Kinetics and Equilibria in the Redox Reaction between Ethylenedinitrilotetra-acetate Complexes of Iron(III) and Vanadium(III) in Aqueous Solution

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The kinetics of the reaction $[Fe^{III}(edta)]^- + [V^{III}(edta)]^- \rightleftharpoons [Fe^{II}(edta)]^{2-} + [V^{IV}O(edta)]^{2-} + 2H^+$ (edta = ethylenedinitrilotetra-acetate) have been studied at 25.0 °C in the forward direction at pH 5.4—7.1 and in the reverse direction at pH 2.5—4.0. Similar studies have been made on the corresponding system involving iron complexes with (*trans*-1,2-cyclohexylenedinitrilo)tetra-acetate. Direct measurements of the equilibrium constants at pH 4.2—5.6 yielded values similar to those calculated from the kinetic results. The mechanism is believed to be of the inner-sphere type. At pH $\leqslant$ 1 the reaction $[Fe^{III}(edta)]^- + [V^{III}(edta)]^- \longrightarrow Fe^{2+} + V^{IV} + H_5edta^+$ occurs, the consumption of hydrogen ion and the form of vanadium(IV) depending on $[H^+]$. The kinetics of this reaction show that as well as a bimolecular redox process, probably of the inner-sphere type, two other reaction paths occur. These involve the dissociation of one of the reactant complexes followed by a redox reaction between the cation so formed and the other edta complex.

Studies of the kinetics of several redox reactions involving two metal complexes of ethylenedinitrilotetra-acetate (edta) and related ligands have previously been reported.[1-4] In several cases the data have been interpreted in terms of an outer-sphere mechanism,[1,2] but in others the mechanism is considered to be of the inner-sphere type.[3,4] The redox reaction between the edta complexes of iron(III) and vanadium(III) has not previously been investigated and here we report a kinetic and equilibrium study of various aspects of the reaction, equation (1). The equilibrium constant for the reaction, K_R, is of the order 10^{-10} mol^2 dm^{-6} so that comparable concentrations of the reactant and product complexes coexist in the region of pH 5. In this region protonation and partial hydrolysis of reactants and products are small and the equilibrium constant is easy to obtain. The reaction goes to completion at higher pH values (5.4—7.1) and is quantitative in the reverse direction at pH 2.5—4.0. Above pH 7.1 and below pH 2.5 substantial amounts of partial hydrolysis or protonation of the complexes lead to relatively complicated behaviour. We present in section (1) of this paper our kinetic measurements within these pH ranges, together with equilibrium measurements. Similar experiments involving iron complexes with (*trans*-1,2-cyclohexylenedinitrilo)tetra-acetate (cydta) are also reported in section (1).

$$[Fe^{III}(edta)]^- + [V^{III}(edta)]^- \xrightleftharpoons{H_2O} [Fe^{II}(edta)]^{2-} + [V^{IV}O(edta)]^{2-} + 2H^+ \qquad (1)$$

$$K_R = \frac{[Fe^{II}(edta)^{2-}][V^{IV}O(edta)^{2-}][H^+]^2}{[Fe^{III}(edta)^-][V^{III}(edta)^-]} \qquad (2)$$

Mixtures of $[Fe^{III}(edta)]^-$ and $[V^{III}(edta)]^-$ are stable at pH 2.5—4.0 in the absence of dioxygen and equation (1) implies that this should also be true at lower values of pH. In fact, a redox reaction occurs at pH *ca.* 1 and lower. The decomposition of $[Fe^{II}(edta)]^{2-}$ under such conditions is virtually complete and the removal of this complex is sufficient to displace the equilibrium in equation (1) so that the products are iron(II) and vanadium(IV). We studied the kinetics of this redox reaction at $[H^+] = 0.05$—0.25 mol dm^{-3}; the vanadium(IV) is principally in the form $[V^{IV}O(Hedta)]^-$ at lower values of $[H^+]$ and is largely decomposed to VO^{2+} at higher values. Consequently, the overall equation for the redox reaction is equation (3A) at $[H^+] \geqslant 0.125$ mol dm^{-3} and equation (3B) at $[H^+] < 0.125$ mol dm^{-3}. The lower limit of $[H^+] = 0.05$ mol dm^{-3} was chosen because below this value the reaction is not quantitative, a proportion of both complexes remaining unreacted. For $[H^+] > 0.25$ mol dm^{-3} the proportion of the reactants decomposed to Fe^{3+} or V^{3+} exceeds a few percent and greatly complicates the kinetic behaviour of the system and its interpretation. The kinetics of the reactions (3A) and (3B) are described in section (2).

$$[Fe^{III}(edta)]^- + [V^{III}(edta)]^- + 8H^+ \longrightarrow Fe^{2+} + VO^{2+} + 2H_5edta^+ \qquad (3A)$$

$$[Fe^{III}(edta)]^- + [V^{III}(edta)]^- + 4H^+ \longrightarrow Fe^{2+} + [V^{IV}O(Hedta)]^- + H_5edta^+ \qquad (3B)$$

Experimental

Solid reagents were of AnalaR quality and were used without purification, with the exceptions noted below. Their solutions were standardised by appropriate methods. Solutions of metal perchlorates were obtained as follows. Perchlorates of Cu^{2+}, Mg^{2+}, and Zn^{2+} were prepared by dissolving the corresponding oxide in a small excess of dilute perchloric acid and diluting the filtered solution to give *ca.* 0.1 mol dm^{-3} metal ion. Nickel(II) perchlorate solution (*ca.* 0.1 mol dm^{-3}) was obtained by double decomposition between warm solutions of barium perchlorate (from barium hydroxide and perchloric acid) and nickel sulphate hydrate. Iron(II) perchlorate solution was prepared by dissolving Specpure iron sponge (from Johnson Matthey) in 0.30 mol dm^{-3} perchloric acid under dinitrogen to give $[Fe^{2+}]$ *ca.* 0.1 mol dm^{-3}. The filtered solution was standardised by titration with cerium(IV) sulphate (ferroin). Iron(III) perchlorate (*ca.* 0.1 mol dm^{-3}) in *ca.* 0.1 mol dm^{-3} perchloric acid was obtained by the oxidation with hydrogen peroxide of a similarly prepared solution of iron(II) perchlorate in dilute perchloric acid. Oxovanadium(IV) perchlorate ($VO[ClO_4]_2$) and vanadium(III) perchlorate solutions in dilute perchloric acid were prepared by electrolytic reduction, starting with ammonium metavanadate(V) rather than vanadium(V) oxide as previously employed.[5] The concentration of oxovanadium(IV) was estimated spectrophotometrically and that of vanadium(III) iodimetrically by the reduction of iodate(V).[5] In both solutions the vanadium concentration was *ca.* 0.1 mol dm^{-3} and free perchloric acid was *ca.* 0.5 mol dm^{-3}. The latter concentration was obtained by difference between the equivalent concentration of vanadium and the total equivalent cation concentration determined by ion exchange on Amberlite IR-120(H) resin, after allowing for the contribution of ammonium ion.

The solid edta complexes $Na_2[VO(C_{10}H_{12}N_2O_8)]\cdot 3H_2O$ and $Na[Fe(C_{10}H_{12}N_2O_8)]\cdot 3H_2O$ were prepared from B.D.H. $VOCl_2$ (50% w/v) and AnalaR $Fe(NO_3)_3\cdot 9H_2O$, respectively, as previously described.[6] $Na[V(C_{10}H_{12}N_2O_8)]\cdot 4H_2O$ was obtained by sodium amalgam reduction of the oxovanadium(IV) complex.[7] Analyses of the purified samples were by Dr. Franz Pascher, Bonn, and were satisfactory. Other edta and cydta complexes were made in solution by mixing the metal perchlorate and the disodium salt solutions of the corresponding nitrilocarboxylic acids with appropriate quantities of sodium hydroxide solution. The hydrated acid $H_4cydta\cdot H_2O$ was obtained from K & K Laboratories Inc., Plainview, New York.

Aqueous solutions of edta and cydta complexes of iron(II) are rapidly oxidised by dioxygen while solutions of the edta complex of vanadium(III) are slowly oxidised. These solutions were therefore freshly prepared and maintained under argon. Stock solutions in general were kept in contact with air. They were degassed and transferred under argon into a mixing vessel or directly into an optical cell by using a technique previously described.[8] The same technique was used in preparing solutions for pH titration in a vessel from which air was excluded by an argon atmosphere.

The protonation equilibrium constants K_b^{F2}, K_b^{F2Z}, and K_b^{V4} for $[Fe^{II}(edta)]^{2-}$, $[Fe^{II}(cydta)]^{2-}$, and $[V^{IV}O(edta)]^{2-}$ respectively were obtained by pH titration of 25 cm³ of 0.020 mol dm⁻³ solutions of the complex with 0.40 mol dm⁻³ perchloric acid. {Here $K_b^{F2} = [Fe^{II}(Hedta)(H_2O)^-]/[Fe^{II}(edta)^{2-}][H^+]$, *etc.*} Both the solution of the complex and that of perchloric acid were made up to ionic strength 1.00 mol dm⁻³ with sodium perchlorate. The saturated potassium chloride of the calomel electrode was replaced by saturated sodium chloride to avoid precipitation at the junction with the perchlorate solution. Measurements were made by using a Radiometer pH meter, model 26, and the titration vessel was maintained at 25.0 °C. The glass electrode was standardised against a solution of 0.0100 mol dm⁻³ perchloric acid and 0.99 mol dm⁻³ sodium perchlorate; the pH of this solution was taken to be 2.00.

Similar pH titrations in the presence of air were carried out to find pK_a values for various buffer acids in perchlorate media of ionic strength 1.00 mol dm⁻³. Values obtained were CH_2ClCO_2H, 2.70; HCO_2H, 3.46; CH_3CO_2H, 4.57; $H_2PO_4^-$, 6.23. The probable error is ±0.03 unit for each value.

