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Kinetic Studies of the Acid Hydrolysis of Aquaoxo[*N*-(2-pyridylmethyl)-iminodiacetato]vanadium(IV) and Aqua(nitrilotriacetato)-oxovanadate(IV) in Aqueous Perchloric Acid Solution

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Acid hydrolysis of aquaoxo[*N*-(2-pyridylmethyl)iminodiacetato]vandium(IV) [VO(pmida)H$_2$O], ([H$^+$]=0.1—2.0 M, 1M=1 mol dm^{-3}) and aqua(nitrilotriacetato)oxovanadate(IV) [VO(nta)H$_2$O]$^-$, ([H$^+$]=0.2—2.0 M) has been studied by the stopped-flow method in aqueous perchloric acid solution at an ionic strength 2.0 (LiClO$_4$). The pseudo first-order rate constant k_0 is dependent on the proton concentration. The rate formula is expressed by $k_0=(k_1K_1[H^+]+k_2K_1K_2[H^+]^2)/(1+K_1[H^+]+K_1K_2[H^+]^2)$. A simulation curve fitting treatment gave the figures: $k_1=0.02$ and 0 s^{-1}, $k_2=6$ and 3000 s^{-1}, $K_1=1.5$ and 0.2 M^{-1}, and $K_2=0.2$ and 0.004 M^{-1} at 25 °C for [VO(pmida)H$_2$O] and [VO(nta)H$_2$O]$^-$, respectively. These data indicate that the rate determining step corresponds to the dissociation of the second basal bond of the singly or doubly protonated oxovanadium(IV) complexes.

The ligand substitution reaction of oxovanadium(IV) complexes includes several kinds of mechanistically discriminated reaction on different coordination sites (Fig. 1).[1] We have determined the structure of a new complex aquaoxo[*N*-(2-pyridylmethyl)iminodiacetato]vanadium(IV) [VO(pmida)H$_2$O]·2H$_2$O by X-ray crystallography to find that the tertiary amine occupies the trans site to oxo.[2] The anation reaction of this complex[1] with thiocyanate and azide proceeded much slower ($\simeq 10^{-1}$ s^{-1} at 25 °C) than the reported basal site substitutions[3] ($\simeq 10^3$ s^{-1} at 25 °C). We have thus considered that the hitherto known rates would not represent those of direct basal site substitution but involve the rearrangement from the apical to the basal site.

This new compound is stable toward acid hydrolysis above pH 3, but loses the quadridentate ligand in a more acid solution. Nitrilotriacetate(nta^{3-}) gives aqua(nitrilotriacetato)oxovanadate(IV) [VO(nta)H$_2$O]$^-$ which was found also stable toward acid hydrolysis above pH 3.[4] Acid hydrolysis of these two complexes involve various steps but must include the dissociation of basal metal-ligand bond. This paper deals with the kinetic studies of aquation of [VO(pmida)H$_2$O] and [VO(nta)H$_2$O]$^-$ in perchloric acid solutions containing 0.1 to 2.0 and 0.2 to 2.0 M (1 M=1 mol dm^{-3}) acid, respectively, at an ionic strength 2.0 (LiClO$_4$). The overall reaction is expressed by Eq. 1 (L^{n-2} stands for the quadridentate ligand with n=0 or 1).

$$[VO(L)H_2O]^n + mH^+ \underset{k_f}{\overset{k_d}{\rightleftharpoons}} [VO_{aq}]^{2+} + H_mL^{m+n-2} \qquad (1)$$

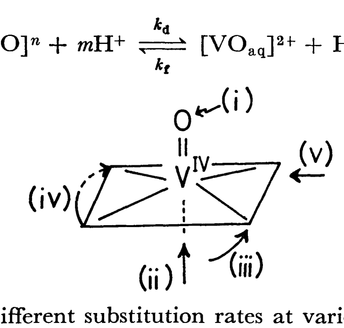

Fig. 1. Different substitution rates at various coordination sites of oxovanadium(IV) ion.
i) Very slow exchange of the oxo ligand, ii) very rapid substitution at the apical site, iii) fairly rapid intramolecular rearrangement from the apical to the basal site, iv) chelate formation at the basal site, v) rather slow direct basal substitution.

Experimental

Materials. The complex [VO(pmida)H$_2$O]·2H$_2$O[2] and K[VO(nta)H$_2$O]·H$_2$O[4] were prepared by the given methods, and the purity was checked by IR, UV, and visible absorption spectra and elemental analysis of carbon, hydrogen, and nitrogen. The ionic strength was adjusted with Special Grade sodium perchlorate and lithium perchlorate. The latter was prepared from the carbonate and perchloric acid and doubly recrystallized. Perchloric acid (Wako Chem. Co., Special Grade 60%) was used without further purification. The acid concentration was determined by the titration with sodium hydroxide.

