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an instrument grant that aided in the purchase of the Bruker HX90 NMR spectrometer.

Registry No. $Rh(PPh_3)_3NO$, 21558-94-1; Rh(ttp)NO, 71411-11-5; Rh(etp)NO, 71411-12-6; Rh(eptp)NO, 71411-13-7; Rh(dppp)(PPh_3)NO, 71411-14-8; Rh(ppH)(PPh_3)NO, 71411-15-9; Rh(ppn)(PPh_3)NO, 71411-16-0; Rh(dmetp)NO, 71411-17-1; Rh(Cyttp)NO, 71411-18-2; Rh(dmdpe)(PPh_3)NO, 71434-85-0; Rh(dppb)(PPh_3)NO, 71411-19-3; Rh(PP_3)NO, 71411-20-6; Rh(P-P*)(PPh_3)NO, 71411-21-7; $[Rh(ttp)(NO)_2]BF_4$, 71411-23-9.

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Reaction of Hydrogen Peroxide with Metal Complexes. 4.[1] Kinetic Studies on the Peroxo Complex Formation of (Polyaminopolycarboxylato)dioxovanadate(V)

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The kinetics of the reactions of hydrogen peroxide with dioxovanadate(V) complexes of ethylenediamine-*N,N,N′,N′*-tetraacetate (EDTA), ethylenediamine-*N,N′*-diacetate (EDDA), and *N,N′*-dimethylethylenediamine-*N,N′*-diacetate (DMEDDA) have been studied spectrophotometrically at an ionic strength of 1.0 M ($NaClO_4$) in the pH range 3–6 between 15 and 35 °C. With a large excess of H_2O_2 over vanadium(V) complex concentration, a faster reaction followed by a slower one was observed. The rate laws for the fast reactions are $k_1^{DMEDDA}(1 + K_{as}^{DMEDDA}[H_2O_2])^{-1}[VO_2(dmedda)^-][H_2O_2][H^+]$, with $k_1^{DMEDDA} = (2.0 \pm 0.5) \times 10^3\ M^{-2}\ s^{-1}$ and $K_{as}^{DMEDDA} = 300 \pm 100\ M^{-1}$ at 25 °C, for the V(V)–DMEDDA system, and $(k_0^{EDDA} + k_1^{EDDA}[H^+])(1 + K_{as}^{EDDA}[H_2O_2])^{-1}[VO_2(edda)^-][H_2O_2]$, with $k_0^{EDDA} = 0.27 \pm 0.04\ M^{-1}\ s^{-1}$ ($\Delta H^* = 49 \pm 3$ kJ mol^{-1}, $\Delta S^* = -90 \pm 5$ J mol^{-1} K^{-1}), $k_1^{EDDA} = (2.8 \pm 0.3) \times 10^4\ M^{-2}\ s^{-1}$, and $K_{as}^{EDDA} = 20 \pm 10\ M^{-1}$ at 25 °C, for the V(V)–EDDA system. K_{as} refers to a formation constant of an associated complex between H_2O_2 and VO_2L. With an excess of V(V)–EDTA complex over $[H_2O_2]$, the rate law for the peroxo complex formation is $(k_1^{EDTA}[VO_2(edta)^{3-}] + k_2^{EDTA}[VO_2(Hedta)^{2-}])[H_2O_2][H^+]$, where $k_1^{EDTA} = (1.5 \pm 0.1) \times 10^6\ M^{-2}\ s^{-1}$ ($\Delta H^* = 47 \pm 4$ kJ mol^{-1}, $\Delta S^* = 29 \pm 8$ J mol^{-1} K^{-1}) and $k_2^{EDTA} = (4.6 \pm 0.8) \times 10^4\ M^{-2}\ s^{-1}$ ($\Delta H^* = 36 \pm 8$ kJ mol^{-1}, $\Delta S^* = -17 \pm 10$ J mol^{-1} K^{-1}) at 25 °C. This rate expression corresponds to one for the fast reaction with excess H_2O_2 conditions. An associative mechanism through a seven-coordinate transition state is most probably operative.

Introduction

Recently, it has been shown that vanadium, which is essential to mammalian life, may be present in muscle tissue at concentrations sufficient to inhibit the sodium and potassium stimulated adenosine triphosphate.[2] There is increasing evidence that vanadium has a significant biological role.[3–6] Kinetic studies of the formation of peroxovanadium(V) complexes in aqueous solution are scarce.[7,8] The main obstacle appears to be uncertainty regarding the precise nature of the vanadium(V) species present in solution. Previously we have reported kinetics of reaction of hydrogen peroxide and vanadium(V) complexes with monoaminopolycarboxylic acids,[9] such as PDA,[10] NTA,[10] and MIDA.[11] Our attention has been drawn to the reactions of hydrogen peroxide with the vanadium(V)–EDTA family[9] complexes, of which the conformation has been established. The X-ray data for $Na_3[VO_2(edta)]\cdot 4H_2O$[12] and $NH_4[VO_2(H_2edta)]\cdot 3H_2O$[13] have given evidence that two oxygen atoms of the VO_2 unit are in the cis configuration and a nitrogen atom of the coordinated EDTA is in a position trans to the oxo oxygen atom of VO_2 (α-cis in the terminology suggested by Garnett et al.[14]) and that all corresponding bond parameters in the coordination groups of these species are nearly identical. According to an NMR study in aqueous solution the EDTA and DMEDDA complexes form a single isomer (α-cis), while the EDDA complex forms both α-cis and β-cis isomers.[15]

The purpose of the present work is to examine differences in the reactivities of the vanadium(V)–EDTA family complexes for peroxo complex formation and to provide new information on the reaction mechanism. We have also determined the protonation constants of the vanadium(V)–EDTA and its peroxo complexes which are necessary to analyze kinetic results.

Experimental Section

Reagents. Solutions of sodium perchlorate and sodium hydroxide were prepared as described previously.[10] Perchloric acid of special

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(9) Ligand abbreviations: PDA, 2,6-pyridinedicarboxylic acid (H_2pda); NTA, nitrilotriacetic acid (H_3nta); MIDA, *N*-methyliminoacetic acid (H_2mida); EDTA, ethylenediamine-*N,N,N′,N′*-tetraacetic acid (H_4edta); EDDA, ethylenediamine-*N,N′*-diacetic acid (H_2edda); DMEDDA, *N,N′*-dimethylethylenediamine-*N,N′*-diacetic acid ($H_2dmedda$). Sometimes we use L for these ligands.

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(15) Amos, L. W.; Sawyer, D. T. *Inorg. Chem.* **1972**, *11*, 2692.

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purity (Wakojunyaku Co., Japan) was used without further purification.

Vanadium(V) Perchlorate. Reagent grade ammonium metavanadate was recrystallized twice from purified ammonia. Pure ammonium metavanadate was heated in a platinum plate to obtain vanadium(V) pentoxide. The vanadium(V) pentoxide dried at 600 °C for 3 h was dissolved in a perchloric acid solution to have a 10^{-2} M vanadium solution containing 0.1 M perchloric acid. The concentration of vanadium was checked titrimetrically with standard potassium permanganate.

