10. REACTIONS OF PORPHYRIN CATIONS IN THE PRESENCE OF NUCLEOPHILES

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Three main classes of porphyrin cations are known. Those derived from N-protonation, \( \pi \)-cation radicals which results from the removal of a bonding electron from the porphyrin \( \pi \)-cloud, and the \( \pi \)-dications in which two bonding electrons are lost from the \( \pi \)-cloud.

Since all nucleophiles possess a pair (or insipient pair) of non-bonding electrons they are by definition Lewis bases and as such are usually incompatible with the conditions under which N-protonation occurs. To our knowledge the only reaction of a protonated porphyrin with a nucleophile, which result in an overall nucleophilic substitution of the porphyrin ring, is the addition of sulfhydryl groups\(^*\) at a methine bridge e.g. 1 → 2. The reaction is favoured by the peripheral electron withdrawing group and by the rehybridization of the \( sp^3 \)-meso carbon atom to an \( sp^2 \) atom with consequent relief of strain amongst the peripheral substituents. It must be noted, however, that it is not clear if this reaction proceeds via the N-protonated porphyrin, for an equally plausible mechanism involving protonation of the peripheral ester can be envisaged. It should be noted in passing that free base and metalloporphyrins do not undergo nucleophilic attack either except

\[ \text{DNCOSH} \]

\[ \text{DNCOSH} \]
perhaps when reduced by hydride to the porphyrinogens.

As we shall see below, the reactions of porphyrin \( \pi \) cations in the presence of nucleophiles are complex and the discussion of this area is left till later. When, however, two electrons are removed from the porphyrin periphery the corresponding \( \pi \)-dication is a powerful electrophile\(^6\), undergoing reactions with a variety of nucleophiles. When the \( \pi \)-dication of zinc meso-tetraphenylporphyrin 3 (Zn(II)TPP)\(^{3+} \) was treated with methanol an immediate change in color, and optical spectrum (Fig. 1), occurred from that of a typical \( \pi \)-dication (diffuse end absorption in the visible and near infrared) to a species having two strong bands in the near infrared. Isolation, and characterisation\(^4\), showed the compound to be the isoporphyrin\(^5\) (4). Inspection of the nmr spectrum of 4 (Fig. 2) confirms the structure of the species.

Figure 1: Optical absorption spectra, in CH\(_2\)Cl\(_2\), of (Zn(II)TPP)\(^{3+} \) 2Cl\(_{104} \) (3)) before (\( \rightarrow \)) and after (\( \cdots \cdots \)) treatment with methanol to give (4).

Figure 2: 100 MHz nmr spectrum of 4 in benzene-d\(_6\).
and shows two sets of AB quartets for the β-protons of the methoxyisoporphyrin which has essentially C2v symmetry. These AB quartets are well resolved in benzene, which acts as a shift reagent, whereas in carbon tetrachloride (Fig. 3a) one of the AB quartets almost collapses to a singlet. In methylene dichloride the isoporphyrin 4 exhibits (Fig. 3b) an nmr spectrum similar to that observed in benzene though not as well resolved. Isoporphyrins are cationic and might be expected to undergo further nucleophilic attack, and indeed this is the case. When 4, in CH2Cl2, is treated with a concentrated solution of sodium methoxide in methanol the green solution of the isoporphyrin changes to an orange color, similar to that of a pyrromethene, and the product 5, which crystallized from solution, had an optical spectrum with λmax at 458 nm (Fig. 4) similar to that of pyrromethene. The nmr spectrum in CD2Cl2 of the β-protons (Fig. 3c) shows only a single AB quartet (8 protons) and a sharp singlet at 3.30 6 (six H O-CH3. The only structure consistent with this data is the dimethoxyporphodimethene 5 which results from the addition of methoxide to the meso position opposite the one already bearing a methoxyl group. Treatment of 5, in methylene dichloride, with acetic acid immediately regenerated the isoporphyrin 4, (Scheme 1).