Kinetic Runs. The UV absorption spectra at the initial and the final stage of the acid hydrolysis reaction are shown in Fig. 2. The rate was measured by monitoring the decrease of absorbance at 350 and 330 nm for the pmida and nta complexes, respectively, by the stopped-flow technique mainly at 25 °C and I=2.0 (LiClO$_4$). The difference in absorption at the given wave lengths before and after the acid hydrolysis coincided with those calculated from pure

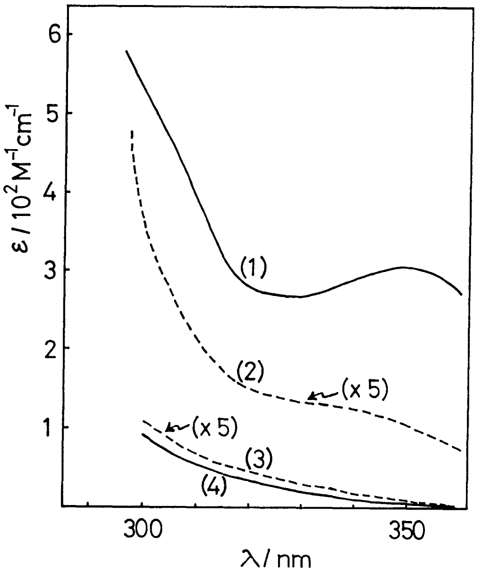

Fig. 2. UV absorption spectra in aqueous solution. 1) [VO(pmida)H$_2$O] at pH 4.7, 2) [VO(nta)H$_2$O]$^-$ at pH 4.7, 3) after equilibration of [VO(nta)H$_2$O]$^-$ containing 1 M acid, 4) after equilibration of [VO(pmida)H$_2$O] containing 1 M acid.

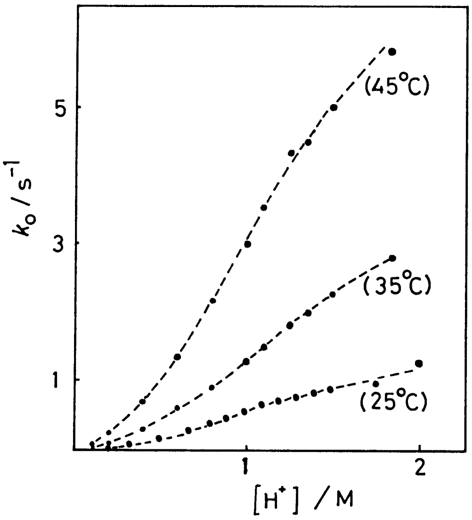

Fig. 3. Dependence of the first-order rate constant k_o upon the acid concentration for [VO(pmida)H_2O] (I=2.0, $LiClO_4$ at 25, 35, and 45 °C). ———; Simulation (see the text).

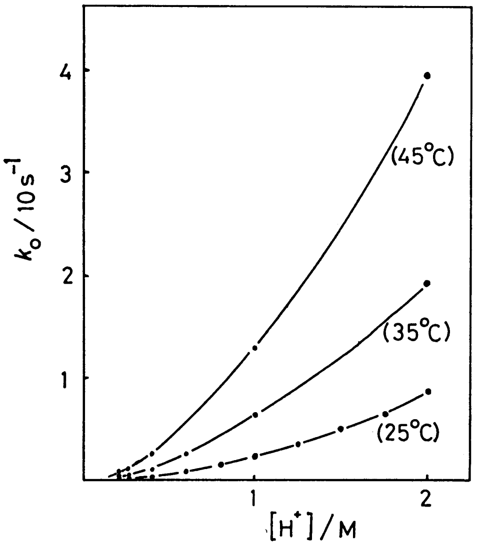

Fig. 4. Dependence of the first-order rate constant k_o upon the acid concentration for [VO(nta)H_2O]$^-$ (I= 2.0, $LiClO_4$ at 25, 35, and 45 °C).

solutions of $[VO(L)H_2O]^n$ and $[VO(H_2O)_5]^{2+}$, and the free ligand. The absorption spectra of all the reaction mixtures 5 min after mixing were the same with those of the complexes in 5 M perchloric acid solutions. Plots of $\ln(A_t-A_\infty)$ against time were linear until the reaction reached 85% completion, where A_t and A_∞ stand for the absorptions at the given wave length at time t and infinity, respectively. The first-order rate constants k_o were obtained from the slopes by the least squares method. The apparatus (Union Giken, RA 601 stopped-flow spectrometer) was used on different time scales, and the reproducibility was satisfactory within an error ±3%.