EDTA and EDDA. EDTA and EDDA, purchased from Dojindo Laboratories (Kumamoto, Japan), were recrystallized from distilled water. Care was taken to use a fresh solution of EDDA because cyclization of the free ligand is known to occur.[16]

DMEDDA. DMEDDA was prepared by the method described previously.[17] We recrystallized the acid form of DMEDDA twice from aqueous methanol. The product was dried at 100 °C under reduced pressure. To check the purity we titrated DMEDDA in glacial acetic acid containing about 30% acetonitrile with a standard perchloric acid in acetic acid with Crystal Violet indicator.[18] The purity was again confirmed by NMR spectra and elemental analysis of C, H, and N.

Hydrogen Peroxide. A 60% hydrogen peroxide solution without added stabilizers (Mitsubishi Edogawa Kagaku Co., Japan) was purified by distillation under reduced pressure. A solution of hydrogen peroxide was titrated with standard permanganate.

Preparation of Complexes. V(V)–EDTA. The crystals were prepared according to the directions of Amos and Sawyer.[15] Analysis indicated that the complex was isolated as $Na_3[VO_2(edta)]\cdot 4H_2O$. Anal. Calcd for $Na_3VC_{10}H_{20}N_2O_{14}$: Na, 13.47; C, 23.44; H, 3.91; N, 5.47. Found: Na, 13.5; C, 23.5; H, 3.4; N, 5.5. Sodium was determined with a flame photometer (Evans Electroselenium Ltd., England).

Monoperoxo Complex of V(V)–EDTA. To a solution of 2.40 g (4.67 mmol) of $Na_3[VO_2(edta)]\cdot 4H_2O$ in 20 cm^3 of water was added gradually 2.3 cm^3 of 2.03 M H_2O_2 solution under vigorous stirring. The acidity of the solution was kept at about pH 5. The resulting mixture was stirred further for 3 h and filtered, and 95% ethanol was added dropwise until complete precipitation. The red powder collected on a filter was washed with 95% ethanol. The product was recrystallized from aqueous ethanol and dried at 65 °C under reduced pressure. Analysis indicated that the complex was isolated as $Na_3[VO(O_2)(edta)]\cdot 4H_2O$. Anal. Calcd for $Na_3VC_{10}H_{20}N_2O_{15}$: C, 22.75; H, 3.79; N, 5.30. Found: C, 23.4; H, 4.0; N, 4.3.

Measurements. All measurements were made in a thermostated room. Temperature of the reaction solution was controlled to within ±0.1 °C by using a thermoelectric circulating bath. Ionic strength was maintained at 1.00 M with sodium perchlorate and perchloric acid. Spectra were recorded on a highly sensitive spectrophotometer (Type SM401, Union Giken Co., Osaka, Japan) to characterize species spectrally.

Protonation constants of V(V)–EDTA and its peroxo complexes were determined potentiometrically by titrating about 10^{-2} M complex solutions prepared by dissolving $Na_3[VO_2(edta)]\cdot 4H_2O$ and $Na_3[VO(O_2)(edta)]\cdot 4H_2O$ in about 1.5 equivalent moles of perchloric acid solution with ca. 1 M sodium hydroxide solution using a piston buret (Metrohm, Switzerland).

Vanadium complex solutions for kinetic measurements were prepared by mixing a vanadium ion solution and a polyaminopolycarboxylic acid solution in excess. We used excess ligand with which vanadium ion forms vanadium(V) complexes quantitatively. Under our experimental conditions the vanadium(V) complexes are stable at least for 1 week and the corresponding peroxo complexes are stable at least for 1 month. The maximum wavelengths of the monoperoxo complexes are 420 nm (ϵ 280), 415 nm (ϵ 290), and 405 nm (ϵ 320) for EDTA, DMEDDA, and EDDA complexes, respectively.

Fast reactions were followed spectrophotometrically as a function of time at some wavelengths (mainly, the maximum wavelengths of the monoperoxo complexes) by stopped-flow spectrophotometers (Type RA401 and Type RA1100, Union Giken). Slower reactions were followed by recording visual spectra or absorbance at some wavelengths after starting the reaction by a sample mixing device (Type MX7, Union Giken).

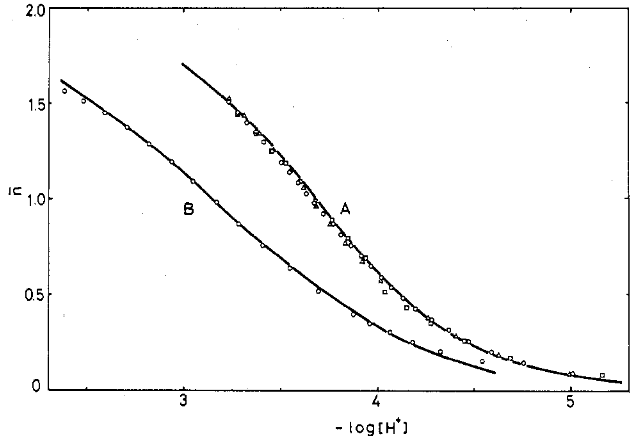

Figure 1. Plots of $\bar{n}$ against $-\log [H^+]$: (A) $VO_2(edta)^{3-}$ at 30 °C (□), 25 °C (○), 20 °C (△); (B) $VO(O_2)(edta)^{3-}$ at 25 °C. The solid curves were calculated with the obtained protonation constants.

Hydrogen ion concentration was determined by an Orion Research pH meter with a glass electrode (Type 91-01-00) and a reference electrode (Type 90-01) filled with a saturated sodium chloride solution. A 1.00 × 10^{-2} M perchloric acid at an ionic strength of 1.00 M ($Na,HClO_4$) was used as a standard solution.

Results

Protonation Equilibria of the V(V)–EDTA Complex and Its Monoperoxo Complex. The four available coordination sites of the VO_2^+ ion are occupied by two nitrogen and two acetate oxygen atoms of EDTA. The two other acetate groups of EDTA are not bonded to the metal and protons attach to the free acetate groups to form $VO_2(Hedta)^{2-}$ and $VO_2(H_2edta)^-$. The protonation of the V(V)–EDTA complex is expressed as

$$VO_2(edta)^{3-} + H^+ \rightleftharpoons VO_2(Hedta)^{2-} \qquad K_1 \qquad (1)$$

$$VO_2(Hedta)^{2-} + H^+ \rightleftharpoons VO_2(H_2edta)^- \qquad K_2 \qquad (2)$$

The plot of $\bar{n}$ (the average number of H^+ bound to V(V)–EDTA) vs. $-\log [H^+]$ is shown in Figure 1. The solid curve is calculated with the obtained constants: $\log K_1 = 3.91 \pm 0.05$, $\log K_2 = 3.45 \pm 0.05$ at 25 °C, and $I = 1.00$ M with $NaClO_4$. Data at 20 and 30 °C do not differ from the value at 25 °C within experimental error limits. Thermodynamic parameters were thus evaluated as $\Delta H_1 = 0 \pm 0.5$ kJ mol^{-1} and $\Delta S_1 = 75 \pm 1$ J mol^{-1} K^{-1} for K_1 and $\Delta H_2 = 0 \pm 0.5$ kJ mol^{-1} and $\Delta S_2 = 66 \pm 1$ J mol^{-1} K^{-1} for K_2.[19] Enthalpy values close to zero may be taken as evidence for the protonation at the free carboxylate.

