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Multidentate Ligand Kinetics. III. The Formation and Dissociation of Triethylenetetraminenickel(II) and Tetraethylenepentaminenickel(II) and their Exchange with Radionickel Ion

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The kinetics of the formation and dissociation reactions of triethylenetetraminenickel(II) and of tetraethylenepentaminenickel(II) as well as their exchange reactions with radionickel ion have been studied at 25°, $\mu = 0.1$, pH 4.5 to 7.5, using spectrophotometric, titrigraphic, and radiochemical methods. It is proposed that these 4- and 5-dentate ligands react with nickel by the stepwise formation of coördinate bonds, where the rate-determining step is the formation of the first Ni–N bond and the subsequent bonding is rapid. Similarly, the dissociation mechanism proposed involves the pre-equilibration of intermediately bonded species leading to the rate step of breaking the last Ni–N bond. On this basis it is possible to estimate the equilibrium constants for each of the reaction intermediates. The differences in the reaction-rate constants of the straight-chain polyamimes (having from 2 to 6 nitrogens), as well as their protonated species, can be attributed entirely to statistical and electrostatic effects. This model should be applicable to complexes containing other metal ions and other unbranched multidentate ligands.

Introduction

Previous papers in this series have dealt with the kinetic behavior of electrophilic attack on complexes of metal ions with ethylenediaminetetraacetic acid and related derivatives.[1] The present investigation was undertaken to gain a more detailed understanding of the variables involved in multiple ring formation between a metal ion and a multidentate ligand. This study has taken advantage of the relative sluggishness of nickel(II) complexes of the polyamines. These complexes possess the added advantage of involving a single type of coördination bond, thus simplifying the analysis of the rates of bond breakage and formation.

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

$$Ni^{+2} + HT^{+} \longrightarrow NiT^{+2} + H^{+} \qquad (1)$$

$$Ni^{+2} + H_2Te^{+2} \longrightarrow NiTe^{+2} + 2H^{+} \qquad (2)$$

$$^{63}Ni^{+2} + NiT^{+2} \longrightarrow {}^{63}NiT^{+2} + Ni^{+2} \qquad (3)$$

$$^{63}Ni^{+2} + NiHTe^{+3} \longrightarrow {}^{63}NiHTe^{+3} + Ni^{+2} \qquad (4)$$

where T represents the quadridentate polyamine, triethylenetetramine (trien), and Te is the quinquedentate polyamine, tetraethylenepentamine (tetren).

In this work a mechanism is proposed for reactions 1 and 2 which involves the stepwise formation of coordinate bonds in the multidentate ligands much as the stepwise addition of monodentate ligands occurs in the equilibria of metal ammines.

In the kinetics of the polyamines the rate-determining step occurs in the formation of the first Ni–N coördinate bond. Electrostatic and statistical factors can account for changes of the reaction-rate constant with different polyamines or with pH. The equilibrium constants for the formation and breakage of the individual coördinate bonds in the multidentate complexes are estimated and successfully applied in predicting the formation and dissociation rates of nickel(II) ion with the other straight-chain polyamines.

Successful resolution of the mechanisms of reactions 3 and 4 has been possible only in the case where no protons are involved.

Experimental

Purification of Polyamines.—For the radionickel exchange studies, reagent grade triethylenetetramine disulfate (J. T. Baker Chemical Co.) was converted to the tetrachloride salt by means of an anion exchange resin and then recrystallized several times from hot alcohol–water solution. Thus, SO_4^{-2} complexes of Ni were avoided. Under the conditions of lower concentration of reactants in the formation rate studies the recrystallized disulfate salt was used. It was shown that variations in SO_4^{-2}, from 0.2 to 0.6 mM, had no effect on the latter reactions.

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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).

Tetraethylenepentamine was obtained in impure form from Union Carbide Chemicals Co. The Cl^- and SO_4^{-2} salts were prepared[2] and recrystallized several times from alcohol–water solution.

Since the starting sample was shown by gas chromatography to have many components and tetren isomers may have been present, we established the purity of the tetren sulfate salt by means of gas chromatography. A 5-ft., 0.25-in. diameter column was packed with hexamethyldisilazane-treated Chromosorb W (Johns-Mansville Co.) coated with 20% SE-30 silicone rubber gum (General Electric Co.). Tetren had a retention time of 11.5 min. when this column was operated at 200° with a flow rate of 50 cc. of helium per min. Salt samples were converted to the amine by dissolving them in water, adding concentrated NaOH to pH 12, and evaporating the water. The original liquid tetren contained at least seven major components, including trien. All impurities detectable by gas chromatography were removed with two recrystallizations.

Polyamine solutions were prepared by dissolving the purified salt in water and were standardized by a spectrophotometric mole-ratio plot with primary standard Cu at 580 mμ.

Radioactive Nickel.—Nickel(II)-63 (half-life, 85 years, maximum β^- energy, 63 kev.) was used for exchange experiments. Its concentration was sufficiently low that the stable decay product, copper(II)-63, did not interfere.

Nickel Polyamine Solutions.—The nickel polyamine complex solutions were prepared by adding a slight excess of recrystallized $Ni(ClO_4)_2$ (prepared from $NiCO_3$) to the polyamine solution and precipitating the excess Ni by addition of NaOH to pH 11.5. The Ni concentration of the filtered solutions was checked by adding excess cyanide ion at pH 9 and measuring the concentration of the resultant $Ni(CN)_4^{-2}$ spectrophotometrically at 267 mμ. The results were in agreement with the original polyamine concentration.

Reaction Conditions.—Acetate buffers ($[OAc^-] \leq 0.025$ M) were used for the radionickel exchange studies and were shown not to affect the rate. A borate–mannitol buffer (10^{-3} M borate ion, 1–3% mannitol) was used for the dissociation rate study of nickel trien with Cu and also was used at slightly higher concentrations for the other spectrophotometric studies. The reactions were unaffected by changes in buffer concentration.

Recrystallized $NaClO_4$ was used to maintain constant ionic strength at $\mu = 0.1$ in all rate solutions. The reactions were studied at 25.0 ± 0.1° using spectrophotometric, titrigraphic, and radiochemical techniques.

Formation Studies.—The rates of formation of the nickel polyamines were followed spectrophotometrically with a thermostated Beckman DU at 235 mμ using the following molar absorptivity values: $\epsilon_{Ni} = 0.5$, $\epsilon_T = 6.4$, $\epsilon_{Te} = 6.0$, $\epsilon_{NiT} = 350$, $\epsilon_{NiTe} = 510$. The protonated complexes did not alter these values significantly in the pH range 5 to 7.5.

The rate of formation of nickel tetren also was followed using a titrigraph (Radiometer, Copenhagen) as a pH-stat where the protons released in the reaction

$$Ni^{+2} + H_xTe^{+x} \longrightarrow NiH_yTe^{+2+y} + (x - y)H^+ \quad (5)$$

were automatically titrated with 0.05 M NaOH to maintain a pre-set pH value. In the range of pH 5 to 6.3, the value of $(x - y)$ varies between 2.95 and 2.98 (2.96 was used for all calculations).

Dissociation Study.—The dissociation rate of nickel trien was studied spectrophotometrically below pH 4.9 and at low copper concentrations, where the reaction

$$Cu^{+2} + NiHT^{+3} \rightleftharpoons CuHT^{+3} + Ni^{+2} \quad (6)$$

is governed entirely by the dissociation rate of the nickel complex, with the Cu^{+2} then reacting rapidly with the free trien.[8] Thus, the data represented a first-order reaction in the nickel polyamine complex. The reaction was followed at 595 mμ using the following molar absorptivity values: $\epsilon_{Cu} = 1.4$, $\epsilon_{Ni} = 0.8$, $\epsilon_{CuT} = 148$, $\epsilon_{NiT} = 5.8$.

Radionickel Exchange Studies.—The exchange reactions were initiated by adding a known amount of $^{63}NiCl_2$ to a solution containing the nickel(II)–polyamine complex. The rate was followed by precipitating $Ni(OH)_2$ from aliquots of the reaction mixture. The precipitate was filtered, washed with dilute base, and dissolved in 1:1 HCl. NaOAc was added and the solution was concentrated almost to dryness. The remaining solids were dissolved in 0.5 ml. of 1.0 M HCl and mixed with 20 ml. of a 95% ethanol–toluene (60:40) scintillation solvent, containing 4.0 g./l. of 2,5-diphenyloxazole (PPO) and 0.1 g./l. of 1,4-di-(2-(5-phenyloxazolyl))-benzene (POPOP). The sample activity was measured at −5° in a Packard Tri-Carb 4 π liquid scintillation counter. The average count rate was taken from a minimum of three countings of 10^5 counts each. Relative counting was used, with standards carried through the same procedure. The standard deviation in count rate was 4.8%, adding to the scatter of the kinetic data.

