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Photochemical Properties of Tin(IV) Phthalocyanines: a Comparison between the Dichloro and Superphthalocyanines

BELA KRAUT and G. FERRAUDI*

Radiation Laboratory, University of Notre Dame, Notre Dame, Ind. 46556, U.S.A.

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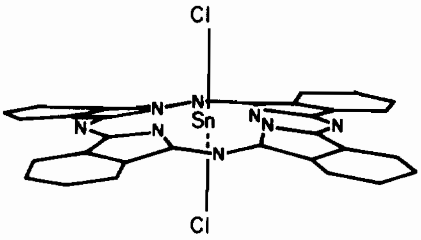
Abstract

The photochemical behavior of Tin(IV) dichlorophthalocyaninate, $Sn(pc)Cl_2$, and tin(IV) super phthalocyanine, $Sn(pc)_2$, has been investigated by flash photolysis. Irradiations, $\lambda_{exc} \sim 640$ nm, of $Sn(pc)Cl_2$ generate the lowest lying triplet state, $(^3\pi\pi^*)Sn(pc)Cl_2$, with a half lifetime, $\tau \sim 40$ μs. Quenching of this excited state with paradinitrobenzene produces a Sn(IV) phthalocyanine radical which isomerizes to a Sn(III) complex in a μs time domain. The photochemistry of $Sn(pc)_2$ can be described in terms of an unreactive $^3\pi\pi^*$ and a reactive CT excited state. Dissociation reactions form $Sn^{II}(pc)$ and $Sn^{IV}(pc)(solvent)_2$. The regeneration of the superphthalocyanine takes place through a Sn(III) intermediate.

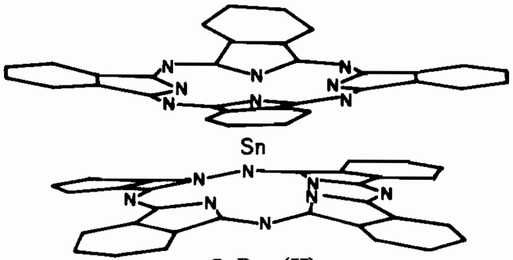
Introduction

A number of photochemical studies have been concerned with the reactivity of the low lying excited states of metallophthalocyanines [1–6]. Although no excited state unimolecular redox reactions have been observed in complexes with low lying ligand centered excited states, e.g. phthalocyanines of Al(III), Cu(II), Rh(III), Ru(II), they undergo rapid electron transfer quenching with appropriate reducing or oxidizing species [1–6]. The presence of low lying pc to metal charge transfer excited states, e.g. Mn(III) phthalocyanines [7], seems to be the reason for rapid relaxation of the ligand centered excited states with no detectable chemical changes in a μs–s time domain [8]. Photoredox reactions have been observed with complexes where the absorption of light populates ligand to metal charge transfer states which largely involve an axially coordinated species. However, this photochemistry is always associated with excitation energies that are above those required for the population of the lowest lying states [8, 9].

Despite that superphthalocyanines, e.g. $M(pc)_2$ [10–13], can be chemically related to simple phthalocyanines whose photochemistry has been characterized in previous studies, no reports are available with regard to the photochemistry of superphthalocyanines. In this regard, results from comparative flash photochemical studies on tin(IV)-dichlorophthalocyaninato (I) and tin(IV)superphthalocyanine (II) are reported in this work.



$SnPcCl_2$ (I)



$SnPc_2$ (II)

Experimental

Photochemical Procedures

The flash photochemical studies were carried out with the apparatus described elsewhere [14, 15]. Time resolved spectral changes or kinetics were investigated in a μs–ms time domain by using a SLL-200 Candela dye laser as the source of 200 ns pulses of monochromatic light. The high photonic fluxes delivered by this system were those required for sequential biphotonic excitations of long lived

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*Author to whom correspondence should be addressed.

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excited species [6]. In this regard, all the experiments were carried out with peak intensities, e.g. less than 100 MWatt/cc, below those where the sequential biphotonic excitations made significant contributions to the observed photochemistry. Transients with lifetimes longer than 30 μs, e.g. in the 30 μs–10 s time domain, were also investigated with a flash photolysis apparatus where two Xe flash lamps were used as sources of polychromatic light pulses. Appropriate filters were used for the irradiation of the phthalocyanines at selected spectral regions. The low photonic densities in the reaction cell prevented from sequential irradiations and the low concentration of excited species produced per pulse underwent decays with first rather than second order kinetics. The computerized detection system allowed us to store, as a final result of monitoring at a given wavelength, the average of a maximum of 20 traces for either kinetic analyses or ensembling time resolved spectra. In all these experiments, solutions of the complexes in halocarbon solvents were deaerated with streams of ultra pure N_2.