The protonation of the monoperoxo complex of V(V)–EDTA is also expressed as

$$VO(O_2)(edta)^{3-} + H^+ \rightleftharpoons VO(O_2)(Hedta)^{2-} \qquad K_{1p} \qquad (3)$$

$$VO(O_2)(Hedta)^{2-} + H^+ \rightleftharpoons VO(O_2)(H_2edta)^- \qquad K_{2p} \qquad (4)$$

The plot of $\bar{n}$ (the average number of H^+ bound to the monoperoxo complex) against $-\log [H^+]$ is shown in Figure 1. The solid curve is calculated with obtained constants: $\log K_{1p} = 3.66 \pm 0.02$, $\log K_{2p} = 2.63 \pm 0.02$ at 25 °C, and $I = 1.0$ M with $NaClO_4$. The biacidic character of the monoperoxo complex suggests that the two acetate groups of coordinated

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(20) Przyborowski, L.; Schwarzenbach, G.; Zimmermann, Th. *Helv. Chim. Acta* **1965**, *48*, 1556.

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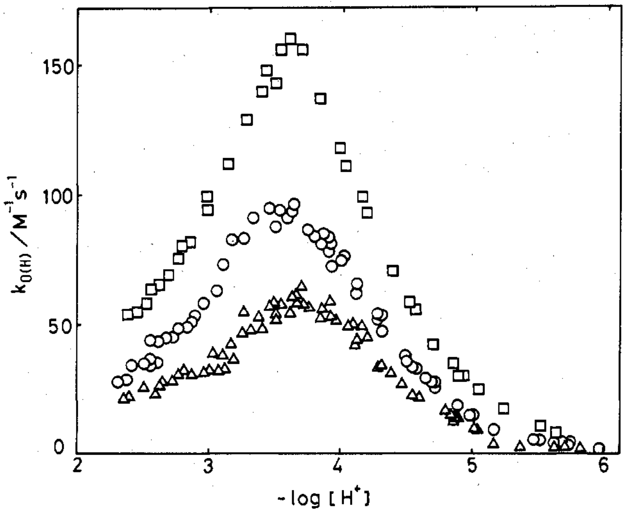

Figure 2. Hydrogen ion dependence of conditional second-order rate constants for reaction of the V(V)–EDTA complex with H_2O_2 at I = 1.0 M ($NaClO_4$) and at 35 °C (□), 25 °C (○), and 20 °C (△).

EDTA are not bonded to the metal and that the vanadium atom environment may be a seven-coordinate pentagonal bipyramid similar to the monoperoxo complex of V(V)–PDA.[22]

Reaction of V(V)–EDTA Complexes with H_2O_2. A distinct isosbestic point (356 nm) is observed in the absorption spectra of solutions resulting from the reaction of a constant concentration of V(V)–EDTA with various concentrations of H_2O_2 ($C_{H_2O_2}/C_{V(V)-EDTA}$ = 0–2). The mole ratio method clearly points to the composition of the peroxo complex: V(V)–EDTA:H_2O_2 = 1:1. The change of the visible absorption spectra with increasing the concentration of H_2O_2 substantially corresponds to the spectral change in the dynamic course of the formation of the peroxo complex by the reaction of V(V)–EDTA and H_2O_2. Furthermore, the spectrum of the peroxo complex formed by the reaction of the V(V)–EDTA complex with H_2O_2 in solution is the same as that of the solution of the authentic crystals $Na_3[VO(O_2)(edta)]\cdot 4H_2O$. The reaction system studied is thus expressed as

$$VO_2(edta)' + H_2O_2 \rightarrow VO(O_2)(edta)' + H_2O \quad (5)$$

where $VO_2(edta)'$ and $VO(O_2)(edta)'$ represent all species of the V(V)–EDTA and monoperoxo complex of V(V)–EDTA, respectively. Equilibrium 5 is much favored to the right under the present experimental conditions, so that the reverse reaction can be neglected in the kinetic study.

The reaction of the V(V)–EDTA complexes with H_2O_2 was followed in the presence of excess V(V)–EDTA ($\sim 5 \times 10^{-4}$ M) over H_2O_2. The rate of formation of the peroxo complex is proportional to the concentrations of the V(V)–EDTA complex and hydrogen peroxide. It is independent of the excess free EDTA concentration (up to 20 times over the complex), but it depends on the hydrogen ion concentration. This is summarized in the rate equation

$$\text{rate} = k_{0(H)}[VO_2(edta)'][H_2O_2] \quad (6)$$

where $[VO_2(edta)']$ represents the total concentration of the V(V)–EDTA complex, i.e., the sum of $[VO_2(edta)^{3-}]$, $[VO_2(Hedta)^{2-}]$, and $[VO_2(H_2edta)^{-}]$, and $k_{0(H)}$ is a conditional second-order rate constant involving hydrogen ion concentration. Values of $k_{0(H)}$ obtained at various hydrogen ion concentrations are plotted as a function of $-\log [H^+]$ in Figure 2. Taking into account that the V(V)–EDTA complex exists in various protonated forms, the reaction[23] appears to proceed as follows:

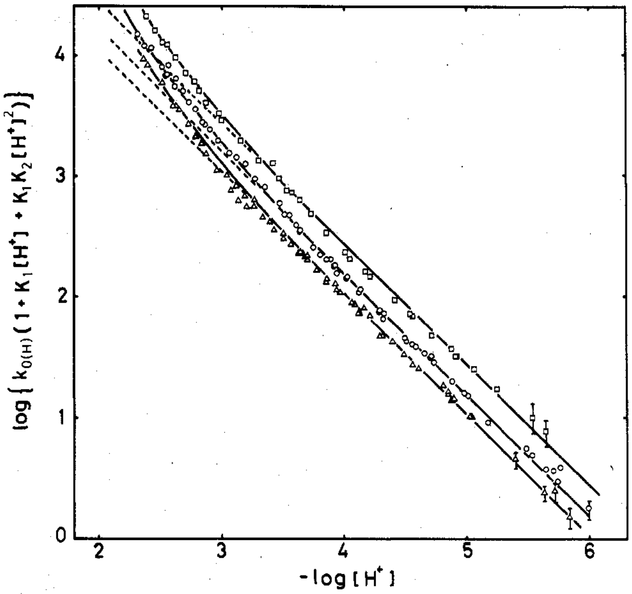

Figure 3. Plots of $\log \{k_{0(H)}(1 + K_1[H^+] + K_1K_2[H^+]^2)\}$ against $-\log [H^+]$: (□) 35 °C; (○) 25 °C; (△) 20 °C. The solid curves were calculated with the rate constants obtained.