Johnson et al.6 have recently reported that treatment of meso-tetraphenylporphyrin (TPP) with a nitrating mixture of nitric and sulfuric acids gave, upon work-up, the dihydroxy porphodimethene (6a). Treatment of 6a with TFA regenerated TPP, and in the presence of zinc and acetic acid 6a gave the hydroxy isoporphyrin 6b. It was suggested7 that 6a was formed by electrophilic ipso nitration followed by hydrolysis of the
nitro group. An equally plausible mechanism, and one which is consistent with the chemistry discussed above, could involve, as depicted in Scheme 2, an initial oxidation of TPP by the nitratating mixture to the dication followed by the addition of water to give 6a, via the hydroxyisoporphyrin. Treatment of 6a with zinc and acetic acid would incorporate a zinc atom into 6a which by analogy with the reactivity of 5 would lose hydroxide to give 6b. In the presence of acetic acid.

When an ethereal solution of the Isoporphyrin A is allowed to stand in contact with aqueous 2N sodium hydroxide the green solution turns blue over a period of about two days (neither light nor oxygen influence the reaction). Chromatography on alumina affords a purple zinc complex 7 while chromatography over silica gel, or treatment of 7, with acid gives a metal free complex 8 which can be converted to 7 with zinc acetate.

The mass spectrum of 7 had a parent peak at m/e 710 (Zn(II)TPP + 2(OH)), while the metal free complex had a parent peak at m/e 648 (H2TPP + 2(OH)). The interconversion of 4 −→ 5
SCHEME 2

suggests a ready mechanism by which the methoxyisoporphyrin 4 could be converted into the hydroxyisoporphyrin 9. Reaction of 9 with a second mole of hydroxide at meso-carbon could generate the compound 6a, but clearly this is not the final purple complex (7) we isolated which, as a result of its color, must have a more conjugated chromophore than a porphodimethene. One can envisage nucleophilic attack not only at a bridging meso-carbon atom but at one of the "angular" carbon atoms 9 → 10 (Scheme 3). Ring opening of 10 would generate the tetrapyrrole 7 which upon demetallation would give 8. The same violet compound (8) has been isolated by Evans et al., who assign a similar structure (as the tautomer 11). Shine et al. have isolated the same compound, and Johnson refers to a violet complex which, considering the reaction conditions, is also presumably 8.

The zinc complex (7) is neutral and whatever the tautomeric structure of 8 there appear to be two principal tautomeric structures for the metal complex, either 7 or the lactim enol 12 which is fully conjugated (and formally a derivative of a bilatriene). Zinc complexes of both biliverdins (13) and phlorins (14), which have chromophores similar to the tautomer 12 have their principal absorptions at 790 and 810 nm, considerably higher than our zinc complex whose principal absorption is at 625 nm (Fig. 5a). Indeed other fully conjugated tetrapyrrolic chromophores such as the magnesium oxaporphyrin (15) (\(\lambda_{max} 825 \text{ nm}\)) (Fig. 5b) and the zinc isoporphyrin 4 (\(\lambda_{max} 825 \text{ nm}\))
Instead of having both oxygen atoms in their enol forms two other tautomers such as 7 or 16 are possible. Both of these are violins\textsuperscript{10} where only three of the pyrrolic rings are conjugated. The optical spectra of the naturally occurring violins such as mesobilviolin IXa (17) \( \lambda_{\text{max}} \text{CHCl}_3, \text{MeOH/NH}_3 \) 329, 570 nm; \( \lambda_{\text{max}} \text{MeOH/HCl} \) 331, 607 nm; \( \lambda_{\text{max}} \text{EtOH/NH}_3/\text{Zn}^{2+} \) 338, 582, 632 nm; and aplysloviolin, are all very similar. Furthermore, the purpurins, which have a chromophore similar to that of the
CHCl₃ (----------) in 5% HCl in ethanol (•••) and in saturated Zn(OAc)₂ solution (-----------------------------).

