Metal-ion Oxidations in Solution. Part IX.[1] Characterisation of the Intermediate formed in the Oxidation of Thiomalic Acid by Iron(III) Ions

By **Keith J. Ellis** and **Alexander McAuley,*** Chemistry Department, The University of Glasgow, Glasgow G12 8QQ

A spectrophotometric stopped-flow study of the redox reaction between iron(III) ions and thiomalic acid (2-mercaptosuccinic acid) has shown the existence of a transient intermediate which is believed to be an iron(III) complex in which thiomalate acts as a bidentate chelate ligand. The visible absorption spectrum of this complex has a maximum at 610—620 nm, values of the absorption coefficient and equilibrium constant being 350 ± 20 l mol^{-1} cm^{-1} and 2·3 ± 0·2 mol l^{-1} respectively at 20 °C at I = 1·0M. Variation of the hydrogen-ion concentration has enabled the derivation of the approximate rate constants at 20 °C of 1 l mol^{-1} s^{-1} for complex formation between Fe^{3+} and thiomalic acid, and 10^4 and 10^6 l mol^{-1} s^{-1} for the reactions of $FeOH^{2+}$ with the undissociated and monodissociated ligand respectively. The proposed mechanism and derived values for the rate constants are consistent with the view that the rate-determining step involves loss of a water molecule co-ordinated to Fe^{III}. Thermodynamic data for the associated equilibria have been evaluated from temperature-dependence studies but the complexity of the rate law, and the limited range of conditions which could be studied without making allowance for the subsequent redox reaction, have not permitted the assignment of activation parameters to the rate data to be made.

PREVIOUS parts of this series have dealt with the mode of oxidation of organic substrates by metal ions [2-4] in aqueous solution and in many systems transient intermediates have been observed. In the case of some iron(III)-ion oxidations, it has been possible both to show that the intermediate is likely to be a metal ion–substrate complex, and to estimate physical properties such as formation constants and absorption coefficients.[5] A notable feature in the iron(III)-ion oxidations of sulphur-containing ligands is the rapid formation of blue-purple intermediates prior to the overall redox process, the kinetics of which are often complex.[6-10] While most of these intermediates exist for only a short time in aqueous solutions, the 'iron(III) thiol' chromophores of 3-mercaptovaline and *N*-(2-mercaptoethyl)-glycine are substantially more stable, and their rates of (redox) decomposition have recently been studied using conventional techniques.[11]

The reaction between iron(III) ions and thiomalic acid (2-mercaptosuccinic acid) is rapid and best studied by the stopped-flow technique. However, in order to evaluate spectrophotometrically the kinetic parameters involved in the consecutive transient formation and redox steps, it is essential to establish the nature of the intermediate present. In this paper we present, therefore, data on the characterisation of the blue transient complex.

EXPERIMENTAL

Iron(III) perchlorate was prepared from iron(III) nitrate (B.D.H., AnalaR) by thrice precipitating iron(III) hydroxide with aqueous NH_4OH, washing the hydroxide with large volumes of distilled water, and then redissolving it in perchloric acid. The iron(III) content in stock solutions, from which reactant solutions were prepared by accurate dilution, was determined by tin(II) chloride reduction and titration with $KMnO_4$. The more dilute iron(III) and iron(II) solutions (as encountered in the stoicheiometry determination) were analysed by iron(III) thiocyanate and $KMnO_4$ methods respectively. Appropriate allowance was made for the slow interaction between these reagents and thiomalic acid and its disulphide.

Stock $HClO_4$ solutions were standardised against disodium tetraborate, and the acid present in iron(III) solutions was determined by titrating to pH 9 with freshly prepared NaOH. Sodium perchlorate solutions, used to adjust the ionic strength of reactant solutions to 1·0M, were prepared from Fluka (puriss p.a.) reagent. Thiomalic acid (2-mercaptosuccinic acid) (99·0%) was used as obtained from Evans Chemetics, New York. Stock solutions were prepared by dissolving a known weight of the solid acid in perchloric acid–sodium perchlorate solutions.