Considerable zero-time exchange (corrected for in the calculations) was noted for both tetren and trien reaction systems varying from 45% at high acidities to 3% at low acidities. This was due mainly to partial acid dissociation of the complex under conditions of the run and re-formation of the complex upon the addition of base to precipitate the excess Ni.

The protonation constants for tetren[4] at 25° and $\mu = 0.075$ gave the relative concentrations of the various protonated species of tetren and nickel tetren at each acidity studied. The trien constants for 25° and $\mu = 0.1$ were estimated from Schwarzenbach's values[5] for 20°, $\mu = 0.1$, by using the heats of ionization calculated from the constants of Jonassen, *et al.*,[6] for 30 and 40° at $\mu = 1.0$ (see Table I).

TABLE I

ACID DISSOCIATION CONSTANTS AND COMPLEX STABILITY CONSTANTS FOR TRIETHYLENETETRAMINE AND TETRAETHYLENEPENTAMINE AT 25°

Acid dissociation constants[a]	trien ($\mu = 0.1$)	tetren ($\mu = 0.075$)
$pK_{(H_5P)}$	. . .	3.15
$pK_{(H_4P)}$	3.25	4.83
$pK_{(H_3P)}$	6.55	8.14
$pK_{(H_2P)}$	9.08	9.38
$pK_{(HP)}$	9.80	9.78
Stability constants[a]		
$\log K_{NiP}^{Ni}$	13.82	17.51
$\log K_{NiHP}^{Ni}$	8.7	12.66
$\log K_{NiHP}^{NiP}$	4.7	4.93

$$K_{(H_5P)} = \frac{[H^+][H_4P]}{[H_5P]}, \text{ etc.}$$

$$K_{NiP}^{Ni} = \frac{[NiP]}{[Ni][P]}, \text{ etc.}$$

where P = polyamine

[a] The terminology for these constants is consistent with the convention used by Bjerrum, *et al.*[7]

Results

Kinetics of the Formation of Tetraethylenepentamine-nickel(II).

—The rate of formation of nickel tetren was

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[2] C. N. Reilley and A. Vavoulis, *Anal. Chem.*, **31**, 243 (1959).

[3] D. W. Margerum and J. J. Latterell, Abstracts of Papers, 142nd National Meeting of the American Chemical Society, Atlantic City, N. J., 1962, p. 19N.

[4] H. B. Jonassen and L. Westerman, *J. Am. Chem. Soc.*, **79**, 4275 (1957).

[5] G. Schwarzenbach, *Helv. Chim. Acta*, **33**, 974 (1950).

[6] H. B. Jonassen, G. Hurst, R. LeBlanc, and A. Meibohm, *J. Phys. Chem.*, **56**, 16 (1952).

[7] J. Bjerrum, G. Schwarzenbach, and L. G. Sillén, "Stability Constants, Part I. Organic Ligands," The Chemical Society, London, 1957.

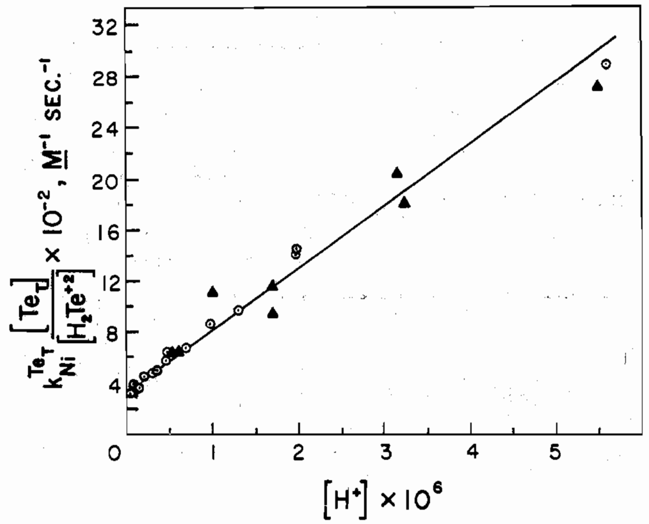

Fig. 1.—Resolution of the rate constants for the formation reaction of tetraethylenepentaminenickel(II) at 25°, $\mu = 0.1$. Plot of the equation

$$k_{Ni}^{Te_T}\frac{[Te_T]}{[H_2Te^{+2}]} = k_{Ni}^{H_2Te} + k_{Ni}^{H_3Te}\frac{[H^+]}{K_{(H_2Te)}}$$

○, spectrophotometric runs; △, titrigraphic runs.

studied spectrophotometrically from pH 4.7 to 7.4. Higher pH values were not practicable due to the rapidity of the reaction and the tendency of $Ni(OH)_2$ to precipitate. At low pH values a very large excess of one reactant is required to force the reaction to completion. The formation reaction also was studied using the titrigraphic method as an independent check on the rate. The range of acidity included in this study was from pH 5.0 to 6.3.

TABLE II

SECOND-ORDER RATE CONSTANTS FOR THE REACTION OF Ni^{+2} AND TRIETHYLENETETRAMINE

25.0°, $\mu = 0.1$

(Spectrophotometric method)

$[Ni^{+2}] = [Te_T] = 0.100$ mM

pH	$k_{Ni}^{Te_T}$, M^{-1} sec.$^{-1}$	pH	$k_{Ni}^{Te_T}$, M^{-1} sec.$^{-1}$
4.68	1.53, 1.60	6.45[a]	9.67
4.70	1.40, 1.43	6.51	10.8
4.97	2.15	6.69	15.5
5.25	2.70	6.88	18.7
5.49	3.22	7.00	24.8
5.70	4.65, 4.60	7.11[a]	31.0, 27.3
5.89	5.00	7.17[b]	30.8, 27.0
6.01	5.93	7.18	36.2, 38.7
6.17	6.72	7.20[c]	31.3, 34.8
6.32	8.97, 8.52	7.40	58.2

(Titrigraphic method)

pH	$[Ni^{+2}]$, mM	$[Te_T]$, mM	$k_{Ni}^{Te_T}$, M^{-1} sec.$^{-1}$
5.00	1.50	0.025	1.62
5.00	1.00	.025	1.20
5.00	0.100	.100	1.53
5.26	.100	.100	2.62
5.49	.100	.100	3.32
5.50	.100	.100	3.90
5.77	.075	.075	3.65, 4.45
6.00	.100	.100	7.52
6.25	.075	.075	7.92
6.27	.050	.050	8.12

[a] $[Ni^{+2}] = [Te_T] = 0.200$ mM. [b] $[Ni^{+2}] = [Te_T] = 0.150$ mM. [c] $[Ni^{+2}] = [Te_T] = 0.075$ mM.

Variation of the amount of excess Ni in the titrigraphic runs showed that the reaction conforms to the second-order equation

$$R_f = \frac{d[NiTe_T]}{dt} = k_{Ni}^{Te_T}[Ni^{+2}][Te_T] \qquad (7)$$

where $[Te_T]$ is the total concentration of all species of free tetren and $[NiTe_T]$ is the total concentration of all species of nickel tetren.

The rate constants obtained from the two methods agree and increase with increasing pH (see Table II). It is possible to resolve the rate into individual components to fit the expression

$$R_f = k_{Ni}^{H_2Te}[Ni^{+2}][H_2Te^{+2}] + k_{Ni}^{H_3Te}[Ni^{+2}][H_3Te^{+3}] \quad (8)$$

where $k_{Ni}^{H_2Te} = 3.2 \times 10^2\ M^{-1}$ sec.$^{-1}$ and $k_{Ni}^{H_3Te} = 3.5\ M^{-1}$ sec.$^{-1}$ (see Fig. 1). Terms involving the other species of tetren do not appear to contribute significantly to the rate of formation in the pH range studied.

Since only the formation-rate constants involving two or three protons are important in this pH interval, the principle of microscopic reversibility dictates that the dissociation-rate constants involving the same number of protons are the only ones of significance at this same acidity level. Considering the fact that $NiHTe^{+3}$ is a stable species in this range, the rate of dissociation can be represented by the equation

$$R_d = k_H^{NiHTe}[H^+][NiHTe^{+3}] + k_{2H}^{NiHTe}[H^+]^2[NiHTe^{+3}] \quad (9)$$

Using the equilibrium constants in Table I these dissociation constants can be calculated from the equilibria

$$Ni^{+2} + H_3Te^{+3} \underset{k_{2H}^{NiHTe}}{\overset{k_{Ni}^{H_3Te}}{\rightleftharpoons}} NiHTe^{+3} + 2H^+ \quad (10)$$

$$Ni^{+2} + H_2Te^{+2} \underset{k_H^{NiHTe}}{\overset{k_{Ni}^{H_2Te}}{\rightleftharpoons}} NiHTe^{+3} + H^+ \quad (11)$$

The values thus calculated are $k_{2H}^{NiHTe} = 2.5 \times 10^5\ M^{-2}$ sec.$^{-1}$ and $k_H^{NiHTe} = 0.17\ M^{-1}$ sec.$^{-1}$.

