The smaller solubility of the *trans* species is to be expected because of its smaller dipole moment in comparison with the *cis* complexes.

We believe, then, on the basis of the experimental evidence obtained, that the following assignments are justified for the IDA–MIDA series of bis complexes: *cis*-$K[Cr(IDA)_2] \cdot 2.5H_2O$; *cis*-$NH_4[Cr(IDA)(MIDA)] \cdot H_2O$; *trans*(facial)-$Na[Cr(MIDA)_2]$.

The distinctive differences between the $Cr(EDTA)(H_2O)^-$ complex and the $Cr(1,3\text{-}PDTA)^-$ complex should be noted. Adding one more methylene link to the backbone of the ligand has apparently relieved almost all strain and has allowed 1,3-PDTA to function apparently as a hexadentate ligand, very much different from the Cr(III)–EDTA complex where EDTA functions as a pentadentate ligand,[13] with a water molecule in the sixth coordination position and an acetate arm remaining free. Molecular models show that strain inherent in the ethylenediamine backbone hinders the ability of EDTA to function as a hexadentate ligand. The symmetry of the $Cr(EDTA)(H_2O)^-$ complex differs from the $Cr(1,3\text{-}PDTA)^-$ complex and this is exemplified in comparing the values of the molar absorptivities for the two complexes. These data are given in Table I. It is also noted that the low-energy absorption band of the EDTA complex has been shifted from the expected value of 510–530 mμ to 545 mμ.

It was also of interest to prepare and compare the visible absorption spectra and molar absorptivities of the mono-IDA and mono-MIDA complexes of chromium(III). Since these species would have a +1 charge, their separation from a reaction mixture containing hexaaquochromium(III) ion (+3 in charge) and the bis complex of the corresponding ligand (−1 in charge) could easily be effected using ion-exchange chromatography. The preparation of these mono species was not clean, some hexaaquochromium(III) ion and the bis complex always being present. The iminodiacetatotriaquochromium(III) ion and the methyliminodiacetatotriaquochromium(III) ion were, however, the major species formed in each case. Both mono species appear to be quite stable with respect to disproportionation into the hexaaquochromium(III) ion and the bis complex. After separation and purification of the mono species by ion exchange and allowing the solutions to sit at room temperature for 1 week, reintroduction of these solutions onto a cation-exchange column showed no or very little evidence for the presence of the hexaaquochromium(III) ion or the bis complex.

The visible absorption spectra and molar absorptivities of these two complexes are given in Table I. The molar absorptivities of the two ions are essentially identical at the two maxima. The only noticeable difference in the two spectra is the fact that in the mono-MIDA complex the low-energy peak has been slightly shifted to longer wavelengths in comparison with the mono-IDA complex.

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Cyclic Voltammetric Study of the Rate of Ligand Exchange between Cadmium Ion and Calcium Ethylenediaminetetraacetate[1a,b]

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The rate of ligand exchange between calcium ethylenediaminetetraacetate complex ion and cadmium ion is measured using the technique known as cyclic stationary electrode polarography. In the presence of excess calcium ion the reaction is found to proceed through (1) a pathway involving a fast, acid-catalyzed dissociation of the calcium complex followed by a rate-limiting combination of the free monoprotonated ligand with cadmium ion and (2) a pathway involving a direct attack of the complex by cadmium ion. At 25° the second-order rate constant for the first pathway is $2.6 \pm 0.7 \times 10^8\ M^{-1}\ \text{sec}^{-1}$ and for the second pathway is $2.3 \pm 0.2 \times 10^2\ M^{-1}\ \text{sec}^{-1}$. The direct reaction is found to proceed through an intermediate in which the multidentate ligand is half-unwrapped and partially bound to both calcium and cadmium ions. The rate-limiting step in both pathways appears to be the formation of the initial cadmium–nitrogen bond.

Introduction

The kinetics and mechanisms of the electrophilic exchange of ethylenediaminetetraacetic acid (EDTA) anion between two metal ions have been studied for several different systems using a variety of techniques. Studies making use of dc polarography,[2-4] radioisotopic

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[1] (a) Taken in part from a thesis submitted by J. R. Kuempel to the Graduate School of Indiana University in partial fulfillment of the requirements for the Ph.D. degree in Chemistry, Sept 1967. (b) Presented in part at the 153rd National Meeting of the American Chemical Society, Miami Beach, Fla., April 9–14, 1967. (c) Author to whom correspondence should be addressed.

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labeling,[5] nmr spectroscopy,[6-8] and visible spectrophotometry[9] have all shown that these exchanges have complex, pH-dependent kinetic expressions containing rate terms involving the concentrations of the attacking metal ion and of both the complex ion and the dissociated EDTA anions. A general mechanism has been proposed by Margerum and coworkers[9,10] for the electrophilic exchange of multidentate ligands between metal ions that involves a dinuclear intermediate species in which the multidentate ligand is partially unwound from the initially complexed metal ion and partially attached to the attacking metal ion.

In this research, we measured the rates of complexation of cadmium ion in solutions containing EDTA in the presence of excess calcium ion using the electroanalytical technique known as cyclic stationary electrode polarography. This technique is especially valuable in studies such as this which are difficult to carry out by spectrophotometric methods because they involve colorless ions or because of the lability of the system. The complexation reaction, which followed a reversible electron transfer, was found to proceed through a dinuclear intermediate.

Experimental Section

The rates of formation of aminepolycarboxylate complexes of cadmium ion were measured in solutions containing ethylenediaminetetraacetic acid (EDTA) or *trans*-1,2-cyclohexanediaminetetraacetic acid (CyDTA) in the presence of excess calcium ion and buffered with boric acid–potassium hydroxide mixtures. Potassium nitrate was used to adjust the ionic strengths of all solutions to 1.0 M. The temperature during all kinetic runs was maintained at 25.0°. Reagent grade ethylenediaminetetraacetic acid obtained from Fisher Scientific Co. was of sufficient purity for use without further purification. *trans*-1,2-Cyclohexanediaminetetraacetic acid was obtained from K & K Laboratories and was purified by dissolution in basic aqueous solution followed by precipitation upon acidification with hydrochloric acid and drying at 1 mm in a drying pistol in the presence of P_2O_5 at 100°. These extreme drying conditions are needed to remove the last mole of water from the cyclohexanediaminetetraacetic acid. The molecular weight of a sample of the anhydrous acid determined by titration with strong base in the presence of excess calcium ion was 344.0, which is in good agreement with the theoretical molecular weight of 346.3. The disodium salt of iminodiacetic acid (IMDA) was obtained from the Eastman Kodak Co. and was used without further purification.

