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Preparation and Characterization of Dipicolinatovanadium(V) Complexes. Kinetics and Mechanism of Their Reaction with Hydrogen Peroxide in Acidic Media

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The preparation and characterization of a dipicolinatooxovanadium(V) complex and a protonated form containing μ -hydroxo bridges are reported. Formation of $[\text{VO}(\text{O}_2)(\text{dipic})\text{H}_2\text{O}]^-$ was monitored for the reaction of this complex which appears to be trimeric in solution with H_2O_2 . With the trimer in excess first-order rate constants k_{obsd} , $[\text{H}^+] = 0.1\text{--}1.0\text{ M}$, fit a rate dependence of $k_{\text{obsd}} = k_a K [\text{H}^+] [\text{trimer}] / (1 + K [\text{H}^+])$, where K , the trimer protonation constant, is 1.37 M^{-1} and k_a for reaction of the protonated complex is $5.25 \times 10^3\text{ M}^{-1}\text{ s}^{-1}$; $\Delta H_a^\ddagger = 5.6\text{ kcal mol}^{-1}$ and $\Delta S_a^\ddagger = -23\text{ cal K}^{-1}\text{ mol}^{-1}$ at 25°C , $\mu = 1.0\text{ M}$ (LiClO_4). At low $[\text{H}^+]$, $10^{-3}\text{--}6.2 \times 10^{-5}\text{ M}$, the unprotonated form reacts with H_2O_2 (k_b) and the much stronger nucleophile HO_2^- (k_c): rate = $(k_b + k_c K_{\text{H}_2\text{O}_2} / [\text{H}^+]) [\text{H}_2\text{O}_2] [\text{trimer}]$, where $K_{\text{H}_2\text{O}_2}$ is the dissociation constant of H_2O_2 ($\sim 10^{-12}\text{ M}$), $k_b = 1.1\text{ M}^{-1}\text{ s}^{-1}$, and $k_c \approx 10^8\text{ M}^{-1}\text{ s}^{-1}$ at 25°C , $\mu = 1.0\text{ M}$. Two different transient diperoxovanadium(V) complexes (HO_2^- being coordinated as a monodentate ligand) are formed with excess H_2O_2 from dipicolinatovanadium(V) fragments which have been generated after reaction of the trimer with one H_2O_2 ligand and subsequent bridge-cleavage processes (rate-determining steps). Each of these diperoxo species is converted to the final $[\text{VO}(\text{O}_2)(\text{dipic})\text{H}_2\text{O}]^-$ product via two kinetically distinguishable steps: rate = $\{1/(a + b[\text{H}_2\text{O}_2])\} [\text{H}^+] [\text{diperoxovanadium(V)}]$. This is consistent with the proton-assisted dissociation of one H_2O_2 ligand and formation of an intermediate monoperoxovanadium(V) complex which is then transformed to the resulting complex V independently of $[\text{H}_2\text{O}_2]$ and inversely dependent on $[\text{H}^+]$ via an intramolecular process. This process is tentatively assigned to the intramolecular ring closure of the peroxo ligand.

Introduction

Kinetic and mechanistic studies of the formation of peroxovanadium(V) complexes in aqueous solution are scarce. Tanaka et al. reported the reaction of (*N*-methyliminodiacetato)dioxovanadate(V) with H_2O_2 in the pH range 3–4 (only an acid independent path was detected).¹⁶ Orhanović and Wilkins reported the kinetics of formation of a red monoperoxovanadium(V) complex from the reaction of the aquated VO_2^+ cation with H_2O_2 again over a limited range of $[\text{H}^+]$ only, 0.1–2.0 M.¹ The complexity of the observed rate law (a dependence on $[\text{H}^+]$, first order and inverse first order, and an $[\text{H}^+]$ -independent path was observed) did not allow detailed mechanistic assignments to be made. The main obstacle appears to be uncertainty regarding the precise nature of the vanadium(V) species present in acidic solution. At the outset of this study we sought to find a simple reaction where the structure of the complex in solution is known and if possible stable over a wide range of H^+ concentrations and where the produced monoperoxo complex is subjected to the same conditions. At least the latter condition seemed to be met by the reaction of pyridine-2,6-dicarboxylic acid (dipicolinic acid, dipic)—a tridentate ligand—and vanadium(V) with H_2O_2 yielding quantitatively the monoperoxovanadium(V) complex $[\text{VO}(\text{O}_2)(\text{dipic})\text{H}_2\text{O}]^-$. Hartkamp had developed this reaction as an efficient and rapid analytical tool for the quantitative determination of small vanadium concentrations.² The structure of the complex has been determined by an x-ray analysis of the ammonium salt to be as in structure V.³

On the other hand, preparative and structural details on the precursor complex containing only vanadium(V) and dipicolinic acid as ligand were not available except for a brief note on the existence of a colorless " $\text{NH}_4[\text{V}(\text{O})_2(\text{dipic})]$ " salt.⁴ The preparation and characterization of what will be shown to be most probably a monomeric dipicolinatovanadium(V) complex in the solid state but trimeric in solution and the kinetics of its reaction with hydrogen peroxide over a wide range of H^+ concentrations are reported in this paper.

Experimental Section

Material and Apparatus. The infrared spectra were recorded on a Beckman IR 12 spectrophotometer as KBr disks. Raman spectra were recorded on a Coderg LRT 800 laser-Raman spectrophotometer using the 514.5-nm exciting line of an Ar-ion laser (Spectra Physics 164). Solid samples were mounted in a spinning cell. UV-visible spectra were recorded on a UNICAM SP 8-100 spectrophotometer.

Triply distilled water was used to make up stock solutions for kinetic experiments. Lithium perchlorate, obtained by neutralization of Li_2CO_3 with perchloric acid, was recrystallized three times. Analytical grade NH_4VO_3 , V_2O_5 , and dipicolinic acid were obtained commercially and used as received. Both stabilized and nonstabilized hydrogen peroxide (prepared from BaO_2 and sulfuric acid) were used. No significant difference of kinetic results was detected. Stock solutions of hydrogen peroxide were titrated by reacting a known volume of the H_2O_2 solution with excess KI in 1 M sulfuric acid and back-titration of I_2 with 0.1 M $\text{Na}_2\text{S}_2\text{O}_3$.

Preparation of Complexes. Elemental analyses were performed for all complexes and are summarized in Table I.¹⁹

1. $\text{NH}_4[\text{V}(\text{O})_2(\text{dipic})]$. This complex has been reported previously without experimental details.⁴ Quantities of 11.6 g of NH_4VO_3 and 16.7 g of pyridine-2,6-dicarboxylic acid (dipicolinic acid, dipic) in 100 mL of water were heated to 80°C until a yellow solution resulted which was cooled to 0°C . Nearly colorless crystals of the desired product precipitated which were filtered off and washed with ethanol and ether.

2. $\text{K}[\text{V}(\text{O})_2(\text{dipic})]$. Quantities of 4.5 g of V_2O_5 and 8.3 g of dipicolinic acid were dissolved in 200 mL of H_2O at 70°C . To the cooled (15°C) and filtered solution 2 drops of 30% H_2O_2 and a saturated solution of KCl were added in small amounts until the precipitation of colorless crystals started. This solution was kept at 0°C for a few hours. The crystals were filtered off and washed with ethanol and ether. The infrared spectrum of this material exhibits no absorption in the $4000\text{--}3100\text{-cm}^{-1}$ region ($\nu(\text{O-H})$ stretching frequencies). In a dry atmosphere of nitrogen no loss of weight was observed up to 200°C .

3. $\text{Cs}[\text{V}(\text{O})_2(\text{dipic})]$. The cesium salt was prepared as the potassium salt but a concentrated solution of CsCl was used instead of KCl and the total reaction volume was only 80 mL. Well-developed, transparent colorless crystals, which contain 0.5 mol of water of crystallization, can be grown if the temperature of a saturated solution of the cesium salt is slowly decreased from 25 to 0°C ($0.5^\circ/\text{h}$).

