Reaction between Hydrogen Ion and 1,10-Phenanthroline. Two Novel Species, HP_2^+ and HP_3^+

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Abstract: The second-order silver|bis(1,10-phenanthroline)silver(I) nitrate, $Ag|AgP_2NO_3$, electrode system has been used to determine the over-all stoichiometric formation constants, β_n, for the 1:1, 1:2, and 1:3 hydrogen–1,10-phenanthroline species. The log β_n values are 5.11, 7.22, and 9.03. Other experimental evidence is shown for the existence of the novel bis(1,10-phenanthroline)hydrogen(I) and tris(1,10-phenanthroline)hydrogen(I) species, and some possible structures are proposed. To show the reliability of the method, the values of β_n for the well-documented CdP_n^{+2} and ZnP_n^{+2} complexes were determined and compared to the literature values. The log β_n values obtained are: Cd, 5.91, 10.70, 14.93; and Zn, 6.36, 12.14, 17.14.

The reaction between 1,10-phenanthroline (P) and hydrogen ion was extensively investigated by Lee, *et al.*[3] They concluded that although 1,10-phenanthroline had two basic nitrogen atoms, it behaved as a monoacidic base. The acid dissociation constant of the mono(1,10-phenanthroline)hydrogen(I) species, HP^+, has been determined potentiometrically[3–11] and spectrophotometrically[12–14] by many workers. These constants are listed in Table II with the values determined in this work.

Spectrophotometric evidence for the existence of a diprotonated species, H_2P^{+2}, in strongly acidic medium has been reported.[12,13,15] The existence of bis(1,10-phenanthroline)hydrogen(I) and tris(1,10-phenanthroline)hydrogen(I) species, HP_2^+ and HP_3^+, has been reported by Grimes[16] and Fullerton.[17]

The $Ag|AgP_2NO_3$ electrode was initially developed by Grimes[16] to measure the concentration of uncombined 1,10-phenanthroline (P). Its utility was further investigated by Fullerton.[17] The mode of operation of the electrode may be described in the following manner

$$AgP_2NO_3(s) \rightleftharpoons AgP_2^+ + NO_3^-$$
$$AgP_2^+ \rightleftharpoons Ag^+ + 2P$$

hence

$$[Ag^+] = \frac{K_{sp}}{\beta_2[P]^2[NO_3^-]}$$

K_{sp} for the insoluble salt and log β_2 for the AgP_2^+ complex were determined by Grimes[16] to be $10^{-8.8}$ and 11.6, respectively, and by Fullerton[17] to be $10^{-8.49}$ and 11.42, respectively. These values were not redetermined in the present work.

The complete electrode reaction is

$$AgP_2NO_3 + e^- \rightleftharpoons Ag^0 + 2P + NO_3^-$$

The Nernst equation for the potential of a silver electrode in a solution saturated in AgP_2NO_3 at 25° is

$$E = E^\circ_{Ag^+|Ag} + 0.059 \log \frac{K_{sp}}{\beta_2} - 0.059 \log [NO_3^-] - 0.118 \log [P] = E^\circ_{Ag|AgP_2NO_3} - 0.059 \log [NO_3^-] - 0.118 \log [P]$$

Hence, the electrode functions as an indicator electrode for 1,10-phenanthroline after correction is made for the contribution to the electrode potential by nitrate ion. $E^\circ_{Ag|AgP_2NO_3}$ was determined by Grimes[16] and Fullerton[17] to be −0.311 and −0.378 v *vs.* sce, respectively.

The experimental method used to obtain the over-all formation constants is essentially a competitive one, between the metal being studied and the competing ion (silver) for the ligand (1,10-phenanthroline). The system is somewhat simplified in that the 1,10-phenanthroline complex with silver forms insoluble AgP_2NO_3 in the presence of nitrate ion; hence, the concentration of uncombined 1,10-phenanthroline is determined directly from the experimental $Ag|AgP_2NO_3$ electrode potential. In most competitive techniques the concentration of uncombined ligand is calculated from the experimentally measured concentration of uncombined competing metal ion and the previously determined formation constants of the complex(es) formed between the competing metal and the ligand.[18]

Anderegg[19] used a technique similar to the one described here. Metal–1,10-phenanthroline systems were studied using a mercury electrode. Upon addition of 1,10-phenanthroline, the amount of ligand which reacted with Hg(I) formed a precipitate of $Hg_2P_2(NO_3)_2$.

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

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Experimental Section

The response plot of the Ag|AgP_2NO_3 electrode was determined by a titration procedure wherein the concentration of nitrate was held constant and the pH and ionic strength were maintained at 10 and 0.1, respectively, while the concentration of uncombined 1,10-phenanthroline was varied from about 1×10^{-4} to 1×10^{-2} *M*. Two solutions were prepared. Each contained 1.000×10^{-4} *M* KNO_3, 1.0×10^{-4} *M* KOH, and 0.0333 *M* K_2SO_4. Solution 1 also contained about 0.015 *M* 1,10-phenanthroline while solution 2 did not contain 1,10-phenanthroline. Solution 2, 40 ml, was titrated with solution 1. From the results of the titration, a standard Ag|AgP_2NO_3 electrode response plot of electrode potential *vs.* log [P] was prepared.