Results

The Overall Rate. The observed rate constant, k_o is expressed by Eq. 2, where [VO] stands for the concentration of the original complex.

Table 1. Results of the simulation curve fitting

	pmida			nta	
Temp/°C	45	35	25	25	25[a)]
K_1/M^{-1}	1.7	1.6	1.5	0.20	0.26
K_2/M^{-1}	0.1	0.1	0.2	0.004	$k_2\cdot K_2$ 12 ± 2 $(M^{-1}\,s^{-1})$
k_1/s^{-1}	0.1	0.05	0.02	0.00	
k_2/s^{-1}	40	20	6	3000	

a) By use of Eq. 9; the apparent ΔH^* and ΔS^* calculated for the product k_2K_2 at 25, 35, and 45 °C are 38±17 kJ mol^{-1} and −96±50 J mol^{-1} K^{-1}, respectively.

$$-d[VO]/dt = k_o[VO] \qquad (2)$$

Since the acid hydrolysis proceeded to completion under the given conditions, only the k_d in Eq. 1 was observed. Addition of excessive H_3nta did not change the k_o values at $[H^+]=0.2$ M. Addition of H_2pmida to the [VO(pmida)H_2O] solution at $[H^+]=0.1$ M increased the observed first-order rate constant and the formula was expressed by Eq. 3. ([$H_x$pmida] stands for the sum of concentration of variously protonated species of free pmida^{2-})

$$k'_o = k_d + k_f[H_x\text{pmida}] \qquad (3)$$

The observed k_d was 0.012 s^{-1}, coinciding with the k_o (0.012 s^{-1}) in the absence of excess of H_2pmida. Hence the formation reaction does not affect the rate of acid hydrolysis and no attention was paid to k_f.

Kinetic Formulae. The observed first-order rate constants for the two complexes showed rather complicated dependence on the acid concentration. (Figs. 3 and 4)

The pmida Complex: The curves in Fig. 3 suggests the participation of two routes involving one and two protons as shown by Eqs. 4, 5, and 6.

$$[VO(L)H_2O]^n \xrightleftharpoons{K_1(H^+)} [VO(HL)H_2O]^{n+1}$$

$$\xrightleftharpoons{K_2(H^+)} [VO(H_2L)H_2O]^{n+2} \qquad (4)$$

$$[VO(HL)H_2O]^{n+1} \xrightarrow{k_1} [VO_{aq}]^{2+} + H_xL \qquad (5)$$

$$[VO(H_2L)H_2O]^{n+2} \xrightarrow{k_2} [VO_{aq}]^{2+} + H_xL \qquad (6)$$

On the basis of Eqs. 4 to 6, the rate formula is written by

$$k_o = (k_1K_1[H^+]+k_2K_1K_2[H^+]^2)/(1+K_1[H^+]+K_1K_2[H^+]^2). \qquad (7)$$

Individual values of k_1, k_2, K_1, and K_2 were obtained by the trial and error method from the experimental values and shown in Table 1. They may involve rather large errors. The broken lines in Fig. 3 drawn by use of these calculated values, however, fit the experimental plots well.

The nta Complex: When the same analysis was applied to the nta complex, the individual values of equilibrium and rate constants were calculated as shown in Table1. It seems as if there is no contribution of the route shown by Eq. 5. The usefulness of such an analysis was verified as follows. The simulated value of k_1 is almost zero, and the product $K_1K_2[H^+]^2$ is very small

TABLE 2. SALT EFFECTS ($[H^+]=0.2$ M, 25 °C)

I	k_o/s^{-1}	
	pmida	nta
0.2	0.020	0.14
1.2	0.037	0.13
2.0	0.042	0.11

under the experimental conditions. Hence the first term of the numerator and the third term of the denominator of Eq. 7 can be ignored to give Eq. 8.

$$k_o = k_2K_1K_2[H^+]^2/(1+K_1[H^+]) \quad (8)$$

This is converted into Eq. 9.

$$[H^+]/k_o = 1/k_2K_1K_2[H^+] + 1/k_2K_2 \quad (9)$$

Plots of $[H^+]/k_o$ against $[H^+]^{-1}$ gave straight lines at the three temperatures, and the K_1 and the product k_2K_2 were obtained from the intercepts and gradients. The K_1 values obtained by such a plot and by the simulation method coincided with each other.

Medium Effects. The salt effect[5] was studied by changing the ionic strength, and the results are included in Table 2. A positive and a slightly negative effect were found for the pmida and the nta complex, respectively.

