

4,¹² w^* is then $(t - s - 4)$. If both the substrate and the transition state have the same degree of hydration, $(t - s)$ is 0 and w^* is -4 , close to the observed values of -3.7 and -4.4 .

Bunnett's ideas⁴ about acid hydrolysis reactions have proved very useful as empirical indicators of mechanism in the present study. Whether the theory^{4c} relating w and w^* values exclusively to hydration changes is correct is not clear at this time. In fact many properties of concentrated acid solutions are related, so that separation of the various factors may be difficult. For example, in this work, fairly good correlations were found between the $\log k_1$ and $\log a_{\text{HCl}}$, where a_{HCl} is the activity of hydrochloric acid, for hydrolysis of *trans*-

(12) K. E. Howlett, *Sci. Progr.*, **53**, 305, 1965, discusses this question.

[Co(en)₂(NO₂)₂]⁺ in this acid. Some caution is necessary in ascribing changes in rate to one factor exclusively.

The effect of the various ligands on the rate of hydrolysis as shown in Table I is not profound, which in itself is quite surprising considering the variety of ligands represented. Any detailed discussion of the relation between structural variation and mechanism, however, cannot be developed at this time.

In conclusion, it is heartening to find that, in general, these results support the mechanism postulated for the acid hydrolysis of *trans*-[Co(en)₂(NO₂)₂]⁺ in a variety of acids and suggest that the Bunnett relations may be useful indicators of mechanism for reactions such as these. The extent to which these relations is valid can be established only by further work.

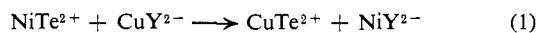
Coordination Chain Reactions. II. The Ligand-Exchange Reaction of Tetraethylenepentaminenickel(II) and Ethylenediaminetetraacetatocuprate(II)

Dale W. Margerum and J. D. Carr

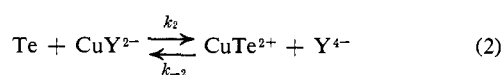
Contribution from the Department of Chemistry, Purdue University, Lafayette, Indiana. Received December 6, 1965

Abstract: The reaction between copper-EDTA and nickel-tetren to produce copper-tetren and nickel-EDTA is catalyzed by traces of either uncomplexed EDTA or tetren and is inhibited by traces of metal ion. A chain-reaction mechanism is proposed where the chain-propagating steps are the reaction of tetren with copper-EDTA and the reaction of EDTA with nickel-tetren. The pH profile of each chain-propagating step is established and used to explain the kinetic behavior in terms of the effect of pH, temperature, reversibility of a propagation step, switch of rate-determining steps, and pseudo-zero-order reactions.

The double ligand-exchange reaction between tetraethylenepentaminenickel(II)¹ and ethylenediaminetetraacetatocuprate(II), shown in eq 1, is thermodynamically favorable but is kinetically sluggish. It is



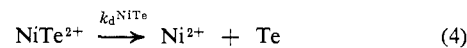
catalyzed by traces of either tetren or EDTA and is inhibited by traces of metal ions. These are the same properties exhibited by the similar exchange between nickel-trien and copper-EDTA which was shown to proceed by a chain-reaction mechanism.² The present work continues the study of coordination chain reactions and the effect which an increase in the dentate number of the polyamine has on the kinetics. The chain-propagating steps (eq 2 and 3 with protons



(1) Abbreviations used are: Te or tetren, tetraethylenepentamine; T or trien, triethylenetetramine; Y⁴⁻ or EDTA, ethylenediaminetetraacetate ion.

(2) D. C. Olson and D. W. Margerum, *J. Am. Chem. Soc.*, **85**, 297 (1963).

omitted) parallel those for trien but the values of the rate constants and their pH dependence are altered using tetren. The tetren chain reaction is of interest for several reasons. (1) The rate of dissociation of nickel-tetren (eq 4) is very much slower than that of nickel-



trien,³ and a higher chain length (rate of propagation/rate of initiation) is possible for the exchange reaction. The greater the chain length, the greater the possible sensitivity to traces of ligands or metals. (2) The nickel-tetren complex is more stable thermodynamically and can be used at lower pH than in the case with nickel-trien. (3) The kinetic effect of the reversibility of a chain-propagating step (eq 2) can be studied. Conditional stability constants⁴ were calculated from the appropriate stability constants⁵ for each complex from pH 4 to 13, and these constants are combined to

(3) D. W. Margerum, D. B. Rorabacher, and J. F. G. Clarke, Jr., *Inorg. Chem.*, **2**, 667 (1963).

(4) A. Ringbom, "Complexation in Analytical Chemistry," Interscience Publishers Inc., New York, N. Y., 1963, pp 38-56.

(5) (a) G. Schwarzenbach, R. Gut, and G. Anderegg, *Helv. Chim. Acta*, **37**, 937 (1954); (b) R. A. Cave and L. A. K. Stavely, *J. Chem. Soc.*, 4571 (1956); (c) P. Paoletti, A. Vacca, and I. Giusti, *Ric. Sci. Rend.*, **A33**, 523 (1963); (d) C. N. Reilly and J. H. Holloway, *J. Am. Chem. Soc.*, **80**, 2917 (1958).

