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Kinetics and Mechanism of the Ligand-Substitution Reaction of the Copper(II)-(Ethylene glycol)bis(2-aminoethyl ether)-*N,N,N',N'*-tetraacetate Complex with 4-(2-Pyridylazo)resorcinol with Special Reference to the Effect of Alkaline Earth Metal Ions

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The kinetics of the ligand-substitution reaction of the copper(II)-(ethylene glycol)bis(2-aminoethyl ether)-*N,N,N',N'*-tetraacetate complex (Cu(II)-EGTA) with 4-(2-pyridylazo)resorcinol (PAR) has been studied spectrophotometrically in the pH range 9.0-10.3 at $\mu = 0.10$ (NaClO₄) and at 25.0°. The rate law of the substitution reaction is

$$\frac{d[\text{Cu}(\text{par})_2^{2-}]}{dt} = k_1^M[\text{Cu}(\text{egta})^{2-}][\text{OH}^-][\text{M}^{2+}] + k_2[\text{Cu}(\text{egta})^{2-}][\text{Hpar}^-] + k_3[\text{Cu}(\text{egta})^{2-}][\text{par}^{2-}] + k_4^M[\text{Cu}(\text{egta})^{2-}][\text{M}^{2+}][\text{Hpar}^-] + k_5^M[\text{Cu}(\text{egta})^{2-}][\text{M}^{2+}][\text{par}^{2-}]$$

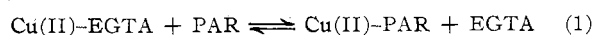
where egta^{4-} , par^{2-} , and M^{2+} refer to tetravalent EGTA, bivalent PAR, and alkaline earth metal ion, respectively. The equilibrium of the present ligand-substitution reaction is favored by the presence of alkaline earth metal ions, which participate kinetically in the substitution reaction. Rate constants at 25.0° and $\mu = 0.1$ are as follows: $k_1^{\text{Ba}} = (1.2 \pm 0.3) \times 10^4 M^{-2} \text{sec}^{-1}$, $k_2 = (1.8 \pm 0.5) M^{-1} \text{sec}^{-1}$, $k_3 = (3 \pm 2) \times 10^2 M^{-1} \text{sec}^{-1}$, $k_4^{\text{Ba}} = (1.5 \pm 0.5) \times 10^3 M^{-2} \text{sec}^{-1}$, $k_5^{\text{Ba}} = (1.9 \pm 0.5) \times 10^6 M^{-2} \text{sec}^{-1}$, $k_1^{\text{Sr}} = (1.1 \pm 0.3) \times 10^4 M^{-2} \text{sec}^{-1}$, $k_4^{\text{Sr}} = (1.2 \pm 0.5) \times 10^3 M^{-2} \text{sec}^{-1}$, $k_5^{\text{Sr}} = (2.0 \pm 0.3) \times 10^6 M^{-2} \text{sec}^{-1}$, $k_1^{\text{Ca}} = (1.8 \pm 0.3) \times 10^5 M^{-2} \text{sec}^{-1}$, $k_4^{\text{Ca}} = (3 \pm 1) \times 10^5 M^{-2} \text{sec}^{-1}$, $k_5^{\text{Ca}} = (7 \pm 3) \times 10^7 M^{-2} \text{sec}^{-1}$. The substitution reaction proceeds through an intermediate in which a central copper ion is bonded with two ligands EGTA and PAR. The role of alkaline earth metal ions is quantitatively interpreted. In connection with the kinetic study the stability constants of the Cu(II)-PAR complexes have been determined spectrophotometrically at $\mu = 0.1$ and 25°: $[\text{Cu}(\text{Hpar})^+]/[\text{Cu}^{2+}][\text{Hpar}^-] = 10^{9.92 \pm 0.05}$, $[\text{Cu}(\text{Hpar})^+]/[\text{Cu}(\text{par})][\text{H}^+] = 10^{6.00 \pm 0.05}$, $[\text{Cu}(\text{par})]/[\text{Cu}^{2+}][\text{par}^{2-}] = 10^{17.22 \pm 0.05}$, $[\text{Cu}(\text{par})_2^{2-}]/[\text{Cu}(\text{par})][\text{par}^{2-}] = 10^{9.1 \pm 0.2}$.

Introduction

Though the kinetics and mechanism of complex formation and substitution of metal chelates with metal ions have been studied in detail, little attention has as yet been given to the substitution of metal chelates with multidentate ligands. Proton nuclear magnetic resonance line-broadening techniques were used to measure the kinetics of the symmetric ligand-exchange reaction.¹⁻⁵ Margerum and Rosen⁶ have utilized a spectrophotometric method for kinetic studies of unsymmetric ligand-exchange reactions. They have pointed out the stepwise process by which one multidentate ligand displaces another from a metal ion in the reactions of Ni(dien)₂²⁺ and Ni(dien)²⁺ with EDTA.

We have studied the ligand substitution of metal chelates with multidentate ligands which are often involved in complexometric titrations and solvent extractions of metal chelates.⁷⁻⁹ The ligand-substitution reaction proceeds through an intermediate in which a central metal ion is bonded to both leaving and entering ligands. The cleavage of the bond between the metal and leaving ligand is the rate-determining step.

The present paper describes the result on the ligand-substitution reaction



where PAR and EGTA represent 4-(2-pyridylazo)resorcinol and (ethylene glycol)bis(2-aminoethyl ether)-*N,N,N',N'*-tetraacetic acid, respectively, and are abbreviated as H₂par (tridentate) and H₄egta (hexadentate), respectively. In order to favor equilibrium 1 to the right, we have carried out the reaction in ligand buffers of egta^{4-} with excesses of alkaline earth metal ions. The free alkaline earth metal ions participate in the reaction and their role in the reaction has been quantitatively accounted for.

Experimental Section

Reagents. Copper(II) Perchlorate.—Reagent grade copper(II) nitrate was recrystallized three times from distilled water. Copper(II) oxide which was obtained by heating pure copper(II) nitrate was dissolved in perchloric acid to prepare copper perchlorate solution. Copper perchlorate obtained was recrystallized three times from distilled water. The copper perchlorate solution was standardized complexometrically against a standard EDTA solution with TAR (4-(2-thiazolylazo)resorcinol)¹⁰ as an indicator. The concentration of copper was also checked by electrolysis of copper.

PAR.—The acid form of PAR, obtained from Dojin-do Chemical Co., Kumamoto, Japan, was recrystallized twice from aqueous ethanol. The purity of PAR was checked by column chromatography.

