from *tert*-butyl methyl ether,[11] and thermochemical data on stabilities of α-silyl radicals[12] are generally consistent with a greater ease of abstraction α to the ether linkage. The competitive substitution observed here is unusual in that the *tert*-butoxy radical/tetraethyltin reaction[10] gave no evidence of ethyl displacement and only a trace of methyl-radical products was observed in the trichloromethyl/2-(trimethylstannyl)butane system.[9] The relatively facile displacement on **1** may suggest a strong steric influence on the course of these substitutions.[13]

That 1,3-ring closure is a general reaction of γ-organotin radicals is demonstrated by the benzophenone-induced photooxidation/decarbonylation[14] sequence shown by trimethyl(4-hydroxybutyl)tin (**2**). Chromatographic analysis of a reaction

$$\underset{\mathbf{2}}{Me_3Sn(CH_2)_4OH} + Ph_2CO^*(T) \xrightarrow{\text{benzene}} \underset{\mathbf{3}}{Me_3Sn(CH_2)_3\overset{O}{\overset{\|}{C}}H} \quad (13)$$

$$3 + Ph_2CO^*(T) \longrightarrow \underset{\mathbf{4}}{Me_3Sn(CH_2)_3^{\bullet}} + CO + Ph_2\dot{C}OH \quad (14)$$

$$4 \longrightarrow \triangle + Me_3Sn^{\bullet} \quad (15)$$

$$2Me_3Sn^{\bullet} \longrightarrow (Me_3Sn)_2 \quad (11)$$

$$2Ph\dot{C}OH \longrightarrow (Ph_2COH)_2 \quad (12)$$

mixture of **2** and benzophenone at varying conversions clearly shows the buildup of **3** as a precursor of the ultimate products of cyclopropane and CO. The photooxidation of trimethyl(3-hydroxypropyl)tin (**5**) also shows the initial conversion to the aldehyde, trimethyl(3-oxopropyl)tin (**6**), and the subsequent decarbonylation of **6** to ethylene and CO. Hexamethylditin and benzopinacol are formed in both photooxidation/decarbonylation sequences in benzene; however, if the reaction is carried out carbon tetrachloride, trimethyltin chloride is the organotin product. Ethylene arises from the facile elimination of Me_3Sn from the (β-trimethyltin) ethyl radical[15] formed by decarbonylation of **6**. Since the ω-trimethyltin-substituted aldehydes[16] are readily available and easily decarbonylated, this reaction may offer a general route to (ω-trimethyltin) alkyl radicals. Interestingly, the benzophenone-induced photooxidation of **5** gave *propanal* as a major product, but **2** showed no butanal! Propanal could arise by an S_H2 reaction of ketone triplet on **5** (or **6**) but since the expected analogous reaction toward **2** (or **3**) did not occur, the more likely source of propanal is the 1,3-ring closure of the intermediate radical, $Me_3SnCH_2CH_2\dot{C}HOH$, to cyclopropanol. Not surprisingly, cyclopropanol was not detected since it undergoes a rapid ketone triplet induced ring opening to form propanal.[17] Thus the formation of propanal from **2** but not butanal from **5** suggests that 1,3-ring closures of the radical $Me_3SnCH_2CH_2\dot{C}HOH$ to yield cyclopropanol and eventually propanal are much faster the 1,4-ring closure of $Me_3SnCH_2CH_2CH_2\dot{C}HOH$.

The lack of strong evidence for the generality of radical adducts of group 4 organometallics[10c] as compared to the corresponding group 3 or 5 elements,[18] the expected large ring strain in stannacyclobutanes,[19] the strain-accelerated ring-opening reactions of stannacyclopentanes,[20] the facile 1,3- and 1,5-ring closures, and the apparent lack of 1,4-ring closure suggest that these reactions are occurring through 3- or 5-membered cyclic transition states involving homolytic substitution at the carbon atom in the carbon–metal bond.

