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Kinetic Studies of the Reactions of the Ferricyanide Ion with Cobalt(II)-Aminopolycarboxylate Complexes

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Kinetic studies of the reactions of the ferricyanide ion with cobalt(II)-aminopolycarboxylate complexes were carried out. The aminopolycarboxylates used in this study were trimethylenediaminetetraacetate (TRDTA), *trans*-1,2-cyclohexanediaminetetraacetate (CyDTA), propylenediaminetetraacetate(PDTA), and *N*-hydroxyethyl ethylenediaminetriacetate(HEDTA). The first step in the reaction is the rapid formation of a binuclear complex intermediate, $[(\text{aminopolycarboxylate})\text{Co}^{\text{III}}\text{NCFe}^{\text{II}}(\text{CN})_5]^{n-}$ (n=5 for TRDTA, CyDTA and PDTA and 4 for HEDTA), followed by the dissociation of the intermediate to ferrocyanide and Co(III)-aminopolycarboxylate ions. The equilibrium constant of the formation reaction and the rate constant of the dissociation reaction of the intermediate at an ionic strength of 0.66 were 6.2×10^2 M^{-1} and 2.0×10^{-2} s^{-1} respectively for the TRDTA system at 5 °C, 3.3×10 M^{-1} and 2.7×10^{-2} s^{-1} for the CyDTA system at 25 °C, and 2.4×10^3 M^{-1} and 3.0×10^{-3} s^{-1} for the PDTA system at 25 °C. The rate constant of the dissociation of $[\text{hedta Co}^{\text{III}}\text{NCFe}^{\text{II}}(\text{CN})_5]^{4-}$ was found to be smaller than 1×10^{-4} s^{-1} at 25 °C and at an ionic strength of 0.66.

It has been reported that the reaction of the ferricyanide ion with ethylenediaminetetraacetatocobaltate(II) (cobalt(II)-EDTA) produced the ferrocyanide ion and the cobalt(III)-EDTA complex as the final products:[1,2]

$$\text{Fe}^{\text{III}}(\text{CN})_6{}^{3-} + \text{Co}^{\text{II}}\text{edta}^{2-} \longrightarrow \text{Fe}^{\text{II}}(\text{CN})_6{}^{4-} + \text{Co}^{\text{III}}\text{edta}^{-} \qquad (1)$$

This reaction proceeds through two consecutive steps. The first step is the formation reaction of a metastable binuclear intermediate, $[\text{edtaCo}^{\text{III}}\text{NCFe}^{\text{II}}(\text{CN})_5]^{5-}$, by an inner-sphere electron-transfer reaction between ferricyanide and cobalt(II)-EDTA. The second step is the dissociation of the intermediate to ferrocyanide and cobalt(III)-EDTA. Analogous reactions of the ferricyanide ion with cobalt(II) complexes containing *trans*-1,2-cyclohexanediaminetetraacetate (CyDTA) and diethylenetriaminepentaacetate (DTPA) were investigated by Huchital and Hodges very recently.[3,4]

This paper will describe kinetic studies of the reactions between the ferricyanide ion and cobalt(II) complexes with several aminopolycarboxylates,[5] studies which have been carried out in order to ascertain how the change in the nature of aminopolycarboxylates influences the features of the reactions.

Experimental

Materials. H_4pdta,[6] H_4trdta,[7,8] $\text{K[Co pdta]}\cdot\text{H}_2\text{O}$,[6] $\text{K[Co cydta]}\cdot3\text{H}_2\text{O}$,[9] and $\text{K[Co trdta]}\cdot2\text{H}_2\text{O}$[7] were prepared by methods described previously. The solution of Co hedta-(H_2O) was prepared in a way similar to that which has been reported for the preparation of $\text{Co}^{\text{III}}\text{trdta}^{-}$.[7] The resulting solution was passed through a cation-exchange resin column, Dowex 50W-X8 (hydrogen-ion form). The effluent was then passed through an anion-exchange resin column, Dowex 1 X-4 (acetate-ion form). The resulting solution was evaporated to a small volume with a rotating evaporator and dried over a phosphorus pentoxide desiccator. Found: C, 32.21; H, 5.27; N, 7.72%. Calcd for $[\text{Co}(\text{C}_{10}\text{H}_{15}\text{N}_2\text{O}_7)(\text{H}_2\text{O})]\cdot\text{H}_2\text{O}$: C, 32.45; H, 5.17; N, 7.57%.

