Comparative photosensitised transformation of polychlorophenols with different sulphonated metallophthalocyanine complexes in aqueous medium

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Abstract

The relative efficiencies for the oxidation of trichlorophenol (TCP) and pentachlorophenol (PCP), sensitised by sulphonated phthalocyanine complexes containing Zn, Al, Sn and Si as central metals, were studied in aqueous solutions. For the first time, sulphonated silicon and tin phthalocyanines were synthesised and their activity towards photosensitisation of singlet oxygen and photo-oxidation of polychlorophenols was examined. The efficiency of the sensitised photo-oxidative degradation of polychlorophenols depends not only on singlet oxygen quantum yield of sensitiser, but also on its stability. The influence of substrate structure and the pH of the solution on the photo-oxidation efficiency, as well as on the sensitiser photodegradation were studied. It was found that the contribution of the Type II (singlet oxygen-mediated) mechanism to the relative efficiency of the photosensitised photo-oxidation of the phenol, decreased from phenol to *p*-chlorophenol, TCP and PCP, whereas Type I radical pathway increased. The results obtained for PCP give evidence that electron transfer from the excited sensitiser to the substrate in its unionised form is responsible for enhanced sensitiser photodegradation. © 2001 Elsevier Science B.V. All rights reserved.

Keywords: Aluminium; Zinc; Tin; Silicon phthalocyanine; Trichlorophenol; Pentachlorophenol; Photosensitization; Singlet oxygen

1. Introduction

Trichlorophenol (TCP) and pentachlorophenol (PCP) are commonly used as pesticides, germicides, fungicides, herbicides, molluscicides, algaecides and insecticides [1]. These polychloroaromatics are well-known environmental pollutants and have been listed [2] as top priority pollutants because of their toxicity, persistence and bioaccummulation in aquatic organisms. Their toxicity and resistance to degradation increase with the number of halogen substituents [3–5]. There have been several reports on the degradation of these compounds under UV irradiation [1,6–9]. Unfortunately, direct irradiation of these complexes in water has been found to generate more toxic and persistent compounds (like the polychlorinated dibenzo-*p*-dioxins) than the parent compound. On the other hand, the use of photocatalysts and photosensitisers has resulted in the production of less harmful photoproducts [10–13].

Metallophthalocyanines (MPc) have proved to be efficient photosensitisers and catalysts for many reactions [14–22]. It has been shown before [22] that due to their superior light absorption and photostability,
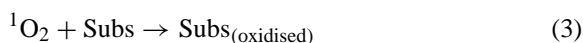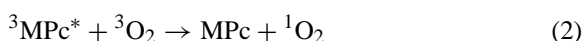
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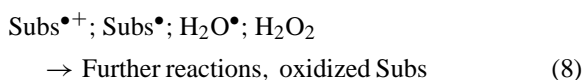fax: +27-46-622-5109.
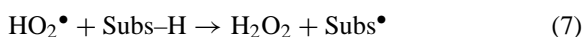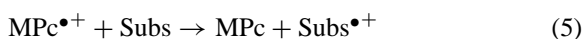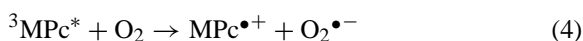*E-mail address:* t.nyokong@ru.ac.za (T. Nyokong).
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these sensitisers have advantages over the commonly used methylene blue and rose bengal.

Generally, under aerobic conditions the photosensitised redox processes involve the interaction of the electronically excited triplet MPc sensitiser (^{3}MPc*) with the ground state oxygen to generate the very active singlet oxygen ($^1O_2$), via triplet–triplet energy transfer process (Type II mechanism, Eqs. (1)–(3)) and/or photo-induced electron transfer process to give the primary radicals (Type I mechanism, Eqs. (4)–(8)):

$$MPc \xrightarrow{h\nu} {}^1MPc* \xrightarrow{isc} {}^3MPc* \tag{1}$$

$$^3MPc* + {}^3O_2 \rightarrow MPc + {}^1O_2 \tag{2}$$

$$^1O_2 + Subs \rightarrow Subs_{(oxidised)} \tag{3}$$

or,

$$^3MPc* + O_2 \rightarrow MPc^{\bullet+} + O_2^{\bullet-} \tag{4}$$

$$MPc^{\bullet+} + Subs \rightarrow MPc + Subs^{\bullet+} \tag{5}$$

$$O_2^{\bullet-} + H^+ \rightarrow HO_2^\bullet \tag{6}$$

$$HO_2^\bullet + Subs–H \rightarrow H_2O_2 + Subs^\bullet \tag{7}$$

$$Subs^{\bullet+}; Subs^\bullet; H_2O^\bullet; H_2O_2$$
$$\rightarrow Further\ reactions,\ oxidized\ Subs \tag{8}$$

where isc is the intersystem crossing, Subs the substrates (in this case TCP or PCP).

Reports show that the route via $^1O_2$ is the predominant process in both photodynamic therapy of cancers and photo-oxidation of many biological and environmental substrates [21,22]. Considerable interest has centred on MPc complexes containing non-transition metal or heavy metal ions because of their tendency to give high singlet oxygen quantum yields. Aluminium, zinc and silicon phthalocyanines, for instance, have particularly received considerable attention [20,21–23].

MPc sensitisers that form dimers and aggregates show lower photosensitization efficiency [24–26]. Aggregation and dimerization reduce the lifetimes of the MPc's excited state, most probably due to enhanced radiationless excited state dissipation [27]

and, therefore, reduce the quantum yields of the singlet oxygen generation. For applications in aqueous systems, water-soluble derivatives of the MPc complexes are of necessity required. The most common water-soluble complexes are the sulphonated MPc complexes [24,28]. Sulphonation often gives the mixture of differently substituted Pc metallocomplexes (MPcS$_{mix}$, where M is the metal ion, $n = 1, 2, 3,$ and 4). The degree of sulphonation, isomeric composition and the nature of the central metal ion affect the extent of aggregation. Studies have shown that AlPcS$_{mix}$ preparations consisting of the least number of isomeric species showed greater tendency to form aggregates, whereas the more complex preparations consisting of a higher number of differently substituted products show more monomeric behaviour in aqueous solutions [28]. In this work we use MPcS$_{mix}$ (M = Al, Zn, Si and Sn) for the photosensitised transformation of TCP and PCP, and compare their behaviour with that of AlPcS$_4$. For the first time, the behaviour of water-soluble, sulphonated silicon and tin phthalocyanines towards photosensitisation of singlet oxygen is reported.

