OXIDATIVE SUBSTITUTION REACTION OF THE OSMOCHROME Os(OEP)[P(OMe)$_3$]$_2$ IN CHLORINATED SOLVENTS

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Summary

Steady state photolysis of Os(OEP)[P(OMe)$_3$]$_2$, where OEP is octa-ethylporphine, in the chlorinated solvents CH$_2$Cl$_2$, CHCl$_3$ and CCl$_4$ at 365 and 405 nm and at 22 °C results in the formation of an osmium(IV) porphyrin identified as Os(OEP)Cl$_2$. The reaction is described as an oxidative substitution reaction. The rate of formation of the photolysis product increases as the solvent varies in the order CH$_2$Cl$_2$ < CHCl$_3$ < CCl$_4$ (in the ratio 1:8:120). The quantum yield of product formation is 0.004 and 1.4 in CH$_2$Cl$_2$ and CCl$_4$ respectively. A possible mechanism involving radicals is suggested and is discussed in terms of the experimental observations.

1. Introduction

The metalloporphyrin complexes M(OEP)LL′ (M ≡ Fe, Ru, Os; OEP ≡ octaethylporphine; L and L′ ≡ various monodentate ligands) form an important and interesting class of compounds owing to the large variations exhibited by their electronic spectra as a function of L, L′ and M. The chemical and spectroscopic properties of these metalloporphyrins have recently been the focus of much activity; some of the work has been reviewed by Buchler and coworkers [1 - 3] and by Gouterman [4] (see also, for example, ref. 5). The osmochromes Os(OEP)LL′ are of particular interest amongst these metalloporphyrins because of their isoelectronic and isosteric resemblance to the biologically important iron porphyrins. Details of the optical absorption and luminescence spectra in organic solvents have been rationalized by Antipas *et al.* [6, 7] on the basis of "iterative extended Huckel" (IEH) calculations. The wide variations in electronic properties have been interpreted [6] in terms of a reciprocation between equatorial back-

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bonding (osmium $d\pi$ to OEP ring $e_g(\pi^*)$ orbitals) and axial backbonding (osmium $d\pi$ to L π^* orbitals). The much stronger backbonding capability of osmium(II) $d\pi$ orbitals over those of iron(II) or ruthenium(II) has also led to the characterization of some unusual osmochromes [2].

Our own interest in these osmochromes rests in elucidating the ultrafast picosecond relaxation phenomena of the excited singlet and triplet states [8] and in testing the recent IEH calculations using the technique of resonance Raman spectroscopy [9]. During the preparation of some of the osmochromes required in these studies we discovered that the trimethyl phosphite compound $Os(OEP)[P(OMe)_3]_2$, the electronic spectrum of which was determined in CH_2Cl_2 and which also was prepared in this solvent, is light sensitive in CH_2Cl_2 under spectrophotometric conditions. This compound is not unique in this regard. Gleria $et\ al.$ [10] have reported that $Ru(bpy)_3{}^{2+}$ (bpy $\equiv$ 2,2'-bipyridine) in chlorinated solvents photolyzes at λ = 436 nm and room temperature to yield $Ru(bpy)_2Cl_2$. More recently, Tyler $et\ al.$ [11] have also reported that photolysis of $Os_3(CO)_{12}$ in chlorinated solvents (CCl_4, $CHCl_3$ and CH_2Cl_2) produces $Os(CO)_4Cl_2$.

We report here on our investigations of the photolysis of the osmium(II) porphyrin compound $Os(OEP)[P(OMe)_3]_2$ in the chlorinated solvents CH_2Cl_2, $CHCl_3$ and CCl_4.

2. Experimental

The chemicals osmium(IV) tetraoxide, OEP, trimethyl phosphite ($P(OMe)_3$), diethyleneglycol monomethyl ether, pyridine (py), hexane, CH_2Cl_2, $CHCl_3$ and CCl_4 were reagent grade and were used as received without further purification. $Os(OEP)[P(OMe)_3]_2$ was prepared from $Os(OEP)CO \cdot py$ and $P(OMe)_3$ in CH_2Cl_2 according to the method of Buchler and Rohbock [12]. UV–visible spectra were recorded on an Aminco–Bowman DW-2 spectrophotometer.

Photolyses were carried out as follows. To 6 ml aliquots of $Os(OEP)$-$[P(OMe)_3]_2$ in hexane (2×10^{-5} M) was added 4 ml of the chlorinated solvent (CH_2Cl_2, $CHCl_3$ or CCl_4) and the solution was subsequently photolyzed at 365 or 405 nm at 22 °C using a 150 W xenon lamp. The exciting radiation was isolated with a 0.25 m Bausch and Lomb monochromator (20 nm bandpass). The samples were prepared in dim red light and a portion of the aliquots was kept in the dark under conditions identical with those employed in the photolyses to assess the thermal component of the reaction.

