

## KINETIC STUDIES OF THE OXIDATIVE PHOTOSUBSTITUTION REACTION IN THE CHARGE TRANSFER PHOTOCHEMISTRY OF $\text{Os}(\text{OEP})[\text{P}(\text{OMe})_3]_2$ (OEP $\equiv$ OCTAETHYLPORPHINE) IN HEXANE-HALOCARBON MIXTURES

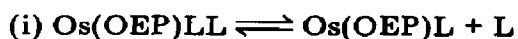
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### Summary

The osmochrome  $\text{Os}^{\text{II}}(\text{OEP})[\text{P}(\text{OMe})_3]_2$ , where OEP is octaethylporphine, undergoes an oxidative photosubstitution reaction in hexane in the presence of chlorinated hydrocarbons ( $\text{CH}_2\text{Cl}_2$ ,  $\text{CHCl}_3$ ,  $\text{CCl}_4$ ,  $\text{CHCl}_2\text{CH}_3$  and  $\text{CH}_2\text{ClCH}_2\text{Cl}$ ) under steady state photolysis. The product has been identified as  $\text{Os}^{\text{IV}}(\text{OEP})\text{Cl}_2$ . Both initial rates of reaction and quantum yields are, within experimental error, independent of whether the hexane-chlorinated hydrocarbon solutions are argon purged, air equilibrated,  $\text{N}_2\text{O}$  purged or oxygen purged. The quantum yields increase with increase in  $\text{CR}_2\text{Cl}_2$  ( $\text{R} \equiv \text{H}$  or  $\text{Cl}$ ) concentration; limiting quantum yields are  $0.0017 \pm 0.0001$  ( $\text{CH}_2\text{Cl}_2$ ),  $0.25 \pm 0.08$  ( $\text{CHCl}_3$ ) and  $0.93 \pm 0.10$  ( $\text{CCl}_4$ ). The reactivity of the chlorinated reactants is  $\text{CCl}_4$  (280)  $\gg$   $\text{CHCl}_3$  (35)  $>$   $\text{CH}_2\text{ClCH}_2\text{Cl}$  (1.4)  $\approx$   $\text{CHCl}_2\text{CH}_3$  (1.1)  $\approx$   $\text{CH}_2\text{Cl}_2$  (1.0) under the experimental conditions used; this order accords with expectations based on the C-Cl bond strengths. A mechanism is postulated in which the three essential steps are ( $\text{L} \equiv \text{P}(\text{OMe})_3$ )



and



The data are treated using both the conventional kinetic theory and the model of Noyes for the scavenging of photoproduced radical pairs in solution.

### 1. Introduction

Recent work [1, 2] from our laboratory on  $\text{Os}(\text{OEP})\text{LL}'$  (OEP is octaethylporphine and L and L' are CO, pyridine (py), O, NO and OMe) has

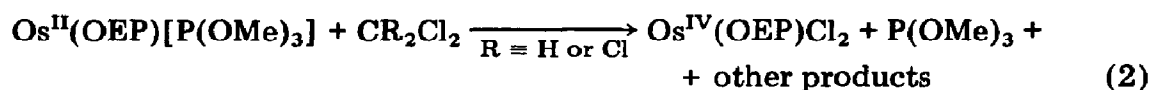
focused on relaxation phenomena of the  $d\pi, \pi^*$  and  $\pi, \pi^*$  excited states in these osmium(II) complexes. In all cases we found both subnanosecond relaxation of an initial excited state  $S_1$  and nanosecond relaxation of a second excited state  $T_1$ . An important result, emanating from those studies, is that the excited state spectra of the six  $Os(OEP)LL'$  osmochromes investigated supported earlier assignments of the nature of the lowest energy excited state in each complex and also lent support to the equatorial-axial back-bonding model described by Gouterman and coworkers [3, 4]. For the osmochromes,  $Os(OEP)(py)_2$ ,  $Os(OEP)[P(OMe)_3]_2$  and  $Os(OEP)CO \cdot py$ , the charge transfer  $d\pi, \pi^*$  states are lower in energy than the  $\pi, \pi^*$  states. By contrast, for the three porphyrin complexes,  $Os(OEP)(NO)(OMe)$ ,  $Os(OEP)(NO)_2$  and  $Os(OEP)O_2$ , the  $\pi, \pi^*$  states are lower in energy than the  $d\pi, \pi^*$  charge transfer states. The spectroscopic properties of these states and indeed their reactivity are understood by considering the highest occupied orbitals  $a_{2u}(\pi)$  and  $a_{1u}(\pi)$  and the lowest unoccupied  $e_g(\pi^*)$  orbitals of a free-base porphyrin and the d orbitals of a metal. Where the metal possesses an  $nd^6$  electronic configuration (e.g. iron(II), ruthenium(II) or osmium(II)), interactions of these d orbitals with the free-base porphyrin orbitals may become important [5 - 7]. Axial ligands L or L' can either enhance or inhibit these metal-porphyrin interactions.

For strong  $\sigma$  donor ligands, such as trimethylamine ( $NMe_3$ ), pyridine or trimethylphosphite ( $P(OMe)_3$ ), the filled  $d\pi$  orbitals in osmium(II) porphyrins lie above the  $a_{2u}(\pi)$  and  $a_{1u}(\pi)$  porphyrin orbitals [3]. A consequence of this is that the  $d\pi$  orbitals of osmium(II) can back bond with the empty higher energy  $e_g(\pi^*)$  porphyrin orbitals. Replacement of the  $\sigma$  donor ligands by good  $\pi$  acceptor ligands, such as CO, pyridine and nitrosonium ion ( $NO^+$ ), shifts the back bonding of the  $d\pi$  electrons from equatorial to axial [4]. This results in a shift of the filled  $d\pi$  metal orbitals and the empty  $e_g(\pi^*)$  porphyrin orbitals to lower energy. The orbital nature of the lowest excited states thus changes from  $d\pi, \pi^*$  to  $\pi, \pi^*$ . The reactivity of the lowest energy excited states is thus *expected* to depend on the orbital nature of these states.

