



Enantioselective electrochemical carbon-chloride bond cleavage of hexachlorocyclohexanes (HCHs) catalyzed by Mn(III)Cl-phthalocyanine

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ABSTRACT

A lipophilic and electron-rich metallophthalocyanine Mn(III)Cl(α,α' -n-OC₅H₁₁)₈Pc has been synthesized and characterized. A series of electrochemical experiments demonstrate that the Mn(III)Cl(α,α' -n-OC₅H₁₁)₈Pc complex can be used as a catalyst for highly efficient carbon-chloride bond cleavage of environmental toxic hexachlorocyclohexanes (HCHs) through electrochemical catalysis, and that the increased catalytic efficiency is related to the enantiomeric carbon-chloride bond of HCHs.

1. Introduction

Over the past few decades, organochlorides, which are organic compounds with at least one covalent C–Cl bond, have been used in a wide range of applications [1–4]. Unfortunately, organochlorides usually do not degrade readily in the environment, so despite restrictions being placed on their use in agriculture by many countries, they are still present globally at significant concentrations as ubiquitous contaminants in soils and waters [5–8]. There has been considerable interest in the development of new techniques to achieve their full degradation through C–Cl bond cleavage reactions including microbial methods [9–14], along with chemical [15–19], photochemical [20–25] and electrochemical approaches [26–30]. More recently, electrocatalytic degradation is becoming more popular due to their facile procedures and low cost. Electrocatalysis usually makes use of transition macrocyclic metal complexes [31,32]. For example, when a transition metal phthalocyanine (Pc) complex is used, a central divalent metal ion is reduced electrochemically to form a [M(I)Pc(–2)][–] species, so it can react with alkyl halides (R–X) to form a σ -bond and a M^{III}-macrocycle [33,34]. This results in the release of a chloride ion through the cleavage of a C–Cl bond. The dissociation energy of the bond is determined by the type of s-p hybridization that is involved. When metalloporphyrins and -corroles are used, efficient dechlorination of environmentally harmful organochlorides can also be achieved through electrochemical catalysis in non-aqueous media [35–40]. We recently demonstrated that when metalloporphyrins are conjugated to the

surface of Fe₃O₄@SiO₂, the catalysts can be successfully recovered by a magnet [41], and that electron rich near infrared (NIR) region absorbing metallophthalocyanines exhibit efficient C–Cl bond cleavage reactions [42], and provide the first example of the full dechlorination of DDT achieved through molecular electrochemical catalysis. In this study, the synthesis and electronic structure of an NIR absorbing Mn(III)ClPc(–2), and a detailed analysis of its electrocatalyzed C–Cl bond cleavage reactions for hexachlorocyclohexane (HCH), which is one of the most important organochlorides. HCHs consist of a six membered ring with a chlorine and hydrogen atom attached to each carbon. Many isomeric structures are possible, which differ according to the stereochemistry of the chlorine atoms. These isomers exhibit various types of reactions that are significant in different fields [43–46]. Within this study, a comparison is made between the C–Cl bond cleavage reactions of the different enantiomers when an electron rich metallophthalocyanine is used as the electrocatalyst.

2. Experimental section

2.1. General

¹H NMR spectra were recorded on a Bruker AVANCE 500 spectrometer (operating at 500.13 MHz) using the residual as an internal reference for ¹H (δ = 7.26 and 5.32 ppm for CDCl₃ and CD₂Cl₂, respectively). All reagents and solvents were of commercial reagent grade and were used without further purification except where noted. Cyclic

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