4. $\text{H}[\text{V}(\text{O})_2(\text{dipic})]\cdot 2\text{H}_2\text{O}$. Quantities of 4.5 g of V_2O_5 and 8.3 g of dipicolinic acid were dissolved in 50 mL of water at 70°C , and a few drops of 30% H_2O_2 was added. To the cooled (0°C) and filtered solution 50 mL of ice-cold concentrated perchloric acid was added with stirring and efficient cooling. The solution was kept in the refrigerator for 12 h. Bright yellow crystals were filtered off and washed rapidly with a minimum amount of ice-cold acetone and ether. The complex is soluble in H_2O and ethanol and slightly soluble in acetone.

5. $\text{H}[\text{V}(\text{O})_2(\text{dipic})]\cdot \text{C}_2\text{H}_5\text{OH}$. The above protonated complex was dissolved in a minimum amount of 90% ethanol at 30°C . The cooled solution (-10°C) was allowed to stand in the refrigerator for 14 h. Bright yellow crystals precipitated which contained one molecule of alcohol of crystallization per vanadium(V) ion.

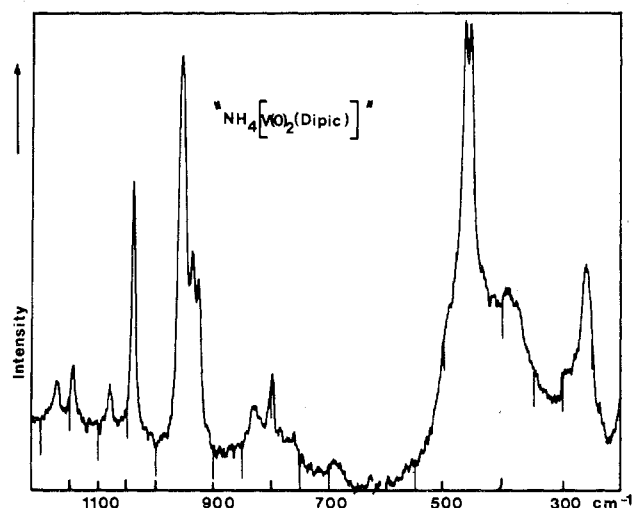


Figure 1. Raman spectrum of solid " $\text{NH}_4[\text{V}(\text{O})_2(\text{dipic})]$ ".

6. $\text{K}[\text{VO}(\text{O})_2(\text{dipic})]\cdot 2\text{H}_2\text{O}$. Quantities of 4.5 g of V_2O_5 and 8.3 g of dipicolinic acid were dissolved in 100 mL of water at 70°C . To the cooled solution (15°C) 5 mL of 30% H_2O_2 was added. A saturated solution of KCl in H_2O was added dropwise until precipitation of red-orange crystals started. The solution was then cooled to 0°C . The crystals were filtered off and washed with ethanol and ether. The complex is stable for weeks if kept in a dark bottle at 0°C .

7. $\text{H}[\text{VO}(\text{O})_2(\text{dipic})\text{H}_2\text{O}]\cdot \text{H}_2\text{O}$. Quantities of 4.5 g of V_2O_5 and 8.3 g of dipicolinic acid were dissolved in 30 mL of water at 70°C . To the cooled solution (15°C) 6 mL of 30% H_2O_2 was added. The deep red solution was cooled to -5°C and 40 mL of ice-cold concentrated perchloric acid was added. Great care was taken to ensure that the temperature never exceeded 0°C in order to prevent decomposition of the red monoperoxovanadium complex with O_2 evolution. This solution was allowed to stand at -5°C in the refrigerator for 24 h. Large red-orange crystals precipitated which were filtered off and washed rapidly with a minimum amount of cold acetone and ether. The complex decomposes at room temperature within hours but is perfectly stable at -5°C . The complex is extremely soluble in H_2O and moderately so in acetone and ethanol.

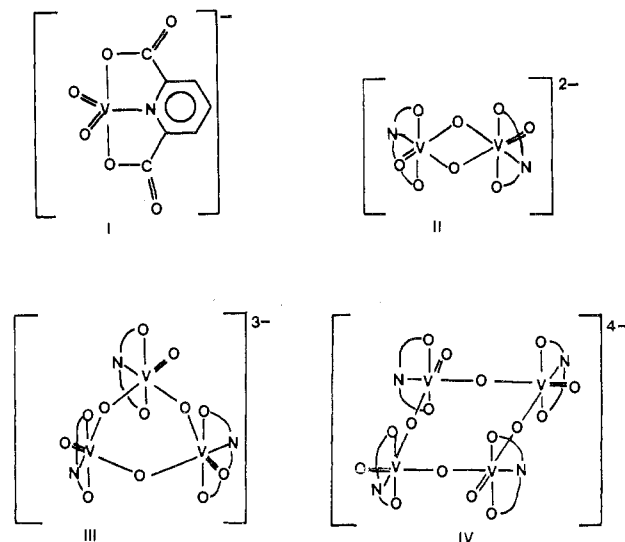
Kinetic Measurements. Fast kinetic runs were followed on a Durrum stopped-flow spectrophotometer; slower runs were measured by conventional spectrophotometric methods. The formation of the red monoperoxovanadium(V) species V was studied by measuring the increase of absorbance at λ 432 nm (ϵ 456 $\text{L mol}^{-1} \text{cm}^{-1}$) as a function of time. A solution containing the desired concentrations of perchloric acid, lithium perchlorate as supporting electrolyte, and $\text{NH}_4[\text{V}(\text{O})_2(\text{dipic})]$ was generally mixed with a second solution containing hydrogen peroxide only. Identical results were obtained by mixing a solution now containing HClO_4 , LiClO_4 , and H_2O_2 with an aqueous solution of the vanadium(V) complex. In a separate experiment a solution of 2 M HClO_4 was mixed in the stopped-flow apparatus with a 2×10^{-3} M aqueous solution of complex. No change of absorbance at λ 340 nm ($\epsilon \sim 200$ for the protonated form and ~ 65 $\text{L mol}^{-1} \text{cm}^{-1}$ for the deprotonated form of the complex) on the stopped-flow time scale was observed. This indicates that the equilibrium of protonated and unprotonated forms (vide infra) is established rapidly.

Values of pseudo-first-order rate constants were obtained from the slopes of $\ln(A_t - A_\infty)$ vs. time plots, where A_t is the absorbance at time t and A_∞ that after the reaction is complete. Such plots were linear for ca. 6 half-lives. When H_2O_2 is the excess component, two or three stages of the reaction are observed depending on the actual $[\text{H}^+]$ and $[\text{H}_2\text{O}_2]$. It has been possible to evaluate pseudo-first-order rate constants for all stages from such traces applying a standard consecutive-reaction treatment.⁵

Results

Preparation and Characterization of Complexes. Pyridine-2,6-dicarboxylic acid reacts in aqueous solution with NH_4VO_3 to form a nearly colorless crystalline complex of the analytical composition $\text{NH}_4[\text{V}(\text{O})_2(\text{dipic})]$.⁴ Reaction of V_2O_5 and dipicolinic acid in aqueous solution yields upon addition of KCl or CsCl the corresponding potassium salt, $\text{K}[\text{V}(\text{O})_2(\text{dipic})]$, or $\text{Cs}[\text{V}(\text{O})_2(\text{dipic})]$. The three salts do not contain water of crystallization or coordinated H_2O . No loss of weight occurs when they are heated in an atmosphere of dry nitrogen to 200°C . The structure of the complex anion is not known. A five-coordinate monomeric species I con-

taining a *cis*-dioxovanadium(V) entity is conceivable⁶ as well as dimeric, II, trimeric, III, or tetrameric, IV,^{6c} anions assuming six-coordinate vanadium(V) centers. A higher degree of polymerization is not considered to be likely in view of the good solubility of all salts in water.



