high-spin (low-field axial ligand) [14]-diene Fe(II) complexes.[40] It was also established for Fe(II) porphyrins by Hoard and coworkers;[2] in addition, James and Stynes have suggested a similar process is important in axial substitution of the ligands on Fe(II) in some complexes.[41] What differs in our case from that of these other studies is the fate of the high-spin species. For Fe(TIM)$(H_2O)_2{}^{2+}$ a proton attacks the five-coordinate Fe(II) complex at the incipient lone pair on an imine nitrogen, causing the Fe(II) to be completely lost and subsequently leading to hydrolysis of the ligand.

We postulate that this process is less efficient in the other metal complexes of TIM because of their smaller size and smaller change in size upon a spin change (Co(II) and Fe(III))[42] or because of their failure to undergo a spin change that results in a dramatic increase in tetragonal plane size (Ni(II) and Cu(II)). Our spin-change-dependent mechanism is consistent with the observations that the rate of reaction is very small when π-acceptor ligands such as CH_3CN or CO are in axial positions: These ligands stabilize the d_{xz} and d_{yz} orbitals such that conversion to high spin is energetically more difficult and hence the steric drive to remove the Fe(II) from the ring is correspondingly less.

Acknowledgment. This work was funded in part by a grant from E. I. du Pont de Nemours and Co. We thank Professor E. C. Lingafelter for providing structural data and Professor J. F. Endicott and M. Perkovic for performing the MM2 calculations.

Registry No. Fe(TIM)$(CH_3CN)(H_2O)^{2+}$, 93184-90-8; Fe(TIM)$(H_2O)_2{}^{2+}$, 90461-84-0; TIM, 59969-61-8.

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[40] It has also been shown that spin equilibrium exists in a saturated 14-member macrocyclic compound of Fe(II): Dabrowiak, J. C.; Merrell, P. H.; Busch, D. H. *Inorg. Chem.* **1972**, *11*, 1979–1988. See also the summary of spin crossover in Fe(II) complexes: Gütlich, P. *Struct. Bonding (Berlin)* **1981**, *44*, 83–195.

[41] Stynes, D. V.; James, B. R. *J. Am. Chem. Soc.* **1974**, *96*, 2733–2738.

[42] Thuery, P.; Zarembowitch, J.; Michalowicz, A.; Kahn, O. *Inorg. Chem.* **1987**, *26*, 851–855.

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Equilibrium and Kinetic Studies of the Complexing of Iron(III) by 1,2-Dihydroxybenzene Derivatives

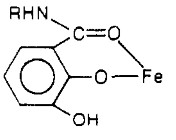
Jinhuang Xu and R. B. Jordan*

Received June 5, 1985

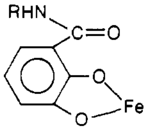
The equilibrium constants and kinetics for complexing of aqueous iron(III) by 2,3-dihdyroxybenzoic acid (DHB) and 1,2-dihydroxy-3,5-benzenedisulfonate (Tiron) have been studied in 1 M $NaClO_4$–$HClO_4$ between 0.01 and 0.7 M H^+ under conditions of [iron(III)] $\gg$ [ligand]. The formation constants for the reaction $Fe^{3+} + H_2L \rightleftarrows Fe{=}L + 2H^+$ are 3.15 ± 0.23 and 6.95 ± 0.60 M for Tiron and DHB, respectively. Formation constant comparisons indicate that DHB complexes in a mode analogous to that for salicylate. The reaction rate shows the $[H^+]$ dependence typical for iron(III) complexation, but there is an unusual contribution from a kinetic term second order in [iron(III)]. The kinetic results are discussed and compared to previous work on related systems.

Introduction

In plants and unicellular organisms, iron is made accessible at near neutral pH by efficient complexing of iron(III) by siderophores. The iron subsequently is released by reduction to the much less strongly complexed iron(II). For catecholate siderophores such as enterobactin, the mechanism and mode of complex formation and reduction remain controversial. The various proposals have been discussed recently by Hider et al.[1] There is a question as to whether the binding is through the salicylate mode (I) or the catecholate mode (II) and what is the site and effect of protonation of the ligand in the iron(III) complex, as well as what the ultimate iron reduction mechanism is.

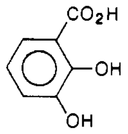


I

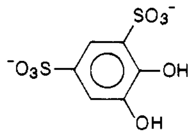


II

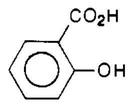
The purpose of this work is to provide some guidelines for answering the above questions by studying simple ligand model systems. The kinetics and equilibrium constants for complexing of aqueous iron(III) by 2,3-dihydroxybenzoic acid (DHB, III) and 1,2-dihydroxy-3,5-benzenesulfonate (Tiron, IV) are compared to the previously studied salicylic acid system (V).[2,3] These ligands provide a series in which the binding mode of iron(III) may be only salicylate (V), only catecholate (IV), or either (III). The presence of $-CO_2H$, $-CO_2{}^-$, and $SO_3{}^-$ substituents may provide useful comparisons for the kinetic results.



III



IV



V

Some features of the equilibrium constants for the iron(III)–Tiron system remain uncertain despite several previous studies.[4-6] The condition of [iron(III)] $\gg$ [ligand] has been used here to simplify the analysis. The same conditions are used in a reexamination of the kinetics, and the acid range has been extended from that of earlier work[7] to examine ligand protonation effects.

Although DHB is a known therapeutic siderophore,[8] the iron(III)–DHB system has not been satisfactorily characterized.[9,10] The potentiometric titration results of Avdeef et al.[9] give an unusually wide variation in the formation constants, which seem

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[1] Hider, R. C.; Bickar, D.; Morrison, I. E. G.; Silver, J. *J. Am. Chem. Soc.* **1984**, *106*, 6983.

[2] Dash, A. C.; Harris, G. M. *Inorg. Chem.* **1982**, *21*, 2336.

[3] Jordan, R. B. *Inorg. Chem.* **1983**, *22*, 4160.

