9CO]+, 372 [Re$_2$]+, 226 [4,4'-dimethylthiobenzophenone].

Thermolysis of 4,4'-Dimethylthiobenzophenonedirhenium Nonacarbonyl [5, $R_1 = R_2 = CH_3$]. A methylcyclohexane solution (100 ml) of the dirhenium nonacarbonyl complex **5** [$R_1 = R_2 = CH_3$] was refluxed for 24 h. Work-up as described for **5**, $R_1 = R_2 = OCH_3$, gave the orange-red ortho-metalated complex **2**, $R_1 = R_2 = CH_3$, as an oil in 68% yield.

Anal. Calcd for $C_{19}H_{13}O_4SRe$: C, 43.58; H, 2.50; S, 6.10. Found: C, 43.99; H, 2.57; S, 6.06.

Ir (CHCl$_3$), ν_{CO}: 2085 (m), 1988 (vs), 1975 (vs), 1928 (s) cm^{-1}. Mass spectrum (m/e): 523 [M]$^+$, 495 [M – CO]$^+$, 467 [M – 2CO]$^+$, 439 [M – 3CO]$^+$, 411 [M – 4CO]$^+$.

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Registry No. $Re_2(CO)_{10}$, 14285-68-8; **2** ($R_1 = R_2 = OCH_3$), 57652-82-1; **2** ($R_1 = R_2 = N(CH_3)_2$), 57652-83-2; **2** ($R_1 = OCH_3$; $R_2 = H$), 57652-84-3; **5** ($R_1 = R_2 = OCH_3$), 57652-85-4; **5** ($R_1 = R_2 = CH_3$), 57652-86-5; **2** ($R_1 = R_2 = CH_3$), 57652-87-6; **1** ($R_1 = R_2 = N(CH_3)_2$), 1226-46-6; **1** ($R_1 = R_2 = OCH_3$), 958-80-5; **1** ($R_1 = R_2 = CH_3$), 1141-08-8; **1** ($R_1 = OCH_3$; $R_2 = H$), 1141-07-7.

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Kinetics and Mechanism of the Complexation Reactions of Pervanadyl Ion with Some Aminopolycarboxylates

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The kinetics of the complex formation reaction of pervanadyl ion with ethylenediamine-*N,N'*-diacetic acid (EDDA), *N*-methyliminodiacetic acid (MIDA), and nitrilotriacetic acid (NTA) has been studied spectrophotometrically by means of a stopped-flow technique. The rate of formation of the pervanadyl aminopolycarboxylate is expressed as $d[VO_2Y^{1-n}]/dt = k^+[VO_2^+][H_mY^{m-n}] - k^-[VO_2Y^{1-n}][H^+]^m$, where $k^+ = 10^{8.03}$ M^{-1} s^{-1}, $k^- = 10^{3.16}$ M^{-1} s^{-1}, $m = 1$, and $n = 2$ for EDDA; $k^+ = 10^{3.39}$ M^{-1} s^{-1}, $k^- = 10^{2.76}$ M^{-1} s^{-1}, $m = 1$, and $n = 2$ for MIDA; $k^+ = 10^{5.13}$ M^{-1} s^{-1}, $k^- = 10^{2.70}$ M^{-2} s^{-1}, $m = 2$, and $n = 3$ for NTA, all at 25 °C and $I = 1.0$ M (NaClO$_4$). Lower rate constants for the reaction of VO_2^+ with protonated MIDA and NTA are interpreted by the relatively slow step of proton migration from protonated nitrogen. In the case of VO_2^+–EDDA, the reaction proceeds with the loss of the first water molecule from the aquated VO_2^+ as a rate-determining step. Mechanisms are proposed for the complexation reactions of the protonated ligands and some discussions are made on the difference in the reactivities of these ligands.

Introduction

Because of the lack of information concerning the solution equilibria of the vanadium(V) cation (pervanadyl ion is represented as VO_2^+ in acidic solution), few studies of complexation kinetics involving pervanadyl ion have been undertaken. Only the kinetics of complexation reactions with hydrogen peroxide[1] and ethylenediamine-*N,N,N',N'*-tetraacetic acid[2] have been reported so far. The reaction of pervanadyl ion does not seem to be well understood; we hoped to obtain information about the characteristics of this oxo cation from studies on complexation kinetics.

