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## CHEMICAL BIODYNAMICS DIVISION

Submitted to the Journal of Chemical Communications

PREPARATION OF OXOPORPHINATOMANGANESE (IV) COMPLEX

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July 1980

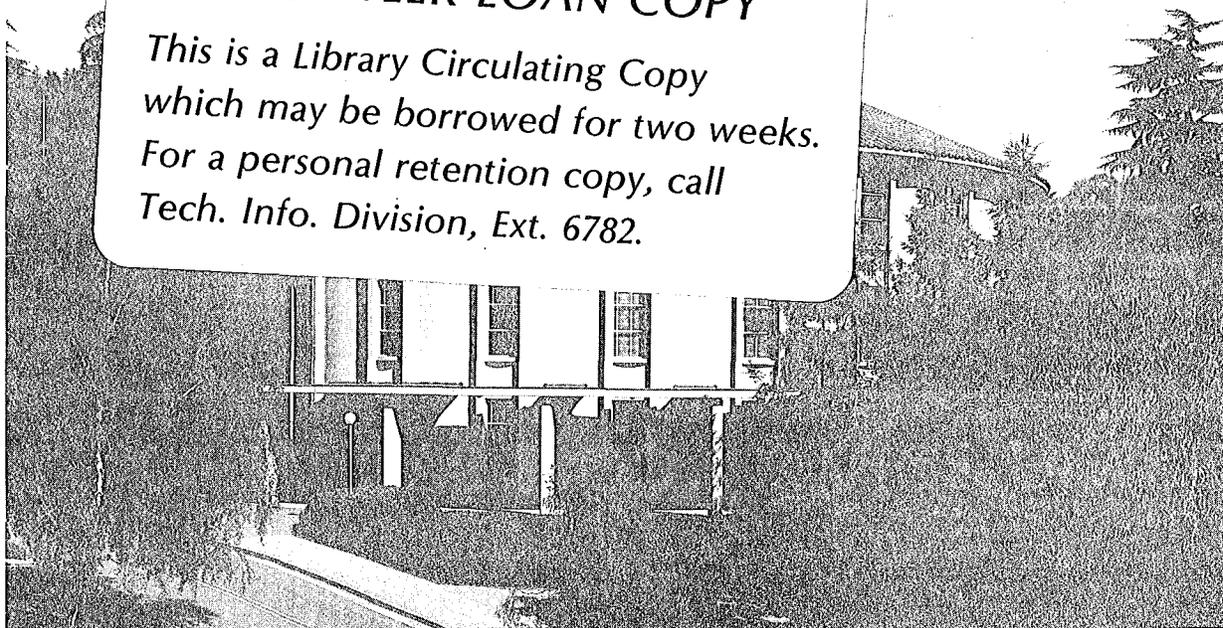
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*LBL-11229 c.2*

## Abstract

Oxo-manganese-tetraphenylporphyrin(1) is prepared by an oxygen-transfer reaction from iodosobenzene to Mn(II)-TPP(3). The oxo-complex(1) is characterized by infra-red spectroscopy and field desorption mass spectroscopy. The spectral characteristics of the oxo-complex are identical to those of a product obtained by direct oxidation of Mn(III)-TPP in an aqueous medium. Oxo-manganese-tetraphenylporphyrin(1) transfers oxygen to triphenylphosphine to produce triphenylphosphine oxide. It is suggested that intermediates similar to (1) are important in oxygen activation by cytochrome P-450 as well as in the photosynthetic evolution of oxygen.



## Preparation of Oxoporphinatomanganese (IV) Complex

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It has been proposed that the activation of oxygen by cytochrome P-450 hemoprotein enzymes involves oxo-metalloporphyrin intermediates.<sup>1</sup> Several such compounds have been reported including vanadium (IV)<sup>2</sup>, molybdenum (V)<sup>3</sup>, and chromium (V)<sup>4</sup> oxo-porphyrins, but only the last of these has been shown to catalyze oxygen transfer reactions. It is known, however, that Mn-complexes are crucial for oxygen evolution in the photosynthetic process. Although the detailed mechanism is not yet established,<sup>5</sup> it has been suggested that their function might involve a high-valent oxo-manganese species.<sup>6</sup> We report here the preparation of oxo-Mn(IV)-meso-tetraphenylporphyrin(1). This complex is capable of transferring an oxygen atom to an electron-rich substrate. We propose that intermediates of similar nature are important in oxygen activation as well as in photosynthetic O<sub>2</sub> evolution.

