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Vanadium(V) Peroxo Complexes. New Versatile Biomimetic Reagents for Epoxidation of Olefins and Hydroxylation of Alkanes and Aromatic Hydrocarbons

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Abstract: Novel covalent vanadium(V) oxo peroxo complexes of general formula $\text{VO}(\text{O}_2)(\text{O}-\text{N})\text{LL}'$ [type I, $\text{O}-\text{N}$ = pyridine-2-carboxylate (Pic), pyrazine-2-carboxylate; $\text{L}, \text{L}' = \text{H}_2\text{O}, \text{MeOH}$, monodentate or bidentate basic ligands] and anionic complexes with the general formula $[\text{VO}(\text{O}_2)(\text{Pic})_2]^{-}\text{A}^+\text{L}$ [type II, $\text{A}^+ = \text{H}^+, \text{PPh}_4^+$; $\text{L} = \text{H}_2\text{O}$, hexamethylphosphoric triamide (HMPT)] were synthesized and characterized by physicochemical methods and X-ray crystallography. The crystal structure of $\text{VO}(\text{O}_2)(\text{Pic})\cdot 2\text{H}_2\text{O}$ (Ia) revealed a pentagonal-bipyramidal environment, with a significant hydrogen bonding between the peroxo moiety and the equatorial water molecule. Protonated type II complexes ($\text{A}^+ = \text{H}^+$) are dissociated in an aqueous solution and have an acidic nature ($\text{pK}_a = 1.8$) but are undissociated in a nonprotic solution, with a presumably peracid-like oxohydroperoxo structure. While relatively stable in solid state and protic solvents vanadium(V) peroxo complexes decompose in nonprotic solvents, the most unstable ones being the complexes Ia and IIb. Upon decomposition or reaction with hydrocarbons, complex Ia lost one oxygen atom and produced an oxo bis(μ -oxo) vanadium(V) dimeric complex IIIa which reacted with HMPT to give a trigonal-bipyramidal vanadium(V) *cis*-dioxo complex $\text{VO}_2(\text{Pic})(\text{HMPT})$ (IIIb) characterized by an X-ray crystal structure. Vanadium peroxo complexes are effective oxidants in nonprotic solvents under mild conditions. They transform olefins to epoxides and cleavage products in a nonstereoselective fashion (*cis*-2-butene gave a mixture of *cis* and *trans* epoxides). More interestingly, they hydroxylate aromatic hydrocarbons to phenols and alkanes to alcohols and ketones. Complex Ia oxidized benzene to phenol with a 55% yield, without any primary deuterium isotope effect ($k_{\text{H}}/k_{\text{D}} = 1$). Toluene was mainly hydroxylated at the ring positions with a 70% NIH shift value. Alkanes are much less readily hydroxylated than aromatics, this reaction occurring with a relatively low isotope effect ($k_{\text{H}}/k_{\text{D}} = 2.8$) and a significant amount of epimerization at the hydroxylated carbon atom. This reactivity, which appears very different from that of Mo peroxo complexes, was tentatively attributed to a radical $\text{V}^{\text{IV}}-\text{O}-\text{O}\cdot$ species generated from peracid-like forms, which adds to double bonds and aromatic nucleus and abstracts hydrogen atoms from alkanes to give a carbon radical intermediate. These observations are discussed in the context of proposed "oxenoid" mechanisms and enzymic cytochrome P_{450} monooxygenases.

The synthesis of well-defined transition-metal peroxides and the study of their oxidizing properties toward organic substrates provide a heuristic approach to the understanding of catalytic oxidation reactions.³ In contrast to molybdenum peroxo complexes, which are well established as epoxidation reagents,⁴ vanadium(V) peroxo complexes have never been studied as such with regard to their oxidizing properties. In fact, the well-characterized V(V) peroxo complexes, e.g., $[(\text{Dipic})\text{VO}(\text{O}_2)\cdot\text{H}_2\text{O}]\cdot\text{NH}_4^+$ 1,⁵

$[\text{VO}(\text{O}_2)_2\text{NH}_3]\cdot\text{NH}_4^+$ 2,⁶ and related complexes,⁷ are anionic species and generally insoluble in organic solvents. However, vanadium compounds have been widely used as catalysts for the oxidation of olefins by H_2O_2 or ROOH.^{3d,e} They are generally less efficient and selective catalysts than molybdenum compounds for the epoxidation of unactivated olefins,⁸ but highly active and stereoselective for allylic alcohols.⁹ Interestingly, cyclohexene is mainly oxidized to cyclohex-1-en-3-ol and cyclohex-1-en-3-one by H_2O_2 in the presence of V_2O_5 .¹⁰

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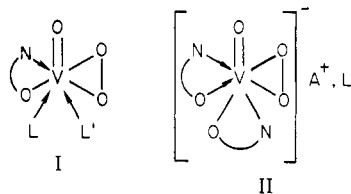
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Table VII. Covalent V(V) Peroxo Complexes VO(O₂)(O-N)LL' (Type I)

| complex | O-N | L | L' | infrared absorption, ^a cm ⁻¹ | | | |
|---------|-----|------------------|------------------|--|--------------------------|--|--|
| | | | | $\nu(\text{V}=\text{O})$ | $\nu(\text{O}-\text{O})$ | $\nu\left(\begin{smallmatrix} \text{O} \\ \diagup \text{V} \diagdown \text{O} \end{smallmatrix}\right)_{s,as}$ | $\nu(\text{X}-\text{O}) (\Delta\nu)^d$ |
| Ia | | H ₂ O | H ₂ O | 975 | 935 | 580, 550 | |
| Ib | | MeOH | H ₂ O | 975 | 940 | 580, 550 | |
| Ic | | py | | 985 | 930 | 595, 550 | |
| Id | | py | py | 945 | 935 | 575, 560 | |
| Ie | | | H ₂ O | 958 | 948 | 580, 540 | 1218 ^b (-10) |
| If | | bpy | | 945 | 935 | 575, 560 | |
| Ig | | | | 960 | 945 | 575, 540 | 1590 ^c (-35) |
| Ih | | | | 975 | 945 | 590, 550 | |
| Ii | | | H ₂ O | 970 | 950 | 580, 550 | 1218 ^b (-10) |
| Ij | | | | 960 | 945 | 575, 545 | 1590 ^c (-35) |

^a KBr disk. ^b X = N. ^c X = C. ^d Frequency shift vs. free ligand.

This paper reports on the synthesis and characterization of two new families of vanadium(V) peroxo complexes: (1) type I—covalent species with the general formula VO(O₂)(O-N)LL'



(O-N = pyridine-2-carboxylate-type bidentate ligand; L, L' = H₂O, MeOH or σ -donor monodentate or bidentate ligands) for which the molecular and crystal structure of Ia (O-N = pyridine-2-carboxylate (Pic), L = L' = H₂O) has been determined; (2) type II—anionic species with the general formula [VO(O₂)(O-N)]⁻A⁺L (A⁺ = H⁺, PPh₄⁺; L = H₂O, HMPT).

These complexes were found to be very effective reagents for the transformation of olefins to epoxides and oxidative cleavage products and unexpectedly for the hydroxylation of alkanes and aromatic hydrocarbons at room temperature.

Results

1. Synthesis, Characterization, and X-ray Crystal Structure of the Covalent VO(O₂)(Pic)·2H₂O (Ia) Complex. In the presence of 1 equiv of picolinic acid per vanadium, V₂O₅ dissolves at 0 °C in 30% H₂O₂, resulting in a deep red solution from which brick-red crystals are deposited. An elemental analysis of this complex indicated the formula VO(O₂)(Pic)·2H₂O (Ia). The infrared spectrum of this complex (Table VII) exhibited absorptions at 975 cm⁻¹ and 935, 580, 550 cm⁻¹ attributable to the characteristic oxo stretching vibration $\nu(\text{V}=\text{O})$ and the C_{2v} peroxo vibrations, respectively. The other infrared absorptions of this complex were assigned to the coordinated water (broad absorption at 3300 cm⁻¹) and the bidentate picolinato group ($\nu(\text{C}=\text{O})_{as}$ 1670 cm⁻¹, ν -

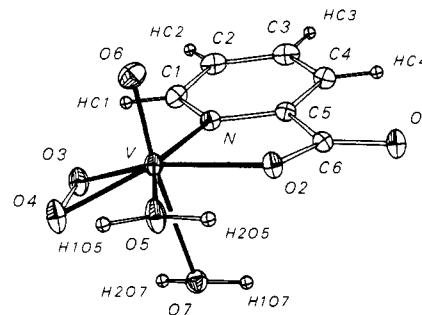


Figure 1. ORTEP plot of the molecule of Ia. Ellipsoids are scaled to enclose 50% of the electronic density; hydrogen atom radii are arbitrary. Principal bond distances (Å): V-N, 2.137 (2); V-O2, 2.016 (2); V-O3, 1.878 (2); V-O4, 1.867 (2); V-O5, 2.046 (2); V-O6, 1.583 (2); V-O7, 2.307 (2); O3-O4, 1.435 (3). Selected bond angles (deg): O3-V-O4, 45.06 (8); V-O3-O4, 67.04 (9); V-O4-O3, 67.90 (9); O6-V-O3, 100.99 (8); O6-V-O4, 104.25 (9).

