Evidence for Contribution of Intermediate Steps to the Limiting Rate in Iron(III) Monomandelate † Complex Formation

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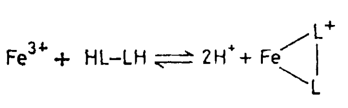
The temperature-jump and stopped-flow methods have been used to study the kinetics of the chelation of iron(III) with mandelic acid at 25.0 °C and ionic strength 1.0 mol dm^{-3} over the acidity range $0.0200 \leqslant [H^+] \leqslant 0.900$ mol dm^{-3}. The observed dependence of the overall forward rate constant on [H$^+$] suggests that only the reaction between the Fe(OH)$^{2+}$ ion and the neutral ligand (HL–LH) contributes significantly to the iron(III) chelate formation and that this reaction occurs through the formation of the intermediate protonated monodentate complex [Fe(OH)(L–LH)]$^+$. At the lowest acidities examined the rate-determining step is the release of the first co-ordinated water molecule, while at high acidities ([H$^+$] > 1.0 mol dm^{-3}) the slow step is the deprotonation of the intermediate monodentate complex. Over the acidity range covered in the present study both steps contribute to the limiting rate in the overall chelate-formation process.

OUR previous temperature-jump kinetic studies [1,2] on the formation of six-membered chelate complexes of iron(III) with various mono- and di-substituted malonic acids showed that two reactions contribute significantly to the complex formation under the experimental conditions used, *i.e.* the reactions of the Fe(OH)$^{2+}$ ion with the neutral and monoanionic ligands. The reactions involving the neutral ligands were found to occur by a ' normal ' dissociative mechanism, the rate constants being similar to those observed for analogous reactions. When the monoanions were the reacting species, the reactions involving the most basic diethylmalonate and cyclopropane-1,1-dicarboxylate monoanions were found to be appreciably slower than those of the remaining malonate ions examined. Two possible mechanisms were then discussed [2] to account for these findings.

In the light of the observed effects of the structural changes of the bidentate ligands on the kinetics and the mechanism of iron(III) chelate formation, we are continuing this type of kinetic investigation using other chelating agents. In the present paper, we report the kinetic data obtained at 25.0 °C and I = 1.0 mol dm^{-3} for the complexation reaction of iron(III) with mandelic acid (hydroxyphenylacetic acid) in aqueous solution. According to equilibrium studies [3] concerning the iron(III)–mandelic acid system in aqueous acidic media, this hydroxyacid (HL–LH) acts as a bidentate ligand forming with iron(III) a five-membered monochelate complex as shown in reaction (1). The same conclusion on the chelation process (1) was recently drawn [4] for the reactions of iron(III) with some other α-hydroxycarboxylic acids. In a previous investigation,[5] mandelic acid was considered as a monoprotic ligand.



K_c (1)

The kinetics were initially followed by the temperature-jump relaxation technique over a wide acidity range ($0.020 \leqslant [H^+] \leqslant 0.900$ mol dm^{-3}). Since the experimental data indicated a kinetic trend different from that observed previously by the stopped-flow method for analogous reactions involving α-hydroxyacids,[4] in order to ascertain the reliability of the kinetic data obtained, stopped-flow measurements were also performed under similar experimental conditions. As it will be seen in what follows, the results obtained by the two techniques are in good agreement, thus providing strong support for the reaction mechanism discussed later.

EXPERIMENTAL

Mandelic acid (Fluka) was recrystallized from water. The purity of the hydroxyacid was checked by its melting point. Stock solutions of iron(III) perchlorate, sodium perchlorate (supporting electrolyte), and perchloric acid were prepared as described elsewhere.[1,2] The solutions of ligand were prepared by weight before use.