From the infrared and Raman spectra of the NH_4^+ , K^+ , and Cs^+ salts which are very similar it is concluded that the dipicolinic anion is bonded as a tridentate ligand via two oxygen atoms of the carboxylic groups ($\nu(\text{C}=\text{O})$ 1690 (vs), 1705 (vs) cm^{-1} ; $\nu(\text{C}-\text{O})$ 1345 (s), 1340 (vs) cm^{-1}) and the heterocyclic nitrogen. It has been possible to discern frequencies due to the coordinated organic ligand from those of the vanadium(V)-oxygen polyhedron by comparison with spectra of $\text{K}[\text{Co}(\text{dipic})_2]$ ⁷ or $\text{NH}_4[\text{Cr}(\text{dipic})_2]$.⁸ The observed frequencies (other than ligand bands) and their assignments are listed in Table II.¹⁹ The Raman spectrum of solid $\text{NH}_4[\text{V}(\text{O})_2(\text{dipic})]$ is shown in Figure 1. The bands arising from vanadium-oxygen (double bond) vibrations are intense and characteristic in the Raman spectrum. A *cis*-dioxo complex I is expected to exhibit a strong polarized band near 950 cm^{-1} ($\nu_s(\text{V}=\text{O})$), and a band of moderate intensity near 900 cm^{-1} ($\nu_{as}(\text{V}=\text{O})$, depolarized).⁹ The IR and Raman spectra of the solid salts are consistent with such an assignment. The intense band at 457 (s, p) cm^{-1} can be assigned to the $\delta(\text{VO}_2)$ deformation frequency. From the kinetic data (vide infra) of the reaction of the complex anion with H_2O_2 it follows that in solution a trimeric species is present. Structure III is proposed where three vanadium(V) ions with a terminal oxygen atom are bonded via three oxo bridges.

A bright yellow microcrystalline compound precipitates from concentrated aqueous solutions of dipicolinic acid and V_2O_5 (1 mol of ligand and 0.5 mol of V_2O_5) upon adding concentrated perchloric acid at -5°C . Aqueous solutions of this species react strongly acidic. From the elemental analysis (Table I) the composition $\text{H}[\text{V}(\text{O})_2(\text{dipic})]\cdot 2\text{H}_2\text{O}$ can be deduced. Recrystallization of this complex from aqueous ethanol (90%) yields a different yellow product, $\text{H}[\text{V}(\text{O})_2(\text{dipic})]\cdot \text{C}_2\text{H}_5\text{OH}$, which contains one molecule of alcohol of crystallization per vanadium(V) which is released when heated in dry nitrogen ($P = 1$ atm) at 97°C . The latter material is better crystallized, and only of this species has it been

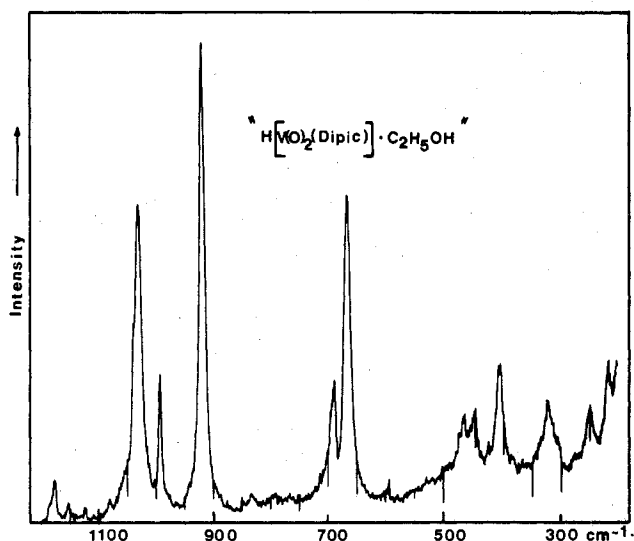
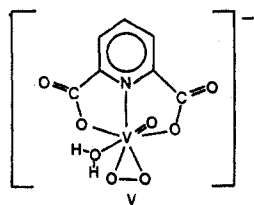


Figure 2. Raman spectrum of solid "H[VO₂(dipic)]·C₂H₅OH".

possible to obtain a Raman spectrum of good quality which is shown in Figure 2. The infrared spectra of both protonated forms exhibit ligand bands at the same wavenumbers as the unprotonated potassium salt indicating that protonation does not occur at the complex-bonded carboxylic groups. This has been discussed previously for a protonated form of the [V(O)₂(C₂O₄)₂]³⁻ ion.¹¹ The presence of a terminal oxo group, V=O, is indicated by a single strong ν (V=O) stretching frequency at 915 cm⁻¹ in the Raman spectrum (Figure 2, the band at 1032 cm⁻¹ is a ligand band). The new bands in the Raman spectrum as compared to the spectrum shown in Figure 1 can be assigned to bridging hydroxo groups: δ (V(OH)V) at 994 cm⁻¹ and ν (V-OH) at 692 (w) and 667 (s) cm⁻¹. This assignment is supported by the fact that the strong δ (VO₂) modes at 452 and 463 cm⁻¹ of the oxo-bridged species are not observed. No information has been obtained concerning the degree of polymerization. Indeed, the observed differences in the infrared spectra of the ethanol-containing sample and the one with two molecules of water of crystallization may be due to different degrees of polymerization.

Vanadium(V) reacts quantitatively with excess dipicolinic acid and excess H₂O₂ in acidic aqueous solution to give the red monomeric monoperoxo complex [VO(O₂)(dipic)H₂O]⁻.^{2,4} The structure of this anion, V, has been established by an x-ray



analysis of the NH₄⁺ salt.³ By reacting V₂O₅, dipicolinic acid, and H₂O₂ and adding a saturated solution of KCl, the potassium salt K[VO(O₂)(dipic)H₂O]·2H₂O has been obtained as well-developed orange-red crystals. It is noted that the infrared-active ν (V=O) stretch frequency of the solid salt is split (Table II)¹⁹ which can only be due to crystal-field effects. The spectrum is in reasonable agreement with that reported for NH₄[VO(O₂)(dipic)H₂O]·H₂O.^{12,13}

If the above reaction mixture is treated with concentrated perchloric acid at -5 °C instead of a KCl solution, large red crystals are obtained which have the composition H[VO(O₂)(dipic)H₂O]·H₂O. These crystals decompose at room temperature with evolution of oxygen. At -5 °C they can be kept for a few days. In the infrared spectrum no bands due to the terminal V=O moiety are detected whereas the

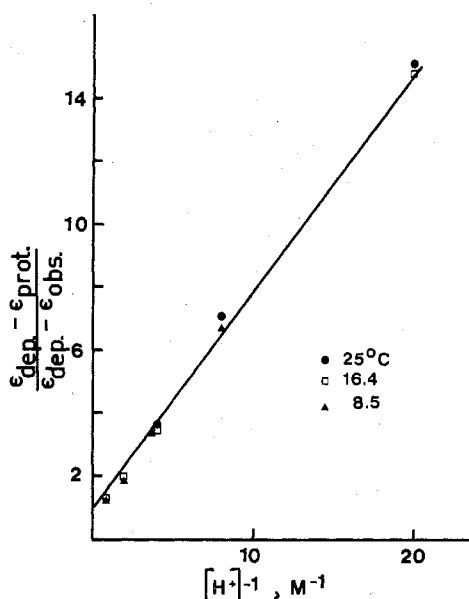
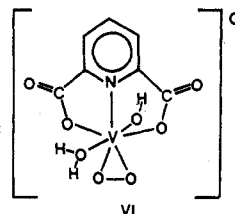


Figure 3. Determination of the constant K for protonation of "NH₄[VO₂(dipic)]", $\mu = 1.0$ M (LiClO₄), according to eq 1.

wavenumbers of characteristic bands of the coordinated carboxylic groups are found to be unchanged compared with the spectrum of III. Therefore, it is concluded that protonation of the complex anion V takes place at the terminal oxygen atom (V=O) and a structure as in VI is proposed.

