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U. Fischer: CYTOCHROMES AND IRON SULFUR PROTEINS IN SULFUR METABOLISM OF PHOTOTROPHIC BACTERIA

Dissimilatory sulfur metabolism in phototrophic sulfur bacteria provides the bacteria with electrons for the photosynthetic electron transport chain and, therefore, with energy. On the contrary, assimilatory sulfate reduction is necessary for the biosynthesis of sulfur-containing cell components, such as amino acids. Sulfide, thiosulfate, and elemental sulfur are the sulfur compounds most commonly used by phototrophic bacteria as electron donors for anoxygenic photosynthesis. Cytochromes or other electron transfer proteins, like high-potential-iron-sulfur protein (HIPIP) function as electron acceptors or donors for most enzymatic steps during the oxidation pathways of sulfide or thiosulfate. Yet heme- or siroheme-containing proteins themselves undergo enzymatic activities in sulfur metabolism. Sirohemes comprise a porphyrin-like prosthetic group of sulfate reductase. Flavocytochromes (cytochrome c reductase, elemental sulfur reductase, or adenylylsulfate (APS) reductase) of phototrophic bacteria react with sulfide. High-spin cytochrome c' exhibits sulfite acceptor oxidoreductase, while sulfite reductases may contain siroheme as a new type of heme prosthetic group.

Reduced sulfur compounds at oxidation levels below that of sulfate serve as electron donors for anoxygenic photosynthesis and carbon dioxide fixation in most phototrophic bacteria. When sulfide is oxidized to sulfate by purple sulfur bacteria (Chromatiaceae) and green sulfur bacteria (Chlorobiaceae), one intermediate product formed is elemental sulfur (S^0). This is stored as sulfur globules inside the cells of Chromatiaceae. The purple sulfur genus *Ectothiorhodospira*, however, stores the S^0 outside cells (as is common for the Chlorobiaceae). Purple nonsulfur bacteria (Rhodospirillaceae) capable of utilizing sulfide as the electron donor oxidize it either to sulfate without the formation of elemental sulfur or only to S^0 which is then deposited outside the cells and which cannot be further oxidized by them to sulfate. The end product of anoxygenic sulfide oxidation by cyanobacteria is S^0 which can be stored inside or outside the cells. As an electron donor for photosynthesis, sulfite (SO_3^{2-}) is used by only a few species of phototrophic bacteria; tetrathionate, as far as known, is used only by the thiosulfate-utilizing green *Chlorobium limicola (forma thiosulfatophilum)*. The ability to consume S^0 is typical of Chromatiaceae and Chlorobiaceae, but not of Rhodospirillaceae and cyanobacteria. The use of thiosulfate as an electron donor is more extensive in Chromatiaceae and Rhodospirillaceae than in Chlorobiaceae.

Sulfur compounds can be either oxidized or reduced by metabolism. Electron carrier proteins are necessary for sulfur redox reactions. Electron transfer proteins include cytochromes, sirohemes, and non-heme iron proteins, such as ferredoxin, rubredoxin, and HIPIP.

Figure I-6.5 summarizes the enzymatic steps of sulfur metabolism where electron transfer proteins are involved.

All enzymatic reactions with the exception of ADP sulfurylase and adenylate kinase involve transfer of electrons. Electron donors or acceptors are necessary for each of these reactions. Cytochromes and iron sulfur proteins, probably components of the plasma or photosynthetic membranes, are able to transfer electrons.

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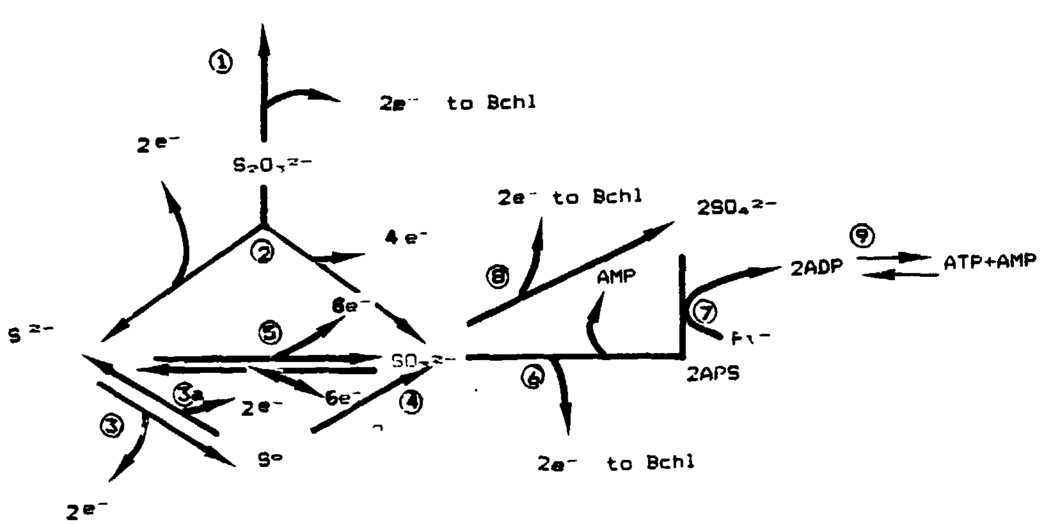

Figure I-6.5. Sulfur oxidation in phototrophic bacteria. 1 = thiosulfate: acceptor oxidoreductase; 2 = thiosulfate reductase; 3 = sulfide oxidizing enzyme; 3a = elemental sulfur reductase; 4 = elemental sulfur-oxidizing enzyme; 5′= sulfite reductase (siroheme); 6 = APS reductase; 7 = ADP sulfurylase; 8 = sulfite: acceptor oxidoreductase; 9 = adenylate kinase. Abbreviations APS = adenosine-5′-phosphosulfate; AMP = adenosine-5′-triphosphate; *Pi* = inorganic phosphate; Bchl = Bacteriochlorophyll.