Treatment of manganese (III) tetraphenylporphyrin acetate (Mn(III)-TPP)(2) with iodosobenzene in methanol did not result in any spectral changes after 10 minutes of contact. However, reduction of (2) with NaBH<sub>4</sub> under nitrogen and subsequent addition of iodosobenzene to the product, Mn(II) tetraphenylporphyrin(3) resulted in an immediate spectral change (Figure 1). Since Mn(III) porphyrin does not react with iodosobenzene, we propose that

the product obtained by the reaction of Mn(II)-porphyrin with iodosobenzene is the oxo-Mn(IV) tetraphenylporphyrin (1), formed via an oxygen transfer process.

The spectral properties of (1) confirm this assignment. The infra-red spectrum of the products in  $\text{CCl}_4$  after removal of the reactants shows a strong absorption at  $1060 \text{ cm}^{-1}$ , attributed to the manganese-oxygen stretching mode. This stretching frequency is in good agreement with those of other reported oxo-metal bonds<sup>3,4,7</sup>. Furthermore, the infra-red spectrum shows stretching bands at  $1023 \text{ cm}^{-1}$  and  $990 \text{ cm}^{-1}$ , characteristic of iodosobenzene. Thus, the presence of a porphyrin complex with iodosobenzene as a ligand can be excluded.<sup>5</sup> Reaction of Mn(II)TPP with iodosobenzene- $^{18}\text{O}$  (30%)<sup>†</sup> shows a decreased intensity of the stretching mode at  $1060 \text{ cm}^{-1}$  and the build-up of a new band at the expected frequency of  $1000 \text{ cm}^{-1}$ , thus confirming the assignment of the band at  $1060 \text{ cm}^{-1}$  to a Mn=O stretching frequency.

Further support for the formation of an oxo-manganese (IV) complex (1) comes from a field desorption mass-spectrum analysis. The spectrum shows a small peak at  $m/e=683$ , corresponding to (1), while the most intense peak ( $m/e = 677$ ) corresponds to the naked Mn-TPP. The oxo-ligand in the complex is probably labile under the conditions of the field desorption analysis. These results are consistent with an oxygen transfer from iodosobenzene to Mn(II)TPP to form oxo-Mn(IV)TPP (1).

It has been previously reported that Mn(IV)-porphyrins, produced by hypochlorite oxidation of Mn(III)-porphyrins, oxidize water to  $\text{H}_2\text{O}_2$  or  $\text{O}_2$  in an acidic medium.<sup>8,9</sup> However, we find that treatment of Mn(III)-TPP (2) with NaOCl yields a product with spectral characteristics similar to those of (1). Therefore, we conclude that Mn(IV)-porphyrins in aqueous solution exist as oxo-products, which could well be the intermediates in the photosynthetic

evolution of oxygen. Addition of triphenylphosphine to (1) resulted in the immediate formation of triphenylphosphine oxide (identified by comparison to an authentic sample by TLC, I.R., M.S.), and Mn(III)-TPP(2).<sup>#</sup> Thus, the oxo-manganese complex (1) can transfer the active oxygen to a substrate.

Scheme I summarizes the formation of the oxo-manganese complex (1) and the oxygen transfer process. The photochemical properties of manganese porphyrins<sup>9</sup> should make possible the production of (1) by photochemical means. This possibility as well as the utilization of (1) in oxy-functionalization of organic substrates are now under current investigation.

