Photo-induced diacid products of octaethylporphyrin probed by resonance Raman and absorption techniques

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The photochemical formation of di- and monoacid derivatives of octaethylporphyrin in CH_2Cl_2 or CCl_4-N alcohol mixtures in the presence of *p*-benzoquinone (p-BQ) has been studied by resonance Raman and optical absorption techniques. The results clearly indicate that the solvent or co-solvent acts as the proton source in the reaction. Simultaneous presence of p-BQ and methanol is found to be essential for diacid formation in CCl_4, while methanol greatly inhibits the process in CH_2Cl_2 solvent. However, in the presence of excess methanol in CH_2Cl_2 and p-BQ, porphyrin monoacid is formed. A chain mechanism is proposed for the photon-induced formation of octaethylporphyrin diacid products.

Porphyrins and their metal derivatives can be oxidized chemically,[1] electrochemically[2] or photochemically[3,4] to form either metal- or porphyrin ring-centered oxidized products. Study of the photochemical formation of these oxidized products has gained much importance due to their involvement in many biological processes such as the primary photoagent in bacterial and plant photosynthesis[5] and in compound I of the peroxidase enzymes in which two-electron oxidation of Fe^{III}-heme takes place.[6] Accordingly, photooxidation of the parent metalloporphyrins by an electron acceptor to give π-cation radical species has been the subject of many studies.[3a,4,7] However, compared to metalloporphyrins, understanding of the metal-free macrocycles, the so-called free base, has remained elusive.[2,7,8]

From EPR studies,[9–11] the π-cation radicals of free base is known to be short lived and highly reactive. A recent investigation[12] has 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 protonated. The transient formation of the free base π-cation radical has also been proposed as the initial step in the photochemical formation of H_2TPP diacid.[13,14] Thus, study of the photochemical formation and characterization of diacid is as important as the π-cation radicals because of the high tendency of the latter to decay into the corresponding acid derivatives.

In the present work, we report results of resonance Raman (RR) and optical absorption studies on the catalytic formation of OEP acid derivatives by irradiating free base octaethylporphyrin within the Soret absorption band in the presence of p-benzoquinone (p-BQ) as electron acceptor in different solvents.

Experimental

Free base octaethylporphyrin (H_2OEP) was commercially purchased from Porphyrin Products Inc., USA, and used without further purification. Methanol and ethanol were dried over anhydrous potassium carbonate and distilled. Carbontetrachloride (CCl_4) was of spectroscopic grade and used as received from SISCO, India. Dichloromethane (CH_2Cl_2) was purified by washing with concentrated H_2SO_4, a 15% solution of potassium carbonate, and a large volume of water, then dried over anhydrous calcium chloride, distilled and stored over molecular shieves. *p*-Benzoquinone (p-BQ) was used as received from Aldrich Co., USA.

The octaethylporphyrin diacid was prepared with concentrated HCl according to the method given in the literature[15] or by addition of dilute Br_2 to the solution of H_2OEP in CH_2Cl_2. The diacid has a characteristic violet color in solution. The monoacid derivative was prepared by dropwise addition of a (MeOH + 5% H_2O) mixture to the solution of diacid in CH_2Cl_2 until the solution color changed from violet to orange red.

Raman spectra were recorded with a SPEX Ramalog 1403 double monochromator equipped with a water-cooled RCA 31034A photomultiplier. A Liconix 4240 HeCd laser provided the excitation line at 441.6 nm. A microprocessor-based SPEX Datamate was used for spectrometer control, data acquisition and processing facilities. The typical laser power at the sample was ~35–40 mW and most of the Raman spectra were measured at a spectral resolution of 4 to 5 cm^{-1}. The position of the Raman peaks was calibrated with indene or the known bands of the solvents used. A minimum of three freeze-pump-thaw cycles was employed whenever anaerobic conditions of the solutions were required.

Electronic absorption spectra were recorded on a Carey 2300 UV-VIS spectrometer using 10 mm path length quartz cuvettes.