Stock solutions of K_2CaY (Y^{4-} is an abbreviation for the tetraacetate anions of EDTA and CyDTA) were prepared by dissolving exactly equimolar amounts of reagent grade K_2CO_3, $CaCO_3$, and H_4Y in water and adjusting the pH of the resulting solution to 5 with nitric acid while bubbling pure nitrogen gas through the solutions to remove the last traces of dissolved CO_2. Stock solutions of $Ca(NO_3)_2$ prepared from reagent grade crystals were standardized by titration in basic solution with standard EDTA using murexide as the indicator. Solutions for the kinetic runs containing the calcium complex in the presence of excess calcium ion were prepared by taking aliquots from the stock solutions, adding the acid form of the buffer system together with sufficient crystalline KNO_3 to bring the ionic strength to 1.0 M, diluting to volume, and finally adjusting the pH to the desired value by adding small volumes of a 10 M KOH solution with a microsyringe.

All pH values were measured with a Sargent Model DR pH meter which was carefully calibrated with standard buffer solutions prepared as described by Bates.[11]

Pseudo-first-order rates were measured using cyclic stationary electrode polarography, for which the theory has been described by Nicholson and Shain.[12] Cadmium ion is introduced into the calcium-EDTA or calcium-CyDTA solutions by oxidation from a cadmium amalgam during an anodic, linear voltage scan. The generated cadmium ion then reacts with complexing species in the calcium–aminepolycarboxylate solutions at a rate dependent upon the concentrations of the reactants to form difficultly and irreversibly reduced cadmium complexes. Before these relatively slow complexation reactions reach completion, the unreacted cadmium ion is quickly reduced back into the amalgam by reversing the direction of the voltage scan. By monitoring the current–time response of the amalgam electrode during the cycle, the amount of cadmium ion that reacts with the ligands between its formation during the anodic scan and its removal during the cathodic scan can be determined from a comparison of the cathodic faradaic current with the anodic faradaic current. The rate of the repetitive anodic and cathodic scans (cps) establishes a time base for the experiment and makes it possible to calculate pseudo-first-order rate constants from the electrochemical data.

The electrochemical cell used in these studies incorporated a strictly planar mercury working electrode and was developed in this laboratory.[13] The saturated calomel reference electrode was equipped with a Luggin capillary probe to minimize uncompensated resistance in the cell. The cadmium amalgam used in the working electrode was prepared by reducing cadmium ion from a cadmium nitrate solution into mercury at a constant applied potential. Transfer of the amalgam to the cell was performed in a closed system under a nitrogen atmosphere to avoid rapid air oxidation of the cadmium from the amalgam.

A conventional three-electrode potentiostatic circuit[14] was used in the current–voltage measurements. The control amplifier was a single Philbrick Model SK2-V operational amplifier (G.A. Philbrick Researches, Inc., Boston, Mass.). The band width of this amplifier was adjusted to be compatible with the electrical characteristics of the cell containing the solutions used in the measurements by adding capacitance between the input and output terminals. The cyclic scan generator used in the experiments was capable of supplying continuously variable cycling rates ranging from 100 sec/cycle to 100 cycles/sec and has been described previously.[15] A Tektronix Model 502 oscilloscope equipped with a Dumont Model 302 Polaroid camera attachment was used to record the current–voltage curves. The oscilloscope was operated in the X–Y mode, the X or voltage axis being driven by the cyclic scan generator and the Y or current axis being driven in the differential mode by the voltage drop across a 1000-ohm precision resistor in the feedback loop of the potentiostat. A Hewlett-Packard Model 523D electronic counter monitored the output of the cyclic scan generator and was used to measure the cycling rates.

In order to determine the second-order dependence of the electrochemically determined pseudo-first-order rate constants and to make certain correlations between rate and stability constants, it was necessary to evaluate the equilibrium constants for the calcium-EDTA and calcium-IMDA systems under the

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[11] R. G. Bates, "Determination of pH, Theory and Practice," John Wiley & Sons, Inc., New York, N. Y., 1964, p 123.

[12] R. S. Nicholson and I. Shain, *Anal. Chem.*, **36**, 706 (1964).

[13] J. R. Kuempel and W. B. Schaap, *ibid.*, **38**, 664 (1966). The cell used was similar to the one shown in Figure 2 of this reference.

[14] G. L. Booman and W. B. Holbrook, *ibid.*, **35**, 1793 (1963).

[15] J. DiSalvo and W. B. Schaap, Abstracts, 153rd National Meeting of the American Chemical Society, Division of Analytical Chemistry, Miami Beach, Fla., April 1967, No. B54.

conditions obtaining during the kinetic experiments. The method used was similar to that originally developed by Schwarzenbach.[16] A solution containing the free acid of EDTA and sufficient potassium nitrate to adjust the ionic strength to 1.0 was titrated in a nitrogen atmosphere with standardized carbonate-free potassium hydroxide solution. The hydrogen ion activity was monitored with a carefully standardized glass electrode which was selected from the several available because of its essentially linear response over the pH range of interest. The titration was then repeated with excess calcium ion present. Similar solutions containing the disodium salt of IMDA, with and without excess calcium ion present, were titrated with standard nitric acid solution. The pH data obtained were then used to calculate both the dissociation constants for the free acid and the formation constants for the calcium complexes. All calculations were performed with an electronic computer, which made it possible to use many data points in order to increase the precision of the results. The results of these calculations are shown in Table I, where the uncertainties given are the average deviations. The CaEDTA constants were then used to calculate the concentrations of all aminepolycarboxylate species present in the solutions used in the kinetic experiments.

