

## Photo-oxidation of phenol and monochlorophenols in oxygen-saturated aqueous solutions by different photosensitizers

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### Abstract

The photo-oxidation of phenol and 2-, 3- and 4-monochlorophenols by irradiation with visible light in aqueous alkaline solution in the presence of photosensitizers and oxygen is described. The reactions were carried out in the absence or presence of detergents. The photosensitizers used were Al(III), Zn(II) and Ga(III) complexes of 2,9,16,23-tetrakisulphthalocyanine (1a-1c), 5,10,15,20-tetrakis(4-carboxyphenyl)porphyrin (2), a cationically charged perylene tetracarboxylic diimide (3), rose bengal (4) and methylene blue (5). The photosensitizers exhibit different activities and photo-oxidative stabilities which are strongly dependent on the pH, hydrolysis sensitivity and aggregation tendency. Singlet oxygen, obtained by photoinduced energy transfer from the excited photosensitizers, dominates the initial steps of photo-oxidation. A reaction sequence is proposed on the basis of the identification of carbonyl dioxide and maleic or fumaric acid as the products of photo-oxidation in the absence of detergent and the evaluated mass balances. © 1997 Elsevier Science S.A.

**Keywords:** Phenols; Photo-oxidation; Photosensitizers; Phthalocyanines

### 1. Introduction

The photo-oxidation of organic and inorganic substrates by oxygen using visible light activation of photosensitizers is of increasing interest. The synthesis of fine chemicals on solar irradiation is one such application. The photo-oxidation of  $\alpha$ -terpinene to ( $\pm$ )-ascaradiol in the presence of chlorophyll as photosensitizer in ethanol has been described [1,2]. Recently, the synthesis of 5-hydroxy-5H-furan-2-one from furfural in the presence of methylene blue or rose bengal as photosensitizer in ethanol (SOLARIS reactor of the solar test centre in Almeria, Spain) [3,4] and the synthesis of pyridines from acetylene and nitriles in the presence of cobalt cyclopentadienyl complexes in water (PROPHIS solar reactor of the DLR in Cologne, Germany) [5] have been reported.

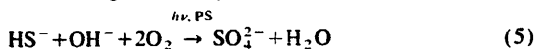
A second application concentrates on the cleaning of wastewater. A well-known example is the removal of halogenated hydrocarbons from water on exposure to solar radiation using TiO<sub>2</sub> as photoexcitable semiconductor [6,7]. Due to the band gap of TiO<sub>2</sub> (3.2 eV), this process works in the UV region where only approximately 4% of solar radiation is effective.

In order to overcome this disadvantage, photosensitizers absorbing in the visible region are used.

In addition to methylene blue and rose bengal mentioned above, other suitable photosensitizers for photo-oxidation include porphyrin analogues, such as 5,10,15,20-tetraphenylporphyrins and phthalocyanines. Photochemical oxidations with porphyrin analogues have been carried out in oxygen-saturated aqueous solutions on thiols, sulfide, thioethers, tryptophan, tyrosine and cholesterol [8-16]. After excitation of the photosensitizer (PS), triplet-triplet energy transfer to triplet oxygen with the formation of singlet oxygen is the dominating initial elementary step, followed by oxidation of the substrate (Sub) (so-called type II reaction) [8,9,17]

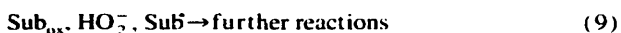


Under alkaline aqueous conditions, thiols are photo-oxidized efficiently to sulfonic acids and sulfide to sulfate [8,9]



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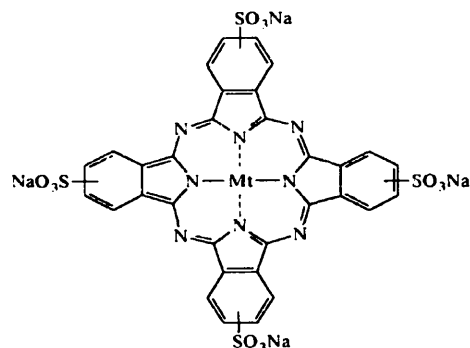
In addition to the singlet oxygen pathway, the formation of the superoxide anion radical by photoinduced electron transfer cannot be ruled out as a side-reaction (so-called type I reaction) [17–19]



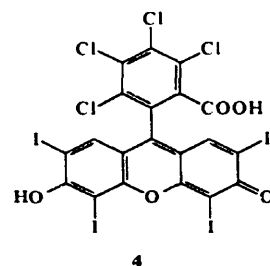
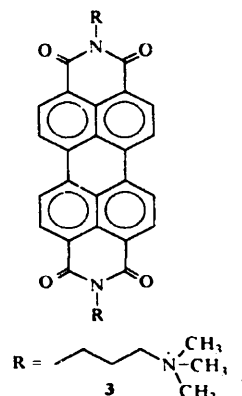
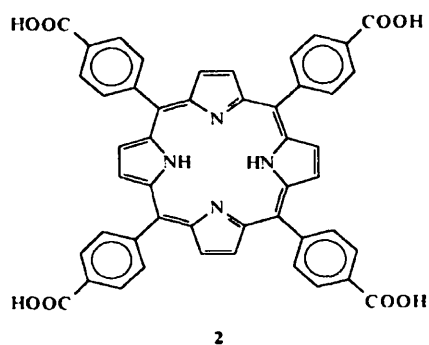
It should be noted that, in the photodynamic therapy of cancer, the oxidation of cellular targets in the presence of photosensitizers on irradiation follows similar pathways [20–24]. The route via singlet oxygen is the dominating process in sensitized photo-oxidation reactions.

