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Racemization Reactions of Cobalt(III) Complexes of Ethylenediaminetetraacetate and Trimethylenediaminetetraacetate

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The kinetics of racemization reactions of ethylenediaminetetraacetatocobaltate(III), $Co^{III}edta^-$, and trimethylenediaminetetraacetatocobaltate(III), $Co^{III}trdta^-$, were investigated in acid solutions. The rate law for the racemization of $(+)_{546}Co^{III}edta^-$ is:

$$\frac{d[(+)_{546}Co^{III}edta^-]}{dt} = -2\frac{k_{r1}K_a+k_{r2}[H^+]}{K_a+[H^+]}[(+)_{546}Co^{III}edta^-]$$

where K_a is the equilibrium constant of the reaction:

$$(+)_{546}Co^{III}(H_2O)Hedta \rightleftarrows (+)_{546}Co^{III}edta^- + H^+$$

The values of k_{r1} and k_{r2} at 120°C and at an ionic strength of 0.53 are 2.0×10^{-5} sec^{-1} and 5.6×10^{-4} sec^{-1} respectively. The rate law for the racemization of $(+)_{589}Co^{III}trdta^-$ is:

$$\frac{d[(+)_{589}Co^{III}trdta^-]}{dt} = -2k'_{r2}[H^+][(+)_{589}Co^{III}trdta^-]$$

The value of k'_{r2} at 120°C and at an ionic strength of 0.53 is 1.9×10^{-5} l mol^{-1} sec^{-1}. It is known that the rate of the racemization reaction of optically-active $Co^{III}edta^-$ is accelerated by the presence of $Co^{II}edta^{2-}$ because of the electron-exchange reaction between these two species. In this paper, the electron-exchange reaction between $Co^{III}trdta^-$ and $Co^{II}trdta^{2-}$ is also investigated by the utilization of the optical activity. This reaction proceeds faster than the reaction between $Co^{III}edta^-$ and $Co^{II}edta^{2-}$.

Bailar[1] proposed a trigonal twist mechanism for the racemization reaction of the optically-active $Co^{III}edta^-$ complex. Cooke, Im, and Busch[2] investigated this reaction in the pH range from 2 to 4 and supported Bailar's proposal on the basis of the facts that this reaction gives a very large and positive entropy of activation and that the reaction rate is insensitive to the pH within the range studied. In this paper, the reaction of the racemization of $Co^{III}edta^-$ and $Co^{III}trdta^-$ will be investigated in solutions containing

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[1] J. C. Bailar, Jr., *J. Inorg. Nucl. Chem.*, **8**, 165 (1958).

[2] D. W. Cooke, Y. A. Im, and D. H. Busch, *Inorg. Chem.*, **1**, 13 (1962).

hydrogen ions in concentrations of more than 0.05M, and the mechanisms will be discussed.

Im and Busch[3] investigated the kinetics of the electron-exchange reaction between $\mathrm{Co^{III}edta^-}$ and $\mathrm{Co^{II}edta^{2-}}$ by the utilization of optical activity. In this work, the kinetics of the electron-exchange reaction between $\mathrm{Co^{III}trdta^-}$ and $\mathrm{Co^{II}trdta^{2-}}$ was followed by a procedure similar to that of Im and Busch.[3] The results will also be presented in this paper.

Experimental

Optically-active $\mathrm{K[Co^{III}edta]\cdot 2H_2O}$[4] and $\mathrm{K[Co^{III}trdta]\cdot 2H_2O}$[5] were prepared by the procedures described in the literature. The ionic strength of the solutions was adjusted with potassium nitrate. The visible absorption spectra were recorded with a Hitachi EPS-3 pen-recording spectrophotometer. A JASCO model ORD/UV-5 spectrophotometer with a CD attachment was used for the kinetic studies of $\mathrm{Co^{III}edta^-}$. In most cases, the rotations were measured at 550 nm. A JASCO model DIP-SL automatic polarimeter was used for the studies of $\mathrm{Co^{III}trdta^-}$; the rotation was measured at the sodium D line unless otherwise stated.

