Inorg. Chem. **1992**, *31*, 240–243

Contribution from the Département de Recherche Fondamentale/Service de Physique/SCPM
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Oxidation Reactions of $[Fe_4S_4(S\text{-}2,4,6\text{-}(i\text{-}Pr)_3C_6H_2)_4]^{2-}$ and an Oxidative Conversion of the Fe_4S_4 Core into an Fe_3S_4 Center

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Received March 15, 1991

The oxidations of the title compound by a variety of chemical oxidants, chosen so as to offer a large range of oxidizing potentials, have been investigated in a selection of reaction media and at room temperature. When moderate oxidants ($[Fe(CN)_6]^{3-}$, Ag^+, I_2, $[C(C_6H_5)_3]^+$) are used in aprotic media (CH_2Cl_2, CH_3CN), a one-electron metal-based oxidation occurs and $[4Fe\text{-}4S]^{3+}$ is quantitatively generated (type I oxidants). The same moderate oxidants in an aqueous medium (DMF/H_2O or CH_3CN/H_2O) give place to an overall two-electron oxidation and generate thus a $[3Fe\text{-}4S]^+$ center (type II oxidants). The oxidative mechanism possibly proceeds via an intermediate $[4Fe\text{-}4S]^{3+}$ species. Oxidation by a stronger oxidant such as air O_2 in aprotic media also produces a $[3Fe\text{-}4S]^+$ center (type II oxidant). The 3Fe species thus created is unstable and decomposes rapidly. Oxidation by an even stronger oxidant, H_2O_2, in an aqueous medium (DMF/H_2O) leads to the immediate formation of a radical ($g_z = 2.051$, $g_y = 2.005$, $g_x = 1.984$) of probable organic nature (type III oxidant). Some implications of these results for the structural interconversions of Fe-S clusters in proteins are discussed.

Introduction

Iron–sulfur clusters can undergo structural interconversions that involve changes in the stoichiometry of Fe and S, when the reaction's medium redox conditions are modified. Thus, in 4Fe proteins, oxidizing conditions either generate a $[4Fe\text{-}4S]^{3+}$ center, as in HP_{ox}[2] (high-potential iron–sulfur protein), or convert the $[4Fe\text{-}4S]^{2+}$ core into a $[3Fe\text{-}4S]^+$ center, as in bacterial ferredoxins[3] and in mammalian aconitase[4] and succinate–ubiquinone oxidoreductase (complex II).[5] In other cases, such as the ferredoxin I from *Azotobacter vinelandii*[6] and lactyl-CoA dehydratase,[7] treatment of the 4Fe cluster by $[Fe(CN)_6]^{3-}$ produces new oxidized species, resembling neither $[4Fe\text{-}4S]^{3+}$ nor $[3Fe\text{-}4S]^+$ centers, currently under investigation. On the other hand, under reducing conditions, some 3Fe proteins tend to convert their active site into a $[4Fe\text{-}4S]^{2+}$ center, even in the absence of Fe^{2+}, as reported for mammalian aconitase[8] and complex II.[5]

In model systems, the oxidative transformation of $[Fe_4S_4X_4]^{2-}$ cubanes into $[Fe_6S_6X_6]^{2-}$ prismanes (X = Cl, Br) has been demonstrated,[9] whereas reducing conditions are known to convert $[Fe_2S_2(SR)_4]^{2-}$ into $[Fe_4S_4(SR)_4]^{2-}$,[10] and the presence of excess halide transforms $[Fe_6S_6Cl_6]^{3-}$ into $[Fe_4S_4Cl_4]^{2-}$ and $[Fe_2S_2Cl_4]^{2-}$.[11] $[Fe_4S_4(SR)_4]^{2-}$ systems have long been known to generate, upon oxidation, the monoanionic $[Fe_4S_4(SR)_4]^-$ species.[12] The stability of this species in solution has been shown to be strongly dependent on the solvent and on the hydrophobicity and steric protection brought around the Fe-S core by the presence of bulky terminal ligands.[13]

