

[CONTRIBUTION NO. 455 FROM THE INSTITUTE FOR ATOMIC RESEARCH AND DEPARTMENT OF CHEMISTRY, IOWA STATE COLLEGE]¹

Kinetics of 1,10-Phenanthroline Chelation. I. Mono-(1,10-phenanthroline)-nickel(II)²

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RECEIVED FEBRUARY 13, 1956

The effect of hydrogen ion concentration on the kinetics of formation and dissociation of the mono-(1,10-phenanthroline)-nickel(II) complex is examined. Two mechanisms are proposed as possible reaction paths. One mechanism is the acid-catalyzed reaction of an unstable intermediate formed between the ligand and nickel(II); the other mechanism is the reaction of the 1,10-phenanthrolium ion with nickel(II) to form an intermediate. Both mechanisms fit the general expression $k_{1f} = ([H^+] + 0.0043)/(2.62 [H^+] + 0.258) 10^6 \text{ l. mole}^{-1} \text{ sec.}^{-1}$. The equilibrium constants of the mono-, bis- and tris-(1,10-phenanthroline)-nickel(II) complexes are $K_1 = 2.5 \times 10^{-9}$, $K_2 = 8 \times 10^{-9}$, $K_3 = 2.8 \times 10^{-8}$, respectively.

Introduction

Although the complexes between nickel(II) and 1,10-phenanthroline have long been known,⁴ no detailed study of the kinetics or equilibrium constants has been reported previously. Vosburgh and Cooper⁵ were able to show the existence of the mono-, bis- and tris-(1,10-phenanthroline)-nickel(II) complexes in aqueous solution by spectrophotometric data. Brandt, Dwyer and Gyarfás⁶ have reviewed the chelate complexes of 1,10-phenanthroline with nickel(II), as well as other ions. Davis and Dwyer⁷ reported from a private communication with Dunstone and Mellor that the pK of the tris-(1,10-phenanthroline)-nickel(II) complex is 18.3, where $K = [Ni^{++}][Ph]^3/[NiPh_3^{++}]$.⁸ This value, which appears to be erroneous, has been in the literature ever since with no experimental confirmation. Equilibrium constants are calculated for these mono, bis and tris complexes in this work.

The kinetics of dissociation of tris-(1,10-phenanthroline)-nickel(II) have previously been shown to proceed at a measurable pace. Basolo, Hayes and Neumann⁹ reported a dissociation rate constant of $5.4 \times 10^{-4} \text{ min.}^{-1}$ in 3 *M* hydrochloric acid at 25°. They observed no major changes in this rate between 2 and 5 *M* hydrochloric acid solutions. However, they did report a hydrogen ion effect on the rate of dissociation of the tris-(2,2'-bipyridine)-nickel(II) complex.

Margerum and Banks¹⁰ showed that the rate of the formation of mono-(1,10-phenanthroline)-nickel(II) is sufficiently slow to allow the separation of trace amounts of iron as tris-(1,10-phenanthroline)-iron(II) perchlorate from nickel solutions.

The reactions between 1,10-phenanthroline and

(1) Work was performed in the Ames Laboratory of the U. S. Atomic Energy Commission.

(2) Abstracted from a portion of the Ph.D. thesis of D. W. Margerum, Iowa State College, 1955. Presented at the Minneapolis Meeting of the American Chemical Society, September 16, 1955.

(3) Department of Chemistry, Purdue University, Lafayette, Indiana.

(4) F. Blau, *Monatsh. Chem.*, **19**, 647 (1898).

(5) W. C. Vosburgh and G. R. Cooper, *THIS JOURNAL*, **63**, 437 (1941).

(6) W. W. Brandt, F. P. Dwyer and E. C. Gyarfás, *Chem. Revs.*, **54**, 959 (1954).

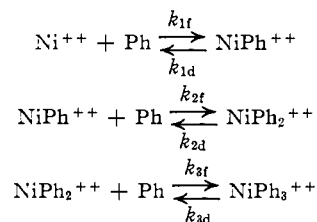
(7) H. R. Davis and F. P. Dwyer, *Trans. Faraday Soc.*, **49**, 180 (1953).

(8) Ph represents 1,10-phenanthroline.

(9) F. Basolo, J. C. Hayes and H. M. Neumann, *THIS JOURNAL*, **75**, 5102 (1953).

(10) D. W. Margerum and C. V. Banks, *Anal. Chem.*, **26**, 200 (1954).

nickel(II) may be written with their rate constants as



where the coordinated water molecules have not been included in the equations. All of these reactions are observed to be measurably slow. The reaction rate of the mono complex is shown in this work to have a complex acid dependence. The mechanisms proposed to explain the observed kinetic data are based on the postulated existence of an unstable intermediate complex between nickel(II) and 1,10-phenanthroline. These mechanisms also appear to fit the acid dependence of other ion-chelate reaction rates.

Experimental and Results

Absorbance measurements were made with a Beckman Model DU quartz spectrophotometer. A Beckman Model G pH meter was used for pH measurements. The kinetic studies were followed with the Beckman spectrophotometer with photomultiplier attachment and using thermospacers for the cell compartment. A water-bath with a circulating pump kept the cell compartment at $25.0 \pm 0.1^\circ$. All glassware used was of class A specifications.

The nickel solution used was prepared from Mond nickel of greater than 99.94% purity which was dissolved in acid and recrystallized as nickel perchlorate. The nickel solutions were analyzed with 1,2-cycloheptanedione dioxime (Heptoxime).¹¹

In acid media, 1,10-phenanthroline forms its conjugate acid, the 1,10-phenanthrolium ion, leaving a low concentration of the free base. Under these conditions the rate of formation of mono-(1,10-phenanthroline)-nickel(II) is sluggish, and the reaction can be followed in 10^{-4} to 10^{-5} molar solutions using ultraviolet spectrophotometry.

