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# Photochemically induced electron transfer between sulfur dioxide and tin(IV) mono- and di-phthalocyanines

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## Abstract

Photolysis, using radiation from a tungsten lamp, of tin diphthalocyanine ($Pc_2Sn(IV)$) in dichloromethane containing $SO_2$ results in the one-electron oxidation of this species to $[Pc(-2)Sn(IV)Pc(-1)]^+$. The relative quantum yields for the formation of the oxidized species were in the order of $10^{-3}$. The one-electron oxidized complex was also formed when $Pc_2Sn$ was photolysed in an acetonitrile/dichloromethane solvent mixture. Photolysis of the monomeric $(L)_2Sn(IV)Pc$ ($L = OH^-, Cl^-, Br^-$ and $F^-$) in pyridine and in the presence of $SO_2$ resulted in the reduction of these species to $(L)_2Sn(IV)Pc(-3)]^-$ with quantum yields in the order of $10^{-2}$.

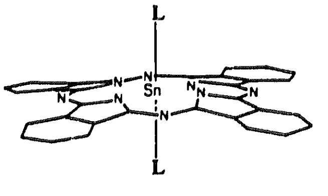
*Keywords:* Photolysis; Photochemically induced electron transfer; Sulphur dioxide; Tin diphthalocyanine

## 1. Introduction

Metallophthalocyanine (MPc, Pc(-2) = phthalocyanine dianion) compounds have attracted a great deal of attention because of their unique properties such as photoconductivity, electrochroism and a variety of catalytic functions [1,2]. The possible use of these complexes as photosensitizers in photodynamic therapy [3–5] and in artificial solar energy devices [6] has been investigated. Metallophthalocyanines are inexpensive and readily available catalysts with a potential for the oxidative degradation of pollutants such as sulfur dioxide and chlorinated aromatic compounds [7,8].

The pathway followed by photochemical reactions of phthalocyanines depends on the specific excited state involved [9]. Excitation into the Q band region populates the lowest-lying triplet excited states, $^3\pi\pi^*$, which may be quenched by electron transfer reactions with electron acceptors or donors [7,9–11]. Visible region photolysis of MPc or porphyrin complexes in the presence of alkyl halides results in the electron transfer from the excited MPc or porphyrin species to the alkyl halide with the formation of $\pi$ cation radical species [12,13].

MPc complexes coordinate axially to many small molecules [14]. The coordination of sulfur containing compounds to MPc species, followed by electron transfer reactions, could provide a useful method for converting harmful sulfur compounds to their less harmful analogues. The oxidation of sulfur dioxide to sulfur(IV) species is of industrial importance. There have been reports on the electrocatalytic oxidation of $SO_2$ by cobalt(II) (CoPc) and iron(II) (FePc) phthalocyanines, in acid media [15,16]. We briefly reported on the photoassisted electron transfer between tin(IV) phthalocyanines and $SO_2$ in our earlier communication [7]. We report in this article on the effects of axial ligands on the quantum yields for the photoreduction of tin(IV) phthalocyanine, $(L)_2Sn(IV)Pc$, complexes ($L = OH^-, Cl^-, Br^-$ and $F^-$, structure I) in the presence of $SO_2$ and in pyridine.



I = $SnPc(L)_2$ ($L = OH^-, F^-, Cl^-$ and $Br^-$)

Although a number of bisphthalocyanines have been synthesized and characterized, their photochemical reactivity has not been extensively investigated. Photolysis of the lanthanide bisphthalocyanine ($Pc_2Ln$) complexes in dichloromethane/acetonitrile solvent mixture resulted in the ring oxidation of these species [17]. Flash photolysis of tin(IV) bisphthalocyanine ($Pc_2Sn$) at wavelengths in the Q band led to the formation of the lowest lying ligand-centred, $^3\pi\pi^*$

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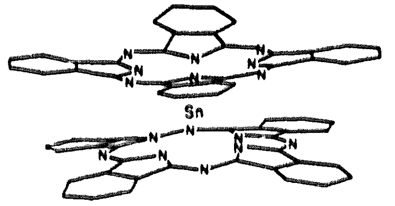
states, whose decay led to the dissociation of the $Pc_2Sn$ and the formation of monomeric products such as Sn(IV)Pc and Sn(II)Pc species [9,10]. The unimolecular redox reactions that are typical of $^3\pi\pi^*$ states of phthalocyanines were not observed. We have recently reported on the electrochemical properties of $Pc_2Sn$ species [18], and in this article, electronic absorption spectra are used in characterising the products of the continuous photolysis of $Pc_2Sn$, structure II, in dichloromethane and in the presence of $SO_2$. The photochemical reactions of these complexes in the presence of $SO_2$ are compared with the observations for the monomeric phthalocyanine complexes.