2. Experimental

2.1. Materials

Chloroaluminium tetrasulphonated phthalocyanine (AlPcS$_4$) was synthesised according to the method of Weber and Bush [29]. Aluminium (AlPcs$_{mix}$), zinc (ZnPcS$_{mix}$), silicon (SiPcS$_{mix}$) and tin (SnPcS$_{mix}$) phthalocyanine complexes containing differently substituted sulphophthalocyanines were synthesised from the ClAlPc, ZnPc, (OH)$_2$SiPc and (OH)$_2$SnPc, respectively, using fuming sulphuric acid (30% SO$_3^-$) according to the reported procedures for AlPc-S$_{mix}$ [30]. The starting materials (OH)$_2$SiPc and (OH)$_2$SnPc, were prepared, purified and characterised according to literature procedures [31–33]. ZnPc and ClAlPc were obtained from Sigma. The sulphonated complexes were further purified by chromatography on silica column. The compounds gave satisfactory spectroscopic characteristics. Triply distilled deionised water was used for all experiments. 2,4,5-Trichlorophenol (TCP), PCP, cetyltrimethylammonium chloride and sodium azide were used as received from

Sigma. 2,5-Dichloro-1,4-benzoquinone and 2,3,5,6-tetrachloro-1,4-benzoquinone (Chloranil), both from Aldrich, were used as standards for high pressure liquid chromatography (HPLC) studies and UV–visible spectrophotometry. Tetrasodium α,α-(anthracene-9, 10-diyl) dimethylmalonate (ADMA) was a gift from Dr. V. Negrimovsky (from Organic Intermediates and Dyes Institute, Russia).

2.2. Photochemical studies

A 1 cm pathlength UV–visible spectrophotometric cell fitted with a tight-fitting stopper was employed for photolysis studies. A volume of $3.0\,\text{cm}^3$ of the solution containing the metallophthalocyanine photosensitiser ($\sim 10^{-6}\,\text{mol}\,l^{-1}$) and polychlorophenol (TCP or PCP, 2.0×10^{-5}–$7.0 \times 10^{-5}\,\text{mol}\,l^{-1}$), was introduced into the cell and then photolysed; oxygen was bubbled through the cell for 20 min before each illumination period. The irradiation was carried out with a General Electric Quartz line lamp (300 W). The lamp output was filtered to eliminate UV light by using a 600 nm glass filter (Schott) and far infrared radiation was filtered by using a water filter. An interference filter (Intor, 670 nm with a bandwidth of 20 nm) was placed in the light path before the sample. The light intensity was measured with a power meter (Lasemate/A) and was found to be 5×10^{16} photons $\text{s}^{-1}\,\text{cm}^{-2}$. ADMA was used as before [34] as chemical scavenger for singlet oxygen in aqueous solution.

The phototransformations of the substrates were analysed by both electronic absorption spectrophotometry and reverse phase HPLC. The separation of the substrates and the photoproducts was achieved within 14 min for TCP and 36 min for PCP using a mobile phase consisting of a mixture of acidified methanol, acetonitrile and water in the ratio of 20:30:50. The volume of injected samples was $20\,\mu l$, and the elution rate was $0.1\,\text{cm}^3$ min. 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 $\lambda = 254\,\text{nm}$) was employed. A Perkin-Elmer 561 chart recorder was connected to the HPLC apparatus. Electronic absorption spectra were recorded with a Cary 500 UV/Vis/NIR spectrophotometer. pH measurements were carried out with the Beckman ϕ 50 pH meter.

2.3. Treatment of data

Quantum yields for the photosensitised phototransformation of the polychlorophenols (Φ_{Subs}) were determined from the initial linear part of the kinetic curves using the usual relationship:

$$\Phi_{\text{subs}} = -\frac{(C_t - C_0)VN_{\text{A}}}{I_{\text{abs}}St} \tag{9}$$

where C_0 and C_t are the chlorophenols concentrations prior to and after irradiation, respectively, C_0 and C_t were monitored by using HPLC. V the reaction volume, t the irradiation time, N_{A} the Avogadro's constant, S the irradiated area ($1.4\,\text{cm}^2$), I_{abs} the overlap integral of the radiation source light intensity and the absorption of the sensitiser (the action spectrum) in the region of the interference filter transmittance (from 650 to 690 nm) and is defined as

$$I_{\text{abs}} = \int (1 - 10^{A_\lambda})I_\lambda \, \text{d}\lambda \tag{10}$$

where I_λ is the light intensity and A_λ the absorbance of the sensitiser at the wavelength λ.

To determine singlet oxygen quantum yields (Φ_Δ) for the sulphonated MPc photosensitisers, the relative method with monomeric AlPcS$_{\text{mix}}$ as reference and ADMA as scavenger of singlet oxygen was used. The equation for the quantum yields for the reaction of ADMA with singlet oxygen (Φ_{ADMA}) is

$$\Phi_{\text{ADMA}} = \Phi_\Delta \frac{k_{\text{r}}[\text{ADMA}]}{k_{\text{d}} + (k_{\text{r}} + k_{\text{q}})[\text{ADMA}]} \tag{11}$$

where k_{d} is the decay rate constant of $^1\text{O}_2$ in water, k_{r} and k_{q} the rate constants for the chemical reaction and physical quenching of singlet oxygen by ADMA, respectively. Using the ratio of Eq. (11) for these MPc complexes with that for the AlPcS$_{\text{mix}}$ complex (reference) and assuming $k_{\text{d}} \gg (k_{\text{r}} + k_{\text{q}})$ [ADMA], gives Eq. (12):

$$^{\text{MPc}}\Phi_\Delta = {}^{\text{AlPcS}_{\text{mix}}}\Phi_\Delta \frac{{}^{\text{MPc}}\Phi_{\text{ADMA}} \times [\text{ADMA}]^{\text{AlPcS}_{\text{mix}}}}{{}^{\text{AlPcS}_{\text{mix}}}\Phi_{\text{ADMA}} \times [\text{ADMA}]^{\text{MPc}}} \tag{12}$$

The value of $^{\text{AlPcS}_{\text{mix}}}\Phi_\Delta$ (0.38) is well known for monomeric AlPcS$_{\text{mix}}$ in aqueous solution [35]. The initial concentration of ADMA was $\sim 7 \times 10^{-5}\,\text{mol}\,l^{-1}$, and its decay was monitored at 380 nm.

