$$\left(\frac{\mathrm{d}[\mathrm{N_2}]}{\mathrm{d}t}\right)_{\max}$$

and t_m are given by

$$\frac{\mathrm{d}^2[\mathrm{N_2}]}{\mathrm{d}t^2} = 0$$

Equation A11 gives

$$\frac{\mathrm{d}^2[\mathrm{N_2}]}{\mathrm{d}t^2} = \frac{k_4[\mathrm{H_2O_2}]\mathrm{e}^{t/\tau}}{2k_7\tau^2(\mathrm{b}e^{t^*/\tau} + e^{t/\tau})^2}\left(b\mathrm{e}^{t^*/\tau} - \frac{k_4}{k_7}\mathrm{e}^{t/\tau}\right) \quad \text{(A19)}$$

Thus, t_m is given by

$$be^{t^*/\tau} - \frac{k_4}{k_7}\mathrm{e}^{t_m/\tau} = 0$$

or

$$t_m = \tau \ln\left(\frac{k_7}{k_4}be^{t^*/\tau}\right) = t^* + \tau \ln\left(\frac{k_7}{k_4}\mathrm{b}\right) \quad \text{(A20)}$$

At $t = t_m$, eq A16 and A17 give

$$[\mathrm{N_2}]|_{t_m} = \frac{1}{2}([\mathrm{H_2O_2}]_0 - [\mathrm{H_2O_2}]_{t_m}) =$$

$$\frac{[\mathrm{H_2O_2}]_0}{2}\left|1 - \left|\frac{b+1}{b + \frac{k_7}{k_4}\mathrm{b}}\right|^{(k_4/k_7)}\right| \quad \text{(A21)}$$

Equation A11 gives

$$\left(\frac{\mathrm{d}[\mathrm{N_2}]}{\mathrm{d}t}\right)_{\max} = \frac{\frac{k_4}{2k_7\tau}[\mathrm{H_2O_2}]|_{t_m}\frac{k_7}{k_4}\mathrm{b}}{b + \frac{k_7}{k_4}\mathrm{b}} =$$

$$\frac{[\mathrm{H_2O_2}]_0}{2\left(1 + \frac{k_7}{k_4}\right)\tau}\left|\frac{b+1}{b + \frac{k_7}{k_4}b}\right|^{(k_4/k_7)} \quad \text{(A22)}$$

Equations A18, A21, and A22 give

$$\tau_e = t^* + \tau \ln\left(\frac{k_7}{k_4}b\right) + \tau\left(1 + \frac{k_7}{k_4}\right)\left|1 - \left|\frac{b + \frac{k_7}{k_4}\mathrm{b}}{b+1}\right|^{k_4/k_7}\right| \quad \text{(A23)}$$

For τ_e to be equal to τ, it is required that t^* be small relative to τ and

$$\ln\left(\frac{k_7}{k_4}b\right) + \left(1 + \frac{k_7}{k_4}\right)\left|1 - \left|\frac{b + \frac{k_7}{k_4}b}{b+1}\right|^{k_4/k_7}\right| = 1.0 \quad \text{(A24)}$$

Experimentally, k_4/k_7 and b are found to be about 0.19 and 5.28, respectively. With these values, RHS of eq A23 = $t^* + \tau$. The results establish that, provided that t^* is negligibly small, $\tau = \tau_e$.

Registry No. N_2H_4, 302-01-2; H_2O_2, 7722-84-1; Cu, 7440-50-8.

Vanadium(V)/Vanadium(III) Redox Couple in Acidic Organic Media. Structure of a Vanadium(III)–Tetraethylene Glycol Pentagonal-Bipyramidal Complex ($[V(teg)(Br)_2]^+Br^-$)

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Contribution from the Casali Institute of Applied Chemistry, The Hebrew University of Jerusalem, Jerusalem, Israel 91904. *Received May 8, 1989*

Abstract: The vanadium(V)/vanadium(III) redox couple was investigated in an acidic organic medium by reduction of sodium metavanadate by hydrogen bromide with 1,2-dichloroethane as solvent in the presence of tetraglyme as a complexing agent. In the absence of dioxygen a vanadium(III)–tetraethylene glycol (teg) pentagonal-bipyramidal complex, $[V(teg)(Br)_2]^+Br^-$, is formed. In the presence of dioxygen a catalytical cycle is initiated whereby vanadium(V) oxidizes hydrogen bromide to molecular bromine. The reduced vanadium(III) species thereby formed is reoxidized by dioxygen to vanadium(V) as confirmed by ESR and UV–vis of the organic phase.