A second titration was performed. This titration was identical with the first except that the system also contained 5.105×10^{-3} *M* H_2SO_4 instead of the KOH. The concentrations of uncombined 1,10-phenanthroline in the hydrogen ion titration were determined graphically from the observed electrode potential values using the standard electrode response plot that was obtained from the former titration.

The procedure for the cadmium and zinc investigations was similar to that described above except that the medium was buffered at a pH of 4.6 with an acetate buffer. The total metal concentrations were 1.079×10^{-3} *M* $CdSO_4$ and 1.080×10^{-3} *M* $ZnSO_4$.

Five Ag|AgP_2NO_3 electrodes were used in every titration, two Beckman silver billet electrodes and three homemade silver wire electrodes. The electrodes were prepared by anodic oxidation for 2 min in a solution containing 1×10^{-3} *M* KNO_3 and 1×10^{-2} *M* 1,10-phenanthroline. A saturated calomel reference electrode was used. The reference and working compartments were separated by a salt bridge employing ultrafine porosity Pyrex disks. The salt bridge contained 0.0333 *M* K_2SO_4 for an ionic strength of 0.1. Potentiometric measurements were made with a Leeds and Northrup No. 7552 Type K-2 potentiometer coupled with a No. 2430-C Type E galvanometer having a sensitivity of 0.005 μa/mm. The temperature was controlled at 25 ± 0.05°. The titration solution was protected from the atmosphere by flushing with carbon dioxide free helium. A sulfate medium was employed in the salt bridge and in the system to control the ionic strength because nitrate and chloride ions would affect the eledtrode system and the perchlorate salts of many metal–1,10-phenanthroline complexes are insoluble.

The electrode system was slow in coming to steady potential values. Frequently the system was equilibrated for more than an hour before steady potentials were obtained. Equilibrium was assumed to have been reached when successive potential readings taken 5 min apart agreed to within 0.15 mv. The long equilibration time was undoubtedly due to the complex nature of the electrode reaction.

A standard response plot was prepared for each Ag|AgP_2NO_3 electrode. The values of uncombined 1,10-phenanthroline used in the computations were the average values from the five electrodes.

The conditional over-all formation constants were calculated using Bjerrum's $\bar{n}$ computational function

$$\sum_{n=0}^{N}(A_i - a_i - nB_i)\beta_n a_i^n = 0$$

and a three-parameter weighted least-squares computer program written by Stagg and Powell,[20] which is similar to the program suggested by Sullivan, *et al.*[21] The computations were performed on an IBM 7074 computer.

The stoichiometric over-all formation constants for the HP_n^+ species were obtained by correcting the conditional constants for the bisulfate ion. The ZnP_n^{+2} and CdP_n^{+2} stoichiometric constants were obtained by correcting the conditional constants for the metal acetate, metal sulfate, and HP_n^+ complexes.

The solubility of 1,10-phenanthroline in water and in aqueous acidic solution was determined. A series of solutions (0 to 0.0526 *M* in HCl) were shaken at 25° with an excess of solid 1,10-phenanthroline. A portion of the saturated supernatant was withdrawn, diluted, and made neutral. The concentration of 1,10-phenanthroline, and hence the solubility, was determined by ultraviolet spectrometry at 265 mμ.

Results and Discussion

The assumption inherent in the preparation of the standard electrode response plots is that under the experimental conditions used, neither hydrogen nor potassium ions are complexed by 1,10-phenanthroline. Hence, the pH was maintained at 10 to inhibit the formation of any HP_n^+ species. Log β_n values of 1.0 and 5.09[16] and 2.09 and 4.93[17] for the KP_1^+ and KP_2^+ species, respectively, have been reported. However, the present authors feel that these results are incorrect because Grimes[16] and Fullerton[17] assumed that the Ag|AgP_2NO_3 electrode had a Nernstian response and, hence, misinterpreted the non-Nernstian response as an indication of complex formation of potassium and other alkali metal ions by 1,10-phenanthroline. To support this hypothesis several studies were conducted. The solubility study described later in this work indicates that the formation of the KP_n^+ species is negligible even in solutions saturated in 1,10-phenanthroline. Further, there is no change in the ultraviolet spectrum of 1,10-phenanthroline even in 1 *M* KCl. In addition, a glass electrode responsive to univalent cations was used to measure the concentration of uncomplexed potassium in the following two solutions: (1) 1×10^{-4} *M* KOH and 5×10^{-4} *M* K_2SO_4, and (2) 1×10^{-4} *M* KOH, 5×10^{-4} *M* K_2SO_4, and 1×10^{-2} *M* 1,10-phenanthroline. Using the previously reported formation constants for the KP_n^+ species, one would expect to observe about a 50-mv difference in electrode potential between these two solutions *vs.* sce. No detectable potential difference was observed indicating that the reported formation constants are indeed excessive. Dale[22] reached the same conclusion in a similar study.