$$\begin{array}{ccc} VO_2(edta)^{3-} + H_2O_2 & \xrightarrow{k_1'} & VO(O_2)(edta)^{3-} \\ H^+ \upharpoonleft\downharpoonright & & H^+ \upharpoonleft\downharpoonright \\ VO_2(Hedta)^{2-} + H_2O_2 & \xrightarrow{k_2'} & VO(O_2)(Hedta)^{2-} \\ H^+ \upharpoonleft\downharpoonright & & H^+ \upharpoonleft\downharpoonright \\ VO_2(H_2edta)^{-} + H_2O_2 & \xrightarrow{k_3'} & VO(O_2)(H_2edta)^{-} \end{array} \quad (7)$$

The protolytic reactions of the complex species are assumed to be very fast compared to the peroxo complex formation steps and can be considered always to be in equilibrium. Therefore the rate of formation of the peroxo complex is expressed as

$$d[VO(O_2)(edta)']/dt = \{k_1'[VO_2(edta)^{3-}] + k_2'[VO_2(Hedta)^{2-}] + k_3'[VO_2(H_2edta)^{-}]\}[H_2O_2] \quad (8)$$

and then the conditional second-order rate constant $k_{0(H)}$ is given as

$$k_{0(H)} = \frac{k_1' + k_2'K_1[H^+] + k_3'K_1K_2[H^+]^2}{1 + K_1[H^+] + K_1K_2[H^+]^2} \quad (9)$$

Plots of $\log \{k_{0(H)}(1 + K_1[H^+] + K_1K_2[H^+]^2)\}$ against $-\log [H^+]$ are shown in Figure 3. The plot indicates that the limiting slope tends to be −2 at higher acidity and −1 at lower acidity, and $k_{0(H)}$ to be the form

$$k_{0(H)}(1 + K_1[H^+] + K_1K_2[H^+]^2) = k_{1H}[H^+] + k_{2H}[H^+]^2 \quad (10)$$

where values of k_{1H} ($M^{-2}\ s^{-1}$) are 1.05×10^6 (20 °C), 1.51×10^6 (25 °C), and 2.75×10^6 (35 °C) ($\Delta H^{*} = 47 \pm 4$ kJ mol^{-1}, $\Delta S^{*} = 29 \pm 8$ J $mol^{-1}\ K^{-1}$) and those of k_{2H} ($M^{-3}\ s^{-1}$) are 2.6×10^8 (20 °C), 3.7×10^8 (25 °C), and 5.6×10^8 (35 °C) ($\Delta H^{*} = 36 \pm 8$ kJ mol^{-1}, $\Delta S^{*} = 38 \pm 10$ J $mol^{-1}\ K^{-1}$).

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[22] Drew, R. E.; Einstein, F. W. B. *Inorg. Chem.* **1973**, *12*, 829.

[23] According to equilibrium data[24] for H_2O_2: $[H^+][H_2O_2]/[H_3O_2^+] \simeq 10^3$, $[H^+][HO_2^-]/[H_2O_2] = 10^{-11.27}$, the reacting species under our experimental conditions is H_2O_2.

[24] Evans, M. G.; Uri, N. *Trans. Faraday Soc.* **1949**, *45*, 224.

Taking into account the catalytic contribution of hydrogen ion, we may expect the following reaction paths: $k_1[VO_2(edta)^{3-}][H_2O_2][H^+]$ and/or $k_2[VO_2(Hedta)^{2-}][H_2O_2]$ for a first-order hydrogen ion dependent path, k_{1H}, and $k_3[VO_2(edta)^{3-}][H_2O_2][H^+]^2$, $k_4[VO_2(Hedta)^{2-}][H_2O_2][H^+]$, $k_5[VO_2(H_2edta)^-][H_2O_2]$, or their combination for a second-order hydrogen ion dependent path, k_{2H}. Expected rate constants are as follows: $k_1 = 1.5 \times 10^6$ M^{-2} s^{-1}, $k_2 = 5.9 \times 10^2$ M^{-1} s^{-1}, $k_3 = 3.7 \times 10^8$ M^{-3} s^{-1}, $k_4 = 4.6 \times 10^4$ M^{-2} s^{-1}, and $k_5 = 1.6 \times 10^1$ M^{-1} s^{-1}. Since the reaction paths for k_1 and k_2, and also the paths for k_3, k_4, and k_5 are kinetically indistinguishable, at this time, we shall try to rationalize which of these appear to be more likely. Since we have no contribution of $VO_2(edta)^{3-}$ even at pH 6, the rate constant (k_0) for the path $k_0[VO_2(edta)^{3-}][H_2O_2]$ is estimated to be smaller than 0.1 M^{-1} s^{-1}. If we assign the k_2 path for the first-order $[H^+]$ dependence and the k_5 path for the second-order $[H^+]$ dependence, k_0 would be 2 to 3 orders of magnitude smaller than k_5 and k_2. Such a large difference seems unreasonable. It is therefore most likely that the first-order acid dependence is due to the catalytic proton contribution and not to the reaction pathway k_2. DMEDDA and EDDA systems having no such proton ambiguity also showed the catalytic proton contribution (vide infra). The second-order acid dependence may correspond to the reaction pathway k_4. Thus the rate law is expressed as

$$d[VO(O_2)(edta)']/dt = (k_1^{EDTA}[VO_2(edta)^{3-}] + k_2^{EDTA}[VO_2(Hedta)^{2-}])[H_2O_2][H^+] \quad (11)$$

where $k_1^{EDTA} = k_1 = (1.5 \pm 0.1) \times 10^6$ M^{-2} s^{-1} ($\Delta H^\ddagger = 47 \pm 4$ kJ mol^{-1}, $\Delta S^\ddagger = 29 \pm 8$ J mol^{-1} K^{-1}) and $k_2^{EDTA} = k_4 = (4.6 \pm 0.8) \times 10^4$ M^{-2} s^{-1} ($\Delta H^\ddagger = 36 \pm 8$ kJ mol^{-1}, $\Delta S^\ddagger = -17 \pm 10$ J mol^{-1} K^{-1}) at 25 °C and $I = 1.0$ M.

Rate of the $VO_2L + H_2O_2$ System (Large Excess H_2O_2). The reactions of V(V)–EDTA, V(V)–DMEDDA, and V(V)–EDDA complexes (VO_2L) with H_2O_2 were followed under pseudo-first-order conditions with at least 10-fold excess $[H_2O_2]$ over the total vanadium(V) complex concentration. In the presence of such a large excess of H_2O_2, we observe two successive reactions of which the rates depend on $[H^+]$ and $[H_2O_2]$. The absorbance at 390 nm increases at first, and it decreases subsequently. At the later stage the absorbance at 420 nm increases. The final spectra are the same as those of the solutions of the authentic monoperoxo complexes.