TABLE I

PROTON AND CALCIUM ION STABILITY CONSTANTS WITH EDTA AND IMDA SPECIES AT 25° AND μ = 1.0 (KNO_3)

Reaction	Constant	Value
$H^+ + EDTA^{4-} \rightleftarrows HEDTA^{3-}$	K_{HEDTA}	$(6.35 \pm 0.2) \times 10^9$
$H^+ + HEDTA^{3-} \rightleftarrows H_2EDTA^{2-}$	K_{H_2EDTA}	$(1.77 \pm 0.05) \times 10^6$
$Ca^{2+} + EDTA^{4-} \rightleftarrows CaEDTA^{2-}$	K_{CaEDTA}	$(4.77 \pm 0.15) \times 10^9$
$H^+ + IMDA^{2-} \rightleftarrows HIMDA^-$	K_{HIMDA}	$(1.79 \pm 0.05) \times 10^9$
$Ca^{2+} + IMDA^{2-} \rightleftarrows CaIMDA^0$	K_{CaIMDA}	$(1.23 \pm 0.05) \times 10^2$

Results

Electrochemical Measurement of Pseudo-First-Order Rate Constants.

—The electrochemical oxidation of cadmium amalgam into calcium-EDTA solutions is an example of a reversible electron-transfer reaction coupled to an irreversible chemical reaction in solution. The diffusion equations applicable to this type of electrode reaction mechanism have been solved for the conditions obtaining in cyclic stationary electrode polarography by Nicholson and Shain.[12] These workers were able to show that for this mechanism the ratio of the maximum cathodic to anodic currents is related to a single parameter, $k_{obsd}\tau$, where k_{obsd} is the observed pseudo-first-order rate constant for the coupled chemical reaction and τ is an elapsed time related to the cycling rate. Specifically, τ is the elapsed scanning time between the polarographic half-wave potential for the uncomplexed ion and the potential at which the direction of the voltage scan is reversed. It is possible to construct a theoretical plot of the ratio of the maximum (peak) cathodic and anodic currents, i_{cp}/i_{ap}, *vs.* $k_{obsd}\tau$, as shown in Figure 1. Since the ratio i_{cp}/i_{ap} can be experimentally evaluated by measuring the peak heights from a cyclic polarogram and τ can be determined from a knowledge of the half-wave potential, the switching potential, and the cycling rate, it becomes possible to evaluate the observed first-order rate constant from a single cyclic polarogram.

The cycling rates were selected to be compatible with the reaction rates. If, for example, k_{obsd} were relatively small, *i.e.*, if the coupled reaction were relatively slow and if the cyclic experiment were performed relatively quickly so that τ is also small, the cycle would be completed before any significant reaction could occur and the ratio i_{cp}/i_{ap} would be essentially 1.0. On the other hand, if k_{obsd} were large, as in the case of a very fast coupled reaction, and if the cyclic experiment were performed relatively slowly so that τ was large, it is possible that the reaction would go essentially to completion and that a vanishingly small cathodic current peak would be observed. These relationships are illustrated in Figure 2, which shows polarograms obtained for the same solution at three different scanning rates.

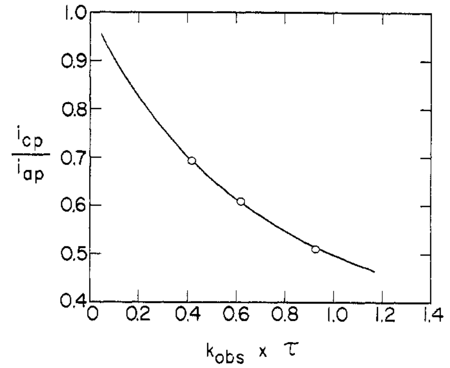
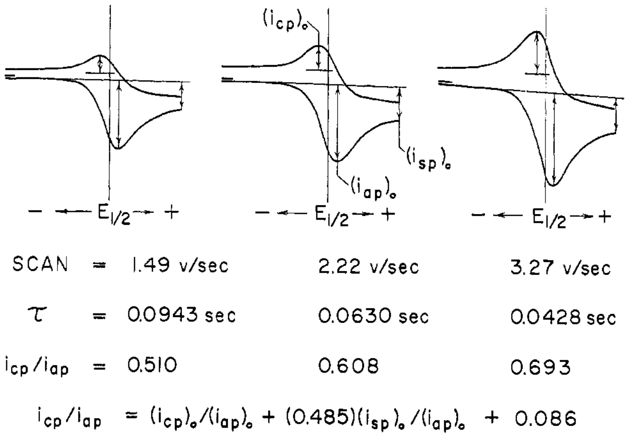


Figure 1.—Dependence of the peak current ratio i_{cp}/i_{ap} on the rate parameter $k_{obsd}\tau$ for a reversible electron-transfer reaction followed by an irreversible coupled chemical reaction. (The line is theoretical and the points are experimental.)



SCAN	=	1.49 v/sec	2.22 v/sec	3.27 v/sec
τ	=	0.0943 sec	0.0630 sec	0.0428 sec
i_{cp}/i_{ap}	=	0.510	0.608	0.693

$$i_{cp}/i_{ap} = (i_{cp})_0/(i_{ap})_0 + (0.485)(i_{sp})_0/(i_{ap})_0 + 0.086$$

Figure 2.—Representative electrochemical data at three cycling rates. The solution contained 0.030 *M* CaEDTA complex ion, 0.029 *M* $Ca(NO_3)_2$, 0.02 *M* H_3BO_3–KOH buffer mixture (pH 8.00), plus sufficient KNO_3 to bring the total ionic strength to 1.0 *M*. The mercury amalgam contained 2×10^{-4} *M* cadmium and the temperature was 25°.

The method used to evaluate the ratios of the peak currents requires the measurement of the faradaic currents at the anodic peak potential, $(i_{ap})_0$, at the switching potential, $(i_{sp})_0$, and at the cathodic peak potential, $(i_{cp})_0$. These values are combined with the equation shown in Figure 2 to obtain the peak current ratios. The equation is an empirical relationship for this mechanism derived by Nicholson.[17] The base lines

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[16] G. Schwarzenbach and H. Ackermann, *Helv. Chim. Acta*, **30**, 1798 (1947).