TABLE 1

Kinetic data obtained by the temperature-jump method[a] (25.0 °C, I = 1.0 mol dm^{-3})

10^2 [H$^+$]/ mol dm^{-3}	10^3 [Fe]$_T$^{b}/ mol dm^{-3}	10^3 [HL–LH]$_T$^{b}/ mol dm^{-3}	10^2D^c/ mol dm^{-3}	10^{-1} k_f^{d} dm^3 mol^{-1} s^{-1}	10^{-1} k_f (calc.)/ dm^3 mol^{-1} s^{-1}
2.00	1.70	35.0	3.34	56	59
2.25	2.20	35.0	3.45	53	52
2.66	2.30	35.0	3.66	41	43
3.50	2.50	30.0	3.67	31	32
4.00	2.00	40.0	4.90	25.5	27.3
5.00	2.00	30.0	4.64	20.3	21.0
6.00	2.00	40.0	6.40	17.4	16.8
7.00	2.00	40.0	7.31	14.7	13.9
10.0	2.00	40.0	10.8	9.3	8.8
15.0	2.50	60.0	21.3	5.2	5.0
20.0	2.50	50.0	32.0	3.6	3.3
30.0	3.00	60.0	66.4	1.75	1.78
40.0	3.00	60.0	113	1.12	1.12
50.0	3.50	60.0	173	0.78	0.77
60.0	3.50	70.0	247	0.52	0.56
80.0	4.00	70.0	434	0.35	0.34
90.0	4.50	80.0	549	0.27	0.27

[a] K_c = 0.15 mol dm^{-3} (ref. 3); K_{OH} = 1.63 × 10^{-3} mol dm^{-3} (R. M. Milburn, *J. Am. Chem. Soc.*, 1957, **79**, 537); K_a = 6.76 × 10^{-4} mol dm^{-3} (A. E. Martell and R. M. Smith, ' Critical Stability Constants,' Plenum Press, New York, 1977, p. 47). [b] Total molar concentration. [c] From equation (6). [d] From equation (5). [e] Calculated by using equation (12).

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† Hydroxyphenylacetate.

Kinetic measurements were performed at 25.0 °C and ionic strength 1.0 mol dm^{-3} with the temperature-jump apparatus and the Durrum stopped-flow spectrophotometer (D-130) used in previous studies [1,2,6] and adopting the same procedure. Stopped-flow measurements were carried out at the wavelength of 350 nm with an excess of ligand ($[Fe^{3+}]_T = 5.00 \times 10^{-4}$ mol dm^{-3}). Owing to the decrease in amplitude of the absorbance change with increasing acidity of the solutions, the maximum acidity used (0.700 mol dm^{-3}) was slightly smaller than that employed in the temperature-jump experiments (0.900 mol dm^{-3}). The observed pseudo-first-order rate constants $k_{obs.}$ were obtained from the linear plots of $\ln(A_{\infty} - A)$ against time (A = absorbance). The observed rate constant $k_{obs.}$ was found to be affected by the ligand concentration only at acidities $\leqslant$ 0.330 mol dm^{-3}. For each solution examined, three determinations were made and the values of $k_{obs.}$ were reproducible within $\pm 3\%$.

Temperature-jump measurements were carried out in the wavelength range 360—400 nm. The relaxation times for the various solutions were determined from at least four photographs of the oscilloscope traces and were affected by an uncertainty of *ca.* $\pm 6\%$. All calculations were made with the help of computer programs run on an HP 9835A.

RESULTS AND DISCUSSION

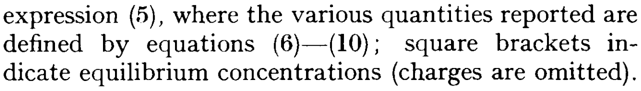
The experimental data obtained in the temperature-jump experiments and the values of the equilibrium constants K_c [reaction (1)], K_{OH} [reaction (2)], and K_a [reaction (3)] at 25.0 °C and ionic strength 1.0 mol dm^{-3} are collected in Table 1.

