrOH(NH_3)_5^{2+}$	2.4×10^2
$CrF(NH_3)_5^{2+}$	2.07
$CrCl(NH_3)_5^{2+}$	2×10^3
$CrBr(NH_3)_5^{2+}$	$>2\times10^3$ [b]
$CrNCS(NH_3)_5^{2+}$	0.2[a]

a) $\mu=1.0$ (NaCl), from Ref. 4.
b) At 15°C.

Table 5 shows the rate constants of the following electron-transfer reaction,

$$*Cr^{2+} + CrX(H_2O)_5^{2+} \xrightarrow{k_{Cr(II)}} *CrX(H_2O)_5^{2+} + Cr^{2+} \quad (18)$$

where *Cr denotes labeled chromium atom. It is known that the values of $k_{Cr(II)}$ given in Table 5 correspond to the rate constants of inner-sphere electron-transfer reactions, in which ligand X acts as an electron-transfer bridge and the product criteria apply.[2,3,14] The comparison of $k_{Cr(II)}$ in Table 5 reveals that the order of the efficiency of the bridging groups in reaction (18) is

$$Br^- > Cl^- > OH^- > F^- > NCS^- > H_2O \;{}^{2,3)}$$

This order is in agreement with that of the rate constants of reaction (3) in Table 3. The plots of log $k_{Cr(II)Y}$ *vs.* log $k_{Cr(II)}$ give at raight line with a slope of approximately unity as shown in Fig. 4,[15] where $k_{Cr(II)Y}$ denotes the rate constant of reaction (3).

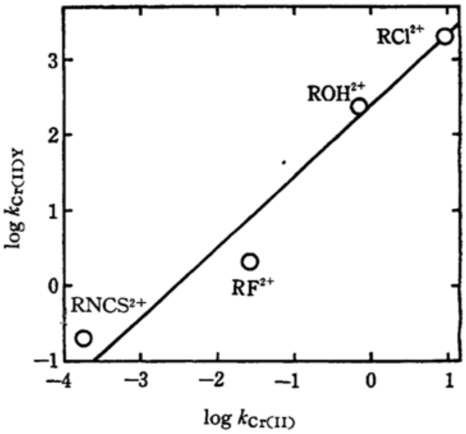

Fig. 4. Relation between the rate constant of reaction 3 ($k_{Cr(II)Y}$) and that of reaction (18) ($k_{Cr(II)}$). R denotes $Cr(NH_3)_5$ for the reaction involving $Cr^{II}(H_2O)edta^{2-}$ and $Cr(H_2O)_5$ for the reaction involving Cr^{2+}.

The facts mentioned above may suggest that the mechanism of the reactions between $Cr^{II}(H_2O)$-$edta^{2-}$ and $CrX(NH_3)_5^{2+}$, except $Cr(NH_3)_6^{3+}$,[4] is of inner-sphere type. This leads naturally to the mechanism expressed as follows for the reaction between $Cr^{II}(H_2O)edta^{2-}$ and $CrX(NH_3)_5^{2+}$:

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14) It should be noted that there is no direct evidence that the reaction between Cr^{2+} and $Cr(H_2O)_6^{3+}$ or $CrOH(H_2O)_5^{2+}$ proceeds through inner-sphere mechanism.

15) In Fig. 4, 9.1 $l\ mol^{-1}\ sec^{-1}$ (at 0°C)[2] is used as the rate constant of the reaction between Cr^{2+} and $CrCl(H_2O)_5^{2+}$, that is, temperature dependence of the rate constant is neglected. On the other hand, the value of one sixth times of the rate constant of the Cr^{2+}-$CrOH(H_2O)_5^{2+}$ reaction should be compared with the rate constants of the other Cr^{2+}-$CrX(H_2O)_5^{2+}$ reactions, the statistical effect being considered. This correction is not made in Fig. 4. The conclusion that the slope of the plots is unity is not affected even by the consideration of these corrections, though the deviation of plots is relatively large.

TABLE 4. KINETIC PARAMETERS OF THE ELECTRON-TRANSFER REACTIONS OF ACIDOPENTAAMMINECHROMIUM(III) COMPLEXES WITH $Cr^{II}(H_2O)edta^{2-}$ (Cr(II)-EDTA SYSTEM) AND WITH Cr^{2+} (Cr^{2+} SYSTEM)

Complex	Cr(II)-EDTA system[a]		Cr^{2+} system[b]	
	$\Delta H^{\ddagger}$ kcal/mol	$\Delta S^{\ddagger}$ e. u.	$\Delta H^{\ddagger}$ kcal/mol	$\Delta S^{\ddagger}$ e. u.
$CrF(NH_3)_5^{2+}$	13.9 ± 0.3	-10.6 ± 0.3	13.4	−30
$CrCl(NH_3)_5^{2+}$	9.1 ± 1.0	-13 ± 3	11.1	−28[c]
$CrBr(NH_3)_5^{2+}$	—	—	8.5	−33

a) This work. Uncertainties represent standard deviations.

b) From Ref. 1.

e) This value was calculated by one of the authors (H. O.) from data on the rate constants reported in the original paper.[1] The original value −23 e. u., should read −28 e. u. (H. Taube, private communication).

