

tainable because of instability of the species in the atmosphere or the limited range of the instrument, crude qualitative spectra were obtained on Nujol mull smears on filter paper using a Beckman Model DK2A ratio-recording spectrophotometer. Visible and near-infrared solution spectra were obtained on the Beckman DK2A. There being no apparent sensitivity of the spectra to temperature, no attempt was made to control it.

Solvents.—Except where noted, solvents were from freshly opened bottles of the reagent grade chemical. Dry CCl_4 was obtained by shaking the reagent grade solvent with P_2O_5 and distilling from fresh P_2O_5 , discarding the first and last portions. Wet CCl_4 was prepared by prolonged shaking with water in a separatory funnel with warming and then allowing the two phases to separate.

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Kinetics of the Ligand Substitution Reaction of the Zinc(II)-4-(2-Pyridylazo)resorcinol Complex with (Ethylene glycol)bis(2-aminoethyl ether)-N,N,N',N'-tetraacetic Acid

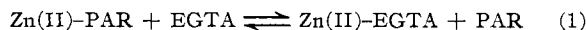
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The kinetics of the ligand substitution reaction of the zinc(II)-4-(2-pyridylazo)resorcinol complex (Zn(II)-PAR) with (ethylene glycol)bis(2-aminoethyl ether)-N,N,N',N'-tetraacetic acid (EGTA) has been studied spectrophotometrically in the pH range 8.7–10 at $\mu = 0.1$ and at 25°. The reaction involves a dissociation equilibrium of the Zn(II)-PAR complex: $-d[\text{ZnR}_2^{2-}]/dt = 10^{6.4}[\text{ZnR}_2^{2-}][\text{H}^+][\text{Y}']/[\text{HR}^-] = 10^{4.4}[\text{ZnR}][\text{Y}']$, where R^{2-} is the divalent anion of PAR (H_2R) and Y' is the free EGTA not combined with any metal. The release of PAR from the reaction intermediate PAR-Zn(II)-EGTA is the probable rate-determining step. The stability constants of sodium- and lithium-EGTA complexes at $\mu = 1.5$ and at 25° are kinetically determined as 24 ± 4 and 15 ± 2 , respectively. The rate of the substitution of Zn(II)-PAR decreases in the order: free EGTA > sodium-EGTA complex > lithium-EGTA complex. The different reactivity of these species is discussed. In connection with the kinetic study the stability constants of the Zn(II)-PAR complexes have been determined spectrophotometrically at $\mu = 0.1$ and at 25°: $[\text{ZnR}]/[\text{Zn}^{2+}][\text{R}^{2-}] = 10^{11.9 \pm 0.1}$, $[\text{ZnR}_2^{2-}]/[\text{ZnR}][\text{R}^{2-}] = 10^{10.3 \pm 0.2}$, $[\text{ZnHR}^+]/[\text{ZnR}][\text{H}^+] = 10^{5.90 \pm 0.05}$, $[\text{ZnHR}_2^-]/[\text{ZnR}_2^{2-}][\text{H}^+] = 10^{7.55 \pm 0.05}$, $[\text{ZnH}_2\text{R}_2]/[\text{ZnHR}_2^-][\text{H}^+] = 10^{6.45 \pm 0.05}$.

Introduction

Though a great number of works have been devoted to the kinetics of the complex formation and the substitution of metal chelates with metal ions, little attention has, as yet, been given to the substitution of metal chelates with multidentate ligands. There are only a few examples such as the works of Bosnich, Dwyer, and Sargeson,¹ of Rogers, Aikens, and Reilley,² and of Margerum, *et al.*^{3–5} Recently Yatsimirskii, *et al.*, have made an account of the kinetics of the reaction of rare earth complexes of xylenol orange with EDTA.⁶ We are interested in the substitution of multidentate ligands, which is often involved in the complexometric titration and the solvent extraction of metal chelates. It seems important to study kinetic phenomena arising from the presence of some different bulky ligands competing for coordination sites on the same metal ion. The system



was chosen for the present study, where PAR and EGTA represent 4-(2-pyridylazo)resorcinol and (ethyl-

ene glycol)bis(2-aminoethyl ether)-N,N,N',N'-tetraacetic acid, respectively, and are abbreviated as H_2R (tridentate) and H_4Y (hexadentate), respectively.

Experimental Section

Reagents. Zinc(II) Perchlorate.—Zinc metal (99.999%) was dissolved in perchloric acid to prepare zinc perchlorate solution.

PAR.—The acid form of PAR was obtained from Dojin-do Chemical Co., Kumamoto, Japan, and purified by recrystallization from aqueous methanol. PAR dried in an air bath at 80° was dissolved in 2 equiv of borax.

EGTA.—Reagent grade EGTA, obtained also from Dojin-do Chemical Co., was purified by recrystallization from distilled water, dried in an air bath at 80°, and dissolved in 2 equiv of borax. The solution was standardized complexometrically against a standard cadmium solution. The values agreed with the theoretical values within 0.3%, and thus the purified EGTA could be used as a primary standard.