[17] R. S. Nicholson, *Anal. Chem.*, **38**, 1406 (1966).

for the anodic scan and the cathodic scan are not the same because of the contribution to the total current by the current associated with the charging of the double layer. If it is assumed that this charging current is constant over the relatively small voltage span of these experiments (400 mV), then the base lines would be parallel and separated by a distance corresponding to the current difference at the switching potential. If the charging current is not constant, nonparallel lines could be constructed to approximate the changes based on measurements with "blank" solutions run at the same cycling rates, *i.e.*, solutions containing all of the electrolytes run with pure mercury rather than with cadmium amalgam to determine independently the fraction of the total current needed for charging the double layer at each potential. When the solutions used in the present kinetic studies were run with a pure mercury electrode, it was found that the charging current was not constant but was essentially linear over the potential range employed. It was possible, therefore, to make the base line corrections by drawing nonparallel straight lines whose ends were separated by distances corresponding to the observed current differences at the extremes of the cycle.

Nicholson has shown[17] that the potential midway between the potentials of the anodic and cathodic peak currents corresponds very closely to the half-wave potential for a reversible electron transfer (uncomplexed cadmium ion, in this case). Thus τ can be obtained from the experimental curves by using the known cycling rate to evaluate the time it takes to scan from a point midway between the anodic and cathodic peak potentials to the switching potential.

The values of the product $k_{\text{obsd}}\tau$ are read from the theoretical plot (Figure 1) at each experimental ratio of peak currents. The value of the product $k_{\text{obsd}}\tau$ in each case is divided by the corresponding value of τ to obtain the observed first-order rate constant. The values of k_{obsd} calculated in this manner from the three experiments represented in Figure 2 are 10.2, 9.9, and 9.8 sec^{-1}, in order of increasing scan rate. The three data points shown on Figure 1 are the experimental peak current ratios plotted *vs.* the products of the average value of k_{obsd} and the experimental values of τ. The agreement of the observed first-order rate constants measured for a given solution over a range of cycling rates and reaction times demonstrates that this chemical system can be studied using the experimental method described and that meaningful pseudo-first-order rate constants can be measured. Replicate experiments showed that values of k_{obsd} could be obtained in this manner with a maximum uncertainty of $\pm 8\%$.

The Second-Order Dependence of the Reaction of Cadmium Ion with Calcium-EDTA Complex.—When reaction rates were measured at constant pH, it was found that the pseudo-first-order rate constants were inversely dependent upon the concentration of the excess calcium ion and directly dependent upon the concentration of the calcium-EDTA complex ion as shown in Table II. The predominant species in solution at the pH values employed in these studies is CaY^{2-}; in fact, $[\text{CaY}^{2-}]$ is, for all practical purposes, equal to the total EDTA concentration in all cases. An inverse dependence upon excess calcium ion concentration suggests a direct dependence upon the concentration of one or more dissociated EDTA species. The appropriate stability constants shown in Table I were used to calculate the concentrations of the various dissociated species, including those shown in Table II.

TABLE II

KINETIC DATA FOR THE REACTION OF CaY^{2-} WITH Cd^{2+} AT $\mu = 1.0\ M$ (KNO_3), 25°, AND pH 8.22

10^2[total EDTA], M	10^2[total calcium], M	$10^9[\text{HY}^{3-}]$, M	k_{obsd}, sec^{-1}
0.60	1.15	8.62	3.9
0.60	1.43	5.74	3.4
0.60	1.98	3.44	2.6
0.60	3.37	1.72	2.2
0.90	1.45	12.9	5.6
0.90	1.73	8.61	4.8
0.90	2.28	5.17	3.8
0.90	3.67	2.58	3.1
1.50	2.05	21.5	9.7
1.50	2.33	14.3	7.6
1.50	2.88	8.61	6.4
1.50	4.26	4.31	5.2
3.00	3.55	43.1	17.3
3.00	3.83	28.7	15.1
3.00	4.38	17.2	11.4
3.00	5.77	8.51	9.2

In Figure 3, the data in Table II are presented in graphical form. The linear relationships between k_{obsd} and $[\text{HY}^{3-}]$ at each concentration of CaY^{2-} suggest a contribution to k_{obsd} by a term of the form

$$k_{\text{Cd}}^{\text{HY}}[\text{dissociated EDTA species}]$$

where $k_{\text{Cd}}^{\text{HY}}$, a second-order rate constant, would be the slope of the parallel lines. It was found that similar plots of k_{obsd} *vs.* $[\text{Y}^{4-}]$ and k_{obsd} *vs.* $[\text{H}_2\text{Y}^{2-}]$ were also straight lines with the same intercepts but with different slopes. To determine which of the dissociated EDTA species was reacting, similar kinetic data were taken at two other pH values, 8.00 and 8.80. The slopes of the plots of k_{obsd} remained most nearly constant as a function of pH when the plots were made *vs.* $[\text{HY}^{3-}]$. This result is not surprising since HY^{3-} is the predominant dissociated EDTA species present in this pH range. The slopes were $1.9 \times 10^8\ M^{-1}\ \text{sec}^{-1}$ at pH 8.00, $2.7 \times 10^8\ M^{-1}\ \text{sec}^{-1}$ at pH 8.22, and $3.3 \times 10^8\ M^{-1}\ \text{sec}^{-1}$ at pH 8.80. The slight pH dependence observed could be caused by a relatively small contribution to the rate of the reaction by the anion Y^{4-}, or by a contribution arising from the presence of CdOH^+, which no doubt exists at these pH values to some extent. We conclude that the principal contribution to the observed first-order rate constant by a dissociative pathway is of the form $k_{\text{Cd}}^{\text{HY}}[\text{HY}^{3-}]$, where $k_{\text{Cd}}^{\text{HY}}$ was found to be $(2.6 \pm 0.7) \times 10^8\ M^{-1}\ \text{sec}^{-1}$ at 25°. Lower values of pH were not obtainable with the buffer system employed, and higher pH values were ruled out because of the possibility of forming precipitated cadmium hydroxide on the elec-