Sodium Perchlorate.—Sodium perchlorate was prepared by dissolution of sodium carbonate in perchloric acid. Heavy-metal impurities in the sodium perchlorate were precipitated as hydroxides at pH 9 and extracted as PAN complexes (PAN =

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- (1) J. L. Sudmeier and C. N. Reilley, *Inorg. Chem.*, **5**, 1047 (1966).
- (2) J. D. Carr, K. Torrance, C. J. Cruz, and C. N. Reilley, *Anal. Chem.*, **39**, 1358 (1967).
- (3) R. J. Kula and G. H. Reed, *ibid.*, **38**, 697 (1966).
- (4) R. J. Kula and D. L. Rabenstein, *J. Amer. Chem. Soc.*, **89**, 552 (1967).
- (5) D. L. Rabenstein and R. J. Kula, *ibid.*, **91**, 2492 (1969).
- (6) D. W. Margerum and H. M. Rosen, *Inorg. Chem.*, **7**, 299 (1968).
- (7) M. Tanaka, S. Funahashi, and K. Shirai, *ibid.*, **7**, 573 (1968).
- (8) S. Funahashi and M. Tanaka, *Bull. Chem. Soc. Jap.*, **43**, 763 (1970).
- (9) S. Funahashi, S. Yamada, and M. Tanaka, *ibid.*, **43**, 769 (1970).

(10) H. Wada and G. Nakagawa, *Bunseki Kagaku*, **14**, 29 (1965).

1-(2-pyridylazo)-2-naphthol) with purified carbon tetrachloride four times at pH 9 and as oxinates with carbon tetrachloride four times at pH 7. Sodium perchlorate was then recrystallized once from distilled water. The concentration of sodium ion in the sodium perchlorate solution was determined gravimetrically as sodium sulfate. The concentration of sodium ion was also checked by ion exchange.

Barium Perchlorate.—Barium perchlorate was prepared by dissolution of barium hydroxide in perchloric acid. Heavy-metal impurities in the barium perchlorate were precipitated as hydroxides at pH 9 and extracted as PAN complexes with carbon tetrachloride four times at pH 9. The concentration of the barium perchlorate solution was determined gravimetrically as barium sulfate.

Calcium Perchlorate.—Calcium chloride was dissolved in perchloric acid and chloride was expelled by evaporation, excess perchloric acid being removed by an infrared lamp. Heavy-metal impurities in calcium perchlorate were precipitated as hydroxides at pH 9 and extracted as PAN complexes with benzene at pH 9. The concentration of the calcium perchlorate solution was determined complexometrically by a standard EDTA solution with methylthymol blue as an indicator.

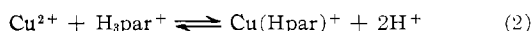
Strontium Perchlorate.—Strontium perchlorate was prepared from reagent grade strontium chloride in the same way as calcium perchlorate.

Methods of preparation of the other reagents (EGTA, boric acid, borax, and sodium hydroxide) have been described previously.⁷

Apparatus.—The following instruments were used: a Hitachi Perkin-Elmer 139 UV-VIS spectrophotometer with a thermostated 5.3-cm cell; a Beckman Model DU spectrophotometer with a thermostated ($\pm 0.2^\circ$) cell compartment; a JASCO Model ORD/UV-5 optical rotatory dispersion recorder; a Hitachi Model QPD-53 recorder; a Horiba Model P pH meter; a Radiometer PHM-4d (Copenhagen) with a glass electrode, Type G202 B, and a calomel electrode, Type K401; a Sharp Model TEB-10 thermoelectric circulating bath.

Determination of the Stability Constants of Cu(II)-PAR Complexes.—It is necessary to determine the stability constants of Cu(II)-PAR complexes in connection with the equilibria involved in the ligand-substitution reaction.

PAR forms a 1:1 complex with copper ion at lower pH under conditions where the concentration of copper is in sufficient excess compared with that of PAR. The isosbestic point at 485 nm in absorption spectra during the formation of the protonated 1:1 Cu(II)-PAR complex points to the equilibrium



Typical data of absorbance of the system (2) at various pH's are given in Table I. The constant for equilibrium 2 $K_{\text{Cu}(\text{Hpar})\text{H}_3\text{par}^+}$

TABLE I
ABSORBANCE OF THE SYSTEM (2) AT VARIOUS pH'S^a

pH	Absorbance at 515 nm	pH	Absorbance at 515 nm
0.70	0.561	0.52	0.462
0.66	0.530	0.50	0.435
0.63	0.517	0.48	0.419
0.60	0.507	0.44	0.410
0.57	0.487	0.40	0.368
0.55	0.465	0.36	0.357

^a $C_{\text{Cu}} = 3.81 \times 10^{-3} M$; $C_{\text{PAR}} = 4.00 \times 10^{-5} M$; $\mu = 0.6$ (NaClO₄-HClO₄); temperature 25°C; cell length 1 cm.

is expressed as

$$K_{\text{Cu}(\text{Hpar})\text{H}_3\text{par}^+} = \frac{[\text{Cu}(\text{Hpar})^+][\text{H}^+]^2}{[\text{Cu}^{2+}][\text{H}_3\text{par}^+]}$$

which leads to the logarithmic form

$$\log K_{\text{Cu}(\text{Hpar})\text{H}_3\text{par}^+} = \log \frac{[\text{Cu}(\text{Hpar})^+]}{[\text{H}_3\text{par}^+]} - \log [\text{Cu}^{2+}] - 2 \text{pH} \quad (3)$$

The plot of $\log \{ [\text{Cu}(\text{Hpar})^+]/[\text{H}_3\text{par}^+] \}$ vs. pH yields a straight line with a slope of 2 in accordance with eq 3 (Figure 1). The molar absorption coefficient of H_3par^+ , $\epsilon_{\text{H}_3\text{par}^+}$, and that of $\text{Cu}(\text{Hpar})^+$, $\epsilon_{\text{Cu}(\text{Hpar})^+}$, at 515 nm are 1.91×10^3 and 1.69×10^4 ,

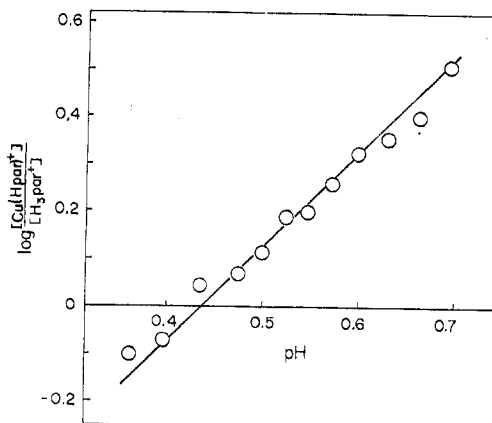


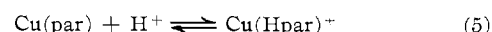
Figure 1.—Dependence of $\log \{ [\text{Cu}(\text{Hpar})^+]/[\text{H}_3\text{par}^+] \}$ on pH according to eq 3 at $\mu = 0.6 M$ and 25° . The slope of the straight line is 2.

