

PHOTOCHEMICAL ELECTRON TRANSFER: REDUCTION OF TIN PORPHYRINS  
IN THE PRESENCE OF STANNOUS CHLORIDE

David G. Whitten and Joseph C. N. Yau<sup>1</sup>

Department of Chemistry, University of North Carolina

Chapel Hill, North Carolina 27514

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The conversion of porphyrins to chlorins, phlorins and other reduced forms has received considerable attention. Chemical reduction of porphyrin iron or tin complexes produces chlorins and tetrahydroporphyrins in relatively poor yields.<sup>2-5</sup> Irradiation of porphyrins in the presence of hydrogen atom donors such as ascorbic acid leads to phlorins and other reduced products<sup>6</sup> while irradiation of certain metal complexes under similar conditions leads to the corresponding chlorins as well as to other products.<sup>2,7</sup> In the present communication we report the surprisingly clean photoreduction of tin porphyrins in the presence of stannous chloride to yield first the corresponding chlorin and subsequently the cis-dihydrochlorin (5,6,7,8-tetrahydroporphyrin).

Solutions of the tin complex of octaethylporphyrin<sup>8</sup> were prepared by introducing  $\text{SnCl}_2 \cdot 2\text{H}_2\text{O}$  into degassed pyridine or ethanol solutions of octaethylporphyrin. Irradiation of these degassed solutions with light absorbed only by the metalloporphyrin leads slowly [ $\phi = 10^{-4}$  for a  $\text{SnCl}_2 \cdot 2\text{H}_2\text{O}$  saturated pyridine solution,  $\lambda = 405 \text{ nm}$ , (porphyrin) =  $8 \times 10^{-5} \text{ M}$ ] to production of the blue tin octaethylchlorin. The chlorin is subsequently photoreduced more rapidly ( $\phi^0 = 2 \times 10^{-4}$ )<sup>9</sup> than the porphyrin to yield a relatively light-stable (in the absence of oxygen) product (I). The chlorin and I are the only products detected in the course of the photoreduction. Conversion of the chlorin to I is quantitative as revealed by the occurrence of several isosbestic points when tin octaethylchlorin is the starting material. The spectrum of I is remarkably similar to that of the chlorin (figure); its identity as the tin complex of 5,6,7,8-tetrahydrooctaethylporphyrin (or cis-bacteriooctaethylchlorin) was revealed by its nmr spectrum and by elemental analysis of its isolated tin (IV) dichloride (table). The "magenta" tetrahydrooctaethylporphyrin assigned the cis structure by Eisner<sup>3</sup> and by Inhoffen<sup>5</sup> yields I on treatment with  $\text{SnCl}_2 \cdot 2\text{H}_2\text{O}$  in pyridine.

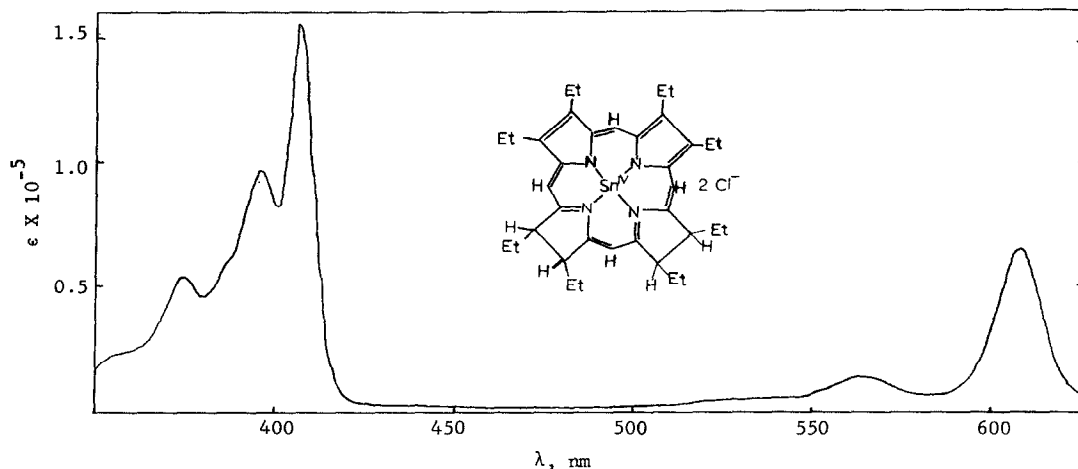


Figure: Electronic Absorption Spectrum of I in Pyridine.

