

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^{MY} , $M^{-1} \text{sec}^{-1}$	k_M^{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

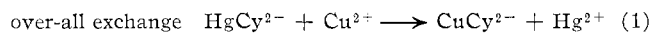
showed that the reaction of Ni-CyDTA with copper(II) was zero order in copper and preceded by the complete dissociation of the CyDTA from nickel ion before

(1) Correspondence to be addressed to this author.

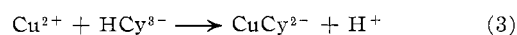
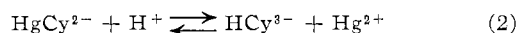
(2) D. W. Margerum, D. L. Janes, and H. M. Rosen, *J. Am. Chem. Soc.*, **87**, 4463 (1965).

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

copper reacted to form the copper-CyDTA complex. Although copper ion did not affect the rate of dissociation of CyDTA from nickel, hydrogen ion assisted the dissociation. Subsequent work with CyDTA complexes of eight other metal ions shows the same kinetic behavior.⁴ In every case the initial metal-CyDTA complex did not react with the exchanging metal ion. Thus, the rate of the over-all exchange reaction in eq 1 is independent of copper ion but depends on the hydrogen ion concentration.

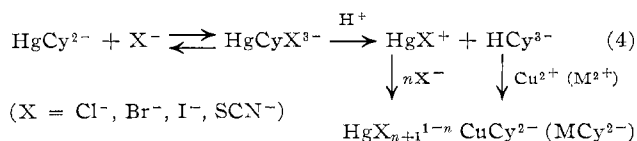


The mechanism proposed for this reaction is the complete dissociation of mercury from CyDTA followed by the formation of the copper-CyDTA complex. Re-



action 1 can be made to proceed despite the fact that $\log K_{\text{HgCy}}$ is 24.95 and $\log K_{\text{CuCy}}$ is 21.95.⁵ Even at pH 4 the hydrolysis of mercury to form soluble hydroxide complexes, HgOH^+ and $\text{Hg}(\text{OH})_2$ ($\log *K_1 = 13.7$, $\log *K_2 = -2.6$ in $0.5 M \text{NaClO}_4$), is quite important while the corresponding hydrolysis of copper is negligible. Thus, the initial rate of reaction 1 was followed in perchlorate media, pH 3.8–5.7, using a 30-fold excess of copper ion. Under these conditions the rate-limiting step was the acid dissociation reaction given in eq 2, and the reaction was independent of the copper ion concentration. A study of the reverse reaction in eq 1 supports the mechanism given in eq 2 and 3, where CyDTA completely dissociates from one metal before reacting with the other.

The primary interest in the present study is the effect which mercury-complexing anions have on the rate of dissociation of CyDTA from mercury. Halide and thiocyanate ions are shown to form 1:1 complexes with Hg-CyDTA, and these mixed complexes speed the loss of CyDTA (eq 4). The subsequent steps



leading to the formation of Cu-CyDTA (or other metal-CyDTA complexes) and anionic complexes of mercury are shown to be after the rate-determining dissociation reaction. Substitution of zinc ion or lead ion as a scavenger gave the same rates as copper ion in reaction 4. In the studies with iodide ion, the reaction rates were the same with and without a metal scavenger present.

In the presence of complexing anions the mercury which dissociates from CyDTA forms complex ions which help to drive eq 4 to completion. Typical constants⁷ for these complexes are: $\log \beta_4 = 16.2$ for

Cl^- , $\log \beta_4 = 21.6$ for Br^- , $\log \beta_4 = 29.8$ for I^- , and $\log \beta_4 = 21.2$ for SCN^- .

In this study the direct effect of a monodentate-coordinated anion on the bond breaking of a multidentate ligand can be assessed to determine what properties of the anion affect the rate of the reaction.

