

Zinc phthalocyanine photocatalyzed oxidation of cyclohexene

Nthapo Sehlotho, Tebbello Nyokong*

Department of Chemistry, Rhodes University, P.O. Box 94, Grahamstown 6140, South Africa

Received 30 March 2004; received in revised form 10 May 2004; accepted 10 May 2004

Available online 17 June 2004

Abstract

Cyclohexene photooxidation catalyzed by zinc phthalocyanine (ZnPc) using either red or white light results in the formation of cyclohexenone, cyclohexenol, *trans*-cyclohexanediol, cyclohexene oxide and cyclohexene hydroperoxide. The product yield increased as follows: cyclohexenone > cyclohexenol > *trans*-cyclohexanediol > cyclohexene oxide > cyclohexene hydroperoxide. The mechanism for the formation of these products involves both singlet oxygen and radicals (Type II and Type I mechanisms, respectively). The catalyst degraded slowly when low light intensities were employed. The product yields were found to depend on the light intensity, the nature of solvent, irradiation time and the rate of photodegradation of the catalyst.

© 2004 Elsevier B.V. All rights reserved.

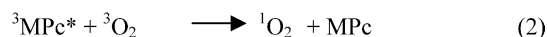
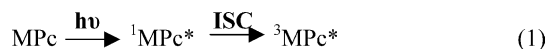
Keywords: Cyclohexene; Zinc phthalocyanine; Photocatalysis; Cyclohexene oxide; Cyclohexenol; Cyclohexenone; Cyclohexanediol; Cyclohexene hydroperoxide

1. Introduction

Alkanes and alkenes are produced in thousands of tones 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]. 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 to achieve desired properties. Enzyme-like catalysis by iron perchlorophthalocyanine for cyclohexane oxidation using hydrogen peroxide, *tert*-butylhydroperoxide and *m*-chloroperoxybenzoic acid as oxidants has been reported [3]. The same molecule has been used in comparison with the unsubstituted iron and cobalt phthalocyanine for the oxidation of cyclohexene using *tert*-butylhydroperoxide and *m*-chloroperoxybenzoic acid as oxidants [4]. In this work, we report on photo-initiated catalysis of oxidation of cyclohexene by zinc phthalocyanine (ZnPc).

Porphyrin complexes have been employed as photocatalysts for oxygen mediated oxidation of cyclohexane [5,6] yielding cyclohexanone and cyclohexanol. These complexes have been used in photocatalyzed oxidation of cyclohexene using water as an oxygen donor [7]. Photoexcited porphyrins generate singlet oxygen which then reacts with substrates, in this case cyclohexene to form products such as cyclohexene hydroperoxide, cyclohex-2-en-1-ol, *trans*-1,2-cyclohexanediol and cyclohexene oxide [8].

It is known that when MPc complexes containing metal ions, such as Zn or Al are irradiated with red light, they get excited to the singlet state ($^1\text{MPc}^*$) which then undergoes intersystem crossing to the triplet state ($^3\text{MPc}^*$). This triplet state then interacts with ground (triplet) state molecular oxygen ($^3\text{O}_2$) generating excited singlet oxygen ($^1\text{O}_2$), which subsequently oxidizes the substrate by Type II mechanism according to Scheme 1 [9];

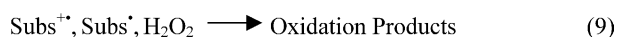
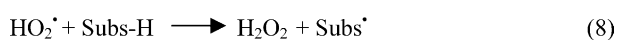
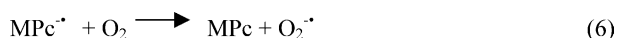
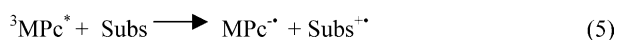
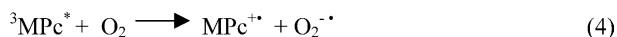


Scheme 1. Type II mechanism.

* Corresponding author. Tel.: +27 46 603 8260; fax: +27 46 622 5109.
E-mail address: t.nyokong@ru.ac.za (T. Nyokong).

where MPc is the metallophthalocyanine, ISC the intersystem crossing and subs the substrate (cyclohexene in this work).