(C=O), 1380 cm⁻¹). The infrared spectrum of Ia treated with H₂O¹⁸ revealed a decrease in the $\nu(\text{V}=\text{O})$ absorption at 975 cm⁻¹ and an increase in the 935 cm⁻¹ absorption, which is due to the superposition of the displaced $\nu(\text{V}=\text{O})$ ($\Delta\nu$ -40 cm⁻¹)¹¹ and the undisplaced $\nu(\text{O}-\text{O})$ vibrations. Cerimetric titration indicated the presence of one peroxidic oxygen per vanadium. The very low conductivity of Ia in CH₃CN (Λ = 0.9 Ω^{-1} mol⁻¹ cm²) confirmed its covalent nature. This complex is stable in the solid state for weeks in a refrigerator and is not explosive even when heated. It is soluble in water, methanol, acetonitrile, and basic solvents, e.g., DMF, HMPT, etc., but decomposes in nonprotic solution at room temperature (see below).

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Table VIII. Anionic Vanadium(V) Peroxo Complexes (Type II)

| complex | infrared absorptions, ^a cm ⁻¹ | | | conductivity, ^b Λ Ω ⁻¹ mol ⁻¹ cm ² | |
|---|---|--------|---|---|--------------------|
| | ν(V=O) | ν(O-O) | ν($\begin{smallmatrix} \text{O} \\ \diagup \text{V} \diagdown \\ \text{O} \end{smallmatrix}$) _{s,cs} | H ₂ O | CH ₃ CN |
| Ia [VO(O ₂)(Pic) ₂] ⁻ ·H ⁺ ·H ₂ O | 965 | 935 | 580, 540 | 209 | 6.7 |
| Ib [VO(O ₂)(Pic) ₂] ⁻ ·H ⁺ ·HMPT | 965 | 940 | 580, 540 | 190 | 9.9 |
| Ic [VO(O ₂)(Pic) ₂] ⁻ ·PPh ₄ ⁺ ·H ₂ O | 960 | 935 | 575, 545 | ^c | 95 |

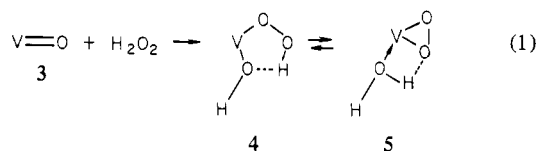
^a KBr Disk. ^b Temperature 23 °C. Concentration = 2.5 × 10⁻³ mol L⁻¹. ^c Iic insoluble in water. The conductivity of PPh₄Br was found to be equal to 142 Ω⁻¹ mol⁻¹ cm² in CH₃CN and to 86 Ω⁻¹ mol⁻¹ cm² in H₂O.

The crystal structure of Ia consists of discrete molecules linked only by hydrogen bonds and van der Waals interactions. Figure 1 shows an ORTEP¹² plot of one molecule, the labeling scheme used, and principal bond lengths and angles.

The coordination polyhedron of the vanadium atom is a distorted pentagonal bipyramid, the equatorial positions of which are occupied by the oxygen atoms of the peroxo group, an oxygen and a nitrogen atom of the picolinate ligand, and a water molecule. The apical positions are occupied by an oxygen atom and a water molecule. The peroxo group is trans to the oxygen atom O2 of the picolinate moiety: a disposition also found in a molybdenum(VI) peroxo complex MoO(O₂)Cl(Pic)-HMPT,¹³ but opposite to that found in a titanium(IV) peroxo dipicolinate complex¹⁴ where the peroxo group is trans to the nitrogen atom.

The geometry of the peroxo group is normal compared to the other vanadium peroxo complexes 1⁵ and 2⁶, with a mean V-O peroxo bond length of 1.872 (2) Å, and mean O3-V-O4 and V-O-O bond angles of 45.06° and 57.47 (9)°, respectively.

A complex network of hydrogen bonds link the various molecules together (see Table I). HC1 is at 2.33 Å from O3 (O3-C1 = 2.794 (3) Å), and this hydrogen atom together with nitrogen, carbon C1, oxygen O3, and vanadium form a five-membered ring. The two hydrogen atoms H1O5 and H2O5 are involved in intramolecular hydrogen bonds: H1O5 is at 2.55 Å from O4 and H2O5 at 2.40 Å from O2; thus, two four-membered rings are formed, containing V-O4-H1O5-O5 and V-O5-H2O5-O2, respectively. The existence of the equatorially distorted five-membered ring V-O3-O4-H1O5-O5 suggests that the formation of peroxo compounds 5 from the reaction of H₂O₂ with oxo compounds 3 occurs through the hydroxo-hydroperoxo intermediate 4, as shown in eq 1.^{3a,b}

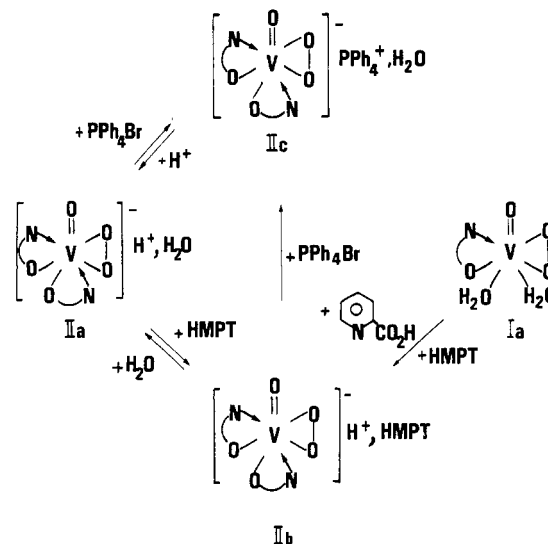


The vanadium(V) hydroxo-hydroperoxo species 4 is similar to 2-hydroperoxyhexafluoro-2-propanol, obtained from the reaction of hexafluoroacetone with H₂O,^{15a} a most effective reagent for epoxidation of olefins,^{15a,b} lactonization of ketones,^{15c} and hydroxylation of mesitylene.^{15c}

2. Substituted Covalent Peroxo Complexes VO(O₂)(O-N)LL' (Type I). One or two coordinated water molecules in Ia can be easily replaced by methanol or monodentate and bidentate basic ligands. Table VII lists the various substituted peroxo complexes bearing monodentate (Ia-e,i) or bidentate ligands (If-h,j) and their infrared characteristics.

Attempts to prepare complexes with L = HMPT, DMF, Ph₃PO, and L' = H₂O led to much less stable complexes, pre-

Scheme I



sumably due to oxidation of the ligand by the peroxo species (see below).

In the infrared, these complexes exhibited similar vibrations: ν(V=O) in the range 945–975 cm⁻¹ and ν(O-O) in the range 935–950 cm⁻¹. In compounds Ie and II, the 4-picoline N-oxide is coordinated through the oxygen atom, as shown by the displacement of the ν(N-O) vibration to the lower frequencies.¹⁶ In complexes Ig and Ij, the N,N-diethylpicolinamide is coordinated in a bidentate fashion, as shown by the displacement of the amide ν(C=O) vibration toward low frequencies. The complex Ic having a monodentate pyridine ligand has no coordinated water, as do CrO₅ complexes.¹⁷

Elemental analysis and peroxidic oxygen content (cerimetric titration) are in agreement with the proposed structure Ia-j. The ¹H NMR spectra of Ia-h is characterized by a downfield shift of ca. 0.7 ppm of the doublet corresponding to the proton in position 6 in the coordinated pyridine-2-carboxylate ligands (see Experimental Section).