For each kinetic run a 1,10-phenanthroline blank was measured to determine the molar absorptivity of the 1,10-phenanthrolium ion under the particular conditions of that run. The molar absorptivity of the mono-(1,10-phenanthroline)-nickel(II) was determined by using a large excess of nickel(II) over 1,10-phenanthroline at low acidity. The absorbances of perchloric acid solutions of 1,10-phenanthroline were measured as a function of time of standing, area of silica surface (using glass beads) and of acidity. These tests indicated that 1,10-phenanthroline was kept in solution as the 1,10-phenanthrolium ion throughout the acidity range used in this work. However, 1,10-phenanthroline does show an affinity for silica surfaces, and at very low acidities this interferes with rate studies.

(11) R. C. Voter and C. V. Banks, *ibid.*, **21**, 1320 (1949).

In all reactions perchlorate was the only anion present. The nickel solution and the acid were mixed and diluted in a volumetric flask. After reaching temperature equilibrium in a water-bath, the required amount of 1,10-phenanthroline solution was added and the reaction solution was diluted to volume, shaken thoroughly, and a portion transferred to an absorbance cell. Unless the time of reaction was quite long, all readings were taken on this sample. The time required for dilution, mixing, and transfer was about two minutes.

Figure 1 shows the effect of time on the absorption spectra between 200 and 300 $m\mu$ when 1,10-phenanthroline and

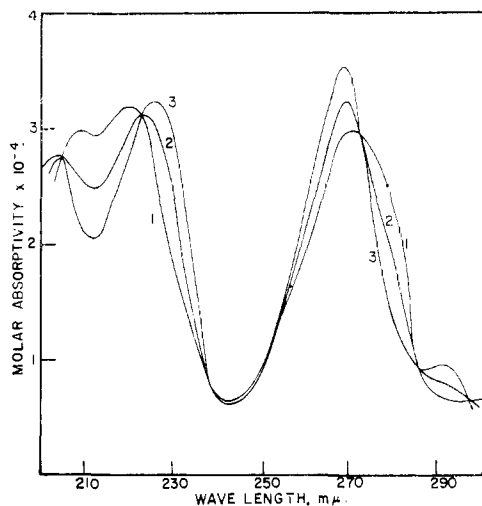


Fig. 1.—Absorption spectra of 1,10-phenanthroline showing the reaction with nickel(II) in acid solution: $Phr = 1.63 \times 10^{-5} M$, $Ni_T = 9.53 \times 10^{-4} M$, $H^+ = 0.509 M$; curve 1 began 2.5 min. after mixing, curve 2 began 17.0 min. after mixing and curve 3 began 108.0 min. after mixing; recording speed = 30 $m\mu$ /min.; all curves started at 300 $m\mu$.

nickel(II) are mixed in acid solutions. The appearance of seven well-defined isosbestic points clearly indicates that there are only two absorbing species present in the solution, namely, the 1,10-phenanthroline ion and the mono-(1,10-phenanthroline)-nickel(II) complex. In this region, 277.5 $m\mu$ is relatively free from interferences and is a suitable wave length for observing a large change in absorbance as the reaction proceeds. Another wave length which is highly suitable is 310 $m\mu$ as seen in Fig. 2.

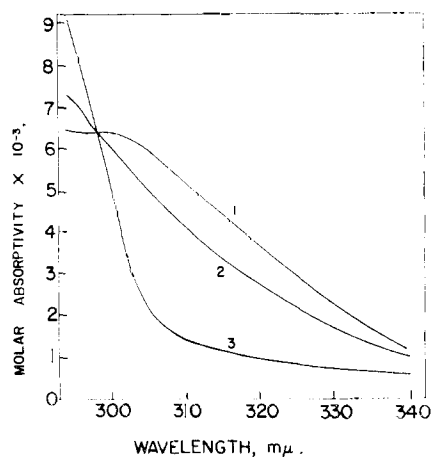


Fig. 2.—Absorption spectra in vicinity 310 $m\mu$ of 1,10-phenanthroline in equilibria with varying nickel(II) in acid solution: $[H^+] = 0.010$; curve 1 has no Ni^{++} ; curve 2 has 10:1 excess Phr ; curve 3 has 4000:1 excess Ni^{++} .

The reaction rate was studied under varying conditions from a large excess of nickel(II) perchlorate to a slight excess of 1,10-phenanthroline and from 0.75 to 0.005 molar perchloric acid. The reaction rate was observed by following the absorbance of the 1,10-phenanthroline ion and, therefore, it was not possible to use a large excess of 1,10-phenanthroline to nickel(II). The rapidity of the reaction prevented the use of a large excess of nickel(II) at low acidities. The visible spectrum is not a suitable region for studying the reaction because the molar absorptivity there is quite small. The insolubility of 1,10-phenanthroline perchlorate and the rapidity of the reaction also become prohibitive factors.

Table I gives a summary of the reaction conditions for the formation reaction and Table II gives a summary of the reaction conditions for the dissociation reaction. The rates of dissociation were followed in much the same manner as the rates of formation. The 1,10-phenanthroline and excess nickel(II) were allowed to reach equilibrium in weakly acidic solutions so that virtually all of the 1,10-phenanthroline was present as the mono-(1,10-phenanthroline)-nickel(II) complex. This solution was then aliquoted into a strong acid environment and the initial dissociation rate observed. When very acid solutions were used, such as 4.5 M (H^+), the molar absorptivity used for 1,10-phenanthroline was a composite of the two protonated 1,10-phenanthroline species as determined experimentally.

