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A STUDY OF THE MECHANISM OF THE LIGAND EXCHANGE BETWEEN TRIETHYLENETETRAMINENICKEL(II) AND 1,10-PHENANTHROLINE

by

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James A. Boersma

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INTRODUCTION

The mechanism of metal polyamine formation and dissociation reactions has been thoroughly studied for nickel[1]. For the reactions involving nickel and the polyamines trien and tetren (see Table 1 for abbreviations), the dissociation involves the following two steps repeated sequentially: metal-nitrogen bond breakage followed by metal-solvent bond formation. The sequence continues until the polyamine has completely dissociated from the metal ion. The rate-determining step is the last metal-nitrogen bond rupture. Similarly, the rate-determining step for the formation reaction is the rate of metal-water loss immediately preceding the first metal-nitrogen bond formation.

Rorabacher[2] has shown that the experimentally measured rate of formation of some metal polyamines is faster than that predicted from the Eigen mechanism[3] which involves outer-sphere association followed by metal-water loss and subsequent rapid metal-ligand bond formation. This is attributed to an internal conjugate base mechanism (ICB). The nature of this enhancement, what causes it and how other coordinated ligands affect its magnitude is presently unknown.

Ligand exchange reactions involving $Ni(trien)^{+2}$ and EDTA have also been studied[4] and shown to preceed through an intermediate having both ligands coordinated to the central metal ion. The

TABLE 1

Ligand Abbreviations

LIGAND	ABBREVIATIONS
Triethylenetetramine	trien, T
Tetraethylenepentamine	tetren
1,10-phenanthroline	phen, P
Ethylenediaminetetraacetic acid	EDTA

degree of coordination to the central metal ion is very sensitive to steric effects.

In order to further study both the ICB mechanism and steric effects of coordinated ligands, the kinetics of the following reactions were investigated in this study.

$$\mathrm{Ni(trien)^{+2} + 3phen \rightleftarrows Ni(phen)_3^{+2} + trien} \qquad (1)$$

From a consideration of the established mechanism of $\mathrm{Ni(trien)^{+2}}$ dissociation, and of EDTA attack on $\mathrm{Ni(trien)^{+2}}$, it was thought that reaction 1 would reveal some additional insight on the steric requirements attacking ligands have on ligand exchange. Further, the measured rate of dissociation in conjunction with a stability constant leads to an experimental value of the formation rate constant. Considering the reverse of reaction 1, if a mixed ligand species forms before the rate-determining step, the effect of phenanthroline upon the formation of $\mathrm{Ni(trien)^{+2}}$ could be seen. An increase or decrease of the ICB effect would thus be attributed to the phenanthroline.

The study of reaction 1 showed the formation of a mixed ligand intermediate, $\mathrm{Ni(trien)(phen)^{+2}}$, which preceded the rate-determining step. Further, phenanthroline is shown to enhance the ICB effect and, after the addition of one phenanthroline molecule, requires that trien dissociate completely before adding a second molecule of phenanthroline. The ICB effect can be made insignificant by varying the pH, in which case the experimental and theoretical rate constants of reaction 1 are in excellent agreement. This is believed to be the first study showing ICB enhancement by a coordinated ligand.

APPARATUS AND REAGENTS

Apparatus

All spectra and kinetic reactions were studied on a Cary Model 14 spectrophotometer equipped with thermostated cells capable of maintaining a constant temperature ±0.05°C at 25°C. The instrument was operated at maximum slit height and a slit width of 0.3 mm.

A Precision Scientific electronic relay was used to control a constant temperature bath for the stability constant study. This controlled the temperature within ±0.1°C.

All pH measurements were made on a Beckman Model 1019 Research pH Meter using a saturated calomel reference electrode which was filled with a saturated solution of NaCl.

Reagents

All reagent grade chemicals were used unless otherwise specified and all solutions were prepared with deionized water prepared by passing distilled water through a mixed bed ion exchange column (Amberlite MB-3).

Standard copper(II) nitrate

B and A Quality copper wire (99.90%) was washed with nitric acid, sulfuric acid, water, ethanol and allowed to air dry. It was then dissolved in a minimum of 6 M nitric acid and diluted to volume.

Ethylenediaminetetraacetic acid

Matheson Coleman and Bell, Reagent, A.C.S., powder (ethylenedinitrilo) tetraacetic acid, disodium salt was used without further purification. It was standardized with standard copper(II) at a pH of 10 using murexide as an indicator[5].

Nickel(II) nitrate

Nickel nitrate solutions were prepared from J. T. Baker Analyzed Reagent nickel nitrate hexahydrate and standardized with EDTA at a pH of 10 and murexide.

1,10-phenanthroline

Phenanthroline solutions were prepared from the monohydrate which was obtained from G. F. Smith, and standardized spectrophotometrically with standard iron solution at a pH of 5.

Triethylenetetraminenickel(II)

J. T. Baker Analyzed Reagent triethylenetetramine disulfate and nickel salts were used to prepare the nickel polyamine solutions[6]. A slight excess of nickel(II) was added to the trien solution and then the pH was raised to 11.5 by the addition of sodium hydroxide to precipitate the excess nickel. The solution was filtered through a 0.45μ Millipore filter and the pH lowered to between 7.5 and 8.0. The concentration was determined by analyzing the complex for the amount of nickel it contained. This was accomplished by adjusting the pH to 9, adding a 1000-fold excess of cyanide and comparing the absorbance at 267 nm with a standard $Ni(CN)_4^{-2}$ solution.

Nickel monophenanthroline

To prepare the nickel monophenanthroline, 50 grams of nickel nitrate hexahydrate was dissolved in 50 ml of hot water and 4 grams of 1,10-phenanthroline monohydrate was added. This corresponds to a 9 to 1 molar ratio of nickel to phenanthroline. A light blue solid was formed which was separated from the solution after it had cooled to room temperature. The solid was washed with t-butyl alcohol to remove excess nickel, and dried under vacuum at 55°C for three hours. The composition of the compound was determined by analyzing for both nickel and phenanthroline.

A weighed portion of the compound was placed in a 100-ml volumetric flask followed by the addition of a pH 10 buffer and 1000-fold excess of cyanide. This solution was then extracted with four 10 ml portions of $CHCl_3$ to remove the phenanthroline. The absorbance of the aqueous portion was measured at 267 nm and compared with a standard $Ni(CN)_4^{-2}$ solution. The $CHCl_3$ extracts were combined and its absorbance measured at 265 nm. This was compared with a standard phenanthroline solution which had been carried through the same procedure. The analysis showed 44.9% phenanthroline and 15.6% nickel while the theoretical values for $Ni(phen)(H_2O)_2(NO_3)_2$ are 45.1% phenanthroline and 14.7% nickel.

Lutidene - lutidene hydrochloride buffer

2,6-lutidene was distilled and the fraction boiling from 143 to 144°C was collected. A modification of the procedure of Pritchard and Long[7] was used to prepare the hydrochloride salt. The 2,6 lutidene was slowly added with stirring to ethyl ether which was saturated with hydrogen chloride. The hydrochloride salt formed was recrystallized from a mixture of methylene chloride and ethyl ether. The base and its salt constitute a buffer of low nucleophilicity in the pH range of 5.9 to 7.4.

Boric acid - sodium borate buffer

An equimolar mixture of boric acid and sodium borate ($Na_2B_4O_7 \cdot 10H_2O$) with varying amounts of mannitol yielded a buffer with a pH range from 4.5 to 9.0. (See Table 2)

Acetic acid - sodium acetate buffer

27.3 grams of $NaC_2H_3O_2 \cdot 3H_2O$ was dissolved in 1 liter of water which contained 60 ml of 1 N HCl[5]. This yielded a buffer of a pH of 5.

TABLE 2

pK_a of H_3BO_3 as a Function of % Mannitol Added

% Mannitol	pK_a
14	4.9
6.8	5.4
3.4	6.4
1.7	7.7

pK_a values were obtained from the titration of 0.5 M H_3BO_3 with 0.1 M NaOH.

Ammonia - ammonium chloride buffer

A pH 10 buffer was produced by dissolving 70 grams of NH_4Cl in 1 liter of water containing 570 ml of NH_3[5].

EXPERIMENTAL

Spectrophotometric Study of Reactants and Products

The spectra of all reactants and products were obtained from 650 to 200 nm. Table 3 lists the principle absorption maxima of reactants and products. Comparison of these spectra showed that the greatest change in molar absorptivity between reactants and products occurred at 343 nm or 295 nm depending on the concentration of $Hphen^{+}$. For the concentrations used in this study, 343 nm was more suitable and all reactions were followed at this wavelength.

The molar absorptivities of all reactants and products were determined at 343 nm. Sodium chloride was used to maintain an ionic strength of 0.1 M. The pH was adjusted using either a boric acid, sodium borate, mannitol buffer or a lutidene HCl buffer. The molar absorptivity of $Ni(trien)^{+2}$ was determined by measuring the absorbance of each stock solution under the above conditions. The slope of a plot of concentration vs. absorbance was used to determine the molar absorptivity of phen, $Hphen^{+}$ and $Ni(phen)^{+2}$ (See Table 4). The molar absorptivity of a proposed mixed ligand complex, $Ni(trien)(phen)^{+2}$, was measured by adding an excess of trien to a solution of $Ni(phen)^{+2}$. The absorbance of this solution was measured and the molar absorptivity calculated. All values used in this study are listed in Table 3.