CH₂Cl₂ (-----------); and b) the optical spectra of 19 in saturated Zn(OAc)₂ solution (-----------------------------).

Figure 5: a) Optical spectra of 8 in CH₂Cl₂ (…….), 7 in CH₂Cl₂/CH₃OH/TFA (•••) and 16 (the zinc complex of 8) in CH₃Cl (--------); and b) the optical spectra of 19 in CHCl₃ (--------) in 5% HCl in ethanol (•••) and in saturated Zn(OAc)₂ solution (-----------------------------).

violins (e.g. mesobilipurpurin (18), also exhibit electronic spectra similar to violins. Moreover, Fuhrhop⁹ converted 15 to 19 and the optical spectra of 19 as both the free base, protonated salt, and zinc complex (5b) are very similar to those of the system described here; which may thus be represented by the violin structures 7, 8, 16. The mass spectrum of the purple violin (8) has a parent peak at 648 and other strong peaks at 543, 479, 389 and 236 while the zinc complex (7) has a strong parent peak at 710 and major peaks at 603 and 430. The ease of fragmentation of these systems and their fragmentation patterns are consistent with the ring open structures suggested here. However, Smith¹¹ informs us that a 220 MHz nmr spectrum on the free base is consistent with the fully conjugated chromophore (11), the apparent differences in structure suggested by the various spectral data must await further resolution.
Returning to the reactions of the \( \pi \)-dication we find that a variety of nucleophiles will generate isoporphyrins. The principal limitation being the competition between nucleophilic attack and electron transfer from the nucleophile to give the \( \pi \)-cation radical and other reduced species.

While the \( \pi \)-dication of a porphyrin containing a meso-carbon atom substituted by hydrogen is treated with a nucleophile the intermediate isoporphyrin (20), which is cationic, loses a proton to regenerate the fully aromatic porphyrin (21) now meso-substituted by the original nucleophile\(^{12}\) (Scheme 4). Once again this appears to be a general reaction with the same limitations that reduction of the \( \pi \)-cation by the nucleophile may occur along with substitution. Two specific examples are discussed here, one which has some significance in chlorophyll biosynthesis, the other which relates to reactions of \( \pi \)-cation radicals in the presence of nucleophiles (see below).

Apart from the oxidation level of the chlorin and bacteriochlorin rings the only major structural difference between chlorophyll a (22), bacteriochlorophyll a 23, and protoporphyrin 24 is the isocyclic ring of the photosynthetic pigments. Both Woodward\(^{5}\) and Kenner\(^{13}\) had earlier suggested that conversion of
a propionate side chain of protoporphyrin into a $\beta$-keto ester side chain (24 → 25) would generate a nucleophile (the enolate anion) which could attack the porphyrin periphery and generate the isocyclic ring (Scheme 5). This hypothesis, however, requires nucleophilic attack at the periphery of an unoxidized porphyrin (a reaction which has still not been adequately documented), as well as an overall oxidation. Pursuing this line of reasoning Kenner et al. using iodine as oxidant, and more recently thallium(III) and photolysis, have caused cyclization of a $\beta$-keto ester side chain to an isocyclic ring. While the mechanisms of their cyclization are not clear, parallel experiments that we have carried out suggest a possible route for these cyclizations and provide a logical sequence to explain the biosynthesis of the isocyclic rings in the photosynthetic pigments.

Magnesium protoporphyrin (cf. 24) is the biogenetic precursor of chlorophyll a. We have already suggested why magnesium plays a central role in the initial photochemical step of photosynthesis, and a second role for the magnesium can be assigned to it during the isocyclic ring formation. Most metalloporphyrins undergo two separate and reversible one-electron oxidations to the $\pi$-cation radical and $\pi$-dication. The potentials at which these oxidations occur is dependent upon the centrally coordinated metal, and Fuhrhop has developed an electrostatic model to describe these systems. Of all coordinated metals, magnesium results in the lowest potentials for macrocycle oxidation. Indeed in many cases the potential required to remove two electrons from a specific magnesium porphyrin (to generate the $n$-dication) is frequently lower than the potential required to remove one electron from other metal complexes of the same porphyrin. This suggested to us that
oxidation of a β-keto ester containing metalloporphyrin to a π-dication (26) should allow the enol to attack the periphery generating an isoporphyrin (27) which by analogy to the isoporphyrin 28 should lose a proton to give the porphyrin 28 bearing an isocyclic ring (Scheme 6). The reactions outlined in scheme 6 do indeed occur14 and provide a good model for the in vivo conversion of magnesium protoporphyrin to chlorophyll a.