For EDDA and EDTA complexes, the first reaction is much faster than the subsequent reaction so that rate constants for respective reactions were determined independently. On the other hand, the kinetic data for DMEDDA were analyzed by a plot of log $\{(A_\infty - A_0)/(A_\infty - A_t)\}$ vs. t, where A_0 and A_t are the absorbances at respective times 0 and t and A_∞ is absorbance after the reaction is complete. The observed value of A_∞ was found to be in excellent agreement in all cases with the calculated value assuming complete conversion of the starting complex to the peroxo complex. The rate constant of the slower reaction, k_{II}, is given by the slope of the plot for the later stage of the reaction. This plot was extrapolated to zero time to obtain the absorbance of the product of the first reaction, $A_{I\infty}$. Then log $\{(A_{I\infty} - A_0)/(A_{I\infty} - A_t)\}$ is plotted against time. From the slope we obtain the negative of the first-stage rate constant $-k_I$. The k_I value thus obtained is in good agreement with that obtained from the absorption change of reaction at 392 nm, the isosbestic point for the second-stage reaction, and also that obtained from a initial-rate method.[25]

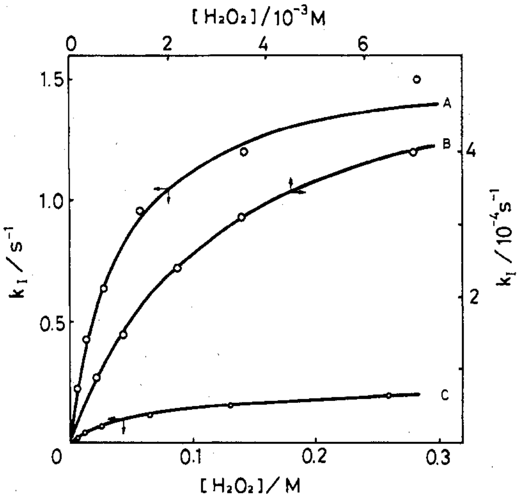

Figure 4. Conditional first-order constants (k_I) as a function of the total H_2O_2 concentration. With H_2O_2 in excess at 25 °C and I = 1.0 M ($NaClO_4$) the following conditions apply: (A) V(V)–EDTA system, $-\log [H^+] = 4.55$; (B) V(V)–DMEDDA system, $-\log [H^+] = 4.03$; (C) V(V)–EDDA system, $-\log [H^+] = 4.05$. The solid lines were calculated from eq 14 and the constants in Table I.

Plots of k_I vs. $[H_2O_2]$ at constant pH (Figure 4) indicate that the rate constants increase with increasing concentration of H_2O_2 up to a limiting value. Such a situation is accommodated in a rate equation of the form

$$\text{rate} = k_I[VO_2L] = \frac{b[H_2O_2]}{1 + a[H_2O_2]}[VO_2L] \quad (12)$$

In fact, plots of the reciprocal k_I vs. $[H_2O_2]^{-1}$ are linear as seen in Figure 5. Thus we may postulate mechanism I:[26]

$$VO_2L + H_2O_2 \overset{K_{as}}{\rightleftharpoons} VO_2L\cdots H_2O_2 \xrightarrow{k} \text{intermediate} \quad (13)$$

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(25) Wilkins, R. G. "The Study of Kinetics and Mechanism of Reactions of Transition Metal Complexes"; Allyn and Bacon: Boston, 1974; p 5. Almost all values of k_I for DMEDDA were obtained by a initial-rate method because the reaction is very slow under our experimental conditions.

(26) There are some mechanisms in which the rate behavior of the form of eq 12 may arise.[27] The rate law is consistent with mechanism II suggested by one of the reviewers

$$VO_2L \underset{k_{-1}}{\overset{k_1}{\rightleftharpoons}} VO_2L^*$$

$$VO_2L^* + H_2O_2 \xrightarrow{k_2} \text{intermediate}$$

in which VO_2L^* is a reactive species (probably a species with a coordination site open by dissociation of a carboxylate bond). In this mechanism, K_{as} and k in mechanism I in the text correspond to k_2/k_{-1} and k_1, respectively. We should expect large proton dependence of k_{-1} because the protonation of dissociated carboxylate groups may occur in our pH range 2.5–6. However actual values of K_{as} are almost constant over a wide pH range (see Table I). The thermodynamic parameters for the formation of the MIDA, NTA, and EDDA complexes of vanadium(V)[28] are useful in order to estimate thermodynamic parameters for preequilibrium of partial dissociation preceding the rate-determining step. We can deduce the ΔH and ΔS values per coordinated carboxylate which forms a chelate ring to be about 0 kJ mol^{-1} and 40–50 J mol^{-1} K^{-1}, respectively,[28] and this is usually the case for other metals.[29] In the V(V)–NTA and V(V)–EDDA systems, it is necessary to dissociate a carboxylate bond as shown as VO_2L^*. On the other hand, in the V(V)–MIDA and V(V)–PDA systems the reactions may proceed without such partial dissociation because MIDA and PDA are both tridentate. Thus in mechanism II $\Delta S^\ddagger$ values negatively larger by ca. 45 J mol^{-1} K^{-1} are expected for the NTA and EDDA systems than for the MIDA and PDA systems. However, the values of $\Delta S^\ddagger$ for a $k[VO_2L][H_2O_2]$ reaction are almost the same ($VO_2(mida)^-$, −79;[11] $VO_2(pda)^-$, −97;[10] $VO_2(pda)(OH)^{2-}$, −100;[10] $VO_2(nta)^{2-}$, −96;[10] $VO_2(edda)^-$, −90 J mol^{-1} K^{-1}). After all consideration, we rule out mechanism II.

(27) Reference 25, pp 25–31.

(28) Yamada, S.; Nagase, J.; Funahashi, S.; Tanaka, M. *J. Inorg. Nucl. Chem.* **1976**, *38*, 617.

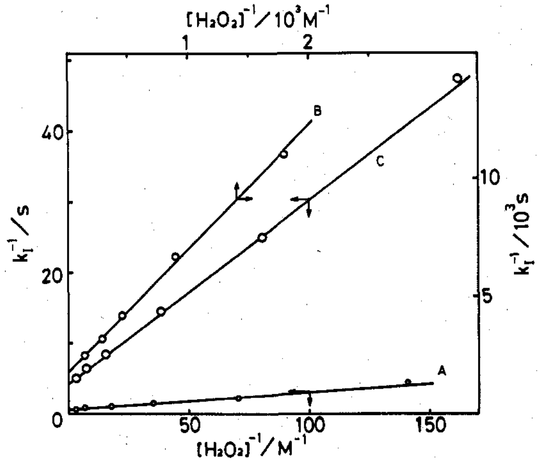

Figure 5. Plots of k_I^{-1} against $[H_2O_2]^{-1}$. The data correspond to those in Figure 4.

