aqueous O_2^- is also useful for nonaqueous solvents. Moreover, by adding reductants that compete with O_2^- for $Ru(bpy)_3^{3+}$, it is possible to study the oxidation of O_2^- by other reagents. Such studies are in progress.

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Note Added in Proof. After this work was completed, the rate constant for the $Ru(bpy)_3^{3+}$–O_2^- reaction was reported as 3.5×10^{10} M^{-1} s^{-1} at $\sim 1 \times 10^{-3}$ M ionic strength, in good agreement with our value 1.4×10^{10} M^{-1} s^{-1} at a higher (0.10 M) ionic strength: Sassoon, R. E.; Aizenshtat, Z.; Rabani, J. *J. Phys. Chem.* **1985**, *89*, 1182.

Registry No. O_2, 7782-44-7; $Ru(bpy)_3^{3+}$, 18955-01-6; O_2^-, 11062-77-4; $Ru(bpy)_3^{2+}$, 15158-62-0; methylviologen, 1910-42-5.

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Stopped-Flow and Rapid-Scan Spectral Examination of the Iron(III)–Acetohydroxamic Acid System

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Kinetic and thermodynamic parameters for the hydrolysis of tris- and bis(acetohydroxamato)iron(III) complexes at I = 2.0 M and 25 °C have been obtained by stopped-flow and rapid-scan spectral methods. Hydrolyzed iron(III) species are not believed to be involved. The results are compared with those already available for the hydrolysis of the mono(acetohydroxamato)iron(III) complex. The rate constants for reaction of $FeA_2(H_2O)_2^+$, $FeA(H_2O)_4^{2+}$, and $FeOH^{2+}$ with acetohydroxamic acid (HA) are very similar, all $\sim 2 \times 10^3$ M^{-1} s^{-1}, and an I_d mechanism is preferred.

Microbial iron transport is mediated by low-molecular-weight multidentate ligands termed siderophores, which have been extensively studied.[3] The naturally occurring siderophore desferrioxamine B is currently used as a drug ("Desferal") for the treatment of chronic iron poisoning, which can result from repeated massive blood transfusions (as with patients suffering from the genetic disease known as Cooley's anemia).[4] The interaction of iron(III) with desferrioxamine has been thoroughly investigated,[5-9] and the results are important in advancing an understanding of the molecular basis for iron availability in microorganisms, as well as the mechanisms for siderophore-mediated microbial iron transport[10,11] and siderophore chelation therapy.

The synthetic hydroxamic acids, $R_1C(O)N(OH)R_2$, are excellent model ligands for the siderophores, and their interaction with iron(III) has been well-studied.[3-5,12-19] The mono(hydroxamate)–iron(III) complexes have been the subject of several kinetic investigations.[12-14,16,17,19] We report in this paper equilibria and kinetic data for the formation and hydrolysis of bis- and tris(acetohydroxamato)iron(III) cations in perchlorate and chloride media. Because of the lability of the system, the use of rapid-scan stopped-flow spectrophotometry has proved very useful for measuring the spectrum of the bis species and for determining the hydrolysis constants of the three stages of complex formation. The results can be used for probing the intimate mechanism of ligand substitution in iron(III)[20] and for understanding the decidedly more complicated ferrioxamine–iron(III) system and iron(III) interchange kinetics involving ferrioxamine B[21] and tris(acetohydroxamato)iron(III).[22,23]

Experimental Section

Reagents were chemically pure. Acetohydroxamic acid was recrystallized from ethyl acetate. Ferric perchlorate solutions were standardized with use of a molar extinction coefficient of 4.16×10^3 M^{-1} cm^{-1} at 240 nm.[24] Perchloric acid solutions were obtained by dilution of 70% perchloric acid. In all experiments, the solvent was water containing NaCl or $NaClO_4$ to produce a final ionic strength of 2.0 M. For the determination of the hydrolysis constants, ferric perchlorate (0.2–0.5 mM) and acetohydroxamic acid (10–100 mM) were equilibrated at pH 6.0 and mixed in a rapid-scan stopped-flow apparatus with the sodium perchlorate solution containing various concentrations of perchloric acid (0–16 mM for tris → bis; 6–400 mM for bis → mono, and 0.2–2.0 M for mono → Fe^{3+}). In each case, a spectrum was recorded that corre-

