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MECHANISM OF PHOTO-OXYGENATION OF MESO-TETRAPHENYLPORPHYRIN METAL COMPLEXES

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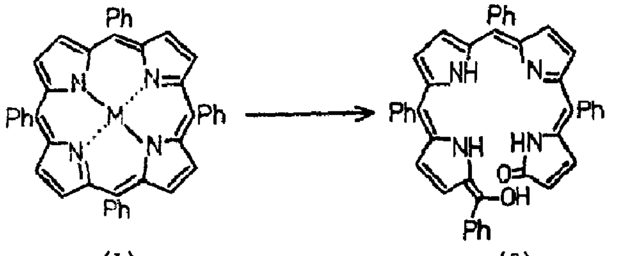
Photo-oxygenation of magnesium(II) meso-tetraphenylporphyrin (1a) to give open-chain benzoylbilitriene (2) is shown to proceed by way of a mechanism involving only one oxygen molecule.

We recently showed[1] that photo-oxygenation of certain <u>meso</u>-methylpheophorbides related to the bacteriochlorophylls-c, to give open-chain acetylbiliverdins, proceeded by way of a mechanism involving only one oxygen molecule. Our method employed photo-oxygenations under an atmosphere enriched with ^{18}O containing $^{18,18}O_2$ and $^{16,16}O_2$, but none of the mixed species $^{16,18}O_2$, and the presence of oxygen labels in the products was verified using repeated-scan mass spectrometry, as described elsewhere.[2] There are three oxidative mechanisms which can be effectively differentiated in this way, namely a *One-Molecule Mechanism* (in which the oxygen atoms inserted into the product are derived from a single oxygen molecule), a *Two-Molecule Mechanism* (in which the atoms are derived from two oxygen molecules), and a *Hydrolytic Mechanism* (in which one oxygen is derived from oxygen, and the other from water). In the present Letter we demonstrate that the photo-oxygenation of metallo-<u>meso</u>-tetraphenylporphyrins (1) affords open-chain benzoylbilitriene (2) by a *One-Molecule Mechanism*. This was unexpected since the production of (2) involves a reduction as well as demetalation, and a *Hydrolytic Mechanism* had been postulated.[3] However, this proposal was readily excluded from further consideration by carrying out the photo-oxygenation of magnesium(II) <u>meso</u>-tetra-



(1)
a, M = Mg
b, M = Zn

(2)
and keto tautomer

phenylporphyrin[4] in methylene chloride under an atmosphere consisting almost entirely of ^{18,18} and comparing the mass spectrum with that obtained under $^{16,16}O_2$. Figure 1A shows a partial ma spectrum of compound (2) prepared under $^{16,16}O_2$; the major peak is clearly the molecular ion a *m/e* 648, and the small peak at 646 may relate to a small impurity due to compound (5). A fulle consideration of the intermediacy of compound (3) will be reported elsewhere. Figure 1A also shows the *m/e* 650 peak to be greater than expected from the naturally abundant isotopes ^{13}C an ^{15}N, and this must be allowed for in assessing ^{18}O incorporations. Figure 1B shows the mass spectrum of (2) prepared by photo-oxygenation of (1a) under 97% $^{18,18}O_2$. Clearly, the major peak now appears *m/e* 652, which indicates that *both* oxygen atoms insert are derived from di-oxygen, and eliminates the *Hydrolyt Mechanism*. The small peak at *m/e* 650 probably correspo to incorporation of two ^{18}O atoms into the small impuri at *m/e* 646 (Figure 1A). Figure 1C shows the mass spect of (2) obtained from a mixture of 60% $^{16,16}O_2$ and 40% $^{18,18}O_2$. Comparison with Figure 1A shows that the majo incorporation occurs at *m/e* 652, and is consistent with *One-Molecule Mechanism*. A *Two-Molecule Mechanism* would require the major incorporation at *m/e* 650.[2] Quantitat determination of the ^{18}O incorporation at *m/e* 652 was o tained for the two enrichments by the averaging of repe ed scans.[2] For the reaction carried out under 97% ^{18,1} the mole percent of (2) at *m/e* 648 and *m/e* 652 was 4% a 96% respectively, in excellent agreement with the predi ions for a *One-Molecule Mechanism* (3% and 97%, respecti ly). For photo-oxygenation under 40% $^{18,18}O_2$, the mole percent of (2) at *m/e* 648 and *m/e* 652 was 61% and 39%, again in good agreement with the 60% and 40% prediction for a *One-Molecule Mechanism*, but totally inconsistent with the predictions (36% and 16% respectively) for the *Two-Molecule Mechanism*. Our results clearly and definitively favor a *One-Molecule Mechanism*.

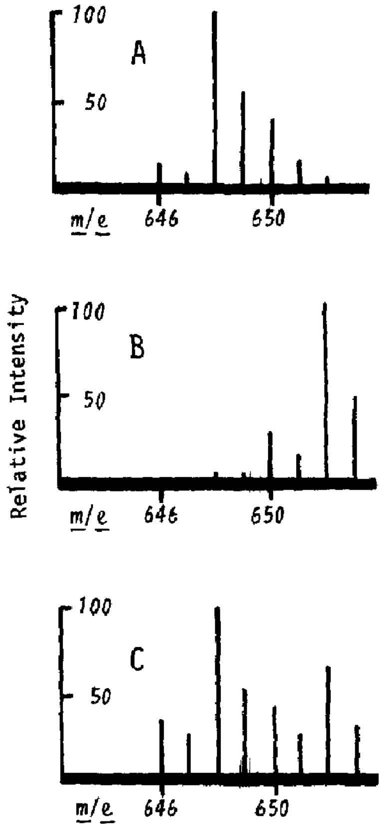
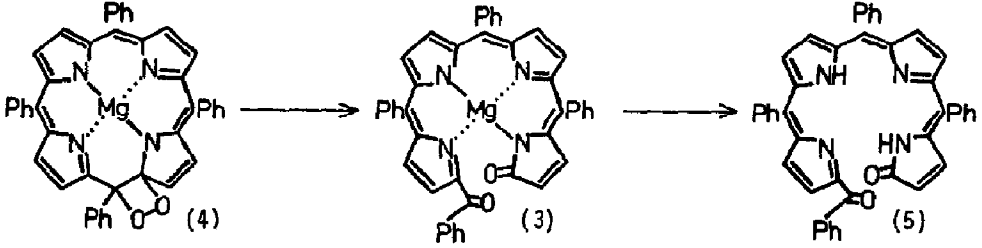