Results

The UV-VIS absorption spectra of H_2OEP and its diacid $(H_4OEP)^{2+}2Cl^-$ in CH_2Cl_2 are shown in Fig. 1(A,C). Neutral H_2OEP displays a Soret band at 399 nm and four bands in the visible region at 499, 534, 567 and 620 nm, similar to the reported ones.[12] In the diprotonated form, as is well-documented,[12,15] the visible spectral region is dominated by two major bands at 554 and 600 nm with a weaker band at 582 nm, which appears as a shoulder to the main peak at 554 nm. The spectral simplification from H_2OEP to the diacid $(H_4OEP)^{2+}$ is a result of the approach towards square symmetry (*i.e.*, D_{4h}) in

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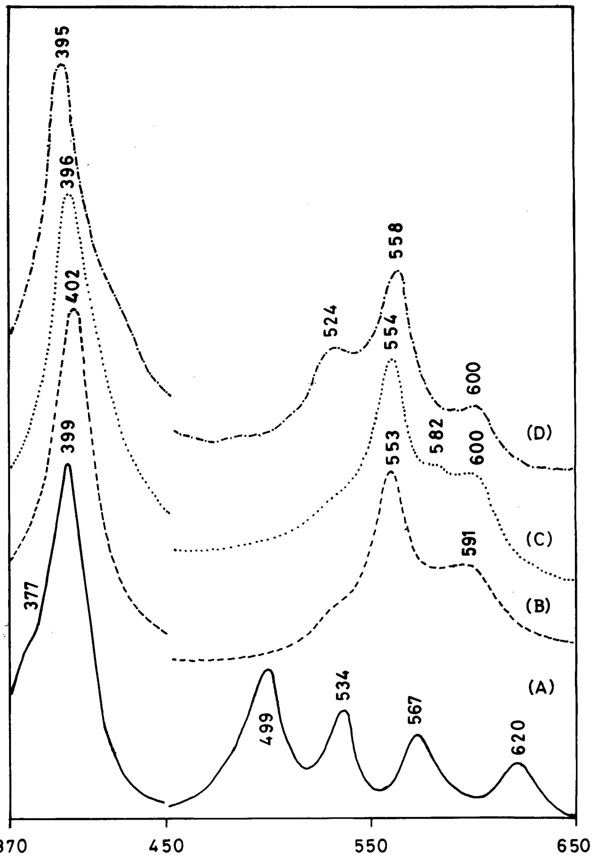

Fig. 1 Electronic absorption spectra of H_2OEP and its chemically prepared acid derivatives in CH_2Cl_2: A (——) H_2OEP; B (– – – –) $(H_4OEP)^{2+}2Br^-$; C (······) $(H_4OEP)^{2+}2Cl^-$; D (–·–·–) $(H_3OEP)^+Cl^-$.

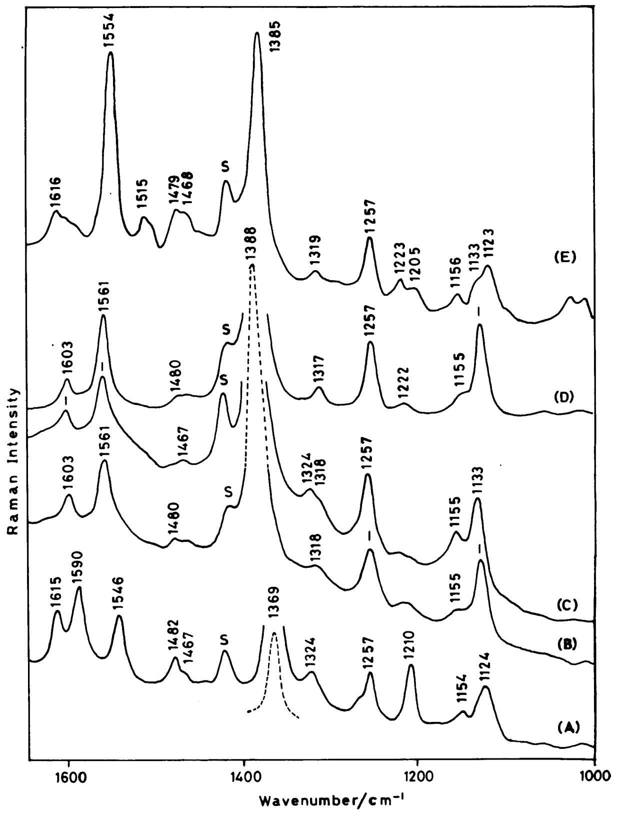

Fig. 2 The 441.6 nm excited RR spectra (1000–1650 cm^{-1}) in CH_2Cl_2 of: (A) H_2OEP (*ca.* 1 mM); (B) with p-BQ (*ca.* 8 mM) under aerobic conditions; (C) same solution as in (B) but under anaerobic conditions; (D) $(H_4OEP)^{2+}2Cl^-$; (E) $(H_3OEP)^+Cl^-$. The letter "S" indicates solvent band.

