CONTRIBUTION FROM THE DEPARTMENT OF CHEMISTRY,
PURDUE UNIVERSITY, LAFAYETTE, INDIANA

Multidentate Ligand Kinetics. VI. The Exchange of Ethylenediaminetetraacetate Ion with Triethylenetetraminenickel(II) and Tetraethylenepentaminenickel(II)

BY D. B. RORABACHER AND D. W. MARGERUM[1]

Received May 28, 1963

The displacement of triethylenetetramine and of tetraethylenepentamine from their nickel complexes by EDTA is several orders of magnitude faster than the aqueous dissociation of these complexes at the same pH. The rapid EDTA exchange reactions are studied at 25°, $\mu = 0.1$, from pH 5.6 to 11.5 using a cyanide quench and a coordination chain reaction method. The reactions are first order in EDTA and first order in the nickel polyamine. A reaction mechanism is proposed involving a series of mixed ligand intermediate complexes where steric effects prevent full chelation of the six coordination sites of the nickel ion by the two multidentate ligands. The postulated rate-determining step is applicable to EDTA reactions with other metal complexes and with aqueous metal ions. The relative rates of reaction of the polyamine complexes are a direct function of dentate number. The effects of protonation, steric hindrance, rate of water loss, and rotational barriers are analyzed.

Introduction

Previous papers in this series have analyzed the mechanisms of metal ion exchange reactions[2] and formation and dissociation reactions[3] involving multidentate ligands and transition metal ions. In the present paper we undertake the analysis of the exchange reactions involving one multidentate ligand replacing another in a metal complex. These reactions are shown to share many of the phenomena found in the previous systems as well as some unique properties arising from the presence of two different bulky ligands competing for coordination sites on the same metal ion.

The reactions investigated (shown here with protonation representative of the predominant reactions in neutral solutions) were

$$HY^{-3} + NiT^{+2} \longrightarrow NiY^{-2} + HT^{+} \quad (1)$$

$$HY^{-3} + NiHTe^{+3} \longrightarrow NiY^{-2} + H_2Te^{+2} \quad (2)$$

where T represents the quadridentate polyamine, triethylenetetramine (trien), Te represents the quinquedentate polyamine, tetraethylenepentamine (tetren), and Y^{-4} represents ethylenediaminetetraacetate ion (EDTA).

A mechanism for the exchange reactions is proposed which involves a series of mixed ligand intermediate complexes where in each succeeding intermediate the nickel ion increases its coordination to the EDTA and decreases the number of coordinate bonds to the polyamine. From comparisons of the rate constants obtained in this study, and from calculations based on the stabilities of the mixed ligand intermediates and the rate constants for water loss and metal–donor bond breakage, the intermediate preceding the rate-determining step is characterized as having three nitrogens of the polyamine and one acetate of the EDTA bonded to the nickel ion with the other two coordination sites occupied by water molecules. Despite the availability of eleven possible amine or carboxylate donor groups from the two multidentate ligands, this proposed reaction intermediate utilizes only four of these donor groups because of steric hindrance, and water molecules complete the octahedral coordination sphere. The rate-determining step is the loss of one of the water molecules from nickel followed by the rapid bonding of a nitrogen of the EDTA ligand.

In agreement with the proposed mechanism and the mechanism for complex formation which we reported previously,[3] a close correlation is shown to exist between the rate constants for the exchange reaction and the rate constants for nickel EDTA formation. A correlation is also established between the constants for the nickel exchange reaction reported in this paper and the previously reported exchange reaction of the same two chelates with copper ion.[4] The failure to obtain a correlation between the rate constants for the copper exchange reaction and the constants for copper EDTA formation is explained in terms of two rates of water loss from the copper ion.

In connection with the study of the nickel trien exchange reaction, constants have been determined for two hydroxide complexes, $Ni(OH)T^{+}$ and $Ni(OH)_2T$.

Experimental

The purification of the polyamines and the preparation and standardization of the nickel polyamine solutions were carried out by methods previously reported.[3] Reagent grade ethylenediaminetetraacetic acid (EDTA), which was recrystallized twice from water and dried before use, was standardized by titration against primary standard copper solution using murexide indicator.

Borate–mannitol buffer (2.5 mM boric acid and sodium borate; 0–2% mannitol) was used to maintain constant acidity in the pH region 5.6 to 9.1. For higher pH values a buffer of reported

---

[1] Correspondence to be addressed to this author.

[2] (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) T. J. Bydalek and D. W. Margerum, *ibid.*, **2**, 678 (1963); (d) D. W. Margerum and T. J. Bydalek, *ibid.*, **2**, 683 (1963).

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

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

low nucleophilicity,[5] 2,6-dimethylpiperidine and its perchlorate salt, was used for the chain reaction study of the nickel trien reaction. Due to the high absorbance of this buffer in the ultraviolet region, higher pH values for the nickel tetren reaction were maintained by using an automatic titrigraph as a pH-stat. The ionic strength was maintained at 0.1 with reagent grade KCl. All absorption measurements were made with a Beckman DU spectrophotometer which was equipped with a thermostated (±0.1°) cell compartment.

Direct spectrophotometric measurement of the exchange reactions was of limited value due to a lack of sufficient sensitivity at the concentration levels required to follow the reaction. To circumvent this difficulty two different indirect methods were used.

EDTA Exchange with Nickel Tetren.—A method for quenching fractions of the rate solution with cyanide was developed on the basis of the large difference in the rates of the reactions

$$\mathrm{NiTe^{+2} + 4CN^- \xrightarrow{fast} Ni(CN)_4{}^{-2} + Te} \qquad (3)$$

$$\mathrm{NiY^{-2} + 4CN^- \xrightarrow{slow} Ni(CN)_4{}^{-2} + Y^{-4}} \qquad (4)$$

From the reported rate constants,[6] the latter reaction does not proceed further than 1% in 24 hr. with the concentration levels of cyanide and nickel EDTA which were present in the quenched fractions (0.5 m*M* NaCN, a maximum of 0.005 m*M* $\mathrm{NiY^{-2}}$, and pH 9.0). Test runs showed that reaction 3 was complete within a few seconds under the same conditions. Furthermore, the addition of a mixture of cyanide and EDTA to a solution of nickel tetren resulted in a quantitative conversion of the polyamine complex to $\mathrm{Ni(CN)_4{}^{-2}}$. Thus, this method of quenching proved very effective for detecting the reactant in the presence of the product by conversion to the tetracyanonickelate complex, the absorbance of which was then measured at 267 mμ ($\epsilon_{\mathrm{Ni(CN)_4}}$ 11,600).

