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Reactions of Hydrogen Peroxide with Metal Complexes. 2. Kinetic Studies on the Peroxo Complex Formation of Nitrilotriacetatodioxovanadate(V) and Dioxo(2,6-pyridinedicarboxylato)vanadate(V)

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Received November 4, 1976

AIC60797C

The kinetics of the reactions of hydrogen peroxide with nitrilotriacetatodioxovanadate(V) (V^VNTA, $VO_2(nta)^{2-}$) and dioxo(2,6-pyridinedicarboxylato)vanadate(V) (V^VPDA, $VO_2(pda)(H_2O)^-$) have been studied spectrophotometrically using a stopped-flow technique at an ionic strength of 1.0 mol dm^{-3} ($NaClO_4$) in the pH range 1.5–5 between 15 and 35 °C. The rate of the peroxo complex formation of V^VNTA is expressed as $d[VO(O_2)(nta)^{2-}]/dt = (k_1 + k_2[H^+])[VO_2(nta)^{2-}][H_2O_2]$ where $k_1 = 7.41$ mol^{-1} dm^3 s^{-1} ($\Delta H^{\ddagger} = 39 \pm 1$ kJ mol^{-1}, $\Delta S^{\ddagger} = -96 \pm 9$ J K^{-1} mol^{-1}) and $k_2 = 1.86 \times 10^4$ mol^{-2} dm^6 s^{-1} ($\Delta H^{\ddagger} = 39 \pm 1$ kJ mol^{-1}, $\Delta S^{\ddagger} = -33 \pm 9$ J K^{-1} mol^{-1}). The rate of the peroxo complex formation of V^VPDA is as follows: $d[VO(O_2)(pda)(H_2O)^-]/dt = \{k_1[H^+][VO_2(pda)(H_2O)^-] + k_2[VO_2(pda)(H_2O)^-] + k_3[VO_2(pda)(OH)^{2-}]\}[H_2O_2]$ where $k_1 = 4.1 \times 10^2$ mol^{-2} dm^6 s^{-1} ($\Delta H^{\ddagger} = 24 \pm 1.5$ kJ mol^{-1}, $\Delta S^{\ddagger} = -114 \pm 9$ J K^{-1} mol^{-1}), $k_2 = 0.39$ mol^{-1} dm^3 s^{-1} ($\Delta H^{\ddagger} = 46 \pm 2$ kJ mol^{-1}, $\Delta S^{\ddagger} = -97 \pm 9$ J K^{-1} mol^{-1}), and $k_3 = 28$ mol^{-1} dm^3 s^{-1} ($\Delta H^{\ddagger} = 35 \pm 2$ kJ mol^{-1}, $\Delta S^{\ddagger} = -100 \pm 9$ J K^{-1} mol^{-1}). Mechanisms are proposed for the H_2O_2 insertion reaction and in terms of activation parameters some discussions are made on the difference in the reactivities of these complexes. We have studied the protonation equilibria of PDA where $\log K_1 = 4.62 \pm 0.02$ ($\Delta H_1 = -27 \pm 4$ kJ mol^{-1}, $\Delta S_1 = -2 \pm 10$ J K^{-1} mol^{-1}), $\log K_2 = 2.18 \pm 0.02$, and $\log K_3 = 0.49 \pm 0.02$, the complexation equilibrium of the V^V–PDA complex where $[VO_2(pda)(H_2O)^-]/[VO_2^+][pda^{2-}] = 10^{8.65\pm0.10}$, and the hydrolysis of the V^V–PDA complex where $[VO_2(pda)(OH)^{2-}][H^+]/[VO_2(pda)(H_2O)^-] = 10^{-5.87\pm0.02}$ ($\Delta H = 7 \pm 7$ kJ mol^{-1}, $\Delta S = -78 \pm 20$ J K^{-1} mol^{-1}).

Introduction

Reactions of hydrogen peroxide with various chemical species have been extensively studied.[2,3] From the chemical point of view, the redox reaction of H_2O_2 has been the subject matter of many investigations. Especially because of its biochemical significance, there has been a good deal of interest in kinetic studies on formation, decomposition, and substrate reactions of peroxo compounds of biologically important metal complexes such as catalase and peroxidase.[4-8] However, relatively little attention has been drawn to the processes of coordination of hydrogen peroxide to metal complexes preceding the decompositions of hydrogen peroxide.[9,10] There is increasing evidence that vanadium has a significant biological role,[11,12] although it has been established to be an essential element only for a few organisms.[13,14]

The kinetics of formation of the pentavalent vanadium complex has been little investigated. Recently the kinetics of formation of vanadium(V) complexes with aminopolycarboxylate ions have been reported.[15] Since some data are available on the kinetics of vanadium(V) reactions, we attempt to compare the water-exchange rate with hydrogen peroxide insertion rates for vanadium(V).