$$5 + Ph_2CO^*(T) \longrightarrow \underset{\mathbf{5a}}{Me_3SnCH_2CH_2\dot{C}HOH} + Ph_2\dot{C}OH \quad (16)$$

$$\mathbf{5a} + Ph_2CO \longrightarrow \mathbf{6} + Ph_2\dot{C}OH \quad (17)$$

$$\mathbf{5a} + \longrightarrow \triangleright\!\!-OH + Me_3Sn^{\bullet} \quad (18)$$

$$\triangleright\!\!-OH + Ph_2CO^*(T) \longrightarrow CH_3CH_2CH_2\overset{O}{\overset{\|}{C}}H \quad (19)$$

$$6 + Ph_2CO^*(T) \longrightarrow \underset{\mathbf{6a}}{Me_3SnCH_2CH_2\overset{O}{\overset{\|}{C}}\cdot} \longrightarrow$$

$$\underset{\mathbf{6b}}{Me_3SnCH_2\dot{C}H_2} + CO \quad (20)$$

$$\mathbf{6b} \longrightarrow Me_3Sn^{\bullet} + CH_2{=}CH_2 \quad (21)$$

$$2Me_3Sn^{\bullet} \longrightarrow (Me_3Sn)_2 \quad (11)$$

$$2Ph\dot{C}OH \longrightarrow (Ph_2COH)_2 \quad (12)$$

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^{17}O ENDOR of Horseradish Peroxidase Compound I

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Hydrogen peroxide treatment of peroxidases and catalase produces an enzymic intermediate, called compound I, which is oxidized by 2 equiv above the ferriheme resting state.[1-3] Recently we employed electron nuclear double reasonance (ENDOR)[4] to prove that one oxidizing equivalent of horseradish peroxidase compound I (HRPI) exists as the porphyrin π-cation radical,[5] as proposed.[3] We now report the observation of ^{17}O ENDOR from HRPI prepared with $H_2{}^{17}O_2$. This result proves that one oxygen atom from the oxidant remains with the intermediate and therefore

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shows the second oxidizing equivalent to be associated with an oxyferryl center, as suggested by earlier ^{18}O isotopic substitution studies on chloroperoxidase.[6] It also allows us to characterize the bonding within this center.

Preparation of HRPI(^{16}O) and HRPI(^{17}O) followed published procedures.[7] $H_2{}^{17}O_2$ was prepared by reacting $^{17}O_2$ (50% enriched) with Na metal.[8] Details of the EPR–ENDOR spectrometer have been discussed.[9] An ENDOR signal represents a NMR absorption which is observed as a change in EPR signal intensity at a fixed magnetic field, H_0.[10] The normal ENDOR pattern for a set of magnetically equivalent protons is a single pair of lines separated in frequency by the orientation-dependent hyperfine coupling constant, A^H, and mirrored about the free-proton Larmor frequency, ν_H.[10] In contrast, the $\Delta m = \pm 1$ transitions for nucleus i, i = ^{14}N ($I = 1$) or ^{17}O ($I = {}^5/_2$), are expected to obey the expression[10]

$$\nu_{\pm}(m) = |A^i/2 \pm \nu_i + P^i(2m - 1)| \qquad (1)$$

where $-I + 1 \leq m \leq I$, P^i is the orientation-dependent quadrupole interaction constant, and all parameters are to be taken as positive (absolute values). When the parameters obey the inequality $A^i/2 > \nu_i > P^i(2I - 1)$, as will be shown to occur for HRPI(^{17}O), the equation describes a pattern consisting of two groups of $2I$ lines each, centered at $A^i/2$ and separated by $2\nu_i$. Within each group the resonances are separated by P^i.

The EPR absorption envelope of HRPI has a maximum at $g \sim 2$ and decreases both to high and low field without the "step" characteristic of a well-defined g tensor. The spectrum taken at pH 6.8 by Schulz et al.[7] was interpreted by assuming the components of the g tensor to have a Gaussian distribution around the values $(g_x, g_y, g_z) = (2.13, 1.73, 2.0)$. We now report that the spectrum and the resulting values of g_x and g_y are pH dependent. The samples employed here had pH values of 6.2, and their spectrum is more symmetric than reported, with g_x slightly larger and g_y smaller; the spectrum becomes less symmetric at elevated pH.