II = $Pc_2Sn$

## 2. Experimental

### 2.1. Materials

(Phthalocyaninato)tin(IV) complexes, $(L)_2Sn(IV)Pc$ ($L = OH^-$, $F^-$, $Cl^-$ and $Br^-$) were prepared by following literature procedures [19–21]. $(Cl)_2Sn(IV)Pc$: IR (KBr disc): $\nu$(Sn–Cl) 295 $cm^{-1}$. UV/Vis in pyridine: $\lambda_{max}$ (log $\epsilon$) = 696 (5.0), 664(4.2), 626(4.3), 336 (4.6) nm. $(OH)_2Sn(IV)Pc$: IR (KBr disc): $\nu$(Sn–OH) 560 $cm^{-1}$. UV/Vis in pyridine: $\lambda_{max}$ (log $\epsilon$) = 698 (5.1), 661(4.3), 631(4.4), 358(4.7) nm. $(Br)_2Sn(IV)Pc$: IR (KBr disc): no $\nu$(Sn–Br) was observed within the instrumental range. UV/Vis in pyridine: $\lambda_{max}$ (log $\epsilon$) = 698 (5.2), 661(4.6), 629(4.4), 359(4.8) nm. $(F)_2Sn(IV)Pc$: IR (KBr disc): $\nu$(Sn–F) 527 $cm^{-1}$. UV/Vis in pyridine: $\lambda_{max}$ (log $\epsilon$) = 695 (5.2), 628(4.4), 375(4.6) nm.

Tin(IV) bisphthalocyanine ($Pc_2Sn$) was prepared by the procedure of Ohno et al. [22] and characterized as described before [18]. UV/visible in $CH_2Cl_2$: $\lambda_{max}$ (log $\epsilon$) = 337(5.08), 568(4.50), 624(5.00) and 779(4.60) nm. The extinction coefficient for the oxidized, $[Pc(-1)Sn(IV)Pc(-2)]^+$, species was estimated from the absorption spectra to be 180 000 $dm^3$ $mol^{-1}$ $cm^{-1}$. This value was used in the calculations of the quantum yields. The electrochemistry of the $Pc_2Sn$ complex and the characterization of its redox products have been reported [18].

All solvents employed in this work were freshly distilled. $SO_2$ gas was purchased from Messer Griesheim.

### 2.2. Electrochemical methods

Cyclic voltammetry data for the $(L)_2Sn(IV)Pc$ complexes dissolved in pyridine and in the presence of tetraethylammonium perchlorate [TEAP] electrolyte, were collected with the Bio Analytical Services (BAS) CV-50W Voltammetric Analyser. The potentials were referenced internally to the ferrocenium/ferrocene couple using procedures described in detail before [11,18]. Concentrations of the phthalocyanines of approximately $10^{-4}$ M were employed for cyclic voltammetry.

### 2.3. Photochemical methods

Solutions of $Pc_2Sn(IV)$ in dichloromethane or $(L)_2Sn(IV)Pc$ in pyridine, were added to 1 cm pathlength UV/vis cell (fitted with a stopper) and were degassed. Sulfur dioxide was dissolved in dichloromethane or pyridine and allowed to equilibrate, and a known volume of the $SO_2$ solution or acetonitrile was then added to the cell and the solution degassed again. The solutions were then irradiated with a 50 watt tungsten lamp, a 590 nm filter was used for irradiations into the Q band region. Changes in the concentration of the $Pc_2Sn(IV)$ or $(L)_2Sn(IV)Pc$ with photolysis time were monitored spectrophotometrically. Sulfur dioxide concentrations were determined by treatment with standardized iodine and titration with aqueous sodium thiosulphate. $SO_2$ concentrations ranging from 0.001–8.0 mol $dm^{-3}$ were employed. Ferric oxalate actinometry [23] was used to estimate the intensity of the radiation incident on the cell, $I_0 = 1.1 \times 10^{-8}$ einstein $s^{-1}$.

Electronic absorption spectra were recorded with a Cary 1E UV-VIS spectrophotometer. Infra-red spectra (KBr discs) were collected with a Perkin Elmer Model 180 IR spectrometer.

## 3. Results and discussion

### 3.1. Photolysis of $Pc_2Sn$ in the presence of sulfur dioxide

Electronic absorption spectra have been used successfully in characterising the various cationic and anionic species of metal bisphthalocyanine complexes [2,24]. The spectra of the neutral Pc(-2)Sn(IV)Pc(-2) species shows an extensive splitting of the Q band and an increased intensity in the Soret band when compared with the spectra of the monomeric MPc complexes. The Q band splitting is due to the coupling between the phthalocyanine rings. Electrochemical studies have shown that the one-electron oxidation of the blue Pc(-2)Sn(IV)Pc(-2) gives the green $[Pc(-1)Sn(IV)Pc(-2)]^+$ species [18], the spectra of these complexes are typical of Pc(-2)MPc(-2) and Pc(-1)MPc(-2) complexes, respectively [2]. We use electronic absorption spectra to characterize the products of the photolysis of $Pc_2Sn$. The spectra of the photolysis products are compared with the spectra of the electrochemically generated oxidation products.

