Oxidation of Chromium(III) Porphyrins to their π -Radical Cations or to Oxochromium(IV) Porphyrins

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One-electron oxidation of several chromium(III) porphyrins has been studied by steady-state and pulse radiolysis techniques under different conditions. Two types of products are observed: those exhibiting intense broad absorptions at $\lambda \ge 600$ nm, ascribed to the π -radical cations, and others exhibiting minor shifts of the porphyrin bands, ascribed to chromium(IV) porphyrins. Cr¹¹¹OEP (octaethylporphyrin), Cr¹¹¹TPP (tetraphenylporphyrin), and Cr¹¹¹TMP (tetramesitylporphyrin) in CH₂Cl₂ undergo one-electron oxidation on the ligand to give π -radical cations, which are stable after ligation, and further oxidation gives the dications. In the presence of KOH, however, they form Cr¹¹²-porphyrins and further radiolysis gives Cr²¹-porphyrins. Cr¹¹¹TSPP [tetrakis (4-sulfonatophenyl)porphyrin], Cr¹¹¹T3PyP [tetrakis(3-pyridyl)porphyrin], and Cr¹¹¹MSP (mesoporphyrin-IX), oxidized in 1 mol dm⁻³ aqueous HCI, form unstable π -radical cations which decay by disproportionation. The pulse radiolysis results indicate that the initial step in the oxidation of all Cr¹¹¹P and O=Cr¹¹²P species occurs at the porphyrin π -system and that, under certain conditions, the initial π -radical cation may undergo intramolecular electron transfer from the metal centre to the ligand to form the higher oxidation state Cr-porphyrin.

There is much current interest in the reactivity of high-valent oxidation states of metalloporphyrins which are important models for biological transport of oxygen and of electrons. One of the dominant reasons for the electron-transport properties of metalloporphyrins is their ability to undergo a series of well defined one-electron transfer processes.¹ The redox potentials for the reduction and the oxidation are significantly dependent upon the nature of the porphyrin ligand and the metal ion, as well as on axial ligation and medium properties. Oxidation of a metalloporphyrin occurs either at the porphyrin ring, resulting in the formation of a π -radical cation, or at the central metal ion if this is capable of forming a higher oxidation state. The parameters that determine the site of reduction²⁻⁴ and oxidation⁵ of Ni^{II}-porphyrins have recently been examined.

Under aerobic conditions, the preferred oxidation state of chromium porphyrins is the trivalent state.⁶⁻⁹ Recently we have found that the reduction path of Cr^{III} -porphyrins, leading to formation of either Cr^{II} -porphyrins or Cr^{III} -porphyrin π -radical anions, is dependent on the structure of the porphyrin and the axial ligands;¹⁰ reaction (1b) is favoured as the electron affinity of P increases and as the strength of the axial ligands L_1 and L_2 increases.

$$L_1 \longrightarrow L_1 L_2 Cr^{II} P \qquad (1a)$$

$$\begin{array}{c} L_1 \xrightarrow{-1} + C \xrightarrow{-1} L_1 L_2 Cr^{III} P^{-1} \end{array} (1b)$$

Since the oxidation of Cr^{III} -porphyrins has been previously studied only in chemical and electrochemical experiments, we investigated the time-resolved radiolytic oxidation of various Cr^{III} -porphyrins and identified their stable products, as well as the species produced immediately upon the first oneelectron oxidation. We find that some of these species undergo changes in axial ligation and/or in the site of oxidation to give the stable products.

Experimental

The following abbreviations are used for the porphyrins: TPP, tetraphenylporphyrin; TMP, tetramesitylporphyrin; TSPP, tetrakis(4-sulfonatophenyl)porphyrin; T3PyP, tetrakis(3-pyridyl)porphyrin; OEP, octaethylporphyrin; MSP, mesoporphyrin-IX; and MSPDME, mesoporphyrin-IX dimethylester. Cr^{III}TPP(Cl) was prepared by the method described previously.¹¹ Cr^{III}OEP(Cl), Cr^{III}TMP(Cl), Cr^{III}T3PyP(Cl), and Cr^{III}MSPDME(Cl) were prepared by similar procedures. The water-soluble Cr^{III}MSP was made by hydrolysis of the dimethylester, and Cr^{III}TSPP (Na salt) was prepared by literature methods.¹² Pyridine was vacuum distilled prior to use. All other solvents and reagents were of analytical-grade purity and were used as received. Water was purified with a Millipore Super-Q system.[†]

