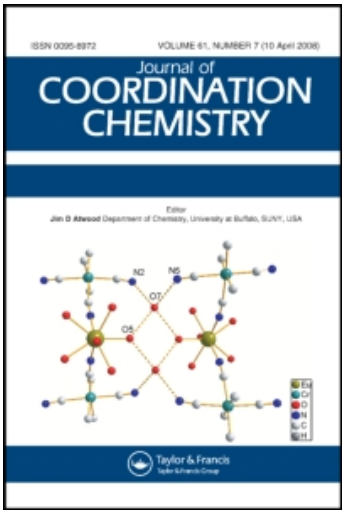

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THERMODYNAMIC AND KINETIC STUDIES ON THE IRON(III)-HYDROXAMATE INTERACTION IN ACID MEDIA

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Thermodynamics and kinetics of 1:1 complexation of iron(III) with benzo- and several ortho-substituted (CH_3, NH_2, Cl and OH) benzohydroxamic acids (HL) forming FeL^{2+} have been investigated spectrophotometrically in aqueous perchloric acid solution. Under the experimental conditions ($[H^+] \gg T_{Fe} \gg T_{HL}$) complexation involves reactions of HL with Fe^{3+} (k_1 path) and $FeOH^{2+}$ (k_2 path) ions leading to an equilibrium. Both k_1 and k_2 have been evaluated by stopped-flow spectrophotometry following the formation of FeL^{2+} and the dissociation of FeL^{2+} in acid solution. The ΔH^* value (42.5 ± 4.8 kJmol^{-1}) for the k_2 path is close to that for the water exchange of $FeOH^{2+}$ species, suggesting essentially a dissociative (I_d) process, but that (54.5 ± 3.8 kJmol^{-1}) corresponding to the k_1 path is perceptibly lower than that for the water exchange of Fe^{3+} species indicating associative (I_a) character. The reverse rate constants (k_{-1} and k_{-2}) for the dissociation of the complexes by the two paths have also been evaluated from experimental values of k_1, k_2, and equilibrium constants (Q) for formation of FeL^{2+} from Fe^{3+} and HL, and the hydrolysis constant (K_h) of the Fe^{3+} ion. There is good agreement for Q values determined by equilibrium and kinetic experiments. Q follows an increasing value of k_1 and a decreasing order of k_{-1} and thus both contribute favourably to the stability of the complex. Formation of a 1:1:1 ternary complex $Fe(Nta)L^-$ in the reaction of Fe(Nta) with benzohydroxamic acid (HL) has also been studied. Results indicate that Nta^{3-} considerably destabilizes the iron(III)-hydroxamate interaction which is due to a considerable increase in the dissociation rate by a factor of *ca* 5×10^3, whereas the formation rate is enhanced by a factor of only *ca* 4 at 25°C. Thus the strong sigma donor Nta^{3-} labilizes the strong sigma donor hydroxamate more than H_2O bound to iron(III).

Keywords: Iron(III), hydroxamic acids, kinetics, stability constants, complexes

INTRODUCTION

Even in fairly strongly acid media iron(III) forms intensely coloured and highly stable complexes with hydroxamic acids which are useful for qualitative and quantitative analysis. Siderophores are biological chelating agents involved in the transportation of iron in microbial systems. Several of the siderophores characterized so far have the hydroxamate group as the iron binding site,[1,2] a fact which accounts for the biological significance of such complexes.[3-6] The great affinity of hydroxamate for iron(III) is also the basis for the use of such substances in the treatment of iron imbalance in the human body[7-9] and some hydroxamic acid-based drugs have been found to be satisfactory on clinical trials.[6] Hence, studies on the thermodynamics and kinetics of complexation of iron(III) by hydroxamic acids are worthy of investigation. From results of X-ray crystallographic studies[10-12] it is known

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that the hydroxamate group behaves as a bidentate (O,O) ligand forming a five-membered chelate ring. These complexes are also stable with respect to redox and photochemical degradation under normal conditions.