Fig. 1 shows the absorption spectral changes observed when solutions of $Pc_2Sn$ in $CH_2Cl_2$ containing $SO_2$ were

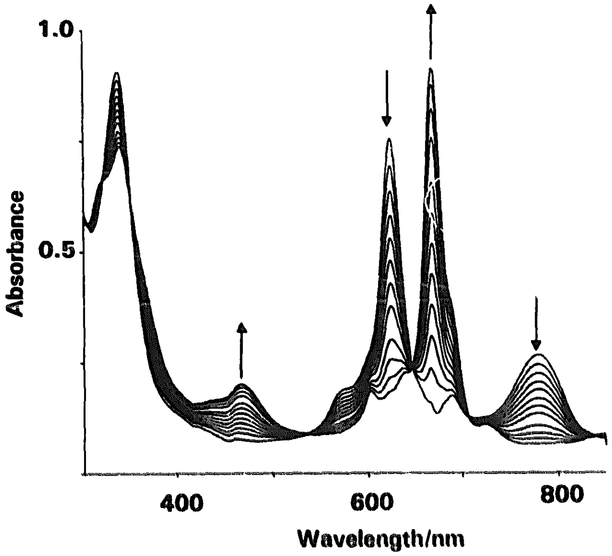


Fig. 1. Absorption spectral changes observed during the photolysis of $Pc_2Sn$ in $CH_2Cl_2$ containing $SO_2$, using unfiltered radiation from the tungsten lamp, $I_0 = 1.1 \times 10^{-8}$ einstein $s^{-1}$. $[Pc_2Sn]_0 = 7.5 \times 10^{-6}$ and $[SO_2] = 0.006$ mol $dm^{-3}$.

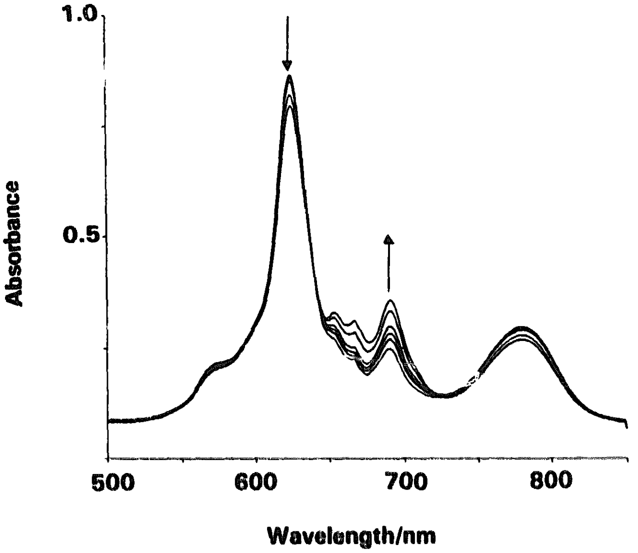


Fig. 2. Absorption-spectral changes observed during the photolysis of $Pc_2Sn$ in $CH_2Cl_2$ containing $SO_2$, with irradiation light of $\lambda > 590$ nm. $[Pc_2Sn]_0 = 8.3 \times 10^{-6}$ and $[SO_2] = 0.008$ mol $dm^{-3}$.

photolysed with the unfiltered radiation from the tungsten lamp. The original bands in the Q band region located at 573, 624, 692 and 779 nm decrease in intensity and three new bands are formed isosbestically at 669, 603 and 470 nm. Another absorption band is observed as a shoulder at 691 nm. The color of the solution goes from blue to green during photolysis. Except for the absorption band at 691 nm, the spectral changes shown in Fig. 1 are similar to the changes observed on one-electron oxidation of $Pc_2Sn$ to $[Pc(-1)Sn(IV)Pc(-2)]^+$ by bulk electrolysis [18]. The absorption band located at 470 nm is characteristic of the transition into the semi-occupied molecular orbital (SOMO) level in $[Pc(-1)Sn(IV)Pc(-2)]^+$ complexes [25], absorption bands in this region are associated with the formation of $\pi$ cation radical species in phthalocyanine complexes. The absorption bands for the electrochemically oxidized species were observed at 669, 604 and 471 nm [18]. The final product on photolysis of $Pc_2Sn$ in the presence of $SO_2$ is thus assigned to the one-electron oxidation product, $[Pc(-1)Sn(IV)Pc(-2)]^+$. The reduction of the oxidized species with sodium borohydride regenerated more than 80% of the original species. The nature of the 691 nm absorption band was investigated by photolysing $Pc_2Sn$ in $CH_2Cl_2$ containing $SO_2$ (0.008 mol $dm^{-3}$), at wavelengths of the Q band ($\lambda > 590$ nm). Spectral changes that occurred were very slow, Fig. 2, however, the observed changes show the 691 nm band as the prominent absorption. The absorption at 691 nm could not be identified with any of the electrochemically oxidized or reduced species of the $Pc_2Sn$ complex. Earlier studies on the flash photolysis of $Pc_2Sn$ in the visible region ($\lambda = 640$ nm) showed [10] that the decay of the excited $(^3\pi\pi^*)Pc_2Sn$ resulted in the formation of monomeric phthalocyanine products such as $[PcSn(IV)]^{2+}$ and Sn(II)Pc species, and a new absorption band located at 694 nm was assigned to the formation of these products. In comparison with the observations from the flash photolysis experiments [10], we assign the 691 nm band to the monomeric phthalocyanine species. The preceding discussion suggests that the monomeric species is formed as a result of the visible irradiation of the $Pc_2Sn$ species.