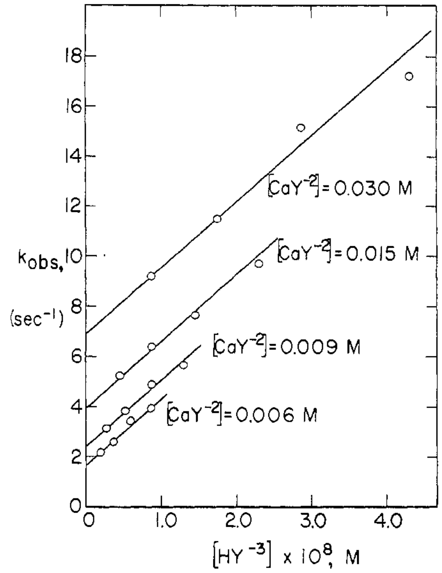


Figure 3.—Dependence of k_{obsd} on the concentration of the monoprotonated EDTA anion at several stoichiometric concentrations of the CaEDTA complex at μ = 1.0 M, 25°, and pH 8.22.

trode surface during the kinetic runs. An independent polarographic experiment showed that a solution containing 10^{-4} M Cd^{2+} begins to precipitate $Cd(OH)_2$ at pH 9.1.

The fact that all plots of k_{obsd} *vs.* the concentration of dissociated EDTA species had nonzero intercepts suggests an additional contribution to the rate expression. The plots indicate a direct dependence of the rate on the concentration of the CaEDTA complex. If the intercept (limiting) values of k_{obsd} are plotted *vs.* $[CaY^{2-}]$, the line in Figure 4 is obtained which has, within experimental error, a zero intercept and demonstrates that the remaining contribution to k_{obsd} has the form $k_{Cd}{}^{CaY}[CaY^{2-}]$. Also included in Figure 4 are the points representing the intercept values found at pH 8.00 and 8.80. The agreement among the data at all pH values shows that the dependence of the rate on the concentration of CaY^{2-} is independent of pH in this range. The slope of the plot of $(k_{obsd})_{lim}$ *vs.* $[CaY^{2-}]$ is equal to the constant $k_{Cd}{}^{CaY}$ and is $(2.3 \pm 0.2) \times 10^2$ M^{-1} sec^{-1}.

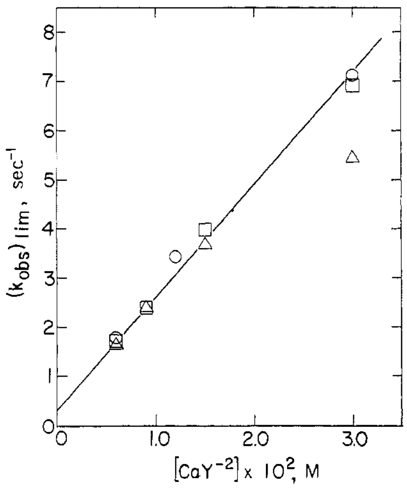


Figure 4.—Dependence of the limiting values of k_{obsd} on the concentration of the calcium-EDTA complex ion at μ = 1.0 M and 25°: ○, pH 8.00; □, pH 8.22; △, pH 8.80.

We conclude from these results that the complete rate expression for the complexation of cadmium ion in solutions containing EDTA in the presence of excess calcium ion at 25°, at an ionic strength of 1.0 (KNO_3), and in the pH range 8.00–8.80 is

$$-\frac{d[Cd^{2+}]}{dt} = k_{obsd}[Cd^{2+}]$$

where

$$k_{obsd} = (2.6 \times 10^8)[HY^{3-}] + (2.3 \times 10^2)[CaY^{2-}]$$

Ligand Exchange with *trans*-1,2-Cyclohexanediaminetetraacetic Acid.—The rate of the complexation reaction was studied with *trans*-1,2-cyclohexanediaminetetraacetic acid (CyDTA) in place of EDTA. In this case, the reaction rate was measured in the presence of 0.03 M CyDTA and varying small amounts of excess calcium ion at a pH of 8.00 and an ionic strength of 1.0 adjusted with potassium nitrate. A relatively slow reaction was detected when the cycling rates were decreased to between 4 and 10 sec/cycle. The experimental ratios of peak currents in this case did not follow the theoretical line in Figure 1, indicating that the reaction was not first order in cadmium ion. The CaEDTA complex under identical conditions underwent a pseudo-first-order reaction with cadmium which was about 100 times faster than the reaction of CaCyDTA with cadmium ion.

Discussion

In a solution containing 0.01 M calcium-EDTA complex ion and 0.01 M excess calcium ion at pH 8.0, the concentration of the monoprotonated dissociated anion, HY^{3-}, is approximately 10^{-8} M. In spite of the six orders of magnitude difference in the concentrations of the complex ion and the dissociated anion, it is found that both species react with cadmium ion in this solution at about the same absolute rate. This large difference in second-order rate constants ($k_{Cd}{}^{HY} = 2.6 \times 10^8$ M^{-1} sec^{-1} and $k_{Cd}{}^{CaY} = 2.3 \times 10^2$ M^{-1} sec^{-1}) is consistent with the mechanisms proposed previously for similar multidentate ligand-exchange reactions involving less labile metal ions.[9,10]

Dissociative Pathway.—The dissociative pathway of the reaction can be outlined as

$$\{CaY^{2-} \underset{-H^+}{\overset{+H^+}{\rightleftharpoons}} CaHY^-\} \underset{k_{Ca}{}^{HY}}{\overset{k_d}{\rightleftharpoons}} Ca^{2+} + HY^{3-} \qquad (1)$$

$$K_{eq} = \frac{k_d}{k_{Ca}{}^{HY}} = \frac{[Ca^{2+}][HY^{3-}]}{[CaY]_{total}} \qquad (2)$$

$$HY^{3-} + Cd^{2+} \xrightarrow{k_{Cd}{}^{HY}} CdY^{2-} + H^+ \qquad (3)$$

The species within the braces in eq 1 are assumed to be in rapid equilibrium. If a small, steady-state concentration of HY^{3-} is assumed, it is possible to derive the following expression for the observed pseudo-first-order rate constant

$$k_{\text{obsd}} = \frac{-d[\text{Cd}^{2+}]}{dt}/[\text{Cd}^{2+}] = \frac{k_{\text{Cd}}^{\text{HY}}k_{\text{d}}[\text{CaY}]_{\text{total}}}{k_{\text{Ca}}^{\text{HY}}[\text{Ca}^{2+}] + k_{\text{Cd}}^{\text{HY}}[\text{Cd}^{2+}]} \quad (4)$$

