concentrated and dilute solutions.

Discussion

We believe that the decomposition of **1** in the absence of olefin occurs by a reversible loss of chlorine atoms as in (2). The free

$$VCl_4(g) \rightleftharpoons VCl_3(s) + Cl^{\bullet} \quad (2)$$

$$\Delta G = 13.05 \text{ kcal/mol at } 25\ ^{\circ}C^{2,6}$$

energy change is estimated from published data.[2,6] UV light or high temperatures accelerate the forward process. The presence of solvents, particularly those with reactive tertiary or allylic hydrogens, leads to more efficient scavenging of Cl$^{\bullet}$ free radicals, thereby promoting the decomposition. However perdeuterio solvents are less efficient than the corresponding protonated solvents in reacting with Cl$^{\bullet}$ because of the deuterium isotope effect—hence, the use of cyclohexane-d_{12} is less effective at promoting decomposition. The increase in the rate of decomposition in the presence of olefins is explained by the formation of a unstable adduct $VCl_4 \cdot x$(olefin), which then rapidly decomposes to the corresponding insoluble VCl_3 product by loss of a chlorine atom. This is parallel to the reaction of **1** with Lewis bases.[1,5] The explanation is consistent with our observation that easily coordinated olefins such as ethylene and 1-octene have the greatest effect on the decomposition rate. Alternate schemes for the reduction of **1** such as direct chlorination of the allylic hydrogen of the olefin by **1** are not supported by the data; thus, 2-octene with five allylic hydrogens is less effective than 1-octene with two and ethylene with none.

The most important conclusion in this study has been the need to invoke the presence of chlorine atoms in the reaction mixture in order to understand the product distribution and the kinetics. The presence of chlorine radicals is supported by the formation of solvent chlorination products (with preference for the allylic or tertiary positions) as well as the formation of polyethylene in the ethylene assisted decomposition. Further support for this scheme is provided by our observation that free radical chlorinators (CCl_4, for example) in solution retard[7] the decomposition of **1**. Alternate reactions such as 1, which do not require the formation of chlorine atoms, will account for most of the reaction products but do not explain the increase in the decomposition rate in the presence of solvents nor the dependence of this rate on the reaction medium.

Experimental Section

VCl_4 was obtained from Stratcor, Niagara Falls, NY, or from Metaux Speciaux S.A., Paris, France: both of these samples contained less than 4% of chlorine. No difference in the decomposition rates or products was noted between these samples. *n*-Hexane was obtained from Phillips Petroleum and contained 5-7% of isomers, principally 2- and 3-methylpentane, 2,3-dimethylbutane, and cyclohexane. Cyclohexane and isooctane were obtained from Burdick and Jackson. All solvents were purified to 2 ppm of moisture and oxygen prior to use. All other chemicals were obtained from Aldrich Chemical Co.

Decomposition of **1** was conducted in a thermostated reaction vessel; temperature control was obtained with a Neslab 610 constant-temperature bath with an accuracy of ±2 °C. UV-vis spectra were obtained on a Perkin-Elmer Lambda 7 spectrophotometer at ambient temperature between 300 and 700 nm. GC, GC-MS, and elemental analysis were performed internally.

Polyethylene and polynorbornene formed during decomposition were isolated by extracting the solid residue with dilute (7%) HCl and then drying the polymer in a vacuum oven. The polymer was identified by IR spectroscopy.

Decomposition Experiment. The decomposition experiment was conducted by dissolving 10 mL (18.2 g) of **1** in 1 L of the solvent under nitrogen at the reaction temperature. The olefin, if necessary, is added at this stage. The thermostated reaction mixture was protected from light, and samples of the solution were syringed out through a in-line filter at predetermined intervals and introduced into a 0.1-mm-pathlength quartz UV-vis solution cell under nitrogen. Spectra were obtained at ambient temperature, and interference from solid precipitates in the reaction vessel was not observed. All of the spectra had a single absorption with a maxima at 412 nm. All data reported in this paper have been normalized by the initial absorption of the solution at 412 nm: this eliminates scatter in the data due to the variation in the real concentration of **1** or inaccuracies of dilution and transfer. We estimate that the extent of this variation is about 5%. These data correspond to the fraction of **1**, compared to the initial amount, left in solution at any stage of the decomposition and are reported as such. Evolved HCl was removed by slowly bubbling a stream of nitrogen through the reaction mixture, followed by absorption into a measured volume of 0.1 M NaOH. Other organic decomposition products were measured by GC or GC-MS analysis after the decomposition of **1** was complete. Experiments in deuteriocyclohexane were conducted at the same concentration of **1** but in a volume of 20 mL of liquid in appropriately scaled equipment.