Values of pH below 1 were necessary to obtain substantial protonation of $[Fe^{III}(edta)]^-$ and $[V^{III}(edta)]^-$ in the measurement of their protonation equilibrium constants, K_b^{F3} and K_b^{V3}. The simple pH titration was unsatisfactory under these conditions and use was made of a cell without liquid junction (see below). A solution (25 cm³) of the sodium salt of the

$$Ag(s)|AgCl(s)|Cl^-, ClO_4^-, [M^{III}(edta)]^-, Na^+, H^+|glass$$

complex (0.25 mol dm⁻³) containing 0.0100 mol dm⁻³ sodium chloride and made up to ionic strength 1.00 mol dm⁻³ with sodium perchlorate was titrated with 0.99 mol dm⁻³ perchloric acid solution containing 0.0100 mol dm ³ sodium chloride at 25.0 °C. The potential was measured after each of about 25 successive additions of acid up to a total added volume of 10 cm³. A calibration curve of apparent pH (calculated from $[H^+]$) against potential was obtained by a similar experiment in the absence of the complex. By assuming a value of K_b^{F3}, a curve of pH against volume of acid solution added was constructed, making allowance for dilution during the titration. Comparison of a set of such curves corresponding to different assumed values of K_b^{F3} with the experimental curve enabled the value of K_b^{F3} to be found within ±10%. The same procedure was adopted for the vanadium(III) complex. There was evidence of the occurrence of a further protonation towards the end of these titrations, especially with the iron(III) complex. Approximate values of the corresponding second protonation equilibrium constants could be obtained from our data, but owing to their low values these constants are not significant in the interpretation of the kinetic experiments. The various values of K_b obtained are summarised in Table 1 together with acid dissociation constants, K_a, reported by others {*e.g.* $K_a^{F3} = [Fe^{III}(OH)(edta)^{2-}][H^+]/[Fe^{III}(edta)^-]$}.

Table 1. Equilibrium constants used in the kinetic analysis [a]

(*a*) Protonation constants for metal complexes [b]

Complex	K/dm³ mol⁻¹	Symbol
$[Fe^{II}(edta)]^{2-}$	801 ± 40	K_b^{F2}
$[Fe^{II}(cydta)]^{2-}$	765 ± 44	K_b^{F2Z}
$[V^{IV}O(edta)]^{2-}$	1 446 ± 109	K_b^{V4}
$[Fe^{III}(edta)]^-$	3.3 ± 0.3	K_b^{F3}
$[V^{III}(edta)]^-$	1.67 ± 0.08	K_b^{V3}

(*b*) Acid dissociation constants for metal complexes

Complex	$10^{10}K$/mol dm⁻³	Symbol
$[Fe^{III}(edta)]^-$	263 ± 26 [c]	K_a^{F3}
$[Fe^{III}(cydta)]^-$	4.79 ± 0.48 [c]	K_a^{F3Z}
$[V^{III}(edta)]^-$	2.69 ± 0.33 [d]	K_a^{V3}

[a] At 25.0 °C and ionic strength = 1.0 mol dm⁻³ ($NaClO_4$). [b] This work. [c] Ref. 9. [d] Ref. 12.

Redox equilibrium and kinetic measurements were made spectrophotometrically at 25.0 °C and ionic strength 1.00 mol dm⁻³ ($NaClO_4$) by using a Perkin-Elmer model 402 spectrophotometer fitted with a temperature-controlled cell holder for 1 cm silica cells. In all experiments the dominant absorbing species was the iron(III) complex. Wavelengths used were 394 nm for experiments involving $[Fe^{III}(edta)]^-$ for pH 2.5—7.1 (ε = 251 dm³ mol⁻¹ cm⁻¹ at pH 2.5—6 and decreases to 229 dm³ mol⁻¹ cm⁻¹ at pH 7.1); 350 nm for experiments involving $[Fe^{III}(edta)]^-$ from $[H^+]$ = 0.05 mol dm⁻³ (ε = 1 450 dm³ mol⁻¹ cm⁻¹) to 0.25 mol dm⁻³ (ε = 1 270 dm³ mol⁻¹ cm⁻¹); 410 nm for experiments involving $[Fe^{III}(cydta)]^-$ for pH 2.7—7.2 (ε = 224 dm³ mol⁻¹ cm⁻¹). In calculating concentrations of iron(III) in the solutions, corrections were made for the small contributions to the optical density from other complexes present.

In kinetic experiments starting with mixtures of $[Fe^{III}(edta)]^-$ or $[Fe^{III}(cydta)]^-$ and $[V^{III}(edta)]^-$ in the pH range 5.4—7.1, the pH of the portion of reaction solution remaining was measured immediately after filling the optical cell for spectrophotometric measurements. Knowing the total concentration of the buffer components and pK_a of the buffer acid, the pH at 50% reaction was calculated. The correction is necessary because hydrogen ions liberated in the forward reaction [equation (1)] react with the buffer base. The amount of correction was between −0.05 and −0.10 pH unit, depending on the buffer concentrations employed. In the system $[Fe^{III}(cydta)]^- + [V^{III}(edta)]^-$, spectrophotometric measurements of the position of equilibrium were made within the pH range 4.4—5.9. A similar pH correction was applied, but in this case the measured pH was corrected to allow for the concentration of hydrogen ions liberated when equilibrium has been attained. For kinetic experiments at pH 2.5—4.0, starting with mixtures of $[Fe^{II}(edta)]^{2-}$ or $[Fe^{II}(cydta)]^{2-}$ and $[V^{IV}O(edta)]^{2-}$, pH was measured at the completion of reac-

Table 2. Rate constants [a] for the reaction of $[Fe^{III}(edta)]^-$ with $[V^{III}(edta)]^-$ [b] at pH 5.4—7.1

pH	$k^f_{obs.}$/ $dm^3\ mol^{-1}\ s^{-1}$	$k^f_{calc.}$/ $dm^3\ mol^{-1}\ s^{-1}$
5.43	0.153	0.158
5.51 [c]	0.188	0.189
5.54	0.215	0.202
5.63	0.235	0.248
5.69	0.295	0.283
5.74	0.345	0.321
5.76	0.375	0.334
5.85	0.431	0.409
5.90	0.465	0.461
6.01	0.615	0.592
6.17	0.852	0.766
6.24	1.10	0.989
6.33	1.36	1.19
6.49	1.50	1.68
6.49	1.57	1.70
6.50	1.65	1.72
6.53	1.81	1.83
6.54	1.67	1.87
6.60	1.91	2.14
6.65	2.05	2.38
6.70	1.92	2.60
6.74	2.37	2.83
6.86	2.81	3.58
6.92	3.09	4.02
7.03	3.58	4.91
7.04	3.98	5.01
7.14	4.48	5.96

[a] At 25.0 °C and ionic strength 1.0 mol dm^{-3} ($NaClO_4$). [b] Initial concentrations: $[Fe^{III}]_0 = 3.0 \times 10^{-3}$ mol dm^{-3}, $[V^{III}]_0 = 6.0 \times 10^{-3}$ mol dm^{-3}. [c] In ethanoate buffer; remainder in phosphate buffers; total buffer concentration = 0.120 mol dm^{-3}.

tion with iron(II) absent. This pH was corrected to the value at 50% reaction, the amount of correction being again between −0.05 and −0.10 pH unit. Most experiments to determine equilibrium constants for the reactions in pH range 4.2—5.5 involved iron(II) and oxovanadium(IV) complexes as the species initially present. It was not convenient with such mixtures to make pH measurements with exclusion of air at the beginning or end of the reaction, as would be necessary to avoid the oxidation of iron(II) by atmospheric dioxygen. For these equilibrium measurements the reaction was initiated by adding under argon a solution of iron(II) perchlorate in dilute perchloric acid to part of a mixture of all other reagents including $Na_2H_2(edta)$ or $Na_2H_2(cydta)$. Once this addition had been completed and the final solution introduced into the optical cell, an appropriate volume of a solution of zinc(II) perchlorate in dilute perchloric acid, of the same concentrations as the iron(II) perchlorate stock solution, was added to the remaining part of the mixture. This gave a solution of exactly the same composition and pH as the initial reaction solution, but containing $[Zn(edta)]^{2-}$ or $[Zn(cydta)]^{2-}$ instead of the corresponding iron(II) complexes. Such a solution being stable to air, the pH was measured and corrected to that obtaining at the position of equilibrium in the system containing the corresponding iron(II) complex.

(1) Redox Reactions at pH 2.5—7.1

Results.—Kinetics of the forward reaction; pH 5.4—7.1. Experiments were done with 3.0×10^{-3} mol dm^{-3} $[Fe^{III}(edta)]^-$ and 6.0×10^{-3} mol dm^{-3} $[V^{III}(edta)]^-$ in $H_2PO_4^-$–HPO_4^{2-} buffer of total concentration 0.120 mol dm^{-3}. Reaction was followed spectrophotometrically to about 90% of completion. Plots of $\log\{[Fe^{III}]/[V^{III}]\}$ against time were linear showing the reaction to be of the first order in each complex and to be unaffected by the product complexes at concentrations up to *ca.* 3×10^{-3} mol dm^{-3}. From the gradient G of each plot the corresponding second-order rate constant $k^f_{obs.}$ for the particular pH was found by using the relationship, $k^f_{obs.} = 2.303G/\{[Fe^{III}(edta)^-]_0 - [V^{III}(edta)^-]_0\}$, where subscripts zero indicate initial concentrations. Values of $k^f_{obs.}$ and pH corrected to 50% reaction are summarised in Table 2.

Table 3. Rate constants [a] for the reaction of $[Fe^{III}(cydta)]^-$ with $[V^{III}(edta)]^-$ [b] at pH 5.6—7.2 [c]

pH	$10^2k^{fZ}_{obs.}$/ $dm^3\ mol^{-1}\ s^{-1}$	$10^2k^{fZ}_{calc.}$/ $dm^3\ mol^{-1}\ s^{-1}$
5.63	1.35	1.50
5.81	2.15	2.29
5.94	3.27	3.06
5.99	3.36	3.49
6.17	5.64	5.25
6.30	7.57	7.09
6.46	10.3	10.2
6.65	17.3	15.7
6.87	27.1	26.3
7.07	41.5	41.2
7.17	49.1	52.9

[a] At 25.0 °C and ionic strength 1.0 mol dm^{-3} ($NaClO_4$). [b] Initial concentrations: $[Fe^{III}]_0 = 3.0 \times 10^{-3}$ mol dm^{-3}, $[V^{III}]_0 = 6.0 \times 10^{-3}$ mol dm^{-3}. [c] In phosphate buffers, total concentration = 0.120 mol dm^{-3}.