Solutions containing $(0.5-1) \times 10^{-4}$ mol dm⁻³ chromium porphyrin in the desired medium were freshly prepared before use and were irradiated under air or after purging with N₂O. Steady-state irradiations were done in a Gammacell 220 ⁶⁰Co source with a dose rate of 95 Gy min⁻¹. Absorption spectra before and after irradiation were recorded with a Cary 219 spectrophotometer. Pulse radiolysis experiments were performed with the apparatus described before,^{3,5} which utilizes 50 ns pulses of 2 MeV electrons from a Febetron Model 705 pulser. The dose per pulse, determined by KSCN dosimetry, was varied between 7 and 40 Gy, which, in aqueous solutions, gives between 4 and 24 × 10⁻⁶ mol dm⁻³ of radicals.

Results and Discussion

Radiolytic Oxidation Reactions

The chromium porphyrins (CrP) were oxidized by radiolytically produced radicals in various media. In aerated CH_2Cl_2 solutions they are oxidized mainly by the two peroxyl radicals, $CH_2ClO_2^{\circ}$ and $CHCl_2O_2^{\circ}$, formed in the radiolysis of

[†] The identification of commercial equipment or material does not imply recognition or endorsement by the National Institute of Standards and Technology, nor does it imply that the material or equipment identified are necessarily the best available for the purpose.

this solvent.13

$$CH_2Cl_2 \rightarrow [CH_2Cl_2]^{*+} + e^-$$
 and $CH_2Cl + Cl$ (2)

$$Cl + CH_2Cl_2 \rightarrow CHCl_2 + HCl$$
 (3)

$$e^{-} + CH_2Cl_2 \rightarrow CH_2Cl + Cl^{-}$$
(4)

$$[CH_2Cl_2]^{+} \rightarrow CHCl_2 + H^+$$
(5)

$$CH_2Cl + O_2 \rightarrow O_2CH_2Cl \tag{6}$$

$$^{\circ}CHCl_{2} + O_{2} \rightarrow ^{\circ}O_{2}CHCl_{2} \tag{7}$$

 $O_2CH_2Cl/O_2CHCl_2 + CrP \rightarrow$

$$CHCl_2O_2^-/CH_2ClO_2^- + (CrP)^+$$
 (8)

 $(CrP)^+$ denotes an oxidized chromium porphyrin, without specifying the site of oxidation. Similarly, in CH_2Br_2 they are oxidized by the corresponding peroxyl radicals and also by the Br atom complex, $CH_2Br_2 \cdot Br.^{14}$ In 2-PrOH–CCl₄ solutions the porphyrins are oxidized by $CCl_3O_2^{\bullet}$ radicals, produced by reduction of CCl_4 in the presence of oxygen.

$$CCl_3O_2^{\bullet} + CrP \rightarrow CCl_3O_2^{-} + (CrP)^+$$
(9)

Rate constants for oxidation of several metalloporphyrins by various peroxyl radicals were found to be generally in the range 10^7-10^9 dm³ mol⁻¹ s⁻¹.¹⁵ In aqueous solutions, the porphyrins were oxidized by Cl₂⁻, Br₂⁻, or N₃ radicals produced in N₂O-saturated solutions containing Cl⁻, Br⁻, or N₃⁻ ions (see, *e.g.* ref. 16).

$$Cl_{2}^{-} + CrP \rightarrow 2Cl^{-} + (CrP)^{+}$$
 (10)

$$N_{3}^{*} + CrP \rightarrow N_{3}^{-} + (CrP)^{+}$$
 (11)

These reactions are generally quite rapid, with rate constants ca. 10^8-10^9 dm³ mol⁻¹ s⁻¹, and result in one-electron oxidation. The metalloporphyrins were not oxidized with OH radicals, produced directly by water radiolysis, since this reaction leads to ligand addition products with only a small fraction giving the desired one-electron oxidation product.