The formation of the $[Pc(-1)Sn(IV)Pc(-2)]^+$ species in the presence of $SO_2$ is attributed to the photoredox processes that occur following the excitation of the $Pc_2Sn$ species. Under our experimental conditions, we cannot rule out the possibility that $CH_2Cl_2$ is also excited by the ultra-violet radiation. However, earlier studies showed that the oxidized species was formed for the lanthanide bisphthalocyanine complexes on photolysis at wavelengths that were high enough to exclude the possibility of exciting $CH_2Cl_2$ [17]. The photooxidation of $Pc_2Sn$ in the presence of $SO_2$ was also observed when other solvents such as chlorobenzene, chloronaphthalene and nitrobenzene were employed, hence suggesting that the $SO_2$ is the quencher of the excited state. The quantum yields for the formation of the $[Pc(-1)Sn(IV)Pc(-2)]^+$ species were relatively low but increased with the increase in the concentration of $SO_2$, Fig. 3(a), confirming the involvement of $SO_2$ as a quencher in these photoredox reaction. The quantum yields for the formation of the $[Pc(-1)Sn(IV)Pc(-2)]^+$ species in the presence of non-chlorinated solvents, e.g. nitrobenzene, were also low and were of the order of $10^{-4}$. We suggest the following mechanism for the electron transfer quenching reaction of the excited $Pc_2Sn$ by $SO_2$:

$$\mathrm{Pc(-2)SnPc(-2)} \overset{h\nu}{\rightleftharpoons} {}^*[\mathrm{Pc(-2)SnPc(-2)}] \tag{1}$$

$$ {}^*[\mathrm{Pc(-2)SnPc(-2)}] + \mathrm{SO_2} \xrightarrow{k_q} [\mathrm{Pc(-2)SnPc(-1)}]^+ + \mathrm{SO_2}^- \tag{2}$$

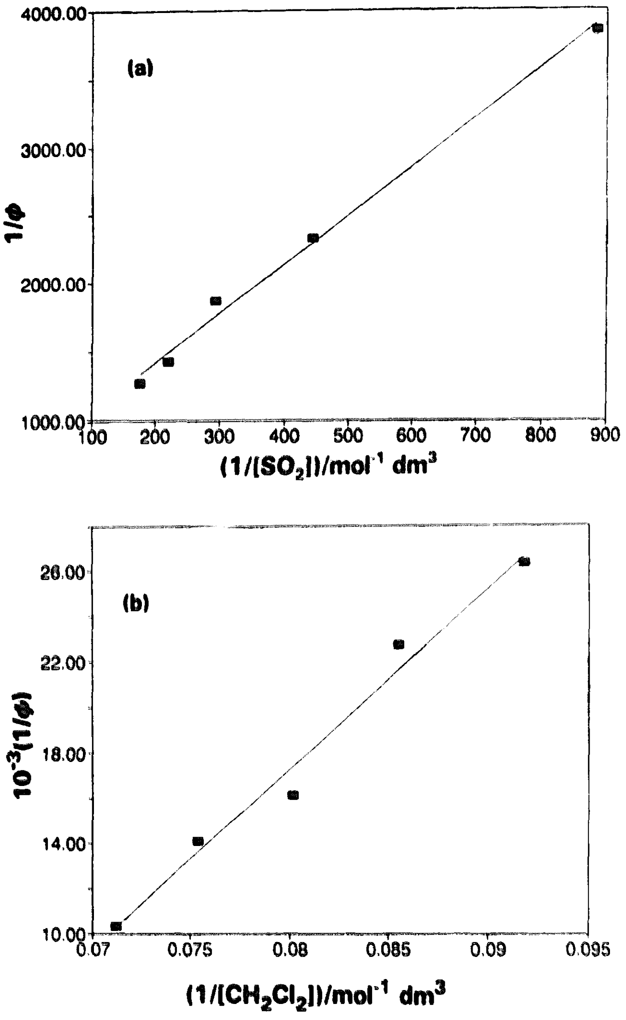


Fig. 3. Plots of reciprocal quantum yields for photooxidation of $Pc_2Sn$ against reciprocal concentration of (a) $SO_2$; $[Pc_2Sn] = 7.5 \times 10^{-6}$ mol dm$^{-3}$ and (b) $CH_2Cl_2$; $[Pc_2Sn] = 4.1 \times 10^{-6}$ mol dm$^{-3}$.

In general, irradiation of metallophthalocyanine dimers, $(MPc)_2$, at wavelengths in the Q band produce the same low-lying $^3\pi\pi^*$ of the monomers, but irradiation in the Soret region generally induces photoredox reactions of the type [9]:

$$(M(II)Pc)_2 \xrightarrow{h\nu} [M(I)Pc(-2)]^- + [M(III)Pc(-2)]^+ \quad (3)$$

$$(M(II)Pc)_2 \xrightarrow{h\nu} [M(II)Pc(-3)]^- + [M(II)Pc(-1)]^+ \quad (4)$$

From the discussion above and comparison with flash photolysis experiments, it is evident that the $(^3\pi\pi^*)Pc_2Sn$ state which is populated by excitation in the Q band, forms monomeric species on decay. The electron transfer quenching reactions observed on photolysis of $Pc_2Sn$ in $CH_2Cl_2$ and in the presence of $SO_2$ using unfiltered radiation from the tungsten lamp, Fig. 1, may thus be mediated by states other than the $(^3\pi\pi^*)Pc_2Sn$. Charge transfer states are most likely involved in these electron transfer reactions [10]. Population of charge transfer, $n\pi^*$, states, by ultra-violet irradiation of monomeric MPc complexes results in reactions that are mediated by hydrogen abstraction [9].