According to the main equilibria (1)—(3) existing in the solutions under study, the formation of the iron(III)

$$Fe^{3+} \rightleftharpoons Fe(OH)^{2+} + H^+ \qquad K_{OH} \qquad (2)$$

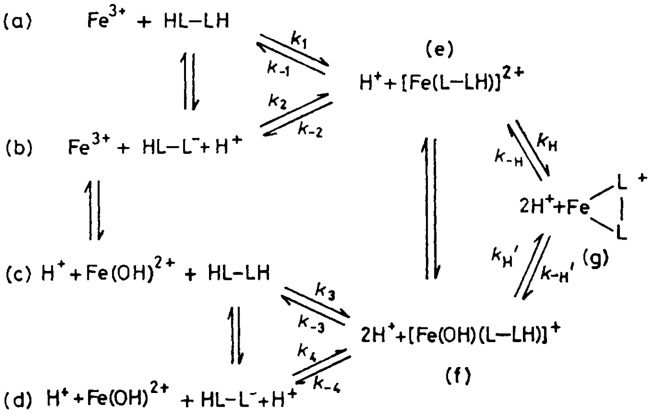
$$HL{-}LH \rightleftharpoons HL{-}L^- + H^+ \qquad K_a \qquad (3)$$

monochelate may be considered to occur, in the most general case, through the four reactions shown in the Scheme, that is the reactions of the ions Fe^{3+} and $Fe(OH)^{2+}$ with the anionic ligand ($HL{-}L^-$) and its conjugate acid ($HL{-}LH$). In the Scheme, co-ordinated water molecules are omitted for simplicity and the species $[Fe(L{-}LH)]^{2+}$ and $[Fe(OH)(L{-}LH)]^+$ represent monodentate complexes. The protolytic reactions (vertical steps) can be assumed to be very fast compared with the complexation reactions and the intermediate species can be considered to be in a steady state. Moreover, step (f)→(g) might be written alternatively as (4).



$$[Fe(OH)(L{-}LH)]^+ \rightleftharpoons H^+ + Fe(OH)\!\left<\begin{matrix}L\\ |\\ L\end{matrix}\right. \xrightleftharpoons{\text{fast}} Fe\!\left<\begin{matrix}L\\ |\\ L\end{matrix}\right.^{+} \qquad (4)$$

Examining now the temperature-jump data, under the experimental conditions used the relaxation time (τ) can be related to the rate constants for complex formation by expression (5), where the various quantities reported are defined by equations (6)—(10); square brackets indicate equilibrium concentrations (charges are omitted). The quantity $1/\tau D$ represents the overall forward rate constant k_f such as it is usually given in the stopped-flow experiments. It should be noted that expression (5) is different from that derived previously for the reactions of iron(III) with substituted malonic acids,[1,2] because in the present case the second dissociation of the acid ligand is insignificant and intermediate steps have been also taken into account.



SCHEME

$$\frac{1}{\tau D} = k_f = \frac{a + b/[H^+]}{c[H^+] + d} + \frac{p/[H^+] + q/[H^+]^2}{r[H^+] + s} \qquad (5)$$

$$D = \frac{[Fe]\beta}{1 + \beta} + \frac{[HL{-}LH]}{1 + \alpha} + \frac{A}{K_c} \qquad (6)$$

$$\alpha = \frac{K_{OH}(K_a + [H] + [HL{-}L]) + [Fe(OH)](K_a + 2[H])}{[H](K_a + [H] + [HL{-}L]) - K_{OH}[Fe]} \qquad (7)$$

$$\beta = \frac{[H]\{K_{OH} + [H] + [Fe(OH)]\} - K_a[HL{-}LH]}{K_a\{K_{OH} + [H] + [Fe(OH)]\} + [HL{-}L](K_{OH} + 2[H])} \qquad (8)$$

$$A = \frac{2[\overline{Fe(L{-}L)}][H](1 + 2\beta + \alpha\beta)}{(1 + \alpha)(1 + \beta)} + [H]^2 \qquad (9)$$

$$\left.\begin{aligned} &a = k_1k_H;\ b = k_2k_HK_a;\ c = k_{-1};\ d = k_{-2} + k_H \\ &p = k_3k_H'K_{OH};\ q = k_4k_H'K_{OH}K_a;\ r = k_{-3};\ s = k_{-4} + k_H' \end{aligned}\right\} \qquad (10)$$