The chloride ion concentration did not affect the rate. The thiocyanate ion slightly accelerated the reactions of both complexes. The kinetic formula is too complicated to be analysed, but the anion seems to replace, at least partly, the coordinated water of the original complexes.[1,4]

Discussion

Whenever a substitution reaction of oxovanadium(IV) complexes is to be analysed, participation of mechanistically discriminated reactions should be considered (Fig. 1). They include i) very inert oxoanion exchange,[6] ii) extremely labile apical site substitution,[7,8] iii) basal ligand substitution involving intramolecular rearrangement of a ligand from apical to basal site,[3] iv) chelation at basal site,[9] and v) direct basal substitution.[1,4] For the present reactions, process iii and v should be considered.

Kinetic formulae for both the complexes indicate that proton catalysed bond breaks are the rate determining steps. Since coordinated nitrogen atoms have no lone pair of electrons, the protonation should take place on the oxygen of the acetate branch of the ligand.[10]

The pmida Complex. The X-ray structure has been determined and the bond lengths are known. The kinetic formula suggests the presence of two parallel paths, accompanied by single and double protonation. For the process iii to operate, break of at least two basal bonds should be needed. A plausible reaction mechanism is illustrated in Fig. 5.

The V–O bond lengths are 2.02 and 1.98 Å at the trans and cis site of the aqua ligand, respectively, in the crystalline state (Fig. 6). If the difference were preserved in the aqueous solution, the first protonation should take place at the trans site. The protonated acetate branch will leave the coordination sphere rapidly, so that the observed K_1 corresponds to the product of the equilibrium constant of the first protonation (I to II) and the break of the trans V–OH bond to the aqua (II to III).[11] The k_1 step can take place at either the V–O (cis to aqua) or the V–N (pyridine) bond. Their lengths are 1.98 and 2.11 Å respectively in the crystalline state. If a similar difference existed in the aqueous solution, the V–N bond would be broken at a rate k_1 [III]. The observed k_1 value is not very different from the ordinary rate constant of direct basal bond break (process v).[1]

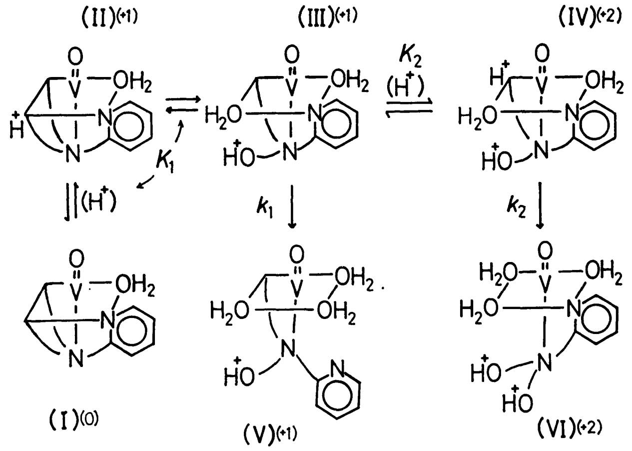

Fig. 5. Plausible reaction mechanism for [VO(pmida)H_2O]. (The overall charges of the complex and the intermediates are in parentheses).

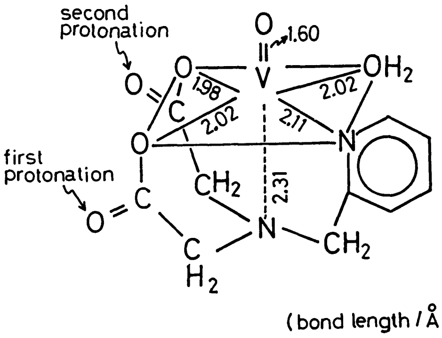

Fig. 6. X-Ray structure data of [VO(pmida)H_2O]·$2H_2O$ and plausible protonation site in solution.

The k_2 step involving the doubly protonated complex (IV) must be the break of the acetate arm cis to the aqua ligand. The larger k_2 than k_1 must be due to protonation. After the two basal bonds are broken, the tertiary nitrogen can dissociate very quickly (process ii) and the third basal bond (V–O and V–N-(pyridine) for the intermediates V and VI, respectively) can move to the apical site (process iii) to result in complete dissociation of $H_x$pmida.

The contribution of the two paths depends on the acid concentration. The k_2 is much greater than k_1, but the small K_2 decreases its contribution, which however predominates at a high acid concentration.