Eigen has shown that the values of the characteristic rate constants for the replacement of water in the inner sphere of hydrated cadmium and calcium ions are of the same order of magnitude,[18] so it might be expected that $k_{\text{Ca}}^{\text{HY}}$ and $k_{\text{Cd}}^{\text{HY}}$ are also of comparable magnitude. An nmr determination reported by Kula and Reed,[8] however, indicates that $k_{\text{Ca}}^{\text{HY}}$ ($1.3 \times 10^7\ M^{-1}\ \text{sec}^{-1}$) is significantly less than $k_{\text{Cd}}^{\text{HY}}$ ($2.6 \times 10^8\ M^{-1}\ \text{sec}^{-1}$).

The solutions used in all of the kinetic experiments reported here contain calcium ion at a concentration in excess of $5 \times 10^{-3}\ M$. The cadmium amalgam employed in the measurements contained $2 \times 10^{-4}\ M$ Cd, so that, upon oxidation of the amalgam, the maximum concentration of Cd^{2+} close to the electrode surface was about $2 \times 10^{-4}\ M$. If it is assumed for the moment that the condition

$$k_{\text{Ca}}^{\text{HY}}[\text{Ca}^{2+}] >> k_{\text{Cd}}^{\text{HY}}[\text{Cd}^{2+}] \quad (5)$$

was experimentally realized, eq 4 simplifies to

$$k_{\text{obsd}} = \frac{k_{\text{Cd}}^{\text{HY}}k_{\text{d}}[\text{CaY}]_{\text{total}}}{k_{\text{Ca}}^{\text{HY}}[\text{Ca}^{2+}]} \quad (6)$$

Combination of eq 2 and 6 yields

$$k_{\text{obsd}} = k_{\text{Cd}}^{\text{HY}}[\text{HY}^{3-}] \quad (7)$$

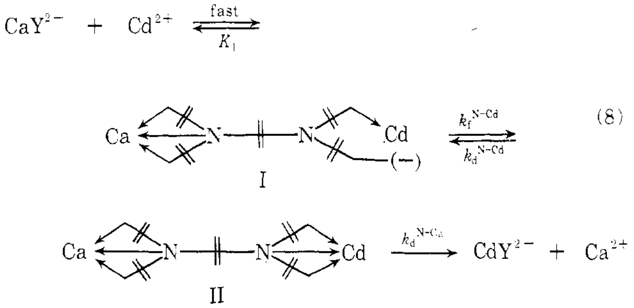
This expression predicts the dependence on dissociated EDTA species experimentally observed; thus, within the uncertainties of our measurements, eq 5 seems to be a valid approximation. If this approximation were not valid, the data in Figure 3 would show a slight downward curvature as the concentration of calcium ion decreases (and $[\text{HY}^{3-}]$ increases) owing to the increasing importance of the second term in the denominator of eq 4. Nevertheless, in view of the results of Kula and Reed, it is probably best to interpret our value of $k_{\text{Cd}}^{\text{HY}}$ as a lower limit, the true value being somewhat greater. Our value agrees well with those listed in Table III,[7,19-21] though it is slightly lower than the others.

The large value for the second-order rate constant for the reaction of cadmium ion with protonated EDTA is comparable to the characteristic first-order water-exchange rate constant measured for aqueous cadmium ion ($2.5 \times 10^8\ \text{sec}^{-1}$),[18] making it probable that the rate-limiting step in the reaction is the formation of the first cadmium–nitrogen bond with attending loss of water of hydration. None of the authors referred to in Table III speculates on the rate-limiting step for this particular reaction, though a similar mechanism has been proposed for the correspondingly fast reaction of copper ion with HY^{3-} ($k_{\text{Cu}}^{\text{HY}} = 1.3 \times 10^9\ M^{-1}\ \text{sec}^{-1}$) by Margerum and coworkers.[22,23]

A similar type of dissociative rate law is not observed with the calcium complex of CyDTA because the rate-limiting step in this exchange is the protonation of the complex, in contrast to the fast preequilibrium step shown in eq 1.[24] The reaction with calcium-CyDTA becomes independent of cadmium ion concentration and thus cannot be studied using the present methods.

Direct Transfer Pathway.—The second pathway of the reaction involves the direct attack on the CaEDTA complex by cadmium ion. This reaction proceeds through a transition state in which the EDTA ligand has half unwrapped itself by rotation about the ethylenic bond between the two nitrogen atoms and has one nitrogen still bound to calcium and the other available for bonding with approaching cadmium ion. Possible rate-limiting intermediates in which partial unwrapping of the nitrogens does not occur (as would be the case if the principal bonding in the transition state complex were through acetate groups) are ruled out by the large observed decrease in the rate and by the change in the mechanism when CaEDTA is replaced by CaCyDTA in the kinetic experiment. The cyclohexane ring in CyDTA prevents rotation about the ethylenic bond between the two nitrogen atoms, making nitrogen-bound dinuclear intermediates sterically impossible.[9] The presence of the ring does not appreciably affect the stability of the metal ion complexes and does little to hinder rotation about any of the other bonds in the molecule. Intermediate species that are predominantly nitrogen bonded are also consistent with predictions based on results of stability,[25] infrared,[26] and nmr[7,27] studies of bonding in alkaline earth–EDTA complexes.

The mechanism of the direct ligand transfer reaction can be represented by the series of steps in eq 8.



