Kinetic Study of Acid Dechelation of some Vanadium(V)–Amino-carboxylate Complexes in Aqueous Solution

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Kinetic studies of the acid hydrolysis of vanadium(V) complexes of ethylenediaminetetra-acetic acid (H_4edta), ethylenediamine-*N*,*N'*-diacetic acid (H_2edda), and nitrilotriacetic acid (H_3nta) have been carried out by stopped-flow spectrophotometry in aqueous solution (I = 3 mol dm^{-3}, $NaClO_4$). The observed first-order (with respect to chelate) rate constant increases as a hyperbolic-type function with H^+ concentration. Discussion of the differences in reactivity of the chelates indicates that the dissociation of the chelate complexes would proceed by a pre-equilibrium step leading to the formation of an intermediate for which the ketonic oxygen of one carboxylate group of the chelate is protonated. This first step is followed by rupture of a metal–oxygen bond, rupture of a metal–nitrogen bond, and then by complete cleavage of the multidentate ligand.

Some studies have reported on the hydrolysis kinetics of chelate complexes in acidic media. Generally, the rate of dissociation increases with the acid concentration. In particular, the phenomenon was observed by Wilkins and co-workers [1-6] on diamine complexes of Ni^{II} or Co^{II}, by Margerum and co-workers [7-10] on polyamine and polyaminocarboxylate complexes of Ni^{II}, and by Nishizawa and Saito [11] on polyaminocarboxylate complexes of V^{IV}. Two general mechanisms are proposed in these papers to explain the acid hydrolysis of chelate complexes. Either attack by H^+ occurs on the chelate by protonation of a ligand donor group after the solvent molecule has separated it from the metal,[1-6] or protonation of the reacting species occurs before (or during) the solvation of the metal.[7-11] Recently, Read and Margerum [7,9] suggested that no solvent molecule replaces the ligand after the first ligand–metal bond rupture. In this first step of the mechanism, an intermediate is produced in which the metal has a reduced co-ordination number. The opening in the ring is not sufficient to move the free chelate group out of the first co-ordination sphere. Thus the protonation of the free chelate group is observed, followed by rapid chelate opening, and metal-ion solvation.

The purpose of the present study is to investigate in detail this mechanism of protonation during acid hydrolysis on chelates of VO_2^+ having different structures. Tanaka and co-workers [12] studied kinetically the complex formation of some aminocarboxylates with V^V and showed that dechelation is dependent on H^+ concentration.

The present paper describes [equation (1)] the dissociation, at low pH, of vanadium(V) complexes of ethylenediaminetetra-acetic acid (H_4edta), nitrilotriacetic acid (H_3nta), and ethylenediamine-*N*,*N'*-diacetic acid (H_2edda).

$$\left.\begin{array}{r}[VO_2(H_2edta)]^- + H^+ \longrightarrow VO_2^+ + \Sigma\, H_iedta^{(4-i)-}\\ [VO_2(edda)]^- + H^+ \longrightarrow VO_2^+ + \Sigma\, H_iedda^{(2-i)-}\\ [VO_2(nta)]^{2-} + H^+ \longrightarrow VO_2^+ + \Sigma\, H_inta^{(3-i)-}\end{array}\right\} \quad (1)$$

Previous results [13] have shown the complexation of VO_2^+ as the central complexed group. In the edta or edda complexes the four available co-ordination sites of VO_2^+ are occupied by two nitrogen and two acetate oxygen atoms of the multidentate ligand.[14] In the nta complex one nitrogen and three acetate oxygen atoms are bonded to the VO_2^+ ion. Each of the three ligands should be tetradentate when co-ordinated to VO_2^+. For edta, two acetate groups are free and not bonded to the metal. Therefore we observe that in all three complexes, there is no water molecule bonded to the central metal, and there is no very weak metal–ligand bond. This structure without solvent bonded to the metal in the first co-ordination sphere allows us to show the importance of the second co-ordination sphere during the substitution. The effect of the solvent shell in these oxovanadium(V) complexes has been previously pointed out for basic hydrolysis [15] and ligand interchange reactions.[16] These reactions show the formation of an intermediate between the complex and OH^- (basic hydrolysis) and between the complex and the entering ligand (ligand interchange).