Boric Acid and Borax.—Boric acid and borax were recrystallized twice from distilled water.

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 8.5 and extracted as oxinates with chloroform four times at pH 8.5. Sodium perchlorate was then recrystallized twice from distilled water.

Sodium Hydroxide.—Sodium hydroxide solution was prepared by electrolysis of the solution of sodium perchlorate obtained as described above. About 2 M aqueous sodium perchlorate solution with a slight excess of perchloric acid was taken in a polyethylene bottle and electrolyzed at about 30 mA with platinum foil electrodes. The polyethylene bottle was connected with an anode chamber by a bridge containing sodium perchlorate.

- (1) B. Bosnich, F. P. Dwyer, and A. M. Sargeson, *Nature*, **186**, 966 (1962).
- (2) D. W. Rogers, D. A. Aikens, and C. N. Reilley, *J. Phys. Chem.*, **66**, 1582 (1962).
- (3) D. B. Rorabacher and D. W. Margerum, *Inorg. Chem.*, **3**, 382 (1964).
- (4) R. A. Libby and D. W. Margerum, *Biochemistry*, **4**, 619 (1965).
- (5) J. D. Carr, R. A. Libby, and D. W. Margerum, *Inorg. Chem.*, **6**, 1083 (1967).
- (6) K. B. Yatsimirskii, T. V. Mal'kova, and L. I. Budarin, "Proceedings of the Xth International Conference on Coordination Chemistry," Tokyo and Nikko, Japan, Sept 1967, p 290.

Nitrogen gas bubbled continuously through the solution during the electrolysis. About 0.2 M sodium hydroxide solution was obtained.

Potassium Chloride.—Heavy metal impurities in potassium chloride were removed as hydroxides at pH 9 and extracted as PAN complexes (PAN: 1-(2-pyridylazo)-2-naphthol) at pH 5 and as oxinates at pH 8.5 with chloroform. The solution of potassium chloride was then concentrated and potassium chloride was recrystallized from distilled water.

Sodium Chloride.—Pure sodium chloride was precipitated by dissolving dry hydrochloric acid in a saturated solution of sodium chloride. The sodium chloride was then heated at 150° to expel hydrochloric acid.

Lithium Chloride.—Heavy metal ions in lithium chloride were removed as PAN complexes with chloroform at pH 5. Lithium chloride was then recrystallized twice from distilled water.

Apparatus.—The following instruments were used: a Horiba Model P pH Meter; a pK Meter from Hitachi Ltd. which comprised an apparatus for the automatic recording of absorbance against pH; a Sharp Model TEB-10 thermoelectric circulating bath; 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 Perkin-Elmer 139UV-VIS spectrophotometer with a 5.3-cm cell thermostated at $25 \pm 0.2^\circ$; and a Hitachi Model QPD-53 recorder.

Determination of the Stability Constants of Zinc(II)-PAR Complexes.—It is necessary to determine the stability constants of zinc(II)-PAR complexes in connection with the equilibria involved in the substitution reaction. These stability constants were determined at ionic strength $\mu = 0.1$ (sodium perchlorate) and at 25°.

PAR forms a 1:1 complex with the zinc ion under conditions where the concentration of zinc is in sufficient excess compared with that of PAR. Curves 1-5 in Figure 1 show the change of

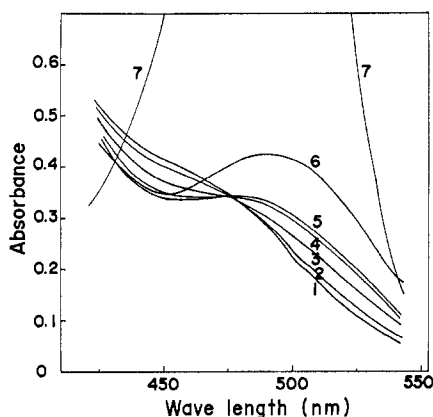


Figure 1.—Spectral change in the course of the formation of the protonated 1:1 zinc(II)-PAR complex. $C_{Zn} = 1.00 \times 10^{-3} M$; $C_R = 3.00 \times 10^{-5} M$; $\mu = 0.1$ (NaClO₄); temperature, 25°; cell length, 1 cm: 1, pH 2.91; 2, pH 3.09; 3, pH 3.18; 4, pH 3.33; 5, pH 3.40; 6, pH 3.91; 7, pH 7.03.

absorption spectra during the formation of the protonated 1:1 zinc(II)-PAR complex. The isosbestic point at 476 nm indicates the equilibrium $Zn^{2+} + H_2R \rightleftharpoons ZnHR^+ + H^+$ ($\epsilon_{H_2R} 5.3 \times 10^3$ and $\epsilon_{ZnHR} 1.1 \times 10^4$ at 500 nm). The change from curve 6 to curve 7 in Figure 1 is attributable to proton release of the protonated 1:1 zinc(II)-PAR complex. The spectra have distinct isosbestic points at 328, 430, and 538 nm and indicate a simple acid-base equilibrium: $ZnR + H^+ \rightleftharpoons ZnHR^+$ ($\epsilon_{ZnR} 3.18 \times 10^4$ and $\epsilon_{ZnHR} 1.07 \times 10^4$ at 490 nm). Typical data of absorbance of the 1:1 zinc-PAR complex in solutions of various pH's are given in Table I.

