COMPARISON OF THE REACTIVITIES OF \([\text{Fe}_4\text{S}_4(\text{SPh})_4]^{2-}\) AND \([\text{Fe}_2\text{S}_2(\text{SPh})_4]^{2-}\)

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The reactivities of the model complexes, \([\text{Fe}_4\text{S}_4(\text{SPh})_4]^{2-}\) (1) and \([\text{Fe}_2\text{S}_2(\text{SPh})_4]^{2-}\) (2), of nonheme iron-sulfur proteins were compared. Complex 1 catalyzed the oxidation of benzenethiol to diphenyl disulfide with the reduction of dioxygen to \(\text{H}_2\text{O}\). 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 \(\text{N}-(4\text{-nitrophenyl})\text{hydroxylamine}\) (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. These proteins are classified by their active sites as rubredoxin ([1Fe]) and ferredoxins ([2Fe-2S], [4Fe-4S], [3Fe-3S], and [3Fe-4S]) types. Many analogues of the active sites of such proteins have been prepared since the successful synthesis of \((\text{Et}_4\text{N})_2[\text{Fe}_4\text{S}_4(\text{SCH}_2\text{Ph})_4]\) by Holm and his coworkers. These analogues have contributed to the understanding of the physical properties of the protein active sites. 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.

We reported previously that \((\text{n-But}_4\text{N})_2[\text{Fe}_4\text{S}_4(\text{SPh})_4]^{6-}\) (1) catalyzes the oxidation of benzenethiol to diphenyl disulfide with dioxygen and also on the reduction of aromatic nitro compounds to amines with benzenethiol. As part of our research on the catalytic properties of iron-sulfur analogues, the reactivity of \((\text{Et}_4\text{N})_2[\text{Fe}_2\text{S}_2(\text{SPh})_4]^{2-}\) (2) 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). 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. However, Coucouvanis et al. reported that 2 is reduced by sodium hydrosulfite and crown ether to form 1. Complex 2 is probably

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reduced to \([\text{Fe}_2\text{S}_2\text{(SPh)}_4]^3^-\), 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 FeCl₃ or FeCl₄ 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

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2[\text{Fe}_2\text{S}_2\text{(SPh)}_4]^2^- + 2\text{PhSH} \rightarrow 2[\text{Fe}_2\text{S}_2\text{(SPh)}_4]^3^- + \text{PhSSPh} + 2\text{H}^+ \\
2[\text{Fe}_2\text{S}_2\text{(SPh)}_4]^3^- \rightarrow [\text{Fe}_4\text{S}_4\text{(SPh)}_4]^2^- + 4\text{PhS}^-
\]

**Chart 3**

<table>
<thead>
<tr>
<th>Catalyst</th>
<th>4</th>
<th>5</th>
<th>6</th>
</tr>
</thead>
<tbody>
<tr>
<td>((\text{n-Bu}_4\text{N})_2[\text{Fe}_4\text{S}_4\text{(SPh)}_4] (1))</td>
<td>21</td>
<td>16</td>
<td>0</td>
</tr>
<tr>
<td>((\text{Et}_4\text{N})_2[\text{Fe}_2\text{S}_2\text{(SPh)}_4] (2))</td>
<td>7</td>
<td>0</td>
<td>92</td>
</tr>
<tr>
<td>(\text{FeCl}_3 + \text{Na}_2\text{SCl})</td>
<td>4</td>
<td>4</td>
<td>8</td>
</tr>
<tr>
<td>(\text{FeCl}_3)</td>
<td>5</td>
<td>0</td>
<td>0</td>
</tr>
<tr>
<td>-</td>
<td>4</td>
<td>0</td>
<td>1</td>
</tr>
</tbody>
</table>

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) \(\text{FeCl}_3\) (0.25 mmol) and \(\text{Na}_2\text{S}\) (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.

REFERENCES AND NOTES

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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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