Materials

The tin complexes, Snpc, $Sn(pc)Cl_2$ and $Sn(pc)_2$ were prepared and purified by literature reports [12, 13]*. The purity of these materials was established from elemental analyses and comparisons with the reported UV–Vis spectra [10, 11]. Other materials were reagent grade and used without further purification.

Results

Photochemical Properties

The 640 nm flash photochemical irradiation of the tin(IV) phthalocyanines has revealed that the compounds undergo different photochemical transformations. These observations are described below for each particular compound.

Photolysis of $Sn(pc)Cl_2$

The flash photochemical irradiation of the dichloro complex in deaerated chlorobenzene solutions, at wavelengths of the phthalocyanine Q band, induces a transient spectrum, Fig. 1, which has features corresponding to the lowest lying ligand centered excited state, $^3\pi\pi^*$, in other metallo phthalocyanines [1, 2, 4, 5]. In deaerated solutions where chlorobenzene, bromobenzene, dichloromethane or mixtures of them are used as solvents, the maximum of the band experiences solvent-induced batho or hipsochromic shifts of *ca.* 10 nm while its decay always obeys a first order rate law with $k = (2.4 \pm 0.2) \times 10^4$ s^{-1}. The spectrum shifts toward longer wavelengths, e.g. to *ca.* 540 nm, in experiments with high laser intensities and large concentrations of excited state in accord with excited state disproportionation and biphotonic reactions already reported for various phthalocyanines [6, 16, 17]. Moreover, the excited state quenching with paradinitrobenzene, PDNB, takes place with a nearly diffusion controlled rate, $k \sim 10^9$ M^{-1} s^{-1}. This quenching reaction produces a new transient species whose absorption spectrum, Fig. 2, is the one expected for a phthalocyanine radical, $Sn(p\dot{c})Cl_2^+$ [18]. Time resolved spectra shows that the radical is converted with a first order kinetics, $k = (5.0 \pm 0.4) \times 10^4$ s^{-1}, into a new species, λ_{max} 540 and 470 nm, which (based on its spectral features) can be assigned as a Sn(III) complex where the phthalocyanine ligand has experienced the removal of two electrons, *i.e.* $Sn^{III}(pc^0)Cl_2^+$ [18].

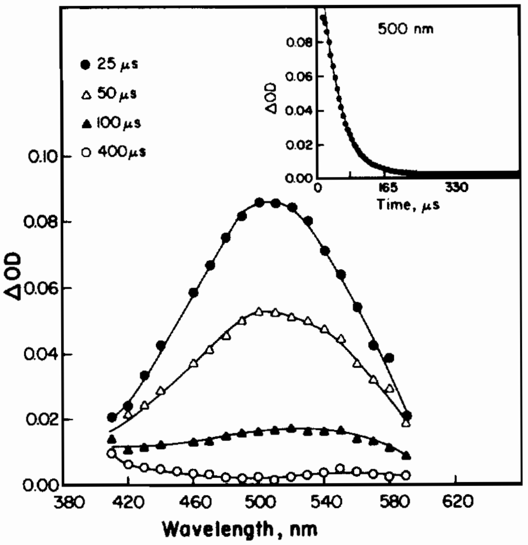

Fig. 1. Transient differential spectra assigned to $(^3\pi\pi^*)Sn(pc)Cl_2$. Measurements were carried out in 640 nm laser flash irradiations of 3.0×10^{-5} M $Sn(pc)Cl_2$ in deaerated chlorobenzene. The insert shows the decay of the 500 nm optical density with a first order curve fitting.

Photolysis of $Sn(pc)_2$

Flash irradiations ($\lambda_{exc} = 640$ nm) of $Sn(pc)_2$ in deaerated solutions produce transient spectra, $\lambda_{max} = 460$ nm, of the lowest lying, $^3\pi\pi^*$, ligand centered state, Fig. 3. In experiments where the concentration of complex was kept constant ($[Sn(pc)_2] = 1.0 \times 10^{-4}$ M) and irradiations were carried out with various laser intensities, $30 < I < 100$ MW/cc, the concentration of excited state exhibited a non linear dependence on the light intensity, Fig. 3. By contrast, the excited state lifetime, ~5 μs, remains invariant under these experimental conditions. Such a non

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*Abbreviations: pc^{2-}, phthalocyanine ligand; $pc^{\cdot -}$, phthalocyanine radical anion (product of one electron oxidations) and pc^0, two electron-oxidized phthalocyanine ligand.

