

Efficient photocatalytic oxygenation of alkenes by water soluble sensitizer in organic–water biphasic media

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ABSTRACT: A new green, environmentally and economically photooxygenation of olefins by molecular oxygen in the presence of 4-carboxyl tetra phenyl porphyrin (H₂TCPP), Rose Bengal (RB), Methylene Blue (MB) and some metallosensitizers (MS) such as cobalt phthalocyaninesulfonate (Coph(SO₃H)₄), MnTCPPCl, FeTCPPCl and SbTPP(OH)₂ as water–soluble sensitizers in organic–water biphasic media at room temperature under visible light was illustrated. The products were obtained with 100% conversion by H₂TCPP and 100% selectivity by Coph(SO₃H)₄. Also in this study, singlet oxygen production as the major route for oxidation of olefins was proved.

KEYWORDS: olefine photooxygenation, singlet oxygen, water-soluble porphyrins, biphasic media, green chemistry.

INTRODUCTION

Oxygenated compounds are useful synthetic intermediate in the laboratory and in industries [1-6]. Many reactions have been studied for conversion of alkanes to corresponding oxygenated products [7]. The popular conventional method to achieve carboxylic acids is Jones reagent [8] and epoxidation of alkenes is carried out by peracids and alkyl peroxides [9]. Although, all these methods have one or some of disadvantages such as the requirement of strong acidic or basic conditions, stoichiometric or super stoichiometric amounts of costly or hazardous oxidizing agents, heavy-metal toxicity and high-temperature [10]. At the century of industrialization, global warming and environmental pollution, using renewable energy, in the chemical industry to environmentally friendly approach is important. For achieving this magnificent goal, solar energy which is abundant, clean and safe can be used. However, molecular oxygen using as cheap and economical regent for oxidation or epoxidation in photooxygenation reaction without no by-product (or its by-product is H_2O which is green and sustainable) is also interesting [11]. However spin rule forbids reaction of air/O₂ with hydrocarbon. For this purpose, photochemical reactions applied use porphyrins and MSs as regent require efficient energy to convert air/³O₂ to singlet oxygen/¹O₂, as an active regent [12]. The key issues for using air/O₂ as an oxidizing regent are applying porphyrins and light that cause oxygen to change to active species for oxidation [13].

Porphyrins and MSs complexes have received great attention, due in part to their direct relevance to many biological systems. The photosensitized production of singlet oxygen has significance in the areas of the photooxidation of organic compounds, DNA damage, and photodynamic therapy [13, 14]. Therefore a variety of photosensitizers have been developed and their photochemical and photo-physical properties have been extensively studied [15]. There are two main factors which dictate the photo-activity of porphyrin sensitizers: (i) quantum yields of the excited triplet states and its singlet oxygen generation from ground state ${}^{3}O_{2}$ and (ii) stability toward oxidative degradation (photobleaching) [16]. In our previous studies, we introduced efficient systems for the aerobic oxidation of alcohols, aldehydes and alkenes under visible light or sunlight [11, 14c, 17].

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Scheme 1. Photooxidation of different olefins in the presence of H_2TCPP in organic–water media

The current study develops the photocatalytic oxygenation of alkenes by using air under visible light irradiation with water soluble photosensitizers in organic–water biphasic media at room temperature (Schemes 1 and 2).

EXPERIMENTAL

Cyclohexene, cyclooctene, α -methyl styrene, cisstilbene, manganese(II) chloride (MnCl₂·4H₂O), iron(II) chloride and solvents were purchased from Fluka and Merck and used without further purification. RB and MB purchased from Fluka. 4-carboxyl tetra phenyl porphyrin (H₂TCPP), FeTCPPCl and MnTCPPCl, Coph(SO₃H)₄ and SbTPP(OH)₂ were synthesized according to the literature [18]. For photooxygenation of olefins, 2 cc water-soluble photosensitizer (1 \times 10⁻³ M) H₂TCPP, MnTCPPCl, FeTCPPCl, Coph(SO₃H)₄, RB, MB, SbTPP(OH)₂ and 4.9×10^{-3} mol cyclohexene, 3.83×10^{-3} mol cyclooctene, 2.8×10^{-3} mol *cis*-stilbene, 3.8×10^{-3} mol α -methylstyrene) were added to 10 cc acetonitrile and 5 cc water (2 acetonitrile:1 water) in a test tube. Reactions were irradiated with the sun simulator light (288 power LED lamps, 1 W, 2.3 V (59660 LUX)) for 64 h at room temperature under 1 atm of bubbling of air in the solution. The stability of sensitizers was monitored by UV-vis (Shimadzu 2100 spectrophotometer) during the reaction by following soret intensity of porphyrin and MS. At the end of the reaction, products were analyzed by



Scheme 2. Structure of different water soluble photosensitizers in photooxygenation of alkenes in acetonitrile-water media

Thermo Quest Finnigan AQA GC-MS. For investigation of mechanism of photooxygenation of alkenes, 4.9×10^{-3} mol cyclohexene was added to 2.5×10^{-3} mol 30% H₂O₂ by using UV light from a high pressure 500 W mercury lamp ($\lambda = 200-280$ nm) in 2 acetonitrile: 1 water for generation of OH[•] [19]. Also 0.44 gr of KO₂ dissolved in dried DMSO and added to 4.9×10^{-3} mol cyclohexene for generation of O₂⁻ [20].