Kinetic runs were carried out on a modified version of the stopped-flow apparatus described previously.[12] All points on the oscilloscope trace were converted to absolute optical density by comparison with a point (usually at $t = 0$) of known optical density.[5] Prior to use, all solutions were degassed thoroughly by freezing, evacuating on a vacuum line, and melting under reduced pressure. As well as preventing cavitation [13] in the mixing chamber, this reduced the concentration of dissolved oxygen to less than 10^{-6}M. Some experiments were also performed using the scale-expansion accessory on a Unicam SP 800 spectrophotometer as described previously.[14]

RESULTS AND DISCUSSION

Stoicheiometry.—The stoicheiometry of the overall reaction, as measured by the decrease in iron(III) concentration and the corresponding increase in iron(II) concentration under conditions of an excess of metal

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[1] Part VIII, A. McAuley, M. N. Malik, and J. Hill, *J. Chem. Soc.* (*A*), 1970, 2461.

[2] J. Hill and A. McAuley, *J. Chem. Soc.* (*A*), 1968, 2405.

[3] J. Hill, A. McAuley, and W. F. Pickering, *Chem. Comm.*, 1967, 573.

[4] W. F. Pickering and A. McAuley, *J. Chem. Soc.* (*A*), 1968, 1173.

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[6] F. P. Page, *Trans. Faraday Soc.*, 1960, **56**, 398.

[7] I. Baldea and G. Niac, *Proc. 9th Internat. Conf. Co-ordination Chem.*, St. Moritz, Switzerland, 1966, p. 272.

[8] A. McAuley, *Co-ordination Chem. Rev.*, 1970, **5**, 245.

[9] H. Lamfrom and S. O. Nielson, *J. Amer. Chem. Soc.*, 1957, **79**, 1966.

[10] D. L. Leussing and I. M. Kolthoff, *J. Amer. Chem. Soc.*, 1953, **75**, 3904.

[11] C. M. Bell, E. D. McKenzie, and J. Orton, *Inorg. Chim. Acta*, 1971, **5**, 109.

[12] J. Hill and A. McAuley, *J. Chem. Soc.* (*A*), 1968, 156.

[13] See 'Rapid Mixing and Sampling Techniques in Biochemistry,' eds. B. Chance, R. H. Eisenhardt, Q. H. Gibson, and K. K. Lonberg-Holm, Academic Press, 1964, pp. 41, 96.

[14] G. S. Laurence and K. J. Ellis, *J.C.S. Dalton*, 1972, 2229.

ion, showed that for each mole of thiomalic acid consumed 0·93 ± 0·05 mol of iron(III) were reduced. This is in reasonable agreement with reaction (1) (HRSH = thiomalic acid).

$$2Fe^{III} + 2HRSH \longrightarrow 2Fe^{II} + HRS\text{-}SRH \quad (1)$$

Spectrum of the Intermediate.—Preliminary experiments indicated that under conditions of high hydrogen-ion concentration, the rate of complex formation greatly exceeded that of the redox step, thus facilitating the measurement of the spectrum of the intermediate by the process described previously.[5] The spectrum is shown in Figure 1. At lower hydrogen-ion concentrations, although the rate of the redox step became significant, the spectrum as measured at any point in time showed no change.

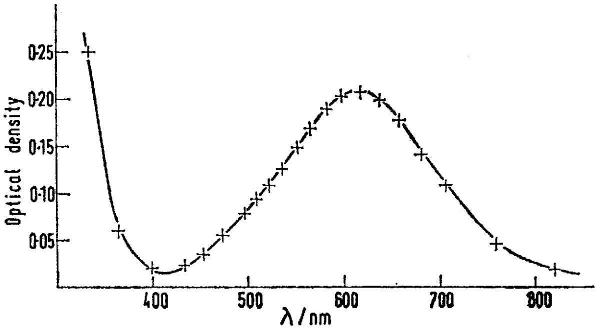

FIGURE 1 Spectrum of intermediate: [Fe^{3+}] = 0·042M; [HRSH] = 0·004M; [H$^+$] = 0·5M; I = 1·0M; 25 °C; l = 2 mm

Characterisation of the Intermediate: Equilibrium Constants and Absorption Coefficient.—Under the experimental conditions used ([H$^+$] > 0·3M), reaction profiles indicated that, at a wavelength of 610 nm, the maximum optical density reached (OD$_{max.}$) must correspond closely to the equilibrium conditions for complex formation. Using OD$_{max.}$ as a function of various metal-to-ligand ratios, it was possible to construct a Job's plot. The position of the maximum in this plot corresponded to the formation of a 1 : 1 complex between iron(III) and thiomalic acid, but the accuracy of the measurements did not preclude the possibility of some asymmetry which would indicate the presence of a 1 : 2 species at high ligand concentrations.[15,16] For this reason, it was decided to maintain an excess of metal ion in the present study.

