Metal-ion Oxidations in Solution. Part XIV.[1] The Formation of Intermediates in the Reaction of Iron(III) with 2-Mercaptocarboxylic Acids

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The oxidation of thiols by iron(III) in perchlorate media proceeds *via* formation of transient blue-purple intermediates. Stopped-flow studies on the reactions with mercaptoacetic (thioglycolic), 2-mercaptopropionic (thiolactic), and 2-mercapto-2-methylpropanoic acids have been made over the temperature range 10—25 °C. Under conditions of high acidity, $[\mathrm{H}^+] > 0.3\,\mathrm{M}$, and in excess of oxidant, optical-density changes have been interpreted by considering the formation of chelated 1 : 1 complexes, the kinetic parameters being consistent with the rate-determining step (i) (HORSH = thiol acid). Rate and thermodynamic parameters are described in terms of a predominantly

$$[\mathrm{Fe(OH)}]^{2+} + \mathrm{HORSH} \underset{k_{12}}{\overset{k_{11}}{\rightleftharpoons}} [\mathrm{Fe(ORS)}]^{+} + \mathrm{H}^{+} \qquad \text{(i)}$$

dissociative mechanism involving rate of water loss on the $\mathrm{Fe^{III}}$. Visible-absorption spectra for the intermediates have been derived, the maxima occurring in the region 610—640 nm. Considerable variation of the absorption coefficients with methyl substituents on the ligand has been observed, the data being interpreted in terms of increasing strain in the chelate ring. Thermodynamic parameters obtained from optical-density changes are in accord with those predicted from activation data derived from rate constants.

THE formation of highly coloured intermediates in reactions of iron(III) with sulphur-containing substrates has been known for a considerable time.[2] The first attempts to characterise these intermediates in acidic media were made on the iron(III)–thiosulphate reaction [3] using an early flow system with which the purple transient $[\mathrm{Fe(S_2O_3)}]^+$ complex was described. A notable feature of $\mathrm{Fe^{III}}$ oxidations of this type [4-12] is rapid formation of such blue-purple intermediates prior to the overall redox processes which are often kinetically complex. In a previous study [13] the stopped-flow technique was used to obtain both kinetic and spectrophotometric information on the intermediate in the reaction with dibasic 2-mercaptosuccinic acid ($\mathrm{H_3msa}$, thiomalic acid) under acidity conditions where it was possible to treat separately the formation and redox steps. Equilibrium data are consistent with bidentate chelate formation involving both oxygen- and sulphur-donor atoms.

In order to simplify the effects of hydrogen ion and to eliminate the possibility of six-membered ring structures which were considered in the case of 2-mercaptosuccinic acid, studies have been made on the series of monocarboxylic acids $\mathrm{HS{\cdot}C(X,Y){\cdot}CO_2H}$ (X,Y = H or Me) where five-membered chelate rings would be formed. Such a series also provides information on ligand-substituent effects which have been noted [10,11] in reactions of this type.

EXPERIMENTAL

Iron(III) perchlorate (Fluka, purum) was recrystallised from perchloric acid solution. Stock solutions were standardised by reduction of aliquot portions using a Jones reductor and subsequent $\mathrm{K[MnO_4]}$ titration. The hydrogen-ion content of such solutions was determined by titration with standard NaOH to pH 9, due allowance being made for the $\mathrm{Fe^{III}}$ present. Perchloric acid (B.D.H., AnalaR) and $\mathrm{Na[ClO_4]}$ (Fluka, Puriss p.a.) solutions were prepared and standardised as described previously.[13] Mercaptoacetic acid ($\mathrm{H_2maa}$, thioglycolic acid) (B.D.H., reagent grade) was distilled and stored under nitrogen but reaction rates obtained using both the original and purified material were identical within experimental error. 2-Mercaptopropionic acid ($\mathrm{H_2mpa}$, thiolactic acid) (Koch–Light, pure) and 2-mercapto-2-methylpropanoic acid ($\mathrm{H_2mmpa}$) (Koch–Light, pure) were stored in a nitrogen atmosphere and used without further purification. Stock solutions of mercaptocarboxylic acids were prepared immediately before use by dissolving a known weight of acid in $\mathrm{HClO_4}$–$\mathrm{Na[ClO_4]}$ solutions.