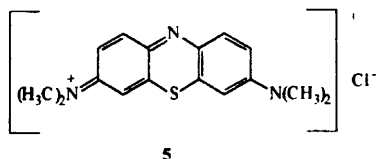
Another class of toxic compound in the wastewater of paper and dye manufacturing industries and oil refineries is phenol and its derivatives. One process for the mineralization of phenols uses the photoexcitation of the semiconductor  $\text{TiO}_2$  in the UV region [6,7]. Furthermore, studies have been carried out on the oxidation of phenols by irradiation with visible light in the presence of photosensitizers and oxygen, concentrating mainly on the selective preparation of *p*-benzoquinone and on the mechanisms and kinetics of these photo-oxidations. Singlet oxygen for the oxidation of different substituted phenols (methyl-, dimethyl- and trimethylphenols, di-(tert-butyl)-phenol, dinitrophenols, chlorophenols) is generated in organic solvents, such as  $\text{CH}_3\text{OH}$ ,  $\text{CCl}_4$ ,  $\text{CH}_2\text{Cl}_2$  and benzene, using different photosensitizers, e.g. eosin, rose bengal, methylene blue, riboflavin and the Zn(II) complex of tetraphenylporphyrin [25–33]. Work by García and coworkers [34,35] has investigated the mechanistic and kinetic aspects of the photo-oxidation of di- and trichlorophenols sensitized by rose bengal and methylene blue in aqueous solutions, but without identification of the reaction products.

This paper describes the photo-oxidation of phenol and monochlorophenols in aqueous alkaline solutions on irradiation with visible light in an oxygen atmosphere. Various photosensitizers were used, e.g. aluminium(III), zinc(II) and gallium(III) complexes of 2,9,16,23-tetrakisulphophthalocyanine (**1a–1c**), metal-free 5,10,15,20-tetrakis(4-carboxyphenyl)porphyrin (**2**), di-(*N,N*-trimethylammonium-propylene)-3,4,9,10-perylenebis-carboximide (**3**), rose bengal (**4**) and methylene blue (**5**). All photosensitizers exhibit, due to the negative or positive charges, good water solubility. In those cases in which the photosensitizers aggregate in water, oppositely charged detergents were added to monomerize the compounds [8,9]. The aims of this work were to investigate the photoactivity and photostability of the photosensitizers, follow the influence of the pH values on the activity, identify the photo-oxidation products and discuss the mechanism of the photo-oxidation of phenols.



sample	Mt
<b>1a</b>	Al(III)OH
<b>1b</b>	Zn(II)
<b>1c</b>	Ga(III)OH





## 2. Materials and methods

### 2.1. Chemicals

Phenol and monochlorophenols (Fluka), rose bengal (4), methylene blue (5) and all other commercially available compounds were of reagent grade and were employed as supplied. The photosensitizers **1a–1c** [8], **2** [36] and **3** [37] were prepared as described elsewhere and were characterized by IR and UV–visible spectroscopy. For the photo-oxidation experiments, doubly distilled water was used. The detergents cetyltrimethylammonium chloride (CTAC, Aldrich) and sodium dodecylsulphate (SDS, Roth) and the borate and phosphate buffers (pH 7 and pH 10, Kraft) were used without further purification.

### 2.2. Photo-oxidation experiments

The photo-oxidation experiments were carried out in an automatic apparatus as described previously [8,9]. In the case of the photo-oxidation of *p*-benzoquinone, for the addition of the substrate to the apparatus a septum was used. The oxygen consumption was followed continuously during stirring and illumination with visible light at  $180 \text{ mW cm}^{-2}$  (halogen lamp, 250 W). For experiments at pH 13, 6 mmol of NaOH was added to doubly distilled water (50 ml). For measurements at pH 10 and pH 7, 25 ml of phosphate or borate buffer and 25 ml of doubly distilled water were used. Photo-oxidations in micellar solutions were carried out in the presence of  $0.1 \text{ mol l}^{-1}$  of detergent (CTAC, SDS). Investigations to confirm singlet oxygen participation were conducted in 25 ml of  $\text{D}_2\text{O}$  or 25 ml of  $\text{H}_2\text{O}$  containing  $0.01 \text{ mol l}^{-1}$  of sodium azide. In most photo-oxidation experiments, the concentrations of the phenols and photosensitizers were  $7.16 \text{ mmol l}^{-1}$  and  $5 \text{ } \mu\text{mol l}^{-1}$  respectively (phenol to photosensitizer molar ratio, 1432 : 1).

After bubbling of the aqueous solutions for 10 min with oxygen, the phenols dissolved in ethanol were added. All measurements were carried out at  $25^\circ\text{C}$ .

For all photo-oxidation experiments, the reaction rates (RRs) were calculated in micromoles of  $\text{O}_2$  per minute from the initial linear slope of the oxygen consumption over time.

The degradation of the photosensitizers was followed by visible spectroscopy. The absorbances of the photosensitizers in the reaction solutions before and after photo-oxidation were compared, and from the change in absorbance the degradation of the photosensitizers was determined. In some

cases, it was impossible to determine the stability of the photosensitizers because of the very strong absorbance of the photoproducts at the maximum absorbance of the photosensitizers.

The absolute singlet oxygen quantum yields of the photosensitizers in *N,N*-dimethylformamide (DMF) were determined using 1,3-diphenylisobenzofuran as chemical quencher as described elsewhere [37,38], with the exception of **5** [39,40].

### 2.3. Spectra

IR spectra were taken on a Bio-Rad SPC-3200 spectrometer and UV–visible spectra on a Perkin–Elmer Lambda 9 spectrophotometer. Product identifications were obtained by gas chromatography/mass spectrometry (GC/MS) using a Finnigan MAT IST 40 and by MS (DCI,  $\text{NH}_3$ , negative) on a Finnigan MAT 8222.

### 2.4. Determination of the reaction products

The quantitative and qualitative confirmation of the reaction products in the photo-oxidation experiments was only possible in the absence of detergents. The products of photo-oxidation at pH 13 in the absence of detergent using **1a** as photosensitizer were isolated from the reaction solution by the addition of hydrochloric acid to pH 1, followed by extraction with ethylacetate. The reaction products dissolved in ethylacetate were identified by MS (DCI,  $\text{NH}_3$ , negative) and GC/MS.