Experimental

Reagents.—Sodium perchlorate, sodium monovanadate, perchloric acid, ethylenediaminetetra-acetic acid, and nitrilotriacetic acid were obtained from Merck; the chemicals were analytical reagent grade and were used without any purification. Ethylenediamine-*N*,*N'*-diacetic acid was purchased from Fluka and recrystallized twice from distilled water. Perchloric acid solutions were standardized against $K[HCO_3]$. Vanadium(V) solutions were titrated against a standard iron(II) sulphate solution. Solutions of nta were standardized complexometrically with an excess of zinc sulphate against a standard sodium hydroxide solution, edta solutions with zinc sulphate in ammonia buffered solution, and edda solutions by pH titrations. The ionic strength was maintained at 3 mol dm^{-3} with sodium perchlorate.

Measurements.—All kinetic measurements were carried out, at various temperatures in the range 10—40 °C, with a stopped-flow spectrophotometer of the type Durrum 131 equipped with a Datalab DL 905 transient recorder interfaced to an Olivetti P 652 microcomputer. This system and the computer programs used for data treatment have been previously described.[17,18]

In all kinetic studies, the solutions of the aminocarboxylate complex contained the chelating agent in a sufficient excess at a given pH (generally *ca.* 3) to ensure that only the 1 : 1 complex was entirely formed,[13] *i.e.* $[VO_2(H_2edta)]^-$, $[VO_2(edda)]^-$, or $[VO_2(nta)]^{2-}$. The H^+ concentration of acid solutions used for hydrolysis reactions was calculated to obtain instantaneously the neutralization of the free ligand excess, and to ensure that reactions were pseudo-first-order with respect to the reacting chelate (at least a ten-fold excess of acid in each run).

Results and Discussion

Experimental Rate Law of Acid Hydrolysis.—To study reactions (1), we performed a series of kinetic runs by stopped-

Table 1. Observed rate constants (s^{-1}) for the acid dissociation of $[VO_2(edda)]^-$. The reactions were followed at 295 nm. All concentrations are given at the initial time after mixing and neutralization of the ligand excess: $[VO_2(edda)^-]_0 = 10^{-4}$ mol dm^{-3}; $[V^V]_0 = 10^{-4}$ mol dm^{-3}; $[ligand]_0 = 3.1 \times 10^{-3}$ mol dm^{-3} ($[V^V]_0$ and $[ligand]_0$ = total metal and ligand concentrations in all solutions formed)

$[H^+]_0$/ mol dm^{-3}	15 °C		25 °C		35 °C	
	$k_{obs.}^{exp.}$	$k_{obs.}^{calc.}$	$k_{obs.}^{exp.}$	$k_{obs.}^{calc.}$	$k_{obs.}^{exp.}$	$k_{obs.}^{calc.}$
0.30	105 ± 8	109	218 ± 22	219		395
	106 ± 8		215 ± 24			
0.25	100 ± 6	100	210 ± 20	203		369
	100 ± 6		222 ± 18			
0.20	88.7 ± 5	88.5	182 ± 15	183		336
	88.8 ± 3		187 ± 17			
0.15	74.0 ± 4	74.6	160 ± 13	158		293
	74.6 ± 3		157 ± 11			
0.10	56.3 ± 4	56.8	120 ± 9	123	226 ± 24	233
	56.9 ± 3		127 ± 10		230 ± 25	
0.075	46.4 ± 5	45.9	99 ± 8	101	196 ± 16	193
	45.5 ± 3		104 ± 9		188 ± 15	
0.050					144 ± 11	144
					146 ± 11	

Table 2. Observed rate constants (s^{-1}) for the acid dissociation of $[VO_2(nta)]^{2-}$. The reactions were followed at 290 nm. All concentrations are given at the initial time after mixing and neutralization of the ligand excess: $[VO_2(nta)^{2-}]_0 = 10^{-4}$ mol dm^{-3}; $[V^V]_0 = 10^{-4}$ mol dm^{-3}; $[ligand]_0 = 6 \times 10^{-4}$ mol dm^{-3} ($[V^V]_0$ and $[ligand]_0$ = total metal and ligand concentrations in all solutions formed)

