

# Photosensitized transformation of 4-chlorophenol in the presence of aggregated and non-aggregated metallophthalocyanines

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## Abstract

The photosensitizing properties of various water-soluble zinc and aluminum phthalocyanines towards the phototransformation of 4-chlorophenol (4-Cp) are presented. The complexes studied are the zinc (ZnPcS<sub>4</sub>) and aluminum (AlPcS<sub>4</sub>) tetra-sulfophthalocyanines; the zinc and aluminum complexes containing a mixture of differently substituted sulfophthalocyanines (represented as zinc (ZnPcS<sub>mix</sub>) and aluminum (AlPcS<sub>mix</sub>), respectively); the zinc (ZnOCPC) and aluminum (AlOCPC) octacarboxy phthalocyanines. The AlPcS<sub>mix</sub> and ZnPcS<sub>mix</sub> complexes showed the best photocatalytic activity towards the transformation of 4-Cp. The values of singlet oxygen quantum yields of the sensitizers were obtained, and it was found that the rates of 4-Cp photooxidation, in general, follow the efficiency of singlet oxygen photosensitization by the phthalocyanine complexes. At 4-Cp concentration below 10<sup>-4</sup> mol l<sup>-1</sup>, photooxidation by singlet oxygen is the dominating mechanism of substrate photodegradation, while at 4-Cp concentration above 10<sup>-3</sup> mol l<sup>-1</sup> the role of Type I mechanism increases. Kinetic analysis indicates that interaction of 4-Cp with singlet oxygen mainly results in “physical” quenching with (k<sub>q</sub> + k<sub>r</sub>) = (13.5 ± 3) × 10<sup>8</sup> mol<sup>-1</sup> s<sup>-1</sup> and k<sub>r</sub> = (2.7 ± 0.3) × 10<sup>8</sup> mol<sup>-1</sup> s<sup>-1</sup> for the phenolate form of 4-Cp, which significantly limits the rates and quantum yields of 4-Cp photooxidation. © 2001 Published by Elsevier Science B.V.

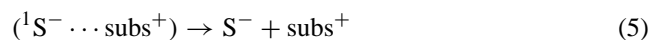
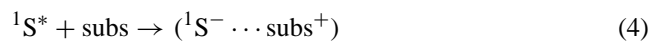
**Keywords:** Aluminum; Zinc; Phthalocyanine; Chlorophenol; Photosensitization; Singlet oxygen

## 1. Introduction

Chlorinated phenols are listed among top priority pollutants [1,2]. The degradation of chlorinated phenols occurs via chemical, photochemical and biological processes [3–8]. Direct irradiation of some chlorinated phenols in water often results in complexes that are more toxic than the starting compounds [9]. It has been demonstrated before [10–12] that the use of photocatalysts results in less harmful photodegradation products. Transformations of chlorophenols using semi-conductive photocatalysts such as TiO<sub>2</sub> have been studied by several researchers [3,13,14]. The use of polyoxometalates and zinc oxide for the photodegradation of chlorophenols has also been reported [1,2].

Photooxidation of substrates by singlet oxygen in the presence of light activated photosensitizer is a growing area of research. The photosensitizer (S) in its triplet state reacts with ground (triplet) state oxygen, <sup>3</sup>O<sub>2</sub>, generating the singlet excited state of oxygen (<sup>1</sup>O<sub>2</sub>) followed by oxidation of

the substrate by Type II mechanism, Eqs. (1)–(3). For phenol and substituted phenols, it has been shown that in addition to Type II mechanism the direct quenching of the <sup>1</sup>S\* by the substrate occurs according to Eqs. (4)–(6) [15]



or



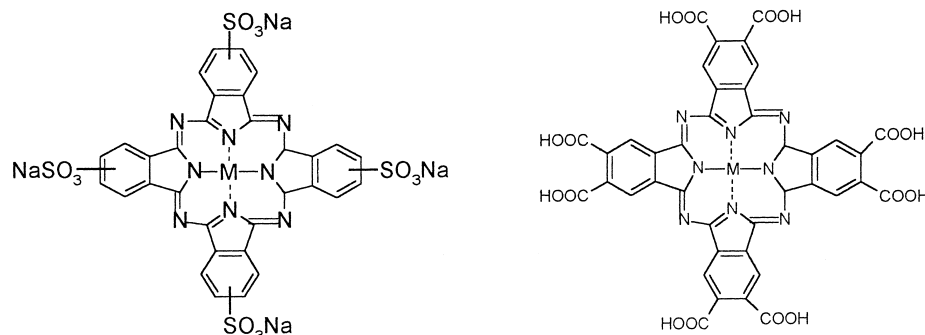
where isc is the intersystem crossing and subs the substrate. The substrate in this case is 4-chlorophenol (4-Cp).

Metallophthalocyanines (MPc) containing non-transition metals have proved to be very good photosensitizers for Type II processes. Aluminum and zinc phthalocyanines have in particular received considerable attention [10,15–21], because they exhibit high triplet life times and give high quantum yields for singlet oxygen formation.