Radiolytic Oxidation Products

To examine the stable products we carried out γ -radiolysis experiments on the different porphyrins and recorded the optical absorption spectra before and after several irradiation intervals (Fig. 1 and 2). In all cases, the peaks of the starting Cr^{III}P disappeared gradually upon irradiation and new absorptions were formed. Two typical spectra were observed. (a) New broad absorptions in the 600-840 nm region are attributed to the π -radical cations, Cr^{III}P⁺⁺, based on some of the previous results with Cr-porphyrins combined with additional evidence discussed below and also in parallel with absorption spectra of other metalloporphyrin π -radical cations (see, e.g. ref. 16, 17). (b) Minor shifts of the Q-band without strong absorption in the long wavelength region are attributed to species oxidized at the metal centre, based on previous assignments of Cr^{IV}-porphyrins. Furthermore, it is generally found that changes in the redox state of the metal in a metalloporphyrin result in minor shifts of the peaks without strong absorption in the red.9,16-18

In the case of $Cr^{III}TPP$, $Cr^{III}TMP$, and $Cr^{III}OEP$ in CH_2Cl_2 , radiolysis leads to clean and quantitative formation of products which exhibit intense broad absorptions at 600–840 nm [Fig. 1(a) and 2(a)], indicating the formation of the



Fig. 1 Spectral changes upon γ -radiolytic oxidation of Cr^{III}OEP. (----), Spectra before irradiation, (- - -), after various irradiation times. (a) 6.5×10^{-5} mol dm⁻³ Cr^{III}OEP in aerated CH₂Cl₂, irradiated for 6, 12, 24 s. (b) 1.5×10^{-4} mol dm⁻³ Cr^{III}OEP⁺⁺, produced as in (a) in aerated CH₂Cl₂, and further irradiated for 26, 52, 68 s. (c) 8.7×10^{-5} mol dm⁻³ Cr^{III}OEP in aerated CH₂Cl₂ stirred with KOH, irradiated for 6, 12, 18 s. (d) 8.7×10^{-5} mol dm⁻³ O=Cr^{IV}OEP, produced as in (c) in aerated CH₂Cl₂, and irradiated for 6, 18 s

 π -radical cations. These products are stable under these conditions but can be further oxidized by continued radiolysis. Another set of good isosbestic points are seen [Fig. 1(b) and 2(b)] and the final products absorb mainly at longer wavelengths, with maxima between 750 and 820 nm. These pro-



Fig. 2 Spectral changes upon γ -radiolytic oxidation of Cr^{III}TPP. (a) 2.5 × 10⁻⁵ mol dm⁻³ Cr^{III}TPP in aerated CH₂Cl₂, irradiation times 6, 12, 18 s. (b) 6.3 × 10⁻⁵ mol dm⁻³ Cr^{III}TPP⁺⁺, produced as in (a) in aerated CH₂Cl₂, and further irradiated for 16, 32, 48, 64 s. (c) 3.5 × 10⁻⁵ mol dm⁻³ Cr^{III}TPP in aerated CH₂Cl₂, stirred with KOH, irradiated for 6, 12, 18 s. (d) 3.5 × 10⁻⁵ mol dm⁻³ O=Cr^{IV}TPP, produced as in (c) in aerated CH₂Cl₂, and irradiated for 6, 18, 42 s

ducts are very likely the result of two-electron oxidation of the porphyrin ring.

$$Cr^{III}P \rightarrow Cr^{III}P^{*+} \rightarrow Cr^{III}P^{2+}$$
 (12)

The dications produced in this process probably add one of the anions produced by radiolysis to give more stable products.^{17,19} The lifetime of the π -radical cation was significantly shortened in the presence of base; radiolysis of the above solutions in the presence of 0.01% pyridine (serving as a base, not as an axial ligand at this concentration) did not yield stable π -radical cations but rather produced directly the more stable two-electron-oxidation product.