The resulting electrode response plots consisted of two regions, both of which were in themselves colinear, but the two regions had slightly different, non-Nernstian slopes. The inflection point consistently occurred near 2×10^{-3} *M* 1,10-phenanthroline. The slope of the low 1,10-phenanthroline region was always greater than the slope of the high 1,10-phenanthroline region. The average value of the slopes for these two regions were 105 and 96 mv compared to the theoretical Nernstian value of 118.3 mv. This type of two-slope, non-Nernstian behavior has been reported by Bishop and Dhaneshwar[23] in their investigation of the response of silver and silver halide electrodes to the concentrations of silver and halide ions. A typical electrode response plot for a specific Ag|AgP_2NO_3 electrode is shown in Figure 1.

Figure 2 shows typical titration plots of electrode potential *vs.* log [P_T] for the hydrogen–, cadmium–, and zinc–1,10-phenanthroline studies.

The results for the conditional over-all formation constants, β_n', with their estimated standard deviations, as they were obtained from the computer program, are given in Table I. Three experimental trials were conducted on the hydrogen–1,10-phenanthroline system, and two trials were conducted on each metal–1,10-phenanthroline, MP_n^{+2}, system. In order to obtain meaningful results, the experimental data for the MP_n^{+2} complexes had to be corrected for the HP_n^+

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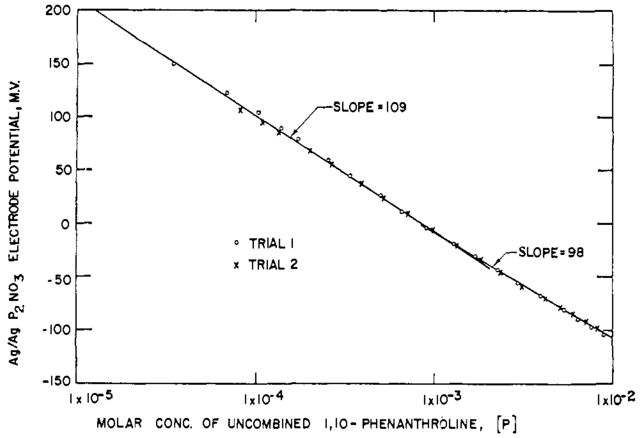

Figure 1. Standard Ag|AgP$_2$NO$_3$ electrode response plot.

species before the data were programmed in the computer.

Table I. Over-all Conditional Formation Constants[a]

Metal	Trial	Log β_1'	Log β_2'	Log β_3'
H[b]	1	4.74 ± 0.01	6.84 ± 0.03	8.83 ± 0.04
	2	4.76 ± 0.01	6.88 ± 0.02	8.63 ± 0.04
	3	4.76 ± 0.01	6.90 ± 0.01	8.57 ± 0.03
Cd[c]	1	5.55 ± 0.02	10.40 ± 0.02	14.53 ± 0.02
	2	5.60 ± 0.03	10.33 ± 0.04	14.65 ± 0.04
Zn[c]	1	6.03 ± 0.04	11.83 ± 0.03	16.76 ± 0.03
	2	6.11 ± 0.03	11.88 ± 0.03	16.95 ± 0.03

[a] μ = 0.1, 25 ± 0.05°. [b] Values not corrected for the bisulfate ion. [c] Values corrected for the HP$_n^+$ species but not for the metal sulfate or metal acetate complexes.

The results for the stoichiometric over-all formation constants, β_n, wherein the conditional constants for HP$_n^+$ have been adjusted in the usual manner[18] for the presence of bisulfate ion[24] and the conditional constants for MP$_n^{+2}$ have been adjusted for the presence of HP$_n^+$, metal acetate,[25] and metal sulfate[26] complexes, are compared in Table II with values reported by other workers.

The investigation was undertaken principally to study the novel HP$_n^+$ system. The MP$_n^{+2}$ systems were included to show the scope of the method and to check the reliability of the method by comparing the well-documented values of log β_n for the MP$_n^{+2}$ species with those obtained in this study.

Figure 3 compares the experimentally determined $\bar{n}$ values with the $\bar{n}$ formation function curve calculated in the computer program from the log β_n' values and the experimental values of [P].

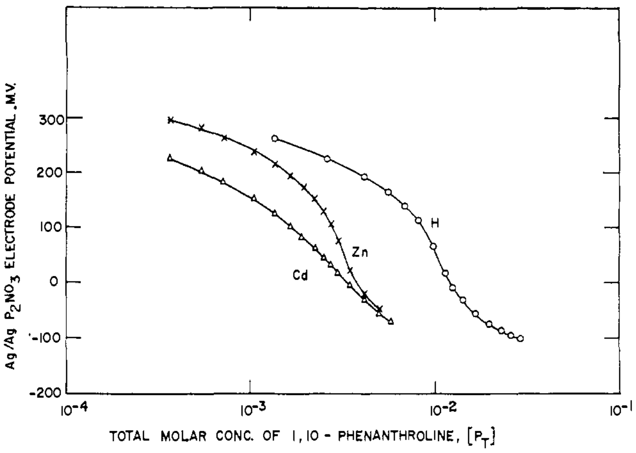

Figure 2. Titrations of hydrogen, cadmium, and zinc with 1,10-phenanthroline.