[4] Schwarzenbach, G.; Willi, A. *Helv. Chim. Acta* **1951**, *34*, 528.

[5] McBryde, W. A. E. *Can. J. Chem.* **1964**, *42*, 1917.

[6] Morin, M.; Scharff, J. P. *Anal. Chim. Acta* **1972**, *60*, 101.

[7] (a) Mentasti, E.; Pelizzetti, E.; Saini, M. *Inorg. Nucl. Chem.* **1976**, *38*, 785. (b) Mentasti, E.; Secco, F.; Venturini, M. *Inorg. Chem.* **1982**, *21*, 602.

[8] Tyson, C. A.; Levalley, S. E.; Chan, R.; Hobbs, P. D.; Dawson, M. I. *J. Pharmacol. Exp. Ther.* **1984**, *228*, 676.

[9] Avdeef, A.; Sofen, S. R.; Bregante, T. L.; Raymond, K. N. *J. Am. Chem. Soc.* **1978**, *100*, 5362.

[10] Hider, R. C.; Mohd-Nor, A. R.; Silver, J.; Morrison, I. G.; Rees, L. V. C. *J. Chem. Soc., Dalton Trans.* **1981**, 609.

to depend on the direction of the titration. Our experience is that redox processes could be a complicating factor in acidic solution. The color and spectrophotometric observations of Hider et al.[10] are consistent with our experience, but the interpretation is different. We find the yellow product reported by Hider et al.[10] for pH <2 is due to DHB oxidation subsequent to formation of a blue complex. We find that the blue product (λ_{max} 575 nm), which they report for pH 2–4 as an iron(II) complex, is an iron(III) species and is also formed at pH <2. The interpretation of Hider et al. seems to have been confused by the redox reactions. These reactions are of considerable interest as models for the enterobactin system and will be the subject of a separate publication.

Experimental Section

Materials. All solutions for kinetic and equilibrium studies were prepared in deionized water distilled from alkaline permanganate in an all-glass apparatus. The iron(III) perchlorate solutions were prepared by dissolving analytical grade iron wire (Fisher Scientific Co.) in excess perchloric acid followed by oxidation of iron(II) with hydrogen peroxide. The excess peroxide was decomposed by heating. The iron(III) stock solutions were standardized by reduction with tin(II) chloride followed by oxidation with potassium dichromate following standard procedures. The iron(III) concentration agreed with that predicted from the weight of metal dissolved. Tests for iron(II) with phenanthroline were negative, so that $[\text{iron(II)}]/[\text{iron(III)}] \leq 5 \times 10^{-3}$. The acid content of the stock solutions was measured by titration to pH 9 with standardized NaOH and verified by displacement of H^+ from Dowex 50W-X8 (H^+) cation-exchange resin. The solutions of 2,3-dihydroxybenzoic acid (Aldrich Chemical Co.) were prepared by weight and used the same day.

Kinetic Measurements. The two solutions mixed on the stopped-flow apparatus contained iron(III) (2×10^{-3}–6×10^{-3} M) and ligand (2×10^{-4} M), respectively, in the same $NaClO_4$–$HClO_4$ medium to give an ionic strength of 1.00 M. The iron(III) concentration was at least 10 times larger than that of the ligand to provide pseudo-first-order conditions and to avoid formation of bis or tris complexes. The optimum observation wavelengths of 600 nm for DHB and 662 nm for Tiron were determined from preliminary observations on a Cary 219 spectrophotometer. A standard Aminco-Morrow stopped-flow system was used with modified output facilities described elsewhere.[11] The recorded rate constants are the average of eight replicate determinations.

Equilibrium Measurements. Solutions of iron(III) in $NaClO_4$–$HClO_4$ were mixed with ligand solutions in the same medium and the absorbances recorded at the chosen wavelength on a Cary 219 spectrophotometer. The absorbance quickly rises to a maximum value and then decreases slowly due to oxidation subsequent to complexing. The maximum absorbance was used for the equilibrium constant determinations. Due to the speed of the second reaction some measurements with DHB at low acidity were done on a Hewlett-Packard 8451 diode array spectrophotometer.

Results

Qualitative observations show that iron(III) and 1,2-dihydroxybenzoic acid (DHB) react in a three-stage process. The initially colorless solution turns blue in a few seconds, yellow after 5–10 min, and finally brown after a few hours for initial concentrations 3×10^{-3} M iron(III), 2×10^{-4} M DHB, and 0.15 M $HClO_4$ at ambient temperature. Tests for iron(II) with 1,10-phenanthroline as an indicator show that the second reaction is an oxidation–reduction process, which will be the subject of another publication. The iron(III)–Tiron product is green, and the color does not change, but the absorbance at 662 nm decreases during the second slower reaction. The measurements reported here refer to the first step only.

Equilibrium Constants. Previous studies[4-6] on the iron(III)–Tiron system suggest that the complex may exist in protonated and unprotonated forms for $[H^+]$ in the range 0.01–0.50 M. Kinetic results on the iron(III)–salicylate system also indicate protonated species are present.[2,3] Therefore, the equilibrium results are interpreted in terms of reactions 1 and 2 where $n = 2$, $z = 2$ for Tiron, $n = 3$, $z = 0$ for DHB, and higher complexes are ignored because $[Fe^{3+}] \gg [\text{ligand}]$.

$$\mathrm{Fe}^{3+} + \mathrm{H}_n\mathrm{L}^{z-} \rightleftarrows \mathrm{Fe(LH}_{n-1})^{3-z-1} + \mathrm{H}^+ \quad K_1 \qquad (1)$$

$$\mathrm{Fe}^{3+} + \mathrm{H}_n\mathrm{L}^{z-} \rightleftarrows \mathrm{Fe(LH}_n{}^{-2})^{3-z-2} + 2\mathrm{H}^+ \quad K_2 \qquad (2)$$