Vanadium Oxidation State. Insoluble vanadium residues from the decomposition were removed by filtration under a nitrogen atmosphere, washed with hexane, and dissolved at 0 °C in deaerated 1 M HCl. Clear solutions were obtained in 1 h. Visible spectra of these solutions showed a broad absorption centered at 580 nm for V(3+). All solid decomposition residues were found to contain V(3+) as the only oxidation state.

Photochemical Experiments. Photochemical decomposition was conducted in a vented quartz reactor containing 100 mL of a 1% v/v hexane solution of **1**. The sample was irradiated at 22 °C with a 150-W high-pressure mercury lamp. Onset of decomposition was rapid, with the walls of the reactor being coated with a dark layer of **2**. Complete decomposition was observed in 20 h.

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^{1}H NMR Hyperfine-Shifted Resonances from the Exchange-Coupled Fe_4S_4-Siroheme of the Assimilatory Sulfite Reductase from *Desulfovibrio vulgaris* (Hildenborough)

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Introduction

^{1}H NMR spectroscopy is a powerful probe of structure and mechanism in biochemical studies of proteins and enzymes.[1,2] In the presence of a paramagnetic prosthetic group, hyperfine-shifted resonances can be observed outside of the normal diamagnetic envelope and so provide a probe of active-site environment.[3-5] There have been several studies of heme proteins (predominantly on myoglobins and a variety of *c*-type cytochromes),[6] cobalt-substituted proteins,[3] HiPIP's, and ferredoxins,[7,8] in which the protons on chromophores and residues ligating the paramagnetic center have been assigned. These resonances can subsequently be used to monitor the magnetic and electronic properties of metal ions (by variable-temperature experiments) or to identify neighboring ionizable residues (by pH titration).

The understanding of the interactions of electronically coupled metal ions is of importance in traditional coordination chemistry, materials science, and biological chemistry (in particular metalloredox proteins). In the latter case, both electron transfer and redox chemistry are of relevance. Many metalloenzymes possess

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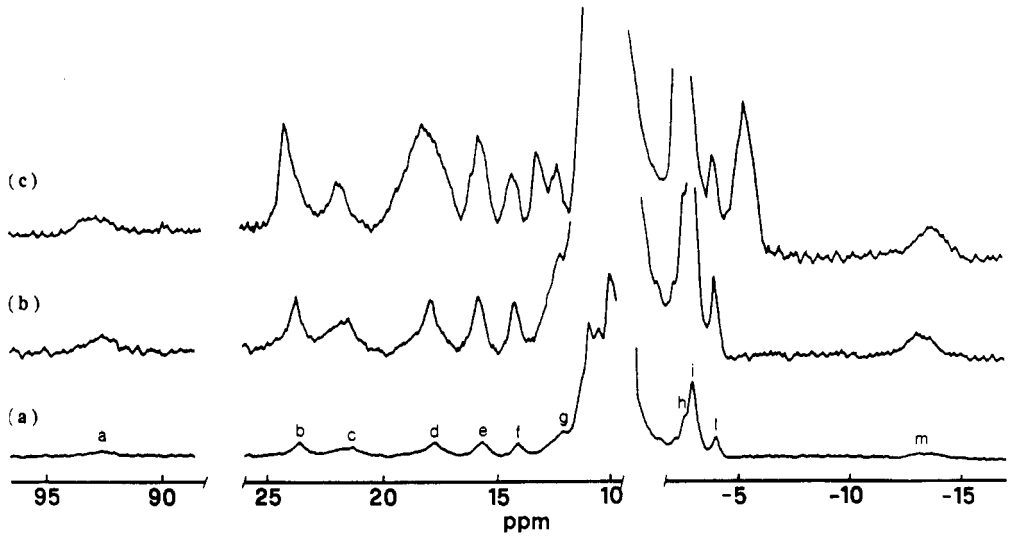