TABLE 3

Principle Absorption Maxima and Molar Absorptivities of all Reactants and Products

Compound	Wavelength, nm	Molar Absorptivities
$Hphen^+$	343	1080 ± 24
	272	30000
	220	32000
	207	31000
$Ni(phen)_3^{+2}$	343	1430 ± 35
	327	2600
	267	120000
	226	140000
phen	343	53.7 ± 0.9
	324	630
	265	31000
	228	44000
$Ni(trien)^{+2}$	925	10.8
	565	6.5
	360	8.6
	343	approximately 7(a)
$Ni(trien)(phen)^{+2}$ (b)	343	373
	327	(d)
	270	(d)
	225	(d)
$Ni(trien)(phen)^{+2}$ (c)	343	335
	325	(d)
	269	(d)
	225	(d)

(a) Molar absorptivity varies with the amount of NO_3^- present.

(b) Complex was prepared by adding excess trien to $Ni(phen)(H_2O)_4(NO_3)_2$.

(c) Complex was prepared by adding excess phen to $Ni(trien)(H_2O)_2(NO_3)_2$.

(d) Values were not determined.

TABLE 4

Absorbance and Concentration Data Used To Calculate Molar Absorptivities

Concentration, M	Cell length, cm	Absorbance
	phen	
0.364×10^{-3}	10	0.194
0.542×10^{-3}	10	0.281
1.09×10^{-3}	10	0.585
1.45×10^{-3}	10	0.771
	$Ni(phen)_3^{+2}$	
1.00×10^{-5}	10	0.157
2.00×10^{-5}	10	0.298
4.00×10^{-5}	10	0.570
5.01×10^{-5}	10	0.736
	$(Hphen)^{+1}$	
1.49×10^{-4}	1	0.135
2.34×10^{-4}	1	0.237
3.84×10^{-4}	1	0.390
4.44×10^{-4}	1	0.457

Reaction Rates and Conditions

All rates of reaction of equation 1 were studied by following the increase in absorbance due to the formation of $Ni(phen)_3^{+2}$ under the same conditions as described above. Kinetic data were obtained over the pH range of 4.99 to 6.75. The pH remained constant throughout a given run. This was demonstrated at a pH of 5.10 and 6.60 by mixing the reactants and monitoring the pH as the reaction proceeded. The ratio of phen/$Ni(trien)^{+2}$ was varied from 3.2/1 to 31/1. Ranges of experimental conditions used in reaction rate studies are given in Table 5.

To initiate the reaction an aliquot of a $Ni(trien)^{+2}$ solution was poured into a beaker containing phen, sodium chloride and buffer. After thorough mixing the solution was poured into a spectrophotometer cell. All solutions were equilibrated at 25°C before mixing. The majority of the reactions were followed for 10 half-lifes and no reversibility was observed.

In all cases the initial absorbance was found to be higher than the calculated value based on the molar absorptivities of the reactants. By assuming the immediate formation of a mixed ligand species, $Ni(trien)(phen)^{+2}$, the higher absorbance can be predicted. This is not unusual as $Ni(phen)^{+2}$ is known to form mixed complexes with diethylenetriamine and nitrilotriacetate[8]. Further evidence for this species comes from a comparison of the spectra of the products of reactions 2 and 3.

TABLE 5

Experimental Conditions Used For Reaction Rate Studies

$Ni(trien)^{+2}$	2.05 to 18.2 x 10^{-5}M
phen	1.89 to 9.44 x 10^{-4}M
Ionic strength	0.1 M
pH range	4.99 to 6.75
Temperature	25.0 ± 0.05°C
Wavelength	343 nm
Cell path length	5.0 and 10.0 cm

$$\mathrm{Ni(trien)^{+2} + phen \rightarrow products} \qquad (2)$$

$$\mathrm{Ni(phen)^{+2} + trien \rightarrow products} \qquad (3)$$

The two spectra were practically identical but different from the spectra of either $\mathrm{Ni(trien)^{+2}}$ or $\mathrm{Ni(phen)_3^{+2}}$ (See Table 4). Finally a stability constant was obtained for the species $\mathrm{Ni(trien)(phen)^{+2}}$.

With the immediate formation of a mixed complex the reaction actually followed is given in equation 4 with protons omitted.

$$\mathrm{Ni(trien)(phen)^{+2} + 2phen \rightleftarrows Ni(phen)_3^{+2} + trien} \qquad (4)$$

The final absorbances were in agreement with those calculated, assuming $\mathrm{Ni(phen)_3^{+2}}$ and trien as final products.

The rate expression tested is given in equation 5.

$$-d(\mathrm{NiTP})/dt = d(\mathrm{NiP_3})/dt = k(\mathrm{NiTP})^n(\mathrm{P})^m \qquad (5)$$

Integration of equation 5 with respect to time and concentration and n and m equal to 1 gave equation 6.

$$\frac{1}{b-a} \log \frac{a(b-x)}{b(a-x)} = \frac{kt}{2.303} \qquad (6)$$

Here, a is the initial concentration of $\mathrm{Ni(trien)(phen)^{+2}}$, b is the initial concentration of free phen and x is the $\mathrm{Ni(phen)_3^{+2}}$ concentration at any time, t. With a 10-fold excess of phen over $\mathrm{Ni(trien)(phen)^{+2}}$ the concentration of phen remains essentially constant during the reaction and integration of equation 5 with respect to time and concentration with n=1 gave equation 7.

$$\log(\mathrm{NiTP}) = \log(\mathrm{NiTP})_0 - k_0 t/2.303 \qquad (7)$$

Here $(\mathrm{NiTP})_0$ refers to the initial concentration and k_0 is a pseudo first-order rate constant.

$$k_0 = k(\mathrm{phen})^m \qquad (8)$$

The loss of $\mathrm{Ni(trien)(phen)}^{+2}$ is equal and opposite to the gain of $\mathrm{Ni(phen)}_3^{+2}$ and can be obtained from the change in absorbance as the reaction proceeds. Equation 9 (See Appendix Part I for derivation) relates the concentration of $\mathrm{Ni(trien)(phen)}^{+2}$ at any time, t, to the final absorbance, A_f, the absorbance at any time t, A_t, the molar absorptivities of reactants and products, and the cell path length, b.

$$(\mathrm{NiTP}) = \frac{A_f - A_t}{b(\epsilon_{\mathrm{NiP_3}} - 2\epsilon_P - \frac{2\epsilon_{HP}(H)}{K_a} - \epsilon_{\mathrm{NiTP}})} \qquad (9)$$

Figure 1 shows the excellent first-order plots of equation 7 that were obtained, thus establishing a first-order reaction in $\mathrm{Ni(trien)(phen)}^{+2}$.

To obtain the kinetic order in phen, reactions were run with less than a 10-fold excess of phen over $\mathrm{Ni(trien)(phen)}^{+2}$. The data were plotted according to equation 6. These plots showed curved lines indicating that m did not equal 1. However, excellent straight lines were obtained when these runs were plotted according to equation 7. Further, plots of equation 7 with varying amounts of phen all gave the same value of k_0. (See Table 6, pH of 4.96-5.00)

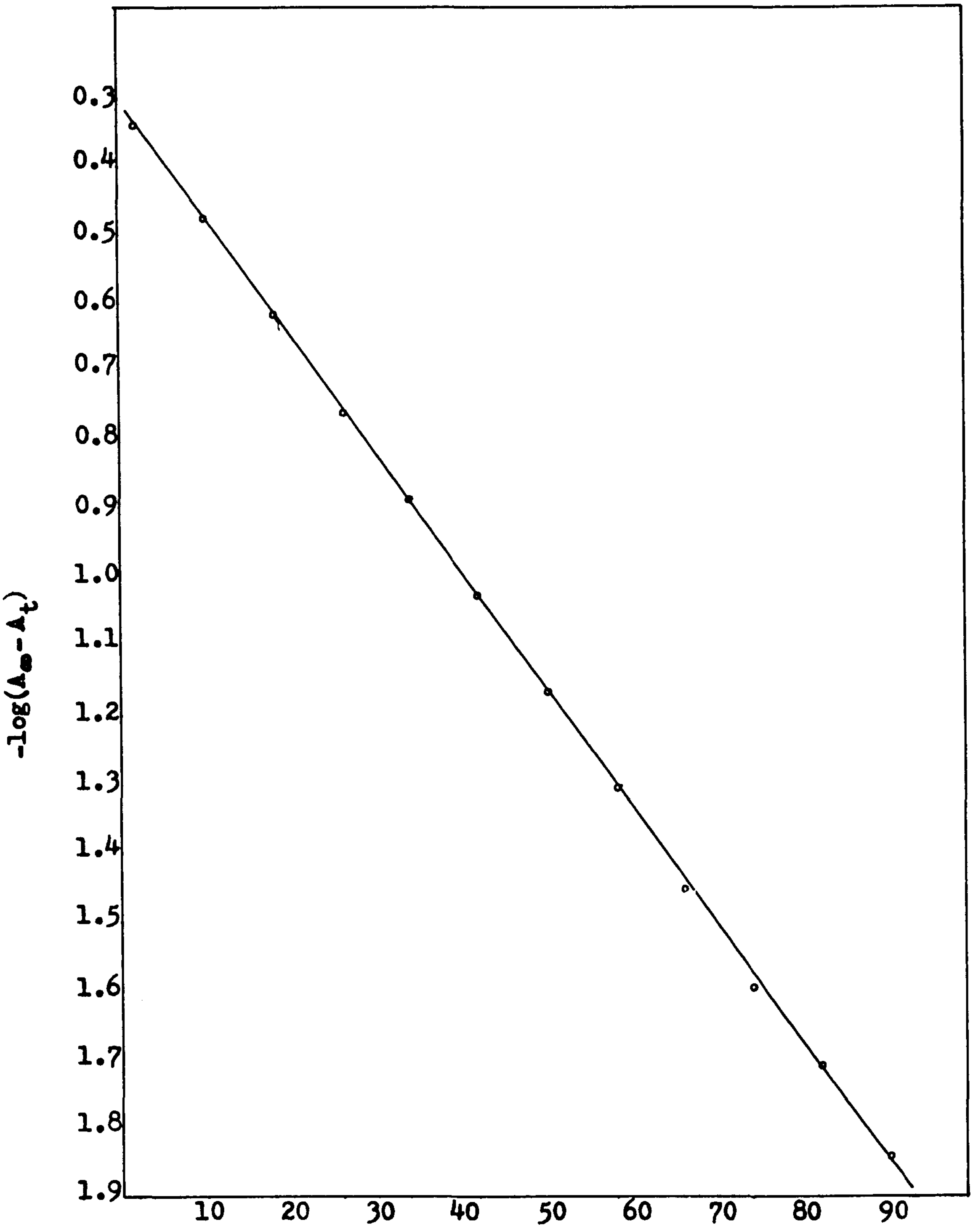

FIGURE 1 A Typical First-Order Rate Plot

(NiT)= 8.44 x 10^{-5}M, (phen)= 2.69 x 10^{-4}M
pH= 5.55, μ = 0.1 M, Temp = 25°C

Thus, the reaction is over-all first-order, first-order in $Ni(trien)(phen)^{+2}$, and zero-order in phen and $k_0 = k$. The slope of the first-order plots times 2.303 gave values of k which are listed in Table 6 along with the phen concentration and the pH.