The rate-limiting step in this sequence could be either the formation of the cadmium–nitrogen bond in proceeding from structure I to structure II or the dissociation of the calcium–nitrogen bond in proceeding from structure II to the products. The results of the present experiments do not allow an unambiguous choice to be made between these alternatives, although we believe the former to be the more reasonable in view of the results of other studies of metal ion attack on

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TABLE III

SUMMARY OF RATE CONSTANTS DETERMINED BY VARIOUS METHODS FOR THE REACTIONS OF CADMIUM ION WITH MONOPROTONATED EDTA ANION

Value of rate const, $k_{\mathrm{Cd}}{}^{\mathrm{HY}}$, M^{-1} sec^{-1}	Ionic strength, M	Temp, °C	Method	Ref
3.7×10^9	0.5	25	Dc pol	19
8.5×10^8	0.1	25	Dc pol	20
5.3×10^8	0.5	25	Dc pol	21
6.1×10^8	0.5	25	Ac pol	21
1×10^9	1.6	28	Nmr	7
2.6×10^8	1.0	25	Cyclic polarog	This study

relatively labile EDTA complexes[9,22,23] and in view of the quantitative comparison between the rate constants $k_{\mathrm{Cd}}{}^{\mathrm{HY}}$ and $k_{\mathrm{Cd}}{}^{\mathrm{CaY}}$ made below. Ligand-exchange mechanisms in which the rate-limiting step is analogous to that between I and II in eq 8 have been proposed by Margerum and coworkers for the reactions between nickel ion and zinc-EDTA[9] and between copper ion and zinc-EDTA.[23]

If it is assumed that intermediate I is the type of species which immediately precedes the rate-limiting step in the reaction of cadmium ion with both the calcium-EDTA complex and protonated EDTA, it is possible to make an approximate comparison of the two rate constants $k_{\mathrm{Cd}}{}^{\mathrm{HY}}$ and $k_{\mathrm{Cd}}{}^{\mathrm{CaY}}$ measured in this study. To make this comparison it is necessary to assume that cadmium ion first associates with an unwound acetate group either as an ion pair or as a complex and that the proton or calcium ion initially present remains attached to the other half of the EDTA molecule. If the rate-limiting step in both cases is the formation of a cadmium–nitrogen bond, then the relative tendencies of the initial HEDTA and CaEDTA complexes to form the partially unwound dinuclear intermediates, such as I, should be proportional to the rate constants.

The rate constant $k_{\mathrm{Cd}}{}^{\mathrm{CaY}}$ can be expressed by the relation

$$k_{\mathrm{Cd}}{}^{\mathrm{CaY}} = \frac{K_{\mathrm{I}} k_{\mathrm{f}}{}^{\mathrm{N-Cd}}}{K_{\mathrm{CaEDTA}}} = \frac{K_{\mathrm{Ca\ segment}} K_{\mathrm{Cd\ segment}} k_{\mathrm{f}}{}^{\mathrm{N-Cd}}}{K_{\mathrm{CaEDTA}}} \tag{9}$$

where K_{I}, the stability constant of the intermediate, is represented by the product of the stability constants of the segment bonded to calcium ion and the segment bonded to cadmium ion, and $k_{\mathrm{f}}{}^{\mathrm{Cd-N}}$ is the rate constant for the formation of the cadmium–nitrogen bond. Similarly, the rate constant $k_{\mathrm{Cd}}{}^{\mathrm{HY}}$ can be written

$$k_{\mathrm{Cd}}{}^{\mathrm{HY}} = \frac{K_{\mathrm{I(H)}} k_{\mathrm{f}}{}^{\mathrm{N-Cd}}}{K_{\mathrm{HEDTA}}} = \frac{K_{\mathrm{H\ segment}} K_{\mathrm{Cd\ segment}} k'_{\mathrm{f}}{}^{\mathrm{N-Cd}}}{K_{\mathrm{HEDTA}}} \tag{10}$$

in which $K_{\mathrm{I(H)}}$ refers to the stability constant of the intermediate attached to both a proton and a cadmium ion.

Bydalek and Margerum[9] have shown that the stability constants of segments of EDTA intermediates can be successfully approximated by the products of known stability constants of smaller complexes which correspond in structure to the unwound EDTA segments. Thus, K_{I} in eq 9 may be replaced by the product $K_{\mathrm{CaIMDA}} K_{\mathrm{CdOAc}} K_{\mathrm{el}}$, where K_{CaIMDA} is the stability constant of calcium ion with imidodiacetic acid (half of an EDTA molecule), K_{CdOAc} is the constant for the cadmium–acetate interaction, and K_{el} is an electrostatic term to correct for electrostatic contributions to the stabilities of the actual intermediates which are not present in the isolated complexes chosen as models. By analogous reasoning, $K_{\mathrm{I(H)}}$ in eq 10 can be replaced by $K_{\mathrm{HIMDA}} K'_{\mathrm{CdOAc}} K'_{\mathrm{el}}$, where K_{HIMDA} is the proton association constant of imidodiacetic acid. Making these replacements, which admittedly neglect some steric, electrostatic, and statistical factors, the ratio of rate constants becomes

$$\frac{k_{\mathrm{Cd}}{}^{\mathrm{HY}}}{k_{\mathrm{Cd}}{}^{\mathrm{CaY}}} = \frac{K_{\mathrm{HIMDA}} K_{\mathrm{CaEDTA}} K'_{\mathrm{CdOAc}} K'_{\mathrm{el}} k'_{\mathrm{f}}{}^{\mathrm{N-Cd}}}{K_{\mathrm{HEDTA}} K_{\mathrm{CaIMDA}} K_{\mathrm{CdOAc}} K_{\mathrm{el}} k_{\mathrm{f}}{}^{\mathrm{N-Cd}}} \tag{11}$$

which can be further simplified by assuming that the rate constants for the formation of the cadmium–nitrogen bond and the affinity of cadmium ion for an unwound acetate group of the intermediate are the same in both bases and would cancel out. This last assumption is not strictly true in the case of the two intermediates being compared because the single negative charge of the protonated half of the HEDTA intermediate would stabilize the cadmium acetate bond more than would the uncharged half of the CaEDTA intermediate containing the calcium ion. Such differences due to charge are included in the electrostatic terms, but their magnitudes are difficult to estimate quantitatively because the steric orientations and charge distributions within these complexes are not precisely known.[22] Calculations of electrostatic corrections attempted by Bydalek and Margerum[9] using a Born-type equation indicate that for a unit difference of charge acting at a typical distance of 6 Å, the stability constant would change by a factor of 3, assuming the dielectric constant to be that of water. If these K_{el} terms are in fact of this small magnitude, no significant error is introduced by omitting their ratio in the present comparison, so that the ratio of rate constants becomes

$$\frac{k_{\mathrm{Cd}}{}^{\mathrm{HY}}}{k_{\mathrm{Cd}}{}^{\mathrm{CaY}}} \simeq \frac{K_{\mathrm{HIMDA}} K_{\mathrm{CaEDTA}}}{K_{\mathrm{HEDTA}} K_{\mathrm{CaIMDA}}} = 11 \times 10^6 \tag{12}$$

