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Multidentate Ligand Kinetics. VIII. The Effect of Hydroxide, Acetate, and Azide Complexes of Copper(II) in Its Reaction with Ethylenediaminetetraacetate Complexes

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The kinetics of the reaction of copper(II) with the ethylenediaminetetraacetatozincate(II) and -nickelate(II) complexes are studied in the presence of various anions at 25.0° and an ionic strength of 0.10. From pH 5 to 7, the rate of the exchange reaction of Cu^{+2} with Zn-EDTA increased about 10-fold with increase in pH. This is attributed to the reaction of hydroxocopper(II). On the other hand, the azide and acetate ion complexes of Cu(II) reduce the rate of the exchange reaction with Zn-EDTA. The rate of reaction of Cu(II) with Ni-EDTA also is accelerated above pH 5 and the effect is attributed to $CuOH^+$. Thus, in EDTA exchange reactions the kinetic reactivity is $CuOH^+ \gg Cu^{+2} > CuAc^+, CuN_3^+$.

Introduction

Previous papers in this series[1] have dealt with the effect of the bonding of the multidentate ligand in exchange reactions. The structure of the ligand and the ability of segments of the ligand to bond to metal ions have been used to characterize the reaction path. In the present work attention is turned to the metal ion and the kinetic effect of substituting a simple monoanionic complex for the aquo metal ion in the exchange of EDTA between two metals. The reactions studied are

$$Cu^{+2} + ZnY^{-2} \longrightarrow CuY^{-2} + Zn^{+2} \tag{1}$$

$$CuOH^+ + ZnY^{-2} \longrightarrow CuY^{-2} + Zn^{+2} + OH^- \tag{2}$$

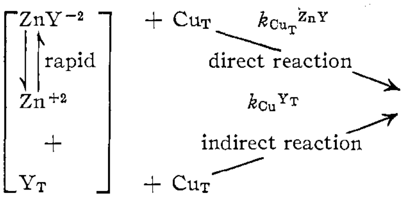
$$CuAc^+ + ZnY^{-2} \longrightarrow CuY^{-2} + Zn^{+2} + Ac^- \tag{3}$$

$$CuN_3^+ + ZnY^{-2} \longrightarrow CuY^{-2} + Zn^{+2} + N_3^- \tag{4}$$

$$CuOH^+ + NiY^{-2} \longrightarrow CuY^{-2} + Ni^{+2} + OH^- \tag{5}$$

In eq. 2 and 5 the reactant is written as $CuOH^+$ although a thorough study by Perrin[2] showed that hydrolyzed copper exists as $Cu_2(OH)_2^{+2}$. However, his copper solutions were greater than 10^{-4} *M* while in the present study many reactions have 10^{-5} *M* copper(II), and, as will be seen, the monomer is more apt to be the reactive species. The exchange of copper with zinc-EDTA previously has been examined in acetate media,[3] where it was assumed that the reaction of the copper acetate species was negligible compared to the reaction of the hydrated metal ion. The present work confirms this assumption but shows that in contrast to the acetate complex the monohydroxocopper(II) complex is much more reactive than the aquo copper ion.

The system studied is



(6)

where ZnY^{-2} is in rapid equilibrium with EDTA compared to the rate of either copper(II) reaction. The term Cu_T refers to all species of Cu(II) not complexed with EDTA, while the term Y_T refers to the sum of the acid forms of EDTA.

The copper exchange with nickel-EDTA is extended[1a] to higher pH at an ionic strength of 0.1 in order to compare the results with the zinc-EDTA reaction.

Experimental Section

The experimental procedures were similar to those reported previously. The temperature was 25.0 ± 0.1° and sodium perchlorate was used to adjust the ionic strength to 0.10 *M* in all cases. Reactions 1, 2, and 5 were followed spectrophotometrically at 260 mμ where ϵ_{CuY} was 3100 and the absorption of the other species was very small. The effect of acidity on the reactions in eq. 6 was examined from pH 4.8 to 7.3. At high pH reaction times were 1 min. or less and reactants were mixed in the cell compartment by a syringe technique. No buffer was needed at lower pH but a borate–mannitol buffer was used above pH 5.7. There was spectrophotometrically observable interaction between copper ($1–3 \times 10^{-5}$ *M*) and mannitol (0.36–0.75%) above pH 6.4, but 95% of this interaction was removed by presence of the borate (a mixture of 2.5×10^{-3} *M* $Na_2B_4O_7$ and 2.5×10^{-3} *M* H_3BO_3). This buffer also was used for reaction 5. Kinetically the concentration of the borate–mannitol buffer had no effect. Reactions 3 and 4 were studied in the presence of excess acetate and azide ions which served as their own buffers.