The excited triplet state of the MPc can also produce radicals on interaction with the ground state molecular oxygen (Eq. (4)). The $^3\text{MPc}^*$ species can interact with the substrate molecule generating radical ions (Eq. (5)), which then further forms superoxide (Eq. (6)) and hydroperoxyl radicals (Eq. (7)). The latter subsequently afford oxidation of the substrate by Type I mechanism (Scheme 2) [10,11];



Scheme 2. Type I mechanism.

It has been reported that Type II mechanism is more prevalent [8] in photo-initiated oxidation reactions, thus the magnitude of singlet oxygen quantum yield (ϕ_Δ) which expresses the amount of singlet oxygen generated per quanta of light is often employed as a main criteria in choosing photosensitizers used in photocatalytic reactions. It is for this reason that ZnPc is used in this work, since it has been reported to have high ϕ_Δ in different organic solvents [12]. Triplet lifetime of the photosensitizer in a particular reaction medium should also be considered so as to maximize efficiency of the reaction.

Enzyme-like oxidation of cyclohexene catalyzed by MP and MPc catalysts has been reported [13,14] to give cyclohexene oxide as the main product, and traces of cyclohexenol and cyclohexenone. The formation of cyclohexanone as the main product of cyclohexene oxidation has been reported [4]. The use of MPc complexes as photocatalysts for the oxidation of cyclohexene has not been explored and we show in this work that when ZnPc is employed as a photocatalyst, a wider range of products is formed, which comprises of *trans*-1,2-cyclohexanediol and cyclohexene hydroperoxide in addition to those formed by biomimetic oxidation.

2. Experimental

2.1. Materials

ZnPc was synthesized, purified and characterized using literature methods [15]. Cyclohexene was purchased from Aldrich and distilled before use. Cyclohexene oxide, cyclohexen-2-ol, cyclohexen-2-one, *trans*-1,2-cyclohexanediol, stilbene, styrene, styrene oxide, stilbene oxide, phenylacetaldehyde, benzaldehyde, sulphuric acid,

potassium iodide, 2-propanol, glacial acetic acid, potassium thiosulphate, diazabicyclooctane (DABCO), diphenylbenzofuran (DPBF), were purchased from Aldrich and used as received. 1,4-dioxane, THF (tetrahydrofuran), DMF (dimethylformamide), dichloromethane and benzene were of gas chromatography (GC) or high pressure liquid chromatography (HPLC) grade.

2.2. Photocatalytic reactions

Reactions were conducted in a number of solvents, namely benzene, THF, 3:7 DMF-CH₂Cl₂ and 1,4-dioxane. However, catalytic reactions were studied mainly in the latter solvent. The reaction mixtures consisting of known amounts of the catalyst (ZnPc) and the substrate (cyclohexene) were prepared in 5 ml glass sample vials and their gas chromatograph (GC) traces recorded. This was followed by irradiation of the reaction mixtures with either red or white light, while stirring. Reactions were run at least in triplicates and with varying amounts of reagents used and irradiation periods. GC traces were recorded periodically during the course of the reaction. Similarly, UV-vis absorption spectra were recorded periodically but the solutions had to be diluted before recording the spectra. For monitoring the fate of the catalyst, experiments were conducted in a 1 cm path-length spectrophotometric cell fitted with a tight fitting stopper. Concentrations of the catalyst were determined using its molar extinction coefficient. This was determined spectrophotometrically and was found to be $1.8 \times 10^5 \text{ dm}^3 \text{ mol}^{-1} \text{ cm}^{-1}$ in 1,4-dioxane at 665 nm.

Irradiation in the visible region (the Q band region of ZnPc, Fig. 1) was carried out with a General Electric Quartz line lamp (300 W), with a 600 nm glass cut off filter (Schott) being used to filter off ultraviolet light. For irradiation using white light, the 600 nm glass filter was left out. The light intensity was measured with a power meter (POWER MAX5100-with incorporated Molelectron detector) and unless otherwise stated the white light intensity used was $5.2 \times 10^{16} \text{ photons s}^{-1} \text{ cm}^{-2}$. In order to determine the catalytic effect of ZnPc under white light, GC traces for the photolysis of cyclohexene in the absence of ZnPc were subtracted from those in the presence of the catalyst.