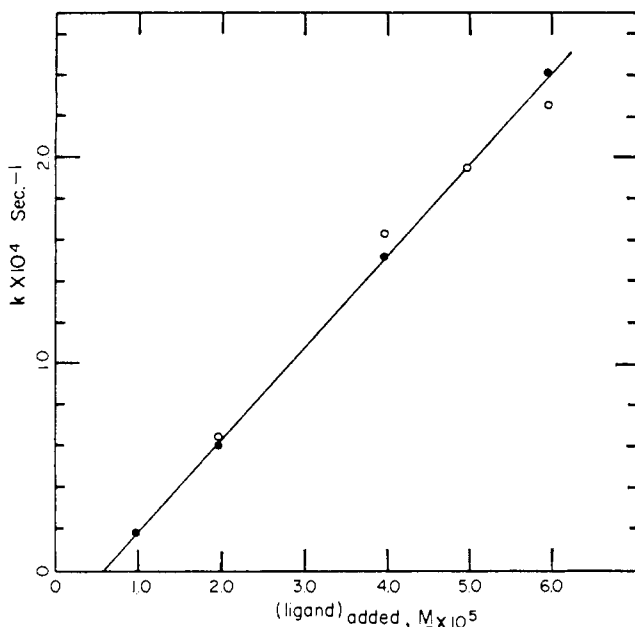


Figure 1. The effect of added free ligand on the observed pseudo-first-order rate constant for the exchange of nickel-tetren and copper-EDTA: $[\text{NiTe}]_0 = 2.38 \times 10^{-4} M$, $[\text{CuY}]_0 = 5.90 \times 10^{-3} M$ (pH 7.48, 25.0° , $\mu = 0.05$); \circ , catalysis by tetren; \bullet , catalysis by EDTA.

give the conditional equilibrium constants for reactions 1, 2, and 3 at each pH in Table I. Although the overall exchange reaction, with a $-\Delta G^\circ$ value of 6–7 kcal/mole, favors product formation at all pH values, one of the chain-propagating steps (eq 2) is very unfavorable thermodynamically at low pH.

Table I. Equilibrium Constants for the Over-all Exchange Reaction and for Each Chain-Propagation Step

pH	Log K_1 (over-all exchange)	Log K_2	Log K_3
4.0	4.54	-2.18	6.72
5.0	4.40	-1.51	5.91
6.0	4.61	-0.60	5.21
7.0	4.77	0.99	3.78
8.0	4.80	2.73	2.07
9.0	4.80	3.91	0.89
10.0	4.80	4.21	0.59
11.0	4.80	4.05	0.75
12.0	4.80	4.01	0.79
13.0	4.80	4.00	0.80

Experimental Section

A standard copper nitrate solution was prepared from copper wire and used to prepare the copper-EDTA solution and to standardize tetren and EDTA solutions.

Tetren and nickel-tetren were prepared as described previously.³ Throughout the experiments, precautions were taken to avoid the introduction of trace metal ion or ligand impurities into any reagent solution.² Constant ionic strength was maintained with KCl. A 0.005 to 0.01 *M* sodium borate-boric acid or mannitol-boric acid buffer system was used for pH control.

The exchange reaction in eq 1 was followed spectrophotometrically (550 *mμ*) in 10-cm cells thermostated to $\pm 0.1^\circ$. In the reactions used to determine the pH profile of the exchange rate, the initial copper-EDTA concentration was $4.70 \times 10^{-3} M$, a 20-fold excess over the initial concentration of nickel-tetren. Reactions were catalyzed with $0.2\text{--}7.0 \times 10^{-5} M$ EDTA to increase the rates of reaction in eq 2 and 3 and to eliminate any possible kinetic effects

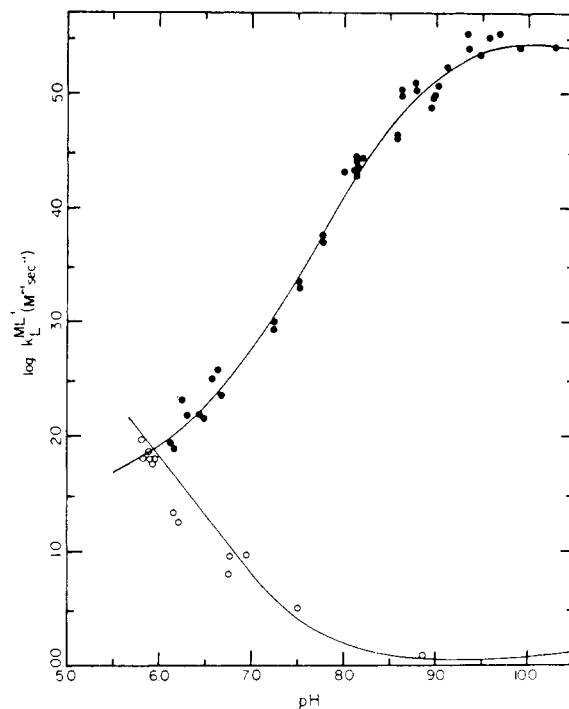


Figure 2. The pH profiles of the chain-propagating steps (25.0° , $\mu = 0.1$): \circ , k_L^{ML} was measured by the chain reaction and follows k_3 ; \bullet , k_2 was measured by stopped-flow techniques. The solid lines are best fits for k_2 and k_3 determined independently of the chain reaction.