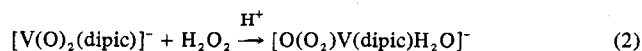


Determination of a Protonation Constant. At wavelengths <350 nm an intense charge-transfer band is observed which shows a bathochromic shift upon protonation of the complex III. Thus a solution of the complex ($\sim 10^{-3}$ M) in 1 M perchloric acid is yellow. The variation in the spectrum at 340 nm with [H⁺] (0.06–1.0 M) was used for determining a protonation constant (K , M⁻¹) of the complex anion at an ionic strength of 1.0 M using LiClO₄ as supporting electrolyte. Absorption coefficients ϵ_{dep} (unprotonated complex), ϵ_{prot} (protonated complex), and ϵ_{obsd} (measured at various [H⁺]) are related by expression 1. Values of ϵ_{prot} and ϵ_{dep} were

$$\frac{\epsilon_{\text{dep}} - \epsilon_{\text{prot}}}{\epsilon_{\text{dep}} - \epsilon_{\text{obsd}}} = \frac{1}{K[\text{H}^+]} + 1 \quad (1)$$

measured by dissolving the complex in 6 M HClO₄ and 1 M LiClO₄, respectively. Within experimental error limits ϵ_{dep} , ϵ_{prot} , and ϵ_{obsd} were found to be independent of the temperature (8.5–25 °C). Figure 3 shows a linear plot of the left-hand side of eq 1 vs. [H⁺]⁻¹. From the slope a value for K was evaluated using a least-squares program (the origin was held fixed at +1 according to eq 1): $K = 1.37 \pm 0.05$ M⁻¹ ($\mu = 1.0$ M (LiClO₄), 8.5–25 °C).

Kinetics of the "NH₄[VO₂(dipic)]"–H₂O₂ Reaction. (a) Kinetics in Acidic Perchlorate Media, [H⁺] 1.0–0.1 M. The kinetics of the formation of the red monoperoxo species V from "NH₄[VO₂(dipic)]" and hydrogen peroxide in perchloric acid media (eq 2) were studied at λ 432 nm (charge-transfer



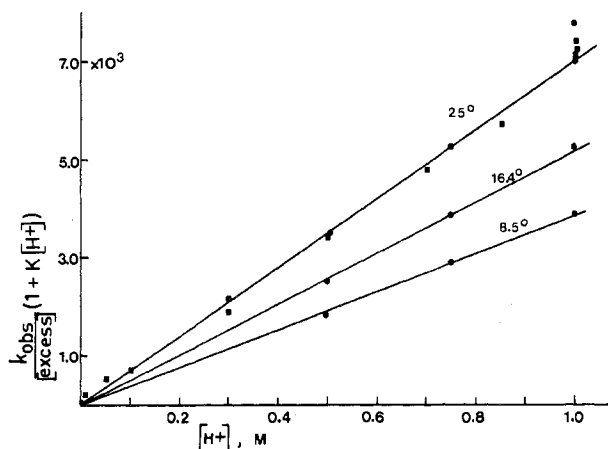


Figure 4. Dependence of k_{obsd} for the first rapid stage of the " $\text{NH}_4[\text{V}(\text{O})_2(\text{dipic})]$ "- H_2O_2 reaction on $[\text{H}^+]$, eq 3. [excess] denotes $[\text{H}_2\text{O}_2]$ (\bullet) or $1/3 [\text{V}]_{\text{T}}$ (\blacksquare) is the excess component using pseudo-first-order conditions.

maximum of V), 25 °C, and an ionic strength of 1.0 M (adjusted with LiClO_4). Stopped-flow traces were obtained using pseudo-first-order conditions with the total vanadium(V) concentration in at least 15-fold excess over H_2O_2 . Under these conditions only a single stage of the reaction was observed. Pseudo-first-order rate constants, k_{obsd} (s^{-1}), are listed in Table III.¹⁹ A first-order dependence on the vanadium(V) concentration was established as in eq 3 ($[\text{V}]_{\text{T}} = 2.5 \times 10^{-3}$ – 2.5×10^{-2} M; $[\text{V}]_{\text{T}}$ denotes the total concentration of vanadium(V) irrespective of possible polymeric structures of the complex). On varying the H^+ concentration, $[\text{H}^+] = 0.01$ – 1.0 M, a nonlinear dependence on $[\text{H}^+]$ was observed:

$$\text{rate} = k[\text{V}]_{\text{T}}[\text{H}_2\text{O}_2]$$

$$k = \frac{k_a K [\text{H}^+]}{1 + K [\text{H}^+]} \quad (3)$$

k_a is the rate constant for the reaction of the protonated complex with H_2O_2 and K is the equilibrium constant for the protonation. A plot of $(k_{\text{obsd}}/[\text{V}]_{\text{T}})(1 + K[\text{H}^+])$ vs. $[\text{H}^+]$ is linear using the value of 1.37 M^{-1} of the spectrophotometrically determined protonation constant. The slope of this straight line is $2360 \text{ M}^{-1} \text{ s}^{-1}$.

In a second set of experiments the first-order dependence of the rate on $[\text{H}_2\text{O}_2]$ was established using pseudo-first-order conditions with $[\text{H}_2\text{O}_2]$ in at least 10-fold excess over $[\text{V}]_{\text{T}}$ at 25 °C and $\mu = 1.0 \text{ M}$ (Table III).¹⁹ Under these conditions ($[\text{H}^+] = 0.3$ – 1.0 M) three distinct stages of the reaction are discernible. At $\lambda 430 \text{ nm}$ the absorbance increases 3 times. But at $\lambda 340 \text{ nm}$ only the first rapid stage is accompanied by an increase of absorbance whereas a decrease is observed for the slower second and third stages. Only the kinetics of the first rapid step exhibit a first-order dependence on $[\text{H}_2\text{O}_2]$ and the same nonlinear dependence on $[\text{H}^+]$ as before when vanadium(V) has been the excess component. The plot of $(k_{\text{obsd}}/[\text{H}_2\text{O}_2])(1 + K[\text{H}^+])$ vs. $[\text{H}^+]$ is linear using again the value 1.37 M^{-1} for the protonation constant K , but the numerical value of the slope of this straight line, $7193 \text{ M}^{-1} \text{ s}^{-1}$, is 3 times that obtained for the slope if $[\text{V}]_{\text{T}}$ is in excess. This is regarded as kinetic evidence that the vanadium(V) complex is trimeric in solution as is shown in structure III. If the concentration of complex is one-third of the total V(V) concentration, the observed rate law is as in eq 3 irrespective of the actual excess concentration.

The temperature dependence of the rate of this first stage has been studied at 25, 16.4, and 8.5 °C. From the slopes of the straight lines ($=k_a K$) in Figure 4 second-order rate constants, k_a ($\text{M}^{-1} \text{ s}^{-1}$), for the reaction of the protonated

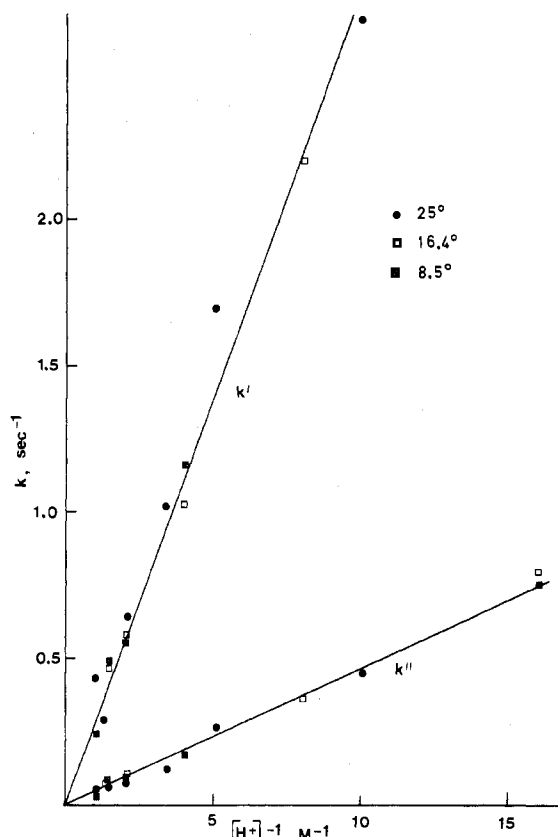


Figure 5. Dependence of k' and k'' for the second and third stages of the " $\text{NH}_4[\text{V}(\text{O})_2(\text{dipic})]$ "- H_2O_2 reaction on $[\text{H}^+]^{-1}$, eq 4 and 5.

trimeric vanadium(V) complex have been determined (Table VI).¹⁹ From these the activation parameters were calculated using a least-squares program: $\Delta H_a^\ddagger = 5.6 \pm 0.6 \text{ kcal mol}^{-1}$ and $\Delta S_a^\ddagger = -23 \pm 2 \text{ cal K}^{-1} \text{ mol}^{-1}$.

