

formed from $(n + 1)s$ and $(n + 1)p$ atomic orbitals and σ -type ligand orbitals, but it might also be strongly localized along the z axis normal to the plane of the three phosphorus atoms. Indeed, according to some authors²² a tricoordinated, trigonal structure gives rise to a better π -bonding distribution than in a tetrahedral structure, not so much as far as the number of possible π bonds²³ is concerned, but certainly as far as the strength of such bonds is concerned.

This hypothesis is supported by the results of kinetic study of CO exchange in nickel carbonyl: here the activation energy for the S_N1 process was found to be lower than the energy found for the Ni-C bond.²⁴ In the case of $[\text{Pt}((\text{C}_6\text{H}_5)_3\text{P})_3]$ there should be directional back-donating bonds, formed from hybrid $6p_z$, $5d_{z^2}$, and $5d_{yz}$ platinum orbitals and $3d$ phosphorus orbitals.

(22) S. Ahrland and J. Chatt, *Chem. Ind. (London)*, 96 (1955); Y. Kimball, *J. Chem. Phys.*, **8**, 188 (1940).

(23) F. A. Cotton, *J. Chem. Soc.*, 5269 (1960).

Such bonds, however, are not very strong, since phosphorus is not a strong π acceptor, so that a $6p_z$ orbital is engaged only slightly in these bonds and is able to hybridize with the $5d_{z^2}$ orbital, in which there is a non-bonding electron pair; charge is then mainly directed along the z axis. The amount of energy required for $d^{10} \rightarrow d^9p^1$ promotion is a good deal lower than $d^{10} \rightarrow d^9$ ionization energy;²¹ this amount of energy is a good measure of the possibility of $(n + 1)p$ and nd hybridization and could be taken as a rough measure of the activation energy for protonation reaction.

Using this picture, tricoordinated compounds appear with structures like those of bases of group V-B with a strong density of directional negative charge.

In any case the results of this research confirm that basic properties of coordination compounds are enhanced when the ligands are poor π acceptors as cyclopentadienyls^{2,3} and phosphines.⁵

(24) F. Basolo and A. Wojcicki, *J. Am. Chem. Soc.*, **83**, 520 (1961).

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Kinetics of the Reaction of Nickel(II) with Ethylenediaminetetraacetatocobaltate(II)

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Received June 4, 1965

Kinetics of the reaction of nickel(II) with ethylenediaminetetraacetatocobaltate(II) is investigated in detail in the pH range 3 to 4.5. The reaction is found to proceed through three independent paths, and the rate constants for each path are determined. The rates of nickel ion attack of normal and protonated cobalt-EDTA complexes are consistent with the binuclear intermediate model proposed by Bydalek and Margerum.

The kinetics of displacement reactions involving metal-ethylenediaminetetraacetato (EDTA, L^{4-}) complexes have been studied by several workers,¹⁻⁵ and the reaction rates for acid-dependent and acid-independent paths have been measured for some metal-EDTA complex systems. Recently Bydalek and Margerum⁶ proposed that the acid-independent path proceeds through a binuclear reaction intermediate, MLM', where the multidentate ligand is partially unwrapped and the iminodiacetate segment is partly or completely coordinated to the attacking ion prior to the rate-determining step, and the stability of this species greatly influences the exchange rate. These authors have shown that the exchange rates in Ni-L-Cu⁷ and Ni-L-Zn⁸ systems can be satisfactorily explained on the basis of this mechanism. In the present

study the kinetics of Ni²⁺ attack of Co-EDTA was investigated in detail mainly to check the applicability of the "binuclear reaction intermediate" mechanism to this system.

Experimental Section

The experimental procedure for the preparation of metal perchlorates, purification of EDTA, standardization, etc., have been described earlier.⁹ Temperature was maintained at the desired value with variation of $\pm 0.1^\circ$, and ionic strength was kept at $\mu = 0.5$ by addition of sodium perchlorate. No buffer was used in order to avoid its possible influence on the exchange rate, and all pH adjustments were made by addition of either perchloric acid or sodium hydroxide. pH measurements were made with a Beckman Model G pH meter using glass-calomel electrodes. All spectral readings were taken with a Beckman DU spectrophotometer using quartz cells. The exchange reaction was followed spectrophotometrically by measuring the absorbance at 980 m μ , which corresponds to the spectral peak of the nickel complex.

(1) G. Schwarzenbach and H. Ackermann, *Helv. Chim. Acta*, **35**, 485 (1962).

