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Photocatalytic oxidation of 1-hexene using GaPc and InPc octasubstituted derivatives

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ABSTRACT

Photocatalytic oxidation of 1-hexene by GaPc (**1a**–**1c**) and InPc (**2a**–**2c**) derivatives (Pc = phthalocyanine) is hereby presented. The derivatives studied are Pc octasubstituted with phenoxy (**a**), 4-*tert*-butylphenoxy (**b**) or benzyloxyphenoxy (**c**) at the peripheral positions. The photocatalytic oxidation products for 1-hexene were 1,2-epoxyhexane and 1-hexen-3-ol. The %conversion values of 1-hexene and %selectivity of 1,2-epoxyhexane were generally higher for InPc derivatives. Even though InPc derivatives showed better photocatalytic results than GaPc derivatives, the former were less stable relative to the latter. Both type I and type II mechanism were implicated in the photocatalysis mechanism.

1. Introduction

Alkanes and alkenes are produced in thousands of tons by petroleum industrial companies as by-products [1]. Because of the increasing need to conserve natural resources, it is imperative that such products be used as starting materials in other industrial processes. Alkanes and alkenes can be partially oxidized to fine chemicals such as alcohols, ketones and aldehydes to mention but a few [2]. The oxidation of alkenes, in particular, results in useful intermediates such as epoxides, which are of great interest in industries. These intermediates are use in, for example, the manufacturing of ethylene glycol, automobile antifreeze, fine chemicals and polymers [2]. Porphyrins and phthalocyanines are known to catalyze the oxidation of alkenes and alkanes. Substituents and central metals can be introduced on these complexes to change both physical and chemical properties in order to achieve desired properties. Pophyrins have been used as photocatalysts for oxygen driven oxidation of cyclohexane [3–5]. The oxidation of alkenes using phthalocyanines and oxygen or other oxidants has not received much attention [6,7]. Thus, in this work we explore the use of GaPc and InPc derivatives as catalysts for the photooxidation of 1-hexene.

Metallophthalocyanines (MPcs) are able to generate single oxygen species through the process of photosensitization. Upon absorbing light, phthalocyanines get excited to the singlet state ($^1MPc^*$) and through intersystem crossing (ISC), they move to the triplet state ($^3MPc^*$) where energy is transferred from the energy rich phthalocyanine to molecular oxygen ($^3O_2$) in its triplet state to yield singlet oxygen ($^1O_2$), which subsequently oxidizes the substrate (Scheme 1). This is called Type II mechanism [8].

The excited MPc in the triplet state can also interact with the substrate molecule to generate radical ions which then continues to form superoxides and hydroperoxyl radicals which can oxidize the substrate [8,9]. This is known as the Type I mechanism (Scheme 2 [8,9]), and is less common compared to Type II.

This work reports on the photocatalytic oxidation of 1-hexene using GaPc (**1a**–**1c**) and InPc (**2a**–**2c**) derivatives (Fig. 1). Ga and In are large metals hence they are expected to enhance intersystem crossing resulting in high triplet yields and hence high singlet oxygen quantum yields. This should result in increased activity towards the oxidation of 1-hexene by Type II mechanism.

2. Experimental

2.1. Materials and instrumentation

The syntheses, purification and characterization of GaPc (**1a**–**1c**) and InPc (**2a**–**2c**) derivatives have been reported [10–12]. 1-Hexene, 1-hexen-3-ol, 1,3-diphenylisobenzofuran (DPBF) and 1,4-diazobicycle-octane (DABCO) were purchased from Aldrich. Dichloromethane (DCM) was of high performance liquid chro-

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