Kinetics of the Formation of Triethylenetetraminenickel(II).—The rate of formation was studied spectrometrically from pH 5.0 to 7.0. As with tetren this formation reaction is second order, which agrees with the first-order dependence of the dissociation reaction.[8] The effective stability constant of the nickel trien complex is sufficiently small that the reaction did not go to completion at the lower pH values with the concentration levels used. Therefore, the initial slopes of the second-order rate plots were used to calculate the rate constants (see Table III). At the lowest pH value the reaction proceeded less than 50% and in general the rate constants at low pH are less accurate than at high pH.

The data were resolved to fit the rate expression

$$R_f = k_{Ni}^{HT}[Ni^{+2}][HT^+] + k_{Ni}^{H_2T}[Ni^{+2}][H_2T^{+2}] \quad (12)$$

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(8) J. J. Latterell, M.S. Thesis, Purdue University, 1962.

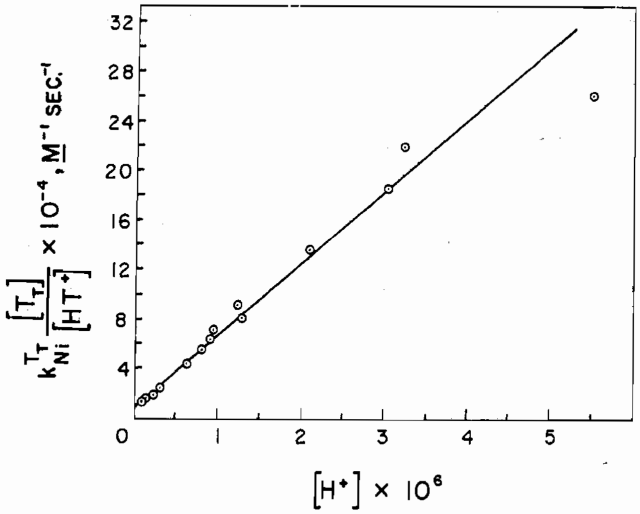

Fig. 2.—Resolution of the rate constants for the formation reaction of triethylenetetraminenickel(II) at 25°, μ = 0.1. Plot of the equation

$$k_{Ni}{}^{T_T}\frac{[T_T]}{[HT^+]} = k_{Ni}{}^{HT} + k_{Ni}{}^{H_2T}\frac{[H^+]}{K_{(H_2T)}}$$

Table III

Second-Order Rate Constants for the Reaction of Ni^{+2} and Triethylenetetramine

(Spectrophotometric method)

25.0°, μ = 0.1, $[Ni^{+2}] = [T_T] = 0.100$ mM

pH	$k_{Ni}{}^{T_T}$, M^{-1} sec.$^{-1}$	pH	$k_{Ni}{}^{T_T}$, M^{-1} sec.$^{-1}$
4.99	1.30	6.03	14.3, 13.8
5.26	2.83	6.09	14.3
5.49	4.50	6.20	17.3
5.52	4.00	6.52	32.2
5.68	6.50	6.68	41.7
5.89	9.33	6.87	69.3
5.91[a]	11.7	6.99	86.2

[a] $[Ni^{+2}] = [T_T] = 0.025$ mM.

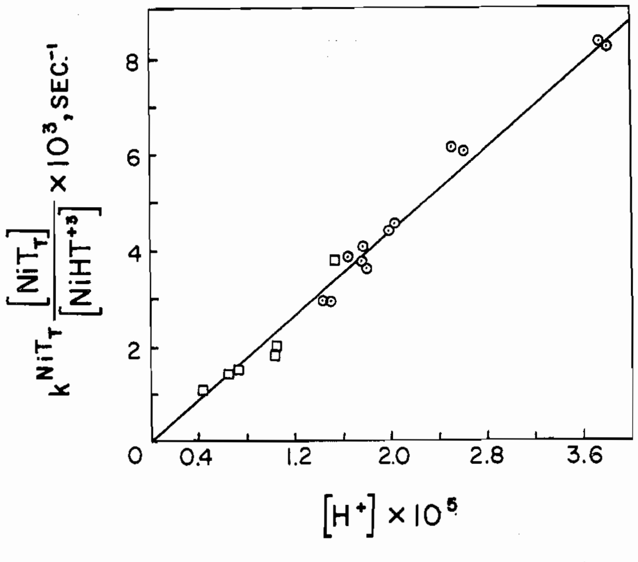

Fig. 3.—Resolution of the rate constants for the dissociation reaction of triethylenetetraminenickel(II) at 25°, μ = 0.1. Plot of the equation

$$k^{NiT_T}\frac{[NiT_T]}{[NiHT^{+3}]} = k^{NiHT} + k_H{}^{NiHT}[H^+]$$

□, runs with slight interference from second-order Cu(II) attack.

where $k_{Ni}{}^{HT} = 9.3 \times 10^3$ M^{-1} sec.$^{-1}$ and $k_{Ni}{}^{H_2T} = 45$ M^{-1} sec.$^{-1}$ (see Fig. 2). The other species of trien do not appear to contribute significantly to the rate in the pH range studied.

The corresponding dissociation-rate constants again can be calculated in the same manner as employed in the nickel tetren system to yield the constant $k^{NiHT} = 1.8 \times 10^{-5}$ sec.$^{-1}$ and $k_H{}^{NiHT} = 1.1 \times 10^2$ M^{-1} sec.$^{-1}$ for the expression

$$R_d = k^{NiHT}[NiHT^{+3}] + k_H{}^{NiHT}[H^+][NiHT^{+3}] \quad (13)$$

The value for $k_H{}^{NiHT}$ was calculated from $k_{Ni}{}^{H_2T}$ which was not known as accurately as desired because the formation reaction rate at low pH was affected by back reaction as discussed above. Therefore, $k_H{}^{NiHT}$ was measured more directly as described in the following section.

Kinetics of the Dissociation of Triethylenetetramine-nickel(II).—A direct measurement of $k_H{}^{NiHT}$ was obtained by using reaction 6 under conditions where there is no appreciable attack by Cu^{+2} on the complex and the rate is governed only by the dissociation of nickel trien. The reaction was first order and the data (see Table IV) were resolved to fit eq. 13, giving k^{NiHT} $<< 1 \times 10^{-4}$ sec.$^{-1}$ and $k_H{}^{NiHT} = 2.3 \times 10^2$ M^{-1} sec.$^{-1}$ (see Fig. 3). It will be noted that the latter constant is twice the value calculated from the formation data, which is in good agreement considering the difficulties inherent in the formation measurements. Since the dissociation method of measuring the more acidic constant is believed to be the more accurate, the value thus obtained was used to recalculate the corresponding formation constant. This value, as well as the best values for the two dissociation constants, is listed in Table VII.

Table IV

First-Order Rate Constants for the Dissociation of Nickel Triethylenetetramine (Using Cu^{+2} as Scavenger)

25.0°, μ = 0.1

pH	$[NiT_T] = [Cu^{+2}]$, mM	$k^{NiT_T} \times 10^3$, sec.$^{-1}$
4.44[a]	0.0910	5.33, 5.30
4.58	.103	3.45
4.60	.0618	3.42
4.69	.0618	2.30
4.70	.103	2.20
4.74	.103	1.68
4.75	.0618	1.92
4.75	.103	1.77
4.78	.0618	1.75
4.82	.103	1.25
4.84	.0618	1.23

[a] $[Cu^{+2}] = 0.126$ mM.

Radionickel Exchange with Tetraethylenepentamine-nickel(II).—The rate of nickel exchange with the nickel tetren complex was studied from pH 4.6 to 6.1 using a constant concentration of $^{63}NiCl_2$ as outlined in the Experimental section. The reaction also was studied by varying the radionickel ion concentration while maintaining constant pH at 4.85 and 5.62 (see Table V).