Experimental Section

Perchlorate salts of all metals used were prepared and recrystallized. Reagent grade sodium salts of Cl^- , Br^- , I^- , and SCN^- were used without further purification. The acid form of CyDTA (Lamont Chemical Co.) was recrystallized several times and dissolved in sodium hydroxide solution. The solution was standardized by titration with copper using Murexide indicator. Hg-CyDTA was prepared by stoichiometric addition to $\text{Hg}(\text{ClO}_4)_2$ solution. The Hg^{2+} solution was standardized using CyDTA and a back titration with zinc using Eriochrome Black T indicator.

Buffers of borate-mannitol ($5.0 \times 10^{-3} M$ total boron with varying amounts of mannitol to adjust the pH) were used as well as 2,6-lutidine perchlorate ($5.0 \times 10^{-3} M$ with NaOH to adjust pH). The borate-mannitol buffer had a slight accelerating effect on the rate of reactions with low chloride ion concentration. Therefore, the 2,6-lutidine buffer, which was shown to have no kinetic effect, was used with this system.

All reactions were followed spectrophotometrically (Cary Model 14) by observing the formation of the products. Reactions with copper were observed at $310 m\mu$ when 2,6-lutidine was the buffer. Using copper, with borate-mannitol as the buffer, $270 m\mu$ was used for bromide, chloride, and perchlorate and $280 m\mu$ for the thiocyanate study. The bromide reaction also was studied with zinc at $265 m\mu$. The iodide study used lead perchlorate and wavelengths of 280 and $290 m\mu$. Ionic strength was held constant at $0.10 M$ using NaClO_4 . All reactions were at $25.0 \pm 0.1^\circ$. A Beckman Research Model 1016 pH meter was used.

First-order rate constants were obtained from plots of $\log (A_t - A)$ against time, where A_t is the final absorbance and A is the absorbance at any time. The reactions usually were followed for 1–2 half-lives except in the case where only perchlorate ion was present at low pH.

Results

Determination of the Stability Constants of HgCyX^{3-} .

—The ultraviolet spectrum of mercury-CyDTA shown in Figure 1 has an absorption shoulder or plateau at $250 m\mu$ which changes in molar absorptivity when anions coordinate to the complex. This plateau decreases in absorbance with chloride ion and increases for all other anions studied. The stability constant, K_{HgCyX} (eq 5), was determined in each case from the

$$K_{\text{HgCyX}} = \frac{[\text{HgCyX}^{3-}]}{[\text{HgCy}^{2-}][\text{X}^-]} \quad (5)$$

spectral shift using eq 6–8, where ΔA is the observed change in absorbance for a single mixed complex. Plots of eq 8 with a large excess of $[\text{X}^-]$ (where the

$$\Delta A = A_{\text{mixture}} - A_{\text{reactants}} = \Delta \epsilon b [\text{HgCyX}^-] \quad (6)$$

$$\Delta \epsilon = \epsilon_{\text{HgCyX}} - \epsilon_{\text{HgCy}} - \epsilon_{\text{X}} \quad (7)$$

$$\frac{[\text{HgCy}^{2-}]_i b}{\Delta A} = \frac{1}{\Delta \epsilon} + \frac{1}{\Delta \epsilon [\text{X}^-] K_{\text{HgCyX}}} \quad (8)$$

species are reversed when HgCy^{2-} is in excess) gave excellent straight lines in agreement with a 1:1 complex with intercepts of $(\Delta \epsilon)^{-1}$ and slopes of $(K_{\text{HgCyX}} \Delta \epsilon)^{-1}$. The $\Delta \epsilon$ value was confirmed in the case of thiocyanate by the addition of a sufficient excess of the anion to

(4) D. W. Margerum, D. L. Janes, and P. J. Menardi, to be published.

(5) G. Anderegg, *Helv. Chim. Acta*, **46**, 1833 (1963).

(6) S. Hietanen and L. G. Sillén, *Acta Chem. Scand.*, **6**, 747 (1952).

(7) L. G. Sillén and A. E. Martell, "Stability Constants of Metal-Ion Complexes," The Chemical Society, London, 1964.