EDTA Exchange with Nickel Trien.—The EDTA exchange with nickel trien is much more rapid than the exchange with nickel tetren. When the concentrations of the reactants were lowered sufficiently (2.5×10^{-6} *M*) to allow measurement of the reaction by the cyanide quench method, trace metal impurities within the reaction solutions caused severe deviations in the second-order rate plots. To circumvent this difficulty this reaction was followed by use of the coordination chain reaction between nickel trien and copper EDTA[4] where reaction 1 is one of the chain-propagating steps. When a 12-fold or greater excess of $[\mathrm{CuY^{-2}}]$ is used and free EDTA is added to the solution, the rate equation takes the integrated form

$$-\log\,[\mathrm{NiT_T}] = \left(\frac{k_{\mathrm{Y_T}}{}^{\mathrm{NiT_T}}[\mathrm{Y_T}]_0}{2.3}\right) t - \log\,[\mathrm{NiT_T}]_{\mathrm{i}} \qquad (5)$$

where $[\mathrm{Y_T}]_0$ is the concentration of uncomplexed EDTA present in solution and $k_{\mathrm{Y_T}}{}^{\mathrm{NiT_T}}$ is the second-order rate constant for the rate equation

$$R_{\mathrm{e}} = -\frac{\mathrm{d}[\mathrm{NiT_T}]}{\mathrm{d}t} = k_{\mathrm{Y_T}}{}^{\mathrm{NiT_T}}[\mathrm{Y_T}]_0[\mathrm{NiT_T}] \qquad (6)$$

(T, used as a subscript, indicates the summation of all species, including proton and hydroxide terms.) A plot of −2.3 log $[\mathrm{NiT_T}]$ against t gives an observed first-order rate constant as the slope which is equal to the product $k_{\mathrm{Y_T}}{}^{\mathrm{NiT_T}}[\mathrm{Y_T}]_0$. From a series of runs with varying amounts of EDTA added, the value of $k_{\mathrm{Y_T}}{}^{\mathrm{NiT_T}}$ can be calculated as previously described.[4] In this way it is possible to correct for any trace metal ion contamination.

Hydroxide Complexes.—A shift in the visible spectrum of the nickel trien complex was noted for solutions above pH 9. When a series of solutions from pH 7.4 to 12.1 was measured at 370 mμ, a definite increase in absorbance was observed which appeared to have two inflection points, one at about pH 9.5 and the other at pH 12.0 or greater (see Fig. 1). These were interpreted as reresulting from the formation of two hydroxide complexes, $\mathrm{Ni(OH)T^+}$ and $\mathrm{Ni(OH)_2T}$, the latter of which has been previously reported.[7] These complexes, with

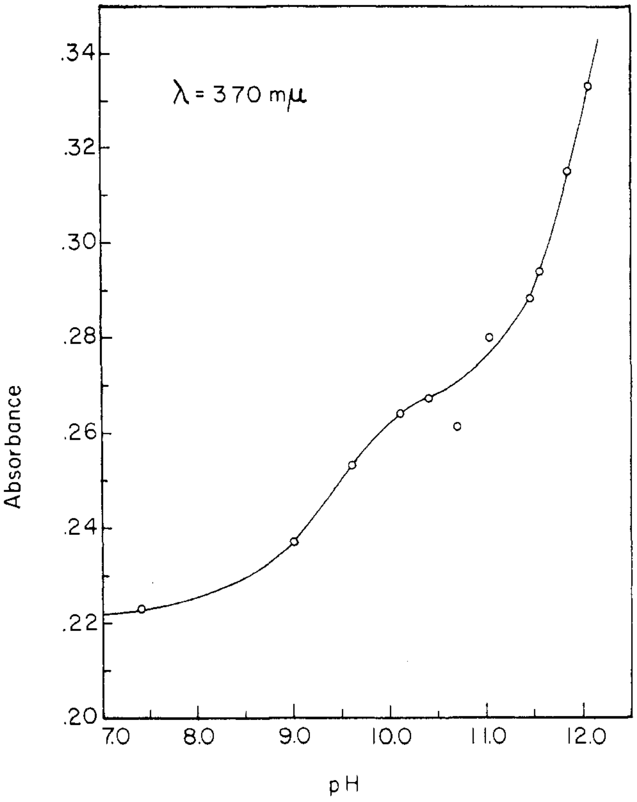

Fig. 1.—Absorbance of nickel trien *vs.* pH for 370 mμ.

$$K_{\mathrm{Ni(OH)T}}{}^{\mathrm{NiT}} = \frac{[\mathrm{Ni(OH)T^+}]}{[\mathrm{NiT^{+2}}][\mathrm{OH^-}]} = 10^{4.5}$$

$$K_{\mathrm{Ni(OH)_2T}}{}^{\mathrm{NiT}} = \frac{[\mathrm{Ni(OH)_2T}]}{[\mathrm{NiT^{+2}}][\mathrm{OH^-}]^2} \cong 10^{4.0}$$

were taken into account in treating the nickel trien data. The spectrum of nickel tetren did not show a shift below pH 11 and no attempt was made to evaluate a stability constant for a hydroxide species.

Protonation and Stability Constants.—The equilibrium constants for the protonated polyamines and nickel polyamine complexes were previously listed.[3] The acid constants for EDTA at 25°, $\mu = 0.1$, were calculated from the values reported by Schwarzenbach and Ackermann[8] for 20° by correcting for the heats of ionization.[9] The resulting values are $\mathrm{p}K_{\mathrm{H_4Y}} = 1.99$, $\mathrm{p}K_{\mathrm{H_3Y}} = 2.69$, $\mathrm{p}K_{\mathrm{H_2Y}} = 6.10$, and $\mathrm{p}K_{\mathrm{HY}} = 10.19$.

Results

Kinetics of EDTA Exchange with Nickel Tetren.—The rate of EDTA exchange with nickel tetren was studied from pH 5.6 to 11.5 using the cyanide quench.

A method of initial rates[10] gave the reaction orders of 1.0 for EDTA and 1.2 for nickel tetren which were interpreted to indicate that the reaction is first order in each reactant in accordance with the equation

$$R_{\mathrm{e}} = \frac{-\mathrm{d}[\mathrm{NiTe_T}]}{\mathrm{d}t} = k_{\mathrm{Y_T}}{}^{\mathrm{NiTe_T}}[\mathrm{Y_T}]\,[\mathrm{NiTe_T}] \qquad (7)$$

---

[5] J. G. Pritchard and F. A. Long, *J. Am. Chem. Soc.*, **79**, 2365 (1957).

[6] D. W. Margerum, T. J. Bydalek, and J. Bishop, *ibid.*, **83**, 1791 (1961).

[7] V. V. Ramanujam, *Dissertation Abstr.*, **20**, 1571 (1959).

[8] G. Schwarzenbach and H. Ackermann, *Helv. Chim. Acta*, **30**, 1798 (1947).

[9] M. J. L. Tillotson and L. A. K. Staveley, *J. Chem. Soc.*, 3613 (1958).

[10] A. A. Frost and R. G. Pearson, "Kinetics and Mechanism," John Wiley and Sons, Inc., New York, N. Y., 1953, p. 44.