Table 4. Rate constants [a] for the reaction of $[Fe^{II}(edta)]^{2-}$ with $[V^{IV}O(edta)]^{2-}$ [b] at pH 2.5—4.0 [c]

pH	$k^b_{obs.}$/ $dm^3\ mol^{-1}\ s^{-1}$	$k^b_{calc.}$/ $dm^3\ mol^{-1}\ s^{-1}$
2.50	9.36	9.72
2.61	9.30	8.89
2.65	8.17	8.60
2.73	7.96	7.94
2.80	7.01	7.38
2.86 [d]	6.98	6.90
2.87	6.73	6.77
2.92	6.59	6.40
2.97	6.14	6.00
3.06 [d]	5.20	5.27
3.10	5.16	4.98
3.16	4.83	4.49
3.24	4.20	3.96
3.39	2.96	2.99
3.42	2.89	2.82
3.48 [d]	2.90	2.52
3.58 [e]	1.80	2.08
3.58 [e]	1.86	2.06
3.84 [e]	1.23	1.20
3.87 [d]	1.19	1.13
3.96 [e]	0.918	0.919

[a] At 25.0 °C and ionic strength = 1.0 mol dm^{-3} ($NaClO_4$). [b] Initial concentrations: $[Fe^{II}]_0 = 3.0 \times 10^{-3}$ mol dm^{-3}, $[V^{IV}]_0 = 6.0 \times 10^{-3}$ mol dm^{-3}. [c] In chloroethanoate buffers, unless otherwise stated. Total buffer concentration = 0.120 mol dm^{-3}. [d] In methanoate buffers. [e] In ethanoate buffers.

Parallel experiments were done with 3.0×10^{-3} mol dm^{-3} $[Fe^{III}(cydta)]^-$ and 6.0×10^{-3} mol dm^{-3} $[V^{III}(edta)]^-$ in the pH range 5.6—7.2. The rate constants $k^{fZ}_{obs.}$ obtained are summarised in Table 3.

Table 5. Rate constants [a] for the reaction of $[Fe^{II}(cydta)]^{2-}$ with $[V^{IV}O(edta)]^{2-}$ [b] at pH 2.7—4.6 [c]

pH	$10^2k^{bZ}_{obs.}$/ dm^3 mol^{-1} s^{-1}	$10^2k^{bZ}_{calc.}$/ dm^3 mol^{-1} s^{-1}
2.72	208	198
2.76	191	187
2.82	185	173
2.83	163	170
2.91	152	150
2.99 [d]	128	132
3.10 [d]	105	107
3.17 [d]	86.2	91.8
3.29 [d]	69.0	70.3
3.41 [d]	56.3	54.2
3.81 [e]	21.4	19.9
3.86 [e]	16.0	17.3
4.21 [e]	7.08	7.28
4.38 [e]	4.78	4.73
4.55 [e]	3.27	3.13

[a] At 25.0 °C and ionic strength = 1.0 mol dm^{-3} ($NaClO_4$). [b] Initial concentrations: $[Fe^{II}]_0 = 3.0 \times 10^{-3}$ mol dm^{-3}, $[V^{IV}]_0 = 6.0 \times 10^{-3}$ mol dm^{-3}. [c] In chloroethanoate buffers, unless otherwise stated. Total buffer concentration = 0.120 mol dm^{-3}. [d] In methanoate buffers. [e] In ethanoate buffers.

Kinetics of the back reaction; pH 2.5—4.0. Experiments were done with 3.0×10^{-3} mol dm^{-3} $[Fe^{II}(edta)]^{2-}$ and 6.0×10^{-3} mol dm^{-3} $[V^{IV}O(edta)]^{2-}$ in ethanoate, methanoate, or chloroethanoate buffers of total concentration 0.120 mol dm^{-3}. Concentrations of $[Fe^{III}(edta)]^-$ were obtained from the optical densities measured at various times, enabling the corresponding concentrations of the reactants to be obtained. Plots of $\log\{[Fe^{II}]/[V^{IV}]\}$ against time were linear to 90% completion. Second-order rate constants $k^b_{obs.}$ were obtained similarly to those for the forward reaction by using the relationship $k^b_{obs.} = 2.303G/\{[Fe^{II}(edta)^{2-}]_0 - [V^{IV}O(edta)^{2-}]_0\}$. Values of $k^b_{obs.}$ and pH corrected to 50% reaction are summarised in Table 4.

Parallel experiments were done with 3.0×10^{-3} mol dm^{-3} $[Fe^{II}(cydta)]^{2-}$ and 6.0×10^{-3} mol dm^{-3} $[V^{IV}O(edta)]^{2-}$ in the pH range 2.7—4.6. The rate constants $k^{bZ}_{obs.}$ are summarised in Table 5.

Determination of position of equilibrium of the redox reaction; pH 4.2—5.6. Solutions of $[Fe^{II}(edta)]^{2-}$ and $[V^{IV}O(edta)]^{2-}$ for equilibrium measurement were made up by the same technique as that used in the kinetic experiments at pH 4.0 and less. The optical density in each experiment was monitored until it became constant and the equilibrium concentration of $[Fe^{III}(edta)]^-$ and hence of the other complexes was obtained. The initial concentration of $[Fe^{II}(edta)]^{2-}$ was always 3.0×10^{-3} mol dm^{-3}, but several different concentrations of $[V^{IV}O(edta)]^{2-}$ were used and $[V^{III}(edta)]^-$ was present initially in some experiments. In Table 6 are summarised values of the equilibrium constant $K_{obs.} = [Fe^{II}][V^{IV}]/[Fe^{III}][V^{III}]$, obtained at different pH values. Here each symbol represents the sum of the concentrations of unprotonated and protonated complexes of the metal in the given oxidation state.

Similar equilibrium measurements were made for the system involving complexes of iron with cydta. In addition, experiments were done starting with mixtures of $[Fe^{III}(cydta)]^-$ and $[V^{III}(edta)]^-$ as indicated in Table 7 in which values of $K^Z_{obs.}$, defined in the same way as $K_{obs.}$, are summarised.

Table 6. Equilibrium constants [a] in the reaction of $[Fe^{II}(edta)]^{2-}$ with $[V^{IV}O(edta)]^{2-}$ [b] at pH 4.2—5.6 [c]

pH	$10^3[V^{III}(edta)^-]_0$/ mol dm^{-3}	$10K_{obs.}$	$10^{10}K_R$/ mol^2 dm^{-6}
4.21	0	0.301	1.02
4.23	10.0	0.263	0.81
4.23	20.0	0.266	0.80
4.25	0	0.301	0.82
4.26	0	0.333	0.90
4.28	10.0	0.380	0.94
4.29	3.0	0.394	0.94
4.29	3.0	0.332	0.77
4.30	10.0	0.334	0.76
4.30	15.0	0.342	0.76
4.34	10.0	0.444	0.83
4.35	0	0.447	0.81
4.35	10.0	0.428	0.77
4.40	0	0.532	0.79
4.43	10.0	0.692	0.89
4.44	10.0	0.916	1.10
4.44	10.0	0.935	1.12
4.45	0	1.03	1.22
4.46	10.0	0.719	0.82
4.48	5.0	0.766	0.80
4.48	0	0.950	0.95
4.49	0	0.790	0.79
4.49	10.0	0.907	0.89
4.49	10.0	0.990	0.97
4.55	0	1.19	0.90
4.56	0	1.42	1.03
4.59	0	1.44	0.90
4.72	0	2.48	0.85
4.82	0	3.59	0.80
4.94	0 (4.5) [d]	9.23	1.21
4.94	0	6.58	0.83
4.95	0 (9.0) [d]	8.18	1.02
4.94	0 (12) [d]	9.30	1.20
4.94	0 (15) [d]	8.36	1.06
4.99	0	11.7	1.22
4.99	10.0	8.49	0.88
5.00	0	8.31	0.83
5.01	0	8.16	0.78
5.01	0	11.7	1.08
5.02	0	11.7	1.04
5.04	0	9.78	0.81
5.10	0	13.7	0.87
5.11	0	16.2	0.97
5.20	0	24.9	0.97
5.21	0	26.2	0.96
5.28	0	33.9	0.95
5.31	0	37.9	0.90
5.32	0	38.9	0.88
5.35	0	48.5	0.97
5.36	0	50.3	0.96
5.41	0	58.1	0.88
5.47	0	71.9	0.81
5.48	0	74.6	0.81
5.49	0	96.2	0.98
5.57	0	143	1.02

[a] $K_{obs.} = [Fe^{II}][V^{IV}]/[Fe^{III}][V^{III}]$ at 25.0 °C and ionic strength = 1.0 mol dm^{-3} ($NaClO_4$). [b] Initial concentrations: $[Fe^{III}]_0 = 0$, $[Fe^{II}]_0 = 3.0 \times 10^{-3}$ mol dm^{-3}, $[V^{IV}]_0 = 6.0 \times 10^{-3}$ mol dm^{-3} except as indicated in footnote *d*. [c] In ethanoate buffers of total concentration 0.09 to *ca.* 1.0 mol dm^{-3}. [d] Figures in parentheses indicate $10^3[V^{IV}]_0$/mol dm^{-3}; values of $[V^{IV}]_0$ for other experiments as in footnote *b*.

Discussion.—pH Dependence of the redox reactions. We have interpreted the pH dependence of the second-order rate constants for both forward and back reactions by assuming that one or more of the various binary combinations of partially hydrolysed and normal (unhydrolysed) species or of protonated and normal (unprotonated) species may react through bimolecular redox steps. In the forward reaction

Table 7. Equilibrium constants[a] in the reaction of $[Fe^{II}(cydta)]^{2-}$ with $[V^{IV}O(edta)]^{2-}$ and of $[Fe^{III}(cydta)]^{-}$ with $[V^{III}(edta)]^{-}$ at pH 4.4—6.0[b]

pH	$10K^{Z}_{obs.}$	$10^{11}K^{Z}_{R}$/mol^2 dm^{-6}
(*a*) Reaction of $[Fe^{II}(cydta)]^{2-}$ with $[V^{IV}O(edta)]^{2-}$ [c]		
4.70[d]	0.607	2.34
4.71	0.531	1.90
5.05	3.41	2.61
5.20	5.29	2.09
5.39	11.8	1.95
5.78	60.4	1.69
(*b*) Reaction of $[Fe^{III}(cydta)]^{-}$ with $[V^{III}(edta)]^{-}$ [e]		
4.39	0.131	1.96
4.41	0.162	2.27
4.59	0.272	1.67
4.99	2.38	2.47
5.10	2.98	1.88
5.25	5.65	1.80
5.41	14.9	2.25
5.44	18.8	2.48
5.70	49.8	1.96
5.76[f]	80.7	2.47
5.95[f]	150	1.91

[a] $K^{Z}_{obs.} = [Fe^{II}][V^{IV}]/[Fe^{III}][V^{III}]$ at 25.0 °C and ionic strength = 1.0 mol dm^{-3} ($NaClO_4$). [b] In ethanoate buffers, unless otherwise stated. [c] Initial concentrations: $[Fe^{III}]_0 = [V^{III}]_0 = 0$, $[Fe^{II}]_0 = 3.0 \times 10^{-3}$ mol dm^{-3}, $[V^{IV}]_0 = 6.0 \times 10^{-3}$ mol dm^{-3}. [d] In methanoate buffer. [e] Initial concentrations: $[Fe^{II}]_0 = [V^{IV}]_0 = 0$, $[Fe^{III}]_0 = 3.0 \times 10^{-3}$ mol dm^{-3}, $[V^{III}]_0 = 6.0 \times 10^{-3}$ mol dm^{-3}. [f] In phosphate buffers.