It should be noted that although the maximum experimental value of $\bar{n}$ obtained in the potentiometric study of the HP$_n^+$ species was about 1.9, a three-parameter computer program was employed for the computations. A two-parameter program was tried on the same experimental data, but the agreement between the experimental and calculated values for $\bar{n}$ was poor for values greater than about 1.3. The agreement became poorer as the value of $\bar{n}$ increased, indicating an unsatisfactory fit of the two-parameter program to the data. It will be shown in the discussion of the solubility study that the maximum attainable $\bar{n}$ in the HP$_n^+$ system, for solutions saturated in 1,10-phenanthroline, is 2.23.

Table II. Over-all Stoichiometric Formation Constants[a]

Metal	Trial	Log β_1	Log β_2	Log β_3	Ref[a]
H	1	5.11	7.25	8.93	
	2	5.11	7.23	8.99	
	3	5.10	7.19	9.18	
		5.05	8.40	10.30	16
		5.27	8.01	12.07	17
		4.96			3
		5.2			4
H		4.96			5
		4.92			6
		4.86			7
		4.857			8
		4.92			9
		5.07			10
		4.98			11
		5.02			12
		5.47			13
		4.95			14
Cd	1	5.88	10.74	14.87	
	2	5.93	10.66	14.98	
		5.93	10.52	14.30	*b*
		5.75	10.84	13.91	17
		5.17	10.0	14.26	11
		6.01[19]		15.19[c]	19[c]
Zn		6.32	12.12	17.03	
		6.39	12.16	17.24	
		6.83	12.05	16.92	*b*
		6.31	12.40	17.17	17
		6.30	11.95	17.05	11
		6.36	12.00	17.00	*d*
Zn		6.5	11.95	17.05	*e*
		6.43	12.15	17.0	*f*
		6.47	12.00	13.1	*g*

[a] Values stated without references are from this work. [b] J. M. Dale and C. V. Banks, *Inorg. Chem.*, **2**, 591 (1963). [c] B. E. Douglas, H. A. Laitinen, and J. C. Bailar, *J. Am. Chem. Soc.*, **72**, 2484 (1950). [d] C. V. Banks and R. I. Bystroff, *ibid.*, **81**, 6153 (1959). [e] H. Irving and D. H. Mellor, *J. Chem. Soc.*, 3457 (1955). [f] I. M. Kolthoff, D. L. Leussing, and T. S. Lee, *J. Am. Chem. Soc.*, **73**, 390 (1951). [g] J. H. McClure, Ph.D. Thesis, Iowa State University, 1951.

Figure 4 shows the degree of formation, α, of the metal and MP$_n^{+2}$ complexes as a function of log [P].

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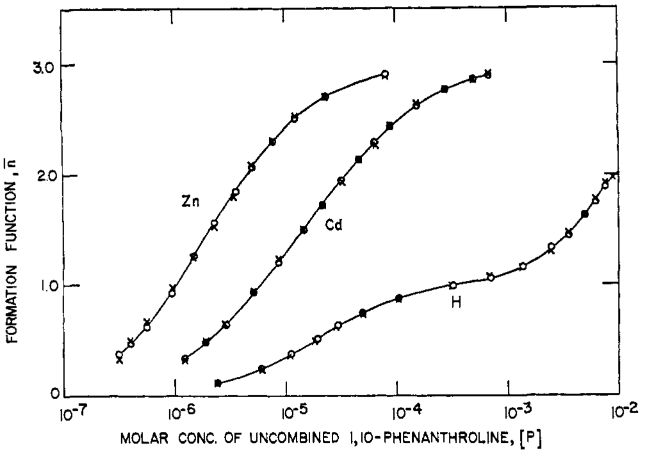

Figure 3. Formation functions of hydrogen–, cadmium–, and zinc–1,10-phenanthroline: O, calculated $\bar{n}$; X, experimental $\bar{n}$.