due to the rate of dissociation of nickel-tetren or of copper-EDTA. Under these conditions the rate expression above pH 6.5 simplifies to eq 5, and excellent first-order plots were obtained for which the

$$\text{rate} = \frac{d[\text{CuTe}^{2+}]}{dt} = k_0[\text{NiTe}^{2+}] \quad (5)$$

value of the observed first-order rate constant, k_0 , depends on the concentration of the free EDTA catalyst present (eq 6). Figure 1

$$k_0 = k_Y^{\text{NiTe}}[\text{Y}] \quad (6)$$

shows a plot of k_0 against the concentration of added EDTA which was used to obtain a value for k_Y^{NiTe} at pH 7.5. The intercept corresponds to the slight amount of free metal ion present in the reagents.⁵ The values of k_L^{ML} determined for the coordination chain reaction were obtained from slopes of similar plots.

The direct reaction of tetren with copper-EDTA was studied using a stopped-flow apparatus similar to a design of Sturtevant.⁶ The mixing cell had a 0.20-cm light path and was attached to a Beckman DU spectrophotometer. The photomultiplier signal was amplified and opposed by a voltage from a mercury battery source so that a selected portion of the percent transmittance could be observed on a Tektronix 564 storage oscilloscope. The stored image was photographed on Polaroid film. Half-lives of reactions measured using the stopped-flow technique ranged from 10 to 300 msec.

The reactions of tetren and copper-EDTA were run under a variety of concentration ratios and levels including equal initial concentrations at both 2.97×10^{-3} and $9.85 \times 10^{-5} M$ and with a large excess of tetren to give pseudo-first-order reactions. These latter reactions were carried out with $[\text{CuY}^{2-}]_0 = 9.85 \times 10^{-5}$, $[\text{Te}]_0 = 2.96 \times 10^{-3}$, and $[\text{CuY}^{2-}]_0 = 2.97 \times 10^{-3}$, $[\text{Te}]_0 = 9.75 \times 10^{-2} M$. All of these conditions were used to establish the pH profile (Figure 2) from pH 6.1 to 10.3. The excellent agreement of the rate constants observed in the different concentration situations shows that reaction 2 is first order in each reactant and second order over-all.

(6) J. M. Sturtevant in "Rapid Mixing and Sampling Techniques in Biochemistry," B. Chance, *et al.*, Ed., Academic Press Inc., New York, N. Y., 1964, p 89.

Rate constants for second-order, equal-concentration situations in the pH range for which reversibility of reaction 2 is significant were calculated from eq 7⁷ using an IBM 7094 computer.

$$Z = \frac{\ln \left[\frac{[\text{CuTe}][\text{CuY}]_0 - 2[\text{CuTe}]_e + [\text{CuY}]_0[\text{CuTe}]_e}{[\text{CuY}]_0([\text{CuTe}]_e - [\text{CuTe}])} \right]}{\left[\frac{2[\text{CuY}]_0([\text{CuY}]_0 - [\text{CuTe}]_e)}{[\text{CuTe}]_e} \right]} = k_2 t \quad (7)$$

Excellent linear plots of Z against time indicated that the reverse reaction was second order as expected and that the rate expression in eq 8 was valid.

$$\text{rate} = \frac{d[\text{CuTe}^{2+}]}{dt} = k_2[\text{Te}][\text{CuY}^{2-}] - k_{-2}[\text{Y}][\text{CuTe}^{2+}] \quad (8)$$

The forward rate constant of reaction 2 was resolved into individual proton dependent terms to fit eq 9 where the pK_a values for HTe^+ , H_2Te^{2+} , and H_3Te^{3+} are 10.0, 9.2, and 8.2, respectively^{8d} (H_4Te^{4+} has a pK_a of 4.1 and need not be considered in this pH range). These calculations were performed with an IBM 7094

$$w = k_2 \left(1 + \frac{[\text{H}^+]}{K_{\text{HTe}}} + \frac{[\text{H}^+]^2}{K_{\text{HTe}}K_{\text{H}_2\text{Te}}} + \frac{[\text{H}^+]^3}{K_{\text{HTe}}K_{\text{H}_2\text{Te}}K_{\text{H}_3\text{Te}}} \right) = k_{\text{Te}}^{\text{CuY}} + k_{\text{HTe}}^{\text{CuY}} \left(\frac{[\text{H}^+]}{K_{\text{HTe}}} \right) + k_{\text{H}_2\text{Te}}^{\text{CuY}} \left(\frac{[\text{H}^+]^2}{K_{\text{HTe}}K_{\text{H}_2\text{Te}}} \right) + k_{\text{H}_3\text{Te}}^{\text{CuY}} \left(\frac{[\text{H}^+]^3}{K_{\text{HTe}}K_{\text{H}_2\text{Te}}K_{\text{H}_3\text{Te}}} \right) \quad (9)$$