The water-soluble $Cr^{III}TSPP$ and $Cr^{III}MSP$ were oxidized by Cl_2^{--} radicals in aqueous HCl (1 mol dm⁻³) and found to give products with broad spectra (Table 1) that are different from those ascribed to the π -radical cations (observed by pulse radiolysis, see below). These products are probably the result of disproportionation of the radical cations and subsequent reaction of the dications with water or chloride.

Cr^{III}MSP and Cr^{III}OEP were oxidized to stable products by γ -radiolysis in 2-PrOH–CCl₄ (9:1). On the other hand, Cr^{III}TPP and Cr^{III}TMP showed little change in their spectra upon irradiation. We attribute this finding to reduction of the π -radical cations by 2-PrOH back to the original Cr^{III}P. Indeed, when the π -radical cation Cr^{III}TPP⁺⁺ was produced in CH₂Cl₂, the addition of 2-PrOH resulted in the reduction of this species to the starting material. This reaction does not occur with the OEP and MSP derivatives because of the lower oxidation potentials of pyrrole-substituted porphyrins as compared with *meso*-substituted porphyrins.^{1,20,21}

Stirring solutions of $Cr^{III}OEP$, $Cr^{III}TPP$, or $Cr^{III}TMP$ in CH_2Cl_2 with solid KOH results in the exchange of the axial Cl^- ligand with OH^- and in a total change in the path of oxidation. Radiolysis of these solutions yields products whose spectra are shifted only slightly from those of the orignal materials [Fig. 1(c) and 2(c)] and are ascribed to the oxochromium(IV) species on the basis of previously reported spectra.²⁰⁻²² The same spectra are also obtained by adding KOH to solutions of the corresponding π -radical cations in CH_2Cl_2 . The $O=Cr^{IV}P$ products can be converted back to $Cr^{III}P^{+}$ by the addition of HCl; stirring with LiCl, however, was less effective. The exact spectra of the $Cr^{III}P^{+}$ species produced from $O=Cr^{IV}P$ were slightly different to those produced by oxidation of $Cr^{III}P$ in the above experiments, owing to differences in axial ligation.

$$\begin{array}{ccc} Cl & Cl & Cl & Cl \\ \downarrow & & \uparrow \\ Cr^{III}P & \underbrace{\gamma^{-rad.}}_{CH_2Cl_2} & Cr^{III}P^{*+} & \underbrace{HCl}_{I} & \downarrow \\ & & \downarrow \\ & & Cl \end{array}$$
(13)

$$\begin{array}{cccc}
Cl & Cl & \\
Cr^{III}P^{*+} & \xrightarrow{H_2O} & Cr^{III}P^{*+} & \xrightarrow{OH^-} & O = Cr^{IV}P & (14) \\
Cl & OH & \\
\end{array}$$

An analogous difference was found between the π -radical cations produced in irradiated CH₂Cl₂ and CH₂Br₂ (for example, for Cr^{III}TPP⁺⁺ in CH₂Cl₂ the peaks were at 742, 690, 604, 536 and 424 nm and in CH₂Br₂ at 752, 664, 602, 538 and 430 nm) owing to ligation with Br⁻ instead of Cl⁻.†

Further irradiation of the $O=Cr^{IV}P$ states of OEP and TPP in CH_2Cl_2 gave the $O=Cr^{V}P$ products, as evident from the shifts in the spectra [Fig. 1(d) and 2(d)], in agreement with

[†] Addition of gaseous HBr to a CH_2Cl_2 solution of $Cr^{III}TPP$ was found to cause exchange of the Cl^- with Br^- immediately, shifting the peaks from 445, 524, 564 and 600 nm to 450, 524, 564 and 602 nm.