Apparent first-order kinetics observed for the photo-oxidation ADMA confirmed that the condition $k_d \gg (k_r + k_q)$ [ADMA] applies for the photolysis studies under investigation. The Φ_Δ determination was carried out at the concentration of sensitiser $\sim 5 \times 10^{-6}$ mol l^{-1} and pH 7 conditions.

The error for the quantum yields of transformation of our substrates, as well as for the singlet oxygen quantum yields of the phthalocyanine derivatives, was about 10%. All experiments were performed at ambient temperature (23–25°C).

3. Results and discussion

3.1. Characterisation of photosensitisers

The Q band absorption maxima of sulphonated MPcs under investigation in water solution are presented in Table 1. It was found that only AlPcS$_{mix}$ shows monomeric behaviour (sharp Q band and obeys Beer's law, Fig. 1a). Relatively, high absorption at the short wavelength slope of Q band in the spectra of AlPcS$_4$, ZnPcS$_{mix}$, SnPcS$_{mix}$ and SiPcS$_{mix}$ is typical of aggregation of MPc complexes in aqueous solution [36–39]. These four complexes showed deviations from Beer's law for concentrations ranging from 5×10^{-6} to 1×10^{-4} mol l^{-1}, as shown in Fig. 1b using SnPcS$_{mix}$ as an example. The degree of aggregation of AlPcS$_4$ was studied previously [30] and found to be 37% at a concentration of 5×10^{-7} mol l^{-1}. For ZnPcS$_{mix}$, SnPcS$_{mix}$ and SiPcS$_{mix}$ we have estimated the degrees of aggregation at a concentration of

5×10^{-6} mol l^{-1}, used for sensitised oxidation of polychlorophenols. The increase in the Q band intensity in the presence of cationic surfactant cetyltrimethylammonium chloride was used for the assessment of dye aggregation. Degrees of aggregation, obtained by using this approach were about 5% for SiPcS$_{mix}$, 30% for ZnPcS$_{mix}$ and 21% for SnPcS$_{mix}$ complexes. Thus, the degrees of aggregation of MPcS$_{mix}$ sensitisers in our experiments did not exceed 30%.

Comparative photoactivity of sulphonated MPc complexes as sensitisers towards singlet oxygen formation and photo-oxidation of the chlorophenols was carried out in the absence of surfactants. Singlet oxygen quantum yields, determined in water at pH 7 and at a sensitiser concentration of 5×10^{-6} mol l^{-1}, are summarised in Table 1. The values for AlPcS$_4$, AlPcS$_{mix}$, were quite similar to the ones reported in literature at pH 7.4 [40]. The Φ_Δ for ZnPcS$_{mix}$ is lower than the known data for its monomeric form in organic media [22] due to partial aggregation in aqueous buffer solutions. The Φ_Δ values for SiPcS$_{mix}$ and SnPcS$_{mix}$ have not been reported before this work, and despite partial aggregation, SnPcS$_{mix}$ shows a high value (0.46).

3.2. Relative efficiency of sensitised oxidation of polychlorophenols

Fig. 2 shows the decrease, with time, of the concentration of TCP in the presence of the various MPc sensitisers at pH 7, during the excitation of sensitiser in the Q band. The experimental conditions were kept constant for all the sensitisers. In the absence of sensitiser

Table 1

Photosensitisation data for the TCP and PCP transformation in the presence of the various water-soluble, sulphonated metallophthalocyanine sensitisers (sens) under wavelength, $\lambda = 670$ nm irradiation ([TCP], [PCP] $= 7 \times 10^{-5}$ mol l^{-1})

Sensitisers	Q band λ_{max} (nm)	Φ_Δ[a]	TCP (7×10^{-5} mol l^{-1})		PCP (7×10^{-5} mol l^{-1})	
			$\Phi_{TCP}/10^3$	% of sensitiser degradation[b]	$\Phi_{PCP}/10^3$	% of sensitiser degradation[b]
AlPcS$_{mix}$	675	0.38	11.80	<1	6.80	16
AlPcS$_4$	675	0.18	5.40	<1	4.50	8
ZnPcS$_{mix}$	667	0.48	10.50	21	3.92	32
SiPcS$_{mix}$	672	0.16	3.43	0	4.11	4
SnPcS$_{mix}$	691	0.46	<2.00	38	<2.00	46

[a] Singlet oxygen quantum yields were determined in water at concentration of sensitiser about 5×10^{-6} mol l^{-1} and in the absence of detergent.
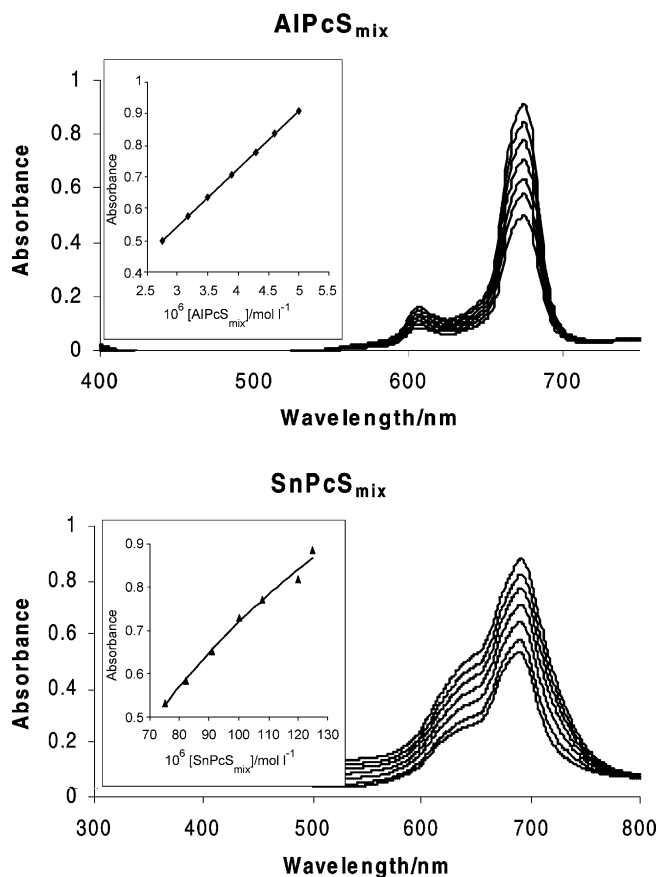
[b] After 270 s of irradiation.