the diacid when protons are added to the pyrrole nitrogen atoms. A similar type of change was observed when dilute Br_2 was added to the solution of H_2OEP in CH_2Cl_2 [Fig. 1(B)]. Titrative addition of MeOH containing 5% H_2O to the solution of $(H_4OEP)^{2+}2Cl^-$ gives the familiar optical spectra[12,15,16] of the monoacid $(H_3OEP)^+$ derivative showing three main visible bands at 524, 558, and 600 nm, and the Soret band at 395 nm [Fig. 1(D)]. It is interesting to note that addition of dry methanol alone to the diacid solution did not result in appreciable formation of monoacid, while water alone gives the neutral form of OEP. It is believed that although water is slightly more acidic than MeOH, it assists in dissociation of the chloride counter ion from the diacid either by H-bonding or due to its high polarity, thereby setting up favorable conditions for monoacid formation in the presence of MeOH.

The resonance Raman (RR) spectra of H_2OEP (*ca.* 1 mM) in CH_2Cl_2 obtained at 441.6 nm excitation under different conditions are shown in Fig. 2. Table 1 gives the tentative mode numbering and assignment based on results[17,18] obtained from isotopic substitution and depolarization ratio measurements. According to the assignment, the RR spectrum of neutral H_2OEP in CH_2Cl_2 shows the ν_4, ν_{11} and ν_{10} mode positions at 1369, 1546 and 1615 cm^{-1}, respectively [Fig. 2(A)]. However, on addition of p-BQ (*ca.* 8 mM) under aerobic or anaerobic conditions [Fig. 2(B,C)], these modes shift to 1388, 1561 and 1603 cm^{-1}, respectively, along with a change in the relative intensities of the bands at 1210 and 1133 cm^{-1}. The RR spectra obtained under these conditions is identical to that of the chemically prepared $(H_4OEP)^{2+}2Cl^-$ [Fig. 2(D)], but different from that of $(H_3OEP)^+Cl^-$ [Fig. 2(E)] for which the ν_4 and ν_{11} modes are observed at 1385 and 1554 cm^{-1}, respectively, with a broad band feature in the ν_{10} mode region. Therefore, it appears that laser excitation of a dichloromethane solution of H_2OEP in the presence of p-BQ results in the formation of the diacid derivative. Similar photochemical changes were also observed with 406 and 514.5 nm laser excitations (not shown).

The optical absorption spectra of H_2OEP in CH_2Cl_2 in the presence of p-BQ before and after laser irradiation at 441.6 nm are shown in Fig. 3. Prior to irradiation the spectral positions are the same as in the absence of p-BQ [Fig. 3(A)]. However, after about 30 min irradiation under aerobic conditions the spectrum becomes similar to that for the diacid

Table 1 Observed RR spectral shifts (in cm^{-1}) of H_2OEP, its acid derivatives and their assignment

H_2OEP	$(H_4OEP)^{2+}2Cl^-$	$(H_3OEP)^+Cl^-$	Mode no. and assignment
1615[a]	1603	1616	ν_{10}, $\nu(C_\alpha{-}C_m)_{asym}$
1590[a]	—	—	ν_{19}, $\nu(C_\alpha{-}C_m)_{asym}$
1546[a]	1561	1554	ν_{11}, $\nu(C_\beta{-}C_\beta)$
—	—	1515	—
1482[a]	1480	1479	ν_{28}, $\nu(C_\alpha{-}C_m)_{sym}$
1467[c]	1467	1468	ν_3, $\nu(C_\alpha{-}C_m)_{sym}$
1369[a]	1388	1385	ν_4, ν(Pyr. half-ring)$_{sym}$
1324[a]	—	—	ν_{20}, ν(Pyr. quarter-ring)
—	1317[b]	1319	$\nu(CH_2)_{wag}$
1257[a]	1257	1257	$\nu(CH_2)_{twist}$
—	1222[c]	1223	δ_{NH}
1210[b]	—	—	ν_{13}, $\delta(C_mH)$
1154[c]	1154	1155	ν_{42a}, $\delta(C_mH)$
—	1133[b]	1133	ν_5, $\nu(C_\beta{-}C_1)_{sym}$
1124[b]	—	1123	ν_{22}, ν(Pyr. half-ring)$_{sym}$

[a] Ref. 17. [b] Ref. 18. [c] Ref. 27.