(2) K. Brill, S. Brill, and P. Krumholz, *J. Phys. Chem.*, **59**, 596 (1955).

(3) N. Tanaka, K. Kato, and R. Tamamushi, *Bull. Chem. Soc. Japan*, **31**, 283 (1958).

(4) K. Kato, *ibid.*, **33**, 600 (1960).

(5) N. Tanaka, H. Osawa, and M. Kamada, *ibid.*, **36**, 530 (1963).

(6) T. J. Bydalek and D. W. Margerum, *Inorg. Chem.*, **2**, 678 (1963).

(7) T. J. Bydalek and D. W. Margerum, *J. Am. Chem. Soc.*, **83**, 4326 (1961).

(8) D. W. Margerum and T. J. Bydalek, *Inorg. Chem.*, **1**, 852 (1962).

(9) T. R. Bhat and M. Krishnamurthy, *J. Inorg. Nucl. Chem.*, **25**, 1147 (1963).

The concentration of nickel complex at different time intervals was calculated using the expression

$$[\text{NiL}_T] = \frac{A - l[\epsilon_{\text{CoLT}}[\text{CoLT}]_i + \epsilon_{\text{Ni}}[\text{Ni}^{2+}]_i]}{l(\epsilon_{\text{NiLT}} + \epsilon_{\text{Co}^{2+}} - \epsilon_{\text{Ni}^{2+}} - \epsilon_{\text{CoLT}})}$$

where A = observed absorbance, l = length of the cell path (1, 2, or 5 cm), and T refers to the total concentration of normal and protonated species. The molar absorptivities, ϵ_M , of different species used in the calculation which are given in Table I were nearly constant in the temperature range studied. The values of ϵ_{NiYT} and ϵ_{CoYT} are pH dependent and hence were determined from the pH vs. ϵ_M curves of NiY and CoY complexes.

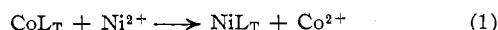
TABLE I
MOLAR ABSORPTIVITIES OF DIFFERENT SPECIES AT 980
m μ , $\mu = 0.5$, AND 25.0°

Species	Molar absorbance	Species	Molar absorbance
NiL ²⁻	32.5	CoL ²⁻	5.0
NiLH ⁻	22.0	CoLH ⁻	4.5
Ni ²⁺	1.2	Co ²⁺	0.9

The rate of the reverse reaction was negligibly small compared to the forward reaction and hence was neglected in calculations. The reaction was followed for more than 50% completion, and the rate constants were reproducible to 6% or better.

Results and Discussion

The exchange reaction



was studied in the concentration range of 0.005 to 0.05 M in Ni^{2+} , Co^{2+} , and CoLT , and in the pH range 3 to 4.5. Under these conditions the reaction obeys the second-order rate law

$$\frac{d[\text{NiLT}]}{dt} = k_0[\text{CoLT}][\text{Ni}^{2+}] \quad (2)$$

Some typical second-order rate law constants are given in Table II. At pH < 3.5, the concentration of the protonated species, CoLH^- , becomes appreciable and hence the rate constant, k , with respect to CoL^{2-} was calculated from the measured k_0 by applying necessary correction taking the formation constant of CoLH^- ($K_{\text{CoLH}^-}^{\text{CoL}^-}$) as $10^{2.6,10}$. These corrected values are also given in Table II.

TABLE II
SECOND-ORDER RATE LAW CONSTANTS FOR THE REACTION
OF Ni^{2+} AND CoLT AT 25° AND $\mu = 0.5$

pH	$10^3[\text{CoLT}]_i, 10^3[\text{Co}^{2+}]_i, 10^3[\text{Ni}^{2+}]_i, M$		$10^3k_0, 10^3k, 10^3k^b, M^{-1} \text{ sec}^{-1}$			
	M	M	M	$M^{-1} \text{ sec}^{-1}$	$M^{-1} \text{ sec}^{-1}$	$M^{-1} \text{ sec}^{-1}$
3.5	50	2.5	10	77	87	86
3.5	10	2.5	50	76	86	86
3.5	5	2.5	10	72	81	86
3.5	10	2.5	5	75	85	86
2.9	15	3.3	10	167	250	260
3.2	10	4.2	10	83	104	103
3.6	10	6.0	15	27	29	30
3.75	10	6.0	10	20	21	21
4.0	10	6.5	10	11	11	11
4.5	20	6.5	20	5	5	4

^a These values were calculated from k_0 using the relation $k = k_0[1 + 10^{2.6}[\text{H}^+]]$. ^b These values were calculated from eq 3 using the values of k_1, k_2 , and k_3 given in Table III.

