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

Prudence Tau, Tebello Nyokong[*]

*Department of Chemistry, Rhodes University, Grahamstown 6140, South Africa*

## 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-hexen-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.
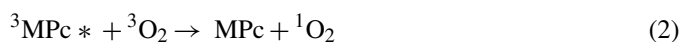© 2007 Elsevier B.V. All rights reserved.

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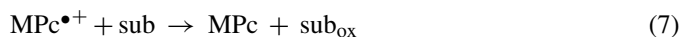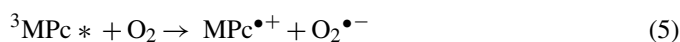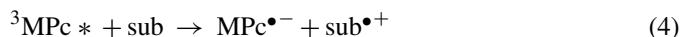
## 1. Introduction

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 sensitiser, 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.
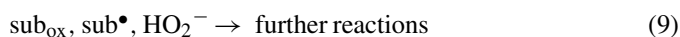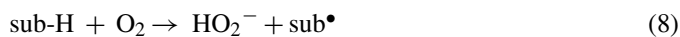
Many photocatalytic olefin oxidations occur in the presence of the highly energetic and oxidative singlet oxygen through the so-called Type II mechanism (Eq. (1)–(3)). On irradiation of the MPc in the visible region, the excited singlet state sensitiser is formed, i.e. $^1$MPc*. By intersystem crossing (ISC), the excited triplet state is formed, i.e. $^3$MPc* which then interacts with the ground state triplet oxygen ($^3$O$_2$) to generate the very active singlet oxygen, i.e. $^1$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.:

$$MPc \xrightarrow{h\nu} {}^1MPc^* \xrightarrow{ISC} {}^3MPc^* \tag{1}$$

$$^3MPc* + {}^3O_2 \rightarrow MPc + {}^1O_2 \tag{2}$$

$$^1O_2 + sub(s) \rightarrow \text{oxidation products} \tag{3}$$

OR

$$^3MPc* + sub \rightarrow MPc^{\bullet-} + sub^{\bullet+} \tag{4}$$

$$^3MPc* + O_2 \rightarrow MPc^{\bullet+} + O_2^{\bullet-} \tag{5}$$

$$MPc^{\bullet-} + O_2 \rightarrow MPc + O_2^{\bullet-} \tag{6}$$

$$MPc^{\bullet+} + sub \rightarrow MPc + sub_{ox} \tag{7}$$

* Corresponding author. Tel.: +27 46 6038260; fax: +27 46 6225109.
*E-mail address:* t.nyokong@ru.ac.za (T. Nyokong).

$$\text{sub-H} + O_2 \rightarrow HO_2^- + \text{sub}^\bullet \tag{8}$$

$$\text{sub}_{ox}, \text{sub}^\bullet, HO_2^- \rightarrow \text{ further reactions} \tag{9}$$

sub = substrate, e.g. alkene.

Interestingly, porphyrins containing iron [9,10], manganese [11,12], osmium [13], niobium [14,15] or molybdenum [16,17] as central atoms tend to yield products of oxidation via a radical mechanism. However, singlet oxygen sensitisers such as porphyrins of oxovanadium and oxotitanium have been reported [5,18].

The efficiency of singlet oxygen which is a key property of a sensitising agent is governed by various factors including aggregation. Aggregation should be avoided as dissipation of energy of the excited state occurs, thus resulting in lower $\Phi_\Delta$ values [19]. Additionally, the presence of heavy atoms promotes ISC – such that the probability of singlet oxygen formation is high – due to increased spin-orbit coupling in the molecule. Furthermore, the stability of the sensitiser is of utmost importance for photocatalytic reactions, since catalyst decomposition may result, leading to the termination of photocatalytic cycles.

To our knowledge, no investigations concerning the use of oxotitanium phthalocyanines as photocatalysts for the oxidation of olefins have been reported. The interest in TiPc complexes is based on the fact that Ti porphyrin complexes show predominantly Type II sensitization. We recently reported the synthesis of various new oxotitanium phthalocyanines which exhibited exceptional photophysical and electrochemical properties [20–22]. It is for this reason that we want to exploit their use as potential catalysts for the photooxidation of 1-hexene. The effects of the nature and position of the substituents on MPc complexes for the oxidation of 1-hexene is investigated. Their efficiencies to generate singlet oxygen as well as their stabilities are explored.

