Redox Reactions of Osmium Porphyrins

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The metal centre in osmium porphyrinates (OsP) can exist in a wide range of oxidation states, each being stabilised by axial complexation with a particular ligand. Thus, Os^{II}P is stabilised by ligation with a CO molecule. Oxidation occurs readily to form the corresponding Os^{III}P which retains the CO ligand and can be reduced quantitatively to the original Os^{II} complex. Further oxidation gives Os^{IV}P which is stabilised by axial ligation of two alcohol or water molecules. These Os^{IV} complexes are stable to both oxidation and reduction. Treating the Os^{II}P with an organic peroxide results in formation of an Os^{VI}P complex which is stabilised by two oxo ligands but can be reduced to the Os^{IV}P species. Photolysis of Os^{II}P and Os^{III}P causes loss of the CO ligand, the naked porphyrin species so formed undergoes oxidative reactions with the solvent, O_2, or trace impurities, in most cases forming an Os^{IV}P complex. The [Os^{VI}P(O)$_2$] species does not oxidise alkanes or alkenes in the dark at room temperature but does oxidise cyclohexene under visible light irradiation.

Considerable attention has been given to the spectroscopic and chemical properties of osmium porphyrins. The central osmium cation can bind a wide variety of small molecules and ions, such as CO, and it can exist in several different oxidation states. Thus, osmium porphyrins have been characterised in which the central cation has a formal oxidation state of 2, 3, 4, or 6, each valency being stabilised by particular ligands.[1–15] Most of these complexes are stable, at least in non-aqueous solvents, and there have been several reports describing their photophysical[16–18] and photochemical[19,20] properties. In the present work, we have employed a variety of experimental techniques to study the redox chemistry of osmium porphyrins with a view to clarifying the extent to which the various oxidation states are interconvertible. It will be shown that the osmium(IV) state presents the 'bottleneck' in the overall cycle.

In related systems, it has been found that certain high-valent metalloporphyrins can mimic the oxidative enzymatic reactions of cytochrome P-450. Fe and Mn porphyrins are known to catalyse the epoxidation and hydroxylation of alkenes under very mild conditions.[21–26] Other metalloporphyrins also possess some catalytic activity for such processes, including Ru, Mo, and Ti complexes,[27–29] although product selectivities tend to be poor. It appears that Os^{VI} porphyrins do not catalyse functionalisation of alkenes but some activity has been observed[30] with lower valent Os porphyrins. We have confirmed such findings and, in addition, we have considered the use of Os^{VI} porphyrins as photosensitisers for alkene oxidations.

Experimental

Osmium(II) ions were inserted into the porphyrin ring using [$Os_3(CO)_{12}$] as the metal carrier so that the final product contains a single molecule of CO bound to the central metal cation. Carbonylosmium(II) 2,3,7,8,12,13,17,18-octaethylporphyrinate [Os^{II}(oep)(CO)] was prepared[2] and purified[7] as described before, the absorption spectrum being in good agreement with earlier reports.[2] The corresponding 5,10,15,20-tetraphenylporphyrinate [Os^{II}(tpp)(CO)] was prepared by a similar procedure and purified by t.l.c. on silica gel using dichloromethane as solvent, the absorption spectrum being similar to that reported[4] for osmium(II) 5,10,15,20-tetrakis(*p*-tolyl)porphyrinate. The presence of the axially bound CO molecule was confirmed by i.r. spectroscopy, intense bands being observed at 1 899 and 1 917 cm^{-1} respectively for the oep and tpp complexes. Satisfactory elemental analyses were obtained only after samples of the osmium porphyrins had been recrystallised from CH_2Cl_2–CH_3OH (1:1). This treatment generates the monomethanol complexes {Found: C, 58.65; H, 6.35; N, 7.10; Os, 24.05. Calc. for [Os(oep)(CO)(CH_3OH)], $C_{38}H_{48}N_4O_2Os$: C, 58.30; H, 6.20; N, 7.15; Os, 24.30%. Found: C, 64.25; H, 3.90; N, 6.40; Os, 21.85. Calc. for [Os(tpp)(CO)(CH_3OH)], $C_{46}H_{32}N_4O_2Os$: C, 64.00; H, 3.75; N, 6.50; Os, 22.05%}.

Authentic samples of the Os^{VI} porphyrins were prepared by reacting the corresponding Os^{II} porphyrins with t-butyl hydroperoxide in CH_2Cl_2–CH_3OH (1:1) at room temperature.[7] The products were chromatographed on silica gel using CH_2Cl_2–acetone (9:1) as eluant and recrystallised from CH_2Cl_2–CH_3OH (1:1). I.r. spectroscopy showed strong bands at 825 and 837 cm^{-1} respectively for the oep and tpp complexes {Found: C, 57.45; H, 6.00; N, 7.40; Os, 25.0. Calc. for [Os(oep)(O)$_2$], $C_{36}H_{44}N_4O_2Os$: C, 57.25; H, 5.85; N, 7.40; Os, 25.20. Found: C, 63.55; H, 3.60; N, 6.50; Os, 22.50. Calc. for [Os(tpp)(O)$_2$], $C_{44}H_{28}N_4O_2Os$: C, 63.30; H, 3.40; N, 6.70; Os, 22.80%}.