Kinetic measurements were made using a stopped-flow apparatus described previously.[14] Use of a Nova 1200 computer enabled evaluation of optical densities (D) at all points in the oscilloscope trace which was recorded using a Polaroid camera. In most instances, solutions were outgassed by freezing and melting under reduced pressure, but in other solutions where such precautions were not taken no effect of dissolved gases was detected.

RESULTS AND DISCUSSION

An excess of oxidant was used to ensure the formation of only 1 : 1 complexes, whilst high hydrogen-ion concentrations prevented hydrolysis and possible dimerisation of the $\mathrm{Fe^{III}}$ species.[15]

(a) *Characterisation of the Intermediates.*—The spectra of the intermediates (Figure 1) were obtained from D against time plots at wavelengths over the range 350—700 nm. The observed rate constants were wavelength independent and the forms of the spectra were identical over the $[\mathrm{H}^+]$ range employed. Kinetic measurements were made at the wavelengths of maximum absorbance of the complexes (Table 1).

Although at the upper end of the accessible acidity

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range the rate of complex formation greatly exceeded that of the redox step, at $[H^+] \leqslant 0.3$M interference from the electron-transfer reaction became important.* At $[H^+] \geqslant 0.4$M the data were consistent with equilibrium (1). Since there is no absorbance associated with either of the reactants in the wavelength range used in the study (λ *ca.* 600 nm), it may be shown [13] that equation (2) applies where $[Fe^{3+}]$ and [L] represent the total Fe^{III} and ligand concentrations respectively, $D_{max.}$ is the maximum absorbance observed in the reaction, ε the absorption coefficient, and l the optical path length. In this derivation it was assumed that $[L] = [FeL^+] + [H_2L]$, the concentration of anion being considered negligible. Under conditions of high $[H^+]$, $[FeL^+] \ll [H_2L]$. Graphical evaluation of equation (2) at various temperatures yielded both ε and K_1 values (Table 1). The values of ε quoted are the average values for all temperatures since any temperature variation was within experimental error. From these data it is apparent that the absorption coefficients at the wavelength maxima are markedly dependent on substituents X and Y. In the case of mercaptoacetic acid (H_2maa), where X = Y = H, little or no repulsion is expected between these atoms, whereas in H_2mmpa, where X = Y = Me, construction of a model indicates considerable interaction between the methyl groups leading to changes in the bond angles and some strain within the five-membered chelate ring. An intermediate value for H_2mpa indicates a larger interaction than in the case of H_2maa but much smaller than in the case of H_2mmpa and is similar to that for H_2msa (ε 350 l mol^{-1} cm^{-1}),[13] suggesting that the latter forms a five-membered ring complex with the group CH_2CO_2H as substituent.

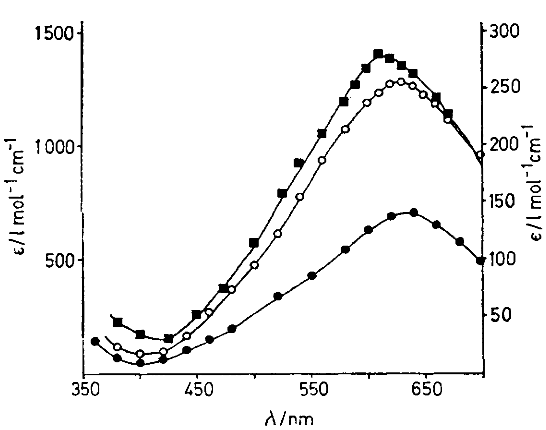
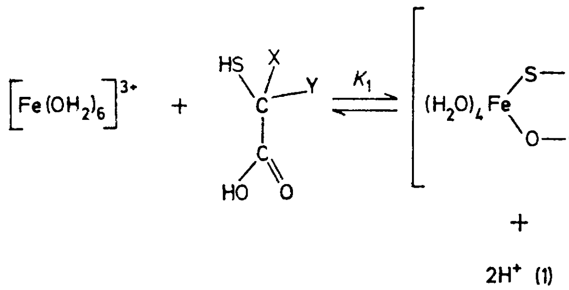


