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

Vongani Chauke, Tebello Nyokong*

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

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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.

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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 (^{1}MPc*) and through intersystem crossing (ISC), they move to the triplet state (^{3}MPc*) where energy is transferred from the energy rich phthalocyanine to molecular oxygen (^{3}O$_2$) in its triplet state to yield singlet oxygen (^{1}O$_2$), 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.
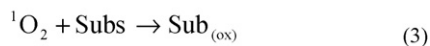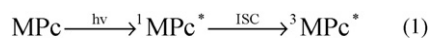
This work reports on the photocatalytic oxidation of 1-hexene using GaPc (**1a–1c**) and InPc (**2a–2c**) derivatives (Fig. 1). Ga and In are large metals hence they are expected to enhance intersystem crossing resulting in high triplet yields and hence high singlet oxygen quantum yields. This should result in increased activity towards the oxidation of 1-hexene by Type II mechanism.
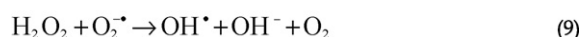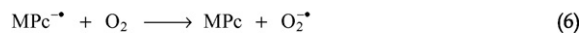
2. Experimental

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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* Corresponding author. Fax: +27 46 622 5109.
E-mail address: T.nyokong@ru.ac.za (T. Nyokong).

$$MPc \xrightarrow{h\nu} {}^1MPc^* \xrightarrow{ISC} {}^3MPc^* \qquad (1)$$

$${}^3MPc^* + {}^3O_2 \rightarrow MPc + {}^1O_2 \qquad (2)$$

$${}^1O_2 + Subs \rightarrow Sub_{(ox)} \qquad (3)$$

Scheme 1. Type II mechanism. ISC = intersystem crossing; subs = substrate (e.g. 1-hexene).

$${}^3MPc^* + O_2 \longrightarrow MPc^{+\bullet} + O_2^{-\bullet} \qquad (4)$$

$${}^3MPc^* + Subs \longrightarrow MPc^{-\bullet} + Subs^{+\bullet} \qquad (5)$$

$$MPc^{-\bullet} + O_2 \longrightarrow MPc + O_2^{-\bullet} \qquad (6)$$

$$O_2^{-\bullet} + H_2O \rightarrow OH^- + HO_2^{\bullet} \qquad (7)$$

$$HO_2^{\bullet} + HO_2^{\bullet} \rightarrow O_2H_2 + O_2 \qquad (8)$$

$$H_2O_2 + O_2^{-\bullet} \rightarrow OH^{\bullet} + OH^- + O_2 \qquad (9)$$
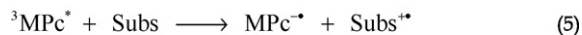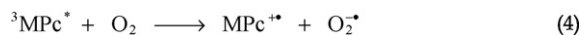
Scheme 2. Type I mechanism. Subs = substrate such as 1-hexene.

matography (HPLC) grade. Products were analyzed using a Hewlett-Packard HP 5890 gas chromatograph (GC), fitted with a flame ionization detector (FID), 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 Funnigan GC–MS using the column used above.

2.2. Photochemical studies

Photolysis was carried out using home-made photochemical set up as described before [10,11] and briefly explained as follows: The reaction mixture containing the MPc and the 1-hexene was irradi-ated 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 was placed in the light pathway before the reaction vessel. The light intensity was measured with a power meter (POWER MAX5100 with incorporated Molelectron detector) and the measured intensity was 4.52×10^{16} photons s^{-1} cm^{-2}.

2.2.1. Singlet oxygen quantum yield (Φ_Δ)

Singlet oxygen quantum yields (Φ_Δ) of GaPc and InPc complexes were determined in DCM, using DPBF as a singlet oxygen quencher. The DPBF quantum yields were (Φ_{DPBF}) were calculated using Eq. (10) [13]:

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

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

$$I_{abs} = \frac{\alpha S I}{N_A} \qquad (11)$$

where α is the fraction of light absorbed, S is the irradiated cell area, I is the intensity of light and N_A is the Avogadro constant. Singlet oxygen quantum yields were calculated using Eq. (12) [13]:

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

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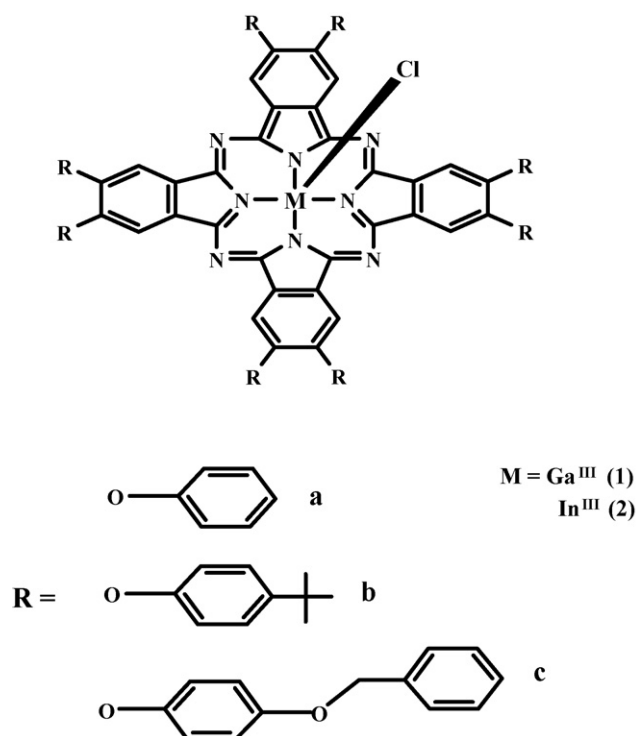

Fig. 1. Structures of Ga and In phthalocyanines.

2.2.2. Photochemical stability

The photostability of GaPc and InPc complexes were determined by monitoring the decrease in the intensity of the Q band. Photodegradation quantum yields were determined using Eq. (10), where change in DPBF concentration was replaced by the change in concentrations of phthalocyanines under investigation. The photobleaching rate constants, k, were determined using Eq. (13). These are a measure of phthalocyanine stability.

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

where ε_0 and ε_t are the extinction coefficients at times $t = 0$ and t, respectively.

2.2.3. Photocatalytic reactions

The photocatalytic oxidation reactions were conducted in a glass vial. The reaction mixture in the glass vial consisted of a phthalocyanine complex in DCM (concentration range $5.6–4.9 \times 10^{-6}$ mol dm^{-3}) and 1-hexene. The reaction mixture was saturated with oxygen before irradiation. The oxidation products were identified using gas chromatographs of the standards. Verification of the oxidation products was achieved by GC–MS. The total reaction time was 6 h.

3. Results and discussion

3.1. Singlet oxygen quantum yield (Φ_Δ) and photostability

The spin allowed triplet–singlet energy transfer from an excited MPc to triplet oxygen affords singlet oxygen. Singlet oxygen plays an important role in photocatalytic oxidation reactions [13–17]. Singlet oxygen quantum yield (Φ_Δ) values (Table 1) were determined using DPBF as the singlet oxygen quencher in DCM. The singlet oxygen quantum yields (Φ_Δ) for GaPc derivatives (**1a–1c**) were lower when compared to the corresponding InPc derivatives (**2a–2c**). This is attributed to the fact than In is larger than Ga and the former therefore encourages intersystem crossing thus resulting in higher Φ_Δ values. The Φ_Δ values were highest for phenoxy derivatives and lowest for the *tert*-butyl derivatives for both InPc and GaPc derivatives and the trend was as follows: phenoxy > benzyloxyphenoxy > *tert*-butylphenoxy. Thus, the *tert*-butyl derivatives gave the lowest singlet oxygen quantum yield values.