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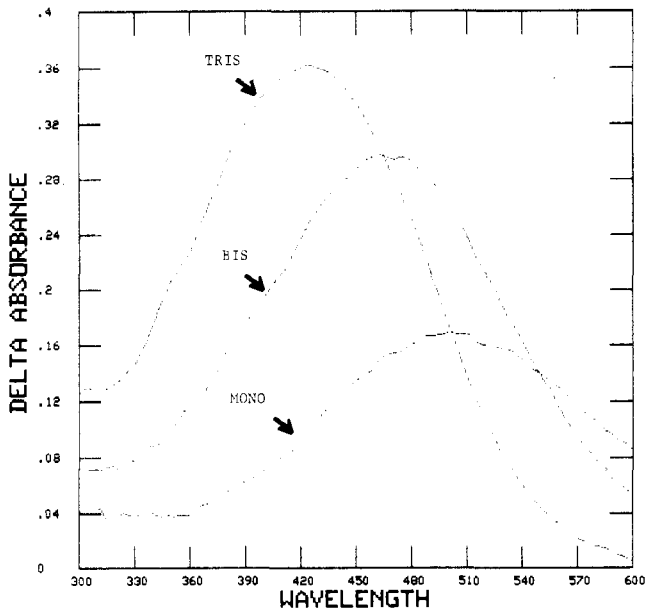

Figure 1. Spectra of tris-, bis-, and mono(acetohydroxamato)iron(III) complexes obtained by rapid-scan stopped-flow spectrophotometry (solvent in all cases at an ionic strength of 2.0 M ($NaClO_4$)). TRIS: 0.18 mM Fe^{3+}, 20 mM acetohydroxamic acid at pH 6.2 in syringe 1 mixed with solvent at pH 6.2 in syringe 2. The spectrum shown was recorded 0.2 ms after flow stop. BIS: 0.18 mM Fe^{3+}, 20 mM acetohydroxamic acid at pH 6.2 in syringe 1 mixed with solvent containing 28 mM $HClO_4$. The spectrum shown was recorded 2.2 ms after mixing (including 2.0-ms mixing time). With these conditions bis will be ~95% formed (tris → bis, $t_{1/2}$ = 0.4 ms) and will barely have started decomposing (bis → mono, $t_{1/2}$ = 19 ms). MONO: 0.18 mM Fe^{3+}, 20 mM acetohydroxamic acid at pH 6.2 in syringe 1 mixed with solvent containing 0.4 M $HClO_4$. The spectrum shown was recorded 20 ms after flow stop. In that time tris → mono was complete and mono → equilibrium mixture $t_{1/2}$ = 6.4 s. The cell path length was 1.72 cm and wavelength accuracy ±3 nm. In all cases, scan time was 3.8 ms.