The coordination and oxidation chemistry of vanadium compounds in liquid organic media has recently received a great deal of research interest. This research has been fueled by the discovery of biological implications of vanadium chemistry. Thus a low-valent vanadium compound is found at the active site of nitrogenase in the bacterium *Azobactor chroococcumm*,[1] and a vanadium(V) complex is present in a bromoxidase enzyme in the marine algae *Ascophyllum nodosum*.[2] The bromoxidase enzyme is capable of catalyzing bromination reactions whereby bromide anions are oxidized by hydrogen peroxide, eq 1. Vanadium is also sequestered from sea water in the marine organisms known as "sea squirts" or tunicates.[3] These tunicates are exceptional in their ability to accumulate vanadium(III)[4] at concentrations of up to 1–2 M by reduction of anionic vanadium(V) species found

$$\mathrm{SH + Br^- + H_2O_2 + H^+ \rightarrow SBr + 2H_2O} \quad (1)$$

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0002-7863/89/1511-8410$01.50/0

Table I. Selected Bond Distances (Å) and Angles (deg) for $[V(teg)(Br)_2]^+Br^-$

V–Br1	2.513 (3)	Br1–V–Br2	178.6 (1)
V–Br2	2.517 (3)	O1–V–O2	72.2 (4)
V–O1	2.08 (1)	O2–V–O3	71.3 (4)
V–O2	2.13 (1)	O3–V–O4	70.8 (5)
V–O3	2.15 (1)	O4–V–O5	73.2 (5)
V–O4	2.14 (1)	O5–V–O1	72.7 (5)
V–O5	2.08 (1)		
O1–Br3	3.118 (3)		

in sea water (about 10^{-7}–10^{-8} M) to vanadium(III) cationic species, which are trapped within the tunicates.[3] There is conflicting evidence that the V(III) oxidation state may be stabilized either by a highly acidic environment or through complexation by polyphenolic ligands called tunichromes.[5,6]

In the context of the vanadium chemistry outlined above, we have undertaken a study of the liquid-phase room-temperature redox chemistry of a vanadium(V) precursor in the presence of gaseous hydrogen bromide and molecular oxygen. A V^{5+}/V^{3+} redox couple is formed where a vanadium(V) species is reduced to a vanadium(III) species by gaseous hydrogen bromide dissolved in a chlorohydrocarbon solvent in the presence of tetraglyme as a complexing agent. In the absence of appreciable amounts of dioxygen red-purple single crystals of the molecular formula $[V^{3+}(teg)(Br)_2]^+Br^-$ (teg = tetraethylene glycol) are formed. This compound has a regular pentagonal-bipyramidal structure with tetraethylene glycol as a pentadentate ligand and two bromide axial ligands. This is the first example where a simple linear polyether analogue of a macrocyclic crown ether has been found as a stabilizing ligand of a reactive transition metal. Under aerobic conditions a catalytic cycle is initiated as witnessed by the formation of molecular bromine. UV–vis and ESR spectroscopic investigations indicate reoxidation by dioxygen of the vanadium(III) species directly to a vanadium(V) product. A vanadium(IV) species generally formed[7] in the oxidation of vanadium(III) compound is conspicuously absent.