Table I. Spectrophotometric Determination of Equilibrium Constants for the Iron(III)–1,2-Dihydroxybenzene-3,5-disulfonate Complex (25 °C, 1.0 M $NaClO_4$)

$10[H^+]$, M	$10^3[Fe^{3+}]$, M	$10^4[\text{Tiron}]$, M	abs[a] obsd	abs[a] calcd[b]
0.30	4.00	2.00	1.510	1.603
0.60	2.00	2.00	1.110	1.086
0.60	2.00	1.00	0.548	0.543
0.60	3.00	1.00	0.613	0.620
0.60	4.00	1.00	0.666	0.667
0.60	5.00	1.00	0.716	0.698
0.60	6.00	1.00	0.759	0.721
2.50	2.00	2.00	0.161	0.157
2.50	4.00	2.00	0.283	0.288
2.50	6.00	2.00	0.388	0.399
2.00	5.00	2.00	0.251	0.256
5.00	6.00	2.00	0.123	0.121

$K_2 = 3.15 \pm 0.23$ M; $\epsilon_2 = (1.73 \pm 0.08) \times 10^{-3}\ \mathrm{M^{-1}\ cm^{-1}}$

[a] Measured at 662 nm in a 5-cm cell. [b] For the least-squares fitting the $[H^+]$ was corrected for the formations of $FeOH^{2+}$ by using a hydrolysis constant of 1.65×10^{-3} M, and the amount of $FeOH_2{}^{3+}$ was adjusted accordingly in the equilibrium constant expression. The least-squares program is from: Marquardt, D. W. IBM Share Program SDA 3094. The parameter correlation coefficient is 0.85.

The structure of the complexes is not defined by the equilibrium measurements alone, but comparisons to ligand systems that lack ambiguities can be very useful in assigning the mode of coordination. With Tiron, there is no doubt that $Fe(L)^-$ is a catechol type chelate, but Fe(LH) might be a protonated chelate or a monodentate phenoxide complex. In the DHB system, $Fe(LH)^+$ might be a salicylate type complex with an uncoordinated –OH or a catecholate analogue with an uncomplexed $-CO_2H$. The $Fe(LH_2)^{2+}$ species could be a monodentate carboxylate, a protonated salicylate, or a protonated catecholate complex. Of course, mixtures of modes of coordination are possible.

Under the acidity conditions of the experiments the ligand acid dissociation constants show that the free ligand will be in the H_nL^{z-} form. Then the total ligand concentration is given by eq 3. The

$$[\mathrm{L_t}] = [\mathrm{H}_n\mathrm{L}] + [\mathrm{Fe(LH}_{n-2})] + [\mathrm{Fe(LH}_{n-1})] \qquad (3)$$

ligand does not absorb at the wavelengths used, so that the measured absorbance is given by eq 4, where l is the cell path

$$A = l(\epsilon_1[\mathrm{Fe(LH}_{n-1})] + \epsilon_2[\mathrm{Fe(LH}_{n-2})]) \qquad (4)$$

length (cm) and ϵ_1 and ϵ_2 are the molar absorptivity coefficients ($\mathrm{M^{-1}\ cm^{-1}}$) of $Fe(LH_{n-1})$ and $Fe(LH_{n-2})$, respectively. From eq 1–4 it can be shown that

$$A = l[\mathrm{L_t}][\mathrm{Fe}^{3+}]\left(\frac{\epsilon_1 K_1[\mathrm{H}^+] + \epsilon_2 K_2}{[\mathrm{H}^+]^2 + [\mathrm{Fe}^{3+}](K_1[\mathrm{H}^+] + K_2)}\right) \qquad (5)$$

Nonlinear least-squares fitting of the variation of A with $[L_t]$, $[Fe^{3+}]$, and $[H^+]$ was used to evaluate the constants in eq 5. The results for Tiron and DHB are given in Tables I and II, respectively. In both systems, the parameters K_1 and ϵ_1 for the protonated complex $Fe(LH_{n-1})$ could not be evaluated because their 95% confidence limits were larger than the values themselves. If the values were fixed at $K_1 = \epsilon_1 = 0$, the standard error of the fit increased by <4%, the calculated absorbances changed by $<2 \times 10^{-3}$ unit, and K_2 and ϵ_2 changed by <1%.

Kinetic Results. There have been several kinetic studies of the reaction of iron(III) and 1,2-dihydroxybenzene derivatives.[7] The present study was done under different conditions of $[\text{iron(III)}] \gg [\text{ligand}]$, and the acidity range has been extended. These conditions allow the dependence of the rate on [iron(III)] to be established and the effect of the protonated complexes on the rate law to be investigated.

The kinetic data cover the acid range from 1.0×10^{-2} to 0.70 M with five iron(III) concentrations between 2.0×10^{-3} and 6.0×10^{-3} M. The hydrogen ion dependence of k_{obsd} for the reaction of 4×10^{-3} M iron(III) with Tiron and DHB is shown in Figure

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[11] Pinnell, D.; Jordan, R. B. *Inorg. Chem.* **1979**, *18*, 3191.

Table II. Spectrophotometric Determination of Equilibrium Constants for the Iron(III)–2,3-Dihydroxybenzoic Acid System (25 °C, 1.0 M $NaClO_4$–$HClO_4$)

			abs[a]	
$10[H^+]$, M	$10^3[Fe^{3+}]$, M	10^4[DHB], M	obsd	calcd[c]
0.10	3.00	2.00	0.293[b]	0.272
0.20	3.00	2.00	0.288[b]	0.268
0.35	3.00	2.00	0.254[b]	0.257
0.50	3.00	2.00	0.247[b]	0.243
1.50	3.00	2.00	0.112[b]	0.131
1.50	2.00	2.00	0.505	0.518
1.50	3.00	2.00	0.630	0.654
1.50	4.00	2.00	0.718	0.752
1.50	5.00	2.00	0.802	0.826
1.50	6.00	2.00	0.877	0.884
3.00	2.00	2.00	0.192	0.182
3.00	3.00	2.00	0.054[b]	0.051
3.00	3.00	2.00	0.270	0.256
3.00	4.00	2.00	0.328	0.321
3.00	5.00	2.00	0.397	0.379
3.00	6.00	2.00	0.432	0.431
5.00	3.00	2.00	0.107	0.105
5.00	4.00	2.00	0.136	0.136
5.00	5.00	2.00	0.168	0.166
5.00	6.00	2.00	0.193	0.195
5.00	4.00	3.00	0.201	0.205
5.00	5.00	3.00	0.238	0.250
5.00	6.00	3.00	0.281	0.292
5.00	3.00	4.00	0.212	0.210
5.00	4.00	4.00	0.281	0.273
5.00	5.00	4.00	0.343	0.333
5.00	6.00	4.00	0.402	0.390

