Optical, NMR and ESR Evidence for the Oxidation of Cobalt Porphyrins in the Presence of an Electron Acceptor

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Studies on the oxidation products of various porphyrins and metalloporphyrins have received attention in recent years because of their unusual electronic properties and reactivity, and their involvement as intermediates in many biological processes [1–3]. Recently, it has been shown that in the presence of molecular oxygen and various donor ligands, oxidation of cobalt(II) protoporphyrins IX dimethyl ester proceeds readily to the corresponding cobalt(III) derivative [4, 5]. It was concluded that the donor ligands coordinate to the metal, promoting electron-transfer from cobalt to molecular oxygen. Here we wish to report our studies on the oxidation of various cobalt(II) porphyrins with different substituents in the presence of an electron acceptor, 4,6-dinitrobenzofuroxan (BFO). The oxidised cobalt(III) porphyrin and the reduced anion radical of BFO have been characterised for the first time in solution using optical, ^{1}H, ^{19}F NMR and ESR techniques.

Experimental

The various cobalt(II) porphyrins used in this study were: cobalt(II) tetraphenylporphyrin, CoTPP; cobalt(II) tetra(*p*-methoxyphenyl)porphyrin, CoTPP(OCH$_3$)$_4$; cobalt(II) octaethylporphyrin, CoOEP; cobalt(II) tetraphenyl-1,3,5,7-tetrabromoporphyrin, CoTPP(Br)$_4$; cobalt(II) tetrakis(pentafluorophenyl)porphyrin, CoTPPF$_{20}$.

The free base porphyrins were either purchased from Aldrich Chemicals, U.S.A. or made in the laboratory using a published procedure [6]. The cobalt(II) derivatives were prepared and purified by column chromatography following the literature procedure [6]. Optical spectra were recorded on a Shimadzu Model UV 160 spectrophotometer. ESR spectra were recorded on a Varian E-109 spectrometer and NMR spectra on a JEOL FX 90Q multinuclear NMR spectrometer.

Results and Discussion

The addition of increasing amounts of BFO to CHCl$_3$ solutions of various cobalt porphyrins decreased the intensity of the Q-bands with the appearance of isosbestic points consistent with the formation of a charge-transfer complex between BFO and cobalt porphyrin. The stoichiometry of the complex, determined as described previously, was found to be 1:1 [7, 8]. However, with time a red shift of the absorption bands [Q-bands ≈14 nm and Soret band ≈20 nm] was observed in all the cobalt porphyrins. Figure 1 shows the absorption changes of a solution containing cobalt(II) tetraphenylporphyrin (3.42×10^{-5} M) and BFO (1×10^{-3} M) with time. The appearance of the new band at 544 nm and the corresponding disappearance of the band at 528 nm clearly indicates the oxidation of cobalt(II) porphyrin to the cobalt(III) derivative. The peak positions are consistent with the spectrum of Co(III)TPPCl in CHCl$_3$. Table 1 lists the absorption maxima of both Q-bands and the Soret band in the presence and absence of BFO, together with the time taken for complete oxidation. It is clearly seen from the Table that the rate of oxidation of cobalt(II) porphyrin to its cobalt(III) derivative depends on the nature of the porphyrin as well as on the substituents present on it.