Fig. 1. Variation of absorbance with concentration and Beer's law behaviour for $AlPcS_{mix}$ and $SnPcS_{mix}$ pH 7 buffer.

no transformation of chlorophenol was observed following photolysis in the visible region. The quantum yields for TCP (Φ_{TCP}) and PCP (Φ_{PCP}) phototransformation, sensitised by sulphonated MPcs, were calculated and are listed in Table 1. Values of Φ_{TCP} depend on the sensitiser as follows: $AlPcS_{mix} > ZnPcS_{mix} > AlPcS_4 > SiPcS_{mix} > SnPcS_{mix}$ (Fig. 2). For PCP, the values of Φ_{PCP} depended on the sensitisers as follows: $AlPcS_{mix} > AlPcS_4 > SiPcS_{mix} \approx ZnPcS_{mix} > SnPcS_{mix}$, a trend slightly different from the one for Φ_{TCP}, since $ZnPcS_{mix}$ is replaced by $AlPcS_4$ in the case of PCP. The results presented in Table 1 show that the trend in photosensitiser activity towards polychlorophenol oxidation differ from the trend in their Φ_Δ values. Apart from the efficiency in $^1O_2$ sensitisation, there are other factors that influence the phototransformation of chlorophenols. One of the important
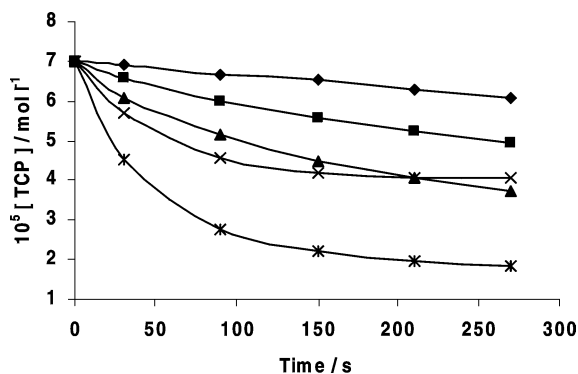

Fig. 2. Kinetic curves for the photo-oxidation of TCP, sensitised by $SnPcS_{mix}$ (◆), $SiPcS_{mix}$ (■), $AlPcS_4$ (▲), $ZnPcS_{mix}$ (×) and $AlPcS_{mix}$ (∗). pH = 7.

factors is the photostability of photosensitiser. From this point of view and considering TCP transformation, the highest activity which is observed for AlPcS$_{mix}$ can be accounted for by its high level of singlet oxygen quantum yield and photostability in aqueous solution. The complex ZnPcS$_{mix}$ is less active despite highest efficiency of $^1O_2$ generation ($\Phi_\Delta = 0.48$), and this behaviour may be caused by its enhanced photodegradation during the course of photolysis (21% photodegradation after 270 s of illumination, Table 1). The activities of the photostable AlPcS$_4$ and SiPcS$_{mix}$ are in accordance with their low Φ_Δ values. SnPcS$_{mix}$ is virtually inactive towards the phototransformation of the substrates even though it showed high a Φ_Δ value. This complex is a characteristic example of an extremely unstable photosensitiser. The slightly different trends in activity observed for photosensitisers towards TCP and PCP oxidation, i.e. the replacement of ZnPcS$_{mix}$ by AlPcS$_4$ for PCP when compared to TCP, can be attributed to the influence of increased rate of sensitiser's degradation in the presence of PCP when compared to TCP. The data shown in Table 1 and the kinetic curves for the photobleaching of the photosensitisers, presented in Fig. 3 for PCP, demonstrate that Si and Al complexes are the most stable of all the sensitisers studied.

3.3. pH dependence

Polychlorophenols are fairly acidic and dissociate in aqueous solutions (pK_a values of TCP and PCP are 6.2 and 4.7, respectively [1,5,41]). There are two
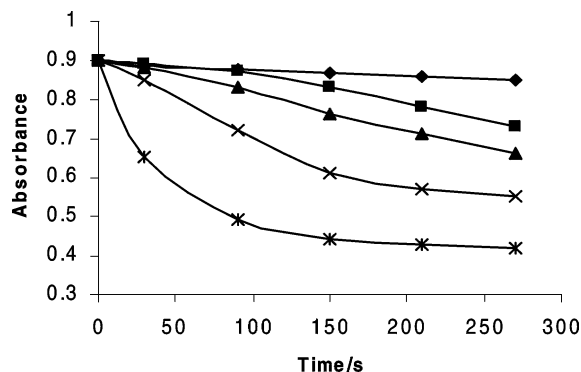
species with different properties which are in equilibrium in PCP or TCP solutions; these are the undissociated phenol (ArOH) and phenoxide ion (ArO$^-$). Since the equilibrium between these two forms is pH dependent, chemical transformations involving these compounds should be pH-dependent as well. We have observed pH dependence of the following photochemical processes: photosensitised degradation of polychlorophenol, formation of *p*-benzoquinone related photoproduct and photobleaching of sensitiser. The results obtained are discussed below.

The dependence on pH of Φ_{Subs} is shown in Fig. 4 for TCP, using AlPcS$_{mix}$ as sensitiser . This dependence is similar to that reported in literatures [11,41] and reflects insignificant contribution of the unionised form of polychlorophenols in their photo-oxidation. In accordance with the pK_a values, the rates and quantum yields of transformation of the chlorophenols increase from pH 6 with a levelling off at pH 8 for TCP and at pH 7 for PCP.