The kinetics of the racemization reaction of $\mathrm{Co^{III}edta^-}$ or $\mathrm{Co^{III}trdta^-}$ was studied in potassium nitrate–nitric acid media. Sealed ampules filled with a solution containing an optically-active cobalt(III) complex, nitric acid, and potassium nitrate were placed in a thermostated oil-bath. The ampules were withdrawn at intervals from the oil-bath and cooled immediately. The solutions were then transferred to optical cells and submitted to measurements of the optical rotations. The kinetic stiudes of the electron-exchange reaction between $\mathrm{Co^{II}trdta^{2-}}$ and optically-active $\mathrm{Co^{III}trdta^-}$ were carried out at 90°C. To avoid the evaporation of the solution, the reaction vessel shown in Fig. 1 was employed.

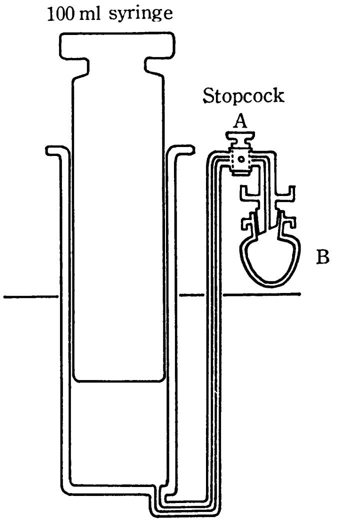

Fig. 1. Reaction vessel used for the kinetic study of the electron-exchange reaction between $\mathrm{Co^{III}}$ trdta$^-$ and $\mathrm{Co^{II}}$ trdta^{2-}.

in an oil-bath of a given temperature. Portions of the solution were removed at intervals from the reaction vessel by opening the stopcock, A, and collected in a vessel, B. The solutions were then transferred to optical cells and submitted to measurements of the optical rotations. The pH of the solution was maintained with an acetate buffer. A Hitachi-Horiba F-5 pH meter was used for the measurement of the pH of the solution. It was found that $\mathrm{Co^{II}trdta^{2-}}$ was slowly oxidized at 90°C. Therefore, air was expelled from the solution by passing through a stream of nitrogen gas before it was placed in a reaction vessel.

Results and Discussion

Racemization Kinetics of $\mathrm{Co^{III}edta^-}$. The rate constants of the racemization reaction of $\mathrm{Co^{III}edta^-}$ were determined by this equation:

$$-\log\left(\frac{\alpha_t}{\alpha_0}\right) = \frac{2}{2.303}k_r t \qquad (1)$$

where α_t and α_0 represent the optical rotations at time t and at time zero respectively. k_r denotes the observed rate constant of the racemization reaction. An example of the plots of $-\log(\alpha_t/\alpha_0)$ *vs.* time is shown in Fig. 2.

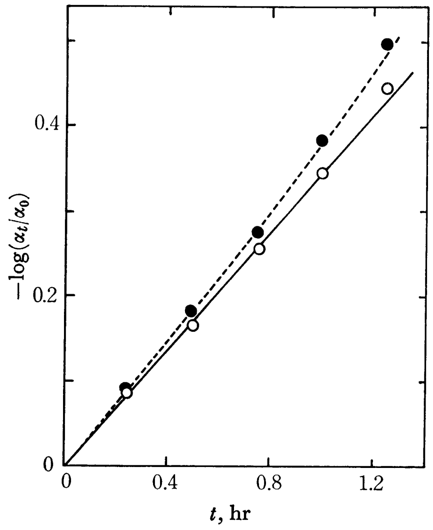

Fig. 2. Relation between $-\log(\alpha_t/\alpha_0)$ and t(solid circles). Open circles represent the values of $-\log(\alpha_t/\alpha_0)$ plotted after correction for the decreases in $\mathrm{Co^{III}}$ edta$^-$ by the decomposition reaction. Experimental condition: $[\mathrm{H^+}]=0.421$M, $\mu=0.53$, 120°C.

It is apparent that the plots do not give a linear relation. The measurements of the visible spectra showed that the cobalt ions in $\mathrm{Co^{III}edta^-}$ were gradually reduced to the divalent state with time. The decrease in the concentrations of $\mathrm{Co^{III}edta^-}$ by this decomposition reaction was determined by the measurement of the visible absorption spectra, and the values of $-\log(\alpha_t/\alpha_0)$ were corrected. The values thus corrected were plotted against the time. The plots gave a straight line, as shown by the solid line in Fig. 2. The rate constant of the racemization, k_r, was calculated from the slope of this straight line. The values of k_r increased with the hydrogen ion concentrations.