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Photochemical transformation of chlorophenols in the presence of oxygen using MPc complexes as photosensitizers has been reported [10,15]. The photosensitizing effectiveness of MPc complexes is substantially reduced by aggregation of these complexes [16,20]. The excited triplet state is quenched in aggregated MPc complexes and the quantum yield for singlet oxygen production is decreased significantly. The photosensitizers that are commonly used for the generation of singlet oxygen are the zinc ( $\text{ZnPcS}_n$ ) or aluminum ( $\text{AlPcS}_n$ ) sulfophthalocyanines. These complexes are water-soluble since they are negatively charged. Positively charged detergents are normally added to solutions of the photosensitizer in order to form monomeric species [10]. There is a need to synthesize water-soluble phthalocyanine complexes which are monomeric in aqueous solution without the addition of detergents. Studies have shown that the degree of aggregation of the  $\text{AlPcS}_n$  species depends on the synthetic method and on the degree of sulfonation [22]. Preparations of  $\text{AlPcS}_n$  consisting of the least number of differently substituted species were found to show a higher tendency to aggregate, whereas  $\text{AlPcS}_n$  consisting of a higher number of differently substituted products showed monomeric behavior [19]. In this respect, aluminum ( $\text{AlPcS}_{\text{mix}}$ ) containing a mixture of di-, tri- and tetra-sulfo products were found to exhibit monomeric behavior. In this work we use  $\text{AlPcS}_{\text{mix}}$  and zinc ( $\text{ZnPcS}_{\text{mix}}$ ) species for the photosensitized oxidation of 4-Cp and we compare the photosensitizing abilities of these complexes with those of the aluminum ( $\text{AlPcS}_4$ ) and zinc ( $\text{ZnPcS}_4$ ). We also study the photosensitizing properties of zinc ( $\text{ZnOCPc}$ ) and aluminum ( $\text{AlOCPc}$ ) octacarboxy phthalocyanines (Scheme 1) towards the oxidation of 4-Cp. Octacarboxy phthalocyanine complexes are water-soluble and are known to be monomeric in aqueous solutions [23]. Photosensitized oxidation of phenols is dependent on pH [6,24], hence, in this work we report on the effects of pH on the quantum yields for the photooxidation of 4-Cp and some details of the kinetics and mechanisms of the process. In the presence of oxygen, 4-Cp is known to be oxidized mainly to benzoquinone [15].



Scheme 1. Molecular structures of  $\text{MPcS}_n$  and  $\text{MOCPc}$ .

## 2. Experimental

### 2.1. Materials

$\text{AlPcS}_4$  and  $\text{ZnPcS}_4$  tetra-sulfophthalocyanines were synthesized according to the method of Weber and Busch [25]. The  $\text{AlPcS}_{\text{mix}}$  and  $\text{ZnPcS}_{\text{mix}}$  phthalocyanine complexes containing mixtures of differently substituted sulfophthalocyanines were synthesized from  $\text{ClAlPc}$  and  $\text{ZnPc}$ , respectively, using fuming sulfuric acid (30%  $\text{SO}_3$ ), according to reported procedures [26].  $\text{ZnOCPc}$  and  $\text{AlOCPc}$  octacarboxy phthalocyanines were synthesized and characterized according to literature methods [23,27]. The compounds gave satisfactory spectroscopic characteristics. Phosphate buffers were employed for pH studies,  $0.1 \text{ mol l}^{-1}$  NaOH or HCl being added to adjust the pH. Triply distilled Millipore water was used for all experiments. 4-Cp (Aldrich) and sodium azide (Aldrich) were used as received. 1,4-Benzoquinone (Aldrich), hydroquinone (May and Baker Ltd.), 4-chlorocatechol (Aldrich), phenol (BDH) and 4-chlororesorcinol (Aldrich) were used as standards for high performance liquid chromatography (HPLC) studies. Tetra-sodium  $\alpha, \alpha'$ -(anthracene-9,10-diyl)bimethylmalonate (ADMA) was a gift from Dr. V. Negrimovsky (from Organic Intermediates and Dyes Institute, Russia).

### 2.2. Photochemical studies

Photochemical transformation of 4-Cp was carried out in a 1 cm pathlength spectrophotometric cell, fitted with a tight fitting stopper. A 2.5 ml solution containing the photosensitizer ( $1 \times 10^{-6}$  to  $7 \times 10^{-6} \text{ mol l}^{-1}$ ) and 4-Cp ( $1 \times 10^{-5}$  to  $2 \times 10^{-3} \text{ mol l}^{-1}$ ) was added to the cell and then photolyzed. The solutions with 4-Cp concentration below  $10^{-4} \text{ mol l}^{-1}$  were irradiated under aerobic conditions without bubbling oxygen. It was confirmed that oxygen present in water was enough for the phototransformation experiments under these conditions. Experiments with 4-Cp concentration above  $10^{-4} \text{ mol l}^{-1}$  were carried out in oxygen saturated solutions, oxygen was bubbled for 20 min before

each illumination period. Irradiation was carried out with a General Electric Quartz line lamp (220 W). A 600 nm glass filter (Schott) and a water filter were used to filter off ultra-violet radiation. An interference filter (Intor, 670 nm with a bandwidth of 20 nm) was placed in the light path. The light intensity was measured with a powermeter (Lasermate/A) and was found to be  $5 \times 10^{16}$  photons  $s^{-1} cm^{-2}$ . For some experiments the interference filter was not employed.

ADMA was used as a chemical scavenger for singlet oxygen in aqueous solutions [28].