RESULTS AND DISCUSSION

Photooxygenation of cyclohexene was investigated as a typical standard sample to evaluate the different factors involved in the reactions (Table 1). It is important to note that the oxidation of substrate stopped in the absence of porphyrin (Table 1 entry 5) or when the irradiation was interrupted (Table 1 entry 6). Therefore, the presence of a porphyrin, light and O_2 are essential for the conversion alkenes to corresponding products (Table 1 entry 1).

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Throughout the photolysis, this was also studied in modified solvent mixtures with variable water to acetonitrile ratios, and high conversion was observed in 2 acetonitrile:1 water media (Table 2).

High turnover number (TON) of the photooxygenation of alkenes to corresponding products was observed with H_2TCPP in the presence of visible light (Table 3 entry 1). It is clear that this reaction proceed under solar radiation because the spectral distribution curve of a fluorescent lamp is similar to that of sunlight (Table 3 entry 2).

Figure 1 shows the reaction of cyclohexene vs. time in an oxygenated solution of CH₃CN: H₂O under visible light irradiation in the presence of H₂TCPP. The Soret band of

Entry	Condition	Conversion, %
1ª	Cyclohexene + light + air + $H_{2}TCPP$	100
2	Cyclohexene + light + air + DMSO + H_2TCPP	22.89
3	Cyclohexene + light + air + NaN_3 + H_2TCPP	22.59
4	Cyclohexene + light + H_2TCPP	8.32
5	Cyclohexene + light + air	Trace
6	Cyclohexene + air + H_2TCPP	Trace
7 ^b	Cyclohexene+ OH•	0
8°	Cyclohexene + O_2^{\bullet}	0
9^{d}	Cyclohexene + H_2O_2	0

Table 1. Photooxygenation of cyclohexene in different reaction conditions

^a 2×10^{-6} mol H₂TCPP, 4.9×10^{-3} mol cyclohexene, air (1 atm) and 288 power LED lamps, 1 W, 2.3 V (59660 LUX) in 2 acetonitrile: 1 water biphasic media. ^bOH[•] produced from photolysis of 2.5×10^{-3} mol 30% H₂O₂ with using light from a high pressure 500 W mercury lamp in 2 acetonitrile: 1 water biphasic media ($\lambda = 200-$ 280 nm) [19]. ^cO₂[•] was prepared by dissolving K₂O in dried DMSO [20]. ^d 4 mmol 30% H₂O₂ dissolved in the reaction solution for generation of hydrogen peroxide.

Table 2. Solvent mixtures with variable water to acetonitrile for cyclohexene photooxygenation^a

Entry	Solvent ratio (H ₂ O:CH ₃ CN)	Selectivity, %	Selectivity, %	Selectivity, %	Conversion, %
1 ^b	1:2	44.83	41.75	13.40	100
2°	2:1	100	—		17.18
3 ^d	1:1	90.59	9.41	—	7.87

 $^a2\times10^{-6}$ mol H₂TCPP, 4.9×10^{-3} mol cyclohexene, air (1 atm) and 288 power LED lamps, 1 W, 2.3 V (59660 LUX). b 10 mL CH₃CN and 5 mL H₂O. c5 mL CH₃CN and 10 H₂O. $^d7.5$ mL CH₃CN and 7.5 mL H₂O.

Entry	Photosensitizers	Selectivity, %	Selectivity, %	Selectivity, %	Conversion, %	TON ^b	TOF ^c
		\diamondsuit	ОН	o			
1	H ₂ TCPP	44.83	41.75	13.40	100	2450	38.28
2^d	H ₂ TCPP	Trace	77.09	10.80	88.72	2250	35.15
3	$Coph(So_3H)_4$	100	_	_	85.46	2050	32.03
4	Rose Bengal	74.61	25.38	_	73.5	1800	28.12
5	Methylene Blue	100	_	_	63.83	1500	23.43
6	SbTPP(OH) ₂	100	_	_	48.32	1250	19.53
7	MnTCPPCL	100	_	_	5.79	140	2.18
8	FeTCPPCL	Trace	_	_	Trace	Trace	Trace

 Table 3. Effect of photosensitizer on the cyclohexene photooxygenation^a

^a2 cc sensitizer 1×10^{-3} M, 4.9×10^{-3} mol cyclohexene, air (1 atm) and 288 power LED lamps, 1 W, 2.3 V (59660 LUX) in 2 acetonitrile:1 water media). ^bTurn over number of the catalyst. ^cTurn over frequency of catalyst (h⁻¹). ^d sunlight (91000LUX).