Table I. Half-Wave Potentials (V)[a] of Chemical Oxidants Used To Oxidize $[NEt_4]_2[Fe_4S_4(Stibt)_4]$

oxidant	CH_2Cl_2 (9.1; 0)[b]	CH_3CN (37.45; 14.1)[b]	DMF (37.65; 26.6)[b]	H_2O (78.5; 18)[b]	$E°$[c]
Ag^+		0.220	0.270[e]		−0.019
I_2					0.295
$[C(C_6H_5)_3]^+$	0.120[f]	0.260			
Fc^{+}[d]	0.390	0.460[f]			0.159
$[Fe(CN)_6]^{3-}$	−0.940	−0.860	−0.900	0.190	0.117
O_2					1.229
H_2O_2					1.776

[a] Determined by cyclic voltammetry (scan rate 0.1 V/s). $[NH_4][PF_6]$ was the supporting electrolyte in the case of H_2O. [b] The first number corresponds to the dielectric constant ϵ; the second number, to the donor number.[18] [c] Standard redox potential (*Handbook of Chemistry and Physics*, 64th ed.; CRC Press: Boca Raton, FL, 1983–4). [d] Ferrocenium. [e] Irreversible reduction wave. [f] Quasi-reversible redox cycle.

In this paper, we have undertaken a more complete investigation of the redox behavior of $[Fe_4S_4(Stibt)_4]^{2-}$ (Stibt = 2,4,6-triisopropylbenzenethiolate) as a function of the oxidizing power of the oxidants and of the solvents used. Use of this sterically encumbered thiolate has recently allowed for the isolation[14] and subsequent studies of the magnetic properties[15] of a stable monooxidized $[4Fe\text{-}4S]^{3+}$ cluster. This model system is therefore a particularly suitable candidate for the study of oxidation reactions.

Experimental Section

$[NEt_4]_2[Fe_4S_4(Stibt)_4]$ was synthesized by the ligand-exchange method,[16] $[NEt_4][Fe_4S_4(Stibt)_4]$ was obtained by controlled-potential elec-

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trolysis,[15b] and $[NEt_4]_3[Fe(CN)_6]$ was prepared according to a published method.[17] All other chemicals were used as purchased. Acetonitrile, dichloromethane, and methanol were predried and distilled after refluxing with calcium hydride. Dimethylformamide (Merck) was degassed prior to use. All procedures were carried out under an inert atmosphere using Schlenk techniques or a Jacomex glovebox filled with prepurified argon.

X-band EPR spectra were recorded on a Varian E 109 spectrometer, and samples cooled in a stream of helium gas, temperature-regulated by an Oxford Instruments ESR 900 cryostat. *g* factors were determined by simultaneously measuring the microwave frequency (EIP 548A frequency counter) and the magnetic field (Varian NMR gaussmeter). Spin integrations were made against a 1 mM $CuSO_4$/EDTA standard.

Cyclic voltammetry and electrolysis experiments were performed with a PAR 273 potentiostat. Working and counter electrodes were of platinum, a saturated calomel electrode was the reference electrode, and $[NBu_4][PF_6]$ (0.1 M) was the supporting electrolyte. All half-wave potentials are given relative to the SCE. In a typical experiment, 10 mL of a 5 mM solution of the Fe-S cluster (77.75 mg) was treated at room temperature with 1, 2, 3, 5 or 10 equiv of oxidant (I_2, $AgPF_6$, $[C(C_6H_5)_3][PF_6]$, $[Et_4N]_3[Fe(CN)_6]$). At regular intervals of time, 0.2-mL filtered aliquots were quickly frozen with liquid nitrogen for EPR measurements. In the case of oxygen, air was admitted to the above solution for various lengths of time, after which the system was flushed with argon and an aliquot frozen at 77 K for EPR measurements.

In the case of hydrogen peroxide, 50 mL of a 1 mM solution of the Fe-S cluster (77.75 mg) was treated with 1 equiv of H_2O_2 (30%) and a 0.2-mL aliquot was then transferred into an EPR tube and frozen at 77 K; the whole reaction time being kept at 1 min. Care was taken to avoid using any metal needles during the whole procedure.

