

# Hydrogen peroxide oxidation of 2-chlorophenol and 2,4,5-trichlorophenol catalyzed by monomeric and aggregated cobalt tetrasulfophthalocyanine

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## Abstract

Cobalt tetrasulfophthalocyanine (CoTSPc) was used to catalyze the oxidation of 2-chlorophenol (2-CP) and 2,4,5-trichlorophenol (TCP) using hydrogen peroxide ( $H_2O_2$ ) as the oxidant. This CoTSPc catalyzed hydrogen peroxide oxidation of chlorophenols resulted in the formation of different types of oxidation products depending on the solvent conditions. In water/methanol conditions (where CoTSPc is mainly monomeric, and unionized forms of the phenols), phenol and hydroquinone were the main oxidation products, while in phosphate buffer solutions (pH 7 and 10 for TCP and 2-CP, respectively, where CoTSPc is mainly aggregated, and ionized forms of the phenols), benzoquinone was the main product. In contrast to CoTSPc, other MTSPc complexes studied (AlTSPc, CuTSPc and NiTSPc) exhibited no detectable catalytic effect on the oxidation of chlorophenols under the experimental conditions employed, thus proving the effect of the central metal ions on efficient catalysis of chlorophenol. Reaction pathways are proposed based on the relative time of oxidation products formation. © 2004 Elsevier B.V. All rights reserved.

**Keywords:** 2-Chlorophenol; 2,4,5-Trichlorophenol; Cobalt tetrasulfophthalocyanine; Hydrogen peroxide; Catalysis

## 1. Introduction

Chlorinated organic compounds such as 2-chlorophenol (2-CP) and 2,4,5-trichlorophenol (TCP) are well known recalcitrant pollutants, despite their useful applications as pesticides, lubricants and solvents [1]. Polychlorinated aromatics in particular are resistant to biotransformation in the environment to less harmful analogues, and the toxicity and resistance to degradation of chlorinated organic compounds increases with the number of halogen substituents [2–5]. Efficient chemical catalysts are needed to convert chlorinated phenols to more biodegradable molecules. Complete degradation to carbon dioxide ( $CO_2$ ) is desirable. It is also desirable that the catalyst is active but does not completely self-destruct through oxidation.

Some metallophthalocyanine (MPc) complexes are important industrial dyes hence readily available. MPc complexes containing electroactive central metals are preferred catalysts

for the oxidation of chlorophenols since these complexes have a wide range of readily available oxidation states. Iron and manganese tetrasulfophthalocyanines complexes have been extensively studied as biomimetic catalysts for the oxidation of chlorophenols in the presence of an environmentally clean hydrogen peroxide ( $H_2O_2$ ) oxidant [6–12]. Cobalt tetrasulfophthalocyanine (CoTSPc) has however, not been explored for the catalytic oxidation of chlorophenols, even though it is produced industrially in large amounts as a catalyst for the oxidation of mercaptans in gasoline fraction [13–16]. CoPc complexes have rich redox chemistry and, because of their high catalytic activities, have been more widely employed in electrocatalytic reactions than their FePc or MnPc counterparts. It is surprising therefore that, up to date, there have been no detailed literature reports on the catalytic oxidation of chlorinated phenols by any CoPc complex. FeTSPc and MnTSPc catalysts exist as  $\mu$ -oxo dimers, which have to undergo cleavage before the formation of the active form of the catalysts. CoTSPc on the other hand does not form  $\mu$ -oxo dimers. For MPc catalyzed reactions, the nature of the catalyst would be dependent on the nature of the

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