Octaethylporphyrin tin (IV) chloride, prepared in the air,<sup>4</sup> undergoes photochemical reduction in degassed pyridine solution but the reduction is extremely slow ( $\phi < 10^{-6}$ ) and several unidentified products are formed in addition to the chlorin and I. The tin (IV) complex photoreduces rapidly in degassed solutions to which  $\text{SnCl}_2 \cdot 2\text{H}_2\text{O}$  has been added to yield I quantitatively via the chlorin. In contrast to zinc, cadmium and magnesium porphyrins,<sup>2</sup> the tin (IV) complex does not photoreduce in the presence of hydrogen atom donors such as ascorbic acid or benzhydrol.

Though precise kinetic details of the photoreduction have not been investigated, it is clear that the reaction proceeds via photochemical electron transfer to the porphyrin and subsequent protonation. The electron donor could be either tin (II) within the complex or external  $\text{SnCl}_2$ . The oxidation state of tin within the porphyrin complexes is uncertain. Since tin must be introduced into the porphyrin as tin (II), the first product formed must be the tin (II) complex. However, the tin complex prepared by introduction of  $\text{SnCl}_2 \cdot 2\text{H}_2\text{O}$  into degassed ethanol or pyridine solutions has absorption and fluorescence spectra nearly identical to those of octaethylporphyrin tin (IV) dichloride. No intermediates are detectable in metallation with  $\text{SnCl}_2 \cdot 2\text{H}_2\text{O}$  in pyridine solution. However, when degassed pyridine solutions of octaethylporphyrin are treated with anhydrous  $\text{SnCl}_2$ , the first species observed

upon heating as a broad, intense absorption at 495 nm.<sup>10</sup> This material forms the metallo-porphyrin on further heating while on irradiation it yields a complicated mixture of products.<sup>10</sup> It appears that the "495" species is an intermediate in metallation but not octaethylporphyrin tin (II). It is possible that octaethylporphyrin tin (II) exists only as an intermediate in the reduction.<sup>4</sup> Interestingly, electrochemical reduction of tin porphyrins has been suggested to proceed via ring reduction rather than via reduction at the metal.<sup>11</sup>

While results of this study are formally and perhaps even mechanistically similar to those obtained in the sodium-alcohol reduction of tin (IV) porphyrins,<sup>4</sup> the photochemical reduction is essentially quantitative and proceeds to the tetrahydroporphyrin. Preliminary experiments indicate that copper, zinc and magnesium porphyrins are not photoreduced to chlorins under conditions used for the tin complex. Octaethylporphyrin cobalt (III) undergoes reduction at the metal while free base porphyrins undergo photometallation followed by . reduction.

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TABLE

## NMR SPECTRAL DATA \*

I	$\delta$	1.07	triplet	(12 H)	$\text{CH}_3\text{CH}_2-$	reduced ring
		1.67	triplet	(12 H)	$\text{CH}_3\text{CH}_2-$	"pyrrole" ring
		2.17	quartet of doublets	(8 H)	$\text{CH}_3\text{CH}_2-$	reduced ring
		3.55	quartet	(8 H)	$\text{CH}_3\text{CH}_2-$	"pyrrole" ring
		4.07	multiplet	(4 H)	Chlorin H	
		7.30	singlet	(1 H)	Bridge	H
		8.02	singlet	(2 H)	Bridge	H
		9.03	singlet	(1 H)	Bridge	H

ANALYSIS: For  $\text{C}_{36}\text{H}_{48}\text{N}_4\text{SnCl}_2$ ; %C 59.31; calcd. 59.50; %H 6.61; calcd. 6.61.

\*Varian A-60 Spectrometer;  $\text{CDCl}_3$  as solvent.

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