## 2. Experimental

### 2.1. Materials and instrumentation

The synthesis, purification and characterisation of arylthio and aryloxy oxotitanium(IV) phthalocyanines were recently reported by us [20–22]. 1-Hexene, 1,2-epoxyhexane, 1-hexen-3-ol, 1,3-diphenylisobenzofuran (DPBF), 1,4-diazabicyclo-octane (DABCO), 2,6-di-*tert*-butyl-4-methylphenol (BHT) were purchased from Aldrich. Dichloromethane (DCM) was of high performance liquid chromatography (HPLC) grade. Product analyses were performed on a Hewlett-Packard HP 5890 gas chromagraph (GC) fitted with an FID detector, using a PONA (crosslinked methyl siloxane) capillary column (50 m length, 0.2 mm internal diameter, 0.5 μm film thickness and 100 phase ratio). Mass spectra were recorded with Finnigan GC–MS using the same column as above.

### 2.2. Photochemical procedures

Detailed experimental methods were performed with a home-made photochemical set-up as described before [23,24].

### 2.2.1. Singlet oxygen quantum yield

The singlet oxygen quantum yields ($\Phi_\Delta$) of the OTiPcs were determined in DCM, using DPBF as chemical quencher. The DPBF quantum yields ($\Phi_{DPBF}$) were firstly calculated using Eq. (10) for each irradiation cycle:

$$\Phi_{DPBF} = \frac{(C_0 - C_t)V}{t I_{abs}} \tag{10}$$

where $C_0$ and $C_t$ are the DPBF concentrations before and after irradiation respectively, $t$ the irradiation time and $V$ is the volume of the sample in the cell. $I_{abs}$ is determined by Eq. (11), i.e.:

$$I_{abs} = \frac{\alpha S I}{N_A} \tag{11}$$

where $\alpha$ is the fraction of light absorbed, $S$ the irradiated cell area, $I$ the light intensity and $N_A$ is the Avogadro's constant. The singlet oxygen quantum yield is then calculated according to Eq. (12) [25]:

$$\frac{1}{\Phi_{DPBF}} = \frac{1}{\Phi_\Delta} + \frac{1}{\Phi_\Delta} \frac{k_d}{k_a} \frac{1}{[DPBF]} \tag{12}$$

where $k_d$ and $k_a$ are respectively, the singlet oxygen decay rate constant and reaction rate constant of DPBF in the presence of singlet oxygen. Using a plot of $1/\Phi_{DPBF}$ versus $1/[DPBF]$, the value of $1/\Phi_\Delta$ is obtained from the intercept.

### 2.2.2. Photochemical stability

The photostabilities of the OTiPc complexes were determined by monitoring the decay of the Q-band intensity in the visible region of light. The respective solutions were irradiated with visible light in DCM. To determine the number of molecules degraded per photon of light, photodegradation quantum yields $\Phi_P$ were calculated from Eq. (10), where the change in MPc concentration instead of DPBF is determined.

Since the time decay of the Q-band maxima for each OTiPc obeyed first-order kinetics, the photobleaching rate constants $k$, which are a measure of phthalocyanine stability, were calculated from Eq. (13):

$$\ln \frac{\varepsilon_0}{\varepsilon_t} = kt \tag{13}$$

where $\varepsilon_0$ and $\varepsilon_t$ are the extinction coefficients measured at time $t = 0$ and $t$, respectively.