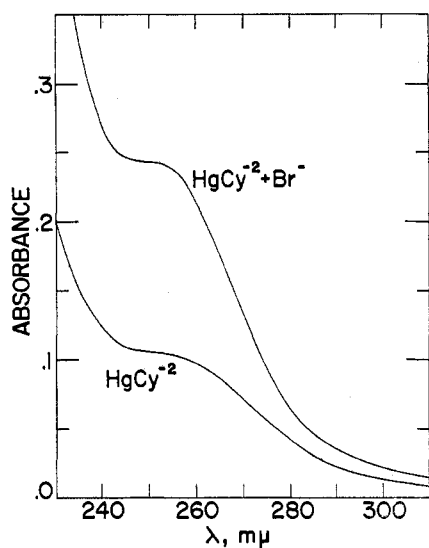


Figure 1.—Effect of bromide ion on the spectrum of HgCy-DTA²⁻; 10-cm cell, $8.40 \times 10^{-6} M$ HgCy²⁻, $1.12 \times 10^{-3} M$ NaBr, 25.0°, 0.10 μ .

form HgCySCN³⁻ quantitatively. With the halides there was no evidence for the addition of more than one anion except in the case of iodide at concentrations above $10^{-4} M$. The slopes were evaluated by a weighted regression analysis program (WRAP)⁸ using from six to nine data points with the weights taken as $(\Delta A)^2$. Table I summarizes the conditions used, the

TABLE I
STABILITY CONSTANTS FOR HgCyX³⁻
25.0°, 0.10 μ (NaClO₄)

X ⁻	K_{HgCyX}	$[\text{HgCy}^{2-}]_i \times 10^4$	$[\text{X}^-]_i \times 10^4$	pH	λ , m μ	$\Delta\epsilon^a$	No. of data points
OH ⁻	$(1.59 \pm 0.18) \times 10^3$ ^a	0.21	1.3–18.2	...	240	810 ± 60	7
Cl ⁻	$(1.44 \pm 0.16) \times 10^2$	4.20	22.7–454	6.5	285	86 ± 4	6
Br ⁻	$(1.60 \pm 0.14) \times 10^3$	0.168	1.12–22.4	8.9	250	3250 ± 180	6
I ⁻	$(1.80 \pm 0.45) \times 10^5$	0.124–0.824	0.0173	8.9	250	7140 ± 290	6
SCN ⁻	$(1.96 \pm 0.24) \times 10^4$	0.0840–0.168	0.222–22.0	8.9	250	4570 ± 200	9

^a The limits are standard errors calculated by a weighted regression analysis program (WRAP).

stability constants measured, and the precision of the measurements.

Kinetics with Perchlorate Ion Present.—Sodium perchlorate was used to control ionic strength and was assumed not to complex Hg-CyDTA. Reactions of Hg-CyDTA with copper ion at constant pH gave first-order rates (eq 9) consistent with eq 2. The copper was present in 30-fold excess and at high pH reaction 1 was not reversible. At low pH the first 25% of the reaction was followed. The large excess of copper ion and the hydrolysis of mercury ion are sufficient to make reaction 3 much faster than the reverse of reaction 2. With only perchlorate ion present the last term in eq 10 can be dropped. The second term also can be

$$\text{rate} = k_0[\text{HgCyT}] \quad (9)$$

$$[\text{HgCyT}] = [\text{HgCy}^{2-}] + [\text{HgCyOH}^{3-}] + [\text{HgCyX}^{3-}] \quad (10)$$

dropped since it is less than $1 \times 10^{-3}\%$ in the pH range studied. The observed rate depends on the hydrogen ion concentration as expressed in eq 11 and

(8) J. D. Carr, Ph.D. Thesis, Purdue University, 1966.

