Kinetics of the Decomposition and Formation of Ethylenedinitrilotetra-acetatovanadate(III) in Dilute Aqueous Perchloric Acid

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The kinetics of the title reaction $V(Y) \rightleftharpoons V^{3+} + HY$ have been studied spectrophotometrically in the forward direction at $[H^+] = 0.6$—4.0 mol dm^{-3} and in the reverse direction at $[H^+] = 0.1$—1.0 mol dm^{-3}. V(Y) represents $[V(edta)]^-$ together with [V(Hedta)] and $[V(H_2edta)]^+$; the corresponding protonation equilibrium constants have been measured by using an e.m.f. cell under the conditions of the kinetic experiments, *viz.* ionic strength $I = 4.0$ mol dm^{-3} ($NaClO_4$) and 25.0 °C. HY represents H_4edta together with H_5edta^+ and H_6edta^{2+}. Two reaction paths have been identified for both the forward and the reverse reaction. The equilibrium constant for the reaction has been measured directly at $[H^+] = 0.5$—1.0 mol dm^{-3} and its value is similar to that obtained from kinetic parameters.

In a study of the redox reaction between ethylenedinitrilotetra-acetatovanadate(III), $[V(edta)]^-$, and ethylenedinitrilotetra-acetatoferrate(III), $[Fe(edta)]^-$,[1] we observed that this vanadium(III) complex decomposes in dilute acid solution to give the metal cation and protonated forms of the ligand much more slowly than do most edta complexes of triply-charged cations normally regarded as giving substitution-labile complexes. Actually such a slow reaction is not unexpected for a triply-charged cation of d^2 configuration. Here we report a spectrophotometric study of the dependence of this decomposition upon the hydrogen-ion concentration. To establish the rate equation it was necessary to extend this concentration up to 4.0 mol dm^{-3}. Consequently all experiments reported are at the high ionic strength of 4.0 mol dm^{-3}, the supporting anion being perchlorate. Complementing the study of the decomposition, we have also studied the formation from V^{3+} and protonated forms of edta in a lower range of hydrogen-ion concentration. In the region where the two ranges overlap an equilibrium is set up and we obtained approximate values of the equilibrium constant from the optical density at the conclusion of reaction.

Experimental

Solid reagents were of AnalaR quality or were prepared by standard methods from AnalaR materials. The preparation and standardisation of several of the reagents and solutions employed in this work have been described by us previously.[1] An additional stock solution required for the present work was lithium perchlorate (4.2 mol dm^{-3}), obtained by dissolving the trihydrate in water, and standardised after suitable dilution *via* ion exchange on Amberlite IR-120(H) resin followed by subsequent titration against standard sodium hydroxide. Twice distilled water was used for this and all other solutions. The trihydrate was obtained by dissolving anhydrous lithium carbonate in 60% perchloric acid at 90 °C to give pH 6—7 followed by rapid filtration and slow cooling to give the solid. The stock solution of *ca.* 0.1 mol dm^{-3} vanadium(III) perchlorate in *ca.* 0.5 mol dm^{-3} perchloric acid was kept under dinitrogen and, after initial iodimetric standardisation,[2] samples were regularly monitored at 760 nm (VO^{2+}: $\varepsilon = 17.2$ dm^3 mol^{-1} cm^{-1}) and discarded when >0.5% of V^{3+} had been oxidised, possibly by ClO_4^-, to VO^{2+}.