### 2.2.3. Photocatalytic studies

In a typical experiment, a 5 ml glass vial was charged with a phthalocyanine complex (1 μmol) and 1-hexene (molar ratio of photosensitiser to substrate was 1:500) in oxygen saturated DCM. The reaction vessel was irradiated (under intensive magnetic stirring) with a General Electric Quartz lamp (300 W), with a 600 nm glass (Schott) and water filters used to filter off the UV and far infrared radiations, respectively. An interference filter (Intor, 700 nm with a bandwidth of 40 nm) was placed in the light path before the reaction vessel. The light intensity was measured with a power meter (POWER MAX51100—with incorporated Molectron detector) and was

found to be $\sim 4.0 \times 10^{16}$ photons s$^{-1}$ cm$^{-2}$. At appropriate intervals, aliquots were removed and immediately analysed by GC. The identification of the reaction products was verified by co-injection with authentic samples and GC–MS analyses. The total reaction time was 8 h at room temperature. The GC conversions (%) and oxidation product selectivities (%) were measured relative to the starting substrate, 1-hexene.

## 3. Results and discussion

### 3.1. Efficiency of singlet oxygen generation

Fig. 1 shows the MPcs used in this study. The complexes were selected because they bore similar substituents, however they differed in their ether (C–O–C) and thiol (C–S–C) bond linkages. Following irradiation of MPc with light at an appropriate wavelength, energy ($h\nu$) is absorbed and subsequently excitation from the singlet ground state to the singlet excited state to produce $^1$MPc* occurs, followed by ISC to form $^3$MPc*. A triplet–triplet energy transfer from $^3$MPc* to triplet oxygen, results in the formation of the energetically rich and chemically more reactive singlet oxygen ($^1$O$_2$). It is this singlet oxygen that is responsible for many photooxidation reactions [26].

The generation of singlet oxygen by the OTiPc complexes was determined in DCM in the presence of a chemical singlet oxygen quencher, DPBF. The decay of DPBF was monitored spectrophotometrically at $\lambda = 416$ nm since the rate of singlet oxygen generation is directly proportional to the rate of DPBF bleaching. The Q-band intensity of each complex was not degraded during the $\Phi_\Delta$ determinations. The singlet oxygen quantum yields of the complexes were relatively high, ranging from 0.61 to 0.86 (Table 1) and are comparable to those in

Table 1
Singlet oxygen quantum yields, photobleaching quantum yields and rate constants of the oxotitanium(IV) phthalocyanine complexes in DCM

| Compound | $\Phi_{DPBF}$ | $\Phi_\Delta$ | $\Phi_P$ | $k$ (min$^{-1}$) |
|---|---|---|---|---|
| **1a** | 0.58 | 0.84 | $3.8 \times 10^{-4}$ | $3.1 \times 10^{-2}$ |
| **1b** | 0.54 | 0.73 | $3.5 \times 10^{-4}$ | $3.4 \times 10^{-2}$ |
| **1c** | 0.56 | 0.86 | $5.3 \times 10^{-4}$ | $2.7 \times 10^{-1}$ |
| **1d** | 0.51 | 0.77 | $5.0 \times 10^{-4}$ | $2.4 \times 10^{-1}$ |
| **2a** | 0.53 | 0.63 | $2.7 \times 10^{-4}$ | $4.2 \times 10^{-2}$ |
| **2b** | 0.54 | 0.61 | $2.2 \times 10^{-4}$ | $3.8 \times 10^{-2}$ |
| **2c** | 0.55 | 0.69 | $4.8 \times 10^{-4}$ | $3.2 \times 10^{-1}$ |
| **2d** | 0.50 | 0.64 | $4.5 \times 10^{-4}$ | $2.9 \times 10^{-1}$ |

literature. Interestingly, the $\Phi_\Delta$ values of the peripherally substituted complexes were larger than those of the non-peripherally substituted complexes considering the same substituents. Additionally, $\Phi_\Delta$ values of the arylthio-substituted complexes were marginally larger than those of the aryloxy-substituted complexes. The presence of the heavier sulphur atoms may promote ISC, thus leading to higher singlet oxygen quantum yields for complexes **c** and **d** compared to **a** and **b**. The large $\Phi_\Delta$ values are sufficient for photooxidation reactions since all the complexes exhibited excellent efficiencies in the singlet oxygen generation under the employed experimental conditions.