When the dication of zinc octaethylporphyrin (Zn(II)OEP)++ (prepared by electrolysis of Zn(II)OEP in CH2Cl2/tetra n-propy lammonium perchlorate at 1.1 V versus Ag/AgCl) is treated with an excess of pyridine the green solution turns red. Separation of the reaction mixture on grade III basic alumina (after removal of solvent and supporting electrolyte) gave Zn(II)OEP (upon elution with CH2Cl2) recovered in 25% yield and (upon elution with methanol) gave, after treatment with Cl- and crystallisation, a product obtained in a yield of 70%. Anal: Found C, 61.2; H, 6.97; N, 9.88; Cl, 5.00, Calcd for C41H48ClN5Zn, C, 61.19; H, 6.80; N, 9.84; Cl, 5.091. λ max at 406, 537, and 572. The nmr spectrum (CDCl3, δ) showed peaks at 10.15 (s, 2-meso H), 10.03 (s, 1 meso H), 9.72 (d, 2-py H), 9.05 (t, 1-py H), 8.34 (t, 2-py H), 7.86 (2q, 12H-CH2-CH2), 2.18 (q, 4H-CH2-CH3), 1.89 (18H-CH2-CH2), 1.20 (t, 6H-CH2-CH3). The cationic nature of the macrocycle was confirmed electrophoretically as described previously.15 Removal of the zinc by treatment with HCl yielded the free base (30) identical to that described earlier,16 which had been prepared by treating the π-cation radical of Mg(II)OEP (generated by iodine oxidation) with excess pyridine followed by demetallation.

When the π-dication of Zn(II)TPP is treated with excess pyridine the solution turns red and exhibits a spectrum typical of a metalloporphyrin. When the π-dication is treated with
approximately two equivalents of pyridine the spectrum of the dication changes to that of an isoporphyrin (Fig. 6). Upon addition of more pyridine the isoporphyrin changes to a metalloporphyrin (Fig. 7). This metalloporphyrin can be isolated in yields of greater than 70% to give a compound (29) which has the optical spectrum shown in Fig. 7 (insert) and which proved to be identical to the β-pyrindinium substituted porphyrin prepared by Shine\(^*\) from the reaction of the \(\pi\)-cation radical of Zn(II)TPP with excess pyridine.

The rate of appearance of isoporphyrin was determined using stopped flow techniques by measuring the increase in absorption at 780 nm when the dication was treated with pyridine. Plots of \(\log (A_\infty - A_t)\) vs. time were linear (Fig. 8).
and the pseudo first-order rate constants \( (k_{\text{obs}}) \) gave a straight line when plotted vs. \((\text{py})^2\) (Fig. 9) showing that the rate

\[
\frac{-d[(\text{Zn(II)TPP})^2]}{dt} = k(\text{py})^2[(\text{Zn(II)TPP})^2] \\
\text{where } k = 2.76 \times 10^5 \text{ M}^{-2}\text{s}^{-1} \text{ at } 25^\circ C
\]

This suggests that during the formation of isoporphyrin one molecule of pyridine coordinates to the zinc while the second reacts at the periphery. The question then arises as to whether the pyridine reacts with the dication to give the isoporphyrin.
31a which rearranges to 31b, or if the pyridine reacts directly at the \( \Theta \) position to give the species 31b which goes directly to 29 by the loss of a proton (Scheme 7). As a suprafacial 1,3-sigmatropic shift 31a \( \rightarrow \) 31b is not allowed, however other

\[ 31a \rightarrow 31b \]