We have studied the hydrolysis reaction of pervanadyl ion[3] and the complexation equilibria with some aminopolycarboxylates.[4] The present paper describes the kinetic results on the complexation reaction

$$VO_2^+ + Y' \rightleftharpoons VO_2Y$$

where Y' refers to aminopolycarboxylate ion such as ethylenediamine-*N,N'*-diacetate (EDDA), *N*-methyliminodiacetate (MIDA), and nitrilotriacetate (NTA). We have utilized the stopped-flow technique to study the reaction.

Experimental Section

Reagents. Methods of preparation and standardization of the reagents (pervanadyl perchlorate, EDDA, MIDA, NTA, sodium perchlorate, and sodium hydroxide) have been described previously.[4]

Measurements. All experiments were carried out in a room thermostated at experimental temperature to ±0.5 °C. The ionic strength was maintained at 1.0 M with sodium perchlorate. Hydrogen ion concentration was determined by a Radiometer pH meter (PHM 22 Type) with a calomel electrode filled with saturated sodium chloride as an internal solution instead of saturated potassium chloride. A 1.000×10^{-2} M perchloric acid solution containing 0.99 M sodium perchlorate was employed as a standard of hydrogen ion concentration ($-\log [H^+] = 2.000$) and the liquid junction potential was taken into consideration.[4]

The kinetics of complexation were studied spectrophotometrically by means of a stopped-flow analyzer, RA 1100 (Union, Ltd., Hirakata, Japan) equipped with a transient recorder (Union RA 108 S). The pervanadyl and the aminopolycarboxylate solutions were brought to temperature equilibrium in a bath kept at a given temperature to ±0.1 °C and then transferred to the thermostated mixing syringes. The changes in absorbance at 270 nm were recorded as a function of reaction time. In all kinetic studies aminopolycarboxylates were present in sufficient excess to ensure the pseudo-first-order reaction.

Results

Under the present experimental conditions the complex formation equilibrium is written as[4]

$$VO_2^+ + Y' \underset{k^-_{o(H,Y)}}{\overset{k^+_{o(H,Y)}}{\rightleftharpoons}} VO_2Y \qquad (1)$$

Table I. Conditional Rate Constants $k^{+}_{o(H,edda)}$ and $k^{-}_{o(H,edda)}$ of the Complexation Reaction of VO_2^+ with EDDA at 25 °C[a]

$10^3 C_{EDDA}$, M	$-\log [H^+]$	$k^{+}_{o(H,edda)}$, s^{-1}	$k^{-}_{o(H,edda)}$, s^{-1}
4.99	2.89	68.3	2.0
	2.82	50.2	2.0
	2.77	40.4	2.3
	2.66	31.7	3.3
	2.56	24.1	4.4
	2.50	19.2	4.9
	2.41	12.8	5.7
	2.31	8.8	7.3
	2.27	6.8	7.5
	2.23	5.7	7.9
	2.16	3.8	8.5
2.00	2.28	2.9	7.3
3.19	2.27	4.2	7.3
3.99	2.32	7.0	6.8
5.99	2.33	10.5	6.4
7.18	2.35	13.6	6.1
7.98	2.35	14.2	5.7

[a] $C_{VO_2} = 1.23 \times 10^{-4}$ M; $I = 1.0$ M ($NaClO_4$).