#### Acknowledgements

This work was supported by the Division of Chemical Sciences, Office of Basic Energy Sciences of the U.S. Department of Energy under contract W-7405-ENG-48. I.W. thanks the Weizmann Institute of Science for a Dr. Chaim Weizmann Fellowship.

<sup>†</sup> Prepared by hydrolysis of iodosobenzene dichloride with H<sub>2</sub>O<sup>18</sup> (30%).

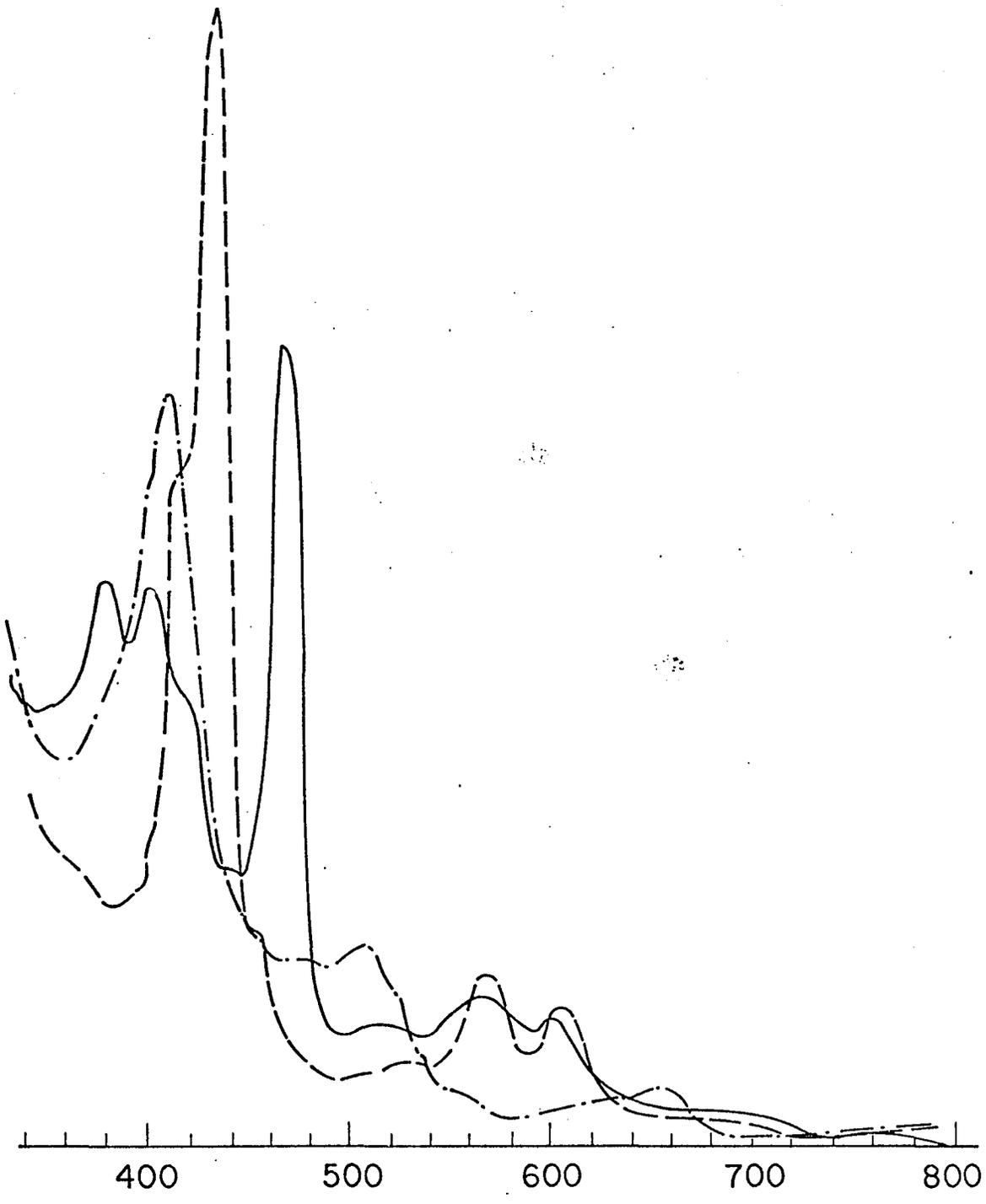
<sup>§</sup> The possible coordination of iodosobenzene to iron porphyrins has been recently proposed cf., J.T. Groves, T.E. Nemo and R.S. Myers, J. Amer. Chem. Soc., 101, 1032 (1979).