The experimental data of Table 1 indicate that the overall forward rate constant k_f ($= 1/\tau D$) is not related in a simple manner to the hydrogen-ion concentration over the whole acidity range investigated, that is it does not show any direct proportionality neither to $1/[H^+]$ nor to $1/[H^+]^2$. In a previous study [4] of analogous reactions involving some α-hydroxyacids, a linear trend was obtained in every case by plotting k_f against $1/[H^+]$ over the acidity range examined ($0.010 \leqslant [H^+] \leqslant 0.10$ mol dm^{-3}). The intercepts of these plots were considered to be insignificant. However, we calculate from the kinetic data of that study that at least for lactic and benzilic acids the intercepts are indeed negative, taking values of -21 ± 15 and -65 ± 8, respectively. If we consider now the temperature-jump kinetic data, it is possible to see from Figure 1 that the plot of k_f against $1/[H^+]$ yields a curved trend, which is more evident at high acidities. A straight line can be however drawn through the experimental points in the acidity range 0.1—0.02 mol dm^{-3},

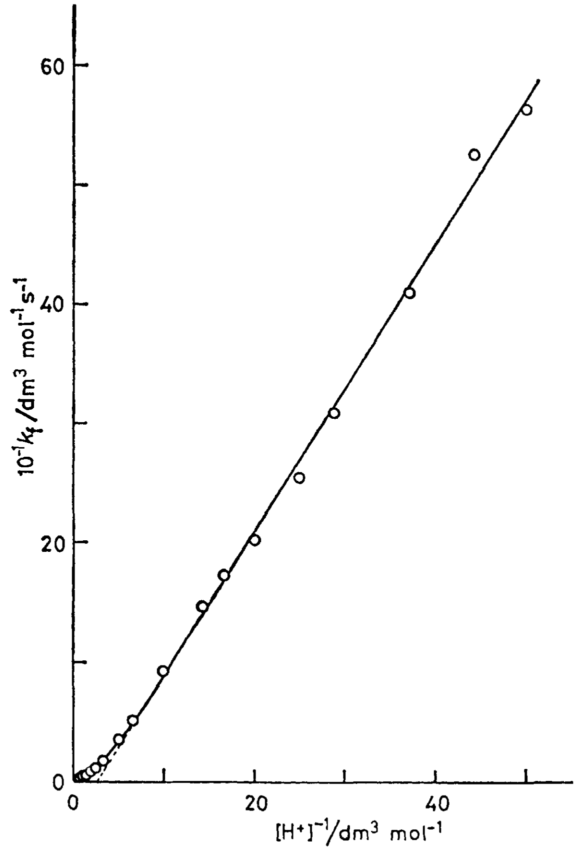


FIGURE 1 Plot of k_f against $1/[H^+]$ using temperature-jump data

yielding the intercept = -31 ± 10. These findings indicate that the linear portion of the plots of k_f against $1/[H^+]$ must be a particular case of a rate law more complex than that derived previously.[4] According to equation (5), where the contribution of intermediate steps is taken into account, a linear trend between k_f and $1/[H^+]$ can be obtained for the cases when $c[H^+] \ll d$, $r[H^+] \ll s$, and $q/[H^+]^2 \ll p/[H^+]$. Moreover, equation (5) reduces to the expression reported in the previous study[4] if the *a priori* assumption is made that $k_H \gg k_{-2}$ and $k_H' \gg k_{-4}$.