As a suprafacial 1,3-sigmatropic shift 31a \( \rightarrow \) 31b is not allowed, however other 1,3-sigmatropic shifts are well documented. The optical spectrum of the intermediate (31a or b) is very similar to that of other isoporphyrins (Fig. 1 and 6) suggesting that
sp² and which still contain an inner conjugated chromophore exhibit “chlorin-like” spectra. When the intermediate (31a or b) is treated with a large excess of pyridine it is cleanly converted (Fig. 7) to the porphyrin 29, with half the reaction being completed in 15 minutes, the isoporphyrin (31a or b) is not, however, sufficiently stable to be isolated.

It is not surprising that the π-dications, which possess an empty bonding π-molecular orbital, are powerful electrophiles. However the π-cation radicals which have lost only one electron from a bonding molecular orbital have no simple mechanism by which they can react with a two electron nucleophile. The first report of a porphyrin π-cation radical reacting in the presence of a nucleophile was that of Barnett and Smith who reported that meso-nitrilation of magnesium OEP occurred when the π-cation radical (Mg(II)OEP)⁺ reacted with nitrite ion. We have found, however, that reaction of Mg(II)OEP⁺ with nitrite brought about the reduction of the cation radical to Mg(II)OEP⁻. Similarly, reaction of the dication (Mg(II)OEP)²⁺ with NO₂ involves initially an electron transfer to give the cation radical Mg(II)OEP⁺ and NO₂. When Mg(II)OEP was treated with NO₂ a series of stepwise reactions ensued whereby mono- di- tri- and finally tetranitro OEP were formed. When the reaction was followed spectroscopically it was observed that the first step was an electron transfer to give the π-cation radical and (presumably) NO₂⁻ (eq. 1, Scheme 8).

Treatment of Mg(II)OEP⁺ (generated electrochemically) with NO₂ gave 5-nitro magnesium OEP (35) and we envision this reaction as a coupling of the radicals to give the isoporphyrin (34) which loses a proton to give the product (35) (eq. 2, Scheme 8). It would appear that radical coupling between an aromatic π-
cation radical and NO$_2$ is a common reaction. Indeed Perrin$^{26}$ has suggested that most electrophilic substitution of aromatic systems by NO$_2^+$ involves an initial electron transfer between the aromatic system and NO$_2^+$ to give NO$_2$ and the π cation radical (eq. 3, Scheme 9) a reaction whose rate is encounter controlled, followed by collapse of these two radicals to give the carbenium ion (an isoporphyrin when a metalloporphyrin is involved) and then loss of a proton to give the substituted aromatic (eq. A, Scheme 9). Clearly the reactions outlined in eq. 1 and 2 are a special case of the more general reactions of eq. 3 and 4.

**Scheme 9**

As important as these radical dimerizations are they do not answer the question as to how porphyrin π-cation radicals react in the presence of two electron nucleophiles. The π-cation radical of Zn(II)TPP is indefinitely stable in the presence of pure methanol, yet both Shine$^{20}$ and Smith$^{19}$ have shown that when porphyrin π-cation radicals are treated with a variety of nucleophiles, including pyridine which we shall discuss in detail below, a peripheral substitution ensues.

It has been shown$^{20}$ that the perchlorate salt of the π-cation radical (Zn(II)TPP)$^+$ when treated with an excess of pyridine in acetonitrile gave a 33% yield of the β-substituted porphyrin 29 coupled with a 61% recovery of Zn(II)TPP, this being consistent with the stoichiometry of the reaction

$$2 \left(\text{Zn(II)TPP}^+\right) \text{ClO}_4^- + \text{Py} \rightarrow 29 + \text{ZnTPP} + \text{HClO}_4.$$

