Kinetics of Reaction of Iron(III) Ions with Ethylenediaminetetra-acetic and Carboxymethyliminobis(ethylenenitrilo)tetra-acetic (Diethylenetriaminepenta-acetic) Acids in Aqueous Perchloric Acid Solution

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The kinetics of reaction of iron(III) ions with ethylenediaminetetra-acetic (H_4edta) and carboxymethyliminobis(ethylenenitrilo)tetra-acetic acids (diethylenetriaminepenta-acetic, H_5dtpa) have been studied in aqueous acid solution ($[HClO_4] = 0{\cdot}200$—$0{\cdot}010$M) with a stopped-flow technique, at ionic strength 1·0M and different temperatures. The reactions are first order with respect to both reactants, and the pH dependence of the rate of reaction indicates that complex formation takes place between the ion $[Fe(H_2O)_5OH]^{2+}$ and two differently protonated species of each ligand. The rate-determining step is a release of a water molecule from the co-ordination sphere of the metal ion. Rate constants obtained are discussed in terms of different apparent charges and statistical possibilities for co-ordination of the ligand species, and it is concluded that chelate-ring closure is not rate determining. An estimate of the equilibrium constant of the reaction $H_6dtpa^+ \rightleftharpoons H_5dtpa + H^+$ has been obtained from kinetic data; $K = (4{\cdot}0 \pm 0{\cdot}6) \times 10^{-2}$ mol l^{-1} at 25·0 °C.

THE kinetics of iron(III) complex formation have recently been the subject of a number of papers.[1] These support the dissociation mechanism postulated by Eigen;[2] *i.e.* the rate-determining step is essentially loss of a water molecule co-ordinated to the metal ion. Nevertheless the chelate-ring-closure has been found to be rate determining in some Co^{II},[3a] Mn^{II},[3a] and Ni^{II} complexes.[3b,c] It therefore was of interest to in-

[1] (*a*) G. Saini and E. Mentasti, *Inorg. Chim. Acta*, 1970, **4**, 210; (*b*) *ibid.*, p. 585; (*c*) F. P. Cavasino and E. Di Dio, *J. Chem. Soc.* (*A*), 1971, 3176; (*d*) E. Mentasti and E. Pelizzetti, *J.C.S. Dalton*, 1973, 2605.

[2] M. Eigen in 'Advances in the Chemistry of the Co-ordination Compounds,' ed. S. Kirschner, Macmillan, New York, 1961, p. 373.

[3] (*a*) K. Kustin, R. F. Pasternack, and E. M. Weinstock, *J. Amer. Chem. Soc.*, 1966, **88**, 4610; (*b*) H. Hoffmann, *Ber. Bunsengesellschaft Phys. Chem.*, 1969, **73**, 432; (*c*) G. Calvaruso, F. P. Cavasino, and E. Di Dio, *J.C.S. Dalton*, 1972, 2632.

vestigate the complex-formation kinetics of Fe^{III} ions with ethylenediaminetetra-acetic (H_4edta) and carboxymethyliminobis(ethylenenitrilo)tetra-acetic (H_5dtpa) acids, in order to compare their behaviour with a previous study on iminodiacetic (H_2ida) and nitrilotriacetic (H_3nta) acids.[4]

EXPERIMENTAL

Perchloric acid and sodium perchlorate (C. Erba RP) were used for adjusting the hydrogen-ion concentration and ionic strength ($I = 1{\cdot}0$M). Iron(III) perchlorate (C. Erba R), recrystallized from perchloric acid, was used to prepare an acid stock solution of iron(III) perchlorate, as previously described.[1d] The disodium salt of H_4edta (C. Erba RP) and carboxymethyliminobis(ethylenenitrilo)-tetra-acetic acid (Merck p.a.) were used without further purification. Doubly distilled water was employed throughout the study.