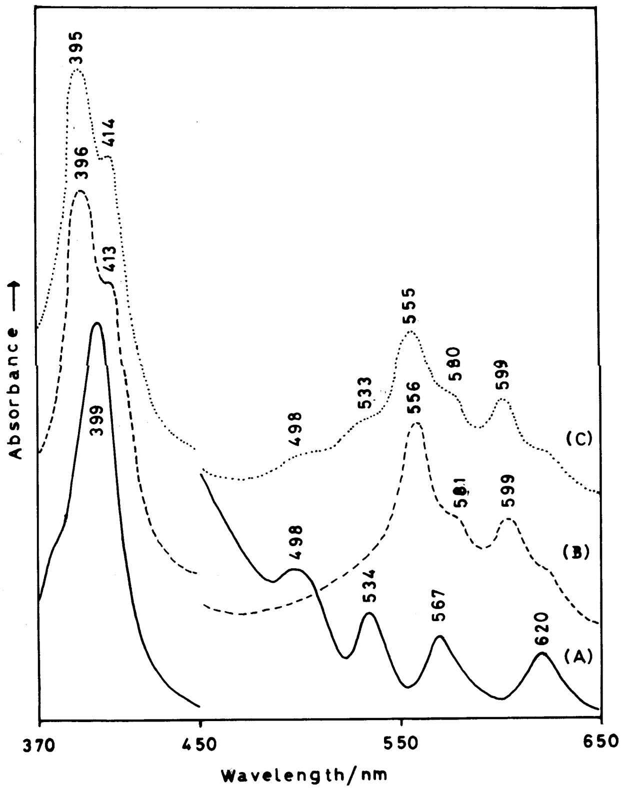

Fig. 3 Electronic absorption spectra of $H_2OEP + p\text{-}BQ$ (1 : 8) in CH_2Cl_2: A (——) before laser irradiation (aerobic); B (– – – –) after 30 min laser irradiation (aerobic); C (······) after 15 min laser irradiation (anaerobic). $\lambda_{ex} = 441.6$ nm.

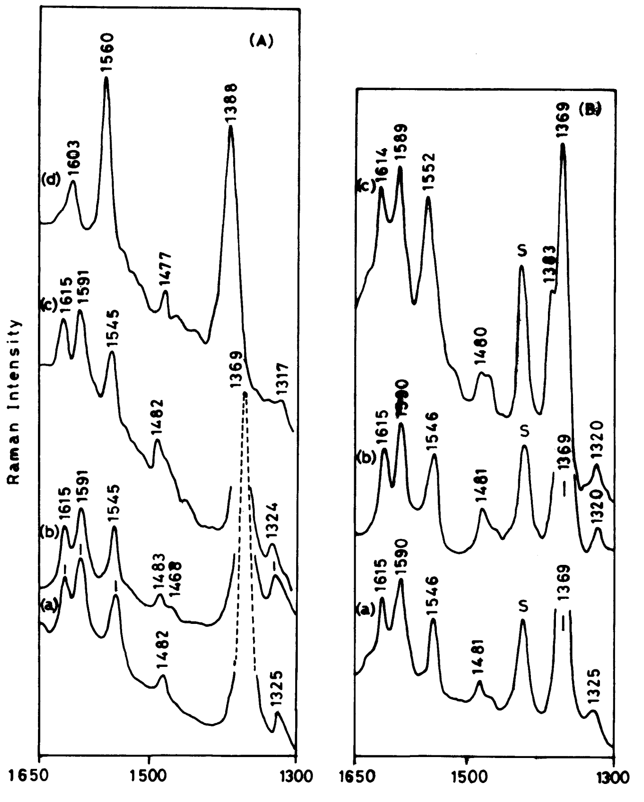

Fig. 4 (A) The 441.6 nm excited RR spectra (1300–1650 cm^{-1}) of H_2OEP (*ca.* 1 mM) in CCl_4: (a) as is; (b) with p-BQ (*ca.* 8 mM); (c) with 15% (v/v) MeOH; (d) with p-BQ (*ca.* 8 mM) and 15% (v/v) MeOH. (B) The 441.6 nm excited RR spectra (1300–1650 cm^{-1}) of H_2OEP (*ca.* 1 mM) in CH_2Cl_2; (a) as is; (b) with p-BQ (*ca.* 8 mM) and 15% (v/v) MeOH; (c) with p-BQ (*ca.* 8 mM) and 30% (v/v) MeOH. The letter "S" indicates solvent band.