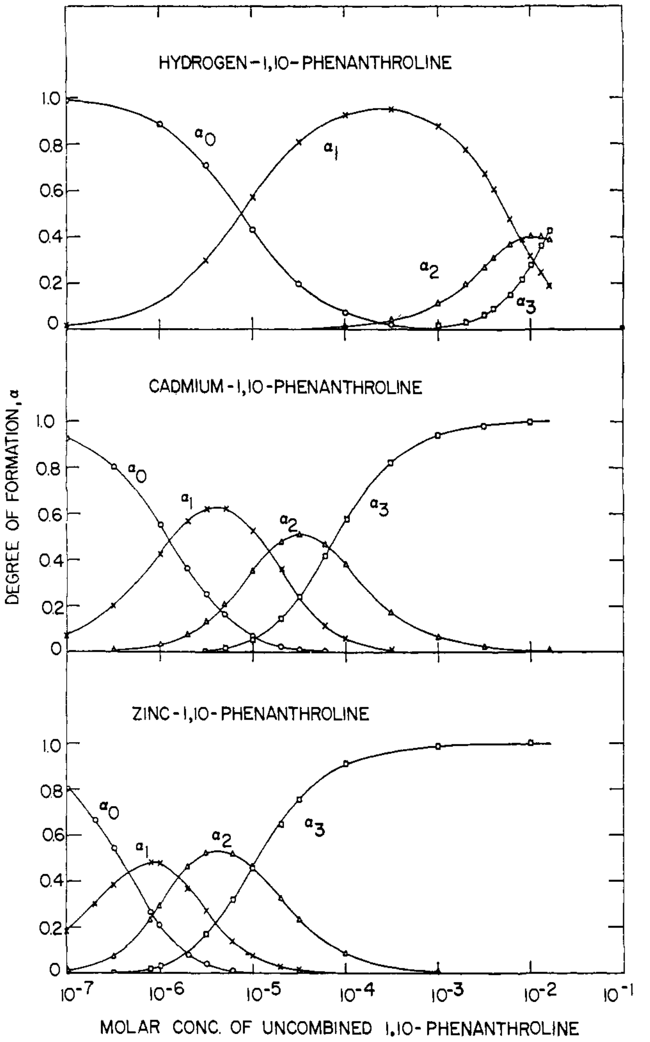

Figure 4. Degree of formation, α, of hydrogen–, cadmium–, and zinc–1,10-phenanthroline.

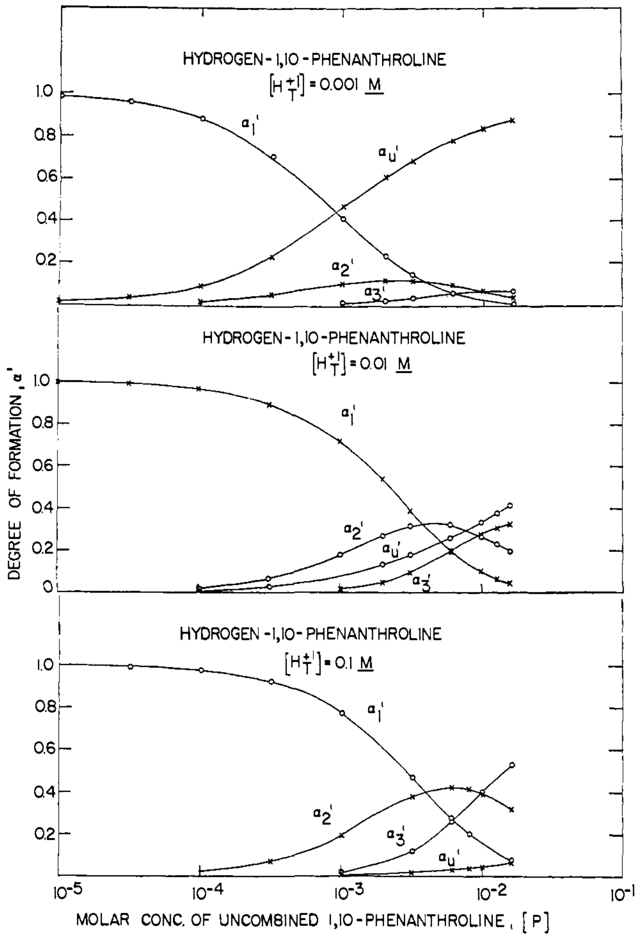

Figure 5. Degree of formation, α', of hydrogen–1,10-phenanthroline.

It should be noted that in the HP_n^+ system the HP^+ species predominates except for the highest values of [P] where the higher order species, HP_2^+ and HP_3^+, become more and more significant. The solubility of 1,10-phenanthroline in water is 0.0160 *M;* this limits the formation and degree of formation plots to a maximum value of [P] of 0.0160 *M*. The log β_n values for the MP_n^{+2} complexes are orders of magnitude greater than those for the HP_n^+ species, which markedly affects the α plots.

Another type of degree of formation, α', was calculated from the α values which may be defined as the fraction of the total ligand that is uncombined, α'_u.

$$\alpha'_u = \frac{[P]}{[P_T]} = \frac{[P]}{[P] + [H_T^+]\sum_{n=1}^{3} n\alpha_n}$$

or in the form of the HP_n^+ species,

$$\alpha'_n = \frac{n[HP_n^+]}{[P_T]} = \frac{n\alpha_n[H_T^+]}{[P] + [H_T^+]\sum_{n=1}^{3} n\alpha_n}$$

Hence, the α' values are a function of the total concentration of the central ion, specifically hydrogen ion. Figure 5 shows the resulting α' values as a function of [P] for $[H_T^+]$ values of 0.1, 0.01, and 0.001 *M*. Again, it should be noted that the higher order species become more significant the greater the [P] and $[H_T^+]$.