3. Anionic Vanadium(V) Peroxo Complexes [VO(O₂)(Pic)₂]⁻A⁺L (Type II). A procedure similar to that used for the synthesis of Ia, but with a picolinic acid:vanadium ratio equal to 2:1, produced a complex with the formula [VO(O₂)(Pic)₂]⁻·H⁺·H₂O (IIa) with a 93% yield. The water molecule in IIa can easily be replaced by basic ligands such as HMPT to produce the complex IIb which is soluble in most organic solvents (Scheme I). IIb can also be obtained from the reaction of Ia with picolinic acid and HMPT with an 80% yield.

Addition of PPh₄Br to the aqueous solution of IIa or IIb results in the precipitation of Iic in which the acidic proton has been replaced by the tetraphenylphosphonium cation.

Complexes IIa-c were characterized by elemental analysis, peroxidic oxygen cerimetric titration, infrared and NMR spectroscopy, and conductimetry (see Table VIII and Experimental Section).

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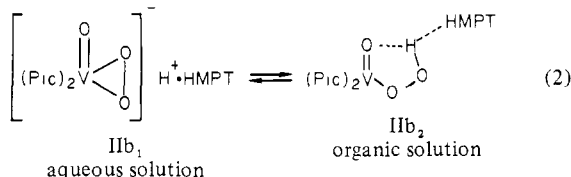
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The characteristics of complex I**IIb** are worthy of note. Its infrared spectrum exhibited characteristic vibrations at 965 cm⁻¹ ($\nu(\text{V}=\text{O})$) and 940, 580, 540 cm⁻¹ (peroxo group). The presence of HMPT, clearly revealed by the spectral print in the $\nu(\text{C}-\text{H})$ 2800–3000 cm⁻¹, appeared less sharply in the other regions. A broad absorption at 1700–1900 cm⁻¹ was attributed to a strongly delocalized O–H vibration. The ¹H NMR spectrum of I**IIb** in CD₂Cl₂ solution showed the presence in the aromatic region of two nonequivalent pyridine-2-carboxylato groups. A broad resonance at 10.9 ppm was assigned to a strongly delocalized OH group (one OH for two picolinate groups). HMPT appeared as a doublet at 2.44 ppm, corresponding to an upfield shift of 0.19 ppm with respect to the free ligand, thus precluding its direct coordination with the d⁰ vanadium(V) metal.⁴ The ¹³C NMR spectrum of I**IIb** indicated that the two pyridine-2-carboxylato ligands are both bonded in a bidentate fashion to the metal, as shown by the downfield shift of the carboxylic carbon atom at 168.8 and 169.1 ppm, with respect to the pyridine-2-carboxylic acid–HMPT charge-transfer complex (δ 163.8).¹⁸

The aqueous solution of I Ib has an acidic nature. The results of alkalimetric titration showed one inflection point at pH 5.2 which required 1 equiv of NaOH per mole of I Ib. This corresponds to the neutralization of the outer-sphere proton of I Ib ($pK_a = 1.8 \pm 0.1$). The conductivity of I Ib in water ($\Lambda = 190 \Omega^{-1} \text{ mol}^{-1} \text{ cm}^2$) is in the range expected for a two-ion conductor and is much greater than the conductivity measured in CH_3CN ($\Lambda = 9.9 \Omega^{-1} \text{ mol}^{-1} \text{ cm}^2$). This suggests the existence of I Ib in a dissociated form in water and in an essentially undissociated form in organic solution, as shown in eq 2.^{18a}



The undissociated IIB₂ form may have a percarboxylic acid structure and the bonding of HMPT in IIB₂ is presumably a hydrogen bonding with the V—OOH moiety, similar to that existing between oxygen bases and percarboxylic acid,¹⁹ which has been found in crystal structure of the 4-NO₂PhCO₃H—Ph₃PO complex.²⁰

4. Decomposition of Vanadium(V) Peroxo Complexes. The stability of peroxo complexes I and II depends on the nature of the solvent and the nature of the ligands bound to the metal. While the complex Ia is relatively stable in protic solvents such as methanol or water, it rapidly decomposes in CH_3CN with evolution of molecular oxygen and formation of a yellow insoluble complex IIIa (see below). Figure 2 shows the decomposition curves of different peroxo complexes, monitored by measuring the decrease of the characteristic visible absorbance at $\lambda = 450\text{--}465\text{ nm}$.^{5b} The nature of the decomposition is autocatalytic, with an induction period and an inflection point. Type I substituted complexes Ic (pyridine) and Ig (*N,N*-diethylpicolinamide) are more stable than the unsubstituted complex Ia. Concerning Type II species, the peracid-like complex IIb is considerably more unstable than the anionic complex IIc.

In fact the acidity of the medium decreases the stability of the complexes. Addition of 1 equiv of MeSO_3H to a CH_2Cl_2 solution of Ig results in a rapid change in color from red to green, and addition of 0.1 equiv results in an important increase in the decomposition rate (Figure 2). The decomposition of complex Ia in CH_3CN has been monitored at 20 °C in the presence of various hydrocarbon substrates (hydrocarbon:complex = 40:1). Olefins (norbornene, 2-methyl-2-pentene, 1-octene) and benzene speed

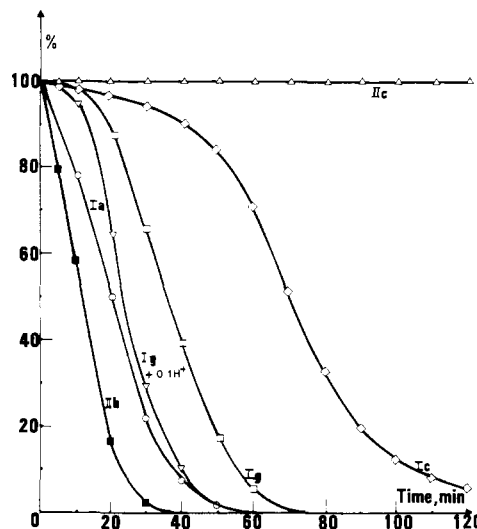
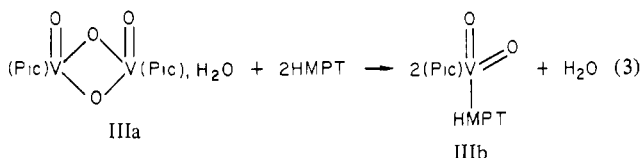


Figure 2. Decomposition of complexes I and II at 20 °C. Concentration: 0.01 mol/L⁻¹; solvent = CH₃CN (for Ia, IIb, IIc) and CH₂Cl₂ (for Ic, Ig); H⁺ = MeSO₃H.

up the decomposition of Ia, while cyclohexane strongly retards this reduction.

The decomposition of the V(V) peroxo complexes appears close to that of organic percarboxylic acids, with a similar solvent and acid effect.²¹ The most unstable complexes Ia and Ib, which will be found the most reactive ones, are those having the more pronounced peracid nature. The autocatalytic nature of this decomposition is presumably due to a chain-radical reaction, radical $V^{IV}-O-O\cdot$ species being generated in solution (see below).

5. X-ray Crystal Structure of the Vanadium(V) *cis*-Dioxo Complex VO₂(Pic)(HMPT) (IIIb) Derived from the Reduced Form of Ia. The decomposition of the peroxo complex Ia or its reaction with olefins, alkanes or aromatics in CH₃CN produced a yellow insoluble complex IIIa. This complex analyzed as VO₂(C₆H₄N-O₂)·0.5 H₂O and exhibited in the infrared one absorption at 985 cm⁻¹ (shifted to 955 cm⁻¹ after exchange with H₂¹⁸O) attributable to ν(V=O) and one absorption at 740 cm⁻¹ (shifted to 710 cm⁻¹ with H₂¹⁸O) which may be assigned to ν(V-O-V).²² This suggests for IIIa the dimeric structure shown in eq 3.