The stability constants obtained by a conventional plot were refined by the HITAC 5020 computer by means of the least-squares method. The following values were obtained

$$K_{ZnHR^+H_2R} = \frac{[ZnHR^+][H^+]}{[Zn^{2+}][H_2R]} = 1.0 \pm 0.1$$

$$K_{ZnHR^+H} = \frac{[ZnHR^+]}{[ZnR][H^+]} = 10^{5.90 \pm 0.05}$$

$$K_{ZnR^2-} = \frac{K_{ZnHR^+H_2R} K_{H_2R} K_{HR^+H}}{K_{ZnHR^+H}} = \frac{[ZnR]}{[Zn^{2+}][R^{2-}]} = 10^{11.9 \pm 0.1}$$

where $K_{H_2R^+H} = [H_2R]/[HR^-][H^+] = 10^{5.30}$ and $K_{HR^+H} = [HR^-]/[R^{2-}][H^+] = 10^{12.30,7}$

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

pH	Absorbance at 490 nm	pH	Absorbance at 490 nm
4.18	0.240	5.69	0.380
4.61	0.260	5.91	0.428
4.99	0.282	6.09	0.485
5.32	0.313	6.55	0.615
5.53	0.347		

^a $C_{Zn} = 1.00 \times 10^{-3} M$; $C_R = 2.10 \times 10^{-5} M$; acetate buffer; $\mu = 0.1$ (NaClO₄); 25°; cell length, 1 cm.

PAR forms a 1:2 complex with zinc under conditions where PAR is in large excess compared to zinc. Beer's law is obeyed for the zinc-PAR complex at constant pH. Under the conditions $C_{Zn} = 1.00 \times 10^{-5} M$, $C_R = 5.00 \times 10^{-5} M$, $C_Y = 1.11 \times 10^{-4} M$, $C_{Mg} = 1.4 \times 10^{-3}$ to $7 \times 10^{-4} M$ at pH 9 (borate buffer), $\mu = 0.1$ (sodium perchlorate), and 25°, the equilibrium constant of the following equilibrium was measured by the spectrophotometry of the ZnR_2^{2-} complex: $ZnR_2^{2-} + MgY^{2-} \rightleftharpoons ZnY^{2-} + 2R' + Mg^{2+}$, where R' is free PAR not combined with any metal. With knowledge of the stability constants of zinc(II)-EGTA and magnesium(II)-EGTA complexes,⁸ the over-all stability constant was determined

$$\beta_{ZnR_2} = \frac{[ZnR_2^{2-}]}{[Zn^{2+}][R^{2-}]^2} = 10^{22.2 \pm 0.2}$$

Thus we have

$$K_{ZnR_2R} = \frac{[ZnR_2^{2-}]}{[ZnR][R^{2-}]} = \frac{\beta_{ZnR_2}}{K_{ZnR^+R}} = 10^{10.3 \pm 0.2}$$

Figure 2 shows the absorbance of a 1:2 zinc(II)-PAR complex as a function of pH. Protonation of the zinc-PAR complex results in the decrease of absorbance at 495 nm. The stability constants of protonated 1:2 zinc-PAR complexes and molar absorptivities at $\mu = 0.1$ (sodium perchlorate) and at 25° were evaluated by means of a curve fitting. The values were refined by the HITAC 5020 computer by means of the least-squares method. The following values were obtained

$$K_{ZnHR_2^+} = \frac{[ZnHR_2^+]}{[ZnR_2^{2-}][H^+]} = 10^{7.55 \pm 0.05}$$

$$K_{ZnH_2R_2} = \frac{[ZnH_2R_2]}{[ZnHR_2^+][H^+]} = 10^{6.46 \pm 0.05}$$

$\epsilon_{ZnR_2} = 9.58 \times 10^4$, $\epsilon_{ZnHR_2} = 6.74 \times 10^4$, and $\epsilon_{ZnH_2R_2} = 1.75 \times 10^4$ at 495 nm.

Stability constants obtained in 50 vol % dioxane-water at $\mu = 0.1$ and at 25° by the present method agree with the previous ones determined potentiometrically under the same conditions by Corsini, Fernando, and Freiser.⁹ They showed the existence of two species of protonated 1:2 zinc-PAR complex in 50% dioxane. In the present case, although the pH-absorbance curve has apparently only one inflection point, the existence of mono- and diprotonated 1:2 zinc-PAR complexes in the aqueous solution was confirmed by curve fitting.

Procedure of Measurement of the Substitution Reaction Rate.