In order to obtain support for the reliability of the above experimental data and then, of the observed curved trend in the plot of k_f against $1/[H^+]$, we performed stopped-flow measurements over the acidity range 0.020—0.700 mol dm^{-3} (see Experimental section). The kinetic data, obtained using an excess of ligand, are summarized in Table 2. Under these experimental conditions, the observed pseudo-first-order rate constant $k_{obs.}$ is related to the overall forward rate constant by equation (11), where $[HL\text{–}LH]_T$ represents the total molar concentration of the ligand. It can be easily seen from the data of Table 2 that the plot of k_f, estimated by equation (11), against $1/[H^+]$ shows a

$$k_{obs.}/\{[HL\text{–}LH]_T[H^+]/([H^+] + K_{OH}) + [H^+]^2/K_c\} = k_f \quad (11)$$

curved trend equal to that observed with the temperature-jump data. In the acidity range 0.1—0.02 mol dm^{-3} the rate constant k_f can be considered to be a linear function of $1/[H^+]$ with an intercept -33 ± 17. Therefore these findings, in spite of the different experimental technique used and the completely different expression derived for the evaluation of k_f, are in excellent agreement with the temperature-jump data and, consequently, confirm the observed dependence of k_f on the hydrogen-ion concentration.

TABLE 2

Kinetic data obtained by the stopped-flow method[a] (25.0 °C, I = 1.0 mol dm^{-3})

10^2 $[H^+]$/ mol dm^{-3}	10^2 $[HL\text{–}LH]_T$[b]/ mol dm^{-3}	Number of experiments	10^{-1} k_f[c]/ dm^3 mol^{-1} s^{-1}	10^{-1} k_f (calc.)/[d] dm^3 mol^{-1} s^{-1}
2.00	1.00	1	51	52
2.50	1.00—4.00	3	42 [e]	41
3.00	2.00	1	29.5	33.7
4.00	2.00	1	25.5	24.4
5.00	2.00—4.00	3	17.7 [e]	18.8
7.50	1.00—4.00	3	10.6 [e]	11.5
10.0	1.00—7.50	3	8.4 [e]	8.0
13.0	5.00	1	6.2	5.7
16.0	5.00	1	4.0	4.3
20.0	7.50	1	3.20	3.10
23.0	10.0	1	2.57	2.51
33.0	2.50—10.0	3	1.49 [e]	1.45
40.0	10.0	1	1.08	1.06
50.0	2.50—10.0	3	0.73 [e]	0.74
70.0	10.0	1	0.40	0.41

[a] Equilibrium constants K_c, K_{OH}, and K_a as in Table 1. [b] Total molar concentration. [c] From equation (11). [d] Calculated by using equation (14). [e] Mean value.

It remains now to explain the observed trend in k_f by by means of equation (5). Several types of possible plots have been drawn in an attempt to evaluate the rate constants. The final plots, which can reasonably explain the acid dependence of k_f, are shown in Figures 2 and 3. A straight line (Figure 2) is obtained by plotting $1/k_f[H^+]$ against $[H^+]$ according to equation (12) with correlation coefficient 0.996 9 and standard deviation 8.64×10^{-3}. Moreover, when the quantity $k_f[H^+]^2$ is plotted against $[H^+]$ a curved trend is obtained with zero intercept (Figure 3), and with $k_f[H^+]^2$ increasing less

$$1/k_f[H^+] = I + G[H^+] = 7.7 \times 10^{-2} + 36.8 \times 10^{-2}[H^+] \quad (12)$$

$$k_f[H^+]^2 = ([H^+]/I)/(1 + G[H^+]/I) = 13.0[H^+]/(1 + 4.8[H^+]) \quad (13)$$

rapidly than as directly proportional to $[H^+]$ and tending to become independent of the hydrogen-ion concentration at high acidities. This trend is in accordance with equation (12). In fact this equation can be rearranged, yielding equation (13). We can see from Figure 3 that the curve drawn in the plot, obtained using the latter equation, fits well the experimental points. Equation (12) [or (13)] has been also used to calculate the overall forward rate constant k_f(calc.) for the various solutions examined and the agreement between the values of k_f and those of k_f(calc.) is very satisfactory (Table 1).