Fig. 1. (a) Time vs. conversion percent of cyclohexene, degradation percent and absorption of H_2TCPP in cyclohexene photooxygenation. (b) UV-vis spectra of H_2TCPP degradation

the H_2 TCPP was followed at 414 nm with UV-vis method. This method showed that sensitizer bleaching for H_2 TCPP was complete after 64 h in our reaction conditions. After the disappearance of the porphyrin Soret band, the formation of the oxidation products stopped.

According to the literature, there are two major pathways for photooxygenation reaction in the presence of non-metal sensitizers, Type I and Type II (Scheme 3) [21]. For investigation of the type I mechanism, we performed our reactions in the presence H_2O_2 , OH[•] and O_2^{\bullet} . In the presence of these reactive oxygen species, the rates of reaction significantly decreased (Table 1 entry 7–9).

Singlet oxygen generation (Type II) and its reaction with the substrates is the foremost mechanism that occurs in our circumstances, since conversions of cyclohexene obey the order of $H_2TCPP > MnTCPPCI>FeTCPPCI$.



Scheme 3. The mechanisms for producing reactive oxygen species in the presence of non-metallosensitizers

Paramagnetic metals are claimed to quench singlet oxygen by energy transfer mechanism from oxygen to the low-lying d electron levels and have very short

Entry	Substrate	Selectivity, %	Conversion, %	Time, h	TON	TOF
1	$4.9 \times 10^{-3} \text{ mol}$	 ♦ 44.84 ♦ ♦	100	64	450	8.28
2	3.83×10^{-3} mol	<u>A</u> 13.40				
	\bigcirc	0.8	98.33	192	626.66	3.26
		, ,				
		90.10				
3	2.8×10^{-3} mol	сно				
	$\bigcirc \bigcirc \bigcirc$	100	44.32	304	310	11.02
4	$3.8 \times 10^{-3} \text{ mol}$	9.92				
		64.14	73.58	304	675	22.22
		сон 25.91				

	DI (· 11	•	•	1. 9
Table 4	Photooxvge	nation of	alkenes	1n OI	rganic_adiia	media ^e
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 $^{a}2 \times 10^{-6}$ mol H₂TCPP and 0.5 cc substrate, air (1 atm) and 288 power LED lamps, 1 W, 2.3 V (59660 LUX).

triplet lifetimes (Table 3, entry 7, 8) [22]. In addition, in the presence of N_3^- , which is a well-known singlet oxygen scavenger [23] (Table 1, entry 3) conversion was inhibited. In the presence of NaN_3^- degradation of the porphyrin sensitizers was also inhibited. Table 1 entry 2 indicates that in the presence of DMSO conversion of cyclohexene considerably diminished. According to the literature for the m-THPC (5,10,15,20-tetra (m-hydroxyphenyl)chlorin) sensitizer, the singlet oxygen lifetime in DMSO is 19 µs compared to 65 µs in acetonitrile [24]. It is interesting Coph(SO₃H)₄ was the best sensitizer for selectivity in organic–aqua media (Table 3, entry 3). To check the generality of this method, the oxidation of photocatalytic oxidation of cyclooctene, *cis*-stilbene and α -methyl styrene with H₂TCPP were accomplished (Table 4).

Olefins bearing aromatic substituents are also not as much reactive because their allylic forms are to smaller extent stable [25]. Based on the variation in the oxidation products, production of singlet oxygen in our reaction condition and the literature the proposed mechanism of ${}^{1}O_{2}$ reactions with substrates are shown in Scheme 4 [26]. Also the proposed mechanism for the Coph(SO₃H)₄ sensitizer is presented in Scheme 5 [16c].



Scheme 4. Photooxygenation mechanism of alkenes by molecular oxygen in the presence of none-metallated photosensitizers under visible light in acetonitrile: water biphasic media



Scheme 5. Proposed mechanism for photooxygenation of cyclohexene with $Coph(SO_3H)_4$ in organic–aqua biphasic media

CONCLUSION

In the present study, we applied an organic–aqua media for photooxygenation of alkenes with reasonable and good conversion, in the presence of water soluble sensitizer by type **II** mechanism for generation of singlet oxygen. H₂TCPP as none metal photosensitizer was the finest photo catalyst for conversion of cyclohexene to oxygenated products. Also Coph(SO₃H)₄ was the optimal catalyst for conversion of cyclohexene to cyclohexene t

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