Preparation of an Oxoporphyrinatomanganese(IV) Complex

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Summary Oxo-manganese-tetraphenylporphyrin (O=Mn^{IV}-TPP) has been prepared by an oxygen-transfer reaction from iodosylbenzene to Mn^{II}TPP and characterized by its i.r. and field desorption mass spectra, which are identical to those of the product obtained by direct oxidation of Mn^{III}(TPP) in an aqueous medium; it transfers oxygen to triphenylphosphine to produce triphenylphosphine oxide, and it is suggested that similar intermediates are important in oxygen activation by cytochrome P-450 as well as in the photosynthetic evolution of oxygen.

IT has been proposed that the activation of oxygen by cytochrome P-450 hemoprotein enzymes involves oxo-metalloporphyrin intermediates.[1] Several such compounds have been reported including vanadium(IV),[2] molybdenum(V),[3] and chromium(V)[4] oxo-porphyrins, but only the last of these has been shown to catalyse oxygen-transfer reactions. It is known, however, that Mn-complexes are crucial for oxygen evolution in photosynthetic processes. Although the detailed mechanism is not yet established,[5] it has been suggested that their function might involve a high-valent oxo-manganese species.[6] We report here the preparation of oxomanganese(IV) mesotetraphenylporphyrin (**1**). This complex is capable of transferring an oxygen atom to an electron-rich substrate. We propose that intermediates of a similar nature are important in oxygen activation as well as in photosynthetic O_2 evolution.

Treatment of manganese(III) tetraphenylporphyrin acetate (Mn^{III}TPP) (**2**) with iodosylbenzene in methanol did not result in any spectral changes after 10 min. However, reduction of (**2**) with $NaBH_4$ under nitrogen and subsequent addition of iodosylbenzene to the product, Mn^{II}TPP (**3**), resulted in an immediate spectral change (Figure). Since the Mn^{III}-porphyrin does not react with iodosylbenzene, we propose that the product obtained by the reaction of the Mn^{II} porphyrin with iodosylbenzene is the oxomanganese(IV) tetraphenylporphyrin (**1**), formed *via* an oxygen-transfer process.

The spectral properties of (**1**) confirm this proposition. The i.r. spectrum of the products in CCl_4, after removal of the reactants, shows a strong absorption at 1060 cm^{-1}, attributed to the Mn=O stretching mode. This stretching frequency is in good agreement with those of other reported oxo-metal bonds.[3,4,7] Furthermore, the i.r. spectrum shows stretching bands at 1023 and 990 cm^{-1}, characteristic of iodobenzene. Thus, the presence of a porphyrin complex with iodosylbenzene as a ligand can be excluded.† Reaction of Mn^{II}TPP (**3**) with [30% ^{18}O]iodosylbenzene‡ leads to a

† The possible co-ordination of iodosylbenzene to iron porphyrins has been proposed recently, *cf.*, J. T. Groves, T. E. Nemo, and R. S. Myers, *J. Am. Chem. Soc.*, **1979**, **101**, 1032.

‡ Prepared by the hydrolysis of iodosylbenzene dichloride with $H_2{}^{18}O$ (30%).

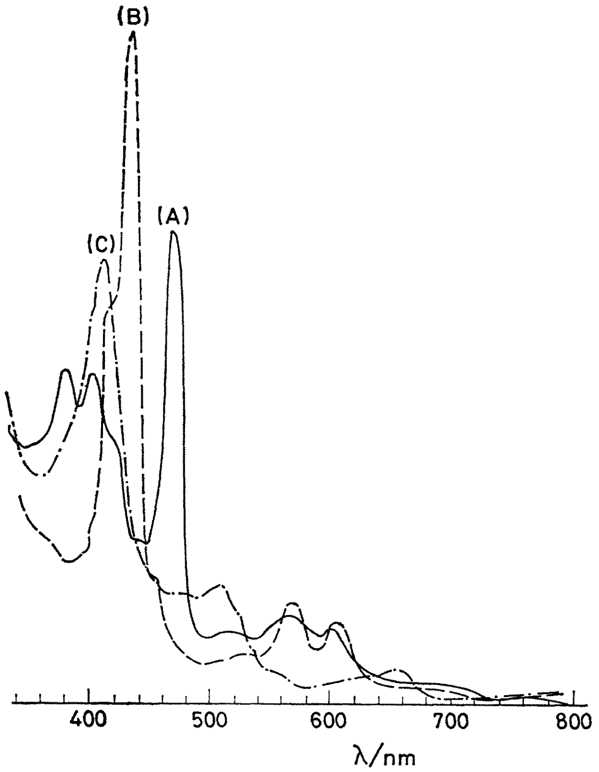
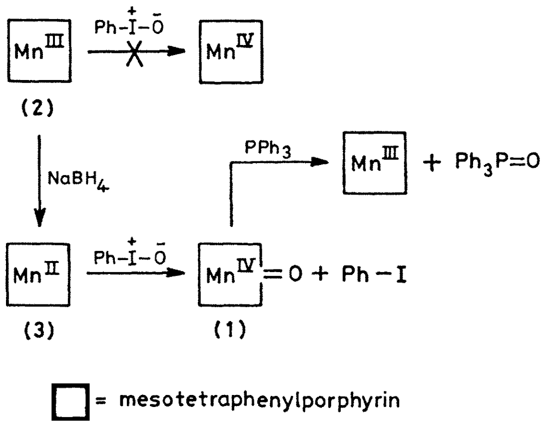