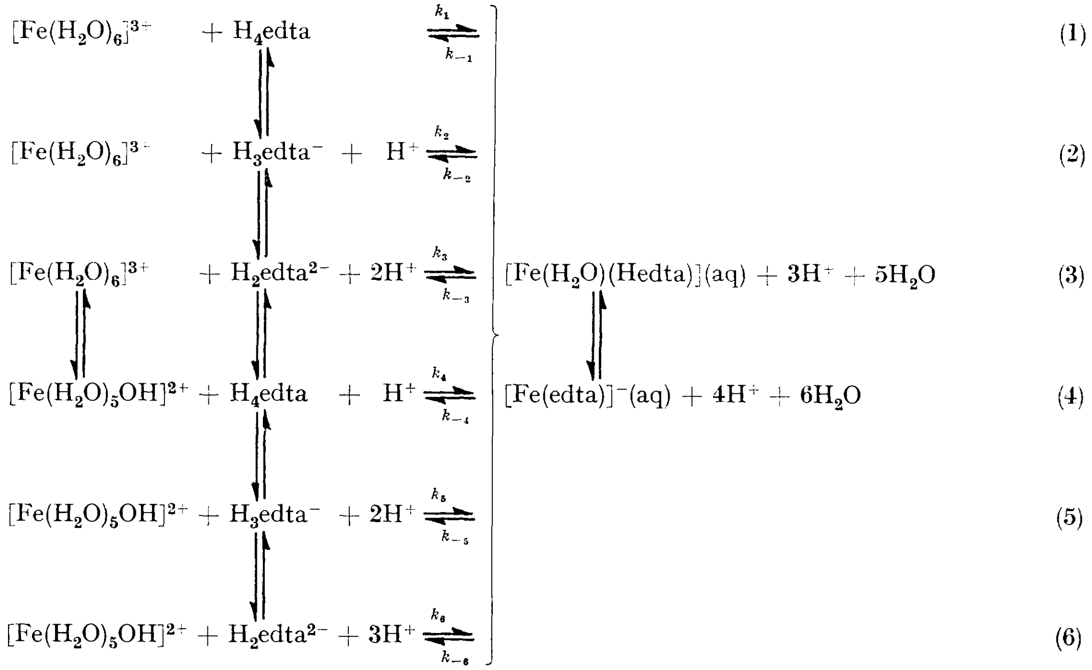
Kinetic runs were carried out on a Durrum–Gibson stopped-flow spectrophotometer, equipped with a 564 Tektronix storage oscilloscope; stored traces were photographed when at least triplicate measurements had been made. pH Measurements were made with a Metrohm potentiometer (E 388) equipped with glass and saturated-calomel (NaCl saturated bridge) electrodes.

Procedure.—Kinetic runs were carried at 15·0, 25·0, and 35·0 °C for $Fe^{III} + H_4edta$ and at 25·0 °C for $Fe^{III} + H_5dtpa$. The reactions were followed at 330 nm (H_4edta) and 350 nm (H_5dtpa). At these wavelengths the uncoordinated ligands contributed negligibly to the measured absorbance; the same holds for iron(III) ions, at the concentrations and $[H^+]$ investigated, whereas the products of reaction exhibited significant absorption.

Hydrogen-ion concentrations ranged from 0·200 to 0·010M for H_5dtpa, whereas no kinetic runs with H_4edta were made at greater than 0·050M owing to the low solubility of the ligand. In the range of concentrations of Fe^{III} (*ca.* 10^{-4}M) and hydrogen ions used, the presence, in appreciable concentration, of hydrolysed species of the metal ion higher than $[FeOH]^{2+}$(aq) can be ruled out; K_{OH}, the equilibrium constant for $[FeOH]^{2+}$(aq) formation, has been computed, at the temperatures investigated, from data of Milburn[5] ($K_{OH} = 1{\cdot}65 \times 10^{-3}$ mol l^{-1} and $\Delta H = 10{\cdot}2$ kcal mol^{-1} at 25 °C and $I = 1{\cdot}0$M).* The dissociation constants, K_i, of H_6edta^{2+} ($H_iedta^{(i-4)+} \rightleftharpoons H_{i-1}edta^{(i-5)+} + H^+$) have been assumed[6] to be $pK_6 = -0{\cdot}12$, $pK_5 = 1{\cdot}4$, $pK_4 = 2{\cdot}2$, $pK_3 = 2{\cdot}3$, and $pK_2 = 6{\cdot}28$ at 20 °C, $I = 1{\cdot}0$M, and 15—35 °C and those of H_8dtpa^{3+} ($pK_5 = 2{\cdot}5$, $pK_4 = 2{\cdot}5$, and $pK_3 = 4{\cdot}19$ at 20 °C and $I = 1{\cdot}0$M)[6] have been assumed to hold at 25·0 °C.† These approximations do not significantly affect the kinetic results since the effect of temperature on the above equilibria is negligible compared with that on rates of reaction. No data are available in the literature for the deprotonation constants K_6, K_7, and K_8 of carboxymethyliminobis(ethylenenitrilo)tetra-acetic acid; H_7dtpa^{2+} and H_8dtpa^{3+} species were assumed to be present in very low concentration, and a value of K_6 was derived from the kinetic data (as described below).