Carbon dioxide, one of the reaction products, was quantitatively determined by precipitation as  $\text{BaCO}_3$  from an aqueous  $\text{Ba}(\text{OH})_2$  solution as follows. Photo-oxidation of phenol in the absence of detergent at pH 13 was performed using **1a** as photosensitizer with a reaction time of 12 000 s. Concentrated aqueous hydrochloric acid was added to pH 1. Nitrogen was bubbled for 4 h through the solution and  $\text{CO}_2$  was precipitated by passing the gas stream through an aqueous  $\text{Ba}(\text{OH})_2$  solution. The precipitate of  $\text{BaCO}_3$  was isolated by filtration, washed with water and dissolved in hydrochloric acid. After neutralizing the solution with NaOH, the amount of  $\text{Ba}^{2+}$  was determined by titration with ethylenediaminetetraacetic acid (EDTA) using phthalein purpur/naphthol green B/methyl red as indicator system [41]. A blank experiment was carried out with an unirradiated solution and the small amount of  $\text{CO}_2$  determined was subtracted from the value for the photo-oxidation experiment.

The determination of hydrogen peroxide was carried out according to a modified method of Egerton et al. [42] using titanil sulphate and determining the UV absorption at 408 nm of the  $[\text{Ti}(\text{O}_2) \cdot \text{aq}]^{2+}$  complex.

### 2.5. Molecular orbital (MO) calculations

All calculations were carried out with the commercially available program HYPERCHEM (Release 4.5) from

Hypercube Inc. (Waterloo, Ont., Canada). The calculation method PM3 was used, comprising MNDO based on the neglect of diatomic differential overlap (NDDO) and an additional class of electron repulsion integrals including the overlap density between two orbitals centred on the same atom interacting with the overlap density between two orbitals also centred on a single (but possibly different) atom, i.e. considering the effects of electron–electron interactions on different atoms. PM3 differs from AM1 only in the values of the parameters, which were derived by comparing a much larger number and wider variety of experimental vs. computed molecular properties. Typically, non-bonded interactions are less repulsive in PM3 than in AM1. PM3 is primarily used for organic molecules, but also parametrized for many main group elements.

The considered MO energies and ionization potentials are based on Koopmann's theorem stating that the first ionization energy of a closed-shell molecule is approximated to second order by the energy of the highest occupied molecular orbital (HOMO). During ionization, the remaining electrons are recognized, contributing an additional term and enabling interpretations of photoelectron spectra to be made from MO calculations. In addition, the orbital energies can reasonably be approximated in the case of higher ionization potentials. Errors in the ionization potentials are typically a few tenths of an electronvolt, i.e. a small percentage of the total value.

For all compounds, a full geometry optimization was carried out until a gradient of less than  $0.01 \text{ kcal } \text{\AA}^{-1} \text{ mol}^{-1}$  was reached. On the basis of this structure, single point calculations were carried out using the PM3 method (convergence limit, 0.01; charge on the system, 0). Additional configuration interaction (CI) calculations were not performed.

### 3. Results

#### 3.1. Photo-oxidation of phenol in the absence of detergent

The photo-oxidation of phenol in the absence of detergent was carried out in alkaline solution at pH 13 employing different photosensitizers. The results are summarized in Fig. 1 and Table 1. In aqueous alkaline solution without irradiation in the presence of a photosensitizer, or with irradiation in the absence of a photosensitizer, no oxygen consumption was observed.

The different activities observed for the photo-oxidation of phenol, i.e. initial RRs evaluated from the linear slopes of the oxygen consumption over time and the final oxygen consumption, may be determined predominantly by three factors:

1. the singlet oxygen quantum yield ( $\Phi_{\Delta}$ );
2. the degradation (photo-oxidative stability) of the photosensitizer;
3. the aggregation of the photosensitizer.

In order for a photosensitizer to be photoactive, it must exist as a monomer because, in aggregates, the dissipation of

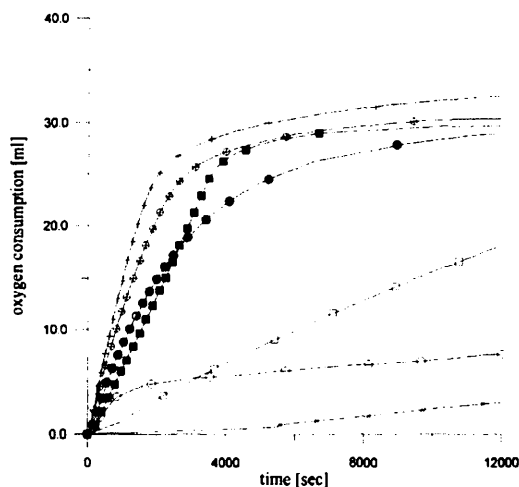


Fig. 1. Photo-oxidation of 0.358 mmol phenol in aqueous solution (50 ml) in the absence of detergent at pH 13 using 0.25  $\mu\text{mol}$  of different photosensitizers: +, 1a;  $\square$ , 1b;  $\bullet$ , 1c;  $\circ$ , 2;  $\times$ , 3;  $\blacksquare$ , 4;  $\circ$ , 5.

Table 1

Oxygen consumption, normalized consumption  $\text{O}_2/\text{Ph}$  (consumed oxygen (mol)/initial concentration of phenol (mol)), reaction rate (RR), degradation of photosensitizer and singlet oxygen quantum yield ( $\Phi_{\Delta}$ ) in the photo-oxidation of phenol (0.358 mmol) in aqueous solution (50 ml) in the absence of detergent at pH 13 using different photosensitizers (PS) (0.25  $\mu\text{mol}$ )

PS	Oxygen consumption <sup>a</sup> (ml)	$\text{O}_2/\text{Ph}^a$	RR ( $\mu\text{mol O}_2 \text{ min}^{-1}$ )	Degradation of PS <sup>a</sup> (%)	$\Phi_{\Delta}^b$
1a	32.4	3.7	41	0	0.20
1b	18.0	2.0	4.7	33.3	0.52
1c	28.8	3.3	23	100	0.41
2	30.2	3.4	35	84	0.47
3	2.9	0.3	0.84	66.7	0.23
4	29.9	3.4	17	100	0.64
5	7.7	0.9	2.9	100	0.37

<sup>a</sup> After 12 000 s of irradiation with visible light.