TABLE I
FORMATION REACTIONS OF THE MONO-(1,10-PHENANTHROLINE)-NICKEL(II) COMPLEX

(H^+)	$Phr^b \times 10^5$	$Ni_T^b \times 10^4$	$k_{11} \times 10^{-4}$ (l. mole ⁻¹ sec. ⁻¹)
0.750	10.35	118.0	3.05
.747 ^a	1.304	305.2	2.84
.531 ^a	1.304	132.6	3.15
.531 ^a	1.304	132.6	3.34
.535 ^a	1.304	305.2	3.28
.498	11.53	61.2	3.17
.376	10.35	58.0	3.02
.376 ^a	10.35	58.0	2.52
.298	11.53	7.65	2.75
.217	6.52	30.6	2.80
.106	6.52	4.59	1.98
.0686	6.52	4.59	1.74
.0686 ^c	6.52	4.59	1.60
.0270	6.52	4.59	0.867
.0213	13.04	4.59	.911
.0207	6.52	4.59	.800
.0064	0.501	5.90	.210

^a These runs were followed at 277.5 $m\mu$ and all others were at 310 $m\mu$. ^b Phr and Ni_T refer to the total concentration of all species of 1,10-phenanthroline or nickel present in solution. ^c These runs were in a 0.5 M $NaClO_4$ solution.

TABLE II
DISSOCIATION REACTIONS OF THE MONO-(1,10-PHENANTHROLINE)-NICKEL(II) COMPLEX

(H^+)	$Phr \times 10^5$	$Ni_T \times 10^4$	$k_{-1} \times 10^3$ (sec. ⁻¹)
4.5 ^a	2.303	1.526	9.15
1.00 ^a	1.153	8.40	9.83
0.50	5.76	1.905	6.55
.20	5.76	1.905	3.95
.020	5.76	1.905	1.52

^a These runs were followed at 277.5 $m\mu$ and all others were at 310 $m\mu$.

The acid dissociation constant for the mono-protonated 1,10-phenanthroline

$$K_a = \frac{(Ph)(H^+)}{(HPh^+)} = 1.1 \times 10^{-9}$$

has been measured by several previous workers¹² and this value is used in all calculations.

Spectrophotometric evidence in Fig. 3 and Fig. 4 indicates that in solutions above 1 M in HClO₄, the diprotonated 1,10-phenanthrolium ion, H₂Ph⁺⁺, begins to form.

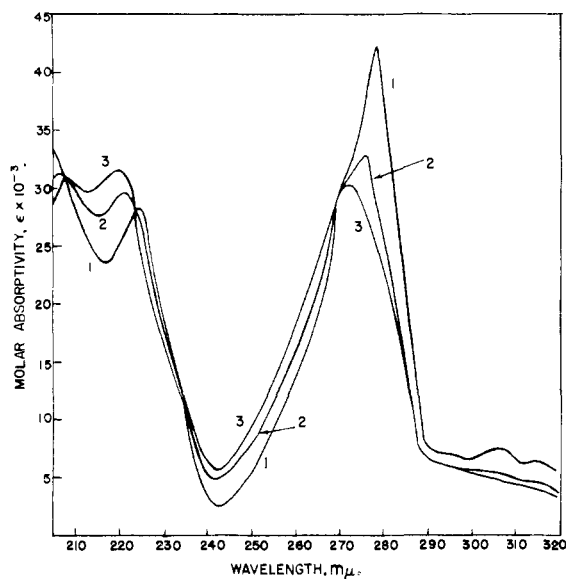


Fig. 3.—Ultraviolet absorption spectra of 1,10-phenanthroline with varying acidity: 1, [H⁺] = 11.5 M; 2, [H⁺] = 3.55 M; 3, [H⁺] = 0.1 M.

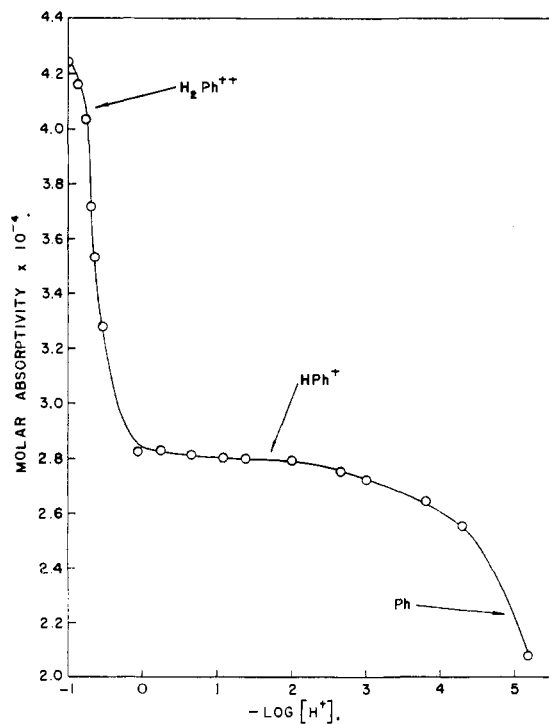


Fig. 4.—Spectrophotometric evidence at 277.5 m μ of mono- and diprotonated 1,10-phenanthroline.