RESULTS AND DISCUSSION

$Fe^{III} + H_4edta$ *Reaction*.—According to equilibria existing in aqueous acid solutions containing H_4edta and Fe^{III} ions,[7] the following reaction scheme can be written,



where vertical protolytic reactions are assumed to be at equilibrium since they are very fast compared with

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* 1 cal = 4·184 J.

† The abbreviations H_6edta^{2+} and H_8dtpa^{3+} represent fully protonated forms of the acids in which all carboxylato-groups and N atoms are protonated.

[4] E. Mentasti, E. Pellizzetti, and G. Saini, *Gazzetta*, 1974, **104**, 201.

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

[6] G. Anderegg, *Helv. Chim. Acta*, 1967, **50**, 2333.

[7] L. G. Sillén and A. E. Martell in 'Stability Constants of Metal-ion Complexes,' Special Publ. Nos. 17 (1964) and 25 (1971), The Chemical Society, London; M. T. Beck in 'Chemistry of Complex Equilibria,' Van Nostran, London, 1970, p. 145.

complex-formation reactions. Taking into account the mass-balance equation for the metal ion, that the ligand is in excess, and that the pH does not change appreciably during the reaction, the integrated expression (7) can be derived from the scheme. Here c_{edta} is the stoicheiometric concentration of ligand and $\alpha_{\mathrm{H_4edta}}$ is the fraction of ligand present in the form $\mathrm{H_4edta}$.

$$\ln\,[c_{\mathrm{eq}}/(c_{\mathrm{eq}} - c_t)] = k_{\mathrm{obs}}\,.\,t \qquad (7)$$

where

$$c = [\mathrm{Fe(Hedta)}] + [\mathrm{Fe(edta)}^-]$$

and

$$k_{\mathrm{obs}} = \left(k_1 + k_2\frac{K_4}{[\mathrm{H^+}]} + k_3\frac{K_4K_3}{[\mathrm{H^+}]^2} + k_4\frac{K_{\mathrm{OH}}}{[\mathrm{H^+}]} + k_5\frac{K_{\mathrm{OH}}K_4}{[\mathrm{H^+}]^2} + k_6\frac{K_{\mathrm{OH}}K_4K_3}{[\mathrm{H^+}]^3}\right)$$

$$\left(\frac{[\mathrm{H_4edta}]_{\mathrm{eq}}\,.\,[\mathrm{Fe^{3+}}]_{\mathrm{eq}}}{c_{\mathrm{eq}}} + c_{\mathrm{edta}}\,.\,\alpha_{\mathrm{H_4edta}}\,.\,\frac{[\mathrm{H^+}]}{[\mathrm{H^+}] + K_{\mathrm{OH}}}\right)$$

Plotting $\ln[A_{\mathrm{eq}}/(A_{\mathrm{eq}} - A_t)]$ as a function of time (A_{eq} and A_t are absorbances at equilibrium and at time t), straight lines were obtained and from the gradients values for k_{obs} were derived (Table 1). This procedure is correct if the molar absorption coefficients of the complexes $[\mathrm{Fe(Hedta)}]$(aq) and $[\mathrm{Fe(edta)}]^-$(aq) are approximately equal. This was shown to be the case, no significant difference in absorbance being found for solutions containing $\mathrm{Fe^{III}}$ ions and an excess of edta between pH 1 and 2; under these conditions $\mathrm{Fe^{III}}$ is almost completely in the forms $[\mathrm{Fe(Hedta)}]$(aq) and $[\mathrm{Fe(edta)}]$(aq), whereas the ratio of the two forms changes appreciably with pH. Figure 1 shows plots of k_{obs} against c_{edta} at constant $[\mathrm{H^+}]$. The straight lines are in agreement with a first-order dependence on the ligand. It is noteworthy that such lines showed no significant intercept, so that the term $[\mathrm{H_4edta}]_{\mathrm{eq}}$-$[\mathrm{Fe^{3+}}]/c_{\mathrm{eq}}$ in equation (7), due to reverse reactions, appears to be negligible.