As we previously showed, when the magnetic field is set to the peak of the EPR spectrum of HRPI(^{16}O), at $g = g_z$, well-resolved ENDOR patterns from ^{14}N and ^1H are observed.[5] This spectrum, reproduced in the inset to Figure 1, appears to be pH independent. When the magnetic field is increased to the high-field edge of the spectrum corresponding to $g \sim 1.5$, the proton ENDOR pattern shifts appropriately to higher frequency and loses resolution, as does the ^{14}N pattern (Figure 1A). When HRPI(^{17}O) is examined under the same conditions, the ^1H and ^{14}N resonances are unchanged, but a strong new ^{17}O resonance at 11 MHz is also observed (Figure 1B). We interpret this as an unresolved set of $2I = 5$ quadrupole lines and assign their center as $\nu_+ = A^O{}_y/2 + \nu_0$. Assignment to ν_+, rather than $\nu_- = A^O{}_{1/2} - \nu_0$, is based on the observation that the line shifts appropriately to *higher* frequency when ENDOR spectra (not shown) are taken at a higher microwave frequency (11.7 GHZ vs. 9.6 GHz). The unobserved partner resonance, center at ν_-, is expected to be less intense; in addition, it is calculated to fall within the ^{14}N resonances, and cross-relaxation could also prevent its observation.[10] This interpretation requires that quadrupole coupling be small and is supported by molecular orbital calculations[11] from which we predict the spread of these 5 lines ($4P^O$) to be less than the ENDOR line width (~1.5 MHz).[12]

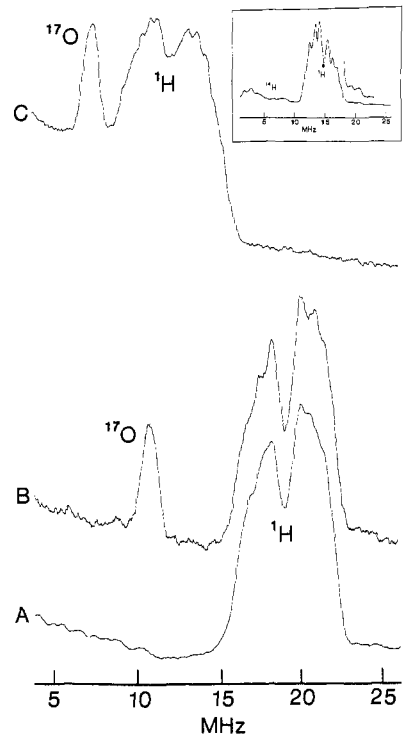

Figure 1. ENDOR spectra of HRPI. Inset: ^1H and ^{14}N ENDOR at $g = 2.0$, after ref 5. (A) HRP(^{16}O) and (B) HRP(^{17}O) at $g \simeq 1.5$; (C) HRP(^{17}O) at $g \simeq 2.4$. The emergence of strong ^{17}O signals is apparent. Conditions: 2-μW microwave power, $T = 2$ K, field modulation $\simeq 3$ G, scan rate ~2 MHz/s. Each spectrum represents the average of approximately 300 scans.

Upon changing H_0 to the low-field edge of the EPR signal, $g \sim 2.4$, the ENDOR spectrum of HRPI(^{17}O)(Figure 1C) is obtained. In addition to the proton and nitrogen signals, an intense ^{17}O resonance, absent in a HRPI(^{16}O) spectrum, is again seen. It is also assigned as the ν_+ transition, by the means described. Observation of ^{17}O ENDOR in HRP compound I, along with our earlier ^1H and ^{14}N ENDOR results, unambiguously establishes the composition of this center. The spin-triplet Fe^{IV} portion of compound I retains an oxygen atom from the oxidant, and thus is in fact an oxyferryl (Fe^{IV}=O) moiety; the spin-coupled doublet moiety is a porphyrin π-cation radical. The observation of the ^{17}O resonance further establishes that the iron-bound oxygen does not exchange with the natural abundance $H_2{}^{16}O$, at least during the 1–2 min subsequent to $H_2{}^{17}O_2$ addition and prior to freezing. In this regard, HRPI is similar to chloroperoxidase compound I.[6]