It has been known that $\mathrm{Co^{III}edta^-}$ is converted into

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[3] Y. A. Im and D. H. Busch, *J. Amer. Chem. Soc.*, **83**, 3357 (1961).

[4] F. P. Dwyer and F. L. Garvan, "Inorganic Syntheses," Vol. 6, (1960), p. 192.

[5] H. Ogino, M. Takahashi, and N. Tanaka, This Bulletin, **43**, 424 (1970).

$Co^{III}(H_2O)Hedta$ in acid solutions.[6] Shimi and Higginson showed the formation of $Co^{III}(H_2O)Hedta$ by the measurement of the visible spectra of $Co^{III}edta^-$ in acid solutions.[7] The equilibrium constant of the reaction:

$$Co^{III}(H_2O)Hedta \rightleftharpoons Co^{III}edta^- + H^+ \qquad (2)$$

was determined to be 1.28 at 25°C and at an ionic strength of 1.0.[6,8] The formation of $Co^{III}(H_2O)Hedta$ is also shown on the circular dichroism curves (CD curves). In Fig. 3, a CD curve of $(+)_{546}Co^{III}edta^-$ measured in 4.21 M HNO_3 (Curve A) is given and is compared with that of $(+)_{546}Co^{III}edta^-$ measured in a neutral solution (Curve B). Curve A is clearly different from Curve B.

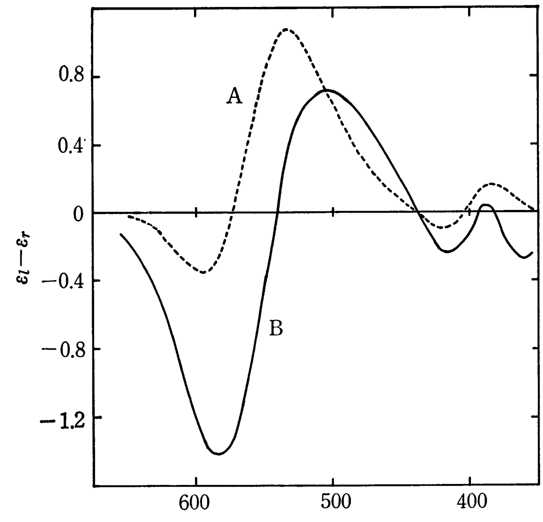

Fig. 3. CD curves of $(+)_{546}$ Co^{III} $edta^-$ in 4.21 M HNO_3 (Curve A) and in water (Curve B).

The change in the k_r value with the hydrogen ion concentrations may be explained by considering the formation of $Co^{III}(H_2O)Hedta$ as follows:

$$(+)_{546}Co^{III}(H_2O)Hedta \rightleftharpoons (+)_{546}Co^{III}edta^- + H^+ \qquad (3)$$

$$(+)_{546}Co^{III}edta^- \xrightarrow{k_{r1}} (-)_{546}Co^{III}edta^- \qquad (4)$$

$$(+)_{546}Co^{III}(H_2O)Hedta \xrightarrow{k_{r2}} (-)_{546}Co^{III}(H_2O)Hedta \qquad (5)$$

In this reaction mechanism, k_r can be expressed as:

$$k_r = \frac{k_{r1}K_a + k_{r2}[H^+]}{K_a + [H^+]} \qquad (6)$$

where K_a represents the equilibrium constant of Reaction (3). The plot of $k_r\ (K_a+[H^+])$ *vs.* $[H^+]$ is given in Fig. 4, which shows a linear relation. The values of k_{r1} and k_{r2} were determined from the intercept and the slope of the straight line respectively. The K_a values used here were calculated from the data reported by Dyke and Higginson.[6] The kinetic parameters are summarized in Table 1.

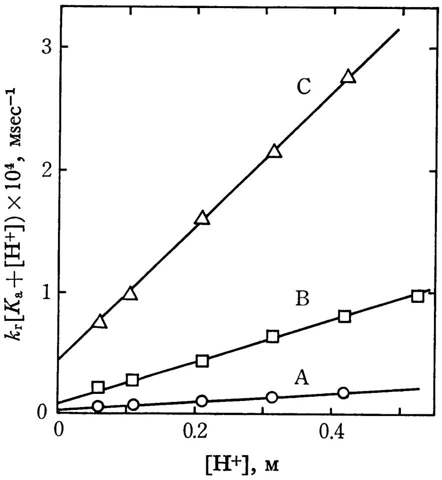

Fig. 4. Relation between $k_r(K_a+[H^+])$ and hydrogen ion concentration for $(+)_{546}$ Co^{III} $edta^-$. Temperature: 100°C (A), 110°C (B), and 120°C (C).