TABLE 1

k_{obs} Values ($\mathrm{s^{-1}}$) for the $\mathrm{Fe^{III}} + \mathrm{H_4edta}$ reaction at $c_{\mathrm{Fe}} = 1 \times 10^{-4}$M

	10^3c_{edta}/	$[\mathrm{H^+}]$/M					
t/°C	M	0·010	0·015	0·020	0·030	0·040	0·050
15·0	0·50	1·11	0·74	0·43	0·24	0·14	0·10
	0·75	1·79	1·02	0·64	0·33	0·21	0·15
	1·0	2·47	1·34	0·83	0·46	0·28	0·22
	1·5	4·01	2·09	1·61	0·73	0·42	0·28
	2·0	5·54	2·75	1·73	0·90	0·57	0·38
	2·5	6·15	3·86	2·34	1·25	0·75	0·50
	3·0	7·09	4·37	2·55	1·47	0·88	0·60
25·0	0·50	3·30	1·75	1·30	0·66	0·49	0·25
	0·75	4·66	2·85	2·03	1·10	0·69	0·45
	1·0	6·15	3·70	2·69	1·41	0·98	0·55
	1·5	8·67	5·43	3·77	2·06	1·45	0·83
	2·0	12·4	7·48	5·84	2·40	1·85	1·07
	2·5	16·1	8·44	6·71	2·73	2·63	1·39
	3·0	19·6	10·2	9·16	3·87	2·90	1·61
35·0	0·50	8·75	4·74	3·02	1·87	0·95	0·81
	0·75	14·3	7·53	5·38	2·59	1·64	1·21
	1·0	19·2	11·0	7·08	3·76	2·26	1·67
	1·5	27·9	16·0	9·63	5·53	3·64	2·63
	2·0	37·1	19·5	14·5	7·62	4·83	3·63
	2·5	49·5	26·4	18·3	8·89	6·06	4·52
	3·0	57·2	33·0	20·8	11·5	7·59	5·36

For evaluating the dependence of the reaction rate on $[\mathrm{H^+}]$, experimental data were treated according to equation (7) rewritten as (8). A plot of k_{obs}' as a

$$k_{\mathrm{obs}}' = \frac{k_{\mathrm{obs}}([\mathrm{H^+}] + K_{\mathrm{OH}})}{c_{\mathrm{edta}}\,.\,\alpha_{\mathrm{H_4edta}}\,.\,[\mathrm{H^+}]} = k_1 + k_2\frac{K_4}{[\mathrm{H^+}]} + k_3\frac{K_4K_3}{[\mathrm{H^+}]^2} + k_4\frac{K_{\mathrm{OH}}}{[\mathrm{H^+}]} + k_5\frac{K_{\mathrm{OH}}K_4}{[\mathrm{H^+}]^2} + k_6\frac{K_{\mathrm{OH}}K_1K_2}{[\mathrm{H^+}]^3} \qquad (8)$$

function of $[\mathrm{H^+}]$ on a logarithmic scale was linear with a gradient of $-1{\cdot}6$ (*i.e.* $k_{\mathrm{obs}}' = A[\mathrm{H^+}]^{-1\cdot6}$) suggesting a form such as (9). The validity of equation (9) was

$$k_{\mathrm{obs}}' = A'[\mathrm{H^+}]^{-1} + A''[\mathrm{H^+}]^{-2} \qquad (9)$$

assessed from linear plots of $k_{\mathrm{obs}}'[\mathrm{H^+}]$ against $[\mathrm{H^+}]^{-1}$ (Figure 2).

