

Iron perchlorophthalocyanine and tetrasulfophthalocyanine catalyzed oxidation of cyclohexane using hydrogen peroxide, chloroperoxybenzoic acid and *tert*-butylhydroperoxide as oxidants

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Abstract

Polychlorophthalocyanine ($\text{Cl}_{16}\text{PcFe}^{\text{II}}$) and tetrasulfophthalocyanine ($[\text{Fe}^{\text{II}}\text{TSPc}]^{4-}$) complexes of iron are employed as catalysts for the oxidation of cyclohexane using *tert*-butyl hydroperoxide (TBHP), *m*-chloroperoxybenzoic acid (*m*-CPBA) and hydrogen peroxide as oxidants. Catalysis using the $\text{Cl}_{16}\text{PcFe}^{\text{II}}$ was performed in a dimethylformamide:dichloromethane (3:7) solvent mixture. For the $[\text{Fe}^{\text{II}}\text{TSPc}]^{4-}$ catalyst, a water:methanol (1:9) mixture was employed. The products of the catalysis are cyclohexanone, cyclohexanol and cyclohexanediol. The relative yields of the products depended on oxidant and the catalyst. TBHP was found to be the best oxidant since minimal destruction of the catalyst and higher selectivity in the products were observed when this oxidant was employed. The mechanism of the oxidation of cyclohexane in the presence of the $\text{Cl}_{16}\text{PcFe}^{\text{II}}$ and $[\text{Fe}^{\text{II}}\text{TSPc}]^{4-}$ involves the oxidation of these catalysts, forming an Fe(III) phthalocyanine species as an intermediate. Higher yields were observed when $[\text{Fe}^{\text{II}}\text{TSPc}]^{4-}$ was employed as a catalyst, which is more soluble than the perchlorinated iron phthalocyanine catalyst. © 2002 Elsevier Science B.V. All rights reserved.

Keywords: Iron phthalocyanine; Cyclohexane; Cyclohexanone; Cyclohexanol; Cyclohexanediol

1. Introduction

The search for biomimetic analogs of cytochrome P-450 [1] for selective oxidation of hydrocarbons has been a subject of several investigations in recent years. Metalloporphyrin complexes have been studied extensively for use as catalysts for hydrocarbon oxidation [2–10]. Halogenated metalloporphyrin complexes have been used successfully as catalysts for hydrocarbon oxidation due to increased stability (induced by the halogens) of the porphyrin ring towards degradation. Metallophthalocyanine (MPc) complexes have a

similar structure to the porphyrins, but the former are more stable to degradation. MPc complexes are also cheaper and more readily available than porphyrins. Both the porphyrins and phthalocyanines are useful catalysts that allow control of the active form of oxygen, resulting in selectivity of the products formed.

The use of MPc complexes as catalysts for the chlorinated phenols, using oxidants such as hydrogen peroxide, has received considerable attention in recent years [11–17]. Iron(II) tetrasulfophthalocyanine was in particular found to efficiently catalyze the oxidation of trichlorophenol with high turnover rates. Studies on the use of MPc complexes as catalysts for the oxidation of alkanes or alkenes has received less attention [6,18,19]. The use of supported PdPc as a catalyst for the partial oxidation of methane resulted in the

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