values of $k^{f}_{obs.}$ and $k^{fZ}_{obs.}$ increase with decrease in $[H^+]$, and potential reactant species are the normal and the partially hydrolysed complexes. We have therefore assumed that $k^{f}_{obs.}$ can be expressed in terms of a parallel set of bimolecular reactions as in equation (4) with a corresponding equation for $k^{fZ}_{obs.}$. Here, $[Fe^{III}] = [Fe^{III}(edta)^-] + [Fe^{III}(OH)(edta)^{2-}]$ and $[V^{III}] = [V^{III}(edta)^-] + [V^{III}(OH)(edta)^{2-}]$. By introducing the appropriate acid dissociation constants for the two complexes, equation (4) can be transformed into equation (5);

$$\begin{aligned}\text{Rate} &= k^{f}_{obs.}[Fe^{III}][V^{III}] \\ &= k_1[Fe^{III}(edta)^-][V^{III}(edta)^-] \\ &\quad + k_2[Fe^{III}(OH)(edta)^{2-}][V^{III}(edta)^-] \\ &\quad + k_3[Fe^{III}(edta)^-][V^{III}(OH)(edta)^{2-}] \\ &\quad + k_4[Fe^{III}(OH)(edta)^{2-}][V^{III}(OH)(edta)^{2-}] \quad (4)\end{aligned}$$

$$k^{f}_{obs.} = \frac{k_1[H^+]^2 + (k_2K^{F3}_{a} + k_3K^{V3}_{a})[H^+] + k_4K^{F3}_{a}K^{V3}_{a}}{([H^+] + K^{F3}_{a})([H^+] + K^{V3}_{a})} \quad (5)$$

there is a similar equation for $k^{fZ}_{obs.}$. For the system involving $[Fe^{III}(cydta)]^-$, we find by weighted least-squares analysis that the experiments in Table 3 are in accord with equation (5) with $k^{Z}_{1} = k^{Z}_{4} = 0$; $(k^{Z}_{2}K^{F3Z}_{a} + k^{Z}_{3}K^{V3}_{a}) = (3.51 \pm 0.10) \times 10^{-8}$ s^{-1}, by taking values of K^{F3Z}_{a} and K^{V3}_{a} from Table 1. Values of $k^{fZ}_{calc.}$ calculated from equation (5) with these values of the constants are included in Table 3. The relative standard deviation, comparing corresponding values of $k^{fZ}_{calc.}$ and $k^{fZ}_{obs.}$, is ±6.7%.

In the system $[Fe^{III}(edta)]^- + [V^{III}(edta)]^-$ a substantial proportion of the iron(III) complex is hydrolysed in the region of pH 7 as is apparent from the value of K^{F3}_{a} (Table 1). Further, there is considerable dimerisation of this hydroxo-complex at higher values of pH. Even at pH 6.6 the proportion of total iron(III) present as dimer half-way through the reaction ($[Fe^{III}] = 1.5 \times 10^{-3}$ mol dm^{-3}) is 2.3%, calculated from the constants in ref. 9. Above this pH the proportion of dimer increases substantially. We have therefore restricted the experiments used in fitting $k_{obs.}$ to equation (5) to those at pH 6.6 or less (Table 2). We again find that $k_1 = k_4 = 0$. The value of $(k_2K^{F3}_{a} + k_3K^{V3}_{a})$ is $(5.91 \pm 0.35) \times 10^{-7}$ s^{-1}. Values of $k^{f}_{calc.}$ in Table 2 in the pH range 5.45—6.60 fit the corresponding values of $k^{f}_{obs.}$ with a relative standard deviation of ±8.2%. Values of $k^{f}_{calc.}$ calculated at pH values exceeding 6.6 by using equation (5) are all larger than the corresponding values of $k^{f}_{obs.}$. This is to be expected if the dimer does not participate in a redox path.

Results for the back reaction show an increase in $k^{b}_{obs.}$ and $k^{bZ}_{obs.}$ as $[H^+]$ is increased. The potential reactant species present are the normal unprotonated forms of the iron(II) and vanadium (IV) complexes together with small proportions of the corresponding protonated forms. We have assumed that $k^{b}_{obs.}$ can be expressed by equation (6) where $[Fe^{II}] = [Fe^{II}(edta)^{2-}] + [Fe^{II}(Hedta)(H_2O)^-]$ and $[V^{IV}] = [V^{IV}O(edta)^{2-}] + [V^{IV}O(Hedta)^-]$, with a corresponding equation for $k^{bZ}_{obs.}$. This equation can be transformed into (7) by introducing the appropriate protonation constants. We found by weighted least-squares analysis, with values of K^{F2}_{b} and K^{V4}_{b} from Table 1, that the results in Table 4 fit equation (7) with $k_5 = 0$, $(k_6K^{F2}_{b} + k_7K^{V4}_{b}) = 8\,900 \pm 600$ dm^6 mol^{-2} s^{-1}, and $k_8 = 14.1 \pm 0.8$ dm^3 mol^{-1} s^{-1}. Values of $k^{b}_{calc.}$ in Table 4 are calculated from equation (7) with these values of rate constants and protonation constants. The relative standard deviation, comparing corresponding values of $k^{b}_{calc.}$ with $k^{b}_{obs.}$, is ±6.1%. Similarly, we found that terms in $[H^+]$ and $[H^+]^2$ were required in fitting results for the system $[Fe^{II}(cydta)]^{2-} + [V^{IV}O(edta)]^{2-}$ to the equation corresponding to (7). Values obtained were $k^{Z}_{5} = 0$, $(k^{Z}_{6}K^{F2Z}_{b} + k^{Z}_{7}K^{V4}_{b}) = 1\,060 \pm 60$ dm^6 mol^{-2} s^{-1}, and $k^{Z}_{8} = 4.05 \pm 0.22$ dm^3 mol^{-1} s^{-1}. Values of $k^{bZ}_{calc.}$ calculated from these rate constants and the appropriate protonation constants from Table 1 are included in Table 5. The relative standard deviation, comparing corresponding values of $k^{bZ}_{calc.}$ and $k^{bZ}_{obs.}$, is ±4.6%.

$$\begin{aligned}\text{Rate} &= k^{b}_{obs.}[Fe^{II}][V^{IV}] \\ &= k_5[Fe^{II}(edta)^{2-}][V^{IV}O(edta)^{2-}] \\ &\quad + k_6[Fe^{II}(Hedta)(H_2O)^-][V^{IV}O(edta)^{2-}] \\ &\quad + k_7[Fe^{II}(edta)^{2-}][V^{IV}O(Hedta)^-] \\ &\quad + k_8[Fe^{II}(Hedta)(H_2O)^-][V^{IV}O(Hedta)^-] \quad (6)\end{aligned}$$

$$k^{b}_{obs.} = \frac{k_5 + (k_6K^{F2}_{b} + k_7K^{V4}_{b})[H^+] + k_8K^{F2}_{b}K^{V4}_{b}[H^+]^2}{(1 + K^{F2}_{b}[H^+])(1 + K^{V4}_{b}[H^+])} \quad (7)$$

The equilibrium constant K_R for reaction (1) is defined in equation (2). By making allowances for the significant proportion of protonated forms of iron(II) and vanadium(IV) complexes at the lower end of the pH range (4.2—5.6) at which the equilibrium was investigated directly, we obtain equation (8) whence the values of K_R in Table 6 were obtained from $K_{obs.}$. Similarly, values of K^{Z}_{R} are shown in Table 7. By equating the forward and backward rates of reactions under conditions in which a measurable equilibrium is established, the relationship between K_R and appropriate rate constants can be found. In the region of pH 5 the term in k_8 (or k^{Z}_{8}) is negligible for the back reaction and the relationship is simply

$$K_R = K_{obs.}[H^+]^2/\{(1 + K^{F2}_{b}[H^+])(1 + K^{V4}_{b}[H^+])\} \quad (8)$$

Table 8. Equilibrium constants [a] and limiting rate constants [b] for selected redox reactions

Reaction	X	For forward reaction	For back reaction
(i) $[Fe^{III}(OH)(X)]^{2-} + [V^{III}(edta)]^- \rightleftharpoons [Fe^{II}(HX)(H_2O)]^- + [V^{IV}O(edta)]^{2-}$	edta	$K_1 = 2.03, k_2 = 22.5$	$K_{-1} = 0.49, k_6 = 11.1$
	cydta	$K_1^Z = 54, k_2^Z = 74$	$K_{-1}^Z = 0.0187, k_6^Z = 1.38$
(ii) $[Fe^{III}(OH)(X)]^{2-} + [V^{III}(edta)]^- \rightleftharpoons [Fe^{II}(X)]^{2-} + [V^{IV}O(Hedta)]^-$	edta	$K_2 = 3.7, k_2 = 22.5$	$K_{-2} = 0.273, k_7 = 6.1$
	cydta	$K_2^Z = 101, k_2^Z = 74$	$K_{-2}^Z = 0.0099, k_7^Z = 0.73$
(iii) $[Fe^{III}(X)]^- + [V^{III}(OH)(edta)]^{2-} \rightleftharpoons [Fe^{II}(HX)(H_2O)]^- + [V^{IV}O(edta)]^{2-}$	edta	$K_3 = 198, k_3 = 2\,200$	$K_{-3} = 0.0050, k_6 = 11.1$
	cydta	$K_3^Z = 95, k_3^Z = 132$	$K_{-3}^Z = 0.0105, k_6^Z = 1.38$
(iv) $[Fe^{III}(X)]^- + [V^{III}(OH)(edta)]^{2-} \rightleftharpoons [Fe^{II}(X)]^{2-} + [V^{IV}O(Hedta)]^-$	edta	$K_4 = 360, k_3 = 2\,200$	$K_{-4} = 0.0028, k_7 = 6.1$
	cydta	$K_4^Z = 180, k_3^Z = 132$	$K_{-4}^Z = 0.0056, k_7^Z = 0.73$

$K_1 = 1/K_{-1} = K_R K_b^{F2}/K_a^{F3}$ $K_3 = 1/K_{-3} = K_R K_b^{F2}/K_a^{V3}$ $K_1^Z = 1/K_{-1}^Z = K_R^Z K_b^{F2Z}/K_a^{F3Z}$ $K_3^Z = 1/K_{-3}^Z = K_R^Z K_b^{F2Z}/K_a^{V3}$