$K_2 = 6.95 \pm 0.60$ M; $\epsilon_2 = (1.37 \pm 0.08) \times 10^3$ M^{-1} cm^{-1}

[a] Measured at 600 nm in a 5.00-cm cell unless indicated otherwise. [b] Measured in a 1-cm cell on an HP 8451 diode array spectrophotometer. [c] For fitting details see footnote *b* of Table I. The parameter correlation coefficient is 0.91.

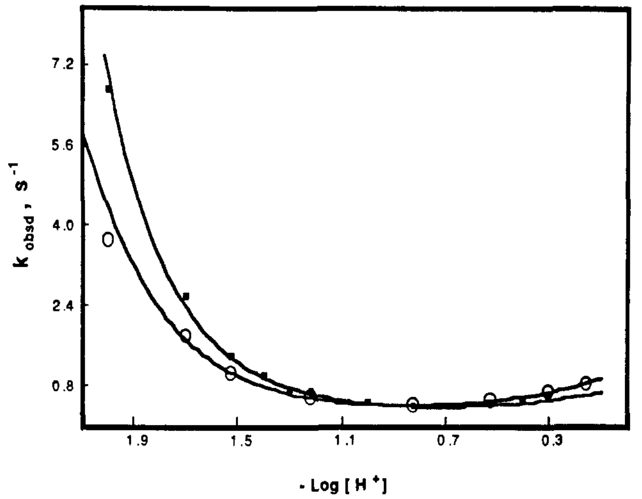


Figure 1. Variation of k_{obsd} with $-\log [H^+]$ for the reaction of iron(III) with 2,3-dihydroxybenzoic acid (■) and 1,2-dihydroxy-3,5-benzenesulfonate (○) for [iron(III)] = 4.0×10^{-3} M in 1.0 M $NaClO_4$ at 25 °C.

1, and the complete data are given in the supplementary material. The hydrogen ion dependence is similar to that from many previous studies and is discussed later in terms of specific reaction schemes.

The unusual feature of the rate law is a term dependent on the square of the iron(III) concentration that is dominant at low $[H^+]$ ($\lesssim$0.03 M) for the two 1,2-dihydroxybenzene derivatives studied here. The only previous suggestion of such a kinetic terms appears in the work of Birus et al.[12] on the acetohydroxamate system. The $[Fe^{3+}]^2$ dependence is sufficiently unusual to require special attention. Figure 2 shows the variation of k_{obsd} with $[Fe^{3+}]$ at 2.0 $\times 10^{-2}$ M H^+ for Tiron and DHB. The plot is not linear but shows the rapidly increasing slope consistent with an $[Fe^{3+}]^2$ dependence.

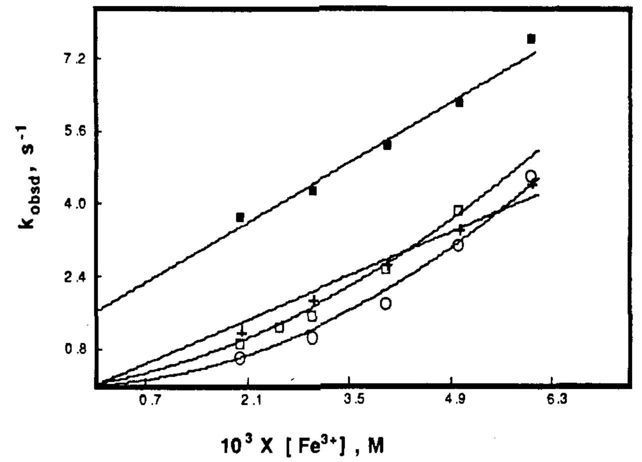


Figure 2. Variation of k_{obsd} with [iron(III)] in 2.0×10^{-2} M $HClO_4$, 1.0 M $NaClO_4$ at 25 °C for 1,2-dihydroxy-3,5-benzenedisulfonate (○) 2,3-dihydroxybenzoic acid (□), salicylic acid (+), and catechol (■).

To check that the observed iron(III) dependence was not a peculiarity of our solutions, the kinetics of the iron(III)–salicylate system was reinvestigated. These results are plotted also in Figure 2 and appear to be consistent[13] with the first-order iron(III) dependence reported originally.[2] A similar study with catechol also gives a first-order iron dependence[13] as shown in Figure 2. The possible mechanistic significance of these observations will be discussed later.

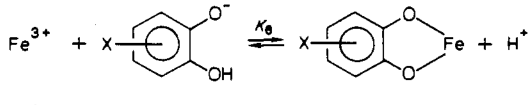
Discussion

The equilibrium constants will be discussed in relationship to previous work and the mode of complexing of DHB. Then the kinetic data will be analyzed for specific reaction schemes and the results discussed in terms of probable mechanisms.