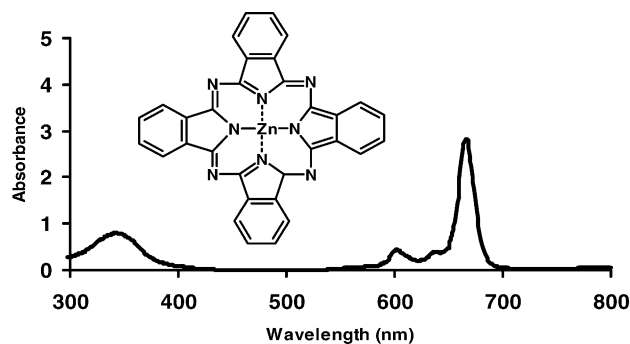


Fig. 1. UV-vis spectrum of ZnPc in 1,4-dioxane. Insert: molecular structure of ZnPc.

The oxidation products were identified by spiking using standards and by measurements of retention times in gas chromatography. Product yields were based on the substrate, cyclohexene. The nature of the products were further confirmed by mass to charge ratios of molecular ion peaks and fragmentation patterns as obtained from a gas chromatograph connected to a mass spectrometer (GC/MS). Cyclohexene hydroperoxide was identified using iodine liberation methods, followed by titration of iodine with sodium thio-sulfate or recording of the ultra violet spectra of iodine at 351 nm [16,17].

2.3. Physical measurements

The GC traces were recorded with a Hewlett-Packard HP 5890 Gas Chromatograph fitted with an FID detector, using a cross-linked methyl siloxane capillary column (30 m length, 0.32 mm internal diameter and 0.25 μm film thickness). The parameters for analysis were: carrier gas N_2 at 30.7 cm s^{-1} , injector temperature = 200°C , detector temperature = 250°C , oven temperature programmed from 40 to 45°C at 1°C min^{-1} and 45 to 250°C at $15^\circ\text{C min}^{-1}$. Mass spectra were recorded with Finnigan LCQ-MS coupled with J & W Scientific column of 30 m length, 0.32 mm internal diameter and 0.25 μm film thickness. UV-vis spectra were recorded with the Cary 1E UV-vis spectrophotometer. Absorbance measurements for detection of hydroperoxides iodometrically were done with a Pharmacia Biotech Novaspec II spectrophotometer. For determination of photo-bleaching quantum yields (ϕ_p), the usual equation (10) was employed:

$$\phi_p = \frac{(C_0 - C_t)VN_A}{I_{\text{abs}}St} \quad (10)$$

where C_0 and C_t in mol L^{-1} are the Pc concentrations before and after irradiation, respectively. V is the reaction volume, S the irradiated sample vial area, t the irradiation time, N_A the Avogadro's number and I_{abs} , the overlap integral of the radiation source intensity and the absorption of the Pc (the action spectrum) [18].

Triplet life times (τ_T) were recorded with a laser flash photolysis system. The excitation pulse was provided by a Nd-Yag laser, providing 400 mJ, 9 ns pulses of laser light at 10 Hz, pumping Lambda-Physik FL3002 dye laser. Single pulse energy was 7 mJ. A 300 W xenon arc lamp (Thermo Oriol) provided the analyzing light. The kinetic curves were averaged over 256 laser pulses using a Tektronix TDS 360 Digital Oscilloscope. The triplet life time values were determined by exponential fitting of the kinetic curves using the program ORIGIN. The solutions for triplet state life times were introduced into a 0.2 mm path length UV-vis spectrophotometric cell, deaerated using nitrogen and photolyzed at the Q band maxima.

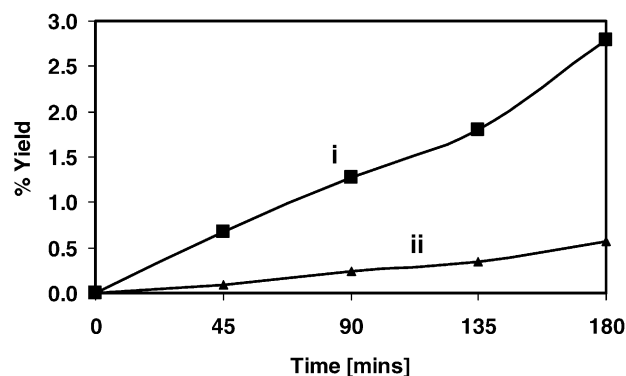


Fig. 2. Variation of cyclohexenone with time on photolysis with white (i) or red (ii) light and in the presence of ZnPc photocatalyst. Reaction time is 3 h with white and red ($\lambda > 600 \text{ nm}$) light irradiation. Starting concentrations in dioxane; cyclohexene = 0.9 mol/dm^{-3} , ZnPc catalyst = 0.004 mg/mL . Experiments were performed in air.