computer using a weighted regression analysis program.⁸ Weighting of the data was necessary because the standard deviation of the observed rate constant is not constant throughout the pH range, but rather is proportional to the observed rate constant. The term $1/w^2$ was used as the weighting factor in the regression analysis in order to give a statistical agreement with the relative experimental error of the rate constants which is approximately constant throughout the pH range.

Results and Discussion

Tetren with Copper-EDTA and EDTA with Nickel-tetren. The rate of reaction 2 was measured independently of the chain reaction using stopped-flow techniques as discussed. Table II gives the experimental values of the equilibrium constant, K_2 , determined by the extent of reversibility observed in the

Table II. Experimental Equilibrium Constants for Reaction 2 (25.0°, 0.10 M KCl)

pH	K_2^a
6.12	0.076
6.17	0.064
6.30	0.365
6.43	0.285
6.48	0.259
6.68	0.582
7.60	33.6
8.00	132

^a Values of K_2 calculated from the values in Table I are larger by a factor of 5, but they were obtained from a combination of results of different workers and not all at the exact conditions used here.

(7) A. A. Frost and R. G. Pearson, "Kinetics and Mechanism," 3rd ed, John Wiley and Sons, Inc., New York, N. Y., 1961, p 188.

(8) This program was obtained from D. Fimble, Sandia Corp., Albuquerque, N. M., and was adapted for the present study as shown by J. D. Carr, Ph.D. Thesis, Purdue University, 1966.

kinetic runs. There are some differences between the observed K_2 values and those calculated in Table I, but the change with pH is consistent. The calculated values used stability constants obtained by different workers under differing experimental conditions. Our data showed no evidence of any mixed complexes and are the results of direct competition of the ligands for copper.

The upper curve in Figure 2 gives the pH profile of the second-order rate constant, k_2 , which increases by a factor of 20,000 from pH 6 to 10 as the tetren becomes less protonated. The curve drawn through the experimental points was fitted from the resolved rates constants which were $k_{\text{Te}}^{\text{CuY}} = 2.2 \times 10^5$, $k_{\text{HTe}}^{\text{CuY}} = 3.7 \times 10^5$, $k_{\text{H}_2\text{Te}}^{\text{CuY}} = 6.7 \times 10^3$, and $k_{\text{H}_3\text{Te}}^{\text{CuY}} = 34 M^{-1} \text{sec}^{-1}$. Another report⁹ discusses the significance of the values for these rate constants as well as those for other polyamine reactions with metal complexes of EDTA and derivatives.

Figure 2 also includes the pH profile for k_3 (or $k_{\text{Y}}^{\text{NiTe}}$) which was obtained earlier¹⁰ by direct reaction of EDTA with nickel-tetren.

After a steady state has been achieved under the chain-reaction conditions the two chain-propagating steps (eq 2 and 3) must proceed at the same rate, but one of the two still is rate limiting. Figure 2 shows that at pH 6 the rate constants k_2 and k_3 are nearly equal but that above this pH, reaction 3 is clearly the rate-limiting reaction. The ratio of the two rate constants reaches a maximum ($k_2/k_3 = 3 \times 10^5$) at pH 10.

Chain Reaction above pH 6.5. The exchange reaction in eq 1 fits the rate expressions in eq 5 and 6 with a first-order dependence in nickel-tetren concentration and a first-order dependence in added ligand concentration. Figure 1 shows that it makes no difference whether EDTA or tetren is initially added to catalyze the reaction. Both ligands act identically after the short time necessary to establish a steady-state condition with reactions 2 and 3. Table III includes three sets of data at 0.05 M ionic strength with the rate con-

Table III. Second-Order Rate Constants Obtained from Varying Nickel-tetren and Trace EDTA Show No Dependence upon Copper EDTA (25.0°, $\mu = 0.05$, $[\text{EDTA}]_{\text{added}} = 1.0\text{--}6.0 \times 10^{-5} M$)

pH	$[\text{NiTe}]_0$, M $\times 10^4$	$[\text{CuY}]_0$, M $\times 10^4$	$k_3 = k_{\text{Y}}^{\text{NiTe}}$, $M^{-1} \text{sec}^{-1}$
7.47	2.38	59.0	4.5
7.50	3.57	59.0	4.4
7.57	2.38	29.5	4.7

stant k_3 determined in each case from the slope of a graph similar to Figure 1. Within the experimental error there is zero-order dependence in the copper-EDTA concentration and a first-order dependence in EDTA and in nickel-tetren. Figure 2 shows experimental points for $k_{\text{L}}^{\text{ML}'}$ at 0.1 M ionic strength determined in a similar manner. These experimental points for the exchange reaction follow closely the previously determined values for $k_{\text{Y}}^{\text{NiTe}}$. Thus, reactions 2 and 3 are the chain-propagating steps as expected and reaction 3 is rate limiting.