Authentic samples of the corresponding Os^{IV} porphyrins were obtained by reduction of the Os^{VI} porphyrins with $SnCl_2$ in CH_2Cl_2–CH_3OH (1:3) at room temperature.[7] The products were chromatographed on silica gel using CH_2Cl_2–CH_3OH (5:1) as eluant and recrystallised from CH_2Cl_2–CH_3OH (1:1). I.r. spectroscopy showed strong bands at 1 010 and 535 cm^{-1} for the oep complex and at 1 013 and 532 cm^{-1} for the tpp complex {Found: C, 58.20; H, 6.45; N, 7.05; Os, 24.05. Calc. for [Os(oep)(OCH_3)$_2$], $C_{38}H_{50}N_4O_2Os$: C, 58.15; H, 6.40; N, 7.15; Os, 24.25. Found: C, 64.00; H, 4.15; N, 6.20; Os, 21.70. Calc. for [Os(tpp)(OCH_3)$_2$] $C_{46}H_{34}N_4O_2Os$: C, 63.85; H, 3.95; N, 6.45; Os, 22.00%}.

Dichloromethane, methanol, and propan-2-ol were obtained from Mallinckrodt, carbon tetrachloride from Kodak, and tin(II) chloride from Fisher; materials used in the photochemical studies were obtained from BDH and were of spectroscopic grade. All other compounds were of the highest available purity and used as received. Water was purified by a Millipore Super-Q system. All solutions were prepared fresh and protected from undue illumination.

Absorption spectra were recorded with Cary 219 and Perkin-Elmer 554 spectrophotometers. Gamma radiolyses were made with a Gammacell 220 ^{60}Co source with a dose rate of 90 Gy min^{-1}. Photochemical experiments were made with an Applied Photophysics 950 W Xe lamp filtered to remove i.r. and light of $\lambda < 350$ nm. In both studies, the course of reaction was followed by absorption spectroscopy. Cyclic voltammetry studies were carried out with a Rank E611 potentiostat driven by a purpose-built triangle wave generator. A glassy-carbon working electrode was used together with a Pt counter electrode and an s.c.e. reference and the solution contained tetrabutylammonium perchlorate (0.1 mol dm^{-3}) as electrolyte.

Certain commercial equipment, instruments, or materials are identified in this paper in order to specify adequately the experimental procedure. Such identification does not imply recognition or endorsement by the National Bureau of Standards, nor does it imply that the materials or equipment are necessarily the best available for the purpose.

Results and Discussion

Cyclic Voltammetry.—Redox potentials for one- and two-electron oxidation of the two Os$^{\mathrm{II}}$ porphyrins were determined by cyclic voltammetry. Detailed studies were made for [Os$^{\mathrm{II}}$(tpp)(CO)] since such measurements have not been reported previously for this compound whereas there have been several determinations[8,9] of redox potentials for [Os$^{\mathrm{II}}$(oep)(CO)]. By comparison to this earlier work, the overall electrochemistry of [Os$^{\mathrm{II}}$(tpp)(CO)] in dichloromethane solution can be summarised by equations (1)—(4). Identical

$$[\mathrm{Os^{II}(tpp)(CO)}]^- + \mathrm{e} \longrightarrow [\mathrm{Os^{II}(tpp)(CO)}]^{2-}; E_{\frac{1}{2}} = -1.17 \text{ V } vs. \text{ s.c.e.} \tag{1}$$

$$[\mathrm{Os^{II}(tpp)(CO)}] + \mathrm{e} \longrightarrow [\mathrm{Os^{II}(tpp)(CO)}]^-; E_{\frac{1}{2}} = -0.72 \text{ V } vs. \text{ s.c.e.} \tag{2}$$

$$[\mathrm{Os^{III}(tpp)(CO)}]^+ + \mathrm{e} \longrightarrow [\mathrm{Os^{II}(tpp)(CO)}]; E_{\frac{1}{2}} = 0.51 \text{ V } vs. \text{ s.c.e.} \tag{3}$$

$$[\mathrm{Os^{IV}(tpp)(CO)}]^{2+} + \mathrm{e} \longrightarrow [\mathrm{Os^{III}(tpp)(CO)}]^+; E_{\frac{1}{2}} = 1.31 \text{ V } vs. \text{ s.c.e.} \tag{4}$$

measurements made with [Os$^{\mathrm{II}}$(oep)(CO)] gave half-wave potentials for one- and two-electron oxidations of 0.36 and 0.90 V *vs.* s.c.e. Thus, the oep complex is easier to oxidise than the corresponding tpp complex.

Addition of pyridine, which complexes strongly to the Os$^{\mathrm{II}}$ ion without dislodging the CO ligand,[8] leads to a substantial increase in $E_{\frac{1}{2}}$ for the first oxidation step. Thus, $E_{\frac{1}{2}}$ values of 0.67 and 0.89 V *vs.* s.c.e. were observed for the oep and tpp complexes, respectively, as compared to 0.36 and 0.51 V in the absence of pyridine. Similarly, the presence of a co-ordinating solvent, such as propan-2-ol, increases the half-wave potentials for one-electron oxidation. Indeed, for [Os$^{\mathrm{II}}$(oep)(CO)] an $E_{\frac{1}{2}}$ value of 0.64 V *vs.* s.c.e. was observed in CH_2Cl_2–propan-2-ol (4:1) whilst the corresponding value observed for [Os$^{\mathrm{II}}$(tpp)(CO)] was 0.83 V *vs.* s.c.e.