The plots of $\log k$ vs. $\log [\text{H}^+]$ gave slope of nearly unity indicating that the rate is dependent on the first

(10) T. R. Bhat and D. Radhamma, unpublished results.

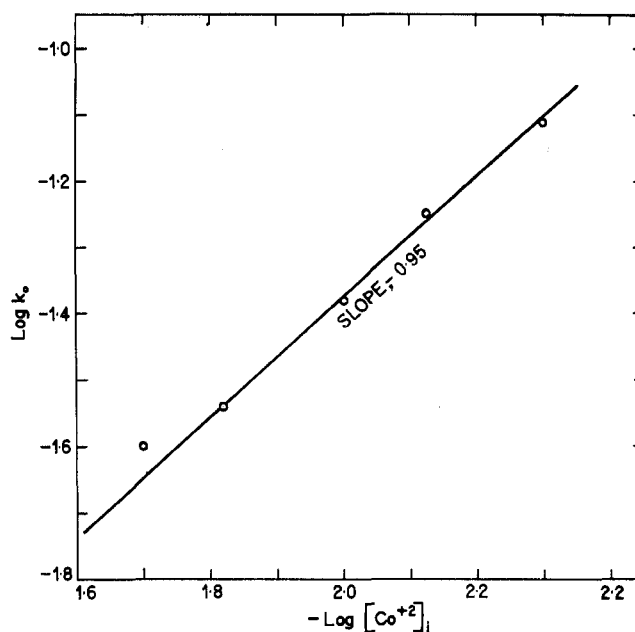


Figure 1.—Variation of k with the initial concentration of Co^{2+} ; $[\text{Ni}^{2+}]_i = 0.01 M$, $[\text{CoLT}]_i = 0.01 M$, at 29.5° and pH 3.5.

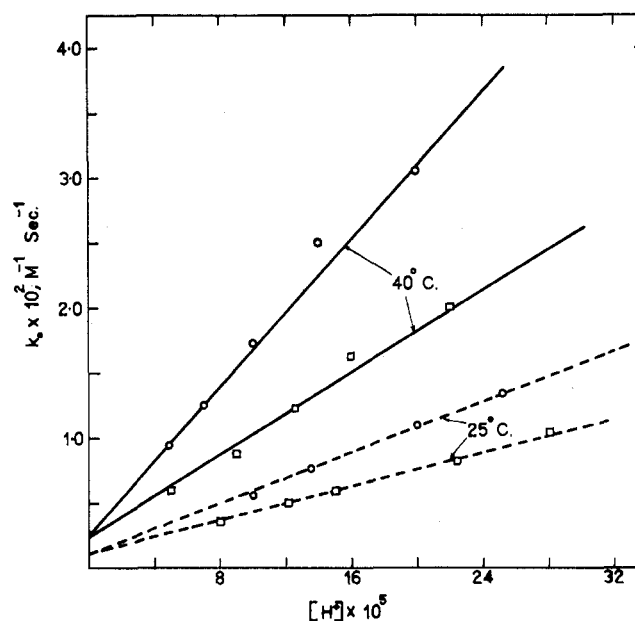


Figure 2.—Variation of k with $[\text{H}^+]$ at 25 and 40° for two different initial concentrations of Co^{2+} : $[\text{CoLT}]_i = 0.01 M$, $[\text{Ni}^{2+}]_i = 0.01 M$. O, $[\text{Co}^{2+}]_i = 0.02 M$; □, $[\text{Co}^{2+}]_i = 0.04 M$.

power of $[\text{H}^+]$ in the pH range studied. Inverse dependence of k on the amount of Co^{2+} initially added, $[\text{Co}^{2+}]_i$, can be seen from the data given in Figure 1. The plots of k vs. $[\text{H}^+]$ (Figure 2) give straight lines which again indicate the first-power dependence on $[\text{H}^+]$. The positive intercepts of these lines in the k axis give the contribution from the $[\text{H}^+]$ -independent path. Also, the slopes of these lines are dependent on $[\text{Co}^{2+}]_i$. These results suggest that k can be resolved into three components corresponding to three independent reaction paths: (1) $[\text{H}^+]$ independent, (2) $[\text{H}^+]$ dependent, and (3) directly dependent on $[\text{H}^+]$ and