# The formation of Mn(II)-TPP (3) is expected in the oxygen transfer process from (1) to triphenylphosphine. Since (3) is a strong reductant while (1) is a strong oxidant, their mutual reaction produces (2). Similar reactions have been reported and shown to be very rapid cf., K.H. Nill, F. Wasgestian and A. Pfiel, *Inorg. Chem.*, 18, 564 (1979); B.A. Moyer and T.J. Meyer, *J. Amer. Chem. Soc.*, 101, 3601, (1979).

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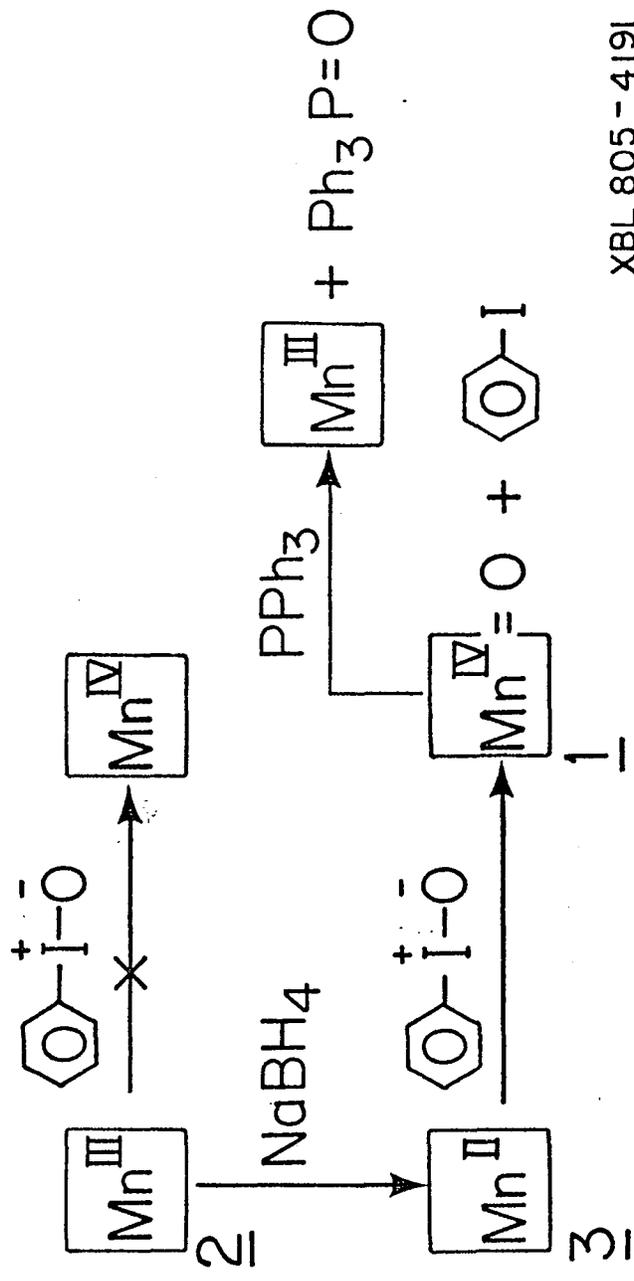
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XBL 805-4196

Willner et al.  
Figure 1



XBL 805 - 4191

This report was done with support from the United States Energy Research and Development Administration. Any conclusions or opinions expressed in this report represent solely those of the author(s) and not necessarily those of The Regents of the University of California, the Lawrence Berkeley Laboratory or the United States Energy Research and Development Administration.