Results

Copper(II) and Ethylenediaminetetraacetatozincate(II).—The reactions showed first-order dependence in both $[ZnY^{-2}]$ and $[Cu_T]$ and inverse dependence in $[Zn^{+2}]$ below pH 5.7. Excellent second-order plots were obtained in the presence of excess zinc ion under conditions where the reverse reaction in eq. 1 was not appreciable. The reactions were followed over the first 40% completion. Figure 1 shows the variation of the observed rate constant, k_0 (defined in eq. 7 and 8), with pH at three different zinc concentrations. Below pH 5.7, the curves were resolved using eq. 8 where K_{ZnY}' is the conditional stability constant[4] of zinc-EDTA at the

$$d[CuY^{-2}]/dt = k_0[Cu_T][ZnY^{-2}] \tag{7}$$

$$k_0 = k_{Cu}{}^{ZnY} + k_{Cu_T}{}^{Y_T}[Zn^{+2}]K_{ZnY}' \tag{8}$$

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[1] (a) T. J. Bydalek and D. W. Margerum, *J. Am. Chem. Soc.*, **83**, 4326 (1961); (b) D. W. Margerum and T. J. Bydalek, *Inorg. Chem.*, **1**, 852 (1962); (c) D. W. Margerum, D. B. Rorabacher, and J. F. G. Clarke, Jr., *ibid.*, **2**, 667 (1963); (d) T. J. Bydalek and D. W. Margerum, *ibid.*, **2**, 678 (1963); (e) D. W. Margerum and T. J. Bydalek, *ibid.*, **2**, 683 (1963); (f) D. B. Rorabacher and D. W. Margerum, *ibid.*, **3**, 382 (1964).

[2] D. D. Perrin, *J. Chem. Soc.*, 3189 (1960).

[3] K. Kato, *Bull. Chem. Soc. Japan*, **33**, 600 (1960).

[4] A. Ringbom, "Complexation in Analytical Chemistry," Interscience Publishers, New York, N. Y., 1963.

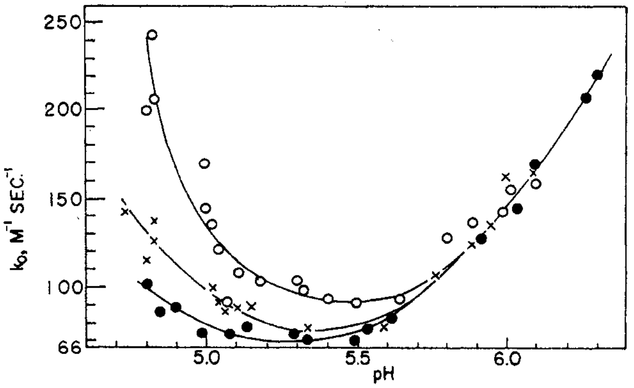


Figure 1.—The effect of pH and $[Zn^{+2}]$ on the observed second-order rate constant for the reaction between copper(II) and ZnY^{-2}: 25.0°, 0.10 μ, $Cu_T = ZnY_T = 1.10 \times 10^{-5}$ *M*; $[Zn^{+2}] = 1.46 \times 10^{-4}$ *M* (open circles), $[Zn^{+2}] = 3.05 \times 10^{-4}$ *M* (crosses), $[Zn^{+2}] = 6.16 \times 10^{-4}$ *M* (solid circles). The curves fit the values of $k_{Cu}{}^{Y_T}$, $k_{Cu_T}{}^{ZnY}$, and the conditional stability constants of ZnY^{-2}.

pH in question. A series of plots was made of k_0 against $1/[Zn^{+2}]$ at different pH values using points taken from the smooth curves drawn through the experimental points. A value of $k_{Cu}{}^{ZnY}$ equal to 67 M^{-1} sec.$^{-1}$ was found from the intercept of eq. 8 over the pH range from 5.0 to 5.4. Values of $k_{Cu}{}^{Y_T}$ were obtained from the slopes of eq. 8 at different pH and were resolved in terms of the acid forms of EDTA giving a value of 1.3×10^9 M^{-1} for the rate constant for the reaction of Cu^{+2} with HY^{-3}. Compared to this reaction, the Cu^{+2} reaction with H_2Y^{-2} was not significant. This is in agreement with the ratio of these rate constants found by Ackermann and Schwarzenbach[5] at 0° in polarographic studies uncorrected for acetate complexation.

Effect of Hydroxide.—At pH values greater than 5.8, the rate was independent of $[Zn^{+2}]$ because K_{ZnY}' (eq. 8) increases with pH and the indirect reaction became negligible. Although there is no significant change in the possible forms of zinc-EDTA in this pH range, the hydrolysis of copper ion begins to become significant[2] and as seen in Figure 1 the observed reaction rate constant increases with pH. The effect is even more striking at higher pH and $k_{Cu_T}{}^{ZnY}$ reaches a value of 2100 M^{-1} sec.$^{-1}$ at pH 7.3. The zinc ion or the pH has been adjusted so that only the direct reaction path is appreciable for the data in Table I. A rate expression including species that might be applicable is given in eq. 9 and some related constants are defined in eq. 10–12.