The lifetime of the lowest energy excited state  $T_1$  of charge transfer  $d\pi, \pi^*$  character in  $Os(OEP)(py)_2$  in tetrahydrofuran (THF) is  $1 \pm 0.3$  ns; this was the shortest lifetime yet observed for a  $T_1$  state of an osmochrome species [2]. The lifetime of corresponding states of other osmium porphyrins ranged from 6 to 16 ns at 295 K. Such a short lifetime as found in the bispyridine complex made possible a direct search for photoproducts after the decay of the  $^3(d\pi, \pi^*)$  excited states. In fact, transient absorption was still significant even after 99% decay of the  $T_1$  state. We suggested [2] that this transient absorption arises from pyridine loss. This notion was supported from the change in absorbance spectra of  $Os(OEP)(py)_2$  in THF solutions containing 50 vol.% pyridine; transient absorption was suppressed in the 4 - 5 ns range. In the presence of 10 vol.% pyridine, transient absorption was intermediate between 0% and 50% pyridine in THF. No net photochemistry was observed on a seconds' time scale [2]. To the extent that the nature of

the lowest energy excited states in  $\text{Os}(\text{OEP})[\text{P}(\text{OMe})_3]_2$  is also  $d\pi, \pi^*$  in nature, light excitation should also induce loss of a  $\text{P}(\text{OMe})_3$  ligand in this complex. The 6 ns lifetime of the  $T_1(d\pi, \pi^*)$  state of this complex precluded [1] observation of any photoproduct since the time range accessible with the picosecond laser instrument was from 10 ps to 5 ns [1, 2].

During the preparation of some of the osmium(II) porphyrin complexes required in our picosecond relaxation studies [1], we noted that the  $\text{P}(\text{OMe})_3$  complex reacts photochemically in chlorinated solvents; addition of excess  $\text{P}(\text{OMe})_3$  inhibited the reaction in hexane-carbon tetrachloride ( $\text{CCl}_4$ ) mixtures [8]. In a preliminary report [8] of this photochemical reaction, we identified the final product as  $\text{Os}^{\text{IV}}(\text{OEP})\text{Cl}_2$  on the basis of its characteristic osmium(IV) spectrum. The first steps



of the probable reaction mechanism were described as light-activated  $\text{P}(\text{OMe})_3$  release followed by solvent ( $\text{CR}_2\text{Cl}_2$ ;  $\text{R} \equiv \text{H or Cl}$ ) attack on the five-coordinate osmium(II)-porphyrin complex.

In this paper, we report our recent findings on this oxidative light-induced photosubstitution reaction of  $\text{Os}^{\text{II}}(\text{OEP})[\text{P}(\text{OMe})_3]_2$  in hexane- $\text{CR}_2\text{Cl}_2$  solutions. In particular, we attempt to quantify the mechanistic details of the reaction. Use of radical scavengers and determination of quantum yields have proved useful in this regard. The pathway to the formation of  $\text{Os}(\text{OEP})\text{Cl}_2$  is more complicated than first envisaged [8]. The data are treated using both the conventional kinetic theory and the Noyes model [9] which was developed to treat the scavenging of photoproducted radical pairs in solution.

## 2. Experimental details

Osmium(VIII) oxide,  $\text{P}(\text{OMe})_3$ , pyridine, hexane, dichloromethane ( $\text{CH}_2\text{Cl}_2$ ), chloroform ( $\text{CHCl}_3$ ),  $\text{CCl}_4$ , 1,2-dichloroethane ( $\text{CH}_2\text{ClCH}_2\text{Cl}$ ) and octaethylporphine were all of reagent grade quality and were employed as received; 1,1-dichloroethane ( $\text{CHCl}_2\text{CH}_3$ ) was vacuum distilled once before use. Diethylene glycol monomethyl ether was vacuum distilled and stored over molecular sieves. The complex  $\text{Os}(\text{OEP})[\text{P}(\text{OMe})_3]_2$  was prepared from  $\text{Os}(\text{OEP})\text{CO}\cdot\text{py}$ ,  $\text{P}(\text{OMe})_3$  and pyridine in  $\text{CH}_2\text{Cl}_2$  according to the procedure of Buchler and Rohbock [10]. The purity of the products was checked by their absorption spectra, recorded on either an Aminco-Bowman DW-2 or a Perkin-Elmer 552 spectrophotometer.

Photolyses were carried out at 365 nm (unless otherwise noted) and 22 °C using a 1000 W Hg-Xe lamp. The exciting radiation was isolated with

a 0.25 m Bausch and Lomb monochromator (22 nm bandpass); a distilled water cell was used to remove the IR radiation. Photolysis samples were prepared in dim red light; 3 ml aliquots were taken from a stock solution of  $\text{Os}(\text{OEP})[\text{P}(\text{OMe})_3]_2$  in hexane to which was added 2 ml of the chlorinated hydrocarbon ( $\text{CH}_2\text{Cl}_2$ ,  $\text{CHCl}_3$ ,  $\text{CCl}_4$ ,  $\text{CHCl}_2\text{CH}_3$  or  $\text{CH}_2\text{ClCH}_2\text{Cl}$ ). The volume of sample irradiated was 3.00 ml. An identical sample was kept in the dark to assess the thermal component of the reaction. This was necessary only for the hexane- $\text{CCl}_4$  runs. Samples were argon purged for about 5 min or were degassed by three freeze-pump-thaw cycles. In experiments employing radical scavengers (oxygen or  $\text{N}_2\text{O}$ ), argon-purged solutions were also treated with either oxygen or with  $\text{N}_2\text{O}$  for about 5 min. The concentration of  $\text{Os}(\text{OEP})[\text{P}(\text{OMe})_3]_2$  was  $9.1 \times 10^{-5}$  M in the solvent mixture.

