Oxidation of Dibenzothiophene Catalyzed by Heme-Containing Enzymes Encapsulated in Sol-Gel Glass

A New Form of Biocatalysts

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ABSTRACT

We have encapsulated several hemoproteins in the sol-gel glass to catalyze the oxidation reaction of dibenzothiophene (model for organic sulfur compounds in coal) with hydrogen peroxide. In addition to cytochrome c and myoglobin, which have previously been encapsulated in sol-gel glasses, two other hemoproteins, horseradish peroxidase and bovine blood hemoglobin, have now been successfully immobilized in sol-gel media with the retention of their spectroscopic properties. All four hemoproteins studied also demonstrate similar catalytic activities toward the oxidation of dibenzothiophene as compared with the results obtained with the proteins in solution. In the case of encapsulated cytochrome c, the more water-soluble S-oxide was obtained with much higher selectivity over the less water-soluble sulfone (S-oxide/sulfone = 7.1) as compared to what was obtained in the aqueous/organic medium (S-oxide/sulfone = 2.3). Because of the advantage of easy separation of the encapsulated proteins from the liquid reaction mixture, it is clear from these studies that the immobilization of active hemoproteins in the solid glass media could serve as more practical biocatalysts.

Index Entries: Dibenzothiophene; biooxidation; biocatalyst; encapsulation; sol-gel glass, hemoglobin; cytochrome c; horseradish peroxidase; myoglobin.

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INTRODUCTION

The hemoproteins catalyze the oxidation of the organic sulfides at the expense of hydrogen peroxide (1-6). Organic sulfur-containing compounds from the combustion of coal represent an important class of environmental chemicals, whose presence often causes poisoning of catalysts, corrosion of surfaces, and air pollution. Biocatalytic sulfoxidation often produces products with increased water solubility and enhanced reactivity, which can then be readily removed from the substrate, e.g., coal.

Among the proteins studied, it has been shown that chloroperoxidase, lactoperoxidase, and horseradish peroxidase catalyze the oxygenation of benzyl methyl sulfide, thioanisole, and thiobenzamide to their respective sulfoxides (2-6). A very recent study has demonstrated that dibenzothiophene can be oxidized to form its S-oxide and sulfone (S-dioxide) by hydrogen peroxide in the presence of horseradish peroxidase, cytochrome c, and bovine blood hemoglobin, and so on (1).

Dibenzothiophene is a widely accepted model compound for organic sulfur in coal because of its poor water solubility (< 10 μM) and the difficulties associated with its transformation into other products by chemical methods (1).

Recently, successful encapsulation of a series of proteins in sol-gel glass has been reported (7-9). It was shown that the encapsulated biomolecules retained their characteristic enzymatic activities inside the glass matrix. These studies have provided excellent prospects for the use of these solid state composite materials containing biochemically active macromolecules as potential bio-devices, such as biosensors or biocatalysts.

In this paper, we report the oxidation of dibenzothiophene catalyzed by cytochrome c, horseradish peroxidase, hemoglobin, and myoglobin encapsulated in a solid sol-gel glass matrix. It is found that all four encapsulated hemoproteins possess similar catalytic activities as compared with the proteins present in solution. The apparent advantages of using the encapsulated proteins are easy separation of the catalyst from the liquid reaction mixture as well as stabilization of the catalysts in the glass matrix. This work should extend the use of hemoproteins as catalysts for sulfoxidation to more practical applications. It also offers the exciting possibility of encapsulated biomacromolecules as the potential biocatalysts.