THE REACTIONS OF MAGNESIUM OCTAETHYLPORPHYRIN AND ITS π-CATIONS WITH NITROGEN DIOXIDE AND NITRITE.

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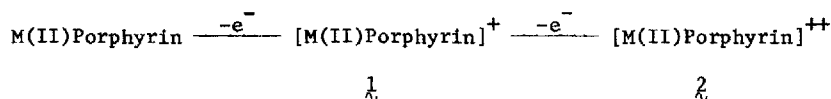Department of Chemistry

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The electrochemical oxidation of a variety of metalloporphyrins proceeds via reversible one and two electron oxidations to generate the corresponding π-cation radical(1) and the π-dication(2)[1,2]

$$M(II)Porphyrin \xrightarrow{-e^-} [M(II)Porphyrin]^+ \xrightarrow{-e^-} [M(II)Porphyrin]^{++}$$

$$\underset{1}{} \qquad\qquad \underset{2}{}$$

We have shown that the π-dications are powerful electrophiles which rapidly react with a variety of nucleophiles to generate isoporphyrins. When the meso-carbon atom is substituted by a phenyl group the isoporphyrin (3,R=∅) is stable, but when the meso-carbon bears a hydrogen atom (3,R=H) then the loss of a proton regenerates a neutral meso-substituted metalloporphyrin (4).[3]
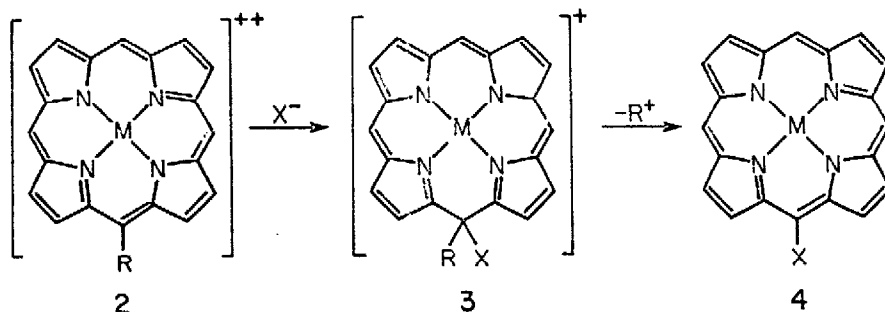
However, we have found no evidence for the reaction in which the π-cation radical functions as a electrophile and earlier such reports have been explained and reinterpreted in other mechanistic terms. Indeed one would anticipate that the reactions between a metalloporphyrin π-cation radical and a two-electron nucleophile would be energetically unfavourable since attainment of the transition state for such a reaction requires the promotion of an electron to an antibonding orbital. Nonetheless it was recently reported[4] that in the presence of excess oxidant meso-nitration of octaethyl-porphyrins and -chlorins was effected by the nucleophilic attack of nitrite

upon metalloporphyrin π-cation radicals, which it was suggested was then followed by the removal

of a second electron and subsequent loss of a proton from the resultant metalloisoporphyrin.

Since this sequence of reactions appeared to be mechanistically untenable we have re-examined

this and related reactions.

In order to more effectively determine the reactions of the porphyrin cations, electro-

chemical methods were employed to generate the reacting species. This allows quantitative

generation of both the cation radical and the dication without contamination by excess oxidant.

All electrochemical experiments were carried out in CH_2Cl_2 as described elsewhere[3] using standard

three-electrode operational amplifier circuitry. The supporting electrolyte was tetra-n-

butylammonium hexafluorophosphate and as reference a Ag/AgCl couple.

Reaction of the π-cation radical $[Mg(II)OEP]^{+\cdot}$ with a stoichiometric (1:1) amount of $NaNO_2$

caused its reduction and gave, after demetallation, a quantitative yield of OEP. The reaction

of excess $NaNO_2$ with $[Mg(II)OEP]^{+\cdot}$ gave once again, after demetallation, OEP as the only porphyrin

product. Thus under the above conditions nitrite acts as a reducing agent to produce the neutral

magnesium OEP. The reaction of aliquots of $NaNO_2$ with the π-dication $[Mg(II)OEP]^{++}$ resulted in

an initial reduction to $[Mg(II)OEP]^{+\cdot}$ followed by partial demetallation and meso-nitration.

After addition of a 4:1 excess of nitrite to the dication, the isolable porphyrin products were

OEP and mixtures of 5,10- and 5,-15 dinitro OEP.[5] In the case of the dication, however, the

potential of $[Mg(II)OEP]^{++}$ ($\sim$1.2 vs NHE) is apparently high enough to effect an initial oxidation

of the NO_2^- moiety to NO_2 which can then further react as described below.