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porphyrin ^a	conditions	porphyrin peaks (λ/nm)	product peaks ^b (λ/nm)	product
Cr ^{III} TSPP (-4)	1 mol dm ⁻³ HCl	442, 520, 558, 594, 630	630 sh, 670, 740 sh	c
Cr ^{III} TPP (0)	CH ₂ Cl ₂	445, 524, 564, 600	424, 536, 604, 650 sh, 742 424, 700 sh, 750, 800 sh	Cr ^{III} P' + Cr ^{III} P ^{2 +}
	CH_2Cl_2 , stirred with KOH	438, 524 sh, 564, 600	430, 500 sh, 542, 575 sh, 602 420, 540, 600 sh	$O = Cr^{IV}P$ $O = Cr^{V}(Cl)P$
	CH ₂ Br ₂ toluene, 10% CCl ₄ 2-PrOH, 10% CCl ₄	450, 524, 564, 602 446, 560, 602 446, 520, 560, 598	430, 538, 602, 664 sh, 752 430, 542, 575 sh, 602	$Cr^{III}P'^+ O = Cr^{IV}P$
Cr ^{III} TMP (0)	CH_2Cl_2 CH_2Cl_2 , stirred with KOH 2-PrOH, 10% CCl ₄	445, 524, 564, 600 438, 524, 564, 602 438, 522, 560, 596	428, 542, 608, 660 sh, 766 432, 500 sh, 542, 576 sh, 600	$Cr^{III}P^{+}$ $O = Cr^{IV}P$
Cr ^{III} T3PyP (+4) (0)	1 mol dm ⁻³ HCl 2-PrOH, 10% CCl ₄	440, 510 sh, 558, 588 sh, 755 442, 518, 560, 596, 750	520 sh, 590, 628, 685, 756 ^e	c d
Cr ^{III} OEP (0)	CH ₂ Cl ₂	434, 490, 540, 572, 750	418, 544, 584, 656, 760, 810 400, 490, 540, 660, 730 sh, 810	Cr ^{III} P'+ Cr ^{III} P ²⁺
	CH_2Cl_2 , stirred with KOH	416, 494, 532, 570, 730	416, 494, 532, 570 ^f 404, 490, 530	$O = Cr^{IV}P$ $O = Cr^{V}(CI)P$
	CH_2Cl_2 , 0.01% pyridine 2-PrOH, 10% CCl_4	448, 490, 544, 574, 760 435, 492, 540, 574, 755	458, 490 sh, 544, 680, 816 418, 460 sh, 590, 670, 750, 800 sh	Cr ^{III} P ²⁺ Cr ^{III} P' ⁺
Cr ^{III} MSP (0) (-2)	1 mol dm ⁻³ HCl 2-PrOH, 10% CCl ₄	430, 490 sh, 538, 570, 750 432, 538, 572, 750	434, 590 sh, 620 sh, 656, 746 440, 546, 570 sh, 620 sh, 654, 750	с с

a See Experimental for the abbreviations of the porphyrins. The charge on the porphyrin ligand is given in parentheses, the overall charge on the porphyrin depends also on the axial ligands. ^b The peaks are given for the initial product in the first line and for the subsequent product in subsequent lines. ^c A product of the dication, probably after reaction with water or Cl⁻. ^d No change was observed upon γ -irradiation. ^e The peaks at 440 and 558 nm of the starting materials were also observed. ^f The peak positions of this product are similar to those of the starting material but the peak intensity ratios are very different.

previous observations following chemical oxidation.^{20,22} The $O=Cr^{v}P$ products, however, were relatively short-lived (several minutes, under the present experimental conditions) and reverted to the stable tetravalent state.

Chemical Oxidation

The γ -radiolytic results indicate that the path of oxidation is strongly influenced by the nature of the anion present in solution or formed by radiolysis. The presence of an oxygen donor in the system is crucial for formation of the tetravalent, or higher valent, oxoporphyrin. To confirm the assignment of the different absorption spectra and to compare their behaviour with that reported in the literature,^{22,23} we oxidized Cr^{III}P with various chemical oxidants. We used chemical oxidants that contain oxygen (*tert*-butyl hydroperoxide, sodium hypochlorite, and silver oxide) and one that does not (Br₂).