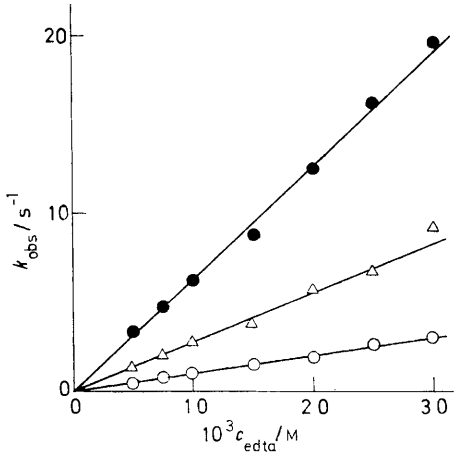


FIGURE 1 Dependence of k_{obs} on c_{edta} for the reaction $\mathrm{Fe^{III}} + \mathrm{H_4edta}$ at 25·0 °C and 0·010 (●), 0·020 (△), and 0·040M (○) $[\mathrm{H^+}]$

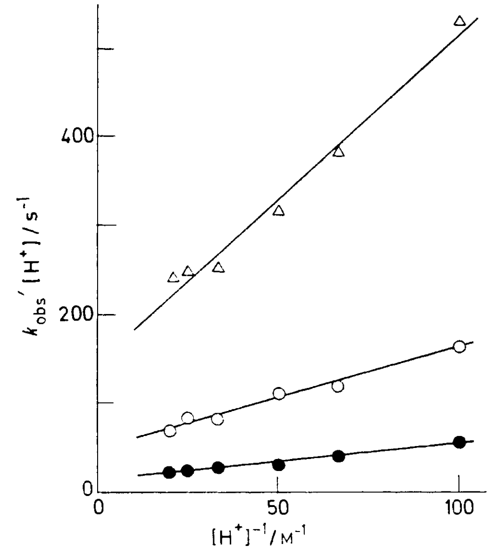
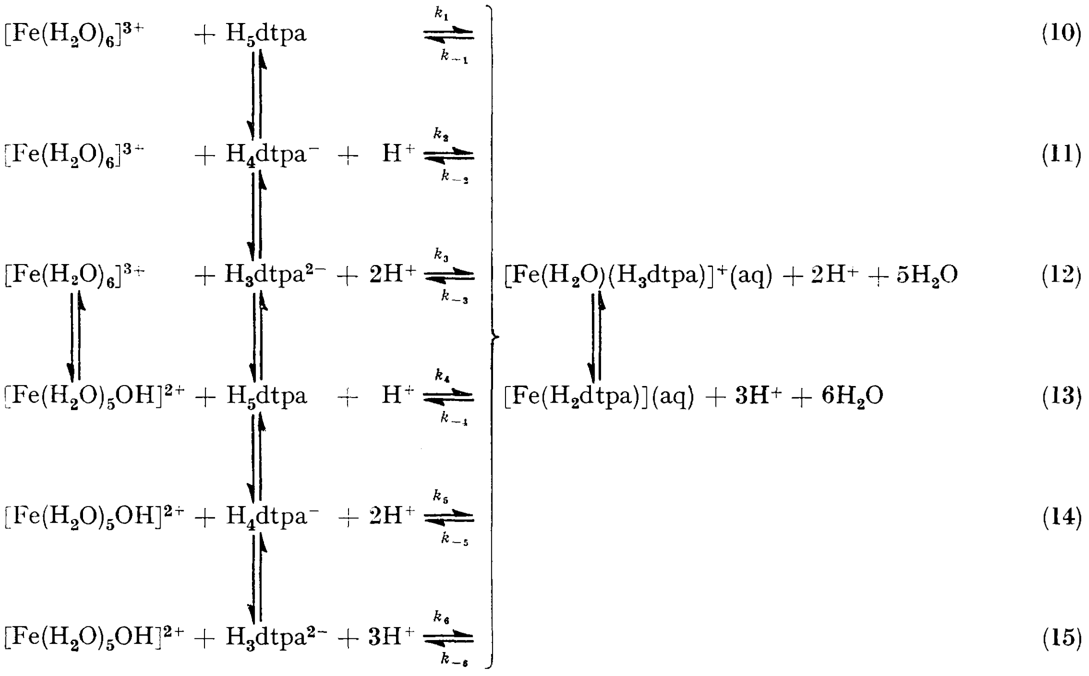


FIGURE 2 Plots of k_{obs}' against $[\mathrm{H^+}]^{-1}$ for the $\mathrm{Fe^{III}} + \mathrm{H_4edta}$ reaction at 15·0 (●), 25·0 (○), and 35·0 °C (△)