Kinetics of the decomposition and formation of $[V(edta)]^-$, including protonated forms, at 25.0 °C were measured spectrophotometrically on a Unicam SP 600 instrument equipped with a temperature-controlled cell holder. The reaction solutions were made up in 2-cm optical cells in an atmosphere of dinitrogen from degassed stock solutions by using calibrated syringes equipped with stainless steel needles. The wavelength was 450 nm; for V^{3+}, $\varepsilon = 3.5$ dm^3 mol^{-1} cm^{-1} at $[H^+] \geqslant 0.6$ mol dm^{-3} and rises to 4.5 dm^3 mol^{-1} cm^{-1} at $[H^+] = 0.1$ mol dm^{-3}; for $[V(edta)]^-$, including protonated forms, $\varepsilon = 26.3$ dm^3 mol^{-1} cm^{-1} at $[H^+] = 0.5$—4.0 mol dm^{-3} and rises to 28.7 dm^3 mol^{-1} cm^{-1} at $[H^+] = 0.1$ mol dm^{-3}. Because of the decomposition, the values of ε for $[V^{III}(edta)]^-$ in the more acid solutions were obtained by extrapolation of measured optical densities to those corresponding to the time of mixing. A few decomposition experiments were done in which repeated spectral scans were obtained over the range 330—700 nm by using a Perkin-Elmer type 402 spectrophotometer. These showed isosbestic points at *ca.* 365, 570, and 650 nm throughout the reaction.

Protonation constants $K^V_{b1} = [V^{III}(Hedta)]/[V^{III}(edta)^-][H^+]$ and $K^V_{b2} = [V^{III}(H_2edta)^+]/[V^{III}(Hedta)][H^+]$ were obtained at ionic strength 4.0 mol dm^{-3} ($NaClO_4$) and 25.0 °C from pH titrations, by using the e.m.f. cell described previously.[1] (Here and subsequently, ligand water molecules are omitted from formulae.) The titration solution contained 0.25 mol dm^{-3} $[V^{III}(edta)]^-$ and 25 readings of pH were taken during the addition of $HClO_4$ (5.0 cm^3 of 4.0 mol dm^{-3}), the final pH being 0.325. Satisfactory agreement between calculated and observed values of pH could not be achieved by assuming a single protonation equilibrium; we obtained the values $K^V_{b1} = 2.86 \pm 0.50$ dm^3 mol^{-1} and $K^V_{b2} = 0.42 \pm 0.11$ dm^3 mol^{-1}, by comparison between calculated and experimental curves of pH against volume of acid added.

Results

Kinetics of the Decomposition; $[H^+] = 0.6$—4.0 *mol dm*$^{-3}$.—In the range $[H^+] = 1.4$—4.0 mol dm^{-3}, decomposition of $[V(edta)]^-$ to V^{3+} and protonated forms of edta proceeds to completion, as shown by the final optical density. With the initial concentrations of the complex *ca.* 0.01 mol dm^{-3}, $[H^+]$ is virtually constant throughout the reaction which follows a first-order law up to at least 90% completion. The rate constant $k^d_{obs.} = -2.303\,d \log[V(Y)]/dt$ was obtained from plots of $\log(D - D_\infty)$ against time t. Here $[V(Y)] = [V(edta)^-] + [V(Hedta)] + [V(H_2edta)^+]$, D is the optical density at time t, and D_∞ that at the end of reaction.

An equilibrium is set up at $[H^+] = 0.6$—1.2 mol dm^{-3}, as shown by equation (1). Here HY represents all uncomplexed

$$V(Y) + xH^+ \rightleftharpoons V^{3+} + HY \qquad (1)$$

Table 1. Rate constants [a] for decomposition of $[V(edta)]^-$ [b] at $[H^+] = 0.6$—4.0 mol dm^{-3}

$[H^+]$/ mol dm^{-3}	$10^4k^d_{obs.}$/ s^{-1}	$10^4k^d_{calc.}$/ s^{-1}
0.60	0.29	0.27
	0.28 [c]	
0.70	0.42	0.41
	0.37 [c]	
0.80	0.55	0.59
	0.54 [c]	
0.90	0.79	0.81
	0.72 [c]	
1.00	1.13	1.07
	1.03 [c]	
	0.95 [c]	
1.20	1.68	1.72
	1.72 [c]	
1.40	2.4	2.6
1.50	3.1	3.1
	3.2 [c]	
1.60	4.1	3.6
1.80	5.3	4.8
2.00	6.4	6.3
	6.0	
	6.4 [c]	
	6.5 [c]	
2.20	8.6	8.0
2.40	9.9	9.9
2.60	12.2	12.0
2.80	14.6	14.3
3.00	16.9	16.9
	18.1 [c]	
	17.3 [c]	
3.25	20	20
3.50	23	24
3.75	28	29
4.00	31	33
	32	
	30	