TABLE 1

Calculated absorption coefficients and equilibrium constants for reaction (2): 20 °C; I = 1·0M; [HRSH] = 4 × 10^{-3}M; [Fe^{3+}] = 0·005—0·04M

[H$^+$] / M	ε / l mol^{-1} cm^{-1}	Equilibrium constant
0·3	344	7·62
0·4	350	5·78
0·5	392	5·00
0·6	380	3·83

Absorption coefficients and equilibrium constants calculated from equation (4)

t / °C	ε / l mol^{-1} cm^{-1}	K_1 / mol l^{-1}
10	343 ± 25	1·65 ± 0·2
14	355 ± 20	1·85 ± 0·2
20	350 ± 20	2·3 ± 0·2
25	366 ± 22	2·55 ± 0·2

For the equilibrium (2), where a, b, and c represent

$$Fe^{3+} + HRSH \rightleftharpoons [(HRS)Fe]^{2+} + H^+ \quad (2)$$

the initial metal, ligand, and hydrogen-ion concentrations, the absorption coefficient ε and the equilibrium constant may be derived from a linear plot of ab/cOD$_{max.}$ against $(a + b)/c$, providing [(HRS)Fe]$^{2+}$ is the only species contributing to the light absorption. Data at various hydrogen-ion concentrations and constant temperature (20 °C) are shown in Table 1, and it is readily seen that, while the calculated absorption coefficient is independent of the hydrogen-ion concentration, the equilibrium constant shows a [H$^+$]$^{-1}$ dependence. This indicates that equation (2) is not a true representation of the system, but on replacing it by equation (3), which is

$$Fe^{3+} + HRSH \rightleftharpoons [Fe(SR)]^+ + 2H^+ \quad (3)$$

consistent with chelate formation, the linear relation becomes (4), where l = optical path length. When

$$\frac{ab}{c^2OD_{max.}} = \frac{1}{\varepsilon l K_1} + \left(\frac{1}{\varepsilon l}\cdot\frac{a+b}{c^2}\right) \quad (4)$$

plotted according to equation (4), all the data at 20 °C were found to be incorporated in a single line (Figure 2) from which the ε and K_1 values were found to be 350 ± 20 l mol^{-1} cm^{-1} and 2·3 ± 0·2 mol l^{-1} respectively. Similar results were obtained at temperatures of 10, 14, and 25 °C and the derived values of K_1 and ε are presented in Table 1.

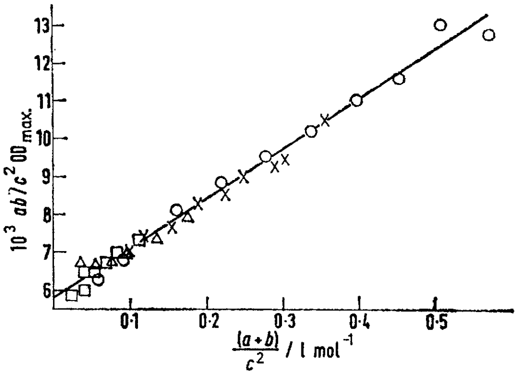

FIGURE 2 Plot for the determination of ε and K at 20 °C, [HRSH] = 0·004M, and [Fe^{3+}] = 5 × 10^{-3}—5 × 10^{-2}M. [H$^+$] = 0·3 (○), 0·5 (△), 0·4 (×), and 0·6M (□)

Kinetic Measurements.—To establish the reaction order with respect to the metal-ion, ligand, and hydrogen-ion concentrations, initial-rate studies were undertaken on the intermediate formation. The data in Figure 3 indicate that the rate of complex formation is dependent on both metal-ion and ligand concentrations to the first

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[15] W. C. Vosburgh and G. R. Cooper, *J. Amer. Chem. Soc.*, 1941, **63**, 437.