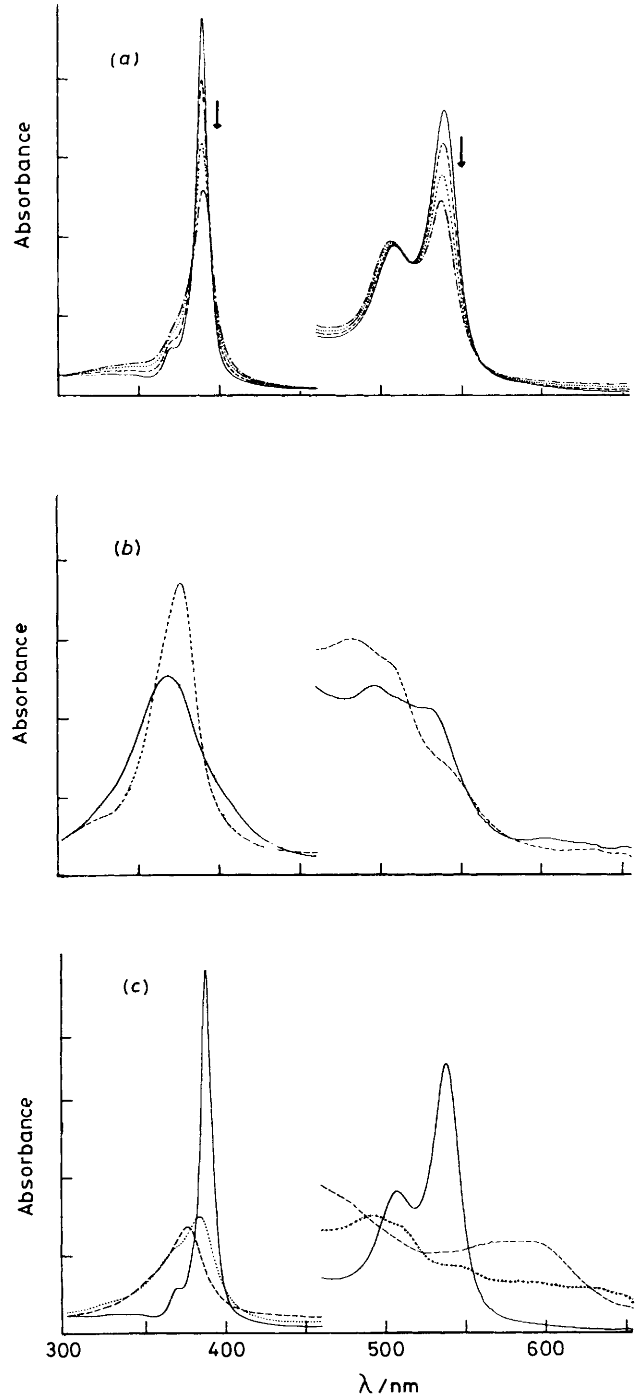


Figure 1. (*a*) Absorption spectra showing the progressive oxidation of [Os$^{\mathrm{II}}$(oep)(CO)] to [Os$^{\mathrm{III}}$(oep)(CO)Cl] following gamma radiolysis in aerated CH_2Cl_2 solution. (*b*) Absorption spectra recorded for [Os$^{\mathrm{IV}}$(oep)(OC_3H_7)$_2$] (——) and the protonated form [Os$^{\mathrm{IV}}$(oep)(C_3H_7OH)$_2$]$^{2+}$ (— — —) as formed by oxidation of [Os$^{\mathrm{II}}$(oep)(CO)] with *p*-cumenyl hydroperoxide in propan-2-ol solution. (*c*) Comparison of absorption spectra recorded for [Os$^{\mathrm{II}}$(oep)(CO)] (——), [Os$^{\mathrm{IV}}$(oep)(OH)$_2$] (· · · ·), and [Os$^{\mathrm{VI}}$(oep)(O)$_2$] (— — —)

Gamma Radiolysis.—One-electron oxidation of [Os$^{\mathrm{II}}$(oep)(CO)] and [Os$^{\mathrm{II}}$(tpp)(CO)] was achieved by gamma radiolysis in air-equilibrated dichloromethane solutions. The absorption spectra recorded after increasing radiation doses exhibit clear isosbestic points as shown in Figures 1(*a*) and 2(*a*). The spectral changes observed in the case of the oep complex are similar to those recorded following electrochemical oxidation,[8] although slight differences are apparent due to the presence of a pyridine ligand in the electrolysis study. The product from our