The purpose of the present work is to examine differences in the reactivities of some vanadium(V) complexes for peroxo complex formation,[16] to determine the energetics of the reaction, and to provide new information on the reaction mechanism. In this paper we describe the results on the reactions

$$V^VNTA + H_2O_2 \rightleftharpoons V^V(NTA)H_2O_2 \qquad (1)$$

$$V^VPDA + H_2O_2 \rightleftharpoons V^V(PDA)H_2O_2 \qquad (2)$$

where NTA and PDA refer to nitrilotriacetic acid (H_3nta) and 2,6-pyridinedicarboxylic acid (H_2pda).

As the data on the equilibrium between vanadium(V) ion and 2,6-pyridinedicarboxylic acid were not available, we have studied the protonation equilibria of PDA and the complexation equilibria of the V^V–PDA complex. We have also determined the thermodynamic parameters for hydrolysis of the V^V–PDA complex which are necessary to analyze kinetic results.

Experimental Section

Reagents. Sodium Perchlorate. Reagent grade sodium perchlorate was prepared by neutralizing 60% perchloric acid with reagent grade anhydrous sodium carbonate. Heavy-metal impurities in the sodium perchlorate solution were precipitated together with active carbon as hydroxides at pH 8.5. After evaporation of the solution crystals of sodium perchlorate were obtained by cooling the solution. Sodium perchlorate was then crystallized twice from distilled water.

Sodium Hydroxide. Sodium hydroxide solution was prepared by electrolysis of the solution of pure sodium perchlorate obtained as described above.

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 a standard permanganate.

Vanadium(V) Perchlorate. Reagent grade ammonium metavanadate was recrystallized twice from purified ammonia water. Pure ammonium metavanadate was dissolved in sodium hydroxide solution and transformed to vanadate ion. Ammonia was expelled by bubbling the solution with nitrogen gas. Vanadium(V) perchlorate solution (ca. 10^{-2} mol dm^{-3}) was prepared by addition of perchloric acid. Vanadium(V) was reduced by sulfur dioxide and the resulting vanadium(IV) was standardized titrimetrically against a standard potassium permanganate.

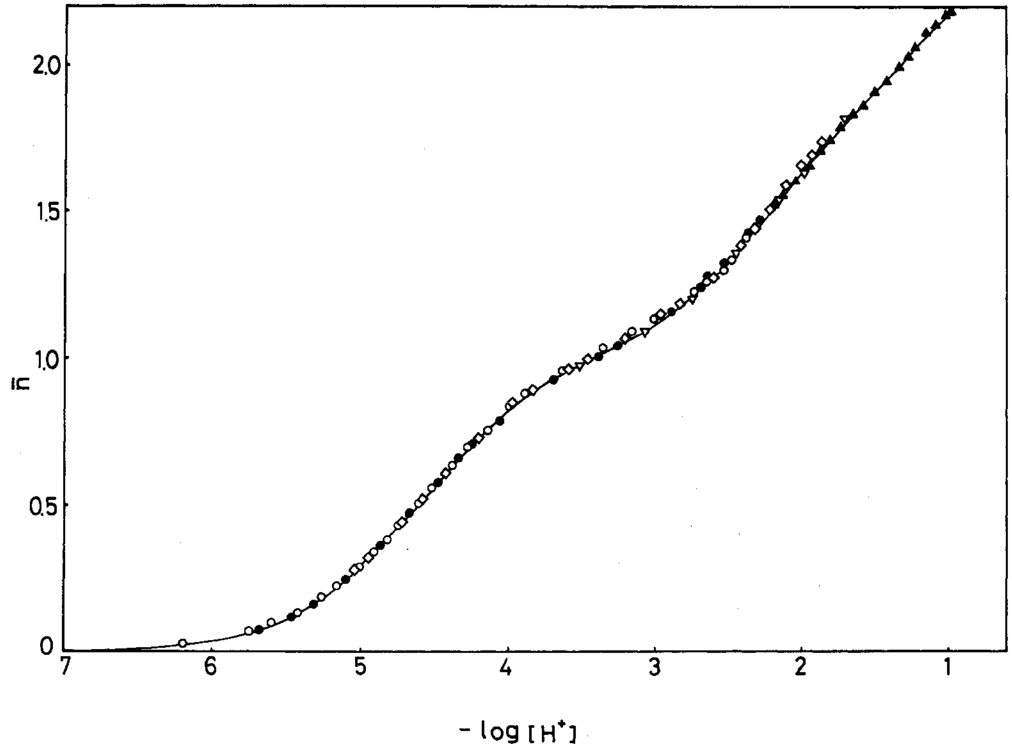


Figure 1. Determination of the protonation constants of PDA at 25 °C and $I = 1.0$ mol dm^{-3} (Na,H)ClO$_4$. Initial concentration of PDA (in mol dm^{-3}): ◊, 6.37×10^{-3}; ○, 9.10×10^{-3}; ●, 9.18×10^{-3}; ▽, 1.01×10^{-2}; ▲, 1.14×10^{-2}. The solid curve is calculated with the constants listed in Table I.