<sup>b</sup> Singlet oxygen quantum yields were determined in DMF as described in Ref. [38].

the energy of the excited state occurs. Therefore the main reason for the low activity of photosensitizers 1b and 3 is their tendency to aggregate in aqueous solution, which is indicated by the shift and increased width of the longest wavelength absorption band in the UV–visible spectrum. In addition, degradation during reaction results in a loss of activity. Methylene blue (5) is a characteristic example of an extremely unstable photosensitizer. After a good initial RR, 5 decomposes completely after around 2000 s, resulting in a loss of activity (Table 1, Fig. 1). The aluminium complex of 2,9,16,23-tetrasulphophthalocyanine (1a) is a characteristic example of a photosensitizer which does not decompose or aggregate, resulting in a high activity for the photo-oxidation of phenol, although the singlet oxygen quantum yield is rel-

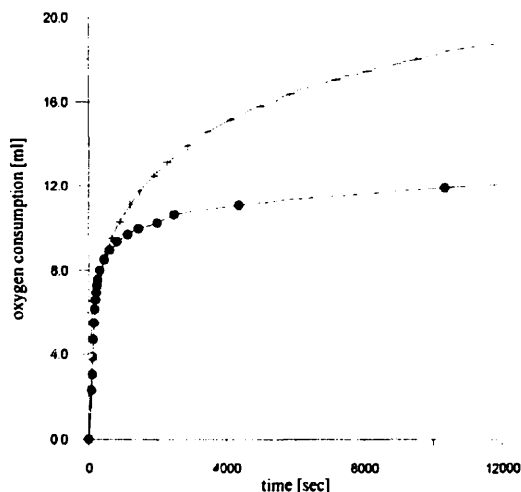


Fig. 2. Photo-oxidation (+) and dark oxidation (●) of *p*-benzoquinone (0.358 mmol) in aqueous solution (50 ml) in the absence of detergent at pH 13 using 0.25  $\mu\text{mol}$  of **1a** as photosensitizer.

Table 2

Oxygen consumption, normalized consumption  $\text{O}_2/\text{Ph}$  (consumed oxygen (mol)/initial concentration of *p*-benzoquinone (mol)), reaction rate (RR) and degradation of photosensitizer in the photo-oxidation and dark oxidation of *p*-benzoquinone (0.358 mmol) in aqueous solution (50 ml) in the absence of detergent at pH 13 using **1a** as photosensitizer (0.25  $\mu\text{mol}$ )

PS	Irradiation (mW $\text{cm}^{-2}$ )	Oxygen consumption <sup>a</sup> (ml)	$\text{O}_2/\text{Ph}$ <sup>a</sup>	RR ( $\mu\text{mol O}_2 \text{ min}^{-1}$ )	Degradation of PS <sup>a</sup> (%)
<b>1a</b>	180	18.7	2.1	140	0
<b>1a</b>	0	12	1.4	110	0

<sup>a</sup> After 12 000 s of irradiation with visible light.

atively low (Table 1). The photosensitizers **2** and **4** are characterized by an excellent singlet oxygen quantum yield; however, photo-oxidative decomposition may be the reason for the lower activities than that of compound **1a** (Table 1). The final oxygen consumption for the most active photosensitizer lies in the range 28–32 ml, which corresponds to a normalized consumption of around 3.3–4.2 mol  $\text{O}_2$  per mole of phenol (see also Table 3). Under the conditions described in Table 1, the phthalocyanine derivative **1a** with the highest RR value also exhibits the highest final oxygen consumption. In most cases, the initial RR correlates with the final oxygen consumption of the photosensitizer.

If *p*-benzoquinone is employed as a possible intermediate at pH 13 in the presence of **1a** (Fig. 2, Table 2), the final oxygen consumption is lower compared with the photo-oxidation of phenol, but the initial RR of photo-oxidation of *p*-benzoquinone is much higher, because *p*-benzoquinone can react even with triplet oxygen (dark reaction) in alkaline aqueous solution [43]. However, the final oxygen consumption of the dark reaction of *p*-benzoquinone is significantly lower than that of photo-oxidation.

### 3.2. Photo-oxidation of phenol in the presence of detergent at different pH values

The photo-oxidation of phenol was also carried out in the presence of detergents. Detergents with a charge opposite to that of the photosensitizer can monomerize these compounds which otherwise aggregate in water [8,9]. This is especially valid for photosensitizers **1b** and **3** which are totally monomeric in oppositely charged detergent solutions (indicated by a decreased width of the Q band in the UV–visible spectrum). The results of the photo-oxidation of phenol at pH 13 in micellar solution are presented in Fig. 3 and Table 3.

The activities of most photosensitizers in micellar solutions at pH 13 are higher than in solutions without detergent, indicated by the higher RR values and final oxygen consumption. The molar ratio of oxygen consumed per mole of phenol

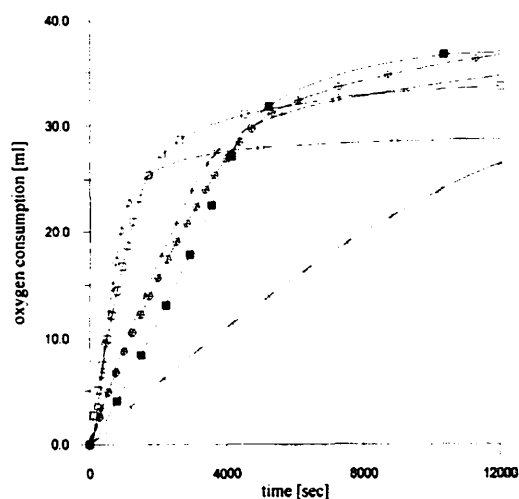


Fig. 3. Photo-oxidation of 0.358 mmol phenol in aqueous solution (50 ml) containing 0.1 M detergent at pH 13 using 0.25  $\mu\text{mol}$  of different photosensitizers: +, **1a**; □, **1b**; ⊕, **2**; ×, **3**; ■, **4**; ○, **5**.