Analysis of the ^{17}O and ^{57}Fe hyperfine constants allows further insight into the properties of this center. The paramagnetism of HRPI was explained by Schulz et al. in terms of spin coupling between two spin systems, one the iron center, which has spin $S_T = 1$ and is subject to a zero field splitting of $D \sim 30$ cm^{-1}, and the other, now shown to be porphyrin radical,[5] which has spin $S_P = {}^1/_2$.[7] In particular, they showed that when the exchange coupling tensor has the form $J = (J_x, J_y, J_z)$ and the radical has an isotropic g value, $g^P = 2$, then the EPR spectrum of the coupled system will be described by the g' tensor, (g'_x, g'_y, g'_z), given by

$$g' = 2 + (\delta g'_x, \delta g'_y, \delta g'_z) \simeq 2 + (\delta g'_x, \delta g'_y, 0) \qquad (2)$$

where $\delta g_i \sim J_i/D$ for $i = x, y$. The ^{17}O and ^{57}Fe hyperfine interactions can also be analyzed within this model. If the triplet spin has ^{17}O hyperfine interaction tensor A^{OT}, then the ^{17}O hyperfine interactions in the coupled system will be described to first order by the tensor[13]

$$A^O = [A'_x, A'_y, A'_z] \qquad (3a)$$

$$A^O \simeq [A^{OT}{}_x \delta g'_x, A_y{}^{OT} \delta g'_y, 0] \qquad (3b)$$

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where the $\delta g'_\alpha$ are defined in eq 2. Thus, it is possible to use the measured hfs tensor, A', to obtain the tensor characteristic of the (Fe^{IV}=O) moiety, A^{OT}. Analogous expressions hold for coupling to the iron.

To fully characterize the ^{17}O hyperfine splitting tensor, ENDOR spectra were obtained at fields across the entire envelope of the EPR spectrum. We show elsewhere[12] that two of the quantities of interest, A^{OT}_x and A^{OT}_y, are simply obtained from the ^{17}O ENDOR spectra observed when the field is set to the low-and the high-field edges of the EPR spectrum (Figure 1). The ν_+ ENDOR signal (Figure 1B,C), when corrected according to eq 1, gives $A'_x \simeq 17$ and $A'_y \simeq 19$ MHz. One treats the magnetic fields as corresponding to the extremal resonance fields of centers with corresponding g-tensor components, namely, $g'_x \simeq 1.5$ and $g'_y \simeq 2.5$, and uses the corresponding $\delta g'_i$ and A'_i in eq 3 to obtain the x and y components of A^{OT}: $A^{OT}_x \simeq 35$ MHz and $A^{OT}_y \simeq 36$ MHz. Thus, the triplet-spin ^{17}O hfs coupling tensor is seen to have no less than axial symmetry ($A^{OT}_x \simeq A^{OT}_y$); the same is true for the ^{57}Fe coupling parameters obtained from Mossbauer measurements.[7,12]

As H_0 approaches the field corresponding to $g_z \simeq 2$ from either above or below, the frequency of the ν_+ resonance is expected to approach $A'_z/2 + \nu_0$. Very close to $g = 2$ the frequency of the resonance approaches zero, indicating that $A'_z \sim 0$ as predicted by the first-order eq 3b, but the intensity also decreases, making it impossible to determine A'_z, and thus A^{OT}_z, with accuracy.