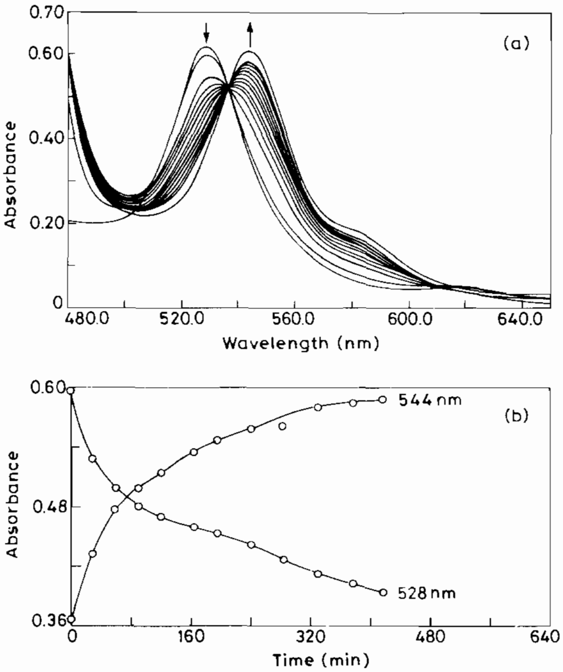

Fig. 1. (a) Absorption changes of CoTPP [3.42×10^{-5} M] in the presence of BFO [1×10^{-3} M] in CHCl$_3$ with time (0–415 min at ~30-min intervals). (b) Plot of absorption changes with time.

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TABLE 1. Absorption maxima of various cobalt porphyrins in the presence and absence of BFO in $CHCl_3$

Porphyrin	Q-band(s) (nm)	Soret band (nm)	Time taken for complete oxidation (min)
CoTPP	528	411	
CoTPP + BFO	544	450	330
$CoTPP(OCH_3)_4$	530	414	
$CoTPP(OCH_3)_4$ + BFO	543	433	270
$CoTPP(Br)_4$	545	424	
$CoTPP(Br)_4$ + BFO	556	453	600
$CoTPPF_{20}$	527	406	
$CoTPPF_{20}$ + BFO	539	430	
CoOEP	552.5, 521	392	
CoOEP + BFO	558, 527	412	25

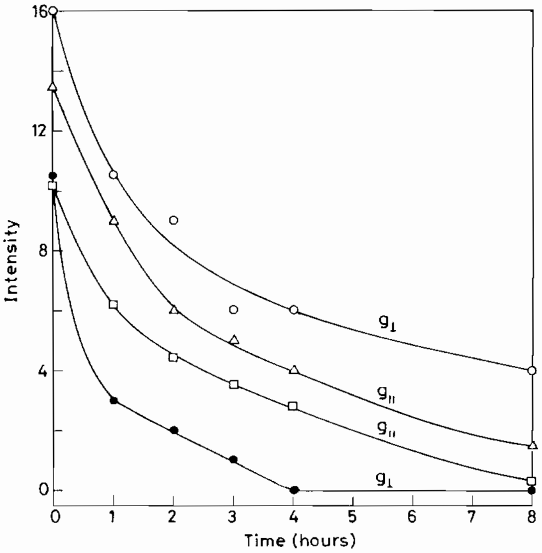

Fig. 2. Variation of intensity of ESR signals upon interaction with BFO as a function of time.

The presence of electron-withdrawing groups as substituents on the porphyrin ring retards the rate of oxidation, while the presence of electron-donating groups as substituents increases the rate of oxidation. There is also a linear correlation between the rate of oxidation and the corresponding $E_{1/2}$ values for the oxidation of cobalt(II) to the cobalt(III) derivative.

The oxidation was also followed in the absence of molecular oxygen. The sample for this was prepared in a high vacuum line. After several freezing and thawing cycles the solutions of BFO and cobalt porphyrins were mixed and the optical cell was vacuum sealed. The spectrum recorded as a function of time clearly shows the existence of both cobalt(II) and cobalt(III) species in solution with an isosbestic point at 424 nm. But the oxidation was not complete even after 24 h. When this solution was exposed to air, a complete conversion to the cobalt(III) species was achieved within an hour of exposure. This observation indicates that the oxidation is facilitated in the presence of molecular oxygen, presumably through the formation of superoxide ion.

The ESR studies also support this observation. The ESR samples were also prepared in a high vacuum line. The eight-line pattern of paramagnetic Co^{2+} ($I = 7/2$) was lost (about 80%) upon interaction with BFO with time and a new free-radical signal at the $g = 2$ region, attributed to the BFO^- radical, was observed at 133 K. Figure 2 shows the decrease in intensity of ESR signals (two lines in the parallel region and two in the perpendicular region) of the cobalt(II) species with time. To make sure that the new radical signal observed was due to the anion radical of the acceptor, BFO was chemically reduced with potassium metal in dimethoxyethane. At room temperature, the ESR signals were well resolved with 15 hyperfine lines due to two nitrogens and two protons [$a_N = 8.5$ G, $a_H = 3.1$ G]. The g value and the linewidth of the new radical signal at 133 K agree well with the chemically reduced BFO, indicating the formation of the BFO^- radical. The g values and the linewidths of the radicals generated by the addition of BFO to cobalt porphyrin and chemically reduced BFO^- were: 2.0434, 21 G and 2.0043, 23 G, respectively.