$(H_4OEP)^{2+}2Cl^-$ in CH_2Cl_2, except for the appearance of a shoulder at 414 nm [Fig. 3(B)]. The 414 nm band was also seen when a freshly prepared solution was irradiated for about 15 min under degassed conditions [Fig. 3(C)]. Since no such band was observed in a photochemically prepared oxidized product of CoTPP with 441.6 nm excitation in the presence of p-BQ as the electron acceptor,[19] the shoulder at 414 nm appearing in the absorption spectra of the photoirradiated sample of H_2OEP could not originate from p-BQ or its radical products. Therefore, the appearance of the shoulder at 414 nm is associated with one of the degradation products formed as a result of photochemical reactions in the system. Slow formation of products other than diacid was also clearly revealed during RR measurements of similar samples with increasing laser irradiation time in the presence of oxygen, but not in the absence of oxygen.[20] These observations indicate that the side-products revealed by RR studies do not correspond to the one characterized by the 414 nm band. However, despite all these complications, it can be clearly pointed out from our RR and optical absorption studies that laser excitation of H_2OEP in CH_2Cl_2 in the presence of p-BQ results in the formation of the OEP diacid derivative, irrespective of the presence or absence of oxygen.

The RR spectrum of H_2OEP (*ca.* 1 mM) in CCl_4 at 441.6 nm excitation is shown in Fig. 4A(a) and is similar to the one in CH_2Cl_2 in the absence of p-BQ [Fig. 2(A)]. Addition of p-BQ (*ca.* 8 mM) or methanol (15% v/v) separately also does not result in any spectral change [Fig. 4A(b,c)]. However, in the simultaneous presence of p-BQ and MeOH [Fig. 4A(d)], certain marker bands associated with the ν_4, ν_{11} and ν_{10} modes at 1369, 1545 and 1615 cm^{-1} for H_2OEP shift to 1388, 1560 and 1603 cm^{-1}, respectively, on laser excitation. Replacing MeOH with ethanol also gives similar RR spectral changes (not shown). On the other hand, in contrast to this, the solution of H_2OEP in a CH_2Cl_2 (85%) + MeOH (15%) mixture in the presence of p-BQ on laser excitation gives an RR spectrum [Fig. 4B(b)] that is the same as for neutral OEP in CH_2Cl_2 [Fig. 4B(a)]. But on increasing the MeOH content from 15% to 30% (v/v), formation of monoacid could be seen as evidenced by the characteristic RR bands at 1383 and 1552 cm^{-1} for the ν_4 and ν_{11} modes, respectively [Fig. 4B(c)].

Discussion

The excited state of OEP directly reached by 441.6 nm excitation is a $^1(\pi,\pi^*)$ singlet state, which is known to relax by an intersystem crossing process to a triplet state with a quantum yield of 0.75.[21] The fact that no ground state chemical reaction occurred between H_2OEP and p-BQ indicates that the excited state quenching of H_2OEP by p-BQ initiates the reaction for OEP diacid formation. Since diacid formation was observed independently of the presence or absence of oxygen, apart from degradation, it appears that the singlet excited state of H_2OEP plays a major role in the process. Quenching of the OEP excited state may occur either by energy transfer to give p-BQ in an excited state (p-BQ*) or by electron transfer to give a one-electron ring-oxidized H_2OEP product. Formation of p-BQ* by energy transfer quenching is unlikely because the process requires overlap of the absorption spectrum of p-BQ with the emission spectrum of H_2OEP, which is not possible since the longest and shortest wavelength absorption[22] and emission[23] bands of p-BQ and H_2OEP are found at 430 nm and 610 nm, respectively. Therefore, the intermediate species responsible for the reaction process is believed to be the $(H_2OEP)^{\cdot+}$ π-cation radical. However, in our system we did not observe any signal that could be attributed to a $(H_2OEP)^{\cdot+}$