The initial rates of reaction and quantum yields were determined using spectrophotometric methods for more than 99% of radiation absorbed and for less than 10% photolysis;  $\text{Cr}(\text{bpy})_3^{3+}$  ( $\text{bpy} \equiv 2,2'$ -bipyridine) was used as a secondary actinometer [8, 11] ( $\Phi_s = 0.10$ ; aqueous air-equilibrated solutions; pH 9.3; Britton-Robinson buffer; 22 °C);  $\Phi_x = \Phi_s(R_x/R_s)$ , where  $\Phi_x$  and  $R_x$  are the quantum yield and initial rate of product  $\text{Os}(\text{OEP})\text{Cl}_2$  formation respectively and  $R_s$  is the initial rate of disappearance of  $\text{Cr}(\text{bpy})_3^{3+}$ . (In our earlier study [8] we reported that  $\Phi_x$  was 0.004 ( $\text{CH}_2\text{Cl}_2$ ) and 1.4 ( $\text{CCl}_4$ ). These values are in error as they were based on an incorrect value of  $\Phi_s$  of 0.18. A recent re-evaluation of  $\Phi_s$  [11] gives  $\Phi_x$  values of 0.002 ( $\text{CH}_2\text{Cl}_2$ ) and about 0.8 ( $\text{CCl}_4$ ) in accord with values in the present study.)

A Shimadzu gas chromatograph model GC-6AM was used to detect possible hydrocarbon products from the photosubstitution reaction. It was equipped with a 2.4 m column with an OV-17 stationary phase on a Chromasorb 750 support; detection was with a flame ionization detector.

### 3. Results

Figure 1 illustrates the spectral changes (350 - 450 nm range) that occur during irradiation at 405 nm of a  $1.6 \times 10^{-5}$  M solution of the  $\text{Os}(\text{OEP})[\text{P}(\text{OMe})_3]_2$  porphyrin complex in hexane- $\text{CHCl}_3$ . The Soret band at 405 nm, characteristic of  $\text{Os}(\text{OEP})[\text{P}(\text{OMe})_3]_2$ , decreases during photolysis while the shoulder at about 385 nm increases in intensity; correspondingly, a band at 395 nm and a shoulder at about 375 nm appear. Isosbestic points are observed at 354, 399 and 416 nm and are maintained for less than 20 min of irradiation. Analogous results have also been observed in hexane- $\text{CH}_2\text{Cl}_2$  where isoabsorption points are observed for about 1.5 h irradiation [8]; in hexane- $\text{CCl}_4$  solutions, isosbestic points are seen but for a few minutes. Irradiating the hexane- $\text{CHCl}_3$  solutions for an additional 47 min leads to loss of these isosbestic points; a band begins to appear at about 420 nm accompanied by loss of intensity of the Soret band at 395 nm together with the appearance of shoulders at about 388 and 376 nm.

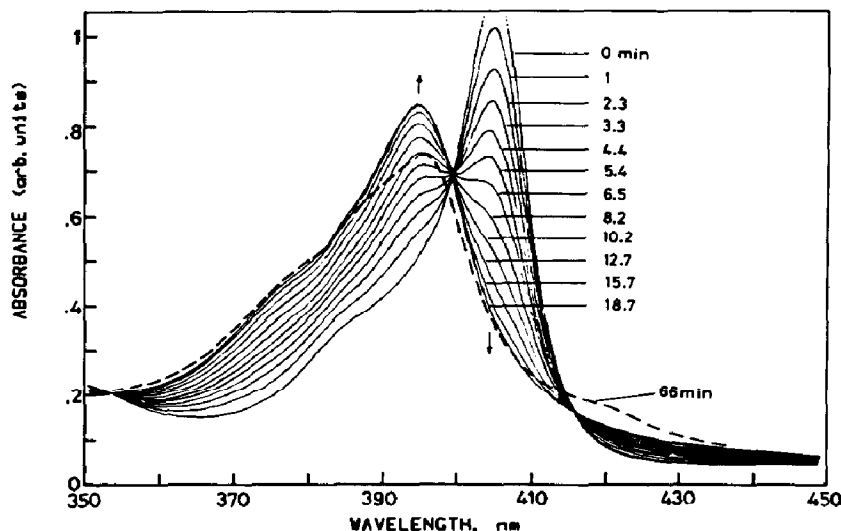
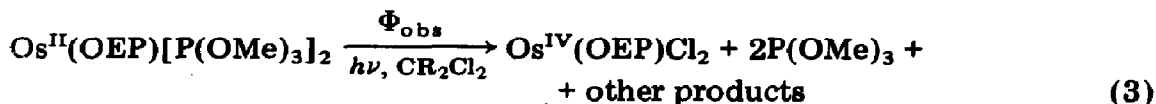


Fig. 1. Spectral changes during irradiation at 405 nm of a hexane- $\text{CHCl}_3$  solution of  $\text{Os}(\text{OEP})[\text{P}(\text{OMe})_3]_2$ .

