to be expected for various leaving groups leads one to anticipate large differences in the relative dissociation rate constant trends as a function of solvent composition upon altering the nature of the leaving group. This factor could then account for the reversal in the relative effect of methanol and water upon the dissociation rate in the current system as contrasted to that reported by Adamson for the Reineckate ion (where NCS$^-$ as the leaving group would serve as a proton acceptor[34a])—a reversal which is difficult to explain within the context of an associative process or of solvent structural effects. Further studies on this aspect are planned.

In view of the evidence supporting the existence of significant outer-sphere effects upon the dissociation of the nickel–ammonia bond, it remains to reconsider the possibility that such effects are also present to a significant degree in the formation rate constant trends observed in this and the previous study.[1] If outer-sphere methanol and water were to have the same relative effect upon nickel–water and nickel–methanol bond dissociation rates as is apparent for nickel–ammonia, then a major contribution to the formation rate constant trend observed in this study could be attributable to changes in the outer-sphere composition. This could lead to the conclusion that the inherent differences in the two nickel–solvent dissociation rate constants are much less than indicated by the values resolved from ignoring outer-sphere effects (*cf.* Figures 5 and 7). By the same token, however, it must then be concluded that inner-sphere effects leading to the observed decrease in nickel–solvent and nickel–ammonia bond dissociations upon replacing coordinated water by methanol[1] are much larger than previously assumed. Thus, to whatever extent outer-sphere effects (including structural effects) are important in nickel–ligand bond rupture rate constants in methanol–water solvents, the magnitude of inner-sphere effects previously reported must be increased accordingly.[38]

Acknowledgment.—The authors wish to thank the National Institute of General Medical Sciences for support of this research under Grant No. GM-12596.

[38] NOTE ADDED IN PROOF.—Suggestive evidence for an interaction between Ni(HEEDTA)S$^-$ and the indicator Chlorophenol Red in solvents of high alcoholic content was brought to our attention by Richard W. Taylor prior to going to press. We are grateful to him and to Louis G. Jambor for subsequently rechecking the relaxation data under alternative conditions in confirming the validity of the original results as reported in Table III of this paper.

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Kinetics of the Exchange Reaction between 1,10-Phenanthroline and Triethylenetetraminenickel(II)

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The kinetics of the ligand substitution of 1,10-phenanthroline (phen) and triethylenetetraminenickel(II) (Ni(trien)$^{2+}$) has been studied spectrophotometrically over the pH range of 4.9–6.7 at 25°. The reaction involves an initial rapid formation of a mixed-ligand intermediate, Ni(trien)(phen)$^{2+}$, which then goes on to products. The reaction is first order in Ni(trien)(phen)$^{2+}$ and zero order in phenanthroline. Experimental rate constants for the dissociation of trien are $k^{\mathrm{NiHTP}} = 3.4 \times 10^{-3}$ sec^{-1} and $k_{\mathrm{H}}^{\mathrm{NiHTP}} = 5.3 \times 10^{2}\ M^{-1}$ sec^{-1}. By comparison to the Ni(trien)$^{2+}$ system, a mechanism is proposed in which breakage of the last trien bond to nickel is rate determining, followed by the rapid addition of two phenanthroline molecules. Formation rate constants for $k_{\mathrm{HT}}^{\mathrm{NiP}}$ and $k_{\mathrm{H_2T}}^{\mathrm{NiP}}$ are both calculated from the above dissociation constants and predicted from the Eigen mechanism. Comparison of these values with the corresponding ones for the Ni(trien)$^{2+}$ system shows that coordinated phenanthroline enhances the internal conjugate base effect by a factor of 80.

Introduction

The mechanism of nickel polyamine formation and dissociation reactions has been thoroughly studied.[1–5] The dissociation involves the following two steps repeated sequentially:[3] nickel–nitrogen bond breakage followed by nickel–solvent bond formation. This sequence continues until the polyamine has completely dissociated from the nickel ion. Excluding strongly acidic conditions, the rate-determining step is the last nickel–nitrogen bond rupture. Similarly, the rate-determining step for the formation reaction is the rate of metal–water loss immediately preceding the first nickel–nitrogen bond formation.

The effect that coordinated nitrogens have upon rate of nickel–water substitution has also been studied.[6–14] Polyamine nitrogens appear to accelerate water loss[7–10] whereas aromatic ones do not.[11–14]

Rorabacher[15] has shown that the experimentally measured rate of formation of some metal polyamines

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[11] M. Eigen and R. G. Wilkins, *Advan. Chem. Ser.*, **No. 49**, 55 (1965).

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is faster than predicted from the Eigen mechanism[16] due to an internal conjugate base effect (ICB). The nature of this enhancement and how other coordinated ligands affect it is presently unknown.

Ligand-exchange reactions involving nickel polyamines and EDTA[17,18] have been studied and shown to proceed through an intermediate having both ligands coordinated to the central metal ion. The reactions are very sensitive to steric effects.

In this study, the kinetics of reaction 1 were investigated to study further the above-mentioned mechanisms and effects. Mixed-ligand intermediates

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

should result as trien dissociates, allowing the effect of coordinated aromatic nitrogens upon the dissociation to be studied.