Thermodynamic and kinetic studies on the complexation of iron(III) with benzohydroxamic acid and some ortho substituted benzohydroxamic acids and the kinetics of dissociation of the complexes in acid media are reported in this communication, which concerns efforts to obtain information on substituent effects on rate and stability. Also reported are the results of corresponding investigations on the influence of a sigma donor (nitrilotriacetate) bound to iron(III) on the binding of benzohydroxamate to form a 1:1:1 ternary complex.

EXPERIMENTAL

Materials and Reagents

Iron(III) perchlorate was prepared from freshly precipitated iron(III) hydroxide and perchloric acid. Iron content of the stock solution was estimated volumetrically.[13] The free acid content of the stock iron(III) solution was determined by passing an aliquot through Dowex 50W–X8 cation exchange resin in the H^+ form, titrating total acid in the eluant and deducting therefrom the acid equivalent of iron(III). $NaClO_4$ (Riedel), twice recrystallized from water and dried at 130°C, was used for maintaining the ionic strength of the experimental solutions. Nitrilotriacetic acid ($NtaH_3$) (Koch-light, England) was used for making a solution of $Fe(Nta)(H_2O)_2$ by mixing a solution of $Fe(ClO_4)_3$ and $NtaH_3$ in equimolar amounts and adjusting the pH of the solution to *ca* 2.7; under these conditions complexation of iron(III) by Nta^{3-} is quantitative.[14] Benzohydroxamic acid (BHA) was prepared following a method described in the literature.[15] The other hydroxamic acids, *viz*, salicylhydroxamic acid (SHA), *o*-chlorobenzohydroxamic acid (CHA), *o*-methylbenzohydroxamic acid (MHA), and *o*-aminobenzohydroxamic acid (AHA) were also prepared following a similar procedure. AHA was purified by recrystallization from ethyl acetate by adding a little chloroform, MHA from a solution of ethyl acetate by addition of petroleum ether. Other acids (BHA, SHA and CHA) were purified by crystallization from ethyl acetate. The hydroxamic acids thus purified had sharp melting points (BHA, 125°; SHA, 169°; CHA, 145°; MHA, 129°; AHA, 144°C) and their purity was checked by nitrogen analysis.

Apparatus and Procedure

A stopped-flow spectrophotometer (Hi-Tech SF-3A) provided with an oscilloscope (Advance Instruments OS 1000A), a transient recorder (Datalab DL-905) and a chart recorder (JJ Lloyds PL-3) system was used for kinetic measurements. The experimental solutions and the mixing chamber were thermostatted at the experimental temperature (±0.05°C). Ionic strength was adjusted to 1 M with an adequate amount of $NaClO_4$ in addition to the $HClO_4$ present in the solution.

pH-measurements were made using a Systronics Digital 335 pH-meter, with a glass and calomel electrode assembly calibrated as usual. Absorbance values were measured with a Carl–Zeiss (VSU–2P) spectrophotometer equipped with thermostatted cell housing.

The pK_a^{NHOH} values for the hydroxamic acids (HL) corresponding to equation (*1*) were evaluated by the usual Bjerrum–Calvin pH-metric method[16] as modified by Irving and Rossotti,[17] under conditions similar to those used for kinetic measurements.

$$RC(=O)—NHOH \rightleftharpoons RC(=O)—NHO^- + H^+ \qquad (1)$$

Owing to the much weaker acidity of the phenolic OH in SHA,[18] application of this method enabled evaluation of pK_a^{NHOH} in this case as well as that corresponding to the dissociation of the phenolic OH group without any complication.

Equilibrium constants (Q) for the iron(III)-hydroxamate complexation (*2a*) in the different cases were evaluated spectrophotometrically.

$$Fe^{3+}_{aq} + HL \rightleftharpoons FeL^{2+}_{aq} + H^+ \qquad (2a)$$

Under the experimental conditions ($[H^+] \gg T_{Fe} \gg T_{HL}$, where T_{Fe} and T_{HL} are the total iron(III) and ligand concentrations respectively in solution), formation of the mono (1 : 1) complex is virtually the only equilibrium of concern[19,20] and it may be shown that for the equilibrium represented by equation (*2a*),

$$T_{HL}/(A_e - A_o) = 1/\varepsilon_{FeL^{2+}} + [H^+]/(QT_{Fe}\varepsilon_{FeL^{2+}}) \qquad (2b)$$

where A_e is the absorbance of the solution at equilibrium and A_o is the absorbance of the iron solution in absence of the hydroxamic acid. Hence, the value of the equilibrium constant Q could be evaluated from a linear plot of $T_{HL}/(A_e - A_o)$ *versus* $[H^+]/T_{Fe}$.