Treatment of IIIa with HMPT in CH_2Cl_2 produced the yellow soluble well-characterized vanadium(V) *cis*-dioxo complex IIIb with an 84% yield. The same complex was synthesized from the reaction of NH_4VO_3 with pyridine-2-carboxylic acid and HMPT in an acidic medium. IIIb exhibited the two absorptions at 948 and 935 cm^{-1} expected for the *cis*-dioxo moiety, together with the vibration at 340 cm^{-1} assignable to the δ *cis* ($\text{O}=\text{V}=\text{O}$) mode.²³ Coordination of HMPT to vanadium through the phosphoryl oxygen atom is clearly revealed by the lowering of the $\nu(\text{P}=\text{O})$ vibration found at 1190 cm^{-1} ($\Delta\nu = -20\text{ cm}^{-1}$) and in NMR by a doublet expected for HMPT at δ 2.79 ($J = 10\text{ Hz}$), corresponding to a deshielding effect of the metal of 0.16 ppm. The crystal structure of IIIb confirmed these observations and revealed a trigonal-bipyramidal environment of the vanadium atom (Figure 3) different from the octahedral structure previously found for V(V) *cis*-dioxo complexes.^{24,25}

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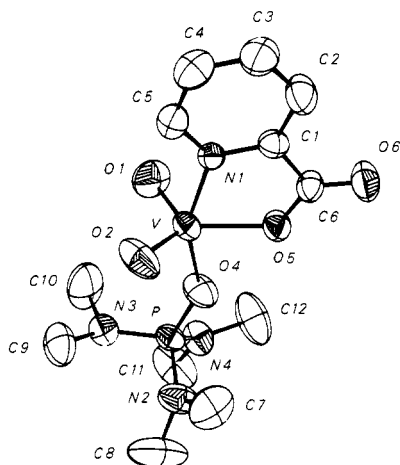


Figure 3. ORTEP plot of one molecule of IIIb. Vibrational ellipsoids are drawn at the 50% probability level. Principal bond distances (Å): V–O1, 1.600 (5); V–O2, 1.606 (5); V–O4, 1.955 (5); V–O5, 2.000 (4); V–N1, 2.147 (4). Selected bond angles (deg): O1–V–O2, 108.7 (3); O4–V–O2, 100.7 (2); N1–V–O5, 75.8 (2); N1–V–O1, 92.6 (2).

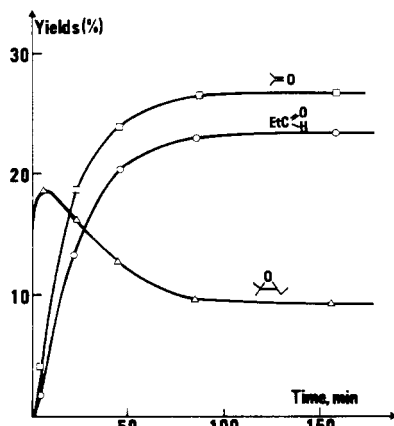


Figure 4. Oxidation of 2-methyl-2-pentene by Ia: temp, 20 °C; solvent, CH₃CN; Ia, 0.04 M; olefin, 2 M. Yields are based on vanadium.

6. Oxidation of Olefins. The stoichiometric oxidation of olefins by vanadium(V) peroxo complexes Ia–j and IIa–c was carried out at room temperature in a nitrogen atmosphere, CH₂Cl₂, or acetonitrile according to the solubility of the complexes. Epoxides and oxidative cleavage compounds were the major products detected from this reaction. Figure 4 shows a typical plot of 2,3-epoxy-2-methylpentane, acetone, and propionaldehyde formation vs. time when 2-methyl-2-pentene was oxidized by Ia in CH₃CN. The epoxide was mainly formed at the beginning of the reaction, but progressively disappeared with time at the expense of the oxidative cleavage compounds. The red solution turned yellow at the end of the reaction and complex IIIa was precipitated. A control experiment showed that the title epoxide was mainly oxidized to acetone and propionaldehyde by the peroxo complex Ia under the same conditions. Equation 4 summarizes the sequence of these reactions.

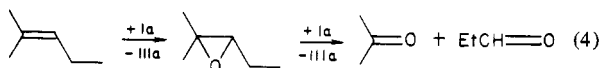


Table XIV lists some representative results obtained when various olefins are stoichiometrically oxidized by complexes of type I and II. The relative amount and the rate of formation of epoxides and oxidative cleavage products depend on the nature of the complex, the nature of the substrate, and the reaction medium. Owing to the different solubility of the reagents and

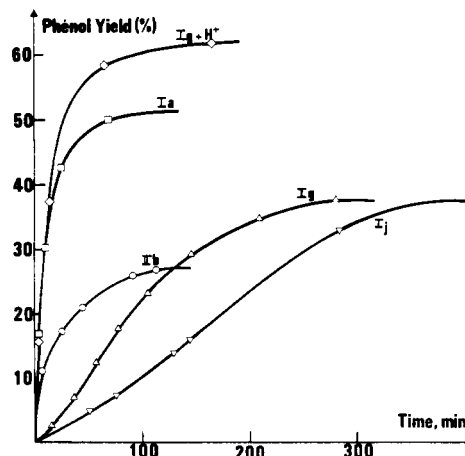


Figure 5. Hydroxylation of benzene: temp, 20 °C; complex, 0.04 M; benzene, 2 M; solvent, CH₃CN (Ia) or CH₂Cl₂ (Ig, Ij, IIb); H⁺ = MeSO₃H.

the consecutive nature of the oxidation, an accurate comparison between the different reactions is rather difficult. Nevertheless, several observations can be drawn from this study depicted in Table XIV.

(1) The reactivity of the peroxo complexes parallels their decomposition rate depicted in Figure 2, the most active ones being the unsubstituted complex Ia and the peracid-like complexes IIa and IIb, while the anionic complex IIc is almost inactive. Substituted complexes such as Ig were found to be much less reactive but gave more epoxide and less cleavage compound than Ia (entries 3,4,16 and 17). Thus, the presence of basic ligands on the metal, by increasing the stability of the complexes, decreases their reactivity but prevents the consecutive oxidation of the epoxide.

(2) The oxidations are best carried out in nonprotic solvents such as CH₂Cl₂ or CH₃CN, the reaction rate being almost the same in these two solvents. Instead, protic solvents such as MeOH strongly retard the reaction (entry 10).

(3) The reactivity of the olefins increases with their nucleophilic nature, following the order: trisubstituted > disubstituted > monosubstituted. Olefins containing phenyl substituents such as styrene, α - and β -methylstyrene gave more oxidative cleavage products than the aliphatic ones. Cyclohexene gave a nonnegligible amount of allylic alcohol and ketone together with epoxycyclohexane; *cis*-2-butene is much more reactive than *trans*-2-butene.

(4) The epoxidation reaction is essentially *nonstereospecific*. *cis*-2-Butene gave an approximately 2:1 mixture of *cis* and *trans* epoxide, whatever the nature of the complex or the advancement of the reaction (entries 3–5) may be. *trans*-2-Butene gave a ca. 6:1 mixture of *trans* and *cis* epoxide (entries 6 and 7).

7. Hydroxylation of Aromatics. One of the most striking features of vanadium(V) peroxo complexes is their ability to transfer oxygen to aromatic hydrocarbons at room temperature. Phenolic compounds were the main products detected from this reaction, without any formation of coupling compounds, such as diphenyl from benzene. Figure 5 shows typical plots of phenol formation vs. time when benzene is oxidized by the peroxo complexes Ia, Ig, Ij, and IIb at 20 °C, and Table XV lists some representative results of the oxidation of benzene, toluene, and mesitylene by various complexes I and II. As for olefins, Ia, IIa, and IIb were found to be the most reactive hydroxylating agents. Complex Ia oxidized benzene in CH₃CN at 20 °C into phenol in ca. 55% yield (based on vanadium). In methanol, Ia was almost inactive, and the solution remained red. The substituted complex Ig reacted rather slowly with benzene, but addition of 1 equiv of MeSO₃H at the beginning of the reaction resulted in an immediate change in color from red to deep green, and the formation of phenol with ca. 60% yield. The anionic complex IIc was reactive only in the presence of 1 equiv of MeSO₃H, and gave a 52% yield of phenol (entries 24 and 25).

The isotope effect k_H/k_D was determined from the competitive hydroxylation of benzene and benzene-*d*₆ (99%) by Ia in CH₃CN.

(25) Edwards, A. J.; Slim, D. R.; Guerschais, J. E.; Sala-Pala, J. J. *Chem. Soc., Dalton Trans.* 1977, 984–989.