The reaction of $Cr^{III}P$ with Br_2 , in CH_2Cl_2 or toluene, resulted in the formation of the broad absorptions in the 600-840 nm region, identical with those formed in the γ radiolysis in CH_2Br_2 and in good agreement with a previous study on the oxidation of $Cr^{III}TPP$,²³ where the corresponding spectrum was attributed to the π -radical cation. The use of Bu'OOH, NaOCl and Ag₂O, however, did not give the broad absorptions of the π -radical cations but only a small change in the porphyrin peaks. It has been suggested that these oxidants lead to the formation of the O= $Cr^{IV}P$ products.²² The reported absorption data for the O= $Cr^{IV}P$ complexes are in good agreement with those found in the present study. This result supports the assumption that the presence of an oxygen donor is important for stabilizing the Cr^{IV} oxidation state as the product of oxidation of $Cr^{III}P$.

Pulse Radiolysis Studies

Pulse radiolysis experiments with kinetic spectrophotometric detection were carried out to characterize the initial species produced by one-electron oxidation of the various Cr^{III}-

porphyrins. Cr^{III}P were pulse irradiated under oxidizing conditions, in most cases in CH₂Cl₂, 2-PrOH-CCl₄ (9:1), or aqueous solutions at different pH values. The species formed upon one-electron oxidation were characterized on the basis of the differential absorption spectra recorded in the 500-840 range immediately after the oxidation reactions were complete ($\leq 200 \ \mu$ s). With all the porphyrins studied the differential spectra indicated bleaching of the Cr^{III}P Q-bands in the 500-600 nm region and formation of broad absorptions in the 600-840 nm region (Fig. 3). The positions and intensities of the new bands were strongly dependent on the porphyrin structure. OEP and MSP, both substituted on the pyrrole ring, gave similar absorption pattern. TPP, TMP and TPPS, which are derived from meso-tetraphenylporphyrin, also show similarity in the spectra of their one-electron-oxidation products. The two groups, however, exhibited somewhat different patterns.

The differential spectra recorded with $Cr^{III}OEP$ and $Cr^{III}TPP$ in CH_2Cl_2 exhibit strong absorptions in the 600–700 nm range ($\lambda_{max} = 600$ and 640 nm for OEP and 620 nm for TPP). Such peaks are characteristic of porphyrin π -radical cations, as observed for Zn-porphyrin and other metalloporphyrins which undergo ring oxidation.^{16,17}

Therefore, we conclude that the initial products of oneelectron oxidation of these two porphyrins are the π -radical cations. The γ -radiolysis results demonstrated the high stability of these products under these conditions. Close comparison of the spectra obtained by the two techniques, however, shows slight differences (ca. 20 nm) in the peak positions (Tables 1 and 2). Therefore, we examined the differential spectrum in the pulse radiolysis after longer times in an attempt to observe its conversion to the final stable product. We found, in fact, that within several seconds after the pulse the initial peak at 640 nm shifts to 660 nm [Fig. 3(a)], indicating formation of the same final product as that formed in the γ -radiolysis experiment. This spectral transformation is ascribed to the following process.



Fig. 3 Transient differential absorpton spectra observed following pulse radiolytic oxidation of chromium porphyrins. (a) Cr^{III}OEP in pulse radiolytic oxidation of chroninan popphysis. (a) Cr OLT in aerated CH_2Cl_2 (\bigcirc) initial spectrum, 0.1 ms after the pulse, (\triangle) final spectrum measured 1 s later. (b) $O=Cr^{IV}OEP$ in aerated CH_2Cl_2 , 0.1 ms after the pulse. (c) $Cr^{II}TPP$ in aerated CH_2Cl_2 , 0.2 ms after the pulse. (d) $O=Cr^{IV}TPP$ in aerated CH_2Cl_2 , 0.2 ms after the pulse. In all cases the dose was 40 Gy per pulse



Fig. 4 Transient differential absorption spectra observed following pulse radiolytic oxidation of several Cr^{III} -porphyrins. (a) CrTSPP, (\bigcirc) initial spectrum, (\triangle) final spectrum. (b) CrT3PyP, (\bigcirc) initial spectrum, (Δ) final spectrum. (c) CrMSP, initial spectrum. All were irradiated in aerated 1 mol dm⁻³ aqueous HCl, with a dose of 40 Gy per pulse, the initial spectra were recorded 0.2 ms after the pulse and the final spectra were recorded ca. 4 ms later