The question then arises as to whether or not the π cation radical reacts directly with the pyridine. Pyridine is electrochemically inert between -1 and +2V versus Ag/AgCl such that electron transfers between it and the π-cation radical to generate either the π-dication or a pyridine anion or cation radical cannot occur. In order to gain a clearer understanding of this reaction we have followed its kinetics. The rate of the reaction was followed by observing the disappearance of the cation radical absorption at 680 nm. Plots of (A$_t$ - A$_\infty$) vs. time (where A$_t$ and A$_\infty$ are the 608 nm absorbancies at time t and infinity) were linear (Fig. 10). The second-order rate constants obtained from such plots give
\[
\frac{-d(Zn(II)TPP)^{++}}{dt} = k(Py)^2(Zn(II)TPP^{+})^2
\]
where \( k = 25 \text{ M}^{-3} \text{s}^{-1} \) at 25°.

Figure 10: Plot of \( (A_i - A_f) \) at 680 nm vs. time for the reaction of \( (Zn(II)TPP)^{+} \) \( \text{CIO}_4^- \) in \( \text{CH}_2\text{Cl}_2 \) with pyridine.

A second order in pyridine was also observed in the reactions of the \( \eta^- \)-dication. In that case we assumed one of the pyridines coordinated to the zinc of the very electron deficient macrocycle. The same assumption is very reasonable in the case of the \( \eta^- \)-cation radical, where in the solid state perchlorate (a notably poor ligand) coordinates to the zinc. In order to test this hypothesis, and to more closely reproduce the initial conditions used by Shine, the kinetics of the
reaction between the cation radical Zn(II)TPP$^+$ and pyridine were followed using acetonitrile as solvent.

Once again plots of $(A - A_\infty)$ versus time were linear (Fig. 12). Now, however, the rate constants from such plots plotted against (Py) gave a straight line (Fig. 13) showing that in acetonitrile the rate law is

$$\frac{-d(Zn(II)TPP^+)}{dt} = (k + k'(Py))(Zn(II)TPP^+)^2$$

where $k = 275$ M$^{-1}$ S$^{-1}$ and $k' = 5230$ M$^{-2}$ S$^{-1}$ at 25°C.

The mechanism outlined in scheme 10 will account for the observed law.

![Figure 12: Plot of $1/(A_t - A_\infty)$ at 680 nm vs. time for the reaction of (Zn(II)TPP)$^{+\cdot}$ ClO$_4^-$ in CH$_3$CN with pyridine.](image)

**SCHEME 10**

Mechanism in CH$_3$CN

\[
\begin{align*}
\text{ZnTPP}^+ & \quad (\text{CH}_3\text{CN}) + \text{Py} \quad \xrightarrow{k_1} \quad \text{ZnTPP}^+ (\text{Py}) + \text{CH}_3\text{CN} \\
2 \text{ZnTPP}^+ (\text{Py}) & \quad \xrightarrow{k_2} \quad \text{products} \\
\text{ZnTPP}^+ & \quad (\text{CH}_3\text{CN}) + \text{ZnTPP}^+ (\text{Py}) \quad \xrightarrow{k_2} \quad \text{products}
\end{align*}
\]

\[
\frac{-d(\text{ZnTPP}^{+\cdot})}{dt} = k_2 K(\text{Py}) (\text{ZnTPP}^{+\cdot})^2 + k_1 K^2 (\text{Py})^2 (\text{ZnTPP}^{+\cdot})^2 \\
\frac{1}{1 + K(\text{Py})}
\]

if $K(\text{Py}) > 1$

\[
\frac{-d(\text{ZnTPP}^{+\cdot})}{dt} = (k_2 + k_1 K(\text{Py})) (\text{ZnTPP}^{+\cdot})^2
\]
Figure 13: Plot of $k_{max}$ vs. (Py) for the reaction of (Zn(II)TPP)$^{+}$ ClO$_4^-$ in CH$_3$CN, with pyridine.