(9) J. D. Carr, R. A. Libby, and D. W. Margerum, to be published.

(10) D. B. Rorabacher and D. W. Margerum, *Inorg. Chem.*, **3**, 382 (1964).

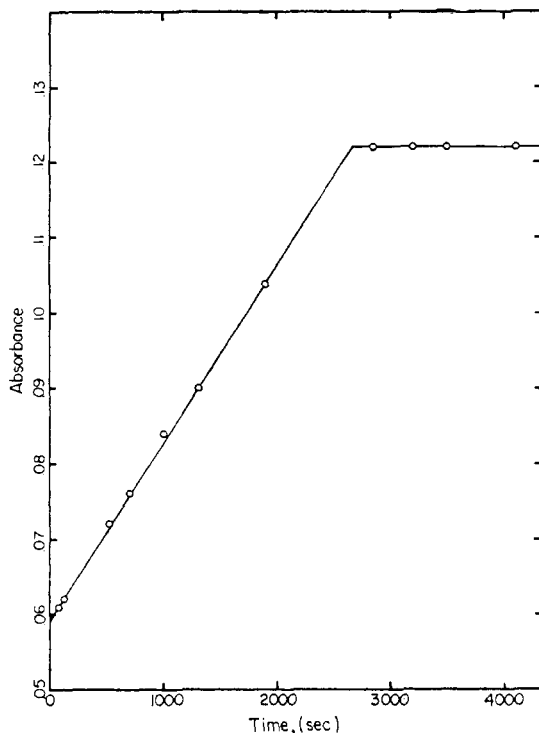


Figure 3. Pseudo-zero-order chain reaction: $[\text{NiTe}]_0 = 1.10 \times 10^{-2} M$, $[\text{CuY}]_0 = 4.50 \times 10^{-4} M$, $[\text{EDTA}]_{\text{added}} = 4.23 \times 10^{-5} M$ (25.0°, pH 9.20, $\mu = 0.10$, 600 μm , 1.0-cm cells).

Pseudo-Zero-Order Chain Reaction. The difference in the rate constants k_2 and k_3 is so large above pH 8 that reaction 3 still may be the rate-limiting step when nickel-tetren is present in large excess over copper-EDTA. Figure 3 shows that the absorbance of products increasing linearly with time at pH 9.2 with a 25-fold excess of nickel-tetren over copper-EDTA. This zero-order plot fits eq 5 and 6 because neither the EDTA concentration nor the nickel-tetren concentrations change appreciably during the reaction. The reaction stops abruptly when the last of the copper-EDTA has reacted.

The higher concentration of nickel-tetren has the advantage of speeding up the otherwise quite slow exchange reaction and giving the simplest possible kinetic form. These are important points in possible applications of the chain reaction to trace analysis. Pseudo-zero-order behavior will not deviate more than 5% for the first 2 half-lives of the reaction if $[\text{NiTe}^{2+}]_0/[\text{CuY}^{2-}]_0 \geq 20$ and if $k_2/k_3 \geq 1600$.

Chain Reaction at Low pH. In Figure 2 the experimental points for the chain reaction below pH 6.5 were obtained by a method of initial slopes because as the reaction progressed it was no longer simple first order. Thus, reactions which formed 50% of the products in 10 min would in some cases require several days for 99% of the products to be formed. Figure 4 shows one reaction plotted with good first-order behavior at pH 7.5 and one with severe deviation at pH 5.8. The primary reason for this behavior is product inhibition due to the reversibility of reaction 2, but the possible switch in the rate-determining step around pH 6 also makes it difficult to obtain simple kinetic behavior.

Effect of Reversibility and of a Switch in the Rate-Determining Step. Table I indicates that the over-all exchange in eq 1 is thermodynamically favored to