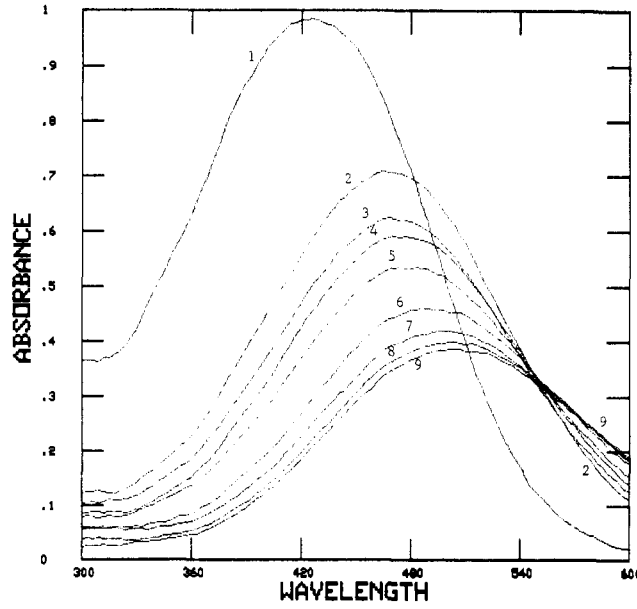

Figure 2. Spectra of equilibria involving bis and mono species: (1) 0.25 mM Fe^{3+}, 50 mM acetohydroxamic acid, pH 6 (tris); (2) 0.25 mM Fe^{3+}, 5.3 mM acetohydroxamic acid, 8 mM $HClO_4$ (bis species recorded 3.8 ms after flow stop). The remaining spectra, used to estimate hydrolysis constants, were 0.25 mM Fe^{3+}, 5.3 mM acetohydroxamic acid, and 3 mM (3), 5 mM (4), 8 mM (5), 24 mM (6), 50 mM (7), 100 mM (8), and 200 mM (9) $HClO_4$. The cell path length was 1.72 cm. In all cases, scan time was 3.8 ms.

sponded to the equilibrium position of the stage being examined. Over longer times, this would change as the next stage occurred. Absorbance readings at 390, 426, and 465 nm were read from the spectra. The kinetics of hydrolysis were determined by mixing ferric perchlorate (0.5 mM) and acetohydroxamic acid (10–200 mM) at I = 2.0 M from one syringe of a Dionex stopped-flow apparatus with various concentrations of $HClO_4$ at I = 2.0 M in the other syringe. Wavelengths of observations were 390 nm (first stage) and 471 nm (second stage), and excellent first-order kinetics were observed. For the formation of enhanced amounts of tris complex from a tris/bis mixture, ferric perchlorate (0.4 mM), acetohydroxamic acid (10 mM), and perchloric acid (1 mM) solution was mixed with solutions of acetohydroxamic acid (10 mM) and various $HClO_4$ concentrations. For the formation of enhanced amounts of bis complex from a bis/mono mixture, ferric perchlorate (0.4 mM), acetohydroxamic acid (3 mM), and perchloric acid (10 mM) solution was mixed with solutions of acetohydroxamic acid (3 mM) and various $HClO_4$ concentrations. In these experiments, $[H^+]$ was determined by measuring the pH of the mixed solutions. Excellent first-order relaxation curves were obtained. Kinetics experiments used a Dionex stopped-flow apparatus, and rapid-scan spectral measurements used a Harrick rapid-scan monochromator linked with a Dionex stopped-flow apparatus. Routine spectra were recorded on a Cary 14 spectrophotometer. All equipment was interfaced with an OLIS data collecting system (On Line Instrument Systems, Jefferson, GA).

Results

The spectra of tris-, bis-, and mono(acetohydroxamato)iron(III) complexes obtained by rapid-scan stopped-flow spectrophotometry are collected in Figure 1. Maxima and molar extinction coefficients, respectively, are as follows: 426 nm, 2.41 × 10^3 M^{-1} cm^{-1} (tris); 465 nm, 1.98 × 10^3 M^{-1} cm^{-1} (bis); 501 nm, 1.13 × 10^3 M^{-1} cm^{-1} (mono). Isosbestic points are at 465 nm (ϵ = 2.0 × 10^3 M^{-1} cm^{-1}), 501 nm (ϵ = 1.15 × 10^3 M^{-1} cm^{-1}), and 552 nm (ϵ = 9.0 × 10^2) for tris/bis, tris/mono, and bis/mono, respectively. The conditions for obtaining these spectra are specified in the legend of Figure 1 and were chosen from a knowledge of hydrolytic equilibria and kinetics parameters.

Hydrolysis of tris(acetohydroxamato)iron(III), FeA_3, proceeds in three separable stages, equilibria 1–3, where HA represents $CH_3CONHOH$. It is possible to isolate the various stages by

$$FeA_3 + H^+ \rightleftharpoons FeA_2^+ + HA \quad k_1, k_{-1}, Q_{h1} \tag{1}$$

$$FeA_2^+ + H^+ \rightleftharpoons FeA^{2+} + HA \quad k_2, k_{-2}, Q_{h2} \tag{2}$$

$$FeA^{2+} + H^+ \rightleftharpoons Fe^{3+} + HA \quad k_3, k_{-3}, Q_{h3} \tag{3}$$

judicious use of concentrations of iron(III), acetohydroxamic acid, and protons, combined with rapid spectral acquisition. Considering the first stage, it is easily shown that the [HA] and $[H^+]$ dependence of the absorbance (1-cm cell) at equilibrium (Abs_e) may be expressed by eq 4, where ϵ_T and ϵ_B are the molar extinction

