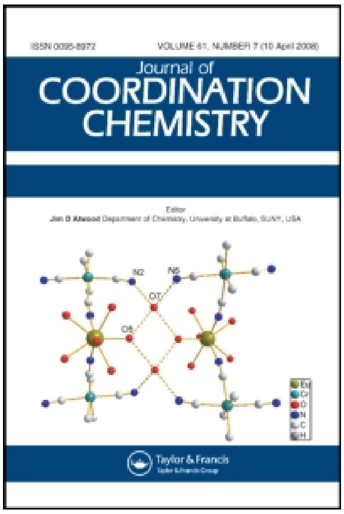

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STABILITY OF THE IRON(III) COMPLEX WITH 2-HYDROXYPYRIDINE

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The formation of the complex formed between 2-hydroxypyridine and ferric ion has been studied in weakly acidic aqueous solution. Prior to the acquisition of the data for this equilibrium study it was necessary to study the equilibrium for the protonation of 2-hydroxypyridine in aqueous solution. A pK value of 0.98 was obtained for the protonation reaction at unit ionic strength at 25°. The formation constant for the 1:1 complex formed by the displacement of hydrogen ion by ferric ion in 2-hydroxypyridine at 25° and unit ionic strength was found to be 5.6. This value is much higher than the corresponding constants for 3- and 4-hydroproxypyridines. This evidence strongly suggests that interaction between the ferric ion and both the oxygen and nitrogen centers in 2-hydroxypyridine enhances complex stability.

INTRODUCTION

Equilibrium studies on iron(III) complexes in aqueous solutions by other workers have been extended to 3- and 4-hydroxypyridine complexes in a previous paper.[5] The latter two ligands provided a situation in which the metal ion is offered a choice between oxygen and nitrogen donor atoms. The study reported below with 2-hydroxypyridine involves a potentially bidentate ligand because of the proximity of the oxygen and nitrogen atoms. It has been shown that only the unprotonated 2-hydroxypyridine reacts with iron(III) under the experimental conditions chosen. Equilibrium constants are reported for the reaction in which 2-hydroxypyridine is protonated and the reaction in which iron(III) displaces a proton in 2-hydroxypyridine.

EXPERIMENTAL RESULTS

Materials

Water and standardized solutions of perchloric acid, sodium perchlorate and iron(III) perchlorate were prepared and purified using previously reported procedures.[2,3] The 2-hydroxypyridine ligand was purchased from the Columbia Chemical Company and, after recrystallization from benzene, had a melting point range of 107–108°.

Reaction Conditions

Equilibrium studies were carried out in aqueous $NaC10_4$-$HC10_4$ media at ionic strength 1.00 and a temperature of 25.0 ± 0.1°.

Protonation Equilibrium Constant for Hydroxypyridine

A value for the equilibrium constant for protonation of the unprotonated 2-hydroxypyridine was required at unit ionic strength in order to interpret other equilibrium data. Relative concentrations of protonated and unprotonated hydroxypyridines were obtained from spectrophotometric measurements at 319 nm for equilibrated solutions. The different absorption peaks, for 2-hydroxypyridine in

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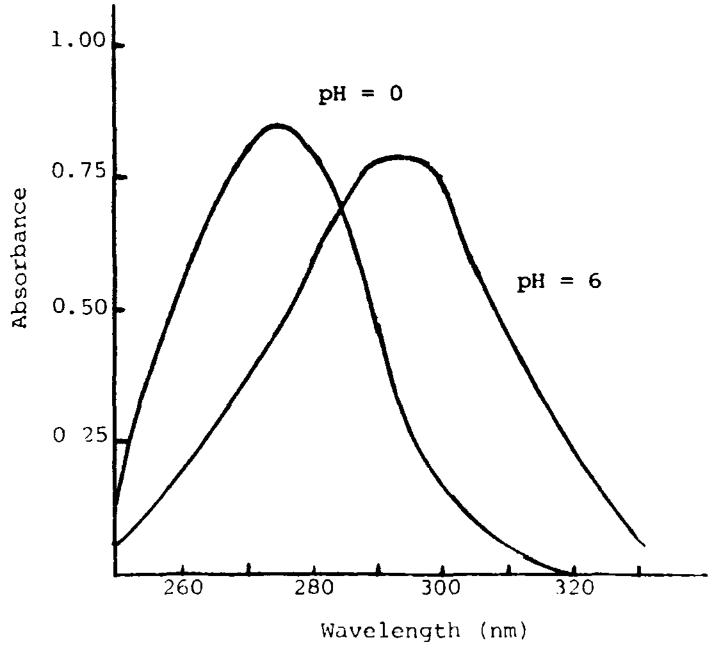

FIGURE 1 Spectrum of a 1.6 mM 2-hyroxypyridine solution as a function of acidity. T = 25°, ionic strength = 1.00. 1 cm cell.

essentially neutral (pH~6) and strongly acidic solutions (pH~0) are shown in Figure 1. The same isosbestic point was also observed for comparable solutions with intermediate pH values suggesting that only two hydroxy-pyridine species were present in solution. The value obtained of 9.46 for the protonation constant shown in Table I compares with a value of 5.7 reported by Albert and Phillips[4] for solutions with much lower ionic strengths.