NTA and PDA. Nitrilotriacetic acid (NTA) and 2,6-pyridinedicarboxylic acid (PDA), purchased from Dojindo Laboratories, were recrystallized twice from distilled water.

Measurements. All measurements were made in a thermostated room. Temperatures were controlled to within ±0.1 °C using a thermoelectric circulating bath. Ionic strength was maintained at 1.0 mol dm^{-3} with sodium perchlorate and perchloric acid. Spectrophotometric measurements were carried out with a Hitachi recording spectrophotometer, Type 323, to characterize species spectrally.

Hydrogen ion concentration was determined by an Orion Research pH meter with a glass electrode, Type 91-01, and a reference electrode, Type 90-01, filled with a saturated sodium chloride solution. A 1.000×10^{-2} mol dm^{-3} perchloric acid at an ionic strength of 1.00 mol dm^{-3} was used as a standard solution. The liquid-junction potential was taken into consideration.

The reaction was followed spectrophotometrically at 432 nm by means of a stopped-flow technique using a rapid-scan spectrophotometer, Type RSP-2 (Hitachi, Ltd., Tokyo), for the V^V–NTA complex; for the V^V–PDA complex, the reaction was followed at 434 nm by a conventional method using a Hitachi Perkin-Elmer 139 UV–VIS spectrophotometer with a thermostated cell compartment. Runs performed at some other wavelengths gave consistent results. Although no buffer was used, the change of pH was negligible due to the buffer capacity of excess NTA or PDA. The kinetic runs were carried out under pseudo-first-order conditions, hydrogen peroxide being in large excess over vanadium(V) complexes.

Stability of Reagents. The decomposition of H_2O_2 is known to be catalyzed heterogeneously by the surface of a container and homogeneously by many transition metal and heavy-metal ions even at very low concentrations. In our case, a spontaneous decomposition of ca. 10^{-2} mol dm^{-3} hydrogen peroxide at room temperature was less than 1% for 1 month. Vanadium(V) can be reduced in an acid medium only on heating in the presence of excess ligands (NTA, PDA). Concentrated hydrogen peroxide (30%) oxidizes the ligands, and the oxidation is complete on boiling. However the V^V–PDA and –NTA complexes are stable at least for 1 week and the corresponding peroxo complexes are stable at least for 1 month under the present experimental conditions.

Results

Table I. Protonation Constants of PDA

$\log K_1$	$\log K_2$	$\log K_3$	Medium	Temp/ °C	Ref
4.68	2.10		0.1 M $NaNO_3$	20	*a*
4.67	2.24		0.10 M KCl	25	*b*
4.532	2.092		0.5 M $NaClO_4$	25	*c*
4.62 ± 0.02	2.18 ± 0.02	0.49 ± 0.02	1.0 M $NaClO_4$	25	*d*
4.72 ± 0.02[f]			1.0 M $NaClO_4$	17	*e*
4.60 ± 0.02[f]			1.0 M $NaClO_4$	25	*e*
4.44 ± 0.02[f]			1.0 M $NaClO_4$	35	*e*

[a] G. Anderegg, *Helv. Chim. Acta*, 43, 414 (1960). [b] W. E. Bennett and D. O. Skovlin, *J. Inorg. Nucl. Chem.*, 28, 591 (1966). [c] A. Napoli, *Talanta*, 15, 189 (1968). [d] This work by potentiometry. [e] This work by spectrophotometry. [f] $\Delta H_1 = -27 \pm 4$ kJ mol^{-1}; $\Delta S_1 = -2 \pm 10$ J K^{-1} mol^{-1}.

Protonation Equilibria of PDA. The protonation constants of PDA were determined potentiometrically. The protonation of PDA is expressed as

$$\mathrm{pda}^{2-} + \mathrm{H}^+ \rightleftharpoons \mathrm{Hpda}^- \quad K_1$$

$$\mathrm{Hpda}^- + \mathrm{H}^+ \rightleftharpoons \mathrm{H_2pda} \quad K_2$$

$$\mathrm{H_2pda} + \mathrm{H}^+ \rightleftharpoons \mathrm{H_3pda}^+ \quad K_3$$

The average number of H^+ bound to pda^{2-}, $\bar{n}$, is given by the expression

$$\bar{n} = \frac{K_1[\mathrm{H}^+] + 2K_1K_2[\mathrm{H}^+]^2 + 3K_1K_2K_3[\mathrm{H}^+]^3}{1 + K_1[\mathrm{H}^+] + K_1K_2[\mathrm{H}^+]^2 + K_1K_2K_3[\mathrm{H}^+]^3}$$

The plot of $\bar{n}$ vs. $-\log[H^+]$ is shown in Figure 1. The protonation constants obtained are summarized in Table I, together with those previously reported. It should be noted that under our experimental conditions considerable amounts of cationic protonated species (H_3pda^+) are present in solution.