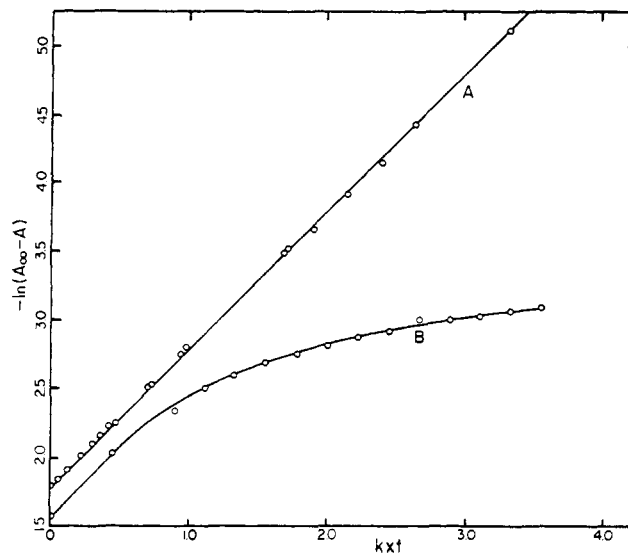


Figure 4. Effect of reversibility on rate of exchange reaction: (A) $[\text{CuY}]_0 = 5.90 \times 10^{-3} M$, $[\text{NiTe}]_0 = 2.38 \times 10^{-4} M$, $[\text{EDTA}]_{\text{added}} = 5.94 \times 10^{-5} M$ ($\mu = 0.10$, pH 7.49); (B) $[\text{CuY}]_0 = 4.73 \times 10^{-3} M$, $[\text{NiTe}]_0 = 2.38 \times 10^{-4} M$, $[\text{EDTA}]_{\text{added}} = 5.94 \times 10^{-5} M$ ($\mu = 0.10$, pH 5.80). The abscissa is shown as the dimensionless quantity $k \times t$ in order that the reactions might be compared on the same scale.

proceed far to the right at all pH values, but that the chain-propagation reaction in eq 2 favors the reactants at low pH. The resulting reversibility of eq 2 leads to a kinetic competition for EDTA by nickel-tetren and copper-tetren. Thus the product of the exchange reaction can suppress its own rate of formation even though the over-all exchange reaction is not significantly reversible.

If even a trace of free ligand has been added to the reaction system, reactions 2 and 3 will produce all the products. These two reactions are coupled and the rate of product formation from each must be equal, regardless of which of the two is rate limiting. Equation 10 and the definition of total free ligand in eq 11 lead to eq 12.

$$\frac{d[\text{NiY}^{2-}]}{dt} = \frac{d[\text{CuTe}^{2+}]}{dt} = k_3[\text{Y}][\text{NiTe}^{2+}] = k_2[\text{Te}][\text{CuY}^{2-}] - k_{-2}[\text{Y}][\text{CuTe}^{2+}] \quad (10)$$

$$[\text{L}]_{\text{T}} = [\text{Te}] + [\text{Y}] \quad (11)$$

$$\frac{\text{rate}}{[\text{L}]_{\text{T}}} = \frac{k_2 k_3 [\text{CuY}^{2-}][\text{NiTe}^{2+}]}{k_2 [\text{CuY}^{2-}] + k_{-2} [\text{CuTe}^{2+}] + k_3 [\text{NiTe}^{2+}]} \quad (12)$$

At high pH $k_2[\text{CuY}^{2-}]$ is much greater than $k_{-2}[\text{CuTe}^{2+}]$ and $k_3[\text{NiTe}^{2+}]$, and eq 12 simplifies to the form used in eq 5 and 6.

At low pH all three terms in the denominator of eq 12 can contribute to the rate expression. Thus, for the reaction B in Figure 4 the relative rates of these terms at 50% reaction are $k_2[\text{CuY}^{2-}] : k_{-2}[\text{CuTe}^{2+}] : k_3[\text{NiTe}^{2+}]$ are 23:3.6:1.0, and, despite the fact that a 20-fold excess of copper-EDTA is present, the reaction rate is suppressed by the formation of copper-tetren. The ratios of these terms indicate that reaction 3 is still the main rate-limiting step under these reaction conditions.

In Figure 5 reaction C also was at low pH but had a 30-fold excess of nickel-tetren over copper-EDTA.

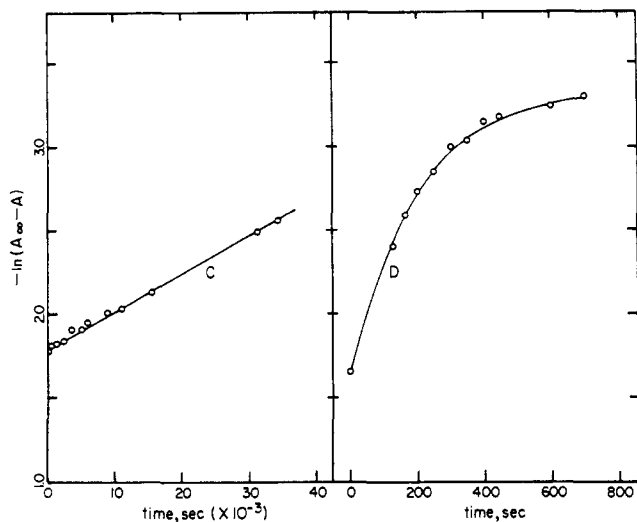


Figure 5. Effect of concentration ratios changing the rate-limiting step at pH 6.1, 25.0°: (C) $[\text{CuY}]_0 = 1.97 \times 10^{-4} M$, $[\text{NiTe}]_0 = 5.95 \times 10^{-3} M$, $[\text{EDTA}]_{\text{added}} = 2 \times 10^{-7} M$ ($\mu = 0.10$, pH 6.12): (D) $[\text{CuY}]_0 = 4.73 \times 10^{-3} M$, $[\text{NiTe}]_0 = 9.86 \times 10^{-5} M$, $[\text{EDTA}]_{\text{added}} = 5.92 \times 10^{-5} M$ ($\mu = 0.01$, pH 6.09).