Quantum yields were determined using spectrophotometric techniques with λ = 365 nm radiation for greater than 99% of radiation absorbed and for less than 10% photolysis; $Cr(bpy)_3{}^{3+}$ was used as a secondary actinometer [13] (Φ = 0.18, aqueous solution, pH 9.3, 22 °C). In one of the photolysis runs in hexane–CCl_4, $P(OMe)_3$ was added to the photolysis solution to assess its effect on the reaction.

3. Results and discussion

Solutions of Os(OEP)[P(OMe)$_3$]$_2$ in neat CH$_2$Cl$_2$, CHCl$_3$ or CCl$_4$ are rapidly photolyzed under normal laboratory fluorescent lighting but hexane solutions of the compound are thermally and photochemically inert. Figure 1 illustrates the spectral changes that occur during irradiation at 405 nm of a 1 × 10^{-5} M solution of Os(OEP)[P(OMe)$_3$]$_2$ in hexane–CH$_2$Cl$_2$. Band maxima at 405 and 520 nm characteristic of Os(OEP)[P(OMe)$_3$]$_2$ decrease during photolysis while the 500 nm band increases in intensity; correspondingly, bands at 396, 570 and approximately 605 nm appear and isosbestic points are observed at 345, 352, 399, 416, 502 and 541 nm. Very similar results were also obtained in hexane–CHCl$_3$ and hexane–CCl$_4$ with isosbestic points (in the 350 - 450 nm range) at 354, 399 and 416 nm and at 351, 399 and 414 nm respectively.

In Fig. 2 we qualitatively compare the spectrum of the starting compound Os(OEP)[P(OMe)$_3$]$_2$ in hexane solution (λ = 405 nm, logε = 5.0; λ = 500 nm, logε = 4.0; λ = 520 nm, logε = 4.1) with that of the photolysis product. Several features are noteworthy. The Soret band in the spectrum of Os(OEP)[P(OMe)$_3$]$_2$ is relatively sharp; however, the α(Q) and β(Q) bands are broad and have underlying tails toward the red, suggesting possible low-lying forbidden transitions [7]. This spectrum has been classified by Antipas et al. [7] as *hypso/hyper*. (Both Gouterman [4] and Buchler [1] have developed a taxonomy for porphyrin spectra: (a) *normal* absorption spectra have N(ππ*), B(ππ*) and Q(ππ*) bands at λ > 320 nm; (b) *hypso* spectra are similar to *normal* spectra but the Q(ππ*) bands are blue shifted to below 570 nm; (c) *hyper* spectra reveal other intense bands at λ > 320 nm in addition to the N(ππ*), B(ππ*) and Q(ππ*) bands.) In contrast, the spectrum of the photolysis product (Fig. 2(a)) shows (1) a blue-shifted broad Soret band at 396 nm, (2) anomalous and broad α and β bands (at 500 and 526 nm; the respective intensities are inverted with respect to the *normal* absorption) and (3) two additional low intensity red bands at approximately 570 and 605 nm.
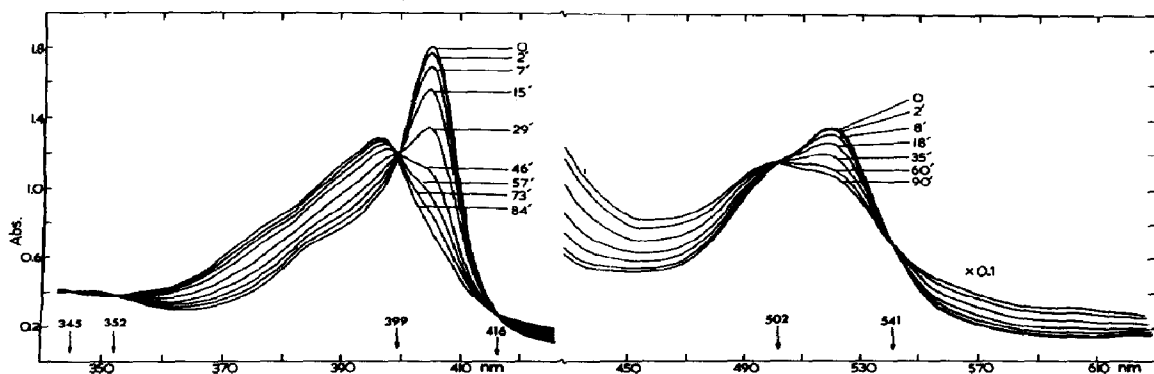