respectively. The value of $K_{\text{Cu}(\text{Hpar})\text{H}_3\text{par}^+}$ is $10^{1.55 \pm 0.03}$ at 25° and $\mu = 0.6 M$; that at 25° and $\mu = 0.1 M$ ^{11,12} is $10^{1.73 \pm 0.03}$. Therefore

$$K_{\text{Cu}(\text{Hpar})\text{H}_3\text{par}^+} = \frac{[\text{Cu}(\text{Hpar})^+]}{[\text{Cu}^{2+}][\text{H}_3\text{par}^+]} = K_{\text{Cu}(\text{Hpar})\text{H}_3\text{par}^+} K_{\text{H}_3\text{par}^+} K_{\text{H}_2\text{par}^+} K_{\text{Hpar}^+} = 10^{9.50 \pm 0.05} \quad (4)$$

where $K_{\text{H}_3\text{par}^+} = [\text{H}_3\text{par}^+]/[\text{H}_2\text{par}^+][\text{H}^+] = 10^{2.69}$ and $K_{\text{H}_2\text{par}^+} = [\text{H}_2\text{par}^+]/[\text{Hpar}^+][\text{H}^+] = 10^{6.50,13}$

At pH from 3 to 6 the spectra of the solution show distinct isosbestic points at 439 and 542 nm attributable to proton release of the protonated 1:1 Cu(II)-PAR complex and indicate a simple acid-base equilibrium



Typical data of absorbance of the 1:1 Cu(II)-PAR complex in solutions of various pH's are given in Table II. The constant

TABLE II
ABSORBANCE OF THE 1:1 Cu-PAR COMPLEX IN SOLUTIONS OF VARIOUS pH'S^a

pH	Absorbance at 515 nm	pH	Absorbance at 515 nm
3.50	0.361	4.93	0.521
3.63	0.354	5.15	0.595
3.81	0.363	5.22	0.592
4.05	0.387	5.36	0.625
4.33	0.407	5.53	0.678
4.47	0.425	5.83	0.712
4.62	0.467	6.12	0.745
4.73	0.482		

^a $C_{\text{Cu}} = 1.90 \times 10^{-3} M$; $C_{\text{PAR}} = 2.00 \times 10^{-5} M$; acetate buffer ($C_{\text{OAc}} = 0.02 M$); $\mu = 0.1$ (NaClO₄); temperature 25° ; cell length 1 cm.

for equilibrium 5 is expressed as $K_{\text{Cu}(\text{Hpar})\text{H}^+} = [\text{Cu}(\text{Hpar})^+]/[\text{Cu}(\text{par})][\text{H}^+]$. In fact the plot of $\log \{ [\text{Cu}(\text{Hpar})^+]/[\text{Cu}(\text{par})] \}$ vs. pH is a straight line with a slope of unity. $\epsilon_{\text{Cu}(\text{Hpar})}$ and $\epsilon_{\text{Cu}(\text{par})}$ at 515 nm are 1.69×10^4 and 3.82×10^4 , respectively. The value of $K_{\text{Cu}(\text{Hpar})\text{H}^+}$ was evaluated by a conventional method

(11) J. Kielland, *J. Amer. Chem. Soc.*, **59**, 1675 (1937).

(12) A. Ringbom, "Complexation in Analytical Chemistry," Interscience, New York, N. Y., 1963, p 24.

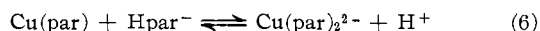
(13) W. J. Geary, G. Nickless, and F. H. Pollard, *Anal. Chim. Acta*, **27**, 71 (1962).

and the value was refined by the HITAC 5020 computer by means of the least-squares method. At 25° and $\mu = 0.1 M$, $K_{\text{Cu}(\text{Hpar})^{\text{H}}} = 10^{8.00 \pm 0.05}$. Therefore

$$K_{\text{Cu}(\text{par})^{\text{par}}} = \frac{[\text{Cu}(\text{par})]}{[\text{Cu}^{2+}][\text{par}^{2-}]} = K_{\text{Cu}(\text{Hpar})^{\text{Hpar}}} K_{\text{Hpar}^{\text{H}}} / K_{\text{Cu}(\text{Hpar})^{\text{H}}} \\ = 10^{17.22 \pm 0.05}$$

where $K_{\text{Hpar}^{\text{H}}} = [\text{Hpar}^-] / [\text{par}^{2-}][\text{H}^+] = 10^{12.80, 13}$

PAR forms a 1:2 complex with copper under conditions where PAR is in a large excess compared to copper. The constant for equilibrium 6, $K_{\text{Cu}(\text{par})_2^{\text{Hpar}}}$, was measured by the spectrophotometry of the $\text{Cu}(\text{par})_2^{2-}$ complex ($\epsilon_{\text{Cu}(\text{par})_2}$ is 6.87×10^4 at 515



nm, Table III). The following values were obtained at 25° and $\mu = 0.1 M$

$$K_{\text{Cu}(\text{par})_2^{\text{Hpar}}} = \frac{[\text{Cu}(\text{par})_2^{2-}][\text{H}^+]}{[\text{Cu}(\text{par})][\text{Hpar}^-]} = 10^{-3.26 \pm 0.12}$$

$$K_{\text{Cu}(\text{par})_2^{\text{par}}} = \frac{[\text{Cu}(\text{par})_2^{2-}]}{[\text{Cu}(\text{par})][\text{par}^{2-}]} = K_{\text{Cu}(\text{par})_2^{\text{Hpar}}} K_{\text{Hpar}^{\text{H}}} = 10^{9.1 \pm 0.2}$$

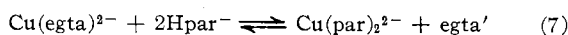
TABLE III

ABSORBANCE OF THE SYSTEM (6) IN SOLUTIONS OF VARIOUS pH'S^a

pH	Absorbance at 515 nm	pH	Absorbance at 515 nm
7.96	0.312	8.91	0.381
8.26	0.330	8.93	0.379
8.35	0.344	9.06	0.385
8.46	0.354	9.10	0.391
8.58	0.359	9.14	0.392
8.62	0.363	9.28	0.401
8.70	0.370	9.34	0.409
8.78	0.370	9.40	0.411
8.85	0.376		

^a $C_{\text{Cu}} = 5.71 \times 10^{-6} M$; $C_{\text{PAR}} = 2.00 \times 10^{-5} M$; borate buffer ($C_{\text{B}} = 0.005 M$); $\mu = 0.1$ (NaClO₄); temperature 25°; cell length 1 cm.