To demonstrate the affect of the higher order HP_n^+ species on the pH of the system, the $\bar{n}$ function was employed to calculate the pH in a hypothetical titration of 100 ml of 0.01 *M* 1,10-phenanthroline with 0.1 *M*

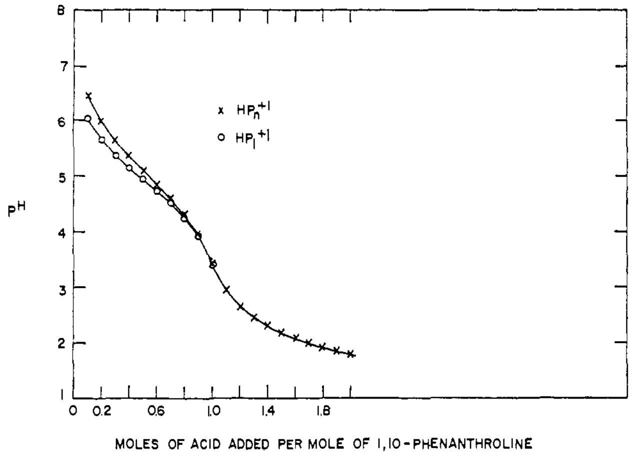

Figure 6. pH study.

acid. The *n* function was rearranged to a fourth-degree polynomial

$$\sum_{n=0}^{4} [\beta_n[n(H_T^+) - (P_T)] + \beta_{n-1}][P]^n = 0$$

where $\beta_0 = 1$ and β_{-1} and $\beta_4 = 0$. Using the resulting real, positive roots for [P], the [H$^+$] can be readily calculated from the α_0 function, [H$^+$] = α_0[H$_T^+$]. The resulting plot of pH *vs.* the ratio of moles of acid added per mole of 1,10-phenanthroline is compared in Figure 6 to the pH calculated in a similar manner when only the HP$^+$ species is considered. Only a slight difference between the two curves is observed. This occurs in the initial region where the concentration of uncombined 1,10-phenanthroline is highest. In either case the equivalence point of the titration would be identical.

Lee, *et al.*,[3] show a similar plot comparing the experimental and calculated pH during a titration of 0.01 *M* 1,10-phenanthroline with 0.2 *M* HCl. Their calculated pH values were obtained by considering only the HP$^+$ species. The agreement between the two curves is good except in the initial region where the concentration of uncombined 1,10-phenanthroline is highest. The experimental pH values are higher than the calculated pH values as would be the case if higher order HP$_n^+$ species were present but unaccounted for.

Krumholz[6] determined the K_a of HP$^+$ by a potentiometric titration of 1,10-phenanthroline with HCl. He noted an increase in K_a of about 30% in passing from the beginning to the end of the neutralization reaction. He noted that a similar trend in K_a was visible in the titration curve presented by Lee, *et al.*[3] This increase in K_a may also be qualitatively explained by considering the higher order species.

Solubility Study

Rossotti and Rossotti[18] have reviewed the utility of solubility studies in the investigation of complex equilibria. The solubility, S_A, of a sparingly soluble ligand, A, in the presence of a central metal ion, B, is

$$S_A = S_A{}^0 + \sum_{n=1}^{N} n[BA_n] \qquad (1)$$

which is of the form

$$A = a + \sum_{n=1}^{N} n[BA_n]$$

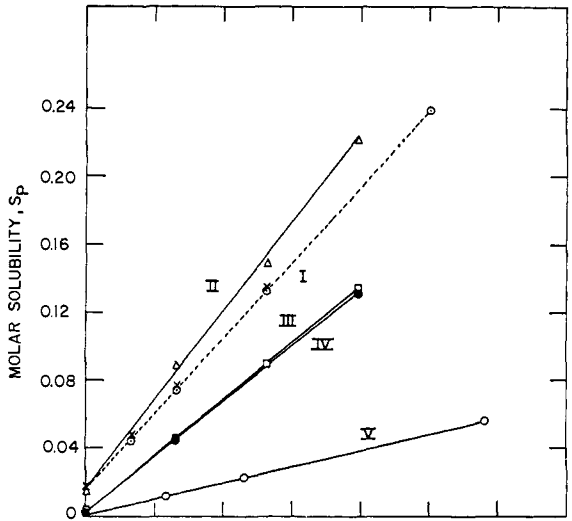

Figure 7. Solubilities of some 1,10-phenanthrolines: I (– – –), $S_P{}^0 + \bar{n}_s[H_T^+]$ (×, μ = 0.1; ⊙, μ not controlled); II, 5-methyl-; III, 5-chloro-; IV, 2,9-dimethyl-; V, 5-nitro-1,10-phenanthroline.

Upon considering the $\bar{n}$ function, eq 1 can be shown to be

$$S_A = S_A{}^0 + \bar{n}_s[B]$$

where $S_A{}^0$ is the solubility of the ligand or the concentration of uncombined ligand, a, in the absence of the central metal, and $\bar{n}_s$ ($\bar{n}$ saturated) is the value of the $\bar{n}$ function for the BA$_n$ system when the system is saturated in ligand.

$$\bar{n}_s = \frac{\sum_{n=1}^{N} n\beta_n(S_A{}^0)^n}{1 + \sum_{n=1}^{N} \beta_n(S_A{}^0)^n}$$

Hence, the solubility of a sparingly soluble ligand in the presence of a central metal ion should be a linear function of [B] with a slope of $\bar{n}_s$. The $\bar{n}_s$ value for the HP$_n^+$ system may be calculated from the β_n values and a value for the solubility of 1,10-phenanthroline in water. An average solubility from the value determined in this work and by other workers[16,27] is 0.0160 *M*. The calculated $\bar{n}_s$ value is 2.23.