Fig. 5 represents spectral changes observed on photolysis of TCP and PCP in the presence of AlPcS$_{mix}$ at pH 7. The spectral changes show the decrease of PCP absorption peaks at 248 and 320 nm and formation of photoproduct with λ_{max} at 290 nm. The TCP peak at 312 nm decreased and a product peak was observed at 272 nm. These transformations proceed with clear isosbestic points, indicating substrate oxidation to the end product with negligible accumulation of intermediates. The products for the phototransformation of PCP and TCP were confirmed with HPLC studies as 2,3,5,6-tetrachloro-1,4-benzoquinone and 2,5-dichloro-1,4-benzoquinone, respectively. Further continuous photolysis at pH 7 lead to photo-oxidation of the primary products and the formation of new products (HPLC retention times of 5 min for TCP and 8.5 min for PCP, Fig. 6). The new products formed are most likely due to further dechlorination of the ring as has been reported before [11]. Photolysis of both TCP and PCP at pH 10 showed diffuse isosbestic points and broad maxima, indicating formation of complicated mixtures of photoproducts absorbing at the same wavelength region. The pH dependence of the relative yield (determined from HPLC traces) for the formation of 2,5-dichloro-1,4-benzoquinone (the photo-oxidation product of TCP) using AlPcS$_{mix}$ as a photosensitiser is shown in Fig. 4. Maximum selectivity and yield of benzoquinone derivative as

Fig. 3. Kinetic curves of photodegradation of SiPcS$_{mix}$ (♦), AlPcS$_4$ (■), AlPcS$_{mix}$ (▲), ZnPcS$_{mix}$ (×) and SnPcS$_{mix}$ (∗) in the presence of PCP (7×10^{-5} mol l^{-1}). pH = 7.
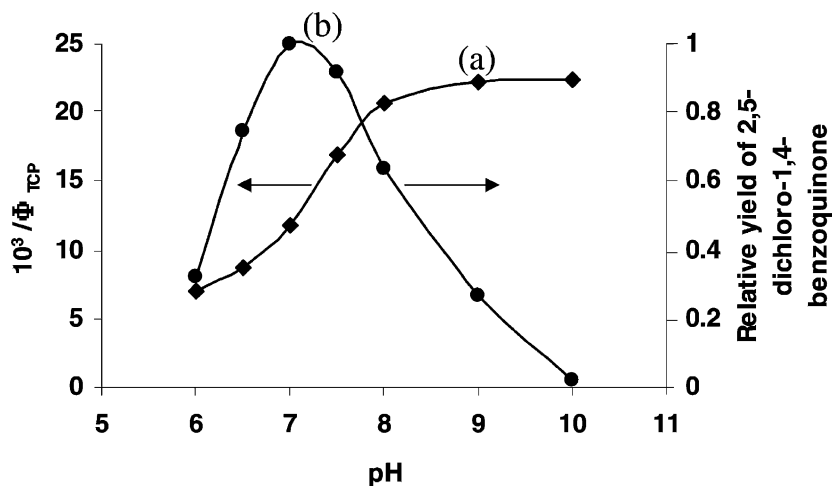
Fig. 4. pH dependence of: (a) quantum yields for photo-oxidation of TCP (7×10^{-5} mol l^{-1}) and (b) relative yield of 2,5-dichloro-1,4-benzoquinone. AlPcS$_{mix}$ as sensitiser.
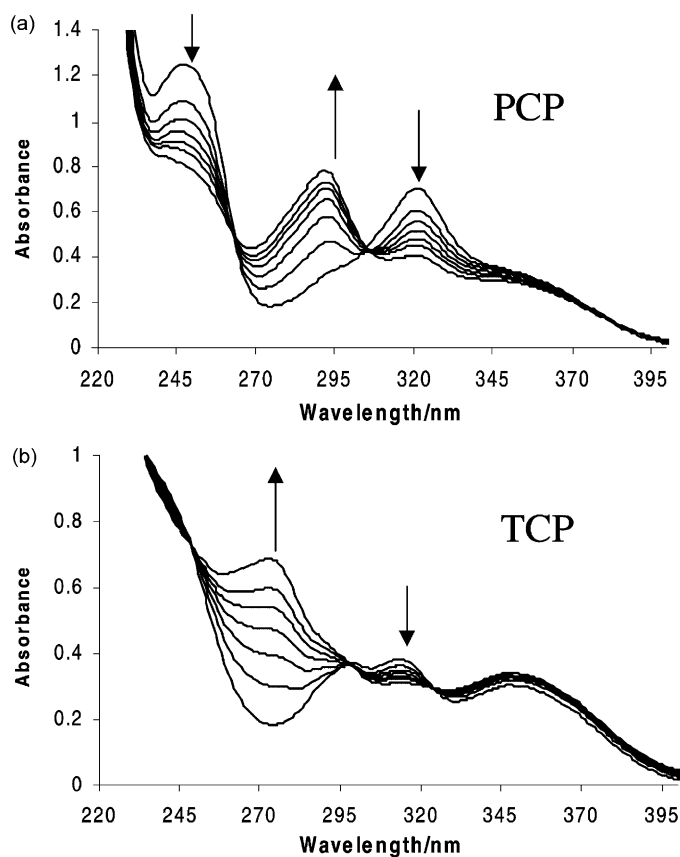

Fig. 5. Electronic absorption spectral changes observed during photolysis of 7×10^{-5} mol l^{-1} solutions of: (a) PCP and (b) TCP in the presence of AlPcSmix ($\sim 5 \times 10^{-6}$ mol l^{-1}). pH = 7.
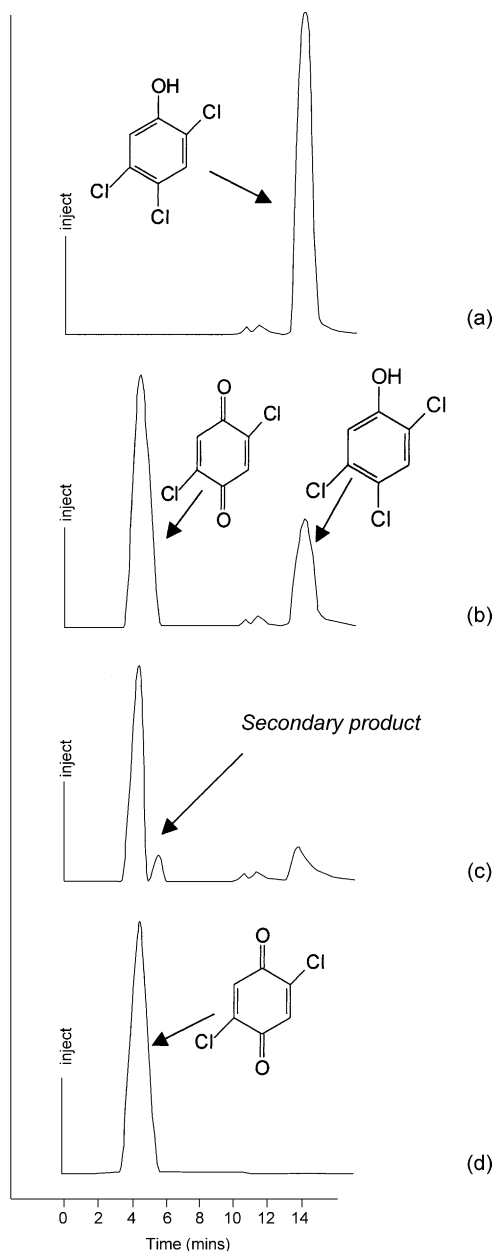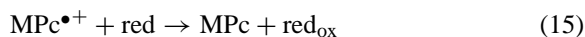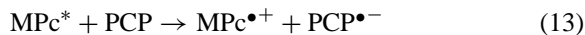
Fig. 6. HPLC traces for the photo-oxidation of TCP ($3.5 \times 10^{-5}\,\mathrm{mol\,l^{-1}}$): (a) before photolysis and (b) after 3.5 min photolysis and (c) after 7 min photolysis, in the presence of AlPcS$_{mix}$ sensitiser (d) corresponds to the HPLC trace for the standard 2,5-dichloro-1,4-benzoquinone. pH 7 conditions.