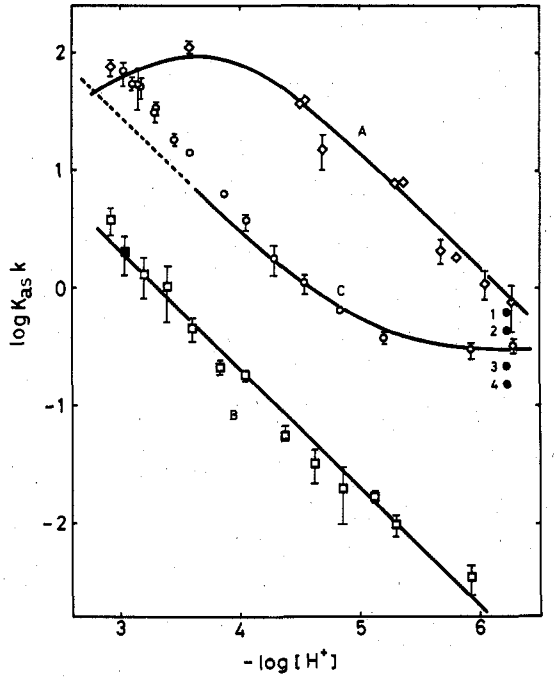

Figure 6. Hydrogen ion dependence of rate constants ($K_{as}k$) for reaction of the VO_2L complex with H_2O_2 in excess at 25 °C and I = 1.0 M ($NaClO_4$). (A) V(V)–EDTA system: The solid curve A was calculated with the rate constants obtained under conditions of excess complex. (B) V(V)–DMEDDA system: Dark square point is a rate constant obtained under excess complex conditions. (C) V(V)–EDDA system. At pH lower than 4 dissociation contributes to processes (see in text): 1 = 35 °C, 2 = 30 °C, 3 = 20 °C, 4 = 15 °C. The solid lines of B and C were calculated with the rate constants obtained.

Table I. Rate Constants ($K_{as}k$) for Reactions of V(V)–L Complexes with H_2O_2 at 25 °C and I = 1.00 M ($NaClO_4$)

$-\log [H^+]$ (±0.03)[a]	$K_{as}k/M^{-1}\ s^{-1}$	k/s^{-1}	K_{as}/M^{-1}
	V(V)–EDTA System[b]		
2.93 (6)[c]	76 ± 10	3.6	23
3.58 (6)	110 ± 10	4.8	24
4.50 (5)	36 ± 3	1.8	20
4.55[d] (6)	40 ± 5	1.6	24
4.69 (5)	15 ± 5	0.63	25
5.29 (5)	7.7 ± 0.8	0.3	25
5.36 (5)	7.9 ± 1	0.59	13
5.67 (6)	2.1 ± 0.5	0.15	14
5.80 (6)	1.8 ± 0.2	0.22	8
6.04 (5)	1.1 ± 0.3	0.07	17
6.26 (5)	0.77 ± 0.3	0.059	15
	V(V)–DMEDDA System[e]		
2.79 (5)	9 ± 1	–[f]	–
2.92 (6)	3.7 ± 1	–	–
3.20 (5)	1.3 ± 0.5	–	–
3.39 (5)	1 ± 0.5	–	–
3.60 (6)	0.45 ± 0.1	1.1×10^{-3}	4.1×10^{2}
3.83 (6)	0.21 ± 0.03	1.2×10^{-3}	1.8×10^{2}
4.03[d] (5)	0.19 ± 0.02	5.7×10^{-4}	3.3×10^{2}
4.37 (7)	$(5.5 \pm 1) \times 10^{-2}$	5.1×10^{-4}	1.1×10^{2}
4.62 (5)	$(3.2 \pm 1) \times 10^{-2}$	4.2×10^{-4}	0.8×10^{2}
4.85 (7)	$(2 \pm 1) \times 10^{-2}$	–	–
5.12 (5)	$(1.7 \pm 0.2) \times 10^{-2}$	1.4×10^{-4}	1.2×10^{2}
5.30 (5)	$(1 \pm 0.2) \times 10^{-2}$	1.2×10^{-4}	0.8×10^{2}
5.93 (5)	$(3.5 \pm 1) \times 10^{-3}$	–	–
	V(V)–EDDA System[g]		
3.03[h] (7)	68 ± 15	1.1	63
3.10[h] (7)	53 ± 7	0.95	55
3.15[h] (7)	52 ± 20	0.85	61
3.17[h] (7)	50 ± 10	0.66	78
3.29[h] (7)	30 ± 5	0.56	53
3.30[h] (7)	33 ± 4	0.64	51
3.45[h] (5)	18 ± 2	0.47	35
3.58[h] (7)	14 ± 1	0.38	35
3.86 (7)	6.3 ± 0.2	0.26	24
4.05[d] (6)	3.9 ± 0.5	0.23	17
4.28 (5)	1.8 ± 0.5	–	–
4.53 (7)	1.1 ± 0.2	–	–
4.82 (7)	0.65 ± 0.05	–	–
5.20 (6)	0.38 ± 0.05	–	–
5.92 (6)	0.30 ± 0.05	–	–
6.28 (6)	0.32 ± 0.05	–	–
6.22[i]			
15 °C (5)	0.16 ± 0.01	–	–
20 °C (5)	0.22 ± 0.02	–	–
30 °C (5)	0.44 ± 0.04	–	–
35 °C (5)	0.63 ± 0.05	–	–

[a] Deviation from an average value of several experimental points. [b] Experimental conditions: $C_V = 2.50 \times 10^{-4}$ M, $C_{EDTA} = 4.00 \times 10^{-4}$ M, $C_{H_2O_2} = 7.10 \times 10^{-3}$–$2.33 \times 10^{-1}$ M. [c] Figure in parentheses indicates the number of various H_2O_2 concentrations. [d] Data for this are given in Figure 4. [e] Experimental conditions: $C_V = 2.50 \times 10^{-4}$ M, $C_{DMEDDA} = 7.15 \times 10^{-3}$–$1.07 \times 10^{-2}$ M, $C_{H_2O_2} = 5.25 \times 10^{-4}$–$4.82 \times 10^{-2}$ M. [f] The intercept of such a plot of Figure 5 was too small to estimate k value. [g] Experimental conditions: $C_V = 2.50 \times 10^{-4}$ M, $C_{EDDA} = 5.66 \times 10^{-3}$–$8.34 \times 10^{-3}$ M, $C_{H_2O_2} = 5.77 \times 10^{-3}$–0.502 M. [h] There is some contribution of dissociation paths (see in text). [i] Experimental conditions: $C_V = 2.50 \times 10^{-4}$ M, $C_{EDDA} = 5.85 \times 10^{-3}$ M, $C_{H_2O_2} = 1.16 \times 10^{-2}$–2.32 M. At 15, 20, 30, and 35 °C. $\Delta H^{\ddagger} = 49 \pm 3$ kJ mol⁻¹, $\Delta S^{\ddagger} = -90 \pm 5$ J mol⁻¹ K⁻¹.