From the K_a^{NHOH} and Q values obtained as above at several temperatures from 20°–50°C, the corresponding ΔH and ΔS values were evaluated graphically.

For kinetic studies the increase (due to formation) or decrease (due to dissociation) in absorbance during the reaction at or around the λ_{max} of the complexes (530 nm for SHA and 515 nm for others) was followed with time. Pseudo-first-order conditions were maintained in the formation reaction by keeping the concentrations of iron(III) and acid in large excess compared to that of the hydroxamic acid in solution. Ionic strength of the experimental solutions was adjusted to 1.0 M using $NaClO_4$. Dissociation was also followed under pseudo-first-order conditions at a fairly high acid concentration.

The Fe–Nta–benzohydroxamate system was investigated similarly at 460 nm which is near the absorbance maximum of the ternary complex $Fe(Nta)L^-$, as formed *via* (*3*).

$$Fe(Nta)(H_2O)_2 + HL \rightleftharpoons Fe(Nta)L^- + H^+ + 2H_2O \qquad (3)$$

RESULTS AND DISCUSSION

Fe(III)-hydroxamate systems

For any of the systems, values of the pseudo-first-order rate constants, k_{obs}, obtained at different concentrations of the reactant with $[H^+] \gg T_{Fe} \gg T_{HL}$ show that k_{obs}

depends on T_{Fe} and acid concentrations but is independent of T_{HL}. Dependence of k_{obs} on $[H^+]$ and T_{Fe} conforms to the following scheme:

$$\begin{array}{l} Fe^{3+} + HL \underset{k_{-1}}{\overset{k_1}{\rightleftharpoons}} FeL^{2+} + H^+;\ k_1/k_{-1} = Q \\ \Big\uparrow\downarrow K_h \\ H^+ + Fe(OH)^{2+} + HL \underset{k_{-2}}{\overset{k_2}{\rightleftharpoons}} FeL^{2+};\ k_2/k_{-2} = Q' = Q/K_h \end{array}$$

Scheme I

The pseudo-first-order rate constant for the formation of the mono-complex according to this scheme, when $[H^+] \gg T_{Fe} \gg T_{HL}$ (where $[FeL^{2+}]$ is negligible compared to T_{Fe}), is

$$k_{obs} = \{k_1[H^+] + k_2K_h\}\{QT_{Fe} + K_h + [H^+]\}/\{K_h + [H^+]\}Q \qquad (4)$$

where k_{obs} is given by

$$\log ([FeL^{2+}]_e/\{[FeL^{2+}]_e - [FeL^{2+}]_t\}) = k_{obs}t/2.303 \qquad (5)$$

Where the subscripts e and t refer to the final equilibrium state and a state at a time interval t from the beginning of the reaction, respectively. Equation (*4*) on rearrangement leads to,

$$k_{obs}\{K_h + [H^+]\}Q/\{QT_{Fe} + K_h + [H^+]\} = k_1[H^+] + k_2K_h \qquad (6)$$

The value of k_{obs} here is that for the system approaching equilibrium and hence it is expected to be independent of the equilibrium being approached from either direction, *viz*, formation and dissociation, and this has been verified in the Fe(III)–hydroxamic acid systems experimentally by the observation that both sets of data fit into the graphical representation of equation (*6*). Plots of left hand side of equation (*6*) *vs* $[H^+]$ yield good straight lines in each case (*cf* Fig. 1, data at 45°C), from the slopes and intercepts of which the k_1 and k_2 values at the experimental temperature and ionic strength could be evaluated from a knowledge of the K_h value (evaluated using literature data[21]). From the k_1 and k_2 values thus determined the reverse rate constants k_{-1} (= Q/k_1) and k_{-2} (= k_2K_h/Q) were calculated. All these constants were determined at three different temperatures (25°, 35° and 45°C) enabling evaluation of the corresponding activation parameters $\Delta H^{\ddagger}$ and $\Delta S^{\ddagger}$. The k values at 25°C together with the pK_a^{NHOH} values for the hydroxamic acids and Q values for the iron(III) complexes are given in Table I. ΔH and ΔS values corresponding to K_a^{NHOH} and Q are given in Table II, while $\Delta H^{\ddagger}$ and $\Delta S^{\ddagger}$ values are given in Table III.