The spectrum of the starting osmochrome  $\text{Os}(\text{OEP})[\text{P}(\text{OMe})_3]_2$  in hexane solution shows bands at  $\lambda = 345$  nm ( $\log \epsilon = 4.3$ ),  $\lambda = 405$  nm ( $\log \epsilon = 5.1$ ),  $\lambda = 500$  nm ( $\log \epsilon = 4.0$ ) and  $\lambda = 520$  nm ( $\log \epsilon = 4.1$ ). In hexane- $\text{CCl}_4$  solutions, new bands are perceptible at 505, 518, 571 and 620 nm while the Soret band is blue shifted. Continued irradiation leads to loss of these bands in the visible region, which leads to one broad band spread over the 450 - 650 nm region; the Soret band continues to blue shift (386 nm) and its intensity decreases drastically. By this time, the solution was a dull greyish red and a fine black suspension formed. This explains the broadened nature of the spectrum and the increased background absorption. The nature of the suspension was not determined.

Earlier [8], we presented the qualitative spectrum of the product,  $\text{Os}^{\text{IV}}(\text{OEP})\text{Cl}_2$ , formed on irradiating hexane- $\text{CH}_2\text{Cl}_2$  solutions of  $\text{Os}^{\text{II}}(\text{OEP})[\text{P}(\text{OMe})_3]_2$ . The band maxima and  $\log \epsilon$  values of the osmium(IV) product in hexane- $\text{CH}_2\text{Cl}_2$  are as follows:  $\lambda = 339$  nm ( $\log \epsilon = 4.4$ ),  $\lambda = 375$  nm (shoulder) ( $\log \epsilon = 4.8$ ),  $\lambda = 393$  nm ( $\log \epsilon = 5.0$ ),  $\lambda = 502$  nm ( $\log \epsilon = 4.0$ ),  $\lambda = 518$  nm ( $\log \epsilon = 4.0$ ),  $\lambda = 563$  nm ( $\log \epsilon = 3.5$ ) and  $\lambda = 605$  nm ( $\log \epsilon = 3.3$ ).

The plots of Fig. 2, in which we depict the ratio  $A_t/A_0$  of the absorbance *versus* the irradiation time, demonstrate the increase in the rate of the reaction



as the solvent is changed in the order  $\text{CH}_2\text{Cl}_2$  (1.0)  $\approx$   $\text{CHCl}_2\text{CH}_3$  (1.1)  $\approx$   $\text{CH}_2\text{ClCH}_2\text{Cl}$  (1.4)  $<$   $\text{CHCl}_3$  (35)  $\ll$   $\text{CCl}_4$  (280). Addition of excess  $\text{P}(\text{OMe})_3$  inhibits reaction (3) [8].

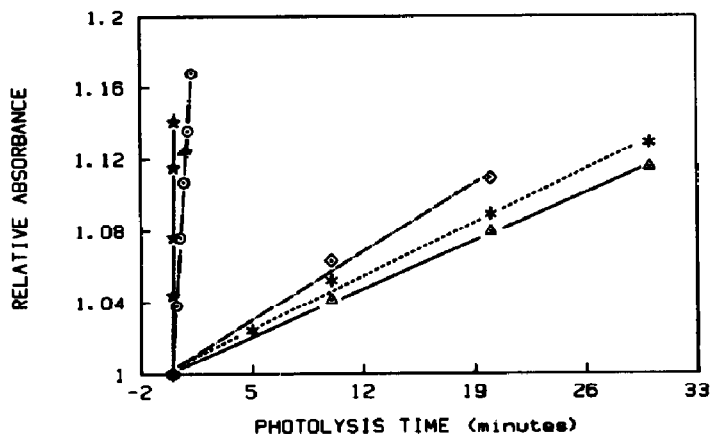


Fig. 2. Plots of relative absorbance vs. irradiation time of hexane-chlorinated hydrocarbon solutions of  $\text{Os}(\text{OEP})[\text{P}(\text{OMe})_3]_2$ . The slopes of the lines reflect the relative rates for the photolysis reaction (3) (see text):  $\star$ ,  $\text{CCl}_4$  (280);  $\odot$ ,  $\text{CHCl}_3$  (35);  $\diamond$ ,  $\text{CH}_2\text{ClCH}_2\text{Cl}$  (1.4);  $*$ ,  $\text{CHCl}_2\text{CH}_3$  (1.1);  $\triangle$ ,  $\text{CH}_2\text{Cl}_2$  (1.0).

TABLE 1

Effect of oxygen and  $\text{N}_2\text{O}$  on the photolysis reaction of hexane solutions of  $\text{Os}(\text{OEP})[\text{P}(\text{OMe})_3]_2$  in the presence of  $\text{CH}_2\text{Cl}_2$ ,  $\text{CHCl}_3$  and  $\text{CCl}_4$ <sup>a</sup>

| Reactants and conditions <sup>b</sup>         | $\Phi_{\text{obs}}$ <sup>c</sup> | C-Cl bond strength<br>(kcal mol <sup>-1</sup> ) |
|---|----------------------------------|---|
| <b>[CH<sub>2</sub>Cl<sub>2</sub>] = 6.2 M</b> |                                  |   |
| Ar purged                                     | 0.0014                           | 75 <sup>d</sup>                                 |
| Air equilibrated                              | 0.0016                           |   |
| Ar purged + N <sub>2</sub> O purged           | 0.0014                           |   |
| O <sub>2</sub> purged                         | 0.0018                           |   |
| Average                                       | 0.0015 ± 0.0002 <sup>e</sup>     |   |
| <b>[CHCl<sub>3</sub>] = 5.0 M</b>             |                                  |   |
| Ar purged                                     | 0.044                            | 71.5 <sup>d</sup>                               |
| Air equilibrated                              | 0.041                            |   |
| Ar purged + N <sub>2</sub> O purged           | 0.033                            |   |
| O <sub>2</sub> purged                         | 0.046                            |   |
| Average                                       | 0.041 ± 0.006                    |   |
| <b>[CCl<sub>4</sub>] = 4.2 M</b>              |                                  |   |
| Ar purged                                     | 0.25                             | 68 <sup>f</sup>                                 |
| Air equilibrated                              | 0.16                             |   |
| Ar purged + N <sub>2</sub> O purged           | 0.20                             |   |
| O <sub>2</sub> purged                         | 0.25                             |   |
| Average                                       | 0.21 ± 0.04                      |   |

