transfer through the stronger metal–metal bond, leading to a higher energy, vacant σ^* orbital.

π Stabilization in the 2:1 Adducts. Equation 1 puts one in the unique position of being able to calculate the σ contribution to the bonding in the 2:1 adduct. Deviations of greater stability in the dirhodium system can be used to probe the influence of coordinating π acceptors on one metal center upon the π back-bonding properties of the second metal. When π- or π^*-back-bond stabilization exists, one can only obtain an estimate on the upper limit of the π stabilization in the second step. This occurs because π back-bonding in the first step enhances σ bonding over that predicted by eq 1. By the assumption that this is not the case, an upper limit of the π stabilization in the second step is calculated. Furthermore, it should be emphasized that although different π-stabilization energies are calculated for the 1:1 and 2:1 steps, both metal–ligand bonds are equivalent in the 2:1 adduct with the sum of these two interactions averaged over the ligands. The $-\Delta H_{2:1}$ value for the second step in the pyridine–$Rh_2(pfb)_4$ system is calculated to be 14.1 kcal mol^{-1} when the k and k' values of $Rh_2(but)_4$ are used. This prediction is in good agreement with the experimental value of 15.0 kcal mol^{-1}, particularly when one considers that π^* back-bonding in the 1:1 adduct is expected to enhance the σ interaction in the 2:1 above that predicted by eq 1. Thus, there is relatively little additional π^* stabilization accompanying the coordination of the second pyridine.

In the acetonitrile system, the $-\Delta H_{2:1}$ for a σ interaction is calculated to be 5.9 kcal mol^{-1}. When compared to the experimental value (7.4 kcal mol^{-1}), this leads to an upper limit for a π^*-stabilization energy of -1.5 kcal mol^{-1}. In contrast to the case for the CH_3CN adducts of the $Rh_2(but)_4$ system (a more effective π-back-donating system with 4.9 kcal mol^{-1} of π^*-back-bonding stabilization), stronger σ coordination to one rhodium center of the stronger acid $Rh_2(pfb)_4$ greatly diminishes the π back-bonding that occurs upon coordination of the second CH_3CN.

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Registry No. $Rh_2(pfb)_4$, 81028-20-8; $Mo_2(pfb)_4$, 24329-24-6; MeCN, 75-05-8; py, 110-86-1; *N*-MeIm, 616-47-7; Me_2SO, 67-68-5; DMA, 127-19-5; THTP, 110-01-0.

Supplementary Material Available: Spectral and calorimetric data for $Rh_2(pfb)_4$ and $Mo_2(pfb)_4$ complexes (15 pages). Ordering information is given on any current masthead page.

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Kinetic Studies of the Reactions of Hydrogen Peroxide with Aqua(nitrilotriacetato)oxovanadate(IV) and Diaquaoxo(2,6-pyridinedicarboxylato)vanadium(IV) in Acidic Aqueous Solution[1]

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The kinetics of the reactions of hydrogen peroxide with aqua(nitrilotriacetato)oxovanadate(IV) (V(IV)–NTA or $VO(nta)(H_2O)^-$) and diaquaoxo(2,6-pyridinedicarboxylato)vanadium(IV) (V(IV)–PDA or $VO(pda)(H_2O)_2$) to form peroxovanadium(V) complexes have been studied spectrophotometrically at an ionic strength of 1.0 mol dm^{-3} ($NaClO_4$) in acidic aqueous solution. The formation rate of the peroxo complexes of V(V)–NTA and V(V)–PDA is first order in vanadium(IV) complexes and hydrogen peroxide and independent of the concentrations of excess ligands (NTA and PDA) and hydrogen ion. The reaction at high pressures up to 1250 kg cm^{-2} was followed by a high-pressure stopped-flow technique. Activation parameters were obtained as follows: for the V(IV)–NTA–H_2O_2 system k_{NTA}(25 °C) = 0.11 ± 0.02 mol^{-1} dm^3 s^{-1}, $\Delta H^\ddagger = 45.2 \pm 1$ kJ mol^{-1}, $\Delta S^\ddagger = -112 \pm 10$ J mol^{-1} K^{-1}, $\Delta V^\ddagger = -10.5 \pm 0.3$ cm^3 mol^{-1}; for the V(IV)–PDA–H_2O_2 system k_{PDA}(25 °C) = 0.55 ± 0.08 mol^{-1} dm^3 s^{-1}, $\Delta H^\ddagger = 36.5 \pm 2$ kJ mol^{-1}, $\Delta S^\ddagger = -125 \pm 15$ J mol^{-1} K^{-1}, $\Delta V^\ddagger = -13.0 \pm 0.2$ cm^3 mol^{-1}. The rate-determining step may be the insertion of a hydrogen peroxide molecule into the first coordination sphere of the vanadium(IV) complex. It is followed by rapid electron transfer and peroxo coordination to thus produce the vanadium(V) complex. An associative interchange mechanism is most probably operative. We have studied the complexation equilibrium of the V(IV)–PDA complex: $K_{VO(pda)} = [VO(pda)(H_2O)_2][VO^{2+}]^{-1}[pda^{2-}]^{-1} = 10^{6.77\pm0.15}$ mol^{-1} dm^3 at 25 °C and $I = 1.0$ mol dm^{-3}.