TABLE I

SECOND-ORDER RATE CONSTANTS FOR THE EXCHANGE OF EDTA WITH NICKEL TETREN; CYANIDE QUENCHING METHOD

$[Y_T] = [NiTe_T] = 2.50 \times 10^{-5}$ M, 25.0°, $\mu = 0.1$

pH	$k_{Y_T}^{NiTe_T}$, M^{-1} sec.$^{-1}$	pH	$k_{Y_T}^{NiTe_T}$, M^{-1} sec.$^{-1}$
5.68	155	8.48	1.23, 1.30
5.88	94.0, 96.7	8.68	1.21
6.03	67.7, 64.7	8.83	1.09
6.22	42.0	9.00	1.18
6.42	26.7	9.25	1.13
6.63	15.4	9.50	1.12
6.82	9.00	9.75	1.15
7.02	5.92	10.00	1.33
7.28	3.62	10.25	1.33
7.48	2.75	10.50	1.37
7.68	2.00	10.75	1.43
7.89	1.72	11.00	1.58
8.08	1.52	11.50	1.20
8.27	1.32		

This later was confirmed in integrated rate plots in which the concentrations of each of the reactants were varied. The second-order rate plots were linear for over 50% of the reaction and extrapolated through the theoretical intercept. A slight tendency for the plots to deviate for later points in the reaction was due to the contribution of the back reaction which is expected on the basis of the stability constants for $NiTe^{+2}$ and NiY^{-2} ($K_{NiTe}^{Ni} = [NiTe^{+2}]/[Ni^{+2}][Te] = 10^{17.51}$; $K_{NiY}^{Ni} = [NiY^{-2}]/[Ni^{+2}][Y^{-4}] = 10^{18.6}$). To avoid any error due to this slight curvature, the initial slopes were used to determine the rate constants.

The resulting rate constants (Table I) show that the reaction rate decreases rapidly with decreasing acidity in the pH range 5.6 to 8.3 and then remains fairly constant up to pH 11.5. On the basis of the acid dissociation constants for EDTA and nickel tetren, the following rate equation is postulated.

$$R_e = (k_Y^{NiTe} + k_{Y,H}^{NiTe}[H^+] + k_{Y,2H}^{NiTe}[H^+]^2 + k_{Y,3H}^{NiTe}[H^+]^3)[Y^{-4}][NiTe^{+2}] \quad (8)$$

Since it was not immediately clear how many protons should be assigned to each reactant, the initial resolution was made with the protons unassigned.

In the pH region above 8.8 the terms involving two and three protons are negligible and eq. 7 and 8 can be combined and simplified to give

$$k_{Y_T}^{NiTe}\ \frac{[Y_T][NiTe_T]}{[Y^{-4}][NiTe^{+2}]} = k_Y^{NiTe} + k_{Y,H}^{NiTe}[H^+] \quad (9)$$

where

$$\frac{[Y_T]}{[Y^{-4}]} = \left\{1 + \frac{[H^+]}{K_{HY}} + \frac{[H^+]^2}{K_{HY}K_{H_2Y}} + \frac{[H^+]^3}{K_{HY}K_{H_2Y}K_{H_3Y}} + \frac{[H^+]^4}{K_{HY}K_{H_2Y}K_{H_3Y}K_{H_4Y}}\right\} \quad (10)$$

$$\frac{[NiTe_T]}{[NiTe^{+2}]} = 1 + [H^+]K_{NiHTe}^{NiTe} \quad (11)$$

A plot of the left side of eq. 9 against $[H^+]$ yields the values

$$k_Y^{NiTe} = \text{intercept} = 1.5\ M^{-1}\ \text{sec.}^{-1}$$

$$k_{Y,H}^{NiTe} = \text{slope} = 1.7 \times 10^{10}\ M^{-2}\ \text{sec.}^{-1}$$

TABLE II

SECOND-ORDER RATE CONSTANTS FOR THE EXCHANGE OF EDTA WITH NICKEL TRIEN; CHAIN REACTION METHOD

$[CuY_T] = 2.88 \times 10^{-3}$ M, $[NiT_T] = 1.00 \times 10^{-4}$ M,
$[Y_T] = 3\text{–}16 \times 10^{-6}$ M, 25.0°, $\mu = 0.1$

pH	$k_{Y_T}^{NiT_T} \times 10^{-2}$, M^{-1} sec.$^{-1}$	pH	$k_{Y_T}^{NiT_T} \times 10^{-2}$, M^{-1} sec.$^{-1}$
5.98	18.7	8.01	4.5
6.34	21.3	8.89	7.5
6.62	17.8	9.08	12.0
6.90	15.7	10.17	18.3
7.19	7.3	10.79	44.7
7.33	9.3	11.07	39.7
7.56	7.0	11.09	54.5
7.72	9.3		

The terms involving two and three protons were evaluated in a similar manner except that correction was made for the contribution of the other two terms by plotting the equation

$$\{B - (k_Y^{NiTe} + k_{Y,H}^{NiTe}[H^+])\}\ \frac{1}{[H^+]^2} = k_{Y,2H}^{NiTe} + k_{Y,3H}^{NiTe}[H^+] \quad (12)$$

where B represents the left side of eq. 9. The values for the rate constants calculated from this plot are

$$k_{Y,2H}^{NiTe} = \text{intercept} = 7.5 \times 10^{17}\ M^{-3}\ \text{sec.}^{-1}$$

$$k_{Y,3H}^{NiTe} = \text{slope} = 2.0 \times 10^{24}\ M^{-4}\ \text{sec.}^{-1}$$

Kinetics of EDTA Exchange with Nickel Trien.—The rate of EDTA exchange with nickel trien was studied from pH 6.0 to 11.1 by means of the coordination chain reaction with copper EDTA and nickel trien. Excellent first-order plots of eq. 5 were obtained for the individual runs, which were linear for more than 98% of the reaction. For a series of runs at the same pH, the plot of the observed rate constants against the amounts of free EDTA added generally gave good straight lines with an intercept which indicated the metal ion impurity level was on the order of 3–4 × 10^{-6} M.

The resulting values for $k_{Y_T}^{NiT_T}$ (see eq. 6) decrease with decreasing acidity in the pH range 6.0 to 7.5 and then increase again above pH 9 with a minimum occurring in the region of pH 8.0 (Table II). On the basis of the acid dissociation constants for EDTA and nickel trien and the constant determined for the hydroxide complex of nickel trien, the following rate equation is postulated.

$$R_e = (k_{Y,OH}^{NiT}[OH^-] + k_Y^{NiT} + k_{Y,H}^{NiT}[H^+] + k_{Y,2H}^{NiT}[H^+]^2)[Y^{-4}][NiT^{+2}] \quad (13)$$

Once again the protons were not assigned to either reactant for the initial resolution of the data.

Below pH 8.5 the reaction is essentially independent of the terms which do not involve protons and eq. 6 and 13 can be combined and simplified to give

$$k_{Y_T}^{NiT_T}\ \frac{[Y_T]}{[Y^{-4}]}\ \frac{[NiT_T]}{[NiT^{+2}]}\ \frac{1}{[H^+]} = k_{Y,H}^{NiT} + k_{Y,2H}^{NiT}[H^+] \quad (14)$$

where $[Y_T]/[Y^{-4}]$ is defined by eq. 10 and

$$\frac{[NiT_T]}{[NiT^{+2}]} = \{[H^+]k_{NiHT}^{NiT} + 1 + [OH^-]K_{Ni(OH)T}^{NiT} + [OH^-]^2K_{Ni(OH)_2T}^{NiT}\} \quad (15)$$

TABLE III

EVALUATED RATE CONSTANTS WITH ALTERNATE ASSIGNMENT OF PROTONS[a]