<sup>a</sup>Concentration of  $\text{Os}(\text{OEP})[\text{P}(\text{OMe})_3]_2$ ,  $1.8 \times 10^{-4}$  M; excitation wavelength, 365 nm; 293 K.

<sup>b</sup>Purging for about 5 min with the appropriate gas.

<sup>c</sup>Estimated errors, about ±15% - 20%.

<sup>d</sup>From ref. 12.

<sup>e</sup>One standard deviation.

<sup>f</sup>From ref. 13.

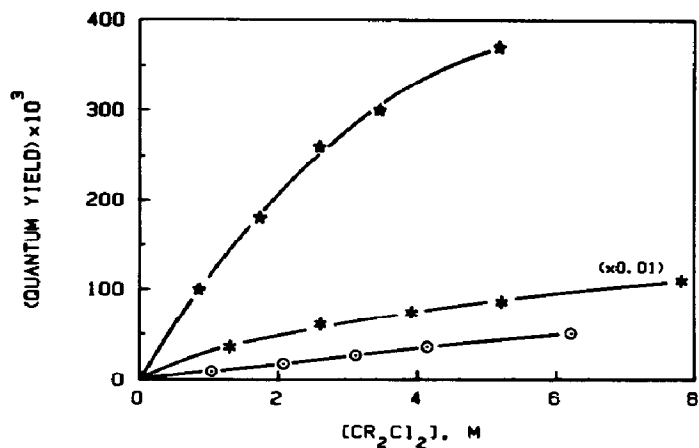


Fig. 3. Quantum yields vs. the concentration of  $\text{CH}_2\text{Cl}_2$  (\*),  $\text{CHCl}_3$  (○) or  $\text{CCl}_4$  (★) in hexane solutions of  $\text{Os}(\text{OEP})[\text{P}(\text{OMe})_3]_2$ .

The effects of oxygen and  $\text{N}_2\text{O}$  on the quantum yields of reaction (3) are collected in Table 1 for  $\text{CH}_2\text{Cl}_2$ ,  $\text{CHCl}_3$  and  $\text{CCl}_4$ . Within experimental error, the initial rates  $R_x$  are independent of whether the hexane- $\text{CR}_2\text{Cl}_2$  solutions of  $\text{Os}(\text{OEP})[\text{P}(\text{OMe})_3]_2$  are argon purged, air equilibrated,  $\text{N}_2\text{O}$  purged or oxygen purged. The rates are  $(8.3 \pm 0.9) \times 10^{-7} \text{ M min}^{-1}$  ( $\text{CH}_2\text{Cl}_2$ ),  $(2.2 \pm 0.3) \times 10^{-5} \text{ M min}^{-1}$  ( $\text{CHCl}_3$ ) and  $(1.4 \pm 0.3) \times 10^{-4} \text{ M min}^{-1}$  ( $\text{CCl}_4$ ). The values of the quantum yields are different from those reported earlier [8] owing to the dependence of  $\Phi$  on  $[\text{CR}_2\text{Cl}_2]$ .

The quantum yields of product formation increase with increase in  $[\text{CR}_2\text{Cl}_2]$  (Fig. 3). These data were least-squares fitted in linear plots of  $\Phi^{-1}$  versus  $[\text{CR}_2\text{Cl}_2]^{-1}$  illustrated in Fig. 4. Curve fitting gives  $\Phi_{\text{obs}}^{-1} = \Phi_0^{-1} + B[\text{CR}_2\text{Cl}_2]^{-1}$ , where  $\Phi_0^{-1}$  is the intercept and  $B$  is the slope. The values of

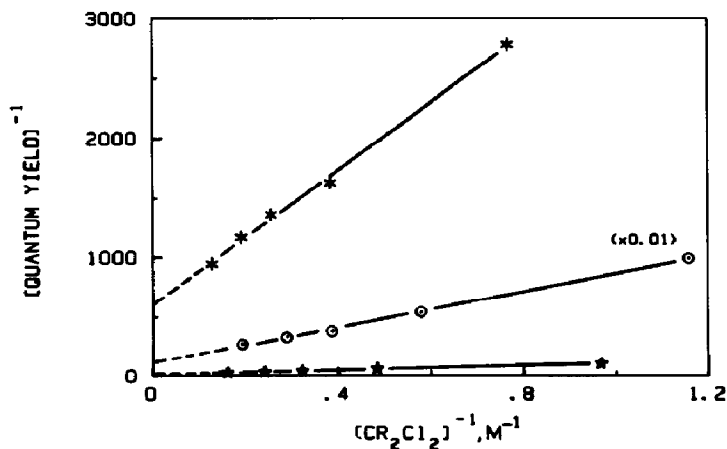


Fig. 4.  $(\text{Quantum yield})^{-1}$  vs.  $[\text{CR}_2\text{Cl}_2]^{-1}$  plots. Extrapolation of the linear least-squares plots to large concentrations of  $\text{CR}_2\text{Cl}_2$  gives the intercept, the reciprocal of which gives the limiting quantum yield (see text): \*,  $\text{CH}_2\text{Cl}_2$ ; ○,  $\text{CCl}_4$ ; ★,  $\text{CHCl}_3$ .