### 3.2. Photostabilities

Photobleaching of Pcs is a process by which Pc macrocycles oxidatively decompose or degrade with time in the presence of singlet oxygen upon irradiation with visible light [27]. Generally, in the presence of oxygen-containing solvents, $\pi$-conjugated molecules undergo photooxidation by attack of $^1$O$_2$ on the $\pi$-electron system. The photostabilities were deter-
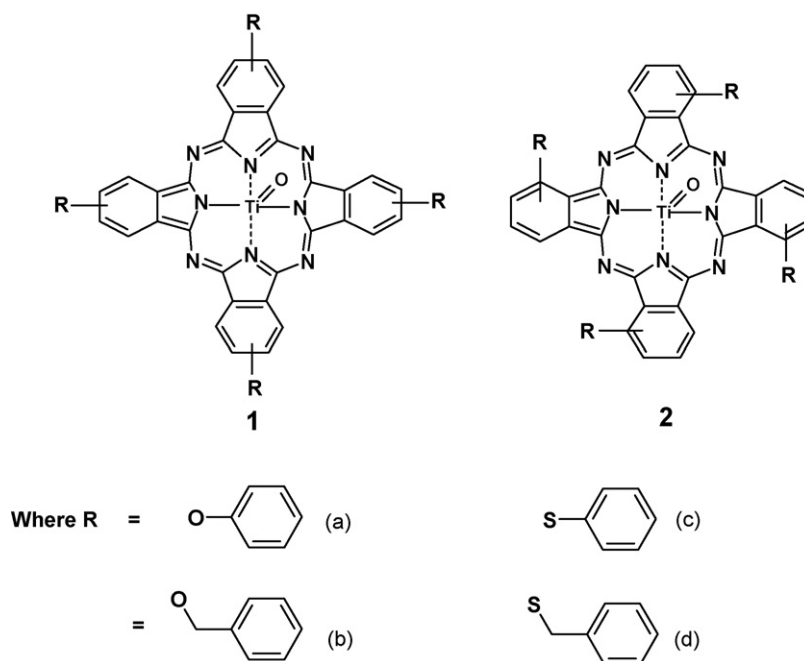


Fig. 1. Peripherally (**1a–d**) and non-peripherally (**2a–d**) substituted oxotitanium(IV) phthalocyanine complexes used in this study.

mined in DCM in order to determine the effect of the substituents on the stability of the complexes.

The photobleaching quantum yield ($\Phi_P$) values of the complexes were found to range from $2.2 \times 10^{-4}$ to $5.3 \times 10^{-4}$ with the arylthio-substituted complexes (**c** and **d**) slightly less stable than the corresponding aryloxy-substituted complexes (**a** and **b**). The electronic effects of the substituents could explain the slight variation in the $\Phi_P$ values, i.e. the arylthio groups are more electron-donating that their corresponding aryloxy groups and thus tend to enhance the probability of the photobleaching process [28]. Furthermore, the non-peripherally substituted complexes (**2a–d**) are slightly less stable than their peripherally substituted counterparts (**1a–d**) since the latter have a stabilising effect than the former.

The photobleaching rate constants ($k$) of the complexes were calculated from Eq. (13) (Table 1) where smaller values of $k$ correspond to a higher photostability. It is obvious that the aryloxy-substituted complexes exhibit a higher photostability compared to the corresponding arylthio-substituted complexes. The observed trend is as a result of the more electron-donating arylthio groups slightly reducing the stabilities of the complexes as discussed above. A relation between the photostabilities and singlet oxygen quantum yields could exist. For example, the arylthio-substituted complexes generate higher yields of singlet oxygen than the aryloxy-substituted complexes, thus the probability of photobleaching is higher in the former than in the latter, since photobleaching is initiated by singlet oxygen. The dependence of the photocatalytic oxidation of 1-hexene on the complex photostabilities is discussed below.