The definite changes of the spectrum with acidity clearly show the formation of a new species. These changes are specific to hydrogen ion concentration and do not occur by merely increasing the ionic strength of the solution. It is

(12) (a) W. W. Brandt and D. K. Gullstrom, *THIS JOURNAL*, **74**, 3532 (1952); (b) T. S. Lee, I. M. Kolthoff and D. L. Leussing, *ibid.*, **70**, 2348 (1948).

possible to estimate a concentration equilibrium constant from these data

$$K = \frac{(H^+)(HPh^+)}{(H_2Ph^{++})} = 5$$

To the first approximation the formation rate can be expressed as first order with respect to both nickel(II) and 1,10-phenanthroline, the latter having a prior equilibrium with its conjugate acid. The dissociation rate can be expressed as first order with respect to the mono complex. Then

$$\frac{d(NiPh^{++})}{dt} = k_{1f}(Ni^{++})(Ph) - k_{1d}(NiPh^{++})$$

and for

$$(H^+) \gg K_a, (Ph) = \frac{K_a}{(H^+)} (Ph_T - (NiPh^{++}))$$

If a large excess of nickel(II) is used, the over-all kinetics become first order and it can be shown that

$$t = \frac{2.3(H^+)}{k_{1f}K_aNi_T + K_1(H^+)}$$

$$\log \frac{1}{1 - \left[\frac{Ni_T K_a + K_1(H^+)}{Ni_T K_a Ph_T} \right] (NiPh^{++})}$$

where $K_1 = k_{1d}/k_{1f}$. Since K_1 can be measured at equilibrium, the only variables are t and $(NiPh^{++})$. At lower nickel(II) concentrations the reaction rate is observed over a sufficiently small fraction of the total reaction time so that the dissociation of the mono complex may be neglected. It can then be shown that

$$t = \frac{2.3(H^+)}{k_{1f}K_a(Ph_T - Ni_T)} \log \left[\frac{Ph_T - (NiPh^{++})}{Ni_T - (NiPh^{++})} \times \frac{Ni_T}{Ph_T} \right]$$

The NiPh⁺⁺ is determined by absorbance measurement

$$(NiPh^{++}) = \frac{\epsilon_{HPh}Ph_T - A_0/l}{\epsilon_{HPh} - \epsilon_{NiPh}}$$

where ϵ is the molar absorptivity of the species indicated by the subscript, l is the cell length and A_0 is the observed absorbance corrected for any cell length.

The rate of dissociation of the mono complex can similarly be followed over a small fraction of the total dissociation to give the expression

$$\log \frac{1}{\epsilon_{HPh}Ph_T l - A_0} = \frac{k_{1d}t}{2.3} - \log [l(\epsilon_{HPh} - \epsilon_{NiPh})(NiPh^{++})_{t=0}]$$

The values obtained for k_{1f} and k_{1d} appear in Tables I and II. Typical reaction studies for the complex formation are shown in Fig. 5. The manner in which the value of k_{1f}

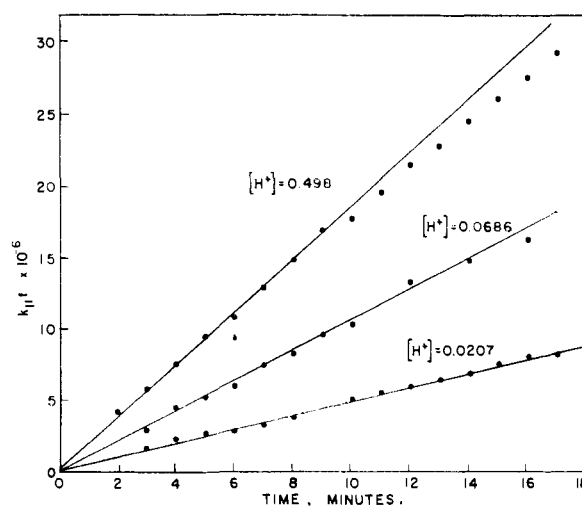


Fig. 5.—Second-order plot of rate of formation reactions of mono-(1,10-phenanthroline)-nickel(II) at different acidities.

changed with acidity is shown by the points in Fig. 6. In the calculation of k_{1f} no correction has been made for ionic strength effects on the activities of H^+ and HPh^+ . Previous estimates of these activities in KCl solutions have been made by assuming the Ph activity to be constant.^{12b}

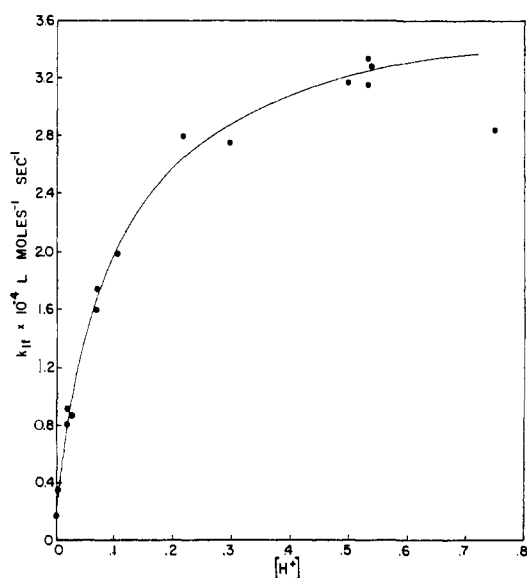


Fig. 6.—Effect of acidity on the formation rate constant of mono-(1,10-phenanthroline)-nickel(II).

The use of these corrections has little over-all effect on the change of k_{1f} with acidity, tending only to give higher values at high acidity. The decrease in k_{1f} at 0.75 M $HClO_4$ could be due to a combination of ionic strength effect on the 1,10-phenanthroline equilibrium and the start of H_2Ph^{++} formation.

Equilibrium constants were determined by absorbance measurements at various hydrogen ion, nickel(II) and 1,10-phenanthroline concentrations. Table III gives values for K_1 and Table IV values for K_3 determined in this manner. The standard deviation, σ , of these data is also given. The value $K_2 = 8 \times 10^{-9}$ was determined by calculations from absorbance data using either the average K_1 or K_3 value.