The axial symmetry of the observed ^{17}O and ^{57}Fe hfs tensors naturally suggests that we interpret the data in terms of a triplet oxyferryl (Fe^{IV}=O) center whose axis lies normal to the porphyrin cation plane. If we assume the two odd electrons of Fe^{IV}=O) to be in antibonding π-molecular orbitals

$$\Psi_x = (1 - c^2)^{1/2} d_{xz}^{Fe} - c p_x^{O}$$
$$\Psi_y = (1 - c^2)^{1/2} d_{yz}^{Fe} - c p_y^{O} \quad (4)$$

and utilize the previously determined reference hfs tensor for a single odd electron in an ^{17}O p-π orbital,[14] one obtains an ^{17}O hfs tensor for the triplet system (Fe^{IV}=O) of $A^{OT} \simeq |c|^2$-[140,140,0] MHz. From the measured coupling constants and eq 3 one arrives at the estimate $c^2 \sim 0.25$, corresponding to an oxyferryl center whose unpaired odd electrons are substantially delocalized between the two atoms through d_π-p_π bonding, in excellent accord with theoretical expectations.[11]

Two alternatives to the symmetrical oxyferryl moiety may be considered, namely, Fe^{IV}-O-H and the recently proposed structure in which oxygen bridges the Fe and a porphyrin nitrogen.[15] However, the axial symmetry of both ^{57}Fe and ^{17}O hfs tensors is evidence against these alternative models. Furthermore, the failure to observe a large proton coupling in HRPI[5] argues against Fe^{IV}-O-H,[16] and the optical spectrum of HRPI is not reproduced by the carbenoid model for the protoporphyrin oxygen-bridged structure.[15] All this leads us to prefer the model discussed here for the oxyferryl moiety of the HRP compound I enzymic intermediate.

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Heterogeneous One-Electron Reduction of Metal-Containing Biological Molecules Using Molecular Hydrogen as the Reductant: Synthesis and Use of a Surface-Confined Viologen Redox Mediator That Equilibrates with Hydrogen

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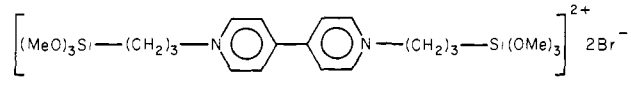
Study and use of metal-containing biological reagents often involves the need to manipulate the redox level. We report herein the synthesis of a heterogeneous catalyst system that allows the use of H_2 as a reductant for the one-electron reduction of horse-heart ferricytochrome *c* (cyt c_{ox}), sperm whale myoglobin, and stellacyanin from the lacquer of *Rhus vernicifera*. Application of the principles illustrated by our catalyst in other systems is possible inasmuch as the reducing power of H_2 is sufficiently great that many biological systems are thermodynamically reducible with H_2. An advantage in using H_2 as a source of reducing power is that the oxidation product is H^+ which is acceptable since most biological systems are studied in buffered media. A heterogeneous catalyst is desirable to facilitate the separation of the catalyst from the product.

A catalyst for one-electron reductions using H_2 must include functionality that will allow equilibration of the substrate with the H_2O/H_2 couple without the undesirable result of hydrogenating the substrate. The aim is to have a catalyst that equilibrates H_2 in such a way that two e^-'s and two H^+'s are available from H_2, not two H atoms. A heterogeneous catalyst must also include the functionality that overcomes the usual kinetic and adsorption problems typically encountered in heterogeneous electron-exchange processes involving large biological molecules.[1-3] For example, the rapid electrochemical reduction of cyc c_{ox} is only possible with certain types of electrodes.[4,5]

We have prepared the heterogeneous catalyst system represented by Scheme I. Basically, the catalyst is a redox-active polymer that (i) can be equilibrated with H_2O/H_2 via the dispersed Pt(0), (ii) reduces biological molecules when reduced, and (iii) can be anchored to a large number of surfaces including glass. Most of our work concerns the use of ordinary 13- × 100-mm Pyrex test tubes functionalized on the inside surface with the catalyst system. The catalyst could be anchored to higher surface area supports to achieve faster observed rates but the functionalized test tubes allow us to illustrate the principles of operation and synthesis. Synthesis of the surface-confined polymer begins with reaction of an *N,N'*-dialkyl-4,4'-bipyridinium (PQ^{2+}) derivative (I)[6-9] with pretreated Pyrex glass: (1) 13- × 100-mm



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