Since $Ni(trien)^{+2}$ exists as both an unprotonated and a monoprotonated complex in the pH range used in this study, it is conceivable that $Ni(trien)(phen)^{+2}$ would likewise exist as two species. A potentiometric titration was used to show this to be true.

The stability constants for reactions 10 and 11 have been measured at 20°C,[9] $\mu = 0.1$ M and estimated for 25°C from the heats of ionization (1,10).

$$Ni^{+2} + Htrien^{+2} \rightarrow Ni(Htrien)^{+2} \tag{10}$$

$$Ni(trien)^{+2} + H^{+} \rightarrow Ni(Htrien)^{+3} \tag{11}$$

Analogous constants for the mixed ligand complex $Ni(trien)(phen)^{+2}$ were obtained using the method of Schwarzenbach[9], described by Jonassen and Westerman[10]. A 10-fold excess of metal complex to free ligand was mixed in a four-neck round bottom flask which was immersed in a constant temperature bath regulated to 25.0 ± 0.1°C. Enough NaCl was added to yield an ionic strength of 0.1 M when the solution was diluted to 100 ml. This solution was titrated using carbonate-free 0.1378 M NaOH. There was no danger of $Ni(phen)^{+2}$ dissociation because at a pH of 1.7 it has a half-life of 7×10^4 sec. and it increases at higher pH[11]. The time required

TABLE 6

First-Order Rate Constants for the Dissociation of Ni(trien)(phen)$^{+2}$

pH	phen x 10^5, M	Ni(trien) x 10^5, M	k_0 x 10^4, sec^{-1}
6.75$^{(a)}$	94.4	4.09	0.366
6.73$^{(a)}$	94.4	4.09	0.297
6.59$^{(a)}$	47.2	4.09	0.389
6.45	47.2	2.05	0.691
6.18$^{(a)}$	56.6	18.2	0.941
5.76	56.6	18.2	3.60
5.62	29.1	9.12	4.79
5.61	29.1	9.12	4.73
5.59	29.1	9.12	4.83
5.55	26.9	8.44	6.63
5.51	26.9	8.44	6.72
5.51	26.9	8.44	6.95
5.38	27.5	8.61	10.7
5.38	27.5	8.61	10.4
5.37	27.5	8.61	10.4
5.30	26.9	8.44	14.8
5.29	26.9	8.44	14.1
5.26	26.9	8.44	14.0
5.26	29.1	8.59	17.0
5.19	29.1	8.59	17.6
5.00	56.6	18.2	31.2
5.00	29.1	9.12	27.6
5.00	29.1	9.12	29.4
4.99	29.1	9.12	27.6
4.96	7.27	0.228	30.4

(a) Lutidene - lutidene hydrochloride buffer.
All others used boric acid - mannitol buffer.

for the titration was approximately 45 minutes. The data obtained are given in Table 7 and a plot of pH vs. the apparent degree of neutralization, a, is given in Figure 2.

Following Jonassen and Westerman[10], four equations were solved simultaneously for the four apparent basicity constants of trien. Points were selected from the titration curve at low pH and high pH where the apparent constants which were important in these regions were also the ones necessary to calculate the needed stability constants. Twelve different combinations of seven points were used to calculate twelve sets of apparent basicity constants. The average values and the experimental points used to calculate them are listed in Table 8. From the average apparent basicity constants, stability constants for the following reactions can be calculated. The equations used to calculate the stability constants from values of a and pH are given in the Appendix Part II.

$$\mathrm{Ni(trien)(phen)^{+2} + H^{+} \rightleftarrows Ni(Htrien)(phen)^{+3}} \qquad (12)$$

$$\mathrm{Ni(phen)^{+2} + (Htrien)^{+1} \rightleftarrows Ni(Htrien)(phen)^{+3}} \qquad (13)$$

$$\mathrm{Ni(phen)^{+2} + trien \rightleftarrows Ni(trien)(phen)^{+2}} \qquad (14)$$

These values are listed in Table 9 along with the analagous $\mathrm{Ni(trien)^{+2}}$ values and the protonation constants for trien.

The data of Table 6 shows that the reaction is pH dependent. In the pH range for which rate constants were obtained, two species of the complex exist, $\mathrm{Ni(trien)(phen)^{+2}}$ and $\mathrm{Ni(Htrien)(phen)^{+3}}$.

TABLE 7

Titration Data Used in the Determination of Stability Constants for $(NiTP)^{+2}$ Species

$Ni(phen)^{+2}$ = 1.383×10^{-2}M, trien= 1.310×10^{-3}M, NaOH= 1.378×10^{-1}M

ml base	pH	ml base	pH
0.00	3.24	2.10	4.85
0.10	3.30	2.20	4.87
0.20	3.37	2.30	4.89
0.30	3.46	2.40	4.92
0.40	3.58	2.50	4.94
0.50	3.72	2.60	4.96
0.60	3.85	2.70	4.98
0.70	4.00	2.80	5.01
0.80	4.14	2.90	5.03
0.90	4.28	3.00	5.06
1.00	4.40	3.10	5.09
1.10	4.48	3.20	5.13
1.20	4.55	3.30	5.17
1.30	4.60	3.40	5.21
1.40	4.64	3.50	5.28
1.50	4.68	3.60	5.36
1.60	4.72	3.70	5.47
1.70	4.74	3.80	5.68
1.80	4.77	3.90	8.58
1.90	4.80	4.00	8.74
2.00	4.82		

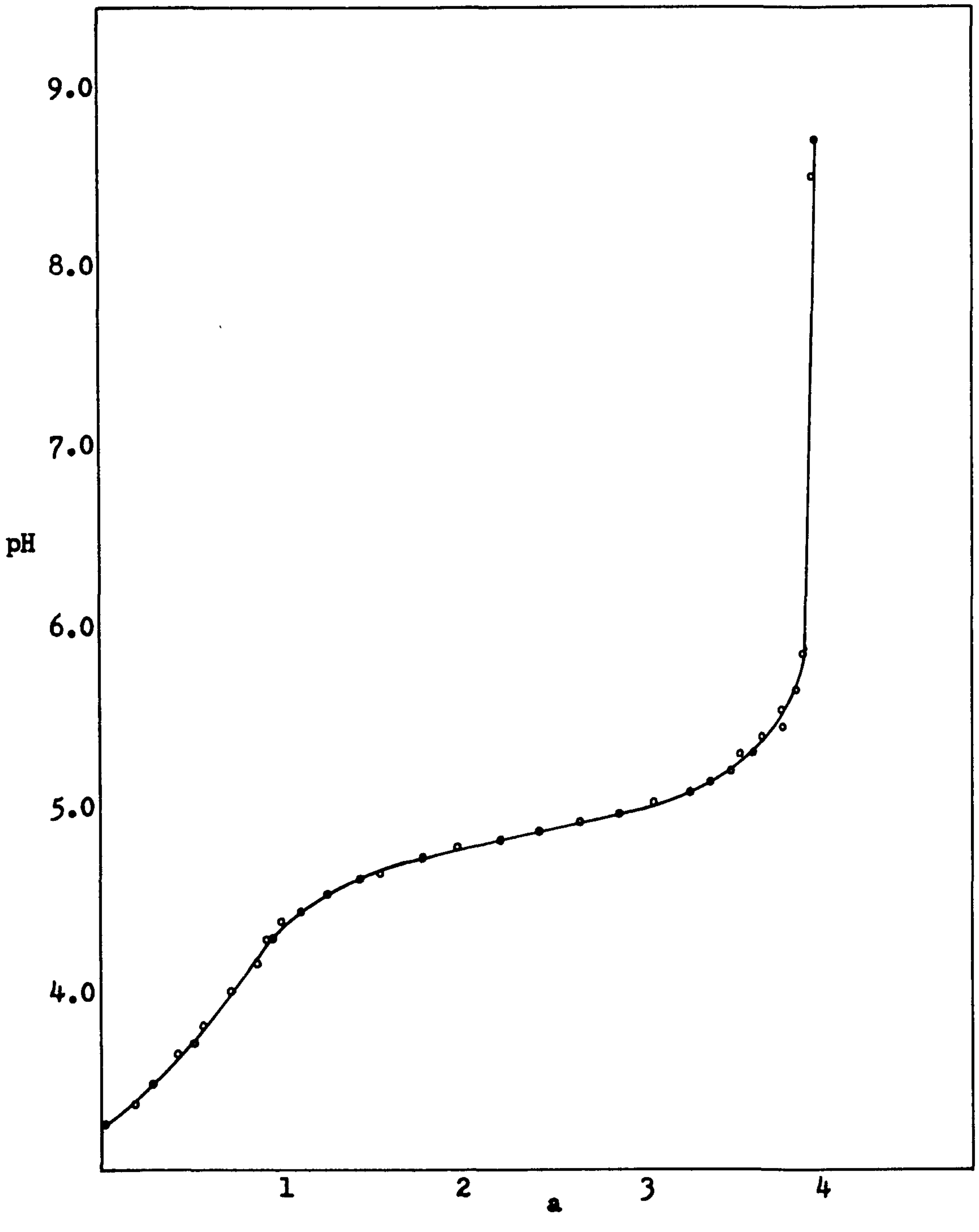

FIGURE 2 Titration of (NiTP) with NaOH

a = the apparent degree of neutralization

TABLE 8

Experimental Points Used to Calculate the Apparent Basicity Constants for Ni(trien)(phen)$^{+2}$