species. But according to recent investigations[12] the π-cation radical is short lived and highly reactive, leading to a follow-up reaction in which the acid derivative of OEP is the final product. Moreover, the π-cation radical of H_2TPP was also proposed to play an intermediate role in the photochemical formation of the corresponding diacid derivative.[13,14] Although we could not detect the $(H_2OEP)^{\cdot+}$ π-cation radical directly in our experiments, its transient formation is believed to initiate the reaction. In this reaction either p-BQ or the solvent can act as proton donor. But RR spectra characteristic of diacid were also found in $CHCl_3$ and $C_2H_2Cl_4$ solvents in the presence of p-BQ, but not in CS_2 and CCl_4[24] under otherwise similar conditions, suggesting that the solvent used is the proton source. This is further supported by diacid formation in CCl_4 only in the simultaneous presence of p-BQ and MeOH on laser excitation. Diacid formation in CH_2Cl_2 in the presence of Br_2 observed in our case and similar to reports in the literature[1] also gives further support to cation radical initiated proton removal from the solvent. In light of the above discussion, the following mechanism for diacid formation is proposed, which is in consonance with proposals in the literature.[13]

$$H_2OEP \overset{h\nu}{\rightleftharpoons} {}^1(H_2OEP)^* \qquad (1)$$

$$\begin{aligned} {}^1(H_2OEP)^* + \text{p-BQ} &\rightarrow {}^1[(H_2OEP)\cdots(\text{p-BQ})^* \\ &\rightarrow (H_2OEP)^{\cdot+} + \text{p-BQ}^- \end{aligned} \qquad (2)$$

$$(H_2OEP)^{\cdot+} + \text{p-BQ} \rightarrow H_2OEP + \text{p-BQ} \qquad (3)$$

$$(H_2OEP)^{\cdot+} + CH_2Cl_2 \rightarrow H_2OEP + {}^{\cdot}CHCl_2 + H^+ \qquad (4)$$

$$\text{p-BQ}^- + CH_2Cl_2 \rightarrow \text{p-BQ} + {}^{\cdot}CH_2Cl + Cl^- \qquad (5)$$

$$H_2OEP + 2H^+ + 2Cl^- \rightarrow (H_4OEP)^{2+}2Cl^- \qquad (6)$$

The photochemical formation of diacid is generally found to be accompanied by degradation products in the presence of strong electron acceptors like p-BQ. These side-reactions are likely to involve radicals originating from both p-BQ and the solvent.

In CCl_4, our results suggest that CCl_4 could not directly remove an electron from H_2OEP in the excited state, otherwise it should lead to diacid formation in the presence of MeOH, similarly to that observed in the H_2TPP[13] system. Even at 406 nm excitation no photooxidation was observed for H_2OEP in the presence of CCl_4 as electron acceptor.[24] Therefore, observation of diacid formation only in the simultaneous presence of p-BQ and MeOH leads to a mechanism whereby MeOH acts as proton source in analogy to the suggestion given above.

$$(H_2OEP)^{\cdot+} + CH_3OH \rightarrow H_2OEP + CH_3O^{\cdot} + H^+ \qquad (7)$$

$$\text{p-BQ}^- + CCl_4 \rightarrow \text{p-BQ} + {}^{\cdot}CCl_3 + Cl^- \qquad (8)$$

$$H_2OEP + 2H^+ + 2Cl^- \rightarrow (H_4OEP)^{2+}2Cl^- \qquad (9)$$

The $CH_3O^{\cdot}$ [eqn. (7)] and ${}^{\cdot}CCl_3$ [eqn. (8)] radicals are expected to finally decay to formaldehyde and chloroform according to the well-documented[13,25] mechanism for oxidation of ethanol.

$${}^{\cdot}CCl_3 + CH_3OH \rightarrow CHCl_3 + {}^{\cdot}CH_2OH \qquad (10)$$

$$CH_3O^{\cdot} + CH_3OH \rightarrow CH_3OH + {}^{\cdot}CH_2OH \qquad (11)$$

$${}^{\cdot}CH_2OH + CCl_4 \rightarrow {}^{\cdot}CCl_3 + Cl^- + HCHO + H^+ \qquad (12)$$

The lack of signal for diacid species in the presence of p-BQ alone in CCl_4 is attributed to the highly unstable nature of the $(H_2OEP)^{\cdot+}$ radical, which quickly reverts to the neutral form by a fast back-electron transfer process in the absence of protic co-solvent.