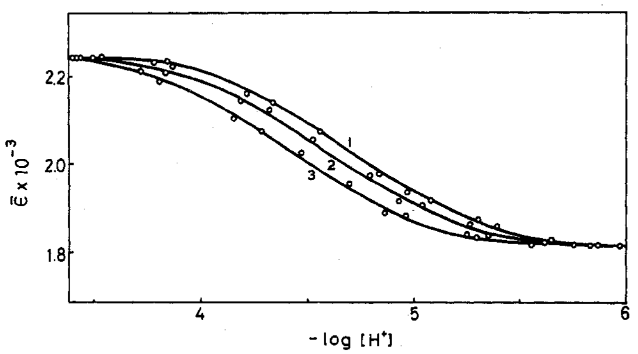


Figure 2. Apparent molar extinction coefficient $\bar{\varepsilon}$ of PDA at 245 nm as a function of $-\log [H^+]$ at $I = 1.0$ mol dm^{-3} ($NaClO_4$). $C_{PDA} = 2.05 \times 10^{-4}$ mol dm^{-3}. Temperature: 1, 17 °C; 2, 25 °C; 3, 35 °C. The solid curves are calculated with the obtained constants.

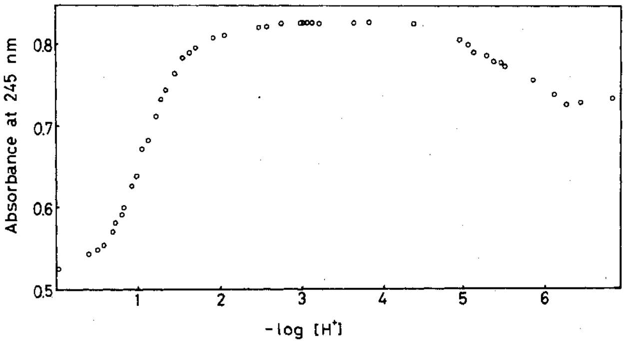


Figure 3. Absorbance of the system at 245 nm as a function of $-\log [H^+]$. $C_V = 1.51 \times 10^{-4}$ mol dm^{-3}, $C_{PDA} = 2.05 \times 10^{-4}$ mol dm^{-3}, $I = 1.0$ mol dm^{-3} ($NaClO_4$), 25 °C.

In addition, values for K_1 of PDA at 17, 25, and 35 °C were determined spectrophotometrically. The absorbance change of PDA as a function of $-\log [H^+]$ (Figure 2) will be used later for estimating the hydrolysis of the V^V–PDA complex.

Complexation Equilibrium of the V^V–PDA Complex. With knowledge of the protonation constants of PDA we have studied spectrophotometrically the complexation equilibria of the vanadium(V) ion with PDA. Absorbance change of the system at 245 nm as a function of $-\log [H^+]$ is shown in Figure 3. The sharp absorbance change near $-\log [H^+] = 1$ is attributable to the equilibrium

$$VO_2^+ + pda' \rightleftharpoons VO_2(H_{3-n}pda)^{(2-n)+} + nH^+ \tag{3}$$

The formation constant of the V^V–PDA complex is given as

$$\frac{[VO_2(H_{3-n}pda)^{(2-n)+}][H^+]^n}{[VO_2^+][pda']} = \frac{K_{VO_2(pda)}}{\alpha_{H_3pda(H)}}$$

where [pda′] refers to the total concentration of PDA not combined with vanadium and $\alpha_{H_3pda(H)}$ is the side reaction coefficient taking into account the proton dissociation of H_3pda^+: $[pda'] = \alpha_{H_3pda(H)}[H_3pda^+]$. The plot of the value of $\log [VO_2(H_{3-n}pda)^{(2-n)+}]\alpha_{H_3pda(H)}/[VO_2^+][pda']$ vs. $-\log [H^+]$ yields a straight line with a slope of 3 over the range of $-\log [H^+]$ from 0.5 to 2.0. Therefore we have $[VO_2(pda)^-][H^+]^3/[VO_2^+][H_3pda^+] = 10^{1.36}$ and then $K_{VO_2(pda)} = [VO_2(pda)^-]/[VO_2^+][pda^{2-}] = 10^{8.65 \pm 0.10}$.

Hydrolysis of the V^V–PDA Complex. The absorbance change near $-\log [H^+] = 5.5$ in Figure 3 is attributable to the hydrolysis reaction of the V^V–PDA complex

$$VO_2(pda)(H_2O)^- \rightleftharpoons VO_2(pda)(OH)^{2-} + H^+ \quad K^{-H}{}_{VO_2(pda)(OH)} \tag{4}$$

The absorbance change due to eq 4 is shown in Figure 4, where the absorbance change of excess PDA is corrected for (see Figure 2). Hydrolysis constants and thermodynamic parameters are as follows: $10^{-5.91\pm0.03}$ (17 °C), $10^{-5.87\pm0.03}$ (25 °C), $10^{-5.82\pm0.03}$ (35 °C), $\Delta H = 7 \pm 7$ kJ mol^{-1}, and $\Delta S = -78 \pm 20$ J K^{-1} mol^{-1}. At higher pH, the V^V–PDA complex dissociates giving rise to vanadate (HVO_4^{2-}) and free PDA ions;[17] this tendency is shown with a dotted line in Figure 4.