### 3.3. Photocatalytic oxidation of 1-hexene

The photocatalytic activities of the various OTiPc complexes for the oxidation of 1-hexene in the presence of oxygen were investigated. The transformation of 1-hexene was found to yield 1,2-epoxyhexane as a major product, identified by GC (Fig. 2) and GC–MS. In addition, the allylic oxidation product, i.e. 1-hexen-3-ol was obtained as a minor product. The resultant 1-hexene conversions and 1,2-epoxyhexane selectivities are summarised in Table 2, typically after 8 h. The arylthio-substituted complexes enhance the catalytic activities
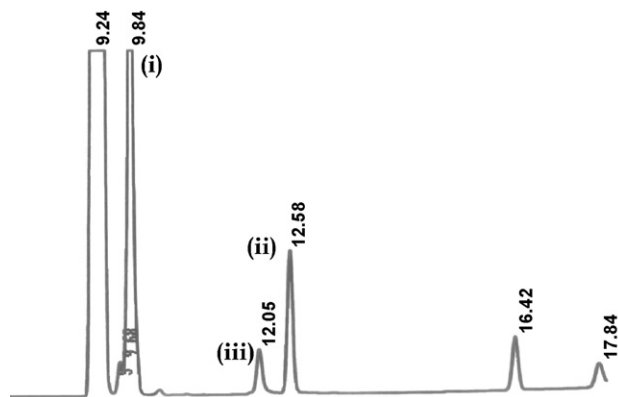
Fig. 2. The GC trace showing the photocatalytic transformation of (i) 1-hexene to (ii) 1,2-epoxyhexane and (iii) 1-hexen-3-ol.

Table 2
Photocatalytic oxidation of 1-hexene by oxotitanium(IV) phthalocyanines in DCM

| Compound | % conversion[a] | % selectivity for 1,2-epoxyhexane[b] |
|---|---|---|
| **1a** | 17.56 | 87.1 |
| **1b** | 15.91 | 80.5 |
| **1c** | 18.02 | 90.8 |
| **1d** | 16.11 | 82.2 |
| **2a** | 12.97 | 76.4 |
| **2b** | 11.92 | 73.7 |
| **2c** | 13.66 | 78.0 |
| **2d** | 12.36 | 75.5 |

[a] $\% \text{ conversion} = \frac{(1-\text{hexene}_{\text{initial}})-(1-\text{hexene}_{\text{remaining}})}{(1-\text{hexene}_{\text{initial}})} \times 100$.

[b] $\% \text{ selectivity} = \text{epoxide}_{\text{obtained}}/[(1-\text{hexene}_{\text{initial}})-(1-\text{hexene}_{\text{final}})]$.