Figure 1. (a) Hyperfine-shifted signals in the 500-MHz ^1H NMR spectra of oxidized assimilatory sulfite reductase (*Desulfovibrio vulgaris*) in μ = 0.1 M sodium phosphate buffer in D_2O (pH 7.0, 296 K). Protein concentration ca. 0.5 mM. (b) Spectrum as in (a) but with a 4-fold increased vertical scale. (c) Spectrum in buffer made up in H_2O.

sets of coupled chromophores and metal ions that serve to turn over small substrate molecules such as oxygen, nitrogen, nitrate, nitrite, sulfate, and sulfite.[9-12] In many instances the enzymes catalyzing these reactions possess a set of well-defined coupled prosthetic groups. An understanding of one example might therefore provide valuable insight into the magnetoelectronic phenomena and mechanistic chemistry exhibited by a variety of complex redox enzymes. To date, only a cobalt-substituted $[Cu_2Co_2]$-SOD has been studied in detail.[3] In this paper, we illustrate the use of high-field ^1H NMR of paramagnetically shifted resonances to study the assimilatory sulfite reductase from *Desulfovibrio vulgaris* (Hildenborough). This enzyme is one of the smallest multielectron (>2$^-$) metalloredox enzymes in nature; possessing a siroheme and an exchange-coupled Fe_4S_4 cluster. We describe the first example of NMR experiments on a protein containing such an exchange-coupled prosthetic center, discuss preliminary assignments of resonances and the likely identity of the sixth ligand to the siroheme, and also identify a signal that displays an unusually large downfield shift that may be a reflection of the exchange coupling between the chromophores.

Experimental Section

Bacterial Growth and Protein Isolation. *D. vulgaris* (Hildenborough, NCIB 8303) was grown in an enriched Baars medium [ATCC medium No. 1249] at the Fermentation Laboratory, Department of Biochemistry, University of Wisconsin. The preparation of the cell extract and isolation of the protein followed the procedure of Peck and co-workers.[13]

NMR Methods. ^1H NMR spectra were obtained on a Bruker AM-500 spectrometer operating at 500 MHz, using 16 K data points over a 125-KHz bandwidth. The super-WEFT sequence (180-τ-90-AQ)[14] was used for suppression of the water signal, with a recycle time of 80 ms and τ values varying from 60 to 70 ms. The reported spectra required about 300 000 scans. A line broadening of 25 Hz was applied. Protein concentration was ca. 0.5 mM. Peaks are referenced to the residual water

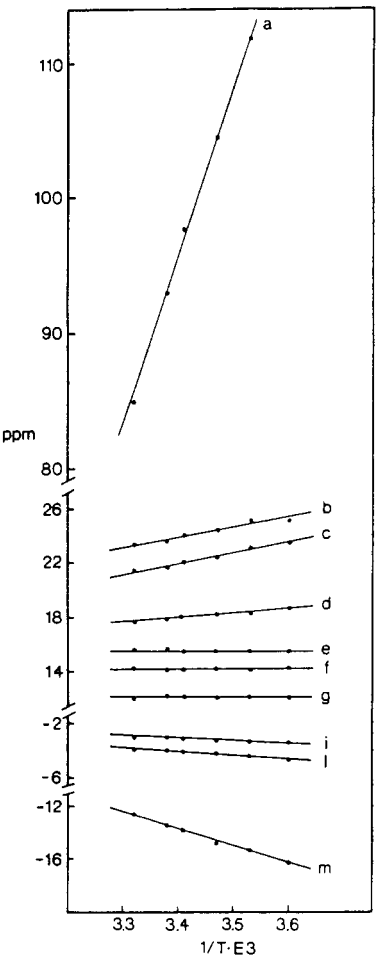

Figure 2. Temperature dependence of the hyperfine-shifted signals of oxidized assimilatory sulfite reductase from *Desulfovibrio vulgaris* in μ = 0.1 M sodium phosphate buffer (pH 7.0). Protein concentration ca. 0.5 mM.