[a] At 25.0 °C and ionic strength $I = 4.0$ mol dm^{-3}. [b] Initial concentration: 0.010 mol dm^{-3}. [c] $NaClO_4$ supporting electrolyte, $LiClO_4$ in others.

edta species, $[HY] = [H_4edta] + [H_5edta^+] + [H_6edta^{2+}]$, and $x \sim 4.5$. The short range of $[H^+]$ over which this equilibrium can be measured is consistent with this high value of x. From the optical densities D and D_∞, the corresponding concentrations c and c_∞ of V(Y) can be obtained, while c_0 the initial concentration is known. For a reaction such as (1), with $[H^+]$ constant, the integrated rate equation [3] is (2) in which $k^d_{obs.}$ is

$$2.303 \log\left\{\frac{c_0{}^2 - c_\infty c}{c_0(c - c_\infty)}\right\} = k^d_{obs.}\left\{\frac{c_0 + c_\infty}{c_0 - c_\infty}\right\} t \quad (2)$$

the first-order rate constant for the reaction proceeding from left to right. Plots of the left-hand side of equation (2) against t thus enable $k^d_{obs.}$ to be obtained for these experiments. These results together with those at $[H^+] = 1.4$—4.0 mol dm^{-3} are summarised in Table 1.

Kinetics of the Formation; $[H^+] = 0.1$—1.0 *mol dm*$^{-3}$.—Equal initial concentrations of V^{3+} and HY (0.010 mol dm^{-3}) were used. At $[H^+] = 0.10$—0.35 mol dm^{-3} the formation reaction, equation (1) from right to left, proceeds to at least 95% completion and follows the simple rate law $-d[V^{3+}]/dt = k^f_{obs.}[V^{3+}]^2$. For each experiment $k^f_{obs.}$ was obtained from a plot of $1/[V^{3+}]$ against t, values of $[V^{3+}]$ being obtained from corresponding values of D.

Table 2. Rate constants [a] for formation of $[V(edta)]^-$ [b] at $[H^+] = 0.1$—1.0 mol dm^{-3}

$[H^+]$ [c]/ mol dm^{-3}	$k^f_{obs.}$/ dm^3 mol^{-1} s^{-1}	$k^f_{calc.}$/ dm^3 mol^{-1} s^{-1}
0.094	0.75	0.83
0.143	0.36	0.40
	0.38	
0.192	0.23	0.23
	0.25	
	0.25	
	0.23	
0.242	0.152	0.153
	0.149	
0.291	0.107	0.108
	0.112	
0.340	0.091	0.080
0.387	0.071	0.063
	0.061	
0.485	0.040	0.040
	0.038	
0.582	0.029	0.028
	0.028	
0.679	0.021	0.021
	0.0188	
0.776	0.0160	0.0160
0.875	0.0127	0.0127
0.973	0.0106	0.0103

[a] At 25.0 °C and ionic strength $I = 4.0$ mol dm^{-3} ($NaClO_4$). [b] Initial concentrations: $[V^{3+}] = [HY] = 0.010$ mol dm^{-3}. [c] Values apply to 50% completion of reaction.

In the range $[H^+] = 0.40$—1.0 mol dm^{-3}, the equilibrium of equation (1) is set up from the right-hand side. The appropriate integrated rate equation [3] for constant $[H^+]$ is (3) in which $k^f_{obs.}$ is the second-order rate constant for reaction (1) proceeding from right to left, s is the known initial concentration of both V^{3+} and HY, while c and c_∞ are defined

$$2.303 \log\left\{\frac{c_\infty(s^2 - c_\infty c)}{s^2(c_\infty - c)}\right\} = k^f_{obs.}\left\{\frac{s^2 - c_\infty{}^2}{c_\infty}\right\} t \quad (3)$$

above and are again obtained from D and D_∞. The kinetic results for the formation reaction are summarised in Table 2.