The solubility of 1,10-phenanthroline as a funtion of the total concentration of HCl (0 to 0.526 *M*) has been determined. In trial 1 the ionic strength was controlled at 0.1 with KCl, and in trial 2 the ionic strength was not controlled. The experimental results are shown in Figure 7 with a plot of the theoretical solubility determined using the calculated $\bar{n}_s$ value.

A least-squares method was used to calculate the slope of the experimental points. The calculated values were 2.23 and 2.24 for trials 1 and 2, respectively. The solubility of 1,10-phenanthroline is about 15 times greater in 0.1 *M* HCl (0.239 *M*) than in water (0.0160 *M*). This is far greater than the "salting-in" phenomena reported by Long and McDevit.[28]

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The solubility of 1,10-phenanthroline in 0.1 *M* KCl was about 2% lower than in water. This further indicates that the formation of any KP_n^+ species, even in solutions saturated in the ligand, is negligible. The 2% decrease is about what one would expect upon considering the Setschenow equation[28] with KCl having a salting factor, k_s, of about 0.1.

The solubility of several substituted 1,10-phenanthrolines as a function of the total [HCl] has been determined in an analogous manner. The experimental results are shown in Figure 7, and the experimental slope values are listed in Table III with a consistent set of pK_a values for the HP^+ species.[5,7]

Table III. Slopes of the Experimental Solubility Plots[a]

Substituted 1,10-phenanthroline	Slope	pK_a[b]
2,9-Dimethyl	1.64	6.17
5-Methyl	2.64	5.23
Unsubstituted (μ = 0.1)	2.23	4.96
Unsubstituted	2.24	4.96
5-Chloro	1.69	4.26
5-Nitro	0.49	3.57

[a] Values obtained at 25 ± 0.05°. Except where noted, the ionic strength was not held constant. [b] pK_a values reported by Brandt and Gullstrom[5] and Schilt and Smith.[7]

A slope greater than one for the solubility curve is an indication that the ligand forms higher order species. The results indicate that the more basic the substituted ligand, the greater the average number of ligands interacting with the hydrogen ion. The 2,9-dimethyl-1,10-phenanthroline is the exception; undoubtedly, steric factors cause it to be out of line.

The $\bar{n}_s$ values are essentially the maximum attainable $\bar{n}$ value for the particular system. This value is realized only in solutions saturated in ligand. Hence, 2.23 is the maximum $\bar{n}$ value for the HP_n^+ system in aqueous medium. Greater S_A^0 values and correspondingly larger $\bar{n}_s$ values could be attainable in a mixed-solvent system. The S_A^0 for 1,10-phenanthroline in a 20% dioxane–water solvent is about ten times greater than in water (about 0.13 *M*). The corresponding $\bar{n}_s$ value is 2.9. The solubility of 1,10-phenanthroline as a function of the total [HCl] in 20% dioxane–water was determined. An experimental slope of 3.1 was obtained, which further substantiates the HP_3^+ species. The agreement between the experimental and calculated slopes is good considering that the β_n values determined in an aqueous system were used to calculate a $\bar{n}_s$ value in a mixed-solvent experimental system.

The infrared spectra of several aqueous solutions containing 2 *M* 1,10-phenanthroline and 1 to 6 *M* HCl were obtained. The ratio of $[P_T]/[HCl_T]$ ranged from 2 to 0.33. In the spectra of the solutions where $[P_T]/[HCl_T]$ exceeded one, there were several spectral changes which are a function of the $[P_T]/[HCl_T]$ ratio. These changes occurred in the region characteristic of ring vibrations of aromatic compounds.[29] New bands appear at 1570, 1515, and 1145 cm^{-1}, and the band at 1425 cm^{-1} increases markedly in intensity.

Proposed Structure for the HP_n^+ Species

No complete description of the bonding in HP^+ was found in the literature. However, 2,2′-bipyridine, B, which also contains the ferroin functional group, has been studied. Baxendale and George[30] have suggested that 2,2′-bipyridine does not add a second proton because hydrogen bonding stabilizes the HP^+ species. Westheimer and Benfey[31] concluded that the hydrogen bonding was insignificant. Nakamoto[32] found no positive evidence for hydrogen bonding in solid hydrochlorides of 2,2′-bipyridine. One must use caution in comparing 1,10-phenanthroline to 2,2′-bipyridine because the former is rigidly planar, while the latter has free rotation of the two "pyridine" rings which alters the alignment and separation of the two ring-nitrogen atoms.

Smith and Richter[27] report that 1,10-phenanthroline monohydrate is bonded together by two N···H–O hydrogen bonds. Fritz, *et al.*,[33] determined a value of 14.50 kcal/mole for the heat of dissociation of 1,10-phenanthroline monohydrate. They explained this result in terms of the energy necessary to rupture two N···H–O bonds having an average bonding energy of 7.25 kcal/mole.

Beattie and Webster[34] have shown infrared evidence for the existence of 1,10-phenanthroline monohydrate in an ethereal solution. They also prepared the solid 1,10-phenanthroline monohydrate monohydrochloride. They propose a structure consiting of a hydronium ion bonded to 1,10-phenanthroline by two N···H···O hydrogen bonds for the cation of the above compound.