Phototransformation of 4-Cp was monitored with HPLC. The separation of 4-Cp and intermediates was achieved within 16 min using a mobile phase, comprising of an acidified 60:40 mixture of water:methanol, flowing at a rate of  $0.1 cm^3 min^{-1}$ . Absolute retention times and spiking of peaks with standards were used in assigning the HPLC peaks. Spectra-Physics HPLC apparatus, Spectra Series P100, equipped with an analytical column GL Wakosil C18 ( $150 mm \times 1 mm$ ) and connected to a variable wavelength UV–VIS detector (set at  $\lambda = 280 nm$ ) was employed. A Perkin-Elmer 561 chart recorder was connected to the HPLC apparatus. Electronic spectra of the solutions containing the photosensitizer and 4-Cp were monitored with a Cary 500 UV–VIS /NIR spectrophotometer during the course of the photolysis in order to monitor the effect of photolysis on the photosensitizer. pH studies were carried out with the Beckman  $\phi 50$  pH meter.

### 2.3. Treatment of data

Quantum yields for the transformation of 4-Cp ( $\phi_{4-Cp}$ ) were determined from the initial linear part of kinetic curve of 4-Cp photooxidation using the relationship

$$\phi_{4-Cp} = -\frac{(C_t - C_0)VN_A}{I_{abs}St} \quad (7)$$

where  $C_0$  and  $C_t$  are 4-Cp concentrations before and after irradiation, respectively;  $V$  the reaction volume,  $t$  the irradiation time,  $N_A$  Avogadro's constant,  $S$  the irradiation area ( $1.4 cm^2$ ),  $I_{abs}$  the overlap integral of the light intensity of the radiation source and the absorption of the sensitizer (the action spectrum) in the region of the interference filter transmittance.  $I_{abs}$  is defined as

$$I_{abs} = \int (1 - 10^{-A_\lambda}) I_\lambda d\lambda \quad (8)$$

where,  $I_\lambda$  is the intensity of light and  $A_\lambda$  the absorbance of the sensitizer at the wavelength  $\lambda$ .

Singlet oxygen quantum yields ( $\phi_\Delta$ ) for the phthalocyanine complexes under discussion were determined in pH 10 buffer, from  $\phi_{ADMA}$  (quantum yield for the reaction of ADMA with singlet oxygen) using Eq. (9)

$$\phi_{ADMA} = \phi_\Delta \frac{k_r[ADMA]}{k_d + (k_r + k_q)[ADMA]} \quad (9)$$

where  $k_d$  is singlet oxygen decay rate constant in water,  $k_r$  and  $k_q$  are the rate constants for the reaction and physical quenching of singlet oxygen by ADMA, respectively. The value of  $\phi_\Delta$  (0.38) is well known for monomeric AlPcS<sub>mix</sub> in aqueous solutions at pH 7.4 [29]. Thus, AlPcS<sub>mix</sub> at pH 7.4 was used as a standard for the determination of  $\phi_\Delta$  for the phthalocyanine complexes under discussion in this work. Using the ratio of Eq. (9) for these phthalocyanine complexes with that for the AlPcS<sub>mix</sub> complex and assuming  $k_d \gg (k_r + k_q)[ADMA]$ , gives Eq. (10)

$${}^{MPc} \phi_\Delta = {}^{AlPcS} \phi_\Delta \frac{{}^{MPc} \phi_{ADMA} [ADMA]^{AlPcS}}{{}^{AlPcS} \phi_{ADMA} [ADMA]^{MPc}} \quad (10)$$

Initial concentration of ADMA was about  $7 \times 10^{-5} mol l^{-1}$ , ADMA decay was monitored at 380 nm. The observed first order kinetics for ADMA photooxidation proves that the condition  $k_d \gg (k_r + k_q)[ADMA]$  applies for photolysis studies under investigation.

The error of 4-Cp phototransformation quantum yields and of singlet oxygen quantum yields for phthalocyanine derivatives was 10%. All experiments were conducted at ambient temperature (23–25°C).

### 3. Results and discussion

We studied the effect of concentration on the absorption spectra for ZnOCpC, AlOCpC, AlPcS<sub>mix</sub> and ZnPcS<sub>mix</sub>, as shown in Fig. 1 for AlPcS<sub>mix</sub>. Beer–Lambert law was obeyed for all of these complexes in the concentrations ranging from  $1.5 \times 10^{-6}$  to  $7.0 \times 10^{-5} mol l^{-1}$ . The Beer–Lambert relationship is shown as an inset for AlPcS<sub>mix</sub> in Fig. 1. In Fig. 2 absorption spectra of ZnOCpC, ZnPcS<sub>mix</sub> and ZnPcS<sub>4</sub> at a concentration of  $5 \times 10^{-6} mol l^{-1}$  and pH 10 are compared. The spectrum of ZnOCpC with sharp Q band is typical for monomer phthalocyanine complex. The formation of aggregates in sulfophthalocyanine complexes is normally accompanied by an absorption band at a low wavelength (near 630 nm) as shown in Fig. 2 for ZnPcS<sub>4</sub>. The spectra

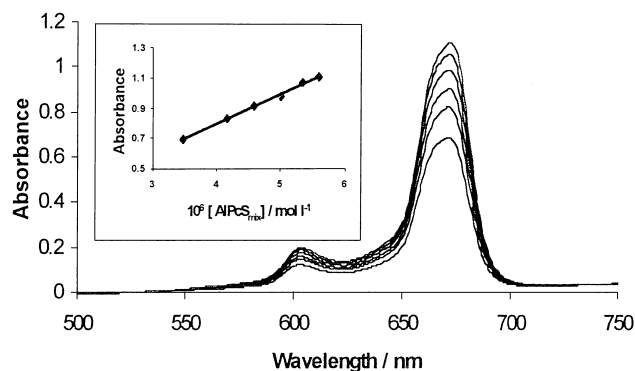


Fig. 1. Variation of absorbance with concentration and Beer–Lambert law dependence for AlPcS<sub>mix</sub> under pH 10 conditions.