We have noted earlier that (Zn(II)TPP)$^{+}$ is stable in the presence of methanol. Shine notes however that the isoporphyrin (A) can be prepared from (Zn(II)TPP)$^{+}$ when the reaction is carried out in acetonitrile. We suggest that an initial coordination of acetonitrile (or pyridine) assists these reactions which in the absence of a good coordinating ligand proceed only slowly if at all (as in the case of electrochemically generated (Zn(II)TPP)$^{+}$ ClO$_4^-$ in methylene dichloride which is stable towards nucleophilic attack by methanol).

What role can such a coordinating ligand play and by what mechanism does the reaction proceed to account for the second order in the $\pi$-cation radical? Three possible mechanisms suggest themselves and are outlined in scheme 11. The first

scheme 11

\[ \text{P}^+ \cdot \text{Py} \rightarrow \text{Py}^+ \rightarrow \text{products} \quad \text{(5)} \]
\[ \text{P}^+ + \text{P}^+ \rightarrow \text{P} + \text{P}^++ \rightarrow \text{products} \quad \text{(6)} \]
\[ \text{P}^+ + \text{P}^+ \rightarrow (\text{P} + \text{P}^+) \rightarrow \text{product} \quad \text{(7)} \]

mechanism (eq. 5) requires attack of a pyridine at the periphery of the $\pi$-cation radical (to give a radical where the unpaired electron can no longer be placed on a bonding molecular orbital delocalised over the whole aromatic framework) followed by the transfer of this unpaired electron to a second $\pi$-cation radical to regenerate Zn(II)TPP and the peripherally substituted porphyrin. Intuitively this mechanism appears energetically
unfavorable to us, and although it cannot be excluded on kinetic grounds it will not be discussed further here. The second mechanism (eq. 6) would require all of the reaction to proceed via the dication formed by disproportionation of the cation radical. While the equilibrium concentration of the dication is exceedingly small we have already seen that the dication itself reacts rapidly with nucleophiles. If one is prepared to accept this disproportionation mechanism then what role does pyridine or acetonitrile play such that reactions will occur in their presence but not in pure methanol? An obvious solution is that the coordinating ligands could change the potentials for oxidation to the $\pi$-cation radical and $\pi$-dication and thereby change the equilibrium concentration of the dication. When a cyclic voltammogram was taken for Zn(II)TPP in CH$_2$Cl$_2$ and 0.1 M tetra-n-butylammonium perchlorate a behaviour typical of metalloporphyrins (Fig. 14) was observed with two reversible waves at $\epsilon_1^{1/2} = 0.84$ (DEp = 130mV) and $\epsilon_2^{1/2} = 1.14$ (DEp = 140mV). Addition or acetonitrile gave a cathodic shift to the $\epsilon_1^{1/2}$ value to 0.81V (DEp = 110mV) with a slight anodic shift for $\epsilon_2^{1/2}$ 1.16V (AEp = 110mV). When pyridine was added, in place of acetonitrile, a typical reversible couple was found at $\epsilon_1^{1/2} = 0.77$V (DEp = 140mV). Anodic sweeps beyond 1.1V gave an oxidation which is broad, totally irreversible, and coupled with a decrease in the cathodic peak of $\epsilon_1^{1/2}$. Clearly then both acetonitrile and pyridine modify the electrochemistry of Zn(II)TPP and will therefore affect the position of equilibrium of the disproportionation as well as the rate of disproportion. These changes do not, however, cast any definitive evidence on the mechanism by which the $\pi$-cation radicals react with pyridine to give peripheral substitution.