25°, $\mu = 0.1$

	EDTA + NiT	
$k_{\mathrm{Y}}^{\mathrm{Ni(OH)T}} = 4.8 \times 10^3$		
$k_{\mathrm{Y}}^{\mathrm{NiT}} \cong 10^4$		
$k_{\mathrm{HY}}^{\mathrm{NiT}} = 5.0 \times 10^2$	$k_{\mathrm{Y}}^{\mathrm{NiHT}} = 1.5 \times 10^8$	
$k_{\mathrm{H_2Y}}^{\mathrm{NiT}} = 6.2 \times 10^3$	$k_{\mathrm{HY}}^{\mathrm{NiHT}} = 1.6 \times 10^5$	$k_{\mathrm{Y}}^{\mathrm{NiH_2T}} = 2.7 \times 10^{11}$
	EDTA + NiTe	
$k_{\mathrm{Y}}^{\mathrm{NiTe}} = 1.5$		
$k_{\mathrm{HY}}^{\mathrm{NiTe}} = 1.1$	$k_{\mathrm{Y}}^{\mathrm{NiHTe}} = 2.0 \times 10^5$	
$k_{\mathrm{H_2Y}}^{\mathrm{NiTe}} = 38$	$k_{\mathrm{HY}}^{\mathrm{NiHTe}} = 5.7 \times 10^2$	$k_{\mathrm{Y}}^{\mathrm{NiH_2Te}} = 9.7 \times 10^8$
$k_{\mathrm{H_3Y}}^{\mathrm{NiTe}} = 2.2 \times 10^3$	$k_{\mathrm{H_2Y}}^{\mathrm{NiHTe}} = 1.2 \times 10^3$	$k_{\mathrm{HY}}^{\mathrm{NiH_2Te}} = 1.7 \times 10^5$
		$k_{\mathrm{Y}}^{\mathrm{NiH_3Te}} = 2.5 \times 10^{12}$

[a] All rate constant values in M^{-1} sec.$^{-1}$.

From a plot of the left side of eq. 14 against $[\mathrm{H}^+]$ we calculate the values

$$k_{\mathrm{Y,H}}^{\mathrm{NiT}} = \text{intercept} = 7.7 \times 10^{12}\ M^{-2}\ \text{sec.}^{-1}$$

$$k_{\mathrm{Y,2H}}^{\mathrm{NiT}} = \text{slope} = 1.2 \times 10^{20}\ M^{-3}\ \text{sec.}^{-1}$$

The other two terms can be evaluated from the data at higher pH values by correcting for the contribution of the proton terms using the equation

$$\{D - (k_{\mathrm{Y,H}}^{\mathrm{NiT}}[\mathrm{H}^+] + k_{\mathrm{Y,2H}}^{\mathrm{NiT}}[\mathrm{H}^+]^2)\} = \frac{k_{\mathrm{Y,OH}}^{\mathrm{NiT}}K_{\mathrm{w}}}{[\mathrm{H}^+]} + k_{\mathrm{Y}}^{\mathrm{NiT}} \quad (16)$$

where D represents $[\mathrm{H}^+]$ times the left side of eq. 14. The rate constant values calculated from this plot are

$$k_{\mathrm{Y,OH}}^{\mathrm{NiT}} = \text{slope}/K_{\mathrm{w}} = 1.3 \times 10^8\ M^{-2}\ \text{sec.}^{-1}$$

$$k_{\mathrm{Y}}^{\mathrm{NiT}} = \text{intercept} \cong 1 \times 10^4\ M^{-1}\ \text{sec.}^{-1}$$

In Fig. 2 the theoretical curves for $k_{\mathrm{Y_T}}^{\mathrm{NiT_T}}$ and $k_{\mathrm{Y_T}}^{\mathrm{NiTe_T}}$ predicted from the evaluated rate constants are compared with the experimental values. Logarithmic plots are used because of the wide range of values included. In both cases a good fit of the data is obtained with the scatter of the nickel trien data giving less confidence in the values calculated for this system.

The protons can be assigned to the rate constant terms in eq. 8 and 13 in several ways. The alternate assignments are listed in Table III with the corresponding values for each assignment.

Discussion

Assignment of the Reaction Mechanism.—Calculations based on our previous study of the formation and dissociation of the nickel polyamines[3] indicate that the rate of dissociation of these complexes is much too slow to account for the data observed with the EDTA exchange reactions. Therefore, the presence of the EDTA in solution aids in the removal of the polyamine from the coordination sphere of the nickel ion. It is proposed that the EDTA performs this function by forming coordinate bonds with the nickel ion prior to the complete dissociation of the polyamine from the nickel ion. In this way the EDTA blocks the re-formation of the nickel polyamine bonds in a manner similar to the function of protons in the dissociation reaction and thus greatly increases the rate of dissociation of the polyamine.

This mechanism results in the formation of one or more mixed ligand complexes as intermediates in the reaction. Such intermediates have been postulated for other multidentate ligand exchange studies.[4,11] Thus, the mechanism for the ligand exchange reactions is similar to the mechanism involving dinuclear intermediates which was proposed for metal exchange reactions.[2]

Since the stability of nickel complexes of polyamine and polyaminocarboxylate ligands increases as the number of dentates increases (up to a maximum of six), each intermediate species should form as many coordinate bonds to the two multidentate ligands as steric factors will permit. This argument leads to the hypothesis that a number of mixed ligand intermediate species may occur in the exchange reaction with successive intermediates exhibiting more coordinate bonds to the EDTA and fewer to the polyamine being displaced.

Structural models show that, in forming the first bond between the nickel ion (which is still coordinated with the polyamine) and an EDTA ion, a carboxylate donor group is highly favored over a nitrogen due to the steric configuration of the EDTA molecule and the hindered access to the nickel coordination sites. This preference is enhanced by the electrostatic attraction between the carboxylate group and the nickel ion.

For the formation of the second and subsequent bonds between the nickel ion and EDTA, the potential barriers for the internal rotation of the chelate ligands and the steric requirements for each at the coordination site greatly decrease the probability that an EDTA donor atom will be in a position to form a coordinate bond at the time of rupture of a nickel–polyamine bond. However, water, being present as the solvent, is readily available for coordination at the vacated site. As a result the favored mechanism consists of the repetition of two alternating steps—the rupture of a polyamine bond with rapid coordination of a water (solvent) molecule followed by the rupture of a water bond and the rapid coordination of an EDTA donor atom which has rotated into a position favorable for bond formation. Thus, the rate-determining step should depend on either (a) the rate constant for water loss (similar to metal chelate formation) or (b) the rate constant

---

(11) D. W. Rogers, D. A. Aikens, and C. N. Reilley, *J. Phys. Chem.*, **66**, 1582 (1962).