TABLE 1. KINETIC PARAMETERS OF THE RACEMIZATION REACTION OF Co^{III} EDTA COMPLEX ($\mu=0.53$ (KNO_3))

	k_{r1} sec^{-1}	k_{r2}, sec^{-1}
100°C	1.9×10^{-6}	3.9×10^{-5}
110°C	6.1×10^{-6}	1.6×10^{-4}
120°C	2.0×10^{-5}	5.6×10^{-4}
$\Delta H^{\ddagger}$(kcal/mol)	32.9	38.5
$\Delta S^{\ddagger}$(e.u.)	3.1	3.9

Cooke *et al.*[2] reported 3.9×10^{-6} sec^{-1} as the rate constant of the racemization reaction of $Co^{III}edta^-$ at 100°C, which corresponds to the k_{r1} in this work. They also reported that the activation energy and the entropy of activation were 40.6 kcal/mol ($\Delta H^{\ddagger}=39.9$ kcal/mol) and 20.6 e.u. respectively. There is a significant discrepancy between the kinetic parameters determined in this work and those reported by Cooke *et al.* It should be recognized, however, that the gradual decomposition of $Co^{III}edta^-$ was not considered in the studies by Cooke *et al.*

Recently, it was found in this laboratory that the decomposition of $Mn^{III}edta^-$ in an aqueous solution led to the formation of $Mn^{II}edta^{2-}$, $Mn^{II}edtra^-$, Mn^{II}-edda, and some other products,[9] where edtra and edda denote $(^-O_2CH_2C)_2NCH_2CH_2NH(CH_2CO_2^-)$ and $(^-O_2CH_2C)NHCH_2CH_2NH(CH_2CO_2^-)$ respectively. It is not unreasonable that the decomposition products of $Co^{III}edta^-$ contain $Co^{II}edta^{2-}$, $Co^{II}edtra^-$, Co^{II}edda, and some other products similar to the decomposition products of $Mn^{III}edta^-$. In this work, the concentration of the hydrogen ion is kept higher than 0.05 M. Under this experimental condition, divalent cobalt ions produced during the reaction are present in the form of aquo ions, Co^{2+}, so that the contribution of the electron-exchange reaction to the racemization reaction of $Co^{III}edta^-$ can be neglected. As Cooke *et al.* studied the racemization reaction in the pH range from 2 to 4,

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[6] R. Dyke and W. C. E. Higginson, *J. Chem. Soc.*, **1960**, 1998.

[7] I. A. W. Shimi and W. C. E. Higginson, *ibid.*, **1958**, 260.

[8] In this work, the determination of the equilibrium constant was repeated. The constant was found to the 1.31 at 25°C and at an ionic strength of 2.0 ($NaClO_4$), which is in good agreement with the value reported by Dyke and Higginson.[6]

[9] H. Ogino, T. Shirakashi, and N. Tanaka, presented at the 24th Annual Meeting of the Chemical Soceity of Japan, Osaka (Apr. 1971).

the electron-exchange reaction between $Co^{III}edta^-$ and decomposition products might have accelerated the racemization reaction. Therefore, the kinetic parameters given in Table 1 seem to be more reliable than those reported by Cooke *et al.*

Although the entropy of activation for Reaction (4) is not a large positive value, this value may suggest that the acid-independent racemization of $Co^{III}edta^-$ proceeds through the trigonal twist mechanism, because it is expected that a dissociative mechanism will give a negative value for the entropy of activation.[2,7,10] Furthermore, it is unlikely that the acid-independent path is detectable in the range of hydrogen ion concentrations employed in this work (0.05—0.5M), because this mechanism requires the breaking of at least two Co–O bonds without protonation in an acid solution and rapid recombination after the inversion reaction. A similar situation exists even for the acid-dependent path. The entropy of activation of k_{r2} is a very large positive value. Therefore, it seems reasonable to say that the racemizations of $Co^{III}edta^-$ and $Co^{III}(H_2O)$-Hedta proceed through the trigonal twist mechanism. The values given in Table 1 indicate that $Co^{III}(H_2O)$-Hedta racemizes from 20 to 28 times faster than Co^{III}-$edta^-$. This implies that the decrease in the number of chelate rings in the EDTA complex makes the twist easier.