Table XIV. Oxidation of Olefins^a

| entry | complex | time, min | olefin | products, ^b % yield ^c | | |
|-----------------|---------|-----------|--------------|---|---------------------|----------------|
| | | | | $C_6H_{13}CH=CH_2$ | $C_6H_{13}-CH-CH_2$ | $C_6H_{13}CHO$ |
| 1 ^d | Ig | 450 | $Ph-CH=CH_2$ | 13 | 2 Ph-CHO | |
| 2 ^d | IIb | 240 | | 12 | 31 | MeCHO |
| 3 ^e | Ia | 15 | | 19 | 8 | 20 |
| 4 ^d | Ig | 400 | | 29 | 13 | 10 |
| 5 ^d | IIb | 100 | | 16 | 8 | 8 MeCHO |
| 6 ^e | Ia | 120 | | 2 | 12 | 3 |
| 7 ^d | IIb | 120 | | 3 | 18 | 1 |
| | | | | | | |
| 8 ^d | IIb | 15 | | 30 | 7 | 7 |
| 9 ^e | Ia | 9 | | 22 | | |
| 10 ^f | Ia | 120 | | 1.8 | | |
| 11 ^d | IIb | 60 | | 45 | Ph-CHO | MeCHO |
| 12 ^e | Ia | 90 | | 6 | 45 | 40 |
| 13 ^e | IIa | 90 | | 13 | 30 | 26 |
| 14 ^d | IIb | 90 | | 30 | 25 | 20 |
| | | | | | | |
| 15 ^d | IIb | 60 | | 15 | 20 | EtCHO |
| 16 ^e | Ia | 90 | | 10 | 27 | 23 |
| 17 ^d | Ig | 90 | | 24 | 10 | 7 |
| | | 120 | | 34 | 15 | 10 |
| 18 ^e | IIa | 90 | | 22 | 18 | 12 |
| 19 ^d | IIb | 90 | | 31 | 15 | 9 |

^a Reaction conditions: temperature, 20 °C; complex, 0.04 M; olefin, 2 M. ^b Identified by GLC-MS coupling. ^c GLC determination using various internal standards (columns A or B). ^d Solvent, CH₂Cl₂. ^e Solvent, CH₃CN. ^f Solvent, MeOH.

The ratio C₆H₅OH:C₆D₅OH was found by GLC-MS to be equal to 1 ± 0.05, indicating that the C-H bond cleavage is not the rate-determining step of the hydroxylation of benzene. It is noteworthy that the same low isotope effect was observed in the hydroxylation of benzene by O(³P) atoms,^{36a} trifluoroperacetic acid,^{32a} and liver microsomal cytochrome P₄₅₀.⁴⁸

Hydroxylation of toluene mainly occurs at the ring positions, yielding *o*-, *m*-, and *p*-cresols in the ratios of 48:20:32, respectively, for Ia. Complexes Ig and IIb gave a similar mixture of isomers. Only traces of benzaldehyde or benzylic alcohol were detected, indicating a strong preference for the attack on the aromatic positions rather than on the aliphatic ones.

Hydroxylation of 4-deuteriotoluene by Ia (20 °C, CH₃CN, substrate:Ia = 50) occurred with a 70% retention and migration of deuterium in the formation of *p*-cresol. This high NIH shift^{30a} value is in the same range as those observed in the hydroxylation of toluene by liver microsomal cytochrome P₄₅₀^{30b} and by photolysis of pyridine *N*-oxide.^{35a}

8. Hydroxylation of Alkanes. Table XVI shows that alkanes are much less readily hydroxylated by V(V) peroxo complexes than aromatic hydrocarbons, and lower yields of alcohols and








ketones result from these oxidations. Cyclohexane was transformed into a mixture of cyclohexanol and cyclohexanone, the relative ratios of which depend on the nature of the reagent. Ia gave more alcohol than ketone, while the reverse was observed with Ig or IIb.

The kinetic isotope effect k_H/k_D was determined from the competitive hydroxylation of cyclohexane and cyclohexane-*d*₁₂ by Ia in CH₃CN. GLC-MS analysis at the end of the reaction revealed, for cyclohexanol, a C₆H₁₁OH:C₆D₁₁OH ratio equal to 2.3 and, for cyclohexanone, a C₆H₉O:C₆D₉O ratio equal to 6.2, for an overall cyclohexanol:cyclohexanone ratio equal to 3.3. This indicated for the hydroxylation of cyclohexane by Ia a primary hydrogen isotope effect k_H/k_D of 2.77.

Hydroxylation of alkanes preferentially occurs at the tertiary positions, as shown in the case of isobutane (entry 34) and decalin (entry 35). *n*-Octane gave a rather statistical mixture of 2-, 3-, and 4-octanols and octanones, without noticeable amounts of terminal oxygenated products.





Cyclohexyl chloride was formed when the oxidation of cyclohexane by Ia was carried out in a 90:10 CH₃CN-CCl₄ mixture (entry 31), indicating that cyclohexyl radicals are produced in

Table XV. Hydroxylation of Aromatic Hydrocarbons^a

| entry | complex | time, min | substrate | product(s), ^b % yield ^c | | | | |
|-------------------|----------------------|-----------|---|---|---|---|---|--|
| | | | C ₆ H ₆ | C ₆ H ₅ OH | | | | |
| 19 ^d | Ia | 120 | | 56 | | | | |
| 20 ^f | Ia | 360 | | 3 | | | | |
| 21 ^e | Ig | 360 | | 45 | | | | |
| 22 ^{e,g} | Ig + H ⁺ | 100 | | 60 | | | | |
| 23 ^e | IIb | 100 | | 27 | | | | |
| 24 ^e | IIc | 360 | | 3 | | | | |
| 25 ^{e,g} | IIc + H ⁺ | 360 | | 52 | | | | |
| | | |  |  |  |  |  | |
| 26 ^d | Ia | 45 | | 24 | 10 | 16 | 2 | |
| 27 ^e | Ig | 360 | | 8 | 3 | 5 | 1 | |
| 28 ^e | IIb | 150 | | 8 | 4 | 6 | 1 | |
| | | |  |  | | | | |
| 29 ^d | Ia | 15 | | 31 | | | | |

^a Reaction conditions: temperature, 20 °C; complex, 0.04 M; substrate, 2 M. ^b Identified by GLC-MS coupling. ^c GLC determination using nitrobenzene as internal standard (column C). ^d Solvent, CH₃CN. ^e Solvent, CH₂Cl₂. ^f Solvent, MeOH. ^g Addition of 1 equiv of CH₃SO₃H.

Table XVI. Hydroxylation of Alkanes^a

| entry | complex | time, min | substrate | products, ^b % yield ^c | | |
|-----------------|---------|-----------|--|--|--|--|
| | | |  |  |  |  |
| 30 ^d | Ia | 280 | | 17 | 8 | |
| 31 ^f | Ia | 180 | | 13 | 10 | 2 |
| 32 ^e | Ig | 720 | | 7 | 18 | |
| 33 ^e | IIb | 120 | | 4 | 9 | |
| 34 ^d | Ia | 300 | isobutane | <i>t</i> -BuOH | | |
| 35 ^d | Ia | 180 | <i>cis</i> -decalin | <i>cis</i> -9-decalol, 6.9; <i>trans</i> -9-decalol, 1.0; 1-decalol, 2.4; 2-decalol, 0.4; 1-decalone, 3.7; 2-decalone, 2.2 | | |
| 36 ^d | Ia | 300 | <i>n</i> -octane | 2-octanol, 1.5; 3-octanol, 0.5; 4-octanol, 0.5; 2-octanone, 2.4; 3-octanone, 2.9; 4-octanone, 2.8 | | |

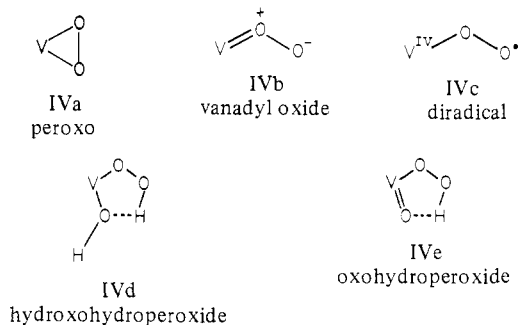
^a Reaction conditions: temperature, 20 °C, complex, 0.04 M; alkane, 2 M. ^b Identified by GLC-MS coupling. ^c GLC determination using *o*-dichlorobenzene as internal standard. ^d Solvent, CH₃CN. ^e Solvent, CH₂Cl₂. ^f Solvent, CH₃CN + 10% CCl₄.

solution and intercepted by chlorine atoms coming from CCl₄.²⁶ A significant epimerization at the C₉ position was also observed in the hydroxylation of *cis*-Decalin by Ia (*cis*-*trans*-9-decalol = 7:1), indicating formation and substantial inversion of *cis*-9-decalyl radical.²⁷ This contrasts with the highly stereospecific hydroxylation of alicyclic alkanes by *p*-nitroperbenzoic acid.²⁸

Discussion

Vanadium(V) peroxo complexes are unique well-defined reagents which can both epoxidize olefins and hydroxylate alkanes and aromatic hydrocarbons. In these oxidations, the transferred

oxygen atom is of a peroxidic nature, since the reduced vanadium(V) species (e.g., IIIa,b from Ia) are inactive. The possible active forms of V(V) peroxidic reagents can be written as IVa-e, and their reactivity can be compared to that of the inorganic and organic peroxidic analogues.