$(H^+) \times 10^6$, M	g	$(H^+) \times 10^4$, M	g
4.27	0.30	3.39	3.40
4.79	0.35	4.27	3.45
5.37	0.40	5.02	3.50
5.76	0.45		

Apparent Basicity Constants (mean ± σ)

$${}'\bar{K}^{H}_{TH} = 5.14 \pm 1.7 \times 10^{4} M^{-1}$$

$${}'\bar{K}^{H}_{TH_2} = 2.44 \pm 2.0 \times 10^{9} M^{-2}$$

$${}'\bar{K}^{H}_{TH_3} = 3.12 \pm 1.4 \times 10^{14} M^{-3}$$

$${}'\bar{K}^{H}_{TH_4} = 6.38 \pm 2.8 \times 10^{17} M^{-4}$$

g = number of protons which appear on the average to be bound to Ni(trien)(phen)$^{+2}$

TABLE 9

Complex Stability Constants for $Ni(trien)(phen)^{+2}$ and $Ni(trien)^{+2}$ and Acid Dissociation Constants for trien

Stability Constants[a]

$\log K^{Ni}_{NiT}$	=	13.82	$\log K^{NiP}_{NiTP}$	=	12.7
$\log K^{Ni}_{NiHT}$	=	8.7	$\log K^{NiP}_{NiHTP}$	=	7.6
$\log K^{NiT}_{NiHT}$	=	4.7	$\log K^{NiTP}_{NiHTP}$	=	4.7

Acid Dissociation Constants[1]

$pK_{(H_4T)} = 3.25$

$pK_{(H_3T)} = 6.55$

$pK_{(H_2T)} = 9.08$

$pK_{(HT)} = 9.80$

$K^{Ni}_{NiT} = (NiT)/((Ni)(T))$

$K_{(H_4T)} = ((H)(H_3T))/(H_4T)$

[a] The terminology for these constants is consistent with reference 15.

Further, each species can undergo an unassisted or proton assisted dissociation. The rate constants in Table 6 represent over-all constants which can be resolved into constants for each of the above mentioned reactions. Thus, the rate of reaction can be represented by the following equation:

$$k_0(\mathrm{NiTP})_T = k_H^{\mathrm{NiTP}}(\mathrm{H})(\mathrm{NiTP}) + k_H^{\mathrm{NiHTP}}(\mathrm{H})(\mathrm{NiHTP}) \qquad (15)$$

where k_X^Y represents the second-order rate constant for X reacting with Y. Equation 17 is obtained by combining equations 15 and 16.

$$(\mathrm{NiHTP}) = K_{\mathrm{NiHTP}}^{\mathrm{NiTP}}(\mathrm{NiTP})(\mathrm{H}) \qquad (16)$$

$$\frac{k_0(\mathrm{NiTP})_T}{(\mathrm{H})(\mathrm{NiTP})} = k_H^{\mathrm{NiTP}} + k_H^{\mathrm{NiHTP}}\ K_{\mathrm{NiHTP}}^{\mathrm{NiTP}}\ (\mathrm{H}) \qquad (17)$$

The ratio $(\mathrm{NiTP})_T/(\mathrm{NiTP})$ can be calculated by substituting equation 16 into equation 18 to yield equation 19.

$$(\mathrm{NiTP})_T = (\mathrm{NiTP}) + (\mathrm{NiHTP}) \qquad (18)$$

$$\frac{(\mathrm{NiTP})_T}{(\mathrm{NiTP})} = 1 + K_{\mathrm{NiHTP}}^{\mathrm{NiTP}}\ (\mathrm{H}) \qquad (19)$$

Substitution of equation 19 into equation 17 yields equation 20.

$$\frac{k_0}{(\mathrm{H})}\ (1 + K_{\mathrm{NiHTP}}^{\mathrm{NiTP}}(\mathrm{H})) = k_H^{\mathrm{NiTP}} + k_H^{\mathrm{NiHTP}}\ K_{\mathrm{NiHTP}}^{\mathrm{NiTP}}(\mathrm{H}) \qquad (20)$$

A plot of the left side of equation 20 versus (H) gave a straight line whose intercept was k_H^{NiTP} and whose slope was

$k_H^{NiHTP} K_{NiHTP}^{NiTP}$. A least squares fit using the data from Table 6 plotted according to equation 20 is shown in Figure 3. The values of k_H^{NiTP} and k_H^{NiHTP} obtained from Figure 3 are $(1.8 \pm .1) \times 10^{8} M^{-1} sec^{-1}$ and $(5.3 \pm 1.7) \times 10^{2} M^{-1} sec^{-1}$ respectively. Other rate constants can be calculated from these two values and the stability constants listed in Table 9. In order to do this it is convenient to consider the product of reaction 4 as simply $Ni(phen)^{+2}$ and a trien species. The actual products are $Ni(phen)_3^{+2}$ and a trien species; however, the addition of the last two phen molecules occurs after the rate determining step since the reaction is zero-order in phen. The stability constant for the following reaction:

$$NiTP + H \rightleftarrows NiP + HT \qquad (21)$$

can be calculated from K_{HT} of trien and K_{NiTP}^{NiP}. Combination of that stability constant with k_H^{NiTP}, known from Figure 3, allows calculation of k_{HT}^{NiP}.

The following equation illustrates the dissociation of $Ni(Htrien)(phen)^{+2}$

$$NiHTP \rightleftarrows NiP + HT \qquad (22)$$

from $Ni(phen)^{+2}$ and $(Htrien)^{+1}$. Combination of k_{HT}^{NiP} previously calculated, and the stability constant for $Ni(Htrien)(phen)^{+2}$ from Table 9 allows calculation of the unassisted dissociation of $Ni(Htrien)(phen)^{+2}$. Similarly, a two proton assisted dissociation

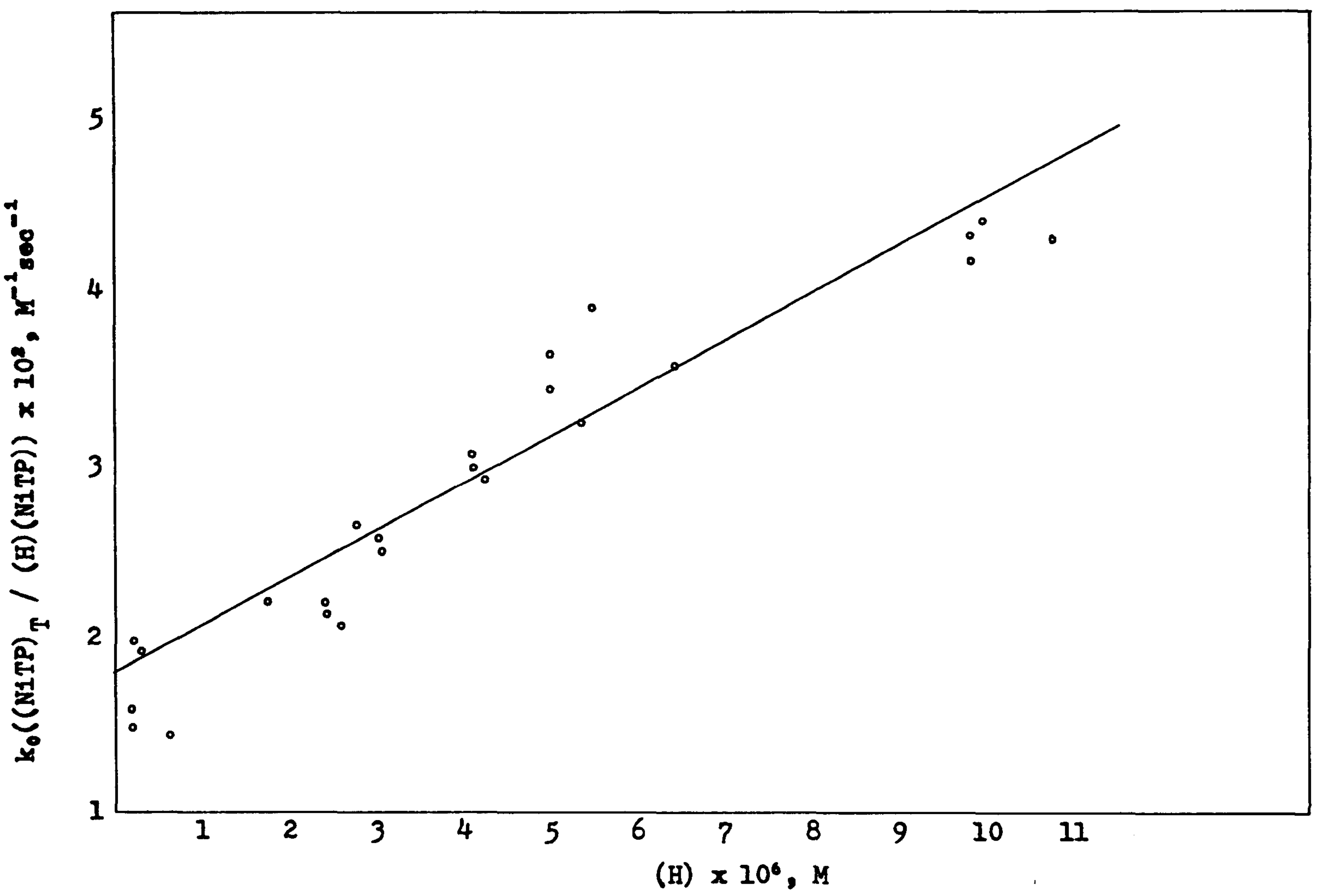

FIGURE 3 Resolution of Rate Constants for the Dissociation of (NiTP)

of Ni(trien)(phen)$^{+2}$ may be calculated. These dissociation rate constants along with the formation rate constant calculated from stability constants and the experimentally resolved dissociation rate constants are listed in Table 10.