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

(8) R. W. Schmid and C. N. Reilly, *Anal. Chem.*, **29**, 264 (1957).

(9) A. Corsini, Q. Fernando, and H. Freiser, *Inorg. Chem.*, **2**, 224 (1963).

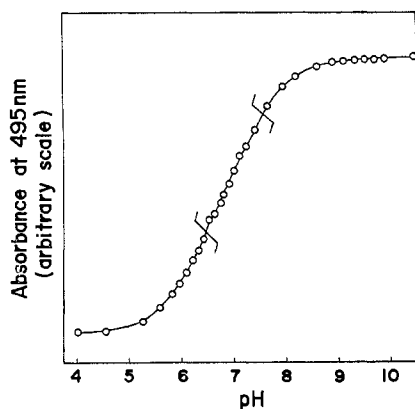


Figure 2.—Determination of stability constants of the protonated 1:2 zinc(II)-PAR complexes. $C_{Zn} = 2.50 \times 10^{-6} M$; $C_R = 7.50 \times 10^{-6} M$; $\mu = 0.1$ (NaClO₄); temperature, 25°. Solid line is the theoretical curve.

—The zinc(II)-PAR solution containing PAR in excess was buffered with borax and sodium hydroxide or boric acid. The ionic strength was maintained constant at 0.1 or 1.5 *M*. A silica beaker (light path, 5.3 cm) containing the zinc(II)-PAR solution was placed in a thermostated compartment of a spectrophotometer capable of temperature control at $25 \pm 0.2^\circ$. The EGTA 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 absorbance at 495 nm of the reaction system was recorded automatically as a function of the reaction time. All experiments were carried out in a room thermostated at $25 \pm 1^\circ$.

Under conditions where the ligands involved were in large excess compared to zinc, the rate plots were linear for over 80% of reaction. As the reaction proceeds, the plots tend to deviate from the linearity in the experiments with insufficient excess of ligands. To avoid any error due to this deviation, the plots for the first half of the reaction were used to determine the rate constants. Alternatively, corrections were made, if necessary, for the variation of concentrations of the ligands in determining the rate constants. Thus the error of the rate constants obtained is less than 10% or better.

Results

Under the present experimental conditions, equilibrium 1 is much favored to the right so that the substitution reaction of the zinc(II)-PAR complex with EGTA goes to completion and the reverse reaction can be neglected in the kinetic study. Beer's law is obeyed for the zinc(II)-PAR complex. Therefore, if the reaction with PAR and EGTA in large excesses is of the *p*th order with respect to zinc-PAR, the following rate equation holds

$$-\frac{d(E_t - E_\infty)}{dt} = \frac{E_0 - E_\infty}{C_{ZnR_2}} k_{0(R,Y,H)} \left(C_{ZnR_2} \frac{E_t - E_\infty}{E_0 - E_\infty} \right)^p \quad (2)$$

where $k_{0(R,Y,H)}$ is the conditional rate constant¹⁰ involving the concentrations of PAR, EGTA, and hydrogen ion; *t* is the time after the beginning of the reaction; E_0 , E_t , and E_∞ are the absorbances of the reaction system at $t = 0$, *t*, and ∞ , respectively; C_{ZnR_2} is the initial concentration of the zinc-PAR complex. The order of the reaction with respect to

(10) As the observed reaction rate depends upon the experimental conditions and the rate constant involves various concentration terms, it seems appropriate to use the term "conditional rate constant" (cf. M. Tanaka, S. Funahashi, and K. Shirai, *Anal. Chim. Acta*, **39**, 437 (1967)) and to indicate clearly the concentration terms involved.

zinc-PAR is given by the slope *p* of the straight line obtained in a plot of

$$\log \left\{ -\frac{d(E_t - E_\infty)}{dt} \right\} \text{ vs. } \log (E_t - E_\infty)$$

Values of $-d(E_t - E_\infty)/dt$ were calculated by Newton's interpolation formula. The plot gave a straight line of slope 1. Therefore the reaction is of the first order in zinc(II)-PAR. Under the present experimental conditions, the zinc(II)-PAR complex exists stoichiometrically as ZnR_2^{2-} . Thus for the reaction with large excesses of PAR and EGTA the rate law is expressed as

$$-\frac{d[ZnR_2^{2-}]}{dt} = k_{0(R,Y,H)} [ZnR_2^{2-}] \quad (3)$$

Then the conditional rate constant $k_{0(R,Y,H)}$ was determined at various concentrations of PAR, at a constant concentration of EGTA, and at constant pH. In Table II the values of conditional rate constants $k_{0(R,Y,H)}$ are given. These data indicate clearly a linear relationship between $k_{0(R,Y,H)}$ and the reciprocal of the concentration of PAR with the zero intercept. Therefore, the rate law is expressed as

$$-\frac{d[ZnR_2^{2-}]}{dt} = k_{0(Y,H)} \frac{[ZnR_2^{2-}]}{[HR^-]} \quad (4)$$

where HR^- is the singly charged species of PAR. In the pH range 8.7–10, the predominant species of PAR is HR^- as evident from the stability constants of PAR ($\log K_{HR^H} = 2.69$, $\log K_{H_2R^H} = 5.50$, $\log K_{HR^H} = 12.30$).