3.2. Photobleaching quantum yields (Φ_p)

Photobleaching is a process where a phthalocyanine is degraded under light irradiation. Photobleaching will affect the photocatalytic abilities of the MPc derivatives, hence the need to study it. The process of photobleaching is driven by oxidative attack in the triplet state of an MPc by singlet oxygen [18,19], giving phthalimide as the photodegradation product [19]. The photobleaching stabilities were determined in DCM by monitoring the decrease in the intensity of the Q band under irradiation with increasing time, as shown in Fig. 2. Several factors can influence Φ_p, such as the nature of the solvent and the substitutents on the phthalocyanine ring.
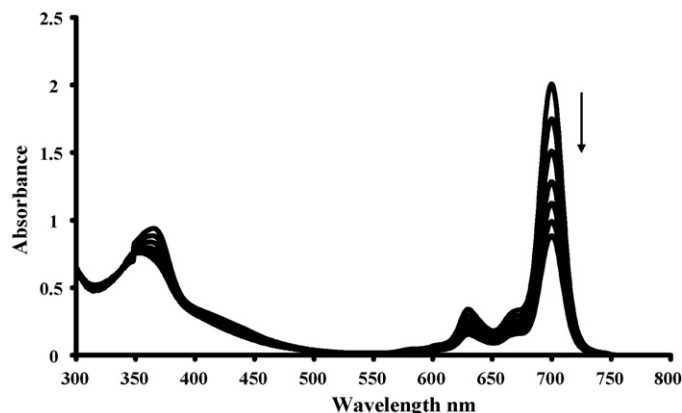

Fig. 2. Photobleaching spectrum of complex **2a**. Concentrations = 1.04×10^{-5}.

The photobleaching quantum yields (Φ_p) for the GaPc and InPc derivatives are listed in Table 1. The Φ_p values fell within the acceptable stability range for phthalocyanines of ~10^{-5}, thus the InPc and GaPc derivatives showed relatively good stability. Photobleaching quantum yields for GaPc derivates were much smaller (in the 10^{-6} range) than those for InPc (**2a–2c**) derivatives, indicating that they are more stable than InPc derivatives. This could be due to the high singlet oxygen quantum yields for the InPc derivatives since photobleaching is initiated by singlet oxygen attack. Photobleaching rate constants (k), also listed in Table 1, matched up photobleaching quantum yields in that the smaller k constants were obtained for smaller photobleaching quantum yields.

3.3. Photocatalytic oxidation of 1-hexene

As mentioned before, singlet oxygen is responsible for the process of photooxidation. The products from the photooxidation of 1-hexene have been reported to be 1,2-epoxyhexane and 1-hexen-3-ol [7] and these products were obtained in this work as evidenced by the spiking with standards and by using GC–MS. Fig. 3 shows a GC chromatogram of complex **1a** after 6 h of irradiation. Mass spectral peaks were observed at $m/z = 99$ amu (M-1) for 1,2-epoxyhexane and $m/z = 97$ amu (M-3); 83 amu (M-OH) for 1-hexen-3-ol.

Fig. 4 shows the %conversion of 1-hexene for GaPc and InPc derivatives. For GaPc derivatives, within the first 4 h of photocatalysis, complex **1c** gave the highest %conversion, while **1a** was the lowest throughout. Of the GaPc derivatives **1a** had the highest singlet oxygen quantum yield and was the most stable in terms of photobleaching quantum yields (Table 1), hence **1a** would have
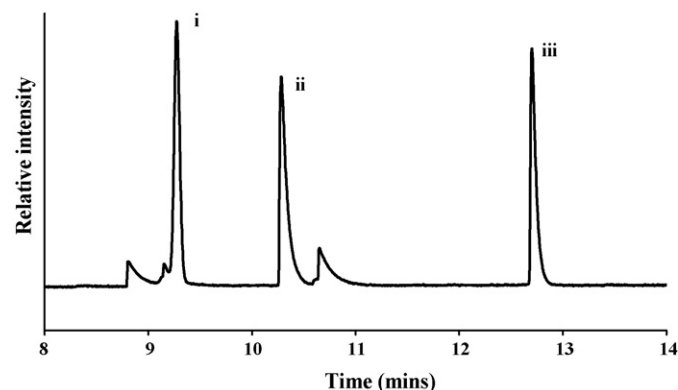
Table 1
Singlet oxygen and photobleaching quantum yields and rate constants in DCM