FIGURE 1 Spectra of intermediate complexes at $[Fe^{III}] = 10^{-2}$, $[Thiol] = 2 \times 10^{-3}$, $[H^+] = 0.4$, $I = 1.0$M, 20 °C, $l = 0.5$ cm: (■), H_2mmpa (left-hand ordinate); (○), H_2mpa; and (●), H_2maa



(1)

$$\frac{[Fe^{3+}][L]}{[H^+]^2 D_{max.}} = \frac{1}{\varepsilon l K_1} + \frac{1}{\varepsilon l} \cdot \frac{[Fe^{3+}] + [L]}{[H^+]^2} \qquad (2)$$

TABLE 1

Absorption coefficients and equilibrium constants [equations (1) and (2)] at $I = 1.00$M

Ligand	$\lambda_{max.}$/nm	ε/l mol^{-1} cm^{-1}	K_1/mol l^{-1} 10	15	20	25 °C
H_2maa	640 ± 5	140 ± 20	1.9 ± 0.2	2.2 ± 0.2	2.7 ± 0.2	
H_2mpa	630 ± 5	260 ± 30	0.99 ± 0.1	1.19 ± 0.1	1.31 ± 0.1	
H_2mmpa	615 ± 5	1 400 ± 100	0.28 ± 0.05	0.33 ± 0.05	0.35 ± 0.05	0.43 ± 0.05

(b) *Kinetics of Complex Formation*.—Initial-rate studies were undertaken to determine the order of reaction with respect to each component. The data were consistent with expression (3), and the results obtained at 20 °C are in Table 2.

$$\text{Initial rate} = \frac{k_{i.r.}[Fe^{3+}][HORSH]}{[H^+]} \qquad (3)$$

In the studies of the overall complex formation, rate data were derived from logarithmic plots which showed linearity to at least three half-lives. The following reaction scheme is consistent with the kinetic observations where the thiol is denoted as HORSH, the protons released on complex formation being derived from the sulphydryl and carboxyl groups as shown in equilibrium (1). Providing the protolytic reactions are

$$Fe^{3+} + HORSH \underset{k_2}{\overset{k_1}{\rightleftharpoons}} [Fe(ORS)]^+ + 2H^+;\ K_1 \qquad (4)$$

$$Fe^{3+} + {}^-ORSH \underset{k_4}{\overset{k_3}{\rightleftharpoons}} [Fe(ORS)]^+ + H^+;\ K_2 = K_1/K_a \qquad (5)$$

$$[Fe(OH)]^{2+} + HORSH \underset{k_{12}}{\overset{k_{11}}{\rightleftharpoons}} [Fe(ORS)]^+ + H^+;\ K_3 = K_1/K_h \qquad (6)$$

$$[Fe(OH)]^{2+} + {}^-ORSH \underset{k_{14}}{\overset{k_{13}}{\rightleftharpoons}} [Fe(ORS)]^+;\ K_4 = K_1/K_aK_h \qquad (7)$$

$$[Fe(OH_2)_6]^{3+} \rightleftharpoons [Fe(OH_2)_5OH]^{2+} + H^+;\ K_h \qquad (8)$$

$$HORSH \rightleftharpoons {}^-ORSH + H^+;\ K_a \qquad (9)$$

rapid, under conditions of excess of metal ion and constant $[H^+]$, the rate of complex formation may be described by equations (10)—(12) where $[Fe^{3+}]$ is the total Fe^{III} concentration.