[16] R. L. Moore and R. C. Anderson, *J. Amer. Chem. Soc.*, 1945, **67**, 167.

power only, but that there is a non-linear dependence on hydrogen-ion concentration. The overall kinetics may be adequately represented by the following reaction scheme {$[Fe(RS)]^+$ denotes bidentate attachment}. It is recognised that reactions of further hydrolysed species of iron(III) and the di- and tri-dissociated thiomalic acid have not been included, but under the conditions employed, the concentrations of such species are negligible.[17]

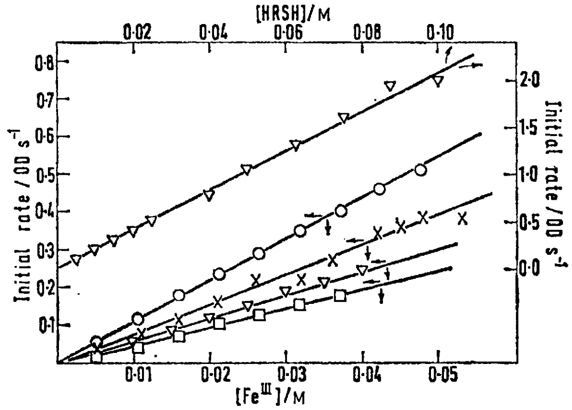

FIGURE 3 Initial-rate data at various acidities: upper and right-hand ordinates refer to ligand dependence, with $[Fe^{3+}] = 0{\cdot}02$M, lower and left-hand ordinates refer to metal-ion dependence, with $[HRSH] = 0{\cdot}004$M. $[H^+] = 0{\cdot}3$ (○), 0·5 (▽), 0·4 (×), and 0·6M (□)

$$Fe^{3+} + HRSH \underset{k_2}{\overset{k_1}{\rightleftharpoons}} [Fe(SR)]^+ + 2H^+ \quad K_1 \qquad (5)$$

$$Fe^{3+} + HRS^- \underset{k_4}{\overset{k_3}{\rightleftharpoons}} [Fe(SR)]^+ + H^+ \quad K_2 = K_1/K_A \qquad (6)$$

$$[Fe(OH)]^{2+} + HRSH \underset{k_{12}}{\overset{k_{11}}{\rightleftharpoons}} [Fe(SR)]^+ + H^+ \quad K_3 = K_1/K_h \qquad (7)$$

$$[Fe(OH)]^{2+} + HRS^- \underset{k_{14}}{\overset{k_{13}}{\rightleftharpoons}} [Fe(SR)]^+ \quad K_4 = K_1/K_hK_A \qquad (8)$$

$$[Fe(H_2O)_6]^{3+} \overset{K_h}{\rightleftharpoons} [Fe(OH)]^{2+} + H^+ \qquad (9)$$

$$HRSH \overset{K_A}{\rightleftharpoons} H^+ + HRS^- \qquad (10)$$

Providing the protolytic reactions are sufficiently fast, the electron-transfer step sufficiently slow, and an excess of iron(III) is maintained, the rate of formation of complex may be described as in equation (11). That

$$d[Fe(SR)^+]/dt = (k_a[Fe^{3+}] + k_b)\{[Fe(SR)^+]_{eq} - [Fe(SR)^+]\} \qquad (11)$$

where $k_a =$

$$\frac{K_1}{[H^+]^2 + K_A[H^+]}\{k_2[H^+]^2 + (k_4 + k_{12})[H^+] + k_{14}\}$$
$$\simeq k_1 + (k_3K_A + k_{11}K_h)/[H^+] + k_{13}K_hK_A/[H^+]^2$$

and $k_b = k_2[H^+]^2 + (k_4 + k_{12})[H^+] + k_{14}$

is, the pseudo-first-order rate constant k_{obs} is of the form (12) and, at constant acidity, a linear variation of

$$k_{obs} = k_a[Fe^{III}] + k_b \qquad (12)$$

k_{obs} with $[Fe^{III}]$ would be expected. All kinetic runs showed good linearity of first-order plots to at least 90% completion of reaction and, at each hydrogen-ion concentration studied, the data were in accord with equation (12). Some measured values of k_{obs}, and the derived values of k_a and k_b at each temperature and hydrogen-ion concentration, are listed in Table 2.