$[H^+]_0$/ mol dm^{-3}	10 °C		15 °C		25 °C		35 °C		40 °C	
	$k_{obs.}^{exp.}$	$k_{obs.}^{calc.}$	$k_{obs.}^{exp.}$	$k_{obs.}^{calc.}$	$k_{obs.}^{exp.}$	$k_{obs.}^{calc.}$	$k_{obs.}^{exp.}$	$k_{obs.}^{calc.}$	$k_{obs.}^{exp.}$	$k_{obs.}^{calc.}$
0.30	9.16 ± 0.30	8.70	11.7 ± 0.4	11.40	29.9 ± 0.8	27.5	63.2 ± 2.9	60.0	91.6 ± 5.0	88.8
	9.17 ± 0.27		11.6 ± 0.4		27.9 ± 0.5		64.4 ± 3.2		86.5 ± 4.8	
0.25	7.43 ± 0.35	7.25	9.92 ± 0.31	9.50	24.0 ± 0.3	22.9	50.9 ± 2.0	50.0	71.1 ± 3.5	74.0
	7.31 ± 0.39		9.98 ± 0.30		24.1 ± 0.3		50.4 ± 2.4		73.7 ± 3.6	
0.20	5.64 ± 0.23	5.80	7.62 ± 0.28	7.60	18.2 ± 0.3	18.3	38.9 ± 1.9	40.0	62.1 ± 3.2	59.2
	5.66 ± 0.21		7.65 ± 0.26		17.9 ± 0.4		38.8 ± 2.2		61.6 ± 3.4	
0.15	4.16 ± 0.17	4.35	5.43 ± 0.24	5.70	13.4 ± 0.4	13.7	28.9 ± 1.3	30.0	42.8 ± 2.4	44.4
	4.33 ± 0.16		5.51 ± 0.19		13.1 ± 0.3		29.3 ± 1.5		44.3 ± 2.4	
0.10	2.68 ± 0.13	2.90	3.70 ± 0.16	3.80	8.79 ± 0.27	9.17	19.7 ± 0.8	20.0	31.0 ± 1.9	29.6
	2.71 ± 0.15		3.68 ± 0.16		9.01 ± 0.28		19.6 ± 0.7		31.3 ± 2.3	

Table 3. Observed rate constants (s^{-1}) for the acid dissociation of $[VO_2(H_2edta)]^-$. The reactions were followed at 270 nm. All concentrations are given at the initial time after mixing and neutralization of the ligand excess: $[VO_2(H_2edta)^-]_0 = 10^{-4}$ mol dm^{-3}; $[V^V]_0 = 10^{-4}$ mol dm^{-3}; $[ligand]_0 = 6 \times 10^{-4}$ mol dm^{-3} ($[V^V]_0$ and $[ligand]_0$ = total metal and ligand concentrations in all solutions formed)

$[H^+]_0$/ mol dm^{-3}	10 °C		20 °C		25 °C		30 °C		40 °C	
	$k_{obs.}^{exp.}$	$k_{obs.}^{calc.}$	$k_{obs.}^{exp.}$	$k_{obs.}^{calc.}$	$k_{obs.}^{exp.}$	$k_{obs.}^{calc.}$	$k_{obs.}^{exp.}$	$k_{obs.}^{calc.}$	$k_{obs.}^{exp.}$	$k_{obs.}^{calc.}$
0.30	0.248 ± 0.025	0.275	0.615 ± 0.032	0.625	0.989 ± 0.030	1.01	1.51 ± 0.02	1.56	3.60 ± 0.08	3.46
	0.279 ± 0.030		0.628 ± 0.027		0.998 ± 0.028		1.59 ± 0.03		3.46 ± 0.09	
0.20	0.285 ± 0.020	0.275	0.634 ± 0.035	0.625	1.05 ± 0.031	1.01	1.52 ± 0.01	1.56	3.50 ± 0.10	3.46
	0.271 ± 0.025		0.615 ± 0.028		0.987 ± 0.026		1.61 ± 0.03		3.42 ± 0.09	
0.15	0.260 ± 0.035	0.275	0.626 ± 0.021	0.625	0.983 ± 0.033	1.01	1.57 ± 0.02	1.56	3.64 ± 0.11	3.46
	0.284 ± 0.015		0.625 ± 0.038		1.02 ± 0.025		1.54 ± 0.02		3.28 ± 0.08	
0.10	0.273 ± 0.030	0.275	0.607 ± 0.034	0.625	1.01 ± 0.018	1.01	1.60 ± 0.03	1.56	3.48 ± 0.10	3.46
	0.300 ± 0.020		0.650 ± 0.023		1.04 ± 0.032		1.54 ± 0.02		3.30 ± 0.07	