3. Results and discussion

3.1. Product formation

It was observed that cyclohexene gets oxidized in dioxane by white light in the absence of a catalyst to cyclohexene oxide, cyclohexenol and cyclohexenone. The increase in the products was insignificant after 45 min. When ZnPc was employed as a catalyst for oxidation of cyclohexene in dioxane in the presence of white or red light, the yields of cyclohexene oxide, cyclohexenol and cyclohexenone increased as shown in Fig. 2 (using cyclohexenone as an example). For the curves in Fig. 2, the oxidation of cyclohexene in the absence of the catalyst and for the same photolysis period were subtracted, so as to show only ZnPc catalyzed yields. In the presence of the catalyst, *trans*-cyclohexanediol and cyclohexene hydroperoxide were observed in addition to cyclohexene oxide, cyclohexenol and cyclohexenone, which are observed in the absence of the catalyst. Thus the presence of the catalyst results in the formation of a wider range of products. The products formed using ZnPc as a photocatalyst are similar to those formed during the photo-oxygenation of cyclohexene in the presence of titanium(IV) porphyrins except that *trans*-cyclohexanediol was not obtained using the latter catalyst [19]. As explained in the experimental section, the products (cyclohexene oxide, cyclohexenol, cyclohexenone and *trans*-cyclohexanediol) were identified by comparison of their GC retention times with those of standards. Further product confirmation was afforded by GC/MS which showed $M - 1$ peak at $m/z = 97$ for cyclohexene oxide and cyclohexenol, and M^+ at $m/z = 96$ and a major α cleavage fragment at $m/z = 68$ for cyclohexenone. Cyclohexene hydroperoxide was identified using the iodine liberation method described in Section 2. No peroxide was obtained on photolysis of solutions containing ZnPc in the absence of cyclohexene, confirming that the peroxide was not due to Type I mechanism (Scheme 2)

Table 1

Comparison of product yields in the various solvents at light intensity = 0.52×10^{17} photons $s^{-1} cm^{-2}$, unless stated otherwise*

Solvent	Product yields (%) ^a				
	Cyclohexenone	Cyclohexenol	<i>trans</i> -Cyclohexane diol	Cyclohexene hydroperoxide	Cyclohexene oxide
Dioxane					
$I = (10^{17} \text{ photons } s^{-1} cm^{-2})$					
(i) 0.52	4.4	1.0	0.30	1.1	0.08
(ii) 1.0*	4.6	1.2	0.37	1.8	0.04
(iii) 1.9*	5.1	1.6	0.27	1.4	0.02
THF	4.3	1.0	0.58	2.8	0.19
Benzene	1.8	0.4	0.11	0.4	0.03
DMF/CH ₂ Cl ₂	6.6	1.6	0	0.7	0.08

Reaction time is 3 h with white light irradiation. Starting concentrations are; cyclohexene = 0.9 mol/dm^3 and ZnPc catalyst = 0.2 mg/mL ^a Product yields based on the substrate, cyclohexene.

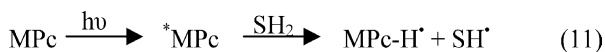
discussed above. Also lack of readily available hydrogen in dioxane may make the formation of hydrogen peroxide through Type I mechanism unfavorable in this solvent.

Only cyclohexene oxide, cyclohexenol and cyclohexenone have been obtained as products using phthalocyanines as enzyme-like catalysts in the presence of oxygen donors [4,13]. Thus photocatalysis results in a wider variety of products compared to the more commonly employed enzyme-like catalytic oxidation of alkenes. The products formed by white light irradiation of cyclohexene in the presence of ZnPc in dioxane were similar to those observed when red light was employed, except the product yields were higher for white light. Table 1 shows the yields obtained for white light in the presence of ZnPc catalyst and after 3 h irradiation. The yields for cyclohexene photooxidation are lower than those observed (after extended periods) during oxidation using MPc complexes and an oxidant [4]. It is however important to note that the yields will be highly dependent on the nature of the catalyst and on reaction time.