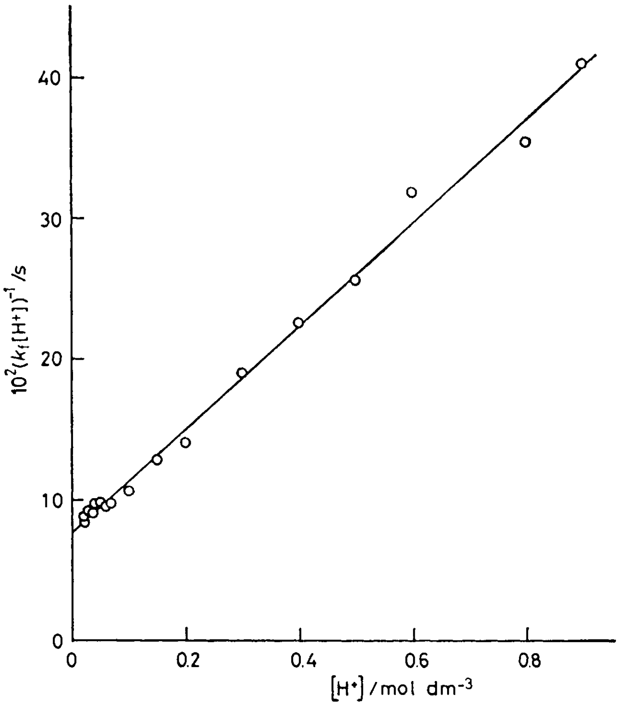


FIGURE 2 Plot of $1/k_f[H^+]$ against $[H^+]$ according to equation (12) and using temperature-jump data

As to the stopped-flow data, the trends of the plots of $1/k_f[H^+]$ and of $k_f[H^+]^2$ against $[H^+]$ are equal to those seen above. The corresponding equations which fit the experimental data in the present case are (14) and (15), and the values of k_f(calc.) are reported in Table 2. The results obtained with the two techniques are in excellent agreement.

$$1/k_f[H^+] = 8.8 \times 10^{-2} + 37 \times 10^{-2}[H^+] \quad (14)$$

$$k_f[H^+]^2 = 11.4[H^+]/(1 + 4.2[H^+]) \quad (15)$$

According to equation (13) [or (15)], an approximately linear dependence of k_f on $1/[H^+]$ may be observed at $[H^+] < 0.1$ mol dm^{-3}, that is when the term 4.8 $[H^+]$ (or 4.2 $[H^+]$) becomes small with respect to unity, as it was shown above.

It can be easily seen that equation (5) reduces to the expression (12) or (13) found experimentally, either when we consider the limiting case $(a + b/[H^+])/(c[H^+] + d) \gg (p/[H^+] + q/[H^+]^2)/(r[H^+] + s)$ with $a \ll b/[H^+]$ or when we assume the opposite limiting case $(p/[H^+] + q/[H^+]^2)/(r[H^+] + s) \gg (a + b/[H^+])/(c[H^+] + d)$ with $q/[H^+]^2 \ll p/[H^+]$. According to these two extreme possible cases, the use of equations (10) and of the estimated values given in equation (13) yields (16) and (17) or (18) and (19), respectively.

$$\frac{b}{d} = \frac{k_2 k_H K_a}{k_{-2} + k_H} = \frac{1}{I} = 13.0 \text{ s}^{-1} \quad (16)$$

$$\frac{c}{d} = \frac{k_{-1}}{k_{-2} + k_H} = \frac{G}{I} = 4.8 \text{ dm}^3 \text{ mol}^{-1} \quad (17)$$

$$\frac{p}{s} = \frac{k_3 k_H' K_{OH}}{k_{-4} + k_H'} = \frac{1}{I} = 13.0 \text{ s}^{-1} \quad (18)$$

$$\frac{r}{s} = \frac{k_{-3}}{k_{-4} + k_H'} = \frac{G}{I} = 4.8 \text{ dm}^3 \text{ mol}^{-1} \quad (19)$$