flow spectrophotometry at various concentrations of chelate and hydrogen ion. Under our experimental conditions (always a large excess of H^+) we can neglect the backward reaction of complex formation and the neutralization of excess ligand which is quasi-instantaneous. The kinetic data are independent of the concentration of the free ligand in excess. Each reaction was found to be first order with respect to the reacting chelate over 95% of the reaction. The values of $k_{obs.}^{exp.}$, the pseudo-first-order rate constant, presented in Tables 1, 2, and 3 are the average of at least three determinations. For the V^V–edda complex, precipitation at low temperature and rate constants greater than 250 s^{-1} at high temperature limited the studied temperature range to 15—35 °C.

For the edta chelate, protonation of non-bonded acetate groups is possible and we observed [13] the formation of three complexes $[VO_2(H_2edta)]^-$, $[VO_2(Hedta)]^{2-}$, and $[VO_2(edta)]^{3-}$. Preliminary kinetic experiments showed that the reactions of protonation or deprotonation of these complexes are instantaneous with the stopped-flow technique. Thus equation (1) summarizes the acid hydrolysis reaction of the three complexes.

The variations of $k_{obs.}^{exp.}$ *versus* $[H^+]$ are different according to the chelate decomplexation studied; we observed (*a*) a hyperbolic variation for the V^V–edda complex, (*b*) a linear variation for the V^V–nta complex, and (*c*) no variation for the V^V–edta complex.

Table 4. Determination of $k_{obs.} = (kK[H^+])/(1 + K[H^+])$. At 25 °C, we estimate $K \approx 0.2$ dm^3 mol^{-1} and $k \approx 500$ s^{-1} for V^V–nta and $K \approx 100$ dm^3 mol^{-1} for the V^V–edta complex

Chelate	Temp./ °C	k/s^{-1}	K/dm^3 mol^{-1}	kK/dm^3 mol^{-1} s^{-1}
$[VO_2(edda)]^-$	15	200	3.97	794
	25	357	5.29	1 888
	35	606	6.23	3 776
$[VO_2(nta)]^{2-}$	10	—	$\ll 1$	29
	15	—	$\ll 1$	38
	25	—	$\ll 1$	92
	35	—	$\ll 1$	200
	40	—	$\ll 1$	296
$[VO_2(H_2edta)]^-$	10	0.275	$\gg 1$	—
	20	0.625	$\gg 1$	—
	25	1.01	$\gg 1$	—
	30	1.56	$\gg 1$	—
	40	3.46	$\gg 1$	—

However, all these results may be summarized by the general mechanism scheme shown by equations (2a) and (2b), where

$$VO_2L + H^+ \overset{K}{\rightleftharpoons} VO_2(HL) \quad (2a)$$

$$VO_2(HL) \xrightarrow{k} \text{products} \quad (2b)$$

L is the multidentate ligand. Under our conditions, the pseudo-first-order rate constant is given by equation (3). The values

$$k_{obs.} = \frac{kK[H^+]}{1 + K[H^+]} \quad (3)$$

of k and K were determined by linear regression analysis as explained in a previous paper.[15] Table 4 gives the values of k and K at different temperatures for the three chelates studied. These values allowed us to recalculate the pseudo-first-order rate constants which have been experimentally measured. Tables 1—3 give these recalculated values ($k_{obs.}^{calc.}$).