Figure 1: Mass spectra of (2) prepared under:
A, $^{16,16}O_2$
B, 97% $^{18,18}O_2$
C, 40% $^{18,18}O_2$.

Given that the mechanism for photo-oxygenation of magnesium(II) meso-tetraphenylporphyrin (1a) involves only one oxygen molecule, we are forced to the conclusion that the initial stable photoproduct (λ_{max} ~790 nm; Figure 2) is compound (3), probably formed via the dioxetane (4), which, in the magnesium(II) octaethylporphyrin series, has been shown to have a very short lifetime by Fuhrhop.[5] Figure 2 shows the absorption spectra of (1a) and the initial photoproduct. The final product (2) isolated from the photo-oxygenation following purification by TLC, has been previously identified by ourselves[6] and by others,[3] the same compound having been obtained by treatment of (1b) with thallium(III) salts.[7] Clearly the product (2) is not derived simply by demetalation of our proposed initial photoproduct (3) [which would give (5)]. It is necessary to replace the metal ion with two protons, and to add two extra hydrogen atoms. Figure 3 shows the absorption spectrum of the benzoylbilitriene (2) and the zinc(II) complex derived from it.[7] The cadmium(II) complex also has a similar spectrum. There is clearly a discrepancy between the spectrum of the initial photoproduct (3), λ_{max} ~790 nm, and the zinc(II) [or cadmium(II) and presumably magnesium(II)] complex derived from (2).[8] Our conclusion is, therefore, that during the work-up procedure, the initial photo-product (3) suffers addition of two hydrogens as well as demetalation, to afford (2) rather than (5) (the logically expected product). These conclusions



(4) (3) (5)

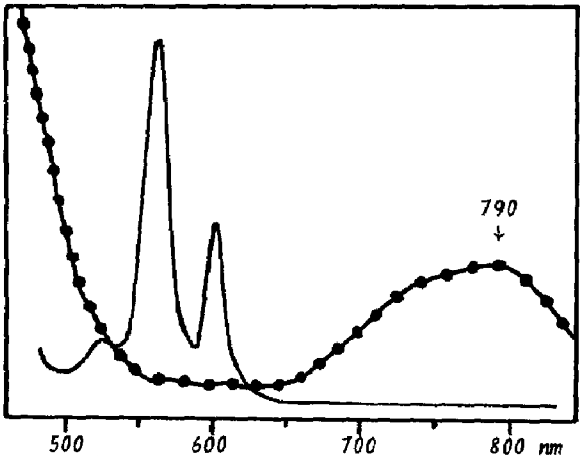


Figure 2: Visible absorption spectrum (CH$_2$Cl$_2$) of — MgTPP (1a); and -●- the initial photoproduct, assigned structure (3).

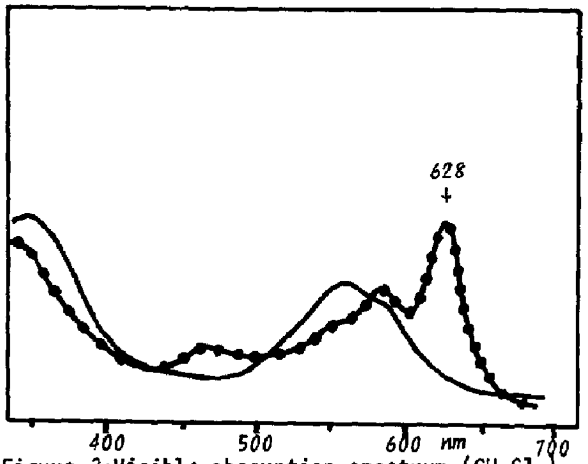
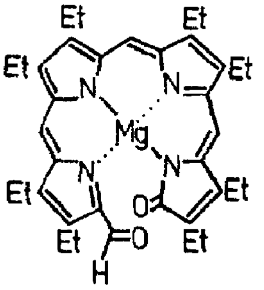


Figure 3: Visible absorption spectrum (CH$_2$Cl$_2$) of — benzoylbilitriene (2); and -●- the zinc(II) complex of compound (2).

are further supported by Fuhrhop's work[5] on the photo-oxygenation of magnesium(II) octaethylpc phyrin, which gave the extremely unstable magnesium(II) formylbilitriene (6), λ_{max} 820 nm, as initial photoproduct. An X-ray study[9] has confirmed the structur of (6). Significantly, the metal-free derivative of (6) has a λ_{π} at 730 nm[5] [indicating the expected hypsochromic shift from (6) c 90-100 nm], which does not compare with the λ_{max} 565 nm for (2), having suffered a 225 nm hypsochromic shift from the initial phot product. This shift is unusually large for a simple demetalation Work on the isolation and characterization of the initial photoproduct is underway.



(6)

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