A third mechanism (eq. 7, Scheme 11) involves the initial dimerization of two cation radicals to give a dimeric diamagne-

![Figure 14: Cyclic voltammogram of Zn(II)TPP in methylene dichloride/tetra-n-butylammonium perchlorate (0.1M).](image-url)
tic dication. We have previously characterized such dimeric species. Thus Mg(II)OEP\(^+\) dimerizes, and the optical spectrum changes from that of the green solution typical of \(\pi\)-cation radicals to a red solution having the spectrum shown in Fig. 15. Formation of the dimer is dependent upon both the solvent and counter ion. Thus for the reaction \(2 \text{Mg(II)OEP}^+ \rightarrow \text{Mg(II)OEP}^+\)\(^+\), an equilibrium constant of \(4.7 \times 10^3\) mole\(^{-1}\) was measured for the formation of the perchlorate dimer at 0\(^\circ\) in CH\(_2\)Cl\(_2\). Dimerization is essentially complete at -20\(^\circ\) for Mg(II)OEP\(^+\)\(^+\) ClO\(_4\)\(^-\) in CH\(_2\)Cl\(_2\) and at -75\(^\circ\) in CH\(_3\)OH. Mg(II)OEP\(^+\) Br\(^-\) in either CH\(_2\)Cl\(_2\) or CH\(_3\)OH is not completely dimerized until -70\(^\circ\). Similar behaviour for (Zn(II)OEP)\(^+\) ClO\(_4\)\(^-\) has been observed.

So far we have been unable to obtain clean and reproducible data on the reaction of [Mg(II)OEP]\(^+\)\(^+\) with pyridine. Some runs have shown a rate which is, as we had anticipated, second order in porphyrin \(\pi\)-cation radical. We concluded that since this system provides for ready dimerization the inconsistent results might be circumvented if we could produce only diamagnetic dimer, and study its reaction with pyridine. We anticipated that while we could vary dimer concentration by lowering the temperature, interpretation of kinetic studies over a range of temperatures coupled with consequent changes in the kinetic and thermodynamic parameter associated with both dimer formation and its subsequent reactions with pyridine might prove to be too complex. Instead we chose to facilitate dimer formation by making the process intramolecular rather than Intermolecular. The bis magnesium complex of the covalently linked dimeric porphyrin (36 n=8)\(^39\) showed a cyclic voltammogram typical of that of a monomeric magnesium porphyrin. Bulk electrolysis at the potential of the first oxidation wave brought about a reversible two electron oxidation (one electron per porphyrin ring) to give the bis- \(\pi\)-cation radical which to our delight was
almost exclusively a dimeric diamagnetic species at room temperature as shown by its optical spectrum (Fig 16). When this
diamagnetic dimer was treated with pyridine the kinetics did
nothing to simplify the situation. The rate law is \(-\frac{d[36^{2+}]}{dt} = \frac{36^{2+}[\text{Py}]}{2}\). The dimer has merely added to the complexity
of the reaction. We had anticipated that the oxidized dimer
would adopt a conformation like that represented in 37, instead
it more probably looks like 38 which would account for the
second order in oxidized dimer. We have examined the dimer
36(n=6). But bulk electrolysis at the potential of the first
oxidation wave removed four electrons to give an unstable and
uncharacterisable material.

While we feel that the most reasonable path for reaction
of porphyrin n-cations with nucleophiles proceeds via the
diamagnetic dimers we cannot, at this time, give definitive
proof. Nonetheless when Zn(II)TPP⁺ is treated with pyridine
an isoporphyrin appears as an intermediate having an optical
spectrum identical to the isoporphyrin observed from the reaction of Zn(II)TPP$^{++}$ with pyridine (vide supra). Such that whatever the path by which the $\pi$-cation radical reacts with pyridine, once the electronic reorganization has occurred the intermediate formed and its conversion to 29 are the same as those for the $\pi$-dication reactions.

A question that one might reasonably ask is are the diamagnetic dimers observed with Zn(II)TPP$^{++}$ as they are with Mg(I)OEP$^{++}$. The answer is no. Nevertheless dimer formation vis: $2 \text{Zn(II)TPP} \rightleftharpoons (\text{Zn(II)TPP})_2^{++}$ is unfavoured electrostatically. We suggest that coordination of pyridine to these systems would better localise the charge on the cation radical and favour dimer formation by lowering the electrostatic repulsion. Unfortunately, those ligands best able to stabilise the charge also react at the periphery making dimer detection difficult.

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