

Comparative photocatalytic efficiency of oxotitanium(IV) phthalocyanines for the oxidation of 1-hexene

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Abstract

The comparative photocatalytic activities of aryloxy and arylthio tetrasubstituted oxotitanium(IV) phthalocyanine complexes for the oxidation of 1-hexene in DCM are reported for the first time. The singlet oxygen quantum yield, photostability and photocatalytic properties are investigated. The catalysts effectively catalyse 1-hexene to 1,2-epoxyhexane and 1-hexene-3-ol as major and minor products respectively. The photooxidation products are formed via two reaction mechanisms, namely via singlet oxygen (Type II) and radical (Type I) reaction pathways. These are also dependent on the singlet oxygen quantum yields and photostabilities of the phthalocyanines. Complex **1a** that is peripherally substituted with phenoxy groups exhibited the best activity in terms of overall performance.

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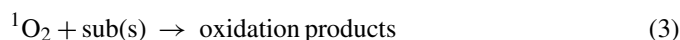
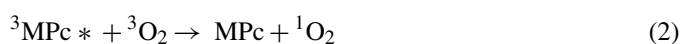
Keywords: 1-Hexene; Oxotitanium(IV) phthalocyanines; Photocatalysis; Singlet oxygen; Photostability; Kinetics

1. Introduction

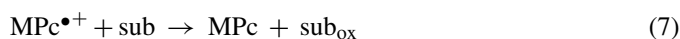
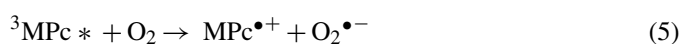
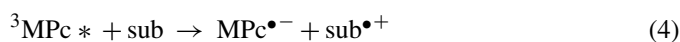
Oxidation of olefins into useful products is of immense interest. For example, epoxides are useful intermediates obtained on catalytic oxidation of alkenes that are widely used for petrochemicals, fine chemicals and polymers such as oxygen-containing natural products or production of epoxy resins. Use of molecular oxygen as an oxidant for transformation of alkenes is preferred as it is cheap, environmentally clean and readily available [1,2].

Excited state oxidation reactions of alkenes using phthalocyanines and molecular oxygen are rare [3] compared to those catalysed by porphyrins [4–7]. There is thus a need of exploring the use of phthalocyanine complexes such as those containing titanium as the central metal atom. Photocatalytic oxidation reactions usually selectively proceed at room temperatures using light, oxygen and a sensitizer, e.g. metallophthalocyanine (MPc). The active species is often singlet oxygen such that a variety of useful compounds can be obtained from starting compounds, e.g. olefins.

Many photocatalytic olefin oxidations occur in the presence of the highly energetic and oxidative singlet oxygen through the so-called Type II mechanism (Eq. (1)–(3)). On irradiation of the MPc in the visible region, the excited singlet state sensitizer is formed, i.e. $^1\text{MPc}^*$. By intersystem crossing (ISC), the excited triplet state is formed, i.e. $^3\text{MPc}^*$ which then interacts with the ground state triplet oxygen ($^3\text{O}_2$) to generate the very active singlet oxygen, i.e. $^1\text{O}_2$. Alternatively, radicals such as superoxides may be generated through the Type I mechanism (Eq. (4)–(9)), however their participation is generally limited. Both Types I and II processes may operate simultaneously since they take place independently of each other [8], i.e.:



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