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Iron (III)-Salen-Catalyzed H_2O_2Oxidation of Dibenzyl Sulfide in Reverse Micelles

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Abstract

Iron(III)-salen complexes {salen = N,N'bis(salicylidene)ethylenediaminato} efficiently catalyze the H_2O_2 oxidation of organic sulfides. This reaction leads to the formation of sulfoxides as the major product. The spectrophotometric kinetic study shows that the reaction follows Michaelis-Menten kinetics. The reactions are then performed in the presence of anionic reverse micelle AOT to understand the rate changes of the reactions in the reverse micelles. The reactions in the micellar medium are faster than in the pure solvent. Based on the spectral and kinetic studies a suitable electron transfer mechanism is proposed.

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Keywords: Iron(III)-salen catalyst ;H2O2oxidation; dibenzyl sulfide

1. Introduction

Several surfactants are able to aggregate in non-aqueous solvents to yield reverse micelles in which the polar head group of the surfactant monomers cluster to form a micelle core and are directed towards the centre of the assembly and the hydrophobic tails extend outwards into the bulk organic phase [1-3]. Both experimental and theoretical approaches show that key structural parameter of reverse micelle is the [water]/[surfactant] molar ratio(W_0) which determines the micellar size as well as the unique physicochemical properties of the entrapped water. Among the anionic surfactants that form reverse micelles, the best known are the systems derived from the AOT (sodium 1, 4-bis-2-ethylhexylsulfosuccinate) in different nonpolar media. AOT has a well-known V-shaped geometry, giving rise to stable reverse micelles without co surfactant. AOT has the remarkable ability to solubilize a

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large amount of water with values of W_0(W_0=[H_2O]/[AOT]),as large as 40-60 depending on the surrounding nonpolar medium, the solute, and the temperature; however the droplets size depends only on the water amount W_0 [4-6]. Several transition metal complexes have been used for studying electron-transfer reactions. Iron is the most prominent transition metal in biological perspective, as many enzymes containing ferrous or ferric ion catalyze various bio-transformations [7-22]. Therefore it is desirable to study the catalytic activities of iron (III) complexes. In this context Rajagopal etal [23] have used iron (III)-salen complexes as enzyme models for the selective oxidation of organic sulfides to sulfoxides using PhIO as the oxygen source. It is advantageous to use H_2O_2 as the oxidant instead of PhIO as H_2O_2 is a safe, readily available and cheap reagent. Further this eco-friendly redox system may serve as peroxidases model and leaves water as the only by product. With this aim of using eco-friendly reagents, six iron(III)-salen complexes are synthesized and used as catalysts. The reaction is facile and organic sulfoxides are the major product of the reaction. The effect of reverse micellar environment on the electron transfer rate has also been examined and is presented.

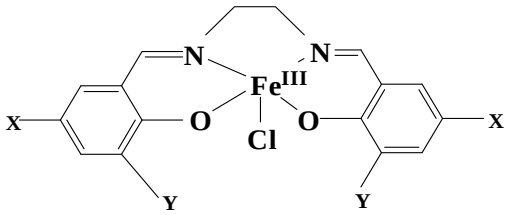
2. Experimental

2.1. Materials

Salicylaldehyde and the substituted salicylaldehyes (5-methyl, 5-bromo, 5-chloro, 3, 5-di-tert butyl, 5-methoxy) were purchased from Aldrich and used as such. Dibenzyl sulfide purchased from Sigma-Aldrich was used as received. CH_3CN, Isooctane of HPLC grade were purchased and used as such. Sodium bis(2-ethylhexyl)sulfosuccinate (AOT), (99%) purity was purchased from Merck and used as such. All other reagents were of Analar grade. The kinetic study of the reaction was performed after the purities of the reactants and solvents used in the system were confirmed.

2.2. Synthesis of ligands and iron(III)-salen complexes

Various salen ligands were prepared from ethylenediamine and the corresponding salicylaldehyde by standard methods [24-27]. Iron(III)-salen complexes I-VI(eq.1) were synthesized using established procedures [28-30]. The complexes were characterized by IR and UV-Visible absorption spectral techniques.



1

I X=Y=H II X=Cl,Y=H
III X=Br,Y IV X=CH_3, Y=H
V X=OCH_3, Y=H VI X=Y=t-butyl

2.3. Procedures

Stock solutions of AOT reverse micelle were prepared by weighing and dilution in isooctane. Stock solutions of 1M surfactant were agitated in a sonicating bath until the reverse micelle was optically clear. The appropriate amount of stock solution to obtain a given concentration of surfactant in the micellar media was transferred into the cell. The addition of water to the corresponding solution was performed using a calibrated microsyringe. The amount of water present in the system is expressed as the molar ratio between water and the surfactant present in the reverse micelle (W_0=[H2O]/[surfactant]). The lowest value of W_0, called W_0=0, corresponds to a system with no addition of water.