Table 3

Oxygen consumption, normalized consumption  $\text{O}_2/\text{Ph}$  (consumed oxygen (mol)/initial concentration of phenol (mol)), reaction rate (RR), degradation of photosensitizer and detergent (0.1 mol  $\text{l}^{-1}$ ) used in the photo-oxidation of phenol (0.358 mmol) in aqueous solution (50 ml) at pH 13 using different photosensitizers (0.25  $\mu\text{mol}$ )

PS	Oxygen consumption <sup>a</sup> (ml)	$\text{O}_2/\text{Ph}$ <sup>a</sup>	RR ( $\mu\text{mol O}_2 \text{ min}^{-1}$ )	Degradation of PS <sup>a</sup> (%)	Detergent
<b>1a</b>	34.6	3.9	23	21.4	CTAC
<b>1b</b>	33.6	3.8	53	97.5	CTAC
<b>1c</b> <sup>b</sup>	–	–	–	100	CTAC
<b>2</b>	36.6	4.2	24	12.6	CTAC
<b>3</b>	26.5	3.0	7.8	19.3	SDS
<b>4</b>	37.0	4.2	15	58.2	CTAC
<b>5</b>	28.7	3.3	71	100	SDS

<sup>a</sup> After 12 000 s of irradiation with visible light.

<sup>b</sup> **1c** is unstable in micellar solution.

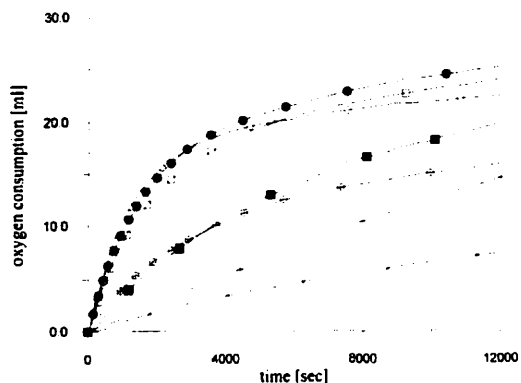


Fig. 4. Photo-oxidation of 0.358 mmol phenol in aqueous solution (50 ml) containing 0.1 M detergent at pH 10 using 0.25  $\mu\text{mol}$  of different photosensitizers: +, 1a;  $\square$ , 1b;  $\bullet$ , 1c;  $\odot$ , 2;  $\times$ , 3;  $\blacksquare$ , 4;  $\circ$ , 5.

Table 4

Oxygen consumption, normalized consumption  $\text{O}_2/\text{Ph}$  (consumed oxygen (mol)/initial concentration of phenol (mol)), reaction rate (RR), degradation of photosensitizer and detergent (0.1 mol  $\text{l}^{-1}$ ) used in the photo-oxidation of phenol (0.358 mmol) in aqueous solution (50 ml) at pH 10 using different photosensitizers (0.25  $\mu\text{mol}$ )

PS	Oxygen consumption <sup>a</sup> (ml)	$\text{O}_2/\text{Ph}$ <sup>a</sup>	RR ( $\mu\text{mol O}_2 \text{ min}^{-1}$ )	Degradation of PS <sup>a</sup> (%)	Detergent
1a	14.5	1.7	3.4	10.5	CTAC
1b	23.9	2.7	24	44.6	CTAC
1c	25.0	2.8	29	11.2	CTAC
2	15.9	1.8	9.6	23.1	CTAC
3	7.3	0.8	2.1	8	SDS
4	19.7	2.3	8.8	13	CTAC
5	22.3	2.5	30	29.3	SDS

<sup>a</sup> After 12 000 s of irradiation with visible light.

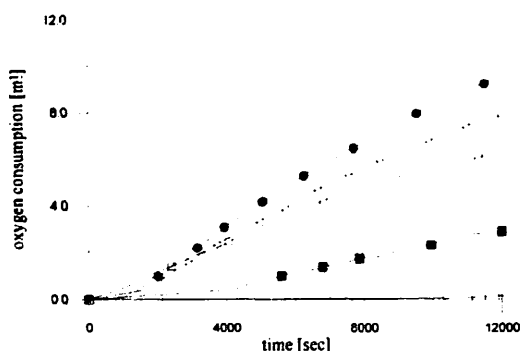


Fig. 5. Photo-oxidation of 0.358 mmol phenol in aqueous solution (50 ml) containing 0.1 M detergent at pH 7 using 0.25  $\mu\text{mol}$  of different photosensitizers: +, 1a;  $\square$ , 1b;  $\bullet$ , 1c;  $\blacksquare$ , 4;  $\circ$ , 5.

employed is 4.2 or less. The Al(III) complex of 2,9,16,23-tetrasulphophthalocyanine, characterized as an active and stable photosensitizer in water (Table 1), exhibits lower RR values and significant degradation in micellar solution (Table

Table 5

Oxygen consumption, normalized consumption  $\text{O}_2/\text{Ph}$  (consumed oxygen (mol)/initial concentration of phenol (mol)), reaction rate (RR), degradation of photosensitizer and detergent (0.1 mol  $\text{l}^{-1}$ ) used in the photo-oxidation of phenol (0.358 mmol) in aqueous solution (50 ml) at pH 7 using different photosensitizers (0.25  $\mu\text{mol}$ )

PS	Oxygen consumption <sup>a</sup> (ml)	$\text{O}_2/\text{Ph}$ <sup>a</sup>	RR ( $\mu\text{mol O}_2 \text{ min}^{-1}$ )	Degradation of PS <sup>a</sup> (%)	Detergent
1a	0.2	0.02	0.03	14.6	CTAC
1b	6.4	0.7	1.5	65.3	CTAC
1c	9.6	1.1	2.4	5.3	CTAC
2 <sup>b</sup>	-	-	-	-	CTAC
3	0	0	0	0	SDS
4	2.9	0.3	0.98	32.4	CTAC
5	7.8	0.9	2.1	39.2	SDS

<sup>a</sup> After 12 000 s of irradiation with visible light.