compared to the corresponding aryloxy-substituted derivatives. Also, the peripherally substituted derivatives exhibited excellent catalytic activities compared to their corresponding non-peripherally substituted counterparts. A correlation between the observed photocatalytic trends and singlet oxygen quantum yields exists (Table 1 and Table 2), whereby complexes **1** (peripherally substituted) show larger $\Phi_\Delta$ values than complexes **2** (non-peripherally substituted). Furthermore, the phenoxy- and phenylthio substituted complexes **1a** and **1c** show the highest conversions, Fig. 3(i) and (ii), respectively, as well as epoxide selectivities (Table 2). Whilst benzyloxy and benzylthio substituted complexes **2b** and **2d** show the lowest activities
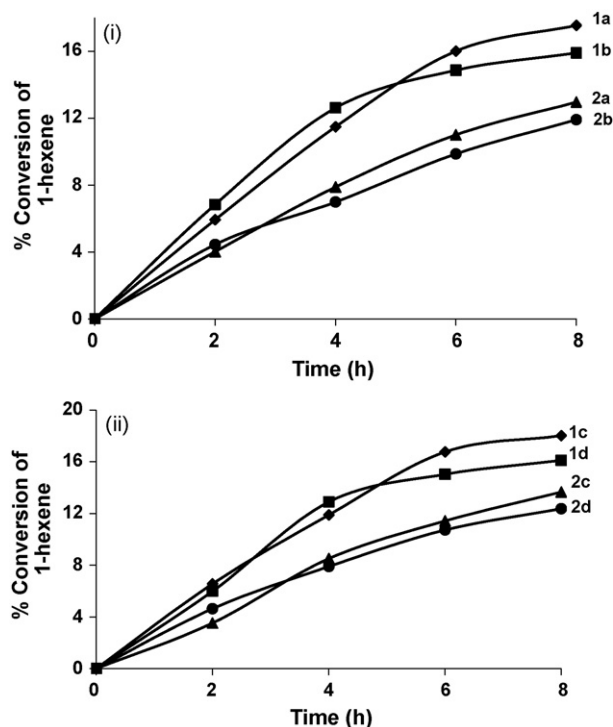
Fig. 3. (i) % conversion plots of 1-hexene over time for the photocatalytic oxidation of (0.5 mmol) 1-hexene in the presence of (1 μmol) aryloxy substituted oxotitanium phthalocyanines (**1a**, **1b**, **2a**, **2b**) in DCM. (ii) % conversion plots of 1-hexene over time for the photocatalytic oxidation of (0.5 mmol) 1-hexene in the presence of (1 μmol) arylthio substituted oxotitanium phthalocyanines (**1c**, **1d**, **2c**, **2d**) in DCM.
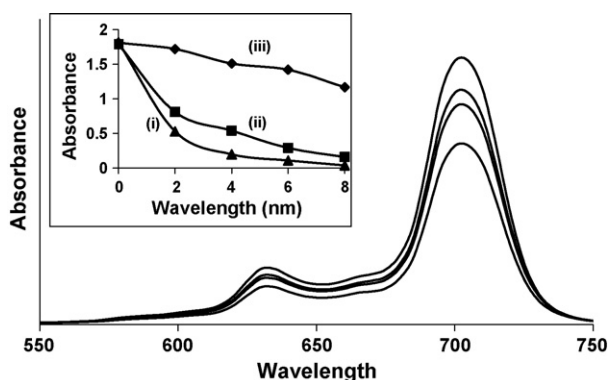
Fig. 4. UV/vis spectral changes of **1b** observed during photocatalytic transformation of 1-hexene (0.5 mmol). Inset: changes in absorbance observed with variation of light intensities: (i) $6.5 \times 10^{16}$, (ii) $5.2 \times 10^{16}$ and (iii) $4.0 \times 10^{16}$ photons $s^{-1}$ cm$^{-2}$ during the photocatalysis of 1-hexene.

and epoxide selectivities (Table 2). No oxidation product was observed in the absence of catalyst thus confirming the need to utilise OTiPcs as photocatalysts. The fate of the OTiPc complexes during the photocatalysis of 1-hexene was monitored by UV/vis spectroscopy. The rate of photostability was found to be dependent on the light intensity as shown in Fig. 4. As mentioned in the experimental section, the optimum intensity of light used was $4.0 \times 10^{16}$ photons $s^{-1}$ cm$^{-2}$, which was high enough to effectuate the photocatalysis and low enough to avoid photodegradation of the catalyst. Overall, all the complexes exhibited excellent photocatalytic activities.

A point to consider is the relationship between the photocatalytic activities and the catalyst photostability. A plot of 1-hexene conversion versus catalyst photobleaching rate constant is shown in Fig. 5. The peripherally substituted complexes **1a–d** show higher activities than the corresponding non-peripherally substituted complexes **2a–d**, which show moderate activities. However, complexes **1c** and **1d** are relatively unstable, while complexes **1a** and **1b** are more stable. It is obvious from the plot that the phenoxy and benzyloxy substituted complexes **1a** and **1b** are better catalysts as they combine good photocatalytic activity, singlet oxygen and photostability.
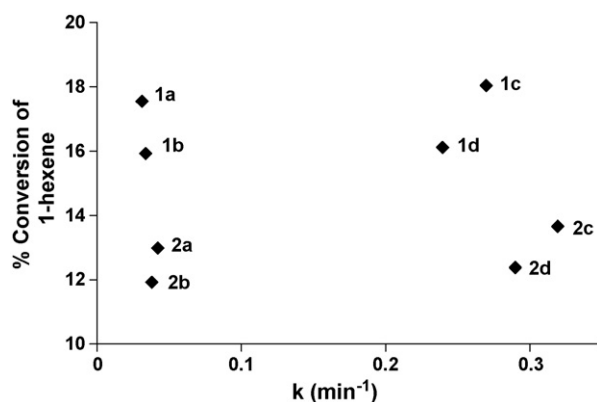