$K_2 = 1/K_{-2} = K_R K_b^{V4}/K_a^{F3}$ $K_4 = 1/K_{-4} = K_R K_b^{V4}/K_a^{V3}$ $K_2^Z = 1/K_{-2}^Z = K_R^Z K_b^{V4}/K_a^{F3Z}$ $K_4^Z = 1/K_{-4}^Z = K_R^Z K_b^{V4}/K_a^{V3}$

Equilibrium constants, K_1 to K_{-4}^Z for the reactions shown are dimensionless quantities. [b] Bimolecular rate constants; units are dm^3 mol^{-1} s^{-1}. At 25.0 °C and ionic strength = 1.0 mol dm^{-3} ($NaClO_4$).

equation (9). Both terms in brackets have been obtained from the analysis of the kinetic results for the forward and back

$$K_R = (k_2 K_a^{F3} + k_3 K_a^{V3})/(k_6 K_b^{F2} + k_7 K_b^{V4}) \qquad (9)$$

reactions, so that ' kinetic ' values of K_R can be obtained and compared with those found by measuring equilibrium concentrations. We find $K_R = (6.66 \pm 0.57) \times 10^{-11}$ and $(9.09 \pm 1.25) \times 10^{-11}$ mol^2 dm^{-6}; for the system with iron complexes with cydta, $K_R^Z = (3.35 \pm 0.21) \times 10^{-11}$ and $(2.06 \pm 0.31) \times 10^{-11}$ mol^2 dm^{-6}; in both pairs the ' kinetic ' value is given first. The disparities within the two pairs of values are in opposite senses, suggesting that experimental errors are responsible rather than the admitted uncertainty of extrapolating kinetic data to a pH range different from that in which the data were determined.

Mechanistic aspects of the reaction. In these systems, for adjacent pH ranges, we have obtained the equilibrium constant for the overall reaction and, subject to the assumption mentioned above, apparent forward and backward bimolecular rate constants. However, these do not all correspond to reaction between a particular pair of complexes. For the forward reaction the term $(k_2 K_a^{F3} + k_3 K_a^{V3})[H^+]$ in equation (5) arises because two distinct reaction paths depend in the same way on $[H^+]$. The contribution of each of these cannot be established from our experiments, but by assuming successively $k_3 = 0$ and $k_2 = 0$, upper limits can be obtained. Similarly for the back reaction, upper limits for k_6 and k_7 can be found. From the overall equilibrium constant, by using the appropriate hydrolysis and protonation constants, an equilibrium constant can be obtained for each of various possible redox reactions between the pairs of potentially reacting complexes. Here, the term redox reaction implies a reaction between a pair of complexes in which the principal difference between a reactant complex and its product appears as a change of one unit in the oxidation state of the metal atom. The term includes mechanisms of the outer-sphere electron-transfer type, as well as inner-sphere reactions with or without transfer of the bridging group.

The various rate constants with related calculated equilibrium constants are summarised in Table 8. For consistency we have used ' kinetic ' values of K_R and K_R^Z, but our qualitative comparisons lead to the same conclusions if the alternative values are used. Comparisons of the rate constant and equilibrium constant for each reaction in the iron–edta system with those for the reaction between corresponding species in the iron–cydta system may indicate that certain routes of reaction or types of mechanism are more probable than others. We had in mind observations that certain redox reactions involving edta and cydta complexes show marked differences in rates which can be ascribed to the pronounced steric effects in bridged transition states when edta is replaced by cydta.[10] In other redox reactions there is little abnormal kinetic effect when edta is replaced by cydta, taking into account any changes in the equilibrium constants. Such cases are thought to involve outer-sphere mechanisms.[1,11] Before making such comparisons, the structure of certain species requires comment. Despite contrary views [12] we believe that species represented in this paper as $[V^{III}(edta)]^-$, $[Fe^{III}(edta)]^-$, $[Fe^{II}(edta)]^{2-}$, and the corresponding cydta complexes of iron are predominantly sexidentate in solution and do not contain ligand water molecules. Our views are partly based upon the magnitudes of the pK_a values of these complexes relative to those of various quinquedentate and sexidentate cobalt(III) complexes.[13] However, the iron and vanadium(III) complexes considered here are substitution-labile for equilibria between sexidentate and aquaquinquedentate forms, so that the predominant form in solution may not be directly involved in a redox step. A special situation arises with the vanadium(IV) species in equations (ii) and (iv) of Table 8. The equilibrium constants and back reaction rate constants for these redox reactions are calculated for the species $[V^{IV}O(Hedta)]^-$ whereas the isomer $[V^{IV}(OH)(edta)]^-$ would be directly involved, both in the transfer of an OH group in reaction (ii) and in the electron transfer (iv). Lacking a reliable value for the ratio $K_5 = [V^{IV}(OH)(edta)^-]/[V^{IV}O(Hedta)^-]$ (which we estimate is *ca.* 0.01) we cannot correct the values of K_2, K_{-2}, K_4, K_{-4}, k_7 and the corresponding constants for the iron–cydta system in Table 8. Fortunately, the following arguments depend upon comparisons of values of rate and equilibrium constants when cydta takes the place of edta in the iron complexes. Uncertainty about K_5 will affect corresponding constants in the two systems in the same way and so does not vitiate the comparisons, the change from edta to cydta being on iron only.

Considering the four redox reactions shown in Table 8, only reaction (iv) {with $[V^{IV}(OH)(edta)]^-$ as the vanadium(IV) complex} is possibly an outer-sphere electron-transfer reaction. Bearing in mind the values of the forward and reverse equilibrium constants, with both iron–edta and iron–cydta complexes, the rate constants for the latter system are unexpectedly low relative to those of the former system, if the reactions involve simple electron transfer between metal atoms in which adjustment of the primary co-ordination sphere is facile (in contrast to Co^{III} complexes). On the other hand, if an inner-sphere reaction occurs *via* an OH bridge, the lower rate constants for the latter system can be ascribed to the steric effect of cydta relative to edta. Similarly, reaction (iii) shows the relatively low values of rate constants in the iron–cydta system to be expected for a reaction involving bridging. Reactions (i) and (ii) involve bridging with transfer of oxygen between iron and vanadium in (i) and of an OH group in (ii). Here the backward rate constants do not appear to show the expected consequences of the steric effects characteristic of cydta. The change from the edta to the cydta complex of iron(II) decreases the equilibrium constants K_{-1} and K_{-2} by a factor of *ca.* 0.04 whereas the effect on the corresponding rate constants k_6 and k_7 is smaller, a factor of *ca.* 0.12.

Summarising, these results enable us to exclude an outer-sphere electron-transfer mechanism in these reactions. We have restricted consideration of inner-sphere mechanisms to those involving vanadyl oxygen as a bridging atom. For these, although the evidence is not so compelling, we conclude that oxygen or OH group transfer does not occur from iron(III) to vanadium(III) as part of the redox process. Both the preferred mechanisms (iii) and (iv) involve bridging *via* an oxygen which remains bonded to vanadium. These mechanisms differ only in the fate of the proton of the vanadium(III) hydroxo-group. In reaction (iii) the proton is transferred to the carboxylate group which is necessarily detached from the iron atom to permit formation of the hydroxo-bridge; in reaction (iv) the proton remains a part of the vanadium complex. Both reactions (iii) and (iv) in the forward direction involve k_3, equations (4) and (5). It is therefore possible that the group-transfer mechanisms (i) and (ii), corresponding to k_2, may occur to a minor extent. In this case the ratio k_2^Z/k_2 could differ substantially from the value of *ca.* 3.3 which led to the rejection of mechanisms (i) and (ii) as major contributors to the overall reaction.

In the region of pH 3, the redox reaction between the iron(II) and vanadium(IV) complexes occurs predominantly by a reaction path in which two protons are incorporated in the transition state. We have assumed that a bimolecular redox reaction occurs between $[Fe^{II}(Hedta)(H_2O)]^-$ or $[Fe^{II}(Hcydta)(H_2O)]^-$ and $[V^{IV}O(Hedta)]^-$ in evaluating the two rate constants k_8 and k_8^Z. The ratio k_8^Z/k_8 is *ca.* 0.28 and would be unaltered if $[V^{IV}(OH)(edta)]^-$ reacts, rather than its isomer. It is possible that the active species are $[Fe^{II}(edta)]^{2-}$ or $[Fe^{II}(cydta)]^{2-}$ and $[V^{IV}(OH)(Hedta)]$; in this case the ratio of the corresponding bimolecular rate constants k_9^Z/k_9 remains *ca.* 0.28 because the values of K_b^{F2} and K_b^{F2Z} are very similar (Table 1). In contrast, the equilibrium constants for electron transfer within either of these differently protonated pairs of potential reactants are larger for the systems including iron(II)–cydta complexes than those for the corresponding systems with edta. We regard this as evidence against an outer-sphere electron-transfer mechanism. However, these results do not enable us to choose between these two possible pairs of reactants, or to make other conclusions about the mechanisms of this reaction path.

(2) Redox Reaction at $[H^+] = 0.05$—0.25 mol dm^{-3}

Results.—Kinetic experiments were done with 5.0×10^{-4} mol dm^{-3} $[Fe^{III}(edta)]^-$ and 0.010—0.040 mol dm^{-3} $[V^{III}(edta)]^-$. The overall reaction at $[H^+] = 0.125$—0.25 mol dm^{-3} is given in equation (3A) showing a decrease of *ca.* 4×10^{-3} mol dm^{-3} in $[H^+]$ occurs during the course of reaction. At $[H^+] = 0.10$ mol dm^{-3} and below, the decrease in $[H^+]$ is (2—3) $\times$ 10^{-3} mol dm^{-3} in accordance with the dominance of reaction (3B). Plots of log $[Fe^{III}]$ against time were linear up to *ca.* 75% of reaction when curvature occurred corresponding to an apparent increase in the first-order rate constant. At higher values of $[H^+]$ this curvature occurred at an earlier stage, *e.g.* at 50% reaction for $[H^+] = 0.30$ mol dm^{-3}. Final values of optical density showed at least 96% completion except for experiments with 0.010 mol dm^{-3} $[V^{III}(edta)]^-$ at $[H^+] = 0.050$ and 0.075 mol dm^{-3} in which only *ca.* 90% of iron(III) was reduced. These observations led us to limit the range of $[H^+]$ studied in detail to 0.050—0.250 mol dm^{-3}. As described in the ensuing discussion, we found that plots linear up to 95% reaction could be obtained if log ($[Fe^{III}] + q$) was plotted against time, the parameter q for a particular reaction being obtained by trial and error. The values of $k_{obs.} = -2.303G$ in Table 9 were obtained from the gradients G of such plots. These rate constants are somewhat smaller than the corresponding pseudo-unimolecular constants obtained from the initial linear portion of the simple plot of log $[Fe^{III}]$ against time. The biggest proportional differences appear at the higher values of $[H^+]$ and $[V^{III}]$, *e.g.* at $[H^+] = 0.250$ mol dm^{-3} and $[V^{III}(edta)^-] = 0.040$ mol dm^{-3}, $k_{obs.}$ from the simple logarithimic plot exceeds by 16% that from the plot of log ($[Fe^{III}] + q$) against time. The mean excess for all the experiments for which q is not zero is 6.9%.