TABLE 2

Kinetic data and derived k_a and k_b values: $I = 1{\cdot}0$M; $[HRSH] = 2{\cdot}0 \times 10^{-3}$—$4{\cdot}0 \times 10^{-3}$M

$10^2[Fe^{III}]$ / M	$[H^+]$ / M	k_{obs} / s^{-1}	$10^2[Fe^{III}]$ / M	$[H^+]$ / M	k_{obs} / s^{-1}
10 °C					
0·98	0·40	0·90	1·53	0·45	1·02
1·12	0·40	0·89	1·12	0·45	1·02
1·96	0·40	1·05	1·84	0·45	1·07
2·45	0·40	1·14	2·45	0·45	1·22
2·45	0·40	1·19	1·68	0·50	1·09
4·09	0·40	1·31	2·51	0·50	1·19
3·35	0·50	1·31	0·72	0·50	0·97
4·19	0·50	1·39			
14 °C					
0·98	0·30	1·27	1·74	0·45	1·57
1·96	0·30	1·60	1·57	0·45	1·56
2·45	0·30	1·70	2·45	0·45	1·74
2·94	0·30	1·82	1·68	0·50	1·59
3·92	0·30	2·04	2·51	0·50	1·73
0·98	0·40	1·35	2·93	0·50	1·84
1·96	0·40	1·61	3·35	0·50	1·92
2·45	0·40	1·71	3·77	0·50	2·00
2·93	0·40	1·78	1·84	0·50	1·67
3·92	0·40	2·07	2·25	0·50	1·70
0·88	0·45	1·45	1·40	0·60	1·77
1·12	0·45	1·48	2·01	0·60	1·95
1·30	0·45	1·52	2·34	0·60	1·92
2·00	0·60	1·92	1·33	0·60	1·81
3·35	0·60	2·13			
20 °C					
0·53	0·30	2·03	0·50	0·50	2·73
1·06	0·30	2·33	1·00	0·50	2·85
1·58	0·30	2·60	1·50	0·50	3·00
2·11	0·30	2·93	2·00	0·50	3·06
2·64	0·30	3·26	2·50	0·50	3·38
3·17	0·30	3·48	3·00	0·50	3·43
3·70	0·30	3·57	3·50	0·50	3·64
4·75	0·30	4·23	4·00	0·50	3·80
0·53	0·40	2·26	0·53	0·60	2·93
1·06	0·40	2·52	1·06	0·60	3·13
1·58	0·40	2·68	1·58	0·60	3·29
2·11	0·40	3·03	2·11	0·60	3·41
2·64	0·40	3·17	3·17	0·60	3·71
3·60	0·40	3·63	3·70	0·60	3·94
4·45	0·40	3·91			
5·28	0·40	4·20			
25 °C					
0·98	0·30	3·59	1·68	0·50	4·78
1·96	0·30	4·72	1·53	0·50	4·65
2·45	0·30	4·98	2·25	0·50	5·15
2·94	0·30	5·50	2·93	0·50	5·46
3·92	0·30	6·28	3·35	0·50	5·58
0·98	0·40	3·90	3·77	0·50	5·91
1·96	0·40	4·54	1·33	0·60	5·01
2·45	0·40	5·01	2·00	0·60	5·33
0·71	0·40	3·62	1·40	0·60	4·95
1·12	0·40	4·02	2·33	0·60	5·56
1·74	0·40	4·45	2·01	0·60	5·25
2·94	0·40	5·44	2·68	0·60	5·66
3·92	0·40	6·12	3·01	0·60	6·00
			3·35	0·60	6·09

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[17] A. McAuley and K. J. Ellis, unpublished work.