$$\frac{Abs_e}{[iron]_{total}} = \frac{\epsilon_T[HA] + \epsilon_B Q_{h1}[H^+]}{[HA] + Q_{h1}[H^+]} \tag{4}$$

coefficients of the tris and bis species, respectively. Raw experimental data are contained in Table I. Best values of ϵ_T, ϵ_B, and Q_{h1} were obtained from 390- and 426-nm observations with the iterative pitmapping (Newton–Raphson) method. The value of Q_{h1} is shown in Table II. Interpretation of data for the bis → mono stage (equilibrium 2), shown in Table I and Figure 2, must allow for small amounts of tris complex in the equilibrium mixture, particularly at lower perchloric acid concentrations. Combining equilibria 1 and 2 leads to (5). With use of Q_{h1}, ϵ_T, and ϵ_B values

$$\frac{Abs_e}{[iron]_{total}} = \frac{\epsilon_T[HA]^2 + \epsilon_B Q_{h1}[HA][H^+] + \epsilon_M Q_{h1}Q_{h2}[H^+]^2}{[HA]^2 + Q_{h1}[HA][H^+] + Q_{h1}Q_{h2}[H^+]^2} \tag{5}$$

determined from the first stage, the best fits of data at 426 and 465 nm for ϵ_M (molar extinction coefficient of the mono species) and Q_{h2} were obtained. The value of Q_{h2} is shown in Table II. Finally, data for the third hydrolysis stage (Table I) were analyzed at 426 nm with use of (6) and $\epsilon_{Fe^{3+}} = 0$ and gave results for Q_{h3} shown in Table II.

$$\frac{Abs_e}{[iron]_{total}} = \frac{\epsilon_B[HA]^2 + \epsilon_M Q_{h2}[HA][H^+]}{[HA]^2 + Q_{h2}[HA][H^+] + Q_{h2}Q_{h3}[H^+]^2} \tag{6}$$

Table I. Hydrolysis Constants Obtained Spectrally at 25 °C and I = 2.0 M (ClO_4^-)[f]

[Fe(III)], M	[HA], M	[H⁺], M	Abs_e 390 nm	Abs_e 426 nm	Abs_{calcd} 390 nm[a]	Abs_{calcd} 426 nm[b]
0.0001	0.05	0.0006	0.195	0.227	0.195	0.226
		0.001	0.177	0.211	0.176	0.211
		0.002	0.152	0.191	0.154	0.193
		0.004	0.138	0.180	0.138	0.179
		0.006	0.136	0.177	0.132	0.174
		0.008	0.129	0.172	0.128	0.171
		0.015	0.121	0.165	0.123	0.167

[Fe(III)], M	[HA], M	[H⁺], M	Abs_e 426 nm	Abs_e 465 nm	Abs_{calcd} 426 nm[c]	Abs_{calcd} 465 nm[d]
0.00025	0.0053	0.003	0.290	0.363	0.299	0.376
		0.005	0.263	0.341	0.261	0.337
		0.008	0.230	0.307	0.226	0.302
		0.024	0.170	0.252	0.165	0.243
		0.05	0.145	0.223	0.142	0.221
		0.10	0.128	0.206	0.130	0.209
		0.20	0.120	0.196	0.124	0.203

[Fe(III)], M	[HA], M	[H⁺], M	Abs_e 426 nm	Abs_{calcd} 426 nm[e]
0.00025	0.005	0.16	0.110	0.111
		0.20	0.100	0.102
		0.26	0.094	0.091
		0.34	0.082	0.079
		0.38	0.073	0.075
		0.50	0.066	0.064
		0.70	0.048	0.051
		0.90	0.043	0.043
		1.0	0.037	0.039