Previous studies have shown that photolysis (at $\lambda > 320$ nm) of lanthanide bisphthalocyanine, $Pc_2Ln$, in the presence of $CH_2Cl_2$ resulted in the electron transfer from the photoexcited $^*Pc_2Ln$ to the $CH_2Cl_2$ [17]. Electron transfer reactions between alkyl halides and porphyrins or monomeric phthalocyanines are known [12,13]. The role of dichloromethane in the photolytic reaction needs to be established. When solutions of $Pc_2Sn$ in $CH_2Cl_2$ in the absence of $SO_2$ were photolysed with unfiltered radiation from the tungsten lamp, spectral changes shown in Fig. 4 were observed. Two new bands are observed in the visible region at 669 and 691 nm. These absorption bands are at the same wavelength as the bands attributed to the oxidized $[Pc(-1)Sn(IV)Pc(-2)]^+$ (Fig. 1) and the monomeric $(L)_2SnPc$ species [9] (Fig. 2), respectively. The presence of the weak band associated with electronic transition into the SOMO level, located at 470 nm, confirms the formation of the one-electron oxidized, $[Pc(-1)Sn(IV)Pc(-2)]^+$, species. The formation of this species was very slow in the absence of $SO_2$. The quantum yield for the formation of the $[Pc(-1)Sn(IV)Pc(-2)]^+$ species, $\phi = 0.81 \times 10^{-4}$ was lower than the values observed for the formation of this species in $CH_2Cl_2$ and in the presence of $SO_2$, Fig. 3(a). No significant spectral changes were observed when solutions of $Pc_2Sn$ in $CH_2Cl_2$, in the absence of $SO_2$, were irradiated at wavelengths of the Q band, $\lambda > 590$ nm.

From the discussion above, it is possible that both $CH_2Cl_2$ and $SO_2$ quench the excited $^*Pc_2Sn$ species and form both the one-electron oxidized, $[Pc(-1)Sn(IV)Pc(-2)]^+$ complex and monomeric MPc species to a varying extent. Irradiation with unfiltered radiation shows that the one-electron

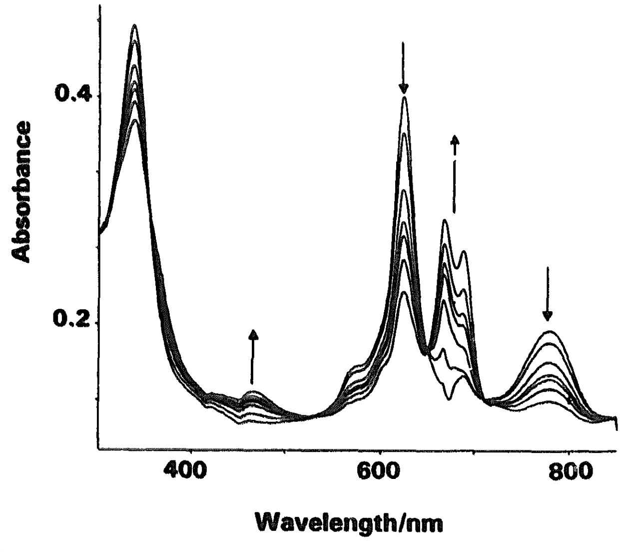


Fig. 4. Absorption spectral changes observed during the photolysis of $Pc_2Sn$ in $CH_2Cl_2$, using unfiltered radiation from the tungsten lamp. $[Pc_2Sn]_0 = 5.0 \times 10^{-6}$ mol dm$^{-3}$.

oxidized product is favored by $SO_2$. The increase of quantum yield with $SO_2$ concentration, Fig. 3(a), shows that $SO_2$ quenches the excited state when solutions of $Pc_2Sn$ are photolysed in $CH_2Cl_2$ in the presence of $SO_2$. This implies that $SO_2$ is a better one-electron quencher of the excited state of the $Pc_2Sn$ species than $CH_2Cl_2$. $SO_2$ has a relatively high electron affinity, and it is generally even better than $O_2$ as an acceptor [26,27]. It is thus reasonable to assume that $SO_2$ will be a better electron transfer quencher than dichloromethane.

### 3.2. Photolysis of $Pc_2Sn$ in $CH_3CN/CH_2Cl_2$ solvent mixture

Fig. 5 shows the spectral changes observed when solutions of $Pc_2Sn$ in $CH_2Cl_2$ containing acetonitrile were photolysed with unfiltered radiation from the tungsten lamp. These changes are similar to those shown in Fig. 1, in that the main product formed is the $[Pc(-1)Sn(IV)Pc(-2)]^+$ species with absorption band maxima at 669 and 470 nm. The isosbestic point in the visible region in Fig. 5 is not as clear as in Fig. 1. The shoulder to the low energy side of the Q band can again be attributed to the formation of the monomeric phthalocyanine products. The formation of the $[Pc(-1)Sn(IV)Pc(-2)]^+$ on photolysis of $Pc_2Sn$ is consistent with the reported formation of one-electron oxidized products of photolysis of lanthanide phthalocyanine in the acetonitrile/dichloromethane solvent mixture [17]. The relative quantum yield for the formation of the $[Pc(-1)Sn(IV)Pc(-2)]^+$ increased with the increase in the concentration of dichloromethane, Fig. 3(b), showing that dichloromethane was the quencher of the excited state. The $[Pc(-1)Sn(IV)Pc(-2)]^+$ species was not formed unless the dichloromethane was in excess in the acetonitrile/dichloromethane solvent mixture. It is most likely that the role of acetonitrile is to stabilize the excited states [28]. Spectral changes similar to those shown in Fig. 1 or Fig. 5 were also observed when $Pc_2Sn$ was photolysed in the chlorobenzene/methanol solvent mixture. In comparison with the lanthanide bisphthalocyanines and with porphyrins [13,17], the photolysis of $Pc_2Sn$ in $CH_2Cl_2/CH_3CN$ mixture may be represented by Eq. (5) and (6):