The Decomposition Equilibrium; $[H^+] = 0.5$—1.0 *mol dm*$^{-3}$.—Appreciable concentrations of reactants and products coexist at the conclusion of reaction for experiments in the range $[H^+] = 0.5$—1.0 mol dm^{-3}. The extraction of $k^d_{obs.}$ or $k^f_{obs.}$ from kinetic results in this range by the use of equations (2) or (3) requires the appropriate value of c_∞. Consequently a value of the equilibrium constant $K_{obs.}$, equation (4), can be

$$K_{obs.} = [V^{3+}][HY]/[V(Y)] \quad (4)$$

obtained from c_∞ in each such experiment. Values of $K_{obs.}$, obtained from both decomposition and formation experiments, are summarised in Table 3.

Discussion

Dependence of the Decomposition Kinetics upon $[H^+]$.—The complex species present in appreciable proportions are $[V(edta)]^-$, $[V(Hedta)]$, and $[V(H_2edta)]^+$. Because of the large changes in $k^d_{obs.}$ when $[H^+]$ is changed, we have assumed that this constant can be expressed in terms of $[V(H_2edta)]^+$ alone although two terms are necessary, equation (5). We

Table 3. Equilibrium constants [a] for decomposition of $[V(edta)]^-$ at $[H^+] = 0.5$—1.0 mol dm^{-3}

$[H^+]$ [b]/ mol dm^{-3}	Percentage conversion [b]	$10^3K_{obs.}$/ mol dm^{-3}	$10^3K_{calc.}$/ mol dm^{-3}
(*i*) Decomposition: reactant V(Y) [c]			
0.578	31	1.42	0.95
0.577	32	1.52 [d]	0.94
0.672	42	3.3	1.93
0.675	35	1.95 [d]	1.97
0.768	47	4.1	3.6
0.768	48	4.5 [d]	3.6
0.864	57	8.3	6.3
0.866	51	5.6 [d]	6.3
0.961	62	10.7	10.2
0.962	59	9.0 [d]	10.3
(*ii*) Formation: reactants V^{3+} and HY [e]			
0.504	82	0.41	0.50
0.599	73	1.02	1.12
0.693	62	2.4	2.2
0.788	52	4.5	4.1
0.886	48	5.4	7.0
0.981	40	9.2	11.3
0.981	38	10.2	11.3

[a] At 25.0 °C and ionic strength $I = 4.0$ mol dm^{-3}. [b] Values apply at equilibrium. [c] Initial concentration: $[V(Y)] = 0.010$ mol dm^{-3}. [d] $NaClO_4$ supporting electrolyte, $LiClO_4$ in others. [e] Initial concentrations: $[V^{3+}] = [HY] = 0.010$ mol dm^{-3}; $NaClO_4$ supporting electrolyte.

eliminate $[V(H_2edta)^+]$ by using equation (6) and can then introduce the overall rate constant $k^d_{obs.}$ to obtain equation (7).

$$-d[V(Y)]/dt = k_1[H^+][V(H_2edta)^+] + k_2[H^+]^2[V(H_2edta)^+] \quad (5)$$

$$[V(H_2edta)^+] = K^V_{b1}K^V_{b2}[H^+]^2[V(Y)]/(1 + K^V_{b1}[H^+] + K^V_{b1}K^V_{b2}[H^+]^2) \quad (6)$$

$$k^d_{obs.}(1/K^V_{b1}K^V_{b2}[H^+]^3 + 1/K^V_{b2}[H^+]^2 + 1/[H^+]) = k_1 + k_2[H^+] \quad (7)$$

The left-hand side can be evaluated by using our measured values of K^V_{b1} and K^V_{b2} and hence k_1 and k_2 are obtained by weighted least-squares analysis. We find $k_1 = (1.46 \pm 0.08) \times 10^{-4}$ dm^3 mol^{-1} s^{-1} and $k_2 = (3.06 \pm 0.10) \times 10^{-4}$ dm^6 mol^{-2} s^{-1}. By substituting these values together with those of K^V_{b1} and K^V_{b2} into equation (7) the values of $k^d_{calc.}$ included in Table 1 can be obtained from $[H^+]$. The relative standard deviation, comparing values of $k^d_{calc.}$ and $k^d_{obs.}$ for all experiments, is $\pm$ 5.9%.