For the complex formation under the conditions $[H^+] \gg K_h$ equation (*6*) reduces to

$$k_{obs}Q[H^+]/(QT_{Fe} + [H^+]) \approx k_1[H^+] + k_2K_h \qquad (7)$$

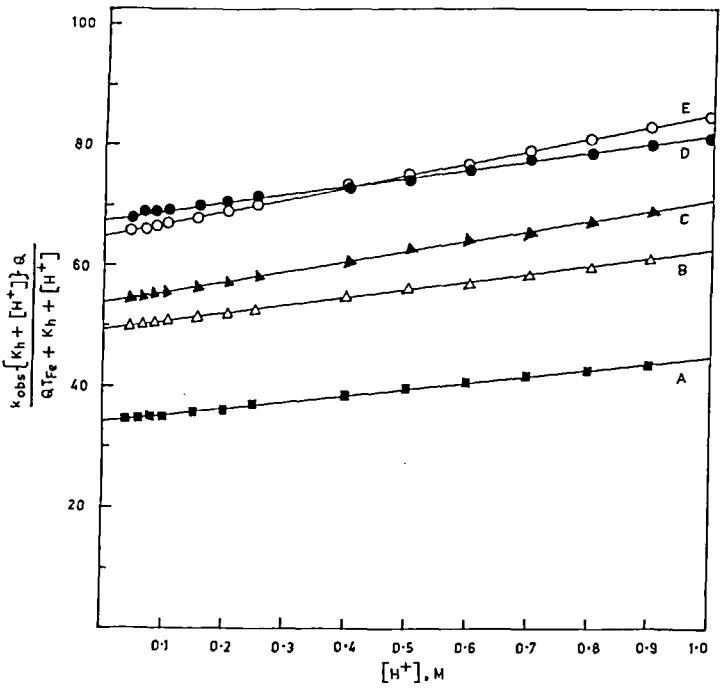

FIGURE 1 Evaluation of k_1 and k_2 in Fe(III)–hydroxamate systems. T = 45 ± 0.05°C; I = 1 M. (A), CHA; (B), AHA; (C), MHA; (D), SHA and (E), BHA. $T_{Fe} = (1.0–4.0) \times 10^{-3}$ M; $T_{HL} = (0.5–1.0) \times 10^{-4}$ M; $[H^+] = 0.04–0.25$ M (formation experiments) and 0.4–1.0 M (dissociation experiments).

TABLE I

Values of pK_a^{NHOH} for the hydroxamic acids (HL), Q for the iron(III) complexes and the formation and dissociation rate constants, k_1, k_2, k_{-1} and k_{-2} for the complexes (25°C, I = 1 M).

HL[a]	pK_a^{NHOH}[b]	Q[c]	$k_1, M^{-1}s^{-1}$	$10^{-3}k_2, M^{-1}s^{-1}$	$10^2k_{-1}, M^{-1}s^{-1}$	$10^2k_{-2}, s^{-1}$
BHA	8.60 ± 0.03	133.0 ± 2.0 (130.5 ± 4.6)	4.43 ± 0.05	4.59 ± 0.02	3.33 ± 0.03	5.87 ± 0.05
MHA	8.56 ± 0.05	53.0 ± 1.0	4.00 ± 0.17	3.53 ± 0.01	7.54 ± 0.02	11.30 ± 0.04
AHA	8.20 ± 0.04	29.2 ± 0.5	3.00 ± 0.13	2.85 ± 0.01	10.26 ± 0.04	16.57 ± 0.05
CHA	8.14 ± 0.04	11.8 ± 0.1 (11.3 ± 0.08)	2.50 ± 0.10	2.29 ± 0.01	22.12 ± 0.05	34.45 ± 0.06
SHA	8.00 ± 0.03	214.5 ± 3.2	3.67 ± 0.40	4.98 ± 0.03	1.71 ± 0.02	3.95 ± 0.03

[a] For the ligands see text. [b] This is the pK_a value corresponding to dissociation of a proton from the NHOH group of the hydroxamic acid. In the case of salicylhydroxamic acid (SHA) the second dissociation constant corresponding to the phenolic OH group has a pK_a value of 9.25 ± 0.05 (25°C, I = 1 M). [c] Values within parentheses were obtained from kinetic experiments (see text).