Integration of eq 4 yields

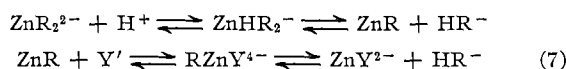
$$C_R \ln \frac{E_0 - E_\infty}{E_t - E_\infty} - 2C_{ZnR_2} \frac{E_0 - E_t}{E_0 - E_\infty} = k_{0(Y,H)} t \quad (5)$$

where C_R refers to the total concentration of PAR: $C_R = 2[ZnR_2^{2-}] + [HR^-]$. The conditional rate constants $k_{0(Y,H)}$ were obtained by the plot according to eq 5. In Figure 3, the values of $k_{0(Y,H)}$ determined at various pH's and concentrations of EGTA are plotted against the hydrogen ion concentration and some data of $k_{0(Y,H)}$ are tabulated in Table II.

It is evident from Figure 3 that $k_{0(Y,H)}$ is linearly related to hydrogen ion concentration. The rate increases with increasing EGTA concentration, and the plots give the zero intercept. Figure 4 represents a plot of $k_{0(Y,H)}$ obtained at pH 9.00 (dashed line in Figure 3) vs. $[Y']$, the total concentration of EGTA not combined with any metal. According to Figures 3 and 4 the substitution reaction is of first order with respect to EGTA and hydrogen ion. Thus the rate law is expressed as

$$-\frac{d[ZnR_2^{2-}]}{dt} = k_0 \frac{[ZnR_2^{2-}][H^+][Y']}{[HR^-]} \quad (6)$$

This rate law is consistent with the reaction mechanism



EGTA reacts with ZnR rapidly formed from ZnR_2^{2-} through the equilibrium process. Substituting the

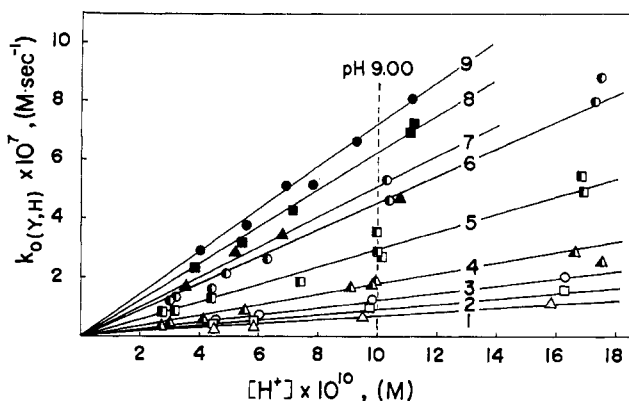


Figure 3.— $k_0(Y,H)$ as a function of hydrogen ion concentration. $C_{Zn} = 3.00 \times 10^{-6} M$; $C_R = 1.02 \times 10^{-5} M$; C_Y : 1, $2.18 \times 10^{-5} M$; 2, $3.23 \times 10^{-5} M$; 3, $4.27 \times 10^{-5} M$; 4, $5.50 \times 10^{-5} M$; 5, $1.09 \times 10^{-4} M$; 6, $1.62 \times 10^{-4} M$; 7, $2.13 \times 10^{-4} M$; 8, $2.54 \times 10^{-4} M$; 9, $3.14 \times 10^{-4} M$; $\mu = 0.1$; temperature, 25° .

TABLE II

CONDITIONAL RATE CONSTANTS

$k_0(R,Y,H)$, AND $k_0(Y,H)$, AT 25° AND $\mu = 0.1$		
$C_{Zn} = 3.00 \times 10^{-6} M$, $C_Y = 1.09 \times 10^{-4} M$		
$10^3 C_R, M$	pH	$10^3 k_0(R,Y,H), \text{sec}^{-1}$
1.02	9.00	3.5
2.02	9.03	1.9
3.03	9.03	1.3
4.04	9.03	1.0
5.05	9.03	0.80
$C_{Zn} = 3.00 \times 10^{-6} M$, $C_R = 1.02 \times 10^{-5} M$		
$10^4 C_Y, M$	pH	$10^7 k_0(Y,H), M \text{sec}^{-1}$
3.14	8.95	8.0
	8.95	8.0
	9.11	5.1
	9.25	3.7
	9.40	2.8
2.54	8.95	7.2
	9.15	4.2
	9.27	3.1
	9.42	2.3
	9.57	0.77
1.09	8.78	5.4
	9.00	3.5
	9.00	2.8
	9.22	1.8
	9.36	1.3
0.427	9.51	0.93
	9.57	0.77
	8.79	2.0
	9.01	1.3
	9.22	0.61
9.34	0.50	