The terms $A''[H^+]^{-2}$ and $A'[H^+]^{-1}$ correspond to reactions (3) + (5) and (2) + (4), respectively. Assuming that reactions (4) and (5) can be neglected, values calculated for k_2 and k_3 were respectively *ca.* 8×10^3 and *ca.* 4×10^4 l mol^{-1} s^{-1} at 25·0 °C, too high for complex-formation reactions of the ion $[Fe(H_2O)_6]^{3+}$ (literature data range from *ca.* 1 to *ca.* 10^2 l mol^{-1} s^{-1})[8] suggesting that the reaction goes through paths (4) and (5).

$Fe^{III} + H_5dtpa$ *Reaction*.—This reaction was also found to obey the first-order equation $-d[Fe^{III}]/dt = k_{obs}[Fe^{III}]$, where k_{obs} represents the pseudo-first-order rate constant obtained from plots of $\ln[A_{eq}/(A_{eq} - A_t)]$ as a function of time for runs carried out for at least a five-fold excess of ligand; the data are collected in Table 2. For complex-formation reactions of Fe^{III} ions and H_5dtpa under the conditions investigated,[7] the following scheme can be written. Under the assumptions previously described, the pseudo-first-order kinetic equation (16) can be obtained, where $c = [Fe(H_3dtpa)^+] + [Fe(H_2dtpa)]$ and c_{dtpa} is the stoicheiometric concentration of ligand.



$$[Fe(H_2O)_6]^{3+} + H_5dtpa \underset{k_{-1}}{\overset{k_1}{\rightleftharpoons}} \quad (10)$$

$$[Fe(H_2O)_6]^{3+} + H_4dtpa^- + H^+ \underset{k_{-2}}{\overset{k_2}{\rightleftharpoons}} \quad (11)$$

$$[Fe(H_2O)_6]^{3+} + H_3dtpa^{2-} + 2H^+ \underset{k_{-3}}{\overset{k_3}{\rightleftharpoons}} [Fe(H_2O)(H_3dtpa)]^+(aq) + 2H^+ + 5H_2O \quad (12)$$

$$[Fe(H_2O)_5OH]^{2+} + H_5dtpa + H^+ \underset{k_{-4}}{\overset{k_4}{\rightleftharpoons}} [Fe(H_2dtpa)](aq) + 3H^+ + 6H_2O \quad (13)$$

$$[Fe(H_2O)_5OH]^{2+} + H_4dtpa^- + 2H^+ \underset{k_{-5}}{\overset{k_5}{\rightleftharpoons}} \quad (14)$$

$$[Fe(H_2O)_5OH]^{2+} + H_3dtpa^{2-} + 3H^+ \underset{k_{-6}}{\overset{k_6}{\rightleftharpoons}} \quad (15)$$

$$k_{obs} = \left(k_1 + k_2\frac{K_5}{[H^+]} + k_3\frac{K_5K_4}{[H^+]^2} + k_4\frac{K_{OH}}{[H^+]} + k_5\frac{K_{OH}K_5}{[H^+]^2} + k_6\frac{K_{OH}K_5K_4}{[H^+]^3}\right)\left(\frac{[H_5dtpa]_{eq}[Fe^{3+}]_{eq}}{c_{eq}} + c_{dtpa} \cdot \alpha_{H_5dtpa} \cdot \frac{[H^+]}{[H^+] + K_{OH}}\right) \qquad (16)$$

The same linear behaviour, without a significant intercept, as for H_4edta, was found on plotting values of k_{obs} against c_{dtpa} at constant $[H^+]$, indicating first-order dependence on the ligand and no significant contribution from reverse reactions. The overall dependence of the reaction rate on $[H^+]$ was found again to agree with an equation of the form (17). The validity of equation (17) is shown in Figure 3 where $k_{obs}'[H^+]$ is plotted against $[H^+]^{-1}$. For the evaluation of α_{H_5dtpa} in equations (16) and (17), H_8dtpa^{3+} and H_7dtpa^{2+} species were assumed to be present in very low concentration, and for the reaction $H_6dtpa^+ \rightleftharpoons H_5dtpa + H^+$ a value for K_6 of $(4{\cdot}0 \pm 0{\cdot}6) \times 10^{-2}$ mol l^{-1} was found to fit the behaviour in Figure 3 (values of 3×10^{-2} and 5×10^{-2} mol l^{-1} gave the trends also given in the Figure). It is to be noted that this estimated value is very close to that for the corresponding deprotonation of H_5edta^+ ($pK_5 = 1{\cdot}4$). With the same treatment as for H_4edta, the paths involved in the reaction are found to be (13) and (14), in accord with the $[H^+]$ dependence.

