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Short Report

Biomimetic Hydrogen Generation Catalyzed by Triironnonacarbonyl Disulfide Cluster

Charles A. Mebi,* Kyra E. Brigance and Robert B. Bowman

Department of Physical Sciences, College of Natural and Health Sciences,
Arkansas Tech University, 1701 N. Boulder Ave, Russellville, Arkansas 72801 USA

O “cluster” dissulfeto de triferrononacarbonila, um precursor sintético e estável para modelos do sítio ativo da enzima hidrogenase [Fe-Fe], foi avaliado como catalisador para a geração eletroquímica de hidrogênio por voltametria cíclica. Na presença de ácido acético, $Fe_3S_2(CO)_9$ catalisa a redução do próton para hidrogênio em – 2,24 V (*vs.* Fc/Fc^+) com um sobrepotencial de –0,78 V (acetonitrila como solvente). O sobrepotencial é comparável àqueles relatados para os modelos diferrocarbonila de hidrogenase [Fe-Fe].

Triironnonacarbonyl disulfide cluster, a stable and synthetic precursor for active site models of [Fe-Fe] hydrogenase enzyme, has been evaluated as catalyst for the electrochemical generation of hydrogen by cyclic voltammetry. In the presence of acetic acid, $Fe_3S_2(CO)_9$ catalyzes the reduction of proton to hydrogen at –2.24 V (*vs.* Fc/Fc^+) with an overpotential of –0.78 V (acetonitrile as solvent). The overpotential is comparable to those reported for diironcarbonyl models of [Fe-Fe] hydrogenase.

Keywords: electrocatalysis, hydrogen, iron-cluster, metalloenzyme, transition metal

Introduction

Iron-sulfur clusters, diverse in composition (containing one to eight iron atoms) and structure, are ubiquitous in biological systems. These clusters are involved in electron transfer and biocatalytic processes. The chemistry of iron-sulfur clusters has been associated with the development of life on planet Earth.[1-3] Iron-sulfur clusters can be coordinated to organic ligands through iron-carbon bonds to form organometallic clusters. A typical example of an organometallic iron-sulfur cluster is triironnonacarbonyl disulfide [$Fe_3S_2(CO)_9$], Figure 1.[4]

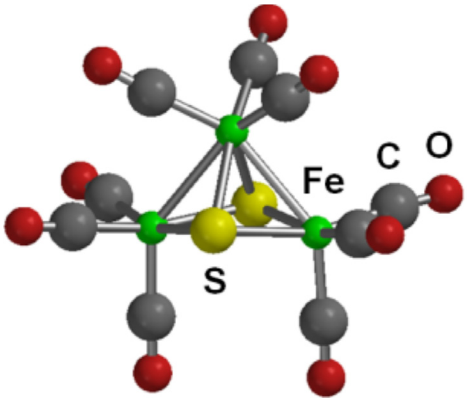

Figure 1. Triironnonacarbonyl disulfide, [$Fe_3S_2(CO)_9$].

The chemistry of $Fe_3S_2(CO)_9$ has drawn a lot of attention over the past few decades.[1] Triironnonacarbonyl disulfide was first prepared in 1958 by Hieber and Beck[5] by the reaction of $[HFe(CO)_4]^-$ and sulfite ion. However, $Fe_3S_2(CO)_9$ has been identified as a common product from reactions between iron-carbonyls and sulfur supplying agents.[1] Wei and Dahlz[6] structurally characterized $Fe_3S_2(CO)_9$ using X-ray crystallography revealing its *nido*-type square pyramidal or trigonal bipyramidal arrangement. $Fe_3S_2(CO)_9$ is stable and its electronic structure and electrochemical properties have been extensively investigated using photoelectron spectroscopy,[7] computational methods,[7,8] cyclic voltammetry,[9] and spectroelectrochemical technique.[10] The reactivity of $Fe_3S_2(CO)_9$ has been explored and continues to be of great interest.[1,11-14] Some important reactions of $Fe_3S_2(CO)_9$ are depicted in Scheme 1: (a) the reaction of $Fe_3S_2(CO)_9$ with formaldehyde and amines to form diiron clusters of the type, $Fe_2[(SCH_2)_2NR](CO)_6$, models for the active site of [Fe-Fe] hydrogenase enzyme (Figure 2)[14] and (b) the photochemical transformation of $Fe_3S_2(CO)_9$ in the presence of $Fe(CO)_5$ to the tetrairon cluster, $Fe_4S_2(CO)_{11}$.[13]