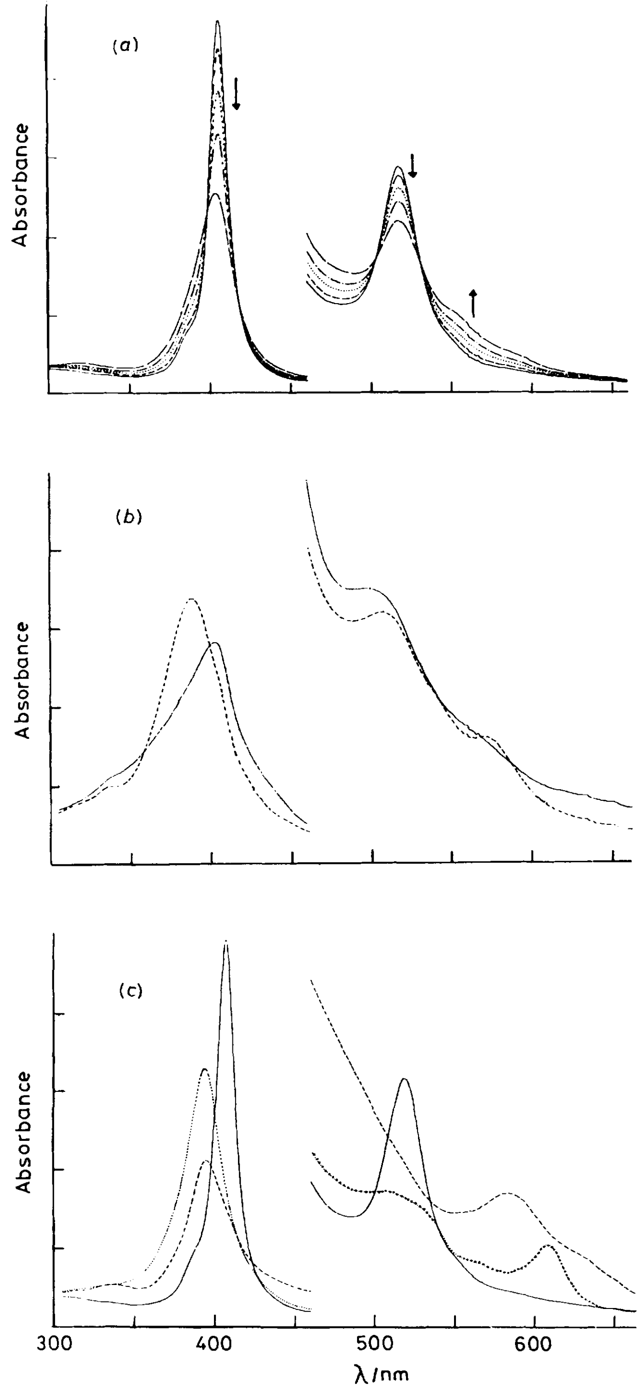


Figure 2. (*a*) Absorption spectral profile showing the conversion of $\mathrm{[Os^{II}(tpp)(CO)]}$ into $\mathrm{[Os^{III}(tpp)(CO)Cl]}$ upon gamma radiolysis in aerated $\mathrm{CH_2Cl_2}$ solution. (*b*) Absorption spectra recorded for $\mathrm{[Os^{IV}(tpp)(OC_3H_7)_2]}$ (——) and the protonated form $\mathrm{[Os^{IV}(tpp)(C_3H_7OH)_2]^{2+}}$ (— — —) formed by oxidation of $\mathrm{[Os^{II}(tpp)(CO)]}$ with *p*-cumenyl hydroperoxide in propan-2-ol solution. (*c*) Comparison of absorption spectra recorded for $\mathrm{[Os^{II}(tpp)(CO)]}$ (——), $\mathrm{[Os^{IV}(tpp)(OH)_2]}$ (· · · ·), and $\mathrm{[Os^{VI}(tpp)(O)_2]}$ (— — —)

experiments is assigned the composition $\mathrm{[Os^{III}(oep)(CO)Cl]}$. Similarly, in the parallel experiment with tpp the product is assigned to $\mathrm{[Os^{III}(tpp)(CO)Cl]}$. It was observed that both $\mathrm{Os^{III}}$ porphyrins could be reduced quantitatively to the original $\mathrm{Os^{II}}$ porphyrins upon addition of $\mathrm{SnCl_2}$.

Radiolysis of aerated dichloromethane solutions results in formation of peroxyl radicals due to a complex sequence of reactions involving intermediate carbon-centred radicals.[31] These chlorinated peroxyl radicals are strong one-electron oxidising agents and are known to oxidise many different metalloporphyrins.[32–34] Presumably, these radicals are responsible for oxidation of the $\mathrm{Os^{II}}$ porphyrins under our experimental conditions [equations (5) and (6); P = porphyrin-

$$\mathrm{CHCl_2O_2 + [Os^{II}P(CO)] \longrightarrow CHCl_2O_2^{-} + [Os^{III}P(CO)]^{+}} \qquad (5)$$

$$\mathrm{CH_2ClO_2 + [Os^{II}P(CO)] \longrightarrow CH_2ClO_2^{-} + [Os^{III}P(CO)]^{+}} \qquad (6)$$

ate]. It is likely that the initial oxidation product is the positively-charged $\mathrm{Os^{III}}$ porphyrin, which quickly combines with a chloride ion to form the neutral complex, equation (7).

$$\mathrm{[Os^{III}P(CO)]^{+} + Cl^{-} \longrightarrow [Os^{III}P(CO)Cl]} \qquad (7)$$

Radiolytic oxidation of the $\mathrm{Os^{II}}$ porphyrins in aerated dichloromethane solution beyond the stage of the $\mathrm{Os^{III}}$ porphyrins leads to formation of a mixture of products and clear isosbestic points are not observed. It appears that, under these conditions, the $\mathrm{Os^{III}}$ porphyrins are partly oxidised to the corresponding $\mathrm{Os^{IV}}$ porphyrins but there is also extensive irreversible oxidation of the porphyrin ring. In an attempt to direct the oxidation towards the metal centre in a more quantitative manner, the solvent system was varied.