inversely dependent on $[\text{Co}^{2+}]_i$. Thus, k can be expressed as

$$k = k_1 + k_2[\text{H}^+] + k_3[\text{H}^+]/[\text{Co}^{2+}] \quad (3)$$

The value of k_1 was obtained from the intercept at $[\text{H}^+] \rightarrow 0$ of k vs. $[\text{H}^+]$ plots (Figure 2). From the slopes of these lines (which give $k_2 + k_3/[\text{Co}^{2+}]_i$) at two different initial concentrations of Co^{2+} , the values of k_2 and k_3 were evaluated and these are summarized in Table III. It can be seen from the data given in Table II that there is over-all agreement between the experimental values of k and these calculated according to eq 3.

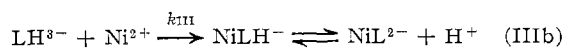
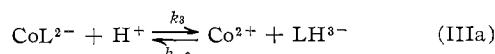
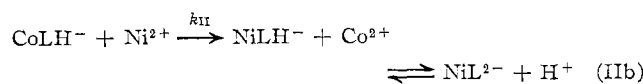
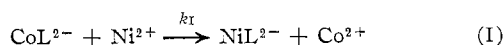
TABLE III
TEMPERATURE DEPENDENCE OF RATE CONSTANTS

Temp, °C	Rate constants, $M^{-1} \text{sec}^{-1}$				
	$10^2 k_1$	k_2	k_3	k_{III}	k_{III}
25	0.83	5.0	0.66	0.0125	1.65×10^6
29.5	1.16	8.3	1.167
35.0	1.66	11.0	1.667
40.0	2.5	16.67	2.67

	Kinetic parameters			
	kcal			$M^{-1} \text{sec}^{-1}$
E_{a1}	13.8	A_1		1.05×10^7
E_{a2}	16.1	A_2		7.8×10^9
E_{a3}	17.0	A_3		1.84×10^{18}

The temperature dependences of k_1 , k_2 , and k_3 were measured by studying the reaction at 25, 29.5, 35, and 40°. The results given in Table III follow the Arrhenius expression and give E_a values of 13.8, 16.1, and 17.0 kcal/mole for k_1 , k_2 , and k_3 , respectively.

The general kinetic behavior of this reaction is similar to those observed by earlier workers in other metal-EDTA systems. The over-all reaction can be explained on the basis of the following three reaction paths



According to this mechanism, applying the steady-state approximation for $[\text{LH}^{3-}]$ and assuming¹¹ $k_{-3}[\text{Co}^{2+}] \gg k_{\text{III}}[\text{Ni}^{2+}]$, one can derive the expression for the formation of NiL_T as

$$\frac{d[\text{NiL}_T]}{dt} = \left[k_1 + k_{\text{II}}K_{\text{CoLH}^{\text{CoL}}}[\text{H}^+] + \frac{k_{\text{III}}[\text{H}^+]}{k_{\text{CoL}}K_{\text{LH}}[\text{Co}^{2+}]} \right] \times [\text{CoL}][\text{Ni}^{2+}] \quad (4)$$

A comparison of eq 3 and 4 shows that the rate constants for the individual paths IIb and IIIb can be calculated from the measured k_2 and k_3 using the relations

(11) This assumption is valid since Ni^{2+} is known to be very sluggish in its reactions compared to Co^{2+} : F. Basolo and R. G. Pearson, "Mechanism of Inorganic Reactions," John Wiley and Sons, Inc., New York, N. Y., 1958, p 111.

$$k_2 = k_{\text{II}}K_{\text{CoLH}^{\text{CoL}}} \quad (5)$$

$$k_{\text{III}} = k_3K_{\text{CoL}}K_{\text{LH}} \quad (6)$$

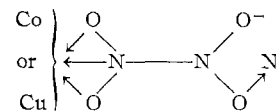
where K_{CoL} and K_{LH} are the formation and dissociation constants of CoL and LH, respectively. These data obtained at 25° using the values $\log K_{\text{CoLH}^{\text{CoL}}} = 2.6$,¹⁰ $\log K_{\text{CoL}} = 16.2$,¹⁰ and $\log K_{\text{LH}} = -9.8$ ¹² are given in Table III. The value of $1.65 \times 10^6 M^{-1} \text{sec}^{-1}$ observed here for k_{III} is very much lower compared to those of 5.8×10^9 and $1.9 \times 10^{10} M^{-1} \text{sec}^{-1}$ reported for reactions of LH^{3-} with Cu^{2+} ³ and Pb^{2+} ,¹³ respectively, at 25° and $\mu = 0.2$. This is to be expected from the general sluggish behavior of nickel ion.