Since the resolved rate constants involve terms in one and two protons, the over-all rate can be expressed as such with various assignments of protons as shown in equations 23 through 26.

$$\text{Rate} = k_0(\text{NiTP})_T = k_H^{\text{NiTP}}(\text{H})(\text{NiTP}) + k_{2H}^{\text{NiTP}}(\text{H})^2(\text{NiTP}) \qquad (23)$$

$$= k_H^{\text{NiTP}}(\text{H})(\text{NiTP}) + k_H^{\text{NiHTP}}(\text{H})(\text{NiHTP}) \qquad (24)$$

$$= k^{\text{NiHTP}}(\text{NiHTP}) + k_{2H}^{\text{NiTP}}(\text{H})^2(\text{NiTP}) \qquad (25)$$

$$= k^{\text{NiHTP}}(\text{NiHTP}) + k_H^{\text{NiHTP}}(\text{H})(\text{NiHTP}) \qquad (26)$$

Using any of the above equations with the appropriate constants and concentration the over-all rate can be theoretically calculated. Excellent fits are obtained in all cases. Figure 4 is a plot of equation 24. The excellent agreement gives confidence in the resolved rate constants.

TABLE 10

Experimental and Predicted Rate Constants for Ni(trien)(phen) and Ni(trien) Systems at 25°C, μ = 0.1 M

Dissociation Constants

Ni(trien)(phen)$^{+2}$ System	Ni(trien)$^{+2}$ System
$k^{NiHTP} = 3.5 \times 10^{-3} sec^{-1}$	$k^{NiHT} = 1.8 \times 10^{-5} sec^{-1}$
$k_{H}^{NiTP} = 1.8 \times 10^{2} M^{-1} sec^{-1}$	$k_{H}^{NiT} = 0.91\ M^{-1} sec^{-1}$
$k_{H}^{NiHTP} = 5.3 \times 10^{2} M^{-1} sec^{-1}$	$k_{H}^{NiHT} = 2.3 \times 10^{2} M^{-1} sec^{-1}$
$k_{2H}^{NiTP} = 2.6 \times 10^{7} M^{-2} sec^{-1}$	$k_{2H}^{NiT} = 1.2 \times 10^{7} M^{-2} sec^{-1}$

Formation Constants

Experimental	Predicted
Ni(trien)(phen)$^{+2}$ System	
$k_{NiP}^{HT} = 1.3 \times 10^{5} M^{-1} sec^{-1}$	$8.8 \times 10^{2} M^{-1} sec^{-1}$
$k_{NiP}^{H_2T} = 17\ M^{-1} sec^{-1}$	$44\ M^{-1} sec^{-1}$
Ni(trien)$^{+2}$ System	
$k_{Ni}^{HT} = 9.3 \times 10^{3} M^{-1} sec^{-1}$	$1.1 \times 10^{3} M^{-1} sec^{-1}$
$k_{Ni}^{H_2T} = 97\ M^{-1} sec^{-1}$	$54\ M^{-1} sec^{-1}$

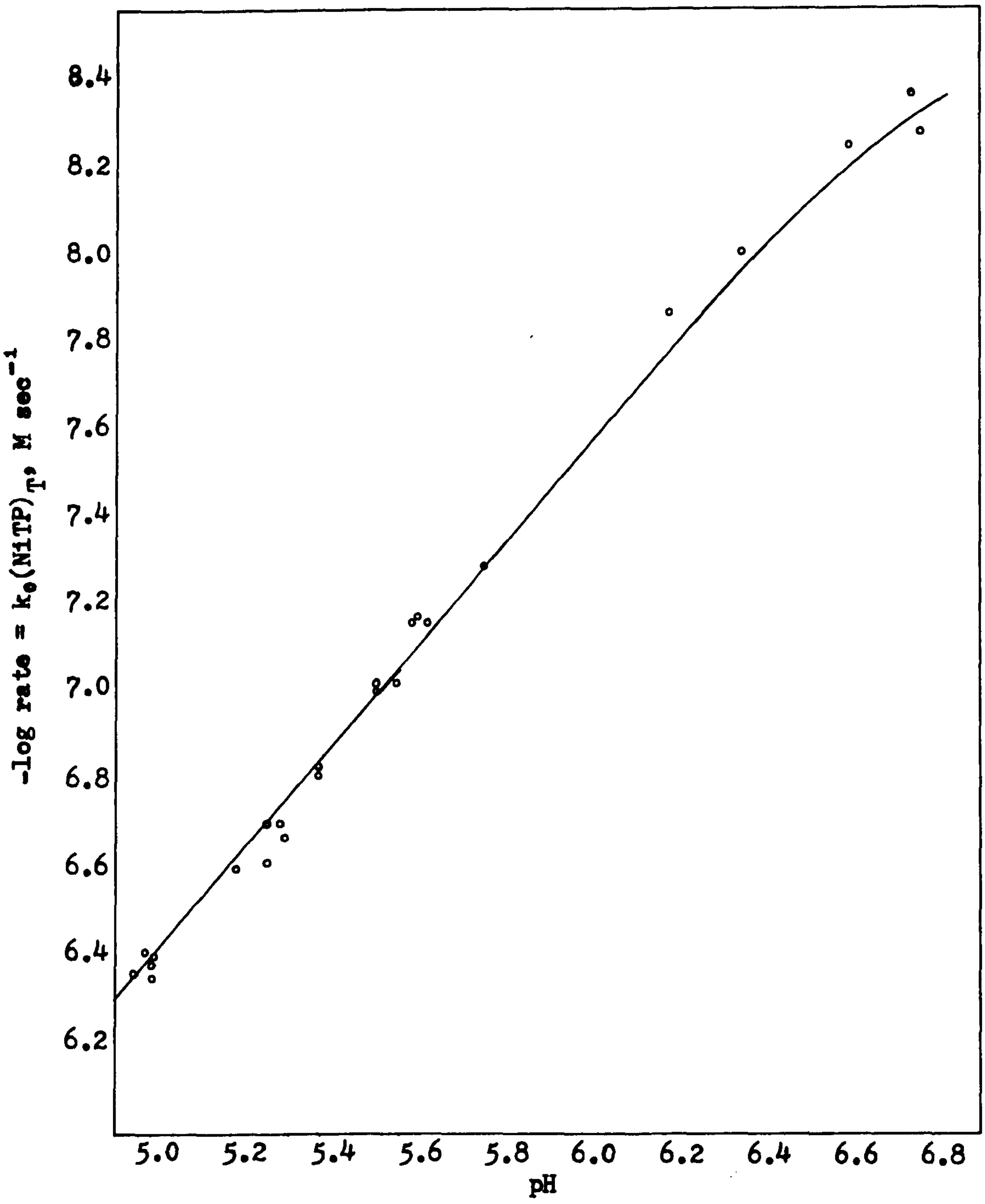

FIGURE 4 Experimental Points for Dissociation of (NiTP) Solid line is theoretical curve. (NiTP)= 1.40×10^{-4}M

DISCUSSION

Reaction Mechanism

A reaction mechanism similar to that for the dissociation of Ni(trien)$^{+2}$ [1] can be shown to apply to this reaction despite the presence of phenanthroline. The rate-determining step must lie after the addition of a phenanthroline to Ni(trien)$^{+2}$ and after two nickel polyamine bonds are broken since a two proton dependence is seen in resolving the over-all rate constant and since Ni(trien)(phen)$^{+2}$ was found to form rapidly as Ni(trien)$^{+2}$ and 1,10-phenanthroline were mixed. Further, the rate-determining step must lie before the addition of a second phenanthroline since no phenanthroline dependence is seen in the rate expression. This leaves rupture of either the third or fourth nickel polyamine bonds as rate-determining. Figure 5 shows the proposed reaction mechanism which involves a rapid addition of 1,10-phenanthroline to Ni(trien)$^{+2}$ followed by a stepwise and complete dissociation of trien from Ni(trien)(phen)$^{+2}$ before the rapid addition of two more 1,10-phenanthroline molecules to form tris-(1,10-phenanthroline)-nickel(II).