Catalysis by cations. Various kinetic experiments were done at $[H^+] = 0.150$ mol dm^{-3} in the presence of a doubly charged cation, Cu^{2+}, Fe^{2+}, Mg^{2+}, Ni^{2+}, VO^{2+}, or Zn^{2+}. The optical absorption of these ions at 350 nm is such that little or no correction was necessary in evaluating concentrations of iron(III) from optical densities. Although these cations showed catalytic effects, the curvature of the simple logarithmic plots after 75% reaction was not noticeably changed, except with VO^{2+}. At $[H^+] = 0.150$ mol dm^{-3} in the absence of catalysts, rate constants obtained from the simple logarithmic plot were 1.4—3.5% higher than those obtained from the plot of log ($[Fe^{III}] + q$) (Table 9). Since the correction obtained by introducing q would be small in most cases of cation catalysis, the values of $k_{obs.}$ summarised in Table 10 are each derived from the linear portion of the simple logarithmic plot. In the case of VO^{2+}, more pronounced curvature showed that higher values of q than those normally found at this acidity would be required; this aspect was not investigated further.

Discussion.—Dependence of $k_{obs.}$ *upon* $[V^{III}]$ *and* $[H^+]$. At each value of $[H^+]$ the various values of $k_{obs.}$ in Table 9 were found to be related to $[V^{III}]$ through equation (10). Here k_g is a bimolecular constant for reaction between iron(III) and vanadium(III) species, while k_h is a unimolecular constant apparently involving iron(III) species alone in the rate-determining step of the corresponding reaction path. In the range $[H^+] = 0.05$—0.25 mol dm^{-3} the predominant species are $[Fe^{III}(edta)]^-$ and $[V^{III}(edta)]^-$, but significant proportions of $[Fe^{III}(Hedta)(H_2O)]$ and $[V^{III}(Hedta)(H_2O)]$ are also present. We have therefore interpreted the dependence of k_g upon $[H^+]$ by assuming redox reactions may occur between one or more of the various combinations of normal and protonated complexes, equation (11). Here and subsequently

$$k_{obs.} = k_g[V^{III}] + k_h \qquad (10)$$

$$\begin{aligned}\text{Rate (bimolecular path)} &= k_g[Fe^{III}][V^{III}]\\ &= k_{10}[Fe^{III}(edta)^-][V^{III}(edta)^-]\\ &\quad + k_{11}[Fe^{III}(Hedta)(H_2O)][V^{III}(edta)^-]\\ &\quad + k_{12}[Fe^{III}(edta)^-][V^{III}(Hedta)(H_2O)]\\ &\quad + k_{13}[Fe^{III}(Hedta)(H_2O)][V^{III}(Hedta)(H_2O)] \qquad (11)\end{aligned}$$

$[Fe^{III}] = [Fe^{III}(edta)^-] + [Fe^{III}(Hedta)(H_2O)]$ and $[V^{III}] = [V^{III}(edta)^-] + [V^{III}(Hedta)(H_2O)]$. By introducing the appropriate protonation constants we then obtain equation (12). Taking the values of the protonation constants from Table 1, we found by weighted least-squares analysis that

$$k_g = \frac{k_{10} + (k_{11}K_b^{F3} + k_{12}K_b^{V3})[H^+] + k_{13}K_b^{F3}K_b^{V3}[H^+]^2}{(1 + K_b^{F3}[H^+])(1 + K_b^{V3}[H^+])} \qquad (12)$$

Table 9. Rate constants[a] for reaction of $[\mathrm{Fe^{III}(edta)}]^-$ [b] with $[\mathrm{V^{III}(edta)}]^-$ at $[\mathrm{H^+}]$ = 0.050—0.250 mol dm^{-3}

$10^3[\mathrm{V^{III}(edta)^-}]_0$/mol dm^{-3}	10^6q/mol dm^{-3}	$10^4k_{\mathrm{obs.}}$/s^{-1}	$10^4k_{\mathrm{calc.}}$/s^{-1}
(*a*) $[\mathrm{H^+}]$ = 0.250 mol dm^{-3}			
10	10	2.23	2.16
15	25	2.53	2.62
20	35	2.97	3.08
25	40	3.72	3.54
30	45	4.26	3.99
35	50	4.58	4.45
40	55	4.96	4.91
(*b*) $[\mathrm{H^+}]$ = 0.200 mol dm^{-3}			
10	10	1.45	1.47
15	15	1.84	1.90
20	20	2.31	2.33
25	25	2.78	2.76
30	30	3.16	3.19
35	35	3.51	3.62
40	40	3.83	4.05
(*c*) $[\mathrm{H^+}]$ = 0.175 mol dm^{-3}			
10	10	1.24	1.22
20	20	2.06	2.04
30	30	2.85	2.86
40	40	3.61	3.67
(*d*) $[\mathrm{H^+}]$ = 0.150 mol dm^{-3}			
10	8	0.992	1.01
15	10	1.38	1.40
20	12	1.80	1.78
25	15	2.16	2.16
30	16	2.53	2.54
35	18	2.87	2.92
40	20	3.33	3.31
(*e*) $[\mathrm{H^+}]$ = 0.125 mol dm^{-3}			
10	5	0.761	0.838
20	10	1.51	1.54
30	15	2.15	2.23
40	20	2.74	2.93
(*f*) $[\mathrm{H^+}]$ = 0.100 mol dm^{-3}			
10	0	0.685	0.684
15	0	0.972	0.991
20	0	1.29	1.30
25	4	1.52	1.61
30	6	1.84	1.91
35	10	2.12	2.22
40	20	2.39	2.53
(*g*) $[\mathrm{H^+}]$ = 0.075 mol dm^{-3}			
10	0	0.518	0.538
20	0	1.01	1.05
30	0	1.64	1.56
40	5	2.26	2.07
(*h*) $[\mathrm{H^+}]$ = 0.050 mol dm^{-3}			
10	0	0.388	0.386
15	0	0.637	0.575
20	0	0.813	0.764
25	0	1.04	0.953
30	0	1.28	1.14
35	0	1.48	1.33
40	0	1.72	1.52

[a] At 25.0 °C and ionic strength 1.0 mol dm^{-3} ($\mathrm{NaClO_4}$); $k_{\mathrm{obs.}}$ obtained from plots of log ($[\mathrm{Fe^{III}}] + q$) against time. [b] Initial concentration: $[\mathrm{Fe^{III}}]_0 = 5.0 \times 10^{-4}$ mol dm^{-3}.

$k_{10} = k_{13} = 0$ and $(k_{11}K_\mathrm{b}^{\mathrm{F}3} + k_{12}K_\mathrm{b}^{\mathrm{V}3}) = (9.55 \pm 0.46) \times 10^{-2}$ dm^6 mol^{-2} s^{-1}.

The rate constant k_h increased rapidly with increase in $[\mathrm{H^+}]$, so that terms involving $[\mathrm{Fe^{III}(edta)^-}]$ were omitted from the rate equation. Two terms differing in their dependence on $[\mathrm{H^+}]$ were required, equation (13); the introduction of $K_\mathrm{b}^{\mathrm{F}3}$ then yields equation (14) from which, by weighted least-squares analysis, we find $k_{14} = (1.79 \pm 1.53) \times 10^{-3}$ dm^6 mol^{-2} s^{-1} and $k_{15} = (1.03 \pm 0.74) \times 10^{-2}$ dm^9 mol^{-3} s^{-1}.

$$\text{Rate (unimolecular path)} = k_\mathrm{h}[\mathrm{Fe^{III}}] = (k_{14}[\mathrm{H^+}]^2 + k_{15}[\mathrm{H^+}]^3)[\mathrm{Fe^{III}(Hedta)(H_2O)}] \quad (13)$$

$$k_\mathrm{h} = (k_{14} + k_{15}[\mathrm{H^+}])K_\mathrm{b}^{\mathrm{F}3}[\mathrm{H^+}]^3/(1 + K_\mathrm{b}^{\mathrm{F}3}[\mathrm{H^+}]) \quad (14)$$

By using the values of $(k_{11}K_\mathrm{b}^{\mathrm{F}3} + k_{12}K_\mathrm{b}^{\mathrm{V}3})$, k_{14} and k_{15} given above, values of $K_\mathrm{b}^{\mathrm{F}3}$ and $K_\mathrm{b}^{\mathrm{V}3}$ from Table 1, together with equations (10), (12), and (14), calculated values $k_{\mathrm{calc.}}$ of the overall rate constant $k_{\mathrm{obs.}}$ were obtained from initial values of $[\mathrm{V^{III}}]$ and $[\mathrm{H^+}]$. These values of $k_{\mathrm{calc.}}$ are included in Table 9; their relative standard deviation from the corresponding values of $k_{\mathrm{obs.}}$ is ±5.02%.

Mechanism of the bimolecular path. From the above value of the composite rate constant $(k_{11}K_\mathrm{b}^{\mathrm{F}3} + k_{12}K_\mathrm{b}^{\mathrm{V}3})$ we obtained upper limits of 0.029 and 0.057 dm^3 mol^{-1} s^{-1} for k_{11} and k_{12}, respectively. We consider the most plausible mechanism involves formation of a hydroxo-bridged transition state from $[\mathrm{Fe^{III}(Hedta)(H_2O)}]$ and $[\mathrm{V^{III}(OH)(Hedta)}]^-$. The latter species is present in constant proportion to $[\mathrm{V^{III}(edta)}]^-$ so that the appropriate rate constant is simply related to k_{11} [equation (11)]. Following an earlier discussion [14] of the value of the ratio $[\mathrm{Co^{III}(OH)(Hedta)^-}]/[\mathrm{Co^{III}(edta)(H_2O)^-}]$ we conclude $[\mathrm{V^{III}(OH)(Hedta)^-}]/[\mathrm{V^{III}(edta)^-}]$ is *ca.* 3×10^{-7}. Correcting k_{11} to take into account this value, we obtain $k'_{11} \sim 10^5$ dm^3 mol^{-1} s^{-1} for redox reaction between $[\mathrm{Fe^{III}(Hedta)(H_2O)}]$ and $[\mathrm{V^{III}(OH)(Hedta)}]^-$. This reaction is formally similar to reactions (iii) and (iv) in Table 8. The rate constant for these reactions, which we consider to be the most probable redox steps at pH 5.4—7.1, is k_3 = 2 200 dm^3 mol^{-1} s^{-1}. This value is only 0.02 k'_{11}, but this can be understood because bridge formation in reactions (iii) or (iv) involves breaking an iron(III)–carboxylate bond in the sexidentate complex $[\mathrm{Fe^{III}(edta)}]^-$. In the presumed reaction between $[\mathrm{Fe^{III}(Hedta)(H_2O)}]$ and $[\mathrm{V^{III}(OH)(Hedta)}]^-$ this bond is already broken, the fourth carboxylate ligand being replaced by the weaker aqua-ligand.