Introduction

Vanadium has been thought for some years to be an essential element in both animals and plants.[2] There have been many reports on the physiological effect of vanadium exogenously added to tissues of animals[3-9] and on the vanadate inhibition of the sodium- and potassium-stimulated adenosine triphosphatase.[10-14] For an understanding of the significant biological role of vanadium and the reaction mechanism of vanadium complexes from the viewpoint of coordination chemistry, kinetic studies on vanadium complexes in aqueous solution are required.

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(1) Reactions of hydrogen peroxide with metal complexes. 6. Part 5: Funahashi, S.; Ishihara, K.; Tanaka, M. *Inorg. Chem.* **1981**, *20*, 51.

(2) Underwood, E. J. "Trace Elements in Human and Animal Nutrition"; Academic Press: London, 1971; pp 416–424.

(3) Erdmann, E.; Krawietz, W.; Philipp, G.; Hackbarth, I.; Schmitz, W.; Scholz, H. *Nature (London)* **1979**, *278*, 459.

(4) Borchard, U.; Fox, A. A. L.; Greeff, K.; Schlieper, P. *Nature (London)* **1979**, *279*, 339.

(5) Grupp, G.; Grupp, I.; Johnson, C. L.; Wallick, E. T.; Schwartz, A. *Biochem. Biophys. Res. Commun.* **1979**, *88*, 440.

(6) Schwabe, U.; Puchstein, C.; Hannemann, H.; Söchtig, E. *Nature (London)* **1979**, *277*, 143.

(7) Cantley, L. C., Jr.; Aisen, P. *J. Biol. Chem.* **1979**, *254*, 1781.

(8) Macara, I. G.; Kustin, K.; Cantley, L. C., Jr. *Biochim. Biophys. Acta* **1980**, *629*, 95.

(9) Sakurai, H.; Shimomura, S.; Fukuzawa, K.; Ishizu, K. *Biochem. Biophys. Res. Commun.* **1980**, *96*, 293.

(10) Cantley, L. C., Jr.; Josephson, L.; Warner, R.; Yanagisawa, M.; Lechene, C.; Guidotti, G. *J. Biol. Chem.* **1977**, *252*, 7421.

(11) Cantley, L. C., Jr.; Cantley, L. G.; Josephson, L. *J. Biol. Chem.* **1978**, *253*, 7361.

(12) Bond, G. H.; Hudgins, P. M. *Biochemistry* **1979**, *18*, 325.

(13) Bowman, B. J.; Slayman, C. W. *J. Biol. Chem.* **1979**, *254*, 2928.

(14) Hansen, O. *Biochim. Biophys. Acta* **1979**, *568*, 265.

0020-1669/82/1321-2202$01.25/0

Previously we have reported the kinetics of reaction between hydrogen peroxide and vanadium(V) complexes with aminopolycarboxylic acids[15] such as MIDA,[16] PDA,[17] NTA,[17,18] EDDA,[19] DMEDDA,[19] and EDTA.[19] Our attention has been extended to the reactions of hydrogen peroxide with tetravalent vanadium complexes, which involve oxidation of vanadium(IV) to vanadium(V) and peroxo coordination. The purpose of the present work is to provide new information on the mechanism of reactions involving peroxo complexes of vanadium. The high-pressure stopped-flow technique was a useful tool to obtain information about the reaction mechanism.