Kinetic Measurements. Kinetic measurements were made by recording the change in the absorbance at a given wavelength as a function of the time, using a Hitachi EPS-3 pen-recording spectrophotometer. The solution containing given amounts of cobalt(II) ions, aminopolycarboxylate, and an acetate buffer was placed in a quartz spectrophotometer cell, which was then sealed with a serum cap. The reaction was initiated by the addition of a potassium ferricyanide solution using a syringe. The mixing was performed by the passage of a rapid stream of nitrogen gas. The concentration of aminopolycarboxylate was kept at five to ten times that of the cobalt(II) ions. The temperature of the optical cell was controlled at 25.0 °C for the PDTA, CyDTA, and HEDTA systems and 5.0 °C for the TRDTA system. The pH of the solution was adjusted to 5.0 with the acetate buffer solution, and the ionic strength was regulated at 0.66 with sodium acetate.

Results

Spectral Change in the Reactions of the Ferricyanide Ion with Cobalt(II)-Aminopolycarboxylates. Figure 1 shows the change in the absorbance at 550 nm with the time which was obtained for the reaction of $\text{Fe}^{\text{III}}(\text{CN})_6{}^{3-}$ with $\text{Co}^{\text{II}}\text{pdta}^{2-}$. The absorbance at zero time which was calculated from the initial concentrations and the molar extinction coefficients of the two reactants is 0.196. However, this calculated value was much smaller than the actual value which was obtained from the extrapolation of the absorbance-time

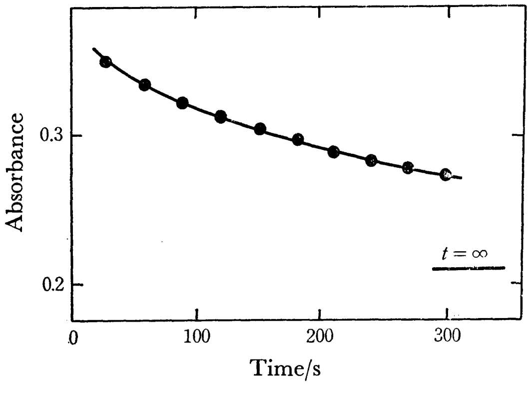

Fig. 1. Absorbance at 550 nm as a function of time obtained for the reaction of ferricyanide ion with cobalt(II)-PDTA complex. Initial concentrations are: $[\text{Fe}(\text{CN})_6{}^{3-}]_{t=0}=0.500$ mM and $[\text{Co}^{\text{II}}\text{ pdta}^{2-}]_{t=0}=8.63$ mM.

curve in Fig. 1 to zero time. This suggested that an intermediate was rapidly formed and then converted to the other species. The final reaction products were identified spectrophotometrically as $Fe^{II}(CN)_6{}^{4-}$ and $Co^{III}pdta^-$. Similar phenomena were also observed for the CyDTA and the TRDTA system. These observations mean that the reaction proceeds in a fashion similar to that of the EDTA system;[1,2] that is, it proceeds through two consecutive steps:

$$Fe^{III}(CN)_6{}^{3-} + Co^{II}Y^{2-} \overset{K_a}{\rightleftharpoons} YCo^{III}NCFe^{II}(CN)_5{}^{5-} \quad (2)$$