The ^1H NMR spectrum of $Co(II)TPP(OCH_3)_4$ shows two broad resonances at 15.99 and 13.11 ppm attributed to pyrrole and the *ortho*-H of the phenyl rings. The *meta*-H resonate at 9.45 ppm. Upon interaction with BFO, after 24 h the broad resonances of paramagnetic cobalt(II) were lost and well-resolved sharp resonances of a diamagnetic cobalt(III) derivative were observed [pyrrole (singlet), 9.013 ppm; *ortho*- and *meta*-protons (multiplet), 7.9 ppm]. To make sure that this was the cobalt(III) derivative, Co(III)TPPCl was prepared and the ^1H NMR spectrum of this was also recorded. Both

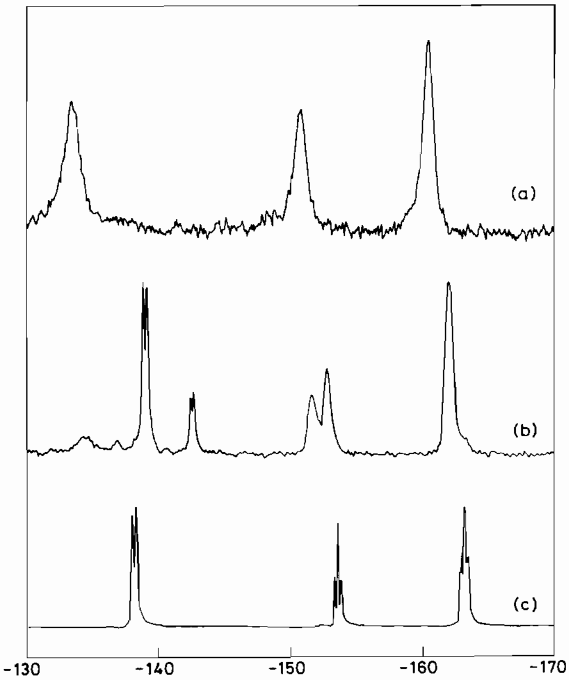

Fig. 3. ^{19}F NMR spectra of: (a) $CoTPPF_{20}$; (b) $CoTPPF_{20}$ containing BFO (spectrum recorded after 48 h of mixing); and (c) $ZnTPPF_{20}$ in $CDCl_3$.

spectra agree well, indicating that the oxidised product is diamagnetic cobalt(III) porphyrin.

^{19}F NMR spectra of penta-fluorinated Co(II)TPP both in the presence and absence of BFO were recorded. Figure 3 shows a comparison of Co(II)-$TPPF_{20}$ in the presence and absence of BFO, together with diamagnetic Zn(II)$TPPF_{20}$. Co(II)$TPPF_{20}$ shows three relatively broad resonances (typical of paramagnetic Co(II) porphyrins) at −133, −160.14 and −150.41 ppm (with external reference CF_3COOH at −76.5 ppm), attributed to *ortho*-, *meta*- and *para*-fluorines of the phenyl rings. These assignments were made on the basis of the ^{19}F NMR spectrum of pentafluorinated benzene [9]. Upon interaction with BFO, the spectrum was well resolved as in the diamagnetic Zn(II) derivative and all the fluorine resonances experienced an upfield shift [−137.55, −161.70 and −152.85 ppm, J_{o-m} 19.5 Hz]. These chemical shifts and the coupling constants are comparable to that of the diamagnetic $ZnTPPF_{20}$ [−137.49, −162.67 and −153.015 ppm and J_{o-m} 19.53 and J_{m-p} 19.5 Hz], indicating the formation of a diamagnetic Co(III) derivative. Further experiments with different electron acceptors and solvent compositions are in progress in an attempt to understand the kinetics and mechanism of electron transfer.

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