The 441.6 nm excitation wavelength used in most of our experiments is also in resonance with the longest wavelength absorption band (430 nm)[22] of p-BQ. It is not clear at this stage how far direct excitation of p-BQ will have implications on the photochemical reaction. However, observation of similar diacid formation with 514.5 nm excitations[24] strongly suggests that the primary process in the reaction involves excited state quenching of H_2OEP by p-BQ [eqn. (2)]. Therefore, it is proposed that in the initial stage of the process, p-BQ acts only as a catalyst, which appears to be the most consistent with the experimental results.

Another interesting aspect of the photochemical process is the different effect of MeOH in CH_2Cl_2 and CCl_4 solvents. In CCl_4, presence of MeOH is essential for the formation of diacid since it acts as the proton source [eqn. (7)]. On the other hand, addition of MeOH greatly inhibits the diacid formation in CH_2Cl_2. However, at higher concentration of MeOH (about 30%), the RR spectra show the presence of monoacid. As in CCl_4, the higher rate of formation of monoacid with increasing concentration of MeOH in CH_2Cl_2 indicates that MeOH also acts as the proton donor in CH_2Cl_2. Therefore, it is most likely that the inhibitory effect of MeOH on OEP diacid formation is due to a lower scavenging power of CH_2Cl_2 for the methoxy radicals produced in the process, resulting in a lower yield of H^+ and Cl^- ions, and hence formation of only monoacid in the presence of a high concentration of methanol.

It is surprising that no photooxidation of OEP is observed in CCl_4 or $C_2H_2Cl_4$,[24] while very clean photooxidation[3b,14] could be obtained for H_2TPP on laser excitation in the Soret absorption region. Since both of these porphyrins have almost the same values for the oxidation potentials[12] and excited state energies,[23] it appears that the observed difference arises mainly from difference in the lifetimes of the excited states, apart from differences in size, shape or solvation effects.

In Table 1 the wavenumber of the modes are listed for neutral, monoacid and diacid OEP. It is seen that OEP acid formation is accompanied by large upshifts of the ν_{11} and ν_4 modes by about 8–15 and 16–19 cm^{-1}, respectively. The frequency shift pattern of the ν_{11} mode, involving mainly the C_β–C_β bond, is in accord with the antibonding character of the a_u (a_{1u} in D_{4h} symmetry) orbital with respect to the C_β–C_β bond as expected for OEP complexes.[26] However, a large upshift in the frequency of the ν_4 (pyrrole half-ring stretch)$_{sym}$ mode in which the C_α–N and C_α–C_β bonds stretch out-of-phase, is inconsistent with these expectations since the a_u orbital is nonbonding and bonding, respectively, with respect to these bonds. From an NMR study,[15] it was shown that protonation of H_2OEP results in deshielding of the N–H protons and hence in a higher electron density on the methine C atom due to migration of negative charge from the anion counter ions to the positively charged porphyrin core. Therefore, it is most likely that the effect also increases electron densities in the C_α–N and C_α–C_β bonds of the acid derivatives, as reflected in the observed large upshift of the ν_4 mode.

From the above observations, we can conclude that in the photochemical reaction of H_2OEP with p-BQ induced by selective laser excitation, diacid is the most stable product of the reaction and the process is very sensitive to the solvent composition. Although formation of OEP π-cation radicals was not detected directly in our experiments, its transient formation as an intermediate in the process is proposed. The abnormal deviation of the ν_4 mode frequency of OEP acids from that expected for a_u character suggests that the ring oxidized and protonated species may not be comparable in H_2OEP due to a deshielding effect on the N–H protons.

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24. The RR spectra of H_2OEP remain unchanged when excited at 406 and 441.6 nm in CH_2Cl_2 in the presence of CCl_4 or $C_2H_2Cl_4$, or even in neat CCl_4 or $C_2H_2Cl_4$. No RR spectral feature was found for the monoacid or diacid derivative of H_2OEP in the presence of p-BQ in C_6H_6, CS_2 and CCl_4, while clean photochemical formation of diacid was observed in CH_2Cl_2, $CHCl_3$, $C_2H_4Cl_2$ and $C_2H_2Cl_4$ at 441.6 nm excitation under aerobic or anaerobic conditions. The 514.5 nm excited sample of H_2OEP in CH_2Cl_2 in the presence of p-BQ under aerobic conditions gave a violet color and absorption spectral changes characteristic of OEP diacid. But the RR spectrum was poorly resolved due to excitation within the Q band region.
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