Experimental Section

Reagents. Solutions of sodium perchlorate, sodium hydroxide, hydrogen peroxide (unstabilized 60% H_2O_2, given by Mitsubishi Gasukagaku Co., Ltd.), vanadium(V) perchlorate, NTA, and PDA were prepared as previously described.[17]

Vanadium(IV) Perchlorate. The stock solution of vanadium(IV) perchlorate was prepared by electrolysis of vanadium(V) perchlorate solution and then by complete reduction of V(V) to V(IV) by sulfur dioxide. The chloride and sulfate ions involved were lower than $^1/_{100}$th of the vanadium concentration. The vanadium(IV) was standardized titrimetrically against a potassium permanganate standard.

Measurements. Temperature of the reaction solution was controlled to within ±0.1 °C. Ionic strength was maintained at 1.00 mol dm^{-3} with sodium perchlorate and perchloric acid. Spectra were recorded on a highly sensitive spectrophotometer (Type SM401, Union Giken Co.) to characterize species spectrally. Hydrogen ion concentration was determined with an Orion Research pH meter. A 1.000×10^{-2} mol dm^{-3} perchloric acid at $I = 1.00$ mol dm^{-3} was used as a pH standard solution.

Vanadium(IV) complex solutions for kinetic measurements were prepared by mixing a vanadium(IV) ion solution and an excess of NTA or PDA solution. In the presence of excess ligand vanadium(IV) ion forms vanadium(IV) complexes quantitatively, as confirmed on the basis of equilibrium constants. Under our experimental conditions vanadium(IV) complexes were stable at least for 2 days, even when they were exposed to oxygen atmosphere.

When an excess of hydrogen peroxide solution was added to the blue acidic solution of $VO(nta)(H_2O)^-$ or $VO(pda)(H_2O)_2$, the solution turned yellow to form peroxovanadium(V) complexes. Fast reactions were followed spectrophotometrically as a function of time at appropriate wavelengths by a stopped-flow spectrophotometer (Type RA401, Union Giken). The progress of slower reactions was measured by monitoring the visual spectra or absorbance at some wavelengths after starting the reaction by a sample-mixing device (Type MX7, Union Giken). Peroxovanadium(V) complexes, produced under our experimental conditions, were stable at least for 1 month.

Reactions under various pressures up to 1250 kg cm^{-2} were followed with a high-pressure stopped-flow apparatus, which was exploited in our laboratory.[18]

Results

Complexation Equilibrium of the V(IV)–PDA System. We have studied spectrophotometrically the complexation equilibria of vanadium(IV) ion with PDA. Absorbance change of the system at 623 nm as a function of $-\log [H^+]$ was measured over the pH range 0.5–3.0, where vanadium(IV) ion does not hydrolyze as judged from its hydrolysis constants.[20,21] The absorbance change is thus attributable to the equilibrium

$$VO^{2+} + pda' \rightleftharpoons VO(pda) + nH^+ \tag{1}$$

The formation constant of the V(IV)–PDA complex is given as

$$K_{VO(pda)} = \frac{[VO(pda)]}{[VO^{2+}][pda^{2-}]} = \frac{[VO(pda)]\alpha_{pda(H)}}{[VO^{2+}][pda']}$$

where [pda′] refers to the total concentration of PDA not combined with vanadium(IV) and $\alpha_{pda(H)}$ is the side-reaction coefficient taking into account the protonation of pda^{2-}: $[pda'] = [pda^{2-}]\alpha_{pda(H)}$. The protonation constants of PDA under the same condition are available.[17] Uncomplexed ligand pda′ does not absorb at 623 nm. We have

$$\log K_{VO(pda)} = \log \frac{A - A_{VO}}{A_{VO(pda)} - A} - \log \left(C_{PDA} - C_{VO}\frac{A - A_{VO}}{A_{VO(pda)} - A_{VO}} \right) + \log \alpha_{pda(H)} = Y + \log \alpha_{pda(H)} \tag{2}$$

where C_{PDA} and C_{VO} represent the total concentrations of PDA and vanadium(IV), respectively, and A_{VO} and $A_{VO(pda)}$ are absorption coefficients of VO^{2+} and VO(pda), respectively. The plot of the 16 values of Y vs. $\log \alpha_{pda(H)}$ yielded a straight line with a slope of −1 over the range of $-\log [H^+]$ from 0.5 to 3.0. We obtained $K_{VO(pda)} = 10^{6.77 \pm 0.15}$ mol^{-1} dm^3 at 25 °C and $I = 1.0$ mol dm^{-3}.