For the nta chelate, under our experimental conditions, we observed $K[H^+] \ll 1$; then $k_{obs.}$ reduces to a linear function of $[H^+]$. Only the kK parameter may be calculated. If the H^+ concentration increases ($0.3 \leqslant [H^+] \leqslant 3$ mol dm^{-3}) in the chelate hydrolysis reaction, we might be able to obtain k and K separately. However, in this case, we cannot neglect the variation of activity coefficients of the species involved in the reaction (variation produced by changing the supporting electrolyte from 3 mol dm^{-3} $NaClO_4$ to 3 mol dm^{-3} $HClO_4$). Discussions on the mechanism and analogous result for basic hydrolysis [15] show that k for the nta or edda chelate may be of the same order of magnitude, leading to an estimated value for K of 0.2 dm^3 mol^{-1} (25 °C).

For the edta chelate, we observed $K[H^+] \gg 1$, and $k_{obs.}$ reduces to k. The value of K might be obtained if we studied the chelate hydrolysis at lower H^+ concentrations ($[H^+] < 0.1$ mol dm^{-3}). However, for these concentrations, the backward reaction is not negligible. Nevertheless, this mechanism is supported by results obtained for the same hydrolysis reaction in water–dimethyl sulphoxide (dmso) mixtures (40—60%; 30—70%) as solvent where k and K may be obtained separately.[19] By extrapolation, a value for K of 100 dm^3 mol^{-1} is estimated.

Proposed Mechanism.—Two pathways may commonly be observed in these hydrolysis reactions: the water dissociation pathway and the protonation pathway. For the hydrolysis of the nta and edda chelates, the experimental curves, $k_{obs.}^{exp.} = f[H^+]$, pass through the origin. Therefore the water dissociation pathway does not contribute to the observed rate. We may assume that analogous results would be obtained for the edta chelate if its hydrolysis could be studied for values of $[H^+]$ of less than 0.1 mol dm^{-3}. However, this experimental investigation is not possible in this range of $[H^+]$, since the back reaction is no longer negligible. Hydrolysis of the V^V–edta chelate in water–dmso medium confirms that the direct solvent dissociation pathway is negligible.[19]

Three remarks may be made. (*a*) For the hydrolysis of the edta and edda chelates, the rate of reaction seems to be almost independent of $[H^+]$ above a certain value. This kinetic result is also observed for complexation of VO_2^+ with edta or nta,[17,20] for the decomplexation of vanadium(v) aminocarboxylates by hydroxide ions,[15] and for ligand interchanges of vanadium(v) aminocarboxylate.[16] We have in previous papers [15—17,20] explained this observation by proposing that there is a fast pre-equilibrium step between the reacting species and the entering group. Rearrangement gives the final products of the reaction. (*b*) Since co-ordinated nitrogen atoms have no available pair of electrons in the chelate, it seems that during the protonation pathway H^+ is most probably fixed on the oxygen of the acetate branch of the ligand.[11] (*c*) Generally, the mechanism of the decomplexation reaction of the chelate involves consecutive steps each of which includes a cleavage of one bond between the metal and the multidentate ligand until the complete dissociation of the chelate. Thus the acid hydrolysis of the V^{IV}–nta chelate shows two consecutive steps where a metal–ligand bond is broken before the other metal–ligand bonds can break very quickly.[11]

These three remarks (*a*)—(*c*) allow us to propose two different hypotheses for the protonation pathway which are consistent with the general expression of $k_{obs.}$ given in equation (3).

Hypothesis 1. This is described by Figure 1: rupture of the metal–oxygen bond, rapid protonation of the free branch of the ligand, rupture of metal–nitrogen bond, and then cleavage of all the metal–ligand bonds by a ' chain ' of rapid reactions leading to the complete decomplexation of the chelate. This hypothesis, for which the break of a metal–ligand bond is observed before protonation is commonly accepted [21] to explain chelate acid hydrolysis.