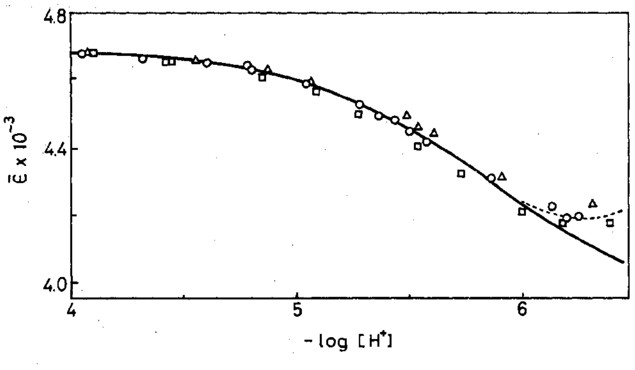


Figure 4. Apparent molar extinction coefficient $\bar{\varepsilon}$ of the V^V–PDA complex at 245 nm as a function of $-\log [H^+]$ at $I = 1.0$ mol dm^{-3} ($NaClO_4$). Temperature: △, 17 °C; ○, 25 °C; □, 35 °C.

Equilibria of Peroxo Complexes. We prepared ammonium oxoperoxo(2,6-pyridinedicarboxylato)vanadate(V) hydrate, $NH_4[VO(O_2)(H_2O)(C_5H_3N(COO)_2)]\cdot xH_2O$, by the method first reported by Hartkamp.[18] This was dried at 80 °C for 4 h under reduced pressure. Anal. Calcd for $NH_4[VO(O_2)(H_2O)(C_5H_3N(COO)_2)]$: C, 28.01; H, 3.02; N, 9.33. Found: C, 27.75; H, 3.06; N, 8.93; dec pt ca. 240 °C. The crystal structure of the peroxo complex was shown to be a distorted pentagonal-pyramidal geometry:[19] the vanadium atom environment is a seven-coordinate distorted pentagonal bipyramid, with a vanadyl oxygen and a water molecule at the apices and a peroxo group, the nitrogen from the pyridine ring, and one oxygen atom from each carboxylate group forming an approximate pentagonal plane. The spectrum of the solution obtained by dissolving the crystals of the peroxo complex is the same as that of the peroxo complex formed by the reaction of the V^V–PDA complex with H_2O_2 in solution.

A distinct isosbestic point is observed in the absorption spectra of solutions resulting from the reaction of $VO_2(nta)^{2-}$ with various concentrations of H_2O_2. The mole ratio method clearly points to the composition of the peroxo complex: vanadium(V):NTA:H_2O_2 = 1:1:1. The change of the absorption spectra substantially corresponds to the spectral change in the dynamic course of the formation of the peroxo complex. This is the case for the reaction of $VO_2(pda)^-$ with H_2O_2. Wavelengths of the absorption maximum and molar absorption coefficients at the same wavelength for the peroxovanadium(V) complexes are 434 nm and 491 for PDA, 432 nm and 352 for NTA, and 425 nm and 359 for MIDA.

Kinetics of the Peroxo Complex Formation of V^VNTA. The reaction system studied is

$$VO_2(nta)^{2-} + H_2O_2 \rightleftharpoons VO(O_2)(nta)^{2-} + H_2O \tag{5}$$

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 rate of formation of the peroxo complex is first order with respect to the V^V–NTA complex under pseudo-first-order conditions in the presence of a large excess of H_2O_2. Thus we have

$$d[VO(O_2)(nta)^{2-}]/dt = k_{0(H_2O_2,H)}[VO_2(nta)^{2-}] \tag{6}$$

where $k_{0(H_2O_2,H)}$ is a conditional first-order rate constant which depends on the concentrations of H_2O_2 and H^+. Over the