TABLE III
EQUILIBRIUM CONSTANTS FOR THE MONO-(1,10-PHENANTHROLINE)-NICKEL(II) COMPLEX

(H ⁺)	Phr × 10 ³	Nit × 10 ³	K ₁ × 10 ⁹
0.747	1.304	0.191	1.45
.535	1.304	.191	1.04
.531	1.304	.191	4.38
.531	1.304	.306	4.45
.510	1.16	1.526	2.44
.217	6.52	1.526	2.24
.498	5.76	1.55	2.95
.199	5.76	3.052	2.22
.202	5.76	3.052	1.48
av. K ₁ = 2.5 × 10 ⁻⁹			
σ = 1.1 × 10 ⁻⁹			

Discussion

The individual reaction rates studied followed a good second-order plot as is seen in Fig. 5. The variation of k_{1f} with acidity cannot be due to the formation of the 1,10-phenanthroline ion since the prior equilibrium between this ion and 1,10-phenanthroline has already been taken into account in the rate expression. Nor can the variation of k_{1f} with acidity be attributed to the hydrolysis of

TABLE IV
EQUILIBRIUM CONSTANTS FOR THE TRIS-(1,10-PHENANTHROLINE)-NICKEL(II) COMPLEX

(H ⁺) × 10 ³	Phr × 10 ³	Nit × 10 ³	K ₃ × 10 ⁸
1.02	9.78	0.382	4.60
1.02	9.78	0.765	1.07
1.02	9.78	1.15	2.62
1.02	9.78	1.53	6.48
1.29	12.21	1.53	2.21
1.29	12.21	2.30	0.71
1.26	12.21	3.06	1.97
1.29	12.21	3.85	2.21
1.29	12.21	4.59	3.58

$$\text{av. } K_3 = 2.8 \times 10^{-8}$$

$$\sigma = 1.6 \times 10^{-8}$$

nickel(II), for according to previous studies¹³ there is no appreciable nickel hydrolysis below pH 8. Furthermore, reactions run at various ionic strengths and the same acidity show only a slight change in k_{1f} , insufficient to account for the variation noted in Fig. 6. A kinetic expression is needed that is still first order with respect to both 1,10-phenanthroline and nickel(II) and also is a function of acid strength. Since 1,10-phenanthroline is a bidentate ligand, it might be reasonable to assume that its reaction with nickel(II) proceeds in a stepwise fashion, one nitrogen-nickel bond forming in each step with the replacement of one coordinated water molecule. Usually this stepwise replacement of water molecules by a chelate would be expected to follow in rapid sequence with no way of distinguishing the individual steps. However, it is possible to postulate an acid catalysis, where the intermediate formed by the replacement of one water molecule goes to product faster by the elimination of a hydronium ion. This mechanism is pictured in Fig. 7 where N-N represents 1,10-

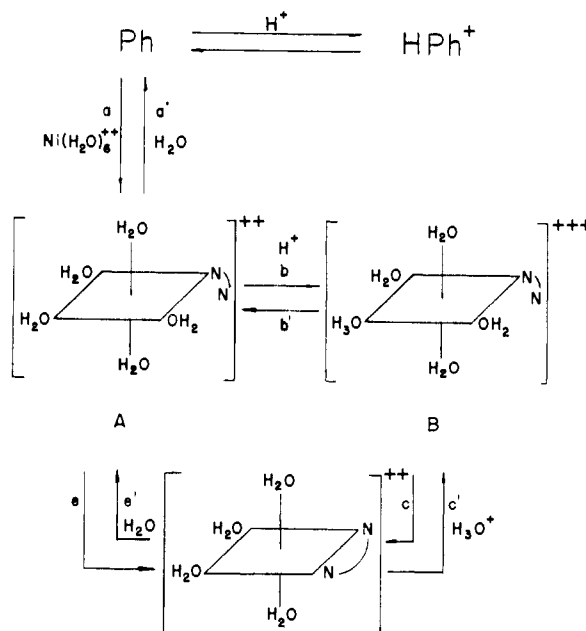


Fig. 7.—Mechanism for acid catalysis of reaction between 1,10-phenanthroline and aqueous nickel(II).

(13) K. H. Gayer and L. Wootner, THIS JOURNAL, 74, 1436 (1952).

phenanthroline. This mechanistic picture is not in itself intended to be realistic but is presented to illustrate the type of push-pull mechanism that may be possible with high acidity. Since A and B are both presumed to be unstable intermediates, it is possible to make the steady-state approximation, setting both of their rates of formation equal to zero. Neglecting the reverse reactions c' and e' , it can be shown that

$$\frac{d(\text{NiPh}^{++})}{dt} = \frac{abc(\text{H}^+) + ae(b' + c)}{bc(\text{H}^+) + (a' + e)(b' + c)} (\text{Ni}^{++})(\text{Ph})$$

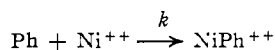
The observed rate constant, k_{1f} , is now dependent on the hydrogen ion concentration and can be written

$$k_{1f} = \frac{(\text{H}^+) + m}{n(\text{H}^+) + p} \quad (1)$$

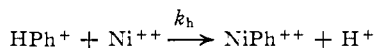
where

$$m = \frac{e(b' + c)}{bc}, n = \frac{1}{a} \text{ and } p = \frac{(a' + e)(b' + c)}{abc}$$

Before illustrating the applicability of such an expression, it is desirable to consider another possible mechanism for this reaction. Krumholz¹⁴ interpreted the rate data for iron(II) and 2,2'-bipyridine as a reaction between iron(II) and both 2,2'-bipyridine and the protonated 2,2'-bipyridinium ion. For the nickel(II)-1,10-phenanthroline system a parallel mechanism would be



and



However, this interpretation fails for both the iron(II)-2,2'-bipyridine and the nickel(II)-1,10-phenanthroline systems. The calculated rate constants would be equal to $k + (\text{H}^+)/K_a K_h$. However, k_{1f} does not continue to increase as the acidity increases, but instead levels off. It can be seen from Table I that contrary to previous suggestion¹⁴ this failure cannot be attributed to ionic strength effects. If affected at all, increasing ionic strength would be expected to increase the reaction rate between two ions of the same charge.