<sup>b</sup> 2 is not soluble in water at pH 7.

3). The Ga(III) complex of 2,9,16,23-tetrasulphophthalocyanine (1c) decomposes within a few seconds in micellar solution at pH 13, and is not suitable for use as a photosensitizer under these conditions.

In micellar solutions, the photo-oxidation of phenol was also carried out at pH 10 and pH 7 (Fig. 4, Fig. 5, Table 4 and Table 5). In general, the activities (RR values and final oxygen consumption) decrease with decreasing pH, whereas the photo-oxidative stabilities increase. The gallium phthalocyanine derivative 1c, showing no activity at pH 13 due to rapid degradation, exhibits increasing stability and activity with decreasing pH, and is the most active photosensitizer at pH 7. Surprisingly, the aluminium phthalocyanine derivative 1a exhibits a strongly decreased activity at pH 10 (Table 4) and no activity at pH 7 (Table 5), although its photostability is largely maintained.

### 3.3. Determination of singlet oxygen

There are several possibilities for the qualitative demonstration of whether or not singlet oxygen is involved in the photo-oxidation. Firstly, singlet oxygen has a longer lifetime in  $\text{D}_2\text{O}$  than in water and, secondly, it is possible to quench singlet oxygen in the presence of the physical quencher sodium azide [8,9]. Employing the very active photosensitizer 1a in water at pH 13 without detergent, the photo-oxidation of phenol was carried out in  $\text{D}_2\text{O}$  and in water containing sodium azide. The initial RR and final oxygen consumption are increased in  $\text{D}_2\text{O}$ , but decreased in  $\text{NaN}_3$  solution (Fig. 6, Table 6).

### 3.4. Determination of reaction products

For the photo-oxidation of phenols in organic solvents, *p*-benzoquinone derivatives were observed as the final reaction products [25-32,34,35,44]. For the oxidation of 1 mol phenol to 1 mol *p*-benzoquinone, the amount of consumed oxy-

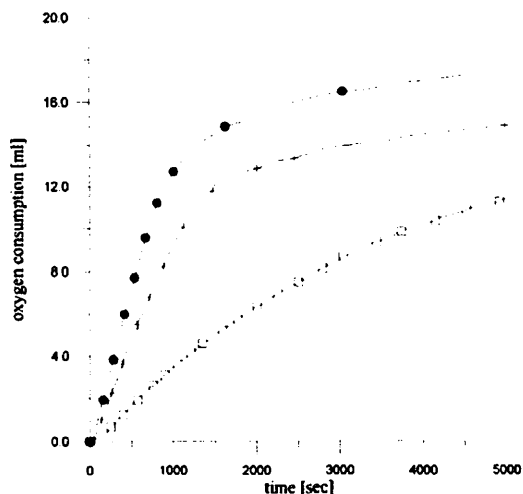


Fig. 6. Photo-oxidation of 0.179 mmol phenol in the absence of detergent at pH 13 in aqueous solution (25 ml) with (□) and without (+) 0.25 mmol of sodium azide and in 25 ml D<sub>2</sub>O (●).

Table 6

Oxygen consumption, normalized consumption O<sub>2</sub>/Ph (consumed oxygen (mol)/initial concentration of phenol (mol)) and reaction rate (RR) in the photo-oxidation of phenol (0.179 mmol) in the absence of detergent in aqueous solution (25 ml) with and without sodium azide at pH 13 and in D<sub>2</sub>O (25 ml) at pH 13 using **1a** as photosensitizer (0.125 μmol)

PS	Solvent	Sodium azide (mmol)	Oxygen consumption <sup>a</sup> (ml)	O <sub>2</sub> /Ph <sup>a</sup>	RR (μmol O <sub>2</sub> min <sup>-1</sup> )
<b>1a</b>	H <sub>2</sub> O	-	14.9	3.4	24
<b>1a</b>	H <sub>2</sub> O	0.25	11.3	2.6	9.2
<b>1a</b>	D <sub>2</sub> O	-	17.4	4.0	35

<sup>a</sup> After 5000 s of irradiation with visible light.

gen would be 1 mol. The higher value of consumed oxygen per mole of phenol of approximately 4 mol shows that further oxidation steps occur.

In order to determine the photo-oxidation products, the reaction solution of phenol photo-oxidation at pH 13 without detergent using **1a** as photosensitizer was analysed after a reaction time of 12 000 s. The solution was acidified to pH 1 and then extracted with ethylacetate. The reaction products dissolved in ethylacetate were analysed by MS and GC/MS. No phenol or *p*-benzoquinone was found. An intensive peak at *m/z*=116 indicated the formation of maleic acid or fumaric acid. This result was confirmed by GC/MS.

Furthermore, photo-oxidation at pH 7 in the presence of detergent and with **1c** as photosensitizer was carried out in order to demonstrate whether or not *p*-benzoquinone was generated as the final product in neutral solution. The reaction solution was analysed by UV-visible spectroscopy, and *p*-benzoquinone was detected after a reaction time of 12 000 s by its characteristic absorption at 245 nm.

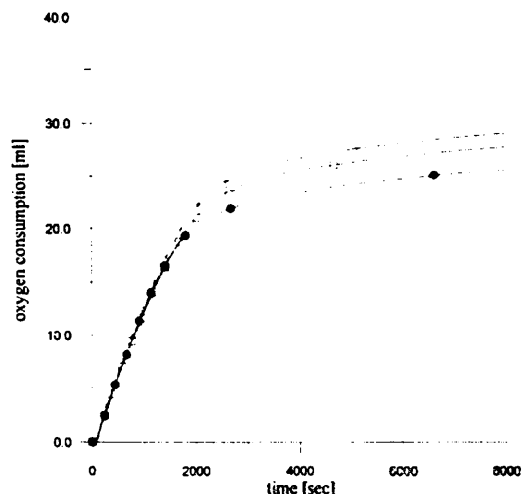


Fig. 7. Photo-oxidation of 0.358 mmol 2-chlorophenol (+), 3-chlorophenol (□) and 4-chlorophenol (●) in aqueous solution (50 ml) in the absence of detergent at pH 13 using 0.25 μmol of **1a** as photosensitizer.