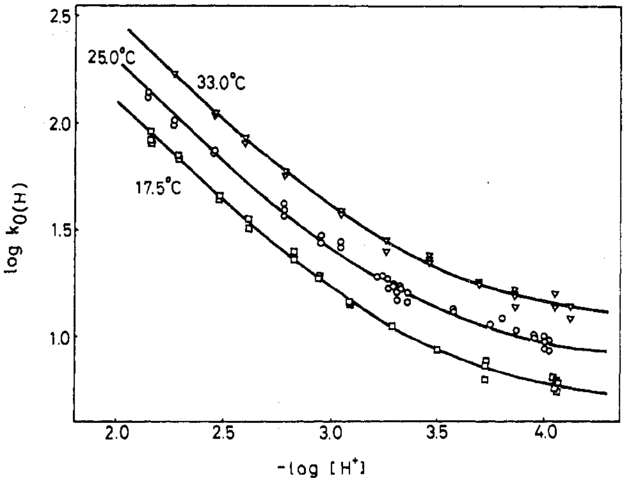


Figure 5. Plot of log $k_{0(H)}$ vs. –log [H^+]. $C_V = 2 \times 10^{-4}$–6×10^{-4} mol dm^{-3}, $C_{NTA} = 4 \times 10^{-4}$–$1.5 \times 10^{-3}$ mol dm^{-3}, $C_{H_2O_2} = 1 \times 10^{-3}$–$2.5 \times 10^{-2}$ mol dm^{-3}, $I = 1.0$ mol dm^{-3} ($NaClO_4$). The solid curves are calculated with the rate constants listed in Table II.

Table II. Rate Constants and Activation Parameters for Peroxo Complex Formation of V^VNTA

Temp/°C	k_1/mol^{-1} dm^3 s^{-1}	k_2/mol^{-2} dm^6 s^{-1}
17.5	4.79	1.20×10^4
25.0	7.41	1.86×10^4
33.0	11.5	2.88×10^4
$\Delta H^‡$/kJ mol^{-1}	39 ± 1	39 ± 1
$\Delta S^‡$/J K^{-1} mol^{-1}	−96 ± 9	−33 ± 9

range of [H_2O_2] from 10^{-3} to 1.5×10^{-2} mol dm^{-3} the reaction is exactly first order in [H_2O_2] at a fixed acidity; $k_{0(H_2O_2,H)} = k_{0(H)}[H_2O_2]$. $k_{0(H)}$ is found dependent on the concentration of hydrogen ion and independent of the excess NTA concentration. A plot of log $k_{0(H)}$ vs. –log [H^+] (Figure 5) indicates that the limiting slope tends to be –1 at higher acidity and 0 at lower acidity. This dependence can be accounted for by the rate equation

$$d[VO(O_2)(nta)^{2-}]/dt = (k_1 + + k_2[H^+])[VO_2(nta)^{2-}][H_2O_2] \qquad (7)$$

The rate constants at various temperatures and activation parameters are summarized in Table II.

Kinetics of the Peroxo Complex Formation of V^VPDA. The reaction appears to proceed as

$$\begin{array}{l} VO_2(pda)(H_2O)^- + H_2O_2 \searrow \\ -H^+ \Updownarrow \qquad\qquad VO(O_2)(pda)(H_2O)^- \qquad (8) \\ VO_2(pda)(OH)^{2-} + H_2O_2 \nearrow \end{array}$$

The rate is proportional to the concentrations of the V^V–PDA complex and hydrogen peroxide. It is also dependent on the hydrogen ion concentration, but independent of the excess PDA concentration. This is summarized in the rate law

$$d[VO(O_2)(pda)(H_2O)^-]/dt = k_{0(H)}[V^V\text{-}PDA][H_2O_2] \qquad (9)$$

where [V^V–PDA] is the total concentration of the V^V–PDA complex, i.e., the sum of [$VO_2(pda)(H_2O)^-$] and [$VO_2(pda)(OH)^{2-}$]. Conditional second-order rate constants $k_{0(H)}$ obtained at various hydrogen ion concentrations are plotted as a function of hydrogen ion concentration in Figure 6.

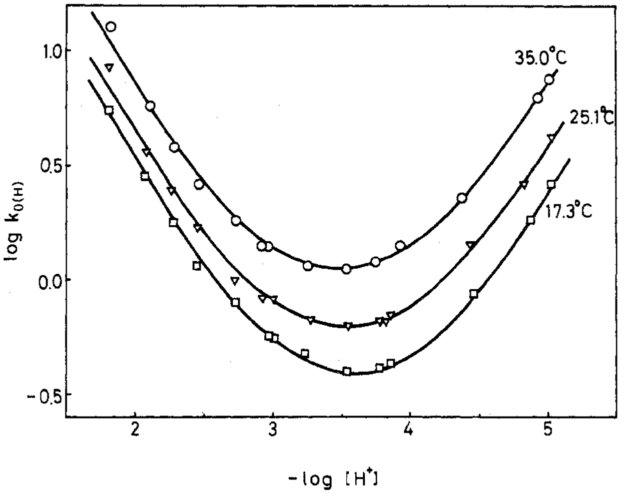


Figure 6. Plot of log $k_{0(H)}$ vs. –log [H^+]. $C_V = 2 \times 10^{-4}$–6×10^{-4} mol dm^{-3}, $C_{PDA} = 2 \times 10^{-4}$–$8 \times 10^{-4}$ mol dm^{-3}, $C_{H_2O_2} = 6 \times 10^{-4}$–$2 \times 10^{-2}$ mol dm^{-3}, $I = 1.0$ mol dm^{-3} ($NaClO_4$). The solid curves are calculated with the rate constants listed in Table III.