$$k_{Cu_T}{}^{ZnY}[Cu_T][ZnY^{-2}] = k_{Cu}{}^{ZnY}[Cu^{+2}][ZnY^{-2}] + k_{CuOH}{}^{ZnY}[CuOH^+][ZnY^{-2}] + k_{Cu_2(OH)_2,H}{}^{ZnY}[Cu_2(OH)_2][H^+] \times [ZnY^{-2}] + k_{Cu_2(OH)_2}{}^{ZnY}[Cu_2(OH)_2][ZnY^{-2}] \quad (9)$$

$$[Cu_T] = [Cu^{+2}] + [CuOH^+] + 2(Cu_2(OH)_2{}^{+2}] \quad (10)$$

$$*K_{CuOH} = \frac{[CuOH^+][H^+]}{[Cu^{+2}]} = 10^{-8} \text{ (value uncertain)} \quad (11)$$

$$*\beta_{22} = \frac{[Cu_2(OH)_2{}^{+2}][H^+]^2}{[Cu^{+2}]^2} = 10^{-11.0} \; (\mu = 0.1, 25°)^2 \quad (12)$$

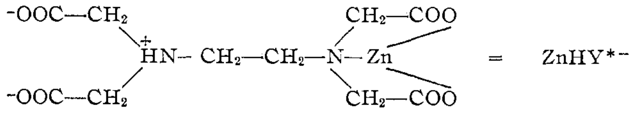
TABLE I

EFFECT OF pH ON $k_{Cu_T}{}^{ZnY}$ AT 25.0°, $\mu = 0.10$

pH	Conditions[a]	$k_{Cu_T}{}^{ZnY}$, M^{-1} sec.$^{-1}$
5.88	B	122
5.91	C	127
5.95	B	136
5.99	A	143
6.00	B	162
6.02	A	155
6.03	C	144
6.09	B	165
6.09	C	168
6.10	A	159
6.27	C	208
6.30	C	220
6.66	D	515
6.80	E	795
7.03	D	1030
7.05	E	1380
7.28	D	1940
7.33	E	2120

[a] Condition (initial concentration of reactants (*M*), added $[Zn^{2+}]$ (*M*): A, 1.1×10^{-1}, 1.46×10^{-4}; B, 1.1×10^{-5}, 3.05×10^{-4}; C, 1.0×10^{-5}, 6.16×10^{-4}; D, 3.0×10^{-5}, 0; E, 1.2×10^{-5}, 0.

According to Pedersen[6] the value of $*K_{CuOH}$ is 10^{-8} while Perrin[2] suggests the value is much less than 10^{-8} but admits his measurements were not sufficiently accurate to assign a new value for the hydrolyzed monomer. Under our reaction conditions the copper ion concentration was varied threefold so that the per cent of dimer varied significantly at the same pH. The reaction rate did not increase with increased dimer concentration but appeared to decrease slightly. Secondly, the reaction rate increased with $1/[H^+]$ and not with $1/[H^+]^2$ as would be required by the last term in eq. 9. Therefore, on both counts this term can be dropped. The next to last term in eq. 9 would correspond to a reaction between $Cu_2(OH)_2{}^{2+}$ and a protonated form of zinc-EDTA. The value of K_{ZnHY} is 10^3 so that $[ZnHY^-]$ is only 0.1 to 0.01% of $[ZnY_T]$ from pH 6 to 7 and is an unlikely reactant. However, if zinc-EDTA must unwrap an iminodiacetate group in order to react as is the case with nickel-EDTA,[7] then the free nitrogen might be protonated.



Thus, a reaction between $Cu_2(OH)_2{}^{2+}$ and $ZnHY^{*-}$ might be imagined that would depend on $1/[H^+]$. However, this would require the protonation constant of ZnY^{*-2} to have a log *K* greater than 8 because ZnY^{*-2} should be much more reactive to copper than $ZnHY^{*-}$. However, the p*K* values of EDTA are 10.26, 6.16, 2.67, etc., and it is most unlikely that ZnY^{*-2} would add a proton so much more readily than HY^{-3}. Therefore, the next to last term on the right-hand side of eq. 9 can be dropped. It does not have the proper

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[5] H. Ackermann and G. Schwarzenbach, *Helv. Chim. Acta*, **35**, 485 (1952).

[6] K. J. Pedersen, *Kgl. Danske Videnskab Selskab*, **20**, 7 (1943).

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

copper dependence and the necessary protonated intermediates are unlikely.

The other terms in eq. 9 fit the observed kinetics. If $^*K_{\mathrm{CuOH}} = 10^{-8}$ then the reactions have from 1 to 10% CuOH^+ between pH 6 and 7 and even if $^*K_{\mathrm{CuOH}} < 10^{-8}$ it is very likely $> 10^{-9}$, so that the $[\mathrm{CuOH}^+]$ would not be unreasonably low for a reactant. Of course, the hydroxide ion could be assigned as ZnYOH^{-3} but Kula[8] reports $K_{\mathrm{ZnOHY}} = [\mathrm{Zn(OH)Y}^{-3}]/[\mathrm{ZnY}^{-2}]\cdot[\mathrm{OH}^-] = 10^{2.0}$. At pH 6 ZnYOH^{-3} would be only 0.0001% of $\mathrm{ZnY_T}$. Similarly, in the metal iminodiacetate complexes hydroxide ion adds to copper but not to zinc.[9]

Finally, the reaction mechanism cannot involve both CuOH^+ and ZnHY^{*-} because in this case there would be no pH effect.