The second and third stages of the reaction are observed only when H_2O_2 is in large excess over complex concentration and $[\text{H}^+] = 0.1$ – 1.0 M . First-order rate constants, k' and k'' (s^{-1}), were obtained from stopped-flow traces and are listed in Table IV.¹⁹ k' and k'' were found to be independent of $[\text{H}_2\text{O}_2]$ ($(2.1$ – $21.3) \times 10^{-3} \text{ M}$), and on varying $[\text{H}^+]$, 0.1– 1.0 M , an inverse dependence on $[\text{H}^+]$ was observed as in eq 4

$$\text{rate} = a[\text{I}_1][\text{H}^+]^{-1} \quad (4)$$

$$\text{rate} = b[\text{I}_2][\text{H}^+]^{-1} \quad (5)$$

and 5 where $[\text{I}_1]$ and $[\text{I}_2]$ denote the concentrations of the intermediates of unknown structures. Small variations of the starting complex concentration, $[\text{V}]_{\text{T}} = (1.0$ – $5.0) \times 10^{-4} \text{ M}$, at constant $[\text{H}^+]$ had no effect on the rates of the second and third stages of the reaction. Figure 5 shows a plot of k' and k'' vs. $[\text{H}^+]^{-1}$ at three temperatures. Values of $a = 0.265 \pm 0.02 \text{ M s}^{-1}$ and $b = (4.97 \pm 0.01) \times 10^{-2} \text{ M s}^{-1}$ were evaluated from the slopes of the straight lines. The values a and b are within experimental error independent of the temperature range 8.5–25 °C.

(b) Kinetics in Acidic Perchlorate Media, $[\text{H}^+] = 0.05$ – $6.2 \times 10^{-5} \text{ M}$. At low H^+ concentrations, 10^{-3} – $6.2 \times 10^{-5} \text{ M}$, the first observable stage of the reaction on the stopped-flow time scale is again first-order in $[\text{H}_2\text{O}_2]$ and [complex III], respectively. The rate of reaction appears to be accelerated at low $[\text{H}^+]$. It has not been possible to establish this reaction step over a wide range of $[\text{H}^+]$ as would have been desirable. Indeed, only kinetic runs at $[\text{H}^+] = 0.001$ and 0.0005 M were executed in acidic perchlorate media with excess H_2O_2 over complex ($[\text{V}]_{\text{T}} = 10^{-4} \text{ M}$). A few experiments were carried

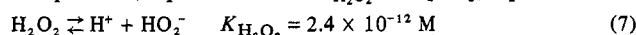
Table V. Pseudo-First-Order Rate Constants k^4 and k^5 of the "[V(O)₂(dipic)]⁻-H₂O₂ Reaction at [H⁺] = 0.05–0.0005 M and Excess H₂O₂ over Complex^a

T, °C	[H ⁺], M	10 ² [H ₂ O ₂], M	k^4 , s ⁻¹	10 ³ k^5 , s ⁻¹
16.4	0.001	2.75	Not determined	2.48
		5.5		1.55
		11.0		0.83
25.0	0.05	0.225	Not detected	720
		1.10		1.08
		2.50		0.94
		5.00		0.63
		7.50		0.56
		9.00		0.54
		15.00		0.33
0.01	0.01	0.225	Not detected	135
		1.10		0.184
		9.00		0.101
0.005	0.005	0.44	0.092	44.0
		1.10		22.3
		2.75		9.91
		5.50		5.86
		11.00		4.0
		0.001		0.44
0.0005	0.0005	2.75	0.092	3.76
		5.50		2.21
		11.00		1.15
		0.44		4.00
35.6	0.001	5.50	0.092	1.12
		11.00		0.60
		0.44		20.62
		2.75		6.66
		5.50		3.47
		11.00		1.96

^a [Complex] = 1 × 10⁻⁴ M; μ = 1.0 M.

out in an innocuous acetate buffer, 0.1 M, at 25 °C and μ = 1.0 M (LiClO₄), which confirmed the first-order dependence on [H₂O₂] and the trimeric nature of the reacting complex III in this medium. In Table VII pseudo-first-order rate constants k'_{obsd} (s⁻¹) are summarized. A plot of $k'_{\text{obsd}}/[H_2O_2]$ vs. [H⁺]⁻¹ (Figure 8) is reasonably linear according to eq 6 rate = ($k_b + k_c K_{H_2O_2} [H^+]^{-1}$)[H₂O₂][complex] (6)

taking into account the relatively large uncertainty of [H⁺] of the buffered reaction medium which was determined potentiometrically with a glass electrode. At [H⁺] < 0.001 M the predominant species of complex is its unprotonated form III which does not contain acidic protons. Therefore, the inverse dependence of the rate on [H⁺] is only consistent with a mechanism where the strong nucleophile HO₂⁻ reacts with complex III, eq 7–9. Since $K_{H_2O_2} \ll [H^+]$, eq 10 reduces



$$\frac{d[III]}{dt} = \left(\frac{k_b [H^+] + k_c K_{H_2O_2}}{K_{H_2O_2} + [H^+]} \right) [H_2O_2][III] \quad (10)$$

Table VI. Summary of Kinetic Data of the "[V(O)₂(dipic)]⁻-H₂O₂ Reaction^a

	8.5 °C	16.4 °C	25.0 °C	35.6 °C
k_a (eq 3), M ⁻¹ s ⁻¹ ^b	2.86 × 10 ³	3.83 × 10 ³	5.25 × 10 ³	
a (eq 4), M ⁻¹ s ⁻¹	0.265	0.265	0.265 ± 0.02	
b (eq 5), M ⁻¹ s ⁻¹	0.049	0.049	0.049 ± 0.001	
k_b (eq 10), M ⁻¹ s ⁻¹			1.1	
$k_c K_{H_2O_2}$ (eq 10), s ⁻¹			5.3 × 10 ⁻⁴	
c (eq 11), M s			0.041 ± 0.003	
d (eq 11), s			0.68 ± 0.04	
e (eq 12), M s		0.103 ± 0.02	0.067 ± 0.02	0.033 ± 0.01
f (eq 12), M s		9.99 ± 0.3	7.15 ± 0.2	4.39 ± 0.1

^a μ = 1.0 M (LiClO₄). ^b Activation parameters: $\Delta H_a^\ddagger = 5.6 \pm 0.6 \text{ kcal mol}^{-1}$; $\Delta S_a^\ddagger = -23 \pm 2 \text{ cal K}^{-1} \text{ mol}^{-1}$.