Results and Discussion

We present here the oxidations of $[Fe_4S_4(Stibt)_4]^{2-}$ by a variety of chemical oxidants. These were chosen so as to offer a large range of oxidizing potentials (see Table I[18]). Ferricyanide was also chosen for its redox potential tunability[17,19,20] and because of the fact that it is a frequently used oxidant for Fe-S proteins.[3-5] Hydrogen peroxide was chosen because it has been recently used, under physiological conditions, to oxidize the Fe-S cluster of a plant mitochondrial aconitase into a $[3Fe\text{-}4S]^+$ core.[21]

In the case of $AgPF_6$ (in CH_3CN), I_2, and $[C(C_6H_5)_3][PF_6]$ (in CH_2Cl_2), and as already observed with ferrocenium,[14] addition of 1–3 equiv of oxidant produces a one-electron oxidation of the Fe_4S_4 core,[15a,22] and the quantitative formation of $[Fe_4S_4(Stibt)_4]^-$ is observed after 10-min reaction time (Figure 1a, Scheme A).

$$[4Fe\text{-}4S]^{2+} \xrightarrow{-1e^-} [4Fe\text{-}4S]^{3+} \qquad \text{Scheme A}$$

$$[4Fe\text{-}4S]^{2+} \xrightarrow{-1e^-} [4Fe\text{-}4S]^{3+} \xrightarrow{-1e^-} [3Fe\text{-}4S]^+ + \text{"}Fe^{2+}\text{-}\dot{S}R\text{"} \qquad \text{Scheme B}$$

$$[4Fe\text{-}4S]^{2+} \xrightarrow{-xe^-} [3Fe\text{-}4S]^0 + Fe^{3+} \xrightarrow{-1e\text{-}} [3Fe\text{-}4S]^+ + Fe^{3+} \qquad \text{Scheme C}$$

$$[4Fe\text{-}4S]^{2+} \xrightarrow{-ye^-} \text{"organic radical"} \qquad \text{Scheme D}$$

These reagents are therefore considered as oxidants of type I. This species is stable for a few hours at room temperature but becomes unstable (the signal at $g = 2.06$ disappears rapidly) when a strong excess (10 equiv) of oxidant is used.

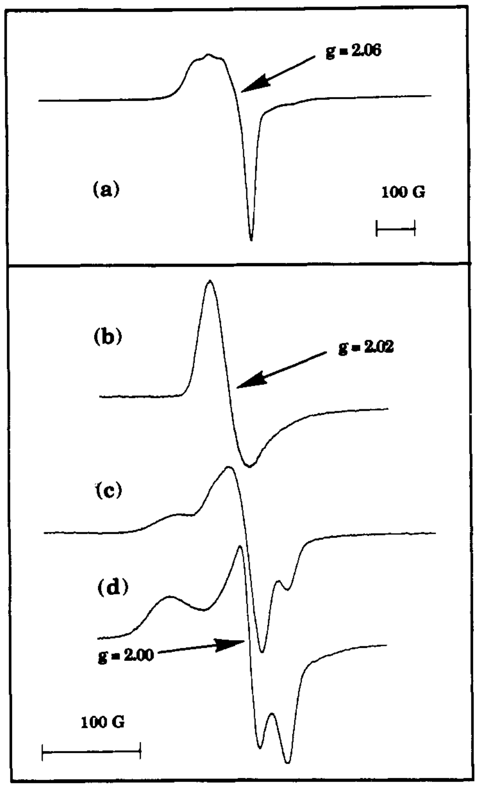

Figure 1. EPR spectra of a frozen solution of $[Fe_4S_4(Stibt)_4]^{2-}$ oxidized by $[Fe(CN)_6]^{3-}$ in (a) CH_3CN/CH_3OH (7.3/1) and (b) DMF/H_2O (4/1) or CH_3CN/H_2O (5/1). Spectra c and d represent the evolution of spectrum b after 3 and 5 min of incubation at room temperature, respectively [T = 9 K, microwave power 0.5 mW (0.05 mW for (a)), modulation 10 G, microwave frequency 9.222 GHz].

When $[Fe(CN)_6]^{3-}$ is used, the reaction outcome varies, as a function of its oxidizing power and of the physical properties of the reaction medium.

In pure CH_3CN, addition of 1 equivalent of oxidant ($E_{1/2}$ = –0.86 V) produces no oxidation, even after 1-h reaction time, and the EPR spectrum of the solution shows only a large signal centered at $g = 2.13$, characteristic of the unreduced oxidant.