The Rây and Dutt mechanism[11] has been known to be an intramolecular racemization mechanism. It should be noted that, when the Rây and Dutt mechanism is applied to at least $Co^{III}edta^-$ and related complexes, this mechanism is identical with the mechanism proposed by Bailar.[1]

Racemization Kinetics of $Co^{III}trdta^-$. The reaction was followed by the procedure described for the Co^{III}-$edta^-$ complex. The plots of $-\log(\alpha_t/\alpha_0)$ *vs.* time after correction for the decomposition of $Co^{III}trdta^-$ with time gave a good linear relation. The plots of k_r *vs.* $[H^+]$ indicate linear dependencies, as shown in Fig. 5. The intercepts of the plots are essentially zero at all temperatures. Therefore, k_r can be expressed as:

$$k_r = k'_{r2}[H^+] \tag{7}$$

If $K_a \gg [H^+]$ is assumed, this relation can be formally derived from Eq. (6).

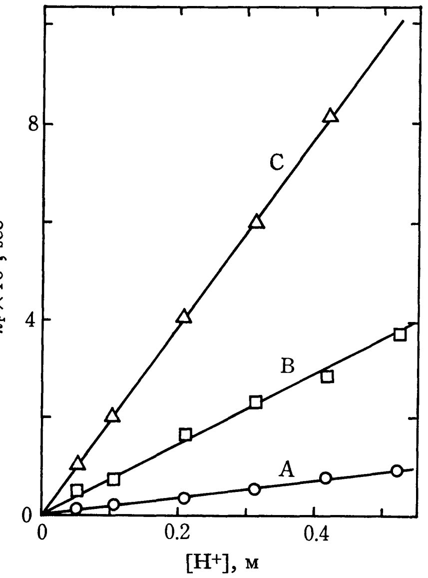

Fig. 5. Relation between k_r and hydrogen ion concentration for $(+)_{546}Co^{III}trdta^-$. Temperature: 120°C (A), 130°C (B), and 140°C (C).

The visible spectra and CD cruves of $Co^{III}trdta^-$ did not show any changes with the increase in the hydrogen ion concentration up to 5M of nitric acid. This is quite different from the behavior of $Co^{III}edta^-$ in an acid solution. That is, the formation of $Co^{III}(H_2O)$-Htrdta is very unfavorable.

TABLE 2. KINETIC PARAMETERS OF THE RACEMIZATION REACTION OF Co^{III} TRDTA COMPLEX (μ=0.53 (KNO_3))

	k'_{r2}, l mol^{-1} sec^{-1}
120°C	1.9×10^{-5}
130°C	6.7×10^{-5}
140°C	2.0×10^{-4}
$\Delta H^{\ast}$(kcal/mol)	37.5
$\Delta S^{\ast}$(e.u.)	14.8

The values of k'_{r2}, the enthalpy of activation, and the entropy of activation are given in Table 2. The racemization reaction of $Co^{III}trdta^-$ is characterized by the facts that an acid-independent path is absent and that the over-all reaction rate is much smaller than that of $Co^{III}edta^-$. As the value of the acid dissociation constant of $Co^{III}(H_2O)$Htrdta is not known, a comparison between the k'_{r2} value for $Co^{III}trdta^-$ and the k_{r2} value for $Co^{III}edta^-$ is not possible. Figure 5 shows that the acid-independent racemization reaction is extremely slow. One reason for this may be that, if $Co^{III}edta^-$ and $Co^{III}trdta^-$ racemize through the trigonal twist mechanism, the diamine chelate rings must be inverted, as shown in Fig. 6. The absolute configurations of $(-)_{546}Co^{III}edta^-$ [12] and $(-)_{546}Co^{III}$-