Equilibria.—Under the present experimental conditions for the kinetic study, copper(II) forms with PAR the 1:2 complex $\text{Cu}(\text{par})_2^{2-}$ as expected from stability constants described. In the range of pH from 9.0 to 10.3, the dominant species of PAR is the singly charged species (Hpar^-) as evident from the stability constants of PAR. The wavelengths of maximum absorption of $\text{Cu}(\text{par})_2^{2-}$ and Hpar^- are 500 and 415 nm, respectively. As seen from the values of the stability constants of protonated EGTA ($\log K_{\text{Hegta}^{\text{H}}} = 9.43$, $\log K_{\text{H}_2\text{egta}^{\text{H}}} = 8.85$, $\log K_{\text{H}_3\text{egta}^{\text{H}}} = 2.69$, $\log K_{\text{H}_4\text{egta}^{\text{H}}} = \sim 2$),¹⁴ egta^{4-} , Hegta^{3-} , and $\text{H}_2\text{egta}^{2-}$ are present under the experimental conditions. Copper(II) forms with EGTA the 1:1 complex $\text{Cu}(\text{egta})^{2-}$. The stability constant of $\text{Cu}(\text{egta})^{2-}$ at 25° and $\mu = 0.1$ (KNO₃) is $K_{\text{Cu}(\text{egta})} = [\text{Cu}(\text{egta})^{2-}] / [\text{Cu}^{2+}][\text{egta}^{4-}] = 10^{17.8, 16}$. Thus the reaction is written



where egta' denotes the EGTA not combined with copper ion. The ratio of the concentration of Cu(II)-PAR to that of Cu(II)-EGTA in the presence of large excesses of alkaline earth metal ion, EGTA, and PAR is expressed as

$$\frac{[\text{Cu}(\text{par})_2^{2-}]}{[\text{Cu}(\text{egta})^{2-}]} = \frac{K_{\text{Cu}(\text{par})_2^{\text{par}}} K_{\text{Cu}(\text{par})_2^{\text{par}}} \alpha_{\text{egta}(\text{H}, \text{M})} C_{\text{PAR}}^2}{K_{\text{Cu}(\text{egta})} \alpha_{\text{par}(\text{H})}^2 C_{\text{EGTA}}} \quad (8)$$

where $\alpha_{\text{par}(\text{H})}$ and $\alpha_{\text{egta}(\text{H}, \text{M})}$ are the side-reaction coefficients taking into account the protonation of par^{2-} and the protonation and the complexation of egta^{4-} , respectively.¹⁶ Alkaline earth

(14) L. G. Sillén and A. E. Martell, "Stability Constants of Metal-Ion Complexes," Special Publication No. 17, The Chemical Society, London, 1964.

(15) J. H. Holloway and C. N. Reilly, *Anal. Chem.*, **32**, 249 (1960).

(16) $[\text{egta}'] = [\text{egta}^{4-}] + [\text{Hegta}^{3-}] + [\text{H}_2\text{egta}^{2-}] + [\text{M}(\text{egta})^{2-}] = [\text{egta}^{4-}](1 + K_{\text{Hegta}^{\text{H}}}[\text{H}^+] + K_{\text{H}_2\text{egta}^{\text{H}}}K_{\text{H}_3\text{egta}^{\text{H}}}[\text{H}^+]^2 + K_{\text{M}(\text{egta})}[\text{M}^{2+}]) = [\text{egta}^{4-}]\alpha_{\text{egta}(\text{H}, \text{M})}$.

metal ions M^{2+} coordinate to EGTA and do not combine with PAR under the present experimental conditions. In order to favor equilibrium 7 to the right, *i.e.*, in order to realize a large value of the ratio (8), the reaction was carried out in ligand buffers of egta^{4-} , which have been defined as a system containing a ligand EGTA and an excess of metal ion.¹⁷ In a ligand buffer $[\text{egta}^{4-}]$ is determined by $C_{\text{M}}/C_{\text{EGTA}}$ and pH. Furthermore in the case where egta^{4-} forms a stable chelate with M^{2+} , $[\text{egta}^{4-}]$ is determined only by the ratio $C_{\text{M}}/C_{\text{EGTA}}$ over a wide range of pH. Under the present experimental condition

$$[\text{egta}^{4-}] = (C_{\text{M}}/C_{\text{EGTA}} - 1)^{-1} K_{\text{M}(\text{egta})}^{-1} \quad (9)$$

$[\text{egta}^{4-}]$ is independent of the total concentration of ligand, and $[\text{egta}^{4-}]$ is determined only by the ratio $C_{\text{M}}/C_{\text{EGTA}}$.

Procedure for Measurement of the Substitution Reaction Rate.

—A solution for the kinetic run containing the Cu(II)-EGTA complex in a ligand buffer of egta^{4-} with excess alkaline earth metal ion was prepared as follows. To a mixture of copper and EGTA solutions is added sodium perchlorate solution to maintain the constant ionic strength. The pH of the solution is then adjusted with borate buffer, and the solution is finally diluted to volume. A silica beaker (light path length of 5.3 cm) containing Cu(II)-EGTA solution was placed in a thermostated compartment of a spectrophotometer capable of temperature control at $25 \pm 0.2^\circ$. The PAR solution was brought to temperature equilibrium in a bath kept at $25 \pm 0.1^\circ$. The reaction was started by mixing these two solutions in the silica beaker. The temperature during all kinetic runs was maintained at $25.0 \pm 0.2^\circ$. The transmittance at 515 nm of the reaction system was recorded automatically as a function of the reaction time. All pH values were measured in a bath kept at $25 \pm 0.1^\circ$ with standard buffer solution (borax, 0.01 M) prepared as described by Bates.¹⁸ All experiments were carried out in a room thermostated at $25 \pm 1^\circ$.

Results

The ligand-substitution reaction was studied spectrophotometrically at pH from 9.0 to 10.3. Experiments at higher pH were not practicable because of high absorbance of a species of PAR, par^{2-} . At lower pH it is difficult to form quantitatively copper(II) complexes, especially the 1:2 Cu(II)-PAR complex, and to force the substitution reaction to completion. Under the present experimental conditions for kinetic study, equilibrium 7 is much favored to the right so that the substitution reaction of the Cu(II)-EGTA complex with PAR goes substantially to completion (eq 8) and the reverse reaction can be neglected in the kinetic study.

For the reaction with large excesses of EGTA, barium ion, and PAR the rate equation can be expressed as

$$\frac{d[\text{Cu}(\text{par})_2^{2-}]}{dt} = k_{0(\text{Ba}, \text{H}, \text{par})} [\text{Cu}(\text{egta})^{2-}] \quad (10)$$

where $k_{0(\text{Ba}, \text{H}, \text{par})}$ is the conditional rate constant involving concentrations of barium ion, hydrogen ion, and PAR. The rate plots of $\log [(A_\infty - A_0)/(A_\infty - A_t)]$ vs. t were linear for over 90% of the reaction. Then the conditional rate constant $k_{0(\text{Ba}, \text{H}, \text{par})}$ was determined from the slope of the straight line. The values of conditional rate constants at various concentrations of EGTA, barium ion, and PAR and at various pH's are given in Table IV.

The values of conditional rate constants at various

(17) M. Tanaka, *Anal. Chim. Acta*, **29**, 193 (1963).

(18) R. G. Bates, "Determination of pH, Theory and Practice," Wiley, New York, N. Y., 1964, p 123.