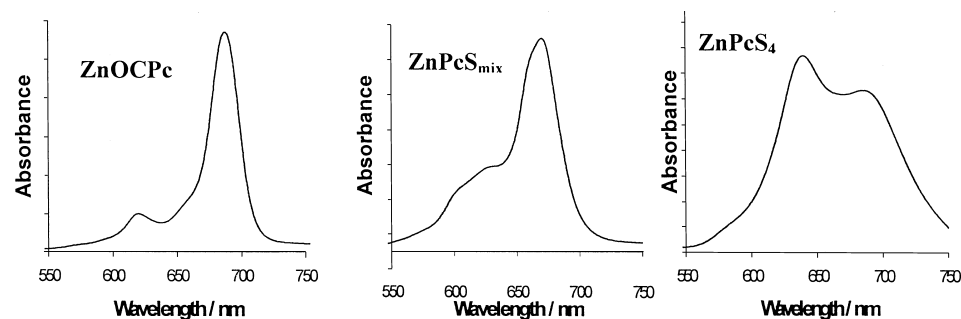


Fig. 2. Electronic absorption spectra of ZnOCPc, ZnPcS<sub>mix</sub> and ZnPcS<sub>4</sub> in water at  $5 \times 10^{-6} \text{ mol l}^{-1}$ , pH = 10.

for ZnPcS<sub>mix</sub> showed some aggregation, as evidenced by a large shoulder to the high energy side of the Q band. However, a linear behavior was observed for the Beer–Lambert law for this complex within the concentration range given above.

### 3.1. pH studies

The stability and photosensitizing abilities of phthalocyanine photosensitizers are known to be dependent on pH [10]. In micellar solutions, the photosensitizing activities towards the phototransformation of phenols were shown to decrease with decrease in pH [10]. The quantum yields for the photooxidation of 4-Cp using AlPcS<sub>4</sub>, AlPcS<sub>mix</sub> and ZnPcS<sub>mix</sub> as photosensitizers were found to increase with pH from pH = 7, with a leveling off at pH = 10, Fig. 3. Hence, pH 10 was employed for subsequent studies. ZnOCPc and AlOCPc were found to be soluble only at pH > 7.

In basic media 4-Cp with  $pK_a = 9.4$  [30] is in its deprotonated phenolate form hence, it is more easily oxidizable, higher quantum yields for the photooxidation of 4-Cp are thus obtained at high pH. The pH dependence of the sensitized photolysis quantum yields demonstrates an insignificant contribution of the unionized form of 4-Cp in the process (Fig. 3).

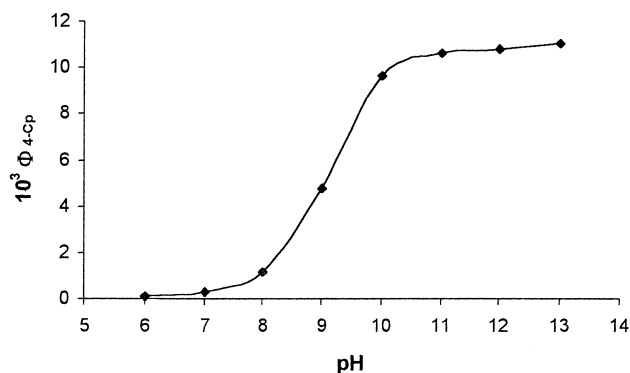
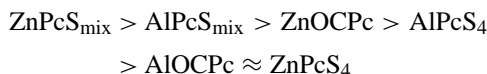


Fig. 3. Dependence of quantum yield on pH for the transformation of 4-Cp in the presence of AlPcS<sub>mix</sub>.  $[4\text{-Cp}] = 3.5 \times 10^{-5} \text{ mol l}^{-1}$ .

### 3.2. Rates and quantum yields of 4-Cp photooxidation

Fig. 4 shows the decrease of the concentration of 4-Cp ( $3.5 \times 10^{-5} \text{ mol l}^{-1}$ ) with time during irradiation in the presence of the various photosensitizers at pH = 10. Irradiation for these studies was performed in the presence of an interference filter, hence, only the Q band was irradiated. The experimental conditions (including intensity of absorbed light) were kept constant for all the photosensitizers. The disappearance of 4-Cp was monitored with HPLC. The results show that photooxidation of 4-Cp occurred faster when ZnPcS<sub>mix</sub> was used as the sensitizer. ZnPcS<sub>4</sub> and AlOCPc showed the least activity towards the photooxidation of 4-Cp. The observed results show that the rate of 4-Cp transformation depends on the photosensitizer as follows:



Values of quantum yields,  $\phi_{4\text{-Cp}}$ , for 4-Cp photosensitized oxidation are summarized in Table 1. It was found that two main factors determine photosensitizer activity: efficiency of singlet oxygen sensitization and sensitizer photodegradation, which will be discussed below.