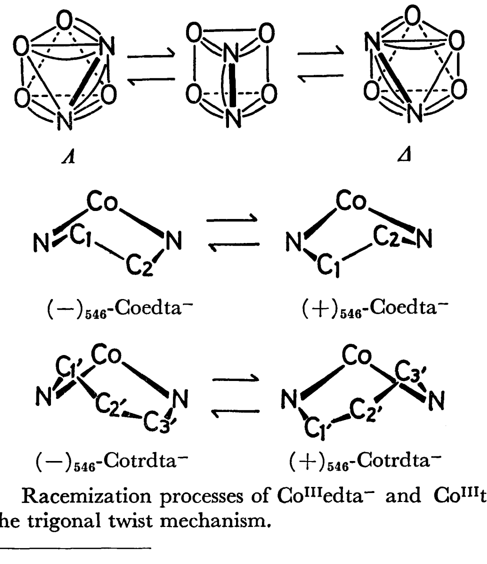

Fig. 6. Racemization processes of $Co^{III}edta^-$ and $Co^{III}trdta^-$ by the trigonal twist mechanism.

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[10] M. L. Morris and D. H. Busch, *J. Phys. Chem.*, **63**, 340 (1959).

[11] P. Rây and N. K. Dutt, *J. Indian Chem. Soc.*, **20**, 81 (1943).

[12] T. E. MacDermott and A. M. Sargeson, *Aust. J. Chem.*, **16**, 334 (1963).

trdta⁻ [5] have been determined to be Λ. In a previous paper,[5] it was shown that the conformation of the trimethylenediamine chelate ring is a twist form. That is, the cobalt(III) ion, two nitrogen atoms, and one central carbon atom of trimethylenediamine (C_2' in Fig. 6) lie on the same plane and there is a two-fold axis through the cobalt(III) ion and C_2'. In the racemization of $(-)_{546}Co^{III}edta^-$, the carbon atom, C_1, above the N–Co–N plane moves downward, while C_2, below the N–Co–N plane moves upward, as shown in Fig. 6. In the case of $(-)_{546}Co^{III}trdta^-$, the C_1' above the N–Co–N plane moves downward and C_3' below the N–Co–N plane, moves upward. In addition, the C_2' atom must be fixed in the N–Co–N plane during the inversion process. Therefore, in the transition state, the cobalt(III) ion, two nitrogen atoms, C_1', C_2', and C_3' must exist on the same plane. It is quite natural that this situation is sterically hindered and leads to the absence of an acid-independent path for $Co^{III}trdta^-$.

Electron-exchange Reaction between $Co^{II}trdta^{2-}$ and $Co^{III}trdta^-$. The electron-exchange reaction between $Co^{II}trdta^{2-}$ and optically-active $Co^{III}trdta^-$ was followed by measurements of the decrease in optical rotation with the time. As the intramolecular racemization of optically-active $Co^{III}trdta^-$ is negligible under these experimental conditions, the reaction can be expressed as follows:

$$Co^{II}trdta^{2-} + \text{optically-active } Co^{III}trdta^-$$
$$\xrightarrow{k_e} \text{racemic } Co^{III}trdta^- + Co^{II}trdta^{2-} \qquad (8)$$

From Reaction (8), these relations:

$$-\log\left(\frac{\alpha_t}{\alpha_0}\right) = \frac{k_{obs}}{2.303}t \qquad (9)$$

$$k_{obs} = k_e[Co^{II}trdta^{2-}] \qquad (10)$$

can be derived. Figure 7 shows some examples of these plots, the slopes of which correspond to $k_{obs}/2.303$. The values of k_{obs} were found to be dependent on both $[Co^{II}trdta^{2-}]$ and $[H^+]$. When the hydrogen ion concentration is kept constant, the k_{obs} values are proportional to $[Co^{II}trdta^{2-}]$, as shown in Fig. 8. The slope of the straight line which is shown in Fig. 8 corresponds to the rate of the electron-exchange reaction, k_e. The k_e values were determined at several pH values; the results are given in Table 3.