TABLE II

Changes in enthalpy (ΔH) and entropy (ΔS) corresponding to K_a^{NHOH} and Q (I = 1 M) from observations in the range of 20°–50°C.

	K_a^{NHOH}		Q	
HL	ΔH, kJmol^{-1}	ΔS, JK^{-1} mol^{-1}	ΔH, kJmol^{-1}	ΔS, JK^{-1} mol^{-1}
BHA	9.1 ± 0.2	−134.9 ± 0.4	6.0 ± 0.3	61.0 ± 0.8
MHA	10.0 ± 0.2	−131.1 ± 0.8	24.7 ± 0.2	116.1 ± 0.5
AHA	9.1 ± 0.2	−127.1 ± 0.4	22.9 ± 0.5	105.0 ± 1.6
CHA	24.5 ± 0.1	−74.2 ± 0.1	41.8 ± 0.4	160.5 ± 1.2
SHA[a]	18.2 ± 0.3	−92.9 ± 0.8	8.1 ± 0.2	72.0 ± 0.6

[a] For the second dissociation constant corresponding to the phenolic OH group, the ΔH and ΔS values are 4.6 ± 0.1 kJmol^{-1} and −162.5 ± 1.5 JK^{-1}mol^{-1}.

Rearrangement of equation (*7*) leads to

$$k_{obs} = \{(k_1[H^+] + k_2K_h)/[H^+]\}\, T_{Fe} + (k_1[H^+] + k_2K_h)/Q \qquad (8)$$

The plot of k_{obs} *versus* T_{Fe} at a fixed $[H^+]$ has been found to be a good straight line for a particular hydroxamic acid under the experimental conditions (T_{Fe}, 0.001–0.006 M; T_{HL}, 0.0002 M; $[H^+]$, 0.1 M; I, 1.0 M ($HClO_4$ + $NaClO_4$)). The slope/intercept ratio of the plot, being $Q/[H^+]$, enabled evaluation of the Q value from kinetic experiments. The method was tested in the case of BHA and CHA at 25° and the Q values so obtained have been found to be in good agreement with those obtained from equilibrium measurements (see Table I). From a consideration of the pK_a^{NHOH} values for the hydroxamic acids (HL) it follows that under the experimental conditions the concentrations of L^- in the experimental solutions will be so insignificant as to make any contribution to the overall complexation process involving its reaction with any of the Fe(III) species negligible.

$\Delta H^{\neq}$ *vs* $\Delta S^{\neq}$ is linear for both k_1 and k_2 paths (Fig. 2) indicating a similarity of mechanism for each path for all the ligands. $\Delta H^{\neq}$ values for the k_2 path (42.5 ± 4.8 kJmol^{-1}; Av. 41.2 ± 1.0) in all the cases are close to the $\Delta H^{\neq}$ value (42.4 ± 1.5 kJmol^{-1}) for the water exchange reaction of $Fe(OH)^{2+}_{aq}$ species,[22] indicating a dissociative (I_d) path. For the k_1 path, however, the $\Delta H^{\neq}$ values (54.5 ± 3.8 kJmol^{-1}; Av. 56.0 ± 1.0) are perceptibly lower than the $\Delta H^{\neq}$ value (64.0 ± 2.5 kJmol^{-1}) for the water exchange reaction of Fe^{3+}_{aq} species[22] indicating an associative (I_a) character for this path. This difference in mechanism is in keeping with earlier conclusions[23,24] regarding associative and dissociative reactions of $Fe(H_2O)_6^{3+}$ and $Fe(H_2O)_5(OH)^{2+}$ species, respectively. $\Delta S^{\neq}$ values are considerably negative for both k_1 and k_2 paths as has been observed previously for some analogous reactions.[20] It is further to be noted that the stability sequence of these Fe(III)–hydroxamate complexes follows (except for the salicylhydroxamic acid) the increasing order of k_1 and decreasing order of k_{-1} and thus both the forward and reverse rates favorably contribute to the stability of the Fe(III)–hydroxamate complex. At 25°C for salicylhydroxamic acid (SHA) the k_1 value is slightly lower but the k_{-1} value is nearly half that of benzohydroxamic acid (BHA) thus leading to the highest value of Q for the Fe(III)–SHA system. Presumably in this case the phenolic OH group is also involved in the complexation in addition to the hydroxamate group.

