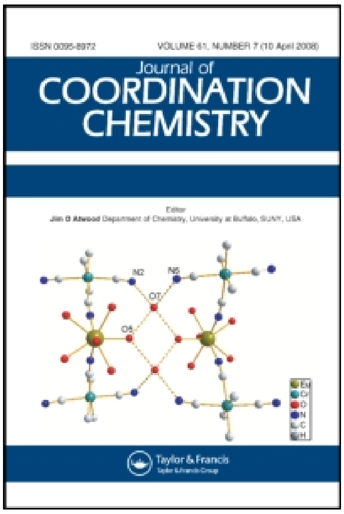

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John E. Teggins[a]; Ronald M. Milburn[a]
[a] Department of Chemistry, Auburn University at Montgomery, Montgomery, Alabama

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STABILITIES OF IRON(III) COMPLEXES WITH 3- AND 4-HYDROXYPYRIDINE

JOHN E. TEGGINS† and RONALD M. MILBURN[1]

Department of Chemistry, Auburn University at Montgomery, Montgomery, Alabama, 36117

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Equilibrium constants for the reaction of 3- or 4-hydroxypyridine with iron(III) were measured in aqueous solution. The experimental method involved the measurement of hydrogen ion concentration and optical absorbance for each of a series of reaction mixtures. The results are consistent with the interpretation that the separate interactions between iron(III) and the hydroxypyridines are of the hard acid-hard base type, with sigma bonding alone being important. Equilibrium constants are reported for both the reactions in which iron(III) displaces a proton in protonated hydroxypyridine and for the direct combination of iron(III) and the hydroxypyridine.

INTRODUCTION

Previous equilibrium studies on iron(III) complexes in aqueous solution have been extended to an examination of the stabilities of the complexes which iron(III) forms with 3- and 4-hydroxypyridines. These ligands offer a simple case in which the metal is offered a choice between oxygen and nitrogen donor atoms. The 3-isomer is also of interest because of its close structural relationship to vitamin B-6.

EXPERIMENTAL AND RESULTS

Materials

Water and standardized solutions of perchloric acid, sodium perchlorate and iron(III) perchlorate were prepared and purified by established procedures.[2] The hydroxypyridines, obtained from the Columbia Chemical Company, were purified by recrystallization; 3-hydroxypyridine from ethanol/diethyl ether (m.p. 127–8°C), 4-hydroxypyridine from dioxane/ethanol (m.p. 146–8°).

Reaction Conditions

Equilibrium studies were carried out in aqueous $NaClO_4$–$HClO_4$ media at ionic strength 1.00 M and a temperature of 25.0(±0.1)°C.

Protonation Equilibrium Constants for Hydroxypyridines

Values of the protonation equilibrium constant for reaction 1, as defined by $K_1 = [LH^+]/[L][H^+]$, where $L = NC_5H_4OH$ and brackets refer to concentrations, were required at unit ionic strength to interpret the other equilibrium data.

$$L + H^+ \rightleftarrows LH^+ \tag{1}$$

For each determination an exactly known quantity of the hydroxypyridine (~1 millimole) was dissolved in distilled water (nitrogen swept to remove oxygen) and a known amount of perchloric acid (~0.5 millimoles) and sufficient sodium perchlorate were then added to give an ionic strength of unity at a final volume of 100 ml. The pH value for each solution was determined at 25.0°C using a Radiometer PHM 4c meter (glass and calomel electrodes) which had been calibrated with 0.05 m potassium hydrogen phthalate solution of pH 4.01. Values of the equilibrium hydrogen ion concentration, $[H^+]$, were obtained from $pH_{meas} = p[H^+] - \log f$, with the activity coefficient term calculated from the Davies equation as before.[2b] Differences between added and measured $[H^+]$ could be attributed to protonation of the hydroxypyridine. For each isomer three closely agreeing values of K_1 were obtained for unit ionic strength. Average values are: 3-hydroxypyridine, $K_1 = 1.23(\pm0.01) \times 10^5$; 4-hydroxypyridine, $K_1 = 3.29(\pm0.04) \times 10.^3$ These values compare with the respective values of $7.2(\pm0.2) \times 10^4$ and $1.86(\pm0.10) \times 10^3$ reported for

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†To whom correspondence should be addressed.

25° and very low ionic strength by Albert and Phillips.[3]

Iron(III) – Hydroxypyridine Complexes

Reaction solutions were prepared by mixing equal volumes of two solutions, one containing the hydroxypyridine and the other containing iron(III) perchlorate, sodium perchlorate and perchloric acid. The final solutions were $\sim 10^{-3}$ **M** in iron(III), $\sim 4 \times 10^{-2}$ **M** in hydroxypyridine, and had pH values in the required range and an ionic strength of 1.00 **M**. The reaction mixtures were equilibrated in a quartz cell in a thermostatted Beckman DU spectrophotometer for one hour prior to optical measurements, which were taken at the absorption maxima for the two iron(III) complexes (3-isomer at 435 nm, 4-isomer at 390 nm). Absorbance values remained unchanged when reaction mixtures were allowed to stand for one day.