The value of $K_2 = 3.1 \pm 0.2$ M for the Tiron system is in reasonable agreement with that of 5.7 M (1.0 M $NaClO_4$) from one interpretation of the data of McBryde,[5] 3 M (0.1 M KCl) from the work of Schwarzenbach and Willi,[4] and 1.45 M (1.0 M $NaClO_4$) reported by Mentasti et al.[7] There is marked disagreement with the result of 0.4 M of Morin and Scharff.[6] It should be noted that some of the disagreements may be due to a second slow reaction between iron(III) and Tiron. This reaction is deceptive because it does not produce a color change but just a decrease in absorbance in the 660-nm region. Once this was recognized during the current study, all absorbance measurements were made within 1 min of mixing. A more casual approach, which would seem consistent with the apparent color stability of the solutions, could lead to significant errors.

The value of $K_2 = 7.0 \pm 0.6$ M for DHB does not agree with that of 4.4×10^{-3} M derived from log $\beta_{111} = 23.5$ reported by Avdeef et al.[9] From our experience with the iron(III)–DHB system, it seems most probable that the relatively rapid oxidation reactions cause substantial uncertainty in the titrimetric results of Avdeef et al. in the acidic region and this probably accounts for the discrepancy. This also explains the dependence of the results[9] on the direction of the titration.

In order to discuss the mode of complexation of DHB, it is useful to consider the equilibrium constant for the reaction



(6)

One might expect K_6 to be fairly independent of the substituent X if the affinities of H^+ and Fe^{3+} for the catecholate dianion are

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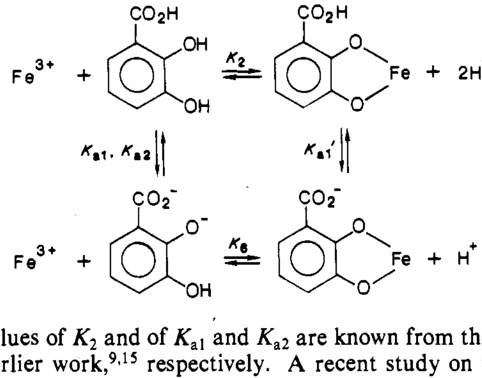
(12) Birus, M.; Kryundzic, N.; Pribanic, M. *Inorg. Chim. Acta* **1980**, *55*, 65.

(13) A reviewer has suggested that there may be some curvature in the plots of these data indicative of some contribution from a term higher than first order in iron(III).

parallel. A survey of systems with X ≡ H, 4-NO_2,[9] 4-$CH_2CO_2^-$,[9] 4-CO_2^-,[14] and 3,5-SO_3^- shows that K_6 is in the range 5×10^6–5×10^8.

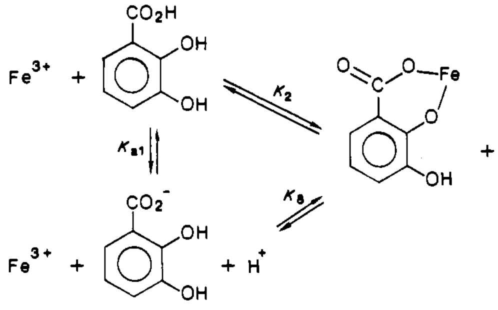
The mode of complexation of DHB may be analogous to that of catechol or salicylate. If catechol complexing is involved, the following reaction scheme can be considered:



(7)

The values of K_2 and of K_{a1} and K_{a2} are known from the present and earlier work,[9,15] respectively. A recent study on the iron(III)-protocatechuic acid system[14] indicated that the $-CO_2H$ group has an ionization constant 2.5 times larger than in the free ligand. Therefore, one would expect $K_{a1}' > 10^{-3}$ M for DHB. Then one calculates that $K_6 = K_2K_{a1}'/K_aK_{a2} > 4 \times 10^{10}$ M. This lower limit is about 100 times larger than expected from the five other systems mentioned above.

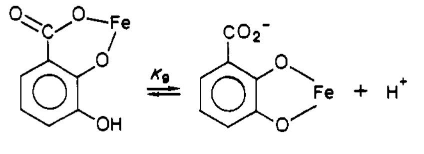
If the complexing of DHB is through the salicylate group, the results can be analyzed by eq 8. For salicylate, 5-sulfosalicylate,



(8)

and 4-hydroxysalicylate, the values of K_8[16] are relatively constant at 0.8×10^3, 0.8×10^3, and 1.5×10^3 M, respectively. It is possible to calculate for DHB that $K_8 = K_2/K_{a1} = 3.5 \times 10^3$ M, which is quite close to the "normal" values.

In summary, the analysis of the formation constants is quite consistent with salicylate type complexing of DHB, while a catechol type complex requires a formation constant at least 100 times larger than expected. The equilibrium constant observations can be used to analyze the following linkage isomerism reaction since $K_9 = K_6K_{a2}/K_8$:



(9)

If K_6 has a value in the normal range of ~5×10^7 M, then $K_9 \approx 1 \times 10^{-6}$ M. Therefore, the catecholate complex will be the dominant form for pH >6.

The reactions necessary to describe the kinetic results for Tiron are given in Scheme I. Although the ionization of the coordinated ligand (K_a'') was not required by the equilibrium studies, it is retained for reasons discussed below.

Scheme I

$$FeOH_2^{3+} \rightleftarrows FeOH^{2+} + H^+ \qquad K_m = 1.65 \times 10^{-3}\ M$$

$$2FeOH_2^{3+} \rightleftarrows Fe_2(OH)_2^{4+} + 2H^+ \qquad K_D = 2.24 \times 10^{-3}\ M$$

$$FeOH^{2+} + H_2L^{2-} \rightleftarrows Fe{=}L^- + H^+ + H_2O \quad k_2, k_{-2}$$

$$FeOH_2^{3+} + H_2L^{2-} \rightleftarrows Fe{=}L^- + 2H^+ \quad k_3, k_{-3}$$

$$Fe_2(OH)_2^{4+} + H_2L^{2-} \rightleftarrows Fe{=}L^- + FeOH_2^{3+} + H_2O \quad k_4, k_{-4}$$

$$Fe{=}LH \rightleftarrows Fe{=}L^- + H^+ \quad K_a''$$

The ionization of H_2L^{2-} has been neglected in Scheme I because the small K_a of the ligand (6.3×10^{-8} M) makes HL^{3-} an insignificant species for $[H^+] > 0.01$ M. For the condition $[Fe^{3+}]$, $[H^+] \gg [H_2L^{2-}]$, Scheme I predicts that the pseudo-first-order rate constant is given by eq 10,[17] where $[Fe^{3+}]_t = [FeOH_2^{3+}] + [FeOH^{2+}] + 2[Fe_2(OH)_2^{4+}]$ and $[H^+]$ takes into account that produced from $FeOH^{2+}$ and $Fe_2(OH)_2^{4+}$ formation.