Iron-Hydroxypyridine Complex

Reaction of equimolar amounts of acidic solutions of ferric ion and 2-hydroxypyridine gave a solution with an absorption maximum at 412 nm. A series of continuous variation experiments suggested that a 1:1 complex formed under these circumstances.

TABLE I

Estimation of K_1 [+] from absorbance at 319 nm in 1 cm cell. Ionic strength = 1.00 M; [2-hydroxypyridine] = 2.00×10^{-4} M.

Hydrogen Ion Conc. (mM)	Absorbance at 319 nm Experiment Solution	 Neutral Solution	%ROH (L)	K_1
50.0	0.163	0.240	67.9	9.46
75.0	0.139	0.235	59.1	9.23
99.9	0.123	0.238	51.7	9.35
199.8	0.085	0.249	34.1	9.67
299.8	0.064	0.249	25.7	9.64
499.8	0.042	0.238	17.6	9.39

Mean value for K_1 = 9.46 (standard deviation = 0.16)

[+] As defined by: $ROH + H^+ = ROH_2^+$.

TABLE II

Calculation of $K^{\dagger}_2$ from absorbance at 412 nm. Ionic strength = 1.00 M: molar extinction coefficient of $FeOR^{+2}$ = 800 M^{-1} cm^{-1} .

	Concentration (mM)			
$[H^+]$	[ROH]	[ROFe]	[Fe]	K_2
9.99	36.5	0.953	0.047	5.55
19.0	33.9	0.911	0.089	5.74
31.6	30.8	0.843	0.157	5.51
33.9	30.4	0.829	0.171	5.41
40.8	28.8	0.805	0.195	5.85
43.1	28.4	0.783	0.217	5.48
51.9	26.8	0.750	0.250	5.81
56.9	26.0	0.710	0.290	5.36
94.4	21.1	0.550	0.450	5.47
199	18.8	0.478	0.522	5.80

Mean value of K_2 = 5.60 (standard deviation = 0.17)

†As defined by: $ROH + Fe^{+3} \rightleftharpoons RoFe^{+2} + H^+$.

In order to estimate the molar absorbance of the iron complex, hydroxypyridine solutions were mixed with solutions containing iron(III) and sodium perchlorate, and perchloric acid. The final solutions were 10^{-3} M in total iron, 4×10^{-2} M in hydroxypyridine, and had ionic strength values equal to 1.00 molar. Absorbance measurements of these solutions varied with acidities. Extrapolation of these result to low hydrogen ion concentrations indicated that a 10^{-3} M complex solution would have an absorbance of very close to 0.800 in neutral solution.

Calculation of Stability Constant for the Complex

Reaction solutions contained known amounts of iron(III), hydroxypyridine, perchloric acid, and sodium perchlorate. After reaction the complex concentrations could be determined from absorbance measurements at 412 nm and hydrogen ion concentrations could be measured directly with a pH meter. The previous determination of the protonation constant (see Table I) enabled the ratios of protonated and unprotonated hydroxypyridine to be estimated. Within the range of conditions reported in Table II all data were consistent with a reaction in which a proton in neutral hydroxypyridine is replaced by ferric ion. The equilibrium constant for this reaction (K_2) was found to be equal to 5.6.

DISCUSSION

The obtained value for the protonation constant (K_1) for 2-hydroxypyridine of 5.7 is much smaller than the corresponding constants for the 3- and 4- isomers of hydroxypyridine which had previously been reported as 1.23×10^5 and 3.29×10^3 , respectively.[5] It has been observed that *keto/enol* tautomerism is important in aqueous solutions of 2-hydroxy-pyridine.[4,6] The relative resistance to protonation of 2-hydroxypyridine could be explained by the stability of the *keto* form of the compound.

The reaction in which iron(III) replaces a proton in unprotonated 2-hydroxypyridine produces a much larger equilibrium constant than the corresponding reactions of other quoted phenolic compounds. On the other hand, the complexes formed between the protonated forms of the 3- and 4-hydroxypyridine and iron(III)

TABLE III
Equilibrium constants for displacement of H^+ by Fe^{+3} at 25.0°.

Reactant	K_2[†]
2 - hydroxypyridine	5.6
3 - hydroxypyridineH$^+$	4.0×10^{-3}
4 - hydroxpyyridineH$^+$	4.3×10^{-3}
phenol	0.8×10^{-3}
p - chlorophenol	1.3×10^{-3}
p - nitrophenol	1.9×10^{-2}
m - nitrophenol	1.4×10^{-3}

[†] Reactions for the two protonated compounds correspond to equation 1, other reactions correspond to equation 2. Ionic strengths were equal to 1.0 M for the hydroxypyridines and 0.1 M for the other compounds. K_2 defined under Table II.

have equilibrium constants comparable to those obtained for many other phenols. These data are given in Table III.

The obvious explanation for the greater stability of the iron(III)-2-hydroxypyridine complex involves the possibility of a strong interaction between the iron(III) ion and both the nitrogen and oxygen atoms in 2-hydroxypyridine. Such a chelate-type interaction would not be possible for the 3- and 4- isomers of hydroxypyridine. These latter two compounds, therefore, react with ferric ion to produce complexes in a manner which is comparable to the other phenols in Table III.

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