The pH values of these solutions were measured at 25° using the Radiometer pH meter. The meter was calibrated with aqueous perchloric acid solutions of known concentration and containing sufficient sodium perchlorate to give an ionic strength of unity, so that the $\mathrm{pH_{meas}}$ value could be here identified with $-\log[\mathrm{H^+}]$.

The spectral measurements on these solutions containing iron(III) and hydroxypyridine, which were in the $[\mathrm{H^+}]$ range $(0.5–5.0) \times 10^{-2}$ **M**, together with independent observations on reactions 1(above) and 2 (equilibrium constant K_2)[2a] indicate that equilibrium reactions 1, 2 and 3 need alone be considered.

$$\mathrm{Fe^{3+} + H_2O \rightleftarrows FeOH^{2+} + H^+} \qquad (2)$$

$$\mathrm{Fe^{3+} + LH^+ \rightleftarrows FeL^{3+} + H^+} \qquad (3)$$

The measurements further allow evaluation of equilibrium constants for reaction 3 (K_3) using an extension of the treatment adopted earlier[4] in determining the stabilities of iron(III)-phenolate complexes.

Thus, for reactions 2 and 3 the total iron concentration is given by

$$[\mathrm{Fe}]_\mathrm{T} = [\mathrm{Fe^{3+}}] + [\mathrm{FeOH^{2+}}] + [\mathrm{FeL^{3+}}] \qquad (4)$$

For the wavelengths employed the absorbances are attributable largely (~90% or more) to the iron(III)-hydroxypyridine complexes; nevertheless, contributions to absorbances from $\mathrm{FeOH^{2+}}$ and $\mathrm{LH^+}$, but not[5] from $\mathrm{Fe^{3+}}$, must be considered. The measured absorbance for a 1 cm path is then given by

$$A = \epsilon_1[\mathrm{LH^+}] + \epsilon_\mathrm{h}[\mathrm{FeOH^{2+}}] + \epsilon_\mathrm{x}[\mathrm{FeL^{3+}}] \qquad (5)$$

Since $[\mathrm{L}]_\mathrm{T}$ (total hydroxypyridine concentration) $\gg [\mathrm{Fe}]_\mathrm{T}$, and $[\mathrm{H^+}] \gg 1/K_1$, $[\mathrm{LH^+}]$ may be taken as equal to $[\mathrm{L}]_\mathrm{T}$. One may then calculate a corrected absorbance, A_corr, defined by:

$$\begin{aligned} A_\mathrm{corr} &= A - \epsilon_1[\mathrm{L}]_\mathrm{T} \\ &= \epsilon_\mathrm{h}[\mathrm{FeOH^{2+}}] + \epsilon_\mathrm{x}[\mathrm{FeL^{3+}}] \end{aligned} \qquad (6)$$

Equations 4 and 6, together with the equilibrium constant expressions corresponding to equations 2 and 3, then readily lead to the relation.

$$1/A_\mathrm{corr} = \{K_2 + K_3[\mathrm{L}]_\mathrm{T} + [\mathrm{H^+}]\}/[\mathrm{Fe}]_\mathrm{T}\{\epsilon_\mathrm{h}K_2 + \epsilon_\mathrm{x}K_3[\mathrm{L}]_\mathrm{t}\} \qquad (7)$$

which predicts a linear relation between $1/A_\mathrm{corr}$ and $[\mathrm{H^+}]$. Good linearity is observed for each ligand, consistent with the view that species of type $\mathrm{FeL^{3+}}$ are the only hydroxypyridine complexes of importance for the conditions examined.

From equation 7 one obtains

$$K_3 = \{(\text{intercept/slope}) - K_2\}/[\mathrm{L}]_\mathrm{T} \qquad (8)$$

which is the same as the expression obtained when $\mathrm{FeOH^{2+}}$ does not contribute to the absorbance.[4] Values of K_3 were then obtained from the intercepts and slopes of the least square straight lines. For our experimental conditions K_2 is [2a]1.60×10^{-3}. The plots of $1/A_\mathrm{corr}$ versus $[\mathrm{H^+}]$ are shown in Figure 1; data employed in the calculation of the stability constants is in Table I. Included are values for the protonation constants (K_1) and for the equilibrium constants for reaction 9 (K_9).