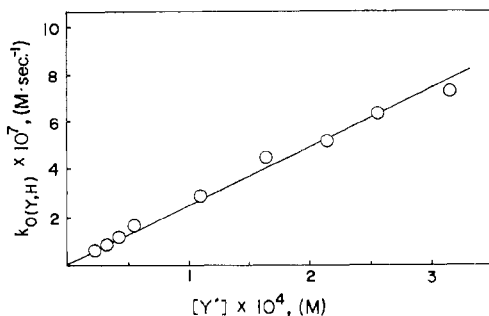


Figure 4.— $k_0(Y,H)$ as a function of uncomplexed EGTA concentration $[Y']$. $C_{Zn} = 3.00 \times 10^{-6} M$; $C_R = 1.02 \times 10^{-5} M$; pH 9.00; $\mu = 0.1$; temperature, 25° .

equilibrium constants into eq 6, the rate law can be expressed as

$$-\frac{d[ZnR_2^{2-}]}{dt} = k_0 \frac{K_{ZnR_2^R}}{K_{HR}^H} [ZnR] [Y'] = k [ZnR] [Y'] \quad (8)$$

As seen from the values of the stability constants of protonated EGTA ($\log K_{HY}^H = 9.43$, $\log K_{H_2Y}^H = 8.85$, $\log K_{H_3Y}^H = 2.68$, $\log K_{H_4Y}^H = 2.0^{(11)}$), Y^{4-} , HY^{3-} , and H_2Y^{2-} are present under the present experimental condition, *i.e.*, in the pH range 8.7–10. However no variation of the rate with varying proportion of these species of EGTA is observed. The rate constants k_0 and k determined in this investigation are 2.6×10^8 and $2.6 \times 10^4 M^{-1} \text{sec}^{-1}$, respectively.¹²

Reactivity and Stability Constants of Sodium- and Lithium-EGTA.—As anticipated the reaction rate varies with ionic strength of the medium because of the variation of activity coefficient. The effect of ionic strength on the rate constant is illustrated in Figure 5, in which potassium chloride, sodium perchlorate, and sodium chloride are used as medium salts. The rate decreases to a greater extent in the presence of sodium salt than in the presence of potassium salt.

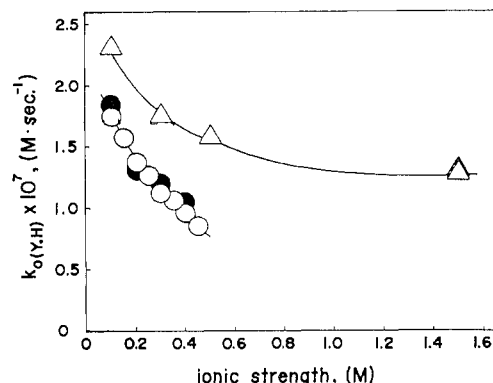


Figure 5.— $k_0(Y,H)$ as a function of ionic strength. $C_{Zn} = 3.00 \times 10^{-6} M$; $C_R = 1.01 \times 10^{-5} M$; $C_Y = 5.50 \times 10^{-5} M$; temperature, 25° ; pH 9.00; Δ , KCl; \circ , NaClO_4 ; \bullet , NaCl.

This fact cannot be interpreted quantitatively in terms of the decrease in $[Y']$ by the formation of the sodium-EGTA complex. It seems quite likely that the complex as well as uncomplexed EGTA participates in the substitution.

The concentration of sodium or lithium chloride is varied from 0 to 0.5 M , ionic strength being maintained constant (1.5 M) with potassium chloride and the relevant chloride. The kinetic effect of chloride is not appreciable (see Figure 5), so, in view of the solubility, potassium chloride was chosen as a medium salt. It may be reasonably assumed that under the present experimental condition the change of the activity coefficient is not appreciable and the potassium-EGTA complex does not exist. The conditional rate constants of the substitution reaction in the presence of sodium and lithium are tabulated in Table III. De-

(11) J. Bierrum, G. Schwarzenbach, and L. G. Sillén, Special Publication No. 6, The Chemical Society, London, 1957, Part I.

(12) Kinetically the concentration (0.06–0.003 M) of the borate buffer gives no effect.

TABLE III

CONDITIONAL RATE CONSTANTS OF THE SUBSTITUTION WITH VARIATION OF SODIUM OR LITHIUM CONCENTRATION^a

NaCl, M	$10^7 k_{0(Y,NaY,H)}$, M sec ⁻¹	LiCl, M	$10^7 k_{0(Y,LiY,H)}$, M sec ⁻¹
0.08	1.22	0.0	1.23
0.18	1.07	0.1	0.94
0.28	1.01	0.2	0.72
0.38	0.98	0.3	0.51
0.48	0.94	0.4	0.43
0.58	0.92	0.5	0.34

^a Each value of conditional rate constant is based on at least two measurements at pH around 9. Then a correction is made for pH to obtain the value at pH 9.00. $C_{Zn} = 3.00 \times 10^{-6}$ M; $C_R = 1.01 \times 10^{-5}$ M; $C_Y = 5.50 \times 10^{-5}$ M; pH 9.00; $\mu = 1.5$; 25°.