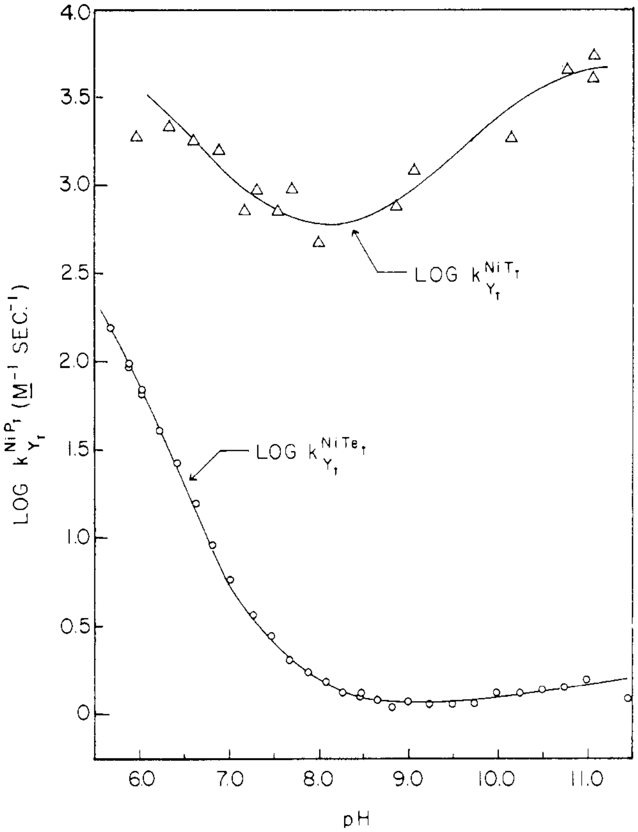

Fig. 2.—Fit of theoretical curves to observed rate constants for EDTA exchange with nickel trien and nickel tetren. Solid lines are curves predicted by eq. 8 and 13. Data shown are for 25.0°, $\mu = 0.1$.

for the rupture of a metal–polyamine bond (similar to metal chelate dissociation).

Since the exchange reactions are reversible, with the forward and reverse reactions involving essentially the same types of bond formation and breakage, and since the reaction order supports the premise that the concentrations of the intermediates are relatively small, the intermediates prior to the rate-determining step may be assumed to be in equilibrium. On this basis, the experimental rate constant can be equated to the relative stability of the intermediate preceding the rate-determining step as follows

$$k_{\text{exptl}} = \frac{K_{(n\text{th intermediate})}}{K_{(\text{reactants})}} k_n \qquad (17)$$

where

$$K_{(n\text{th intermediate})} = \frac{K_{(\text{polyamine segment})} \cdot K_{(\text{EDTA segment})}}{K_{\text{electrostatic}}}$$

The ratio $K_{(n\text{th intermediate})}/K_{(\text{reactants})}$ represents the relative concentration of the nth intermediate compared to the concentration of reactants, for intermediates preceding the rate-determining step. Values used for $K_{(\text{reactants})}$ are $K_{\text{NiT}}{}^{\text{Ni}} = 10^{13.8}$ and $K_{\text{NiTe}}{}^{\text{Ni}} = 10^{17.5}$ (the stability of free EDTA is taken as unity). The stability constants for the ligand segments bonded to the nickel ion are assumed equal to the stability of the corresponding nickel ligand complexes and $K_{\text{electrostatic}}$ was estimtaed in the manner used previously.[2c] Thus, for intermediate species III in Fig. 3, $K_{(\text{polyamine segment})} = K_{\text{NiDien}}{}^{\text{Ni}} = 10^{10.7}$ (Dien = diethylenetriamine), $K_{(\text{EDTA segment})} = K_{\text{Ni(OAc)}_2}{}^{\text{Ni}} = 10^{0.7}$, and $K_{\text{electrostatic}} \approx 0.10$ (a more comprehensive discussion of this type of calculation has been presented previously[2c]).

The value of k_n is taken as the rate constant for nickel–nitrogen or nickel–water bond rupture corrected for the rotational barrier involved.[3] For steps k_2, k_4, k_6, and k_9, involving rupture of a nickel–nitrogen bond and rotation around a C–N or C–C bond,[3] the value for k_n is approximately 80 sec.$^{-1}$. For steps k_5, k_7, and k_8 the corrected value for k_n is taken as 6×10^2 sec.$^{-1}$, while for step k_3, where the preferred rotation is around a C–O bond, k_n is approximately 1×10^4 sec.$^{-1}$.

The value for k_{exptl} calculated for eq. 17 should equal the experimentally observed rate constant for the case where $K_{(n\text{th intermediate})}$ is the stability of the intermediate preceding the rate-determining step k_n.

Equation 17 has been used to test all possible mixed ligand intermediate complexes with the experimentally observed constants. The results of these calculations show that for a mechanism in which the total number of coordination sites on the metal ion occupied by both ligands alternates between six and five, all of the intermediate complexes predict values for k_{exptl} which are much larger than the observed values. On the other hand, for a mechanism in which the total number of sites occupied by both ligands alternates between four and three, all values are much smaller than those which are observed. From this it is concluded that the exchange of EDTA with the nickel polyamine complexes proceeds by a mechanism involving intermediates which have alternately a total of five and four sites on the metal ion occupied by the two multidentate ligands. Such a mechanism is shown in Fig. 3 for the case in which no protons are involved.

Calculations based on the intermediates in this figure show that several of the rate steps give values for k_{exptl} which are very close to the observed values for the two exchange reactions. Of these, step k_3 correlates most closely with the experimental constants and, therefore, appears to be the rate-determining step. The intermediate preceding the rate-determining step is then characterized as having three nitrogens of the polyamine and one acetate of the EDTA coordinated with the nickel ion. The rate-determining step is the loss of a water molecule followed by coordination of the first nitrogen of the EDTA.

Support for this mechanism can be gained by a careful examination of the alternative forms of the rate constants for EDTA exchange with the nickel polyamine complexes as listed in Table III. From such a comparison two pairs of strikingly similar values are noted.

$$k_{\text{HY}}{}^{\text{NiT}} \cong k_{\text{HY}}{}^{\text{NiHTe}} \cong 5 \times 10^2\ M^{-1}\ \text{sec.}^{-1} \qquad (18)$$

$$k_{\text{HY}}{}^{\text{NiHT}} \cong k_{\text{HY}}{}^{\text{NiH}_2\text{Te}} \cong 1.6 \times 10^5\ M^{-1}\ \text{sec.}^{-1} \qquad (19)$$

These similarities are not totally unexpected since the protonated nickel tetren complex bears a high re-

