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COMPARISON OF THE REACTIVITIES OF $[Fe_4S_4(SPh)_4]^{2-}$ AND $[Fe_2S_2(SPh)_4]^{2-}$

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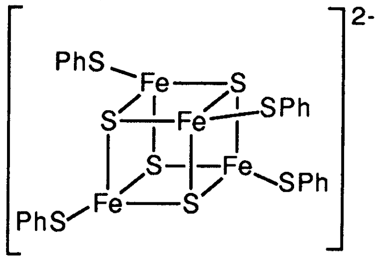
The reactivities of the model complexes, $[Fe_4S_4(SPh)_4]^{2-}$ (**1**) and $[Fe_2S_2(SPh)_4]^{2-}$ (**2**), of nonheme iron-sulfur proteins were compared. Complex **1** catalyzed the oxidation of benzenethiol to diphenyl disulfide with the reduction of dioxygen to H_2O. Complex **2** did not catalyze it, but the reaction proceeded after an induction period during which complex **2** was converted to complex **1**. In addition, complex **1** catalyzed the reduction of 1,4-dinitrobenzene to *N*-(4-nitrophenyl)hydroxylamine (21 %) and 4-nitroaniline (16 %) with the oxidation of benzenethiol to diphenyl disulfide, but complex **2** induced mainly the displacement of nitro group to phenylthio group to give 1-nitro-4-(phenylthio)benzene (92 %). It was revealed that the reactivities of complex **1** and complex **2** are quite different.

KEYWORDS iron-sulfur complex; ferredoxin model; benzenethiol oxidation; diphenyl disulfide; 1,4-dinitrobenzene reduction

Nonheme iron-sulfur proteins act as electron carriers in various processes or cell metabolisms.[2] These proteins are classed by their active sites as rubredoxin ([1Fe]) and ferredoxins ([2Fe-2S], [4Fe-4S], [3Fe-3S], and [3Fe-4S]) types.[3] Many analogues of the active sites of such proteins have been prepared[4] since the successful synthesis of $(Et_4N)_2[Fe_4S_4(SCH_2Ph)_4]$ by Holm and his coworkers.[5] These analogues have contributed to the understanding of the physical properties of the protein active sites.[4] However, there have been no reports of the comparison between the reactivities of such analogues, though it would be interesting for elucidation of the activities of iron-sulfur proteins as electron carriers.



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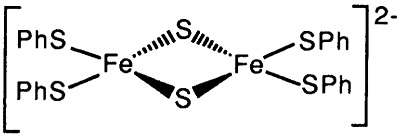


2

Chart 1

We reported previously that $(n\text{-}Bu_4N)_2[Fe_4S_4(SPh)_4]$[6] (**1**) catalyzes the oxidation of benzenethiol to diphenyl disulfide with dioxygen[7] and also on the reduction of aromatic nitro compounds to amines with benzenethiol.[8] As part of our research on the catalytic properties of iron-sulfur analogues,[9] the reactivity of $(Et_4N)_2[Fe_2S_2(SPh)_4]$ (**2**)[10] was compared with that of **1** (Chart 1). We report here that the catalytic activities of **1** and **2** were quite different, surprisingly.

The oxidation of benzenethiol with **1** or **2** as a catalyst was followed by monitoring the consumption of dioxygen (Fig. 1).[11] Diphenyl disulfide was formed quantitatively and other products were not detected. The reaction with **1** started immediately and was completed within ten minutes, and afterwards dioxygen uptake was not observed. The quantity of dioxygen uptake was exactly 1/4 equimolar of benzenethiol (Chart 2). In the reaction with **2** as a catalyst, an induction period was observed, and then the reaction proceeded in a manner similar to that with **1**. The induction period became shorter with higher content of **2**. These results and the visible spectral change of **2** during the reaction show that **2** itself does not catalyze the oxidation of benzenethiol with dioxygen but that **2** dimerizes to **1** during the induction period and then **1** induces the reaction.

Holm *et al.* reported that **2** is stable in aprotic solvent such as dimethyl sulfoxide, *N*,*N*-dimethylformamide, and hexamethylphosphoramide under an anaerobic condition.[12] However, Coucouvanis *et al.* reported that **2** is reduced by sodium hydrosulfite and crown ether to form **1**.[13] Complex **2** is probably