noting as $k_{0(H)}^Y$ and $k_{0(H)}^{MY}$ the conditional rate constants of the substitution reaction by uncomplexed EGTA and by a weak complex MY, respectively,¹³ we have

$$k_{0(Y,MY,H)} = k_{0(H)}^Y[Y'] + k_{0(H)}^{MY}[MY^{3-}] \quad (9)$$

Insofar as $[MY^{3-}] \ll C_M$, eq 9 can be rewritten as

$$k_{0(Y,MY,H)} = k_{0(H)}^Y[Y'] \left(1 + \frac{k_{0(H)}^{MY}}{k_{0(H)}^Y} K_{MY'} C_M \right) \quad (10)$$

where $K_{MY'} = [MY^{3-}]/[M^+][Y']$ is the conditional stability constant of the weak complex MY^{3-} such as sodium- or lithium-EGTA complex.

Since $C_{Zn} \ll C_Y$, it follows that

$$C_Y = [Y'] + [MY^{3-}] \quad (11)$$

In the absence of the weak complex MY^{3-} , eq 9 simplifies to

$$k_{0(Y,H)} = k_{0(H)}^Y C_Y \quad (12)$$

Combining and rearranging eq 10, 11, and 12, we obtain

$$\frac{k_{0(Y,H)}}{k_{0(Y,H)} - k_{0(Y,MY,H)}} = \left(1 - \frac{k_{0(H)}^{MY}}{k_{0(H)}^Y} \right)^{-1} \left(\frac{1}{K_{MY'} C_M} + 1 \right) \quad (13)$$

Thus a plot of $k_{0(Y,H)}/(k_{0(Y,H)} - k_{0(Y,MY,H)})$ vs. the reciprocal of the concentration of sodium or lithium ion ($1/C_M$) should yield a straight line (Figure 6). From the intercept and slope of the straight line $k_{0(H)}^{MY}/k_{0(H)}^Y$ and $K_{MY'}$ may be obtained. The results are tabulated in Table IV.

The stability constant of the sodium complex of an aminopolycarboxylic acid is in general smaller than that of the lithium complex. According to the present study this is not the case in the EGTA complexes. Although the value of the stability constant of the sodium-EGTA complex is larger than that of the lithium-EGTA complex, the kinetic reactivity of the sodium-EGTA complex is larger. The rate of the substitution reaction with the zinc(II)-PAR complex decreases in the order: free EGTA > sodium-EGTA complex > lithium-EGTA complex.

Discussion

Mechanism of the Substitution Reaction.—In the substitution of zinc-PAR with EGTA, ZnR in equi-

(13) Attacking group is specified, if necessary, by the superscript to k_0 .

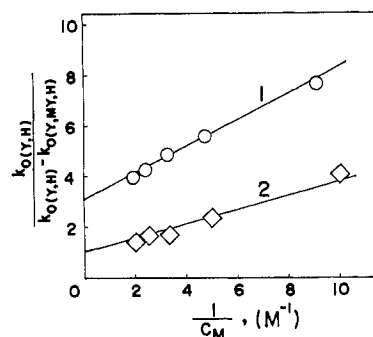


Figure 6.— $k_{0(Y,H)}/[k_{0(Y,H)} - k_{0(Y,MY,H)}]$ as a function of $1/C_M$ according to eq 13: 1, NaCl; 2, LiCl; $C_{Zn} = 3.00 \times 10^{-6}$ M; $C_R = 1.01 \times 10^{-5}$ M; $C_Y = 5.50 \times 10^{-5}$ M; pH 9.00; $\mu = 1.5$; temperature, 25°.

TABLE IV

THE RATIO OF THE RATE CONSTANTS AND THE STABILITY CONSTANTS OF SODIUM- AND LITHIUM-EGTA COMPLEXES AT 25° AND $\mu = 1.5$

	$\frac{k_{0(H)}^{MY}/k_{0(H)}^Y}{k_{MY}^{MY}/k_Y^Y} =$	$K_{MY'}$, at pH 9.00	K_{MY}^a
Na ⁺	0.67 ± 0.03	5.8 ± 0.8	24 ± 4
Li ⁺	<0.05	3.7 ± 0.5	15 ± 2

^a $K_{HYH} = 10^{9.28 \pm 0.05}$ and $K_{H_2YH} = 10^{8.78 \pm 0.05}$ are determined by the present authors at $\mu = 1.5$ (KCl) and 25°.

librium with ZnR_2^{2-} reacts with EGTA to form an intermediate $RZnY^{4-}$. The latter dissociates to yield ZnY^{2-} setting HR^- free. This process involves: (i) bond formation between zinc and donors in EGTA and (ii) breaking of the bonds between zinc and PAR.