Stoichiometry. The peroxo ion in $NH_4[VO(O_2)(pda)(H_2O)]$[17] was successfully determined by titration with a standard permanganate solution, although the reaction was appreciably slow. After completion of the reaction of vanadium(IV) complexes with hydrogen peroxide added dropwise, excess H_2O_2 and coordinated peroxo ion were determined with a standard permanganate solution. The amount of H_2O_2 consumed by oxidation of V(IV) to V(V) was 0.5 mol/mol of vanadium(IV) ion. This means that the OH radical produced by one-electron reduction of H_2O_2 is consumed by the subsequent rapid oxidation of V(IV) ion. Thus with excess vanadium(IV) complexes and H_2O_2 the overall reactions are expressed as

$$VO(nta)(H_2O)^- + {}^3/_2H_2O_2 \rightarrow VO(O_2)(nta)^{2-} + H_3O^+ + H_2O \tag{3}$$

$$VO(pda)(H_2O)_2 + {}^3/_2H_2O_2 \rightarrow VO(O_2)(pda)(H_2O)^- + H_3O^+ + H_2O \tag{4}$$

In the presence of a large excess of H_2O_2, the OH radical should react with H_2O_2 (vide infra).

Reaction of the V(IV)–NTA Complex with H_2O_2. In all kinetic experiments H_2O_2 was used in large excess over V(IV)–NTA. First-order plots were linear for at least 3 half-lives. First-order rate constants showed a linear dependence on the concentration of hydrogen peroxide at constant acidity and at constant concentration of excess NTA.[22] The rate law is thus expressed by eq 5. The second-order rate constant

$$\frac{d[VO(O_2)(nta)^{2-}]}{dt} = k_{NTA}[VO(nta)(H_2O)^-][H_2O_2] \tag{5}$$

k_{NTA} was independent of the concentrations of excess NTA and hydrogen ion under various conditions: $C_{NTA} = (4\text{–}20) \times 10^{-4}$ mol dm^{-3}, $[H^+] = 10^{-2.4}\text{–}10^{-3.4}$ mol dm^{-3}.[22] From the temperature dependence of rate constants,[22] the following activation parameters were obtained: $k_{NTA}(25\ °C) = 0.11 \pm 0.02$ mol^{-1} dm^3 s^{-1}, $\Delta H^\ddagger = 45.2 \pm 1$ kJ mol^{-1}, and $\Delta S^\ddagger = -112 \pm 10$ J mol^{-1} K^{-1}.

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(15) Ligand abbreviations: MIDA, *N*-methyliminodiacetic acid; PDA, 2,6-pyridinedicarboxylic acid (H_2pda); NTA, nitrilotriacetic acid (H_3nta); EDDA, ethylenediamine-*N*,*N*′-diacetic acid; DMEDDA, *N*,*N*′-dimethylethylenediamine-*N*,*N*′-diacetic acid; EDTA, ethylenediamine-*N*,*N*,*N*′,*N*′-tetraacetic acid.

(16) Funahashi, S.; Ito, Y.; Tanaka, M. *J. Coord. Chem.* **1973**, *3*, 125.

(17) Funashashi, S.; Haraguchi, K.; Tanaka, M. *Inorg. Chem.* **1977**, *16*, 1349.

(18) Funahashi, S.; Ishihara, K.; Tanaka, M. *Inorg. Chem.* **1981**, *20*, 51. Funahashi, S.; Inamo, M.; Ishihara, K.; Tanaka, M. *Ibid.* **1982**, *21*, 447.

(19) Funahashi, S.; Midorikawa, T.; Tanaka, M. *Inorg. Chem.* **1980**, *19*, 91.

(20) Rossotti, F. J. C.; Rossotti, H. S. *Acta Chem. Scand.* **1955**, *9*, 1177.

(21) Francavilla, J.; Chasteen, N. D. *Inorg. Chem.* **1975**, *14*, 2860.