In CH_3CN/CH_3OH, where the $E_{1/2}$ potential of $[Fe(CN)_6]^{3-}$ is still relatively low (–0.56 V), it oxidizes the Fe_4S_4 core by one electron and is then also considered as a type I oxidant. No low-field resonances are observed, but a minority of unknown species is sometimes present, with *g* values at g_1 = 2.095 and g_2 = 1.959.

In DMF/H_2O and CH_3CN/H_2O (Figure 1b–d), $[Fe(CN)_6]^{3-}$ becomes a stronger oxidant, and its $E_{1/2}$ potential rises then respectively to –0.38 and –0.09 V. After 1-min reaction time with an equimolar amount of the $[4Fe\text{-}4S]^{2+}$ cluster, all the oxidant has been consumed and a signal (with a relatively narrow bandwidth of 30 G, best visible at 10–12 K and hardly power-saturating at this temperature) indicative of a $[3Fe\text{-}4S]^+$ center[23] has appeared (Figure 1b). This center is apparently generated from the Fe_4S_4 core, since when the reaction is followed by cyclic voltammetry, addition of the oxidant causes the immediate decrease of the $[4Fe\text{-}4S]^{2+/3+}$ redox wave. The 3Fe species is unstable in solution since, after 5-min reaction time, the $g = 2.02$ signal has totally disappeared and been replaced by a signal due to an unidentified radical (Figure 1c,d). Maximum intensity of the 3Fe

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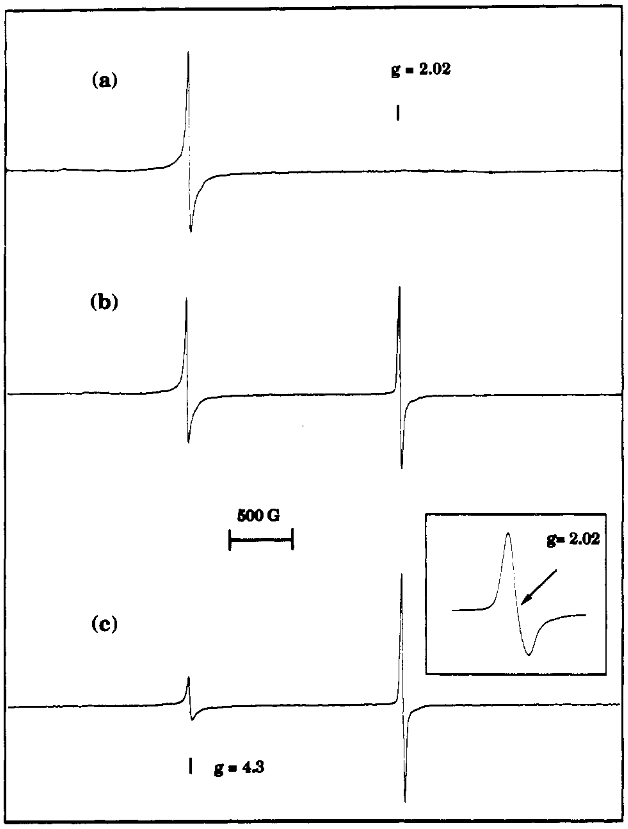

Figure 2. EPR spectra of a frozen solution of $[Fe_4S_4(Stibt)_4]^{2-}$ in CH_2Cl_2, CH_3CN, or DMF after (a) 1, (b) 2, and (c) 3 min of incubation with O_2 at room temperature. The intensity of spectrum c was decreased by a factor of 3. The inset shows the detail of spectrum c in the $g = 2$ region [$T = 5$ K (inset at 10 K), microwave power 0.2 mW, modulation 10 G, microwave frequency 9.221 GHz].

EPR signal is obtained when 2 equiv of $[Fe(CN)_6]^{3-}$ is used, which indicates that an overall two-electron oxidation has occurred and that ferricyanide in aqueous DMF or CH_3CN should be considered as a type II oxidant.