Experimental Section

Materials.—All chemicals were reagent grade and used without further purification with the exception of 2,6-lutidine which was distilled, and the fraction boiling at 143–144° was collected. The hydrochloride salt was prepared using the method of Pritchard and Long.[19] All solutions were prepared by passing distilled water through a mixed-bed ion-exchange column.

$\mathrm{Ni(trien)^{2+}}$.—Solutions of $\mathrm{Ni(trien)^{2+}}$ were prepared by adding a slight excess of $\mathrm{Ni(NO_3)_2}$ to a solution of triethylenetetramine disulfate and raising the pH to 11.5 using NaOH. The excess nickel was filtered off as the hydroxide using a Millipore 6.45-μ filter and the pH of the solution was lowered to 7.5–8.0 using HCl. The concentration of the $\mathrm{Ni(trien)^{2+}}$ was obtained by spectrophotometrically analyzing aliquots for the nickel content as $\mathrm{Ni(CN)_4{}^{2-}}$ using an excess of $\mathrm{CN^-}$. The molar absorptivity of $\mathrm{Ni(CN)_4{}^{2-}}$ was obtained from a standard nickel solution and an excess of $\mathrm{CN^-}$.

Nickel Monophenanthroline.—Crystalline nickel monophenanthroline was prepared according to procedures previously described.[20] Nickel was analyzed spectrophotometrically as $\mathrm{Ni(CN)_4{}^{2-}}$ after the addition of excess cyanide and chloroform extraction of the phenanthroline. The chloroform extracts were combined and analyzed for phenanthroline at 265 nm. *Anal.* Calcd for $\mathrm{Ni(phen)(H_2O)_2(NO_3)_2}$: Ni, 14.7; phen, 45.1. Found: Ni, 15.6; phen, 44.9.

Kinetic Runs.—All kinetic runs were made using a Cary Model 14 spectrophotometer by following the increase in absorbance due to the formation of $\mathrm{Ni(phen)_3{}^{2+}}$ at 343 nm. A spectral study of reactants and products showed the largest change in molar absorptivity at that wavelength. The molar absorptivities of reactants and products measured at 343 nm, $\mu = 0.1\ M$, and 25.0° were as follows ($M^{-1}\ \mathrm{cm^{-1}}$): phen, 54; $\mathrm{Hphen^+}$, 1080; $\mathrm{Ni(trien)^{2+}}$, 7; $\mathrm{Ni(trien)(phen)^{2+}}$, 335; $\mathrm{Ni(phen)_3{}^{2+}}$, 1430. Kinetic data were obtained over the pH range of 4.99–6.75 using lutidine–lutidine hydrochloride or boric acid–mannitol as buffers. The pH held 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 phen:$\mathrm{Ni(trien)^{2+}}$ ratio was varied from 3.2:1 to 31:1. The ionic strength was held constant at 0.1 M using NaCl.

Stability Constants.—Data for the calculation of stability constants for the reactions

$$\mathrm{Ni(trien)(phen)^{2+} + H^+ \rightleftharpoons Ni(Htrien)(phen)^{3+}} \quad (2)$$

$$\mathrm{Ni(phen)^{2+} + Htrien^+ \rightleftharpoons Ni(Htrien)(phen)^{3+}} \quad (3)$$

$$\mathrm{Ni(phen)^{2+} + trien \rightleftharpoons Ni(trien)(phen)^{2+}} \quad (4)$$

were obtained by mixing known amounts of $\mathrm{Ni(phen)(H_2O)_2(NO_3)_2}$ and $\mathrm{trien\cdot 2H_2SO_4}$ in a four-neck round-bottom flask.

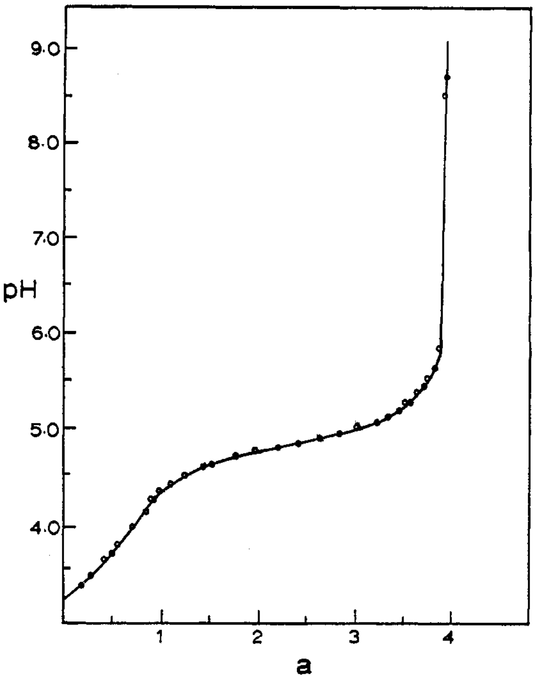

Figure 1.—Neutralization curve of $\mathrm{Ni(trien)(phen)^{2+}}$ with NaOH at 25°, $\mu = 0.1\ M$. a = apparent degree of neutralization of $\mathrm{H_4trien^{4+}}$; pH = (normality of base)(milliliters base added)/(molarity of trien)(milliliters of initial solution).

This was immersed in a constant-temperature bath regulated to 25.0 ± 0.1°. The ionic strength was set at 0.1 M using NaCl and the solution was titrated using carbonate-free NaOH. The time for each titration was about 45 min.