As a result, $k_3[\text{NiTe}^{2+}] \gg (k_2[\text{CuY}^{2-}] + k_{-2}[\text{CuTe}^{2+}])$ and eq 12 simplifies to eq 13 which gives a first-order plot. (Actually, the other two terms are calculated to

$$\frac{\text{rate}}{[\text{L}]_T} \cong k_2[\text{CuY}^{2-}] \quad (13)$$

contribute from 5% initially to 10% after 2 half-lives.) Reaction D in Figure 5 was at the same pH as reaction C but did not have sufficient nickel-tetren to force reaction 2 to be rate limiting, and as a result all three terms in the denominator of eq 12 again contribute and a complicated rate dependence results.

In general the reversibility of one of the chain-propagating steps will be more apt to lead to product suppression of the exchange rate if this step is not rate limiting. When the reversible step also is the rate-limiting step, first-order kinetics can be achieved more easily (*i.e.*, curve C in Figure 5).

Reactions run under conditions which result in a switch in the rate-limiting step as the reaction progresses will give a complicated rate expression whether reversibility is a factor or not. This will be the case if unequal concentrations of copper-EDTA and nickel-tetren are used but neither is in large excess and the reaction is run at a pH for which the rate constants of the two chain-propagation steps are nearly equal. This effect without the complication of reversibility has been observed in other coordination chain-reaction systems.^{5,11}

Temperature Study. At pH 7.5 the exchange rate increases about threefold for a temperature change of 25 to 40°. An Arrhenius plot is given in Figure 6, which includes rate constants from the direct study¹² of reaction 3. Other temperature studies of the NiTe-CuY chain reaction between pH 6 and 8 under conditions for which reaction 3 is rate limiting gave good agreement with the results of the direct study. Table IV gives Arrhenius parameters for the resolved

(11) Paper III: J. D. Carr and D. W. Margerum, *J. Am. Chem. Soc.*, **88**, 1645 (1966).

(12) D. B. Rorabacher, Ph.D. Thesis, Purdue University, Lafayette, Ind., 1963.

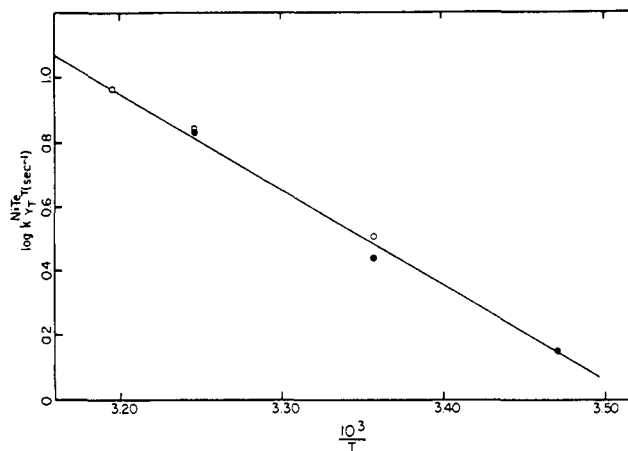


Figure 6. Arrhenius plot of the chain reaction at pH 7.50: O, chain reaction values for $k_L^{\text{ML}'}$ ($[\text{CuY}] = 4.73 \times 10^{-3} M$, $[\text{NiTe}] = 2.38 \times 10^{-4} M$, $\mu = 0.10$); ●, direct study of reaction 3.¹²

rate constants.¹² The large values of E_a suggest a much higher temperature dependence than is observed in Figure 6, but the temperature dependence of the acidity constants of EDTA are an opposing factor. For this reason the exchange reaction rate should have greater sensitivity to temperature changes at pH 10–11.

Table IV. Arrhenius Parameters of Reaction 3 and Temperature Dependence of Acidity Constants of EDTA

	Arrhenius parameters		
	E_{a3} , kcal/mole		Log A, sec ⁻¹
$k_{\text{HY}}^{\text{NiTe}}$	15.8		11.7
$k_{\text{H}_2\text{Y}}^{\text{NiTe}}$	19.6		16.0
$k_{\text{H}_3\text{Y}}^{\text{NiTe}}$	17.8		13.4
Acidity constant	15°	25°	35°
$\text{p}K_{\text{H}_4\text{Y}}$	1.99	1.99	1.99
$\text{p}K_{\text{H}_3\text{Y}}$	2.65	2.69	2.72
$\text{p}K_{\text{H}_2\text{Y}}$	6.22	6.10	6.00
$\text{p}K_{\text{HY}}$	10.33	10.19	10.05

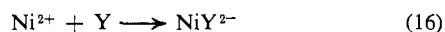
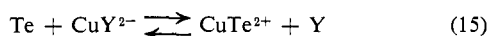
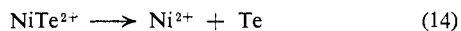
Conclusions

The exchange reaction between nickel-tetren and copper-EDTA has the kinetic sensitivity to traces of free EDTA or free tetren which is characteristic of the previously reported coordination chain reaction. The pH and temperature dependencies of the exchange reaction rate above pH 6 closely follow those of the EDTA reaction with nickel-tetren, demonstrating that reaction 3 is the rate-limiting chain-propagation step. All of the kinetic evidence including the effects of reversibility, switch of rate-determining steps, pseudo-zero-order reactions, and the effect of addition of trace ligands are consistent with the assignment of this exchange reaction as the second example of a coordination chain-reaction system.