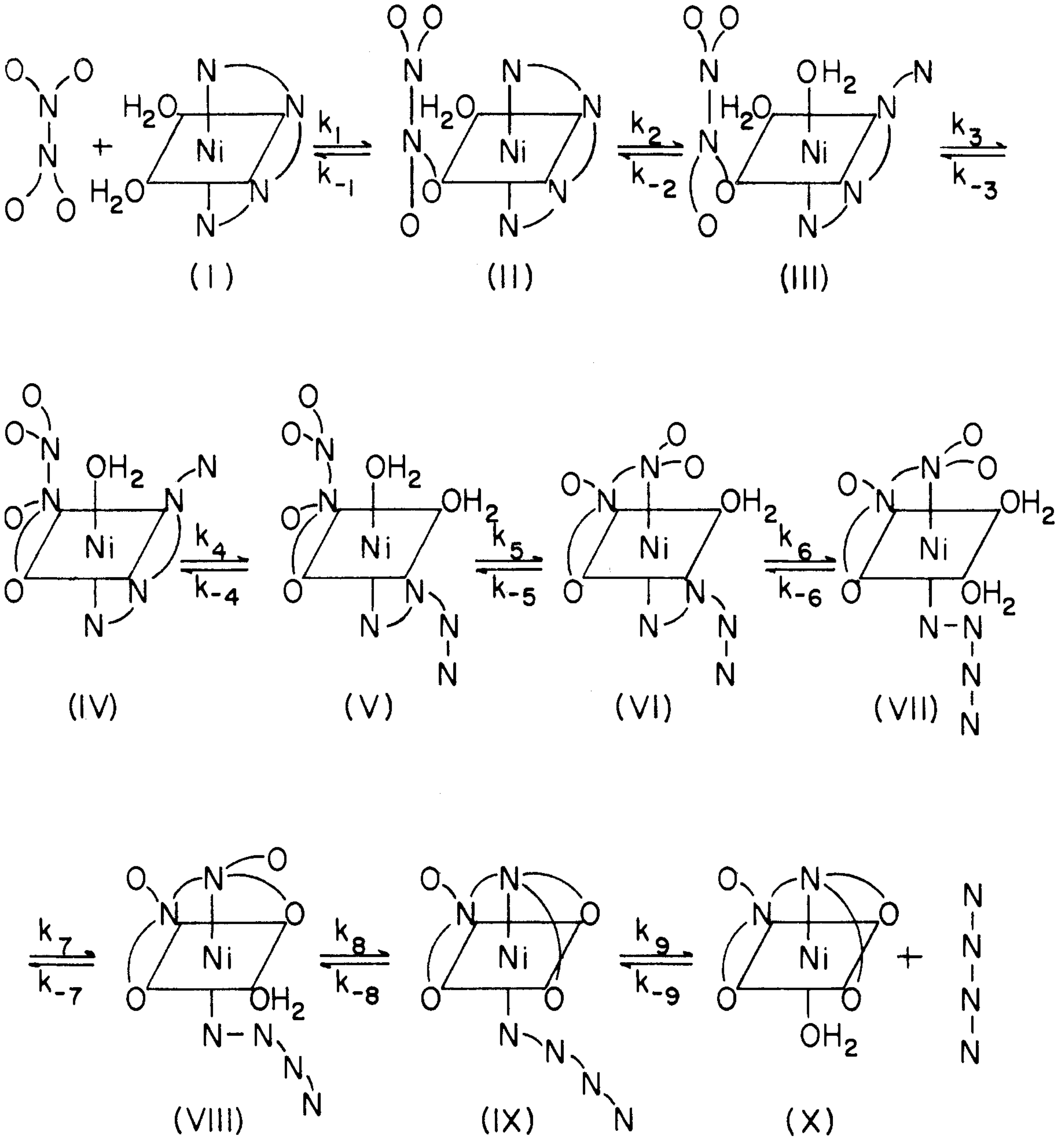

Fig. 3.—Proposed mechanism for EDTA exchange with nickel trien for the term involving no protons. The nickel trien complex is shown in the nonplanar configuration which predominates at 25°, μ = 0.1 [C. K. Jørgensen, *Acta Chim. Scand.*, 11, 399 (1957)].

semblance to the nickel trien complex, as does the diprotonated nickel tetren to the protonated nickel trien. However, it should be noted that no such close correlation is obtained for any of the alternative forms of these constants (*e.g.*, $k_{Y}^{NiH_2Te} \neq k_{Y}^{NiHT}$). Since this correlation is obtained only when one proton is assigned to the EDTA and the others are assigned to the nickel polyamine complex, it is assumed that this represents the state of the reactants at the time of the rate-determining step. Figure 4 shows the structures proposed for the intermediate preceding the rate-determining step (corresponding to intermediate III in Fig. 3) for the terms involving protons. The one and two proton intermediates for the nickel tetren exchange reaction have structures similar to the corresponding nickel trien intermediates.

The basicities of the donor atoms would dictate that the first two protons in the system should go on the nitrogens of EDTA[12] and the third on the nickel polyamine (pK_{HY} = 10.2, pK_{H_2Y} = 6.1, $\log K_{NiHT}^{NiT} \cong \log K_{NiHTe}^{NiTe} < 5.0$). That only one proton appears to be on the EDTA prior to the rate-determining step indicates that one of the EDTA nitrogens is either already bonded or undergoing bond formation at this step so that it cannot be protonated. However, the fact that one proton still remains on the EDTA indicates that the second nitrogen is not yet bonded since the value of $\log K_{NiHY}^{NiY}$, where the proton is on an acetate, is somewhat less than $\log K_{NiH_2Te}^{NiHTe}$ as predicted from our previous paper[3] ($\log K_{NiHY}^{NiY} = 3.1$; $\log K_{NiH_2Te}^{NiHTe} = 3.8$).

The fact that the ratio of the two rate constants

---

(12) D. C. Olson and D. W. Margerum, *J. Am. Chem. Soc.*, **82**, 5602 (1960).

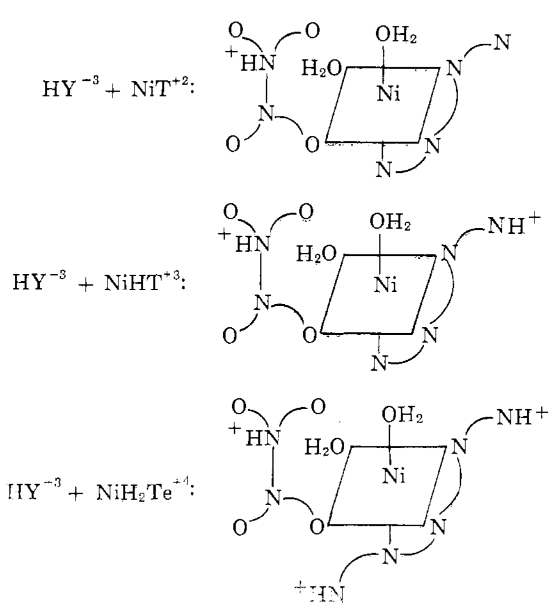

Fig. 4.—Proposed structures for the intermediate preceding the rate-determining step for terms involving protons. These structures show the positions of the protons in the intermediate corresponding to intermediate III in Fig. 3.

which do not involve protons, k_Y^{NiT} and k_Y^{NiTe}, is approximately equal to the ratio of the stability constants of the two polyamine complexes shows that the additional dentate in the nickel tetren complex breaks before the point of the rate-determining step and the two reactions pass through the same intermediate preceding this step. It is further seen that the ratio of the rate constants for the four-bonded polyamine complexes in eq. 18 to the constants for the three-bonded complexes in eq. 19 is essentially equal to the equilibrium constant for the breakage of a single nickel–polyamine bond as evaluated in the study of the formation and dissociation reactions.[3] This indicates that no more than three polyamine nitrogens are coordinated to the nickel at the time of the rate-determining step.

This evidence limits the choice for the rate-determining step to steps k_3 and k_4 in Fig. 3 and lends strong support to the former conclusion that step k_3 determines the reaction rate.

In keeping with the mechanism proposed for the dissociation of the nickel polyamine complexes, it might be assumed that the breakage of the last polyamine bond to the nickel ion would be the most likely rate-determining step. However, comparison of the constants for the reverse exchange reaction with the formation rate constants for the nickel polyamines shows that the exchange reaction constant is about 10^4 times slower than the formation rate constant, thus eliminating this step as rate-determining.

The failure of the metal ion to form more than five coordinate bonds with the two multidentate ligands in the intermediate complexes is attributed to steric hindrance of the bulky chelates. This is supported by molecular models which indicate that full coordination to the chelates is possible only in the case where one of the ligands is singly coordinated and the second ligand has five points of coordination. Other combinations appear to be too sterically hindered to make full chelation possible. However, if a water molecule is bonded at one of the coordination sites it then appears possible, on the basis of steric considerations alone, to bond the EDTA and polyamine at the other five sites in any combination.