a photoproduct was obtained at pH 7 for both PCP and TCP. Thus, the oxidation products of the polychlorophenols are pH-dependent and at high pH, an increase in the rate of further oxidation of primary benzoquinone derivatives is possible.

Finally, the photobleaching of the sensitiser during sensitised polychlorophenol oxidation is also pH dependent. After 270 s of illumination of a water solution of AlPcS$_{mix}$ containing PCP as a substrate, the extent of sensitiser photobleaching was found to be 16% at pH 7 and 6% at pH 10. In the absence of PCP no photobleaching of AlPcS$_{mix}$ was observed. This finding indicates that there is another pathway, probably Type I electron transfer process, in addition to $^{1}O_2$ mediated oxidation of polychlorophenol. Our studies of the dependence AlPcS$_{mix}$ photobleaching on the nature of the substrate have shown that photodegradation of the photosensitiser is most pronounced for PCP, decreasing for TCP and being negligible for p-chlorophenol and phenol. This suggests that electron-acceptor properties of phenols are of main importance in the photobleaching process, electron transfer being directed from the excited sensitiser to polychlorophenol. In agreement with this mechanism is the decrease in the photobleaching rate from pH 7 to 10, which suggests that undissociated PCP is a more efficient electron acceptor than the phenoxide anion. So electron transfer from excited sensitiser to polychlorophenols (Eq. (13)) may be considered as a primary step in the Pc photobleaching process. It was found that addition of reductants stabilised the sensitiser, probably due to recovery of sensitiser from it semioxidised form (Eq. (15)). Addition of 5% (v/v) of ethanol as a reductant resulted in 60% inhibition of AlPcS$_{mix}$ photodegradation in the presence of PCP. No effect of ethanol on the rate of PCP transformation was observed during this experiment. Similar results were observed for other reductants such as sodium borohydride. Based on the results obtained, the mechanism of photosensitiser photodegradation may be represented by the following sequence of reactions (13) and (14):

$$\mathrm{MPc}^* + \mathrm{PCP} \rightarrow \mathrm{MPc}^{\bullet+} + \mathrm{PCP}^{\bullet-} \qquad (13)$$

$$\mathrm{MPc}^{\bullet+} \rightarrow \mathrm{products} \qquad (14)$$

$$\mathrm{MPc}^{\bullet+} + \mathrm{red} \rightarrow \mathrm{MPc} + \mathrm{red_{ox}} \qquad (15)$$

where red is the reductant.

The fate of PCP$^{\bullet-}$ anion radical will be discussed below.

3.4. Efficiency of Type I and Type II processes

As stated above, at pH 7 polychlorophenols are oxidised to give 1,4-benzoquinone derivatives with high selectivity. We studied some aspects of the formation of these products by following their appearance spectrophotometrically at 272 and 290 nm for TCP and PCP, respectively, using AlPcS$_{mix}$ since it is the most active sensitiser used in this work.

Although there has been no study yet on the photo-oxidation of the polychlorophenols using the water-soluble sulphonated metallophthalocyanines, singlet oxygen-mediated photo-oxidation of chlorophenols (Type II mechanism) is an established process [11,22,41]. In order to determine the relative contribution of the Type I radical pathway for the case when sulphonated metallophthalocyanines are employed as sensitisers, experiments were carried out in a solution containing the singlet oxygen quencher, sodium azide (NaN$_3$), in the presence of AlPcS$_{mix}$. The data presented in Fig. 7 show that addition of NaN$_3$ ($2.5 \times 10^{-3} \, \text{mol l}^{-1}$) to $7.0 \times 10^{-5} \, \text{mol l}^{-1}$ solution of PCP, containing AlPcS$_{mix}$, resulted in 76% inhibition of phototransformation of PCP. The same experiments with TCP gave inhibition of Type II

mechanism up to 83%. The extent of inhibition of phototransformation was not changed by increasing the concentration of NaN$_3$ from 2.5×10^{-3} to $5 \times 10^{-3} \, \text{mol l}^{-1}$, thus confirming the full quenching of singlet oxygen in these experiments. The above results show the dominance of the Type II process with about 17% for TCP and 24% for PCP of the Type I process under our experimental conditions. It also suggests the greater participation of PCP to Type I process than TCP. The negative inductive effects of halogen substituents in aromatic rings results in electron-withdrawing effects from the benzene nucleus, deactivating it for an electrophilic attack by singlet oxygen and hence decreasing the contribution of Type II pathway as the number of halogen substituents increase.