Compound	Φ_{DPBF}	Φ_Δ (± 0.05)	Φ_p (± 0.1)/10^5	k (min^{-1})
1a	0.32	0.63	0.14	1.62×10^{-2}
1b	0.25	0.52	0.93	4.42×10^{-2}
1c	0.36	0.56	0.31	5.58×10^{-2}
2a	0.53	0.84	9.08	2.03×10^{-0}
2b	0.39	0.62	4.12	4.19×10^{-1}
2c	0.43	0.66	1.64	2.41×10^{-1}

Fig. 3. GC chromatogram of the photocatalytic reaction by complex **1a** after 6 h of irradiation, for 1-hexen-3-ol (i), 1-hexene (ii) and 1,2-epoxyhexane (iii).
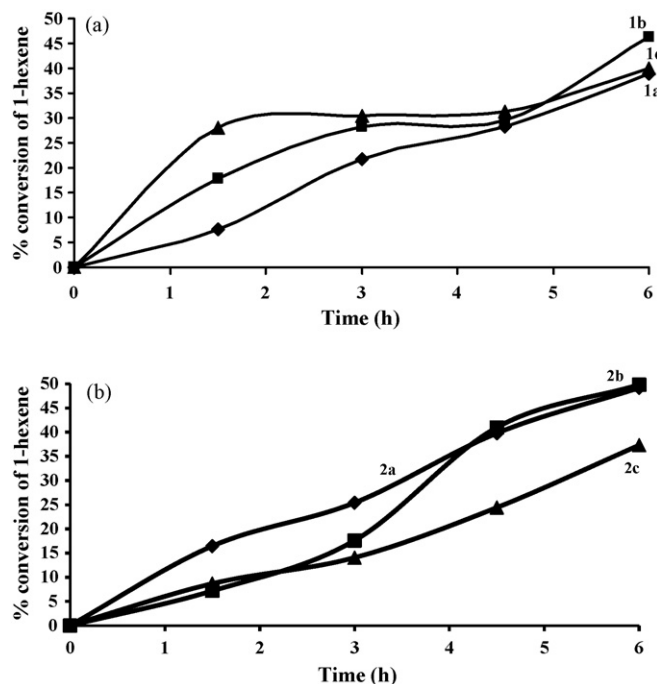
Fig. 4. %Conversion plots of 1-hexene by GaPc (a) and InPc (b) derivatives in DCM.

Table 2
Photocatalytic oxidation of 1-hexene by GaPc and InPc derivatives in DCM

MPc	%Conversion[a]	%Selectivity of 1,2-epoxyhexane[b]
1a	38.7	37.6
1b	46.3	42.8
1c	39.9	22.3
2a	49.2	60.9
2b	49.8	65.6
2c	37.3	68.0

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

[b] $\%\text{Selectivity} = \frac{\text{epoxide}_{obtained}}{1\text{-hexene}_{initial} - 1\text{-hexene}_{final}}$. Where the amounts of 1-hexene and the epoxide were determined from GC peak areas (errors = ±10% for both %selectivity and %conversion).

Fig. 6. %Selectivity plots of 1,2-epoxyhexane in DCM using GaPc derivatives.

been expected to give the highest %conversion if the singlet oxygen mechanism was in the only one operating. Fig. 5a shows that **1a** remained stable throughout the photocatalysis experiment. There was insignificant decrease in the Q band. Aggregation is another factor which may affect the photocatalytic activity of the MPc complexes, however these complexes are known not to form aggregates at concentrations less than 1×10^{-5} M [10,11]. The concentrations employed in the photocatalysis experiments were in the 1×10^{-6} to 1×10^{-5} mol dm^{-3} range hence aggregation is not expected.