$$k_{obsd} = \left(k_2K_m + k_3[H^+] + \frac{k_4K_D[Fe^{3+}]_t}{K_m + [H^+]} \right) \times \left(\frac{[Fe^{3+}]_t}{K_m + [H^+]} + \frac{K_a''[H^+]}{K_2(K_a'' + [H^+])} \right) \quad (10)$$

The results of nonlinear least-squares fits of the k_{obsd} values to eq 10 are summarized in Table III. A value for k_3 could not be distinguished from zero on the basis of the fits. Although the equilibrium studies did not require a protonated species, it was necessary to include FeLH and K_a'' in fitting the kinetic results. If K_a'' is fixed at a much larger value than $[H^+]$, then the predicted rate constants for 0.50 and 0.70 M H^+ are persistently too large by 5–14%. $K_a'' = 1.7$ M is compatible with the equilibrium measurements if ϵ_1 (eq 4) is $\lesssim 8 \times 10^2\ M^{-1}\ cm^{-1}$,[18] so that FeLH is not contributing to the absorbance for $[H^+] \leq 0.50$ M.

For DHB, Scheme I must be modified slightly because the ligand is a tribasic acid (H_3L), and ionization of the carboxylate group ($K_a = 2.0 \times 10^{-3}$ M)[9] means that H_2L^- must be included. Scheme II is adequate to describe the results. The product $Fe{=}LH_2^{2+}$ has the phenol groups protonated, and K_a'' and K_{a2}'' refer to successive ionizations of these groups. The K_a'' value is analogous to that for the salicylate complex.[2,3]

Scheme II

$$FeOH_2^{3+} \rightleftarrows FeOH^{2+} + H^+ \quad K_m$$

$$2FeOH_2^{3+} \rightleftarrows Fe_2(OH)_2^{4+} + 2H^+ \quad K_D$$

$$H_3L \rightleftarrows H_2L^- + H^+ \quad K_a$$

$$FeOH_2^{3+} + H_2L^- \rightleftarrows Fe{=}LH^3 + H^+ \quad k_1, k_{-1}$$

$$FeOH^{2+} + H_3L \rightleftarrows Fe{=}LH^+ + H^+ \quad k_2, k_{-2}$$

$$FeOH_2^{3+} + H_3L \rightleftarrows Fe{=}LH^+ + 2H^+ \quad k_3, k_{-3}$$

$$Fe_2(OH)_2^{4+} + H_3L \rightleftarrows Fe{=}LH^+ + FeOH_2^{3+} \quad k_4, k_{-4}$$

$$Fe_2(OH)_2^{4+} + H_2L^- \rightleftarrows Fe{=}LH^+ + FeOH^{2+} \quad k_5, k_{-5}$$

$$FeLH_2^{2+} \rightleftarrows FeLH^+ + H^+ \quad K_a''$$

$$FeLH^+ \rightleftarrows FeL + H^+ \quad K_{a2}''$$

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(14) Kennedy, J. A.; Kipton, H.; Powell, J. *Aust. J. Chem.* **1985**, *38*, 659.

(15) The pK_a values used are 2.7 and 10.06 (27.1 °C, 0.1 M) from ref 9, in reasonable agreement with 3.1 and 9.84 (25 °C, 0.1 M) from: Harada, H. *Bull. Chem. Soc. Jpn.* **1971**, *44*, 3459.

(16) Martell, A. E.; Smith, R. M. *Critical Stability Constants*; Plenum: New York, 1977; Vol. 3.

(17) A reviewer has noted correctly that dimer formation may not be fast enough to maintain the initial equilibrium concentration. Numerical solution of the appropriate differential equations indicates that the dimer can drop to a steady-state concentration about 20% below the initial value. This will have some quantitative effect on k_3 and k_4 values but does not invalidate the general interpretation.

(18) If $\epsilon_1 = 800$ and $K_a'' = 1.7$, the standard error of the fit is ~15% worse than the best value, and $K_2 = 2.8 \pm 0.2$.

Table III. Summary of Least-Squares Best-Fit Rate Constants (M^{-1} s^{-1}; 25 °C, 1.00 M $NaClO_4$)[a]

	DHB	Tiron
k_1	$(4.0 \times 10^3)^b$	
k_2	$(4.8 \times 10^3)^b$	$(3.08 \pm 0.48) \times 10^3$
k_3		
k_4	$((4.5 \pm 5.5) \times 10^3)^c$	$(10.9 \pm 0.3) \times 10^3$
k_5	$(2.15 \pm 0.88) \times 10^5$	
K_a''	2.10 ± 1.27	1.70 ± 1.30

[a] Errors are 95% confidence limits; fitting methods are described in footnote *b* of Table I. Maximum parameter correlation coefficients are 0.88 between k_4 and k_5 for DHB and 0.86 between k_2 and K_a'' for Tiron. [b] Calculated from $k_1K_a + k_2K_m = 8.01 \pm 0.61$ by assuming the value equals k_1K_a to obtain k_1 or by assuming it equals k_2M_m to obtain k_2 with $K_a = 2.0 \times 10^{-3}$ M[9] and $K_m = 1.65 \times 10^{-3}$ M. [c] The value is not well-defined in view of the confidence limits.

The pseudo-first-order rate constant for Scheme II is given by eq 11.