TABLE V

INITIAL RATES OF EXCHANGE OF $^{63}Ni^{+2}$ WITH NICKEL TRIETHYLENETETRAMINE

25.0°, $\mu = 0.1$, $[^{63}Ni^{+2}] = 0.523$ mM, $[NiTe_T] = 1.05$ mM

pH	Initial rate × 10⁸, M sec.⁻¹	pH	Initial rate × 10⁸, M sec.⁻¹
4.66	9.37	5.58	0.303
4.71	9.63	5.59	.400
4.85	5.37	5.62	.407
4.90	3.02	5.66	.245
5.16	1.24	5.78	.135
5.18	1.57	5.92	.082
5.39	1.26	6.07	.103
5.52	0.168		

pH = 4.85, $[NiTe_T] = 1.05$ mM		pH = 5.62, $[NiTe_T] = 1.05$ mM	
$[Ni^{+2}]$, mM	Initial rate × 10⁸, M sec.⁻¹	$[Ni^{+2}]$, mM	Initial rate × 10⁸, M sec.⁻¹
0.291	3.93	0.261	0.290
.385	4.53	.366	.585
.539	5.37	.523	.407
.692	7.42	.679	.475
.795	7.00	.784	.733
1.05	12.7	1.31	1.12
1.31	8.37	1.57	1.35
1.57	10.28		

The exchange rate data were resolved to fit the expression

$$R_e = k^{\mathrm{NiHTe}}[Ni^{+2}][NiHTe^{+3}] + k_{\mathrm{Ni,H}}^{\mathrm{NiHTe}}[H^+][Ni^{+2}][NiHTe^{+3}] + k_{\mathrm{H}}^{\mathrm{NiHTe}}[H^+][NiHTe^{+3}] + k_{\mathrm{2H}}^{\mathrm{NiHTe}}[H^+]^2[NiHTe^{+3}] \quad (14)$$

where the first two terms represent the attack of Ni^{+2} on the complex and the last two terms involve the acid dissociation of the complex. Using the dissociation rate constants given in Table VII (calculated from the spectrophotometric and titrigraphic methods) the contribution of the last two terms was subtracted from the observed exchange-rate values and the two terms involving Ni^{+2} attack then were resolved to give $k_{\mathrm{Ni}}^{\mathrm{NiHTe}} = 1.7 \times 10^{-2}\ M^{-1}$ sec.⁻¹ and $k_{\mathrm{Ni,H}}^{\mathrm{NiHTe}} = 4.17 \times 10^{3}\ M^{-2}$ sec.⁻¹.

The agreement between the theoretical rate curve based on eq. 14 and the observed rate data is shown in Fig. 4.

Radionickel Exchange with Triethylenetetraminenickel(II).—The rate of nickel exchange with nickel trien was studied from pH 5.3 to 7.2 and the dependence on Ni^{+2} concentration was studied at pH 5.68 (see Table VI). Due to the higher pH it was necessary to include a third exchange term involving the attack of Ni^{+2} on the unprotonated complex in order to account for the data over the entire pH range. The resulting rate equation is

$$R_e = k_{\mathrm{Ni}}^{\mathrm{NiT}}[Ni^{+2}][NiT^{+2}] + k_{\mathrm{Ni}}^{\mathrm{NiHT}}[Ni^{+2}][NiHT^{+3}] + k_{\mathrm{Ni,H}}^{\mathrm{NiHT}}[H^+][Ni^{+2}][NiHT^{+3}] + k^{\mathrm{NiHT}}[NiHT^{+3}] + k_{\mathrm{H}}^{\mathrm{NiHT}}[H^+][NiHT^{+3}] \quad (15)$$

The data were treated in the same manner used for nickel tetren. However, some difficulty was encountered in determining the exchange rate constants due to bad scattering of the rate data and the fact that over most of the pH range studied it was necessary to treat the three exchange terms simultaneously. By plotting the data against both $[H^+]$ and $1/[H^+]$ and using successive approximations, a consistent set of constants was determined as follows

$$k_{\mathrm{Ni}}^{\mathrm{NiT}} = 2 \times 10^{-3}\ M^{-1}\ \mathrm{sec.}^{-1}$$
$$k_{\mathrm{Ni}}^{\mathrm{NiHT}} = 0.3\ M^{-1}\ \mathrm{sec.}^{-1}$$
$$k_{\mathrm{Ni,H}}^{\mathrm{NiHT}} = 3 \times 10^{5}\ M^{-2}\ \mathrm{sec.}^{-1}$$

The accuracy of these values is considered to be limited to a factor of about 2. The agreement between the theoretical rate curve based on eq. 15 and the observed rate data is shown in Fig. 4.

TABLE VI

INITIAL RATES OF EXCHANGE OF $^{63}Ni^{+2}$ WITH NICKEL TRIETHYLENETETRAMINE

25.0°, $\mu = 0.1$, $[^{63}Ni^{+2}] = 0.523$ mM, $[NiT_T] = 1.05$ mM

pH	Initial rate × 10⁸, M sec.⁻¹	pH	Initial rate × 10⁸, M sec.⁻¹
5.28	56.7, 55.5	5.93	2.55
5.31	48.5, 41.8	5.99	2.60, 2.20
5.38	37.2, 32.5	6.45	0.865
5.44	21.0	6.48	.717
5.50	34.0	6.60	.232
5.60	13.0	6.68	.430
5.68	14.7, 12.1	6.92	.253
5.71	7.33	7.00	.213
5.82	5.23	7.12	.293

pH = 5.68, $[NiT_T] = 1.05$ mM

$[Ni^{+2}]$, mM	Initial rate × 10⁸, M sec.⁻¹
0.281	5.63
.381	7.27
.532	11.7
.687	11.3
.791	8.47
1.05	8.47
1.31	15.8
1.57	14.4

TABLE VII

EXPERIMENTAL RATE CONSTANTS AT 25.0°, $\mu = 0.1$

Formation constants

$k_{\mathrm{Ni}}^{\mathrm{HT}} = 9.3 \times 10^{3}\ M^{-1}$ sec.⁻¹
$k_{\mathrm{Ni}}^{\mathrm{H_2T}} = 97\ M^{-1}$ sec.⁻¹
$k_{\mathrm{Ni}}^{\mathrm{H_2Te}} = 3.2 \times 10^{2}\ M^{-1}$ sec.⁻¹
$k_{\mathrm{Ni}}^{\mathrm{H_3Te}} = 3.5\ M^{-1}$ sec.⁻¹

Dissociation constants

$k^{\mathrm{NiHT}} = 1.8 \times 10^{-5}$ sec.⁻¹
$k_{\mathrm{H}}^{\mathrm{NiT}} = 0.91\ M^{-1}$ sec.⁻¹
$k_{\mathrm{H}}^{\mathrm{NiHT}} = 2.3 \times 10^{2}\ M^{-1}$ sec.⁻¹
$k_{\mathrm{2H}}^{\mathrm{NiT}} = 1.2 \times 10^{7}\ M^{-2}$ sec.⁻¹
$k_{\mathrm{H}}^{\mathrm{NiHTe}} = 0.17\ M^{-1}$ sec.⁻¹
$k_{\mathrm{2H}}^{\mathrm{NiTe}} = 1.4 \times 10^{3}\ M^{-2}$ sec.⁻¹
$k_{\mathrm{2H}}^{\mathrm{NiHTe}} = 2.5 \times 10^{5}\ M^{-2}$ sec.⁻¹
$k_{\mathrm{3H}}^{\mathrm{NiTe}} = 2.2 \times 10^{10}\ M^{-3}$ sec.⁻¹

Radionickel exchange constants

$k_{\mathrm{Ni}}^{\mathrm{NiT}} = 2 \times 10^{-3}\ M^{-1}$ sec.⁻¹
$k_{\mathrm{Ni}}^{\mathrm{NiHT}} = 0.3\ M^{-1}$ sec.⁻¹
$k_{\mathrm{Ni,H}}^{\mathrm{NiT}\,a} = 2 \times 10^{4}\ M^{-2}$ sec.⁻¹
$k_{\mathrm{Ni,H}}^{\mathrm{NiHT}} = 3 \times 10^{5}\ M^{-2}$ sec.⁻¹
$k_{\mathrm{Ni,2H}}^{\mathrm{NiT}} = 2 \times 10^{10}\ M^{-3}$ sec.⁻¹
$k_{\mathrm{Ni}}^{\mathrm{NiHTe}} = 1.7 \times 10^{-2}\ M^{-1}$ sec.⁻¹
$k_{\mathrm{Ni,H}}^{\mathrm{NiTe}} = 1.4 \times 10^{3}\ M^{-2}$ sec.⁻¹
$k_{\mathrm{Ni,H}}^{\mathrm{NiHTe}} = 4.2 \times 10^{3}\ M^{-2}$ sec.⁻¹
$k_{\mathrm{Ni,2H}}^{\mathrm{NiTe}} = 3.5 \times 10^{8}\ M^{-3}$ sec.⁻¹

[a] $k_{\mathrm{Ni,H}}^{\mathrm{NiT}} = k_{\mathrm{Ni}}^{\mathrm{NiHT}} K_{\mathrm{NiHT}}^{\mathrm{NiT}}$, etc.