For the InPc derivatives, **2a** and **2b** gave the best %conversion, while **2c** was the lowest (Table 2). This is the reverse of what was

obtained for GaPc derivatives, for the corresponding complexes, hence shows that the nature of the substituent is not influential in determining the %conversion. **2a** was also the least stable in terms of photobleaching quantum yields in Table 1, but had the highest
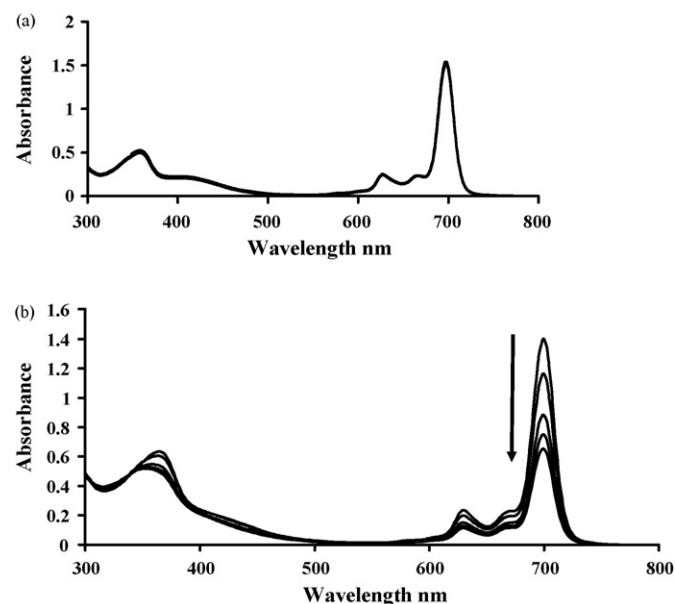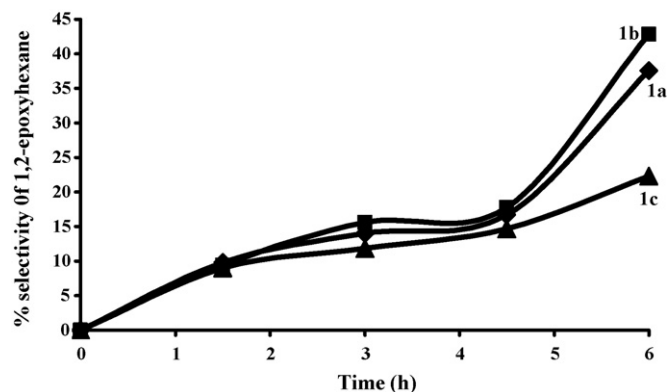

Fig. 5. Electronic absorption spectra showing the degradation of complex **1a** (a) and **2a** (b) and during the photocatalytic oxidation reaction. Concentration = 5.6×10^{-5} mol dm^{-3}.
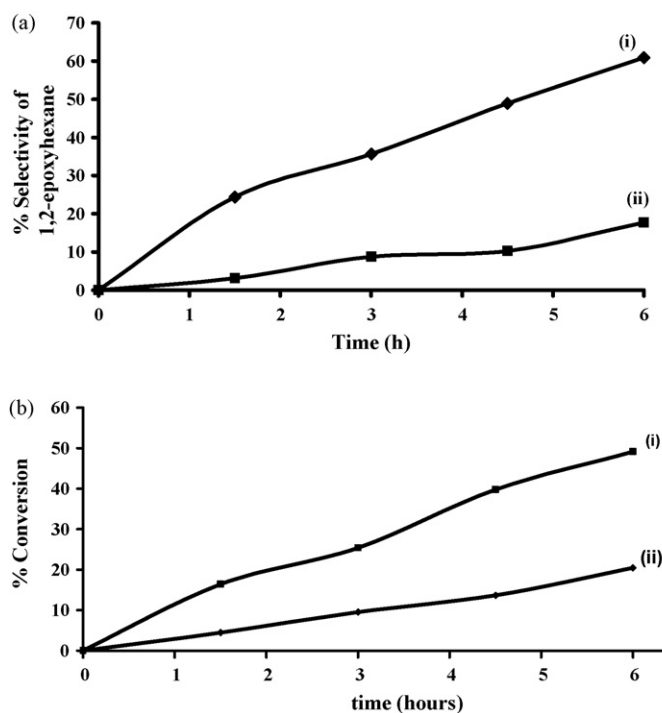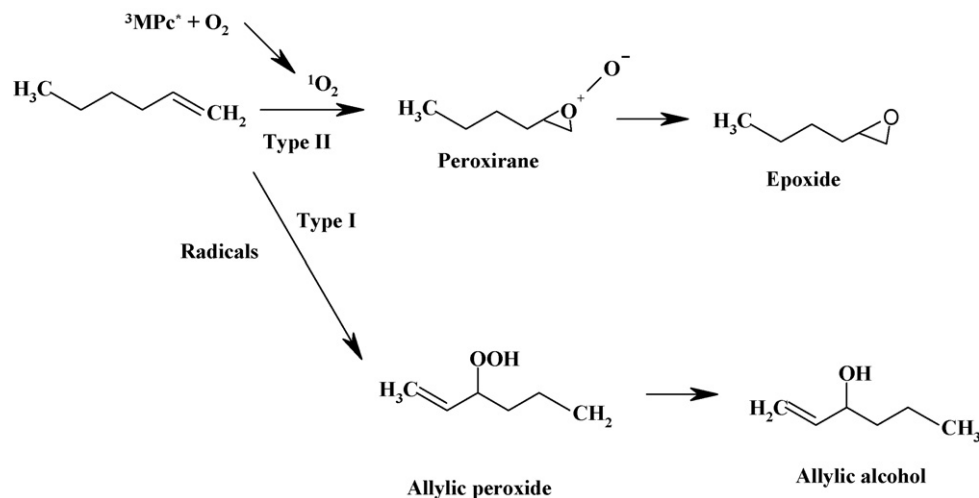