Location of the rate-determining step as either the third or fourth nickel polyamine bond rupture depends upon the relative magnitude of k_{-2a}, k_{2a}, k_{1a} and k_{-1a} for the unprotonated case. The same conclusion, however, applies also to the protonated cases. Equation 27 results from applying the steady state approximation to

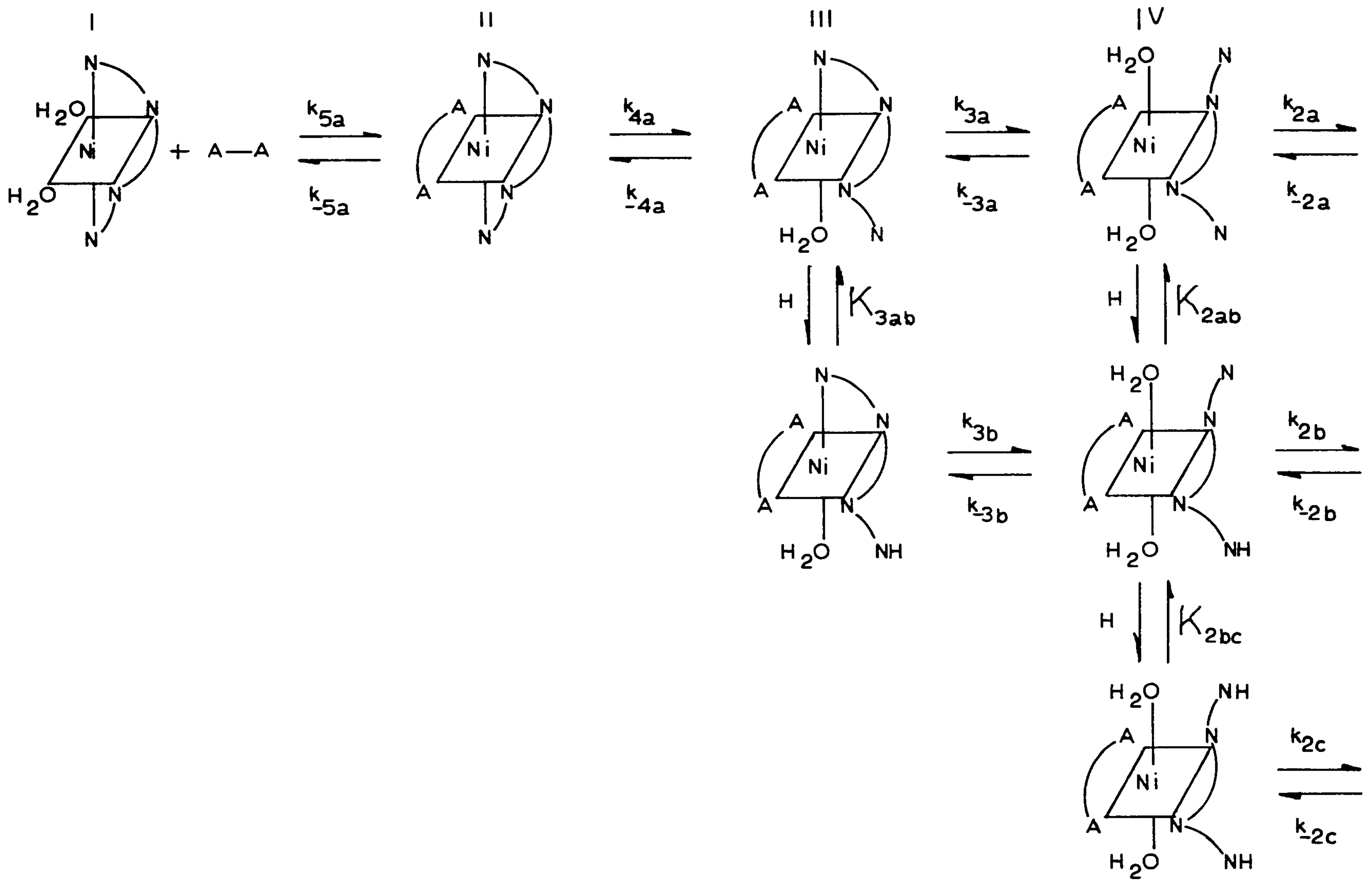

FIGURE 5 Stepwise Dissociation and Formation of (NiTP)

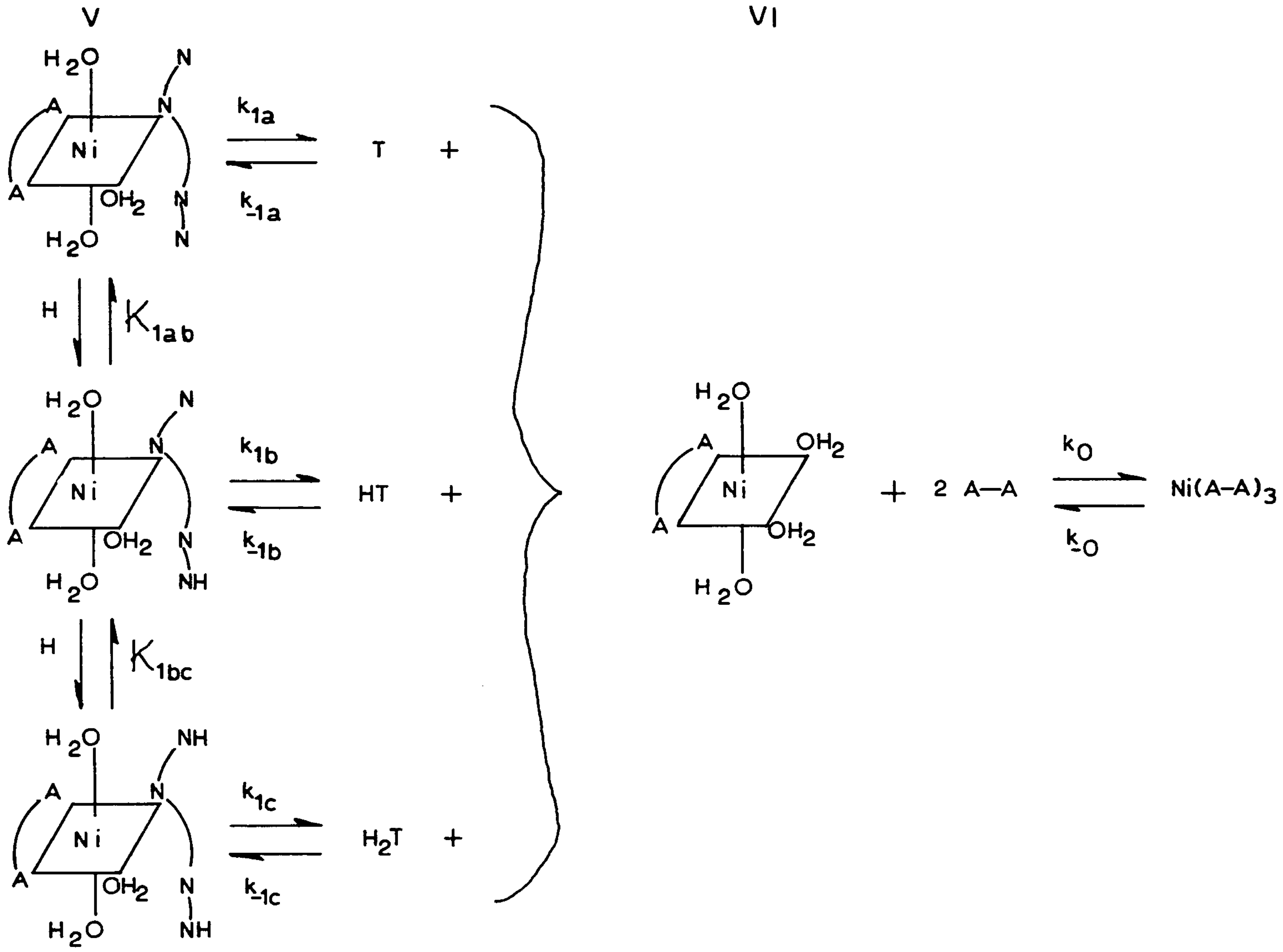

FIGURE 5 Continued

intermediate Va and the assumption that all prior steps are in rapid equilibrium and that II is the reactant.

$$(\mathrm{Va}) = \frac{k_{2a}}{k_{-2a} + k_{1a}} K_{3a}K_{4a}(\mathrm{NiTP}) \tag{27}$$

Combining equation 27 with equation 28 gives equation 29 as the rate of reaction.

$$\frac{-d(\mathrm{NiTP})}{dt} = k_{1a}(\mathrm{Va}) \tag{28}$$

$$\frac{-d(\mathrm{NiTP})}{dt} = \frac{k_{2a}\ k_{1a}}{k_{-2a} + k_{1a}} K_{3a}K_{4a}(\mathrm{NiTP}) \tag{29}$$

An estimate of the value of k_{-2a} can be obtained from the rate of water loss of mono-(1,10-phenanthroline)-nickel(II) followed by a rotational energy barrier factor due to the twisting of the polyamine into a favorable position for bonding. The rate of water loss of mono-(1,10-phenanthroline)-nickel(II) has been measured at 25°C, $\mu = 0.25$ M[11] and found to be $2.2 \times 10^4 \mathrm{sec.}^{-1}$. In the present study there is also one polyamine nitrogen bond to the nickel which would affect step k_{-2a}. There is evidence to show that increased nitrogen coordination enhances the rate of water loss although other factors are also important[13]. From previous work[12,14] it can be estimated that an increase of a factor of from 4 to 40 could be attributed to the coordination of a single nitrogen. The rotational energy barrier for the twisting of a segment of trien into a favorable bonding position has been previously estimated[1] to be 44, based upon the ratio of the rate constants for the first and second bond ruptures of mono-(ethylenediamine)-nickel(II). Thus, k_{-2a} has a maximum value of $1.2 \times 10^4 \text{sec.}^{-1}$ and a minimum value of $1.2 \times 10^3 \text{sec.}^{-1}$.