As mentioned above, the GC trace areas obtained from photolysis by white light in the absence of a catalyst were subtracted from those obtained in the presence of ZnPc, thus ensuring that the data reported is only for the ZnPc catalyzed photooxidations. Increased yields when white light is employed compared to red light could be a result of increased amount of radicals in solution due to occurrence of redox reactions that have been characterized as abstractions of hydrogen from appropriate hydrogen donors (SH₂) by photoexcited MPc complexes, leading to the formation of Pc radicals [20], Scheme 3.

Fig. 3 compares the yields formed with time for the various products. The highest yields were obtained for cyclohexenone. The following trend in product yield was obtained:

Cyclohexenone > cyclohexenol > *trans*-cyclohexanediol > cyclohexene oxide > cyclohexene hydroperoxide.



Scheme 3. Hydrogen abstraction and formation of MPc radicals.

The high yields of cyclohexenone compared to cyclohexenol could be due to the fact that the latter is known to phototransform to the former [21]. Thus, once cyclohexenol has been produced by photolysis, it will be transformed to cyclohexenone with time. This was investigated by photolysing cyclohexenol alone; indeed it was oxidized to cyclohexenone. It is thus possible that both cyclohexenone and cyclohexenol are generated from the parent cyclohexene, but in addition, cyclohexenol is converted to cyclohexenone as photolysis proceeds, hence the much higher yields of the latter relative to the former.

Furthermore, photooxidation of styrene in the presence of ZnPc and under the same conditions as given in Table 1 yielded benzaldehyde, styrene oxide and phenylacetaldehyde, while photooxidation of stilbene yielded benzaldehyde and stilbene oxide as identified using GC and standards. Thus the oxide seems to be the consistent product for oxidation of alkenes. However oxidation of cyclohexene did not give the aldehyde as one of the products.

It was observed that reactions continued in the dark following irradiation of solutions containing cyclohexene and ZnPc. It also was observed that product yields improved with increasing light intensity (Table 1) even though catalyst degradation was enhanced as will be discussed below. These two observations suggest that once reaction inter-

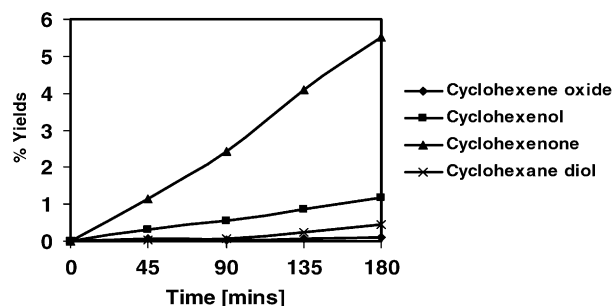
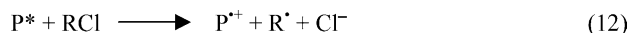


Fig. 3. Variation of product yield with time for 2-cyclohexenone, 2-cyclohexenol, *trans*-cyclohexanediol, and cyclohexene oxide. Starting concentrations in dioxane; cyclohexene = 0.9 mol/dm^3 , ZnPc catalyst = 0.3 mg/mL . White light irradiation conditions. Experiments were performed in air.

mediates are formed upon interaction of singlet oxygen or radicals with the substrate, the reaction can still proceed in the dark in the presence or absence of the original form of the catalyst. Cyclohexene did not form products in the dark in the absence of the catalyst.

3.2. Solvent effects

Studies using porphyrin catalysts [7,8,19,21] have shown that the nature and relative yields of products formed by catalytic photo-oxygenation of cyclohexene vary depending on the type of catalyst, oxidant, solvent, irradiation wavelength and irradiation period and light intensity. The products obtained in this work for the ZnPc photocatalyzed oxidation of cyclohexene in dioxane were similar to those obtained in THF and benzene, except lower yields were obtained for benzene when compared to THF and dioxane (Table 1). When the solvent mixture of DMF and CH₂Cl₂ (3:7) was employed for the photocatalytic reaction, the yields of cyclohexenol and cyclohexenone were generally higher than for THF, benzene and dioxane (Table 1). Chlorinated solvents are known to quench triplet states of porphyrins and phthalocyanines [22–24] according to Scheme 4, hindering generation of singlet oxygen. However photo-oxidation still occurred in the presence of dichloromethane, suggesting that it is not only singlet oxygen which is involved in the generation of products from cyclohexene, but that the radical mechanism is also important as will be discussed below.