TABLE IV
CONDITIONAL RATE CONSTANTS $k_{0(\text{Ba,H,par})}$ OF THE LIGAND-SUBSTITUTION REACTION OF THE Cu(II) -EGTA COMPLEX WITH PAR IN THE LIGAND BUFFERS OF egta^{4-} WITH BARIUM ION, AT 25° AND $\mu = 0.1$ (NaClO_4)^a

Run no.	$10^4 C_{\text{PAR}}$, M	$10^4 C_{\text{Ba}}$, M	$10^3 [\text{egta}^{4-}]$, M	pH	$10^3 k_{0(\text{Ba,H,par})}$, sec^{-1}	$k_{2(\text{Ba,H})}$, $\text{M}^{-1} \text{sec}^{-1}$
1	0.500	3.32	4.31	8.09	0.200	3.32
2	1.00			9.07	0.340	3.07
3	2.00			9.07	0.625	2.96
4	2.50			9.09	0.769	2.93
5	3.00			9.07	0.911	2.93
6	0.500	8.93	1.26	9.08	0.292	3.56
7	1.00			9.04	0.520	4.15
8	1.50			9.08	0.679	3.76
9	2.00			9.05	0.894	3.94
10	2.50			9.08	1.00	3.54
11	3.00			9.06	1.31	4.01
12	0.500	22.3	0.469	9.04	0.608	6.50
13	1.00			9.04	0.905	6.27
14	2.50			9.04	1.78	6.00
15	0.400	8.93	1.26	9.55	0.587	6.30
16	0.500			9.52	0.687	7.46
17	0.500			9.55	0.673	6.70
18	1.00			9.52	0.987	6.70
19	1.00			9.55	0.933	5.93
20	1.20			9.55	1.04	5.83
21	1.50			9.54	1.33	6.67
22	2.00			9.54	1.63	6.51
23	2.50			9.52	1.98	6.66
24	2.50			9.54	1.92	6.34
25	3.00			9.52	2.31	6.65
26	0.500			10.31	2.66	14.6
27	1.00			10.31	4.29	23.7
28	2.00			10.28	6.67	24.3
29	1.00	10.2	1.09	9.93	1.73	7.95
30				9.57	0.976	5.67
31				9.34	0.709	4.68
32				9.05	0.601	4.76
33	2.00			10.20	4.81	15.4
34				9.80	2.19	7.49
35				9.51	1.54	5.90
36				9.16	1.10	4.70
37	3.00			10.03	5.27	13.6
38				9.55	2.65	7.52
39				9.37	1.89	5.44
40				9.30	1.07	4.83
41				9.13	1.45	4.34
42	2.00	1.53	18.9	9.89	0.775	3.63
43				9.57	0.550	2.63
44				9.35	0.458	2.22
45				9.25	0.458	2.24
46		2.55	6.45	10.02	1.37	5.88
47				9.99	1.13	4.75
48				9.66	0.758	3.37
49				9.62	0.667	2.95
50				9.38	0.592	2.74
51				9.28	0.558	2.62
52		5.10	2.44	9.86	1.52	5.81
53				9.51	0.908	3.76
54				9.31	0.792	3.47
55		25.5	1.09	9.77	5.42	19.0
56				9.46	3.17	11.9
57				9.22	2.33	9.35
58				9.13	2.03	8.30
59	1.00	2.55	6.45	9.91	0.608	4.56
60				9.39	0.388	3.42
61				9.28	0.346	3.10
62				9.14	0.342	3.16

^a $C_{\text{Cu}} = 1.00 \times 10^{-6} \text{ M}$ and $C_{\text{EGTA}} = 1.00 \times 10^{-4} \text{ M}$, for all but runs 55-58 where $C_{\text{EGTA}} = 2.50 \times 10^{-4} \text{ M}$.

concentrations of PAR are given in Table IV (run no. 1-28). These data indicate clearly a linear relationship between $k_{0(\text{Ba,H,par})}$ and the concentration of PAR with a nonzero intercept (Figure 2). Thus the conditional rate constant $k_{0(\text{Ba,H,par})}$ is expressed by

$$k_{0(\text{Ba,H,par})} = k_{1(\text{Ba,H})} + k_{2(\text{Ba,H})}[\text{Hpar}^-]$$

$k_{1(\text{Ba,H})}$ is found proportional to the concentration of barium ion and to the reciprocal concentration

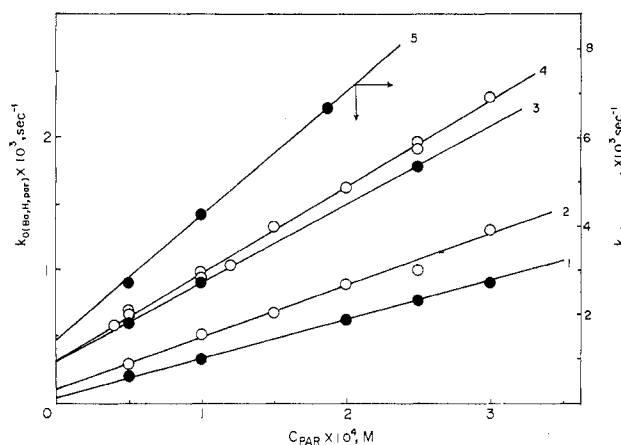


Figure 2.— $k_{0(\text{Ba,H,par})}$ as a function of the concentration of PAR. Conditions: $\mu = 0.1 \text{ M}$ (NaClO_4), 25° , $C_{\text{Cu}} = 1.00 \times 10^{-6} \text{ M}$, $C_{\text{EGTA}} = 1.00 \times 10^{-4} \text{ M}$; (1) $C_{\text{Ba}} = 3.32 \times 10^{-4} \text{ M}$, pH 9.08; (2) $C_{\text{Ba}} = 8.93 \times 10^{-4} \text{ M}$, pH 9.06; (3) $C_{\text{Ba}} = 2.23 \times 10^{-3} \text{ M}$, pH 9.04; (4) $C_{\text{Ba}} = 8.93 \times 10^{-4} \text{ M}$, pH 9.54; (5) $C_{\text{Ba}} = 8.93 \times 10^{-4} \text{ M}$, pH 10.30.

of hydrogen ion. Then we have

$$k_{1(\text{Ba,H})} = k_1 \frac{[\text{Ba}^{2+}]}{[\text{H}^+]} \quad (11)$$

$$= k_1 [\text{OH}^-] [\text{Ba}^{2+}] \quad (12)$$

where $k_1 = k_1'/K_w$ (see Discussion). These facts are also confirmed from the other data.