Results and Discussion

Crystals of $[V^{3+}(teg)(Br)_2]^+Br^-$ were precipitated by bubbling gaseous hydrogen bromide into a mixture containing 0.1 mmol of vanadium(V) species (added as sodium or ammonium metavanadate), 10 mmol of tetraglyme, $CH_3O(CH_2CH_2O)_4CH_3$, and 25 mL of 1,2-dichloroethane. Passage of hydrogen bromide was continued until the solution was saturated as evidenced by the fuming of the solution. The solution was then transferred into vials leaving no space (air) between the liquid and vial cap, which was hermetically closed. After the solution stood for 2–5 days at room temperature and in the dark, red-purple air-sensitive crystals were formed and were identified by X-ray diffraction to be $[V^{3+}(teg)(Br)_2]^+Br^-$. The space group is orthorhombic $P2_12_12_1$ with the cell constants a = 15.328 (4) Å, b = 13.219 (3) Å, c = 7.464 (3) Å, V = 1512.4 (6) Å^3, and ρ_{calc} = 2.13 g cm^{-3} for Z = 4. The structure of the $[V^{3+}(teg)(Br)_2]$ cation is given in Figure 1, and the important bond lengths and angles are given in Table I. The crystal structure reveals several interesting and novel facets. One may note the pentagonal-bipyramidal structure with tetraethylene glycol as an equatorial pentadentate ligand. Vanadium to oxygen atom distances of 2.13 (1)–2.15 (1) Å for the internal oxygen atoms O2, O3, and O4 and 2.08 (1) Å for the terminal oxygen atoms O1 and O5 are found. Bond angles between nearest oxygen atoms and the central vanadium atom O–V–O vary between 70.8 (5)° and 73.2 (5)°. Computation of the average deviation of the oxygen atoms from the least-squares plane gives a value of 0.0518 Å, indicating a highly planar structure. The tetraethylene glycol oxygens form a regular pentagon around the vanadium center. Vanadium to bromine atom distances are 2.513 (3) and 2.517 (3) Å with a Br1–V–Br2 bond angle of 178.6 (1)°. The structure shows that the two axial bromine atoms are equivalent, and therefore the entire cation has a regular pentagonal-bipyramidal structure. The bromide counteranion (not shown) is found to be hydrogen bound to the terminal O1 atom with a O1 to bromide bond distance of 3.118 (3) Å. The finding that tetraethylene glycol is a pentadentate ligand may have been theoretically expected as there are examples of pentadenticity of 15-crown-5, the macrocyclic analogue of tetraethylene glycol, with metal cations such as Na(I),[8] Pb(II),[9] Zn(II),[10] and Co(II).[11] It is, however, exceptional that tetraethylene glycol as a generally accepted poor linear analogue of macrocyclic crowns[12] is able to stabilize a reactive transition-metal species such as vanadium(III).

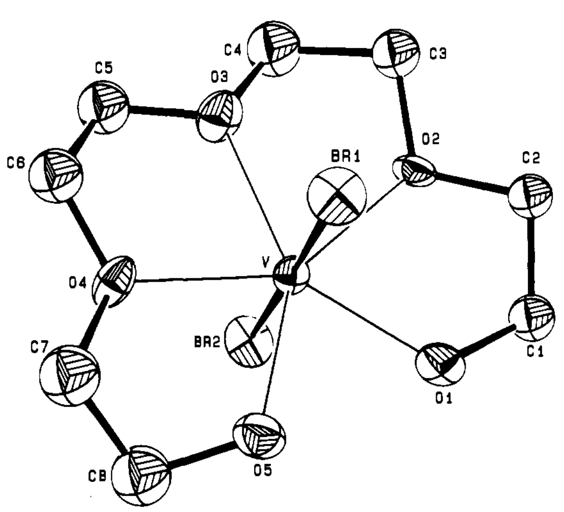

Figure 1. Structure of the $[V^{3+}(teg)(Br)_2]^+$ cation showing the 50% probability thermal ellipsoids and atom-labeling scheme.

In this context it is also worth noting that although the tetraethylene oxide ligand was originally added as a glyme, it forms a stable complex only after removal of the terminal methyl groups of the glyme by scission of the terminal ether bond by hydrogen bromide. This finding seems to indicate that the additional energy gained by hydrogen bonding of the bromide anion to the terminal hydroxyl group is crucial for the stabilization of the vanadium(III) crystalline compound.

Continual passage of hydrogen bromide and air into a mixture of 0.1 mmol of $NaVO_3$, 10 mmol of $CH_3O(CH_2CH_2O)_4CH_3$, and 25 mL of 1,2-dichloroethane yields a catalytic system that oxidizes hydrogen bromide with dioxygen to form bromine and water. The bromine formed was accumulated as the reaction product or alternatively was reacted in situ by addition of 20 mmol of reactive organic substrates, eq 2. Results of such bromination reactions

$$HBr + RH + \tfrac{1}{2}O_2 \xrightarrow{[V]} RBr + H_2O \qquad (2)$$

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(5) For a discussion and summary of both viewpoints, see: Oltz, E. M.; Bruenig, R. C.; Smith, M. J.; Kustin, K.; Nakanishi, K. *J. Am. Chem. Soc.* **1988**, *110*, 6162 and references therein.