It is of special interest to check how far the experimental reaction rates for the nickel ion attack of CoL^{2-} and CoLH^- agree with the value expected from the mechanism of Bydalek and Margerum. For checking the value of k_1 the rate constant for nickel ion attack of another metal EDTA complex is required. Therefore the rate of $\text{Ni}^{2+} + \text{CuL}^{2-} \rightarrow \text{NiL}^{2-} + \text{Cu}^{2+}$ reaction was studied in the pH range 3.5 to 5 where the rate is known to be independent of pH⁷ and the above mechanism was found to hold.⁶ Some typical second-order rate law constants with respect to $[\text{Ni}^{2+}]$ and $[\text{CuL}]$ are given in Table IV from which an average value of $0.011 M^{-1} \text{sec}^{-1}$ was obtained. (This is comparable with the reported⁷ value of $0.0103 M^{-1} \text{sec}^{-1}$ at 25° and $\mu = 1.25$.)

TABLE IV
SECOND-ORDER RATE LAW CONSTANTS FOR THE REACTION
 $\text{Ni}^{2+} + \text{CuL}^{2-} \rightarrow \text{NiL}^{2-} + \text{Cu}^{2+}$ AT 25° AND $\mu = 0.5$

pH	$10^2[\text{Ni}^{2+}], M$	$10^2[\text{CuL}], M$	$k, M^{-1} \text{sec}^{-1}$
3.8	10	20	0.0110
4.0	20	20	0.0115
4.5	25	10	0.0105
4.5	50	10	0.0112
			Av 0.0110

If we assume the applicability of the mechanism of Bydalek and Margerum, then the reaction intermediate will have the structure



and the slowest step is the formation of Ni-N bond. Then the value of k_1 becomes equal to the product of K_R and the rate of Ni^{2+} attack of CuL^{2-} (i.e., 0.011) where K_R is the ratio of the relative stability of the intermediate with respect to the normal cobalt and copper complexes, defined by

$$K_R = \frac{K_{\text{CoIMDA}}K_{\text{NiOAc}}/K_{\text{CoL}}}{K_{\text{CuIMDA}}K_{\text{NiOAc}}/K_{\text{CuL}}}$$

where K_{CoIMDA} , etc., refers to the stability constant of the individual segment in the intermediate structure (IMDA, iminodiacetate; AcO, acetate). Using the stability constant values obtained¹⁰ under the experi-

(12) A. E. Martell and F. F. Carini, *J. Am. Chem. Soc.*, **74**, 5745 (1952).

(13) N. Tanaka and K. Kato, *Bull. Chem. Soc. Japan*, **33**, 1236 (1960).

mental conditions ($\log K_{\text{CuL}} = 18.43$, $\log K_{\text{CoL}} = 16.20$, $\log K_{\text{CuIMDA}} = 10.35$, $\log K_{\text{CoIMDA}} = 6.95$, $\log K_{\text{NiOAc}} = 0.65$) the value of K_R can be obtained as 0.068. This gives a value for k_1 as $7.48 \times 10^{-4} M^{-1} \text{sec}^{-1}$, which is in good agreement with the experimental value of $8.3 \times 10^{-4} M^{-1} \text{sec}^{-1}$. Therefore, it may be concluded that the mechanism proposed by Bydalek and Margerum holds for Ni^{2+} attack of the normal cobalt-EDTA complex.

In case of protonated species, the applicability of the binuclear intermediate mechanism can be tested by comparing the rate of Ni^{2+} attack of CoLH^- with that of CoL^{2-} . This ratio should be equal to the ratio of stability of the intermediate species, CoLHNi and CoLNi . The stability of the protonated intermediate species will be increased by protonation of the carboxyl group of the iminodiacetate segment. Simultaneously it will be reduced, partly owing to lowering of charge (Bydalek and Margerum⁶ have calculated the contribution due to this factor as $\log K_{e1} = 0.5$) and partly to statistical effect. Taking these factors into consideration this kinetic ratio $k_{\text{Ni}}^{\text{CoLH}}/k_{\text{Ni}}^{\text{CoL}}$ can be obtained¹⁴ as 38 which compares favorably with the experimental value of 15. If this type of binuclear mechanism holds also for exchange reactions in other metal-EDTA systems, this ratio must remain constant irrespective of the system. Some of these values reported in the literature and the corresponding ratios are sum-

(14) This value was calculated taking the pK value of iminodiacetic acid as 2.38.¹⁰ Here, an assumption has been made that the proton is attached to the carboxyl group rather than to nitrogen in the protonated intermediate species.

marized in Table V, from which it can be seen that the observed ratio is of the right order of magnitude. In view of the wide variations in the experimental conditions employed by different workers, the agreement is reasonably good.