A mechanism can be postulated with the 1,10-phenanthrolium ion by again considering the stepwise formation of the two bonds from 1,10-phenanthroline to nickel(II). If the 1,10-phenanthrolium ion combines directly with nickel(II), the molecule must lose its proton before completing chelation. This mechanism is pictured in Fig. 8.

Since C and A are again presumed to be unstable intermediates of negligible concentration, it is possible to once more use the steady-state approximation. In this way it can be shown by neglecting e' that

$$\frac{d(\text{NiPh}^{++})}{dt} = \frac{efg(\text{H}^+) + eaK_a(f' + g)}{K_a f' g' (\text{H}^+) + K_a(e + a')(f' + g)} (\text{Ni}^{++})(\text{Ph})$$

The observed rate constant, k_{1f} , is then dependent on (H^+) and again can be written as in eq. 1, where

$$m = \frac{aK_a(f' + g)}{fg}, n = \frac{K_a f' g'}{efg} \text{ and } p = \frac{(e + a')(f' + g)K_a}{efg}$$

(14) P. Krumholz, *Anais. acad. brasil. cienc.*, **22**, 263 (1950).

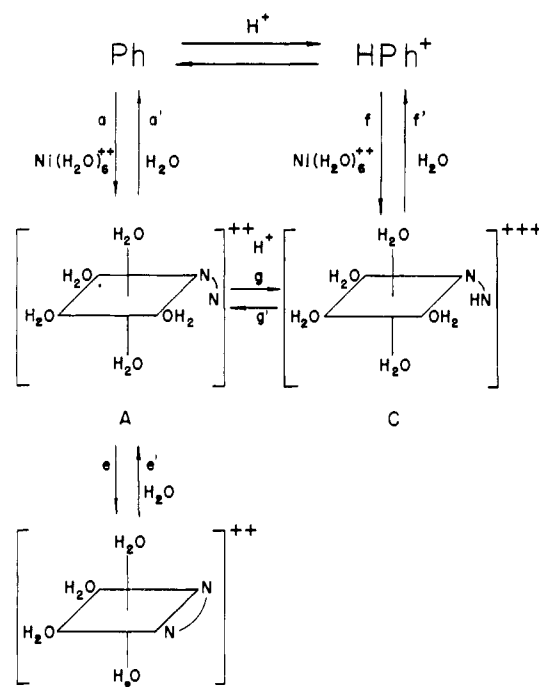


Fig. 8.—Mechanism for reaction between the 1,10-phenanthrolium ion and aqueous nickel(II).

It can be seen that the expression derived from either of these mechanisms corresponds qualitatively to the effect of acid strength on the rate constant. At low acidity $k_{1f} = m/p$, which by either mechanism is $ae/(a' + e)$, and is the hydrogen ion independent portion of the reaction. At intermediate acidity, k_{1f} changes with acidity while at very high acidity k_{1f} again becomes a constant equal to $1/n$. If at high acidity the major fraction of the reaction proceeds through the hydrogen ion dependent path, then $f(\text{HPh}^+)(\text{Ni}^{++}) \gg a(\text{Ph})(\text{Ni}^{++})$ or $c(\text{B}) \gg e(\text{A})$. It can then be seen that $f(\text{H}^+) \gg [aK_a(f' + g)]/g$ or that $c(\text{H}^+) \gg [e(b' + c)]/b$, and hence at high (H^+) , $k_{1f} = (\text{H}^+)/[n(\text{H}^+) + p]$. Therefore, if the assumption that the hydrogen ion dependent path is predominant at high acidities is correct, a plot of $1/k_{1f}$ against $1/(\text{H}^+)$ should give a straight line of intercept n and slope p . This plot is shown in Fig. 9. The following values were obtained for the constants in eq. 1: $n = 2.62 \times 10^{-5}$, $p = 2.58 \times 10^{-6}$, $m = 4.3 \times 10^{-3}$.

The dissociation rate constant, k_{1d} , also increases with increasing acidity. For the acid-catalyzed mechanism

$$\frac{-d(\text{NiPh}^{++})}{dt} = \frac{a'b'c'(\text{H}^+) + a'c'(b' + c)}{bc(\text{H}^+) + (a' + e)(b' + c)} (\text{NiPh}^{++})$$

The observed rate constant, k_{1d} , is therefore dependent on the hydrogen ion concentration and can be expressed as

$$k_{1d} = \frac{(\text{H}^+) + q}{r(\text{H}^+) + s} \quad (2)$$

where

$$q = \frac{e'(b' + c)}{b'c'}, r = \frac{bc}{a'b'c'}, \text{ and } s = \frac{(a' + e)(b' + c)}{a'b'c'}$$

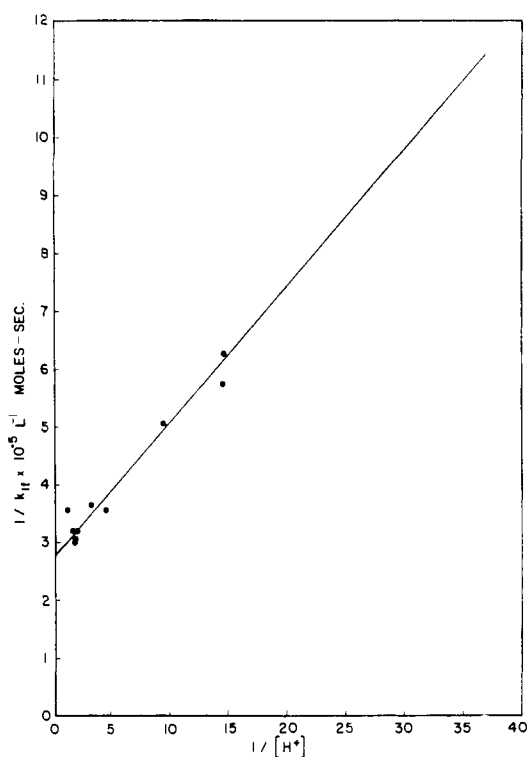


Fig. 9.—Reciprocal rate constant against reciprocal acidity showing the predominance of the hydrogen ion dependent path at high acidity.