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* 1M = 1 mol dm^{-3}, 1 cal = 4.184 J

TABLE 2

Initial rate data * and pseudo-first-order rate constants at 20 °C and I = 1.00M

$[H^+]$ / M	$[Fe^{3+}]$ / M	H_2maa / M	$k_{obs.}$ / s^{-1}	$k_{i.r.}$ * / l mol^{-1} s^{-1}	$[H_2mpa]$ / M	$k_{obs.}$ / s^{-1}	$k_{i.r.}$ * / l mol^{-1} s^{-1}	$[H_2mmpa]$ / M	$k_{obs.}$ / s^{-1}	$k_{i.r.}$ * / l mol^{-1} s^{-1}
0.3	0.01167	0.00256	6.76	34.8	0.00276	4.01	12.7	0.00220	1.61	1.79
	0.01750		7.43	32.3		4.43	14.2		1.85	2.00
	0.02333		9.03	36.0		5.01	15.0		1.69	1.80
	0.02918		10.66	37.5		5.10	13.5		1.86	1.86
	0.03500		11.12	40.1		5.69	15.7		1.82	1.85
	0.04667		12.01	35.1		6.64	16.7		2.01	1.99
	0.05835		15.98	43.7		7.44	17.0		2.03	1.91
0.4	0.01	0.00252	6.48	26.6	0.00261	4.02	12.3	0.00261	2.12	1.70
	0.015		7.34	28.3		4.12	11.8		2.22	1.81
	0.02		7.68	27.2		4.92	13.8		2.23	1.76
	0.025		8.24	27.6		4.94	13.1		2.28	1.83
	0.03		9.06	29.5		5.59	13.7		2.36	1.86
	0.04		10.20	29.7		6.54	16.2		2.34	1.80
	0.05		10.40	29.1		6.92	16.7		2.50	1.86
0.45	0.00917	0.00238	6.33	29.2	0.00289	5.03	13.3	0.00242	2.27	1.70
	0.01375		8.14	36.1		5.42	13.9		2.26	1.69
	0.01833		7.48	33.9		5.24	13.4		2.33	1.70
	0.02292		9.38	37.6		5.68	13.9		2.43	1.77
	0.02750		9.15	35.5		5.95	14.2		2.46	1.76
	0.03667		11.05	39.2		6.18	14.1		2.48	1.77
	0.04583		11.06	36.4		6.76	15.4		2.53	1.77
0.5	0.00833	0.00225	6.70	32.4	0.00226	4.98	16.5	0.00250	2.57	1.72
	0.01250		8.24	36.6		6.83	15.9		2.68	1.81
	0.01667		8.08	33.1		6.02	14.6		2.65	1.81
	0.02088		9.14	36.0		6.08	13.6		2.69	1.81
	0.0250		9.89	37.3		6.46	15.1		2.76	1.85
	0.03333		9.71	36.3		6.36	14.0		2.73	1.77
	0.04175		9.30	31.3		6.35	13.1		2.73	1.77
0.6	0.00667							0.00242	2.99	1.60
	0.01000								3.14	1.74
	0.01333								3.19	1.70
	0.01667								3.08	1.67
	0.02000								2.99	1.62
	0.02667								3.31	1.77
	0.03333								3.21	1.71
0.65	0.0058							0.00229	3.25	1.50
	0.0146								3.42	1.57
	0.0292								3.47	1.61
0.7	0.0050							0.00224	3.29	1.59
	0.0125								3.77	2.00
	0.0250								3.78	1.59

* $k_{i.r.}$ = (initial rate)$[H^+]/[Fe^{III}][HORSH]\varepsilon l$ where l = path length = 5 mm.

The observed rate constant, $k_{obs.}$, derived from the first-order rate expression (10) is thus seen to be of the form (13), and whilst, in general, plots of $k_{obs.}$ against $[Fe^{3+}]$ showed good linearity uncertainties in the gradients, k_α, did not allow a meaningful interpretation. The intercepts, k_β, were, however, derived to a greater degree of accuracy and used to determine the kinetic parameters with equation (12). Data for both these constants at the various temperatures studied are in Table 3.