$$Pc(-2)SnPc(-2) \overset{h\nu}{\rightleftharpoons} {}^*[Pc(-2)SnPc(-2)] \qquad (5)$$

$$^*[Pc(-2)SnPc(-2)] + CH_2Cl_2 \xrightarrow{k_q} [Pc(-2)SnPc(-1)]^+ + {}^{\bullet}CH_2Cl + Cl^- \qquad (6)$$

The quantum yields for the formation of the $[Pc(-1)Sn(IV)Pc(-2)]^+$ species were found to be generally lower in the $CH_3CN/CH_2Cl_2$ solvent mixture as compared with the formation of this species in the presence of $SO_2$. Also the quantum yields reported here were lower than the yields reported for the photooxidation of $Pc_2Ln$ in $CH_3CN/CH_2Cl_2$ solvent mixture [17].

### 3.3. Photolysis of the monomeric $(L)_2Sn(IV)Pc$ complexes in the presence of $SO_2$

The electronic absorption changes observed during the photolysis of $(L)_2Sn(IV)Pc$ species in pyridine and in the presence of $SO_2$, are quite similar for the different axial ligands. As an example, Fig. 6 shows the spectral changes observed for the photolysis of $(Br)_2Sn(IV)Pc$. The Q band observed at 698 nm in the spectra of the unphotolysed species decreased in intensity and two new and weaker bands are formed at 585 and 622 nm with isosbestic points at 624 and 725 nm. The final spectra observed at the end of photolysis is characteristic of MPc(-3) and similar to the spectra of $[(OH)_2Sn(IV)Pc(-3)]^{-\bullet}$ [7]. During the photolysis, the solution turns from greenish blue to the dark blue color typical

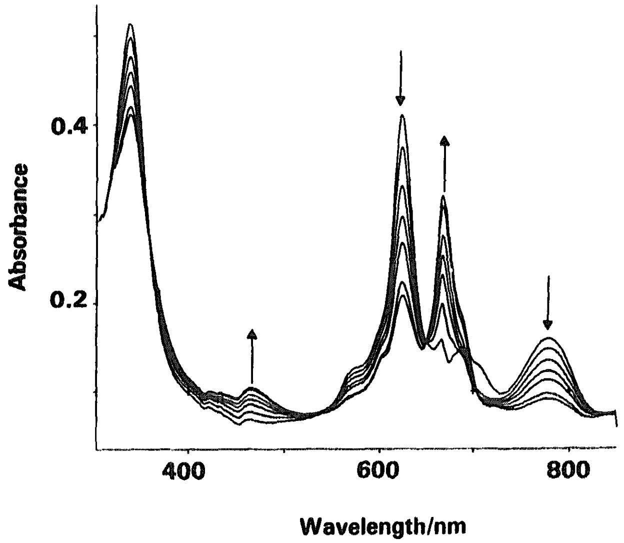


Fig. 5. Absorption spectral changes observed during the photolysis of $Pc_2Sn$ in $CH_2Cl_2/CH_3CN$ solvent mixture, using unfiltered radiation from the tungsten lamp. $[Pc_2Sn]_0 = 4.0 \times 10^{-6}$ mol dm$^{-3}$ and 90% $CH_2Cl_2$.

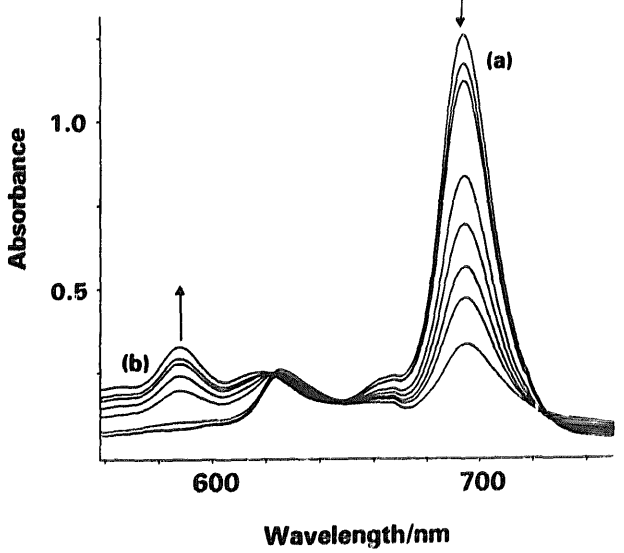


Fig. 6. Absorption spectral changes observed during the photolysis of $(Br)_2Sn(IV)Pc$ in pyridine, in the presence of 1.4 mol dm$^{-3}$ $SO_2$ (dissolved in pyridine); the spectra before (a) and after (b) photolysis.