Confirmation of the Mechanism.—On the basis of the proposed mechanism it should be possible to equate the experimental rate constants to the individual rate steps by means of equations of the type

$$k_Y^{NiT} = K_1K_2k_3 \qquad (20)$$

$$k_{HY}^{NiHT} = K_1'k_3 \qquad (21)$$

where $K_1 = k_1/k_{-1}$, $K_2 = k_2/k_{-2}$ (Fig. 3), and K_1' differs from K_1 by small electrostatic and statistical factors. The first equilibrium constant, K_1 or K_1', can be calculated from the stability constant for nickel acetate and the electrostatic and statistical factors. The values for K_1 (Y^{-4}) and K_1' (HY^{-3}) are roughly 200 and 40, respectively. The second constant, K_2, is the equilibrium for the rupture of a single nickel–polyamine bond and has been previously evaluated[3] as 1.35×10^{-3}. The rate-determining step, k_3, is equal to the rate constant for water loss for which a recently reported value[13] is 2.7×10^4 sec.$^{-1}$ divided by the rotational barrier of the EDTA molecule. The least hindered rotation appears to be rotation about the C–O bond. No values for this potential barrier have been reported but a fair approximation can be obtained by using the C–C rotational barrier in acetone as a model. From the potential barrier values reported for the rotation of this bond,[14] the calculated rotational barrier is a factor of about 3. Thus, the predicted values for k_Y^{NiT} and k_{HY}^{NiHT} are

$$k_Y^{NiT} = 200 \times 1.35 \times 10^{-3} \times \frac{2.7 \times 10^4}{3} = 2.4 \times 10^3\ M^{-1}\ \text{sec.}^{-1}$$

$$k_{HY}^{NiHT} = 40 \times \frac{2.7 \times 10^4}{3} = 3.6 \times 10^5\ M^{-1}\ \text{sec.}^{-1}$$

The values which are calculated by means of equations such as 20 and 21 are compared in Table IV to the experimental values. The excellent correlations, which are obtained in all cases, support the mechanism proposed in Fig. 3 where step k_3 is rate-determining.

Application of the Mechanism to Other Systems

Trien Exchange with Copper EDTA.—The exchange of trien with copper EDTA has been studied by means of the coordination chain reaction.[4] If the rate-determining step is the same for these ligand exchange reactions with both copper and nickel ions, it should be possible to establish a correlation between the rate constants for the nickel trien–EDTA exchange reaction and the constants for EDTA exchange with copper trien (which can be calculated from the rate constants

---

[13] T. J. Swift and R. E. Connick, *J. Chem. Phys.*, **37**, 307 (1962).

[14] J. G. Aston, *Discussions Faraday Soc.*, **10**, 73 (1951).

TABLE IV

COMPARISON OF EXPERIMENTAL RATE CONSTANTS FOR THE EXCHANGE OF EDTA WITH NICKEL POLYAMINES TO VALUES PREDICTED BY PROPOSED MECHANISM[a]

25.0°, $\mu = 0.1$

Rate constant	Experimental value	Predicted value
k_Y^{NiT}	$\sim 1 \times 10^4$	2.4×10^3
k_{HY}^{NiT}	5.0×10^2	4.8×10^2
k_{HY}^{NiHT}	1.6×10^5	3.6×10^5
k_Y^{NiTe}	1.5	3.2
k_{HY}^{NiTe}	1.1	0.7
k_{HY}^{NiHTe}	5.7×10^2	4.8×10^2
$k_{HY}^{NiH_2Te}$	1.7×10^5	3.6×10^5

[a] All rate constant values in M^{-1} sec.$^{-1}$.

for the reverse reaction[4] and the known equilibrium constants[15]). Since electrostatic and statistical factors will be the same for both cases, the relative rates should be a function of the metal–donor bond rupture rates only.

The bond ruptures represented by k_1 and k_{-1} in Fig. 3 should be reflected in the differences of the stability constants for the monoacetate complexes of the two metal ions. This amounts to a factor of about 10 in favor of the copper complex ($\log K_{NiOAc}^{Ni} = 0.7$; $\log K_{CuOAc}^{Cu} = 1.7$).[15] Similarly, the value for K_2 for the copper system can be estimated from the relative stability constants for copper trien and diethylenetriamine,[15] which differ by a factor of about $10^{-4.4}$. Two values have been reported for water loss from copper ion, one for axial water and one for equatorial water.[13] Subsequent reports[16] indicate only axial water loss occurs for the hexaaquo copper ion with a rapid vibrational mode possible between axial and equatorial waters. However, the chelate rings formed by a multidentate ligand such as trien would prevent the rapid conversion of a bound water from an equatorial to an axial type. Thus, the entering EDTA molecule, because of its chelate nature, will form the second bond with copper ion at a position *cis* to the first bond, resulting in the loss of an equatorial water in the rate-determining step corresponding to step k_3 in Fig. 3.

The rate constant expected for loss of equatorial water from copper ion would be approximately the same as that found for nickel.[16a] Since the rotational barrier is independent of the metal ion, step k_3 is assumed to be nearly identical for the two metal ions. Equation 21 then predicts that, for the terms involving two protons, the ratio of the exchange rates for the two metal ions will equal the ratio of the stabilities of their acetate complexes (K_1' in eq. 21). This permits the prediction of k_{HY}^{CuHT} from which, in turn, one can predict the values for the terms involving one and zero protons. The excellent agreement between these constants and the constants for the back reaction of the trien exchange with copper EDTA as shown in Table V further supports the contention that the exchange reactions for the two metal ions proceed by the mechanism outlined in Fig. 3.

TABLE V

COMPARISON OF EXPERIMENTAL RATE CONSTANTS FOR EDTA EXCHANGE WITH COPPER TRIEN TO VALUES PREDICTED FROM DATA FOR EDTA EXCHANGE WITH NICKEL TRIEN[a]

25.0°, $\mu = 0.1$

Rate constant	Experimental[b] value	Predicted value	Basis for prediction
k_Y^{CuT}	1×10^3	7×10^2	$k_Y^{NiT} k_{HY}^{CuT} / k_{HY}^{NiT}$
k_{HY}^{CuT}	10	70	$k_{HY}^{CuHT} K_{CuDien}^{Cu} / K_{CuT}^{Cu}$
k_{HY}^{CuHT}	2×10^6	2×10^6	$k_{HY}^{NiTH} K_{CuOAc}^{Cu} / K_{NiOAc}^{Ni}$

[a] All rate constant values in M^{-1} sec.$^{-1}$. [b] The experimental values were calculated from the values reported for the reverse exchange reaction.[4]

EDTA Complex Formation with Aquonickel Ion.—A comparison of the rate constants for the exchange of EDTA with the nickel polyamines to the corresponding rate constants for the formation of the nickel EDTA complex[17] shows an interesting equality.

$$k_{HY}^{NiHT} \cong k_{HY}^{NiH_2Te} \cong k_{HY}^{Ni} \cong 1.5 \times 10^5 \ M^{-1} \text{ sec.}^{-1} \quad (22)$$