First, the bond formation is considered. In general the rate of release of a water molecule from the aquo-metal ion is rate determining in the complex formation.^{14,16} Furthermore it is demonstrated in several instances^{16,17} that, in the stepwise formation of a complex, the rate of substitution of the second ligand is faster than that of the first.¹⁸ The rate of substitution of water molecules in ZnR with donor atoms of EGTA in the absence of any steric hindrance will be faster than the rate of substitution of the aquozinc ion. In fact structural models show that the substitution of these water molecules with EGTA is not sterically hindered. The probable rate constant of the substitution of the aquozinc ion¹⁵ ranges from 10^6 to 10^8 M⁻¹ sec⁻¹, which is too high a value to interpret the observed rate constant of $10^{4.4}$ M⁻¹ sec⁻¹ for reaction 1. Thus taking into consideration this fact together with equal reactivity of protonated EGTA species (see below), it is quite unlikely that the coordination of EGTA in this stage is the rate-determining step.

Protons in two species of EGTA, HY^{3-} and H_2Y^{2-} ,

(14) M. Eigen and K. Tamm, *Z. Elektrochem.*, **66**, 107 (1962).

(15) M. Eigen and R. W. Wilkins in "Mechanisms of Inorganic Reactions," *Advances in Chemistry Series*, No. 49, American Chemical Society, Washington, D. C., 1965, p 55.

(16) G. G. Hammes and J. I. Steinfeld, *J. Am. Chem. Soc.*, **84**, 4639 (1962); *J. Phys. Chem.*, **67**, 528 (1963).

(17) C. B. Honaker and H. Freiser, *ibid.*, **66**, 127 (1962).

(18) The water-exchange process is not always responsible for the enhanced rate of substitution of a second ligand: G. Gordon and D. Rablen, "Proceedings of the Xth International Conference on Coordination Chemistry," Tokyo and Nikko, Japan, Sept 1967, p 199.

being attached to the nitrogen in EGTA, the rate of coordination with the nitrogen may be different for these species. Actually these species react equally in the substitution reaction. This experimental fact indicates that the substitution of zinc-PAR with the nitrogen in EGTA cannot be rate determining.

Since PAR is not as flexible as aliphatic polyamines, it is less likely to react *via* a stepwise removal of donor atoms of PAR from the central metal as was postulated previously in the substitution of polyamine complexes of nickel with EDTA.³ It is likely therefore that, as soon as one donor atom of PAR is removed from zinc in the intermediate $RZnY^{4-}$, the other two will also be detached. This step should be the rate-determining step.

As stated above, the release of a water molecule from an aquometal ion is an important step in the complex formation, and the rate constants of formation of various zinc complexes fall in a rather narrow range, *i.e.*, 10^6 – $10^8 M^{-1} sec^{-1}$. Though the rate constant for formation of ZnR is not yet available, it will very probably be in this range. The rate of dissociation of ZnR can be estimated from the stability constant of this complex determined in the present study and the rate of formation of ZnR . The estimated value ranges from 10^{-6} to $10^{-4} sec^{-1}$, which is by more than several orders of magnitude lower than the observed rate constant of the substitution of zinc-PAR with EGTA. The high negative charge of the intermediate $RZnY^{4-}$ and the electron donation from EGTA to zinc are responsible for the higher rate of removal of PAR from $RZnY^{4-}$ than from the uncharged ZnR .

According to our preliminary experiments, the substitution with EDTA proceeds, under the same condition, about 100 times faster than with EGTA. If the release of the PAR anion from the intermediate is rate determining, the electrostatic effect, electron donation from aminopolycarboxylate to the metal, and

the steric effect arising from the presence of EGTA or EDTA would be operative in determining the overall reaction rate. Among these effects, the former two may reasonably be assumed to be roughly the same for both EGTA and EDTA. Thus, the lower rate of substitution with EGTA than with EDTA may be attributable to the steric hindrance exhibited by the former ligand which is sterically much more crowded when partially coordinated.

Different Reactivity of Sodium- and Lithium-EGTA Complexes.—Because metal carboxylate in the sodium- or lithium-EGTA complex does not seem to exhibit a greater reactivity than free carboxylate in the same complex, sodium or lithium should remain attached to one of the carboxylates in EGTA until the last stage of substitution of ZnR with EGTA. Then the intermediate in the substitution with these EGTA complexes should be $RZnYNa^{3-}$ or $RZnYLi^{3-}$. Retardation of the removal of the PAR anion from the latter intermediates would result from the electrostatic and steric effects of these alkaline metals attached to carboxylate in EGTA. The electrostatic effect may be assumed to be approximately the same for both alkaline metals. The difference in reactivity of these EGTA complexes should, therefore, be interpreted in terms of the steric effect. That is to say, removal of PAR from $RZnYLi^{3-}$ should be sterically more difficult than from $RZnYNa^{3-}$. This provides a good reason to postulate that most solvating water molecules are retained around the alkaline metal attached to carboxylate in the intermediate and probably in the original complex, because lithium ion is known to be more solvated by water molecules than sodium ion in the aqueous solution.

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