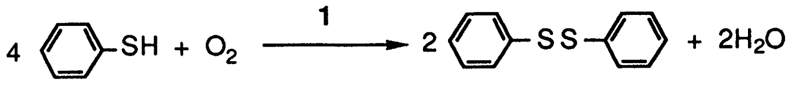


Chart 2

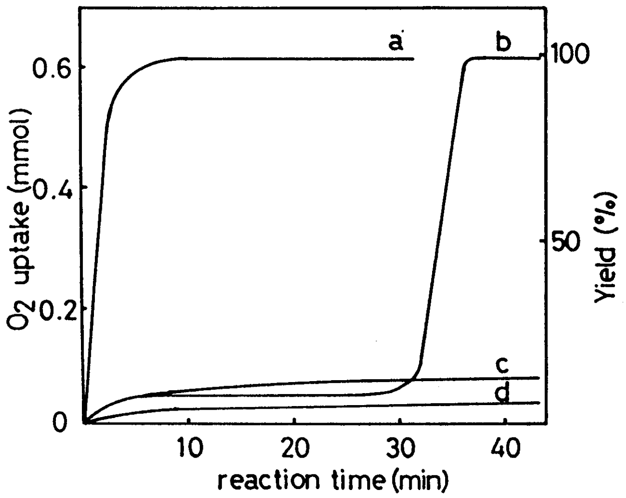


Fig. 1. Catalytic Oxidation of Benzenethiol to Diphenyl Disulfide with Dioxygen in the Presence of **1** or **2**
a) (n-$Bu_4N)_2[Fe_4S_4(SPh)_4]$ (**1**) (0.07 mmol).
b) $(Et_4N)_2[Fe_2S_2(SPh)_4]$ (**2**) (0.03 mmol).
c) $FeCl_2$ (0.09 mmol). d) $FeCl_3$ (0.12 mmol).

reduced to $[Fe_2S_2(SPh)_4]^{3-}$, also, by benzenethiol and then dimerizes to **1** with formation of thiolate anion (Chart 3).

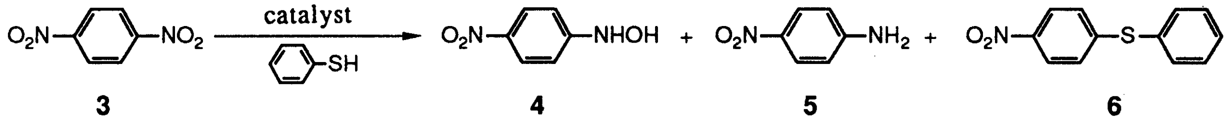
The reaction of 1,4-dinitrobenzene (**3**) with benzenethiol was used for the comparison of the catalytic activities of **1** and **2** (Table I). The reaction with **1** as a catalyst gave reduction products such as *N*-(4-nitrophenyl)hydroxylamine (**4**, 21 %) and 4-nitroaniline (**5**, 16 %). However, in the case of using **2**, the yield of the reduction product [*N*-(4-nitrophenyl)hydroxylamine] (**4**) was only 7 %, but the catalytic displacement of nitro group by phenylthio group proceeded mainly to give 1-nitro-4-(phenylthio)benzene (**6**, 92 %). The displacement and the reduction proceeded with $FeCl_3$ or $FeCl_3$ and sodium sulfide as a catalyst. As the result, it was shown that the catalytic activity of **1** is quite different from that of **2**. Complex **2** catalyzes the conversion of **3** to **6**. Generally, the nitro group of 1,4-dinitrobenzene causes

$$2[Fe_2S_2(SPh)_4]^{2-} + 2PhSH \longrightarrow 2[Fe_2S_2(SPh)_4]^{3-} + PhSSPh + 2H^+$$

$$2[Fe_2S_2(SPh)_4]^{3-} \longrightarrow [Fe_4S_4(SPh)_4]^{2-} + 4PhS^-$$

Chart 3

Table I. Catalytic Reaction of 1,4-Dinitrobenzene with Benzenethiol in the Presence of **1** or **2**[a)]



Catalyst	Yield (%)[b)]		
	4	**5**	**6**
(n-$Bu_4N)_2[Fe_4S_4(SPh)_4]$ (**1**)	21	16	0
$(Et_4N)_2[Fe_2S_2(SPh)_4]$ (**2**)	7	0	92
$FeCl_3$ + Na_2S[c)]	4	4	8
$FeCl_3$	5	0	0
-	4	0	1

a) Reaction conditions: 1,4-Dinitrobenzene (1.0 mmol), catalyst (0.1 mmol), and benzenethiol (10 mmol) in acetonitrile (20 ml) were stirred at 26 °C for 20 h under an argon atmosphere. b) The yield of products was determined by TLC scanner. c) $FeCl_3$ (0.25 mmol) and Na_2S (0.22 mmol).

displacement easily by various nucleophiles.[14)]

In conclusion, **1** reduced dioxygen or dinitrobenzene in the presence of benzenethiol. The reduction efficiency of **1** was revealed to be quite different from that of **2**.

This work shows that **1** has high reduction activities, but 2 does not. **2** catalyzes the displacement rather than the reduction. This is the first report about the difference of the reactivities between [4Fe-4S] and [2Fe-2S] iron-sulfur complexes.

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11) Benzenethiol (0.25 ml, 2.5 mmol) and acetonitrile (1 ml) were placed in a two-necked round-bottom flask equipped with a Suba Seal Septa and a three way stopcock which was connected to a dioxygen cylinder and a gas buret. After dioxygen was substituted in the flask, the solution of analogue in acetonitrile (10 ml) was added through Septa with a syringe. The reaction mixture was stirred at 0 °C and dioxygen consumption was followed.

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