The second mechanism leads to another expression like eq. 2 where

$$q = \frac{a'(f' + g)}{f'g'}, r = 1/e' \text{ and } s = \frac{(a' + c)(f' + g)}{e'f'g'}$$

A plot of the values of $1/k_{1d}$ at high acidity against $1/[\text{H}^+]$ again gives a straight line which aids in evaluating the coefficients of eq. 2. The following values were obtained from these constants: $q = 1.5 \times 10^{-2}$, $r = 8.4 \times 10^3$, $s = 3.6 \times 10^3$. From the theoretical values of these coefficients for either mechanism it can be shown that p/n should equal s/r . However, the numerical values of these coefficients give p/n about one-fourth the value of s/r . It was observed in the dissociation reactions that an immediate increase (within at least three minutes) in absorbance occurred when mono-(1,10-phenanthroline)-nickel(II) was placed in solutions of very high acidity. This increased absorbance cannot be attributed to the formation of 1,10-phenanthrolium ion because the measured dissociation reaction does not proceed that rapidly. Experiments indicated that this absorbance increase cannot be accounted for by merely salt effects and suggest another stable complex between mono-(1,10-phenanthroline)-nickel(II) and hydrogen ion has formed in solutions containing hydrogen ion concentrations greater than 0.5 M. Several workers^{12b,14} have suggested a stable protonated 1,10-phenanthroline-metal ion complex. For instance, the species FeHPh_3^{+4} has been suggested to account for the acid dependence of the ferrin dis-

sociation. It has been suggested¹⁵ that one of the reasons for the unusual stability of the 1,10-phenanthroline complexes is the formation of a double bond between the metal ion and the ligand. This would result in the distribution of a negative charge on the 1,10-phenanthroline molecule. It would then be conceivable that in highly acid solutions a proton is associated with the 1,10-phenanthroline portion of the complex but not directly with the nitrogens. In other words a new complex, $\text{Ni}(\text{H}_2\text{O})_4\text{PhH}^{+++}$, may form.

It is possible to simplify the expressions for the coefficients of eq. 1 and 2 by assuming the simple proton transfer reactions to be very rapid so that $b' \gg c$ or $g \gg f'$. The following values for the individual rate constants can then be estimated

$$\begin{aligned} &\text{Acid-catalyzed mechanism} \\ &a = 3.82 \times 10^4 \text{ l. mole}^{-1} \text{ sec.}^{-1} \\ &e' = 1.89 \times 10^{-6} \text{ sec.}^{-1} \\ &c' = 1.26 \times 10^{-3} \text{ l. mole}^{-1} \text{ sec.}^{-1} \\ &\text{1,10-Phenanthrolium mechanism} \\ &a = 3.96 \times 10^4 \text{ l. mole}^{-1} \text{ sec.}^{-1} \\ &e' = 1.19 \times 10^{-4} \text{ sec.}^{-1} \\ &f = 1.01 \times 10^4 \text{ l. mole}^{-1} \text{ sec.}^{-1} \end{aligned}$$

The values of e' in either mechanism would not permit sufficient dissociation to occur within three minutes to account for the increased absorbance noted for the mono complex at high acidity. However, the product $c'(\text{H}^+)$ from the acid-catalyzed mechanism might be large enough to permit appreciable formation of the species B within three minutes provided this species were stable at high acidity.

It is readily apparent that the effect of hydrogen ion concentration on the kinetics of mono-(1,10-phenanthroline)-nickel(II) is much more complicated than previously supposed. Until the nature of the transient species formed at high acidities has been established, it will be difficult to distinguish between the two suggested mechanisms.

Several other complex ions of the phenanthroline type appear to have an acid dependence similar to that in eq. 1 and 2. The reaction between 2,2'-bipyridine and iron(II)¹⁴ as well as the reaction between 1,10-phenanthroline and iron(II)¹⁶ seem to have a similar hydrogen ion dependence.

The values of the rate constants k_{2f} and k_{3f} are too close to that of k_{1f} to be readily determined under the same experimental conditions. However, it is possible to estimate that these rate constants must fall between 10^2 and 10^3 l. mole⁻¹ sec.⁻¹. The hydrogen ion effect on these constants is not yet known.

The values for the equilibrium constant K_1 indicate that hydrogen ion does not enter the equilibrium expression in the range of acidities in Table III. The product $K_1K_2K_3 = K$ gives a pK value of 24.3 for the tris-(1,10-phenanthroline)-nickel(II) ion. The pK value for this complex is much greater than that previously reported.⁷ Attention has frequently been called to the unusually high stability of tris-(1,10-phenanthroline)-iron(II) ($pK = 21.3$)

(15) (a) F. H. Burstall and R. S. Nyholm, *J. Chem. Soc.*, 3570 (1952); (b) R. S. Nyholm, *Revs. Pure Applied Chem. (Aust.)*, **4**, 32 (1954).