The reactivity of V(V) peroxo complexes is very different from that of Mo analogues, although both are high-valent d⁰ species. Mo(VI) peroxo complexes such as MoO(O₂)₂-HMPT are stable in aprotic (CH₂Cl₂) and protic (MeOH) solutions, but are reactive in both solvents,⁴ while vanadium complexes are reactive only in aprotic solvents, in which they decompose. Mo reagents stereospecifically epoxidize olefins (*cis*-olefins give only *cis*-epoxides) and are not hydroxylating agents.⁴ Further, Mo peroxo complexes bearing equatorial anionic ligands adjacent to the peroxo moiety, e.g., MoO(O₂)Cl(Pic)-HMPT,¹³ MoO(O₂)(Dipic)-HMPT, and MoO(O₂)(OOH)(Pic),^{18a} are completely inactive since coordination of the olefin is precluded, while vanadium complexes IIa,b VO(OOH)(Pic)₂L (L = H₂O, HMPT) are powerful epoxidizing and hydroxylating reagents. Hence, coordination of the substrate to the metal followed by its peroxymetalation^{3b} appears very unlikely in the case of vanadium. Further, such a coordination, while conceivable for nucleophilic substrates such as olefins, is hard to imagine for inert hydrocarbons such as benzene or alkanes.

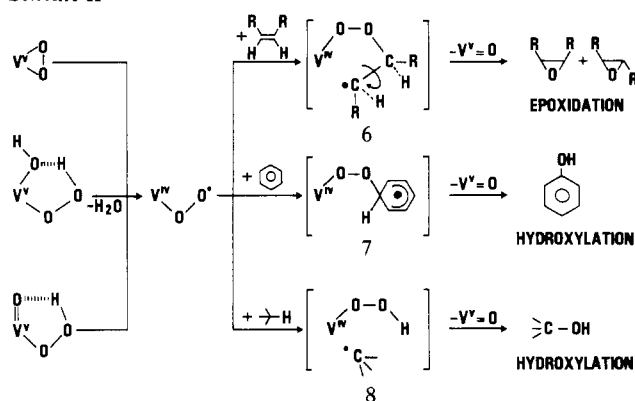
Oxygen transfer from vanadium(V) peroxo complexes to hydrocarbons seems more likely to occur in a bimolecular fashion from the opened forms IVb (vanadyl oxide) or IVc (diradical) generated from the cleavage of IVa or the rearrangement of the intramolecularly hydrogen-bonded hydroxo-hydroperoxide IVd or oxo-hydroperoxide (peracid) IVe. Indeed, configuration IVd is suggested by the X-ray structure of Ia, and configuration IVe has been deduced from the properties of IA,b in aprotic solution.

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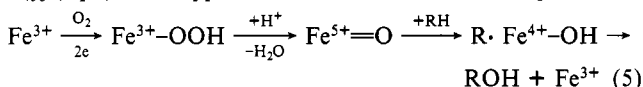
Scheme II



The strong beneficial effect of protons on the reactivity of the substituted complexes Ig or Ij and the anionic complex IVc supports this hypothesis, as does the inhibitory effect of protic solvents which prevent the formation of the intramolecular hydrogen-bonded IVd and IVe species.

Hamilton²⁹ postulated that cytochrome P₄₅₀-dependent monooxygenases interact with O₂ to form peroxidic "oxenoid" species capable of epoxidizing olefins, hydroxylating aromatic hydrocarbons (with a characteristic intramolecular migration and retention of substituents of the aromatic ring called NIH shift),³⁰ and inserting a singlet oxygen atom into an aliphatic C-H bond to produce an alcohol.³¹ Various "oxenoid" reagents comprising trifluoroperoacetic acid,³² carbonyl oxide formed in the ozonolysis of alkynes,³³ or in the photooxidation of diazo compounds,³⁴ pyridine N-oxide + *hν*,³⁵ and O(3P) atoms³⁶ were found suitable models for these monooxygenase enzymes.

On the other hand, Groves and co-workers³⁷ showed that a loss of stereochemistry occurs at the site of hydroxylation by liver microsomal cytochrome P₄₅₀³⁸ and proposed as active species a ferryl ion Fe⁵⁺=O, obtained from the hydrolysis of Fe³⁺-OOH species, capable of abstracting a hydrogen atom from alkanes. This results in the formation of Fe⁴⁺-OH and substrate carbon radical which recombine to give hydroxylated product and ferric P₄₅₀ (eq 5). In support of this mechanism, several epoxidation



and hydroxylation systems using PhIO as the oxygen source, and iron,^{39a} manganese,^{39b} and chromium^{39c} porphyrins as catalysts

(29) Hamilton, G. A. In "Molecular Mechanisms of Oxygen Activation"; Hayaishi, O., Ed.; Academic Press: New York, 1974; pp 405-451 and references therein.

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(37) Groves, J. T. In "Metal Ion Activation of Dioxide"; Spiro, T. G., Ed.; Wiley: New York, 1980; pp 125-162 and references therein.

(38) Groves, J. T.; McClusky, G. A.; White, R. E.; Coon, M. J. *Biochem. Biophys. Res. Commun.* **1978**, *81*, 154-160.

were found, and reactive high-valent oxo species were detected.^{39b,c}

We believe that the reactivity of vanadium peroxo complexes is more reminiscent of that of peroxidic reagents such as carbonyl oxide in its biradical form R₂C=O-O·, and we favor the radical species IVc as being the active epoxidizing and hydroxylating agent, as shown in Scheme II.

Epoxidation of olefins would proceed upon the homolytic addition of IVc to the double bond, giving a freely rotating free radical intermediate 6 which homolytically decomposes to give the epoxide (cis + trans mixture) and vanadium(V) oxo compound. This is consistent with the lack of stereospecificity of this reaction, also observed in the epoxidation of olefins by alkyl peroxy radicals RO₂·⁴⁰ and carbonyl oxide R₂C=O-O·.^{33,34c,d} It is noteworthy that epoxidation of olefins by H₂O₂-Fe(acac)₃⁴¹ and *Pseudomonas Oleovorans*⁴² also proceeds primarily with inversion of the original substrate geometry, in contrast to peracids,⁴³ Mo peroxo complexes,⁴ and ROOH + Mo or V catalytic systems.⁹ The mechanism depicted in Scheme II is also consistent with the observed relative reactivity of olefins toward the electrophilic species IVc.