$$k_{obs}' = \frac{k_{obs}([H^+] + K_{OH})}{c_{dtpa} \cdot \alpha_{H_5dtpa} \cdot [H^+]} = B'[H^+]^{-1} + B''[H^+]^{-2} \qquad (17)$$

TABLE 2

k_{obs} Values (s^{-1}) for the $Fe^{III} + H_5dtpa$ reaction at 25 °C and $c_{Fe} = 1 \times 10^{-4}$M

10^3c_{dtpa}/M	[H+]/M							
	0·010	0·015	0·020	0·030	0·040	0·050	0·100	0·200
0·50	4·74	2·51	1·73	0·94	0·56	0·48	0·13	0·030
0·75	6·22	4·05	2·83	1·57	0·86	0·64	0·17	0·048
1·0	8·57	5·48	3·73	2·07	1·12	0·83	0·24	0·065
1·5	13·3	7·97	5·50	2·92	1·75	1·28	0·36	0·097
2·0	16·8	10·4	7·41	3·93	2·35	1·61	0·48	0·13
2·5	21·4	13·1	8·80	5·07	2·79	2·12	0·59	0·16
3·0	25·0	15·4	10·0	5·85	3·41	2·63	0·71	0·20

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[8] F. Accascina, F. P. Cavasino, and S. D'Alessandro, *J. Phys. Chem.*, 1967, **71**, 2474; F. P. Cavasino, *ibid.*, 1968, **72**, 1378.

In Table 3, values of the second-order rate constants have been collected together with activation parameters, and kinetic data of the $Fe^{III} + H_2ida$ and $Fe^{III} + H_3nta$ reactions. These rate constants, as well as the activation parameters, are in fact composite terms which include contributions from all the reaction steps (*i.e.*, for example, ion-pair formation). From these data it can be inferred that the metal ion reacts in its monohydroxo-form, in agreement with previous findings on the reactivity of the ion $[Fe(H_2O)_5OH]^{2+}$ {*ca.* 10^3 times greater than that of $[Fe(H_2O)_6]^{3+}$}; [8] it is known that Fe–H_2O bonds in $[Fe(H_2O)_5OH]^{2+}$ are weakened by OH^-.[9]

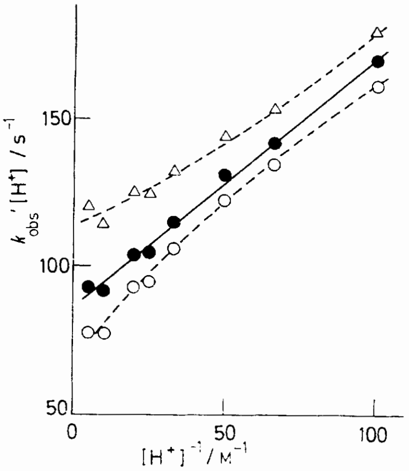

FIGURE 3 Plots of k_{obs}' against $[H^+]^{-1}$ for the $Fe^{III} + H_5dtpa$ reaction (25·0 °C): $K_6 = 3 \times 10^{-2}$ (△), 5×10^{-2} (○), and 4×10^{-2} mol l^{-1} (●)