of MPc(-3)) species [24]. Exposure of the photoreduced species to air resulted in a complete regeneration of the original Sn(IV)Pc(-2)) species, for all the $(L)_2Sn(IV)Pc$ complexes under discussion. Since coordination numbers greater than six are common in tin(IV) phthalocyanine complexes [19], we used the IR spectra to determine the possibility of coordination of $SO_2$ to the SnPc(-2) species. The IR spectra observed when the photoreduced species was exposed to air and the solvent evaporated to dryness showed a broadening of the bands in the 1100 $cm^{-1}$ region and an extra band at 610 $cm^{-1}$, in addition to bands typical of phthalocyanine moiety [19]. These changes are attributed to the presence of free sulfate. Free sulfate bands are located at 1110 and 615 $cm^{-1}$ [29].

It was suggested before that $SO_2$ was coordinated to the central metal during its electrocatalytic oxidation by CoPc and FePc [15]. It is thus likely that $SO_2$ is reversibly coordinated to the photoexcited $(L)_2Sn(IV)Pc^*$ species during the electron transfer and that upon oxidation of the photoreduced Sn(IV)Pc(-3) species by exposure to air, the $SO_2$ is oxidized to a sulfate. There was no evidence for the coordination of the sulfate to the Sn(IV)Pc(-2) species formed by exposure of the Sn(IV)Pc(-3) species to air. Such coordination would be expected to affect the electronic absorption spectra. Studies on porphyrin complexes [29] have shown that monocoordinated sulfate has IR bands at 1147, 1098 and 464 $cm^{-1}$. No new IR bands were observed at these frequencies. There was also no spectroscopic evidence for the coordination of $SO_2$ to the $(L)_2Sn(IV)Pc$ prior to the photolysis. The reduction of the $(L)_2Sn(IV)Pc$ complexes by $SO_2$ could only be achieved in deaerated solutions, hence suggesting that $SO_2$, and not the higher oxides of sulfur, is the species involved in the reduction of the tin(IV) phthalocyanine species.

The reaction between $SO_2$ and metalloporphyrin complexes often result in dimerization of the porphyrins [29,30]. Aggregation in MPc complexes is characterized by a considerable broadening of the Q band [14]. There was no spectral evidence for aggregation following photolysis of the $(L)_2Sn(IV)Pc$ species in the presence of $SO_2$. Unlike the ring oxidized, MPc(-1) species, MPc(-3) species do not dimerize readily in solution. The spectra shown in Fig. 6 for the $[(L)_2Sn(IV)Pc(-3)]^-$ species is typical of monomeric MPc(-3) species [24]. Also the spectra of the species formed by exposure of the photoreduced species to air is similar to the original spectra and does not show the broadening of bands typical of aggregation in phthalocyanines.

Irradiations of the $(Cl)_2Sn(IV)Pc$ species in the visible region, generates the lowest-lying triplet states, ${}^3\pi\pi^*(Cl)_2Sn(IV)Pc$ [10], which may be quenched by electron acceptors or donors. It is expected that the excited triplet states will be populated upon visible photolysis of the $(L)_2Sn(IV)Pc$ complexes. The first step in this reaction is thus expected to be the population of the ${}^3\pi\pi^*$ states, Eq. (7):

$$(L_2)Sn(IV)Pc \overset{h\nu}{\rightleftharpoons} {}^3\pi\pi^*(L)_2Sn(IV)Pc \qquad (7)$$

followed by the electron transfer between $SO_2$ and the ${}^3\pi\pi^*(L)_2Sn(IV)Pc$ state, Eq. (8):

$$SO_2 + {}^3\pi\pi^*(L)_2Sn(IV)Pc \longrightarrow [(L)_2Sn(IV)(SO_2)Pc(-3)]^- \qquad (8)$$