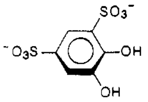
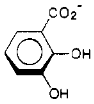
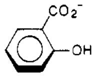
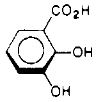
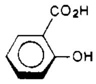
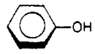
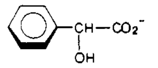
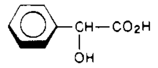
$$\begin{aligned} k_{obsd} = \Big\{&(k_1K_a + k_2K_m) \times \\ &[H^+] + k_3[H^+]^2 + \left(\frac{k_4K_D[H^+] + k_5K_DK_a}{K_m + [H^+]}\right) \times \\ &[Fe^{3+}]_t\Big\}\Big\{\frac{[Fe^{3+}]_t}{(K_m + [H^+])(K_a + [H^+])} + \\ &\frac{K_a''[H^+]}{K_f([H^+]^2 + K_a''[H^+] + K_a''K_{a2}'')}\Big\} \end{aligned} \tag{11}$$

The results of nonlinear least-squares fits of k_{obsd} to eq 11 are summarized in Table II.[19] The value of k_4 is only marginally defined by the data since the 95% confidence limit is almost equal to the value of k_4. A value for K_{a2}'' could not be determined except to show that it must be significantly smaller than the smallest experimental $[H^+]$, so that K_{a2}'' was fixed at 1×10^{-3} M, consistent with the results of Kennedy et al.[14] on the protocatechuic acid–iron(III) system. The kinetic results require $K_a'' \approx 2$, but this is not inconsistent with the equilibrium data if ϵ_1 (eq 4) is $\lesssim 1 \times 10^3$ M^{-1} cm^{-1}.

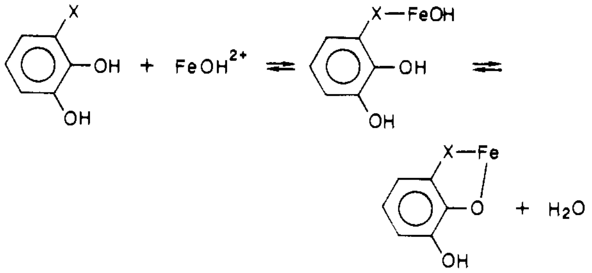
The kinetic results of some structurally related systems from this and earlier studies are summarized in Table IV. The interpretation is clouded by the proton ambiguity problem as indicated by the values in brackets in Table IV, for those cases where a dual interpretation is possible. The growing evidence[20,21] that $FeOH^{2+}$ reacts by dissociative activation can be used in further analysis. The unambiguous cases of Tiron and phenol have similar rate constants of $\sim 2 \times 10^3$ M^{-1} s^{-1} for complexing with $FeOH^{2+}$. The values for salicylic acid, DHB, and hydroxyphenylacetate are only slightly above this value. The difference might be due to some contribution from the $FeOH_2^{3+}$ + deprotonated ligand path for the last three systems. This path could have a rate constant on the order of 10^3 M^{-1} s^{-1}, based on results of $FeOH_2^{3+}$ + haloacetate systems.[22]

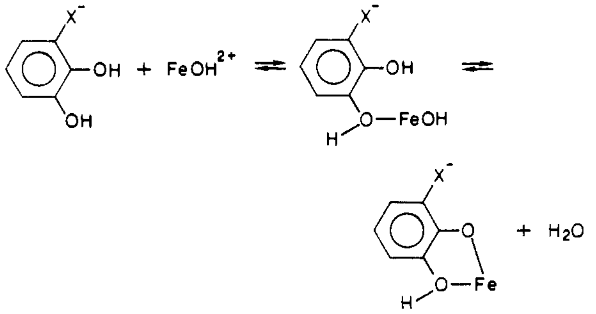
The carboxylate anions salicylate, hydroxyphenylacetate, and possibly DHB^- deviate from the above "normal" pattern since their rate constants are 6–8 times larger than for the neutral acids and Tiron. The ligand charge could be used as an explanation through stabilization of the ion pair precursor, but then the "normal" rate constant for Tiron dianion seems anomalous. Although one $-SO_3^-$ substituent in Tiron is too far from the reaction site to be of influence, the $3\text{-}SO_3^-$ in Tiron is in the same relative position as the $-CO_2^-$ in DHB^-. These observations could be rationalized if first bond formation to the carboxylate anions is a rapid preequilibrium, followed by rate-limiting ring closure as shown in eq 12, where $X^- \equiv CO_2^-$. When $X^- \equiv SO_3^-$, this path would be unfavorable because of the very weak complexing ability of $-SO_3^-$. Then the following competitive path would dominate when $X^- \equiv SO_3^-$:

Table IV. Summary of Kinetic Data for Related Systems[a]

ligand	rate const, M^{-1} cm^{-1} $FeOH_2^{3+}$	 $FeOH^{2+}$	 $Fe_2(OH)_2^{4+}$
	...	3.1×10^3	11×10^3
	(4.0×10^3)	$<3 \times 10^4$	2.2×10^5
	(3.5×10^3)	1.5×10^4	...
	...	(4.8×10^3)	4.5×10^{3c}
	$\lesssim 10$	(3.5×10^3)	...
	...	1.5×10^3	...
	(1.4×10^4)	1.4×10^{4b}	
	...	(5.7×10^3)	

[a] Values in brackets are upper limits as described in the footnote to Table III. [b] This value is not well-defined by the data, as noted in ref 3. [c] This value is not well-defined by the data.


(12)


(13)

The ligands that are fully protonated at the reaction sites do not show detectable reactivity with $FeOH_2^{3+}$. This implies that $k_3[H^+] \ll k_2K_m$ (eq 10 or 11), so that $k_3[H^+] \ll (3 \times 10^3)(1.7$

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(19) The reaction of $FeOH^{2+} + H_2L^-$ is omitted from Scheme II because the rate constant cannot be derived from the data, except to give an upper limit of $\lesssim 3 \times 10^4$ M^{-1} s^{-1}, which causes ~10% increase in the standard error of the fit.