TABLE 2 (*Continued*)

t/°C	$[H^+]$/M	k_a/l mol^{-1} s^{-1}	k_b/s^{-1}
10	0·4	13·8 ± 1·4	0·76 ± 0·04
10	0·45	15·6 ± 1·5	0·81 ± 0·03
10	0·50	12·6 ± 1·8	0·88 ± 0·05
14	0·30	25·8 ± 4·0	1·05 ± 0·10
14	0·40	23·9 ± 4·8	1·12 ± 0·13
14	0·45	19·6 ± 2·1	1·25 ± 0·11
14	0·50	19·0 ± 3·1	1·29 ± 0·08
14	0·60	17·0 ± 4·1	1·57 ± 0·09
20	0·30	51 ± 6	1·81 ± 0·1
20	0·40	41 ± 4	2·08 ± 0·1
20	0·50	33 ± 3	2·50 ± 0·1
20	0·60	28 ± 3	2·82 ± 0·1
25	0·30	90 ± 14	2·80 ± 0·4
25	0·40	77 ± 6	3·11 ± 0·13
25	0·50	53 ± 11	3·88 ± 0·3
25	0·60	54 ± 7	4·24 ± 0·2

Rearrangement of the terms k_a and k_b yields expression (13). Since K_A is much less than $[H^+]$ under the

$$\frac{k_a}{k_b} = \frac{K_1}{[H^+]^2 + K_A[H^+]} \qquad (13)$$

experimental conditions used, a plot of k_a/k_b against $[H^+]^{-2}$ should yield an approximate value of K_1. Although the errors inherent in the term k_a/k_b are large, at 20 °C, for example, a reasonable linear plot was obtained with a least-squares gradient of 2·5 ± 0·3 mol l^{-1}, and a small positive intercept, the significance of which is not readily apparent. It is considered that the agreement between this value of K_1 (derived kinetically) and that obtained using steady-state measurements helps further to substantiate the proposed mechanism.

Although we cannot unambiguously assign rate constants to the individual reactions, it is possible to show that the proposed mechanism is valid, and to make an estimate of the rate constants. If only reaction (5) is considered operative, there should be a simple acidity dependence of both k_{obs} and the initial rate; this is not found experimentally. Since K_h and K_A are approximately equal,[17] one cannot include only $[Fe(OH)]^{2+}$, but must also consider HRS^- in the reaction scheme, and it is the interaction of these species which leads to not just one, but two additional acid-dependent terms. Plots of k_a, k_b, and initial rates against functions of $[H^+]^x$ (where x is integral) all indicate that a distinction cannot be made between, for example, an $[H^+]$ or $[H^+]^2$ dependence, and that expressions for k_a and k_b of the forms given in equation (11) must all be included in order to adequately describe the system.

As mentioned previously, the interference of the redox step in the overall reaction limited an accurate study of the complex formation to a relatively small $[H^+]$ range and this, coupled with the experimental uncertainties in k_a and k_b, did not permit us to obtain unique values for the individual constants by solving simultaneous equations. For the same reasons, solution by a quadratic regression procedure did not yield reliably unique values. However, both the algebraic treatment, and plots of k_b against $[H^+]$ and $[H^+]^2$, indicated that at 20 °C, for example, k_{14} must have a value of 0·8 ± 0·3 s^{-1}, which yields a value of *ca.* 1·5 × 10^6 s^{-1} for k_{13}. Similarly, graphical representations yielded values of *ca.* 1·0 l mol^{-1} s^{-1} and *ca.* 10 s^{-1} for the terms k_1 and $(k_3K_A + k_{11}K_h)$ respectively.

Although reactions (6) and (7) are kinetically indistinguishable, it has been suggested[18] that for most reactions involving iron(III), the rate of reaction is primarily controlled by the elimination of a co-ordinated water molecule, and that $k_{11} > k_3$. Providing this is correct, then k_{11} must have a value of *ca.* 10^4 l mol^{-1} s^{-1}, a figure which fits in well with the limits suggested by Moorhead and Sutin[18] of 3 × 10^3—3 × 10^5 l mol^{-1} s^{-1}. A value of the order of unity for k_1 compares quite favourably also with values at 25 °C of 5 ± 3 l mol^{-1} s^{-1} for hydroxy(phenyl)acetic acid,[19] 4·0 l mol^{-1} s^{-1} for HN_3,[20] and 11·4 l mol^{-1} s^{-1} for HF,[20] and likewise a value of k_{13} somewhat larger than k_{11} is in accord with the negatively charged HRS^- ion assisting in the removal of the first water molecule from the metal ion, a trend which would appear to be shown in the case of sulphate, and perhaps, azide ion.[20]

It will be noted that no attempt has been made to calculate activation parameters from the available data. Although the increase of both k_a and k_b with temperature corresponds to an activation energy of *ca.* 10 kcal mol^{-1}, the accuracy with which one can assign values to the individual rate constants (k_1, k_2, *etc.*) is insufficient to allow any meaningful results to be obtained. It is hoped that a further study of the redox step might permit calculation of k_a and k_b over a much wider range of hydrogen-ion concentration (*i.e.* by making due allowance for the redox reaction instead of neglecting it), and the subsequent more accurate determination of individual rate constants and activation parameters.