$$d[Fe(ORS)^+]/dt = (k_\alpha[Fe^{3+}] + k_\beta)\{[Fe(ORS)^+]_\infty - [Fe(ORS)^+]_t\} \quad (10)$$

$$k_\alpha = \{k_2[H^+]^2 + (k_4 + k_{12})[H^+] + k_{14}\} K_1([H^+]^2 + K_a[H^+])^{-1} \quad (11)$$

$$k_\beta = k_2[H^+]^2 + (k_4 + k_{12})[H^+] + k_{14} \quad (12)$$

$$k_{obs.} = k_\alpha[Fe^{3+}] + k_\beta \quad (13)$$

Using equation (12) a quadratic dependence of k_β on $[H^+]$ would be expected, but, in fact, linear plots of k_β against $[H^+]$ were obtained, the data for H_2mmpa at 20 °C being shown in Figure 2. From this graph it may be seen that the intercept (k_{14}) is zero within experimental error and there is no apparent higher-order dependence on $[H^+]$. It would thus appear that the dissociation reactions proceed *via* (5) and (6) and in this respect complement the initial-rate studies where an

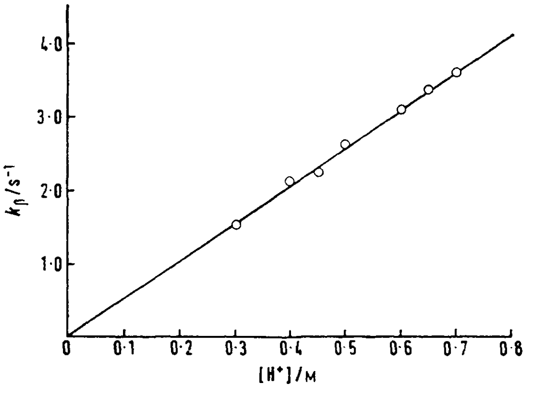

FIGURE 2 Plot of k_β against $[H^+]$ for H_2mmpa at $[Fe^{III}]$ = 5 × 10^{-3}—60 × 10^{-3}, $[H_2mmpa]$ = 2 × 10^{-3}, I = 1.0M, and 20 °C

anticipated $[H^+]^{-1}$ dependence was observed. In the case of the two other thiols, due to the lower absorption coefficients, optical densities were less well resolved at high $[H^+]$. Also greater interference from the subsequent redox reaction was experienced at low $[H^+]$ resulting in a systematic deviation from this linear behaviour. Based on the more reliable initial-rate data, together with the linearity of k_β with $[H^+]$ at higher hydrogen-ion concentrations, we chose, however, to describe the data for all three thiols using a similar mechanism.

TABLE 3

Variation of constants k_α and k_β with temperature *

Ligand	$[H^+]$/M	θ_c/°C	k_α/l mol^{-1} s^{-1}	k_β/s^{-1}
H_2maa	0.4	10	45.0 ± 6.0	2.00 ± 0.15
	0.45		45.2 ± 3.5	2.32 ± 0.10
	0.5		43.6 ± 1.7	2.49 ± 0.04
	0.4	15	71.9 ± 6.0	3.68 ± 0.15
	0.45		59.5 ± 6.5	4.16 ± 0.12
	0.5		49.8 ± 4.5	4.51 ± 0.18
	0.3	20	181 ± 22	4.71 ± 0.63
	0.4		124 ± 13	5.30 ± 0.35
	0.45		131 ± 15	5.82 ± 0.45
	0.5		92 ± 22	6.53 ± 0.55
H_2mpa	0.4	10	20.3 ± 2.5	1.43 ± 0.06
	0.45		13.8 ± 1.5	1.76 ± 0.04
	0.5		13.8 ± 1.8	1.92 ± 0.05
	0.4	15	29.9 ± 2.0	2.58 ± 0.05
	0.45		26.9 ± 2.0	2.82 ± 0.05
	0.5		18.9 ± 2.0	3.26 ± 0.05
	0.3	20	74.4 ± 4.0	3.15 ± 0.15
	0.4		70.2 ± 6.5	3.46 ± 0.20
	0.45		43.6 ± 3.5	4.66 ± 0.13
	0.5		27.8 ± 7.5	5.29 ± 0.20
H_2mmpa	0.3	10	2.2 ± 0.5	0.56 ± 0.02
	0.4		1.8 ± 0.8	0.79 ± 0.02
	0.5		2.2 ± 0.83	0.88 ± 0.01
	0.6		1.3 ± 1.0	1.21 ± 0.03
	0.3	15	4.6 ± 0.7	1.13 ± 0.02
	0.4		3.7 ± 0.7	1.26 ± 0.02
	0.5		2.9 ± 1.0	1.56 ± 0.03
	0.6		1.9 ± 2.0	2.00 ± 0.05
	0.3	20	8.6 ± 1.1	1.53 ± 0.04
	0.4		8.0 ± 0.8	2.10 ± 0.02
	0.45		7.3 ± 0.7	2.24 ± 0.02
	0.5		5.3 ± 0.9	2.60 ± 0.03
	0.6		4.5 ± 1.5	3.08 ± 0.03
	0.65		5.3 ± 4.0	3.34 ± 0.3
	0.7		3.7 ± 3.0	3.72 ± 0.2
	0.3	25	17.1 ± 2.0	3.04 ± 0.07
	0.4		10.3 ± 1.0	3.33 ± 0.03
	0.5		16.7 ± 1.2	3.95 ± 0.03
	0.6		7.5 ± 3.1	5.25 ± 0.07