[a] Equation 4 with $\epsilon_T = 2.66 \times 10^3$ M^{-1} cm^{-1}, $\epsilon_B = 1.17 \times 10^3$ M^{-1} cm^{-1}, and $Q_{h1} = 76.2$. [b] Equation 4 with $\epsilon_T = 2.84 \times 10^3$ M^{-1} cm^{-1}, $\epsilon_B = 1.62 \times 10^3$ M^{-1} cm^{-1}, and $Q_{h1} = 73.8$. [c] Equation 5 using $\epsilon_T = 2.84 \times 10^3$ M^{-1} cm^{-1}, $\epsilon_B = 1.62 \times 10^3$ M^{-1} cm^{-1}, and $Q_{h1} = 75$ (stage 1) and $\epsilon_M = 469$ M^{-1} cm^{-1} and $Q_{h2} = 1.09$. [d] Equation 5 with $\epsilon_T = 2.34 \times 10^3$ M^{-1} cm^{-1}, $\epsilon_B = 1.99 \times 10^3$ M^{-1} cm^{-1}, and $Q_{h1} = 73.8$ (stage 1) and $\epsilon_M = 788$ M^{-1} cm^{-1} and $Q_{h2} = 1.22$. [e] Equation 6 with $\epsilon_B = 1.62 \times 10^3$ M^{-1} cm^{-1}, $Q_{h2} = 1.16$, $\epsilon_M = 6.3 \times 10^2$ M^{-1} cm^{-1}, and $Q_{h3} = 0.015$. [f] Cell path length 1.0 cm (converted from 1.72 cm).

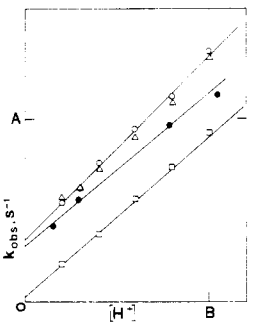

Figure 3. Plot of k_{obsd} (s^{-1}) vs. [H⁺] for tris(acetohydroxamato)iron(III) → bis(acetohydroxamato)iron(III): (○) 100 mM acetohydroxamic acid, I = 2.0 M ($NaClO_4/HClO_4$); (△) 100 mM acetohydroxamic acid, I = 2.0 M ($NaCl/HClO_4$); (□) 5 mM acetohydroxamic acid, I = 2.0 M ($NaClO_4/HClO_4$); (●) 10 mM acetohydroxamic acid, I = 2.0 M ($NaClO_4/HClO_4$) (formation direction). For ●, A = 50 s^{-1} and B = 0.5 mM. For others, A = 500 s^{-1} and B = 5.0 mM.

Kinetics

The hydrolysis of the tris(acetohydroxamato)iron(III) complex in acid proceeds in three discernible stages. Only data for the first and second stages (eq 1 and 2) were collected, since the kinetics of the third stages have been studied in detail.[12-14,16,17,19] For these stages, the observed first-order rate constant, k_{obsd}, is given by (7) (n = 1, 2).[25] Plots of k_{obsd} vs. [H⁺] at constant [HA]

$$k_{obsd} = k_n[H^+] + k_{-n}[HA] \quad (7)$$

are shown in Figures 3 and 4, from which k_n, k_{-n} values (shown in Table II) were obtained.

(25) If (1) is treated as a rapid preequilibrium for (2), then $k_{obsd} = k_2[H^+]^2([H^+] + [HA]Q_{h1}^{-1})^{-1} + k_{-2}[HA]$. Since $[H^+] >> [HA]Q_{h1}^{-1}$, the fuller equation reduces to eq 7 (n = 2).

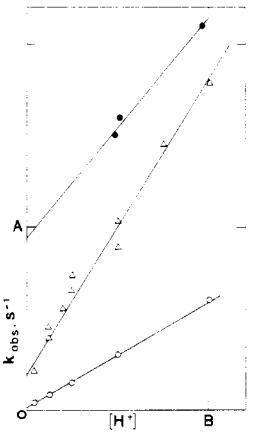

Figure 4. Plot of k_{obsd} (s^{-1}) vs. [H⁺] vs. [H⁺] for bis(acetohydroxamato)iron(III) → mono(acetohydroxamato)iron(III): (○) 5 mM acetohydroxamic acid, I = 2.0 M ($NaClO_4/HClO_4$); (△) 5 mM acetohydroxamic acid, I = 2.0 M ($NaCl/HClO_4$); (●) 3 mM acetohydroxamic acid, I = 2.0 M ($NaClO_4/HClO_4$) (formation direction). For ●, A = 10 s^{-1} and B = 10.0 mM. For others, A = 500 s^{-1} and B = 200 mM.