Fig. 1. Spectral changes during irradiation at 405 nm and 22 °C of a hexane–CH$_2$Cl$_2$ solution of Os(OEP)[P(OMe)$_3$]$_2$.
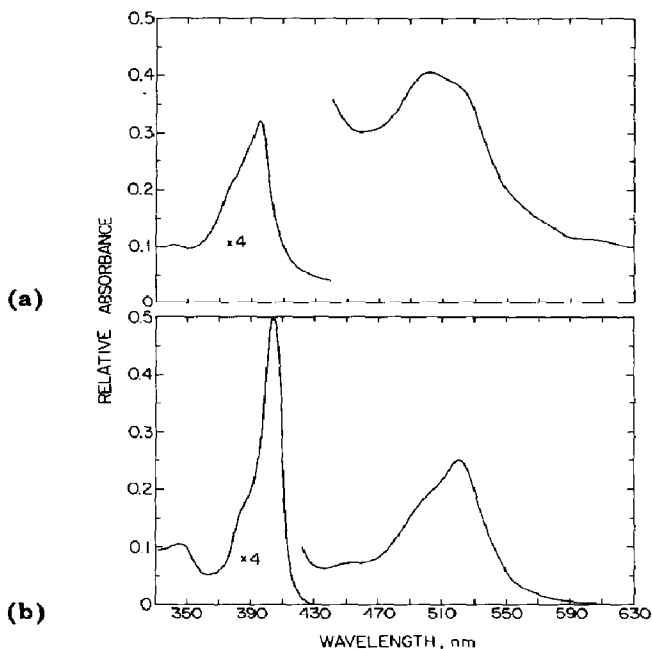
Fig. 2. (a) Absorption spectrum of the final photolysis product in hexane–CH_2Cl_2 solution; (b) spectrum of the starting compound $Os(OEP)[P(OMe)_3]_2$ in hexane solution.

The spectrum is clearly of the *hyper* type and is very unlike other known osmium(II) porphyrin spectra [7]. Rather, it is reminiscent of the spectrum of $Os(IV)(OEP)(OMe)_2$ which has bands at 370, 497, 530 and 610 nm [7]. Therefore we suggest that the final photolysis product also contains osmium(IV). In view of the nature of the reactants, this product is identified as $Os(OEP)Cl_2$.

On the basis of this evidence the photolysis reaction is described as

$$Os(OEP)[P(OMe)_3]_2 \xrightarrow[h\nu,\ CH_2Cl_2]{\Phi_{rx}} Os(OEP)Cl_2 + 2P(OMe)_3 \qquad (1)$$
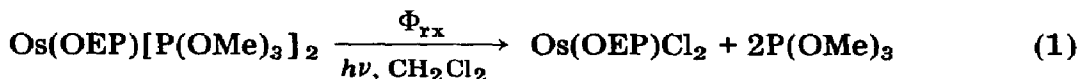
in which the starting osmochrome oxidatively reacts with the chlorinated solvent. Analogous observations were made in $CHCl_3$ and CCl_4.

Figure 3, in which we show the ratio A_t/A_0 of the absorbance *versus* the irradiation time, clearly demonstrates that the rate of reaction (1) increases as the solvent is changed in the order $CH_2Cl_2 < CHCl_3 < CCl_4$ (in the ratio 1:8:120). The figure also shows that the addition of $P(OMe)_3$ to the starting hexane–CCl_4 solution inhibits (by a factor of nearly 5) the rate of reaction with CCl_4. (To verify that this inhibition is definitely a result of the presence of $P(OMe)_3$ and not of the dilution of the aliquot, we carried out two experiments. In the first experiment we irradiated a solution made up of 6 ml of a solution of $Os(OEP)[P(OMe)_3]_2$ in hexane, 4 ml of CCl_4 and 2 ml of $P(OMe)_3$. In the second experiment we irradiated a solution in which the 2 ml of $P(OMe)_3$ were substituted with 2 ml of hexane. The results of
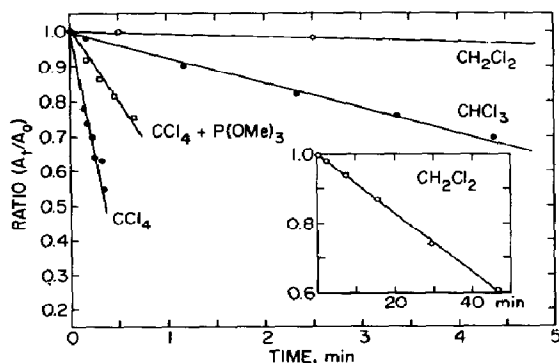
Fig. 3. Plot of absorbance ratio vs. irradiation time of hexane–CH_2Cl_2, hexane–$CHCl_3$, hexane–CCl_4–$P(OMe)_3$ and hexane–CCl_4 solutions of $Os(OEP)[P(OMe)_3]_2$. The slopes indicate relative rates for the photolysis reaction (1) (see text).