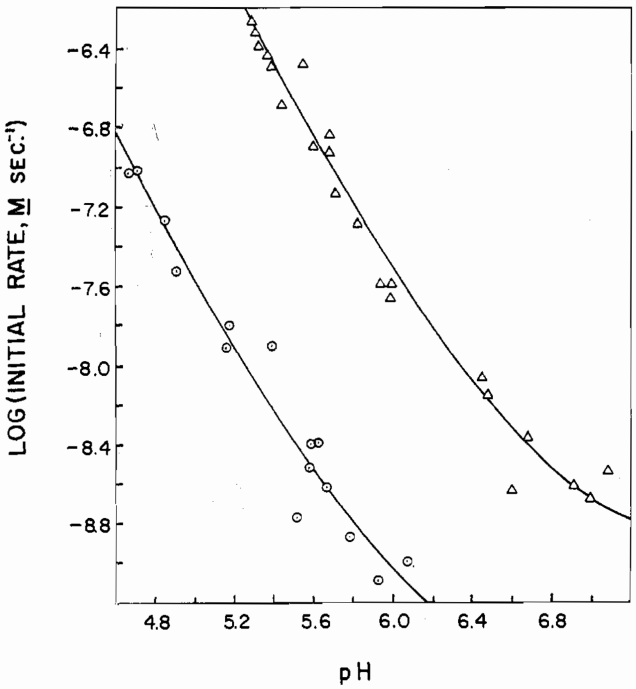

Fig. 4.—Experimental points for radionickel exchange with nickel polyamine complexes at 25°, μ = 0.1. Solid lines represent theoretical curves predicted by eq. 14 and 15. O, data for tetraethylenepentaminenickel(II); △, data for triethylenetetraminenickel(II).

Discussion

Proposed Mechanism for Formation and Dissociation Reaction.—The observed rate constants for the formation and dissociation of the nickel polyamine complexes can be considered to be complex functions involving the stepwise formation and breakage of successive coördinate bonds. Certain of these steps can be eliminated from consideration as the rate-determining step from an examination of the experimental rate equations. First, it is significant that the rate constants can be expressed in terms of the different protonated polyamine species without a more complex acid dependence. Second, the appearance of the terms involving diprotonated trien and triprotonated tetren in the experimental expressions for the formation reactions eliminates the possibility that the rate-determining step could occur after the formation of the second coördinate bond due to the fact that these species cannot form more than two bonds to the nickel and, therefore, must lose protons and hence their identities in later steps of the formation reaction. Thus, the formation of either the first or the second bond (or a combination of the two) must represent the rate step.

Examination of the detailed mechanism for nickel trien as shown in Fig. 5 reveals that the relative magnitudes of k_{1a}, k_{-1a}, k_{1b}, and k_{-1b} determine which of the first two bonds is rate determining in the reaction of nickel with monoprotonated trien.

Applying the steady-state approximation to the one-bonded intermediate results in the following expression for the reaction of nickel ion with the monoprotonated species

$$R_f = \frac{k_{1a}k_{1b}}{k_{-1a} + k_{1b}}[\mathrm{Ni}^{+2}][\mathrm{HT}^+] \qquad (16)$$

The magnitude of k_{-1a}, the rate constant for the dissociation of the last Ni–N bond, is equivalent to the rate constant for the dissociation of mono-(ammine)-nickel(II). This latter constant has been measured by Wilkins at 0° and the activation energy determined.[9] Extrapolating these data to 25° gives a value for the dissociation constant of $k_{-1a} = k^{\mathrm{NiNH_3}} = 5.8$ sec.$^{-1}$.

The value of k_{1b} should depend on the rate of water loss from the nickel ion and the energy barrier imposed by the necessity to twist the polyamine into a configuration favorable for the second bond formation. Connick and Stover have reported a value of 3.2×10^4 sec.$^{-1}$ for the rate of water loss from nickel(II) ion.[10] Ahmed and Wilkins have suggested that the "rate" of the rotation of the polyamine chain is reflected in the difference between the rate constants for the first and second bond breakages of the mono-(ethylenediamine)-nickel(II) complex.[11] These authors have measured the rate constant for the first bond breakage and reported a value (extrapolated to 25°) of 0.27 sec.$^{-1}$. Since the second bond breakage is equivalent to nickel–ammonia bond cleavage, the energy barrier due to the twisting of the polyamine is estimated to be (taking into account the statistical factor relating to the number of nickel–nitrogen bonds available for cleavage): 2(5.8/0.27) = 44, which is equivalent to a potential barrier of 2.3 kcal. mole^{-1}. In order to break the nickel–polyamine bond it is necessary to rotate either a carbon–carbon bond or a carbon–nitrogen bond. The rotational barriers of the ethane and methylamine molecules are reported to be 2.8 and 1.9 kcal. mole^{-1}, respectively.[12,13] This indicates that our estimation of the rotational barrier for the polyamine is of the correct magnitude and the value of k_{1b} is then estimated to be

$$k_{1b} = \frac{k^{\mathrm{Ni(H_2O)}}}{44} = 7.4 \times 10^2 \text{ sec.}^{-1} \qquad (17)$$

Thus it is estimated that k_{1b} is roughly 100 times greater than k_{-1a} and eq. 16 then simplifies to

$$R_f = k_{1a}[\mathrm{Ni}^{+2}][\mathrm{HT}^+] \qquad (18)$$

It is concluded, therefore, that the first bond formation represents the rate-determining step. The proposed mechanism then corresponds to the stepwise outline in Fig. 5 where the rate step is represented by k_{0a}, k_{1a}, etc., for the formation reaction, and k_{-0a}, k_{-1a}, etc., for the dissociation reaction, and the rest of the system is in equilibrium.

Estimation of Stepwise Equilibrium Constants.—The values of all the stepwise equilibrium constants represented in Fig. 5 can be estimated directly from our experimental data, independently from any rate con-

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(9) R. G. Wilkins, private communication, quoted by C. S. Garner and J. Bjerrum, *Acta Chem. Scand.*, **15**, 2055 (1961).

(10) R. E. Connick and E. D. Stover, *J. Phys. Chem.*, **65**, 2075 (1961).

(11) A. K. S. Ahmed and R. G. Wilkins, *J. Chem. Soc.*, 3700 (1959).

(12) K. S. Pitzer, *Discussions Faraday Soc.*, **10**, 66 (1951).

(13) J. G. Aston and F. L. Gittler, *J. Am. Chem. Soc.*, **77**, 3175 (1955).

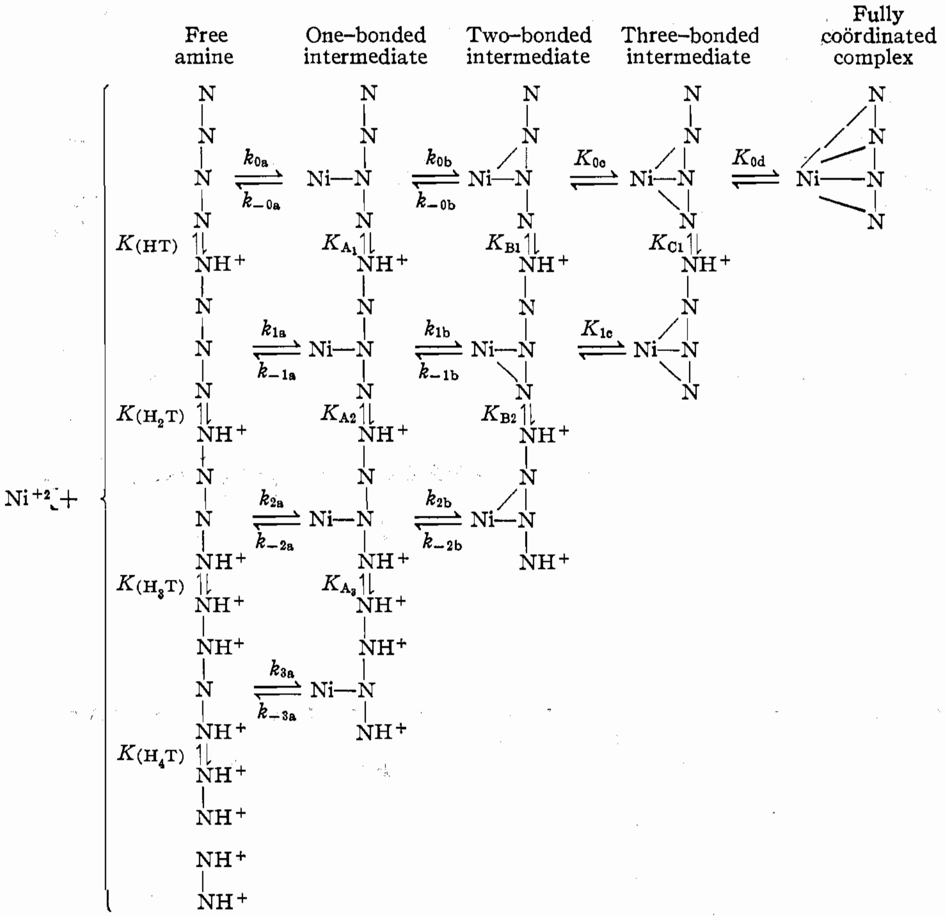

Fig. 5.—Stepwise outline for the formation and dissociation of triethylenetetraminenickel(II). Note that although the dissociation reaction is shown as an unfolding mechanism, no actual distinction is made between unfolding (breaking nickel–nitrogen bonds at both ends) and unwinding (proceeding from one end).

stants contained in the literature, if one makes the following approximations: (1) The rate of a single nickel–nitrogen bond breakage is independent of the degree of protonation on the rest of the complex (*e.g.*, $k_{-1a} = k_{-2a}$). (2) The rate of formation of the second, third, and fourth bonds is unaffected by protonation of the polyamine molecules at positions other than the new bonding site except for a statistical factor (*e.g.*, $k_{1b} = 2k_{2b}$). (3) Although the rates of formation and breakage of bonds are not necessarily independent of the number of nickel–nitrogen bonds already formed, the ratios of breakage rate to formation rate, *i.e.*, the equilibrium constants, remain essentially constant except for a statistical factor (*e.g.*, $K_{1b} = 2K_{1c}$).