Hydroxylation of aromatic hydrocarbons would presumably occur upon the homolytic addition of IVc to the aromatic ring and not by hydrogen atom abstraction from the nucleus C-H bond, since no primary deuterium isotope effect was observed in this reaction. Phenol and V^V oxo compound would result from homolytic decomposition of intermediate 7, possibly with transient formation of arene oxide, as suggested by the observed high NIH shift value.³⁰ A similar radical hydroxylation mechanism has been suggested by Lindsay Smith et al. for the oxidation of aromatics by O₂ in the presence of Fe(II) salts and organic reducing agents⁴⁴ and by H₂O₂/Fe(ClO₄)₂ in CH₃CN,⁴⁵ the latter reaction occurring with a high NIH shift. Support for the existence of intermediate 7 can be derived from the isolation and characterization by X-ray structure of peroxo(*p*-quinolato)cobalt(III) complexes obtained from the reaction of (salpr)Co^{III}-O₂· with 2,4,6-tri-*tert*-butylphenol.⁴⁶

Hydroxylation of alkanes would result from a hydrogen atom abstraction by IVc to give an intermediate carbon radical 8, followed by a recombination with the hydroxyl radical coming from V^{IV}-OOH to give the alcohol and the V(V) oxo complex. Carbon radical intermediate were clearly evidenced by trapping experiment with CCl₄ chlorine atoms giving cyclohexyl chloride, and by the observed epimerization at the C₉ hydroxylated position of *cis*-decaline. The low value of deuterium isotope effect (2.8) found in the hydroxylation of cyclohexane by Ia is in the range expected for abstraction of hydrogen atoms by radical reagents⁴⁷ and close to the value of 2.9 observed with P₄₅₀ liver microsomes.⁴⁸ This abstraction-recombination mechanism of hydroxylation by IVc is similar to the "oxygen rebound" mechanism proposed by Groves for the hydroxylation by high-valent metal oxo species,³⁷ with the important difference, however, that the transferred oxygen atom is of peroxidic nature.

In conclusion, vanadium(V) peroxo complexes which homolytically cleave to give electrophilic reactive V^{IV}-O-O· species behave differently from known peroxo complexes (Mo, Rh) which

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heterolytically cleave to M^+-O-O^- species and only react with coordinated substrates with a peroxymetalation mechanism.³ Owing to their peculiar epoxidizing and hydroxylating properties, and notwithstanding the absence of substrate-enzyme-like interactions which limits their selectivity, they can be regarded as valuable models for P_{450} -dependent monooxygenases. A Fe(III) peroxo complex, obtained upon one-electron reduction of the dioxygen adduct $Fe^{3+}-O_2^-$ and reacting as its homolytically dissociated form $Fe^{II}-O-O^{\cdot}$ in a way similar to that of vanadium analogues (Scheme II), could be considered as a plausible alternative reactive intermediate in enzymic P_{450} oxidations. Further studies directed along these lines to gain more mechanistic details on these reactions and to extend their scope to catalytic synthetic oxidations⁴⁹ are now in progress in our laboratory.

Experimental Section

Materials. Reagent grade V_2O_5 , picolinic acid, 2-pyrazinecarboxylic acid, 4-picoline *N*-oxide (Aldrich) were used without further purification. *N,N*-Diethylpicolinamide⁵⁰ and methyl pyridine-2-carboxylate⁵¹ were prepared according to published procedures. Olefins were passed through a column containing active alumina to remove peroxidic impurities, distilled over sodium, and stored in nitrogen.

Apparatus. Infrared spectra were recorded by a Perkin-Elmer Model 457, UV-visible spectra by a Perkin-Elmer Model 402, and NMR spectra by a Varian CFT 20. Products were identified by GLC-MS coupling (Kratos Model MS80) and comparison with the mass spectra of authentic samples. The conductivities of the complexes in H_2O and CH_3CN were measured on a Methrom Model E365.

Preparation of $[VO(O_2)(Pic)_2] \cdot 2H_2O$ (Ia). V_2O_5 (4.52 g, 25 mmol) and picolinic acid (6.15 g, 50 mmol) were dissolved at 0 °C in 20 mL of 30% H_2O_2 with continuous stirring for 4 h. **CAUTION:** The reaction should be carried out in an open vessel and under rigorous temperature control in order to prevent H_2O_2 decomposition. The orange precipitate was filtered, rapidly washed with a minimum amount of ice-cold water and then with diethyl ether, and dried in vacuo: yield = 90%; 1H NMR (δ , D_2O) 7.5–8.5 (m, 3 H), 9.5 (d, 1 H). Ia is soluble in H_2O , MeOH, and CH_3CN and insoluble in CH_2Cl_2 . Anal. Calcd for $C_6H_8NO_8V$: C, 28.02; H, 3.1; N, 5.45; O (active), 6.22. Found: C, 28.01; H, 3.11; N, 5.44; O (active), 6.1.

Preparation of $[VO(O_2)(Pic)_2] \cdot H^+ \cdot H_2O$ (IIa). V_2O_5 (4.52 g, 25 mmol) and picolinic acid (12.3 g, 100 mmol) were dissolved at 0 °C in 20 mL of 30% H_2O_2 with continuous stirring for 4 h. The brick-red precipitate was filtered, rapidly washed with a minimum amount of ice-cold water and then with diethyl ether, and dried in vacuo: yield, 93%. Anal. Calcd for $C_{12}H_{10}N_2O_8V$: C, 39.7; H, 3.03; N, 7.73; O (active), 4.43. Found: C, 40.5; H, 2.95; N, 7.85; O (active), 4.41.

Preparation of $[VO(O_2)(Pic)_2] \cdot H^+ \cdot HMPT$ (IIb). This complex was prepared by the procedure used for IIa, adding HMPT (13.5 g, 75 mmol) at the end of the reaction. The complex IIb was extracted by 150 mL of CH_2Cl_2 . Addition of diethyl ether to the organic solution dried over Na_2SO_4 and concentrated to 25 mL precipitated a brick-red complex IIb: yield, 85%; 1H NMR (CD_2Cl_2) δ 2.44 (d, 18 H, $J_{H-P} = 10$ Hz (HMPT)), 7.5–8.5 (m, 6 H), 9.46 (d, 1 H), 9.95 (d, 1 H), 10.94 (s, 1 acidic proton); ^{13}C NMR (CD_2Cl_2) δ ring carbons 151.1 (C_2), 151.5 (C'_2), 125.2 (C_3), 127.3 (C'_3), 140.9 (C_4), 141.8 (C'_4), 127.9 (C_5), 129.2 (C'_5), 146.8 (C_6), 147.8 (C'_6); carboxylic carbons 168.8 (C_7), 169.1 (C'_7); pyridine-2-carboxylic acid-HMPT complex (CD_2Cl_2) δ ring carbons 147.6 (C_2), 127.0 (C_3), 142.3 (C_4), 129.2 (C_5), 146.4 (C_6); carboxylic carbon 163.8 (C_7). Anal. Calcd for $C_{18}H_{26}N_2O_8PV$: C, 41.3; H, 5.16; N, 13.38; V, 9.75; O (active), 3.06. Found: C, 41.4; H, 5.18; N, 13.3; V, 9.7; O (active), 3.0. The same complex was prepared from the reaction of Ia (1.28 g, 5 mmol) with picolinic acid (0.65 g, 5 mmol) and HMPT (1.5 mL) in CH_2Cl_2 (40 mL) at 0 °C for 4 h. The complex IIb was precipitated by addition of Et_2O ; yield, 2 g (80%).

Preparation of $[VO(O_2)(Pic)_2] \cdot PPh_4^+ \cdot H_2O$ (IIc). NH_4VO_3 (1.17 g, 10 mmol) and picolinic acid (2.46 g, 20 mmol) were dissolved in 10 mL of H_2O_2 30% for 1 h at 0 °C. Addition of 4.2 g (10 mmol) of tetraphenylphosphonium bromide results in the precipitation of a brick-red complex IIc, which was filtered and washed with H_2O and diethyl ether: yield, 6.5 g (92%); 1H NMR (CD_2Cl_2) δ 7.4–8.5 (m, 26 H), 9.5 (d, 1 H), 9.85 (d, 1 H). Anal. Calcd for $C_{36}H_{30}N_2O_8PV$: C, 61.7; H, 4.28; N, 4.0; P, 4.43; O (active), 2.28. Found: C, 61.3; H, 4.21; N, 4.01; P, 4.39; O (active), 2.20.

Preparation of $[VO_2(Pic)_2] \cdot H_2O$ (IIIa). Complex Ia (1 g, 3.9 mmol) was dissolved in a solution containing 60 mL of CH_3CN and 5 mL of cyclohexane. After the mixture stirred continuously for 3 h in N_2 , a yellow complex precipitated which was filtered and washed with diethyl ether; yield, 0.75 g (88%). Anal. Calcd for $C_{12}H_{10}N_2O_9V_2$: C, 33.64; H, 2.33; N, 6.54. Found: C, 33.2; H, 2.1; N, 6.5.