(22) Supplementary material.

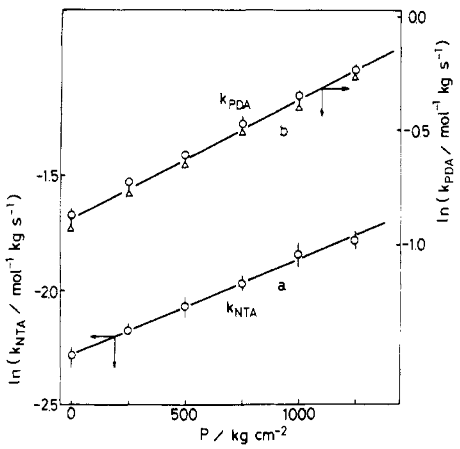

Figure 1. Pressure dependence of the second-order rate constant: (a) (V(IV)–NTA system) $C_{VO} = 3.18 \times 10^{-4}$ mol kg^{-1}, $C_{NTA} = 5.89 \times 10^{-4}$ mol kg^{-1}, $C_{H_2O_2} = 1.11 \times 10^{-1}$ mol kg^{-1}, $[H^+] = 1.18 \times 10^{-3}$ mol kg^{-1}, $I = 1.05$ mol kg^{-1}, 25 °C; (b) (V(IV)–PDA system) $C_{VO} = 3.18 \times 10^{-4}$ mol kg^{-1}, $C_{PDA} = 2.36 \times 10^{-3}$ mol kg^{-1}, $C_{H_2O_2} = 5.43 \times 10^{-2}$ mol kg^{-1}, $I = 1.05$ mol kg^{-1}, 25 °C, (○) $[H^+] = 3.55 \times 10^{-4}$ mol kg^{-1}, (△) $[H^+] = 8.21 \times 10^{-4}$ mol kg^{-1}.

According to the transition-state theory the change in rate constant with pressure is given by eq 6. Pressure dependence

$$(\partial(\ln k_{NTA})/\partial P)_T = -\Delta V_{NTA}^{\ddagger}/RT \tag{6}$$

of ln k_{NTA} is shown in Figure 1. The plot is linear within experimental uncertainty. Thus the volume of activation $\Delta V_{NTA}^{\ddagger}$ for k_{NTA} is assumed to be pressure independent and was determined to be -10.5 ± 0.3 cm^3 mol^{-1}.[23] The value of the rate constant at zero pressure obtained from the intercept in Figure 1 agreed with that obtained at atmospheric pressure by a conventional method.

Reaction of the V(IV)–PDA Complex with H_2O_2. The same analysis was applied to the V(IV)–PDA–H_2O_2 system. The rate is first order in the V(IV)–PDA complex and hydrogen peroxide and independent of the concentrations of excess PDA and hydrogen ion under the following conditions: $C_{PDA} = (2\text{–}10) \times 10^{-3}$ mol dm^{-3}, $[H^+] = 10^{-2.4}\text{–}10^{-3.7}$ mol dm^{-3}.[22] The rate equation is given by eq 7. The second-order rate constant

$$\frac{d[VO(O_2)(pda)(H_2O)^-]}{dt} = k_{PDA}[VO(pda)(H_2O)_2][H_2O_2] \tag{7}$$

k_{PDA} was obtained at various temperatures at $-\log$ ([H$^+$]/mol dm^{-3}) = 3.07 and 3.35[22] and at various pressures at $[H^+] = 3.55 \times 10^{-4}$ and 8.21×10^{-4} mol kg^{-1} (see Figure 1b). The values of activation parameters were the same at two different hydrogen ion concentrations. The hydrogen ion independence of $\Delta V_{PDA}^{\ddagger}$ also supports the proposal that the pH decrease with change in pressure does not affect the rate.[23] The activation parameters obtained were as follows: $k_{PDA}(25\ °C) = 0.55 \pm 0.08$ mol^{-1} dm^3 s^{-1}, $\Delta H^{\ddagger} = 36.5 \pm 2$ kJ mol^{-1}, $\Delta S^{\ddagger} = -125 \pm 15$ J mol^{-1} K^{-1}, and $\Delta V^{\ddagger} = -13.0 \pm 0.5$ cm^3 mol^{-1}.