Table 7

Oxygen consumption, normalized consumption O<sub>2</sub>/Ph (consumed oxygen (mol)/initial concentration of monochlorophenols (mol)), reaction rate (RR) and degradation of photosensitizer in the photo-oxidation of 2-, 3- and 4-chlorophenol (0.358 mmol) in the absence of detergent in aqueous solution (50 ml) at pH 13 using **1a** and **4** as photosensitizers (0.25 μmol)

PS	Substrate	Oxygen consumption <sup>a</sup> (ml)	O <sub>2</sub> /Ph <sup>a</sup>	RR (μmol O <sub>2</sub> min <sup>-1</sup> )	Degradation of PS <sup>a</sup> (%)
<b>1a</b>	2-Chlorophenol	29.1	3.3	36	0
<b>1a</b>	3-Chlorophenol	27.8	3.2	36	0
<b>1a</b>	4-Chlorophenol	25.6	2.9	36	0
<b>4</b>	2-Chlorophenol	29.2	3.3	22	100
<b>4</b>	3-Chlorophenol	28.7	3.3	22	100
<b>4</b>	4-Chlorophenol	25.8	2.9	23	100

<sup>a</sup> After 8000 s of irradiation with visible light.

Carbon dioxide was determined as described in Section 2.4. Employing 0.358 mmol phenol in the reaction, 0.32 mmol CO<sub>2</sub> was determined, which corresponds to 0.9 mol CO<sub>2</sub> formed per mole of phenol. Taking into account the larger standard deviations for the method of CO<sub>2</sub> determination, i.e. liberation as gas from the reaction solution and absorption in an aqueous Ba(OH)<sub>2</sub> solution, we can assume that around 1 mol CO<sub>2</sub> is formed as photo-oxidation product from 1 mol phenol.

Finally, tests for hydrogen peroxide formation as the reduction product of oxygen were carried out in reaction solutions for the photo-oxidation of phenol at pH 13 without detergent employing **1a** as photosensitizer. Titanium sulphate was added to the solution to identify the [Ti(O<sub>2</sub>)<sub>2</sub>·aq]<sup>2+</sup> complex by UV spectroscopy. However, in contrast with the photo-oxidation of sulfide [9], no generation of hydrogen peroxide was detected in several experiments during the photo-oxidation of phenol.

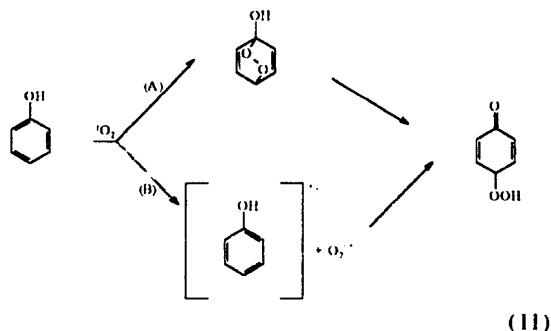
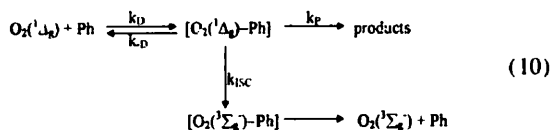
### 3.5. Photodegradation of monochlorophenols

In addition to phenol, the photo-oxidations of 2-, 3- and 4-chlorophenol were investigated (Fig. 7, Table 7). The reactions were carried out in aqueous solution at pH 13 without detergent in the presence of the photosensitizers **1a** and **4**. It can be seen from Fig. 7 that the plots of O<sub>2</sub> consumption over time are comparable with those in Fig. 1. The molar ratios of consumed oxygen to employed phenols are 2.9–3.3 for 4-chlorophenol and 3.3 for 2-chloro- and 3-chlorophenol.

## 4. Discussion

The most important prerequisite for the photo-oxidative activity of a photosensitizer is its monomeric state in solution. The activities of **1b** and **3**, which aggregate in non-micellar solutions, are enhanced in the presence of oppositely charged detergents due to monomerization [8,9]. The photosensitizer **5**, which decomposes in non-micellar solution after approximately 2000 s, exhibits a higher stability (up to approximately 4000 s) in micellar solution and, therefore, a higher consumption of oxygen for the photo-oxidation of phenol. In addition, the porphyrin derivative **2** is characterized by a higher activity and stability in the presence of detergent. The opposite situation is evident for the gallium phthalocyanine derivative **1c**, which is very rapidly degraded in micellar solution at pH 13, and for the aluminium phthalocyanine derivative **1a**, which shows a decrease in stability in the presence of CTAC. In aqueous solutions at pH 10 and pH 7, the Al-containing **1a** shows, in the presence of CTAC, a great loss in activity, and the Ga-containing **1c** shows only a small decrease in activity compared with that at higher pH. It can be assumed that, in strong alkaline solution, the Lewis acid Al(III) in the phthalocyanine core coordinates strongly with OH<sup>-</sup>, resulting in good monomerization even without detergent, but, at pH 7, this monomerization effect is decreased, resulting in the aggregation of **1a** and therefore a lower photo-oxidative activity. At high pH, the gallium phthalocyanine derivative **1c** shows a tendency to demetallate, followed by basic hydrolysis of the macrocycle. At lower pH, **1c** is more stable against demetallation and hydrolysis.