Radiolysis of alcoholic or aqueous alcoholic solutions of $\mathrm{CCl_4}$ in the presence of oxygen results in the formation of $\mathrm{CCl_3O_2}$ radicals,[32] which are strong one-electron oxidising agents. Surprisingly, gamma radiolysis of the $\mathrm{Os^{II}}$ porphyrins dissolved in a mixture of propan-2-ol–water–$\mathrm{CCl_4}$ (80:20:1) containing 0.2 mol $\mathrm{dm^{-3}}$ KOH under air led to quantitative formation of the corresponding $\mathrm{Os^{IV}}$ porphyrins. The oxidation product obtained from $\mathrm{[Os^{II}(oep)(CO)]}$ was found to have a similar absorption spectrum to that characterised[1–3,7,30] for $\mathrm{[Os^{IV}(oep)(OCH_3)_2]}$. This suggests that the $\mathrm{Os^{IV}}$ porphyrins formed by radiolytic oxidation in alkaline aqueous propan-2-ol solution exist with two axially co-ordinated propanoxy ligands.

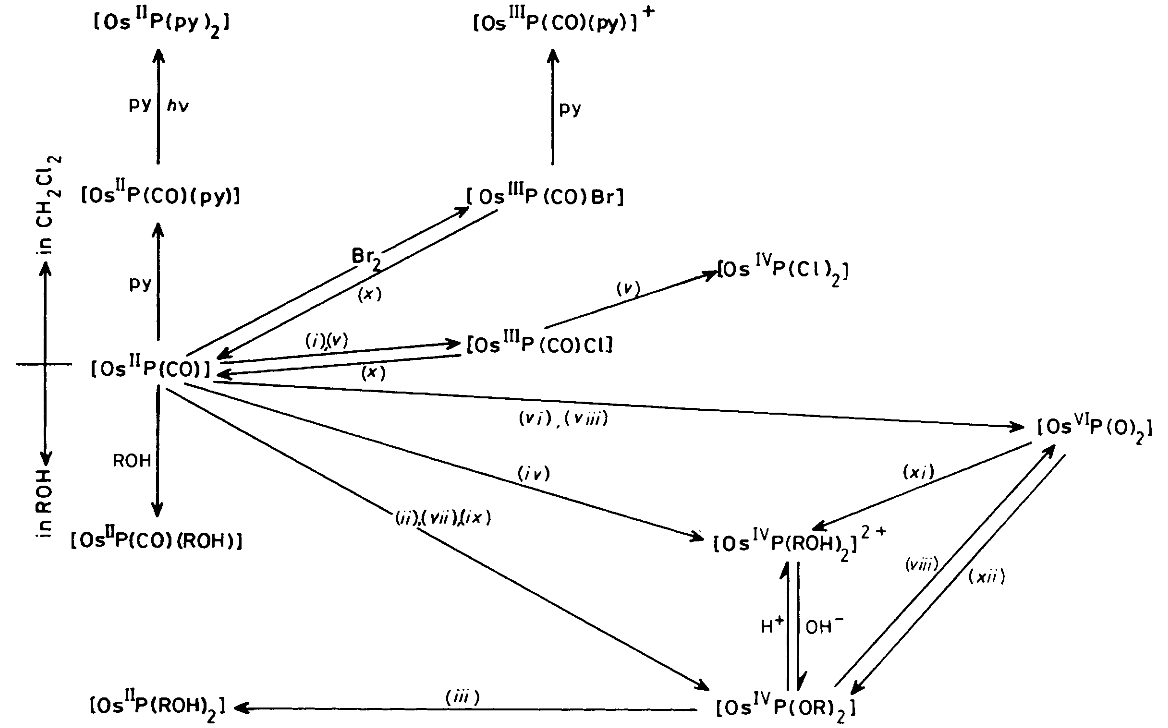
For both oep and tpp complexes, absorption spectra recorded after increasing radiation doses showed clear isosbestic points. This implies that the transition from $\mathrm{Os^{II}}$ to $\mathrm{Os^{IV}}$ proceeds without the intermediacy of a stable $\mathrm{Os^{III}}$ state. This could be explained in terms of the initially formed $\mathrm{Os^{III}}$ porphyrin undergoing rapid disproportionation in alkaline solution [equations (8)—(10)].

$$\mathrm{[Os^{II}P(CO)] + CCl_3O_2 \longrightarrow [Os^{III}P(CO)]^{+} + CCl_3O_2^{-}} \qquad (8)$$

$$\mathrm{[Os^{III}P(CO)]^{+} + C_3H_7OH \longrightarrow [Os^{III}P(CO)(OC_3H_7)] + H^{+}} \qquad (9)$$

$$\mathrm{2[Os^{III}P(CO)(OC_3H_7)] \rightleftharpoons [Os^{II}P(CO)] + [Os^{IV}P(OC_3H_7)_2] + CO} \qquad (10)$$

Alternatively, the intermediate osmium(III) porphyrins might be oxidised by some radiation product. There are several reports[1–4,7,10,30] of $\mathrm{Os^{II}}$ porphyrins being oxidised to $\mathrm{Os^{IV}}$ and $\mathrm{Os^{VI}}$ porphyrins by oxidants that can also transfer oxygen atoms, *e.g.* organic peroxides or iodosylbenzene. The complex radiation chemistry involved with the present multicomponent solvent[32] system could generate organic peroxides that react in a similar fashion.