these parameters are respectively  $(6.0 \pm 0.4) \times 10^2$  and  $(2.83 \pm 0.09) \times 10^3$  M for  $\text{CH}_2\text{Cl}_2$ ,  $4.0 \pm 1.6$  and  $(1.04 \pm 0.03) \times 10^2$  M for  $\text{CHCl}_3$  and  $1.1 \pm 0.1$  and  $7.6 \pm 0.2$  M for  $\text{CCl}_4$ . The operational format of the expression for  $\Phi_{\text{obs}}$  is

$$\Phi_{\text{obs}} = \frac{\Phi_0[\text{CR}_2\text{Cl}_2]}{B\Phi_0 + [\text{CR}_2\text{Cl}_2]} \quad (4)$$

Also, to the extent that addition of  $\text{P}(\text{OMe})_3$  causes a diminution of the rate [8], the concentration of  $\text{P}(\text{OMe})_3$  must also be implicated in eqn. (4) (see Section 4). The intercepts from the plots of Fig. 4 give the limiting quantum yields:  $\Phi_{\text{lim}} = 0.0017 \pm 0.0001$  ( $\text{CH}_2\text{Cl}_2$ ),  $0.25 \pm 0.08$  ( $\text{CHCl}_3$ ) and  $0.93 \pm 0.10$  ( $\text{CCl}_4$ ). The error limits represent standard errors.

#### 4. Discussion

Solutions of  $\text{Os}(\text{OEP})[\text{P}(\text{OMe})_3]_2$  in neat  $\text{CH}_2\text{Cl}_2$ ,  $\text{CHCl}_3$ ,  $\text{CCl}_4$ ,  $\text{CHCl}_2\text{CH}_3$  and  $\text{CH}_2\text{ClCH}_2\text{Cl}$  are rapidly photolysed under normal laboratory fluorescent lighting, but hexane solutions of the osmochrome are thermally and photochemically inert. Clear well-defined isosbestic points obtain for the oxidative light-driven photosubstitution reaction of the metal-porphyrin complex in hexane- $\text{CHCl}_3$  solutions, at least for irradiation times of less than 20 min. The spectral changes illustrated in Fig. 1 are identified with reaction (3) in which the only light-absorbing species are  $\text{Os}(\text{OEP})[\text{P}(\text{OMe})_3]_2$  and the product  $\text{Os}(\text{OEP})\text{Cl}_2$ . The loss of isosbestic points on further irradiation at 405 nm is taken to mean that  $\text{Os}(\text{OEP})\text{Cl}_2$  is also photoactive. More dramatic spectral changes occur, in a shorter time, when hexane- $\text{CCl}_4$  is the solvent. Observation of a fine black suspension in the solution together with a large diminution of the Soret band intensity is indicative of almost complete decomposition of the osmium-porphyrin complex.

Attempts to identify the "other products" of reaction (3) by gas chromatographic analyses were unsuccessful. These products had been anticipated to be hydrocarbons resulting from coupling of the carbenes  $:\text{CR}_2$  or  $\cdot\text{CR}_2\text{Cl}$  radicals with each other or with the original  $\text{CR}_2\text{Cl}_2$  species. Failure to identify these products must arise from their low concentrations. Moreover, the  $\text{CR}_2\text{Cl}_2$  solvents invariably contained "impurities" in the parts per million range that rendered identification of the "products" difficult. Interestingly, in a recent paper by Vogler and Kunkley [14] on the photochemical oxidative addition of chlorine from  $\text{CHCl}_3$  to  $\text{Pt}(\text{bpy})\text{Cl}_2$  to give  $\text{Pt}(\text{bpy})\text{Cl}_4$ , these researchers identified 1,1,2,2-tetrachloroethane by gas chromatographic methods formed by insertion of the monochlorocarbene  $:\text{CHCl}$  into a C-Cl bond of  $\text{CHCl}_3$ . Such insertion reactions are well known in carbene chemistry [15]. We speculate that similar insertions can also occur in reaction (3). In so far as monochlorinated hydrocarbon solvents have no effect on the oxidative substitution reaction (3) [16] the second chlorine ligand on  $\text{Os}(\text{OEP})\text{Cl}_2$  must originate with the  $\cdot\text{CR}_2\text{Cl}$  radical. We did not attempt to trap the carbenes but note that attempts [14] to trap the



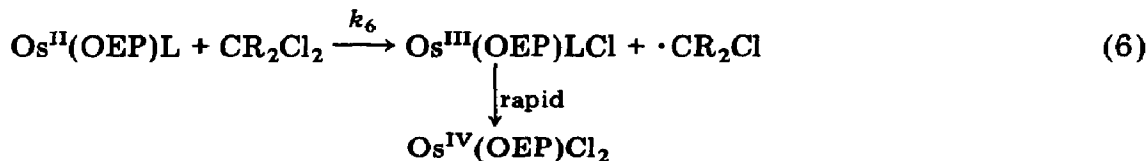
carbene :CHCl with 2,3-dimethyl-2-butene did not lead to unambiguous results.