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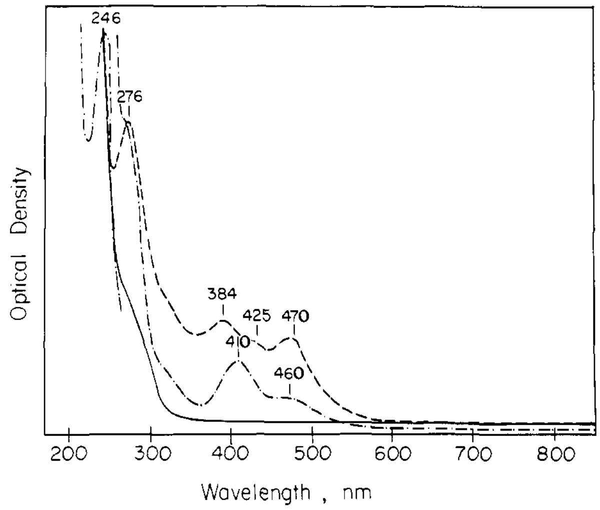

Figure 2. Ultraviolet and visible spectra of the vanadium species: (—) spectrum of the catalytically active vanadium(V) species; (---) spectrum of $[V^{3+}(teg)(Br)_2]^+Br^-$ dissolved in dichloromethane; (–•–) spectrum of $[V^{3+}(teg)(Br)_2]^+Br^-$ dissolved in acetonitrile. The peak at 246 nm is found for the V(III) compound in both acetonitrile and dichloromethane.

with olefins, such as 1-octene or styrene, or with aromatics such as anisole or ethoxybenzene gave a turnover number of 100 ± 10 mol of Br_2/mol of V h^{-1} at 25 °C.

In order to gain further insight as to the mode of operation of the vanadium catalyst, the ESR and UV–vis spectra of the vanadium solution were taken. The ESR spectra show that the catalytic solution is ESR silent at both room temperature and 77 K. The absence of a typical vanadium(IV) signal even at high gains indicates that only vanadium(III) and vanadium(V) may be present in solution since both these oxidation states of vanadium are ESR silent. The UV–vis spectra of the catalytically active solution and those of the vanadium(III) crystal dissolved in dichloromethane and acetonitrile are given in Figure 2. The dissolved vanadium(III) crystal has peaks in the near-ultraviolet and visible regions attributable to charge transfers and d-d ligand transitions.[13] The catalytically active solution and the vanadium(V) precursor on the other hand have *no* peaks in the near-ultraviolet and visible region, indicating that *only* a d^0 or vanadium(V) species is present. It therefore seems reasonable that a catalytic cycle centered around the V^{5+}/V^{3+} redox couple has been formed although the formation of a short-lived intermediate vanadium(IV) moiety cannot be entirely ruled out. A speculative catalytic cycle may be thus represented by the oxidation by dioxygen of a vanadium(III) species, perhaps through a peroxo dimer intermediate, to a vanadium(V) species, which in turn oxidizes hydrogen bromide to bromine, eq 3.

$$2V^{III} + O_2 \rightarrow [V^{III}OOV^{III}] \rightarrow 2V^{V}O$$
$$2V^{V}O + 4HBr \rightarrow 2V^{III} + 2Br_2 + 2H_2O \qquad (3)$$

In the past vanadium(III) species have been shown to interact with dioxygen, yielding a vanadium(III)–dioxygen adduct followed by the formation of vanadium(IV) species.[7] When the isolated $[V(teg)(Br)_2]^+Br^-$ compound is redissolved in 1,2-dichloroethane in the *absence* of HBr, the vanadium(III) compound is likewise slowly (2–3 days) decomposed by oxidation to a blue-green vanadium(IV) species [UV–vis: λ (log ϵ) 725 (3.75), 608 (3.87), 406sh (4.31), 284 (5.33) nm]. One must conclude that the acidity of the organic solution is critical in defining the catalytic pathway. The affect of a strongly noncoordinating acidic media has been noticed in the past where perchloric acid has catalyzed the disproportionation a vanadium(IV) compound to vanadium(V) and vanadium(III) compounds.[14] However, the absence of vanadium(III) or vanadium(IV) in an aerobic solution in our system and the fact that the disproportionation fails for coordinating acids[14] argue for a different pathway. The identity of the halide anion is also of critical importance. For example, under identical reaction conditions the use of hydrogen chloride instead of hydrogen bromide yields a *noncatalytic* reduction of vanadium(V) to a green vanadium(IV) compound, because hydrogen chloride is a weaker reducing agent than hydrogen bromide or iodide, which enable the reduction to the vanadium(III) state.[15] The fact that the vanadium(IV) compound is not reoxidized to a vanadium(V) species and chlorine is not catalytically formed also provides evidence that vanadium(IV) oxidation state is circumvented and is not an intermediate in the catalytic oxybromination reaction.