The first of these approximations is valid for a nickel–nitrogen bond breakage which is dependent on the vibrational mode since a proton must be at least four atoms distant. The second approximation involves a slight error by ignoring the increased electrostatic repulsion resulting in those cases where protons on the polyamine are proximal to the amine group involved in the bond formation. However, calculations indicate that the electrostatic factor involved is not large and highly successful estimates have been obtained with the adoption of these approximations. The validity of the third approximation is attested to by the fact that each addition of an ethylamine group in the series ethylenediamine, diethylenetriamine, triethylenetetramine, tetraethylenepentamine increases the stability of the nickel complex by a nearly constant factor.[4,7]

By comparing the dissociation-rate constants for the various species of trien and tetren and applying the preceding approximations we obtain, for the appropriate equilibrium constants in Fig. 5, the values

$$K_{B2} = 2(k_H{}^{NiT}/k_{2H}{}^{NiT}) = 1.5 \times 10^{-7} \tag{19}$$

$$K'_{C2} = K_{B2} = 1.5 \times 10^{-7} \tag{20}$$

$$K_{C1}/K'_{C2} = k_H{}^{NiHTe}/k_H{}^{NiT} = 0.18$$
$$K_{C1} = K'_{C2} \times 0.18 = 2.7 \times 10^{-8} \tag{21}$$

$$K_{0d} = 1/(K_{C1} \times K_{NiHT}{}^{Ni}) = 7.4 \times 10^{2} \tag{22}$$

$$K_{A3} \cong K'_{B3} = 2 \times k_H{}^{NiHTe}/k_{2H}{}^{NiHTe} = 1.3 \times 10^{-6} \tag{23}$$

where K'_{C2} is the second protonation constant for the three-bonded intermediate of nickel tetren and K'_{B3} is the third protonation constant for the two-bonded intermediate (see Fig. 6).

By invoking the third approximation and applying the appropriate statistical factors, it is possible to evaluate the remaining stepwise equilibrium constants for the nickel–trien system. The values thus obtained are tabulated in Table VIII.

It is to be emphasized that all of the stepwise equilibrium constants have been estimated without recourse to the literature values for k^{NiNH_3} and $k_1{}^{Ni(en)}$ (rate

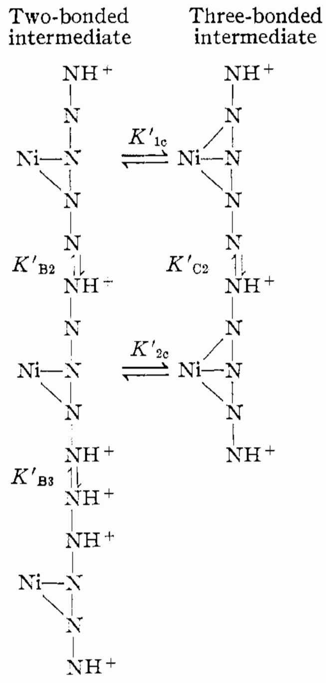

Fig. 6.—A portion of the stepwise outline for the formation and dissociation of tetraethylenepentaminenickel(II) showing K'_{C2} and K'_{B3}.

TABLE VIII

STEPWISE EQUILIBRIUM AND RATE CONSTANTS FOR THE FORMATION AND DISSOCIATION OF NICKEL TRIETHYLENETETRAMINE 25.0°, $\mu = 0.1$

Stepwise equilibrium constants

$$K_{0d} = K_{1c} = K_{2b} = 7.4 \times 10^2$$
$$K_{0c} = K_{1b} = 2K_{0d} = 1.5 \times 10^3$$
$${}^1/_3K_{A1} = {}^1/_2K_{B1} = K_{C1} = 2.7 \times 10^{-8}$$
$${}^1/_2K_{A2} = K_{B2} = 1.5 \times 10^{-7}$$
$$K_{A3} = 1.3 \times 10^{-6}$$

Stepwise formation rate constants

$$k_{0a} = {}^3/_2 \times 30 \times k_{Ni}{}^{HT} = 4.2 \times 10^5\ M^{-1}\ \text{sec.}^{-1}$$
$$k_{1a} = k_{Ni}{}^{HT} = 9.3 \times 10^3\ M^{-1}\ \text{sec.}^{-1}$$
$$k_{2a} = k_{Ni}{}^{H_2T} = 88\ M^{-1}\ \text{sec.}^{-1}$$
$$k_{0b} = k_{1b} = 2k_{2b} = 4.0 \times 10^2\ \text{sec.}^{-1}$$

Stepwise dissociation rate constants

$$k_{-0a} = k_{-1a} = k_{-2a} = k^{NiNH_3} = 5.8\ \text{sec.}^{-1}$$
$$k_{-0b} = k_{-1b} = k_{-2b} = k_1{}^{Ni(en)} = 0.27\ \text{sec.}^{-1}$$

constant for the first bond breakage for mono-(ethylenediamine)-nickel(II)). However, it can now be shown that these equilibrium constants predict nearly the same values for the rate constants as those cited in the literature.

Equating k_{-1b} to Ahmed and Wilkins' value of 0.27 sec.$^{-1}$ for $k_1{}^{Ni(en)}$ we can again estimate k_{-1b} as follows

$$k_{1b} = K_{1b}k_{-1b} = 4.0 \times 10^2\ \text{sec.}^{-1} \qquad (24)$$

which is in very good agreement with the previous estimate made in eq. 17. Conversely, by applying the estimated value for k_{1b} from eq. 17 we obtain a value of 0.49 sec.$^{-1}$ for the rate constant for the breakage of the first nickel–nitrogen bond in the Ni(en) complex.

The stepwise equilibrium constants also can be used to estimate the rate constant for the last nickel–nitrogen bond breakage from equations of the type

$$k_{2H}{}^{NiT} = \frac{k_{-2a}}{K_{0d}K_{C_1}K_{1c}K_{2b}} \qquad (25)$$

The resultant estimates for the nickel–trien system are $k_{-2a} = 19$ sec.$^{-1}$ and $k_{-1a} = 20$ sec.$^{-1}$ and nearly identical values are calculated for the nickel–tetren system. These values are about three times larger than the k^{NiNH_3} value reported by Wilkins, a relatively minor disagreement considering the number of approximations involved.

The close agreement between the literature values for the rates of breakage of the last two nickel–nitrogen bonds and the values which are predicted independently by our experimental data appear to confirm the proposed mechanism and to support the approximations which were used in estimating the stepwise equilibrium constants.

Contributions of Electrostatic and Statistical Factors.—On the basis of the proposed mechanism, the values of the experimental rate constants $k_{Ni}{}^{HT}$, $k_{Ni}{}^{H_2Te}$, etc., must represent the values of k_{1a}, k_{2a}', respectively, where k_{2a}' is the rate constant for the first bond formation of nickel with H_2Te (compare eq. 18 with eq. 8 and 12).

Ratios of these constants should correspond to the contribution of electrostatic repulsion between $Ni(H_2O)_6{}^{+2}$ and the protonated amines and the statistical availability of amine sites for coördination.

An estimation of the electrostatic factor is possible using

$$\Delta S^* = -\frac{20Z_{Ni}Z_H}{r^*} \qquad (26)$$

where r^* represents the distance between the aquonickel ion and a protonated amine site during the first bond formation; Z_{Ni} is +2, Z_H is +1, and the sum of the values for all protons is taken. The electrostatic contribution to the ratio of any two rate constants can then be evaluated by means of eq. 27, where $(\partial \ln D/\partial \ln T)_P = 1.4$ at 25°.[14]

$$-\frac{\Delta(\Delta S^*)}{\left(\dfrac{\partial \ln D}{\partial \ln T}\right)_P} = -\frac{\Delta(\Delta F^*)}{T} = R \ln (k_1/k_2) \qquad (27)$$

We have estimated ΔS^* using eq. 26, calculating the proportion of each structural isomer of a protonated polyamine species and the contribution of nickel attack at each open amine position for each isomer. However, these estimations are quite involved and awkward to use so we have adopted a semi-empirical approximation which gives similar answers and is simple to use. The empirical model assumes that the addition of each proton to the polyamine effectively increases the charge by +1 at a distance of $r^* = 5$ Å. (5 Å. corresponds to the distance between an aquonickel ion and a proton on an amine group adjacent to the bonding site). This does not mean that nickel bonds to nitrogens adjacent to protonated sites but rather that this is, to a first approximation, a model equivalent to the more elaborate one. Equations 26 and 27 then give $k_1/k_2 = 28$

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[14] S. W. Benson, "The Foundations of Chemical Kinetics," McGraw-Hill Book Co., New York, N. Y., 1960, p. 538.

for the ratio of rate constants of two polyamines containing the same number of available coördination sites and differing only by a unit of charge. The experimental ratios are $k_{\mathrm{Ni}}{}^{\mathrm{HT}}/k_{\mathrm{Ni}}{}^{\mathrm{H_2Te}} = 29$ and $k_{\mathrm{Ni}}{}^{\mathrm{H_2T}}/k_{\mathrm{Ni}}{}^{\mathrm{H_3Te}} = 28$, in agreement with our model.