The magnitude of k_{1a} can be obtained directly from the experimental measurement of the rate of dissociation of ammonia from $Ni(phen)(NH_3)(H_2O)_3^{+2}$. That value was found to be 3.8 sec.^{-1} at 25°C, $\mu = 0.25$ M[12]. Thus, k_{-2a} is at least 3.2×10^2 greater than k_{1a} and equation 29 simplifies to

$$\frac{-d(NiTP)}{dt} = k_{1a}(NiTP)\ K_{2a}K_{3a}K_{4a} \tag{30}$$

This shows the rate-determining step to be k_{1a}, or the breakage of the last nickel-polyamine bond. Prior steps are assumed to be in equilibrium.

In this respect, the reaction mechanism is identical with the dissociation of $Ni(trien)^{+2}$ and $Ni(tetren)^{+2}$ [1]. The phenanthroline has no effect on the location of the rate-determining step. This is contrary to the accelerating effect that EDTA has on the dissociation of $Ni(trien)^{+2}$ [4].

In the case of EDTA attacking $Ni(trien)^{+2}$, the attacking ligand forms several mixed ligand intermediate species with nickel, each having a greater degree of coordination to EDTA and a lesser one to trien. The rate-determining step is that one immediately following the intermediate of lowest stability. By analogy to the system under study, two coordination sites are available for

immediate coordination by phenanthroline yielding mono-(1,10-phenanthroline)(trien)-nickel(II). From that point on, trien unwraps forming successively less stable intermediates. Regardless of the configuration of the trien on nickel, after three nickel polyamine bonds have broken, two adjacent coordination sites are open and a second phenanthroline could add to the complex. The order dependence of the reaction shows that, despite the availability of two adjacent sites prior to the rate-determining step, a second phenanthroline does not add to the complex until the trien has completely dissociated. The reason must be attributed to steric factors. However, the addition of a second phenanthroline should not be seen kinetically, regardless of where it occurred in the mechanism. A mixed ligand complex having two phenanthroline molecules would be more stable than one having just one phenanthroline and an ethylenediamine (en) segment of trien bonded (pK_{stab} of $Ni(phen)^{+2} = 8.8$, pK_{stab} of $Ni(en)^{+2} = 7.7$)[15]
Thus, the rate-determining step would occur before the addition of a second phenanthroline since a less stable intermediate would exist before the second phenanthroline added. Since a second phenanthroline does not add to the complex until the trien is completely dissociated, the rate-determining step would follow the least stable intermediate which would be the last nickel polyamine bond as was previously shown.

Mixed Ligand Stability Constants

The stability constants obtained from the potentiometric titration of mono-(1,10-phenanthroline)(trien)-nickel(II) are reasonable compared to the analogous constants for the Ni(trien)$^{+2}$ system. The value $K^{NiTP}_{NiHTP} = 5.14 \times 10^{4}$ is identical with $K^{NiT}_{NiHT} = 5.0 \times 10^{4}$ (See Table 9 for terminology used in the constants). These constants both represent an acid-base reaction involving protonation of a non-bonded trien nitrogen. The presence of phenanthroline should have no effect on this value and the data indicate this. The value of $K^{NiP}_{NiHTP} = 4.44 \times 10^{7}$ is similar to $K^{Ni}_{NiHT} = 5.02 \times 10^{8}$. These constants describe the addition of mono-protonated trien to mono-(1,10-phenanthroline)-nickel(II) and nickel(II) respectively. Outside of a statistical factor of 6/4 and a possible steric factor due to the presence of phenanthroline, both of which would favor the reaction with nickel, the two constants should agree. The factor of 10 difference would account for the above-mentioned effects. Finally, the value of $K^{NiP}_{NiTP} = 5.44 \times 10^{12}$ is similar to $K^{Ni}_{NiT} = 6.6 \times 10^{13}$. These constants describe the same reaction mentioned above except involving unprotonated trien. Thus, the same effects would be present in both reactions whether they involve mono or unprotonated trien. This is evident as can be seen by the same factor of 10 difference between formation constants.

Effect Of Phenanthroline On Nickel Polyamine Formation Reactions

A comparison of the various dissociation constants for mono-(1,10-phenanthroline)(trien)-nickel(II) and Ni(trien)$^{+2}$, shown in Table 10 reveals that the terms involving one proton, k^{NiHTP} and k_{H}^{NiTP} are about a factor of 200 larger than the corresponding constants in the absence of phenanthroline. Since the stability constants involving mono-protonated trien for the two systems are about equal after statistical factors are taken into consideration, the difference in rate of dissociation cannot be explained on this basis. Further, comparison of the rate constants involving two protons, k_{H}^{NiHTP} and k_{2H}^{NiTP} with k_{H}^{NiHT} and k_{2H}^{NiT} shows that here the presence of phenanthroline makes practically no difference at all. Thus, some different effect must be operating when only one proton is present since the slight difference in stability constants cannot account for the increase of 200 seen when phenanthroline is present. The explanation must be in the rate of formation which is enhanced by the presence of phenanthroline.

The rate of formation of mono-(1,10-phenanthroline)(trien)-nickel(II) and of Ni(trien)$^{+2}$ can be obtained from their respective experimentally measured dissociation constants and their stability constants. Despite the fact that the product of the experimentally measured reaction was the formation of tris-(1,10-phenanthroline)-nickel(II), the rate-determining step was the complete dissociation of trien from the complex so just that portion of the reaction can be considered by itself. The addition of the last two phenanthroline molecules occurs rapidly after the rate-determining step and is not included in the stability constant, K_{NiTP}^{NiP}, or the formation rate constant, k_{NiP}^{T}.

The rate of formation of NiHTP, NiH_2TP, NiHT and NiH_2T from NiP reacting with HT or H_2T and Ni reacting with HT or H_2T can also be theoretically calculated from the thoroughly tested general mechanism postulated by Eigen involving the formation of an outer sphere complex between the metal ion and ligand followed by the loss of a coordinated water molecule as the rate-determining step[3]. This is illustrated in reactions 31, 32 and 33 using $Ni(phen)^{+2}$ and $(Htrien)^{+1}$.

$$Ni(phen)(H_2O)_4^{+2} + Htrien \overset{K_{os}}{\rightleftarrows} Ni(phen)(H_2O)_4^{+2} \cdots Htrien \tag{31}$$

$$Ni(phen)(H_2O)_4^{+2} \cdots Htrien \xrightarrow{k^{Ni-H_2O}} Ni(phen)(H_2O)_3^{+2} \cdots Htrien + H_2O \tag{32}$$

$$Ni(phen)(H_2O)_3^{+2} \cdots Htrien \xrightarrow{fast} Ni(phen)(Htrien)(H_2O)_3^{+3} \tag{33}$$

Since the last nickel-polyamine bond rupture is rate-determining in both systems, with or without phenanthroline, the formation of the first nickel-polyamine bond will be rate-determining in the formation reaction. Thus, the formation rate constants for the above mentioned system can be calculated as

$$k_{NiP}^{HT} = K_{os}\, k^{Ni-H_2O} \tag{34}$$

Values of K_{os} can be calculated with fair accuracy from diffusion equations[16] and the k^{Ni-H_2O} values are known from previous work[12]. Equation 35 is used to calculate K_{os} values

$$K_{os} = (4/3)\ \pi\ a^3\ N_a\ \exp(-Z_a Z_b e_o^2\ /\epsilon k T a')\ \times 10^{-3} \qquad (35)$$

where a is the center-to-center distance of closest approach between the nickel ion and the unprotonated nitrogen donor atom of trien, estimated to be 3.5×10^{-8} cm using molecular models, and a' is the center-to-center distance between the nickel ion and the protonated nitrogen of trien, measured to be 14×10^{-8} cm for $(\text{Htrien})^{+}$ and 7×10^{-8} for $(H_2\text{trien})^{+2}$. N_a is Avogodro's number, Z_a and Z_b are the formal charges on the reacting species, e_o is the electronic charge in esu, ϵ is the dielectric constant, k is the Boltzmann constant in ergs/deg and T the absolute temperature. The value of K_{os} for both nickel and mono-(1,10-phenanthroline)-nickel(II) reacting with $(\text{Htrien})^{+}$ is $4.0 \times 10^{-2} M^{-1}$ and for the same two species reacting with $(H_2\text{trien})^{+2}$ is $2.0 \times 10^{-3} M^{-1}$.

Using the above mentioned K_{os} values along with $k^{Ni(phen)-H_2O} = 2.2 \times 10^4$ [12] and $k^{Ni-H_2O} = 2.7 \times 10^4$ [12] formation rate constants can be calculated from equation 34. These are listed in Table 10 along with the formation constants obtained from experimentally measured dissociation constants and stability constants.

Comparison of the experimental and calculated values shows that NiHT forms about a factor of 10 faster than predicted and NiHTP about a factor of 100 faster than predicted, whereas $(NiH_2T)^{+2}$

and $(NiH_2TP)^{+2}$ both form at the predicted rate. The explanation for the enhanced rate of formation involving $(Htrien)^{+1}$ has been attributed to an internal conjugate base mechanism (ICB)[2]. This mechanism involves the usual formation of an outer-sphere complex followed by a hydrogen bond between a coordinated water molecule and a basic donor atom of the ligand. This is followed by loss of an adjacent labilized water molecule from the inner coordination sphere, rapid substitution of a second donor atom from the same multidentate ligand and rupture of the original hydrogen bond. Subsequent bonding steps are rapid, the first metal donor bond being rate-determining. Figure 6 shows the mechanism in detail using $Ni(phen)^{+2}$ and trien.

Further, it has been shown that multidentate ligands with pK_a values less than 8 do not react by the ICB mechanism with nickel as they are not basic enough to form a hydrogen bond[2]. This is seen in the present study where $(H_2trien)^{+2}$, having remaining pK_a values of 6.55 and 3.25 forms at the predicted rate whereas $(Htrien)^{+1}$, having remaining pK_a values of 9.08, 6.55 and 3.25 is sufficiently basic to hydrogen bond and thus forms at a faster rate than predicted.