In order to establish which of the two terms of equation (5) may be neglected with respect to the other, we have to follow an indirect approach based on the use of the known values of the rate constants for analogous reactions. Then, if the first case occurs and consequently $k_2 k_H K_a/(k_{-2} + k_H)$ can be set equal to 13.0 s^{-1} [equation (16)], bearing in mind that the ratio $k_H/(k_{-2} + k_H) \leqslant 1$ (its magnitude depending on whether $k_H \ll k_{-2}$ or $k_H \gg k_{-2}$ respectively), we obtain that $k_2 \geqslant 1.92 \times 10^4$ dm^3 mol^{-1} s^{-1} ($K_a = 6.76 \times 10^{-4}$ mol dm^{-3}; see Table 1). This rate constant appears to be unreasonably larger than those obtained for analogous reactions.[1,2,4,7] On the other hand, if we consider the second limiting case [equation (18)], remembering that $k_H'/(k_{-4} + k_H') \leqslant 1$, the minimum k_3 value estimated ($k_3 \geqslant 8.0 \times 10^3$ dm^3 mol^{-1} s^{-1}) is similar to those found for the rate constants of analogous reactions involving $Fe(OH)^{2+}$ ion and many neutral mono- and bi-dentate ligands of different nature.[1,2,4,7] Moreover, since the value of 8.0×10^3 dm^3 mol^{-1} s^{-1} lies near the upper limit of the range of the values reported for similar rate constants, we can infer not only that the dominant term of equation (5) is $(p/[H^+])/(r[H^+] + s)$, but also that $k_H' \gg k_{-4}$ and, consequently, that equation (18) reduces to $k_3 K_{OH}$. Therefore the final conclusion is that only the route (c) ⟶ (f) ⟶ (g) contributes significantly to the formation of the iron(III) monochelate examined under the acidity range covered. Furthermore, the estimated k_3 value suggests that the step (c) ⟶ (f) occurs by a 'normal' dissociative mechanism.

Bearing in mind that $k_H' \gg k_{-4}$, equation (19) reduces to k_{-3}/k_H'. Using the estimated values of k_3 and k_{-3}/k_H', we evaluate that $k_3 k_H'/k_{-3} = k_H' K_3 = 1.7 \times 10^3$ s^{-1}. Since $K_{OH} K_3 K_H' = K_c$, we can calculate that $k_{-H}' = 18$ s^{-1}. All the rate constants estimated in this work using both the temperature-jump and stopped-flow experimental data are assembled in Table 3. As we have already noted above, the two different techniques yield values of rate constants in excellent agreement.

An interesting result of the present work is the evaluation of the ratio k_{-3}/k_H', which allows us to establish the contribution of the two steps (c) ⟶ (f) and (f) ⟶ (g) to the limiting rate in the overall chelate-formation process. According to the present findings, the rate equation (5) reduces simply to equation (20). It can be then deduced that at the lowest acidities studied the