Fig. 5. % conversion of the photocatalytic oxidation of 1-hexene in relation to the photobleaching rate constants (*k*) of oxotitanium(IV) phthalocyanines in DCM.
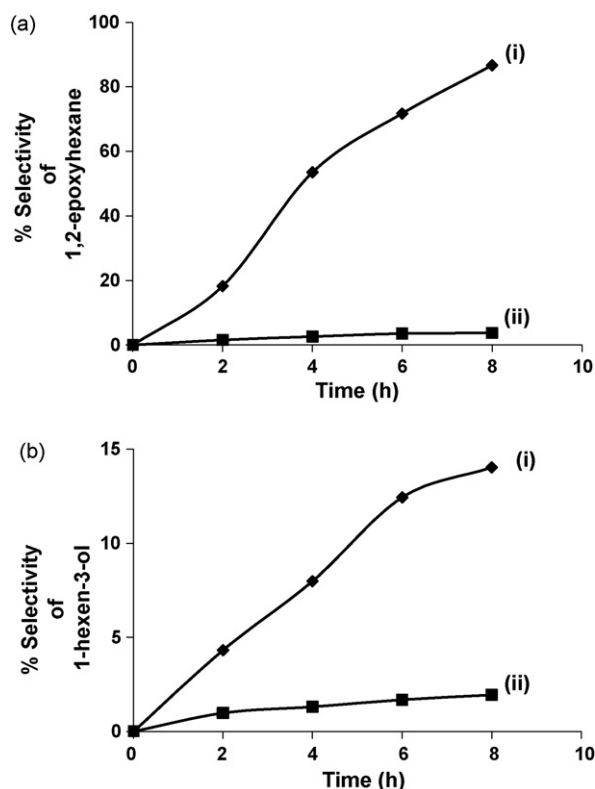


Fig. 6. (a) % selectivity plots of 1,2-epoxyhexane in (i) absence and (ii) presence of DABCO over time during the photocatalysis of 1-hexene by 1a (1 μmol) in DCM. (b) % selectivity plots of 1-hexen-3-ol in (i) absence and (ii) presence of BHT over time during the photocatalysis of 1-hexene by 1a (1 μmol) in DCM.

It is important to note that the formation of the epoxide and the allylic product suggest that there are two possible types of active species, one of which is responsible for the production of the 1,2-epoxyhexane and the other for 1-hexen-3-ol [29]. Thus to determine the mechanisms involved in the production of the oxidation products, photocatalytic reactions were undertaken in the presence of DABCO (singlet oxygen quencher) and a radical quencher, 2,6-di-*tert*-butyl-4-methylphenol (BHT), Fig. 6. Addition of DABCO led to a pronounced decrease of 1,2-epoxyhexane formation, Fig. 6a, while the amount of allylic alcohol was not affected. This observation thus suggests that singlet oxygen is the sole active species in the production of the epoxide. Addition of BHT however deactivated the active species responsible for the formation of the allylic alcohol, thus suggesting that radicals in solution are the active species, Fig. 6b. The formation of the epoxide in the presence of BHT was not affected. The presence of the radicals may also be facilitated by the solvent, DCM, as chlorinated solvents are known to form radicals during photolysis [28]. Thus both Type II (singlet oxygen) and Type I (radicals) mechanisms are involved in the photocatalytic oxidation of 1-hexene mediated by the OTiPc complexes, with the former favouring the formation of epoxide and the latter the allylic alcohol. Type II mechanism however seems to be the dominant process as the selectivity of 1,2-epoxyhexane was over 70%, Table 2 and Fig. 6.