The satisfactory analysis of the dependence of $k^d_{obs.}$ upon $[H^+]$ requires a wide variation in the latter and this leads to large changes in the concentration of the inert cation used to maintain a constant ionic strength. In some reactions even singly charged cations show highly specific salt effects, so that the kinetic effects of making substantial changes in hydrogen-ion concentration at constant ionic strength cannot be interpreted in a simple manner such as that adopted here. Where this complication arises it is usually found that the substitution of Li^+ for Na^+ leads to major changes in rate of reaction. In these circumstances $LiClO_4$ is preferable to $NaClO_4$ as inert electrolyte; unlike those of the latter, the activity coefficients of $LiClO_4$ closely approximate to those of $HClO_4$ over a wide range of ionic strengths.[4] Inspection of the results in Table 1 shows that the differences between $k^d_{obs.}$ values obtained using $LiClO_4$ and $NaClO_4$ are minor and we conclude that specific salt effects which may lead to a false rate equation are absent from this system.

Dependence of the Formation Kinetics upon $[H^+]$.—The principal edta species present are H_4edta, H_5edta^+, and H_6edta^{2+}, while uncomplexed vanadium(III) is almost wholly in the form V^{3+}. Despite its low proportion, less than 5% of total edta at the lowest $[H^+]$ used, H_3edta^- is likely to be a kinetically significant species, judging by the approximately inverse dependence of $k^f_{obs.}$ upon $[H^+]^2$ evident in Table 2. Values of the protonation constants $K_4 = [H_4edta]/[H_3edta^-][H^+]$, $K_5 = [H_5edta^+]/[H_4edta][H^+]$, and $K_6 = [H_6edta^{2+}]/[H_5edta^+][H^+]$ have not been measured under our conditions of ionic strength. However, examination of values obtained under other conditions [5] suggests that approximate values are $K_4 = 60$, $K_5 = 30$, and $K_6 = 2$, all in dm^3 mol^{-1}. With such values, and assuming that the only reactive aquavanadium species is V^{3+}, it is evident that the reaction of H_4edta is important as well as that of H_3edta^-. Also, with little error, the contribution of H_3edta^- can be neglected in evaluating the concentrations of the principal edta species at each value of $[H^+]$; the precise value of K_4 is then unimportant and can be included in a rate constant. Following these considerations, the appropriate rate equation (8) can be transformed into (9)

$$-d[V^{3+}]/dt = k^f_{obs.}[V^{3+}][HY] = k_3[V^{3+}][H_4edta]/[H^+] + k_4[V^{3+}][H_4edta] \quad (8)$$