The experimental value of the rate constant ratio under the conditions of these studies is $\geq 1.1 \times 10^6$, which is in reasonably good agreement with the calculated ratio and supports the similarity in mechanisms. (The agreement between the ratios is even better if the mean of all of the results for $k_{\mathrm{Cd}}{}^{\mathrm{HY}}$ given in Table III is used.) Other possible intermediates preceding the rate-limiting step which involve fewer than three dentate groups attached to the calcium ion (*e.g.*, glycinate or acetate-like structures) are appreciably less stable than CaIMDA and would give less favorable comparisons with the experimental ratio of rate constants.

We conclude, therefore, that the direct attack by cadmium ion on the calcium-EDTA complex proceeds through a partially unwound dinuclear intermediate bonded to both calcium and cadmium ions and that the rate-limiting step in this pathway, as well as in the dissociative pathway, is most likely the formation of the first cadmium-nitrogen bond.

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Absorption and Circular Dichroism Spectral Studies of Chelate Complexes of Praseodymium(III) with α-Amino Acids[1]

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Preparation is described of solutions of amino acid chelate complexes with Pr(III), in the neutral and alkaline pH range. Characteristic absorption and CD spectra are shown for the dominant 1:1 complexes. Differences between spectra for the simple amino acids (alanine, valine, leucine) and the potentially tridentate serine and asparagine are demonstrated. Stability and ease of formation are correlated with the pK of the α-amino group. Data are also given for the basic amino acids, ornithine and lysine. Aspartic and glutamic acids give CD spectra in acid solution which are interpreted as reflecting chelation through the two carboxyl groups. In alkaline solution, this may become chelation through the amino group and the carboxyl β to it, to give a six-membered ring.

The absorption and circular dichroism (CD) spectra of complexes of Pr(III) with a number of optically active hydroxy acids have been described.[2] In these systems, evidence was presented for formation of six- and seven-membered chelate rings. This report extends observations to chelate complexes of Pr(III) with the α-amino acids. Not only is coordination with an amino group introduced, but in these systems five-membered rings must be formed.

Experimental Section

Materials.—Stock solution 0.894 M in $PrCl_3$ was prepared from Pr_6O_{11} (99.9% pure) by digesting a weighed amount of oxide with a small excess of HCl and then diluting the solution to volume with water. The concentration calculated was verified by comparing the extinction values for the maxima at 444.0 and 482.5 nm with those given by Stewart and Kato.[3] In some early experiments, crystalline $PrCl_3$ of uncertain hydration was used, and the stock concentrations were determined from these extinction values alone.

Most of the amino acids were used as supplied by Nutritional Biochemicals Corp. An exception was proline, which was recrystallized from methanol to which ether was added. The other amino acids were glycine, alanine, valine, leucine, serine, ornithine, lysine, arginine, asparagine, aspartic acid, and glutamic acid.

Sample Preparation.—The following procedure was adopted for routine solution preparations after preliminary experiments. This operated smoothly for all of the monocarboxylic acids. A desired weight of the amino acid was dissolved in water, and 5 F ammonia was added to make the solution alkaline. The required volume of stock Pr(III) solution (usually 1–2 ml) was then added dropwise, with mixing. Additional 5 F NH_3 was then added, as required, to achieve the desired final pH, estimated with Hydrion paper. In cases where precipitation limited the pH which might be attained, ammonia was added only until hazy solution showed a trace of permanent precipitate to be formed. This was usually centrifuged down before spectral measurements were made. Occasionally precipitation which was slow in initiation interrupted a spectral scan. Final solutions were about 0.1 F in Pr(III).

Preliminary attempts to prepare samples by dissolving the freshly precipitated Pr(III) hydroxide with excess amino acid solution were only occasionally successful, and even then the stoichiometry of the solution resulting was uncertain. Addition of NaOH to mixtures of Pr(III) and amino acid also was unsatisfactory. Consistent results were obtainable only with the procedure outlined. Dicarboxylic acids presented problems of a different type; glutamic acid preparations in solution above pH 7 were not obtainable.

Spectral Measurements.—Absorption and CD spectra were plotted on the Durrum-Jasco ORD-UV-CD-5, as in previous work.[2] For the CD spectra a 30-mm cell was generally used, and for the absorption measurements, one of 5-mm length was used. No thermostating of the samples was attempted. When spectra were to be analyzed into gaussian components, the Du Pont Model 310 curve analyzer (10 channels) was used. As in the prior study,[2] attention was concentrated on the spectral region, 420–510 nm, in which the ^3P transitions of Pr(III) are found.

Results

The spectral behavior of the monocarboxylic acid–praseodymium(III) mixtures with pH was fairly uniform. As pH increased toward about pH 6, the absorption peaks at 443.5, 468.5, and 482 nm decreased a little in intensity and broadened slightly toward the long-wavelength side. As with the hydroxy acids,[2] the decrease was least in the $^3P_1$ band (468.5 nm). At pH 6–7, depending on the amino acid, the broadening to the long-wavelength side became sharply accentuated, and, in the case of the $^3P_0$ band (482 nm), a definite new peak at 484 nm was initiated. At lower pH values, it

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[1] Based on work performed under the auspices of the U. S. Atomic Energy Commission.

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