With sulphonated methallophthalocyanines as sensitisers and phenols as substrates for Type I mechanism, the primary electron transfer from ionised substrate to the sensitiser in its excited state has been reported [42]. The formation of anion radical AlPcS$_{mix}$$^{\bullet-}$ in the presence of phenol was reported before [43] and the formation of this anion may be considered as confirmation of electron transfer from the substrate to the sensitiser. We have no evidence to enable us to reject this generally accepted process for phenols. However, in the case of polychlorophenols, due to electron-withdrawing effect of chlorine substituents the electron-donating ability of substrate is reduced and electron-acceptor ability is increased substantially. So it is not surprising, that the results obtained provide evidence for opposite direction of electron transfer — from excited sensitiser to polychlorophenol in unionised form (see above and Eq. (13)). This electron transfer leads to formation of polychlorophenol anion radical and sensitiser cation radical as primary species for Type I mechanism. Scheme 1 shows the transformation of the radical anion of polychlorophenol to *p*-benzoquinone derivative, based on reductive dechlorination (reductive defluorination is established process [43]) may be suggested.

It is worth noting that oxidation of ionised PCP by singlet oxygen remains as the main pathway, resulting in the formation 1,4-benzoquinone derivative. The interaction of PCP radical anion with oxygen may result in the recovery of the substrate and the simultaneous production of the superoxide. In the
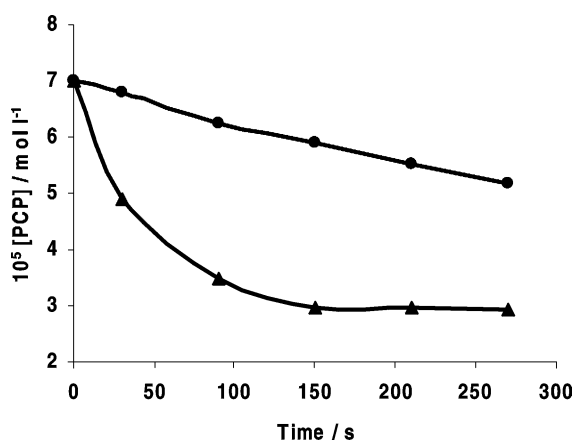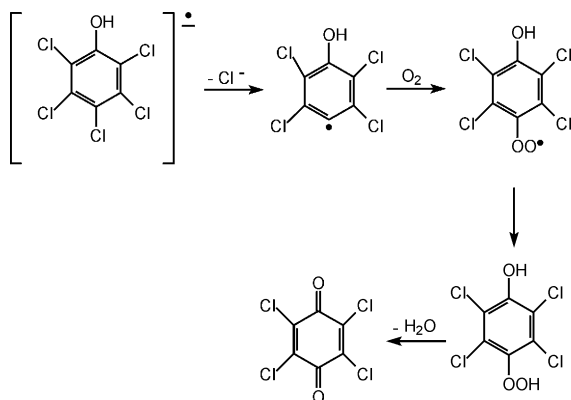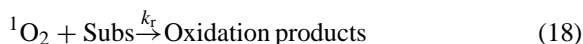

Fig. 7. Effect of the addition of singlet oxygen quencher, NaN$_3$ ($2.5 \times 10^{-3} \, \text{mol l}^{-1}$), on the rate of phototransformation of PCP (starting concentration = $7 \times 10^{-5} \, \text{mol l}^{-1}$), sensitised by AlPcS$_{mix}$. Without NaN$_3$ (▲); with NaN$_3$ (●).

Scheme 1.

Fig. 8. Plots of: (a) $1/\Phi_{TCP}$ vs. $1/[TCP]$ and (b) $1/\Phi_{PCP}$ vs. $1/[PCP]$ for the phototransformation of TCP and PCP, in the presence of AlPcS$_{mix}$ and AlPcS$_4$. pH = 7.

series of substrates from phenol to *p*-chlorophenol, TCP and PCP we have an increase in Type I mechanism which involves electron transfer from the excited sensitiser to the unionised form of the phenol derivative.

Let us consider competitive and dominating Type II pathway. The reaction of singlet oxygen proceeds through the following processes:

$$^1O_2 \xrightarrow{k_d} {}^3O_2 \tag{16}$$

$$^1O_2 + \text{Subs} \xrightarrow{k_q} {}^3O_2 + \text{Subs} \tag{17}$$

$$^1O_2 + \text{Subs} \xrightarrow{k_r} \text{Oxidation products} \tag{18}$$

where k_d, k_q and k_r are the rate constants for the decay of $^1O_2$ in water, "physical" quenching of $^1O_2$ by the substrates (TCP and PCP) and formation of oxidation products, respectively.

The quantum yield for the transformation of the polychlorophenols (Φ_{Subs}) is given by

$$\Phi_{Subs} = \Phi_\Delta \frac{k_r[\text{Subs}]}{k_d + (k_r + k_q)[\text{Subs}]} \tag{19}$$

Rewriting Eq. (19) and rearranging gives Eq. (20):

$$\frac{1}{\Phi_{Subs}} = \frac{1}{\Phi_\Delta}\left(\frac{k_r + k_q}{k_r} + \frac{k_d}{k_r[\text{Subs}]}\right) \tag{20}$$