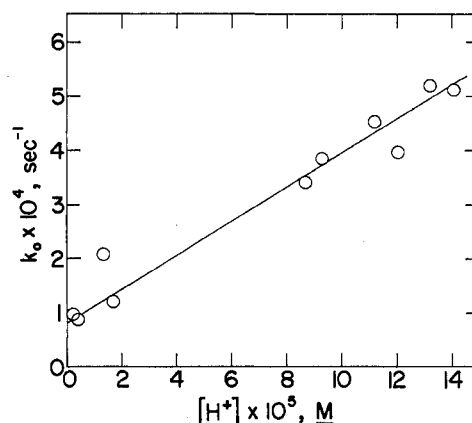


Figure 2.—Effect of hydrogen ion concentration on the first-order rate constant for HgCy²⁻ dissociation. The slope is $k_{\text{H}^{\text{HgCy}}}$; 25.0°, 0.10 μ , $4.20 \times 10^{-6} M$ HgCy²⁻, $1.20 \times 10^{-3} M$ Cu(ClO₄)₂.

$$\text{rate} = k_{\text{H}^{\text{HgCy}}}[\text{H}^+][\text{HgCy}^{2-}] + k_{\text{d}^{\text{HgCy}}}[\text{HgCy}^{2-}] \quad (11)$$

graphed in Figure 2. The slope gave a value of $3.1 M^{-1} \text{sec}^{-1}$ for $k_{\text{H}^{\text{HgCy}}}$ and the intercept gave $0.8 \times 10^{-4} \text{sec}^{-1}$ for $k_{\text{d}^{\text{HgCy}}}$.

Kinetic Effect of Bromide Ion.—The study of the reaction with bromide ion in eq 4 was carried out at such low hydrogen ion concentration that the first term in eq 11 was negligible. At a constant and excess bromide ion concentration of $5.60 \times 10^{-4} M$, the reaction rate follows eq 9 and k_0 has a first-order de-

pendence with hydrogen ion concentration from pH 6.5 to 7.5 (Figure 3 and Table II). The value of k_0 also depends upon the bromide ion concentration (Figure 4) with a first-order dependence at low concentrations which changes to a zero-order dependence at higher concentrations of bromide. This change in reaction order matches the conversion of HgCy²⁻ to HgCyBr³⁻, in accord with the stability constant in Table I. Thus, most of the bromide ion effect results from the reaction of hydrogen ion with HgCyBr³⁻. The small values of the intercepts in Figures 2 and 3 are not quite negligible and eq 12 gives the full kinetic dependence between pH 6 and 8. The second term in eq 12 evaluated from

$$k_0[\text{HgCyT}] = k_{\text{d}^{\text{HgCy}}}[\text{HgCy}^{2-}] + k_{\text{d}^{\text{HgCyBr}}}[\text{HgCyBr}^{3-}] + k_{\text{H}^{\text{HgCyBr}}}[\text{H}^+][\text{HgCyBr}^{3-}] \quad (12)$$

the graphical intercept and the stability constant K_{HgCyBr} gave a value of $k_{\text{d}^{\text{HgCyBr}}} = 2 \times 10^{-4} \text{sec}^{-1}$. This constant is not known with high accuracy because its contribution to the rate is small. The validity of eq 12 is shown in Figure 5, which plots the rearranged

TABLE II
 EFFECT OF pH ON THE DISSOCIATION OF HgCy^{2-} IN THE PRESENCE OF HALIDES AND THIOCYANATE AT 25.0° , 0.10μ

Bromide ^a		Chloride ^b		Iodide ^c		Thiocyanate ^d	
pH	$k_0 \times 10^3, \text{sec}^{-1}$	pH	$k_0 \times 10^3, \text{sec}^{-1}$	pH	$k_0 \times 10^3, \text{sec}^{-1}$	pH	$k_0 \times 10^3, \text{sec}^{-1}$
7.01	0.76	7.03	0.24	8.82	0.30	5.97	1.15 ^f
6.95	0.96	6.74	0.40	8.12	0.46	5.96	1.24 ^e
6.92	0.80	6.51	0.59	7.68	1.01	5.76	1.17 ^g
6.87	0.93	6.41	0.75	7.46	2.7	5.53	2.42 ^e
6.79	1.07	6.32	0.84	7.39	2.8	5.17	4.1 ^e
6.74	1.35	6.13	1.30	7.24	3.1	5.15	5.2 ^e
6.48	2.20	5.91	2.10	7.08	4.1	4.98	8.8 ^e
6.40	2.59			7.07	4.5	4.91	10.7 ^e
6.22	3.9			7.00	5.9	4.79	12.3 ^e
6.16	4.4			6.91	6.8	4.66	19.2 ^f
				6.82	7.7		