In Figure 3, some values of $k_{2(\text{Ba,H})}$ determined at

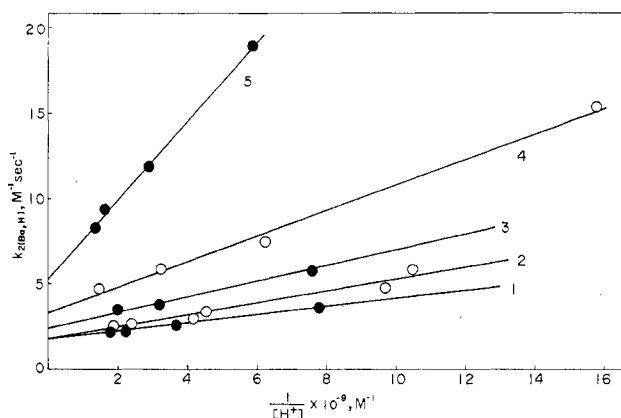


Figure 3.— $k_{2(\text{Ba,H})}$ as a function of $1/[\text{H}^+]$. Conditions: $\mu = 0.1 \text{ M}$ (NaClO_4), 25° , $C_{\text{Cu}} = 1.00 \times 10^{-6} \text{ M}$, $C_{\text{PAR}} = 2.00 \times 10^{-4} \text{ M}$, $C_{\text{EGTA}} = 1.00 \times 10^{-4} \text{ M}$ (1-4), $2.50 \times 10^{-4} \text{ M}$ (5), $C_{\text{Ba}} = 1.53 \times 10^{-4} \text{ M}$ (1), $2.55 \times 10^{-4} \text{ M}$ (2), $5.10 \times 10^{-4} \text{ M}$ (3), $1.02 \times 10^{-3} \text{ M}$ (4), $2.55 \times 10^{-3} \text{ M}$ (5).

various pH's are plotted against the reciprocal concentrations of hydrogen ion. It is evident from Figure 3 that $k_{2(\text{Ba,H})}$ is linearly related to the reciprocal concentration of hydrogen ion and that the rate increases with increasing barium ion concentration at constant concentration of EGTA (1-4 in Figure 3). The nonzero intercept suggests that the rate expression must include $1/[\text{H}^+]$ -independent terms.

The equilibrium $\text{Cu}(\text{egta})^{2-} \rightleftharpoons \text{Cu}^{2+} + \text{egta}^{4-}$ is more favored to the right with increasing concentration of barium ion. Therefore the higher rate in the presence of barium ions would possibly result from the enhanced dissociation of $\text{Cu}(\text{egta})^{2-}$ in the presence

of barium ions. If the reaction path through the dissociation of $\text{Cu}(\text{egta})^{2-}$ were appreciable, the conditional rate constants at the same value of C_M/C_{EGTA} (4 and 5 in Figure 3) should be identical (see eq 9). As apparent from Figure 3, this is not the case. In fact, the conditional rate constant $k_{2(\text{Ba},\text{H})}$ is proportional to the concentration of free barium ion ($[\text{Ba}^{2+}] = C_{\text{Ba}} - C_{\text{EGTA}}$) and independent of the concentration of egta^{4-} (Table IV). The dependence of $k_{2(\text{Ba},\text{H})}$ on the concentrations of hydrogen ion, PAR, and barium ion suggests the expression

$$k_{2(\text{Ba},\text{H})} = k_{2(\text{Ba})} + k_{3(\text{Ba})} \frac{1}{[\text{H}^+]} \quad (13)$$

The intercepts in Figure 3 correspond to $k_{2(\text{Ba})}$ and the slopes to $k_{3(\text{Ba})}$. The resultant values are plotted against the concentration of free barium ion in Figures 4 and 5, respectively. From these plots, relationships

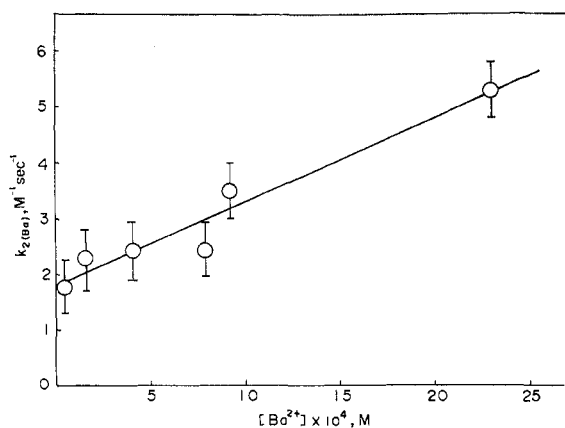


Figure 4.— $k_{2(\text{Ba},\text{H})}$ as a function of the concentration of free barium ion. The intercept and slope give k_2 and k_4 , respectively.

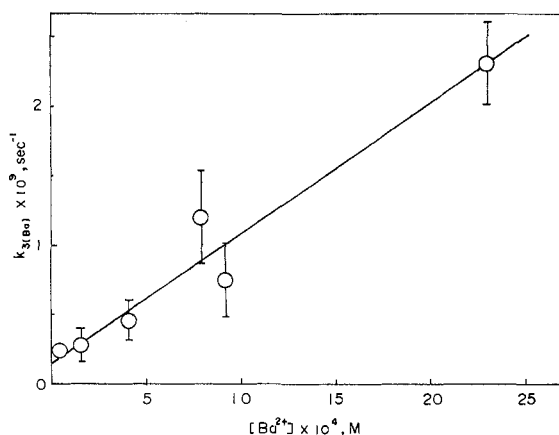


Figure 5.— $k_{3(\text{Ba})}$ as a function of the concentration of free barium ion. The intercept and slope give k_3' and k_5' , respectively.

14 and 15 are evident, and the values of k_2 , k_4 , k_3' , and k_5' were determined. The intercepts and the slopes

$$k_{2(\text{Ba})} = k_2 + k_4[\text{Ba}^{2+}] \quad (14)$$

$$k_{3(\text{Ba})} = k_3' + k_5'[\text{Ba}^{2+}] \quad (15)$$

of all plots were determined by the method of least squares. The proton dependence on the rate is attributable to the dissociation equilibrium of Hpar^- .

TABLE V

CONDITIONAL RATE CONSTANTS $k_{0(\text{Sr},\text{H},\text{par})}$ AND $k_{0(\text{Ca},\text{H},\text{par})}$ OF THE LIGAND-SUBSTITUTION REACTION OF THE Cu(II)-EGTA COMPLEX WITH PAR IN THE LIGAND BUFFERS OF egta^{4-} WITH STRONTIUM AND CALCIUM IONS AT 25° AND $\mu = 0.1$ (NaClO_4)

I. Strontium ^a				
Run no.	$10^4 C_{\text{PAR}}$, M	$10^4 C_{\text{Sr}}$, M	pH	$10^3 k_{0(\text{Sr},\text{H},\text{par})}$, sec ⁻¹
1	0.500	1.05	9.26	0.440
2	1.00		9.26	0.740
3	1.50		9.26	1.05
4	2.50		9.26	1.60
5	3.00		9.27	1.80
6	1.00	0.525	9.93	1.07
7			9.70	0.767
8			9.26	0.533
9		1.05	9.93	1.83
10			9.71	1.33
11			9.36	0.733
12			8.96	0.633
13		3.15	9.70	4.20
14			9.62	3.05
15			9.26	1.76
16			8.96	1.27
17		5.25	9.79	7.44
18			9.14	2.33
19			8.94	1.87