TABLE 3

Equilibrium constants and thermodynamic parameters, I = 1·0M

t/°C	K_1/mol l^{-1}	$10^{-3}K_2$	$10^{-3}K_3$	$10^{-6}K_4$/l mol^{-1}
10	1·65 ± 0·2	1·75	2·54	2·70
14	1·85 ± 0·2	1·90	2·18	2·22
20	2·3 ± 0·2	2·48	1·92	2·07
25	2·55 ± 0·2	2·79	1·55	1·70
$-\Delta G$/kcal mol^{-1}	0·55 ± 0·05	4·7 ± 0·2	4·4 ± 0·2	8·5 ± 0·3
ΔH/kcal mol^{-1}	5·1 ± 1·4	5·1 ± 1·5	−5·0 ± 1·5	−4·8 ± 1·4
ΔS/cal K^{-1} mol^{-1}	20 ± 5	33 ± 10	−2·5 ± 5	12 ± 5

Thermodynamic Parameters for the Equilibrium Constants.—Since the values of K_A[17] and K_h[21] already have been determined under the present experimental conditions, appropriate values of K_2, K_3, and K_4 [associated with equations (5)—(8)] could be readily evaluated, and from the temperature dependences, the thermodynamic parameters were obtained (Table 3). The formation of

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[18] E. B. Moorhead and N. Sutin, *Inorg. Chem.*, 1966, **5**, 1866.

[19] A. D. Gilmour and A. McAuley, *J. Chem. Soc.* (*A*), 1969, 2345.

[20] F. Accascina, F. Cavasino, and S. D'Alessandro, *J. Phys. Chem.*, 1967, **71**, 2474.

[21] R. M. Milburn, *J. Amer. Chem. Soc.*, 1957, **79**, 537.

complexes by reaction of the Fe^{3+} ion is an endothermic process, the larger equilibrium constant for K_2 resulting from an entropy effect. Complexes involving $[Fe(OH)]^{2+}$, however, are formed in exothermic reactions with smaller associated entropies. To our knowledge, there are no other thermodynamic data as yet available for this type of iron–sulphur bonded system with which to make comparisons.

Proposed Structure of the Iron(III) *Thiomalate Complex.*—Reaction of iron(III) with malic acid yields a yellow complex in solution as opposed to the blue thiomalic acid complex. The difference between the malate and thiomalate complexes must be due in some way to the presence of the SH instead of the OH group, and we feel that it is because of the direct involvement of the mercapto-groups in complexation rather than an indirect electronic effect on the carboxy-groups. It has been suggested previously that iron(III) thiol complexes in aqueous solution exhibit a blue-purple colour,[6,8,11] and further evidence for this is shown by the observation [22] that in the presence of silver(I) ions (which are believed to bind preferentially to the thiol group) [23] the reaction between Fe^{III} and thiomalic acid becomes very slow, does not appear to involve a redox step, and leads to a rather complex mixture of products. The other point of attachment of the ligand, which must then be one of the carboxy-group oxygen atoms, is at present uncertain. Structural models suggest that it might be the terminal carboxy-group furthermost from the mercapto-group, even though this gives a six-membered ring, while, in general, a five-membered ring would be considered to be more stable.

Thus, formation of the thiomalate complex agrees with all of our experimental observations and, despite our not being able to say whether sulphur or oxygen atom attachment occurs first, the overall kinetics support the view that the loss of the first water molecule co-ordinated to Fe^{III} is the rate-determining step in the formation of the iron(III) monothiomalate complex, and that the loss of the second water molecule, so as to allow bidentate attachment, is much more rapid. This is similar to the effect noted in the case of some monodentate ligands, where substitution on the monosubstituted complex is faster than on the hydrated metal ion.[24]

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