Hypothesis 2. This is described by Figure 2: formation of an ' outside ' protonated species by a very fast reaction, rupture of the metal–oxygen bond and then cleavage of the metal–nitrogen bond followed by rapid reactions leading to the complete decomplexation of the chelate. Complex formation between a reacting species and a H^+ ion to give an ' outside ' protonated species (Figure 3) was pointed out by some authors in the first step of the mechanism. The interpretation of acid-assisted aquation of the acetatopenta-aquachromium(III) ion shows the existence of a such complex.[22] More recently, Nishizawa and Saito [11] for the acid hydrolysis of a vanadium(IV)–nta chelate, and Margerum [9] for the acid-catalyzed dissociation of a nickel(II)–glycylglycylglycinate complex, proposed a mechanism involving an intermediate with an analogous structure.

The values of k and K obtained for the three chelates allow us to choose between these two reaction mechanisms. Experimentally we observe: K(nta) < K(edda) < K(edta) and k(edda) $\geqslant$ k(edta); k(nta) $\geqslant$ k(edta).

Discussion on hypothesis 1. This mechanism gives a rate law equivalent to equation (3) with $k = k_1$ and $K = (k_3/k_{-1})K_1$. We assume that the V–N bond cleavage (k_3) and the protonation constant (K_1) of an acetate group are practically independent of the ligand. The constant k_{-1} of V–O bond formation is greater for the edta chelate than for the edda and

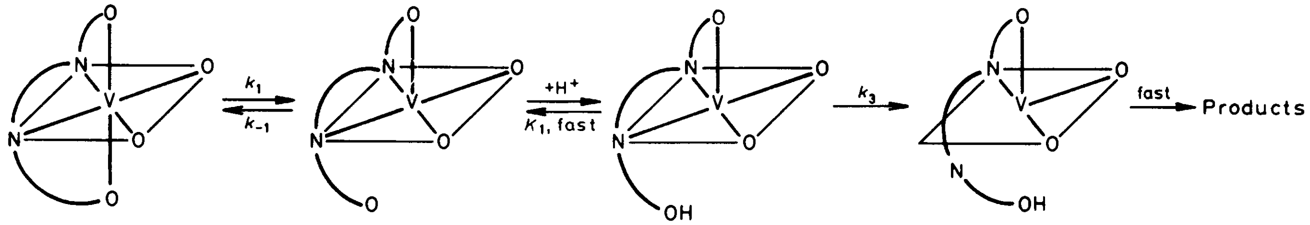

Figure 1. Hypothesis 1: proposed mechanism using $[VO_2(edda)]^-$ as an example

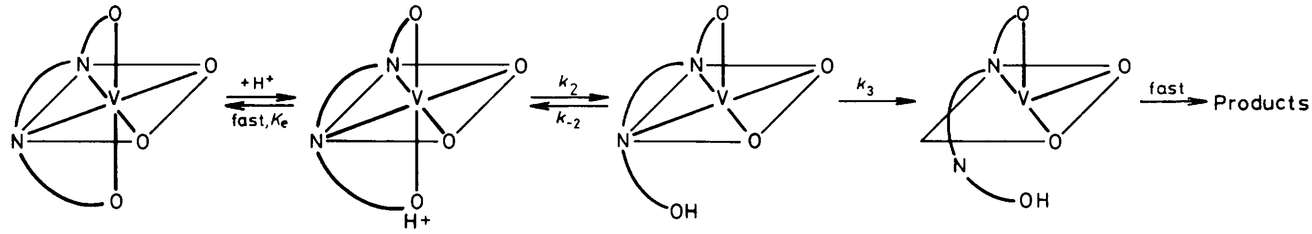

Figure 2. Hypothesis 2: proposed mechanism using $[VO_2(edda)]^-$ as an example

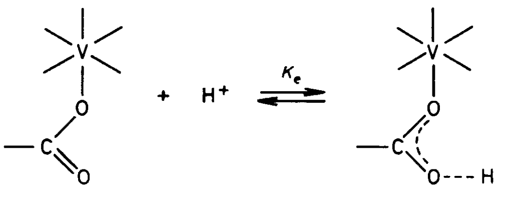

Figure 3. ' Outside ' protonation

nta chelates; the edta chelate possesses two open co-ordination positions (free acetate group) in addition to the free acetate group formed by the V–O bond rupture. Then, we might observe: *K*(edta) < *K*(nta) and *K*(edta) < *K*(edda).