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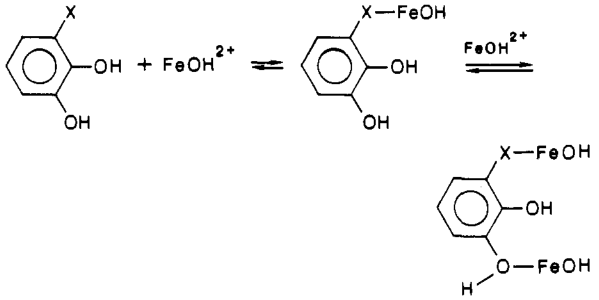
(21) Swaddle, T. W.; Merbach, A. E. *Inorg. Chem.* **1981**, *20*, 4212.

(22) Perlmutter-Hayman, B.; Tapuhi, E. *J. Coord. Chem.* **1976**, *6*, 31.

$\times 10^{-3}$) = 5, and for $[H^+] = 0.7$ M, $k_3 \ll 7$ M^{-1} s^{-1} for the protonated ligands.

The assignment of the $FeOH_2^{3+}$ + carboxylate anion reactions remains ambiguous, and the probable associative activation[20,21] makes comparisons between ligands much less meaningful. The apparently similar rate constants for the DHB^- and salicylate anions with $FeOH_2^{3+}$ seems reasonable, but all of this reactivity could be assigned to $FeOH^{2+}$ with the protonated ligand as discussed above.

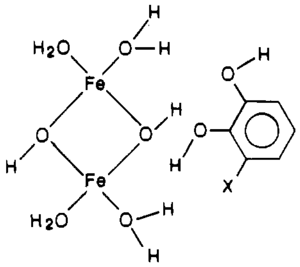
The observation that the complexing of Tiron, DHB, and DHB^- contains a terms second order in $[Fe^{3+}]$ and essentially inverse second order in $[H^+]$ remains to be discussed. As well as being unusual in itself, it is also noteworthy that this kinetic term is not apparent in the complexing of catechol or salicylate. The implication is that the $[Fe^{3+}]^2$ dependence is enhanced or perhaps requires substituents in the 1- and 3-positions of the aromatic ligand. Elimination of either the 1-OH (salicylate) or 3-CO_2H (catechol) suppresses or eliminates this kinetic path. One explanation for the $[Fe^{3+}]^2$ dependence could be in terms of eq 14.



(14)

This possibility seems unlikely in view of the limited complexing ability of $-SO_3^-$ and $-CO_2H$. Furthermore, it is not at all obvious why the addition of the second $FeOH^{2+}$ in eq 14 should be competitive with intramolecular rearrangement of the monoiron(III) complex to products.

An explanation of the $[Fe^{3+}]^2$ term may be formulated in terms of the iron(III) dimer, which is the third most abundant iron species in solution.[23,24] This dimer has been taken to have a bis(μ-hydroxy) structure from potentiometric and NMR relaxation data[24] and from kinetic evidence.[25] However, recent spectroscopic studies[26,27] on much more concentrated solutions have been interpreted to indicate a μ-oxo structure. It may be relevant to note that $Cr(OH_2)_6^{3+}$ produces a bis(μ-hydroxy) species in dilute acid,[28] although the μ-oxo species can be made by other methods. Whatever the structure is, the iron(III) dimer may form a particularly reactive precursor complex when the appropriate ligand substituents are present. The structure may be represented by VI or an analogous form for the μ-oxo structure. The polar substituents at positions 1 and 3 on the ligand provide the possibility of simultaneous interaction with both iron(III) centers to stabilize the precursor complex to substitution. After substitution on one iron, the dimer presumably would dissociate rapidly.[29]



VI

Acknowledgment. We thank the Natural Sciences and Engineering Research Council of Canada for financial support, and J.X. thanks the Peking Medical College for a study leave and financial support.

Registry No. III, 303-38-8; IV, 77310-82-8; Fe^{3+}, 20074-52-6.

Supplementary Material Available: Listings of kinetic results for the reaction of iron(III) with Tiron and DHB (3 pages). Ordering information is given on any current masthead page.

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Notes

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$(Et_3Te^+Ag_4I_5^-)_n$: Synthesis and X-ray Structure of a Layered Polyanion

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Received August 21, 1987

Organotelluronium salts containing a halide or a halogen-rich anion such as MX_4^- or MX_6^{2-} (M = B(III), Al(III), Sb(III), Te(IV), Sn(IV), Ti(IV); X = F, Cl, Br) are well-known.[1,2] In an attempt to prepare a salt with a dithiophosphate anion from Et_3TeI and $Ag^+[S_2P(OEt)_2]^-$, the compound $(Et_3Te^+Ag_4I_5^-)_n$ was obtained in good yield. X-ray structural analysis reveals that the structure has some interesting differences from those of the alkali-metal or ammonium salts, which belong to a class of Ag–I-based solid electrolytes.[3,4] These differences can be ascribed to the Te···I secondary interionic interactions.

Experimental Section

The silver salt of *O,O*-diethyl dithiophosphate (1.72 g, 5.85 mmol) was prepared from equimolar aqueous solutions of $AgNO_3$ and $NH_4^+[S_2P(OEt)_2]^-$ and reacted in situ with an aqueous solution of 2.00 g (5.85 mmol) of Et_3TeI, prepared as described earlier.[2] The reaction mixture was warmed up to 70 °C for ca. 3 h and cooled to room temperature, and the yellow oil that formed as a result of the reaction was separated from the reaction mixture with CH_2Cl_2. The solution was concentrated, and $CHCl_3$ was added to it. A dull yellow crystalline product gradually separated from the solution. (Anal. Found: C, 5.19; H, 0.99. Calcd for $C_6H_{15}TeAg_4I_5$: C, 5.62; H, 1.17. Mp 155–160 °C; yield 0.75 g, 50%.) An X-ray structural analysis of a single crystal showed the com-

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