Reaction Rate in the Presence of Propan-2-ol. The reduction of hydrogen peroxide might yield free OH radical. We used propan-2-ol as an OH-radical scavenger. Second-order rate constants, k_{NTA}, at various concentrations of H_2O_2 in the absence and in the presence of 0.10 mol dm^{-3} propan-2-ol are plotted against the H_2O_2 concentration (Figure 2). At lower concentration of H_2O_2 and in the absence of the alcohol, the rate is faster by a factor of about 2 than that at higher concentration of H_2O_2 or in the presence of the alcohol. On the other hand, in the V(IV)–PDA–H_2O_2 system no such effect has been observed.

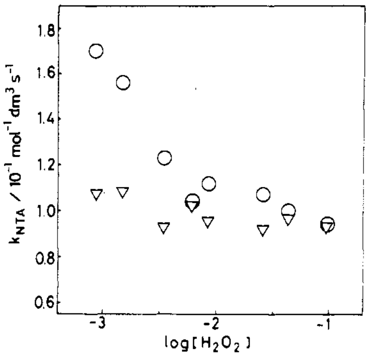

Figure 2. Effect of propan-2-ol on rate constant ($C_{VO} = 3.02 \times 10^{-4}$ mol dm^{-3}, $C_{NTA} = 6.06 \times 10^{-4}$ mol dm^{-3}, $-\log[H^+] = 2.85$): (○) in the absence of propan-2-ol; (▽) in the presence of 0.10 mol dm^{-3} propan-2-ol.

Discussion

The reactions of H_2O_2 with Ti(III)[25] and Fe(II)[26] have been widely used for the generation of organic free radicals in aqueous media. In the present system, the reduction of hydrogen peroxide is thought to take place via two successive one-electron transfers (eq 8 and 9), thus yielding free radicals

$$VO(nta)(H_2O)^- + H_2O_2 \xrightarrow{k_{NTA}} VO_2(nta)^{2-} + H_3O^+ + OH \tag{8}$$

$$VO(nta)(H_2O)^- + OH \rightarrow VO_2(nta)^{2-} + H_3O^+ \tag{9}$$

capable of reacting with various substrates in the reaction mixture. Under experimental conditions where [V(IV)–NTA] > [H_2O_2], it would be reasonable to assume that reaction 8 is followed immediately by reaction 9. The situation is the same for the dropwise addition of H_2O_2 to the V(IV)–NTA solution (vide supra). On the other hand, at [H_2O_2] >> [V(IV)–NTA], reactions 8 and 10–12 seem to take place to an appreciable extent. Available values of k_{10}, k_{11}, and k_{12} are 4.5×10^7, 7.5×10^5, and 7×10^{-9} mol^{-1} dm^3 s^{-1}, respectively.[27–31]

$$OH + H_2O_2 \xrightarrow{k_{10}} HO_2 + H_2O \tag{10}$$

$$HO_2 + HO_2 \xrightarrow{k_{11}} H_2O_2 + O_2 \tag{11}$$

$$OH + HO_2 \xrightarrow{k_{12}} H_2O + O_2 \tag{12}$$

In the present study reactions were followed by the appearance of the peroxo complex of vanadium(V). The rate of peroxovanadium(V) complex formation from V(V) complexes and H_2O_2[17] is much faster than that of the reaction of corresponding V(IV) complexes with H_2O_2. If the OH radicals oxidize the V(IV) complex (reaction 9), the formation rate of the peroxovanadium(V) complex should be twice as fast as that in the case where the OH radicals are consumed by H_2O_2 (reactions 10–12). We verified this assumption by some

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(23) The pH of the reaction system should vary with the change in pressure. The volume changes in the protonation of carboxylate ions in NTA are assumed to be about 10 cm^3 mol^{-1}.[24] Thus the pH of the system will become a little lower with increasing pressure. Since in the present system the reaction is independent of the hydrogen ion concentration over the pH range 2.4–3.4, the pH decrease with change in pressure does not affect the rate.

(24) Asano, T.; le Noble, W. J. *Chem. Rev.* **1978**, *78*, 407.

(25) Shiga, T. *J. Phys. Chem.* **1965**, *69*, 3805.

(26) Po, H. N.; Sutin, N. *Inorg. Chem.* **1968**, *7*, 621.