TABLE III

Activation parameters, ΔH^* and ΔS^*, corresponding to the rate constants for the formation and dissociation of the iron(III)–hydroxamate complexes (I = 1 M).

	k_1		k_2		k_{-1}		k_{-2}	
Ligand	ΔH^*, $kJmol^{-1}$	ΔS^*, $JK^{-1}mol^{-1}$	ΔH^*, $kJmol^{-1}$	ΔS^*, $JK^{-1}mol^{-1}$	ΔH^*, $kJmol^{-1}$	ΔS^*, $JK^{-1}mol^{-1}$	ΔH^*, $kJmol^{-1}$	ΔS^*, $JK^{-1}mol^{-1}$
BHA	57.8 ± 0.8	-39.6 ± 2.5	39.1 ± 0.9	-44.5 ± 2.8	51.5 ± 0.8	-101.6 ± 2.8	74.9 ± 1.1	-18.3 ± 3.7
MHA	56.1 ± 0.8	-46.4 ± 2.5	41.8 ± 0.9	-37.5 ± 3.0	31.0 ± 1.0	-163.6 ± 3.1	59.0 ± 1.3	-66.2 ± 4.2
AHA	57.3 ± 0.8	-44.6 ± 2.5	47.2 ± 1.3	-21.2 ± 4.4	34.5 ± 0.9	-149.2 ± 2.9	66.5 ± 1.3	-37.8 ± 4.3
CHA	58.2 ± 0.8	-43.0 ± 2.5	40.4 ± 1.4	-45.8 ± 4.6	17.0 ± 0.9	-201.5 ± 3.1	41.9 ± 1.3	-114.3 ± 4.3
SHA	50.7 ± 1.6	-65.0 ± 5.0	37.7 ± 0.7	-48.5 ± 2.2	42.6 ± 1.5	-137.0 ± 4.9	71.5 ± 0.8	-33.0 ± 2.4

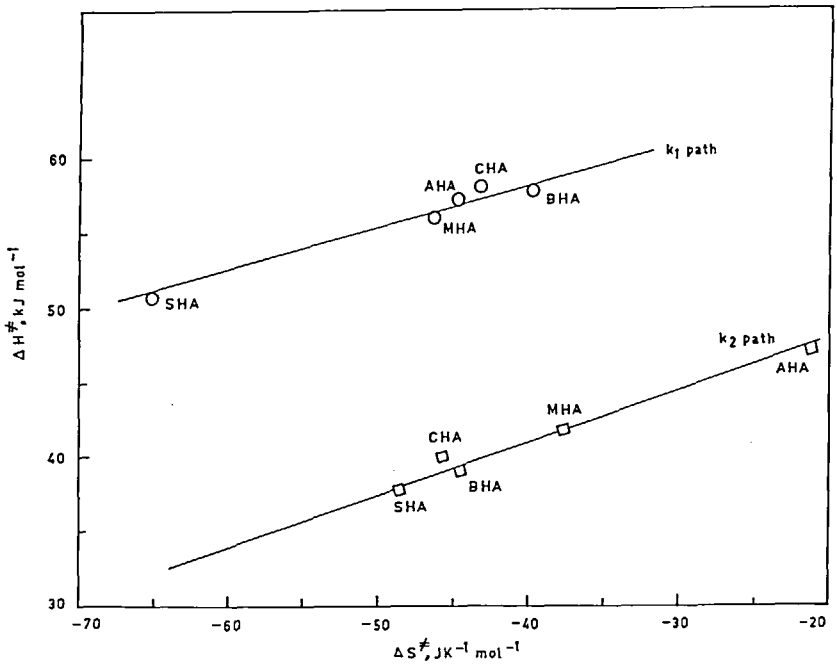

FIGURE 2 $\Delta H^{\neq}$ *vs* $\Delta S^{\neq}$ plots for the Fe(III)–hydroxamate systems (I = 1 M).