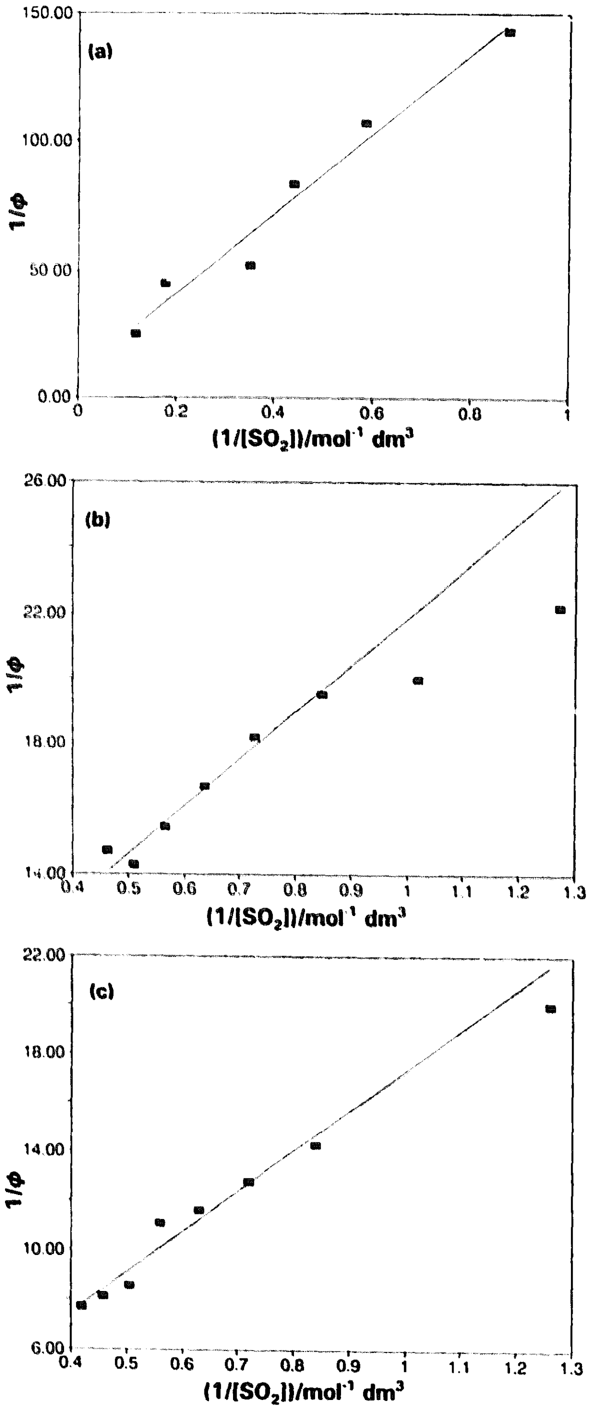


Fig. 7. Plots of reciprocal quantum yields for photooxidation of (a) $(OH)_2Sn(IV)Pc$, (b) $(Br)_2Sn(IV)Pc$ and (c) $(F)_2Sn(IV)Pc$ against reciprocal concentration of $SO_2$.

Table 1
Comparison between half-wave potentials ($E_{1/2}$) for the reduction of $(L)_2Sn(IV)Pc$ complexes and the relative quantum yields for photoreduction of these complexes in the presence of $SO_2$ (1.2 mol $dm^{-3}$)

| Complex | $E^{1/2}$/V vs. SCE [a] | $10^2\phi[SnPc(-3)]$ | Ref. [b] |
|---|---|---|---|
| $(OH)_2Sn(IV)Pc$ | −0.46 | 0.9 | 11 |
| $(F)_2Sn(IV)Pc$ | −0.46 | 5.1 | tw |
| $(Cl)_2Sn(IV)Pc$ | −0.52 | 3.3 | 11 |
| $(Br)_2Sn(IV)Pc$ | −0.68 | 3.2 | tw |

[a] TEAP = electrolyte; solvent = pyridine.
[b] tw = this work.

The quantum yields for the formation of the $[(L)_2Sn(IV)(SO_2)Pc(-3)]^{-\bullet}$ species increased with the increase in $SO_2$ concentration, Fig. 7, confirming the involvement of $SO_2$ in the electron transfer quenching reactions. For the same concentration of $SO_2$, the quantum yields increased with the ease of reduction of the $(L)_2Sn(IV)Pc$ complexes for L = $Br^-$, $Cl^-$ and $F^-$, Table 1.

Attempts to photoreduce other monomeric MPc complexes such as $(L)_2RuPc$ and $(L)RhPc$ in the presence of $SO_2$ were unsuccessful.

### *3.4. Comparisons between the photochemical behaviors of $Pc_2Sn$ and $(L)_2Sn(IV)Pc$*

Even though the monomeric $(L)_2Sn(IV)Pc(-2)$ complexes are photoreduced to the $[(L)_2Sn(IV)Pc(-3)]^-$ in the presence of $SO_2$ and in pyridine, preliminary work shows that new products are formed, prior to photolysis, on the addition of $SO_2$ to pyridine solutions of $Pc_2Sn$. The products formed are still under investigation. The potentials for ring reduction of the $(L)_2Sn(IV)Pc(-2))$ species are not too different from those for the first ring reduction in $Pc_2Sn$ [18]. For example the half-wave potential, $E^{1/2} = -0.44$ V vs. saturated calomel electrode (SCE) for $Pc_2Sn$ in dimethylformamide [18], and −0.46 V vs. SCE for $(OH)_2Sn(IV)Pc(-2)$ in the same solvent, Table 1. The differences in the photochemical behavior of the monomeric and bisphthalocyanines in pyridine and in the presence of $SO_2$ could be attributed to the differences in the relative stability of the excited states.

No absorption spectral changes were observed on photolysis of $(L)_2Sn(IV)Pc(-2)$ dissolved in $CH_2Cl_2$ and in the presence of $SO_2$. The one-electron oxidation product formed for $Pc_2Sn$ under the same conditions was not observed. Cyclic voltammetry of $(L)_2Sn(IV)Pc(-2)$ in solvents such as dichloromethane or acetonitrile containing tetraethylammonium perchlorate as an electrolyte and on platinum electrodes showed no oxidation couples, whereas cyclic voltammetry of $Pc_2Sn$ shows one oxidation couple at 0.35 V vs. SCE [18]. The differences in the photo-oxidation properties of $Pc_2Sn$ and $(L)_2Sn(IV)Pc(-2)$ probably reflect the difficulty in oxidizing the latter species.

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