Equation 13, which is plotted in Figure 2, gives the rate constant dependence on copper and hydrogen ion resulting from the remaining terms in eq. 9 combined with eq. 10, 11, and 12, except that the small and unknown correction for the concentration of CuOH^+ in eq. 10 is omitted. Once the dimer forms at high pH

$$k_{\mathrm{Cu_T}}{}^{\mathrm{ZnY}}(1 + 2^*\beta_{22}[\mathrm{Cu}^{+2}]_{\mathrm{i}}/[\mathrm{H}^+]^2) = k_{\mathrm{Cu}}{}^{\mathrm{ZnY}} + k_{\mathrm{CuOH}}{}^{\mathrm{ZnY}}(^*K_{\mathrm{CuOH}}/[\mathrm{H}^+]) \quad (13)$$

it apparently does not dissociate rapidly enough to react with zinc-EDTA, hence the initial concentration of copper, $[\mathrm{Cu}^{+2}]_{\mathrm{i}}$, is used in eq. 13. The intercept in Figure 2 is $k_{\mathrm{Cu}}{}^{\mathrm{ZnY}} = 50\ M^{-1}\ \mathrm{sec.}^{-1}$, in approximate agreement with the value found at pH 5.0–5.4.

The slope in eq. 14 is $k_{\mathrm{CuOH}}{}^{\mathrm{ZnY}}{}^*K_{\mathrm{CuOH}} = 1.1 \times 10^{-4}$ and if $^*K_{\mathrm{CuOH}} < 10^{-8}$, then $k_{\mathrm{CuOH}}{}^{\mathrm{ZnY}} > 10^4\ M^{-1}\ \mathrm{sec.}^{-1}$, which is more than 200 times the value of $k_{\mathrm{Cu}}{}^{\mathrm{ZnY}}$. The alternate assignment corresponding to $k_{\mathrm{Cu}}{}^{\mathrm{ZnYOH}}$ cannot be used because this rate constant would have to be $10^8\ M^{-1}\ \mathrm{sec.}^{-1}$, which is much too large to permit even partial unwrapping[7] of the coordinated EDTA from zinc.

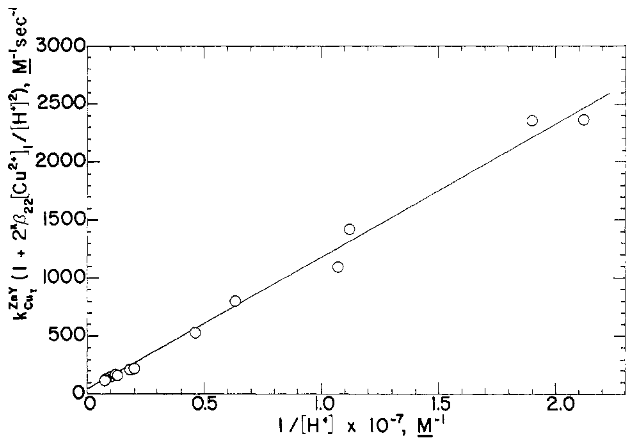

Figure 2.—Resolution of direct reaction rate constant, $k_{\mathrm{Cu_T}}{}^{\mathrm{ZnY}}$, into rate constants for Cu^{+2} and CuOH^+ reaction with ZnY^{-2}. The intercept is $k_{\mathrm{Cu}}{}^{\mathrm{ZnY}}$ and the slope is $k_{\mathrm{CuOH}}{}^{\mathrm{ZnY}}{}^*K_{\mathrm{CuOH}}$ (see eq. 13).

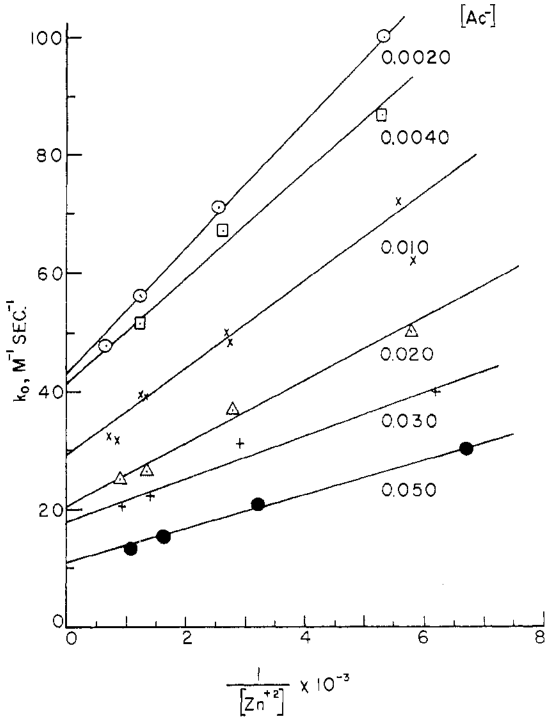

Figure 3.—Effect of acetate ion on the resolution of the observed rate constant into its direct rate constant (intercept = $k_{\mathrm{Cu_T}}{}^{\mathrm{ZnY}}$) and indirect rate constant (slope = $k_{\mathrm{Cu_T}}{}^{\mathrm{Y_T}}/K_{\mathrm{ZnY}}$). The molarity of the acetate ion concentration is shown for each series. The copper acetate complexes can be considered not to react with ZnY^{-2} by comparison to Cu^{+2}; pH 5.02, $\mu = 0.10$, 25.0°.