TABLE 5. RATE CONSTANTS OF THE ELECTRON-TRANSFER REACTIONS BETWEEN Cr^{2+} AND ACIDO- AND AQUOPENTAAMMINECHROMIUM(III) IONS

Complex	$k_{Cr(II)}$ l mol^{-1} sec^{-1}	Temp. °C	Ref.
$Cr(H_2O)_6^{3+}$	$\leq2\times10^{-5}$	24.5	5
$CrOH(H_2O)_5^{2+}$	0.7	24.5	5
$CrF(H_2O)_5^{2+}$	2.6×10^{-2}	27	2
$CrCl(H_2O)_5^{2+}$	9.1	0	2
$CrBr(H_2O)_5^{2+}$	>60	0	2
$CrNCS(H_2O)_5^{2+}$	1.8×10^{-4}	27	2

TABLE 6. COMPARISON OF THE RATE CONSTANTS OF REACTION (21) ($k'_{Cr(II)}$) WITH THOSE OF REACTION (3) ($k_{Cr(II)Y}$)

Complex	$k'_{Cr(II)}$[a] l mol^{-1}sec^{-1}	$k_{Cr(II)Y}/k'_{Cr(II)}$	Temp. °C
$CrF(NH_3)_5^{2+}$	2.7×10^{-4}	7.7×10^{3}	25
$CrCl(NH_3)_5^{2+}$	5.1×10^{-2}	4×10^{4}	25
$CrBr(NH_3)_5^{2+}$	0.191	$>1\times10^{4}$	15

a) From Ref. 1.

$$Cr^{II}(H_2O)edta^{2-} + Cr^{III}X(NH_3)_5^{2+} \xrightarrow{\text{slow}} Cr^{III}Xedta^{2-} + H_2O + Cr^{2+} + 5NH_3 \quad (19)^{16)}$$

$$Cr^{III}Xedta^{2-} + H_2O \xrightarrow{\text{fast}} Cr^{III}(H_2O)edta^{-} + X^{-} \quad (20)$$

Product criteria did not apply to the present cases under the experimental condition. This seems to be due to the lability of $Cr^{III}Xedta^{2-}$, which dissociates rapidly to $Cr^{III}(H_2O)edta^{-}$ and anion X.

Table 6 shows the comparison of $k_{Cr(II)Y}$ with the rate constant of the following electron-transfer reaction[1]:

$$Cr^{2+} + CrX(NH_3)_5^{2+} \xrightarrow{k'_{Cr(II)}} CrX(H_2O)_5^{2+} + Cr^{2+} + 5NH_3 \quad (21)$$

Unfortunately, the comparison is restricted to only a few cases, but it is shown in Table 6 that $Cr^{II}(H_2O)edta^{2-}$ reacts with $CrX(NH_3)_5^{2+}$ faster than chromium(II) ions approximately by ten thousand times. Chromium(II) - EDTA ions are more powerful as reducing agent than chromium(II) ions. Marcus' theory predicts that the rate of electron-transfer reactions increases with free energy of the reactions,[18,19] though the thoery was derived only for outer-sphere electron-transfer reactions. It was shown recently that free energy contributes also to the rate of the inner-sphere electron-transfer reactions.[20] Considering the difference in the standard reduction potentials of $Cr(aq.)^{2+}$ - $Cr(aq.)^{3+}$ couple (−0.412 V *vs.* NHE)[21] and $Cr^{II}(H_2O)edta^{2-}$ - $Cr^{III}(H_2O)edta^{-}$ couple (-0.98_3 V *vs.* NHE),[13] it seems reasonable that $Cr^{II}(H_2O)edta^{2-}$ ions react more rapidly than chromium(II) ions. In addition, the electrostatic interaction between reactants is more favorable in reaction (3) than in reaction (21). If kinetic parameters of these reactions in Table 4 are compared, it will be found that the enthalpy of activation of reaction (3) is essentially identical with that of reaction (21) and that the increase in rate is mainly due to the change of the entropy of activation. For reactions between oppositely charged ions, the charge of the activated complex is reduced and hence the solvent molecules in the solvation shell will be released during the activation process. For reactions between like-charged ions, these

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16) It is known that the rate for the substitution of an water molecule coordinated to chromium(II) ion is extremely rapid.[17] In Eq. (19), it is assumed that an activated complex, $[edtaCr^{II}\text{-}X\text{-}Cr^{III}(NH_3)_5]^{*}$, is formed after release of the coordinated water molecule in $Cr^{II}(H_2O)edta^{2-}$.

17) M. Eigen, *Ber. Bunsenges. Physik. Chem.*, **67**, 753 (1963).

18) R. Marcus, *J. Phys. Chem.*, **67**, 853 (1963).

19) R. Marcus, *J. Chem. Phys.*, **43**, 679 (1965).

20) For instance, A. Haim and N. Sutin, *J. Am. Chem. Soc.*, **88**, 434 (1966); R. D. Cannon and J. E. Earley, *ibid.*, **88**, 1872 (1966).

21) G. Grube and A. Breitinger, *Z. Elektrochem. angew. physik. Chem.*, **33**, 112 (1927).

situation is opposite. If this electrostriction effect[22,23] is considered, the smaller negative entropy of activation for reaction (3) can be understood at least qualitatively.

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

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22) L. Laidler, "Chemical Kinetics," McGraw-Hill, Inc., New York (1965) p. 216.

23) J. Lewis and R. G. Wilkins, ed., "Modern Coordination Chemistry," Interscience Publishers Inc., New York (1960), p. 100.