where Y' denotes the aminopolycarboxylate not combined with pervanadyl ion. For the reaction with a large excess of hydrogen ion and Y', the rate equation can be expressed as

$$d[VO_2Y]/dt = k^{+}_{o(H,Y)}[VO_2^+] - k^{-}_{o(H,Y)}[VO_2Y] \quad (2)$$

where $k^{+}_{o(H,Y)}$ and $k^{-}_{o(H,Y)}$ are the forward and backward conditional rate constants involving concentrations of hydrogen ion and aminopolycarboxylate respectively. The rate plots of $\ln [(A_\infty - A_0)/(A_\infty - A_t)]$ vs. t were linear for over 90% of the reaction (A_0, A_t, and A_∞ are the absorbance of the reaction systems at reaction times 0, t, and ∞, respectively). Then the conditional rate constants ($k^{+}_{o(H,Y)} + k^{-}_{o(H,Y)}$) were determined from the slope of this plot. On the other hand, the ratio of the conditional rate constants is given by eq 3, where K_{VO_2Y},

$$k^{+}_{o(H,Y)}/k^{-}_{o(H,Y)} = K_{VO_2Y}C_Y/\alpha_{Y(H)} \quad (3)$$

C_Y, and $\alpha_{Y(H)}$ refer to the formation constant of a 1:1 pervanadyl–aminopolycarboxylate complex, the total concentration of aminopolycarboxylate, and the side-reaction coefficient of aminopolycarboxylate taking into account its protonation, respectively.

Knowing the hydrogen ion concentration in the reaction mixture, we obtain the ratio of the conditional rate constants from eq 3 (each value is the average of at least three determinations). For the VO_2^+–EDDA system values of the conditional rate constants at various concentrations of hydrogen ion and EDDA are given in Table I.

These data indicate that $k^{+}_{o(H,edda)}$ does not linearly depend upon the concentrations of hydrogen ion and EDDA. Taking into account all the species involved, we have 15 possible reaction paths involving VO_2^+, HVO_3, and VO_3^- for vanadium(V) and H_4edda^{2+}, H_3edda^+, H_2edda, $Hedda^-$, and $edda^{2-}$ for EDDA. Then the overall rate equation for the forward reaction of the V^V–EDDA system is expressed as (4),

$$v^{+}_{EDDA} = k^{+}_{o(H,edda)}[VO_2^+] = (k_1[VO_2^+] + k_2[HVO_3] + k_3[VO_3^-])(k_4[H_4edda^{2+}] + k_5[H_3edda^+] + k_6[H_2edda] + k_7[Hedda^-] + k_8[edda^{2-}]) \quad (4)$$

C_{EDDA} being equal to $\alpha_{edda(H)}[edda^{2-}]$. The conditional rate constant $k^{+}_{o(H,edda)}$ is given as in (5), where β_n^V and β_m^Y refer

$$\alpha_{edda(H)}k^{+}_{o(H,edda)}/C_{EDDA} = (k_1 + k_2\beta_1^V[H^+]^{-1} + k_3\beta_2^V[H^+]^{-2})(k_4 + k_5\beta_1^Y[H^+] + k_6\beta_2^Y[H^+]^2 + k_7\beta_3^Y[H^+]^3 + k_8\beta_4^Y[H^+]^4) \quad (5)$$

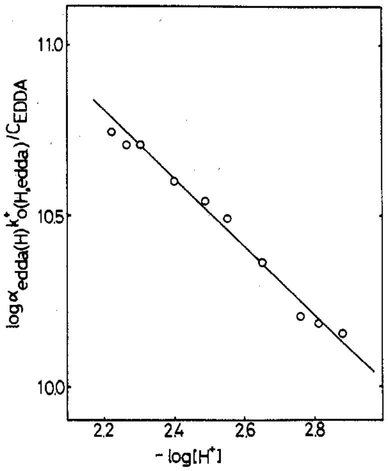


Figure 1. $\alpha_{edda(H)}k^{+}_{o(H,edda)}/C_{EDDA}$ as a function of hydrogen ion concentration; $C_{VO_2} = 1.23 \times 10^{-4}$ M, $C_{EDDA} = 4.99 \times 10^{-3}$ M, $I = 1.0$ M ($NaClO_4$), 25 °C.

to the overall hydrolysis constant for VO_2^+ [3] and the overall protonation constant for EDDA,[4] respectively: $\beta_n^V = [VO_2(OH)_n^{1-n}][H^+]^n/[VO_2^+]$; $\beta_m^Y = [H_medda^{m-2}]/([H^+]^m[edda^{2-}])$. Plot of the logarithmic value of the left-side of eq 5 against $-\log [H^+]$ (Figure 1) yields a straight line with a slope of -1.