TABLE 3

Rate constants and activation parameters at 25·0 °C

Reaction	k / l mol^{-1} s^{-1}	$\Delta H^‡$ / kcal mol^{-1}	$\Delta S^‡$ / cal K^{-1} mol^{-1}	Ref.
$[FeOH]^{2+}(aq) + H_2ida$	$(2\cdot5 \pm 0\cdot3) \times 10^3$	$6\cdot1 \pm 1\cdot0$	-23 ± 3	4
$[FeOH]^{2+}(aq) + Hida^-$	$(8\cdot8 \pm 0\cdot9) \times 10^3$	$4\cdot9 \pm 1\cdot0$	-22 ± 3	4
$[FeOH]^{2+}(aq) + H_3nta$	$(1\cdot5 \pm 0\cdot2) \times 10^4$	$9\cdot9 \pm 1\cdot0$	-5 ± 3	4
$[FeOH]^{2+}(aq) + H_2nta^-$	$(5\cdot6 \pm 0\cdot6) \times 10^4$	$6\cdot3 \pm 1\cdot0$	-16 ± 3	4
$[FeOH]^{2+}(aq) + H_4edta$	$(3\cdot0 \times 0\cdot3) \times 10^4$	$7\cdot3 \pm 1\cdot0$	-15 ± 3	*a*
$[FeOH]^{2+}(aq) + H_3edta^-$	$(1\cdot1 \pm 0\cdot1) \times 10^5$	$5\cdot7 \pm 1\cdot0$	-15 ± 3	*a*
$[FeOH]^{2+}(aq) + H_5dtpa$	$(5\cdot3 \pm 0\cdot6) \times 10^4$			*a*
$[FeOH]^{2+}(aq) + H_4dtpa^-$	$(1\cdot6 \pm 0\cdot2) \times 10^5$			*a*

[a] This work.

By comparing rate constants for two species of the same ligand (that is H_4edta and H_3edta^- as well as H_5dtpa and H_4dtpa^-), it is found that the rate constant is higher for the less-protonated species in agreement with the mechanism put forward by Eigen.[2] An increase in negative charge on a ligand generally raises the equilibrium constant for ion-pair formation, which enters as a factor in the overall rate constant. According to the Fuoss equation,[10] when the charge on a ligand is increased by one unit, the association constant for ion-pair formation becomes *ca.* three times larger, in good agreement with experimental findings.*

A further point which deserves attention is the increase in rate constants in the order $H_2ida < H_3nta < H_4edta < H_5dtpa$ (both for undissociated species and for those with one negative charge) corresponding to the increase in the number of chelate rings formed. Such a trend is not in accord with the hypothesis that the chelate-ring closure step affects the overall rate constants. In fact, if this were to be the case the order would be reversed. One explanation of these findings can be advanced by taking into account the fact that the reacting ligands are in effect zwitterions. When outer-sphere complex formation occurs, carboxylato-groups will approach the ion $[Fe(H_2O)_5OH]^{2+}$ and the ligand will bear, with respect to the metal, an overall negative charge which will be greater on going from H_2ida to H_5dtpa. An increase in the size of the ion-pair association constants is therefore expected, accounting for the increase in overall rate constants. Another possible explanation may be suggested on a statistical basis, taking into account that there is, going from H_2ida to H_5dtpa, an increase in the number of carboxylato-groups able to give rise to the first co-ordination bond with the metal ion, so that the probability of occurrence of reaction is accordingly increased.

The experimental findings in all cases are consistent with the assumption that the rate of formation of the complexes should be ' normal,' *i.e.* the rate-determining step is displacement of the first water molecule from the co-ordination sphere of the metal ion, as shown by the fact that overall rate constants are of the same order as the rate of exchange of one water molecule between $[Fe(H_2O)_5OH]^{2+}$ and water in ' bulk ' (*ca.* 10^4 s^{-1}).[11] Further support to this assumption is given by a comparison of the $\Delta H^‡$ values with those given previously for reaction of the ion $[Fe(H_2O)_5OH]^{2+}$ with other ligands. In fact, for all such reactions so far investigated, the enthalpy of activation is slightly dependent on the entering species.[1b,d,8]

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* The factor of three is obtained, at $I = 1\cdot0$M, by assuming a 5 Å distance of closest approach between the reacting ions (approximately the internuclear distance of a co-ordinate bond plus the effective thickness of a water molecule).

[9] F. P. Cavasino and M. Eigen, *Ricerca Sci.*, 1964, **4**, 509.

[10] R. M. Fuoss, *J. Amer. Chem. Soc.*, 1958, **80**, 5059.

[11] R. E. Connick and E. E. Genser, quoted by D. Seewald and N. Sutin, *Inorg. Chem.*, 1963, **2**, 643.