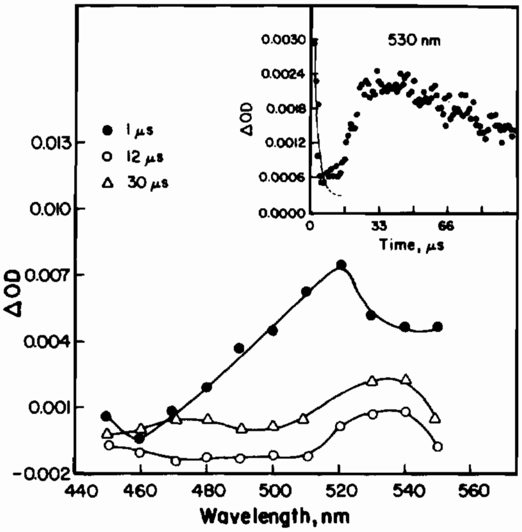

Fig. 2. Transient spectra observed by quenching ($^3\pi\pi^*$)Sn(pc)Cl_2 with PDNB. The spectrum recorded at 1 μs has been assigned to the excited state (see Fig. 1) while curves recorded at longer times have been assigned to a Sn(IV) ligand radical complex (t = 12 μs) and a Sn(III) species (t = 30 μs) respectively. The formation of three different species is also illustrated in the insert showing the time resolved changes in the 530 nm optical density.

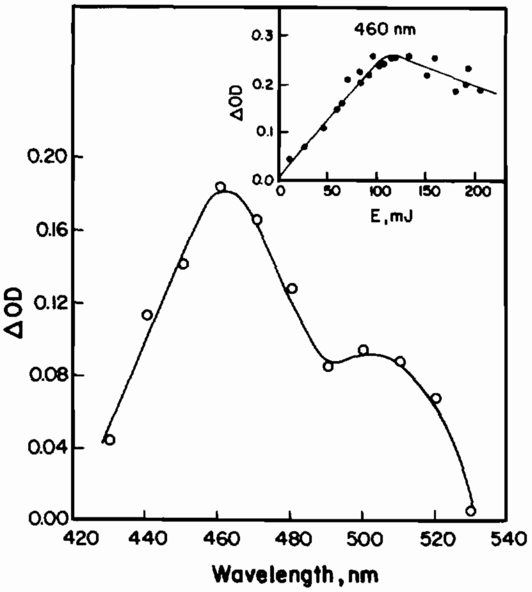

Fig. 3. Short lived transient spectrum generated in 640 nm laser flash irradiations of 1.0×10^{-4} M Sn$(pc)_2$ in deaerated chlorobenzene. The curve has been determined with a delay of 2.5 μs following the flash. The insert shows the non linear dependence of the excited state yield (measured in terms of the 460 nm optical density change 1 μs after the flash) on the light intensity. In these experiments, 10^{-4} M Sn$(pc)_2$ was irradiated in deaerated chlorobenzene.

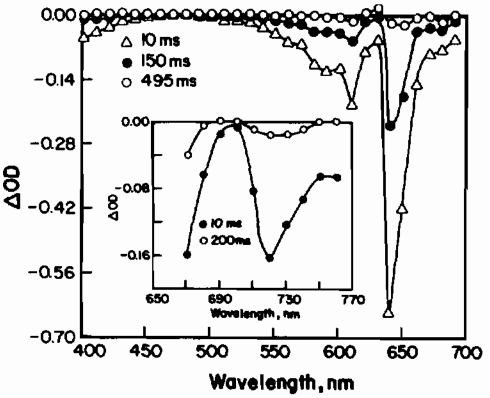

Fig. 4. Long lived transient bleach observed in laser flash irradiations (λ_{exc} = 640 nm) of 3.0×10^{-5} M Sn$(pc)_2$ in deaerated chlorobenzene. The insert shows spectral changes in the 650–750 nm region where a new band at 694 nm has been assigned to the formation of phthalocyanine products. Spectra obtained in flash lamp irradiations of 5.0×10^{-6} M Sn$(pc)_2$ at wavelengths of the Q-band.