the first experiment were identical with those illustrated in Fig. 3 whilst the results of the second experiment were identical with the results obtained without the dilution (see also Fig. 3) for which the volume of solution was approximately 10 ml.) The quantum yields Φ_{rx} for product formation are 0.004 (CH_2Cl_2) and 1.4 (CCl_4) with an error of about ±(10 - 15)%. To the extent that $\Phi_{rx} > 1$ in CCl_4 solutions, the involvement of radical species is indicated in the formation of $Os(OEP)Cl_2$.
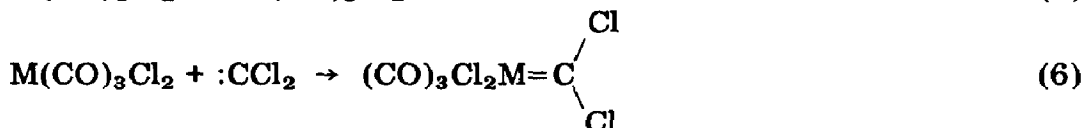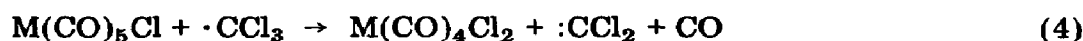
The data presently available afford some preliminary rationalizations of a possible mechanism. Certain points may be noted.

(1) Inasmuch as $P(OMe)_3$ inhibits the formation of $Os(OEP)Cl_2$, it may compete with chlorine atoms for the coordination site(s).

(2) The exciting radiation (365 or 405 nm) cannot induce the formation of radicals from CCl_4.

(3) According to IEH calculations there are no low-lying excited ligand field states in $Os(OEP)[P(OMe)_3]_2$ [7] that might promote dissociation of the axial $P(OMe)_3$ ligands; the lowest energy state is an excited triplet osmium $d\pi$ to porphyrin ring $e_g(\pi^*)$ charge transfer state. Interestingly, the complex $Ru(bpy)_3{}^{2+}$ also has a low-lying excited triplet ruthenium → bpy charge transfer state and also forms a chlorine-containing compound, $Ru(bpy)_2Cl_2$ [10]. According to Durham et al. [14] the source of chlorine atoms in the formation of this compound may be the counter-ion in [$Ru(bpy)_3$] Cl_2 rather than the solvent CH_2Cl_2.

In a recent work on the possible existence of metallodichlorocarbenes
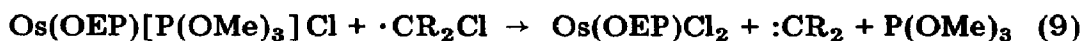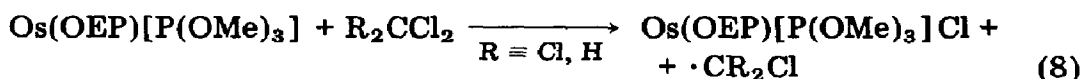
$$\left[M{=}C \diagup_{\diagdown Cl}^{Cl} \right]$$
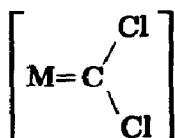
Garnier et al. [15] have demonstrated that where M ≡ W these can be formed by photochemical chlorination of a metal carbonyl compound by CCl_4 according to the mechanism

$$M(CO)_6 \; \xrightleftharpoons[]{h\nu} \; M(CO)_5 + CO \tag{2}$$

$$M(CO)_5 + CCl_4 \; \rightarrow \; M(CO)_5Cl + \cdot CCl_3 \tag{3}$$

$$M(CO)_5Cl + \cdot CCl_3 \; \rightarrow \; M(CO)_4Cl_2 + :CCl_2 + CO \tag{4}$$

$$M(CO)_4Cl_2 \; \rightleftharpoons \; M(CO)_3Cl_2 + CO \tag{5}$$

$$M(CO)_3Cl_2 + :CCl_2 \; \rightarrow \; (CO)_3Cl_2M{=}C \underset{\textstyle Cl}{\overset{\textstyle Cl}{\big\langle}} \tag{6}$$

Analogously, the compound $W[P(OMe)_3]_6$ appears to have an extraordinary photochemical activity on exposure to Pyrex-filtered radiation from a mercury lamp; it decomposes to give substantial quantities of free $P(OMe)_3$ [16].