Of most interest, however, is the factor of 170 between the predicted and experimental constants involving mono-(1,10-phenanthroline)-nickel(II) and $(Htrien)^{+1}$ compared to only a factor of 8.2 between the corresponding constants for the aquo-nickel ion. The presence of phenanthroline in the inner coordination sphere of

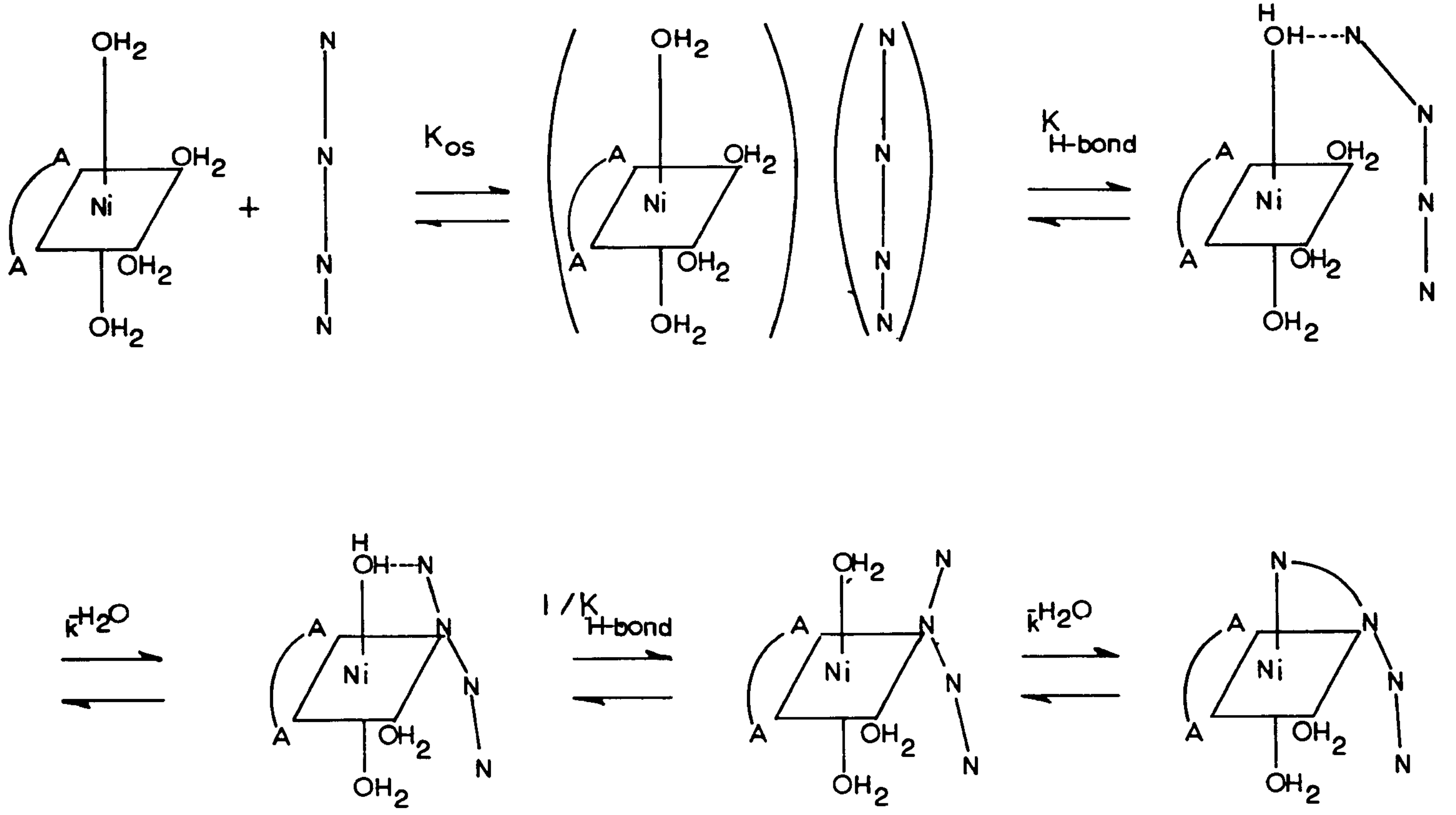

FIGURE 6 Proposed (ICB) Mechanism for the Formation of (NiTP)

nickel has somehow enhanced the ICB effect by a factor of 21. It is possible to account for the increase in formation rate due to the ICB mechanism from either an increase in K_{os}, due to the H-bond, or an increase in k^{-H_2O} due to the labilizing effect of a hydrogen bond on an adjacent water molecule. It is not known whether an increase in both constants or in only one is responsible for the enhanced rates.

The presence of phenanthroline has therefore further enhanced either K_{os} or k^{Ni-H_2O}. The fact that k^{Ni-H_2O} and k^{NiP-H_2O} are about equal[12] shows that the presence of phenanthroline has no effect on the nickel-water bond unless another ligand is present to hydrogen bond by the ICB mechanism. Thus, phenanthroline must somehow facilitate electron redistribution as a result of hydrogen bonding to cause faster nickel-water bond rupture or facilitate hydrolysis of water in the inner coordination sphere of nickel. Present data do not allow a choice between the two explanations. The earlier noted discrepancy between the experimental dissociation constants of $Ni(Htrien)(phen)^{+1}$ and $Ni(Htrien)^{+1}$ is due to an enhanced formation rate caused by the presence of phenanthroline.

APPENDIX

Part I

Relationship of concentration of NiTP at time t, and absorbance

$$A_f = b(\epsilon_1(NiP_3)_f + \epsilon_2(P)_f + \epsilon_3(HP)) \tag{1}$$

$$A_t = b(\epsilon_1(NiP_3)_t + \epsilon_2(P)_t + \epsilon_3(HP)_t + \epsilon_4(NiTP)_t) \tag{2}$$

$$(NiP_3)_t = (NiP_3)_f - (NiTP)_t \tag{2a}$$

$$(P)_t = (P)_f + 2(NiTP)_t \tag{2b}$$

$$(HP)_t = (P)_t(H)/K_a \tag{2c}$$

Substitute equations 2a, 2b and 2c into equation 2

$$\begin{aligned} A_t = b(&\epsilon_1((NiP_3)_f-(NiTP)_t) + \epsilon_2((P)_f + 2(NiTP)_t) + \\ &\epsilon_3(((P)_f + 2(NiTP)_t)(H)/Ka) + \epsilon_4(NiTP)_t) \end{aligned} \tag{3}$$

$$\begin{aligned} A_t = {} & b(\epsilon_1(NiP_3)_f + \epsilon_2(P)_f + \epsilon_3(P)_f(H)/K_a) + \\ & b(-\epsilon_1 + 2\epsilon_2 + (2\epsilon_3(H)/K_a) + \epsilon_4)(NiTP)_t \end{aligned} \tag{4}$$

$$A_f - A_t = b(\epsilon_1 - 2\epsilon_2 - (2\epsilon_3(H)/K_a) - \epsilon_4)(NiTP)_t \tag{5}$$

$$(NiTP)_t = (A_f - A_t)/(b(\epsilon_1 - 2\epsilon_2 - (2\epsilon_3(H)/K_a) - \epsilon_4)) \tag{6}$$

A_f = final absorbance

A_t = absorbance at time t

b = cell length

K_a = acid dissociation constant for phenanthroline

ϵ_1 = epsilon for NiP_3

ϵ_2 = epsilon for P

ϵ_3 = epsilon for HP

ϵ_4 = epsilon for NiTP

APPENDIX

Part II

Calculation of the Stability Constants for the Mixed Ligand Complex

The total concentration of trien is given by equation 1

$$(T)_T = (T) + (HT^+) + (H_2T^{+2}) + (H_3T^{+3}) + (H_4T^{+4}) \qquad (1)$$

and the mass balance on hydrogen by equation 2

$$(T)_T \times g = (HT^+) + 2(H_2T^{+2}) + 3(H_3T^{+3}) + 4(H_4T^{+4}) \qquad (2)$$

where g equals the number of protons which appear on the average to be bound to trien. Equation 3 is obtained by combining equations 1 and 2

$$\begin{aligned} g + (g-1)(H^+)\ {}'\bar{K}^H_{HT} + (g-2)(H^+)^2\ {}'\bar{K}^H_{H_2T} + \\ (g-3)(H^+)^3\ {}'\bar{K}^H_{H_3T} + (g-4)(H^+)^4\,{}'\bar{K}^H_{H_4T} = 0 \end{aligned} \qquad (3)$$

where ${}'\bar{K}^H_{H_xT}$ represents the apparent basicity constants of trien in the presence of a 10-fold excess of $Ni(phen)^{+2}$.

The apparent basicity constants along with the basicity constants of trien are used in equations 4 and 5 to solve for two stability constants.

$$K^{NiP}_{NiTP} = \frac{1}{(NiP^{+2})} \quad \frac{K^{T}_{H_4T}}{{}'\bar{K}^{H}_{H_4T}} - 1 \qquad (4)$$

$$K^{NiP}_{NiHTP} = \frac{1}{(NiP^{+2})} \quad \frac{K^{HT}_{H_2T} \; K^{H_2T}_{H_3T} \; K^{H_3T}_{H_4T}}{{}'\bar{K}^{T}_{H_4T} \; / \; {}'\bar{K}^{T}_{HT}} - 1 \qquad (5)$$

The value of K^{NiTP}_{NiHTP} can be calculated from K^{NiP}_{NiHTP}, K^{NiP}_{NiTP} and K^{T}_{HT}.

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VITA

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