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Table I. NMR Parameters for the Hyperfine-Shifted Resonances in Assimilatory Sulfite Reductase (*Desulfovibrio vulgaris*)[a]

signal	δ, ppm	T_1, ms[b]	signal	δ, ppm	T_1, ms[b]
a	92.5	3	g	12.0	6
b	23.7	6	h	−2.6	15
c	21.5	4	i	−3.1	19
d	17.8	6	l	−4.1	14
e	15.7	9	m	−13.3	4
f	14.1	6			

[a] Protein concentration ca. 0.5 mM in μ = 0.1 M sodium phosphate buffer (pH 7.0, 296 K). [b] Estimated with the super-WEFT sequence (errors are within 15%).

peak (4.8 ppm). The estimated T_1 values were obtained with the same sequence, using a recycle time of 150 ms and different delay times τ.

Results and Discussion

The hyperfine-shifted resonances in the 500-MHz ^{1}H NMR spectrum of the native enzyme are shown in Figure 1 (Table I). Seven downfield-shifted single proton resonances appear in the spectrum recorded in D_2O. Six (b–g) are grouped in the range 12–24 ppm, while a broad resonance (a) lies far downfield at ca. 90 ppm. Four signals were observed upfield in the range −2 to −14 ppm. Signals h, i, and l show an approximate 1–5–1 intensity pattern, while the broad resonance m integrates to one proton. All signals follow a Curie temperature dependence except signals e, f, and g, whose shifts are nearly independent of temperature (Figure 2). Signal a shows a steep decrease of the shift with increasing temperature, with a zero intercept far outside of the diamagnetic region. The narrow range of the isotropic shifts of signals b–m is typical of low-spin ferric heme proteins[6] and related porphyrin model complexes[15] and of oxidized ferredoxins containing one or two Fe_4S_4 cluster(s).[16-19] In addition, the absence of a field dependence of the line widths, when spectra recorded at 300 and 500 MHz are compared, supports the low-spin state of the iron(III) in the siroheme suggested by ESR and Mössbauer measurements.[13] Signal a, however, shows a shift that is not characteristic of the above types of systems. We tentatively suggest that the unusual shift of this signal results from the magnetic coupling between the paramagnetic low-spin iron(III) of the siroheme and the Fe_4S_4 cluster through the bridge (Figure 3). Such a coupling could increase the population of magnetic states of the cluster, and one proton of a β-CH_2 geminal couple of a cysteine ligand could show a sizable hyperfine shift as a result of a very small Fe–S–C–H dihedral angle. Alternatively, but less likely, signal a could arise from a proton of an aromatic residue experiencing a strong π–π interaction with the siroheme ring. In any event, the isotropic shift pattern of this protein is distinctly unique. Another effect that may be ascribed to magnetic coupling is the absence of the characteristic anti-Curie behavior that is normally shown by cysteine protons of oxidized ferredoxins.

The absence of the three-proton resonances corresponding to the two methyl groups of the siroheme in the downfield region of the spectrum may be accounted for by the π-delocalization mechanism of spin transmission that is operative in tetragonal low-spin iron(III):[3] the two methyl groups of the siroheme are both bound to sp^3-hybridized carbons in the two partially saturated pyrrole rings,[20] and so they should not feel a sizable unpaired spin density. The meso protons of the siroheme are unlikely to appear in the hyperfine-shifted portion of the spectrum, in analogy to low-spin Fe(III) heme proteins[6] and model porphyrin[15,21] and