In view of this relationship and the mechanism proposed for the exchange reaction, it is concluded that the mechanism of the nickel EDTA complex formation reaction involves the formation of an acetate-bonded intermediate followed by loss of a water molecule and the bonding of the first nitrogen from EDTA as the rate-determining step. This will be in line with our previous conclusions regarding metal complex formation[3] only if the rate of the metal–acetate bond rupture exceeds the rate of the second metal–nitrogen bond formation, *i.e.*, $k^{NiOAc} > 1 \times 10^4$ sec.$^{-1}$. Considering the stability constant for nickel acetate this would indicate that the formation rate constant for nickel acetate is at least $5 \times 10^4 \ M^{-1}$ sec.$^{-1}$, which is not an unreasonable value in light of the electrostatic attraction between the acetate and the nickel ion and the formation rate constants predicted for the nickel polyamine complexes.[3]

EDTA Complex Formation with Aquocopper Ion.—A remarkable contrast exists in the rate constants for the reactions of HY^{-3} with the two copper species $Cu(H_2O)_6^{+2}$ and $CuHT(H_2O)_3^{+3}$ as compared with the rate constants for the corresponding two nickel species. The rate constants for the latter two species were shown, in eq. 22, to be approximately equal, while for copper the hexaaquo ion has a rate constant which is nearly 1000 times greater[18] than the value for k_{HY}^{CuHT}

$$k_{HY}^{CuHT} = 2 \times 10^6 \ M^{-1} \text{ sec.}^{-1}$$

$$k_{HY}^{Cu} = 1.3 \times 10^9 \ M^{-1} \text{ sec.}^{-1}$$

This fact is consistent with the proposed mechanism and results from the influence of the trien molecule in preventing the rapid interconversion of equatorial and axial positions in the coordination sphere of copper as discussed earlier. This forces the sluggish loss of an equatorial water in the reaction of HY^{-3} with copper trien whereas this restriction does not exist for the

---

(15) J. Bjerrum, G. Schwarzenbach, and L. Sillén, "Stability Constants, Part I. Organic Ligands," The Chemical Society, London, 1957.

(16) (a) M. Eigen and T. S. Swift, private communication; (b) R. E. Connick and T. S. Swift, Inorganic Division, 142nd National Meeting of the American Chemical Society, Atlantic City, N. J., 1962.

(17) D. W. Margerum and B. A. Zabin, *J. Phys. Chem.*, **66**, 2214 (1962).

(18) D. W. Margerum and B. A. Zabin, Abstracts of Papers, Inorganic Division, 144th National Meeting of the American Chemical Society, Los Angeles, Calif., 1963.

aquocopper ion. Thus, the reaction of HY^{-3} with $Cu(H_2O)_6^{+2}$ compared to its reaction with $CuHT(H_2O)_3^{+3}$ would be expected to differ by a factor representing the difference in the rate constants for the two types of water loss with slight corrections for statistical and electrostatic effects.

The rate constant for water loss from aquocopper ion, which is presumed to represent loss from the axial position, has recently been reported to be in the range 2×10^8 sec.$^{-1}$.[16b,19] The difference in the rate constants for the reaction of HY^{-3} with the two copper species is nearly 10^3, which, on the basis of the proposed mechanism, leads to the conclusion that the rate constant for water loss from the equatorial position of copper ion is in the vicinity of 2×10^5 sec.$^{-1}$. This lends support to the earlier contention that water loss from the equatorial position of copper ion should occur with a rate constant which is similar to the rate constant for water loss from nickel ion (3×10^4 sec.$^{-1}$).[16a]

Thus, a consistent mechanism is found for the five cases of HY^{-3} reaction with Ni^{+2}, $NiHT^{+3}$, NiH_2Te^{+4}, Cu^{+2}, and $CuHT^{+3}$, as well as for the other reactions of Y^{-4} already cited.

Conclusions

The multidentate ligand exchange reaction of EDTA displacing a polyamine coordinated to nickel ion is shown to proceed by a mechanism which involves a number of reaction intermediates of mixed ligand complexes. The intermediate prior to the rate-determining step is characterized as having three nitrogens of the polyamine and one acetate of the EDTA bonded to the nickel ion with the other two coordination sites occupied by water molecules. The rate-determining step is then the loss of one of the water molecules followed by the rapid bonding of the first nitrogen dentate from the EDTA.

Bonding of the two chelate molecules at all six coordination sites is not achieved in the mixed ligand intermediate complexes due to the steric hindrance of the large multidentate ligands involved. This fact predicts that exchange reactions of this type will be very sensitive to steric effects. In particular, if the steric hindrance increases to the point that at least two coordination sites must remain unchelated in all intermediates, the reaction will slow down by several orders of magnitude due to the loss in the stability of the intermediates.

The effect of dentate number should be directly analogous to the formation and dissociation reactions. An increase in the number of similar donor atoms on the incoming ligand should increase the reaction rate in an electrostatic and statistical manner whereas a similar increase in the ligand being displaced (compare nickel tetren to nickel trien) should markedly reduce the observed rate constant. This latter generalization is true if the number of bonded donor atoms for the ligand being displaced is equal to or exceeds the number which are bonded at the time of the rate-determining step.

In a series of similar rate steps (*e.g.*, the loss of water or the breakage of a nickel–nitrogen bond) the step following the intermediate of lowest stability will be favored as the rate-determining step. The stability of an intermediate mixed complex is dependent on the stabilities of the segments of the two multidentate ligands involved in the exchange. Often chelate segments will tend to parallel the stabilities of the multidentate ligands of which they are a part. In such a case the succeeding intermediates will tend to increase in stability if the attacking ligand is the stronger chelate or decrease if the attacking ligand forms a complex of lower stability. Therefore, the rate-determining step can be expected to lie near the beginning of the reaction in the former case and near the end in the latter. This may not hold true for chelates whose stabilities vary due to the number of dentates (*e.g.*, trien *vs.* tetren) nor for mixed donor chelates whose segments contain different ratios of the donor types than does the parent ligand. Large variations in the rotational barriers in the different segments can also have a separate influence on the rate-determining step.

The analysis of the present exchange reactions has revealed that several of the intermediate steps proceed at rates of nearly the same order of magnitude. This suggests that the exchange reactions will be much more readily affected by changes in rotational barriers and the substitution of labile donor atoms into the chelate structure than is the case for the formation and dissociation reactions. The analysis of the effect of certain other variables is complicated by the fact that the exchange reactions involve both a formation reaction and a dissociation reaction which are proceeding simultaneously. Thus an increase in acidity produces a dual phenomenon since protonation of the dissociating ligand markedly increases the reaction rate whereas protonation of the incoming ligand tends to slow the reaction (not including the effect of electrostatic factors).

The mechanism proposed for the EDTA exchange with the nickel polyamines is shown to be consistent with the EDTA reactions with aquonickel ion, aquocopper ion, and copper(II) trien. In the last case it is proposed that the polyamine chelate prevents the rapid interchange of axial and equatorial positions around Cu(II), causing the reaction to be relatively sluggish in comparison with other Cu(II) forms.

Acknowledgments.—The authors wish to thank the National Science Foundation for providing a grant (D. W. M.) and a cooperative fellowship (D. B. R.) in support of this research.

---

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