The overall quantum yields Φ_{Subs} involve contributions from both Type I and Type II (dominating) reactions. Nevertheless, to determine limiting values of the qua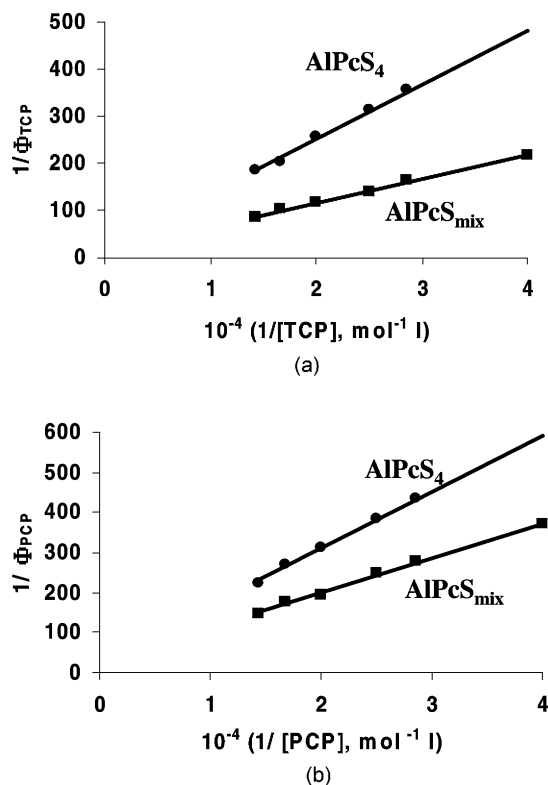ntum yields, Φ_∞, for phototransformation of the chlorophenols we have plotted $1/\Phi_{Subs}$ vs. $1/[\text{subs}]$ for TCP and PCP in the concentrations ranging from 2.5×10^{-5} to $7.0 \times 10^{-5} \, \text{mol}\,l^{-1}$ and in the presence of the efficient and stable sensitisers, AlPcS$_{mix}$ and AlPcS$_4$, under the pH 7 conditions. Fig. 8 shows that the plots $1/\Phi_{Subs}$ vs. $1/[\text{subs}]$ obey a linear relationship. Values Φ_∞ are equal to inversed *y*-intercepts of these plots and were found to be for TCP: $\Phi_\infty = 0.048 \pm 0.015$ with AlPcS$_4$ and 0.07 ± 0.015 with AlPcS$_{mix}$ and for PCP: $\Phi_\infty = 0.032 \pm 0.005$ and 0.031 ± 0.005 with AlPcS$_4$ and AlPcS$_{mix}$, respectively. Hence even the overall limiting quantum yields, consisting of radical and singlet oxygen contributions, are significantly lower than the Φ_Δ of sensitisers (Table 1), indicating that not all the singlet oxygen is involved in the chemical reaction with polychlorophenol. Thus, the physical quenching of the $^1O_2$ by the phenolate ions competes strongly with the chemical reaction.

Neglecting the minor Type I contribution to Φ_{Subs} we have compared the efficiencies of the reactive and physical quenching of $^1O_2$ for TCP and PCP by calculating $(k_r + k_q)/k_r$ ratio from y-intercepts of the plots shown in Fig. 8. With Φ_Δ from Table 1 the ratio $(k_r + k_q)/k_r$ of the phenolate ion was obtained (with an error of $\pm 20\%$) to be about 5 for TCP and 9 for PCP, implying that most of the $^1O_2$ is scavenged by a quenching process. Simply put, PCP for example, can deactivate about nine molecules of $^1O_2$ before being destroyed. This situation is similar to the one obtained for other phenols which quench $^1O_2$ more rapidly than they react with it [44].

From slopes of plots on Fig. 8 (at pH 7) we have calculated k_r, the constant of chemical quenching of $^1O_2$ by TCP and PCP. For TCP the slopes obtained were $0.011 \pm 0.003 \, \text{mol} \, 1^{-1}$ for AlPcS$_4$ and $0.005 \pm 0.001 \, \text{mol} \, 1^{-1}$ for AlPcS$_{\text{mix}}$. For PCP the slopes were $0.014 \pm 0.002 \, \text{mol} \, 1^{-1}$ for AlPcS$_4$ and $0.0085 \pm 0.001 \, \text{mol} \, 1^{-1}$ for AlPcS$_{\text{mix}}$. According to Eq. (20) these slopes 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 [45]). Using values of Φ_Δ from Table 1, the rate constants k_r calculated for the chlorophenolate ions of the chlorophenols were: for TCP; $(1.5 \pm 0.2) \times 10^8 \, \text{mol}^{-1} \, 1 \, \text{s}^{-1}$ for the AlPcS$_4$ and $(1.6 \pm 0.2) \times 10^8 \, \text{mol}^{-1} \, 1 \, \text{s}^{-1}$ for AlPcS$_{\text{mix}}$, while for PCP we had $(1.2 \pm 0.2) \times 10^8 \, \text{mol}^{-1} \, 1 \, \text{s}^{-1}$ for AlPcS$_4$ and $(1.0 \pm 0.2) \times 10^8 \, \text{mol}^{-1} \, 1 \, \text{s}^{-1}$ for AlPcS$_{\text{mix}}$. The reported k_r values for TCP and PCP are within these ranges [41]. The total rate constants $(k_r + k_q)$ were determined from the intercepts of the plots shown in Fig. 9 (i.e. $k_q + k_r/\Phi_\Delta k_r$). The average values obtained for the deprotonated substrates were $(k_r + k_q) = (7.5 \pm 1.5) \times 10^8 \, \text{mol}^{-1} \, 1 \, \text{s}^{-1}$ for TCP and $(10 \pm 2) \times 10^8 \, \text{mol}^{-1} \, 1 \, \text{s}^{-1}$ for PCP. The low solubility of TCP and PCP in acid media did not permit for the effective estimation of the rate constants, $(k_r + k_q)$ for the protonated forms of these substrates.

4. Conclusion

Sulphonated metallophthalocyanines have been proved to be efficient sensitisers of singlet oxygen. Sulphonation of Zn, Al, Si and Sn complexes of Pc leads to a mixture of isomers and differently substituted compounds, which are water-soluble and efficiently sensitise the formation of singlet oxygen in dilute solutions. The use of sulphonated metallophthalocyanines as sensitisers for the photo-oxidative degradation of polychlorophenols shows that the efficiency of the process depends not only on the singlet oxygen quantum yield of sensitiser, but also on its stability. Thus, the new compound, SnPcS$_{\text{mix}}$, turned out to have high singlet oxygen quantum yield, but due to low photostability, the efficiency of this photosensitiser for the oxidation of polychlorophenols is low, hence showing the importance of the photostability factor.

Polychlorophenols are known to be stable towards oxidation and this conclusion was confirmed in present work for sensitised photo-oxidation by singlet oxygen. Therefore, the study of the dependence of the photo-oxidation rate of the substrate depends on a number of factors, and it is important to establish conditions of the highest degradation efficiency. Results obtained show that the majority of processes (rates of polychlorophenol oxidation and of sensitiser photodegradation, and the nature of photoproducts) depend on pH. Hence, substrate ionisation is of crucial importance for any photophysical and photochemical step in the system under investigation.

In general, efficiency of the oxidation of phenolates of polychlorophenol, mediated by singlet oxygen, is lower in comparison with unsubstituted phenol and less chlorinated phenols due to lower constants of chemical reaction and extensive physical quenching of singlet oxygen by substrate. Considering stepwise dechlorination in the course of the process of increasing rates of chemical interaction of substrate with singlet oxygen, it may be suggested, that further oxidation to give final mineralisation of chlorosubstituted phenols should proceed in milder conditions.

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