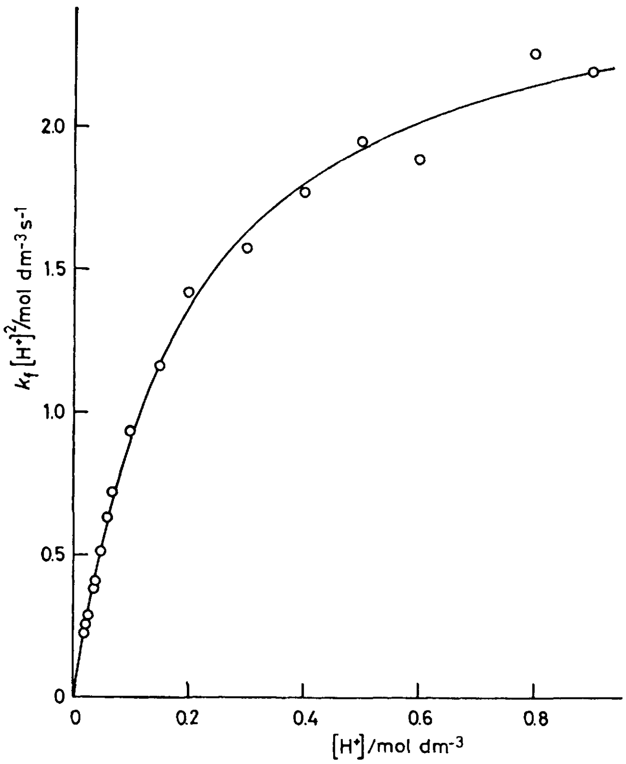


FIGURE 3 Plot of $k_f[H^+]^2$ against [H$^+$] according to equation (13) and using temperature-jump data

term $k_{-3}[H^+]$ becomes negligible with respect to k_H', the

$$k_f = \frac{k_3 k_H' K_{OH}/[H^+]}{k_{-3}[H^+] + k_H'} \qquad (20)$$

rate-limiting step of the overall process is (c) → (f) and, in particular (as described above), is the release of the first water molecule co-ordinated to the metal ion (' normal ' substitution). On the contrary, at high acidities ([H$^+$] > 1.0 mol dm^{-3}), $k_{-3}[H^+] \gg k_H'$, equation (20) becomes equal to $k_H' K_3 K_{OH}/[H^+]^2$, and then the step (f) → (g) is the rate-determining one. Under the acidity range covered in the present work, both steps contribute to the limiting rate in the overall chelate-formation process. As far as we know, this is the first case involving iron(III) monochelates in which the experimental data have provided evidence for the contribution of two consecutive intermediate steps to the overall process rate.

The step (f) → (g) is a composite one because it involves the closure of the chelate ring and an intramolecular proton transfer [in the case of the alternative reaction (4) the proton transfer implies the solvent as proton acceptor]. Whether these two processes occur in two successive steps or simultaneously can not be established. According to Mentasti,[4] since iron(III) can be shown to have a larger affinity for carboxylic than for alcoholic groups, the first metal–oxygen bonding [step (c) → (f)] takes place through the carboxylic group, while the chelate-ring closure involves the alcoholic oxygen. The formation of the second metal–oxygen bond labilizes the alcoholic proton which is subsequently released. Whatever the actual course of the chelate-ring closure and the proton-transfer processes, we deem that, owing to the very high basicity of the alcoholic oxygen, the relatively low rate of the step (f) → (g) [or of the first step of reaction (4)] has to be ascribed to the proton-transfer process. Low rates of deprotonation of intermediate monodentate protonated complexes were also suggested before in the case of nickel(II) and iron(III) chelates with some substituted malonic acids.[2,8]

TABLE 3

Rate constants obtained by temperature-jump and stopped-flow methods (25.0 °C, I = 1.0 mol dm^{-3})

	Temp.-jump	Stopped-flow
$10^2\ I^a$/s	7.7 ± 0.3	8.8 ± 0.3
$10^2\ G^a$/s dm^3 mol^{-1}	36.8 ± 0.7	37 ± 1
$k_3 K_{OH}{}^b$/s^{-1}	13.0 ± 0.5	11.4 ± 0.4
$10^{-3}\ k_3$/dm^3 mol^{-1} s^{-1}	8.0 ± 0.3	7.0 ± 0.2
$k_{-3}/k_H'^c$/dm^3 mol^{-1}	4.8 ± 0.2	4.2 ± 0.2
$10^{-3}\ k_H' K_3$/s^{-1}	1.7 ± 0.1	1.7 ± 0.1
$10^{-1}\ k_{-H}'$/s^{-1}	1.8 ± 0.1	1.8 ± 0.1

[a] From equation (12) or equation (14). [b] From equation (18), with $k_H' \gg k_{-4}$ (see text). [c] From equation (19), with $k_H' \gg k_{-4}$ (see text).

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