The reactivity of the five chlorinated solvents follows the order  $\text{CCl}_4 > \text{CHCl}_3 > \text{CH}_2\text{ClCH}_2\text{Cl} \approx \text{CHCl}_2\text{CH}_3 \approx \text{CH}_2\text{Cl}_2$  (Fig. 2) and is in accord with our earlier findings [8] and with those of others [17, 18]. For example,  $(\eta^5\text{-C}_5\text{H}_5)\text{W}(\text{CO})_3\text{Cl}$  photochemically reacts with  $\text{CCl}_4$ ,  $\text{CHCl}_3$  and  $\text{CH}_2\text{Cl}_2$  to yield  $(\eta^5\text{-C}_5\text{H}_5)\text{W}(\text{CO})_2\text{Cl}_3$ , the rate of formation of which varies as  $\text{CCl}_4 > \text{CHCl}_3 > \text{CH}_2\text{Cl}_2$  [17]. Also, consistent with our observations, spectral changes that take place in seconds in  $\text{CCl}_4$  require several hours in  $\text{CH}_2\text{Cl}_2$ . The same trend in reactivity was reported in the reaction of these chlorinating agents  $\text{CR}_2\text{Cl}_2$  with the superoxide ion in dimethyl sulphoxide and dimethylformamide solutions [18]. The importance of  $\text{CCl}_4$  [19, 20], in particular, and other chlorinated hydrocarbons [21, 22] in oxidative addition reactions [14, 21] and metathetical reactions [19, 22] continues to be documented. In all cases, the reactions have implicated radical species of these halocarbons.

The quantum yields of formation of  $\text{Os}(\text{OEP})\text{Cl}_2$  are dependent on the concentration of  $\text{CR}_2\text{Cl}_2$ , with the limiting yield reaching near unitary values for  $\text{CCl}_4$ . Within experimental error, however, the values of the quantum yields do not appear to be affected by the presence of oxygen or  $\text{N}_2\text{O}$  (*cf.* Table 1). This means that, whatever the mechanism, the presence of oxygen and  $\text{N}_2\text{O}$  is inconsequential in the rate-determining step(s) of reaction (3).

#### 4.1. Mechanistic considerations using conventional kinetic theory

In charge transfer photochemistry, electron transfer (metal to ligand or ligand to metal) can lead to bond weakening, to changes in the oxidation state of the metal with potential labilization of a ligand and/or to production of radical pairs. Reactions that follow such changes are often affected by the nature of the solution medium, the magnitude of which is either not available or not understood. In the present case, metal-to-ligand charge transfer leads to labilization of  $\text{P}(\text{OMe})_3$  from the  $\text{Os}(\text{OEP})[\text{P}(\text{OMe})_3]_2$  species [2, 8]. To account for the quantitative treatment of the medium effects, we first consider the mechanism proposed earlier [8]:



Moreover, we account for  $\text{P}(\text{OMe})_3$  ligand release as a primary step in the photochemical consequence of irradiating  $\text{Os}(\text{OEP})[\text{P}(\text{OMe})_3]_2$  to give the triplet charge transfer state  $^3(d\pi, \pi^*)$  [2]. The reactive intermediate  $\text{Os}^{\text{II}}(\text{OEP})\text{L}$  forms with a quantum yield  $\Phi_5$  from  $\text{Os}(\text{OEP})\text{LL}$ ; it can then

deactivate with rate constant  $k_{-5}$  back to the original complex in competition with reaction with a solvent molecule  $\text{CR}_2\text{Cl}_2$  (rate constant  $k_6$ ) to produce an osmium(III) intermediate species that rapidly continues to products. We note that  $\Phi_5$  incorporates all the usual decay channels of an excited state, namely internal conversion, non-radiative transition to ground state and luminescence (if any). While solution medium may affect these decay channels, the effects are not expected to be as large as those acting on such rate steps as  $k_6$  and  $k_{-5}$ . Application of the steady state approximation on  $\text{Os}^{\text{II}}(\text{OEP})\text{L}$  and rearrangement gives

$$\frac{1}{\Phi_{\text{obs}}} = \frac{1}{\Phi_5} \left( 1 + \frac{k_{-5}[\text{L}]}{k_6[\text{CR}_2\text{Cl}_2]} \right) \quad (7)$$

where  $1/\Phi_5$  yields the limiting quantum yields for reaction (3) (see Section 3) and  $k_{-5}[\text{L}]/\Phi_5 k_6$  contains information regarding the deactivation of  $\text{Os}(\text{OEP})\text{L}$  and the reactivity of  $\text{CR}_2\text{Cl}_2$ . Not surprisingly, addition of  $\text{L}$  ( $\equiv \text{P}(\text{OMe})_3$ ) to the reaction should inhibit reaction (3) [8].

That  $\Phi_5$  should vary by nearly three orders of magnitude (from 0.0017 ( $\text{CH}_2\text{Cl}_2$ ) to 0.93 ( $\text{CCl}_4$ )) and thus should be so dependent on the nature of  $\text{CR}_2\text{Cl}_2$  is enigmatic in as much as  $\Phi_5$  reflects the formation of the five-coordinate  $\text{Os}(\text{OEP})\text{L}$  intermediate. Rather, to the extent that  $\Phi_5$  values vary according to  $\text{CR}_2\text{Cl}_2$  must suggest a more complicated pathway;  $\text{CR}_2\text{Cl}_2$  must also act in some direct way on the formation of  $\text{Os}(\text{OEP})\text{L}$  or its equivalent in a manner that will enhance either formation of  $\text{Os}(\text{OEP})\text{L}$  or formation of the intermediate species  $\text{Os}^{\text{III}}(\text{OEP})\text{LCl}$ . One additional decay channel for the triplet charge transfer state of  $\text{Os}(\text{OEP})\text{LL}$  is direct reaction with  $\text{CR}_2\text{Cl}_2$



where  $\Phi_8$  is the quantum yield of direct formation of the osmium(III) species. Inclusion of this reactive step in the mechanistic scheme leads, after a steady state treatment, rearrangement and with  $k_8[\text{CR}_2\text{Cl}_2](\Phi_5 + \Phi_8)$  taken to be very much greater than  $\Phi_5 k_{-5}[\text{L}]$ , to

$$\frac{1}{\Phi_{\text{obs}}} = \frac{1}{\Phi_5 + \Phi_8} \left( 1 + \frac{k_{-5}[\text{L}]}{k_6[\text{CR}_2\text{Cl}_2]} \right) \quad (9)$$