Fe(Nta)–benzohydroxamate system

In the pH range 2.7–3.9, application of the mole ratio method[25] indicated that BHA (HL) reacts with Fe(Nta) (0.0005 M) to form a 1:1:1 ternary complex $Fe(Nta)L^-$. The equilibrium constant (Q) for the formation of this complex (see equation (*3*)) was evaluated spectrophotometrically as in the case of the iron(III)–hydroxamate system; at 30°C (I = 1 M) the Q value is 0.30 (*cf* 133 for the corresponding FeL^{2+}).

The pseudo-first-order rate constant for the formation of this ternary complex from Fe(Nta) and excess HL in the pH range 2.7–3.9 conforms to $k_{obs} = k_o + k'T_{HL} + k''[H^+]$. This agrees with the equation

$$Fe(Nta)(H_2O)_2 + HL \underset{k_{-1}}{\overset{k_1}{\rightleftharpoons}} Fe(Nta)L^- + 2H_2O + H^+ \qquad (9)$$

where $k_1 = k_0 + k'T_L$ and $k_{-1} = k''$; k_0 and k' are ligand-independent and ligand-dependent paths, respectively. The absence of a path involving the $Fe(Nta)(OH)(H_2O)^-$ complex is due to the extremely low concentration of this hydroxo species in the pH range used in the investigations [pK_a of $Fe(Nta)(H_2O)_2$ at 25°C, I = 1 M, is 5.0[26]] and greater inertness of Fe–OH compared to $Fe–OH_2$. The values of the rate constants at 25°C along with the corresponding $\Delta H^{\neq}$ and $\Delta S^{\neq}$ values are given in Table IV. It is evident that while Nta^{3-} bound to Fe^{3+} somewhat enhances (*ca* 4 times at 25°C) the rate (k_f), of hydroxamate binding presumably due to labilization of the $Fe^{III}–OH_2$ bonds, the dissociation rate (k_d) is enhanced very much

more (*ca* 5000 times at 25°C). Owing to the fact that both Nta^{3-} and hydroxamate (L^-) are essentially strong sigma donors, the quadridentate Nta^{3-} strongly labilizes L^- in the species $Fe(Nta)(L)^-$. It is due to this very much enhanced dissociation rate that the stability of $Fe(Nta)(L)^-$ is very much less than that of FeL^{2+}, as the data in Table V indicate.

TABLE IV

Rate constants (at 25°C) for the formation and dissociation of the Fe^{III}(Nta)-benzohydroxamate complex, along with corresponding activation parameters. $T_{Fe} = T_{NtaH_3} = 5 \times 10^{-4}$ M; $T_{BHA} = 0.005$–0.02 M; pH = 2.7–3.9; I = 1 M ($HClO_4$ + $NaClO_4$).

Rate constants	ΔH^* kJmol^{-1}	ΔS^* JK^{-1}mol^{-1}
k_0, s^{-1} = 0.18 ± 0.02	55.6 ± 1.6	−73.8 ± 2.8
k′, M^{-1}s^{-1} = 18.26 ± 0.25	42.3 ± 1.8	−80.0 ± 3.2
k″, M^{-1}s^{-1} = 168.3 ± 3.2	41.3 ± 2.1	−64.8 ± 4.6

TABLE V

Thermodynamic and kinetic data for the interactions of Fe^{3+}_{aq} and $Fe(Nta)_{aq}$ with benzohydroxamate (L^-), at 25°C, I = 1 M.

	FeL^{2+}	$Fe(Nta)L^-$	${}_kFe(Nta)L^-/{}_kFeL^{2+}$
Q	133 ± 2.0	0.30 ± 0.05	
k_f, M^{-1}s^{-1}	4.43 ± 0.05	18.30 ± 0.15	4.13 ± 0.08
10^2k_d, M^{-1}s^{-1}	3.33 ± 0.03	168.30 ± 1.20	(5.05 ± 0.08)10^2

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