Table III. Rate Constants and Activation Parameters for Peroxo Complex Formation of V^VPDA

Temp/°C	k_1/mol^{-2} dm^6 s^{-1}	k_2/mol^{-1} dm^3 s^{-1}	k_3/mol^{-1} dm^3 s^{-1}
17.3	3.2×10^2	0.22	19
25.1	4.1×10^2	0.39	28
35.0	6.0×10^2	0.71	46
$\Delta H^‡$/kJ mol^{-1}	24 ± 1.5	46 ± 2	35 ± 2
$\Delta S^‡$/J K^{-1} mol^{-1}	−114 ± 9	−97 ± 9	−100 ± 9

As evident from the equilibria of the V^V–PDA complex under the present experimental conditions, the concentration of the protonated complex is extremely low, while we have an appreciable amount of the hydroxo complex at lower acidity. Therefore the rate of formation of $VO(O_2)(pda)(H_2O)^-$ is expressed as

$$\begin{aligned} d[VO(O_2)(pda)(H_2O)^-]/dt = \{&k_1[H^+][VO_2(pda)(H_2O)^-] \\ &+ k_2[VO_2(pda)(H_2O)^-] \\ &+ k_3[VO_2(pda)(OH)^{2-}]\}[H_2O_2] \end{aligned} \qquad (10)$$

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

$$k_{0(H)} = \frac{k_1[H^+] + k_2 + k_3K^{-H}{}_{VO_2(pda)(OH)}/[H^+]}{1 + K^{-H}{}_{VO_2(pda)(OH)}/[H^+]} \qquad (11)$$

The solid lines in Figure 6 are theoretical curves calculated from the obtained rate constants. The results of the kinetic analysis are tabulated in Table III.

Discussion

NMR,[20] x-ray[21-23] and complex formation[17] studies have given evidence that two oxygen atoms of the VO_2 unit in VO_2-aminopolycarboxylate complexes are in the cis configuration and that a nitrogen atom of the coordinated ligand is always in a position trans to the oxo oxygen atom of VO_2. We may thus speculate that the structures of VO_2–aminopolycarboxylate complexes in aqueous solution are

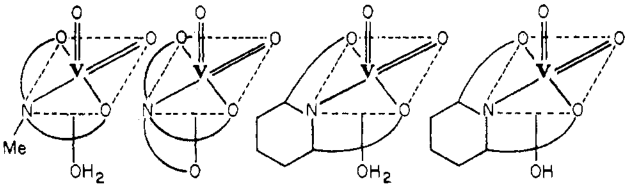
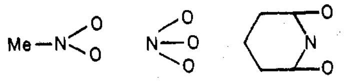


Table IV. Kinetic Parameters for Vanadium(V) Reactions

Reaction (eq no. in text)	Rate eq	Reaction product	k(25 °C)[d]	$\Delta H^{\ddagger}$/kJ mol^{-1}	$\Delta S^{\ddagger}$/J K^{-1} mol^{-1}	Ref
A	$k[VO_2^+][Hedda^-]$	$VO_2(edda)^-$	1.0×10^8	29 ± 5	8 ± 15	*a*
B	$k[VO_2(mida)^-][H_2O_2]$	$VO(O_2)(mida)^-$	9.3×10^3	26 ± 1.5	−79 ± 9	*b*
C (eq 7)	$k[VO_2(nta)^{2-}][H_2O_2]$	$VO(O_2)(nta)^{2-}$	7.41	39 ± 1	−96 ± 9	*c*
D (eq 7)	$k[VO_2(nta)^{2-}][H_2O_2][H^+]$	$VO(O_2)(nta)^{2-}$	1.86×10^4	39 ± 1	−33 ± 9	*c*
E (eq 10)	$k[VO_2(pda)^-][H_2O_2]$	$VO(O_2)(pda)^-$	3.9×10^{-1}	46 ± 2	−97 ± 9	*c*
F (eq 10)	$k[VO_2(pda)^-][H_2O_2][H^+]$	$VO(O_2)(pda)^-$	4.1×10^2	24 ± 1.5	−114 ± 9	*c*
G (eq 10)	$k[VO_2(pda)(OH)^{2-}][H_2O_2]$	$VO(O_2)(pda)^-$	2.8×10	35 ± 2	−100 ± 9	*c*

[a] S. Yamada, Y. Ukei, and M. Tanaka, *Inorg. Chem.*, **15**, 964 (1976). [b] S. Funahashi, Y. Ito, and M. Tanaka, *J. Coord. Chem.*, 3, 125 (1973). [c] This work. [d] For second-order reactions k is given in mol^{-1} dm^3 s^{-1} and for third-order reactions it is given in mol^{-2} dm^6 s^{-1}.

where fully dissociated MIDA, NTA, and PDA anions are symbolized as



respectively. The protonation constant of MIDA ($10^{9.48}$),[17] the formation constant of MIDA with vanadium(V) ($10^{10.16}$),[17] and the reciprocal of the hydrolysis constant for $VO_2(mida)(H_2O)^-$ ($10^{-6.13}$)[17] are larger than the corresponding constant for PDA. This evidently results from a higher electron density on the nitrogen atom of mida^{2-}, as compared with pda^{2-}.