Table II. Summary of Crystallographic Data for $[V(teg)(Br)_2]^+Br^-$

formula	$C_{10}H_{18}Br_3O_5V$
mol wt	484.88
cryst syst	orthorhombic
space gp	$P2_12_12_1$
a, Å	15.328 (4)
b, Å	13.219 (3)
c, Å	7.464 (3)
V, Å^3	1512.4 (6)
Z	4
ρ_{calcd}, g cm^{-3}	2.13
μ(Mo Kα), cm^{-1}	83.96
no. of unique data	1528
no. of obsd data $I \geq 3\sigma(I)$	1101
R	0.054
R_w	0.073
w	$(\sigma_F^2 + 0.003834F^2)^{-1}$

Conclusion

The vanadium-catalyzed oxidation of hydrogen bromide to bromine has revealed a novel V^{5+}/V^{3+} redox couple. In the presence of dioxygen only a vanadium(V) species is observed in solution, whereas in the absence of dioxygen a unique vanadium(III) compound with tetraethylene glycol as a pentadentate ligand crystallizes. This latter compound is certainly related to a reduced vanadium(III) species active in the catalytic cycle described.

Experimental Section

Materials and Instruments. Compounds accessible from commercial sources were of the highest purity available and were used without further purification. The following instruments were used. UV–vis spectra were recorded on a Bausch and Lomb Spectronic 2000 spectrophotometer. Solution ESR spectra were recorded on a Varian 3L spectrometer with a liquid-nitrogen Dewar. DPPH (g = 2.0037) was used as an external standard. FTIR spectra were recorded with an Analect 6260 Fourier transform spectrometer with samples prepared as KBr pellets. Elementary analysis was performed by Atomic Absorption with a GBC 923, and microanalysis was performed at The Hebrew University Microanalysis Center.

Preparation of $[V(teg)(Br)_2]^+Br^-$. Sodium metavanadate (14 mg, 0.1 mmol) and tetraglyme (2.2 g, 10 mmol) were added to 20 mL of deaerated 1,2-dichloroethane. Anhydrous hydrogen bromide was slowly bubbled through the solution for about 15 min until saturation or a fuming solution was obtained. The orange solution obtained was transferred into a 20-mL vial, which was filled, leaving no space for air, and then sealed. The vial was stored at room temperature for 2–5 days wherein red-purple single crystals formed, yield 82%. The elementary analysis of the crystals by a combination of atomic absorption of vanadium and microanalysis of carbon, hydrogen, and bromine gave calculated for $C_{10}H_{18}Br_3O_5V$: C, 19.82; H, 3.74; Br, 49.44; O, 16.50; V, 10.51. Found: C, 19.56; H, 3.83; Br, 48.63; V, 10.76. UV-vis (CH_2Cl_2): λ (log ϵ) 246 (5.30), 276 (5.21), 384 (4.48), 425 sh (447), 470 (4.73) nm. The IR spectra as a KBr pellet has the following absorptions: 1630 s, 1458 m, 1399 w, 1351 w, 1299 vw, 1244 w, 1112 sh, 1093 sh, 1067 vs, 971 m,

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J. Am. Chem. Soc. 1989, 111, 8413-8420

950 m, 911 w, 882 w, 828 w, 666 m, 504 m, cm^{-1}. It may be also noted that the C–H peak expected at about 2900 cm^{-1} was very broad.