The singlet oxygen quantum yields for some of the sensitizers, used in the present work, were reported in literature

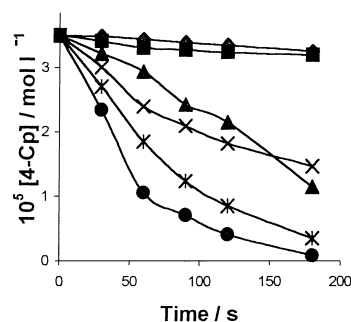


Fig. 4. The dependence of concentration of 4-Cp on time (s) for the ZnPcS<sub>4</sub> (◆); AlOCPc (■); AlPcS<sub>4</sub> (▲); ZnOCPc (×); AlPcS<sub>mix</sub> (\*); ZnPcS<sub>mix</sub> (●), pH = 10. Photolysis in the Q band ( $\lambda = 670 \text{ nm}$ ) in the presence of an interference filter.

Table 1

Photosensitization data for 4-Cp transformation in the presence of the various sensitizers (S) under  $\lambda = 670$  nm irradiation<sup>a</sup>

S	4-Cp photooxidation		$\phi_{\Delta}$	Degradation of S (%) <sup>b</sup>
	Rate, $10^7 \text{ mol l}^{-1} \text{ s}^{-1}$	$\phi_{4\text{-Cp}}$		
ZnPcS <sub>mix</sub>	4.07	0.0140	0.48	35
AlPcS <sub>mix</sub>	2.7	0.0097	0.38	0
ZnOCPc	1.68	0.0059	0.52	51
AlPcS <sub>4</sub>	0.93	0.0040	0.18	0
AIOCPc	<0.5	<0.002	0.12	1.3
ZnPcS <sub>4</sub>	<0.5	<0.002	<0.01	0.5

<sup>a</sup> Conditions: pH 10, [4-Cp] =  $3.5 \times 10^{-5} \text{ mol l}^{-1}$ .

<sup>b</sup> After 3 min of irradiation with visible light.

at pH 7.4 [23]. For sulfonated phthalocyanines, particularly AlPcS<sub>mix</sub>, these values are dependent on the degree of sulfonation. We have not assessed the degree of sulfonation for AlPcS<sub>mix</sub> and ZnPcS<sub>mix</sub> in the present work, however, singlet oxygen quantum yields were determined for all sensitizers under our experimental conditions (pH 10). The values obtained for  $\phi_{\Delta}$  are presented in Table 1. It is worth noting that for ZnOCPc, AIOCPc, AlPcS<sub>4</sub> and the monomeric AlPcS<sub>mix</sub> the  $\phi_{\Delta}$  quantum yields were found to be close to the ones reported at pH 7.4 [23]. The value of  $\phi_{\Delta}$  for ZnPcS<sub>mix</sub> is slightly low in comparison with known data for its monomeric form in organic media [10] due to partial aggregation of this dye in aqueous buffer solutions. ZnPcS<sub>4</sub> is highly aggregated, hence,  $\phi_{\Delta}$  for this compound is less than 0.01.

The data presented in Table 1 show that the rates and  $\phi_{4\text{-Cp}}$  for photooxidation of 4-Cp decrease as  $\phi_{\Delta}$  of the photosensitizers decrease, with the exception of ZnOCPc. The relatively low activity of ZnOCPc when compared to ZnPcS<sub>mix</sub> and AlPcS<sub>mix</sub> is probably due to photodegradation, since its spectral characterization showed monomeric properties and its singlet oxygen quantum yield is relatively high ( $\phi_{\Delta} = 0.52$ ). Table 1 gives the percentage degradation of the photosensitizers and shows that all the AlPc complexes are relatively stable and degradation is not an important factor in their photosensitizing abilities. Aggregation in ZnPc complexes influences photodegradation in that monomeric complexes (e.g. ZnOCPc) show a higher degree of degradation than aggregated species (e.g. ZnPcS<sub>4</sub>), Table 1. The relatively large efficiency of ZnPcS<sub>mix</sub> as shown by Fig. 4, is surprising considering the fact that this complex shows extensive photodegradation. The large efficiency of ZnPcS<sub>mix</sub> could be a result of its relatively high singlet oxygen quantum yield ( $\phi_{\Delta} = 0.48$ ), Table 1. This  $\phi_{\Delta}$  value is higher than for AlPcS<sub>mix</sub> ( $\phi_{\Delta} = 0.38$ ). ZnPcS<sub>4</sub> showed little activity towards the transformation of 4-Cp. This is due to the extensive aggregation of this species in solution. Aggregated MPc complexes are photoinactive due to rapid energy dissipation after excitation. AIOCPc is also virtually inactive towards the transformation of 4-Cp, even though this complex shows monomeric absorption properties and low degradation. This might be due to the

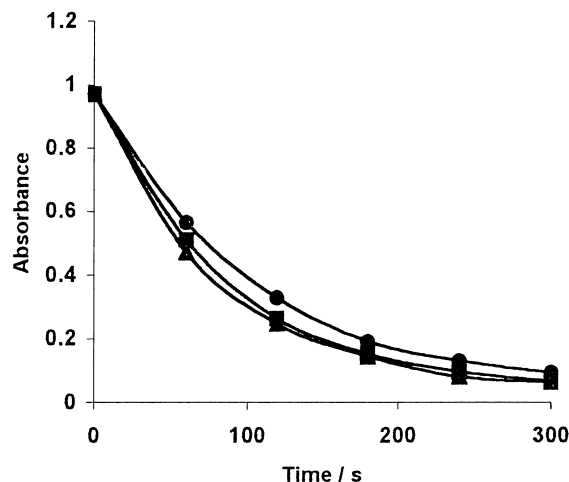


Fig. 5. Changes in the absorbance of ZnOCPc with time in the absence (●); presence of (▲, lower curve)  $1 \times 10^{-4} \text{ mol l}^{-1}$  4-Cp; (■)  $5 \times 10^{-3} \text{ mol l}^{-1}$  NaN<sub>3</sub>, pH = 10. Photolysis in the Q band ( $\lambda = 670$  nm).