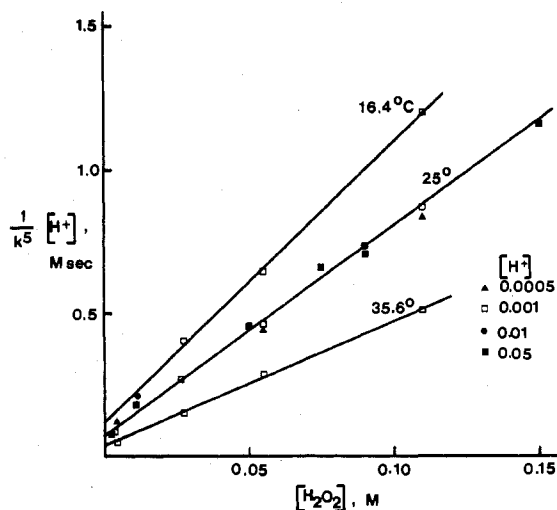


Figure 6. Dependence of k^5 for the slowest step of the "[NH₄[V(O)₂(dipic)]⁻-H₂O₂ reaction on [H₂O₂], eq 12.

to eq 6. From the slope of the straight line (Figure 8) and intercept, values for k_b (1.1 M⁻¹ s⁻¹) and $k_c K_{H_2O_2}$ (5.3×10^{-4} s⁻¹) were determined.

At [H⁺] below 0.05 M and large excess of H₂O₂ over complex III two new steps of the reaction become kinetically relevant. At 430 nm increases in absorbance are observed but at 340 nm two subsequent decreases are observed. Both steps exhibit an *inverse* dependence on [H₂O₂] and a first-order dependence on [H⁺]. The functional dependence of measured pseudo-first-order rate constants k^4 and k^5 (s⁻¹) conforms to eq 11 and 12 (Table V). k^5 in the [H⁺] range 0.005–0.0005

$$k^4 = \frac{1}{c + d[H_2O_2]} [H^+] \quad (11)$$

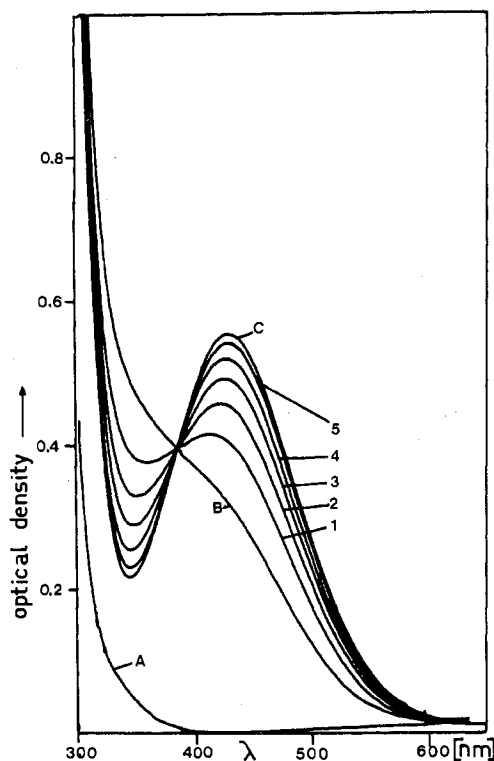
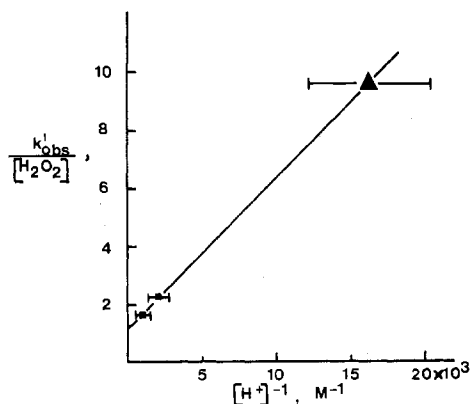
$$k^5 = \frac{1}{e + f[H_2O_2]} [H^+] \quad (12)$$

M has been determined by conventional spectroscopic methods from the slopes of $\ln(A_\infty - A_t)$ vs. time plots where A_t is the absorbance at time t and A_∞ that 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 [VO(O₂)(dipic)H₂O]⁻ (λ_{max} 432 nm, ϵ 456 L mol⁻¹ cm⁻¹). Figure 6 shows a plot of $(1/k^5)[H^+]$ vs. [H₂O₂] at 16.4, 25, and 35.4 °C which is linear. Slopes (d or f) of such straight lines and intercepts (c or e) were determined by means of a least-squares program (Table VI).

At [H⁺] = 0.001 M and [H₂O₂] = 0.3 M the last steps of the reaction are sufficiently slow to enable a conventional scan spectrum to be recorded (Figure 7). An isosbestic point at 385 nm is retained throughout the reaction. Spectrum B is

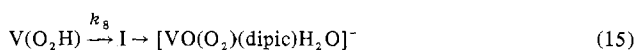
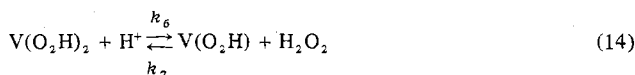
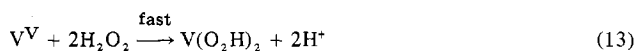
Table VII. Pseudo-First-Order Rate Constants, k'_{obsd} , for the First Stage of the "[V(O)₂(dipic)]⁻-H₂O₂ Reaction at Low [H⁺]^a

[H ⁺], M	10 ² [H ₂ O ₂], M	10 ³ [V ^V] _T , M	k'_{obsd} , s ⁻¹
0.001	15.0	0.2	0.25
0.001	7.5	0.2	0.14
0.0005	11.0	0.2	0.26
0.0005	5.50	0.2	0.125
0.0005	2.75	0.2	0.068
6.2 × 10 ⁻⁵	15.0	0.2	1.35
6.2 × 10 ⁻⁵	7.5	0.2	0.66
6.2 × 10 ⁻⁵	1.25	0.2	0.17
6.2 × 10 ⁻⁵	0.001	26.0	0.14
6.2 × 10 ⁻⁵	0.001	7.0	0.03

^a T = 25 °C; μ = 1.0 M (LiClO₄).**Figure 7.** Scan spectrum of the "NH₄[V(O)₂(dipic)]-H₂O₂ reaction at 20 °C, μ = 1.0 M (LiClO₄) ([H⁺] = 0.001 M, [V]_T = 3 × 10⁻⁴ M, [H₂O₂] = 0.3 M). Curve A is the spectrum of the unreacted complex (3 × 10⁻⁴ M); spectrum B is obtained 20 s after mixing of reactants; spectra 1-5 were recorded after 2, 4, 7, 12, and 21 min and C is the final spectrum of [VO(O₂)(dipic)H₂O]⁻.**Figure 8.** Dependence of $k'_{\text{obsd}}/[H_2O_2]$ for the first stage of the "NH₄[V(O)₂(dipic)]⁻-H₂O₂ reaction on [H⁺]⁻¹ at 25 °C, eq 6: ▲, measurements in acetate buffer (0.1 M) solution at μ = 1.0 M (LiClO₄); ■, measurements in acidic perchlorate media.

obtained 20 s after mixing of reactants. Curve A is the spectrum of unreacted complex III in 0.001 M perchloric acid and curve C is that of the final product V. From eq 11 and 12 the half-lives of the reaction rates are estimated to be 3 and 25 min at 25 °C. Therefore, a substantial portion of spectrum B must arise from transient species which are rapidly formed. The presence of an isosbestic point (Figure 7) suggests that under the present experimental conditions predominantly one intermediate B species is formed which is transformed to a C species according to eq 11.

It is proposed that after the trimeric complex III has reacted in the rate-determining step with H₂O₂ (eq 3 and 6) rapid bridge-cleavage processes occur generating one molecule of [VO(O₂)(dipic)H₂O]⁻ and most probably two different fragments. These two dipicolinatovanadium(V) complexes rapidly form two diperoxovanadium(V) complexes, eq 13,



which are subsequently transformed to the final sole product of the reaction complex V according to rate laws eq 11 and 12. This interpretation is supported by the following experimental findings. After mixture of 20 mL of an aqueous solution of "NH₄[V(O)₂(dipic)]" (0.05 M) with 20 mL of concentrated H₂O₂ (0.6 M) at 2 °C an increase of H⁺ concentration in the yellow solution is observed (production of H⁺, eq 13) which slowly decreases again (two distinct stages were recorded) thereby forming a dark red solution of the monoperoxo complex V (consumption of H⁺, eq 14).