Reactions of NO_2 in CH_2Cl_2 with Mg(II)OEP or $[Mg(II)OEP]^{+\cdot}$ were followed spectrally using

a flow-through optical-electrolysis apparatus.[6] By careful additions of NO_2 to Mg(II)OEP sets

of isosbestic points were observed indicating a series of clean reactions proceeding through at

least three different intermediates, until a limiting spectrum was obtained. Samples, taken at

successive points, gave, after demetallation and work up 5-nitro OEP, 5,10- and 5,15-dinitro

OEP, 5,10,15-trinitro OEP and 5,10,15,20-tetranitro OEP.[5]

Spectroscopic evidence showed that the reaction of Mg(II)OEP with NO_2 proceeds via the

initial formation of $[Mg(II)OEP]^{+\cdot}$ since concentrations of the π-cation radicals quickly reached

a maximum after the addition of one equivalent of NO_2. Further addition of NO_2 caused a decrease

in the intensity of the $[Mg(II)OEP]^{+\cdot}$ band at 665 nm, as well as a red shift in the two metallo-

porphyrin visible absorption bands (Fig. 1). The addition of one equivalent of NO_2 to

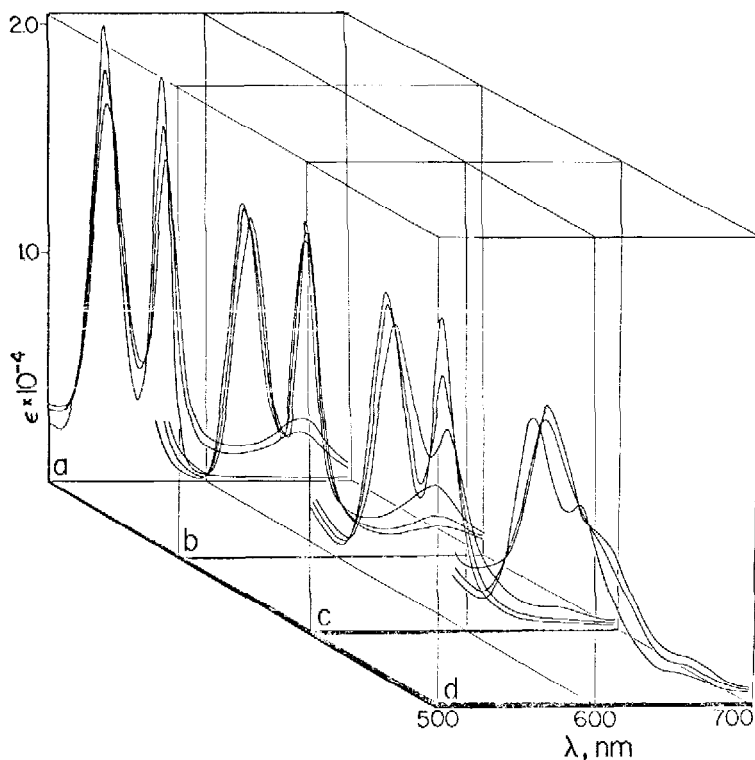$[Mg(II)OEP]^{+\cdot}$ (generated electrochemically) yielded, after demetallation, 5-nitro-OEP as the only

Figure 1 - *Stepwise formation of meso-(nitro) derivatives of MgOEP upon treatment of MgOEP with NO₂ in CH₂Cl₂: a MgOEP plus 1 equivalent of NO₂; b the addition of a second equivalent of NO₂; c the addition of a third equivalent of NO₂; d the addition of a fourth equivalent of NO₂ gives the resulting limiting spectrum.*

porphyrin product.

We envisage the above reactions as an initial oxidation of Mg(II)OEP by NO_2 to generate $[Mg(II)OEP]^{+\cdot}$ followed by a coupling of the radical cation with the NO_2 radical to generate an isoporphyrin (3;R=H;X= NO_2). No spectral evidence was found for formation of the isoporphyrin indicating loss of the meso-proton to be a facile process. Repetition of the same cycle would bring about further meso-nitration and indeed Figure 1 shows the step-wise nitration of all four meso-positions. As each additional nitro group is added its

electron withdrawing properties increase the potential[8] required to generate the next cation radical. This accounts for the stepwise nature of the reaction and the clean isosbestic points observed for each step. The yields were estimated spectroscopically to be quantitative.

In view of the above results we conclude that the reaction observed by Smith et al[4] actually involved the oxidation of NO_2^- to NO_2, by iodine in methanol, followed by the reaction of the NO_2 with either Mg(II)OEP or $[Mg(II)OEP]^{+\cdot}$. In support of this hypothesis we find a high concentration of NO_2, detected by vpc, in the atmosphere above a CH_2Cl_2/MeOH solution of $NaNO_2$ and I_2.

Acknowledgements

References

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7. E. Watanabe, S. Nishimura, H. Ogoshi and Z. Yoshida. *Tetrahedron*, 31, 1385 (1975).

8. The first oxidation potentials of OEP and its meso-nitro substitution products were measured versus the Ag/AgCl reference couple in 0.2 M tetra-n-butylammonium hexafluorophosphate- $-CH_2Cl_2$: OEP 0.86v; 5-nitro OEP 1.1 v; 5,10-dinitro OEP 1.3v; 5,10,15-tri-nitro OEP 1.46v; 5,10,15,20-tetranitro OEP > 1.6v; (this limit was imposed by decomposiition of the solvent-supporting electrolyte system).