* $[Fe^{III}] = 5 \times 10^{-3}$—$60 \times 10^{-3}$, [HORSH] = *ca.* 2×10^{-3}, $I = 1.00$M, and $\lambda = 610$—640 nm.

The gradients of plots of k_β against $[H^+]$ (Figure 2) yield the composite constant $(k_4 + k_{12})$, which indicates that complex formation may take place *via* two kinetically indistinguishable paths (5) and (6), *i.e.* by reaction of Fe^{3+} and $[Fe(OH)]^{2+}$ respectively. This problem has promoted considerable discussion [16,17] on the rates of Fe^{III} reactions, and where resolution has been possible the rates have been in accord with the water-exchange parameters for $[Fe(OH_2)_6]^{3+}$ (150) [18] and $[Fe(OH_2)_5OH]^{2+}$ (*ca.* 10^3—10^4 s^{-1}). Given a postulated rate constant of 10^3 l mol^{-1} s^{-1} for k_3 (the reaction between Fe^{3+} and $^{-}ORSH$), *viz.* an order of magnitude greater than that for water exchange, it may be shown using the equilibrium constant K_2 that k_4 will contribute at most only 4% to the composite rate constant $(k_4 + k_{12})$. The percentage would fall proportionately if the assumed rate constant was reduced to a value comparable to that found in other studies. This observation strongly suggests that the only contributing path to the formation reaction is (6) and the rate constants and thermodynamic parameters derived using this model are in Table 4. Further support for this line of reasoning is provided by the absence of any evidence of equilibrium (7) and by the fact that since the dissociation constants of the carboxylic acids in the ligands are *ca.* 10^{-4} mol l^{-1} (ref. 19) in the concentration range used (*ca.* 10^{-3}M) the amounts of dissociated acid present in solution will be very small indeed.

TABLE 4

Rate constants and activation parameters at 25 °C and $I = 1.00$M

Ligand	θ_c/°C	$(k_{12} + k_4)$/l mol^{-1} s^{-1}	10^3k_{11} [a]/l mol^{-1} s^{-1}	10^3k_{11} [b]/l mol^{-1} s^{-1}
H_2maa	10	5.05 ± 0.5	14.5 ± 1.5	15.6 ± 3
	15	9.10 ± 0.5	21.9 ± 2	20.8 ± 4
	20	13.0 ± 1.0	28.5 ± 3	27.6 ± 6
	25	22.4 ± 1.5	40.6 ± 4	
	$\Delta H^\ddagger$ [c]	15.0 ± 2	10.5 ± 2	11.3
	$\Delta S^\ddagger$ [d]	-2.2 ± 3	-2.1 ± 3	
H_2mpa	10	3.84 ± 0.5	5.75 ± 0.5	5.99 ± 1
	15	6.43 ± 0.5	8.33 ± 1.0	8.35 ± 2
	20	10.5 ± 1.0	11.2 ± 1.0	11.7 ± 2
	25	16.7 ± 1.5	15.6 ± 1.5	
	$\Delta H^\ddagger$ [c]	15.9 ± 2	10.3 ± 2	10.7
	$\Delta S^\ddagger$ [d]	$+0.5 \pm 3$	-4.7 ± 3	
H_2mmpa	10	1.89 ± 0.2	0.80 ± 0.05	0.85 ± 0.2
	15	3.18 ± 0.3	1.10 ± 0.10	1.07 ± 0.2
	20	5.15 ± 0.5	1.50 ± 0.15	1.43 ± 0.3
	25	8.35 ± 0.7	2.20 ± 0.20	2.02 ± 0.4
	$\Delta H^\ddagger$ [c]	16.0 ± 2	10.3 ± 2	9.2
	$\Delta S^\ddagger$ [d]	-0.8 ± 3	-8.7 ± 3	