The proposed mechanism, eq 13-15, for the formation of a monoperoxo intermediate I via dissociation of a diperoxo species leads to the formal kinetic expression eq 16 if the

$$d[I]/dt = \frac{2k_6k_8}{k_8 + k_7[H_2O_2]} [V(O_2H)_2][H^+] \quad (16)$$

steady-state approximation is applied for V(O₂H) in eq 14. This is of the form in eq 11 and 12 where c (or e) = $1/2k_6$ and d (or f) = $k_7/2k_6k_8$. Thus $2c$ and $2e$ represent reciprocal second-order rate constants for the dissociation of one complex-bonded H₂O₂ ligand. It is not to be expected that this process is greatly influenced by the degree of polymerization of V^V centers (monomeric and dimeric diperoxovanadium(V) species are conceivable if the μ-oxo bridge cleavage is rapid), and indeed, the two values of k_6 —evaluated from c and e (Table VI) at 25 °C—are very similar (12.2 ± 1.0 and $7.5 \pm 3 \text{ M}^{-1} \text{ s}^{-1}$). From the temperature dependence of c , activation parameters for k_6 were determined: $\Delta H_6^\ddagger = 10.1 \pm 1.5 \text{ kcal mol}^{-1}$ and $\Delta S_6^\ddagger = -20 \pm 5 \text{ cal K}^{-1} \text{ mol}^{-1}$.

The need to invoke two different relatively stable monoperoxovanadium(V) intermediates I, eq 15, stems from the observation of two stages of the reaction ([H⁺] = 0.1-1.0 M) which are both independent of [H₂O₂] and inversely dependent on [H⁺] (vide supra). These two reaction steps must be assigned to consecutive processes occurring after diperoxovanadium(V) species are generated because they are *not* observed when complex III is in large excess over H₂O₂. In addition, the absorbance changes (increases at 430 nm but *decreases* at 340 nm) can only be rationalized if transient species with an absorption spectrum B (Figure 7) participate in the reaction.

If it is assumed that the deprotonated forms of I react *intramolecularly* to give the final complex V as in eq 17 and 18, eq 19 can be derived which reduces to eq 20 if $K_a \ll H^+$.



$$d[VO(O_2)(dipic)H_2O]/dt = \frac{k_i K_a}{K_a + [H^+]} [I] \quad (19)$$

$$d[VO(O_2)(dipic)H_2O]/dt = k_i K_a [I]/[H^+] \quad (20)$$

Thus the constants a or b of eq 4 and 5 are composite values ($k_i K_a$), where K_a is the equilibrium constant of dissociation of the intermediates I_1 and I_2 .

At high H^+ concentrations the reaction sequence in eq 17 and 18 is sufficiently retarded to become the rate-determining step since the formation of the intermediates I in eq 13–15 is rapid. At low $[H^+]$ the formation of I is rate determining.

Discussion

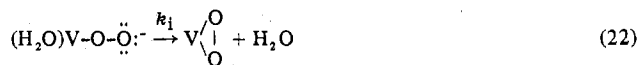
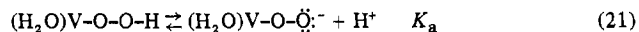
The interpretation of the kinetics of the first stage of the reaction at high $[H^+]$ is straightforward. The red monomeric monoperoxovanadium(V) complex V is generated from a trimeric complex in its protonated form. The rate-determining step is the substitution reaction of an H_2O_2 ligand into the first coordination sphere of a vanadium(V) center. It is noted that each vanadium(V) ion in complex III has achieved an octahedral coordination without binding of labile aquo ligands which could be substituted via a dissociative mechanism. Therefore, an associative mechanism with a seven-coordinate V(V) intermediate is most probably operative. Protonation of a μ -oxo bridge of III affects the electron density of the V(V) centers and improves their susceptibility toward the good nucleophile H_2O_2 . This is clearly demonstrated by the fact that the unprotonated form of III reacts 3 orders of magnitude more slowly at 25 °C with H_2O_2 (Table VI). No kinetic evidence has been obtained for the participation of an $H_3O_2^+$ cation in the reaction since the equilibrium constant of protonation of H_2O_2 ($K \approx 10^{-5} M^{-1}$)¹⁴ is many orders of magnitude different from the kinetically relevant value for K in eq 3.

On the other hand, at low $[H^+]$ the excellent nucleophile HO_2^- reacts with the unprotonated complex III at a very high but not improbable rate ($k_c \approx 10^8 M^{-1} s^{-1}$). Thus the rate of substitution of complex III is dramatically affected by the nucleophilicity of the incoming ligands (H_2O_2 or HO_2^-) which is characteristic for an associative mechanism.

After the reaction of III (protonated or unprotonated) with one molecule of hydrogen peroxide (or HO_2^-) is completed, breakdown of the trimeric structure of III occurs (μ -oxo or μ -hydroxo bridge cleavage). From kinetic experiments with H_2O_2 in large excess over complex it is deduced that two different fragments are generated, relative concentrations of both being dependent on $[H_2O_2]$ and $[H^+]$. The precise structure of these species is not known but each vanadium(V) ion is coordinated to the tridentate dipicolinato anion and one or possibly two terminal oxygen atoms ($V=O$) and at least one, presumably labile, H_2O ligand. Monomeric and dimeric species are conceivable. These fragments react rapidly with H_2O_2 forming two different transient diperoxovanadium(V) complexes. The rate-determining step for the formation of these diperoxo species via the fragmentation of III is the reaction of III with the first H_2O_2 ligand since no further stage of the reaction is observed with a first-order dependence on $[H_2O_2]$.

From the ease with which the diperoxo species are converted via an acid catalysis, eq 11 and 12, to the final monoperoxo complex V, eq 14–16, it is proposed that the hydrogen peroxide is only bonded as a monodentate ligand $V-O-O-H$. This appears to be more reasonable than intermediates containing bidentate peroxo groups because this would imply eight-coordinate vanadium(V) centers.

The mechanistic implications of the two observed stages of the reaction (excess H_2O_2) which are inversely dependent on $[H^+]$ but independent of $[H_2O_2]$ in the range of $[H^+] = 1.0$ – $0.1 M$, eq 4 and 5, are more difficult to assess. The proposed intramolecular rearrangement, eq 17 and 18, of a deprotonated transient monoperoxovanadium(V) complex is tentatively rationalized as follows. If the intermediates I, eq 4, 5, and 15, contain a monodentate HO_2^- ligand, e.g., $V-O-O-H$, it would be plausible to propose that a very rapid ring closure of the deprotonated form occurs:



pK_a values in the range 7–9 are observed for organic peroxo acids.¹⁵ If a roughly similar value for the dissociation constant of the $V-O-O-H$ species is assumed, the intramolecular rate constant for ring closure, k_i , would be of the order of magnitude 10^7 – $10^9 s^{-1}$ according to eq 20. This would be in agreement with the rate constant proposed for the exchange of coordinated water at the $V(O)_2^+$ cation ($\sim 10^8 s^{-1}$).¹⁶