This oxidation proceeds possibly via a monooxidized $[4Fe\text{-}4S]^{3+}$ to produce a $[3Fe\text{-}4S]^+$ center (scheme B), since addition of 1 equiv of $[Fe(CN)_6]^{3-}$ to a 5 mM solution of monooxidized $[NEt_4][Fe_4S_4(Stibt)_4]$ in DMF/H_2O or CH_3CN/H_2O produces the same 3Fe EPR signal. The presence of water without oxidant has no such effect, but it is nevertheless necessary, as verified by a comparative experiment: oxidation of a 5 mM solution of monooxidized $[Fe_4S_4(Stibt)_4]^-$ with 1 equiv of Ag^+ (instead of $[Fe(CN)_6]^{3-}$) in CH_3CN/H_2O (5/1) also produces a 3Fe center, whereas oxidation by Ag^+ in pure CH_3CN, as seen above, generates only the $[4Fe\text{-}4S]^{3+}$ center. Formation of the $[4Fe\text{-}4S]^{3+}$ intermediate is possibly slower (and rate-limiting) than its further oxidation into a 3Fe center, which may account for the fact that it cannot be detected. The 3Fe center thus formed is unstable and therefore present only at low concentration (spin quantitation gives less than 15% yield). The presence of the bulky thiolate Stibt does however stabilize it somewhat, since, in a similar oxidation performed by Weterings et al.[24] on $[Fe_4S_4(S\text{-}t\text{-}Bu)_4]^{2-}$, the 3Fe center was observable only when the reaction was performed at less than −40 °C.

A recent study of the solvent-dependent stability of monooxidized $[Fe_4S_4(SR)_4]^-$ ions[25] shows that, in basic media, the $[4Fe\text{-}4S]^{3+}$ center is unstable and slowly decomposes, presumably because of a nucleophilic attack of a solvent molecule on an iron atom of the iron–sulfur core. In the present case, the combined presence of a polar and protic solvent, such as water, and of an oxidant with increased oxidizing power seems to promote a faster, possibly ligand-based oxidation of $[Fe_4S_4(Stibt)_4]^-$, which could lead to the expulsion of a Fe^{2+}–$\dot{S}R$ fragment. It is unlikely that the Fe is expelled as an Fe^{3+} species, since no signal was detected at $g = 4.3$. Presumably, such coordinated radical thiyl complexes dimerize and cannot therefore be observed by EPR spectroscopy. Ligand-based, rather than metal-based, oxidations have been reported in several systems[26–28] and can be tentatively explained by use of the results of recent MO calculations on Fe_4S_4 clusters by Noodleman.[29] When the changes in charge distribution upon oxidation of a $[4Fe\text{-}4S]^{2+}$ center are considered, almost no charge density is left on the mixed-valence Fe pair,[30] whereas the thiolate sulfurs still have some radical character. As $[4Fe\text{-}4S]^{3+}$ formally contains iron atoms that are already in a fairly oxidized state, it is understandable that they will become more difficult to oxidize ($[4Fe\text{-}4S]^{4+}$ has so far never been shown to exist) and that the thiolates may then become a preferential site of oxidation.

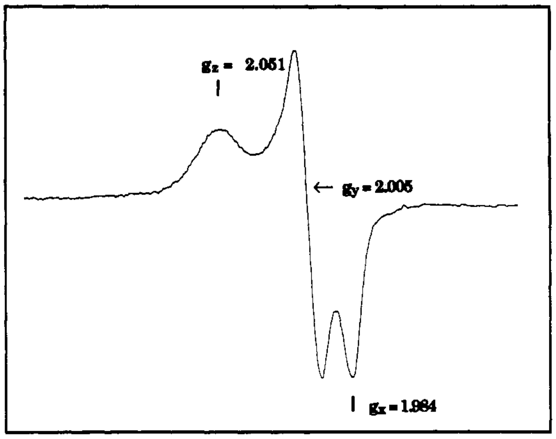

Figure 3. EPR spectrum of a frozen solution of $[Fe_4S_4(Stibt)_4]^{2-}$ in DMF/H_2O (4/1) after 1-min reaction with 1 equiv of H_2O_2 (30%) [$T = 18.5$ K, microwave power 2 mW, modulation 10 G, microwave frequency 9.226 GHz].