Effect of Acetate.—The reaction between copper and zinc-EDTA was examined with variation of both acetate and zinc concentrations while maintaining a constant pH of 5.03 with acetic acid. This pH avoided any contribution from CuOH^+ and permitted the effect of CuAc^+ to be measured for both the direct and indirect reaction paths. Figure 3 shows that an increase in acetate concentration suppressed the observed rate constant. This figure also gives the resolution for the direct and indirect reactions as expressed in eq. 8. The acetate concentration was varied from 2 to $50 \times 10^{-3}\ M$ while the zinc concentration was varied from 0.2 to $1.2 \times 10^{-3}\ M$, and the copper concentration was about $10^{-5}\ M$. The zinc acetate complex ($K = 4.6$) was used to give a corrected $[\mathrm{Zn}^{+2}]$ plotted in Figure 3. The reaction was inverse first order in free acetate concentration and the copper acetate complexes react much slower than (by at least a factor of 10) aquocopper ion with ZnY^{-2} or with HY^{-3}. The constants resolved from Figure 3 ($k_{\mathrm{Cu_T}}{}^{\mathrm{ZnY}}$ and $k_{\mathrm{Cu_T}}{}^{\mathrm{Y_T}}$) are given in Table II with corrections for $[\mathrm{Cu_T}]$ to give $k_{\mathrm{Cu}}{}^{\mathrm{ZnY}}$ and $k_{\mathrm{Cu}}{}^{\mathrm{HY}}$. The stability constants[10] for the copper complexes at ionic strength 0.20 and 25.0° were used: $\log K_{\mathrm{CuAc}} = 1.72$, $\log \beta_{\mathrm{CuAc_2}} = 1.97$. At these concentrations the monoacetatocopper(II) complex was the predominant acetate species. The resolved rate constants are consistent with the values obtained without acetate ion, indicating that CuAc^+ is much less reactive than Cu^{+2}.

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[8] R. J. Kula, *Anal. Chem.*, **37**, 989 (1965).

[9] G. Schwarzenbach, G. Anderegg, W. Schneider, and H. Senn, *Helv. Chim. Acta*, **38**, 1147 (1955).

[10] N. Tanaka and K. Kato, *Bull. Chem. Soc. Japan*, **33**, 417 (1960).

TABLE II

Cu_T REACTION WITH ZnY^{-2} IN THE PRESENCE OF ACETATE ION AT 25.0°; μ = 0.10, $[Cu_T]_{initial} = [ZnY^{-2}]_{initial} = 1.10 \times 10^{-5}$

$[Ac^-]$, M	$\frac{k_{Cu_T}^{ZnY} (M^{-1}\ sec.^{-1})}{(1 + K_{CuAc}[Ac^-] + \beta_{CuAc_2}[Ac^-]^2)}$	$\frac{k_{Cu_T}^{HY} (M^{-1}\ sec.^{-1})}{(1 + K_{CuAc}[Ac^-] + [Ac^-]^2)}$
0.0020	47.7	1.47×10^9
0.0040	50.2	1.32×10^9
0.0100	44.8	1.37×10^9
0.0197	42.6	1.34×10^9
0.0296	47.2	1.16×10^9
0.0492	41.6	1.33×10^9

Av. $k_{Cu}^{ZnY} = 47\ M^{-1}\ sec.^{-1}$; av. $k_{Cu}^{HY} = 1.3 \times 10^9\ M^{-1}\ sec.^{-1}$

Effect of Azide.—A study of the CuN_3^+ reaction with ZnY^{-2} was made in a manner similar to the acetate study. The monoazo complex[11] with a stability constant $K_{CuN_3} = 280$ was used. The limited concentration range of azide possible (10^{-5} to $6 \times 10^{-4}\ M$) and the low stability of the copper complex mean that a maximum of only 14% of the copper was complexed. Nevertheless this is sufficient to answer the question of whether or not CuN_3^+ reacts more readily or less readily than Cu^{+2}. Table III lists the results obtained which show (with some minor fluctuations at very low azide concentration) that the rate constants $k_{Cu_T}^{ZnY}$ and $k_{Cu_T}^{Y_T}$ tend to decrease as the azide concentration increases. When these rate constants are corrected for the CuN_3^+ concentration the resulting values are nearly constant. This suggests that only Cu^{+2} is reacting and that by comparison CuN_3^+ has a negligible reaction with ZnY^{-2}.