Three paths are considered to be possibly relevant to the reaction, i.e.

$$v^{+}_{EDDA} = 10^{8.03}[VO_2^+][Hedda^-] = 10^{5.04}[HVO_3][H_2edda] = 10^{6.47}[VO_3^-][H_3edda^+]$$

at 25 °C. Though we cannot stoichiometrically distinguish these three possibilities, we should be able to choose one reasonable pathway from possible alternatives.

It is generally established that complex formation in aqueous solution involves rapid equilibrium of an outer-sphere complex with a metal ion and a ligand followed by the rupture of an inner-sphere coordinated water molecule (rate-determining step).[5] The effect of the attached group on the exchange rate of coordinated water at metal ion has been successfully interpreted.[6] The relative water-exchange rate is related to the electron-donating properties of the ligand coordinated to the central metal ion[7] by

$$\log (k_{MA}^{-H_2O}/k_M^{-H_2O}) = \gamma E_n$$

where $k_{MA}^{-H_2O}$ and $k_M^{-H_2O}$ denote the rate constants of water exchange at MA and M, respectively, and E_n and γ refer to the electron donor constant of the attached ligand A[8] and the constant characteristic of the metal ion,[7] respectively.[9]

As γ value is around unity for hard and borderline Lewis acids,[10] the reactivity of the hydrolyzed species HVO_3 is anticipated to be only about 10 times as high as that of the corresponding aquo ion VO_2^+. Moreover $Hedda^-$ seems to be much more reactive than H_2edda and H_3edda^+ as indicated by the results from other systems.[11] Thus the respective reactions of H_2edda and H_3edda^+ with minor species HVO_3 and VO_3^- cannot be regarded as important paths: this complexation should proceed through the reaction path involving $Hedda^-$ and the predominant species VO_2^+.

For the backward reaction $k^{-}_{o(H,edda)}$ is found proportional to the concentration of hydrogen ion and independent of the EDDA concentration (Table I). Thus we have

$$v^{-}_{EDDA} = k^{-}_{o(H,edda)}[VO_2(edda)^-] = k^{-}_{EDDA}[VO_2(edda)^-][H^+]$$

Table II. Conditional Rate Constants $k^{+}_{\mathrm{o(H,mida)}}$ and $k^{-}_{\mathrm{o(H,mida)}}$ of the Complexation Reaction of VO_2^+ with MIDA at 25 °C[a]

10^2C_{MIDA}, M	−log [H⁺]	$k^{+}_{\mathrm{o(H,mida)}}$, s^{-1}	$k^{-}_{\mathrm{o(H,mida)}}$, s^{-1}
2.00	1.98	15.4	5.4
	1.87	12.3	6.9
	1.77	10.3	9.3
	1.67	8.0	13.0
	1.60	7.1	16.2
	1.54	6.2	20.8
	1.48	4.3	20.8
	1.43	3.6	22.1
3.00	1.87	17.0	6.4
	1.71	10.6	9.0
	1.59	9.6	15.8
	1.48	7.0	22.3
1.00	1.84	6.0	7.7
	1.64	3.4	15.0

[a] $C_{VO_2} = 2.20 \times 10^{-4}$ M; $I = 1.0$ M ($NaClO_4$).

Table III. Conditional Rate Constants $k^{+}_{\mathrm{o(H,nta)}}$ and $k^{-}_{\mathrm{o(H,nta)}}$ of the Complexation Reaction of VO_2^+ with NTA at 25 °C[a]

10^3C_{NTA}, M	−log [H⁺]	$k^{+}_{\mathrm{o(H,nta)}}$, s^{-1}	$k^{-}_{\mathrm{o(H,nta)}}$, s^{-1}
5.92	1.15	56.2	2.2
	1.05	39.7	3.8
	0.96	29.9	6.3
	0.89	23.4	8.9
	0.82	18.3	13.0
	0.77	14.0	15.5
	0.71	10.1	18.5
	0.68	8.7	20.8
	0.64	7.7	26.3
	0.60	5.8	28.0
2.96	1.18	32.5	2.2

[a] $C_{VO_2} = 2.02 \times 10^{-4}$ M; $I = 1.0$ M ($NaClO_4$).