association of this sensitizer via hydrogen bonding between the axial hydroxyl groups, as suggested before [23] (hence, giving a low value for  $\phi_{\Delta} = 0.12$ , Table 1).

Fig. 5 shows the change in the absorbance of ZnOCPc with photolysis time under Q band excitation and pH 10 conditions. The ZnOCPc readily disappeared showing that this complex is not stable. Photodegradation of ZnOCPc was observed in the absence of 4-Cp and the effect of 4-Cp (concentration  $1 \times 10^{-4} \text{ mol l}^{-1}$ ) on the rate of degradation of ZnOCPc was minimal (Fig. 5). The result shows that interaction between sensitizer and 4-Cp has negligible influence on ZnOCPc photodegradation under experimental conditions. When the solution containing ZnOCPc was photolyzed in the presence of a singlet oxygen quencher, sodium azide ( $5 \times 10^{-3} \text{ mol l}^{-1}$ ), the rate of photodegradation of ZnOCPc did not change (Fig. 5), suggesting that a mechanism other than attack of ZnOCPc by singlet oxygen could be involved in the photodegradation of ZnOCPc. Detailed investigation on the mechanisms of the photodegradation of MPc complexes is underway.

For practical applications of MPc complexes as photosensitizers, it is important to study the photooxidation of 4-Cp without the use of the interference filter. The time dependence of the concentration of 4-Cp during photolysis in the presence of the various photosensitizers and excitation with light of  $\lambda > 600$  nm was studied. Under these conditions both the monomer and dimer components of the Q band were exposed to radiation for the ZnPcS<sub>4</sub> complex, while the dimeric component of the Q band was cut-off in the presence of the interference filter. Absence of the interference filter did not significantly affect the dependence of 4-Cp transformation on the photosensitizers.

The products of the phototransformation of 4-Cp were identified using HPLC as explained in the experimental section. A new peak with a retention time of 3 min was observed when 4-Cp was photolyzed in the presence of AlPcS<sub>mix</sub>,

this peak was identified as benzoquinone. Benzoquinone has been identified before as the product for the photodegradation of chlorophenol [15,31]. The reaction solution was also followed by UV–VIS spectrophotometry, and benzoquinone was detected after a photolysis time of 4 min by its characteristic absorption at 245 nm. Benzoquinone is observed only in the presence of oxygen.

### 3.3. Kinetic studies

The kinetic studies were aimed at answering some questions about the role of phthalocyanine-type sensitizers in photooxidation of 4-Cp. The particular importance of Type I radical pathway and limiting efficiency of Type II photooxidation of 4-Cp with  $\text{AlPcS}_{\text{mix}}$  and  $\text{ZnPcS}_{\text{mix}}$  as photosensitizers were investigated.

Singlet oxygen mediated photooxidation of 4-Cp sensitized by metallosulphthalocyanines process is undoubted and generally accepted. However, Lang et al. [15] using laser flash photolysis have recently found that interaction of aluminum sulphthalocyanine, in its excited singlet state, with the 4-Cp leads to the phthalocyanine anion radical and substrate cation radical both of which can react with  $\text{O}_2$  through the Type I radical pathway. Thus, besides oxidation by singlet oxygen, the interaction of 4-Cp with the excited singlet state of the sensitizer is more important than is generally recognized.

To address the question of relative contribution of Type I reaction pathway in overall quantum yields of 4-Cp photooxidation, sensitized by aluminum sulphthalocyanine particularly, experiments were performed on inhibition of the sensitized reaction by singlet oxygen quencher, sodium azide. As shown on Fig. 6A, addition of sodium azide at a concentration of  $5 \times 10^{-3} \text{ mol l}^{-1}$  to solutions containing low amounts of 4-Cp ( $3.5 \times 10^{-5} \text{ mol l}^{-1}$ , pH 10) and  $\text{AlPcS}_{\text{mix}}$  as a photosensitizer, resulted in strong (92%) inhibition of the transformation of 4-Cp, hence, proving that singlet oxygen mediated, Type II, mechanism is the dominating route under these conditions. At higher concentrations of 4-Cp ( $2.0 \times 10^{-3} \text{ mol l}^{-1}$ ) and in oxygen saturated solutions only 70% inhibition of the photooxidation of 4-Cp by sodium azide was observed (Fig. 6B), hence, about 30% of 4-Cp is transformed through the Type I process. The full inhibition of singlet oxygen in these experiments was confirmed by obtaining the same results with  $5 \times 10^{-3}$  and  $5 \times 10^{-2} \text{ mol l}^{-1}$  concentrations of sodium azide. This data show that the contribution of Type I mechanism to overall quantum yields is concentration dependent and can be neglected only at low concentrations of substrate.

The kinetic scheme for photooxidation of 4-Cp by singlet oxygen is shown below.