Results

Stability Constants of Mixed-Ligand Complexes.—Stability constants for reactions 2–4 were obtained using the method of Schwarzenbach,[21] as described by Jonassen and Westerman.[22] There was no danger of the dissociation of $\mathrm{Ni(phen)^{2+}}$ before it reacted with trien or $\mathrm{Htrien^+}$ because at pH 1.7, the half-life for dissociation is 7×10^4 sec and increases at higher pH.[23] The apparent degree of neutralization as a function of pH is shown in Figure 1. From this, apparent basicity constants were calculated, and from them, stability constants were calculated for reactions 2–4 as previously described.[22] These values along with the analogous $\mathrm{Ni(trien)^{2+}}$ values[3] and the protonation constants for trien[24] are listed in Table I.

Kinetics of Phenanthroline Exchange with $\mathrm{Nickel(trien)^{2+}}$.—In all kinetic runs the initial absorbance was found to be higher than the calculated value based on the molar absorptivities of the reactants. The higher initial absorbance can be predicted by assuming the immediate formation of a mixed-ligand species, $\mathrm{Ni(trien)(phen)^{2+}}$. The molar absorptivity of $\mathrm{Ni(trien)(phen)^{2+}}$ was measured from solutions both of $\mathrm{Ni(trien)^{2+}}$ and phen and of $\mathrm{Ni(phen)^{2+}}$ and trien. This type of species is not unusual as $\mathrm{Ni(phen)^{2+}}$ is known to form mixed complexes with diethylenetriamine and nitrilotriacetate.[20]

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TABLE I

COMPLEX STABILITY CONSTANTS FOR Ni(trien)(phen)$^{2+}$ AND Ni(trien)$^{2+}$ AND ACID DISSOCIATION CONSTANTS FOR trien (25.0°, $\mu = 0.1\ M$)

Stability Constants[a]	
$\log K_{\mathrm{NiT}}^{\mathrm{Ni}} = 13.82^{b}$	$\log K_{\mathrm{NiTP}}^{\mathrm{NiP}} = 13.60^{c}$
$\log K_{\mathrm{NiHT}}^{\mathrm{Ni}} = 8.7^{b}$	$\log K_{\mathrm{NiHTP}}^{\mathrm{NiP}} = 8.22^{c}$
$\log K_{\mathrm{NiHT}}^{\mathrm{NiT}} = 4.7^{b}$	$\log K_{\mathrm{NiHTP}}^{\mathrm{NiTP}} = 4.71^{c}$
Protonation Constants	
$\log K_{\mathrm{H_4T}} = 3.39^{d}$	$\log K_{\mathrm{H_2T}} = 9.31^{d}$
$\log K_{\mathrm{H_3T}} = 6.75^{d}$	$\log K_{\mathrm{HT}} = 10.09^{d}$

[a] The terminology for these constants is consistent with the convention used by L. Sillén and A. B. Martell, "Stability Constants of Metal Ion Complexes," The Chemical Society, London, 1964: $K_{\mathrm{NiT}}^{\mathrm{Ni}} = [\mathrm{NiT}]/[\mathrm{Ni}][\mathrm{T}]$; $K_{\mathrm{H_4T}} = [\mathrm{H_4T^{4+}}]/[\mathrm{H_3T^{3+}}]a_{\mathrm{H}}$. [b] See ref 3. [c] Measured in this study. [d] See ref 24.

The formation of the mixed complex was complete within the time of mixing. Thus, the reaction actually followed is given in eq 5 with protons omitted. The

$$\mathrm{Ni(trien)(phen)^{2+}} + 2\mathrm{phen} \rightleftharpoons \mathrm{Ni(phen)_3^{2+}} + \mathrm{trien} \qquad (5)$$

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

When phen was in tenfold or greater excess over Ni(trien)(phen)$^{2+}$, the data gave excellent first-order plots. This established a first-order behavior in Ni(trien)(phen)$^{2+}$. However, when the phen concentration was only in a threefold excess over Ni(trien)(phen)$^{2+}$, marked curvature was obtained by plotting the data as a second-order reaction, but replotting the data as a first-order reaction gave excellent first-order plots. Further, variation of the excess phen concentration over a tenfold range at pH 5.0 yielded essentially constant values for the rate constant. Thus, the reaction is first order in Ni(trien)(phen)$^{2+}$ and zero order in phen in accordance with the equation

$$\text{rate} = \frac{-d[\mathrm{NiTP^{2+}}]}{dt} = k_0[\mathrm{NiTP^{2+}}] \qquad (6)$$

All rate constants along with reactant concentrations and pH are listed in Table II.

TABLE II

FIRST-ORDER RATE CONSTANTS FOR THE DISSOCIATION OF Ni(trien)(phen)$^{2+}$ (25°, $\mu = 0.1\ M$)

pH	10^5[phen], M	10^5[Ni(trien)], M	$10^4 k_0$, 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, 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, 6.95
5.38	27.5	8.61	10.7, 10.4, 10.4
5.30	26.9	8.44	14.8, 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
5.01	56.6	18.2	31.2
5.01	29.1	9.12	27.6
4.99	29.1	9.12	29.4, 27.6
4.96	7.27	0.228	30.4

[a] Lutidene–lutidene hydrochloride buffer. All others used boric acid–mannitol buffer.