linear dependence of the excited state yield on light intensity shows that for excitations with more than 50 MW/cc, the absorption of light by ($^3\pi\pi^*$)Sn$(pc)_2$ is a significant fraction of the total light absorbed; a problem already studied in connection with the sequential biphotonic photochemistry of phthalocyanines [16, 17]. Under a monophotonic excitation regimen, the decay of the excited state, $k = (1.8 \pm 0.4) \times 10^5$ s^{-1}, is faster than the decay of the ($^3\pi\pi^*$)-Sn(pc)Cl_2 and leads to bleaching of the parent complex spectrum and appearance of a new absorption band at 694 nm, Fig. 4. Comparison of the photoinduced spectral changes with the spectra of Sn phthalocyanines indicates that Sn(pc)(solvent)$_2^{2+}$ and Snpc are generated in the decay of the excited state with very different yields, *i.e.* the Sn(IV) product accounts for only a 15% of the photoconverted superphthalocyanine while *ca.* 85% leads to Snpc formation. In a ms to s time domain, the rate of recovery of the Sn$(pc)_2$ spectrum obeys an apparent first order rate law with k = 10 s^{-1} when one follows it at 600 nm, Fig. 5. The complexity of this process has been revealed, however, from observations made at wavelengths between 400 and 500 nm where the formation and decay of an intermediate, Fig. 5, takes place with first order kinetics, $k_{formation} = 15.2 \pm 0.9$ s^{-1} and $k_{decay} = 3.3 \pm 0.2$ s^{-1}. The decay of such an intermediate leads to an almost complete restoration of the Sn$(pc)_2$ spectrum with minor differences corresponding to the presence of the Sn(IV) product indicated above.

Discussion

Flash irradiations of Sn(pc)Cl_2 at wavelengths of the Q-band result in the generation of the long lived

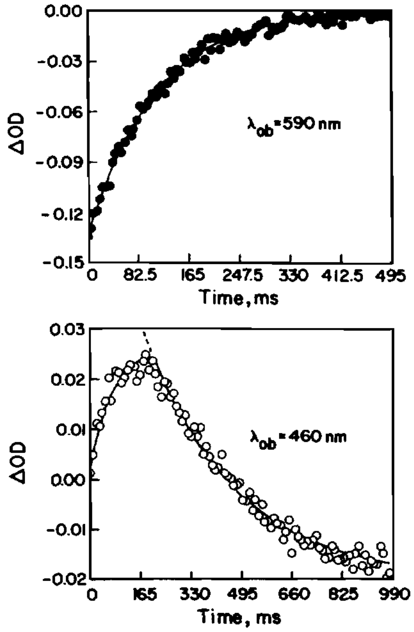

Fig. 5. Traces showing the time resolved recovery of the optical density at 590 and 460 nm respectively in flash irradiations of $\mathrm{Sn(pc)_2}$. (For experimental conditions see Fig. 4.) Solid lines give the least-squares curve fitting of the experimental data for first order kinetics.

($^3\pi\pi^*$)$\mathrm{Sn(pc)Cl_2}$ as in the case of other metallo phthalocyanines where such a ligand centered excited state is placed below various macrocycle to metal or metal to macrocycle charge transfer states. This observation is also supported by the absence of absorption bands (in the $\mathrm{Sn(pc)Cl_2}$ spectrum) below the energies of the Q band, namely bands that in other phthalocyanines, e.g. Co(III) and Mn(III) compounds, have been assigned to charge transfer transitions [7, 8]. Although the behavior of the ($^3\pi\pi^*$)$\mathrm{Sn(pc)Cl_2}$ with respect to electron transfer quenching, eqns. (1) and (2), is similar to the one reported for other phthalocyanines, the intramolecular electronic reorganization, eqn. (3), and electrochemical data [19]* suggests that the reduction of Sn(IV) to Sn(III) may not be energetically prohibitive and that the Sn(III) intermediate could be more stable than the corresponding porphyrin species [20, 21].

$$\mathrm{Sn^{IV}(pc)Cl_2} \overset{h\nu}{\rightleftarrows} (^3\pi\pi^*)\mathrm{Sn^{IV}(pc)Cl_2} \qquad (1)$$

$$(^3\pi\pi^*)\mathrm{Sn^{IV}(pc)Cl_2} + \mathrm{PDNB} \longrightarrow \mathrm{Sn^{IV}(p\dot{c})Cl_2^{+}} + \mathrm{PDNB}^{\cdot -} \qquad (2)$$

$$\mathrm{Sn^{IV}(p\dot{c})Cl_2^{+}} \longrightarrow \mathrm{Sn^{III}(pc)Cl_2^{+}} \qquad (3)$$