[a] Derived from k_{12}, K_1, and K_h. [b] Derived from $k_{i.r.}$, ε, and K_h. [c] In kcal mol^{-1}. [d] In cal K^{-1} mol^{-1}.

The k_{11} values (Table 4) are close to that found for H_3msa (*ca.* 10^4 l mol^{-1} s^{-1}) [13] and lie within the limits suggested for reactions of $[Fe(OH)]^{2+}$ for a dissociative process.[16,20,21] There does, however, appear to be a regular trend of decreasing k_{11} with increasing methyl substitution and whilst some contribution from an associative mechanism cannot be excluded the composite nature of the constant k_{11} does not allow more meaningful interpretation. It has been suggested [16] that the rate-determining step in complex-formation reactions of Fe^{III} is dissociative loss of water from an outer-sphere complex as in (14) where $k_{11} = K_{o.s.}k_0$. The trend in

$$\mathrm{[Fe(OH_2)_5OH]^{2+} + HORSH} \overset{K_{o.s.}}{\rightleftharpoons} \mathrm{[HORSH, H_2OFe(OH_2)_4OH]^{2+}} \overset{k_0}{\rightleftharpoons} \mathrm{[(HORSH)Fe(OH_2)_4OH]^{2+} + H_2O} \quad (14)$$

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k_{11} could thus be attributed to either a change in k_0 or in $K_{o.s.}$. The similarity of the individual values of k_4 to those found in other reactions of $[Fe(OH_2)_5OH]^{2+}$ implies that the reaction proceeds by the dissociative mechanism and that the $K_{o.s.}$ term is the cratic factor in determining the trend with ligand structure.

(c) *Thermodynamic Parameters for Complex Formation.*—Values of ΔH_1 were obtained from temperature-dependence studies of equilibrium (1) from data measured at high $[H^+]$ treated using expression (2). Since values of K_a [19] and K_h [15] have been determined under the present experimental conditions, it is possible to evaluate the constants K_2, K_3, and K_4 and the corresponding thermodynamic parameters are in Table 5. The formation of the complexes is seen to be entropy controlled and while the reactions of $[Fe(OH)]^{2+}$ are exothermic those of Fe^{3+} are endothermic as was observed with the H_3msa analogue.[13] Activation parameters for the various rate constants were derived from an unweighted least-squares Arrhenius treatment. Data for all three ligands are consistent with the following Scheme where the initial hydrolysis interaction has an accompanying enthalpy change (ΔH_h) of 10 kcal mol^{-1}.[15]

TABLE 5

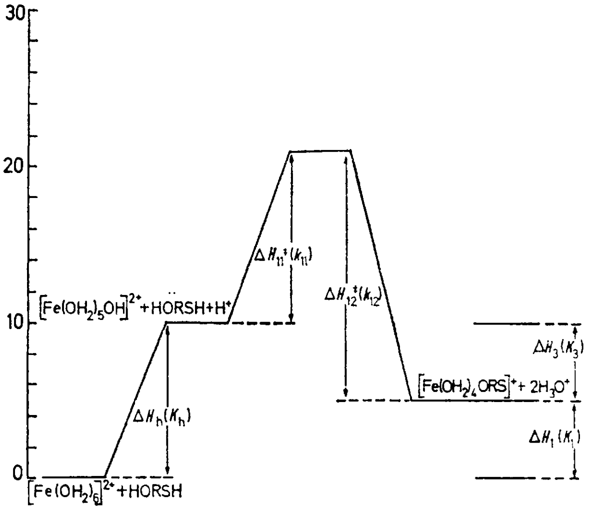
Equilibrium constants and associated thermodynamic parameters at 25 °C and I = 1.0M