Since the original proposal in 1954 by Wicke, *et al.*,[35] the existence of the trihydrated hydronium ion, H_3O^+-$(H_2O)_3$ or $H_9O_4^+$, has been used to explain a host of observed properties of aqueous strong acid solutions.[36–38] It is proposed that the species consists of a pyramidal hydronium ion which is hydrated by three water molecules in the primary hydration sphere and more water molecules, perhaps six, in the secondary hydration sphere.

Tuck[39] suggests that the structure of the H_3O^+-$(H_2O)_3$ species is such that a maximum of three large, moderately basic organic molecules can be bonded to it through hydrogen bonds. The species $(TBP)_3H_9O_4X$ has been characterized in the solvent extraction of tetrachloroaurate(III) ion, X, from HCl solution into a benzene solution of tri-*n*-butyl phosphate (TBP),[40] and in the extraction of chromium(VI) from acidic solution into TBP in cyclohexane.[41] Whitney and Diamond[42] have studied the extraction of $HClO_4$

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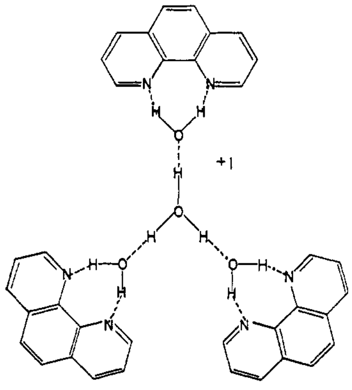

Figure 8. Proposed structure of HP_3^+, $3P\cdot H_9O_4^+$.

into solutions of TBP in inert solvents. They suggest that when the concentration of TBP in the inert solvent is low, the extracted species is $3TBP\cdot H_3O^+\cdots ClO_4^-$, and when the concentration of TBP is high, the extracted species is $3TBP\cdot H_9O_4^+\cdots ClO_4^-$.

It is proposed that in the highest concentration of 1,10-phenanthroline, 1,10-phenanthroline competes with and replaces the water molecules in the secondary hydration sphere about the hydronium ion. Hence, the HP_n^+ species would be represented by $HP_n^+ = nP\cdot H_9O_4^+$. The proposed structure for $3P\cdot H_9O_4^+$ is shown in Figure 8.

It is also possible that the replacement of the water molecules by 1,10-phenanthroline could take place in the primary hydration sphere instead of the secondary hydration sphere. In this case the HP_n^+ species would be represented by $HP_n^+ = nP\cdot H_3O^+(3 - n)H_2O$. A Fisher–Taylor–Hirschfelder model of the hydronium ion was constructed, and a molecule of 1,10-phenanthroline could be arranged about each of the hydrogen atoms of the hydronium ion.

However, this latter proposal seems to be less favorable than the former proposal. The type of bonding in the $nP\cdot H_9O_4^+$ proposal would seem to fit in better with the type of bonding proposed in the 1,10-phenanthroline monohydrate studies.[27,33,34]

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The Hydrogen Isotope Effect in the Thermal Decomposition of Cyclobutane[1]

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Abstract: The thermal decomposition of mixtures of cyclobutane and cyclobutane-d_8 has been studied at pressures from 100 to 0.005 mm at 449° and over the temperature range from 419 to 460° at pressures near 100 mm. The value of the isotope effect (k_H/k_D) for pressures in the neighborhood of 100 mm was observed to be 1.41 ± 0.02 at 449°. The temperature dependence of the isotope effect near 100 mm could be expressed as $k_H/k_D = 0.75 \exp(900/RT)$. It was found that k_H/k_D decreases with decreasing initial pressure and reaches a value of unity near 0.08 mm at 449°. At lower pressures an inverse isotope effect was observed, C_4H_8 reacting about 0.83 times as fast as C_4D_8 at 0.005 mm.

Previous investigations of kinetic isotope effects in gas-phase, unimolecular reactions of cyclic molecules have provided a number of interesting results. Weston[3] showed that in the isomerization of cyclopropane-t_1 the isotope effect decreased with decreasing pressure until it had almost disappeared at 0.4 mm. Blades[4] observed that the isotope effect in the isomerization of a mixture of cyclopropane-d_6 and cyclopropane decreases with a lowering of the initial pressure, k_H/k_D reaching a value of 1.35 at 0.178 mm. Rabinovitch, Setser, and Schneider[5] published a theoretical treatment of the isotope effect in the isomerization of cyclopropane-d_6. Their calculated values showed a decrease with decreasing pressure in agreement with the experimental results of Blades[4] and at pressures below those reached by Blades showed an inverse intermolecular isotope effect. Subsequently, in an experimental study of the cyclopropane system, Rabinovitch, Gilderson, and Blades[6] found values of k_H/k_D less than unity at pressures below 10^{-2} mm. A marked inverse isotope effect has been observed at low pressures also in the thermal isomerization of a mixture of CD_3NC and CH_3NC to the corresponding nitriles.[7]

Langrish and Pritchard[8] measured k_D/k_H for a mixture of cyclobutane-d_8 and cyclobutane at 449° from 36 to 0.7 mm. In this region where the first-order constants for light cyclobutane are pressure dependent,[9]

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