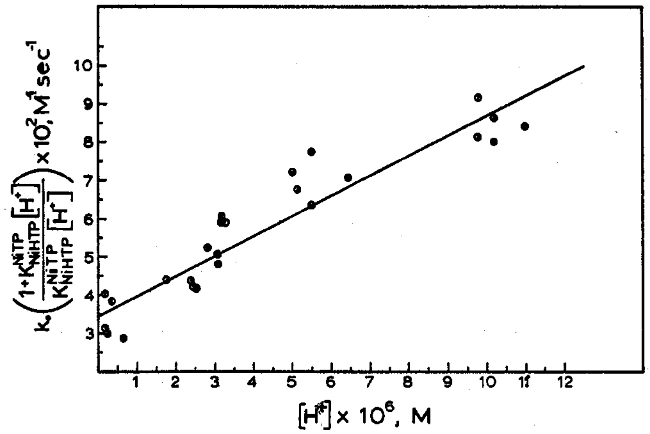

Figure 2.—Resolution of the rate constants for the dissociation of Ni(trien)(phen)$^{2+}$ at 25°, $\mu = 0.1\ M$. Plot of eq 9.

The data in Table II show that the reaction is pH dependent. Values of pH higher than 6.8 were not practicable due to the slowness of the reaction and values less than 5 gave small absorbance changes due to the high molar absorptivity of Hphen$^+$. In the pH range for which rate constants were obtained, the dissociation rate of Ni(trien)(phen)$^{2+}$ can be expressed as a two-term function involving one and two protons, respectively. This can be represented as

$$k_0[\mathrm{NiTP}]_{\mathrm{T}} = (k^{\mathrm{NiHTP}} + k_{\mathrm{H}}^{\mathrm{NiHTP}}[\mathrm{H^+}])[\mathrm{NiHTP^{3+}}] \qquad (7)$$

where

$$[\mathrm{NiTP}]_{\mathrm{T}} = [\mathrm{NiTP^{2+}}] + [\mathrm{NiHTP^{3+}}] \qquad (8)$$

Equation 7 can be rearranged to the form

$$k_0\frac{[\mathrm{NiTP}]_{\mathrm{T}}}{[\mathrm{NiHTP^{3+}}]} = k_0\left(\frac{1 + K_{\mathrm{NiHTP}}^{\mathrm{NiTP}}[\mathrm{H^+}]}{K_{\mathrm{NiHTP}}^{\mathrm{NiTP}}[\mathrm{H^+}]}\right) = k^{\mathrm{NiHTP}} + k_{\mathrm{H}}^{\mathrm{NiHTP}}[\mathrm{H^+}] \qquad (9)$$

which yielded the linear plot shown in Figure 2. From the plot, the values k^{NiHTP} = intercept = $(3.4 \pm 0.2) \times 10^{-3}$ sec^{-1} and $k_{\mathrm{H}}^{\mathrm{NiHTP}}$ = slope = $(5.3 \pm 0.3) \times 10^2\ M^{-1}$ sec^{-1} were obtained. The dissociation reaction can be written several ways depending upon the assignment of the protons. Formation rate constants can also be calculated from the dissociation rate constants and appropriate stability constants. Table III lists the various rate constants for alternate proton assignments.

TABLE III

EXPERIMENTAL RATE CONSTANTS FOR Ni(trien)(phen)$^{2+}$ AND Ni(trien)$^{2+}$ SYSTEMS (25°, $\mu = 0.1\ M$)

Ni(trien)(phen)$^{2+}$ system[a]	Ni(trien)$^{2+}$ system[b]
Dissociation Constants	
$k^{\mathrm{NiHTP}} = 3.5 \times 10^{-3}\ \mathrm{sec^{-1}}$	$k^{\mathrm{NiHT}} = 1.8 \times 10^{-5}\ \mathrm{sec^{-1}}$
$k_{\mathrm{H}}^{\mathrm{NiTP}} = 1.7 \times 10^{2}\ M^{-1}\ \mathrm{sec^{-1}}$	$k_{\mathrm{H}}^{\mathrm{NiT}} = 0.91\ M^{-1}\ \mathrm{sec^{-1}}$
$k_{\mathrm{H}}^{\mathrm{NiHTP}} = 5.3 \times 10^{2}\ M^{-1}\ \mathrm{sec^{-1}}$	$k_{\mathrm{H}}^{\mathrm{NiHT}} = 2.3 \times 10^{2}\ M^{-1}\ \mathrm{sec^{-1}}$
$k_{\mathrm{2H}}^{\mathrm{NiTP}} = 2.7 \times 10^{7}\ M^{-2}\ \mathrm{sec^{-1}}$	$k_{\mathrm{2H}}^{\mathrm{NiT}} = 1.2 \times 10^{7}\ M^{-2}\ \mathrm{sec^{-1}}$
Formation Constants	
$k_{\mathrm{NiP}}^{\mathrm{HT}} = 5.7 \times 10^{5}\ M^{-1}\ \mathrm{sec^{-1}}$	$k_{\mathrm{Ni}}^{\mathrm{HT}} = 9.3 \times 10^{3}\ M^{-1}\ \mathrm{sec^{-1}}$
$k_{\mathrm{NiP}}^{\mathrm{H_2T}} = 43\ M^{-1}\ \mathrm{sec^{-1}}$	$k_{\mathrm{Ni}}^{\mathrm{H_2T}} = 97\ M^{-1}\ \mathrm{sec^{-1}}$

[a] This study. [b] See reference 3.