A statistical factor would be expected for the ratio of rate constants of two polyamine species having the same charge but differing in their relative number of open amine positions. Thus the ratio $k_{\mathrm{Ni}}{}^{\mathrm{H_2Te}}/k_{\mathrm{Ni}}{}^{\mathrm{H_2T}}$ would have a statistical factor of 1.5 with three and two open amine positions for $\mathrm{H_3Te^{+2}}$ and $\mathrm{H_2T^{+2}}$, respectively. The experimental ratio is 3.0, which may reflect a slight electrostatic contribution making it somewhat easier for $\mathrm{Ni^{+2}}$ to approach the longer chain.

From the foregoing discussion it is evident that electrostatic repulsion is the major factor governing the rate of reaction of nickel with the polyamine chelates, whereas a statistical factor contributes only to a slight extent. In making predictions for the other polyamine systems an electrostatic factor of 30 has been assigned for each unit change in the charge of the polyamines and a statistical factor has been assigned for each open amine position.

Predictions for Other Nickel Polyamine Systems.—Setting up stepwise outlines as in Fig. 5 for other nickel–polyamine systems and adjusting the appropriate constants from Table VIII for electrostatic and statistical considerations enables us to estimate the rates of formation and dissociation for any of the straight-chain polyamine complexes of nickel ion as well as their stability constants. In making these estimations, the breakage rate constant for the last nickel–nitrogen bond was assumed to be equal to the literature value for mono-(ammine)-nickel(II) dissociation.

The results are tabulated in Table IX and are compared with literature values where available. It is seen that almost all of the predictions which can be checked against literature values agree to better than a factor of ten and in the case of the dissociation constants a large portion of the error may be attributable to the approximations used to adjust the literature value to 25°. Despite the errors involved, it is felt that the predictions are in sufficiently good agreement with experimental values to verify the validity of the proposed mechanism for the unsubstituted straight-chain polyamines.

Exceptions to Proposed Mechanism.—It is to be noted that since the rate of formation of the second bond is only about 100 times faster than the rate of rupture of the first bond, the rate-determining step may shift with slight alterations in the structure of the multidentate ligand. For example, the substitution of groups on the polyamine chain could slow the formation rate of successive bonds, by interfering with the rotation of the ligand molecule or hindering the closeness of approach to the metal ion, such that later steps would become rate determining. Alternatively, the substitution of weaker complexing groups into the ligand structure would be expected to increase the rate of rupture of the first bond formed which could also result in the rate step appearing at a later stage in the formation reaction.

A third possibility for a shift in the first bond mechanism involves the blocking of coördination sites by protonation or complexation with other metals where the equilibrium for the removal of these groups is unfavorable. This phenomenon appears to be involved in the reaction of nickel ion with the triprotonated trien where it is found, by using the constants in Table VIII, that the loss of a proton from the one-bonded intermediate is sufficiently unfavorable below pH 4.5 to make the rate of second bond formation important. At sufficiently low pH (less than pH 3.5) the reaction rate of nickel ion with $\mathrm{H_3T^{+3}}$ simplifies to the expression

$$R_{\mathrm{f}} = K_{3\mathrm{a}}K_{\mathrm{A3}}k_{2\mathrm{b}}\frac{[\mathrm{H_3T^{+3}}]}{[\mathrm{H^+}]}[\mathrm{Ni^{+2}}] \qquad (28)$$

which can be rewritten as

$$R_{f} = \frac{K_{3\mathrm{a}}K_{\mathrm{A3}}}{K_{(\mathrm{H_3T})}}k_{2\mathrm{b}}[\mathrm{H_2T^{+2}}][\mathrm{Ni^{+2}}] \qquad (29)$$

Using the values from Tables I and VII the value of the coefficient of $(\mathrm{H_2T^+})$ is $2.8 \times 10^2\ M^{-1}\ \mathrm{sec.}^{-1}$, which compares favorably with the experimental value of $k_{\mathrm{Ni}}{}^{\mathrm{H_2T}}$. It is concluded that no term involving $\mathrm{H_3T^{+3}}$ will be observed even at low pH values.

The same considerations lead us to the conclusion that terms involving protonated species with less than two open coördination sites will not be observed in any of the straight-chain polyamines and thus these species have been omitted from Table IX.

Formation Rate Constant of Mono-(ammine)-nickel (II).—Table IX reveals an incongruency with respect to mono-(ammine)-nickel(II) in an otherwise consistent trend of formation-rate constants. On the basis of the dissociation-rate constant[9] and the stability constant[7] for this complex, the calculated formation-rate constant is

$$k_{\mathrm{Ni}}{}^{\mathrm{NH_3}} = K_{\mathrm{NiNH_3}}{}^{\mathrm{NH_3}}k^{\mathrm{NiNH_3}} = 630 \times 5.8 = 4 \times 10^3\ M^{-1}\ \mathrm{sec.}^{-1} \qquad (30)$$

By contrast the formation-rate constant for unprotonated mono-(ethylenediamine)-nickel(II) is

$$k_{\mathrm{Ni}}{}^{\mathrm{en}} = K_{\mathrm{Ni(en)}}{}^{\mathrm{en}}k^{\mathrm{Ni(en)}} = 4 \times 10^7 \times 5 \times 10^{-3} = 2 \times 10^5\ M^{-1}\ \mathrm{sec.}^{-1} \qquad (31)$$

which is in excellent agreement with our predicted value of $1.8 \times 10^5\ M^{-1}\ \mathrm{sec.}^{-1}$.

Wilkins' value for the dissociation-rate constant is supported by measurements made at −25° by Garner and Bjerrum[15] and is consistent with our experimental data.

Thus, $k_{\mathrm{Ni}}{}^{\mathrm{NH_3}}$ is one fiftieth as large as $k_{\mathrm{Ni}}{}^{\mathrm{en}}$, which is a greater difference in properties than might be expected. Our predicted value for $k_{\mathrm{Ni}}{}^{\mathrm{NH_3}}$ also is much too large. Although $\mathrm{NH_3}$ is not a member of the homologous series under comparison, its relative sluggishness seems unusual and deserves further investigation.

Mechanism of Radionickel Exchange.—When the

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(15) C. S. Garner and J. Bjerrum, *Acta Chem. Scand.*, **15**, 2055 (1961).

TABLE IX

PREDICTED FORMATION AND DISSOCIATION RATE CONSTANTS AND STABILITY CONSTANTS FOR NICKEL–POLYAMINE COMPLEXES
25.0°, $\mu = 0.1$

Formation rate constants

Polyamine	Constant	Predicted value, M^{-1} sec.$^{-1}$	Lit. value, M^{-1} sec.$^{-1}$	Ref.
NH_3	$k_{Ni}{}^{NH_3}$	9.2×10^4	4×10^3	7, 9
en	$k_{Ni}{}^{en}$	1.8×10^5	2×10^5	7, 11
dien	$k_{Ni}{}^{D}$	2.8×10^5		
	$k_{Ni}{}^{HD}$	6.2×10^3		
trien	$k_{Ni}{}^{T}$	4.2×10^5		
	$k_{Ni}{}^{HT}$	9.3×10^{3a}		
	$k_{Ni}{}^{H_2T}$	97^a		
tetren	$k_{Ni}{}^{Te}$	4.8×10^5		
	$k_{Ni}{}^{HTe}$	1.3×10^4		
	$k_{Ni}{}^{H_2Te}$	3.2×10^{2a}		
	$k_{Ni}{}^{H_3Te}$	3.5^a		
Pentaethylene-hexamine	$k_{Ni}{}^{Pe}$	5.8×10^5		
	$k_{Ni}{}^{HPe}$	1.6×10^4		
	$k_{Ni}{}^{H_2Pe}$	4.2×10^2		
	$k_{Ni}{}^{H_3Pe}$	5.3		
	$k_{Ni}{}^{H_4Pe}$	0.12		