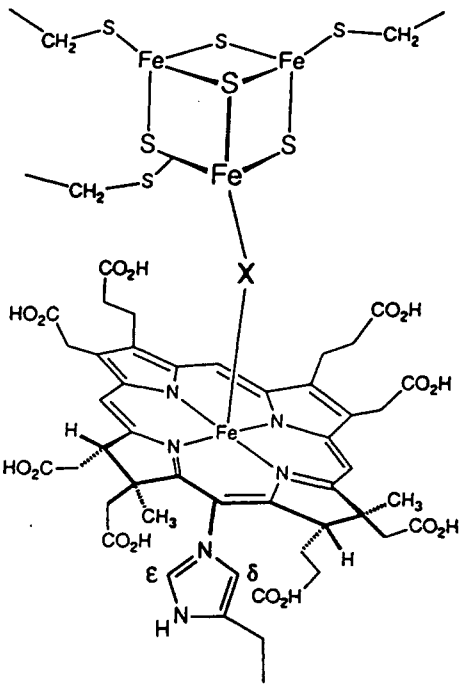

Figure 3. Schematic representation of the exchange-coupled $[Fe_4S_4]$–siroheme in the active site of assimilatory sulfite reductase (*Desulfovibrio vulgaris*) with the proposed histidine ligand at the axial site. On the basis of chemical analysis,[13] the bridging unit X has been identified as sulfide rather than cysteine.[9,10]

chlorin[22] complexes. As a result, signals b–g should arise from the α-methylene groups on the acetate and propionate functions around the siroheme ring and from the β-CH_2 groups of the cysteine binding the Fe_4S_4 cluster. Furthermore, since low-spin Fe(III) porphyrins exhibit a sizable magnetic anisotropy,[6] the presence of isotropically shifted signals from side-chain protons of nonbinding residues in the surroundings of the siroheme cannot be excluded. Since no upfield signals have been detected in oxidized Fe_4S_4 ferredoxins,[16-19] the nonexchangeable resonances h–m can reasonably be assigned to protons near the siroheme. In low-spin Fe(III) heme proteins, the spectral region containing the resonances h, i, and l is usually occupied by β-methylene propionate protons[23-25] or methyl groups or proximal nonbinding residues such as leucine, valine,[26] or isoleucine.[27] At least one methyl resonance must be present in the composite peak i, and so at least one of the latter residues could be in close contact with the siroheme. The shape and position of resonance m is characteristic of the ϵ-H signal from an axial histidine and has been assigned in a number of low-spin Fe(III) heme proteins,[23,25,27-29] model bis(imidazole) complexes of natural[30] and synthetic porphyrins,[31] and also, recently, a chlorin.[22] The resonance of the δ-H imidazole proton in general lies downfield, in the same region as the b–g resonances[25,30-33] or in the diamagnetic region.[22] The His-N-δ-H

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resonance could also lie among the several exchangeable resonances that appear in the spectrum recorded in H_2O (Figure 1c).[28,34-36] The magnetic anisotropy of the siroheme could lead to the presence of numerous exchangeable resonances that frequently arise from proximal or distal histidine, arginine, and backbone NH protons. The data can be interpreted as indicative of a histidine residue as the sixth ligand to the siroheme in sulfite reductase. A methionine as axial ligand is unlikely since there is no evidence for a characteristic three-proton signal due to the iron-bound methionine ϵ-methyl group found at low frequencies (−8 to −25 ppm) in several *c*-type cytochromes.[33,37-40]

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Registry No. His, 71-00-1; siroheme, 52553-42-1; sulfite reductase, 37256-51-2.

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Unusual Synthesis and X-ray Structure of *cis*-Dichloro[1,2-bis(*o*-(diphenylphosphino)phenyl)ethane-1,2-diolato(2−)]technetium(IV) Hemiethanol Solvate

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Technetium phosphine complexes are stable and thus are useful in the design of ^{99m}Tc radiopharmaceuticals.[1,2] In this context the most important properties of phosphine ligands are their ability to reduce the pertechnetate(VII) ion and their ability to stabilize low oxidation states by means of π-back-bonding.[3-6] Technetium-99m phosphine complexes have been investigated for biological purposes,[1,7,8] and a few are very close to being used as radiopharmaceuticals. Chelating ligands containing both phosphorus(III) and other coordinating atoms offer new possibilities in the development of this field.