$$YCo^{III}NCFe^{II}(CN)_5{}^{5-} \xrightarrow{k} Fe^{II}(CN)_6{}^{4-} + Co^{III}Y^- \quad (3)$$

where Y denotes the tetranegative anion of aminopolycarboxylates. The reaction of $Fe^{III}(CN)_6{}^{3-}$ with cobalt(II)-HEDTA, however, was found to be different; an intensely-colored species was formed when the reactants were mixed, and it remained unchanged for at least several hours. Figure 2 shows the spectra of the species related to the reaction of $Fe^{III}(CN)_6{}^{3-}$ with $Co^{II}hedta(H_2O)^-$. Curve A in Fig. 2 is the spectrum for the solution containing $Fe^{III}(CN)_6{}^{3-}$ and $Co^{II}hedta(H_2O)^-$. This does not coincide with the synthetic spectrum (Curve E in Fig. 2) which was calculated by assuming that the following reaction occurred:

$$Fe^{III}(CN)_6{}^{3-} + Co^{II}hedta(H_2O)^- \longrightarrow Fe^{II}(CN)_6{}^{4-} + Co^{III}hedta(H_2O) \quad (4)$$

The shape of Spectrum A is very similar to those of $[edta\ Co^{III}NCFe^{II}(CN)_5]^{5-}$ and $[cydta\ Co^{III}NCFe^{II}(CN)_5]^{5-}$.[1,3] These facts suggest that $[hedta\ Co^{III}NCFe^{II}(CN)_5]^{4-}$ is formed rapidly by the reaction between $Fe^{III}(CN)_6{}^{3-}$ and $Co^{II}hedta(H_2O)^-$ and that Spectrum A corresponds to the sum of the spectra of $[hedta\ Co^{III}NCFe^{II}(CN)_5]^{4-}$ and $Co^{II}hedta(H_2O)^-$, the latter of which is present in a large excess.

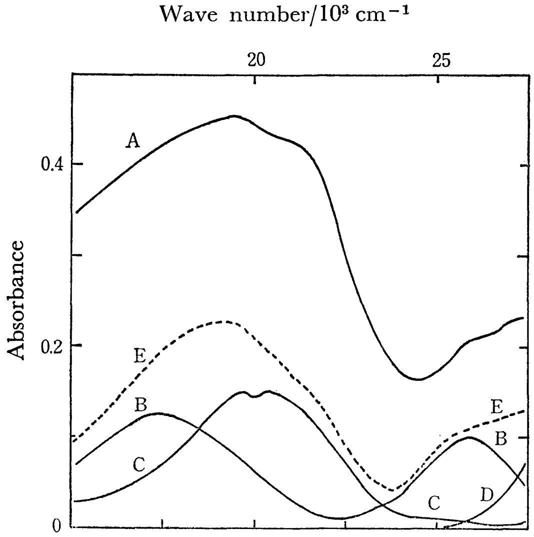

Fig. 2. Spectra of the species related to the reaction of ferricyanide ion with cobalt(II)-HEDTA.
(A) Spectrum obtained for the cobalt(II)-HEDTA solution upon the addition of ferricyanide: $[Co^{II}hedta(H_2O)^-]_{t=0}=8.63$ mM, $[Fe(CN)_6{}^{3-}]_{t=0}=0.500$ mM. (B) Spectrum of 0.500 mM $[Co^{III}hedta(H_2O)]$ (C) Spectrum of 8.13 mM $[Co^{II}hedta(H_2O)^-]$, (D) Spectrum of 0.500 mM $[Fe(CN)_6{}^{4-}]$, (E) Synthetic spectrum resulted from the sum of spectra (B), (C) and (D).