FIGURE. Visible spectra of manganese porphyrins: (A), Mn^{III}TPP (**2**); (B), Mn^{II}TPP (**3**); (C), O=Mn^{IV}TPP (**1**).

decreased intensity in the stretching mode at 1060 cm^{-1} and the build-up of a new band at the expected frequency of 1000 cm^{-1}, thus confirming the assignment of the band at 1060 cm^{-1} to a Mn=O stretching frequency.

Further support for the formation of the oxo-manganese(IV) complex (**1**) comes from a field-desorption mass-spectral analysis. The spectrum shows a small peak at *m/e* 683, corresponding to (**1**), while the most intense peak (*m/e* 667) corresponds to the non-oxygenated MnTPP. 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 iodosylbenzene to Mn^{II}TPP (**3**) to form O=Mn^{IV}TPP (**1**).

It has been reported previously that Mn^{IV}-porphyrins, produced by the hypochlorite oxidation of Mn^{III}-porphyrins, oxidize water to H_2O_2 or O_2 in an acidic medium.[8,9] 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 with an authentic sample using t.l.c., i.r., and m.s.) and Mn^{III}TPP (**2**).§ Thus, the oxo-manganese complex (**1**) can transfer the active oxygen to a substrate.



SCHEME.

The Scheme summarizes the formation of the oxo-manganese complex (**1**) and the oxygen-transfer process. The photochemical properties of manganese porphyrins[9] should enable the production of (**1**) by photochemical reactions. This possibility and the use of (**1**) in the oxygenation of organic substrates are now under investigation.

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

(*Received* 17*th June* 1980; *Com.* 658.)

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§ The formation of Mn^{II}TPP (**3**) is expected in the oxygen-transfer process from (**1**) to PPh$_3$. 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.*, 1979, **18**, 564; B. A. Moyer and T. J. Meyer, *J. Am. Chem. Soc.*, 1979, **101**, 3601.

[1] G. A. Hamilton in 'Molecular Mechanisms of Oxygen Activation,' ed. O. Hayaishi, Academic Press, New York, 1974, p. 405; C. K. Chang and D. Dolphin in 'Bioorganic Chemistry,' Vol. IV, ed. E. E. van Tamelen, Academic Press, New York, 1978, p. 37.
[2] R. C. Pettersen and L. E. Alexander, *J. Am. Chem. Soc.*, 1968, **90**, 3873.
[3] Y. Matsuda, F. Kubota, and Y. Murakami, *Chem. Lett.*, 1977, 1281.
[4] J. T. Groves and W. J. Kruper, *J. Am. Chem. Soc.*, 1979, **101**, 7613.
[5] A. Harriman and J. Barber in 'Photosynthesis in Relation to Model Systems,' ed. J. Barber, Elsevier North-Holland, New York, 1979, pp. 243—280 and references cited therein.
[6] M. Calvin, *Science*, 1974, **184**, 375.
[7] J. A. Elvidge and A. B. P. Lever, *Proc. Chem. Soc., London*, 1959, 195.
[8] I. Tabushi and S. Kojo, *Tetrahedron Lett.*, 1975, 305.
[9] A. Harriman, *Coord. Chem. Rev.*, 1979, **28**, 147.