^a $5.60 \times 10^{-4} M$ NaBr, $8.40 \times 10^{-6} M$ HgCy^{2-} , $1.20 \times 10^{-5} M$ $\text{Cu}(\text{ClO}_4)_2$. ^b $1.13 \times 10^{-2} M$ NaCl, $8.40 \times 10^{-6} M$ HgCy^{2-} , $1.20 \times 10^{-5} M$ $\text{Cu}(\text{ClO}_4)_2$. ^c $8.65 \times 10^{-5} M$ NaI, $4.20 \times 10^{-6} M$ HgCy^{2-} , $1.00 \times 10^{-5} M$ $\text{Pb}(\text{ClO}_4)_2$. ^d $1.11 \times 10^{-4} M$ SCN^- . ^e $4.20 \times 10^{-6} M$ HgCy^{2-} , $1.20 \times 10^{-4} M$ $\text{Cu}(\text{ClO}_4)_2$. ^f $8.40 \times 10^{-6} M$ HgCy^{2-} , $1.20 \times 10^{-4} M$ $\text{Cu}(\text{ClO}_4)_2$. ^g $8.40 \times 10^{-6} M$ HgCy^{2-} , $1.20 \times 10^{-5} M$ $\text{Cu}(\text{ClO}_4)_2$.

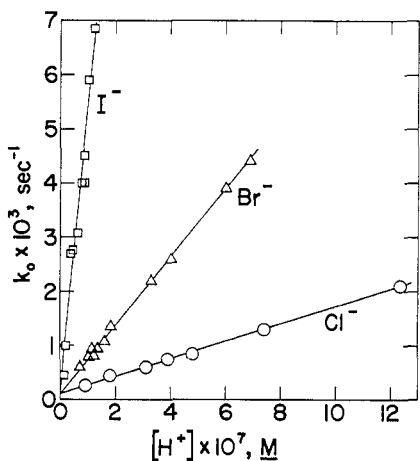


Figure 3.—Effect of hydrogen ion concentration on the first-order rate constant for HgCy^{2-} dissociation in the presence of halide ions. The slopes are $k_H^{\text{HgCyX}} \left(\frac{K_{\text{HgCyX}}[\text{X}^-]}{1 + K_{\text{HgCyX}}[\text{X}^-]} \right)$; 25.0° , 0.10μ . See Table II.

relationship given in eq 13 for a variety of different bromide ion concentrations and a variety of pH values over the range 5.8–7.1. The good fit of eq 13 justifies

$$\frac{k_0}{[\text{H}^+]} = \frac{k_d^{\text{HgCy}} + k_d^{\text{HgCyBr}} K_{\text{HgCyBr}} [\text{Br}^-]}{[\text{H}^+](1 + K_{\text{HgCyBr}} [\text{Br}^-])} = \frac{K_{\text{HgCyBr}} [\text{Br}^-]}{1 + K_{\text{HgCyBr}} [\text{Br}^-]} k_H^{\text{HgCyBr}} \quad (13)$$

the specific assignment of the bromide ion effect to the kinetic reactivity of the mixed complex, HgCyBr^{3-} . The reaction is first order in the concentration of this complex and zero order in free bromide ion. The rate constant for k_H^{HgCyBr} is $1.5 \times 10^4 M^{-1} \text{sec}^{-1}$. This is in good agreement with the value of $1.3 \times 10^4 M^{-1} \text{sec}^{-1}$ calculated from the slope in Figure 4 after correction for the fraction of Hg-CyDTA complexed to bromide.

The concentration of the metal ion used to scavenge the CyDTA released by the mercury did not interfere kinetically. A tenfold range of copper ion concentration was used without a kinetic effect and in a few cases zinc was substituted for copper.