(27) Schwarz, H. A. *J. Phys. Chem.* **1962**, *66*, 255.

(28) Rabani, J.; Matheson, M. S. *J. Phys. Chem.* **1966**, *70*, 761.

(29) Sehested, K.; Rasmussen, O. L.; Fricke, H. *J. Phys. Chem.* **1968**, *72*, 626.

(30) Behar, D.; Czapski, G.; Rabani, J.; Dorfman, L. M.; Schwarz, H. A. *J. Phys. Chem.* **1970**, *74*, 3209.

(31) Field, R. J.; Noyes, R. M.; Postlethwaite, D. *J. Phys. Chem.* **1976**, *80*, 223.

Table I. Rate Constants and Activation Parameters for Various Reactions of Oxovanadium(IV) Complexes

no.	reacn syst	k(25 °C)/ $mol^{-1}\ dm^3\ s^{-1}$	$\Delta H^{\ddagger}$/ $kJ\ mol^{-1}$	$\Delta S^{\ddagger}$/ $J\ mol^{-1}\ K^{-1}$	$\Delta V^{\ddagger}$/ $cm^3\ mol^{-1}$	ref
1	$VO(pmida)(H_2O) + NCS^-$	0.26	49 ± 2	−90 ± 9		35
2	$VO(pmida)(H_2O) + N_3^-$	3.7	47 ± 6	−75 ± 20		35
3	$VO(nta)(H_2O)^- + NCS^-$	0.62	41 ± 1	−112 ± 3		36
4	$VO(nta)(H_2O)^- + N_3^-$	4.1	54 ± 1	−52 ± 2		36
5	$VO(nta)(H_2O)^- + VO_2(nta)^{2-}$	1.36	62 ± 13	−33 ± 41		36
6	$VO(pmida)(H_2O) + NO_2^-$	1.0 (45 °C)	65 ± 2	−41 ± 5		36
7	$VO(nta)(H_2O)^- + NO_2^-$	0.20 (45 °C)	66 ± 2	−48 ± 17		36
8	$VO(nta)(H_2O)^- + H_2O_2$	0.11 ± 0.02	45.2 ± 1	−112 ± 10	−10.5 ± 0.3	this work
9	$VO(pda)(H_2O)_2 + H_2O_2$	0.55 ± 0.08	36.5 ± 2	−125 ± 15	−13.0 ± 0.2	this work

kinetic runs in the presence of propan-2-ol, where all the OH radicals will react with the alcohol, yielding alcoholic radicals, according to reaction 13. The k_{13} value of 1.2×10^9 mol^{-1}

$$(CH_3)_2CHOH + OH \xrightarrow{k_{13}} (CH_3)_2COH + H_2O \quad (13)$$

$dm^3\ s^{-1}$ is known.[32] In the absence of propan-2-ol, competition for OH radicals between V(IV)–NTA (reaction 9) and H_2O_2 (reaction 10) led to an effective decrease in the peroxovanadium(V) formation rate, with increasing H_2O_2 concentration. Since a propan-2-ol concentration of 0.10 mol dm^{-3} immediately traps OH radicals, the rate constant k_{NTA} in the presence of the alcohol should be equal to that at a large excess of H_2O_2. At low concentration of H_2O_2 where the OH radicals react mainly with the V(IV)–NTA complex (reaction 9), the rate is faster by a factor of about 2, as expected. On the other hand, in the V(IV)–PDA–H_2O_2 system no such effect has been observed. This indicates that the rate of the reaction of V(IV)–NTA with OH is faster than that of the reaction of V(IV)–PDA with OH.

A primary aspect of the mechanism of an oxidation–reduction (redox) reaction is the characterization of the redox reaction as an inner-sphere or outer-sphere process. Another pertinent aspect of the details of the mechanism is the question whether the partially bonded species in the inner-sphere reaction is an activated complex or an unstable intermediate.[33] To consider these points, we must dissect a redox reaction into its individual steps. The first step is the diffusion-controlled formation of an encounter complex (I):

$$V^{IV} + H_2O_2 \rightleftharpoons \underset{I}{V^{IV}\cdots H_2O_2} \quad (14)$$