TABLE III

EFFECT OF AZIDE ION ON THE REACTION RATE CONSTANTS FOR Cu_T WITH ZnY^{-2} AT pH 4.8, 0.10 μ, 25.0°

$[N_3^-]$, M	$k_{Cu_T}^{ZnY}$, M^{-1} sec.$^{-1}$	$k_{Cu_T}^{Y_T}$, M^{-1} sec.$^{-1}$ $\times 10^{-9}$	$\frac{k_{Cu_T}^{ZnY}}{(1 + K_{CuN_3} \cdot [N_3^-])}$ M^{-1} sec.$^{-1}$	$\frac{k_{Cu_T}^{Y_T}}{(1 + K_{CuN_3} \cdot [N_3^-])}$ M^{-1} sec.$^{-1}$ $\times 10^9$
2.0×10^{-5} [a]	55.6	1.43	56.4	1.44
5.5×10^{-5} [a]	59.1	1.24	60.2	1.26
10.7×10^{-5} [a]	57.5	1.13	59.4	1.16
11.7×10^{-5} [b]	50.0	1.32	51.5	1.35
22.8×10^{-5} [b]	50.0	0.98	53.0	1.04
60.2×10^{-5} [b]	44.2	1.14	51.7	1.33

Av. $k_{Cu}^{ZnY} = 55$; av. $k_{Cu}^{Y_T} = 1.3 \times 10^9$

[a] $[Cu_T]_{initial} = [ZnY^{-2}]_{initial} = 1.10 \times 10^{-5}\ M$. [b] $[Cu_T]_{initial} = [ZnY^{-2}]_{initial} = 2.21 \times 10^{-5}\ M$.

Copper(II) and Ethylenediaminetetraacetatonickelate(II).—The exchange reaction between copper ion and nickel-EDTA also is catalyzed above pH 5. The data in Figure 4 at $10^{-4}\ M$ reactants show that the initial effect is very similar to that observed with zinc-EDTA. The same pH behavior was found at $10^{-4}\ M$ copper which cannot be the case if $Cu_2(OH)_2^{+2}$ is the reactant. The ratios of slope/intercept in Figures 2 and 4 are 2.2×10^{-6} for zinc and 0.9×10^{-6} for nickel. When $10^{-3}\ M$ copper and nickel-EDTA are used there is no hydroxide ion effect between pH 5.6 and 6.1 (see Table IV). This is due to a sluggish reaction of nickel-EDTA which must precede its reaction with copper.

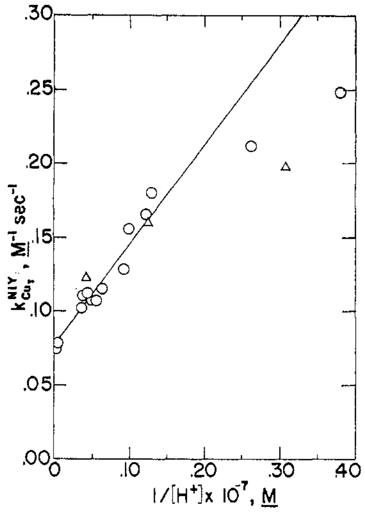

Figure 4.—Resolution of the reaction rate constant, $k_{Cu_T}^{NiY}$ into rate constants for Cu^{+2} and $CuOH^+$ reaction with NiY^{-2}: ○, $10^{-4}\ M$ data; △, $10^{-5}\ M$ data.

The deviation at higher values of $1/[H^+]$ in Figure 4 may be related to the same phenomena but more likely is due to the difficulty in maintaining copper in solution at this high pH. When $10^{-5}\ M$ reactants were used for nickel-EDTA and copper the reaction was exceedingly slow (requiring 1 week for less than 50% reaction) and the results at high pH were erratic—due in part to loss of copper to the walls of the vessels.

TABLE IV

REACTION OF Cu(II) WITH NiY^{-2} AT 25.0°, μ = 0.10

pH	Conditions[a]	k, M^{-1} sec.$^{-1}$	pH	Conditions[a]	k, M^{-1} sec.$^{-1}$
5.49	A	0.044	5.81	A	0.041
5.63	A	0.041	5.81	B	0.045
5.70	A	0.040	5.82	A	0.043
5.73	C	0.045	5.90	C	0.043
5.77	C	0.043	5.98	C	0.044
5.81	C	0.043	6.05	C	0.042

[a] Conditions: A, $1.2 \times 10^{-3}\ M$ reactants; B, $1.5 \times 10^{-3}\ M$ reactants; C, $1.10 \times 10^{-3}\ M\ Cu^{+2}$, $2.50 \times 10^{-3}\ M\ NiY^{-2}$.

Correction for the copper hydroxy dimer in Figure 4 is not given because it is very small. Once again $CuOH^+$ appears to be the reactant.

Discussion

The rate of the reaction between Cu(II) and zinc-EDTA is suppressed by copper acetate and copper azide complexes but is accelerated by increased pH in the region where hydroxide complexes of copper are appreciable. Bydalek[12] has shown that acetate complexes of copper(II) also suppress its reaction with nickel-EDTA. Our initial studies at $10^{-3}\ M$ copper failed to show a pH effect (between pH 5.6 and 6.1) in the reaction with nickel-EDTA.[13] However, a recent study[7] indicates that this was due in large part to a rate-limiting step involving the half-unwrapping of EDTA from nickel. When the copper concentration

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[11] G. Saini and G. Ostacoli, *J. Inorg. Nucl. Chem.*, **8**, 346 (1958).

[12] T. J. Bydalek, *Inorg. Chem.*, **4**, 232 (1965).

[13] D. W. Margerum and B. A. Zabin, Abstracts of Papers, 144th National Meeting of the American Chemical Society, Los Angeles, Calif., 1963, p. 6K.