Kinetic Results. The dissociation of the intermediates was followed under pseudo-first order conditions. The rate constant, k_{app}, was obtained from the slope of plots of log $|D_t - D_\infty|$ *vs.* time, where D_t and D_∞ mean the absorbances at time t and at infinite, respectively. Adamson and Gonick[1] derived the following equation for k_{app} by assuming that the reaction proceeds by means of the mechanism indicated in Eqs. 2 and 3:

$$k_{app} = \frac{kK[Co^{II}Y^{2-}]}{1+K[Co^{II}Y^{2-}]} \quad (5)$$

This equation may be rewritten as:

$$\frac{1}{k_{app}} = \frac{1}{k} + \frac{1}{kK[Co^{II}Y^{2-}]} \quad (6)$$

As is shown in Fig. 3, the plots of $1/k_{app}$ *vs.* $1/[Co^{II}Y^{2-}]$ for various aminopolycarboxylate systems show linear relations which are consistent with the mechanism given in Eqs. 2 and 3. The values of k and K were obtained from the intercepts and slopes of these plots. The results are summarized in Table 1, along with the values reported previously. The values of k and K for the CyDTA system obtained in this work are in good agreement with those obtained by Huchital and Hodges.[3] In the case of the HEDTA system, only a lower limit of the rate constant could be determined.

Discussion

The rate constants of the dissociation of the intermediate, $[YCo^{III}NCFe^{II}(CN)_5]^{n-}$, were found to be

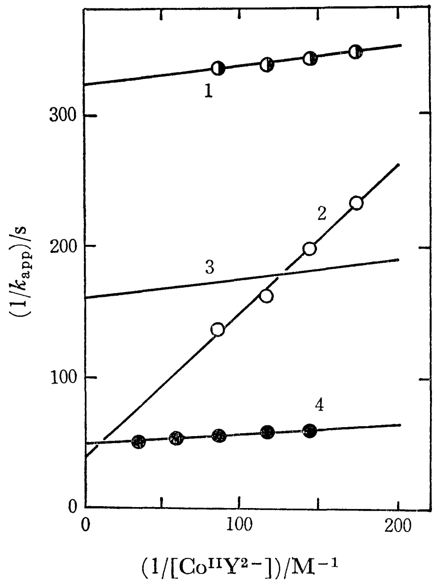

Fig. 3. Plots of reciprocal pseudo-first order rate constant as a function of reciprocal concentrations of cobalt(II)-PDTA (1), -CyDTA (2), -EDTA (3) and -TRDTA (4). Temperature: 25.0 °C for PDTA, CyDTA and EDTA systems and 5.0 °C for TRDTA system. Data for EDTA system are taken from Ref. 1.

TABLE 1. EQUILIBRIUM CONSTANTS K OF REACTION (2) AND RATE CONSTANTS k OF REACTION (3).

Aminopoly-carboxylate	Temp/°C	K/M^{-1}	k/s^{-1}	Ref.
TRDTA	5	6.2×10^2	2.0×10^{-2}	This work
CyDTA	5	4.0×10^2 [a]	1.2×10^{-3} [a]	3
	25	4.4×10	2.2×10^{-2}	3
	25	3.3×10	2.7×10^{-2}	This work
EDTA	5	6.1×10^3 [a]	2.1×10^{-4} [a]	3
	25	8.3×10^2	5.4×10^{-3}	3
PDTA	25	2.4×10^3	3.0×10^{-3}	This work
HEDTA	25	—	$<1\times10^{-4}$	This work
	—	$\sim5\times10^3$	—	4

a) The value was calculated from the data reported in Ref. 3 by the present authors.