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$$\begin{array}{cccc}
Cl & Cl & Cl \\
I & I \\
Cr^{III}P^{+} \xrightarrow{ROO} & I \\
& & Cr^{III}P^{*+} \xrightarrow{HCl} & I \\
& & I \\
ROO & Cl
\end{array}$$
(16)

The initial oxidation of ClCr^{III}P by the peroxyl radicals of CH₂Cl₂ probably takes place via an intermediate adduct.²⁴ The final spectrum is ascribed to the dichloro complex, which is formed by reaction of the initial adduct with the HCl produced in the radiolysis of CH₂Cl₂ [reactions (3)-(5)]. Since both reactants are produced in equal amounts, we expect a second-order rate law for this reaction. The traces, however, appeared to fit better to a first-order rate law, with some

 Table 2
 Pulse radiolytic oxidation of chromium(III) porphyrins

porphyrin"	conditions	peaks (λ/nm)	product
Cr ^{III} TSPP	$1 \text{ mol dm}^{-3} \text{ HCl, air}$	630, 660, 740 790	Cr ^{III} P'+ Cr ^{III} P ²⁺
	$0.01 \text{ mol } \text{dm}^{-3} \text{ NaN}_3$, pH 7.3, N ₂ O	630 sh, 670, 730	Cr ^{III} P'+
Cr [™] TPP	CH ₂ Cl ₂ , air 2-PrOH, 10% CCl ₄ , air	620, 740 sh 640, 740 sh	Cr ^{III} P'+ Cr ^{III} P'+
Cr ^{III} TPP' ⁺ ^b	CH ₂ Cl ₂ , air	810	Cr ^{III} P ²⁺
O=Cr ^{IV} TPP ^c	CH ₂ Cl ₂ , air	620	Cr ^{IV} P ^{•+}
Сг ^ш ТЗРуР	1 mol dm ⁻³ HCl, air	620 sh, 670, 770 800–850	Cr ^{III} P ^{• +} Cr ^{III} P ^{2 +}
Cr ^{III} OEP	CH_2Cl_2 , air CH_2Cl_2 , stirred with KOH, air 2-PrOH, 10% CCl_4 , air	600, 640, 790 590, 640, 770 600, 640	Cr ^{III} P'+ Cr ^{III} P'+ Cr ^{III} P'+
Cr ^{III} OEP ^{++ b}	CH ₂ Cl ₂ , air	740, 800840	Cr ^{III} P ²⁺
O=Cr ^{IV} OEP ^c	CH ₂ Cl ₂ , air	600, 640–680, 760	Cr ^{IV} P ⁺⁺
Cr ^{III} MSP	1 mol dm ⁻³ HCl, air	600 sh, 620 > 840	Cr ^{III} P ^{•+} Cr ^{III} P ²⁺
	$0.01 \text{ mol } \text{dm}^{-3} \text{ NaBr, pH } 10, \text{ N}_2\text{O}$	600 sh, 630	Cr ^{III} P*+

^a See Experimental for the abbreviations of the porphyrins. ^b Prepared by pre-irradiation of solution. ^c Prepared by pre-irradiation of solution and stirring with KOH.

second-order contribution. The rate constant for this process was estimated as $k = 0.4 \pm 0.1 \text{ s}^{-1}$.

The rate of this reaction was found to increase by an order of magnitude in the presence of HCl added prior to irradiation, but it was difficult to obtain a quantitative dependence of the rate constant on the HCl concentration owing to its limited solubility and volatility from this organic solvent. Nevertheless, at all HCl concentrations examined, the spectral change followed a first-order process, indicating no dimerization of the initial product.[†]

Radiolysis of CH₂Cl₂ solutions of Cr^{III}P in the presence of alkali resulted in the formation of $O=Cr^{IV}P$. In the pulse radiolysis, however, the first product was found to be the π radical cation. This product was short-lived in alkaline solutions and presumably forms the $O=Cr^{IV}P$. Pulse radiolysis of Cr^{III}P in 2-PrOH-CCl₄ (9:1) also gave a short-lived π radical cation. This product, however, decayed, probably by oxidizing the solvent, as seen in the γ -radiolysis experiments with CrTPP.