By analogy with this mechanism and on the basis of our observations the photolysis of $Os(OEP)[P(OMe)_3]_2$ in chlorinated solvents to form $Os(OEP)Cl_2$ probably occurs by the following pathway:

$$Os(OEP)[P(OMe)_3]_2 \; \xrightleftharpoons[]{h\nu,\, kT} \; Os(OEP)[P(OMe)_3] + P(OMe)_3 \tag{7}$$

$$Os(OEP)[P(OMe)_3] + R_2CCl_2 \; \xrightarrow[R \equiv Cl,\, H]{} \; Os(OEP)[P(OMe)_3]Cl + \cdot CR_2Cl \tag{8}$$

$$Os(OEP)[P(OMe)_3]Cl + \cdot CR_2Cl \; \rightarrow \; Os(OEP)Cl_2 + :CR_2 + P(OMe)_3 \tag{9}$$

$$:CR_2 \; \rightarrow \; \tfrac{1}{2} R_2C{=}CR_2 \tag{10}$$

Preliminary supportive evidence for this pathway is based on the results of experiments carried out in the presence of free $P(OMe)_3$. For example, the thermal reaction with CCl_4 is suppressed by the addition of $P(OMe)_3$; no spectral changes were observed after 10 min although considerable changes were noted after about 1 min of irradiation. The photolysis reaction is also inhibited by free $P(OMe)_3$ (see Fig. 3). The order of reactivity of $Os(OEP)$-$[P(OMe)_3]_2$ in the three chlorinated solvents employed, $CH_2Cl_2 < CHCl_3 < CCl_4$, probably reflects the order of reactivity of reaction (8) and thus must reflect the reactivity of the R_2CCl_2 ($R \equiv Cl$, H) species in solution. In future studies [17] we will attempt to identify the intermediates and products of reactions (7) - (10) and to quantify the various rate processes.

Acknowledgments

References

1 J. W. Buchler, in K. M. Smith (ed.), *Porphyrins and Metalloporphyrins*, Elsevier, Amsterdam, 1975, Chap. 5, p. 157.
2 J. W. Buchler, W. Kobish and P. D. Smith, *Struct. Bonding (Berlin)*, *34* (1978) 79.
3 J. W. Buchler, in D. Dolphin (ed.), *The Porphyrins*, Vol. I, Part A, Academic Press, New York, 1978, Chap. 10.
4 M. Gouterman, in D. Dolphin (ed.), *The Porphyrins*, Vol. III, Part A, Academic Press, New York, 1978, Chap. 1.
5 D. Dolphin (ed.), *The Porphyrins*, Vols. I - VII, Academic Press, New York, 1978.
6 A. Antipas, J. W. Buchler, M. Gouterman and P. D. Smith, *J. Am. Chem. Soc.*, *102* (1980) 198.
7 A. Antipas, J. W. Buchler, M. Gouterman and P. D. Smith, *J. Am. Chem. Soc.*, *100* (1978) 3015.
8 N. Serpone, T. L. Netzel and M. Gouterman, submitted to *J. Am. Chem. Soc.*
9 R. Felton, N. Serpone and T. L. Netzel, work in progress.
10 M. Gleria, F. Minto, G. Beggiato and P. Bortolus, *J. Chem. Soc., Chem. Commun.*, (1978) 285.
11 D. R. Tyler, M. Altobelli and H. B. Gray, *J. Am. Chem. Soc.*, *102* (1980) 3022.
12 J. W. Buchler and K. Rohbock, *J. Organomet. Chem.*, *65* (1974) 223.
13 M. A. Jamieson, N. Serpone and M. Z. Hoffman, *Inorg. Chem.*, *18* (1979) 214.
14 B. Durham, J. L. Walsh, C. L. Carter and T. J. Meyer, *Inorg. Chem.*, *19* (1980) 860.
15 F. Garnier, P. Kransz and H. Rudler, *J. Organomet. Chem.*, *186* (1980) 77.
16 H. W. Choi, R. M. Gavin and E. L. Muetterties, *J. Chem. Soc., Chem. Commun.*, (1979) 1085.
17 N. Serpone, R. Greenhorn and L. Hutchings, work in progress.