Preparation of $VO_2(Pic)(HMPT)$ (IIIb). A CH_2Cl_2 (60 mL) solution of picolinic acid (1.25 g, 10 mmol) and HMPT (3.5 mL) was added to a suspension of NH_4VO_3 (1.17 g, 10 mmol) in 10 mL of H_2O . After addition of 2 mL of HBf_4 (38%) of vigorous stirring for 15 min, the yellow CH_2Cl_2 solution was decanted, dried over Na_2SO_4 , and concentrated until yellow crystals were formed. Recrystallization of this complex in $CH_2Cl_2-Et_2O$ yielded 3.4 g (88%) of light yellow crystals. Anal. Calcd for $C_{12}H_{22}N_4O_5V$: C, 37.51; H, 5.77; N, 14.58; P, 8.06. Found: C, 37.02; H, 5.77; N, 14.26; P, 8.15. 1H NMR (CD_2Cl_2) δ 2.79 (d, 18 H, $J_{H-P} = 10$ Hz (HMPT)), 7.3–8.3 (m, 3 H), 8.67 (d, 1 H). The same complex was synthesized from the reaction of IIIa (0.5 g, 2.25 mmol) with HMPT (0.7 g, 4 mmol) in CH_2Cl_2 and precipitation with diethyl ether; yield, 84%.

Oxidation Procedures and Product Analysis. The hydrocarbons were oxidized in a small double-jacketed glass flask connected to a vacuum nitrogen line. In a typical procedure, the hydrocarbon solution containing the internal standard was added in N_2 to the complex, and the evolution of the oxidation was followed by GLC analysis of aliquot samples. In the case of aromatics and alkanes hydroxylation, the peroxidic complex in the aliquot samples was reduced at 0 °C by excess PPh_3 in order to prevent further oxidation in the GLC injector. Different columns were used, depending on the requested analysis: Column A (10% DEGS on Chromosorb WHP 4 m) and column B (20% Carbowax on Chromosorb WAW 4 m) were used for the oxidation of olefins. Column C (10% FFAP on Chromosorb WAW 3 m) and column D (FFAP, fused-silica capillary column 25 m) were used for the oxidation of aromatic hydrocarbons and alkanes. The oxygenated products were identified by GLC-MS coupling and comparison of the mass spectra with those of authentic samples.

NIH Shift. Ia (5 mg) was reacted with 4-deuteriotoluene (100 μ L, 95% D content, prepared by deuteriolysis of 4-bromotoluene^{52a}) in CH_3CN (1 mL) for 1 h. The concentrated reaction mixture was analyzed by GLC-MS coupling using the capillary column D. The deuterium content of *p*-cresol was found to be equal to 70% estimated from *m/e* 107 and 108 ($M-1$). The deuterium content of *o*- and *m*-cresol was 90 and 81%, respectively.

X-ray Data Collecting and Processing. Suitable crystals of Ia were obtained by slow crystallization at 4 °C in a diluted reaction medium, and those of IIIb by slow evaporation of a CH_2Cl_2 solution at room temperature. The crystal systems were determined by using an automatic Phillips PW 1100/16 (for Ia) or a Picker FACS-1 (for IIIb) with standard software. The unit cell parameters were refined with 25 carefully selected reflections. The results are summarized in Table XVII. A parallelepipedic crystal of Ia and a spherical-shaped crystal of IIIb were sealed in Lindemann glass capillaries and mounted on rotation-free goniometer heads. Intensities were recorded by using the parameters listed in Table XVII. The raw step-scan data were converted to intensities with their standard deviation, using the Lehman-Larsen algorithm.⁵² These intensities were then corrected for Lorentz and polarization factors; absorption corrections were applied by using the method outlined by Dwiggs⁵³ for IIIb and the numerical integration method for Ia.⁵⁴ For complex Ia, a linear decay correction was applied. All computing was done with the Enraf-Nonius structure determination package.⁵⁵ Both structures were solved with the heavy-atom method and refined with full-matrix least squares and refinement of the heavy atoms. A difference Fourier revealed maxima of residual electronic density close to the positions expected for hydrogen atoms. They were introduced into structure factor calculations by their computed coordinates for the carbon hydrogen ($C-H = 0.95$ Å) and Fourier coordinates for the water molecule hydrogens with isotropic temperature factors but not refined.⁵⁶ Table XI gives the final results.

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Registry No. IA, 85082-23-1; Ib, 85082-29-7; Ic, 85082-30-0; Id, 85082-31-1; Ie, 85032-32-2; If, 85082-33-3; Ig, 85082-34-4; Ih, 85082-35-5; Ii, 85082-36-6; Ij, 85082-37-7; IIa, 85082-24-2; IIb, 85082-25-3; IIc, 85082-27-5; IIIa, 85082-28-6; IIIb, 82371-40-2; $C_6H_{13}CH=CH_2$, 111-66-0; $Ph-CH=CH_2$, 100-42-5; C_6H_5 , 71-43-2; CH_4 , 74-82-8; *cis*-2-butene, 590-18-1; *trans*-2-butene, 624-64-6; cyclohexene, 110-83-8; norbornene, 498-66-8; *trans*-1-phenyl-1-propene, 873-66-5; α -methyl styrene, 98-83-9; 2-methyl-2-pentene, 625-27-4; toluene, 108-88-3; 1,3,5-trimethylbenzene, 108-67-8; *cis*-decalin, 493-01-6; *n*-octane, 111-65-9.

Supplementary Material Available: Complex Ia: contact distances less than 3.5 Å (Table I), distances and angles (Table II), mean planes (Table III), positional and thermal parameters (Tables IV and V), observed and calculated structure factor amplitudes (Table VI). Complex IIIb: description of the structure, distances and angles (Table IX), least-squares mean planes (Table X), positional and thermal parameters (Table XI and XII), observed and calculated structure factor amplitudes (Table XIII). Complexes Ia and IIIb: X-ray experimental data (Table XVII). Experimental Section: preparation and analysis of complexes Ib-j (25 pages). Ordering information is given on any current masthead page.

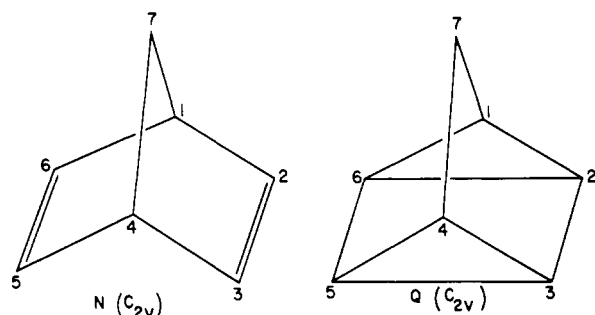
Theoretical Studies in the Norbornadiene-Quadricyclane System

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Abstract: Ab initio molecular orbital theory is used to investigate interesting aspects of the chemistry of norbornadiene (N) and quadricyclane (Q). Effects of polarization functions and electron correlation are included in these calculations. The optimized structures of N and Q are found to be in excellent agreement with those obtained from electron diffraction experiments. N is calculated to be 27 kcal/mol more stable than Q, slightly higher than the experimental thermochemical measurements. Detailed structural information which is not available experimentally is provided for the radical cations of N and Q (N^+ and Q^+). N^+ is calculated to be 11 kcal/mol more stable than Q^+ , in good agreement with the experimental value. The nature of the triplet state is investigated in detail. The structure of the triplet state is found to be distorted to a symmetry (C_s) lower than that of the parent compounds (C_{2v}). An analysis of the orbital correlations for such a distorted triplet state reveals that conversion to Q on the singlet surface is more favorable than conversion to N. This explains the photochemical observations that reveal that the triplet state converts with a high yield ($\approx 90\%$) to Q. Relative spin densities are calculated for both radical cations and are consistent with the measured nuclear spin polarization spectra.

Norbornadiene (N) and quadricyclane (Q) are strained hy-



drocarbons which have been the subject of intense experimental¹⁻¹³

and theoretical¹⁴⁻²¹ investigations. They are structural isomers which can interconvert under appropriate conditions. Thermochemical as well as structural information about both molecules is known experimentally and hence provides a convenient testing ground for theoretical studies.

The cations formed from both N and Q (N^+ and Q^+) have also been observed in photochemical²¹⁻²⁴ and nuclear spin polarization (CIDNP) experiments.^{25,26} From the ionization potentials observed in the case of N and Q, thermochemical information about the cations can be inferred. However, no structural information is available, as is typical for most gas-phase ions. Hence, theory can provide valuable structural information to complement the energetic information known from experiments.

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