The oxidation by air oxygen also creates an oxidized $[3Fe\text{-}4S]^+$ species, albeit under different conditions. In effect, O_2 is a much stronger oxidant than $[Fe(CN)_6]^{3-}$ (Table I), the reaction medium does not contain any water, and the physical properties of the solvents used do not influence the reaction outcome. An oxidized high-spin Fe^{3+} species appears first ($g = 4.3$, Figure 2a) possibly expelled from the Fe_4S_4 core, while the resulting 3Fe center is presumably present under its reduced, EPR-silent $[3Fe\text{-}4S]^0$ form (scheme C). The latter is then also rapidly oxidized by O_2 to the $[3Fe\text{-}4S]^+$ state ($g = 2.02$, Figure 2b,c), which is unstable and decomposes to give the same unidentified radical. Oxygen may therefore also be considered as a type II oxidant. Intermediate binding of O_2 to an iron atom possibly promotes its expulsion from the Fe_4S_4 core, as recently suggested[31] in the case of the reaction sequence $2Mo_3FeS_4 + O_2 + 4H^+ \rightarrow 2MoS_4{}^{4+} + 2Fe^{2+} + 2H_2O$, where the intermediate is believed to be $[Mo_3FeS_4(O_2)]^{4+}$. In order to verify that $[4Fe\text{-}4S]^{3+}$ is indeed not an intermediate state, air oxidation of the monooxidized cluster $[Fe_4S_4(Stibt)_4]^-$ was performed under the same conditions. The $g = 2.06$ signal remained stable until up to 15 min of exposure to oxygen and was then progressively replaced by a signal at $g = 4.3$ (Fe^{3+}) and a

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signal at $g = 2.02$ ([3Fe-4S]$^+$). This indicates that the [4Fe-4S]$^{3+}$ center is only slowly oxidized by O_2 into [3Fe-4S]$^+$ and that, were it an intermediate in scheme C, it should have been observable.

Further evidence for the formation of a 3Fe center with these type II oxidants has been recently provided by oxidizing $[Fe_4S_4(Stibt)_4]^{2-}$ (by O_2 or $[Fe(CN)_6]^{3-}$) in the presence of an equimolar amount of $CoCl_2$. A [3Fe,Co-4S]$^{2+}$ species is then formed,[32] which suggests that the Co^{2+} has been incorporated into the vacant site of a Fe_3S_4 core.

When a H_2O_2 oxidation (scheme D, Figure 3) is performed in DMF/H_2O (4/1), no formation of either [4Fe-4S]$^{3+}$, [3Fe-4S]$^+$, or Fe^{3+} is observed, and only the immediate formation of the same unidentified radical is observed ($g = 2.051, 2.005, 1.984$) up to 60 K (it power-saturates easily at low temperatures and remains stable for approximately 24 h). We were unable to determine whether [4Fe-4S]$^{3+}$ and [3Fe-4S]$^+$ are intermediates of reaction or not, since oxidation by H_2O_2 of the monooxidized cluster $[Fe_4S_4(Stibt)_4]^-$ under the same conditions immediately produced the same radical. The mechanism of action of H_2O_2 as an oxidant has been extensively investigated,[28a,33] and it is assumed therefrom that H_2O_2 oxidizes coordinated thiols via nucleophilic attack of the sulfurs on the O–O bond. The radical observed here could indeed correspond to an oxidized state of the Stibt ligands. Indeed, an EPR signal with similar g values (2.09, 2.01, 1.98) has been reported in the $[Fe(CN)_6]^{3-}$ oxidation of *A. vinelandii* FdI[6] and tentatively attributed to a cysteinyl disulfide radical. The latter has been identified among the products of radiation damage in γ-irradiated cysteine hydrochloride.[34] Its EPR spectrum is also observable at liquid-N_2 temperature, with g values of 2.06, 2.02, and 2.00, not unlike those observed here.

In conclusion, chemical oxidation of an Fe-S cluster with bulky thiolates such as $[Fe_4S_4(Stibt)_4]^{2-}$ can lead to different products when the oxidizing power and the physical properties of the reaction medium are varied:

(A) Moderate oxidants (Ag^+, I_2, $[Fe(CN)_6]^{3-}$, $[C(C_6H_5)_3]^+$) in aprotic media (CH_2Cl_2, CH_3CN) produce a one-electron metal-based oxidation, and [4Fe-4S]$^{3+}$ is quantitatively generated (type I oxidants). An increase of basicity of the solvent will also lead to an increased instability of the Fe-S core.[25]

(B) When the same moderate oxidants (Ag^+, $[Fe(CN)_6]^{3-}$) are used in a medium where H_2O is also present, an overall two-electron oxidation occurs, a 4Fe → 3Fe core conversion is then observed, and [3Fe-4S]$^+$ is generated (type II oxidants). The latter is unstable, which possibly accounts for its low concentration (less than 15%).