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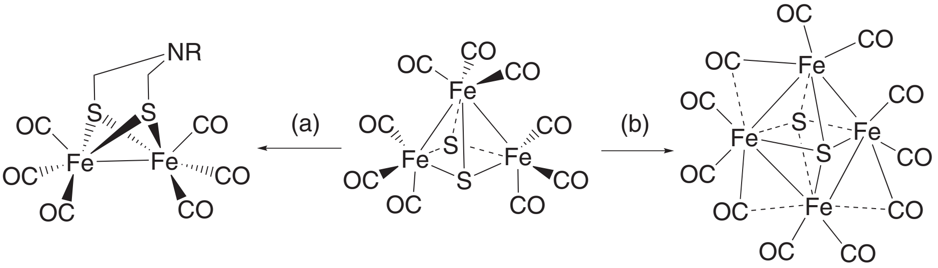
*e-mail: cmebi@atu.edu



Scheme 1. Reactivity of $Fe_3S_2(CO)_9$: (a) $(CH_2O)_n/RNH_2$; (b) h*v*, $Fe(CO)_5$, cyclohexane.

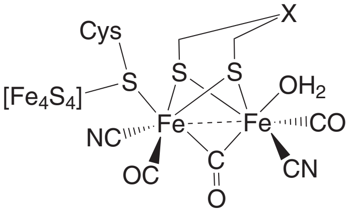


Figure 2. Active site of [Fe-Fe] hydrogenase enzyme (X = NH or CH_2).

Although the reactivity, electrochemical properties, and electronic structure of $Fe_3S_2(CO)_9$ have been investigated, to the best of our knowledge, its catalytic properties remain unexplored. Giving the synthetic and structural relationship between $Fe_3S_2(CO)_9$ and models for the active site of [Fe-Fe] hydrogenase enzyme, it is important to examine the ability of $Fe_3S_2(CO)_9$ to mimic the enzyme. The hydrogenase enzyme efficiently catalyzes the evolution of hydrogen by proton reduction in aqueous media (TOF = 6000-9000 s^{-1}). The reduction potential of the H^+/H_2 couple for [Fe-Fe] hydrogenase has been determined to be –0.36 V *vs.* SCE at pH 6 and 30 °C.[14] Studies on the enzyme and its synthetic models are useful in the development of catalysts for the production of hydrogen, a clean alternative to fossil fuels. In this study, we report on the electrocatalytic reduction of proton to produce hydrogen by $Fe_3S_2(CO)_9$. The catalytic properties of $Fe_3S_2(CO)_9$ are compared to those of some diironcarbonyl models of the enzyme reported in the literature.

Experimental

Electrocatalytic studies were conducted using an Epsilon BAS potentiostat. Cyclic voltammograms of $Fe_3S_2(CO)_9$ were obtained with increasing concentrations of acetic acid (0, 7, 21, 35, 42, 49, 56, 63 mmol L^{-1}) using a three-electrode cell. The electrodes used are glassy carbon working electrode, platinum auxiliary electrode, and Ag/AgCl reference electrode. The platinum and glassy carbon electrodes were polished with aluminum paste and rinsed with water and acetone. A 0.1 mol L^{-1} CH_3CN solution of Bu_4NPF_4 was used as supporting electrolyte. The concentration of $Fe_3S_2(CO)_9$ was 1 mmol L^{-1} and the scan rate was 100 mV s^{-1}. We degassed the electrolyte solution by bubbling nitrogen at room temperature for 5 min before measurement. The potentials obtained with reference to Ag/AgCl electrode are quoted in this report against ferrocene/ferrocenium (Fc/Fc^+) potential except otherwise mentioned. The Fc/Fc^+ reference is used to allow for comparison with reported redox potential values of similar models. All reagents were obtained from commercial sources. Acetonitrile for electrochemical assay was purchased from Aldrich and used without any further purification. We obtained $Fe_3S_2(CO)_9$ as a byproduct from the reaction of $Fe_3(CO)_{12}$ and phenanthrene-4,5-disulfide.[15] The identify of $Fe_3S_2(CO)_9$ was confirmed by infrared and X-ray crystallography.