Dissociation constants

Polyamine	Constant	Predicted value	Lit. value	Ref.
NH_3	k^{NiNH_3}	20 sec.$^{-1}$	5.8 sec.$^{-1}$	9
en	k^{Nien}	8×10^{-3} sec.$^{-1}$	5×10^{-3} sec.$^{-1}$	11
dien	k^{NiD}	5×10^{-6} sec.$^{-1}$		
	$k_H{}^{NiD}$	3×10^2 M^{-1} sec.$^{-1}$		
	k_{diss} (pH 3.5)	0.1 sec.$^{-1}$	1 sec.$^{-1}$	16
	k_{diss} (pH 7)	5×10^{-5} sec.$^{-1}$	1.2×10^{-4} sec.$^{-1}$	16
trien	k^{NiT}	3×10^{-9} sec.$^{-1}$		
	$k_H{}^{NiT}$	0.27 M^{-1} sec.$^{-1}$	0.92 M^{-1} sec.$^{-1}$	This work
	$k_{2H}{}^{NiT}$	3.5×10^6 M^{-2} sec.$^{-1}$	1.2×10^7 M^{-2} sec.$^{-1}$	This work
	k_{diss} (pH 3.5)	0.3 sec.$^{-1}$	2.3×10^2 sec.$^{-1}$	16
tetren	k^{NiTe}	2.5×10^{-12} sec.$^{-1}$		
	$k_H{}^{NiTe}$	2×10^{-4} M^{-1} sec.$^{-1}$		
	$k_{2H}{}^{NiTe}$	2.7×10^3 M^{-2} sec.$^{-1}$	1.4×10^4 M^{-2} sec.$^{-1}$	This work
	$k_{3H}{}^{NiTe}$	3.7×10^9 M^{-3} sec.$^{-1}$	2.2×10^{10} M^{-3} sec.$^{-1}$	This work
Pentaethylene-hexamine^b	k^{NiPe}	2×10^{-15} sec.$^{-1}$		
	$k_H{}^{NiPe}$	1×10^{-8} M^{-1} sec.$^{-1}$		
	$k_{2H}{}^{NiPe}$	2 M^{-2} sec.$^{-1}$		
	$k_{3H}{}^{NiPe}$	3×10^6 M^{-3} sec.$^{-1}$		
	$k_{4H}{}^{NiPe}$	7×10^{11} M^{-4} sec.$^{-1}$		

Stability constants

Polyamine	Constant	Predicted value	Lit. value	Ref
NH_3	$K_{NiNH_3}{}^{NH_3}$	4.6×10^3	6.3×10^2	7
en	$K_{Nien}{}^{en}$	2×10^7	4×10^7	7
dien	$K_{NiD}{}^{D}$	5×10^{10}	5.0×10^{10}	7
	$K_{NiHD}{}^{HD}$	8×10^5		
trien	$K_{NiT}{}^{T}$	1.1×10^{14}	6.6×10^{13}	
tetren	$K_{NiTe}{}^{Te}$	2.0×10^{17}	3.2×10^{17}	4
	$K_{NiHTe}{}^{HTe}$	3.6×10^{12}	4.6×10^{12}	4
Pentaethylene-hexamine^b	$K_{NiPe}{}^{Pe}$	4×10^{20}		
	$K_{NiHPe}{}^{HPe}$	7×10^{15}		
	$K_{NiH_2Pe}{}^{H_2Pe}$	1×10^{11}		
	$K_{NiH_3Pe}{}^{H_3Pe}$	1×10^6		

[a] Experimentally determined constants. [b] Assumes that nickel is bonded to all six amine groups, which may not be valid since Jonassen, *et al.*, have found that copper forms only five-coördinate bonds with pentaethylenehexamine.[17]

concept of the stepwise formation and breakage of bonds is applied to the radionickel exchange with nickel trien or nickel tetren it is found that the reaction path must at some time pass through a symmetrical tinermediate (or a symmetrical transition state) and the rate at which this intermediate proceeds to products should equal its rate of dissociation back to reactants. The resulting rate expression can be represented as

$$R_e = {}^1/_2 k_E[\mathrm{Ni}^{+2}][\mathrm{NiP}] \qquad (32)$$

where k_E is the rate constant for the formation of the symmetrical intermediate and [NiP] is the concentration of the nickel polyamine species in question.

(16) These values are estimated from reaction half-times at 0° as reported by R. Hogg, G. A. Melson, and R. G. Wilkins in S. Kirschner, Ed., "Advances in the Chemistry of the Coordination Compounds," The Macmillan Co., New York, N. Y., 1961, pp. 391–397.

(17) H. B. Jonassen, J. A. Bertrand, F. R. Groves, Jr., and R. I. Stearns, *J. Am. Chem. Soc.*, **79**, 4279 (1957).

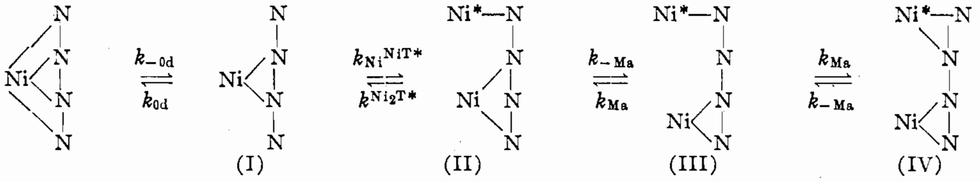

Fig. 7.—Proposed mechanism for radionickel exchange with NiT^{+2} showing formation of symmetrical intermediate.

The mechanism proposed for the formation of the symmetrical intermediate for the case involving radionickel exchange with unprotonated nickel trien is shown in Fig. 7, where the rates of bond formation and breakage should be the same as those listed in Table VIII. From electrostatic and statistical considerations the value of ${k_{Ni}}^{NiT*}$ should be equal to approximately one-half the value of ${k_{Ni}}^{H_2T}$ and it can be shown that species I and II are in equilibrium with the initial complex. Applying the steady-state approximation to species III results in the expression

$$R_e = {}^1/_2 \frac{{K_{Ni_2T*}}^{Ni}}{K_{0a}} \frac{k_{-Ma}}{2} [Ni^{+2}][NiT^{+2}] \qquad (33)$$

where ${K_{Ni_2T*}}^{Ni} = {k_{Ni}}^{NiT*}/k^{Ni_2T*} = 8.3$. This results in a predicted value of ${k_{Ni}}^{NiT}$ (see eq. 15) equal to 7.5×10^{-4} M^{-1} sec.$^{-1}$, which is in good agreement with the experimental value of 2×10^{-3} M^{-1} sec.$^{-1}$.

However, when this treatment is applied to the radionickel exchange terms involving protonated complexes of nickel trien and nickel tetren, the estimated values are consistently lower than the experimentally evaluated constants. One may presume that with the addition of protons to the complex either (a) the exchange reaction proceeds *via* a different mechanism or (b) the effective electrostatic repulsion between the attacking nickel ion and the complex is much less than expected.

Conclusions

(1) The kinetics of the formation and dissociation reactions of the nickel polyamine complexes are consistent with a stepwise process of individual bond breakage and formation between the multidentate ligand and the nickel ion. This parallels the stepwise addition of monodentate ligands in the equilibria of nickel ammines.

(2) However, the formation of the first coöordinate bond represents the rate-determining step in the reaction of nickel ion with the unsubstituted polyamines.

(3) The differences in the rates of reaction of nickel with the various polyamines and their protonated forms is entirely due to statistical and electrostatic factors. Of these, elctrostatic repulsion is the predominant influence.

(4) In the dissociation reaction, the protonation of the polyamine increases the rate by increasing the concentrations of the intermediate species, the formation of species containing non-bonded, unprotonated amine groups being quite unfavorable. The dissociation kinetics can be described to a good approximation as a pre-equilibration of these intermediates, with the last nickel–nitrogen bond breakage as the rate-determining step.

(5) Equilibrium constants for each reaction intermediate species can be evaluated if one assumes that (a) the rate of individual nickel–nitrogen bond breakage is independent of the degree of protonation of the polyamine, (b) the rate of formation of the second, third, and successive bonds is independent of protonation at points other than the coördination site, and (c) the stepwise equilibrium constants are independent of the number of coördinated amine groups. Using the evaluated stepwise constants and applying the electrostatic and statistical factors, one can predict the rates of formation and dissociation of nickel with all the unsubstituted straight-chain polyamines.

General Significance.—This detailed analysis of the nickel polyamine mechanism provides a basis upon which the general kinetic behavior of multidentate ligands can be examined. For example, the fact that one multidentate ligand can rapidly displace another multidentate ligand leading to coördination chain reactions[18] can be explained in terms of the build-up of the concentrations of intermediate species prior to the last bond breakage in a manner similar to that proposed in this work.

The effects of (a) steric hindrance in the rotation of dentate groups, (b) branching in multidentate ligands, (c) different dentates and metal ions on the relative rates of bond formation and rupture, and (d) dentate substitution on subsequent bond rupture will be tested with this model.

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[18] D. C. Olson and D. W. Margerum, *J. Am. Chem. Soc.*, **84**, 680 (1962); *ibid.*, **85**, 297 (1963).