Mechanism of the unimolecular path. The above analysis of the dependence of k_h upon $[\mathrm{H^+}]$ leads to equation (14). Nevertheless, a much simpler relationship, equation (15), fits our results equally well, even though the distribution of iron(III) between $[\mathrm{Fe^{III}(edta)}]^-$ and $[\mathrm{Fe^{III}(Hedta)(H_2O)}]$ is ignored. (In the range $[\mathrm{H^+}]$ = 0.05—0.25 mol dm^{-3} the proportion of the latter species varies from 14% to 45% of $[\mathrm{Fe^{III}}]$.) We find $k_{16} = (7.7 \pm 1.3) \times 10^{-3}$ dm^9 mol^{-3} s^{-1}. In a study of the exchange of labelled iron between $[\mathrm{Fe^{III}(edta)}]^-$ and $\mathrm{Fe^{3+}}$ in acid solution [15] a term $k[\mathrm{Fe^{III}(edta)^-}][\mathrm{H^+}]^3$ appears in the rate equation and is interpreted as a rate-determining acid-promoted dissociation of the complex to give $\mathrm{Fe^{3+}}$. The value of k is 7.8×10^{-3} dm^9 mol^{-3} s^{-1} under similar conditions of temperature and ionic strength to those of our experiments. Consequently, we propose a mechanism in which reaction (16) is rate-determining and is followed by the potentially rapid overall redox reactions (17A) and (17B), their proportion depending upon $[\mathrm{H^+}]$. With $[\mathrm{Fe^{3+}}] = 5 \times 10^{-4}$ mol dm^{-3} and $[\mathrm{V^{III}(edta)^-}]$ = 0.010 mol dm^{-3} at $[\mathrm{H^+}]$ = 0.20 mol dm^{-3}

$$k_\mathrm{h} = k_{16}[\mathrm{H^+}]^3 \quad (15)$$

Table 10. Overall rate constants[a] for reaction of $[Fe^{III}(edta)]^-$ [b] with $[V^{III}(edta)]^-$ in the presence of doubly charged cations, M^{2+}

$10^3[V^{III}(edta)^-]_0$/mol dm^{-3}	$10^3[M^{2+}]$/mol dm^{-3}	$10^4k^M_{obs.}$/s^{-1}
(*a*) M^{2+} absent, constants are $k'_{obs.}$		
10	0	1.01
20	0	1.83
30	0	2.61
40	0	3.44
(*b*) M^{2+} = copper(II)		
10	5.0	1.49
10	10.0	2.10
20	5.0	2.61
20	10.0	3.44
30	5.0	3.54
30	10.0	4.30
40	5.0	4.71
40	10.0	6.10
(*c*) M^{2+} = iron(II)		
10	1.0	1.03
10	5.0	1.26
20	1.0	1.89
20	5.0	2.11
30	1.0	2.71
30	5.0	3.04
40	1.0	3.66
40	5.0	3.95
(*d*) M^{2+} = magnesium(II)		
10	5.0	1.02
10	20.0	1.06
20	5.0	1.84
20	20.0	1.88
30	5.0	2.67
30	20.0	2.72
40	5.0	3.48
40	20.0	3.57
(*e*) M^{2+} = nickel(II)		
10	5.0	1.01
10	10.0	1.01
20	5.0	1.80
20	10.0	1.93
30	5.0	2.65
30	10.0	2.61
40	5.0	3.43
40	10.0	3.55
(*f*) M^{2+} = oxovanadium(IV)		
10	1.0	1.10
10	5.0	1.37
10	10.0	1.74
20	1.0	2.07
20	5.0	2.60
20	10.0	3.30
30	1.0	2.86
30	5.0	3.68
30	10.0	4.78
40	1.0	3.77
40	5.0	4.86
40	10.0	6.37
(*g*) M^{2+} = zinc(II)		
10	5.0	1.00
10	20.0	1.00
20	5.0	1.85
20	20.0	1.92
30	5.0	2.64
30	20.0	2.71
40	5.0	3.49
40	20.0	3.64

[a] At 25.0 °C, $[H^+] = 0.150$ mol dm^{-3}, ionic strength 1.0 mol dm^{-3} ($NaClO_4$); $k^M_{obs.}$ obtained from plots of log $[Fe^{III}]$ against time.
[b] Initial concentration: $[Fe^{III}]_0 = 5.0 \times 10^{-4}$ mol dm^{-3}.

$$[Fe^{III}(edta)]^- + 5H^+ \longrightarrow Fe^{3+} + H_5edta^+ \quad (16)$$

$$Fe^{3+} + [V^{III}(edta)]^- + 3H^+ \longrightarrow Fe^{2+} + V^{IV}O^{2+} + H_5edta^+ \quad (17A)$$

$$Fe^{3+} + [V^{III}(edta)]^- \longrightarrow Fe^{2+} + [V^{IV}O(Hedta)]^- + H^+ \quad (17B)$$

redox was completed within 20 s at 25.0 °C, a much more rapid reaction than that between $[Fe^{III}(edta)]^-$ and $[V^{III}(edta)]^-$. The essentials of this interpretation are unaltered if, as we believe, the rate-determining decomposition of the iron(III)–edta complexes occurs *via* two paths differing in their dependence on $[H^+]$.

The significance of the parameter q. The occurrence of the 'unimolecular' path discussed above points to the possibility of the complementary route involving reaction (18), followed by (19A) and (19B), both of which may occur in several steps. The acid-promoted dissociation of the edta complex may

$$[V^{III}(edta)]^- + 5H^+ \longrightarrow V^{3+} + H_5edta^+ \quad (18)$$

$$[Fe^{III}(edta)]^- + V^{3+} + 3H^+ \longrightarrow Fe^{2+} + V^{IV}O^{2+} + H_5edta^+ \quad (19A)$$

$$[Fe^{III}(edta)]^- + V^{3+} \longrightarrow Fe^{2+} + [V^{IV}O(Hedta)]^- + H^+ \quad (19B)$$

again be rate-determining because the redox reaction, equation (19A) or (19B), was found to be complete within 20 s with 5.0×10^{-4} mol dm^{-3} $[Fe^{III}(edta)]^-$ and $[V^{3+}] = 0.010$ mol dm^{-3} at $[H^+] = 0.20$ mol dm^{-3} and 25.0 °C. If we extend equation (10) to include this route proceeding *via* V^{3+} we obtain equation (20). In our experiments $[V^{III}]$ can be regarded as constant since it greatly exceeds $[Fe^{III}]$. Integrating,

$$-d[Fe^{III}]/dt = k_g[Fe^{III}][V^{III}] + k_h[Fe^{III}] + k_j[V^{III}] \quad (20)$$

we obtain equation (21), the significance of which is obvious, remembering that $k_{obs.}$ in equation (10) is obtained from plots of log ($[Fe^{III}] + q$) against time with q adjusted to give

$$2.303 \log \{[Fe^{III}] + k_j[V^{III}]/(k_g[V^{III}] + k_h)\} = -(k_g[V^{III}] + k_h)t + \text{constant} \quad (21)$$

linearity for each experiment. Equation (21) provides a basis for the interpretation of q which should therefore be defined by equation (22). The values of $k_{obs.}$ are such that q should

$$q = k_j[V^{III}]/(k_g[V^{III}] + k_h) = k_j[V^{III}]/k_{obs.} \quad (22)$$

increase by a factor not exceeding *ca.* 1.7 as $[V^{III}]$ is changed from 0.010 to 0.040 mol dm^{-3} at constant $[H^+]$. Reference to Table 9 shows that larger changes than this occur; we are satisfied that this is not a consequence of the rather high error in obtaining q. We therefore considered other possible causes of the curvature of simple first-order plots. The most probable alternative was catalysis by reaction products and we found that this does occur, as described subsequently in this paper. However, the magnitude of such catalysis was found to be insufficient to lead to appreciable curvature and we have therefore reconsidered the original interpretation. The sequence of reactions (18) and (19) resembles the sequence (16) and (17), but the reactant concentrations do not favour a rate-determining decomposition of the edta complex followed by a rapid, scavenging, redox reaction in the case of the first pair. The concentration of $[\mathrm{Fe^{III}(edta)}]^-$, the scavenger in (19), does not exceed 5.0×10^{-4} mol dm^{-3} in contrast to the higher concentration, 0.010 mol dm^{-3} of $[\mathrm{V^{III}(edta)}]^-$, the scavenger in (17). With inefficient scavenging it is perhaps surprising that the simple modification of the first-order plot by introducing q is sufficient to give plots linear up to 96% of reaction. Experimental values of q should not be substantially less than those calculated from equation (22) which will yield an upper limit. We have investigated the rate of decomposition of $[\mathrm{V^{III}(edta)}]^-$ to $\mathrm{V^{3+}}$ over the range $[\mathrm{H^+}] = 0.6$—4.0 mol dm^{-3} at ionic strength 4.0 mol dm^{-3} ($\mathrm{NaClO_4}$) and at 25.0 °C.[16] Extrapolation of the unimolecular rate constant $k_j = -2.303\, \mathrm{d} \log [\mathrm{V^{III}(edta)^-}]/\mathrm{d}t$ to $[\mathrm{H^+}] = 0.125$ and 0.250 mol dm^{-3} gives values of 3.1×10^{-7} and 2.3×10^{-6} s^{-1}, respectively. By using equation (22) with $[\mathrm{V^{III}}] = 0.040$ mol dm^{-3} we calculate $10^5 q = 4.5$ (2.0) mol dm^{-3} at $[\mathrm{H^+}] = 0.125$ mol dm^{-3} and 18.5 (5.5) mol dm^{-3} at $[\mathrm{H^+}] = 0.250$ mol dm^{-3}; corresponding experimental values from Table 9 follow in parentheses. These comparisons lead to the conclusion that the curvature of plots of log $[\mathrm{Fe^{III}}]$ against time is due to a minor reaction path involving reactions (18) and (19), but that under our conditions its contribution is less than the rate of reaction (18) because the $\mathrm{V^{3+}}$ produced in the latter reaction is not scavenged efficiently by reaction (19).