Results and Discussion

The electrochemical properties of $Fe_3S_2(CO)_9$ have been previously investigated in benzonitrile by cyclic voltammetry.[9] $Fe_3S_2(CO)_9$ is reported to undergo two one-electron reduction processes at –0.43 V (reversible, $E_{1/2}$) and –1.38 V (irreversible, E_{pc}). An irreversible oxidation of $Fe_3S_2(CO)_9$ was observed at +1.30 V *vs.* Ag/AgCl. These results are similar to those obtained by us in acetonitrile (Table 1). We observe *ca.* 0.07 V shift in the electrochemical potentials with the change of solvent from benzonitrile to acetonitrile.

The electrocatalytic generation of hydrogen by $Fe_3S_2(CO)_9$ from acetic acid (a weak acid; pK_a = 22.3 in acetonitrile) has been studied and the results are contained in Table 2 and Figure 3. Figure 3 contains cyclic voltammograms of $Fe_3S_2(CO)_9$ in the absence of acid and with increasing amounts of acetic acid. In the absence of acid, only the three redox events mentioned in Table 1 were observed. On addition of 7 mmol L^{-1} of acetic acid, a new peak at –2.24 V (*vs.* Fc/Fc^+) appears and its current intensity increases with sequential increment of acid concentration (Figure 4). These observations are indicative of electrocatalytic reduction of proton to molecular hydrogen.[16] The overpotential was determined to be –0.78 V using the standard reduction (E^o_{HA}) of –1.46 V (*vs.* Fc/Fc^+) for acetic

Table 1. Electrochemical data for $Fe_3S_2(CO)_9$

Electrochemical Process		Benzonitrile (V *vs* Ag/AgCl)[a]	Acetonitrile (V *vs* Ag/AgCl)[b]	Acetonitrile (V *vs* Fc/Fc$^+$)[b]
$[Fe_3S_2(CO)_9] + e^- \rightleftharpoons [Fe_3S_2(CO)_9]^-$	$E_{1/2}$	–0.43	–0.50	–0.94
$[Fe_3S_2(CO)_9]^- + e^- \longrightarrow [Fe_3S_2(CO)_9]^{2-}$	E_{pc}	–1.38	–1.31	–1.75
$[Fe_3S_2(CO)_9] \longrightarrow [Fe_3S_2(CO)_9]^+ + e^-$	E_{pa}	+1.30	+1.24	+0.80

[a]Reference 9. [b]This work.

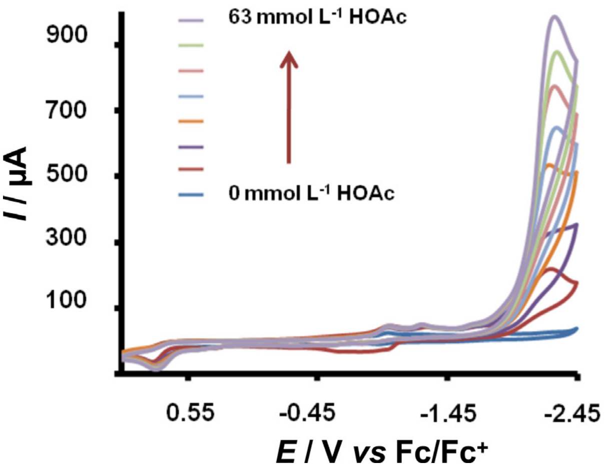


Figure 3. Cyclic voltammograms of $Fe_3S_2(CO)_9$ (1 mmol L^{-1}, 10 mL) with acetic acid (0, 7, 21, 35, 42, 49, 56, 63 mmol L^{-1}) in 0.1 mol L^{-1} BuN_4PF_6/acetonitrile at a scan rate of 100 mV s^{-1}.