Setting K_{as} as formation constant of an associated complex $VO_2L \cdots H_2O_2$ between the complex and hydrogen peroxide, we have

$$k_I = \frac{K_{as}k[H_2O_2]}{1 + K_{as}[H_2O_2]} \qquad (14)$$

and $a = K_{as}$ and $b = K_{as}k$. k_I was independent of the excess ligand concentrations except for data at lower pH in the EDDA system (vide infra). We can determine values of K_{as} and k from the slope and intercept of straight lines in Figure 5. The results are given in Table I. Values of $K_{as}k$ were determined with an appreciable certainty from the slopes. Values of k and K_{as} obtained from plots with small intercept were not very accurate.

Logarithmic values of $K_{as}k$ for each reaction system are plotted against $-\log [H^+]$ in Figure 6. The solid curve for EDTA (Figure 6A) is a theoretical curve calculated with the equilibrium constants K_1 and K_2 and the rate constants ob-

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(29) Funahashi, S.; Tanaka, M. *Bull. Chem. Soc. Jpn.* **1976**, *49*, 2481.

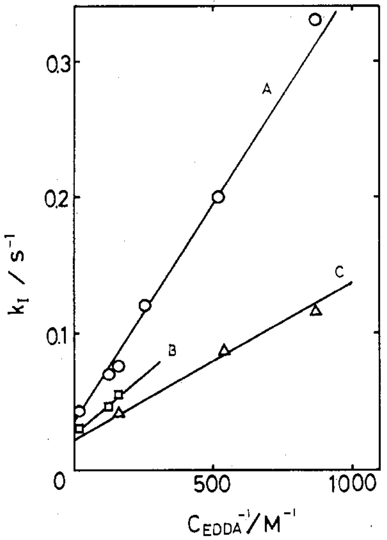

Figure 7. Ligand concentration dependence of conditional first-order rate constant (k_I) for reaction of the V(V)–EDDA complex with H_2O_2. Conditions: 25 °C; $I = 1.0$ M ($NaClO_4$); $C_V = 2.50 \times 10^{-4}$ M; $C_{H_2O_2} = 5.90 \times 10^{-3}$ M; $C_{EDDA} = 1.15 \times 10^{-3}$–$1.64 \times 10^{-2}$ M; $-\log [H^+] = 3.57 \pm 0.03$ (A), 3.67 ± 0.03 (B), 3.80 ± 0.03 (C).

tained with excess complex (vide supra). The plot for DMEDDA (Figure 6B) is reasonably linear, the relatively large uncertainty being taken into account. Thus we have

$$\text{rate} = \frac{k_1^{\text{DMEDDA}}}{1 + K_{\text{as}}^{\text{DMEDDA}}[H_2O_2]}[VO_2(\text{dmedda})^-][H_2O_2][H^+] \tag{15}$$

where $k_1^{\text{DMEDDA}} = (2.0 \pm 0.5) \times 10^3$ M^{-2} s^{-1} and $K_{\text{as}}^{\text{DMEDDA}} = 300 \pm 100$ M^{-1} at 25 °C and $I = 1.0$ M.

In the plot for EDDA (Figure 6C), the slope tends to be less than −1 at lower pH and 0 at higher pH. We confirmed the contribution of dissociation of V(V)–EDDA at pH lower than 4. Plots of k_I vs. the reciprocal C_{EDDA} are linear with intercepts, and both the slope and the intercept increase with increasing H^+ concentrations (Figure 7). This suggests the dissociation of the V(V)–EDDA complex. Under conditions with no contribution of such dissociation processes, the rate law is expressed as

$$\text{rate} = \frac{k_0^{\text{EDDA}} + k_1^{\text{EDDA}}[H^+]}{1 + K_{\text{as}}^{\text{EDDA}}[H_2O_2]}[VO_2(\text{edda})^-][H_2O_2] \tag{16}$$

where $k_0^{\text{EDDA}} = 0.27 \pm 0.04$ M^{-1} s^{-1} ($\Delta H^{\ddagger} = 49 \pm 3$ kJ mol^{-1} and $\Delta S^{\ddagger} = -90 \pm 5$ J mol^{-1} K^{-1}), $k_1^{\text{EDDA}} = (2.8 \pm 0.3) \times 10^4$ M^{-2} s^{-1}, and $K_{\text{as}}^{\text{EDDA}} = 20 \pm 10$ M^{-1} at 25 °C and $I = 1.0$ M.

Conditional first-order rate constant, k_{II}, for the final step exhibits an *inverse* $[H_2O_2]$ dependence. k_{II} tends to increase with increasing hydrogen ion concentration and it is slightly dependent on excess ligand concentrations. Some data for the V(V)–DMEDDA system are given in Table II. However we were unable to establish clear rate equations for the final step. We postulate the scheme

$$VO_2L(H_2O_2)_2' \overset{K'}{\rightleftharpoons} VO_2L(H_2O_2)' + H_2O_2 \tag{17}$$

$$VO_2L(H_2O_2)' \xrightarrow{k'} VO(O_2)L \tag{18}$$

where we do not know the conformation of $VO_2L(H_2O_2)_2'$ and $VO_2L(H_2O_2)'$. Then we have $k_{II} = k'K'^{-1}[H_2O_2]^{-1}$. We tentatively rationalized as follows: the rate-determining step may be the step (eq 18) that the monodentate 1:1 peroxo complex in equilibrium with the intermediate monodentate 1:2 peroxo complex (eq 17) transforms to the bidentate 1:1 peroxo complex. It should be reminded that at the first step the coordination of the first H_2O_2 molecule to the V(V)–L complex is rate determining and that subsequently a second H_2O_2 molecule coordinates rapidly to form an intermediate $VO_2L(H_2O_2)_2'$. Formation of such a monodentate 1:2 peroxovanadium(V) intermediate prior to the formation of a stable monoperoxo complex has been reported in a reaction of the V(V)–PDA complex with H_2O_2.[8]

Table II. Conditional First-Order Rate Constant k_{II} (25 °C, $I = 1.00$ M) for the Reaction of V(V)–DMEDDA with H_2O_2 under Various Conditions

$10^5 \times$ C_V/M	$10^3 \times$ C_{DMEDDA}/ M	$10^3 \times$ $C_{H_2O_2}$/ M	$-\log [H^+]$	$10^5 k_{II}$/ s^{-1}
9.32	5.95	2.26	3.20	23
		3.39		18
		4.52		11
		6.78		8.6
		9.04		6.2
25.0	6.30	5.90	2.72	19
			2.79	19
			2.98	16
			3.25	13
			3.79	13
			4.21	7.7
			4.49	6.2
			4.87	3.7
24.0	6.30	6.40	3.0 ± 0.1	16
	15.0			19
	18.3			28
	22.5			29

Discussion

The crystal structure of the peroxo complex of vanadium(V)–PDA has been determined to be a pentagonal-bipyramidal geometry: the vanadium atom environment is a seven-coordinate pentagonal bipyramid involving a peroxo group in the pentagon.[22] The spectrum of the solution obtained by dissolving the crystals of the peroxo complex of V(V)–PDA is the same as that of the 1:1 peroxo complex formed by the reaction of the V(V)–PDA complex with H_2O_2 in solution.[10] The spectra of the 1:1 peroxo complexes of EDTA, DMEDDA, and EDDA in aqueous solution are very similar to that of the 1:1 peroxo complex of V(V)–PDA. Thus the basic respective arrangement of the oxo, peroxo, and ligands (L) should be substantially the same as in the corresponding peroxo complex of V(V)–PDA for all the products in the present investigation.