In light of this, epoxidation and allylic oxidation are two competing processes that typically take place due to attack at the
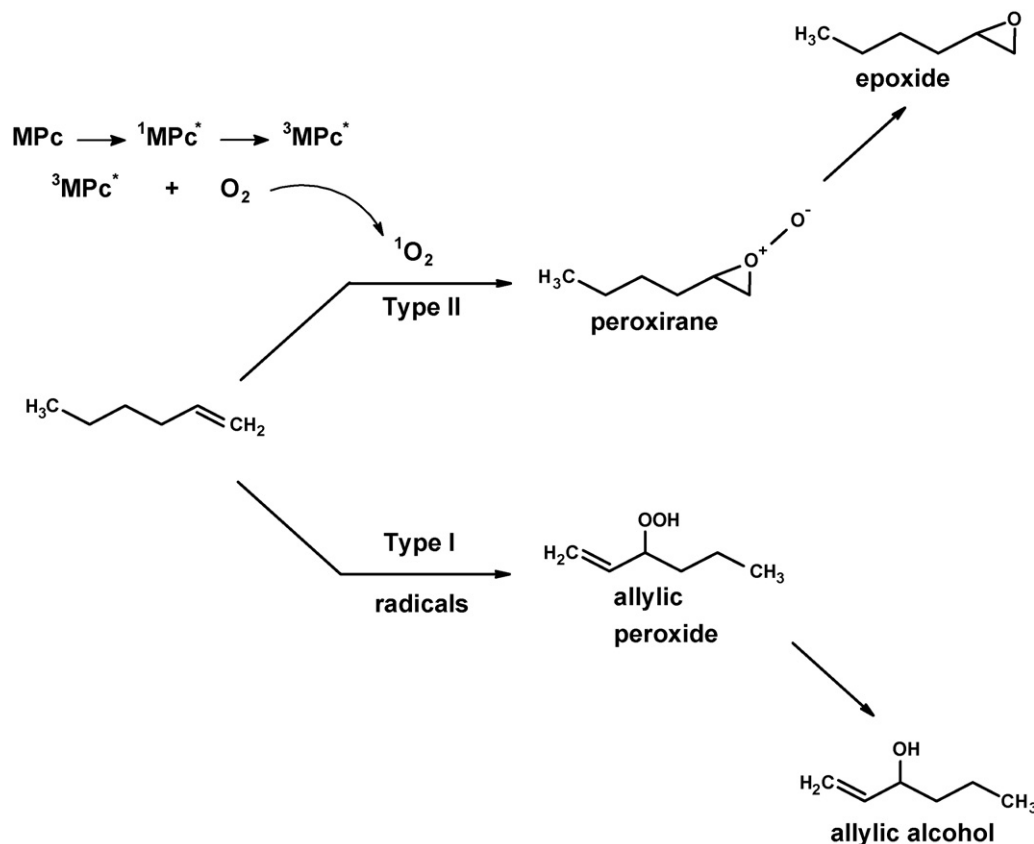
Scheme 1. Proposed mechanism for the formation of the photooxidation products.

1-hexene double bond in the former and hydrogen abstraction in the latter. These processes often occur simultaneously [30]. Although the role of the metal complex as well as the mechanistic route is not clear, the mechanism shown in Scheme 1 is proposed. Following irradiation, the fate of 1-hexene is determined by either Type I or Type II mechanisms. As earlier mentioned the former implies that radicals are the oxidising agents, which form the hydroperoxide intermediate by hydrogen abstraction/hydroxylation, thus yielding the allylic alcohol, i.e. 1-hexen-3-ol as a minor product. Singlet oxygen in the Type II mechanism is the oxidising agent, which probably forms the diradical intermediate, i.e. peroxirane. The abstraction of the terminal oxygen results in the epoxide, i.e. 1,2-epoxyhexane, as the major product. The epoxidation selectivity over hydroxylation might be due to the fact that the former tend to dominate with oxometallic complexes [30].

## 4. Conclusion

Aryloxy and arylthio tetrasubstituted complexes catalyse the photooxidation of 1-hexene by two competing Types I and II mechanisms. The photooxidation products were found to be 1-hexen-3-ol as minor product as well as 1,2-epoxyhexane as the major product with good selectivities (73.7–90.8). The reaction products are dependent on the nature and position of the substituents with the peripherally substituted complexes being better catalysts than the corresponding non-peripherally substi-

tuted counterparts. The generation of singlet oxygen quantum yield was also found to be directly related to the photostability of a complex. Overall the phenoxy substituted complex **1a** was found to be the best catalyst in terms of singlet oxygen quantum yield, photostability and activity. We have demonstrated the use of molecular oxygen as being attractive in these photocatalytic processes for economic reasons.

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