II. Calcium ^b				
Run no.	$10^4 C_{\text{PAR}}$, M	$10^4 C_{\text{Ca}}$, M	pH	$10^3 k_{0(\text{Ca},\text{H},\text{par})}$, sec ⁻¹
1	0.500	4.27	9.24	0.197
2	1.00		9.24	0.320
3	1.50		9.24	0.467
4	2.50		9.24	0.708
5	3.00		9.24	0.833
6	1.00	0.973	9.92	1.07
7			9.50	0.969
8			9.07	0.467
9		1.95	10.25	2.00
10			9.96	1.28
11			9.34	0.867
12		2.92	9.94	2.22
13			9.50	1.80
14			9.38	1.27
15			9.32	0.867
16		3.89	10.22	5.12
17			9.74	2.60
18			9.34	2.08

^a $C_{\text{Cu}} = 1.00 \times 10^{-6}$ M and $C_{\text{EGTA}} = 1.00 \times 10^{-4}$ M. ^b For runs 1-5 $C_{\text{Cu}} = 1.00 \times 10^{-6}$ M and $C_{\text{EGTA}} = 2.00 \times 10^{-5}$ M; for all other runs $C_{\text{Cu}} = 1.00 \times 10^{-6}$ M and $C_{\text{EGTA}} = 2.00 \times 10^{-6}$ M.

This proton transfer is very rapid compared to the other reaction step. Therefore, the conditional rate constant $k_{2(\text{Ba},\text{H})}$ is expressed as

$$k_{2(\text{Ba},\text{H})}[\text{Hpar}^-] = k_2[\text{Hpar}^-] + k_3[\text{par}^{2-}] + k_4^{\text{Ba}}[\text{Ba}^{2+}][\text{Hpar}^-] + k_5^{\text{Ba}}[\text{Ba}^{2+}][\text{par}^{2-}] \quad (16)$$

where $k_3 = k_3'K_{\text{Hpar}^{\text{H}}}$, $k_5^{\text{Ba}} = k_5'K_{\text{Hpar}^{\text{H}}}$, and $K_{\text{Hpar}^{\text{H}}} = [\text{Hpar}^-]/[\text{par}^{2-}][\text{H}^+]$.

Some data for the substitution reaction in the ligand buffers of egta^{4-} with strontium and calcium ions are tabulated in Table V. The rate equation for strontium and calcium is analogous to that for barium. Thus the rate law of the ligand-substitution reaction of the Cu(II)-EGTA complex with PAR in the ligand buffers of egta^{4-} with excesses of alkaline earth metal

ions Ba²⁺, Sr²⁺, and Ca²⁺ is written

$$\frac{d[\text{Cu}(\text{par})_2^{2-}]}{dt} = k_1^M[\text{Cu}(\text{egta})^{2-}][\text{OH}^-][\text{M}^{2+}] + k_2[\text{Cu}(\text{egta})^{2-}][\text{Hpar}^-] + k_3[\text{Cu}(\text{egta})^{2-}][\text{par}^{2-}] + k_4^M[\text{Cu}(\text{egta})^{2-}][\text{M}^{2+}][\text{Hpar}^-] + k_5^M[\text{Cu}(\text{egta})^{2-}][\text{M}^{2+}][\text{par}^{2-}] \quad (17)$$

where M²⁺ refers to barium, strontium, or calcium ions. The rate constants involved in eq 17 are tabulated in Table VI.

TABLE VI

RATE CONSTANTS OF THE LIGAND-SUBSTITUTION REACTION OF THE Cu(II)-EGTA COMPLEX WITH PAR IN THE LIGAND BUFFERS OF egta⁴⁻ WITH BARIUM, STRONTIUM, AND CALCIUM IONS AT 25° AND μ = 0.1 (NaClO₄)^a

	Ba	Sr	Ca
k ₁ , M ⁻² sec ⁻¹	(1.2 ± 0.3) × 10 ⁴	(1.1 ± 0.3) × 10 ⁴	(1.8 ± 0.3) × 10 ⁵
k ₂ , M ⁻¹ sec ⁻¹		1.8 ± 0.5	
k ₃ , M ⁻¹ sec ⁻¹		(3 ± 2) × 10 ²	
k ₄ , M ⁻² sec ⁻¹	(1.5 ± 0.5) × 10 ²	(1.2 ± 0.5) × 10 ²	(3 ± 1) × 10 ⁵
k ₅ , M ⁻² sec ⁻¹	(1.9 ± 0.5) × 10 ⁵	(2.0 ± 0.3) × 10 ⁶	(7 ± 3) × 10 ⁷
K _{ML} ^b	10 ^{2.66}	10 ^{2.84}	10 ^{4.58}

^a Uncertainty is the range. ^b L²⁻ is *N*-(2-methoxyethyl)iminodiacetate; K_{ML} = [ML]/[M²⁺][L²⁻]; G. Schwarzenbach, G. Anderegg, W. Schneider, and H. Senn, *Helv. Chim. Acta*, **38**, 1147 (1955).

Discussion

In previous papers⁷⁻⁹ we have reported that in the ligand-substitution reactions of metal complexes with multidentate ligands the rate-determining step is the loss of a leaving group from an intermediate involving leaving and entering ligands. Especially the ligand-substitution reaction⁹ of the Cu(II)-PAR complex with EGTA, the reverse reaction of the present substitution reaction, has reasonably been interpreted in terms of a mechanism involving a mixed-ligand intermediate.

In Table VI the rate constants involved in eq 17 are summarized together with the stability constant K_{ML} of alkaline earth metal ions with *N*-(2-methoxyethyl)iminodiacetate ion, L²⁻. *N*-(2-Methoxyethyl)iminodiacetate exactly corresponds to the segment of EGTA. The rate constants increase with increasing stability constants K_{ML}. Relations between rate constants and stability constants K_{ML} are shown in Figure 6. The plots lie close to a straight line with a unit slope. This fact suggests that the difference in rates for various alkaline earth metal ions should be attributed to the difference in the equilibrium constants K_{ML}. The effect of magnesium ion on the substitution reaction rate was not appreciable (C_{Mg} = 10⁻⁵ M). This is as expected from the low stability of the magnesium-*N*-(2-methoxyethyl)iminodiacetate complex (log K_{MgL} = 3.31¹⁹). Experiments with higher concentrations of magnesium were not possible because of the reaction of PAR with magnesium resulting in a coloration similar to Cu-PAR.