(16) D. W. Margerum, Ph.D. Thesis, Iowa State College, 1955.

but it is now seen that nickel(II) forms a stronger complex with 1,10-phenanthroline than does iron(II).

Acknowledgments.—The authors wish to thank

Mr. Donn W. Klingman for his technical assistance. We should also like to express our appreciation to Dr. G. S. Hammond for his interest and criticisms. AMES, IOWA

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Electronic and Vibrational States of the Pleiadienes¹

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RECEIVED MARCH 9, 1956

The electronic spectra of acepleiadiene and acepleiadylene have been studied in rigid glassy solution at 77°K., in dilute single mixed crystals with pyrene at 77°K. and at 4°K., and in single crystals at 77°K. The electronic transitions are assigned, using both the symmetry and the semi-empirical (Platt) classifications. Comparisons with theory indicate that the LCAO-MO, FEMO and cyclic polyene (Moffitt) perturbation theories are in good agreement with the observed results. Aromaticity in peri-condensed systems is discussed, and possible extensions of the Hückel rule are suggested. Vibrational analyses and assignments are given for the lowest absorption and fluorescence transitions in acepleiadylene and for the lowest absorption transition in acepleiadiene. A 1890 cm.⁻¹ crystal splitting which is observed for the lowest absorption transition in acepleiadylene is interpreted on the basis of the Frenkel-Davydov exciton theory. The lowest absorption transition of acepleiadiene shows evidence of crystal-induced mixing of molecular transitions. The crystal spectra give information regarding some of the gross features of the crystal structure.

Introduction

The lower electronic transitions of numerous cata-condensed hydrocarbons have been studied by D. S. McClure and co-workers, using single crystals and mixed crystals in polarized light at low temperatures.³ These studies have provided detailed information about the polarization properties and vibrational structure of the transitions, and have clarified earlier discrepancies concerning symmetry assignments of the electronic transitions. Furthermore, from a comparison of the spectra of the ordinary and mixed crystals, it has been possible to arrive at conclusions concerning the nature of the intermolecular forces and their effects on the spectra of molecular crystals.⁴

Recently, Boekelheide and co-workers have reported the synthesis of acepleiadiene,^{5a} pleiadiene and acepleiadylene.^{5b} In addition to their intrinsic interest, these peri-condensed hydrocarbons containing five- and seven-membered rings provide a proving ground for the theories of molecular structure which have been developed primarily for the cata-condensed hydrocarbons. In this paper, the results of the spectral studies of the lower electronic transitions of these molecules are reported. The results are compared with the predictions of previous theories, and additional predictions are made. Finally, the study of the crystal spectra is used to provide some information about the structure of the crystal.

(1) This research was supported by the Office of Ordnance Research, under contract DA-30-115-Ord 620 with the University of Rochester. Presented at the Symposium on Molecular Spectra and Structure at the Ohio State University, Columbus, Ohio, in June, 1956.

(2) Department of Theoretical Chemistry, Cambridge University, England. Post-doctoral fellow under a grant by the Shell Fellowship Committee to the Department of Chemistry of the University of Rochester, 1955-1956.

(3) See, for example, naphthalene in durene: D. S. McClure, *J. Chem. Phys.*, **22**, 1668 (1954).

(4) (a) D. S. McClure and O. Schnepf, *ibid.*, **23**, 1575 (1955); (b) J. W. Sidman, *Phys. Rev.*, **102**, 96 (1956).

(5) (a) V. Boekelheide, W. E. Langeland and C. T. Liu, *THIS JOURNAL*, **73**, 2432 (1951); (b) V. Boekelheide and G. K. Vick, *ibid.*, **78**, 653 (1956).

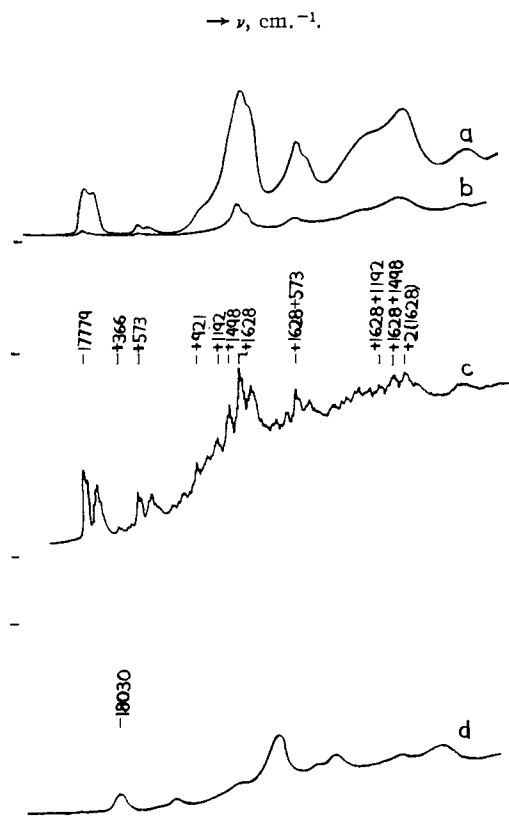


Fig. 1.—The ${}^1L_b \leftarrow {}^1A$ absorption transition of acepleiadylene: (a) single mixed crystal with pyrene, 77°K. for light polarized along the *a*-axis in the *ab* face; (b) same as (a), but for light polarized along the *b*-axis; (c) mixed crystal with pyrene, 4°K.; (d) rigid glass, 77°K.

Experimental

The spectrograph used in this research was a Bausch and Lomb quartz prism Littrow spectrograph. The experimental arrangement used to record the spectra was similar to one which has been previously described.⁶ The rigid

(6) J. W. Sidman and D. S. McClure, *ibid.*, **77**, 6461, 6471 (1953).