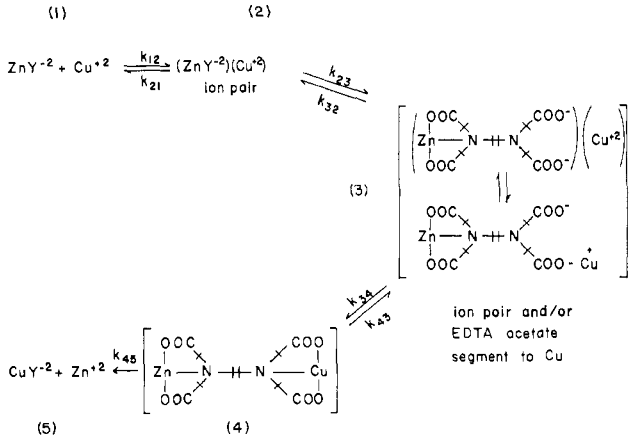


Figure 5.—Proposed mechanism for transfer of EDTA from zinc(II) to copper(II).

is lower (10^{-4} to 10^{-5} *M*) the reaction rate again is copper dependent and there is a similar pH effect for both nickel-EDTA and zinc-EDTA.

It is extremely difficult to assign the pH effect on the rate constants to any phenomenon other than an increasing concentration of a more reactive $CuOH^+$ ion. Copper(II) and its methyliminodiacetate complex both hydrolyze appreciably in this pH range while zinc(II), nickel(II), and their methyliminodiacetate complexes do not.[9] In addition a similar pH effect has been observed for the reaction between Cu(II) and triethylenetetraminenickel(II).[14] Furthermore, we have seen that the pH effects with the nickel- and zinc-EDTA complexes are about the same. But the hydrolysis constants of these EDTA complexes are much different, $10^{0.5}$ and $10^{2.0}$, respectively.[8,15] Thus, the amount of hydroxy species at any given pH differs widely and the acceleration observed would be expected to differ also. Finally, the reaction of Fe(III) and zinc-EDTA has a similar pH effect shifted to lower pH where $FeOH^{+2}$ formation begins, which suggests the pH effect is associated with the reacting metal ion.[16]

A general mechanism for the stepwise unwrapping and transfer of EDTA from nickel to copper has been outlined.[7] A similar mechanism is proposed for zinc-EDTA in Figure 5. Ion-pair association of the reactants is suggested as the first step in the mechanism. This avoids possible diffusion-control limitations because of the very small concentration of half-unwrapped Zn-EDTA. The half-unwrapping of zinc-EDTA is a relatively labile process and the estimated rate constant,[7] k_{23}, is too large to be rate limiting. (This is confirmed by the fact that at lower pH completely dissociated Zn-EDTA contributes to the rate. The half-unwrapping rate is much faster than the full dissociation rate.) Equation 14 results from a steady-state approximation for species 4. However, $k_{45} >> k_{43}$

$$\text{rate} = \frac{k_{34}k_{45}}{k_{43} + k_{45}}[\text{species 3}] \qquad (14)$$

because the dissociation rate constant of zinc from its iminodiacetate complex can be shown to be much greater than the corresponding constant for copper. Thus

$$k_{Cu}^{ZnY} = \frac{[\text{species 3}]}{[Cu^{+2}][ZnY^{-2}]}k_{34} = K_{Cu}'k_{34} \qquad (15)$$

where species 3 is considered in equilibrium with the reactants and K_{Cu}' is its equilibrium constant.

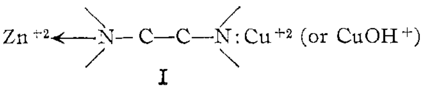
A comparison with the rate constant for the nickel ion reaction with zinc-EDTA[1b] provides one test of this mechanism because step 3, 4 should be rate limiting in both cases, and it is the characteristic water-exchange rate constant for each metal. If species 3 results from

$$\frac{k_{Cu}^{ZnY}}{k_{Ni}^{ZnY}} = \frac{K_{Cu}'k_{Cu}^{-H_2O}}{K_{Ni}'k_{Ni}^{-H_2O}} = \frac{3 \times 10^8 \text{ sec.}^{-1}}{1 \times 10^4 \text{ sec.}^{-1}} = 3 \times 10^4 \qquad (16)$$

ion-pair formation then $K_{Cu}' \cong K_{Ni}'$ and eq. 16 gives the theoretical ratio of rate constants using the characteristic rate of water substitution for each metal.[17] The experimental ratio is 1.5×10^4, which is in excellent agreement. Prior metal bonding to an acetate group of EDTA in species 3 would lead to a larger ratio in eq. 16 because $K_{CuAc} > K_{NiAc}$, but $NiAc^+$ is reported to have a larger water-exchange rate constant than aquo nickel(II).[12] Therefore the ratio of rate constants will not differ greatly for this variation in the mechanism. Unlike the exchange reactions with nickel-EDTA, the experimental ratio $k_{Cu}^{ZnY}/k_{Ni}^{ZnY}$ has no relationship to the ratio of stabilities of the iminodiacetate complexes ($K_{Cu}^{IDA}/K_{Zn}^{IDA}$ is only 190).