In Figure 7, a proposed mechanism is shown for the k₅^M path of the ligand-substitution reaction. Step I-II corresponds to the partial dissociation of EGTA from its metal complex before reacting with alkaline

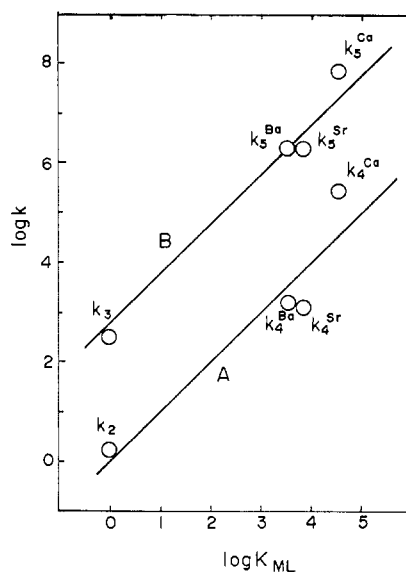


Figure 6.—Relations between rate constants and stability constant K_{ML} of alkaline earth metal ions with *N*-(2-methoxyethyl)iminodiacetate ion. A straight line A for the rate constants concerning Hpar⁻ species and a straight line B for the rate constants concerning par²⁻ species are shown.

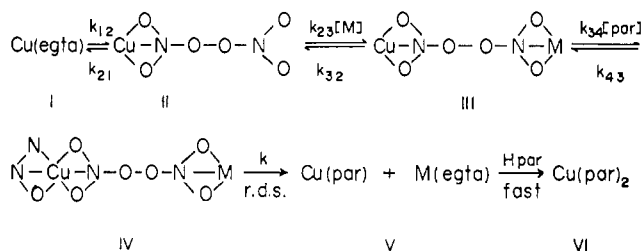


Figure 7.—Proposed stepwise reaction mechanism for the ligand-substitution reaction of the Cu(II)-EGTA complex with PAR in the presence of alkaline earth metal ions. EGTA and PAR are symbolized as $\text{O} \begin{array}{c} \diagup \\ \text{N} \\ \diagdown \end{array} \text{O}-\text{O}-\text{N} \begin{array}{c} \diagdown \\ \text{O} \\ \diagup \end{array}$ and $\text{N}-\text{N}-\text{O}$, respectively. Charges are omitted for simplicity.

earth metal ion. The role of alkaline earth metal ions is to trap the segment of EGTA in the partially unwrapped chelate (step II-III). A similar fact has been observed by Margerum, *et al.*,^{20,21} in the reaction of the Ni(II)-EDTA complex with copper(II) ion. The rate-determining step in this reaction path is perhaps the dissociation of the copper-nitrogen bond in proceeding from the intermediate complex IV involving two metal ions (Cu²⁺, M²⁺) and two ligands (EGTA, PAR) to stage V. The coordination of the second PAR (step V-VI) is fast.^{8,22} The overall rate would then depend on the stability of a dinuclear intermediate IV containing two different ligands. Therefore, the rate constant can be written as the product of the equilibrium constants of reaction intermediates and the rate constant *k* for the loss of EGTA from an intermediate IV

$$k_5^M = \frac{k_{12} k_{23} k_{34} k}{k_{21} k_{32} k_{43}}$$

(20) D. W. Margerum, D. L. Janes, and H. M. Rosen, *J. Amer. Chem. Soc.*, **87**, 4463 (1965).

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It appears reasonable to assume that the equilibrium constants k_{12}/k_{21} and k_{34}/k_{43} and the rate constant k are the same for various alkaline earth metal ions because the mutual effect of metals along the long bond sequence Cu-N-O-O-N-M seems to be unimportant.

The rate of the reaction path corresponding to k_1 is independent of the concentration of PAR. This fact suggests that hydroxyl ion in the OH-Cu(II)-EGTA-M complex prevents the coordination of PAR to copper in this complex. The rate constant for k_1^{Ca} is about one order of magnitude greater than k_1^{Ba} and k_1^{Sr} . The difference in rates for k_1 for alkaline earth metal ions corresponds to the difference in stability constants of complexes of alkaline earth metal ions with the segment of EGTA, *i.e.*, K_{ML} in Table VI. Thus the cleavage of the copper-nitrogen bond in (OH)Cu(egta)M is the rate-determining step in

this reaction path. The resulting Cu(OH)⁺ reacts rapidly with PAR under the present experimental conditions.

The reactivity of par²⁻ is about three orders of magnitude higher than that of Hpar⁻. A similar result has been described by Kodama, *et al.*,²³ in the ligand-substitution reactions of Eriochrome Black T with cobalt(II) and nickel(II) complexes of 1,2-diaminocyclohexanetetraacetic acid and diethylenetriaminepentaacetic acid. This is understandable qualitatively in terms of the difference in constants for the relevant equilibria preceding the rate-determining step. More extensive electron donation of par²⁻ in (par)Cu(egta) than of Hpar⁻ in (Hpar)Cu(egta) would make easier the cleavage of egta⁴⁻ from the intermediate (par)Cu(egta).

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Electron Spin Resonance Study of the Kinetics and Equilibrium of Adduct Formation by Copper(II) Dibutyldithiocarbamate with Nitrogen Bases^{1a}

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The esr spectrum of copper (II) bis(di-*n*-butyldithiocarbamate) [Cu(DnBDC)₂] was measured as a function of temperature and solvent composition in mixtures of methylcyclohexane with piperidine, *n*-hexylamine, and pyridine. Evidence for the formation of a short-lived 1:1 adduct is presented. Equilibrium constants for the adduct formation reaction and adduct lifetimes were obtained from analysis of the line positions and line widths. The fast-exchange-limit solution of the modified Bloch equations was reexamined, and correction terms were derived permitting the application of the fast exchange limit to somewhat slower reactions than usual. Arrhenius plots of the equilibrium constants and the adduct lifetimes gave the thermodynamic parameters for the adduct formation equilibrium and kinetic parameters for the adduct dissociation reaction. In the case of the piperidine adduct at 25°, the equilibrium constant is $K = 3.9 \pm 0.1$ l./mol, $\Delta S^\circ = -22 \pm 1$ eu; the rate of adduct dissociation is $k_r = (3.7 \pm 0.4) \times 10^8$ sec⁻¹, $\Delta H^\ddagger = 7.4 \pm 1.7$ kcal/mol, and $\Delta S^\ddagger = 5 \pm 3$ eu. In general, the rate of the adduct formation reaction seems to be almost entirely limited by entropy of activation, while the dissociation reaction is primarily limited in rate by enthalpy of activation.

Introduction

The past 15 years has seen a considerable amount of interest in the reaction of square-planar copper(II) complexes with nitrogen bases to form five-coordinate adducts. The principal effort has been on the characterization²⁻⁵ and structure^{6,7} of the adducts, on the interpretation of the electronic,^{2,3,8-13} vibrational,¹³

esr,¹³⁻²¹ and nmr²¹⁻²³ spectra of the adducts, and on the

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(1) (a) Taken in part from the Ph.D. thesis of B. J. Corden, Brown University, Providence, R. I., 1970. (b) National Science Foundation Trainee, 1966-1969.

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