The entity I can then progress either through an inner-sphere path (eq 15), giving precursor complex (II), successor complex (III), and product (IV)

$$I \rightleftharpoons \underset{II}{V^{IV}\text{–}H_2O_2} \rightleftharpoons \underset{III}{V^{V}\text{–}(H_2O_2')} \rightleftharpoons \underset{IV}{V^{V} + OH} \quad (15)$$

or through an outer-sphere path

$$I \rightleftharpoons V^{V}\cdots(H_2O_2') \rightleftharpoons V^{V} + OH \quad (16)$$

In the case of the inner-sphere mechanism, precursor formation (I → II), intramolecular electron transfer (II → III), or succesor decomposition (III → IV) may be rate limiting.

Activation volume is very useful in diagnosing the mechanism. The measured volume of activation ΔV^{*} can be expressed as the sum of an intrinsic part ΔV_{intr}^{*} and an electrostrictive part ΔV_{el}^{*}.[34] ΔV_{intr}^{*} represents the contribution to ΔV^{*} arising from alterations in bond lengths and angles during the formation of the transition state. ΔV_{el}^{*} reflects variation in solvation. There seems to be little or no contribution of solvational changes in the present systems with no change of charge in the transition state. In the case of the outer-sphere mechanism the activation volume should be a small positive value. The obtained values of activation volume are considerably large negative values. We can thus rule out the outer-sphere mechanism.

Nishizawa and Saito[35,36] have studied the kinetics of substitution reactions of thiocyanate and azide with water in aquaoxo((2-pyridylmethyl)iminodiacetato)vanadium(IV) (VO(pmida)(H_2O)) and $VO(nta)(H_2O)^-$ in which the sites trans to oxo are blocked by PMIDA and NTA. They also studied the reaction of $VO(nta)(H_2O)^-$ with nitrite to give $VO_2(nta)^{2-}$ and NO and the reaction of $VO(nta)(H_2O)^-$ with $VO_2(nta)^{2-}$ to give a binuclear complex of the composition $[V_2O_3(nta)_2]^{3-}$ with equal oxidation states of the two vanadium ions. Their data are listed in Table I together with our present data.

As apparent from figures in Table I, corresponding activation parameters are similar in all the systems although the types of reactions are not the same. An isokinetic relationship is shown in Figure 3.[22] The isokinetic temperature is ca. 60 °C. The isokinetic plot demonstrates that all reactions proceed via a common mechanism in activation processes.[37] The values of activation entropies are largely negative. This points to an associative mode of activation process. The negative activation volume is consistent with an associative mechanism in which H_2O_2 is entering into the inner coordination sphere of the central metal ion in the activation process. The H_2O_2 does not replace a coordinated water molecule, but the complex forms the seven-coordinate transition state, which does not make use of a normal coordination position in vanadium.

We can conclude that the present redox reaction proceeds by an inner-sphere mechanism, followed by fast electron transfer and successor decomposition, and that the activation mode into the transition state should be associative. The systems with smaller values of activation entropy are expected to show more associative I_a behavior. In fact, ΔV^{*} values parallel those of ΔS^{*} is the present two systems.

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Registry No. H_2O_2, 7722-84-1; $VO(nta)(H_2O)^-$, 12347-63-6; $VO(pda)(H_2O)_2$, 18582-04-2.

Supplementary Material Available: Table S1 giving rate constants under various conditions [(1) hydrogen peroxide dependence, (2) hydrogen ion dependence, (3) excess PDA dependence, (4) temperature dependence, (5) propan-2-ol effect, and (6) pressure dependence] and Figure 3 showing isokinetic relationship (9 pages). Ordering information is given on any current masthead page.

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[32] Anbar, M.; Neta, P. *Int. J. Appl. Radiat. Isot.* **1967**, *18*, 493.

[33] Wilkins, R. G. "The Study of Kinetics and Mechanism of Reactions of Transition Metal Complexes"; Allyn and Bacon: Boston, 1974; pp 269–274.

[34] Swaddle, T. W. *Coord. Chem. Rev.* **1974**, *14*, 217.

[35] Nishizawa, M.; Saito, K. *Inorg. Chem.* **1978**, *17*, 3676.

[36] Nishizawa, M.; Saito, K. *Inorg. Chem.* **1980**, *19*, 2284.

[37] Reference 33, pp 100–101.