in the following order with the natures of the aminopolycarboxylates:

$$\text{TRDTA} > \text{CyDTA} > \text{EDTA, PDTA} \gg \text{HEDTA}$$

where $n=5$ for TRDTA, CyDTA, EDTA, and PDTA, and 4 for HEDTA. This order is parallel to the tendency of aminopolycarboxylates to take a hexadentate structure in the cobalt(III) complexes. Several facts demonstrate that the hexadentate structures of the Co(III)CyDTA and Co(III)-TRDTA complexes are much more stable than the corresponding pentadentate structures, while the hexadentate structures of the Co(III)-EDTA and Co(III)-PDTA complexes are slightly more stable than the pentadentate structures. Complexes of the $\mathrm{Co^{III}Xedta^{2-}}$ and $\mathrm{Co^{III}Xpdta^{2-}}$ types, where X is $\mathrm{Cl^-}$, $\mathrm{Br^-}$, $\mathrm{NO_2^-}$ or $\mathrm{OH^-}$, have also been prepared.[10–13] The ligand X in these complexes is slowly eliminated in a solution, and the complexes come to have the hexadentate structure.[14,15] Dwyer and Garvan observed a rapid conversion of $\mathrm{Co^{III}}$-$\mathrm{Clcydta^{2-}}$ to $\mathrm{Co^{III}cydta^-}$.[9] Van Saun and Douglas failed in preparing complexes in which TRDTA functions as a pentadentate ligand.[16] Therefore, the $\mathrm{[trdtaCo^{III}NCFe^{II}(CN)_5]^{5-}}$ complex detected in this work is the first example of a complex in which TRDTA functions as a pentadentate ligand.

The equilibrium constant of the following acid dissociation reaction may also be a measure of the tendency of aminopolycarboxylates to take a hexadentate structure in cobalt(III) complexes:

$$\mathrm{Co^{III}HY(H_2O)} \overset{K_a}{\rightleftharpoons} \mathrm{Co^{III}Y^-} + \mathrm{H^+} + \mathrm{H_2O} \qquad (7)$$

The value of K_a for the EDTA complex has been determined to be $1.31\ \mathrm{M^{-1}}$ at 25 °C and at an ionic strength of 2.0.[17] In this work, the K_a value for the PDTA complex was determined spectrophotometrically to be $1.04\ \mathrm{M^{-1}}$ at 25 °C and at an ionic strength of 2.0, this value is very close to that of the EDTA complex. The value of K_a for the CyDTA complex has not yet been reported. However, it was found in this work that $\mathrm{Co^{III}cydta^-}$ did not show any spectral change with the increase in the hydrogen-ion concentration up to 5 M in nitric acid. This is the same result as for $\mathrm{Co^{III}}$ $\mathrm{trdta^-}$.[17] Hence, the formations of $\mathrm{Co^{III}Hcydta(H_2O)}$ and $\mathrm{Co^{III}Htrdta(H_2O)}$ are considered to be very unfavored.

The increasing tendency to have a hexadentate structure of the CyDTA and TRDTA complexes compared with the EDTA and PDTA complexes holds also in the corresponding complexes of other metals. Both chromium(III)-EDTA[18] and PDTA[19] complexes contain one water molecule in the first coordination sphere, while both CyDTA[19] and TRDTA[20] function as hexadentate ligands in their chromium(III) complexes.

Higgison determined the proportions of several metal(II) complexes containing EDTA, PDTA, or CyDTA in the hexadentate form, the remaining part being the pentadentate form in which the sixth coordination position of the central metal(II) ion is occupied by an aqua ligand.[21] These data also show the increasing tendency to be of a hexadentate structure of the cobalt(II)-, nickel(II)- and copper(II)-CyDTA complexes compared with the corresponding EDTA and PDTA complexes.

The HEDTA system provides an extreme case in which HEDTA functions as a pentadentate ligand because of the very weak coordination ability of the N-hydroxyethyl group. The rate of the dissociation of $\mathrm{[hedta\ Co^{III}NCFe^{II}(CN)_5]^{4-}}$ was very slow; this is consistent with the interpretation of the order of the dissociation rate of the intermediates presented above. Therefore, the dissociation of the intermediates, $\mathrm{[YCo^{III}}$-$\mathrm{NCFe^{II}(CN)_5]^{n-}}$, may be a S_N2 reaction, as has been proposed by Huchital and Hodges,[3] in which unbound carboxylate assists the elimination of $\mathrm{Fe^{II}(CN)_6^{4-}}$ from the central cobalt(III) ion.