The results for MIDA and NTA systems are summarized in Tables II and III, respectively.

In the VO_2^+–MIDA system the plot of log $\alpha_{\mathrm{mida(H)}} \cdot k^{+}_{\mathrm{o(H,mida)}}/C_{\mathrm{MIDA}}$ against −log [H⁺] yields a straight line with a slope of −1. This result conforms to the rate equation

$$v^{+}_{\mathrm{MIDA}} = k^{+}_{\mathrm{o(H,mida)}}[VO_2^+] = k^{+}_{\mathrm{MIDA}}[VO_2^+][\mathrm{Hmida}^-]$$

For the backward reaction $k^{-}_{\mathrm{o(H,mida)}}$ is found proportional to the concentration of hydrogen ion and independent of the MIDA concentration

$$v^{-}_{\mathrm{MIDA}} = k^{-}_{\mathrm{o(H,mida)}}[VO_2(\mathrm{mida})^-] = k^{-}_{\mathrm{MIDA}}[VO_2(\mathrm{mida})^-][H^+]$$

For the VO_2^+–NTA system the same procedure was followed and we obtained the rate law

$$v^{+}_{\mathrm{NTA}} = k^{+}_{\mathrm{o(H,nta)}}[VO_2^+] = k^{+}_{\mathrm{NTA}}[VO_2^+][H_2\mathrm{nta}^-]$$

$$v^{-}_{\mathrm{NTA}} = k^{-}_{\mathrm{o(H,nta)}}[VO_2(\mathrm{nta})^{2-}] = k^{-}_{\mathrm{NTA}}[VO_2(\mathrm{nta})^{2-}][H^+]^2$$

Then the complexation reaction of pervanadyl ion with aminopolycarboxylates is summarized by eq 6–8. The rate

$$d[VO_2(\mathrm{edda})^-]/dt = k^{+}_{\mathrm{EDDA}}[VO_2^+][\mathrm{Hedda}^-] - k^{-}_{\mathrm{EDDA}}[VO_2(\mathrm{edda})^-][H^+] \quad (6)$$

$$d[VO_2(\mathrm{mida})^-]/dt = k^{+}_{\mathrm{MIDA}}[VO_2^+][\mathrm{Hmida}^-] - k^{-}_{\mathrm{MIDA}}[VO_2(\mathrm{mida})^-][H^+] \quad (7)$$

$$d[VO_2(\mathrm{nta})^{2-}]/dt = k^{+}_{\mathrm{NTA}}[VO_2^+][H_2\mathrm{nta}^-] - k^{-}_{\mathrm{NTA}}[VO_2(\mathrm{nta})^{2-}][H^+]^2 \quad (8)$$

constants obtained for these reactions at 25 °C are summarized in Table IV.

Table IV. Rate Constants of the Complexation Reaction of VO_2^+ with Aminopolycarboxylates at 25 °C and $I = 1.0$ M ($NaClO_4$)

	log k^+	log k^-
EDDA	8.03	3.16
MIDA	3.39	2.76
NTA	5.13	2.70

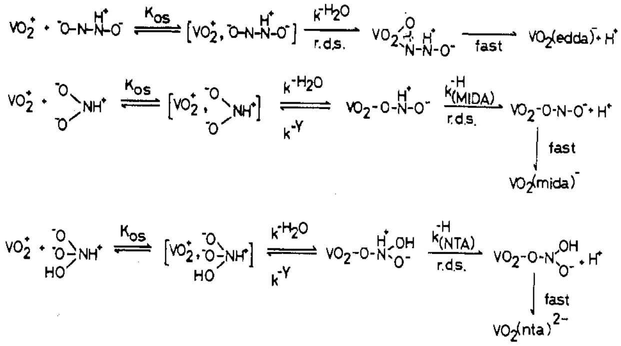
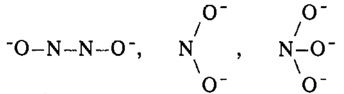


Figure 2. Proposed stepwise reaction mechanism for the complexation reactions of pervanadyl ion with aminopolycarboxylates. Free ions for EDDA, MIDA, and NTA are symbolized respectively as



and K_{os} and k^{-H_2O} refer to the outer-sphere formation constant and the rate constant of the water exchange at VO_2^+.