The overall rate of dissociation can be expressed as any combination of one and two proton terms such as eq 7. Calculation of the overall rate using any of the above-mentioned combinations gave excellent agreement to the experimental data in all cases. Figure 3 is a plot of eq 7. This gives confidence in the resolved rate constants.

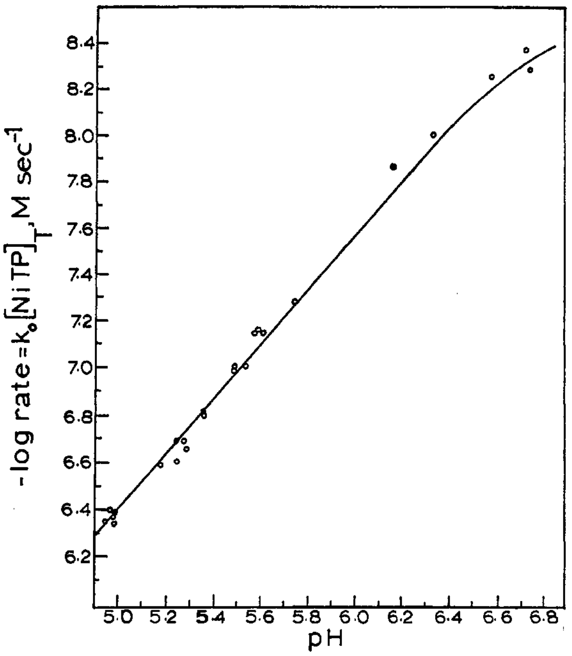

Figure 3.—Fit of theoretical curve to experimental rate constants for the dissociation of Ni(trien)(phen)$^{2+}$ at 25°, μ = 0.01 *M*. Solid line is the curve predicted by eq 7; circled points are experimentally observed values.

Discussion

Since this study involves the dissociation of the trien from Ni(trien)(phen)$^{2+}$, a comparison with the dissociation of trien from Ni(trien)$^{2+}$ [3] will be helpful in determining the mechanism. Comparison of the rate constants for both systems shows that both the dissociation and formation rate constants for all two-proton terms are practically identical. However, all one-proton terms are a factor of about 200 higher for the Ni(trien)(phen)$^{2+}$ system than for the Ni(trien)$^{2+}$ system. Previous studies have shown that when similar rate constants for several related systems are obtained, the same mechanism holds true for those systems.[16,17,25] The similarity of rate constants for the two-proton terms strongly suggests the same type of mechanism holds true for both systems.

The experimental data for the present system show that the rate-determining step must lie after the addition of phenanthroline to Ni(trien)$^{2+}$ and after two nickel–polyamine bonds are broken since Ni(trien)(phen)$^{2+}$ was found to form rapidly as Ni(trien)$^{2+}$ and phenanthroline were mixed and since a two-proton dependence is seen in resolving the overall rate constant. 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 bond as rate determining and is thus far identical with the Ni(trien)$^{2+}$ dissociation.

At this point, two reasonable possibilities exist: (a) breaking of the third nickel–polyamine bond as rate determining, followed by the rapid addition of a second phenanthroline, or (b) breaking of the fourth nickel–polyamine bond as rate determining, as is the case with Ni(trien)$^{2+}$, followed by the addition of a second phenanthroline. These two stepwise pathways are illustrated in Figure 4. The addition of phenanthroline cannot be rate determining since kinetically no phenanthroline dependence is seen. Further, rupture of the third nickel–polyamine bond as rate determining followed by rupture of the fourth and then rapid addition of phenanthroline can be eliminated using steady-state arguments analogous to those for the Ni(trien)$^{2+}$ system.[3]

Pathway A.—Although fitting the experimental kinetic dependence, pathway A would not be the most likely mechanism. It can be shown that a factor of about 70 exists between the breaking of three and of four nickel–polyamine bonds in Ni(trien)$^{2+}$.[3] Since k_{H}^{NiHTP} and k_{2H}^{NiTP} are approximately equal to k_{H}^{NiHT} and k_{2H}^{NiT}, respectively, it must be assumed that, for pathway A to be correct, the presence of phenanthroline is causing diprotonated trien to dissociate at a slower rate than normal.

The presence of phenanthroline basically does not affect the rate of water loss of Ni(phen)(H$_2$O)$_4^{2+}$ [7] or Ni(phen)$_2$(H$_2$O)$_2^{2+}$, [5] nor does it affect the stability constant for the addition of trien (see Table I, $K_{NiPT}^{NiP} \cong K_{NiT}^{Ni}$). Thus, there is no reason to expect phenanthroline to slow down the rate of two-proton dissociation to the point where breakage of the first three nickel–polyamine bonds is equal to breakage of all four without phenanthroline. Phenanthroline would be expected to increase the dissociation of trien both statistically (twofold) and sterically. This would leave an even wider gap between the two-proton terms of both systems. The one-proton terms are about a factor of 200 higher for Ni(trien)(phen)$^{2+}$ than for Ni(trien)$^{2+}$ which would be reasonable assuming pathway A with statistical and steric factors. Thus, in order for pathway A to be correct the similarity of the two-proton terms for both systems must be explained on the basis of the presence of phenanthroline. Experimental work does not support this, so, despite the apparent agreement of the one-proton terms, pathway A must be excluded.