Conversion of mono into bis species and of bis into tris species by mixing solutions of higher acidity with those of lower acidity gave first-order relaxation data (Figures 3 and 4), which led to rate constants in good agreement with those expected from hydrolytic examination (Table I).

Discussion

The spectra of the tris-, bis- and mono(acetohydroxamato)iron(III) complexes obtained by rapid-scan stopped-flow spectrophotometry are shown in Figure 1. Spectral characteristics of FeA_3 ($\epsilon_{426\,nm}^{max} = 2.4 \times 10^3$ M^{-1} cm^{-1}) resemble closely those of ferrioxamine B ($\epsilon_{425\,nm}^{max} = 2.46 \times 10^3$ M^{-1} cm^{-1}).[8] As might be anticipated, an increased degree of complexing by acetohydroxamate is attended by a shift in the maximum to lower

Table II. Kinetic and Thermodynamic Parameters for Hydrolysis of Tris-, Bis-, and Mono(acetohydroxamato)iron(III) Complexes at I = 2.0 M (Sodium Perchlorate) and 25 °C

k_1, M^{-1} s^{-1}	k_{-1}, M^{-1} s^{-1}	Q_{h1}	k_2, M^{-1} s^{-1}	k_{-2}, M^{-1} s^{-1}	Q_{h2}	k_3, M^{-1} s^{-1}	k_{-3}, M^{-1} s^{-1}	Q_{h3}
1.0 (±0.02) × 10^5 [a]	1.7 (±0.07) × 10^3 [a]	59 ± 4 [b]	1.4 (±0.03) × 10^3 [c]	1.6 (±0.6) × 10^3 [c]	0.92 ± 0.50 [b]	0.06 [d]	4.8 [d]	0.0125 [d]
						0.09 [e]	1.2 [e]	0.009 [e]
9.0 (±0.2) × 10^4 [c]	1.1 (±1.0) × 10^3 [c]	82 ± 40 [b]					6.4 [f]	
9.9 (±0.3) × 10^4 [a,g]	1.7 (±0.1) × 10^3 [a,g]	58 ± 5 [b]	4.1 (±0.2) × 10^3 [a,g]	2.0 (±0.27) × 10^4 [a,g]	0.21 ± 0.04 [b]			
8.1 (±0.5) × 10^4 [j]	1.5 (±.02) × 10^3 [j]	56 ± 10 [j]	1.2 (±0.1) × 10^3 [j]	3.2 (±0.2) × 10^3 [j]	0.38 ± 0.05 [j]			
		75 ± 7 [h]			1.16 ± 0.15 [h]			0.015 ± 0.002 [h]
		138 [i]			0.49 [i]			0.009 [i]

[a] In 0.1 M acetohydroxamic acid. [b] Obtained from quotient k_n/k_{-n}. [c] In 0.005 M acetohydroxamic acid. [d] Reference 19, I = 1.0 M ($NaClO_4$/$HClO_4$). [e] Reference 13, I = 0.8–2.0 M ($NaClO_4$/$HClO_4$). [f] Reference 16, I = 1.0 M ($NaClO_4$/$HClO_4$). [g] I = 2.0 M (NaCl/$HClO_4$). [h] Spectral measurements of equilibrated solutions, eq 4, 5, or 6. [i] Reference 5, I = 0.1 M ($NaClO_4$) at 20 °C. [j] From relaxations involving formation of higher species.

wavelengths and higher molar extinction coefficients. There are sufficient differences among all three species and Fe^{3+} ion (transparent in the region displayed) to make the spectral method a viable one for equilibria and kinetic measurements.