According to the experimental evidence given above, the reaction of VO_2L with H_2O_2 is expressed as follows:

$$\begin{tikzcd}
\underset{\text{I}}{VO_2L + H_2O_2} \arrow[r, shift left, "K_{\text{as}}"] & \underset{\text{II}}{VO_2L\cdots H_2O_2} \arrow[l, shift left] \arrow[r, "k"] & {} \\
\underset{\text{III}}{VO_2L(H_2O_2)'} \arrow[r, shift left, "H_2O_2"] \arrow[d, "k'"] & \underset{\text{IV}}{VO_2L(H_2O_2)_2'} \arrow[l, shift left, "K'"] & \\
\underset{\text{V}}{VO(O_2)L} & &
\end{tikzcd}$$

The first stage of the reaction with a large excess of H_2O_2 corresponds to the process I → II → III → IV in which II → III is the rate-determining step. The second stage is the process IV → III → V. The reaction of excess V(V)–EDTA complex with low concentration of H_2O_2 corresponds to the process I → II → III → V with the rate-determining step II → III. As pointed out above, curve A in Figure 6 was drawn with the values of K_1, K_2, k_{1H}, and k_{2H}. This good fitting with experimental values of $K_{\text{as}}k$ over a wide pH range clearly indicates that $k_{0(H)}$ obtained with excess complex corresponds to $K_{\text{as}}k$ obtained with excess H_2O_2. Also in the case of the

DMEDDA complex, a second-order rate constant obtained with excess complex (filled square in Figure 6) is equivalent to $K_{as}k$ obtained with excess H_2O_2.

Although α-cis and β-cis isomers in the V(V)-EDDA complex exist 55 and 45% at 25 °C, respectively,[15] the difference between their reactivity was not observed in the present work. Thus the equilibrium between both isomers is established rapidly in comparison with peroxo complex formation, or there is no difference in reactivity of both isomers.

The formation constants (K_{as}) of associated complexes which are formed prior to the rate-determining steps are 25–10 M^{-1}, 300 ± 100 M^{-1}, and 20 ± 10 M^{-1} for vanadium(V) complexes of EDTA, DMEDDA, and EDDA, respectively, at 25 °C and $I = 1.0$ M. Such considerably large values of K_{as} should not be due to electrostatic interaction such as hydrogen bonding of an oxo oxygen of vanadium(V) complexes with hydrogen peroxide,[30] but they should be due to bonding with covalency. The value of K_{as} for each complex is almost constant at different pH's (see Table I). Thus the associated complex ($VO_2L\cdots H_2O_2$) is a seven-coordinate intermediate involving H_2O_2 weakly bonded as a monodentate at a face of the octahedron of VO_2L. K_{as} of the DMEDDA complex is 1 order of magnitude larger than that for the EDDA complex which is similar to that for the EDTA complex. This is attributable to the inductive effect of the methyl groups in the coordinated DMEDDA. Although the species of the V(V)–EDTA complex varies with H^+ concentrations, corresponding K_{as} values are almost the same (see Table I).

The rate-determining step (II → III) may be the rearrangement to the pentagonal-bipyramidal complex (III) from the associated complex (II) in which an entering ligand H_2O_2 coordinates weakly to the face of the octahedron (VO_2L). In the case of low concentration of H_2O_2, the formation of the monoperoxo complex (V) proceeds rapidly, while in the case of a large excess of H_2O_2 the fast addition of the second H_2O_2 to $VO_2L(H_2O_2)'$ occurs to give rise to the 1:2 complex $VO_2L(H_2O_2)_2'$. $VO_2L(H_2O_2)'$ in equilibrium with the latter is finally converted to the monoperoxo complex.

Since K_{as} is independent of proton concentration, proton dependence of second-order rate constants, $K_{as}k$, may be connected with the addition of a proton to an oxo group or an oxygen atom of coordinated carboxylates in the rate-determining step. The proton thus attached should facilitate the conversion to a pentagonal bipyramid.

If the loss of an oxo oxygen from the dioxovanadium(V) complex is the rate-determining step in the peroxo complex formation, the rate should be higher, the weaker the V=O bond. According to the IR data[15] the respective frequencies for the EDTA, DMEDDA, and EDDA complexes are 935, 895; 935, 900; and 905, 865 cm^{-1} for the two vibrational modes of $\nu_s(VO_2)$ and $\nu_{as}(VO_2)$, respectively.[31] The strength of the V=O bond of these complexes does not correspond to the reactivity of their complexes with H_2O_2. Thus the dissociation of oxo oxygen of the dioxovanadium(V) complex is not rate determining. An associative mechanism through a seven-coordinate transition state is most probably operative.[32] Large negative values of entropy of activation for the k_0^{EDDA} path and others (see Table IV of ref 10) may be taken as an indication of an associative mode of activation. For the proton-dependent paths the activation entropy is not very low probably because of the desolvation of proton in the formation of the activated complex. k_1^{EDTA} is 30 times larger than k_2^{EDTA}, despite the value of activation enthalpy for k_1^{EDTA} larger than that for k_2^{EDTA}. This fact points to a larger contribution of the entropy of activation due to the charge on the complexes.

Acknowledgment. We are grateful to the Ministry of Education of Japan for support of this work through Grant No. 347034.

Registry No. $Na_3[VO_2(edta)]$, 71818-67-2; $Na_3[VO(O_2)(edta)]$, 71818-68-3; $VO_2(dmedda)^-$, 38868-04-1; $VO_2(edda)^-$, 71869-70-0; H_2O_2, 7722-84-1.

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(30) We proposed the mechanism involving an outer-sphere complex in ref 10. One of the reviewers pointed out the impossibility of hydrogen bonding. With $K_{as} = 300$ M^{-1} for the DMEDDA complex, the outer-sphere complex involving hydrogen peroxide is proposed to be ~1.7 × 10^4-fold more stable than analogous species containing a water molecule in the outer sphere. Such a great tendency of H_2O_2 to form the outer-sphere complex as compared with H_2O is unreasonable.

(31) Infrared bands of $Na_3[VO_2(edta)]\cdot 4H_2O$ in Nujol mull between sodium chloride disks on a Jasco Model A-3 infrared spectrometer are 930 and 905 cm^{-1} for ν_s and ν_{as}, respectively.

(32) Recently we have measured the activation volume for the peroxo complex formation of (nitrilotriacetato)dioxovanadate(V) with H_2O_2 by means of a high-pressure stopped-flow technique.[33] We obtained the negative activation volume which is consistent with the proposed mechanism.

(33) Funahashi, S.; Ishihara, K.; Tanaka, M. *Inorg. Chim. Acta* **1979**, *35*, L351.