Pathway B.—This pathway is analogous to the Ni(trien)$^{2+}$ system, followed by the rapid addition of a second phenanthroline, and fits the kinetic order dependence. The two-proton terms of both systems are similar, reflecting rupture of four nickel–polyamine bonds through the rate-determining step in both cases. Previously discussed evidence shows that phenanthroline should have no effect on trien dissociation.

The one-proton terms, however, are about a factor of 200 higher for Ni(trien)(phen)$^{2+}$ than for Ni(trien)$^{2+}$. Since corresponding stability constants for both systems are about equal, the difference in one-proton dissociation rates cannot be explained on this basis.

If the reverse of reaction 1 is considered, the rate of formation of Ni(trien)(phen)$^{2+}$ from Ni(phen)$_3^{2+}$ and trien can be obtained from the experimentally measured dissociation rate constant and stability constants. The rate of formation of Ni(trien)$^{2+}$ from Ni^{2+} and trien has been experimentally determined.[3] The rate of formation of Ni(trien)(phen)$^{3+}$, Ni(H$_2$trien)(phen)$^{4+}$, Ni(Htrien)$^{3+}$, and Ni(H$_2$trien)$^{4+}$ from Ni(phen)$^{2+}$ reacting with Htrien$^+$ or H$_2$trien^{2+} and Ni^{2+} reacting with Htrien$^+$ or H$_2$trien^{2+}, respectively, can be calculated theoretically from the thoroughly tested gen-

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[25] T. J. Bydalek and D. W. Margerum, *Inorg. Chem.*, **2**, 678 (1963).

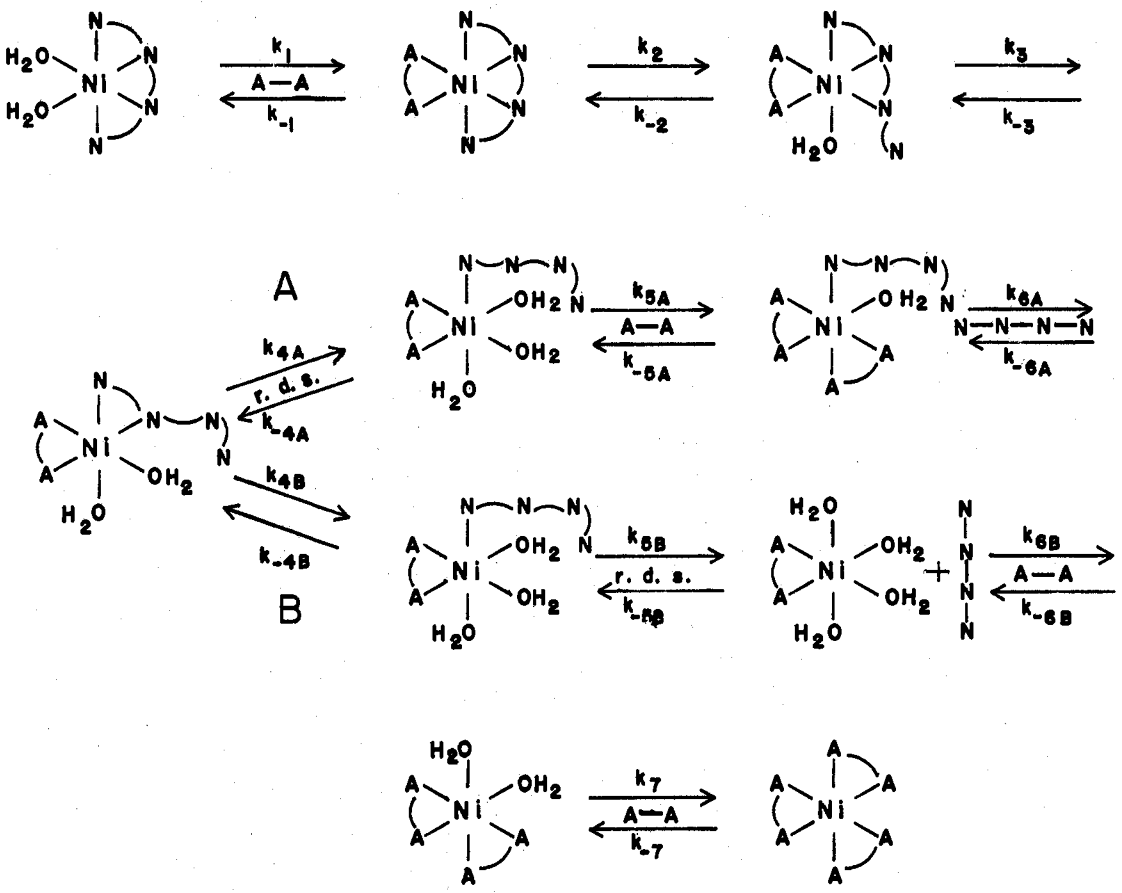

Figure 4.—Proposed stepwise mechanism for the dissociation of Ni(trien)(phen)$^{2+}$ in the presence of phenanthroline. Proton are omitted for the sake of clarity. Phenanthroline is A–A.