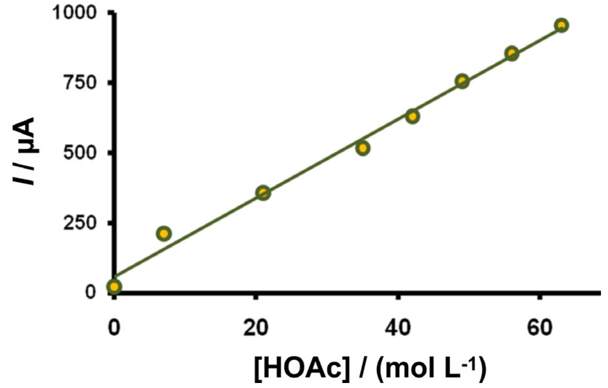
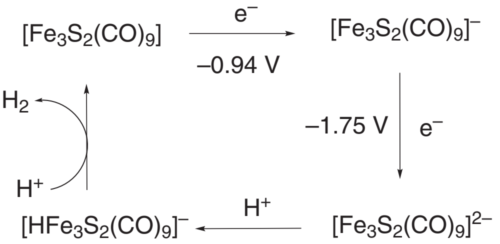


Figure 4. Dependence of current heights of the electrocatalytic peaks of $Fe_3S_2(CO)_9$ on concentration of acetic acid.

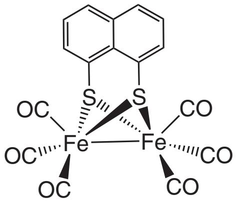
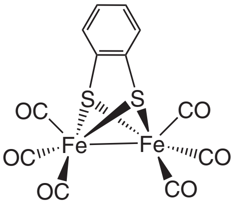
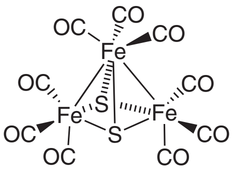
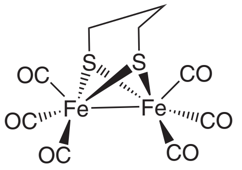


Scheme 2. Proposed mechanism for the electrocatalytic proton reduction of acetic acid to produce H_2 by $Fe_3S_2(CO)_9$.

acid.[17] The overpotential and potential for the reduction of acetic acid to hydrogen (E_{cat}) by $Fe_3S_2(CO)_9$ are contained in Table 2 alongside those of some diironcarbonyl models of [Fe-Fe] hydrogenase.[17,18] As observed in Table 2, the overpotential and E_{cat} for $Fe_3S_2(CO)_9$ are comparable to those of the diironcarbonyl models.

Scheme 2 shows a tentative mechanism for the electrocatalytic hydrogen production by $Fe_3S_2(CO)_9$. The suggested electrochemical-electrochemical-chemical-chemical (EECC) mechanism is based on the results described above and similar reported examples.[16] As depicted in Scheme 2, $Fe_3S_2(CO)_9$ first undergoes successive one-electron reductions to produce $[Fe_3S_2(CO)_9]^{2-}$ which upon protonation affords $[HFe_3S_2(CO)_9]^-$. Subsequent protonation of $[HFe_3S_2(CO)_9]^-$ generates hydrogen.

Table 2. A comparison of electrocatalytic data for $Fe_3S_2(CO)_9$ and some diironcarbonyl models of [Fe-Fe] hydrogenase[a]

Models				
Overpotential / V	–0.54	–0.65	–0.78	–0.89
E_{cat} / V	–2.00	–2.11	–2.24	–2.35

[a]Values for diironcarbonyl models were obtained from references 17 and 18.

Conclusions

$Fe_3S_2(CO)_9$ has been shown to mimic [Fe-Fe] hydrogenase by catalyzing the electrochemical evolution of hydrogen with an overpotential of –0.78 V (*vs.* Fc/Fc$^+$). This overpotential is comparable to those of reported models of [Fe-Fe] hydrogenase. We have proposed an EECC catalytic cycle for the generation of H_2 by $Fe_3S_2(CO)_9$. However, more studies (computational, bulk electrolysis, and spectroelectrochemical) are required to characterize the species involved and ascertain the mechanism.

Acknowledgments

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