Scheme 4. Quenching of excited states by chlorinated solvents.

where RCl is the chlorinated solvent, P stands for porphyrin or phthalocyanine.

As mentioned earlier, catalytic activity was lower in benzene compared to the other solvents. It would be expected that for the reaction to occur effectively, the solvent should be able to stabilize the formed intermediates, suggesting that benzene has lower stabilizing effects for the intermediates than the other solvents. Photostability of the MPc molecule is known to affect the catalytic activity. The less photostable the molecule, the less the catalytic activity. The study of the photostability of ZnPc in dioxane and THF showed ZnPc to be slightly more photostable in the former solvent (with $\phi_{PB} \sim 1 \times 10^{-6}$) than in the latter ($\phi_{PB} = 1.5 \times 10^{-6}$ [25]), probably accounting for comparable yields of the products, except for cyclohexene hydroperoxide. Triplet lifetime (τ_T) of the catalyst is another attributing factor since the longer it is, the larger the generation of singlet oxygen yield. The τ_T values were found to be almost equal in THF and dioxane, i.e. 240 μ s, hence explaining the almost similar product yields in some cases in these solvents.

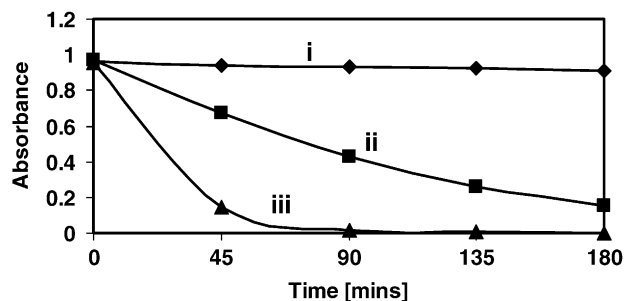


Fig. 4. Variation of absorbance of catalyst with time upon white light photolysis at various light intensities: (i) 0.52; (ii) 1.0; and (iii) 1.9×10^{17} photons $s^{-1} cm^{-2}$. Starting concentrations in dioxane; cyclohexene = 0.9 mol dm^{-3} and ZnPc catalyst = 0.003 mg/mL. Experiments were performed in air.

3.3. The fate of the ZnPc catalyst

The fate of the ZnPc catalyst during the photocatalysis of cyclohexene in dioxane was monitored by UV–vis spectroscopy. The ZnPc complex tended to decompose with photolysis as judged by the decrease in the intensities of both the Q and Soret bands, for both red and white light. However, the degradation was more pronounced with white light when compared with red light. Excitation of phthalocyanines in the visible region populates the triplet state resulting in generation of singlet oxygen, which subsequently attacks the Pc complexes, resulting in decomposition [6]. The rate of decomposition depended on light intensity as shown by Fig. 4. For low light intensity, the decomposition was minimal, and the data reported in this work was undertaken using light intensity of 5.2×10^{16} photons $s^{-1} cm^{-2}$ which was low enough to avoid photodegradation of the catalyst. The rate of photodegradation of ZnPc using red light was the same as when white light was employed at the above-mentioned light intensity. The kinetic curve for red light was similar to that for white light in Fig. 4, suggesting that it is the photoexcitation of the ZnPc complex in the visible region which results in photodegradation.

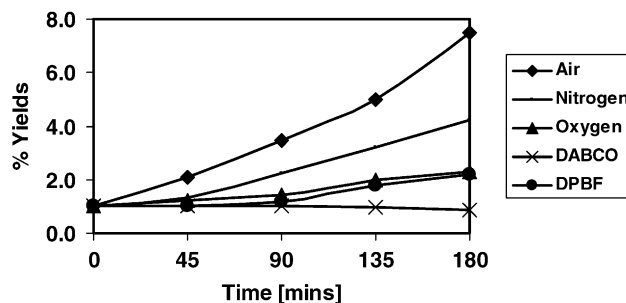
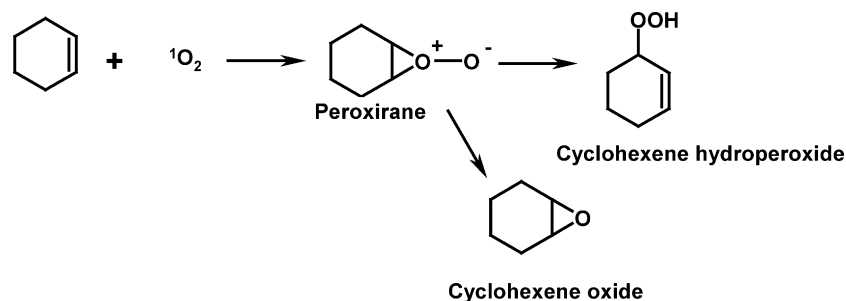