X-ray Crystal Structure Analysis. Crystals were obtained as described and mounted in a glass capillary. Data were measured on a PW1100/20 Phillips Four-Circle computer-controlled diffractometer. Mo Kα (λ = 0.71069 Å) radiation with a graphite crystal monochromator in the incident beam was used. The unit cell dimensions were obtained by a least-squares fit of 24 centered reflections in the range of $10° \leq \theta \leq 15°$. Intensity data were collected using the ω–2θ technique to a maximum 2θ of 50°. The scan width, $\Delta\omega$, for each reflection was 1.00 + 0.35 tan θ with a scan speed of 0.05 deg/min. Background measurements were made for a total of 20 s at both limits of each scan. Three standard reflections were monitored every 60 min. No systematic variations in intensities were found. Intensities were corrected for Lorentz and polarization effects. Absorption was corrected by using the Ψ-scan method. All non-hydrogen atoms were found by using the results of the SHELXS-86 direct method analysis.[16] After several cycles of refinements using a CYBER 855 computer, the positions of the hydrogen atoms were calculated and added with a constant isotropic temperature factor of 0.05 Å^2 to the refinement process. Refinement proceeded to a convergence by minimizing the function $\sum w(|F_o| - F_c|)^2$. A final difference Fourier synthesis map showed several peaks less than 1 e/Å^3 scattered about the unit cell without significant feature. The discrepancy indices $R = \sum||F_o| - |F_c||/\sum|F_o|$ and $R_w = [\sum w(|F_o| - |F_c|)^2/\sum wF_o^2]^{0.5}$ are presented with other pertinent crysallographic data in Table II.

Supplementary Material Available: Tables of positional and thermal parameters and bond lengths and bond angles (5 pages). Ordering information is given on any current masthead page.

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Mechanism of Reactions of Hydrogen Peroxide and Hydroperoxides with Iron(III) Porphyrins. Effects of Hydroperoxide Structure on Kinetics

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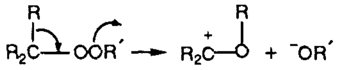
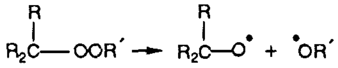
Abstract: The buffer-catalyzed and uncatalyzed reactions of various alkyl hydroperoxides and hydrogen peroxide with chelated protohemin chloride have been studied. The rates of the uncatalyzed reactions show the same dependence on structure as the catalyzed reactions. The rates of reactions of peracids and hydroperoxides show similar dependencies on leaving ion stability. These and other evidence indicate that these reactions proceed by heterolytic cleavage of the oxygen–oxygen bond under the conditions employed.

The cleavage of the oxygen–oxygen bond in peroxides takes two distinct pathways, heterolytic[1-3] or homolytic,[4,5] illustrated by eq 1 and 2 for organic peroxides. Reaction 1 is accelerated



$$R_2\overset{R}{C}{-}OOR' \longrightarrow R_2\overset{+}{C}{-}\overset{R}{O} + {}^{-}OR' \qquad (1)$$

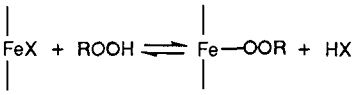


$$R_2\overset{R}{C}{-}OOR' \longrightarrow R_2\overset{R}{C}{-}O^{\bullet} + {}^{\bullet}OR' \qquad (2)$$

by increased electron density in R and decreased electron density in R′ and is catalyzed by acid in those cases where $R'O^-$ is not self-sufficiently stable, i.e., R′ = alkyl or hydrogen.[2,3]

By contrast reaction 2 is accelerated by increased electron repulsion of the oxygen lone pairs and by resonance stabilization of $R'O^{\bullet}$ and $R_3CO^{\bullet}$. Thus any reaction producing $RO^{\bullet}$ will be sensitive to its stability. Electron-withdrawing groups as either R′ or R decrease the rate. Because $RO^{\bullet}$ is a poor base, general or specific acid catalysis of reaction 2 is not to be expected and has not been observed.

Recent interests[6-12] in the metalloenzyme-catalyzed cleavage of peroxide bonds has prompted further investigation of these mechanisms in those cases where the peroxide contains a metal–oxygen bond. A similar dichotomy of mechanisms can be envisioned in the reactions of the biologically important iron(III) porphyrins (PFe^+) with hydroperoxides and peracids to presumably produce an iron(III)–hydroperoxide species (eq 3).



$$\text{FeX} + \text{ROOH} \rightleftharpoons \text{Fe}{-}\text{OOR} + \text{HX} \qquad (3)$$

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