

Laser Induced Oxidation of Free base Mesoporphyrin-IX Dimethyl Ester Probed by Resonance Raman Technique

H.H. Thanga¹ J.Lalnunthari²

^{1,2}Department of Physics

^{1,2}Mizoram University, Aizawl-796004, India

Abstract— Radicals of porphyrins and their metal derivatives serve as transient intermediates in a variety of biological redox processes. As a result there has been great interest in the preparation and characterization of the oxidized/reduced species of porphyrin complexes. The present work reports photochemical generation and resonance Raman characterization of free base mesoporphyrin- IX dimethyl ester (H_2MP) π -cation radical in benzene under selective laser irradiation at 441.6 nm in the presence of CCl_4 as electron acceptor. At low concentration of CCl_4 (20% v/v), both one- and two-electron oxidation products, viz (H_2MP)^{•+} radical and (H_4MP)⁺² diacid can be seen simultaneously from the RR spectrum. Higher concentration of the electron acceptor favours the formation of diacid (H_4MP)⁺². A reaction mechanism for the photo-oxidation process is proposed.

Key words: Mesoporphyrin-IX Dimethyl Ester Probed, Laser Induced Oxidation

I. INTRODUCTION

Porphyrins are a group of heterocyclic macrocycle organic compounds, formed by the linkage of four pyrrole rings through methane bridges. They constitute the chromophore of many biological molecules like hemoglobin, myoglobin, cytochromes, catalases etc. Porphyrins and their metal derivatives can be oxidized or reduced chemically[1], electrochemically[2] or photochemically[3,4] to form either π -cation or anion radicals. Since these radicals serve as transient intermediates in a variety of biological redox processes there has been great interest in the preparation and characterization of the oxidized/reduced species of porphyrin complexes. In particular, photooxidation of the parent metalloporphyrin to give π -cation radical species has been the subject of many studies due to their involvement in many biological processes such as in the primary photoagent in bacterial and plant photosynthesis[5], compound I of peroxidase enzymes[6] and also in artificial photocatalytic systems[7,8]. However, compared to metalloporphyrins, understanding the oxidation process of metal-free macrocycles, the so-called free base, still remain elusive.

From EPR studies [5], the π -cation radicals of free base porphyrins are known to be short lived and highly reactive. Inisan *et.al* [9] had shown that free base π -cation radicals (H_2OEP , H_2TPP , H_2CdiE) electrogenerated in strictly anhydrous solvents are not stable and give rise to a follow-up reaction in which the free bases are finally protonated. Accordingly the transient formation of free-base π -cation radicals has been proposed as the initial step in the photochemical formation of H_2TPP and H_2OEP diacids in the previous report of our group [10,11]. However, we observed that the decay pathways of the radical appear to be strongly influenced by the type of porphyrin, solvent and electron acceptor used in the photochemical system.

In the present study, we report resonance Raman study on the photooxidation of free base mesoporphyrin-IX dimethyl ester (H_2MP) in benzene and dichloromethane under selective laser irradiation within the electronic absorption region of this system in the presence of CCl_4 as electron acceptor. The reaction mechanisms are proposed and discussed.

II. MATERIALS AND METHOD

Raman spectra of the sample was recorded in 90° scattering geometry with a SPEX Ramalog 1403 double monochromator equipped with RCA C-31034-02 photomultiplier tube and photon counting arrangement. The spectrometer control and data processing were achieved with the help of a computer. Excitation wavelength of 441.6 nm was provided by Liconix Model 4240B He-Cd Laser.

The chemical H_2MP -IX DME was obtained commercially from Sigma Chemical Co. USA. The molecular structure of the compound is shown in Figure 1. Analytical grade benzene (C_6H_6) and CCl_4 were used as solvent and oxidizing agent.

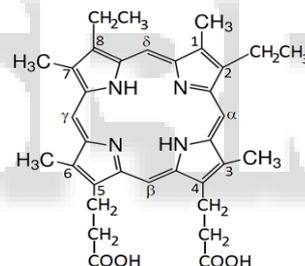


Fig. 1: Molecular structure free base mesoporphyrin-IX dimethyl ester

III. RESULTS AND DISCUSSION

Fig. 2 compares the resonance Raman spectra of H_2MP and its radical in benzene obtained with 441.6nm laser line as excitation source in the presence of CCl_4 as electron acceptor. Excitation with 441.6nm, which is in resonance with Soret (B) absorption band H_2MP and its radical leads to the enhancement of totally symmetric modes having A_{1g} symmetry viz ν_2 , ν_3 , ν_4 . Depolarised bands viz ν_{10} , ν_{11} are also seen with appreciable intensity due to John-Teller effect [12]. The contribution of residual neutral porphyrin to the radical cation spectra is also there as can be seen from the intensity remaining at the positions of band due to H_2MP in the spectra of its radical. But when the relative concentration of CCl_4 is increased, the intensity of bands due to neutral porphyrin decreases while that due to π -radical cation increases significantly. Modes observed for these systems are listed in Table I with their assignment, mode numbering and frequency shifts on radical formation. The RR band positions of a chemically oxidized H_2MP in benzene with bromine are also included in the table for comparison.