The consideration of the mechanism of the photosensitized oxidation of phenol includes the elementary steps of photoexcitation as well as the reaction products and stoichiometry. The reactions in D<sub>2</sub>O and in the presence of sodium azide clearly show that singlet oxygen (O<sub>2</sub>(<sup>1</sup>Δ<sub>g</sub>)), obtained via photoinduced energy transfer from the excited photosensitizer, is involved in the photo-oxidation process of phenol (Eqs. (1)–(3)). It is generally accepted that phenol and various substituted phenols form an exciplex [O<sub>2</sub>(<sup>1</sup>Δ<sub>g</sub>)-Ph] with singlet oxygen (Eq. (10)), which disintegrates on intersystem crossing into the educt molecules (physical quenching) or leads via a [2 + 4]-cycloaddition to a hydroperoxycyclohexadienone (chemical quenching, Eq. (11)) [28–30,33,34,45–49]

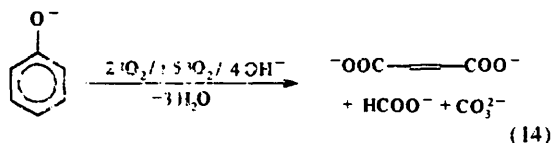
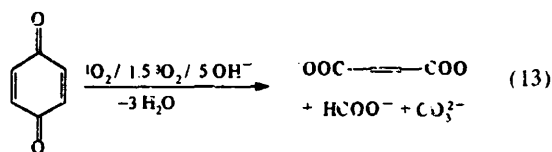
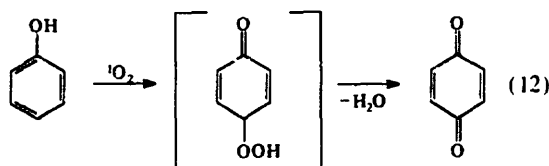


The formation of the same hydroperoxy compound is possible by photoinduced electron transfer (Eq. (6)) via the phenol cation radical and superoxide anion O<sub>2</sub><sup>•-</sup> (Eq. (11)). Therefore the participation of electron transfer under the conditions employed cannot be ruled out, and investigations in this direction will be carried out in the near future. For phenols unsubstituted at position 4, the hydroperoxycyclohexadienone easily decomposes to form *p*-benzoquinone (Eq. (12)). Working in organic solvents, *p*-benzoquinone was found to be the main final photo-oxidation product of phenol [28,31,50]. It was shown previously that, under the aqueous alkaline conditions employed, further oxidation occurs. During the photo-oxidation at pH 13, at longer reaction times, the colour of the solution changes from nearly colourless (weak colour from the small amount of photosensitizer) to deep brown, then yellow and then nearly colourless again. At pH 7, the photo-oxidation proceeds more slowly and *p*-benzoquinone can be detected. The UV-visible spectrum of the brown-coloured solution (photo-oxidation of phenol at pH 7 in the presence of CTAC using **1c** as photosensitizer) shows an intense absorption at 245 nm, which corresponds to the absorption of *p*-benzoquinone in aqueous solution at pH 7. On photo-oxidation at pH 13, this product vanishes, because *p*-benzoquinone can react even with triplet oxygen in alkaline aqueous solution [43]. Carbon dioxide and maleic or fumaric acid are identified as the photo-oxidation products. It is known that naphthoquinone reacts with triplet oxygen in aqueous alkaline solution to give phthalic acid [43], and *p*-benzoquinone in the presence of triplet oxygen (dark oxidation) in alkaline aqueous solution gives maleic or fumaric acid. However, the photo-oxidation of *p*-benzoquinone (Table 2, Fig. 2) consumes more oxygen compared with the reaction without irradiation.

Hydrogen peroxide was not observed which may be due to the immediate reaction of H<sub>2</sub>O<sub>2</sub> with phenol or photoproducts [45].



Approximately 3.5–4 mol of oxygen is consumed per mole of phenol employed at pH 13. In Eq. (14), the photo-oxidation of phenol with 3.5 mol of oxygen on irradiation is summarized. Formic acid is the only product not identified. Singlet oxygen (1 mol), obtained by triplet–triplet energy transfer from the excited sensitizer, is needed for the oxidation of phenol to *p*-benzoquinone (Eq. (12), Table 5 for 1c). Triplet oxygen (1.5 mol) and additional singlet oxygen (1 mol) are consumed in the subsequent oxidation of the quinone (Eq. (13), Table 2, Fig. 2).



The decreasing activity at lower pH, observed in every case for the photo-oxidation of phenol, must be due to a decreasing concentration of phenolate ions. The stabilities of the transition states of phenol or phenolate and singlet oxygen determine the rate of photo-oxidation. The electronic interaction takes place between the calculated lowest unoccupied molecular orbital (LUMO) of singlet oxygen, located at  $-0.98$  eV, and the calculated HOMO of phenolate, located at  $-2.69$  eV, or of phenol, located at  $-9.81$  eV. An increase in the difference between the energy of the LUMO of singlet oxygen and the energy of the HOMO of the organic substrate results in weaker electronic interaction. Therefore phenol is less reactive than phenolate in the photo-oxidative process.

The photoinduced oxidation of phenol is characterized by several consecutive reaction steps and, consequently, by complex kinetics. The strong retardation of the kinetics in the advanced stages of the oxidation process may be due to an inhibition of the photosensitizer by intermediates and products.

The photo-oxidation of monochlorophenols exhibits similar kinetics, oxygen consumptions and stabilities of the photosensitizers as that of unsubstituted phenol (Table 7, Fig. 7). Detailed investigations, including higher chlorinated phenols and other substituted phenols, are underway.

## 5. Conclusions

The mineralization of phenol in alkaline aqueous solution, previously achieved only with titanium dioxide on irradiation with UV light, also proceeds in the presence of photosensitizers which absorb visible light. The photosensitizers used exhibit different activities and stabilities depending on various parameters, such as the pH, hydrolysis sensitivity, aggregation tendency and use of detergents.

Whereas the photo-oxidation in neutral aqueous solution shows *p*-benzoquinone as the final product, at pH 13, carbon dioxide and maleic or fumaric acid are detected, enabling the proposal of a reaction stoichiometry based on the mass balances for the first time.

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