All the hexadentate EDTA, TRDTA, PDTA and CyDTA complexes of cobalt(III) contain two nonequivalent acetate rings. One is in the plane of the diamine chelate ring (in-plane acetate), and the other is perpendicular to the in-plane acetate rings (out-of-plane acetate). In a previous paper,[8] it was suggested that the trimethylenediamine chelate ring in $\mathrm{Co^{III}}$ $\mathrm{trdta^-}$ takes a twist-boat form and that the in-plane acetate rings are more strained than the out-of-plane acetate rings. This was confirmed later by X-ray study.[22] The data revealed that the shape and size of the four acetate rings of $\mathrm{Co^{III}trdta^-}$ are essentially identical to those of $\mathrm{Co^{III}edta^-}$.[23] The in-plane acetate rings show considerable departure from planarity and are strained, while the out-of-plane acetate rings are nearly planar. It has been inferred that the conformational situations of acetate rings in $\mathrm{Co^{III}pdta^-}$ and $\mathrm{Co^{III}cydta^-}$ are similar to those in $\mathrm{Co^{III}edta^-}$.[24,25] This may be true also for $\mathrm{Co^{III}hedta(H_2O)}$, because HEDTA has a structure very similar to that of EDTA.

It is known that X in $\mathrm{Co^{III}Xedta^{2-}}$ replaces an in-plane acetate.[26] Busch *et al.* investigated the reactions of ethylenediamine with $\mathrm{Co^{III}edta^-}$ and $\mathrm{Co^{III}}$-$\mathrm{pdta^-}$ to produce the tris(ethylenediamine)cobalt(III) ion.[24,27,28] They found a satisfactory interpretation for the reaction mechanism on the assumption that the first step of the entry of ethylenediamine to the coordination sphere of the cobalt(III) ion is the replacement of an in-plane acetate group. Therefore, it is reasonable to consider that the cyano group coordinated to the cobalt(III) ion in the intermediate given in Eq. 2 replaces an in-plane acetate group.

Huchital and Hodges reported that the higher value of k for the CyDTA complex than that for the EDTA complex was due to the steric hindrance between the methylene protons of the acetate ring and the axial proton in the 3 position of the cyclohexane ring.[3) However, this does not seem to be the cause of the higher value of k, because the acetate protons which interfere with the axial proton in the 3 position of the cyclohexane ring are out-of-plane protons. There is no steric interaction between the axial proton in the cyclohexane ring and the proton of the in-plane acetate ring which is replaced by the incoming cyano group. The molecular model for the $Co^{III}pdta^-$ complex reveals that there is a steric hindrance between the proton of the out-of-plane acetate ring and the methyl protons. This steric hindrance is similar to that between the proton of the out-of-plane acetate ring and the axial proton in the 3 position of the cyclohexane ring for the CyDTA complex. If the out-of-plane acetate group, which suffers steric hindrance from the proton of the methyl group, is replaced by a cyano group, the value of k for the PDTA system would be expected to be much different from that for the EDTA system. The results given in Table 1 show that this is not true and that the values of k for the two systems are essentially identical. Therefore, it may be concluded that the cyano group coordinated to the cobalt(III) ion in the intermediate replaces the in-plane acetate group.

The equilibrium constant of Reaction 2, K, was found to increase in the following order with the nature of the aminopolycarboxylates:

$$\text{CyDTA, TRDTA} < \text{EDTA, PDTA} < \text{HEDTA}$$

This order is not related to that of the magnitude of the oxidation-reduction potentials of the Co(III)-Y/Co(II)-Y sysetm,[29,30) but it is the reverse of the order found for the values of the rate constant, k, except for TRDTA and CyDTA. Hence, it can reasonably be concluded that the value of K becomes larger for aminopolycarboxylates, which have a stronger tendency to take a pentadentate structure.

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