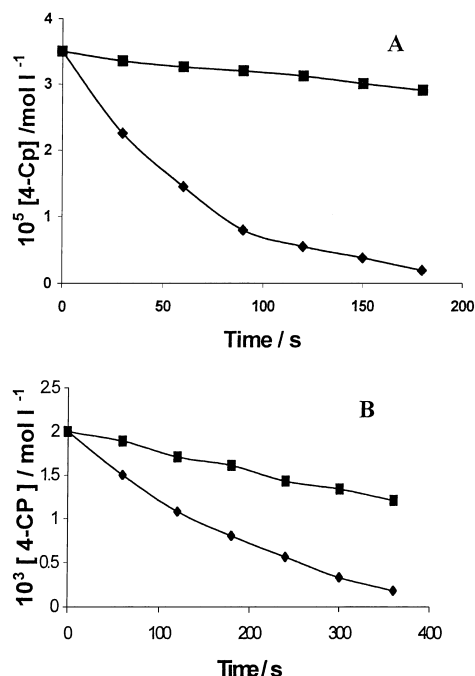


Fig. 6. Effects of addition of singlet oxygen quencher (sodium azide,  $5 \times 10^{-3} \text{ mol l}^{-1}$ ) on the rate of phototransformation of 4-Cp. (A)  $[4\text{-Cp}] = 3.5 \times 10^{-5} \text{ mol l}^{-1}$ ; (B)  $[4\text{-Cp}] = 2.0 \times 10^{-3} \text{ mol l}^{-1}$ . Sensitizer =  $\text{AlPcS}_{\text{mix}}$ . Without sodium azide ( $\blacklozenge$ ); with sodium azide ( $\blacksquare$ ).



where  $k_d$ ,  $k_q$  and  $k_r$  are the rate constants for the decay of  ${}^1\text{O}_2$ , “physical” quenching of  ${}^1\text{O}_2$  by 4-Cp and formation of oxidation products, respectively.

The expression describing the quantum yield of 4-Cp phototransformation ( $\phi_{4\text{-Cp}}$ ) is

$$\phi_{4\text{-Cp}} = \phi_{\Delta} \frac{k_r[4\text{-Cp}]}{k_d + k_q[4\text{-Cp}] + k_r[4\text{-Cp}]} \quad (14)$$

Rewriting Eq. (14) as its double reciprocal and rearranging gives Eq. (15)

$$\frac{1}{\phi_{4\text{-Cp}}} = \frac{1}{\phi_{\Delta}} \left( \frac{k_r + k_q}{k_r} + \frac{k_d}{k_r[4\text{-Cp}]} \right) \quad (15)$$

According to Eq. (15) the plots of  $1/\phi_{4\text{-Cp}}$  versus  $1/[4\text{-Cp}]$  were used for determination of the limiting value of quantum yields  $\phi_{\infty}$  for the Type II phototransformation of 4-Cp in the presence of the most efficient of the photosensitizers studied, particularly  $\text{ZnPcS}_{\text{mix}}$  and  $\text{AlPcS}_{\text{mix}}$ . pH 10 conditions and concentrations of 4-Cp in the range  $1 \times 10^{-5}$  to  $5 \times 10^{-5} \text{ mol l}^{-1}$  (i.e. Type II mechanism conditions), were employed for plots shown in Fig. 7. The values of  $\phi_{\infty}$  equal  $0.10 \pm 0.03$  for  $\text{ZnPcS}_{\text{mix}}$  and  $\phi_{\infty} = 0.07 \pm 0.01$  for  $\text{AlPcS}_{\text{mix}}$  sensitized photooxidation of 4-Cp phenoxide were determined from the inverse of the y-intercepts of the plots shown in Fig. 7. These  $\phi_{\infty}$  values are significantly lower than singlet oxygen quantum yields (Table 1), indicating that

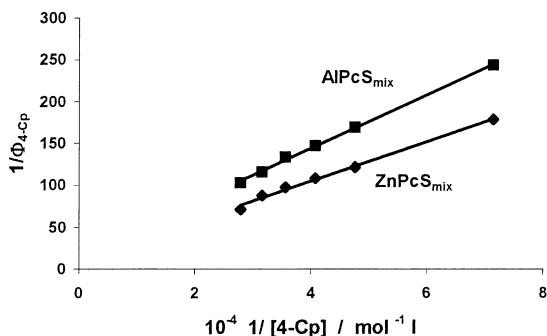


Fig. 7. Plots of  $1/\phi_{4\text{-Cp}}$  vs.  $1/[4\text{-Cp}]$  for the phototransformation of 4-Cp in the presence of  $\text{ZnPcS}_{\text{mix}}$  and  $\text{AlPcS}_{\text{mix}}$  for photolysis in the Q band ( $\lambda = 670 \text{ nm}$ ),  $\text{pH} = 10$ .