The water-soluble Cr^{III}TSPP, Cr^{III}T3PyP and Cr^{III}MSP were oxidized by Cl_2^{-} radicals, produced in 1 mol dm⁻³ aqueous HCl under air, and all formed the π -radical cations (Fig. 4). These products decayed by disproportionation²⁵ leading to the original compound and the dication (or its neutralized product).

$$2Cr^{III}P^{*+} \rightarrow Cr^{III}P + Cr^{III}P^{2+}$$
(17)

The decay of the TSPP and T3PyP radicals took place within several milliseconds and that of the MSP radical within several seconds. $Cr^{III}TSPP$ and $Cr^{III}MSP$ were also oxidized by the N₃ radical in neutral and alkaline solutions, both giving the π -radical cations which decayed within milliseconds to the same final products.

The π -radical cations Cr^{III}OEP⁺⁺ and Cr^{III}TPP⁺⁺ were stable and did not disproportionate under our conditions. They were, however, converted to the dications by further oxidation. Pulse radiolysis experiments with solutions of

Cr^{III}OEP⁺⁺ and Cr^{III}TPP⁺⁺, prepared by prior γ -radiolysis, showed strong absorptions at 780–840 nm; the differential spectra were very similar to those derived from γ -radiolysis [Fig. 1(b) and 2(b)].

Pulse irradiation of $O=Cr^{IV}P$ solutions, produced by γ -radiolysis, led to initial formation of the π -radical cations, before transformation into the final products, $O=Cr^{V}P$.

$$O = Cr^{IV}P \to O = Cr^{IV}P^{*+} \to O = Cr^{V}P$$
(18)

The transformation of the radical cation to the Cr^{v} product again may involve reaction with HCl to provide the additional axial ligand required by the higher oxidation state, *i.e.* to form $O=Cr^{v}(Cl)P$.

Conclusion

 Cr^{III} -porphyrins undergo one-electron oxidation on the ligand to form π -radical cations which are stable in aprotic solvents. In protic solvents, however, they are generally shorter-lived, depending on the structure of the porphyrin ligand, and they may disproportionate to give the dication and the original porphyrin. Some of the π -radical cations were found to be reduced by 2-PrOH to the original compound. Further oxidation of the π -radical cations yields two-electron ligand-oxidized products.

Oxidation under alkaline conditions yields $O=Cr^{IV}P$ and subsequently $O=Cr^{V}P$. Furthermore, Cr^{IIP} ⁺⁺ can be converted into $O=Cr^{IV}P$ by the addition of base and the reaction can be reversed by the addition of acid, *i.e.* changes in the axial ligation result in intramolecular electron transfer between the metal centre and the porphyrin macrocycle.

Time-resolved pulse radiolysis experiments have shown that one-electron oxidation of Cr^{IIP} and $O=Cr^{IV}P$ under all conditions takes place initially at the ligand to form π -radical cations. Subsequently, within milliseconds to seconds, these species either add another ligand anion to give the stable form of the π -radical cation in acidic medium or add OH⁻ and lose HCl in the presence of base to form a higheroxidation-state metal centre. The latter process involves an intramolecular electron transfer from the metal centre to the porphyrin ligand and its rate is controlled by the rate of ligand exchange.

[†] Certain earlier results (e.g. ref. 20) on the oxidation of $Cr^{III}P$ were interpreted to suggest the formation of a dimer, $PCr^{IV}-O-Cr^{IV}P$, which is converted to $O=Cr^{IV}P$ by the addition of base. We support the alternative interpretation that the initial product is the π -radical cation.

The stability of the higher oxidation states depends on the porphyrin and on the medium, and they may be readily reduced to the $Cr^{III}P$ state; $O=Cr^{V}P$ more readily than $O=Cr^{IV}P$. The $O=Cr^{V}P$ state may thus serve as a two-electron oxidant or an oxygen atom donor, which may enable these porphyrins to act as oxidation catalysts.^{20,21,26}

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