After this paper had been submitted for publication an interesting paper by Tanaka et al. appeared which describes the reaction of H_2O_2 with what is claimed to be the mononuclear complex $[V(O)_2(dipic)H_2O]^-$.¹⁸ It would appear that this species has been prepared in situ from dipicolinic acid and vanadium(V) perchlorate. The precise structure has not been established as regards possible polymeric anions or the presence of coordinated H_2O . Contrary to this study only a single stage of the reaction is observed when H_2O_2 is in excess which supports a mononuclear structure. The rate of peroxo complex formation is given in eq 23 (pseudo-first-order conditions with

$$d[VO(O_2)(dipic)H_2O]/dt = \{k_x [H^+][V(O)_2(dipic)H_2O] + k_y [V(O)_2(dipic)H_2O] + k_z [V(O)_2(dipic)OH^{2-}]\} [H_2O_2] \quad (23)$$

excess H_2O_2 have been used only). This has been assigned to the reaction of H_2O_2 with a protonated form of the mononuclear complex. Since the equilibrium constant of protonation has not been determined, a meaningful comparison with the proton-catalyzed reaction of the trimer with H_2O_2 is not possible. However, the unprotonated form ($k_y = 0.39 M^{-1} s^{-1}$, 25 °C, $\mu = 1.0 M$) reacts at nearly the same rate as the unprotonated trimer ($k_b = 1.1 M^{-1} s^{-1}$) taking into account a statistical factor of 3. But contrary to our interpretation of the $[H^+]^{-1}$ dependent path, eq 6 (reaction of the unprotonated trimer with HO_2^-), Tanaka et al. assigned the k_z path, eq 23, solely to the reaction of $[V(O)_2(dipic)OH]^{2-}$ (which is the hydrolyzed form of $[V(O)_2(dipic)H_2O]^-$) with H_2O_2 . A bimolecular rate constant of $28 M^{-1} s^{-1}$ has been calculated for k_z . In the light of the results obtained for the reaction of the trimer (which does not contain acidic protons) the $[H^+]^{-1}$ -dependent reaction path of the mononuclear species can—at least in part—be also attributed to the very rapid reaction with the strong nucleophile HO_2^- .²⁰

Acknowledgment. I am deeply indebted to Professor H. Hartkamp (Gesamthochschule Wuppertal) for communicating unpublished preparative details of his research on dipicolinato metal complexes and for stimulating discussions. I am grateful to Dr. H. Ehrhardt (Technische Universität Hannover) for measuring the Raman spectra. Financial support of this research from the Deutsche Forschungsgemeinschaft and the Fonds der Chemischen Industrie is also acknowledged.

Registry No. $NH_4[V(O)_2(dipic)]$, 64440-63-7; $K[V(O)_2(dipic)]$, 64440-71-7; $Cs[V(O)_2(dipic)]$, 64440-70-6; $H[V(O)_2(dipic)]$, 64440-68-2; $H[V(O)_2(dipic)] \cdot C_2H_5OH$, 64440-69-3; $K[VO(O_2)-$

(dipic) H_2O , 64440-67-1; $\text{H}[\text{VO}(\text{O}_2)(\text{dipic})\text{H}_2\text{O}]$, 64440-66-0; H_2O_2 , 7722-84-1; III, 64475-65-6.

Supplementary Material Available: Table I giving elemental analyses of all complexes, Table II summarizing the vibrational spectra of complexes, and Tables III and IV giving rate constants of the first rapid stage and of the subsequent second and third stages for the reaction of trimeric $[\text{V}(\text{O})_2(\text{dipic})]_3^{3-}$ with H_2O_2 , $[\text{H}^+] = 1.0\text{--}0.1\text{ M}$ (5 pages). Ordering information is given on any current masthead page.

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- (19) Supplementary material.
- (20) The crystal structure of $\text{Cs}[\text{V}(\text{O})_2(\text{dipic})] \cdot 0.5\text{H}_2\text{O}$ has been determined revealing a mononuclear, five-coordinate *cis*-dioxodipicolinatovanadium(V) anion, which does not contain coordinated H_2O ligands: B. Nuber, J. Weiss, and K. Wiegardt, *Z. Naturforsch.*, submitted for publication.

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Anion Dependence of Ring Conformational Equilibria of the Tris(ethylenediamine)nickel(II) Cation. 2. Effect of Anion Base Strength in Aqueous Solution

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Received March 2, 1977

The temperature dependence of the NMR contact shifts of $[\text{Ni}(\text{en})_3](\text{RCO}_2)_2$ ($\text{R} = \text{Cl}_3\text{C}$, Cl_2HC , ClH_2C , and H) in water is interpreted in terms of the chelate ring conformational equilibria. As was found previously for acetate, benzoate, and nitrate, two separate equilibria are exhibited by these systems in the temperature range from 0 to 75 °C. For the high-temperature process a more precise correlation is observed in these new results between the base strength of the anion and the parameters for ring inversion. The large values of ΔH and ΔS for the high-temperature equilibrium are interpreted as the result of the breaking of hydrogen bonds and the dissociation of ion pairs. These observations and recent x-ray crystal results suggest that association of cation and anion plays an important role in ethylenediamine ring conformational behavior.

Introduction

The equilibrium that exists in solution between the δ and λ conformations in the five-membered chelate rings of tris(ethylenediamine)metal complexes has been studied using the technique of NMR spectroscopy during the past decade.²⁻⁴ An excellent review by Beattie⁵ summarizes the methylene proton spectra of several $[\text{M}(\text{en})_3]^{m+}$ complexes. In our studies of the dynamic NMR spectrum of the paramagnetic $[\text{Ni}(\text{en})_3]^{2+}$ complex we have found that solvents⁶ and anions⁷ can shift this equilibrium according to their ability to associate with or hydrogen bond to the cation. For example, at high temperature in aqueous solution the thermodynamic parameters for the $\delta \rightleftharpoons \lambda$ ring inversion observed for $[\text{Ni}(\text{en})_3]\text{X}_2$ ($\text{X} = \text{acetate}$, benzoate , and nitrate) increase with the base strength of these anions.⁷ The large values of ΔH and ΔS found for these systems suggest that association of cation and anion plays an important role in ethylenediamine ring conformational behavior. A subsequent x-ray crystal structure determination⁸ of $[\text{Ni}(\text{en})_3](\text{O}_2\text{C}_2\text{H}_3)_2 \cdot 2\text{H}_2\text{O}$ revealed the $\Delta\delta\delta\delta^9$ configuration of the cation involved in several strong hydrogen bonds to acetate anions and solvate molecules.

While the three anions previously studied do differ in their base strength, their structural diversity precludes firmly ascribing the observed variation to a single parameter. In order to verify a correlation between anion base strength and the ring conformational equilibrium, we have extended our studies to include a series of $[\text{Ni}(\text{en})_3](\text{RCOO})_2$ compounds, where

RCOO^- is a carboxylate anion. These anions have a well-established trend in their base strength but no gross structural differences. We report here the results of this new study along with its comparison to our earlier work.

Experimental Section

Synthesis and Characterization of Compounds. $[\text{Ni}(\text{en})_3](\text{O}_2\text{CH})_2$, **Tris(ethylenediamine)nickel(II) Formate.** A saturated solution was prepared by adding 3.35 g (18 mmol) of nickel(II) formate dihydrate to approximately 90.0 mL of water at 75 °C. A 4-mL volume of 99% ethylenediamine (60 mmol) was slowly added with stirring, and the solution turned from light green to purple. Liquid volume was reduced to approximately 15 mL by warming on a vacuum roto evaporator, and the solution was then refrigerated at 10 °C for 24 h until a precipitate formed. This purple solid was collected and washed with ether; the approximate yield was 68%. This material is stable in aqueous solutions, but the solid is slightly hygroscopic and must be stored with a desiccant.

$[\text{Ni}(\text{en})_3](\text{O}_2\text{C}_2\text{H}_2\text{Cl})_2$, **Tris(ethylenediamine)nickel(II) Monochloroacetate.** A 14-g (150 mmol) amount of crystalline monochloroacetic acid was dissolved in 15 mL of water, and nickel(II) carbonate was added in small portions with warming until effervescence was complete. Approximately 7.50 g (63 mmol) was required. On cooling, a green solid formed which was redissolved with 15 mL of 95% ethanol. This solution was cooled while 15 mL of ethylenediamine (207 mmol) was slowly added, resulting in precipitation of the purple product which was washed with ethanol and dried for 24 h in a vacuum desiccator at 47 °C; the approximate yield was 86%. This material is very hygroscopic to the point of decomposition, and aqueous solutions are unstable, turning from purple to blue in 3 to 4 weeks.