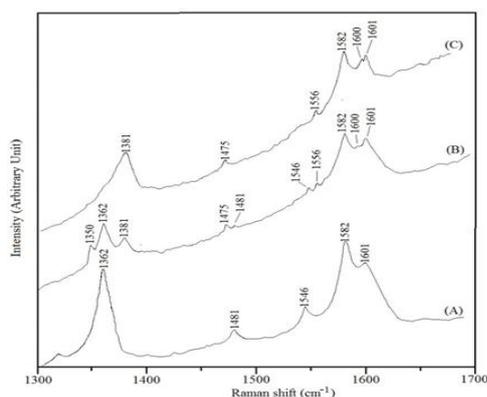
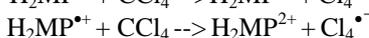
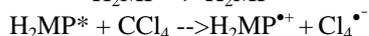
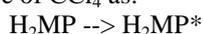


Fig. 2: RR spectra of H₂MP and its cations by excitation at 441.6 nm laser; (A) in C₆H₆ (B) in C₆H₆ with 20% of CCl₄ (C) in C₆H₆ with excess CCl₄.

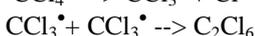
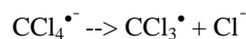
In benzene, under low relative concentration of CCl₄ the spectrum shows a triplet in ν₄ mode region at 1350, 1362 and 1382 cm⁻¹. The band at 1350 cm⁻¹ can be associated with the ν₄ mode of (H₂MP)^{•+}, while the band at 1382 cm⁻¹ is due to diacid (H₄MP)⁺² formed by the protonation of the two hydrogen atoms at the centre of the porphyrin ring. However when the relative concentration of CCl₄ is increases to high value, there is a complete shift of ν₄ mode to the position expected for the ν₄ mode of (H₄MP)⁺². This is due to the fact that the diacid strong Soret absorption band is much closer to laser excitation wavelength which had been used for excitation than that of the radical cation. Consequently, RR scattering from the diacid is dominant even when it is a minor component. It is interesting to note that the intensity of modes involving mainly pyrrole nitrogen atoms and phenyl rings is affected drastically in the RR spectra of (H₄MP)⁺². The benzene solvent thus favours diacid formation. Apart from this, it is also observed that ν₃ mode {ν(C_α-C_β)} shifts down from 1481 cm⁻¹ to 1475 cm⁻¹, while ν₁₁{ν(C_β-C_β)} and ν₂{ν(C_α-C_β)} modes shift up from 1546 cm⁻¹ and 1582 to 1556 cm⁻¹ and 1600 cm⁻¹, respectively.

On the basis of the above discussion, we can suggest the following mechanism of photo-oxidation for H₂MP in the presence of CCl₄ as:



The H₂MP²⁺ finally undergoes protonation to yield H₄MP²⁺ diacid.

According to Saini [3], Cl₄^{•-} breaks into CCl₃[•] and Cl⁻ at room temperature and CCl₃[•] dimerizes to give C₂Cl₆ as the product.



Where Cl⁻ acts as counter ion to stabilize the H₂MP^{•+}Cl⁻ complex.

H ₂ MP in C ₆ H ₆	H ₄ MP ²⁺ in C ₆ H ₆ + CCl ₄	H ₄ MP ²⁺ in C ₆ H ₆ + Br ₂	Frequency shift Δν	Mode no. and Assignment
1582	1600	1601	+18	ν ₂ (A _{1g}); ν (C _β -C _β)
1546	1556	1556	+10	ν ₁₁ (A _{1g}); ν (C _β -C _β)

1481	1475	1473	-6	ν ₃ (A _{1g}); ν (C _α -C _m)sym
1362	1350 1381	1382	-12 +19	ν ₄ (A _{1g}); ν (pyrrole half ring)

Table 1: Mode Assignment of Resonance Raman Frequencies (cm-1) for H₂MP-IX and its Radicals

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