eral 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.[16] Assuming pathway B as being correct, microscopic reversibility predicts that the first nickel–polyamine bond will be rate determining for the formation reaction. Thus the formation rate constants for the above system can be calculated as

$$k_{\mathrm{Ni\,or\,NiP}}{}^{\mathrm{total}} = K_{\mathrm{os}}k^{\mathrm{Ni-H_2O}} \qquad (10)$$

Values of K_{os} can be calculated with fair accuracy[5,26] from diffusion equations and the appropriate values of $k^{\mathrm{Ni-H_2O}}$ are known.[7] Equation 11[26] is used to calculate K_{os} values. The terms have been previously

$$K_{\mathrm{os}} = \frac{4\pi Na^3}{3000}\,\gamma_{\pm}{}^2 \exp(-Z_AZ_Be_0{}^2/DkTa') \qquad (11)$$

defined.[26] Values of $a = 3.5 \times 10^{-8}$ cm and $a' = 14 \times 10^{-8}$ cm for Htrien$^+$ and $a = 3.5 \times 10^{-8}$ cm and $a' = 9 \times 10^{-8}$ [27] for H$_2$trien^{2+} were obtained from molecular models. The a values were also used in calculating $\gamma_{\pm}$. Equation 11 gives values of K_{os} for both Ni(H$_2$O)$_6{}^{2+}$ and Ni(phen)(H$_2$O)$_4{}^{2+}$ reacting with Htrien$^+$ as $2.2 \times 10^{-2}\ M^{-1}$ and, for the same two species reacting with H$_2$trien^{2+}, $1.5 \times 10^{-3}\ M^{-1}$.

TABLE IV

COMPARISON OF PREDICTED AND EXPERIMENTAL VALUES OF FORMATION RATE CONSTANTS (25°, $\mu = 0.1\ M$)

Predicted	Experimental
Ni(trien)(phen)$^{2+}$ System	
$k_{\mathrm{NiP}}{}^{\mathrm{HT}} = 4.8 \times 10^2\ M^{-1}$ sec^{-1} [a]	$k_{\mathrm{NiP}}{}^{\mathrm{HT}} = 5.7 \times 10^5\ M^{-1}$ sec^{-1} [b]
$k_{\mathrm{NiP}}{}^{\mathrm{H_2T}} = 33\ M^{-1}$ sec^{-1} [a]	$k_{\mathrm{NiP}}{}^{\mathrm{H_2T}} = 43\ M^{-1}$ sec^{-1} [b]
Ni(trien)$^{2+}$ System	
$k_{\mathrm{Ni}}{}^{\mathrm{HT}} = 6.1 \times 10^2\ M^{-1}$ sec^{-1} [a]	$k_{\mathrm{Ni}}{}^{\mathrm{HT}} = 9.3 \times 10^3\ M^{-1}$ sec^{-1} [c]
$k_{\mathrm{Ni}}{}^{\mathrm{H_2T}} = 42\ M^{-1}$ sec^{-1} [a]	$k_{\mathrm{Ni}}{}^{\mathrm{H_2T}} = 97\ M^{-1}$ sec^{-1} [c]

[a] Predicted from eq 10. [b] Measured in this study. [c] See ref 3.

Using these K_{os} values along with $k^{\mathrm{Ni(phen)-H_2O}} = 2.2 \times 10^4$ [7] and $k^{\mathrm{Ni-H_2O}} = 2.8 \times 10^4$ [7] formation rate constants can be predicted from eq 10. These are listed in Table IV along with the formation constants obtained from experimentally measured dissociation constants and stability constants.

Comparison of the experimental and calculated values shows that Ni(Htrien)$^{3+}$ forms about a factor of 15 faster than predicted and Ni(Htrien)(phen)$^{3+}$ about a factor of 1200 faster than predicted, whereas Ni(H$_2$trien)$^{4+}$ and Ni(H$_2$trien)(phen)$^{4+}$ both form at the predicted rate. Enhanced formation rates for nickel polyamines have been seen previously and are attributed to an internal conjugate base mechanism (ICBM).[15]

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(26) A. Kowalak, K. Kustin, R. F. Pasternack, and S. Petrucci, *J. Amer. Chem. Soc.*, **89**, 3126 (1967).

(27) The value of a' for H$_2$trien^{2+} is a weighted distance calculated from the fractional concentration of each of the four possible isomers of H$_2$trien^{2+} multiplied by the appropriate center-to-center distance between charges. Fractional concentrations were obtained from D. B. Rorabacher, Ph.D. Thesis, Purdue University, June 1966. It must also be noted that K_{os} for Ni^{2+} and H$_2$trien^{2+} may be calculated from experimental values of $k_{\mathrm{Ni}}{}^{\mathrm{H_2T}}$ and $k^{\mathrm{Ni-H_2O}}$, since the ICB effect is inoperable with H$_2$trien^{2+}. Using these values, eq 10 gives $K_{\mathrm{os}} = 3.5 \times 10^{-3}\ M^{-1}$ which is in excellent agreement with the values of $1.4 \times 10^{-3}\ M^{-1}$ from eq 11.