$$k^f_{obs.} = (k_3 + k_4[H^+])/([H^+] + K_5[H^+]^2 + K_5K_6[H^+]^3) \quad (9)$$

by introducing K_5 and K_6. By assuming values of these constants it is therefore possible to plot $k^f_{obs.}([H^+] + K_5[H^+]^2 + K_5K_6[H^+]^3)$ against $[H^+]$ to obtain corresponding values of k_3 and k_4. This has been done for various combinations of values of K_5 and K_6 in the ranges $K_5 = 10$—60 dm^3 mol^{-1}, $K_6 = 0.5$—5.0 dm^3 mol^{-1}. For each set of values of K_5 and K_6, together with the corresponding values of k_3 and k_4, values of $k^f_{calc.}$ (the overall second-order rate constant for the reaction) can be calculated by using equation (9), with $k^f_{calc.}$ replacing $k^f_{obs.}$. By comparing all the corresponding values of $k^f_{obs.}$ and $k^f_{calc.}$ for a given set of values of K_5, K_6, k_3, and k_4 the relative standard deviation is obtained. In establishing the dependence of the equilibrium constant $k_{obs.}$ upon $[H^+]$, use is again made of K_5 and K_6 and in a similar way comparison between calculated and observed values of the equilibrium constant can be made and the relative standard deviation found. Rather than choose values of K_5 and K_6 which minimise the relative standard deviation for $k^f_{calc.}$ compared with $k^f_{obs.}$ in isolation, we have chosen values which give the best fit for both these kinetic results and the equilibrium results taken together. We find $K_5 = 26 \pm 4$ dm^3 mol^{-1} and $K_6 = 2.2 \pm 0.2$ dm^3 mol^{-1}, the variations within the limits quoted giving negligible changes in the goodness of fit. The values $k_3 = 0.256 \pm 0.034$ s^{-1} and $k_4 = 0.563 \pm 0.043$ dm^3 mol^{-1} s^{-1} are obtained by using $K_5 = 26$ dm^3 mol^{-1} and $K_6 = 2.2$ dm^3 mol^{-1}, and the relative standard deviation, comparing $k^f_{calc.}$ with $k^f_{obs.}$, is 6.12%.

Dependence of the Position of Equilibrium upon $[H^+]$.—The equilibrium constant $K_{obs.}$ is defined in equation (4) without reference to the extent of protonation of the uncomplexed edta and of the vanadium complex. A convenient equilibrium constant which takes into account $[H^+]$ is K_R, defined in equation (10) in which K_1, K_2, K_3, K_4 are the first four consecutive protonation constants for $edta^{4-}$ and β is the

$$K_R = K_1K_2K_3K_4/\beta = [V^{3+}][H_4edta]/[V(edta)^-][H^+]^4 \quad (10)$$

conventional stability constant for $[V(edta)]^-$. The relationship between $K_{obs.}$ and K_R is then given by equation (11). By

$$\frac{K_{obs.}}{K_R} = \frac{(1 + K_5[H^+] + K_5K_6[H^+]^2)[H^+]^4}{1 + K^V_{b1}[H^+] + K^V_{b1}K^V_{b2}[H^+]^2} \quad (11)$$

using the values of K_5 and K_6 adopted in the previous section, a weighted least-squares plot of $K_{obs.}$ against the right-hand side of equation (11) gives $K_R = (7.34 \pm 0.82) \times 10^{-4}$ dm^9 mol^{-3}. Multiplication of the right-hand side of equation (11) for a given value of $[H^+]$ by K_R then enables $K_{calc.}$ to be obtained; values of $K_{calc.}$ are included in Table 3. The relative standard deviation obtained by comparing $K_{calc.}$ with $K_{obs.}$ is 30.87%; as can be seen from Table 3, comparing values of $K_{obs.}$ at similar values of $[H^+]$, there is considerable scatter in the experimental results. At ionic strength 3.0 mol dm^{-3} and 25 °C, the conditions most similar to those of our experiments, $\log(K_1K_2K_3K_4) = 19.01$.[5] Combining this value with our value $\log K_R = -3.1$ gives $\log \beta = 22.1$. This value is considerably lower than that ($\log \beta = 25.9$) previously obtained [6] at ionic strength 0.1 mol dm^{-3} and 20 °C. However, a decrease is to be expected in the equilibrium constant for a reaction between oppositely charged ions when there is a substantial increase in the ionic strength.