$$\mathrm{Fe^{3+} + L \rightleftarrows FeL^{3+}} \qquad (9)$$

DISCUSSION

For the 3- and 4-hydroxypyridines the equilibrium constants for reaction 3 are almost identical (K_3 in Table I), and these values are very similar to the constants corresponding to $\mathrm{Fe^{+3}}$ displacement of a proton from simply substituted phenolates (Table II). A relation of this type between complex stability and proton basicity may be summarized by a unit slope free energy plot, as was noted earlier[4] for the $\mathrm{Fe^{3+}}$ and $\mathrm{H^+}$ associations with phenols. For the hydroxypyridines the points corresponding to a plot of ΔG between reactions 9 and 1 fall close to and parallel to the previously observed[4] unit slope line. This result is consistent with the interpretation that the interaction between $\mathrm{Fe^{3+}}$ and the hydroxypyridines are of the hard acid-hard base type, with σ-bonding being alone important. The situation

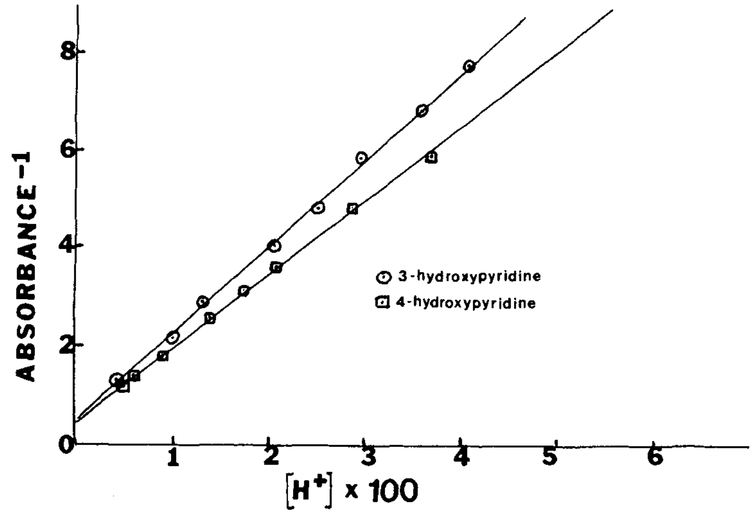
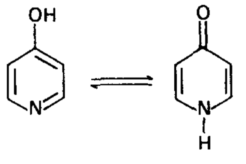


FIGURE 1 Plot of absorbance^{-1} against hydrogen ion concentration for 3- and 4-hydroxypyridine and iron(III). Temp = 25°; Ionic strength = 1.00; total hydroxypyridine concentration = 4 x 10^{-2}M; total iron(III) concentration = 1 x 10^{-3}M.

TABLE I*

	3-Hydroxypyridine	4-Hydroxypyridine
Slope	$173.4(\pm2.1)M^{-1}$	$149.3(\pm0.8)M^{-1}$
Intercept	$0.552(\pm0.054)$	$0.494(\pm0.015)$
K_2	1.60×10^{-3} M	1.60×10^{-3} M
$[L]_T$	4.0×10^{-2} M	4.0×10^{-2} M
K_3	3.96×10^{-2}	4.27×10^{-2}
K_1	$1.23 \times 10^{5} M^{-1}$	$3.29 \times 10^{3} M^{-1}$
$K_9 (=K_1 K_3)$	$4.9 \times 10^{3} M^{-1}$	$1.4 \times 10^{2} M^{-1}$

*uncertainties are standard deviations



(10)

TABLE II
Equilibrium Constants for Displacement of H^+ by Fe^{3+} at 25.0°C.

Reactant	K_3 [a]
3-hydroxypyridine H^+	4.0×10^{-2}
4-hydroxypyridine H^+	4.3×10^{-2}
phenol	0.8×10^{-2}
p-chlorophenol	1.3×10^{-2}
p-nitrophenol	1.9×10^{-2}
m-nitrophenol	1.4×10^{-2}

[a] Ionic strength: 1.0M for 3- and 4-hydroxypyridines; 0.10M for other entries (see ref. 4).

constrasts with that observed for complexes of $(NH_3)_5Ru^{2+}$ with pyridine, pyrazine and related ligands, where, because of the importance of metal-ligand π-bonding, an inverse relation exists between complex stability and ligand basicity.[6]

For K_9 as well as for K_1 there is an approximately 35-fold difference in values in favor of complexed or protonated ligand for the 3-isomer compared to the 4-isomer. In the related comparison between 3- and 4-nitrophenolate associations, the greater stability for the 3-isomer complex has been shown to be entropy controlled, with the differences attributable to solvation effects.

While simple solvation effects could be of importance in the present case, a further consideration is that 4-hydroxypyridine (γ-pyridone) has been shown[7] to exist predominantly in the amide form in aqueous solution. Although an amide(zwitter ion) form is possible for the 3-isomer,[8] it is very much less favored. In consequence, the fact that the 3-isomer is more readily protonated is understandable. Similar considerations provide an explanation for the greater stability of the iron(III) complex of 3-hydroxypyridine compared to 4-hydroxypyridine.

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