The nta Complex. The X-ray structure of this complex is not known, but the tertiary amine was believed to occupy the apical position.[4] The simulated

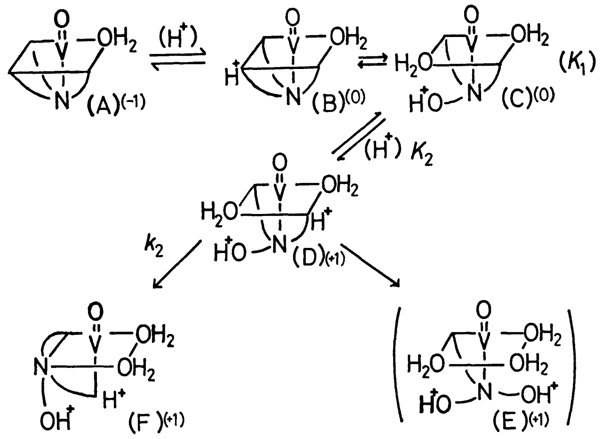

Fig. 7. Plausible reaction mechanisms for [VO(nta)-H$_2$O]$^-$ (see the text). (The overall charges of the complex and the intermediates are in parentheses).

small k_1 implies that the singly protonated species (C in Fig. 7) does not allow the dissociation of the complex. Whenever a similar process is assumed for this complex as for the pmida complex, the K_1 represents the overall equilibrium constant for the two processes, the protonation (form A to B) and the dissociation of a V–OH bond trans to aqua (B to C). The simulated K_1 is much smaller than that for the pmida complex. This fact may result from either the difficulty in first protonation or the ease of the backward reaction from C to B, suggesting in either case a stronger V–O bond than that for the pmida complex. The K_2 value indicating the ease of second protonation at the cis site to the aqua ligand is also smaller than that for the pmida complex. This fact also suggests a stronger V–O bond than that for the pmida complex. These observations are also reflected in the high acid concentration region, in which the acid hydrolysis can be measured. The simulated k_2 vaule ($\simeq 3000\ \mathrm{s}^{-1}$) is, on the other hand, much greater than that of the pmida complex ($\simeq 6\ \mathrm{s}^{-1}$). Although there can be complication from the difference in overall charge, it is unlikely that a stronger bond is more readily broken than a weaker bond under a similarly protonated circumstance. Hence the k_2 must reflect some other process than a mere break of V–OH bond (from D to E in Fig. 7). If the doubly protonated intermediate D underwent intramolecular rearrangement to give F, the protonated arm at the apical site would be readily broken (processes iii and ii). Such an intramolecular change is not generally feasible for a terdentate ligand. Molecular model studies, however, suggest that the nta complex is highly strained. The second protonation will elongate the V–O bond and can bring about the rearrangement of H$_2$nta$^-$ to give F. The simulated k_2 is in the same region as those for the process iii.[12)]

Comparison of the Two Complexes. The faster acid hydrolysis of the more stable nta complex than that of the pmida complex may be accounted for by considering different rate determining steps for both complexes as shown above. The reason why the pmida complex undergoes the intramolecular rearrangement to give F-type intermediate with difficulty may be attributed to the more highly oriented V–N (pyridine) bond brought about by the delocalization of electron between d_{xy} orbital of vanadium(IV) and the π-orbital of pyridine.

The influence of ionic strength upon k_0 indicates the interactions between species with the same and opposite ionic sign for the pmida and the nta complex, respectively. Since interactions involving species without electric charge do not exhibit significant dependence on the ionic strength, the equilibrium constants K_2 and K_1 will be subject to the influence (see Figs. 5 and 7). The K_2 for the pmida complex will increase and the K_1 for the nta complex will decrease with increase in ionic strength. Since the second and third terms of the denominator of Eq. 7 are much less than unity, the influence of ionic strength will be predominating on the numerator. Hence the results of Table 2 are reasonably interpreted by the mechanisms shown in Figs. 5 and 7.

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11) The absorption change corresponding to the step from species (II) to (III) seems too small to be detected. The rate of the bond break from II to III must be greater than those for the k_1 and k_2 paths but can be of similar order to that of the k_2 path.

12) This interpretation is based on the assumption that the first protonation takes place at the trans site to the aqua ligand as presumed for the pmida complex. If the first protonation occurred on the cis site, on the contrary, the intermediate product would involve a facially terdentated Hnta^{2-} species. The nitrogen at the apical site would be labile, and the second protonated acetate arm can squeeze into the apical site while the nitrogen tentatively leaves the apical site. Such a mechanism is also in accord with the given kinetic formula and the simulated values of K_1, K_2, and k_2. So far as the bond lengths remain unknown the two possible reaction mechanisms cannot be discriminated.