Fig. 5. Kinetic curves for product (cyclohexenone) formation from the ZnPc photocatalyzed oxidation of cyclohexene in dioxane in the presence of (♦) air, (—) Nitrogen, (▲) bubbled oxygen, (X) DABCO (0.01 g/mL) and (●) DPBF (0.03 g/mL). Concentrations; cyclohexene = 0.9 mol dm^{-3} , ZnPc catalyst = 0.4 mg/mL. White light irradiation conditions.



Scheme 5. Suggested mechanism for the formation of photolysis products.

3.4. Singlet oxygen versus radical mechanisms

In order to elucidate the mechanism (singlet oxygen Type II or radical Type I) for the ZnPc photocatalyzed oxidation of cyclohexene, experiments were performed in: (i) air; (ii) presence of bubbled oxygen; (iii) nitrogen; (iv) radical and singlet oxygen scavenger DABCO and (v) singlet oxygen scavenger, DPBF, Fig. 5. The experiments were performed in dioxane. For all the products, yields in the presence of DPBF (a singlet oxygen quencher) and DABCO (both a singlet oxygen and radical quencher), were much lower, more especially in the latter situation. This indicates that both singlet oxygen and radicals are needed for the photocatalytic reaction to proceed faster. Fig. 5 shows that the highest yields were obtained in air. When oxygen was bubbled to the solution, faster decomposition of the catalyst was observed than in air. As mentioned above, it is known [6] that singlet oxygen adds to the macrocyclic ring of porphyrins and phthalocyanines leading to cleavage and degradation. The low product yields obtained in the presence of DPBF, show that singlet oxygen generated from ground state oxygen by ZnPc catalyst is needed for the reactions, however, the lower yields obtained in the presence of bubbled oxygen show that photodegradation of the catalyst by the generated singlet oxygen becomes a limiting factor in the formation of the products. Thus, for the photocatalytic reactions discussed in this work, singlet oxygen should be in moderation so as not to cause oxidative degradation of the catalyst. When nitrogen was bubbled through the solution containing ZnPc and cyclohexene, the yields of the products decreased, again confirming that oxygen is needed for the reactions.

It has been reported that intermediates such as dioxetanes, zwitterions, biradicals, endo-peroxides and peroxiranes are formed upon interaction of singlet oxygen with ethylenes [26–30]. Using these types of intermediates, we propose in this work that cyclohexene hydroperoxide, *trans*-cyclohexanediol and cyclohexene oxide are formed as shown by Scheme 5.

Formation of cyclohexene hydroperoxide results from the 'ene' reaction, (proton abstraction and addition) while that of cyclohexene oxide results from loss of oxygen atom inductively. Protonation of dioxetane, which may form as an intermediate, could give *trans*-cyclohexanediol.

4. Conclusions

It has been shown that photooxidation of cyclohexene catalyzed by ZnPc leads to formation of cyclohexene oxide, cyclohex-2-enol, cyclohex-2-enone, *trans*-1,2-cyclohexanediol and cyclohexene hydroperoxide. Product yields are dependent on the nature of solvent, irradiation wavelength, light intensity, and irradiation period. Reaction mechanism involves both the singlet oxygen and radicals. The range of products formed was larger for the photocatalytic transformation of cyclohexene in the presence of ZnPc when compared to enzyme-like catalysis reported before. It could be concluded that the new products; cyclohexene hydroperoxide and *trans*-cyclohexanediol are formed via singlet oxygen mechanism while cyclohexene oxide, cyclohexenol and cyclohexenone are formed via radical mechanism, since the former group of products is observed only in the presence of photogenerated singlet oxygen. Thus the use of photocatalysis could assist the petroleum industry in achieving a wider variety of useful products.

Acknowledgements

This work was supported by Rhodes University and by the Foundation for Research. NS thanks the Lesotho Government for a graduate bursary.