Fig. 7. %Selectivity for 1,2-epoxyhexane (a) and %conversion of 1-hexene (b) plots in the absence (i) and presence (ii) of DABCO in DCM, by complex **2a**.

Scheme 3. Proposed mechanism for the formation of the photooxidation products.

singlet oxygen quantum yield. Fig. 5b shows that **2a** decomposed appreciably during the photocatalysis experiment. Thus, the photocatalytic ability of the complexes towards the transformation of 1-hexene is a balance between singlet oxygen quantum yield and stability. There is no clear trend between the Φ_Δ values for the complexes and %conversion, suggesting that it is not only singlet oxygen mechanism in operation during catalysis. However, complex **2a** with the highest Φ_Δ value, gave a high %conversion. The %conversion values obtained in the work are much higher than reported for TiPc complexes [7]. The %yields of 1,2-epoxyhexane were less than 2% for all MPc derivatives. This is similar to the observation for the photocatalysed transformation oh cyclohexene using ZnPc [6].

Fig. 6 shows plots of %selectivity for 1,2-epoxyhexane versus time. Higher %selectivity values were achieved for InPc derivatives, they range from 60.9 to 68.0%. Fig. 6 shows the %selectivity increases with time for GaPc derivatives. The same was observed for InPc derivatives.

As mentioned before both Types I and II mechanisms may be involved in the photocatalytic oxidation reactions. In order to confirm if both mechanisms are involved, a singlet oxygen quencher, DABCO, was added to solutions containing the MPc derivative and 1-hexene, then the solution photolysed. There was a significant decrease in both %conversion of 1-hexene and %selectivity for 1,2-epoxyhexane Fig. 7a and b. The fact that there was a decrease in both %conversion of 1-hexene and %selectivity for 1,2-epoxyhexane, shows that singlet oxygen is involved in the photocatalysis mechanism. However, since there was still some activity in the presence of DABCO and the activity did not decrease any further than shown in Fig. 7 with increase in the concentration of DABCO, shows that it is not only singlet oxygen (Type II) which is involved in the photocatalysis mechanism and suggest the involvement of Type I mechanism.

The possible mechanism taking into account both Types I and II mechanisms is shown by Scheme 3. The two processes that could be taking place are epoxidation and allylic oxidation. These take place due to the attack at the 1-hexene double bond for epoxidation and hydrogen abstraction in the allylic oxidation process. These processes may occur at the same time (Scheme 3 [7,20]).

4. Conclusion

Singlet oxygen quantum yields were determined and InPc derivatives had better Φ_Δ values relative to GaPc derivatives. The %conversion of 1-hexene was highest for InPc derivatives, which had the largest singlet oxygen quantum yield, suggesting Type II mechanism. However, addition of singlet oxygen quencher showed that Type I mechanism may also be involved. The products of the photooxidation are 1,2-epoxyhexane and 1-hexen-3-ol.

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