Comparisons between the behavior of ($^3\pi\pi^*$)$\mathrm{Sn(pc)Cl_2}$ and that of $\mathrm{Sn(pc)_2}$ following excitations with visible light cannot be simply established unless one assumes that coordination in the superphthalocyanine induces little mixing between the electronic clouds of the two macrocycles; a point supported to some extent by the crystallographic structure, the electrochemistry and spectroscopy of $\mathrm{Sn(pc)_2}$. Indeed the presence of typical phthalocyanine spectral features (Q and Soret bands) in the superphthalocyanine spectrum gives some support to the idea of weak mixing and the appearance of a broad and intense band at $\lambda_{\mathrm{max}} = 750$ nm suggests that there is a significant charge transfer interaction [7]. In this model, the short lifetime of the ligand centered excited state can be attributed to the presence of such lowest lying charge transfer states. The photochemistry can be described, therefore, in terms of a long lived unreactive ligand centered excited state and a short lived reactive charge transfer state, eqns. (4)–(8).

$$\mathrm{Sn^{IV}(pc)_2} \overset{h\nu}{\rightleftarrows} (^3\pi\pi^*)\mathrm{Sn(pc)_2} \qquad (4)$$

$$(^3\pi\pi^*)\mathrm{Sn(pc)_2} \longrightarrow (\mathrm{CT})\mathrm{Sn(pc)_2} \qquad (5)$$

$$(\mathrm{CT})\mathrm{Sn(pc)_2} \longrightarrow \begin{cases} \mathrm{Sn(pc)_2} & (6) \\ \mathrm{Sn^{II}(pc)} + \mathrm{p\mathring{c}} & (7) \\ \mathrm{Sn^{IV}(pc)^{2+}} + \mathrm{pc^{2-}} & (8) \end{cases}$$

It is expected that the excited state with a strong $^3\pi\pi^*$-ligand centered character will not engage in unimolecular redox reactions as in the similar case of the lowest lying $^3\pi\pi^*$ in $\mathrm{Sn(pc)Cl_2}$ and other metallo phthalocyanines [1, 2, 8, 9]. By contrast, a charge transfer state where the electronic clouds of the ligands have experienced a significant repolarization with regard to the ground state is in a better accord with the homolytic and heterolytic nature of the processes, eqns. (7) and (8) that one must formulate in order to account for the formation of the Sn(IV) and Sn(II) products.

The partial restoration of the $\mathrm{Sn(pc)_2}$ absorption spectrum that follows the spectral changes induced by the excited state processes, eqns. (4)–(8), involves an intermediate species whose spectrum corresponds to a phthalocyanine radical [18]. This observation suggests that the transfer of two electrons, required for the regeneration of the Sn(IV) complex, takes

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*Preliminary experiments on the cyclic voltammetry of $\mathrm{Sn(pc)_2}$ show several waves for sweeps between 1 and -1 V *versus* an Ag/AgCl electrode. A reversible one electron wave with $\epsilon_{1/2} = 0.408$ V (*versus* NHE) and a separation between cathodic–anodic waves, $\Delta\epsilon = 0.055$ V, has been assigned to the couple $\mathrm{Sn^{IV}(pc)_2/Sn^{III}(pc)_2}$. In these experiments we use dry $\mathrm{CH_2Cl_2}$ with 0.1 M $\mathrm{(C_4H_9)_4NClO_4}$ as support electrolyte.

place in two independent steps instead of a one step two electron transfer, eqns. (9)–(11).

$$\mathrm{Sn^{II}(pc) + p\overset{\circ}{c}} \underset{\text{(fast)}}{\rightleftharpoons} \mathrm{Sn^{II}(pc)(p\overset{\circ}{c})} \tag{9}$$

$$\mathrm{Sn^{II}(pc)(p\overset{\circ}{c})} \xrightarrow[\text{(slow)}]{} \mathrm{Sn^{III}(pc)(p\dot{c})} \tag{10}$$

$$\mathrm{Sn^{III}(pc)(p\dot{c})} \longrightarrow \mathrm{Sn^{IV}(pc)_2} \tag{11}$$

Moreover, the first order kinetics for the formation and decay of the intermediate signals that a second order reattachment of the two electron-oxidized phthalocyanine fragment to Sn(pc) cannot be the rate determining process namely the electron transfer must be intramolecular as indicated in eqn. (10).

Acknowledgements

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