Kinetic Effect of Chloride Ion.—For the data in

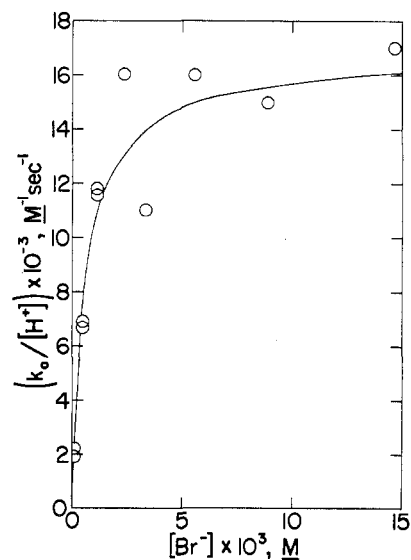


Figure 4.—Effect of bromide ion concentration on the second-order rate constant for hydrogen ion reaction with HgCyT ; 25.0° , 0.10μ .

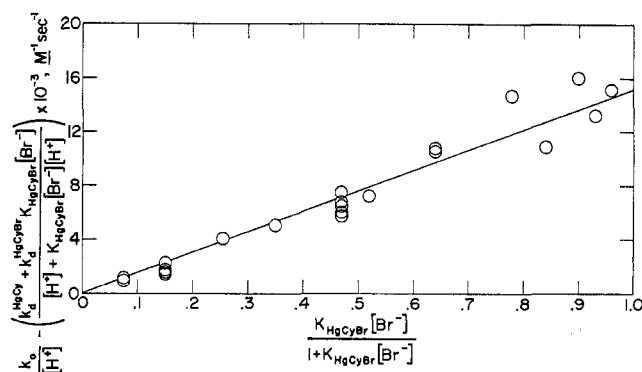


Figure 5.—Second-order rate constant for the reaction between H^+ and HgCyT as a function of fraction of Hg-CyDTA complexed by bromide ion. The slope is k_H^{HgCyBr} ; 25.0° , 0.10μ . See eq 13.

Figure 3 and Table II the chloride ion concentration was $1.13 \times 10^{-2} M$ and the pH range was 5.9–7.0. The rate constant obtained from the fraction of HgCyCl^{3-} present is $k_H^{\text{HgCyCl}} = 2.6 \times 10^3 M^{-1} \text{sec}^{-1}$.

Kinetic Effect of Iodide Ion.—Iodide forms a strong complex with Hg-CyDTA , and the CyDTA dissociates

faster than with the other halogens. Therefore, a low concentration of iodide ($8.65 \times 10^{-5} M$) and a higher pH was used. The value of k_H^{HgCyI} is $5.9 \times 10^4 M^{-1} \text{sec}^{-1}$. When the iodide ion concentration was increased to $1.7 \times 10^{-4} M$ the results agreed with these rate constants, but at higher iodide concentrations the reaction was faster than predicted. This additional kinetic dependence in iodide was not tested further.

Lead ion was used as the scavenger in the iodide ion studies except in some cases where no scavenger was added. This was possible because mercury forms very stable iodide complexes. The reaction rate did not depend on the scavenger concentration.

Kinetic Effect of Thiocyanate Ion.—A series of reactions with $1.11 \times 10^{-4} M$ thiocyanate ion from pH 4.6 to 6.0 gave the kinetic data in Table II. The value of k_H^{HgCySCN} is $2.3 \times 10^3 M^{-1} \text{sec}^{-1}$.

Discussion

Reactions of Hg-CyDTA with copper, lead, and zinc showed no kinetic effect attributed to these metals, but a hydrogen ion dependence was found even at pH 8. This is consistent with the behavior of other metal-CyDTA reactions. The detailed study of the effect of bromide ion showed that a prior equilibrium of HgCy^{2-} and HgCyX^{3-} precedes the slow steps of the reaction. The dissociation of CyDTA from mercury is the rate-determining reaction which can proceed by several paths indicated by the rate constants k_d^{HgCy} , k_d^{HgCyX} , k_H^{HgCy} , and k_H^{HgCyX} . The last constant represents by far the most important path below pH 7–8 in the presence of 10^{-5} to $10^{-2} M$ concentrations of the various complexing anions. The general kinetic behavior of chloride, iodide, and thiocyanate ions was consistent with that of bromide ion, and the same type of mechanism is assumed. The relative contributions of the k_d^{HgCy} and k_d^{HgCyX} terms to the reaction rate were always small. The data with perchlorate ion clearly show that the first term exists, and the data with bromide ion necessitate the second term, but only an approximate value is known. With the other anions the value of the second term is even less certain.