(C) With a stronger oxidant (oxygen) and in aprotic media (CH_2Cl_2, CH_3CN, DMF), the same 4Fe → 3Fe conversion is observed (type II oxidant). The presence of H_2O is not required, and the mechanism of oxidative conversion is possibly different from case B).

(D) Oxidation by an even stronger oxidant (H_2O_2) leads to an immediate oxidation into a radical of possibly organic nature (type III oxidant).

It appears thus that the site of oxidation on the $[Fe_4S_4(Stibt)_4]^{2-}$ cluster can be controlled by a combination of factors, principally the oxidizing strength of the oxidant and the presence of H_2O in the reaction medium. These observations may help to explain why, upon oxidation of a 4Fe protein by $[Fe(CN)_6]^{3-}$, there is either formation of a [4Fe-4S]$^{3+}$ center, conversion into a 3Fe center, or appearance of an organic radical. In the case of proteins, the medium, as well as the oxidizing strength of $[Fe(CN)_6]^{3-}$, is constant. Modulation of the reaction outcome can therefore be brought about by (1) the Fe-S cluster redox potential (the higher it is, the more stable the core with respect to oxidative degradation and the less likely a 4Fe → 3Fe conversion) and (2) the local environment of the 4Fe cluster, that is its degree of hydrophobicity and polarity (the more accessible the 4Fe cluster to water, the more easily it will destabilize and convert into a 3Fe center or even a more oxidized radical). Indeed, when characteristic features of the cluster-binding cavities in HP and in bacterial ferredoxins[2] are compared, it appears that nonpolar side chains surrounding the ferredoxin clusters differ from those found in contact with the HP cluster. Thus, the ferredoxin cavities contain mostly aliphatic chains, while the HP environment includes many aromatic side chains, and whereas the latter will effectively prevent access of solvent molecules, the ferredoxin clusters will be only moderately protected.

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Carbon-13 Nuclear Magnetic Resonance Spectroscopic Study of $Fe_3(CO)_{12}$ and $Ru_3(CO)_{12}$ Supported on Metal Oxide Surfaces[†]

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Received April 23, 1991

^{13}C-enriched $Fe_3(CO)_{12}$ and $Ru_3(CO)_{12}$ supported on a variety of metal oxide surfaces (γ-Al_2O_3, SiO_2, MgO, and HNa-Y zeolite) have been examined by carbon-13 "magic-angle" sample-spinning (MAS) nuclear magnetic resonance (NMR) spectroscopy. Our results show that the γ-Al_2O_3-supported $Fe_3(CO)_{12}$ cluster is fluxional at room temperature, but low-temperature spectra give no evidence in favor of the unusual bridging carbonyl proposed previously by some workers from infrared (IR) spectroscopy. On HNa-Y, $Fe_3(CO)_{12}$ forms a highly mobile chemisorbed species, and the ^{13}C chemical shift is consistent with formation of the dianion $[Fe_3(CO)_{11}]^{2-}$. For $Ru_3(CO)_{12}$ on γ-Al_2O_3 and SiO_2 surfaces, our results are in agreement with IR studies and show that, under anaerobic conditions, highly mobile physisorbed clusters are initially formed. Upon exposure to air or upon thermal activation, divalent tricarbonyl species are generated. The resonances of these chemisorbed species are enhanced by cross polarization and display large chemical shift anisotropies, due to restricted mobility. On MgO, $Ru_3(CO)_{12}$ behaves quite differently, the ^{13}C NMR results being consistent with the formation of highly fluxional hexaruthenium carbonyl clusters.

Introduction

Metal carbonyl clusters supported on high surface area metal oxides are of interest in relation to the cluster–surface analogy between catalytic transition-metal surfaces and molecular metal clusters,[1] as well as being good candidates for extending the study of molecular mobility to species chemisorbed on surfaces.[2-5] Not

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[†] This work was supported by the Solid-State Chemistry Program of the U.S. National Science Foundation (Grant DMR 88-14789).

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