Judging from equilibrium data[24] for H_2O_2, the values of the proton dissociation constants for $H_3O_2^+$ and H_2O_2 are of such magnitude as to preclude inclusion of $H_3O_2^+$ and HO_2^- in the present reaction system: $[H^+][H_2O_2]/[H_3O_2^+] \simeq 10^3$, $[H^+][HO_2^-]/[H_2O_2] = 10^{-11.27}$. The kinetics of hydrogen exchange between H_2O_2 and water have been investigated by the ^{1}H NMR method in the pH range 2.5–6.6. According to the results[25] (rate = $1.6 \times 10^7[H_2O_2][H_3O^+] + 7.3 \times 10^7 \cdot [H_2O_2][H_2O][HO_2^-]$), the hydrogen-exchange reaction is much faster than H_2O_2 insertion reactions relevant to the present study. It has also been shown that no appreciable oxygen exchange occurs between H_2O_2 and H_2O for several days at room temperature. Thus in our studies all protolytic reactions are assumed to be rapid.

Recently it has been pointed out that for the reaction of VO_2^+ ion with EDDA (ethylenediamine-*N,N′*-diacetic acid) to form the $VO_2(edda)^-$ complex, the rate-determining step is water loss from the metal ion.[15] The activation enthalpy and entropy for water dissociation at VO_2^+ are 29 kJ mol^{-1} and 8 J K^{-1} mol^{-1}, respectively (reaction A in Table IV). On the other hand, in Table IV it may be seen that the large negative entropy of activation is characteristic of the H_2O_2 entry reaction. The large negative values of $\Delta S^{\ddagger}$ are ascribed to a highly oriented transition state and provide strong evidence for an associative mechanism for the vanadium(V) complex–H_2O_2 reactions.

In the proton-independent reaction paths, the difference between rate constants for $VO_2(mida)^-$ (reaction B in Table IV) and $VO_2(pda)^-$ (reaction E) is large, namely, about 5 orders of magnitude, whereas there is little difference in values of $\Delta S^{\ddagger}$ for $VO_2(mida)^-$, $VO_2(pda)^-$, $VO_2(nta)^{2-}$ (reaction C), and $VO_2(pda)(OH)^{2-}$ (reaction G). However there is a very interesting trend in values of $\Delta H^{\ddagger}$. The enthalpy of activation increases in the order MIDA (reaction B) < NTA (reaction C) < PDA (reaction E). This sequence may be taken as a result of the different basicities of the oxo group in vanadium(V) complexes. The higher the electron density on the nitrogen atom in coordinated ligands, the more negative the charge on the oxo group. The increased negative charge on the oxo group would result in the increased affinity for H_2O_2 to form a hydrogen-bond complex. In the same sense, the lower activation enthalpy of $VO_2(pda)(OH)^{2-}$ (reaction G) in comparison with that of $VO_2(pda)(H_2O)^-$ (reaction E) is attributable to the electron donation from the hydroxo group. Eventually the variation of enthalpies of activation is parallel with the electron donation from the coordinated ligands in the vanadium(V) complex.

Proton-dependent reactions (reactions D and F) for NTA and PDA complexes are faster than the corresponding proton-independent reactions (reactions C and E) by a factor of ca. 10^3. Such an enhancement of reaction rates by proton catalysis is reflected in the activation entropy term for NTA and in the activation enthalpy term for PDA. The role of the proton might be different mechanistically for these two cases. But sufficient information is not available to explain such a difference. A first-order $[H^+]$ dependence has been established for the reactions involving oxo anions[26] or VO_2^+.[27] It is believed the acid catalysis arises from a reactive species presumably protonated at the oxo group.

Registry No. H_2O_2, 7722-84-1; $VO_2(nta)^{2-}$, 59368-60-4; $VO_2(pda)(H_2O)^-$, 62126-16-3; PDA, 499-83-2; $VO(O_2)(nta)^{2-}$, 62126-17-4; $VO(O_2)(pda)(H_2O)^-$, 62126-18-5.

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(16) Some terminology used in the paper: peroxide, O_2^{2-}; peroxo, covalently bound dioxygen resembling O_2^{2-}; peroxo complex, complex containing metal-bound peroxo ligand(s); oxide, O^{2-} ion; oxo, covalently bound monatomic oxygen resembling O^{2-} (the dioxo, $(O)_2$, is not to be confused with peroxo, (O_2)).
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