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The Redox Photochemistry of Dimeric and Monomeric Copper(II) Tetra(N-octadecylsulfonamide)phthalocyanine in Non Aqueous Media

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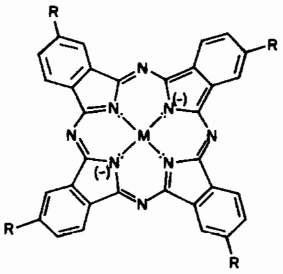
Introduction

Previous studies** [1] have shown that the ultraviolet irradiation of aqueous solutions of the dimeric copper(II) tetrasulfophthalocyanine, (I), induce a photoredox dissociation in oxidized and reduced copper(II)–ligand radicals, eqn. 1.



(I) R = SO_3H

(II) R = $SO_2NH\text{-}C_{18}H_{37}$

$$[Cu^{II}(pts)]_2^{8-} \xrightleftharpoons{h\nu} Cu^{II}(p\dot{t}s)^{5-} + Cu^{II}(p\dot{t}s)^{3-} \quad (1)$$

Moreover, the same reduced copper(II)–ligand radical, $Cu(p\dot{t}s)^{5-}$, is produced when hydrogen is abstracted from 2-propanol by ($n\pi^*$) excited states of monomeric copper(II) sulfophthalocyanine [1]. We have extended these studies in order to investigate the effect of the solvent and ligand substituents on the photochemical properties of the complex.

Results and Discussion

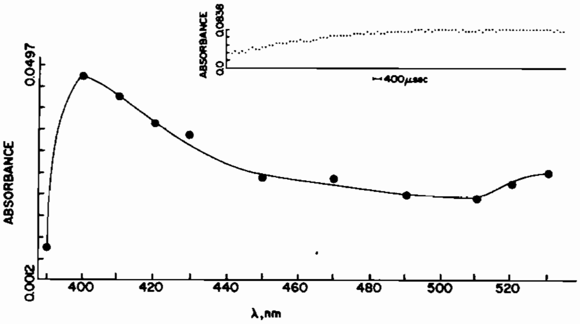


Fig. 1. Transient spectrum obtained 400 μsec after the flash irradiation of copper(II) tetra(N-octadecylsulfonamide)-phthalocyanine in deaerated chloroform. The inset shows a typical trace for the absorbance growth at 420 nm. Irradiatins were carried out at $\lambda_{excit} \geqslant 280$ nm with 250 Joule/pulse flashes.

Flash irradiations of the dimeric copper(II) tetra(N-octadecylsulfonamide)phthalocyanine, (II), in deaerated chloroform, $\lambda_{excit} > 280$ nm, produce a species with $\lambda_{max} \sim 400$ nm, Fig. 1. The 420 nm increases after the 30 μsec irradiation with a rate that has a first order dependence in the zero time concentration of the species, Fig. 1. A rate constant k = 1.3×10^2 sec^{-1} was obtained from measurements with various zero time concentrations. Photolyses of the complex in oxygen saturated chloroform produce a decrease in the yield of the species, namely $\phi_{oxygenated}/\phi_{deaerated} = 0.67$. However, oxygen did not modify the rate of the absorbance growth. Furthermore, maximum absorptions at $\lambda \sim 500$ nm, characteristic of the copper(II)–ligand radicals [2], were not observed in experiments with deaerated or oxygenated solutions. In this regard, the species with $\lambda_{max} \sim 420$ nm has been assigned as a copper(III) phthalocyanine [3] which is produced, in part, during the decomposition of the solvent, eqns. 2–4. Such a decomposition of the solvent generates chloride ions. Indeed Cl^- was detected as a product in 300 nm continuous photolyses.

$$[Cu^{II}(pts\ R)]_2 \overset{h\nu}{\rightleftharpoons} {}^*[Cu^{II}(pts)\ R)]_2 \rightarrow Cu^{I}(pts\ R)^- + Cu^{III}(pts\ R)^+ \quad (2)$$

$$Cu^{I}(pts\ R)^- + CHCl_3 \rightarrow Cu(pts\ R)(CHCl_2) + Cl^- \quad (3)$$

$$Cu(pts\ R)(CHCl_2) \xrightarrow{H^+} Cu^{III}(pts\ R)^+ + CH_2Cl_2 \quad (4)$$

Flash irradiation, $\lambda_{excit} > 280$ nm, of the monomeric phthalocyanine in 2-propanol–chloroform mixtures, namely [2-propanol] $\geqslant 1.0$ *M*, produces a similar copper(III) species with $\lambda_{max} \sim 400$ nm. Also, minor concentrations of copper(II)–ligand radicals with $\lambda_{max} \sim 510$ nm were detected under such conditions. The formation of $Cu^{III}(pts\ R)^+$

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**Abbreviations: pts = tetrasulfophthalocyanine – see (I); pts R = tetra(N-octadecylsulfonamide)phthalocyanine – see (II).

can be related to the reduction of the phthalocyanine complex when ($n\pi^*$) excited states react with 2-propanol, eqns. 5, 6.

$$\mathrm{Cu(pts\,R)} \overset{h\nu}{\rightleftarrows} {}^*\,\mathrm{Cu(pts\,R)}$$

$$\mathrm{(CH_3)_2CHOC} \begin{cases} \rightarrow \mathrm{Cu^{II}(p\dot{t}s\,R{-}H)} + \mathrm{(CH_3)_2\dot{C}OH} & (5) \\ \rightarrow \mathrm{Cu^{I}(pts\,R)} + \mathrm{H^+} + \mathrm{(CH_3)_2\dot{C}OH} & (6) \end{cases}$$

The photochemical formation of copper(I) and copper(III) phthalocyanines in chloroform, eqns. 2, 6, contrasts with the generation of ligand radicals in aqueous solutions, eqn. 1. This behavior suggests that the mono and tripositive states of copper have been stabilized with respect to the oxidation and reduction of the tetra(N-octadecylsulfonamide)-phthalocyanine ligand. It is feasible that such stabilization is provided by a change of the substituents, namely from sulfonic to sulfonamide groups, and solvation effects which affect the energy of the phthalocyanine's π system, [4].

Experimental

Copper(II) tetra(N-octadecylsulfonamide)phthalocyanine was obtained by procedures reported elsewhere [5]. The compound was purified by recrystallization from carbon tetrachloride. Spectroquality chloroform was first separated from the stabilizer, *ca.* 1% ethanol, by distillation of a 2:1 chloroform–sulfuric acid mixture and then washed with distilled water. Solutions of the complex were prepared with chloroform which was previously dried over Na_2SO_4 (anh.) and Molecular Sieves. A dramatic change in the reactivity of the complex was observed when untreated chloroform was used for the preparation of the solutions. The photochemical procedures and apparatuses have been previously described [6].

Acknowledgments

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References

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