Anion complexes of copper could have two opposing effects on the mechanism in Figure 5: (1) The stability of the ion-pair or copper-EDTA segment in species 3 could be lessened. (2) The combined rate of loss of water and nitrogen coordination to copper in step 3, 4 could be increased. For the azide and acetate ions the first factor appears greater than the second, and the net result is a suppression of the reaction rate. On the other hand, hydroxide ion seems to have an enormous effect on the second factor, giving a much faster rate.

The large hydroxide ion effect suggests that $CuOH^+$ loses coordinated water much faster than Cu^{+2} or in some way can react more readily with the accessible nitrogen atom. Electrostatic repulsion between the zinc at one nitrogen atom and the copper near the other nitrogen atom as in I may be important despite



I

the presence of the negative acetate groups. For either an acceleration of water loss or a diminished repulsion between Zn^{+2} and $CuOH^+$, it is clear that hydroxide ion must be acting quite differently from the other anions, neither of which shows such an effect.

If we assign the hydroxide effect entirely to the rate of loss of water from copper(II) then $k_{CuOH}^{-H_2O}$ must be several hundred times larger than $k_{Cu}^{-H_2O}$ because k_{CuOH}^{ZnY} would be this much larger than k_{Cu}^{ZnY} if $^*K_{CuOH}$ equals 10^{-8}. This gives an extraordinarily

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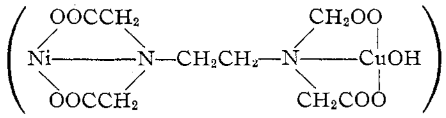
large value (~10^{10} sec.$^{-1}$), which is greater than the characteristic water substitution rate constant of any other metal ion. Only the values for Hg^{+2} and Ba^{+2} are greater than 10^9 sec.$^{-1}$. A constant greater than 10^{10} sec.$^{-1}$ approaches the limiting rate of a first-order transformation.[17] Thus, some but not all of the hydroxide effect might be attributed to an increased water-substitution rate. The accelerating effect of the hydroxo group in coordination compounds was first demonstrated by Brønsted[18a] and has been shown with other cobalt(III) compounds.[18b] It has also been observed with Cr(III)[18c] and with Fe(III).[18d] This increased lability of the hydroxo complexes compared to the aquo complexes is not due simply to the decreased charge of the complex and has been explained in terms of π bonding in the transition state.[18b] However, this is the first evidence to suggest that the rate of ligand loss from a divalent metal ion is strongly affected by hydroxide ion. The effect was not expected for Cu(II) because its H_2O exchange is already extremely rapid.[19,20]

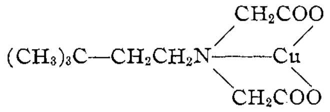
The case for accelerated water loss from $CuOH^+$ is reasonable but runs into another difficulty, namely that a very similar pH effect occurs in the reaction of copper with nickel-EDTA. A great deal of evidence[1] points to the Ni–N bond dissociation rather than Cu–N bond formation as the rate-determining step. The relative reaction rates of Zn^{+2}, Cu^{+2}, Ni^{+2}, H^+, and Fe^{+3} with nickel-EDTA correspond to the stability constants of their iminodiacetate complexes. Thus, unlike the situation with Zn-EDTA, a more labile copper ion should make little difference. On the other hand, the stability constant of $CuOH^+$ with the iminodiacetate segment would be important. Rather unexpectedly, $CuOH^+$ forms complexes nearly as stable as does Cu^{+2} with iminodiacetate, polyamines, bipyridyl, etc. This can be shown from the copper hydrolysis constant of methyliminodiacetate.[9] According to the proposed mechanism[7] $CuOH^+$ must cause a 10^2 to 10^3 decreased repulsion between nickel and copper in intermediate II.

$$\frac{K_{\mathrm{CuL}}}{K_{\mathrm{CuOHL}}} \gtreqless 10^{0.89} \text{ for } K_{\mathrm{CuOH}} \leqq 10^{-8} \qquad (17)$$

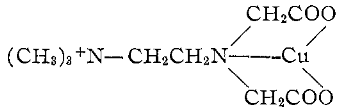


II

Repulsion between charges associated with the nitrogen atoms in EDTA and similar compounds is of appreciable magnitude. The two nitrogen protonation constants in EDTA differ by 4 pK units. For compounds III and IV, Δ log K_{Cu} is 3.76.[9] Thus, a very large repulsion between Cu^{+2} and Ni^{+2} in II might be reduced by hydroxide ion.



III



IV

The anomaly is that the pH effect is so very similar for the copper reaction with zinc-EDTA and nickel-EDTA. In the former case bond formation to copper and in the latter bond dissociation of nickel appear to be rate determining. This suggests that the repulsion is so great in a species such as I that it may be a transition state rather than an intermediate. For nickel the transition state may be closer to the products and for zinc it may be closer to the reactants. Hydroxide ion need not even form a stable $CuOH^+$ entity and still could enter into the transition state. A more complete explanation undoubtedly involves the remarkable stability of the $CuOH^+$ complexes with nitrogen donors. In any case this work clearly shows that for copper and metal-EDTA exchange reactions, hydroxide ion exerts a special effect not found with acetate and azide ions.

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