The values of k_1 (rate constant of the V–O bond cleavage between the metal and the oxygen of an acetate group) may be practically the same for the three chelates. Then all the experimental values of *k* would be of the same order of magnitude: *k*(nta) ~ *k*(edda) ~ *k*(edta).

The two variations of *K* and *k* with the ligand which might be observed in the case of hypothesis 1 are not consistent with the experimental values.

Discussion on hypothesis 2. This mechanism gives a rate law equivalent to equation (3) with $k = (k_2k_3)/(k_{-2} + k_3)$ and $K = K_e$. K_e is the equilibrium constant of formation of an intermediate between the chelate and a H^+ ion. The structure of the chelate shows a dipole moment which decreases from the edta chelate to the nta chelate, reducing the basicity of the C=O group as can be seen in molecular models. If we assume that, for large ions with a large dipole moment, ion–dipole interaction is an important factor [23] in the formation of the ' outside ' protonated intermediate, we may observe the following variation of *K*: *K*(edta) > *K*(edda) > *K*(nta). This theoretical variation is also observed experimentally. We assume that the V–O bond cleavage (k_2) and the V–N bond cleavage (k_3) are practically independent of the ligand; the rate constant of the V–O bond reformation, k_{-2}, is greater for the edta chelate than for the edda and nta chelates: for the edta chelate this bond reformation could occur not only between the metal and the acetate group which has just left its co-ordination site but also between the metal and the other free acetate groups. Then, the following variations might be observed: *k*(edta) < *k*(edda) and *k*(edta) < *k*(nta). These ligand effects are also experimentally confirmed.

Table 5. Thermodynamic and activation parameters of *K* ($\Delta H^\ominus$, $\Delta S^\ominus$) and *k* ($\Delta H^\ddagger$, $\Delta S^\ddagger$)

Chelate	$\Delta H^\ominus$/ kJ mol^{-1}	$\Delta H^\ddagger$/ kJ mol^{-1}	$\Delta S^\ominus$/J K^{-1} mol^{-1}	$\Delta S^\ddagger$/J K^{-1} mol^{-1}
$[VO_2(edda)]^-$	15.5	38.2	65.6	−68.1
$[VO_2(H_2edta)]^-$	—	60.2	—	−43.5
	$\Delta H^\ominus + \Delta H^\ddagger$		$\Delta S^\ominus + \Delta S^\ddagger$	
$[VO_2(nta)]^{2-}$	54.7		−23.4	

The preceding discussion allows us to choose hypothesis 2 as the mechanism for the acid hydrolysis of $[VO_2(H_2edta)]^-$, $[VO_2(edda)]^-$, and $[VO_2(nta)]^{2-}$. Thermodynamic parameters for *K* have been calculated (Table 5). The $\Delta H^\ominus$ and $\Delta S^\ominus$ enthalpy and entropy of formation of the ' outside ' protonated intermediate complex are both small. The activation parameters, $\Delta H^\ddagger$ and $\Delta S^\ddagger$, obtained by analyzing *k* data according to conventional transition-state theory, are presented in Table 5. These values are consistent with those obtained [24] for metal–oxygen bond rupture in acid hydrolysis of Co^{III} chelates.

Conclusions

The mechanism of hypothesis 2 proposed for acid hydrolysis of vanadium(v) chelates indicates the formation of an ' outside ' protonated precursor complex in the first step and shows the great importance of the second solvation shell in the kinetic process of substitution reactions of oxo-metal complexes.

We observe that the hydrolysis rate constant is greatly diminished (about 1 000 times lower) by the presence of an acetate group not bonded to the metal (edta chelate). This effect is due to competition between chelating group–metal bond rupture (k_2) and new bond formation between the acetate group and the metal (k_{-2}). This reversible reaction is followed by V–N bond rupture and complete cleavage of the multidentate ligand.

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