Comparison of Equilibrium Constants obtained by Direct Measurement and from Kinetic Results.—The studies of the decomposition and formation kinetics both include the range $[H^+] = 0.5$—1.0 mol dm^{-3} in which the equilibrium constant K_R has been obtained by the direct measurement of the equilibrium values of [V(Y)]. This value of K_R can be compared with one obtained from the observed rate constants. We commence with equation (12) where the concentrations

$$K_{obs.} = k^d_{obs.}/k^f_{obs.} = [V^{3+}]_e[HY]_e/[V(Y)]_e \quad (12)$$

hold in an equilibrium mixture. By using equations (7), (9), and (11) to eliminate $k^d_{obs.}$, $k^f_{obs.}$, and $K_{obs.}$, respectively, we obtain equation (13). This relationship between K_R

$$K_R = K^V_{b1}K^V_{b2}(k_1 + k_2[H^+])/(k_3 + k_4[H^+]) \quad (13)$$

and constants which we have already obtained should hold at any value of $[H^+]$ within our experimental range and so (13) can be simplified to give equation (14). Values of K_R

$$K_R = K^V_{b1}K^V_{b2}k_1/k_3 = K^V_{b1}K^V_{b2}k_2/k_4 \quad (14)$$

obtained from k_1/k_3 and k_2/k_4 are $(6.85 \pm 0.98) \times 10^{-4}$ and $(6.54 \pm 0.54) \times 10^{-4}$ dm^9 mol^{-3}, respectively. These are in satisfactory concordance with the value of $(7.34 \pm 0.82) \times 10^{-4}$ dm^9 mol^{-3} obtained by direct measurement. The choice of values of K_5 and K_6 outside the ranges cited above leads to greater disparities between values of K_R obtained by direct measurement and from kinetic data.

Reaction Mechanism.—Two reaction paths have been identified for the decomposition, involving $[V(edta)]^-$ plus three or four protons, respectively, in the transition state. In the formally analogous decomposition of $[Fe(edta)]^-$ only one reaction path was identified [7] although we consider [1] that there are two, similarly involving three and four protons, respectively. The low value of K^V_{b1} suggests that the complex $[V(edta)]^-$ is sexidentate; edta complexes with a free carboxylate group show higher protonation constants of *ca.* 10^3 dm^3 mol^{-1}.[8] Even with the sexidentate configuration, the incorporation of a minimum of three protons in the transition state would be sufficient to cause the detachment of a nitrilodiacetato-moiety from the vanadium atom; we suggest that this may be an important stage in the decomposition. However, detailed mechanistic paths are too various for us to suggest a complete mechanistic scheme.

In the formation reaction, two paths have been found, again corresponding to transition states composed of V^{3+}, $edta^{4-}$, and three or four protons, respectively. This differs from the formation of $[Fe(edta)]^-$ in which the two transition states are composed of Fe^{3+}, $edta^{4-}$, and two or three protons, respectively.[9] In such reactions the dominant paths may change with the particular metal cation involved and would of course be expected to change with the range of $[H^+]$ adopted for the experiments. Complex formation with iron(III) is considered [9] to occur through the reactions of $Fe(OH)^{2+}$ with H_3edta^- and with H_4edta, because the rate constants for the kinetically equivalent reactions of Fe^{3+} with H_2edta^{2-} and with H_3edta^- are larger than would be expected for the predominantly S_N1 replacement of water in $[Fe(H_2O)_6]^{3+}$. The question of reactions proceeding *via* $V(OH)^{2+}$ rather than V^{3+} has been discussed [10] where the evidence obtained suggests that $V(OH)^{2+}$ shows no major enhancement in rate of substitution as compared to V^{3+}. From the spread of rate constants observed it is clear that bond-making is important kinetically in complex-formation reactions of vanadium(III). With $k_3'[V^{3+}][H_3edta^-] = k_3[V^{3+}][H_4edta]/[H^+]$, and $K_4 \sim 60$ dm^3 mol^{-1}, k_3' is ~ 15 dm^3 mol^{-1} s^{-1}, a larger rate constant than is found for certain substitution reactions of vanadium(III), but smaller than for others for which the principal reaction path is uncertain.[11] Consequently, the clear-cut identification of the reactive form of the cation in the analogous iron(III) system is not possible for the vanadium(III)–edta system.

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