The equilibrium involving the mono species and uncoordinated Fe(III) ion (eq 3) has been the subject of several investigations (Table II).[5,13,19] Our value for Q_{h3} using the rapid-scan stopped-flow approach is in very good agreement with those obtained by conventional spectrophotometry and potentiometry. This lends confidence in the use of the technique to isolate and examine the two equilibria involving the higher species (eq 1 and 2). The only previous data on the formation constants of the complete system are those of Schwarzenbach and Schwarzenbach at I = 0.1 M and 20 °C (Table II).[5] We confirm the trend that they observed, namely that $Q_{h1} > Q_{h2} > Q_{h3}$. The constants for the formation of mono, bis, and tris species from HA (Q_{h3}^{-1}, Q_{h2}^{-1} and Q_{h1}^{-1}, respectively) are 67 ± 9, 0.86 ± 0.13, and 0.13 ± 0.002, respectively. We have no value for the ionization constant of acetohydroxamic acid in our conditions. If we use the value obtained at I = 1.0 M and 25 °C (1.3×10^{-9} M),[13] then formation constants in terms of A^- for the mono, bis, and tris species are 5.1×10^{10} M^{-1}, 6.6×10^8 M^{-1}, and 1.0×10^7 M^{-1}, respectively, reflecting the usual trend for a normal system. The marked stability of the tris complex (overall formation constant $\sim 3 \times 10^{26}$ M^{-3}) is apparent.

The kinetics of formation of mono(acetohydroxamato)iron(III) ion have been interpreted in terms of reaction of $Fe(H_2O)_6^{3+}$ and $Fe(H_2O)_5OH^{2+}$ reacting with unionized HA, with rate constants 4.8 and 4×10^3 M^{-1} s^{-1}, respectively (I = 1.0 M $NaClO_4$/$HClO_4$ at 25 °C).[19] Only one study of the kinetics of formation of the bis and tris species has been reported. In that work, formate buffers were used and hydroxo- and formate-containing species were invoked as reactants.[15] We employed higher acidities in our studies and do not believe hydrolyzed species are involved for the following reasons. The kinetic data are consistent with the simple equilibria (1) and (2) and give equilibrium constants in good agreement with those obtained by spectral examination of equilibrated solutions (Table II). The ionization constants of $FeA_2(H_2O)_2^+$ and $FeA(H_2O)_4^{2+}$ are likely to be much lower than that of $Fe(H_2O)_6^{3+}$, which is 1.65×10^{-3} M.[15] This would require that rate constants for reaction of $FeA_2(H_2O)(OH)$ and $FeA(H_2O)_3(OH)^+$ with HA would be at least 10^3 greater than those reported for the corresponding aqua species in Table II (k_{-1} and k_{-2}). Such assessed values ($\geq 10^6$ M^{-1} s^{-1}) appear inordinately high. Finally, no hydrolyzed species $FeA(H_2O)_3(OH)^+$ need be postulated for the interpretation of the kinetics of the Fe(III)–acetohydroxamic acid $\rightleftharpoons$ mono system.[13,19] The free acid HA must be the reactive species since it is easily calculated that rate constants for reaction of the mono and bis species with A^- exceed diffusion-controlled values (see also ref 13). The rate constants for reaction of $FeA_2(H_2O)_2^+$, $FeA(H_2O)_4^{2+}$ and $FeOH^{2+}$ [12-14,16,19] (*not* Fe^{3+}) with acetohydroxamic acid are remarkably similar, all $\sim 2 \times 10^3$ M^{-1} s^{-1}. There is overwhelming evidence that $FeOH^{2+}$ reacts by an I_d mechanism, whereas substitution in Fe_{aq}^{3+} is by an I_a or A process.[16,20] These results suggest that replacement of coordinated water by acetohydroxamate in the mono and bis species is dissociative in character and that coordinated acetohydroxamate ion has a labilizing effect similar to that of coordinated hydroxide. The difference in the stabilities of the bis and tris species arise wholly from differences in the hydrolytic rate constants, a common occurrence with dissociative-dominated substitutions.

Chloride ion may serve as a model for small metabolites which can coordinate to the iron(III) center in biomolecules.[10] The increase in reactivity in changing a perchlorate to a chloride medium in the reaction of Fe^{3+} with acetohydroxamic acid has been quantitatively analyzed in terms of the more reactive $FeCl^{2+}$ and $FeCl_2^+$ ions.[19] A similar labilizing of the mono system (particularly in the formation direction) is noted in this work, suggesting chloro complexes are formed with $FeA(H_2O)_4^{2+}$. This effect of chloride over perchlorate is unlikely to be a medium effect, since chloride and perchlorate give the same result in the bis/tris equilibria kinetics. With the latter chloro complex formation would not be anticipated.

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