Scheme. Radiolysis in (*i*) aerated CH_2Cl_2 solution, (*ii*) aerated propan-2-ol–CCl_4–H_2O–KOH, (*iii*) deaerated propan-2-ol–H_2O–KOH, (*iv*) aerated propan-2-ol–CCl_4; photolysis in (*v*) aerated CH_2Cl_2 solution, (*vi*) aerated benzene solution, (*vii*) aerated propan-2-ol–$CHCl_3$ solution; (*viii*) *p*-cumenyl or t-butyl hydroperoxide in CH_2Cl_2 solution; (*ix*) cumenyl hydroperoxide in propan-2-ol–CH_2Cl_2 solution; (*x*) $SnCl_2$ in CH_2Cl_2 solution; (*xi*) $SnCl_2$ in propan-2-ol solution; (*xii*) triphenylphosphine in alcohol solution

Table. Absorption maxima (nm) and molar absorption coefficients (10^{-3} ε/dm^3 mol^{-1} cm^{-1}) of the various complexes

		λ (ε)	
Complex	Solvent	P = oep	P = tpp
$[Os^{II}P(CO)]$	*a*	389 (415), 508 (16), 538 (31)	406 (280), 518 (17)
$[Os^{II}P(CO)(C_3H_7OH)]$	*b*	389 (457), 508 (17), 538 (32)	405 (308), 516 (16)
$[Os^{III}P(CO)Cl]$	*a*	391 (206), 505 (17), 537 (20)	404 (150), 517 (13)
$[Os^{III}P(CO)Br]$	*a*	389 (188), 504 (16), 538 (22)	411 (158), 522 (13)
$[Os^{IV}P(Cl)_2]$	*a*	377 (110), 500 (12), 540 (11)	396 (114), 480 (16), 590 (7)
$[Os^{IV}P(OC_3H_7)_2]$	*b*	369 (125), 496 (12), 530 (10)	403 (89), 498 (11)
$[Os^{IV}P(C_3H_7OH)_2]^{2+}$	*b*	376 (182), 481 (15)	388 (105), 506 (10), 570 (5)
$[Os^{VI}P(O)_2]$	*a*	377 (123), 588 (10)	337 (31), 394 (119), 583 (10)

[a] Recorded in CH_2Cl_2. [b] Recorded in propan-2-ol.

It is also pertinent to note that recent work[35] has shown that oxidation of zinc porphyrins by CCl_3O_2 radicals occurred *via* an inner-sphere electron-transfer mechanism. This reaction involved formation of a complex in which the peroxyl radical was bound to the central zinc cation and it seems probable that a similar mechanism holds for the oxidation of Os^{II} porphyrins. The high affinity that Os ions have for oxygen atoms could help stabilise any such complex and facilitate a second electron-transfer step within the complex.

The radiolytic products were reduced quantitatively to the starting materials when the solutions were bubbled with N_2 (to remove O_2 and CCl_4) and then irradiated within the Gammacell. Radiolysis of aqueous alcohol solutions in the absence of O_2 is known to generate the strongly reducing radical $(CH_3)_2COH$, or its basic form $(CH_3)_2CO^-$, which reduce porphyrins very rapidly.[36,37]

Chemical Transformations.—The various reactions involved in the redox chemistry of osmium porphyrins in CH_2Cl_2 and alcohol solutions are summarised in the Scheme. Careful addition of Br_2 to solutions of the Os^{II} porphyrins in CH_2Cl_2 resulted in oxidation to the corresponding Os^{III} porphyrins, equation (11). Absorption spectral details recorded for these

$$2[Os^{II}P(CO)] + Br_2 \longrightarrow 2\,[Os^{III}P(CO)Br] \quad (11)$$

products are given in the Table; they are similar to those obtained for the chloride complexes as formed by gamma radiolysis. Quantitative reduction to the original compound occurs upon addition of $SnCl_2$ and the retention of the CO ligand was confirmed by i.r. spectroscopy. Addition of pyridine (py) to the Os^{III} porphyrins gave the corresponding pyridine adducts.

Clean oxidation with Br_2 was not observed in propan-2-ol solution or for the $Os^{II}P$ pyridine adducts. After oxidation with the minimum quantity of Br_2 in CH_2Cl_2 solution, the solvent was evaporated and the residue dissolved in propan-2-ol. The product was found to be predominantly the $[Os^{II}P(CO)]$ complex; typical yields being 90 and 65% respectively for the oep and tpp complexes. There was no indication of $[Os^{IV}P(OR)_2]$ at the end of this reaction so that, although $[Os^{III}P(CO)(OR)]$ is clearly unstable in alcohol solvents, disproportionation seems not to occur under such conditions. Rather, it appears that propan-2-ol reduces the $Os^{III}P$ without displacing the CO ligand.

In agreement with earlier studies, stirring a solution of the Os^{II} porphyrins in CH_2Cl_2–CH_3OH with t-butyl hydroperoxide or iodosylbenzene resulted in quantitative formation of the Os^{VI} dioxo porphyrins,[2,7] equations (12) and (13). Absorption

$$[Os^{II}P(CO)] + 2Bu^tOOH \longrightarrow [Os^{VI}P(O)_2] + CO + 2Bu^tOH \quad (12)$$

$$[Os^{II}P(CO)] + 2PhIO \longrightarrow [Os^{VI}P(O)_2] + 2PhI + CO \quad (13)$$

spectral details are presented in the Table and the presence of the Os–O bonds was confirmed by i.r. spectroscopy. Upon treatment with excess triphenylphosphine[2] or $SnCl_2$[7] in the presence of an alcohol (ROH), these Os^{VI} porphyrins were reduced to $[Os^{IV}P(OR)_2]$.