It has been shown that multidentate ligands with $pK_a < 8$ do not react *via* the ICBM with nickel because they are not basic enough to hydrogen bond to a coordinated water.[15] This is seen in both the present study and the Ni(trien)$^{2+}$ system where H_2trien^{2+}, having remaining pK_a values of 6.75 and 3.39, forms at the predicted rate, whereas Htrien$^+$, having remaining pK_a values of 9.31, 6.75, and 3.39, forms at an accelerated rate.

Of more interest, however, is the factor of 1200 between the experimental and predicted formation rate constants involving Ni(phen)$^{2+}$ and Htrien$^+$ compared to only a factor of 15 between the corresponding constants for the aquo nickel ion and Htrien$^+$. The presence of phenanthroline in the inner coordination sphere of nickel has somehow enhanced the ICB effect by a factor of 80. Realizing that K_{os} values may only be correct to within a factor of 2–4[5,27] the effect is still unmistakable. 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 hydrogen bonding, 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 fact that k^{Ni-H_2O} and k^{NiP-H_2O} are about equal[7] shows that the presence of phenanthroline has no effect on the nickel rate of water loss unless another ligand is present to hydrogen bond by the ICB mechanism before initial formation with nickel. Thus, phenanthroline must somehow facilitate either electron redistribution as a result of hydrogen bonding to cause faster nickel–water bond rupture or hydrolysis of water in the inner coordination sphere of nickel. Present data do not allow a choice between the two explanations. The earlier statement that phenanthroline does not affect trien dissociation is still true, provided no hydrogen bonding is possible. This is the case with the two-proton terms and would be true for both the one- and two-proton terms of pathway A.

It must be noted at this point that if an ICBM is also postulated for the formation reaction *via* pathway A, the two-proton terms of both systems should still differ by at least a factor of 70 since the ICBM does not operate when the free nitrogen pK_a values are less than 8.

Thus, it is concluded that pathway B fits the experimental data best, based upon comparison with Ni(trien)$^{2+}$ and upon knowledge of the effect of phenanthroline on formation rates and stability constants.

Comparison to Similar Systems.—It is instructive to compare the Ni(trien)(phen)$^{2+}$ system with other nickel polyamine formation and dissociation studies. The effect of coordinated polyamine nitrogens and ammonia has been shown to accelerate the loss of water from $Ni(H_2O)_{6-x}L_x$ in a linear fashion.[7–10] This is substantiated in a study of the ethylenediamine (en) reaction with Ni(en)$_2^{4+}$.[4] The results of the present study involving coordinated aromatic nitrogens are in contrast to coordinated polyamine nitrogens and show no effect on water lability or polyamide dissociation rate, provided no hydrogen bonding involving the polyamine is possible. This reaffirms previous work in the area.[11–14]

Compared to the Ni(en)$_2^{2+}$ system, the present study also reveals that phenanthroline is able to enhance the ICB effect by a factor of about 80 when hydrogen bonding is possible, whereas the ratio of experimental rate of formation of Ni(en)$_3^{2+}$ from Ni(en)$_2^{2+}$ and en to the predicted rate is only about 1.2 (this includes an estimated ICB effect).[28] Thus, apparently, coordinated polyamines are not able to enhance the ICB effect whereas coordinated aromatic nitrogens are.

The reactions of diethylenetriaminenickel(II) (Ni(dien)$^{2+}$)[18] and of Ni(trien)$^{2+}$[17] with EDTA have also been studied. Both show that the flexible EDTA can coordinate to nickel by occupying sites as they are left open from the partially dissociated polyamine. Thus dien and trien dissociation is enhanced to the point where only one polyamine bond is broken prior to the rate-determining step. This is in contrast to the rigid phenanthroline molecule which apparently requires four open sites.

It has also been noted that due to the bulky nature of the two multidenate ligands involved, exchange reactions should be very sensitive to steric effects.[17] This is seen in the present study and can be used to explain the failure of phenanthroline to coordinate until four sites are available.

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[28] Equation 9 predicts $k_{Ni(H_2O)_6}{}^{en} = 2.8 \times 10^3\ M^{-1}\ sec^{-1}$ using $K_{os} = 0.1\ M^{-1}$[4] and $k^{Ni-H_2O} = 2.8 \times 10^4\ sec^{-1}$.[7] The experimental value of $k_{Ni(H_2O)_6}{}^{en} = 4 \times 10^5\ M^{-1}\ sec^{-1}$.[5] The ICB effect per en is thus 140. Equation 9 predicts $k_{Ni(en)_2}{}^{en} = 1.2 \times 10^5\ M^{-1}\ sec^{-1}$ using $K_{os} = 0.1\ M^{-1}$[4] and $k^{Ni(en)_2-H_2O} = 1.2 \times 10^6\ sec^{-1}$.[8] The experimental value of $k_{Ni(en)_2}{}^{en} = 5.5 \times 10^6\ M^{-1}\ sec^{-1}$.[4] Correcting the predicted value for the ICB effect (140) and a statistical factor ($^1/_3$) gives 5.6×10^6. Thus, there is no ICB enhancement by two coordinated en molecules.