The ligand *o*-(diphenylphosphino)benzaldehyde ($Ph_2PC_6H_4CHO$) is one of the simplest possible bidentate O,P-chelating phosphine ligands. We have studied the reaction of this ligand with oxotetrachlorotechnetate(V) and observed an unexpected Tc(IV) product containing an O_2P_2-tetradentate ligand. The synthesis and X-ray structural characterization of this unusual product are now reported.

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Table I. Crystallographic Data for *cis*-$TcCl_2(Ph_2PC_6H_4CHO)_2 \cdot {}^1/_2EtOH$

formula: $C_{38}H_{30}Cl_2O_2P_2Tc \cdot {}^1/_2EtOH$	diffractometer: Philips PW1100
fw 773.4	T = 22 °C
space group: P$\bar{1}$ (No. 2)	λ = 0.7107 Å
a = 12.460 (8) Å	μ = 6.5 cm^{-1}
b = 15.140 (4) Å	ρ(obsd) = 1.44 (3) g cm^{-3}
c = 10.753 (5) Å	ρ(calcd) = 1.426 g cm^{-3}
α = 86.98 (4)°	no. of obsd ($I > 3\sigma(I)$) rflcns: 1369 (up to 2ϑ = 36)
β = 106.88 (7)°	anisotropy for atoms in "inner core"
γ = 111.67 (6)°	$R(F_o)$ = 0.075
V = 1800.5 (2.7) Å^3	w = 1
Z = 2	

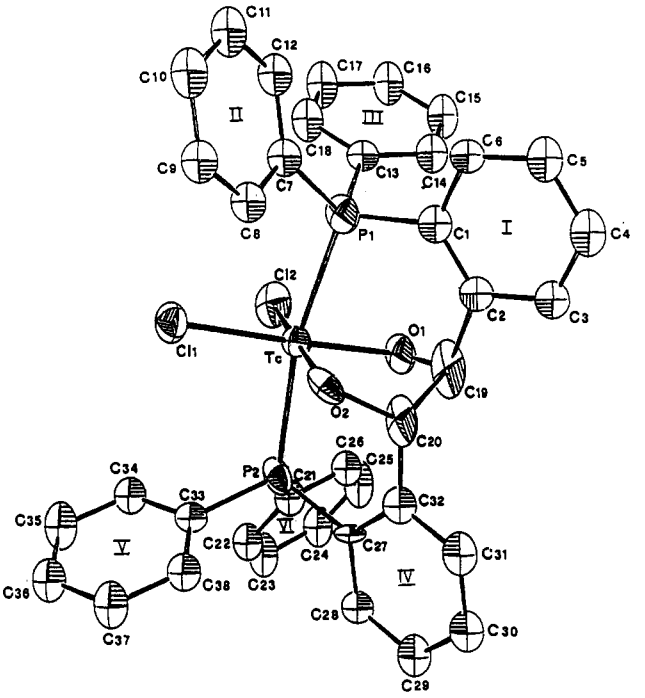

Figure 1. ORTEP drawing of the structure of $TcCl_2(Ph_2PC_6H_4CH(O-)-CH(O-)C_6H_4PPh_2)$. The EtOH molecule has been omitted for clarity.

Synthesis

$N(CH_2CH_2CH_2CH_3)_4[TcOCl_4]$ (50 mg, 0.1 mmol) was dissolved in the minimum amount (2 mL) of ethanol. *o*-(Diphenylphosphino)benzaldehyde (94 mg, 0.35 mmol) was added to this solution. The initial pale green color turned deep purple; after the solution was stirred for 10 min at room temperature, the solids dissolved and the solution was left to evaporate slowly overnight. Red-purple crystals were obtained, and after filtration, they were washed with two 1-mL portions of ethanol and dried under a nitrogen stream (yield: 95% with respect to $[TcOCl_4]^-$).

Elemental analyses, conductivity and magnetic susceptibility measurements, and ^{1}H NMR and IR spectra are consistent with the formulation $TcCl_2L$ (L = $(Ph_2PC_6H_4CHO-)_2$).[9]

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