TABLE V
OBSERVED RATE CONSTANTS FOR THE METAL ION ATTACK
OF NORMAL AND PROTONATED METAL-EDTA COMPLEXES
AND THEIR RATIO

System	Temp, °C	μ	$k_M^{\text{MY}}, M^{-1} \text{sec}^{-1}$	$k_M^{\text{MYH}}, M^{-1} \text{sec}^{-1}$	$\frac{k_M^{\text{MYH}}}{k_M^{\text{MY}}}$	Ref
Cu + CdY	20	0.1	0.056	1.4	25.0	a
	15	0.2	2.20	45.9	20.9	b
Cu + PbY	25	0.2	0.78	8.0	10.3	c
	25	0.2	5.10	60.0	11.8	d
Cu + CoY	15	0.2	15.3	150	9.8	e
Pb + ZnY	25	0.2	5.0	300	60.0	f
Cu + ZnY	15	0.2	19.0	60	3.2	g
Ni + CoY	25	0.5	8.3×10^{-4}	1.25×10^{-2}	15	h

^a See ref 1. ^b N. Tanaka and M. Kamada, *Bull. Chem. Soc. Japan*, **35**, 1596 (1962). ^c See ref 3. ^d N. Tanaka and E. Kato, *ibid.*, **32**, 1376 (1959). ^e See ref 5. ^f N. Tanaka and H. Ogino, *ibid.*, **36**, 175 (1963). ^g K. Kato, *ibid.*, **33**, 600 (1960). ^h Present work.

It may be noted that the rate of nickel ion attack of CuL^{2-} is faster than that of CoL^{2-} even though the latter complex is less stable. This may be attributed, as in the case of the zinc complex,⁸ to the greater stability of the binuclear intermediate in the case of the copper complex.

Acknowledgments.—The authors wish to thank the referees for useful suggestions.

CONTRIBUTION FROM THE DEPARTMENT OF CHEMISTRY,
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Multidentate Ligand Kinetics. IX. The Effect of Coordinated Anions on the Dissociation Rate of 1,2-Diaminocyclohexanetetraacetatomercurate(II)

BY D. L. JANES AND DALE W. MARGERUM¹

Received November 15, 1965

The kinetics of dissociation of *trans*-1,2-diaminocyclohexanetetraacetatomercurate(II), HgCyDTA^{2-} , are studied in the presence of complexing anions at 25°, 0.1 μ . Halide, thiocyanate, and hydroxide ions (X) form mixed complexes, $\text{Hg}(\text{CyDTA})\text{X}^{3-}$, and their stability constants are measured. The $\log K$ values are 2.16 (Cl^-), 3.21 (Br^-), 5.25 (I^-), 4.29 (SCN^-), and 3.20 (OH^-). In each case the dissociation kinetics are first order in $[\text{Hg}(\text{CyDTA})\text{X}^{3-}]$ and first order in $[\text{H}^+]$. The hydrogen ion dependence exists even at pH 8. The resulting second-order rate constants ($M^{-1} \text{sec}^{-1}$) are 3.1 (H_2O), 2.6×10^3 (Cl^-), 1.5×10^4 (Br^-), 5.9×10^4 (I^-), 2.3×10^3 (SCN^-), and a probable value of 10^6 for hydroxide ion. The ability of the anions to complex HgCyDTA^{2-} correlates with a measure of their polarizability. Increasing polarizability of the anions accelerates the rate of the proton-assisted dissociation of CyDTA from mercury(II), except in the case of thiocyanate ion.

Introduction

The exchange of *trans*-1,2-diaminocyclohexanetetraacetate (CyDTA) between two metal ions is a kinetically simple process compared to the parallel reaction with EDTA.² An earlier paper in this series³

showed that the reaction of Ni-CyDTA with copper(II) was zero order in copper and preceded by the complete dissociation of the CyDTA from nickel ion before

(1) Correspondence to be addressed to this author.

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

(3) D. W. Margerum and T. J. Bydalek, *Inorg. Chem.*, **2**, 683 (1963).