The coordination of the anion to mercury greatly speeds the rate at which a proton helps to remove CyDTA. The reaction rate accelerates as the strength of the halide complex increases and HgCyI^{3-} reacts 20,000 times faster than HgCy^{2-} . Table III summarizes the rate constants for HgCyX^{3-} .

Only one anion is involved in the kinetics although

TABLE III

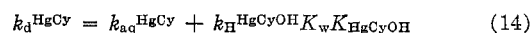
RATE CONSTANTS FOR THE MERCURY-CyDTA COMPLEXES
25.0°, 0.10 M NaClO₄

Complexing anion	$k_H^{\text{HgCyX}}, M^{-1} \text{sec}^{-1}{}^a$
None	3.1
Cl ⁻	2.6×10^3
Br ⁻	$(1.3 \pm 0.04) \times 10^4{}^b$
I ⁻	5.9×10^4
SCN ⁻	2.3×10^3
(OH ⁻)	$< 5 \times 10^6$

^a Determined graphically except as in b. ^b From least-squares analysis and with limits using 95% confidence level.

in the reaction product more than one anion coordinates to mercury. This suggests that the rate-determining step occurs early in the unwrapping of the CyDTA ion and occurs before the mercury ion can place itself in a less hindered position where it can accept additional halide coordination. The exact structures of Hg-EDTA-type complexes are not known but from stability constant measurements both nitrogens and some of the acetate groups are believed to be coordinated to mercury.⁹ The X-ray structures of Ni-EDTA¹⁰ and La-EDTA¹¹ have been determined. Considering the size of mercury ion it is not apt to be completely surrounded by the coordination cage of CyDTA but like La-EDTA it could have one side slightly exposed (La coordinates three H₂O molecules in addition to six-coordination to EDTA). Thus, Hg^{II}-N bond distances of 2.6 Å are reported in one complex¹² compared to about 2.1 Å for Ni-N and about 2.8 Å for La-N in the EDTA complexes. The small exposed portion of the mercury ion is assumed to coordinate water or an anion, and the latter makes it much easier for Hg(II) to break away from the CyDTA coordination cage. As stated earlier the rate-determining step must occur before the mercury ion is so far out of the cage that it could readily accept additional anion ligands. However, the proton path is important at extremely low hydrogen ion concentrations and only a nitrogen atom of CyDTA would be a good proton acceptor under these conditions. Therefore, the mechanism would appear to be a concerted reaction with Hg(II) leaving the vicinity of the nitrogens as a proton is added. The anion makes this process easier, and the stronger the anion complex, the easier it is to break the mercury away from the CyDTA coordination.

Possible Effect of Hydroxide Ion.—The rate constant, k_d^{HgCy} , which was given in eq 12 might not be a simple solvent replacement term but might consist of the two kinetic terms given in eq 14. The first term on the right-hand side of eq 14 represents a solvent replacement of the CyDTA without protonation of the ligand before the rate-determining step. The second term represents the splitting of the solvent molecule with H⁺ going to CyDTA and OH⁻ going to the mercury before the rate-determining step. The second term also can be considered as a reaction of H⁺ with HgCyOH^{3-} . There are several reasons to suggest this: (1) All the HgCyX^{3-} complexes show the importance of the H⁺ path. (2) The HgCyOH^{3-} complex is known to form



and even if it is present in trace quantities it could be sufficiently labile to contribute to the rate. (3) The value of k_d^{HgCyBr} compared to k_d^{HgCy} is not as large as would be expected compared to the bromide ion effect on the hydrogen ion path. This could be explained if a k_H^{HgCyOH} term made an appreciable contribution as

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shown in eq 14. If the major contribution to eq 14 were from the k_H^{HgCyOH} term, then the value of this constant would be $5 \times 10^6 M^{-1} \text{sec}^{-1}$. This would be its maximum possible value, but there is no experimental way to separate the two terms in eq 14.

