BIOCHEMICAL FUNCTIONS OF PERSULFIDES

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NATURE OF PERSULFIDES

In biological systems, persulfides (RSS\(^-\)) are reactive, unstable intermediates in the transformations of sulfur compounds. Persulfides are also referred to as polysulfides, or alkyl/aryl hydrogen disulfides. The persulfide sulfur is commonly termed, "sulfane", to designate sulfur covalently bonded only to other sulfur atoms. The scission of the sulfur-sulfur bond is enhanced by the joint action of electrophilic and nucleophilic groups\(^1\).

Persulfides are formed in a variety of ways. Elemental sulfur and mercaptans combine in a reversible reaction.

\[
RS^- + S^0 \rightleftharpoons RSS^- \tag{1}
\]

The reaction to the right reflects the action of mercaptans in dissolving sulfur from its suspension in water; the reverse results from the intrinsic instability of persulfides and the insolubility of free sulfur.

Hylin and Wood\(^2\) produced persulfides by incubating flowers of sulfur with solutions of mercaptans (Table 1). If an appreciable excess of mercaptan was used, the sulfane sulfur was reduced to sulfide.

\[
RSS^- + RS^- \rightleftharpoons RSSR + S^{2-} \tag{2}
\]

Table 2 shows some properties of persulfides which are useful in their detection. Cyanolysis yields thiocyanate ion which is readily detectable with ferric ion. Alkylation with iodoacetate produces a mixed disulfide\(^3\).

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F. Bossa et al. (eds.), Structure and Function Relationships in Biochemical Systems
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Persulfides transfer sulfur to a variety of anions.

$$\text{RSS}^- + \text{ICH}_2\text{COO}^- \rightarrow \text{RSSCH}_2\text{COO}^- + \text{I}^-$$ \[3\]

Reaction 4 represents cyanolysis. Where R represents an enzyme, the reactions are catalytic.

**PERSULFIDES IN BIOLOGICAL SYSTEMS**

Table 3 shows some persulfides that are found in biological systems. Thiocysteine has been detected by Cavallini et al.\(^4\) as the initial product of the action of cystathionase (EC 4.4.1.1) on cystine.

$$\text{CH}_2\text{-S-S-CH}_2 \overset{\text{cystathionase}}{\longrightarrow} \text{CH}_2\text{-S-SH}$$

Table 1. Formation of Persulfides

<table>
<thead>
<tr>
<th>Precursor</th>
<th>Sulfane Sulfur (µmole/mmole)</th>
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<tbody>
<tr>
<td>Sodium sulfide</td>
<td>12.8</td>
</tr>
<tr>
<td>Mercaptoethanol</td>
<td>9.2</td>
</tr>
<tr>
<td>Mercaptopyruvate</td>
<td>7.3</td>
</tr>
<tr>
<td>Cysteine</td>
<td>14.7</td>
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</tbody>
</table>

Flowers of sulfur (6 mg) and 0.1 M solutions (10 ml) of precursor in 0.1 M buffer, pH 9.1, were incubated at 37°C for 15 min. Sulfane sulfur was determined as thiocyanate after cyanolysis.

Table 2. Some Properties of Persulfides

<table>
<thead>
<tr>
<th>Cyanolyse</th>
<th>Deposit Sulfur</th>
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<tbody>
<tr>
<td>Transfer Sulfur</td>
<td>Absorb at 330-350 nm</td>
</tr>
<tr>
<td>Alkylate</td>
<td>Reduce to Sulfide Ion</td>
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</tbody>
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