In CH_2Cl_2 solution, Os^{II} porphyrins are oxidised to the corresponding Os^{VI} dioxo porphyrins by *p*-cumenyl hydroperoxide. However, in propan-2-ol solution, this hydroperoxide oxidised the Os^{II} porphyrins only to the Os^{IV} state; absorption spectra recorded at the end of the reactions are presented in Figures 1(*b*) and 2(*b*). These were essentially identical to those recorded after gamma radiolysis of the corresponding $[Os^{II}P(CO)]$ complexes in alkaline propan-2-ol containing CCl_4. The absorption spectral details are provided in the Table and are similar to those quoted for the $[Os^{IV}P(OC_3H_7)_2]$ complexes prepared by reduction of $[Os^{VI}P(O)_2]$. Thus, under these conditions, reaction appears to stop at the stable Os^{IV} porphyrins.

Addition of acid to the above products in propan-2-ol solution led to immediate changes in the absorption spectra, as shown by Figures 1(*b*) and 2(*b*). These changes were reversible, the original spectra being recovered upon addition of base. The changes, therefore, are ascribed to protonation of the axially-bound ligands, equation (14), in parallel with earlier studies

$$[Os^{IV}P(OC_3H_7)_2] + 2H^+ \rightleftharpoons [Os^{IV}P(C_3H_7OH)_2]^{2+} \quad (14)$$

carried out with iron(II) porphyrins.[38] The protonated species were formed also by gamma radiolysis of the corresponding $[Os^{II}P(CO)]$ complexes in neutral propan-2-ol–CCl_4 where the acid arises from the primary radiolytic reactions.[38] These various Os^{IV} porphyrins are stable with respect to further reduction by $SnCl_2$.

Photolysis.—In fluid solution at room temperature, $[Os^{II}(tpp)(CO)]$ exhibits weak phosphorescence centred at 650 nm. In outgassed CH_2Cl_2 solution, the phosphorescence quantum yield was found to be 0.005 whilst single photon counting studies showed the emission lifetime to be 12.4 ns. From laser flash photolysis studies performed at room temperature, the triplet excited state lifetime was found to be 14 ± 3 ns, in good agreement with the emission studies. The emission yield and lifetime were essentially unaffected by the presence of O_2 or pyridine. Under similar conditions, neither $[Os^{III}(tpp)(CO)Br]$ nor $[Os^{IV}(tpp)(OC_3H_7)_2]$ showed any detectable emission that could be supported with an excitation spectrum. In contrast, $[Os^{VI}(tpp)(O)_2]$ showed quite intense phosphorescence centred at 745 nm for which the triplet state lifetime was shown to be 9.2 ns.

Photolysis ($\lambda > 350$ nm) of $[Os^{II}(tpp)(CO)(py)]$ in CH_2Cl_2 containing 5% pyridine resulted in quantitative formation of the corresponding bis(pyridine)Os^{II} porphyrin, equation (15). This

$$[Os^{II}(tpp)(CO)(py)]^* + py \longrightarrow [Os^{II}(tpp)(py)_2] + CO \quad (15)$$

complex shows absorption maxima at 405, 490, and 560 nm with prominent shoulders at *ca.* 480 and 515 nm and has been well characterised by Collman *et al.*[20] The overall photoreaction was very inefficient, requiring long irradiation periods, and for excitation into the Soret band the quantum yield was only *ca.* 10^{-6}. The course of reaction was independent of excitation wavelength and the rate of reaction did not increase at higher concentrations of pyridine. Presumably, reaction occurs from the first excited triplet state and, in this case, the very low yield of product is consistent with the finding that pyridine hardly quenches the observed phosphorescence. These findings suggest that the dominant pathway for deactivation of the excited triplet state involves non-radiative intersystem-crossing to the ground state, phosphorescence and decarbonylation being minor deactivation routes. The corresponding oep complex reacted in an identical fashion.

Photolysis of $[Os^{II}(tpp)(CO)]$ and $[Os^{II}(oep)(CO)]$ in chlorinated hydrocarbon solvents gave air-stable products whose absorption spectra resembled those assigned to Os^{III} and Os^{IV} porphyrins. Clear isosbestic points were preserved during the early part of photolysis and absorption spectra indicated that the product was an Os^{III} porphyrin. Upon further photolysis, the isosbestic points were lost and new products accumulated. These products, which were not reduced by triethylamine, were assigned to $[Os^{IV}P(Cl)_2]$ on the basis of their absorption spectra.

The quantum yields for formation of the $Os^{III}P$ products were found to depend upon the irradiation wavelength and the solvent. No reaction was observed for excitation into the porphyrin *Q*-bands but photo-oxidation proceeded, albeit inefficiently, upon excitation into the Soret bands. Reaction was even more efficient for excitation with u.v. light and for irradiation at 313 nm quantum yields for formation of the $Os^{III}P$ products were determined to be 0.052 and 0.044 respectively for the oep and tpp complexes in CH_2Cl_2 solution. These quantum yields were unaffected by the presence of O_2 but they were increased by a factor of about eight upon replacing CH_2Cl_2 with CCl_4.

Quite similar behaviour was observed for photo-oxidation of $[Os^{III}(tpp)(CO)Br]$ and $[Os^{III}(oep)(CO)Br]$. These porphyrins, which are non-luminescent, were readily converted into Os^{IV} porphyrins upon irradiation with u.v. light in CH_2Cl_2 solution. Again, the observed quantum yields increased with decreasing wavelength of excitation; they were much higher in CCl_4 than in CH_2Cl_2 and remained unaffected by the presence of O_2. The corresponding pyridine adducts $[Os^{III}P(CO)(py)]^+$, which do exhibit room temperature phosphorescence, do not undergo photo-oxidation upon irradiation with u.v. or visible light.