References

- [1] T. Dumas, W. Bulani, Oxidation of Petrochemicals: Chemistry and Technology, Applied Science Publishers, London, 1974, p. 1.
- [2] R.J. Fessenden, J.S. Fessenden, Organic Chemistry, fifth ed., Brooks/Cole Publishing Company, 1993, p. 900.
- [3] N. Grootboom, T. Nyokong, J. Mol. Catal. A: Chem. 179 (2002) 113.
- [4] N. Sehlotho, T. Nyokong, J. Mol. Catal. A: Chem. 209 (2004) 51.
- [5] A. Maldotti, C. Bartocci, G. Varani, A. Molinari, P. Battini, D. Mansuy, Inorg. Chem. 35 (1996) 1126.
- [6] J.-W. Huang, W.-Z. Huang, W.-J. Mei, J. Liu, S.-G. Hu, L.-N. Ji, J. Mol. Catal. A: Chem. 156 (2000) 275.
- [7] T. Shiragami, K. Kubomura, D. Ishibashi, H. Inoue, J. Am. Chem. Soc. 118 (1996) 6311.
- [8] A. Maldotti, L. Andreotti, A. Molinari, S. Borisov, V. Vasil'ev, Chem. Eur. J. 7 (2001) 3564.

- [9] R. Bonnett, *Chem. Soc. Rev.* 24 (1995) 19.
- [10] R. Bonnett, Chemical aspects of photodynamic therapy, in: D. Phillips, P.O. Brein, S. Roberts (Eds.), *Advanced Chemistry Texts*, vol. 1, Gordon & Breach, Germany, 2000.
- [11] I. Rosenthal, E. Ben-Hur, *Int. J. Radiat. Biol.* 67 (1995) 85.
- [12] A. Ogunsipe, D. Maree, T. Nyokong, *J. Mol. Struct.* 650 (2003) 131.
- [13] K. Kasuga, K. Tsuboi, M. Handa, T. Sugimori, K. Sogabe, *Inorg. Chem. Commun.* 21 (1999) 507.
- [14] M.H. Lim, S.W. Jin, G. Jhon, W. Nam, C. Kim, *Bull. Korean Chem. Soc.* 22 (2001) 93.
- [15] H. Tomoda, S. Saito, S. Shiraishi, *Chem. Lett.* (1983) 313.
- [16] R.D. Mair, A.J. Graupner, *Anal. Chem.* 36 (1964) 194.
- [17] J. Premkumar, R. Ramaraj, *J. Mol. Catal. A: Chem.* 142 (1999) 153.
- [18] I. Seotsanyana-Mokhosi, N. Kuznetsova, T. Nyokong, *J. Photochem. Photobiol. A: Chem.* 140 (2001) 215.
- [19] P.E. Esser, B. Drießen-Hölscher, W. Keim, *J. Mol. Catal. A: Chem.* 140 (1999) 13.
- [20] G. Ferraudi, in: C.C. Leznoff, A.B.P. Lever (Eds.), *Phthalocyanines, Properties and Applications*, vol. 1, VCH Publishers, 1989 (Chapter 4).
- [21] S. Takagi, T. Okamoto, T. Shiragami, H. Inoue, *J. Am. Chem. Soc.* 116 (1994) 7373.
- [22] I.V. Renge, V.A. Kuz'min, A.F. Mironov, Y.E. Borisevich, *Doklady Akademii Nauk SSSR* 263 (1982) 143.
- [23] Z. Gasyana, W.R. Browett, M.J. Stillman, *Inorg. Chim. Acta* 92 (1984) 37.
- [24] K. Kasuga, H. Morimoto, M. Ando, *Inorg. Chem.* 25 (1986) 2478.
- [25] A. Ogunsipe, D. Maree, T. Nyokong, *J. Mol. Struct.* 689 (2004) 89.
- [26] P.D. Bartlett, A.P. Schaap, *J. Am. Chem. Soc.* 92 (1970) 3223.
- [27] C.S. Foote, J.W. Peters, *J. Am. Chem. Soc.* 93 (1971) 3795.
- [28] P.R. Ogilby, C.S. Foote, *J. Am. Chem. Soc.* 103 (1981) 1220.
- [29] B.M. Monroe, *J. Phys. Chem.* 82 (1978) 15.
- [30] L.E. Manning, C.S. Foote, *J. Am. Chem. Soc.* 105 (1983) 4710.