Correlation with Anion Polarizability.—Mercury(II) is a class b metal¹³ (or a soft acid¹⁴) which forms stronger complexes with more polarizable ligands (soft bases). In the case of the mixed complexes of HgCyX^{3-} there is an excellent correlation between the polarizability of the ligand and the stability constant of the complex as seen in Figure 6. The polarizability in this case is expressed in terms of the electrode potentials as discussed by Edwards.¹⁵ If the molar refractivity (another measure of polarizability) of the halide ions is used, very similar plots result.

The reaction rate also increases with the halide ion polarizability. The relationship in eq 15 is suggested

$$\log \frac{k}{k_0} = \alpha E_n + \beta H \quad (15)$$

by Edwards¹⁵ where E_n is a measure of polarizability of the nucleophile (electrode potential or molar refractivity) and H is the basicity of the nucleophile. The present reaction can be examined in these terms, although Edwards' correlation is for nucleophilic attack whereas in the present case the anions are already present in the complex and influence the metal-ligand dissociation. The value of β for mercury(II) is very small and with the exception of hydroxide ion none of the anions is a good base. Therefore, the second term in eq 15 can be omitted and the value of $\log(k_H^{\text{HgCyX}}/k_H^{\text{HgCy}})$ can be compared to E_n . The rate constants do not give a good linear plot such as the stability constants, but the halide ions fit the general trend with iodide ion being less effective than expected from its polarizability. However, the thiocyanate ion does not fit at all and is less effective than chloride ion despite the fact that its stability constant falls on the line in Figure 6.

The difference between the thermodynamic and kinetic effects of thiocyanate ion and the halide ions may be due to differences in bonding to mercury such as back bonding from the metal or there may be steric factors in the rate of unwrapping the CyDTA from the mercury. The thiocyanate ion is believed to complex through the sulfur so that the metal-sulfur-carbon

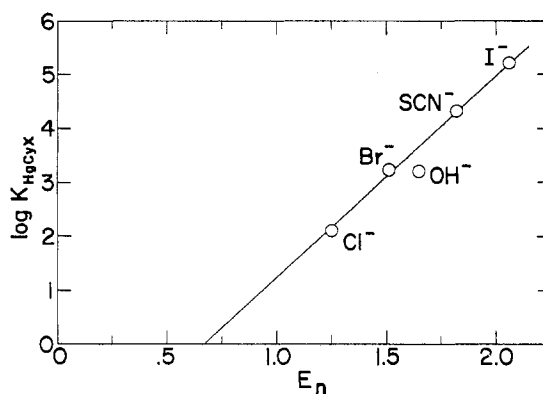


Figure 6.—Correlation of stability constants of mixed complex with polarizabilities. $E_n = E_0 + 2.60$ is used as a function of polarizability; see ref 15.

bonding is not linear, and this has led to effects attributed to steric factors in other complexes.¹⁶ As some of the CyDTA dentate groups break away from the mercury, the thiocyanate ion may make it more difficult for solvent molecules to take their place. This may also occur to a lesser extent with iodide ion where the polarizability is not as effective kinetically as it is thermodynamically. On the other hand, the thiocyanate and halide ions fit into the expected trend in their reaction¹⁷ with CH_3HgOH where steric effects are not as great.

Conclusion

Halide and thiocyanate ions form moderately strong complexes with the mercury-CyDTA complex despite the negative charge of the complex and multidentate character of CyDTA. The stabilities of the resulting complexes increase in a regular fashion with the polarizability of anion. The proton-assisted-dissociation rate of CyDTA from mercury is greatly enhanced by the formation of the anion complexes, and the speed of the reaction also increases with the polarizability of the halide ions. Thiocyanate ion also speeds the dissociation of CyDTA from mercury, but it is not quite as effective as chloride ion. Its kinetic effect does not follow its polarizability, although the thermodynamic stability of HgCySCN^{3-} does correlate with E_n .

Acknowledgment.—The authors wish to thank the National Science Foundation for its support of this research under Grant GP-3406.

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