Catalysis by cations. Catalysis by a product was investigated as an alternative cause of the curvature of plots of log $[\mathrm{Fe^{III}}]$ against time. For $\mathrm{Fe^{II}}$ the complex with edta is virtually completely decomposed, even at $[\mathrm{H^+}] = 0.050$ mol dm^{-3}. Spectrophotometric investigations of solutions of $[\mathrm{V^{IV}O(edta)}]^{2-}$ showed that at the conclusion of the redox reaction the proportion of $\mathrm{V^{IV}}$ product in the form $[\mathrm{V^{IV}O(Hedta)}]^-$ is 88%, 33%, 12% at $[\mathrm{H^+}] = 0.050$, 0.150, 0.250 mol dm^{-3}, respectively, the remaining part being $\mathrm{VO^{2+}}$. The magnitude of q increases with increase in $[\mathrm{H^+}]$, hence vanadium(IV) catalysis is likely to be by $\mathrm{VO^{2+}}$ rather than $[\mathrm{V^{IV}O(Hedta)}]^-$ since the proportion of the latter decreases with increase in $[\mathrm{H^+}]$. Accordingly we have investigated the effect of addition of $\mathrm{VO^{2+}}$ rather than its edta complex. Experiments were also done in the presence of cations other than $\mathrm{Fe^{2+}}$ and $\mathrm{VO^{2+}}$ to establish the general or specific nature of the catalysis.

An obvious effect of catalysis by a constant concentration of a catalyst would be to increase one or more of the rate constants in equation (20). Terms involving dependence on reactant concentrations different from those in the terms in equation (20) were not necessary. Accordingly, the general equation to allow for catalysis by a cation $\mathrm{M^{2+}}$ is equation (23). At $[\mathrm{H^+}] = 0.150$ mol dm^{-3} we can omit the correction averaging *ca.* 2.6% to $k_{\mathrm{obs.}}$, obtained by introducing q, for all cations except $\mathrm{VO^{2+}}$. For these cations the term in $(k_j + k_j^{\mathrm{M}}[\mathrm{M^{2+}}])$ may therefore be omitted and $k_{\mathrm{obs.}}^{\mathrm{M}}$, obtained from

$$-\mathrm{d}[\mathrm{Fe^{III}}]/\mathrm{d}t = (k_g + k_g^{\mathrm{M}}[\mathrm{M^{2+}}])[\mathrm{Fe^{III}}][\mathrm{V^{III}}] + (k_h + k_h^{\mathrm{M}}[\mathrm{M^{2+}}])[\mathrm{Fe^{III}}] + (k_j + k_j^{\mathrm{M}}[\mathrm{M^{2+}}])[\mathrm{V^{III}}] \quad (23)$$

the linear portion of the simple plot of log $[\mathrm{Fe^{III}}]$ against time, is defined by equation (24). By combining equations (10) and (24) we obtain equation (25) in which $k'_{\mathrm{obs.}}$ signifies the first-order constant obtained, without introducing q, from the linear portion of the plot of log $[\mathrm{Fe^{III}}]$ against time at the same value of $[\mathrm{V^{III}}]$ as the corresponding value of $k_{\mathrm{obs.}}^{\mathrm{M}}$. By using equation (25) with the values of $k_{\mathrm{obs.}}^{\mathrm{M}}$ and $k'_{\mathrm{obs.}}$ in Table 10 we evaluated k_g^{M} and k_h^{M} by weighted least-squares analysis; these rate constants are summarised in Table 11.

$$k_{\mathrm{obs.}}^{\mathrm{M}} = (k_g + k_g^{\mathrm{M}}[\mathrm{M^{2+}}])[\mathrm{V^{III}}] + (k_h + k_h^{\mathrm{M}}[\mathrm{M^{2+}}]) \quad (24)$$

$$(k_{\mathrm{obs.}}^{\mathrm{M}} - k'_{\mathrm{obs.}})/[\mathrm{M^{2+}}] = k_g^{\mathrm{M}}[\mathrm{V^{III}}] + k_h^{\mathrm{M}} \quad (25)$$

In the absence of doubly charged cations added initially, if the curvature of the plot of log $[\mathrm{Fe^{III}}]$ against time is caused by catalysis as reaction proceeds, it should be possible to use the appropriate constants from Table 11 to demonstrate this curvature. Making allowance for catalysis by $\mathrm{M^{2+}}$ (which could be either $\mathrm{Fe^{2+}}$ or $\mathrm{VO^{2+}}$) produced in the reaction, as well as $\mathrm{M^{2+}}$ added initially, integration of equation (23) gives equation (26) if k_j and k_j^{M} can be neglected. Here subscripts

$$2.303 \log [\mathrm{Fe^{III}}] - 2.303 \log \left\{ \frac{k_g[\mathrm{V^{III}}] + k_h}{k_g^{\mathrm{M}}[\mathrm{V^{III}}] + k_h^{\mathrm{M}}} + [\mathrm{M^{2+}}]_0 + [\mathrm{Fe^{III}}]_0 - [\mathrm{Fe^{III}}] \right\} = \{(k_g[\mathrm{V^{III}}] + k_h) + (k_g^{\mathrm{M}}[\mathrm{V^{III}}] + k_h^{\mathrm{M}})([\mathrm{Fe^{III}}]_0 + [\mathrm{M^{2+}}]_0)\}t + \text{constant} \quad (26)$$

zero indicate initial concentrations, except for $[\mathrm{V^{III}}]$ which is taken as constant throughout the reaction. When $[\mathrm{M^{2+}}]_0 \gg [\mathrm{Fe^{III}}]_0$, use of this equation yields a linear plot of log $[\mathrm{Fe^{III}}]$ against time, of gradient $-k_{\mathrm{obs.}}^{\mathrm{M}}/2.303$, where $k_{\mathrm{obs.}}^{\mathrm{M}}$ is given by equation (24). With $[\mathrm{M^{2+}}] = 0$, and with appropriate values of the various rate constants, equation (26) was used to calculate values of time t corresponding to chosen values of $[\mathrm{Fe^{III}}]$. The simple plot of log $[\mathrm{Fe^{III}}]$ against t was then constructed from these corresponding values. Simple plots obtained in this way by using the values of k_g^{M} and k_h^{M} found for $\mathrm{Fe^{2+}}$ or $\mathrm{VO^{2+}}$ in equation (26) showed hardly any curvature up to 96% of completion of reaction. The values of $k_{\mathrm{obs.}}^{\mathrm{M}}$ exceeded corresponding values of $k_{\mathrm{obs.}}$ calculated without allowance for catalysis by products by less than 5%. We concluded that catalysis by $\mathrm{Fe^{2+}}$ or $\mathrm{VO^{2+}}$ produced in the reaction does not account for the curvature of plots of log $[\mathrm{Fe^{III}}]$ against time, hence our resort to the explanation discussed previously.

The brief investigation of catalysis by cations other than $\mathrm{Fe^{2+}}$ and $\mathrm{VO^{2+}}$ proved insufficient to indicate the nature of the catalysis. There is substantial catalysis of the 'bimolecular' reaction path by $\mathrm{Cu^{2+}}$, $\mathrm{Fe^{2+}}$, and $\mathrm{VO^{2+}}$, compared with the minor effects of $\mathrm{Mg^{2+}}$, $\mathrm{Ni^{2+}}$, and $\mathrm{Zn^{2+}}$. Of the latter, $\mathrm{Ni^{2+}}$ is a cation of complexing ability comparable to that of $\mathrm{Cu^{2+}}$ and $\mathrm{VO^{2+}}$, and exceeding that of $\mathrm{Fe^{2+}}$. Ability to form complexes, in particular to assist $\mathrm{H^+}$ in the removal of edta from its complexes with the reactants, does not seem the crucial factor. We note that these more active cations are capable of undergoing changes of oxidation state under the conditions of this investigation. Redox mechanisms for the catalysis can be advanced, but require substantiation. Catalysis by the other cations is sufficiently small to be classed as a specific salt effect. We are unable to interpret the observation that only $\mathrm{Cu^{2+}}$ and $\mathrm{Fe^{2+}}$ are capable of increasing the rate of the 'unimolecular' path proceeding by the rate-determining dissociation of $[\mathrm{Fe^{III}(edta)}]^-$. Finally, the extent of curvature of the simple plot of log $[\mathrm{Fe^{III}}]$ against time was altered little by the presence of the various catalysts, except for $\mathrm{VO^{2+}}$. With the latter, there was a marked increase in curvature corresponding to an approximately ten-fold increase in q above its normal value. The use of such a high value of q would lead to slightly smaller values of $k_{\mathrm{obs.}}$ than those in Table 10 and a decrease in k_g^{M}

Table 11. Rate constants * for catalysis by metal cations of the reaction of $[Fe^{III}(edta)]^-$ with $[V^{III}(edta)]^-$

Metal cation	Cu^{2+}	Fe^{2+}	Mg^{2+}	Ni^{2+}	$V^{IV}O^{2+}$	Zn^{2+}
$10^2k_g^M$/dm^6 mol^{-2} s^{-1}	45.3 ± 7.3	17.8 ± 11.3	1.8 ± 1.4	1.4 ± 2.6	73.3 ± 4.0	1.6 ± 1.4
$10^4k_h^M$/dm^3 mol^{-1} s^{-1}	61 ± 14	29 ± 21	0	0	0	0

* At 25.0 °C, $[H^+] = 0.150$ mol dm^{-3}, ionic strength 1.0 mol dm^{-3} ($NaClO_4$). See equation (23) for definition of the rate constants k_g^M and k_h^M.

below the value in Table 11. Insufficient experiments were done to ascertain the best values of k_g^M and q for catalysis by VO^{2+}. Again, we are unable to interpret the finding that VO^{2+}, alone among the cations studied, enhances the rate of the path *via* reactions (18) and (19). However, the observation provides further evidence that q does not arise through catalysis of the 'bimolecular' route by VO^{2+} formed in the reaction. In the presence of a large initial concentration of VO^{2+} (0.01 mol dm^{-3}) compared with that formed in the reaction, such catalysis would lead to almost linear plots of log $[Fe^{III}]$ against time.

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