Discussion

For the reaction of an aquated metal ion with a ligand to form a metal complex, the rate-determining step is, in most cases, water loss from the metal ion. It has been pointed out that in the formation of a metal–aminopolycarboxylate complex from protonated aminopolycarboxylate, the proton plays an important role. In the complexation of metal ion with the aminopolycarboxylates of which nitrogen donors are all protonated,[12–16] the reaction rate is slower than predicted by the Eigen mechanism: this is ascribed to the relatively slower step of the proton migration from the nitrogen atom in a partially bonded reaction intermediate or the presence of small amounts of carboxylate-protonated ligand. On the other hand, the rates of complexation of metal ion by the monoprotonated forms of ethylenediamine-*N*,*N*,*N*′,*N*′-tetraacetic acid[14,17–19] and cyclohexanediamine-*N*,*N*,*N*′,*N*′-tetraacetic acid[14] and the nonprotonated forms of iminodiacetic acid[13,14] and NTA[12,14,16] are all approximately equal to those predicted by the Eigen mechanism.

In the present study it was revealed that the rate law for the complex formation reaction of pervanadyl ion with aminopolycarboxylate ion is generally expressed as

$$d[VO_2Y^{1-n}]/dt = k^+[VO_2^+][H_mY^{m-n}] - k^-[VO_2Y^{1-n}][H^+]^m$$

According to the rate law obtained, pervanadyl ion reacts with Hedda^- for EDDA, $H_2\mathrm{nta}^-$ for NTA, and Hmida^- for MIDA. EDDA, of which one nitrogen atom is protonated and the other is not protonated, reacts extremely faster than the other two cases in which the nitrogen atom is protonated. As in the cases of other monoprotonated diaminopolycarboxylates,[14,17–19] for EDDA reacting with VO_2^+ the rate-determining step is considered as the water loss from VO_2^+ followed by the rapid proton dissociation leading to the coordination of all donor atoms in EDDA (see Figure 2). In fact, the VO_2^+–EDDA complex is not protonated under the present condition.[4] According to available data for a d^0 metal ion the exchange rate of coordinated water is in the range 10^8–10^9 s^{-1}: for Ca^{2+}, Sr^{2+}, and Ba^{2+}, $>10^{7.8}$ M^{-1} s^{-1} (10 °C, $I = 0.1$ M);[20] for Sc^{3+},

$10^{7.7}$ M^{-1} s^{-1} (12 °C, $I = 0.1$ M);[21] for Y^{3+}, $10^{7.1}$ M^{-1} s^{-1} (12 °C, $I = 0.1$ M);[21] for La^{3+}, $10^{7.9}$ M^{-1} s^{-1} (12 °C, $I = 0.1$ M);[21] for $MoO_3(OH)^-$, 10^8 M^{-1} s^{-1} (25 °C, $I = 0.2$ M);[22] for $WO_3(OH)^-$, 10^9 M^{-1} s^{-1} (25 °C, $I = 0.2$ M).[22] Then the constant of $10^{8.03}$ M^{-1} s^{-1} for the VO_2^+–$Hedda^-$ path implies that this reaction involves the exchange of coordinated water at VO_2^+ as a rate-determining step.[23] Considering the role of the proton in these reaction systems, we postulate the mechanism illustrated in Figure 2 with the assumption that, in the cases of MIDA and NTA, the proton migration from the nitrogen atom to bulk water or to the carboxylate oxygen is not rapid compared to the water-exchange rate.[24]