Ligand	θ_c/°C	K_1/mol l^{-1}	10^3K_2	10^3K_3	10^6K_4/ l mol^{-1}
H_2maa	10	1.9 ± 0.2	14.0	2.9	21
	15	2.2 ± 0.2	13.6	2.4	15
	20	2.7 ± 0.2	14.7	2.2	12
	25	3.2 ± 0.2	16.0	2.0	10
	ΔH [a]	5.7 ± 2.0	3.5 ±3.0	−4.5 ±2.1	−6.9 ±3.0
	ΔS [b]	21.5 ± 5.0	31.1 ±20	0.5 ±5.1	−10.1 ±20
H_2mpa	10	0.99 ± 0.1	4.1	1.5	6.2
	15	1.19 ± 0.1	4.4	1.3	4.8
	20	1.31 ± 0.1	4.7	1.1	3.9
	25	1.48 ± 0.1	5.5	0.9	3.3
	ΔH [a]	4.6 ± 2.0	6.9 ±3.0	−5.6 ±2.1	−3.3 ±3.0
	ΔS [b]	16.2 ± 5.0	40.3 ±20	4.8 ±5.1	28.9 ±20
H_2mmpa	10	0.28 ± 0.05	2.2	0.42	3.3
	15	0.33 ± 0.05	2.6	0.36	2.8
	20	0.35 ± 0.05	2.8	0.28	2.3
	25	0.43 ± 0.05	3.5	0.26	2.1
	ΔH [a]	4.5 ± 2.0	5.7 ±3.0	−5.7 ±2.1	−4.5 ±3.0
	ΔS [b]	13.5 ± 5.0	36 ±20	7.5 ±5.1	29.6 ±20

[a] In kcal mol^{-1}. [b] In cal K^{-1} mol^{-1}.

By the arguments proposed above, use of equation (10) provides a value of k_{12} and hence $\Delta H_{12}^{\ddagger} = 16 \pm 2$ kcal mol^{-1}. Initial rate data at the various temperatures allow an independent evaluation of $\Delta H_{11}^{\ddagger} = 11 \pm 2$ kcal mol^{-1} and from this it is possible using the above reaction scheme to predict that ΔH_1 should have a value of 5 ± 3 kcal mol^{-1}. Thermodynamic parameters may be derived from the temperature dependence of the overall optical-density changes, equation (1), observed at $[H^+] >$ 0.4M, the experimental ΔH_1 being 5 ± 2 kcal mol^{-1}.

The fact that this treatment holds for all three thiol acids, with absorption coefficients and equilibrium constants varying by an order of magnitude, would appear to justify our treatment of all reactions by a single mechanism. The scheme also explains the exothermicity for the reaction of $[Fe(OH)]^{2+}$ compared to the endothermic Fe^{3+} complex formation as being derived from the inclusion of ΔH_h in the overall process. Thermodynamic parameters for the complex-formation reaction are similar in magnitude to those observed in other reactions of $[Fe(OH)]^{2+}$ with uncharged species.[21]



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(d) *Stereochemical Effects.*—Variations in k_{11} and K_1 with ligand structure show a similar trend. Consideration of the thermodynamic parameters implies a common source for this effect lending support to our conclusion that the variation in k_{11} may be attributed to the $K_{o.s.}$ term, since both inner- and outer-sphere complex formation may have similar steric requirements.

The results presented above provide a possible explanation for stereochemical effects in the reaction of 2-amino-3-mercapto-3-methylbutyric acid (penicillamine) with Fe^{III} where a ' marked kinetic stabilisation of the iron(III)–thiol chromophore as compared with the 2-amino-3-mercaptopropionic acid (cysteine) species ' [10] has been reported.[10,11] Rather than attributing this effect to the ' inhibition of oxidation-reduction reactions by the two β-methyl groups,' [11] we would suggest that the overall rate of oxidation is reduced by the destabilisation in free-energy terms of the intermediate species in a manner similar to that described for the complexes in this paper.

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