The nickel-tetren chain-reaction system is more sluggish than the corresponding nickel-trien system. Reactions run with the same reactant concentrations and an EDTA concentration of $5 \times 10^{-6} M$ at pH 7.4 (25.0°, $\mu = 0.10$) give half-times of 1200 and 8.5 min, respectively. This difference in reaction rates is

explained by the large difference in the values of the rate constants k_Y^{NiTe} and k_Y^{NiT} . The difference becomes even greater at higher pH because k_Y^{NiTe} decreases (Figure 1) and k_Y^{NiT} increases above pH 8.¹⁰ Thus, the more sluggish chain-reaction rate is a direct consequence of the slower EDTA displacement of tetren from nickel(II). On the other hand, the rate constants of the fast chain-propagating steps, polyamine displacement of EDTA from copper(II), do not show much difference for the two reactions. The values for $k_{\text{Te}^{\text{CuY}}}$ and $k_{\text{T}^{\text{CuY}}}$ both reach a maximum value of $3 \times 10^5 \text{ M}^{-1} \text{ sec}^{-1}$ at high pH, and the observed reactions fall off rapidly as the pH is lowered to give values of approximately $10^2 \text{ M}^{-1} \text{ sec}^{-1}$ at pH 6.

The minimum ligand concentration detectable in this reaction system depends upon the chain length and the equilibrium or steady-state concentrations of the free ligands. A second reaction sequence which could lead to products is



In order for this sequence to account for the formation of less than 5% of the products, it can be shown¹³ that the minimum value of EDTA concentration is given by eq 17, and because $[\text{Y}] \gg [\text{Te}]$, this repre-

$$[\text{EDTA}]_{\text{min}} = \frac{20k_d^{\text{NiTe}}}{k_Y^{\text{NiTe}}} \quad (17)$$

sents the minimum free-ligand concentration necessary in the reaction mixture. Table V indicates the calculated minimum values of EDTA to meet the criteria in eq 17. This is the limiting factor at pH 6–7 but at pH 8–10 the equilibrium concentration of EDTA from the copper-EDTA (see Table V) is higher and therefore determines the lowest level of free-ligand concentration. The tetren concentration in equilibrium with nickel-tetren would be higher, but the steady-state value, because of the large value of k_2 , causes $[\text{Y}] \gg [\text{Te}]$. The result is that at the higher pH the minimum ligand

(13) D. W. Margerum and R. K. Steinhaus, *Anal. Chem.*, **37**, 222 (1965).

concentration detectable by the nickel-tetren chain and the nickel-trien chain are both limited by the stability of copper-EDTA, and there is no advantage in sensitivity offered by the use of nickel-tetren but considerable disadvantage because it is so slow. However, at pH 6–7 the nickel-tetren chain offers the possibility of using $1/10$ to $1/100$ lower concentrations of free ligand than is possible with the nickel-trien chain in this pH region. Although this is the same pH range where the reversibility and switch in the rate-determining step can be troublesome, both difficulties can be avoided by using a sufficient excess of copper-EDTA. Nevertheless, the reaction would be inconveniently slow at the minimum possible EDTA concentrations of 10^{-10} to 10^{-8} M . Nickel-tetren which has only one coordination site available for a second ligand is less subject to the formation of mixed complexes than is nickel-trien. This can be advantageous when the exchange reactions are run in the presence of other complexing ligands.

Table V. Theoretical Minimum Ligand Concentrations Detectable by NiTe-CuY Chain Reaction^a

pH	[EDTA] _{min} for >95% chain path, M	[EDTA] _{equil} with 10^{-4} M CuEDTA, M	Limiting factor
6	1.1×10^{-8}	8.5×10^{-10}	Chain path
7	6.1×10^{-10}	2.4×10^{-10}	Chain path
8	7.0×10^{-11b}	3.9×10^{-10}	[EDTA] _{equil}
9	4.6×10^{-11b}	1.2×10^{-9}	[EDTA] _{equil}
10	3.8×10^{-11b}	5.0×10^{-9}	[EDTA] _{equil}

^a These concentrations are based on the assumption that there is no direct reaction between copper-EDTA and nickel-tetren. This reaction path has not been observed with the nickel-trien chain reaction with free-ligand concentrations as low as 10^{-8} M . ^b From extrapolated values of k_d^{NiTe} , assuming no hydroxide ion acceleration.

At low pH the products of the reaction can severely inhibit the reaction rate despite the favorable thermodynamics of the exchange reaction.

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