Assuming the stationary-state condition for the intermediates protonated at nitrogen, we have the forward rate constant expressed as

$$k^{+}{}_{Y} = K_{os}k^{-H_2O}k^{-H}{}_{Y}/(k^{-Y} + k^{-H}{}_{Y})$$

The formation constant of the nitrogen protonated intermediates ($K = k^{-H_2O}/k^{-Y}$) being low, k^{-H_2O} and k^{-Y} may be of the same order of magnitude and assumed to be much greater than $k^{-H}{}_{Y}$. Then we have

$$k^{+}{}_{Y} = K_{os}Kk^{-H}{}_{Y} \tag{9}$$

This equation suggests that, in the reaction of VO_2^+ with $Hmida^-$ and H_2nta^-, the rate-determining step is not the loss of the first water molecule from VO_2^+. The lower rate of these reactions is attributable to the $k^{-H}{}_{Y}$ step.

$K_{os}K$ in eq 9 being the same for NTA and MIDA systems, the relative rate constant is given by

$$k^{+}{}_{NTA}/k^{+}{}_{MIDA} = k^{-H}{}_{NTA}/k^{-H}{}_{MIDA}$$

pK_a values of the nitrogen-protonated intermediates not being available, we shall estimate the difference in reactivities between these two systems from the protonation equilibria of the ligands. Since, by the coordination of pervanadyl ion to the carboxyl group, the proton basicity on the nitrogen atom seems to be affected to the same extent for both ligands, the value of $k^{-H}{}_{NTA}/k^{-H}{}_{MIDA}$ should be parallel to the reciprocal ratio of the nitrogen protonation constants[4] of the free ligand, i.e., $K_{Hmida}/K_{Hnta} = 10^{9.48}/10^{8.92} = 10^{0.56}$. This ratio is about 1 order of magnitude lower than that of the observed rate constants ($k^{-H}{}_{NTA}/k^{-H}{}_{MIDA} = 10^{1.74}$; see Table IV). This difference points to the effect of the attached groups on the nitrogen atom: one of the free carboxyl groups of NTA being protonated, the proton basicity of the intermediate involving NTA should be lower than predicted from the pK_a of $Hnta^{2-}$. In fact, according to the estimate based on the microscopic equilibrium, the $-CH_2COOH$ group lowers the basicity of nitrogen by 2.0 in pK_a units as compared with the $-CH_2COO^-$ group.[25] After all, the difference in the reactivities of NTA and MIDA is consistent with the reaction mechanism involving the proton transfer as a rate-determining step (Figure 2).

The value of $10^{-0.2}$ being taken for K_{os}, the rate constant of the water exchange at VO_2^+ is estimated to be $10^{8.2}$ s^{-1} from the complexation rate constant of VO_2^+ with $Hedda^-$. Since the value of ΔH_{os} does not significantly contribute to $\Delta H^{\ddagger}{}_{EDDA}$, the activation enthalpy of water exchange at VO_2^+ is roughly estimated to be 29 kJ mol^{-1}.[26] As compared with other transition metal ions, lower activation enthalpy for this oxo cation is close to the corresponding value for Cu^{2+} (~25 kJ mol^{-1}).[27,28] The similarity of these two ions has already been pointed out[4] and attributed to the two labile water molecules: two axial water molecules for copper(II) ion and two water molecules trans to oxygen for pervanadyl ion. These more labile hydrated waters would make the potential energy of these ions high, thus lowering the activation energy in a similar fashion.

Considerably lower rate constants have been reported for the vanadium(V) ion reacting with EDTA ($10^{6.6}[VO_2^+]\cdot[H_2edta^{2-}]$ at 25 °C and $I = 3$ M ($NaClO_4$)[2]; $10^{4.4}[VO_2(OH)_2^-][H_2edta^{2-}]$ and $10^{3.4}[VO_2(OH)_3^-][H_2edta^{2-}]$ at 25 °C and $I = 0.5$ M (NH_4Cl)[29]). In this connection it should be noted that the basic nitrogens in EDTA are both protonated; proton migration from nitrogen should play an important role as in the reaction of MIDA and NTA with VO_2^+.

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Registry No. VO_2^+, 18252-79-4; EDDA, 5657-17-0; MIDA, 4408-64-4; NTA, 139-13-9.

References and Notes

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