not all the singlet oxygen is involved in chemical reaction with the 4-Cp phenoxide. This observation shows that physical quenching of singlet oxygen by the phenolate form of 4-Cp competes strongly with the chemical reaction. The ratio between the rate constant for reactive quenching,  $k_r$  and the total quenching constant ( $k_q + k_r$ ) is strongly dependent on the structure of the phenolic compounds [32], and for 4-Cp the value of this ratio is unknown. To compare efficiencies of chemical reaction and total quenching we have calculated corresponding constants using Eq. (15) and the plots shown in Fig. 7. Plots of  $1/\phi_{4\text{-Cp}}$  versus  $1/[4\text{-Cp}]$  gave straight lines of slopes  $0.0024 \pm 0.0001 \text{ mol l}^{-1}$  for  $\text{ZnPcS}_{\text{mix}}$  and  $0.0032 \pm 0.0008 \text{ mol l}^{-1}$  for  $\text{AlPcS}_{\text{mix}}$ . These slopes are equal to  $k_d/\phi_{\Delta}k_r$  with  $k_d = 1/\tau_{\Delta} = 3.22 \times 10^5 \text{ s}^{-1}$  ( $\tau_{\Delta} = 3.09 \times 10^{-6} \text{ s}$  in water [33]). Using values of  $\phi_{\Delta}$  from Table 1, the constant  $k_r$  was calculated for the phenolate ion of 4-Cp. The value of  $k_r$  was calculated to be  $(2.8 \pm 0.3) \times 10^8 \text{ mol}^{-1} \text{ l s}^{-1}$  from the plot using  $\text{ZnPcS}_{\text{mix}}$  as sensitizer and  $(2.65 \pm 0.3) \times 10^8 \text{ mol}^{-1} \text{ l s}^{-1}$  for  $\text{AlPcS}_{\text{mix}}$ . These two values are close to each other and confirm that the choice of sensitizer has no effect on  $k_r$ , and that direct interaction of 4-Cp with excited sensitizer is negligible under the experimental conditions.

The plots shown in Fig. 7 gave intercepts =  $(k_q + k_r)/\phi_{\Delta}k_r$ . The intercepts were found to be  $9.67 \pm 4.00$  for  $\text{ZnPcS}_{\text{mix}}$  and  $14.33 \pm 3.00$  when  $\text{AlPcS}_{\text{mix}}$  was employed as sensitizer. An average value of  $k_r = (2.7 \pm 0.3) \times 10^8 \text{ mol}^{-1} \text{ l s}^{-1}$  for the phenolate ion of 4-Cp and  $\phi_{\Delta}$  values from Table 1 were used to calculate the rate constant ( $k_q + k_r$ ) for the total quenching of singlet oxygen by deprotonated 4-Cp. Calculated values for ( $k_q + k_r$ ) are  $(12.5 \pm 5.2) \times 10^8$  and  $(14.7 \pm 3.1) \times 10^8 \text{ mol}^{-1} \text{ l s}^{-1}$  when using  $\text{ZnPcS}_{\text{mix}}$  and  $\text{AlPcS}_{\text{mix}}$  as sensitizers, respectively, the average value of singlet oxygen total quenching rate constant is  $(k_q + k_r) = (13.5 \pm 3.0) \times 10^8 \text{ mol}^{-1} \text{ l s}^{-1}$ . The rate constant ( $k_q + k_r$ ) of 4-Cp phenolate ion is five times larger than the rate constant,  $k_r$ , for photooxidation alone thus, most of the singlet oxygen is scavenged by a quenching process. The situation is similar to that of other phenols, which quench singlet oxygen more rapidly than react with it [34].

It is worth noting that the constant of chemical oxidation of 4-Cp by singlet oxygen in water was determined earlier by Tratnyek and Holgne [24]. The method used in [24] was based on  $k_r$  calculations from rates of phenol photooxidation and steady state concentration of singlet oxygen, determined separately with furfuryl alcohol. Thus, the  $k_r$  constants were obtained for a diverse set of phenols, the value for deprotonated 4-Cp was reported to be  $1.93 \times 10^8 \text{ mol}^{-1} \text{ l s}^{-1}$ . However, it was noted that this rate constant for 4-Cp is low due to the depression of steady state concentration of singlet oxygen through physical quenching by the phenolate ion. Indeed, with steady state concentrations of singlet oxygen, determined in the same solution with the 4-Cp, values of  $k_r$  were as high as  $2.7 \times 10^8 \text{ mol}^{-1} \text{ l s}^{-1}$  [24], and are close to  $k_r$ , obtained in the present study. The rate constants from this study appear to be more precise than previously reported by Tratnyek and Holgne [24].

Rates of undissociated 4-Cp photooxidation by singlet oxygen were measured at  $\text{pH} 6.5$  (fraction of 4-Cp dissociated at this  $\text{pH}$  is negligible, about 0.1%). The experiments under comparable conditions show that the rate of 4-Cp reaction with singlet oxygen is a factor of 20 lower than that for 4-Cp phenoxide anion. The estimated value of  $k_r$  for undissociated 4-Cp is about  $10^7 \text{ mol}^{-1} \text{ l s}^{-1}$ , a result which agrees with literature data [24].

In conclusion we have shown in this work that 4-Cp is phototransformed to benzoquinone in the presence of various phthalocyanine photosensitizers. The photosensitizers containing a mixture of differently substituted sulfophthalocyanines ( $\text{ZnPcS}_{\text{mix}}$  and  $\text{AlPcS}_{\text{mix}}$ ) gave the best results for the phototransformation of 4-Cp. At low concentrations of 4-Cp, Type II mechanism predominates for the phototransformation of 4-Cp. Enhanced physical quenching of singlet oxygen by phenoxide form of 4-Cp leads to significant decrease of photooxidation efficiency. Contribution of Type I mechanism to the overall quantum yields is concentration dependent and becomes appreciable at high substrate concentrations.

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