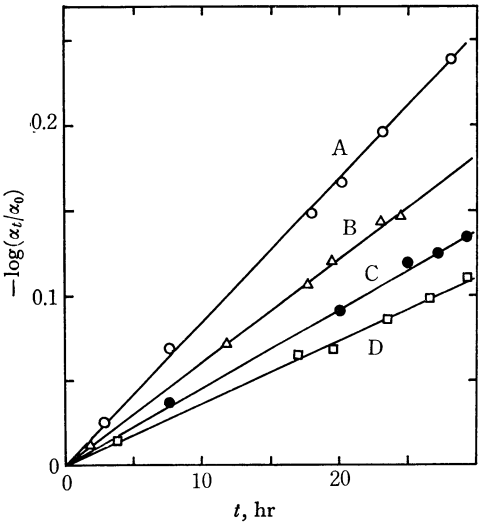

Fig. 7. Relation between $-\log(\alpha_t/\alpha_0)$ and t.
Experimental conditions: $[Co^{II}trdta^{2-}]$=13.45mM (A), 22.97 mM (B), 13.77 mM (C), and 13.80 mM (D); pH=3.04 (A), 3.58 (C), and 3.86 (B) and D)

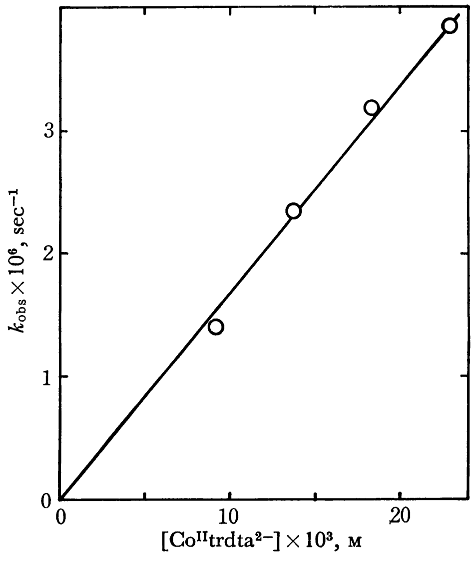

Fig. 8. Relation between k_{obs} and $[Co^{II}trdta^{2-}]$. pH=3.86

TABLE 3. RATE CONSTANTS OF THE ELECTRON-EXCHANGE REACTION OF Co-TRDTA SYSTEM AT μ=0.2 (KNO_3) AND 90°C

pH	k_e, l mol^{-1} sec^{-1}
3.86	1.55×10^{-4}
3.58	1.99×10^{-4}
3.04	3.74×10^{-4}

It is known that $Co^{II}trdta^{2-}$ is in equilibrium with $Co^{II}Htrdta^-$ as follows:[13]

$$Co^{II}Htrdta^- \rightleftarrows Co^{II}trdta^{2-} + H^+ \qquad (11)$$

Therefore, the electron-exchange reaction between $Co^{II}trdta^{2-}$ and $Co^{III}trdta^-$ can be expressed by this mechanism:

$$Co^{II}trdta^{2-} + \text{optically-active } Co^{III}trdta^-$$
$$\xrightarrow{k_{e1}} \text{racemic } Co^{III}trdta^- + Co^{II}trdta^{2-} \qquad (12)$$
$$Co^{II}Htrdta^- + \text{optically-active } Co^{III}trdta^-$$
$$\xrightarrow{k_{e2}} \text{racemic } Co^{III}trdta^- + Co^{II}Htrdta^- \qquad (13)$$

On the basis of this mechanism, the rate law can be derived as:

$$k_e = \frac{k_{e1}K^H + k_{e2}[H^+]}{K^H + [H^+]} \qquad (14)$$

where K^H represents the equilibrium constant of Eq. (11). By use of the data given in Table 3 and Eq. (14), the values of k_{e1}, k_{e2}, and K^H were calculated. The results are given in Table 4, along with the data

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[13] G. Anderegg, *Helv. Chim. Acta*, **47**, 1801 (1964).

Table 4. Rate constants of electron-exchange reaction for Co-TRDTA and Co-EDTA systems (μ=0.2)

	Temp., °C	k_{e1}, l mol^{-1} sec^{-1}	k_{e2}, l mol^{-1} sec^{-1}	K^H, mol/l	Ref.
Co-TRDTA system	90	1.0×10^{-4}	1.1×10^{-3}	2.4×10^{-3}	This work
Co-EDTA system	90	8.1×10^{-5}	2.8×10^{-4}	1.1×10^{-3}	3

reported for the Co-EDTA system.3)

The reactions proceed faster than the reaction between $Co^{II}edta^{2-}$ and $Co^{III}edta^{-}$ for both the acid-independent and the acid-dependent paths.