Overall, the photo-oxidation of $Os^{II}P$ in halogenated hydrocarbon solvents results in decarbonylation and formation of stable $Os^{IV}P$ products. The observed solvent and wavelength dependencies suggest that the reaction proceeds *via* a charge-transfer-to-solvent mechanism, although it is probable that a minor reaction pathway involves photoejection of the CO ligand and oxidative attack by the solvent, equations (16) and (17). The solvent radical CCl_3 can react with atmospheric O_2 to

$$[Os^{II}P(CO)]^* + CCl_4 \longrightarrow [Os^{III}P(CO)Cl] + CCl_3 \quad (16)$$

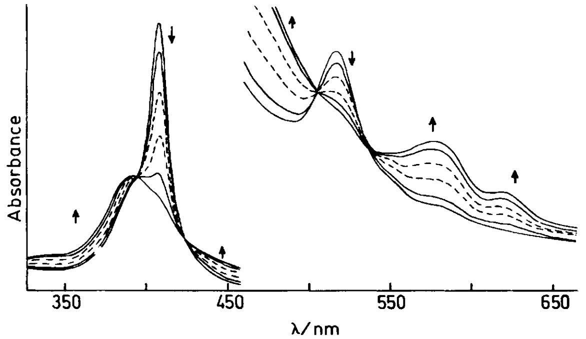


Figure 3. Absorption spectral profile showing the conversion of [Os^{II}(tpp)(CO)] into [Os^{VI}(tpp)$(O)_2$] upon photolysis in N_2-purged benzene solution containing small amounts of O_2

$$[Os^{III}P(CO)Cl]^* + CCl_4 \longrightarrow [Os^{IV}P(Cl)_2] + CO + CCl_3 \quad (17)$$

produce an oxidising radical, oxidise an adjacent $Os^{II}P$ or $Os^{III}P$ molecule or dimerise.

In outgassed benzene solution [Os^{II}(tpp)(CO)] appears to be photochemically unreactive. When the photolysis was carried out under a constant stream of argon gas, however, some decarbonylation occurred although the quantum yield was very low. Photolysis in benzene solution containing small amounts of O_2 resulted in formation of a product having absorption maxima at 392, 580, and 620 nm. Clear isosbestic points were observed (Figure 3), the final absorption spectrum being identical to that of [Os^{VI}(tpp)$(O)_2$] recorded in benzene solution, equation (18). The quantum yield for formation of

$$[Os^{II}(tpp)(CO)]^* + O_2 \longrightarrow [Os^{VI}(tpp)(O)_2] + CO \quad (18)$$

$Os^{VI}P$ was $< 10^{-5}$ and appeared to be independent of irradiation wavelength. However, neither the mechanism nor the stoicheiometry of this reaction was clarified and the presence of even small amounts of ethanol in the solution resulted in formation of [Os^{IV}(tpp)$(OC_2H_5)_2$].

Activation of Alkenes.—Previous work[30] has shown that [$Os^{VI}P(O)_2$] does not transfer oxygen atoms to alkenes such as cyclohexene. We have confirmed this result and, additionally, found that [Os^{VI}(tpp)$(O)_2$] does not oxidise alcohols at room temperature. However, stirring [Os^{II}(tpp)(CO)] in cyclohexene containing iodosylbenzene has resulted in functionalisation of the alkene suggesting that one of the lower oxidation states catalyses this reaction.[30] The apparent inertness of [Os^{VI}(tpp)-$(O)_2$] contrasts with the reactivity of other high-valent metalloporphyrins,[21–29] such as Mn, Fe and Ru, and prevents the employment of this compound as an oxidation catalyst.

Visible light irradiation of [Os^{VI}(tpp)$(O)_2$] in benzene solution causes slow decomposition of the chromophore. In benzene–methanol (1:1) solution, the photoreaction occurs more rapidly and forms [Os^{IV}(tpp)$(OCH_3)_2$] as a major product. The fate of the oxo ligands could not be determined but it appears not to involve formation of molecular O_2 as a permanent product. Repeating the photolysis in the presence of cyclohexene (1 mol dm^{-3}) resulted in formation of [Os^{IV}(tpp)-$(OCH_3)_2$] together with a mixture of cyclohexane oxide (45%), cyclohex-2-en-1-one (35%), and cyclohex-2-en-1-ol (20%). No such products were observed in the absence of light. The mechanism of the process has not been elucidated, as yet, but the poor selectivity for alkene oxidation together with the slow rate of reaction limit the utility of the compound as an oxidant for such systems.

Conclusions

Two noteworthy features have emerged from this study. First, Os^{IV} porphyrins are stabilised by complexation with alcohol ligands to such an extent that the complexes are essentially inert, even under photochemical conditions. They are the final products in most redox systems. Secondly, photolysis of [$Os^{II}P(CO)$] in non-co-ordinating solvents, such as benzene, containing trace amounts of O_2 results in inefficient formation of [$Os^{VI}P(O)_2$]. Unlike other oxo-porphyrins,[21–29] this compound does not transfer O atoms to alkenes at room temperature in the dark. Visible light irradiation activates the molecule sufficiently for it to oxidise cyclohexene, although the selectivity of this process is too low for the system to have any useful synthetic applications.

Acknowledgements

We thank the S.E.R.C. and the Office of Basic Energy Sciences of the U.S. Department of Energy for financial support. D. Y. S. thanks the Egyptian Education Bureau for the award of a studentship.

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Received 12*th November* 1987; *Paper* 7/2009