Now  $\Phi_5$  and  $\Phi_8$  also reflect the quantum yields of loss of the  $^3(d\pi, \pi^*)$  state of  $\text{Os}(\text{OEP})[\text{P}(\text{OMe})_3]_2$  and  $\Phi_5 + \Phi_8 = \Phi_{\text{lim}}$ . In as much as  $\Phi_{\text{lim}}$  is 0.0017 for  $\text{CH}_2\text{Cl}_2$  and  $\Phi_5$  is not expected to be very dependent on the nature of  $\text{CR}_2\text{Cl}_2$ , then  $\Phi_5 < 0.0017$  and  $\Phi_{\text{lim}} \approx \Phi_8$ , i.e. the limiting quantum yield mirrors the magnitude of the direct interaction of  $\text{CR}_2\text{Cl}_2$  with the triplet charge transfer state.

The slope-to-intercept ratios from the plots of Fig. 4 yield values of  $k_{-5}[\text{L}]/k_6$ ; they are 4.7 M ( $\text{CH}_2\text{Cl}_2$ ), 26 M ( $\text{CHCl}_3$ ) and 7.0 M ( $\text{CCl}_4$ ). On the

basis of the C—Cl bond strengths (Table 1) in these halocarbons, the ratios were expected to decrease in the order  $\text{CH}_2\text{Cl}_2 > \text{CHCl}_3 > \text{CCl}_4$ . The value for  $\text{CH}_2\text{Cl}_2$  is anomalous. However, both the  $\Phi_{\text{lim}}$  and the initial rates of formation of  $\text{Os}(\text{OEP})\text{Cl}_2$  accord with the greater reactivity of the chlorinated solvents in the order  $\text{CCl}_4 > \text{CHCl}_3 > \text{CH}_2\text{Cl}_2$  as might be expected on C—Cl bond strength considerations [23, 24].

#### 4.2. Mechanistic considerations using the Noyes model

The Noyes model [9] considers photolytically produced radical species to react via three possible routes: (i) primary recombination within the solvent cage, (ii) secondary recombination following diffusive displacement of the order of a molecular diameter and (iii) complete cage escape. The fact that secondary recombination varies with time as  $t^{3/2}$  precludes a conventional kinetic treatment for (ii). Noyes has derived an expression

$$\Phi_{\text{obs}} = \Phi_r + 2a\Gamma(\pi k_s[\text{CR}_2\text{Cl}_2])^{1/2} \quad (10)$$

that relates the observed quantum yield  $\Phi_{\text{obs}}$  to the square root of the concentration of the entering ligand in a process of radical scavenging by some other species such as transition metal complexes [24]. In the expression (10),  $a$  ( $\leq 10^{-6} \text{ s}^{1/2}$ ) is a constant related to secondary recombination,  $\Gamma$  is the quantum yield of radicals escaping primary recombination,  $\Phi_r$  is the quantum yield in the presence of the scavenger at concentrations sufficient to prevent radical recombination in the bulk but too low to compete with secondary recombination and  $k_s$  ( $\approx 10^{10} \text{ M}^{-1} \text{ s}^{-1}$ ) is the rate constant of product formation [9]. Thus, according to Noyes, a plot of the quantum yield  $\Phi_{\text{obs}}$  of the reaction against the square root  $[\text{CR}_2\text{Cl}_2]^{1/2}$  of the ligand concentration should yield linear plots with a slope of  $2a\Gamma(\pi k_s)^{1/2}$ .

The results on treating the concentration dependence of the chloride abstraction photoreaction following eqn. (10) are illustrated in Fig. 5. In all

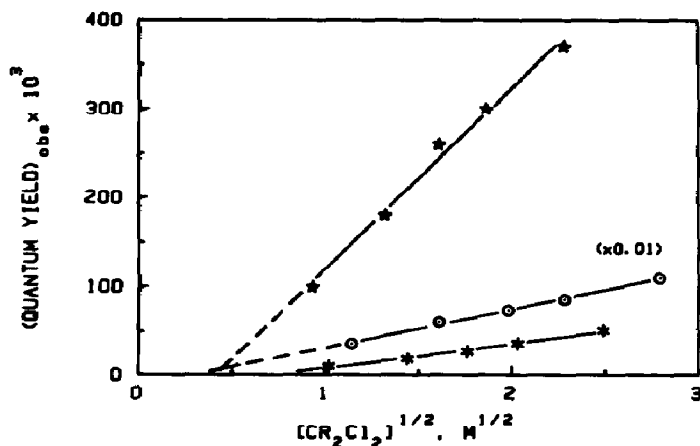


Fig. 5. Noyes plots of the concentration dependence of the halogen abstraction reaction for  $\text{CR}_2\text{Cl}_2$  in hexane: ☆,  $\text{CCl}_4$ ; ⊙,  $\text{CH}_2\text{Cl}_2$ ; \*,  $\text{CHCl}_3$ .

TABLE 2

Slopes and intercepts from Noyes plots of the concentration dependence of  $\Phi_{\text{obs}}$  of Os(OEP)Cl<sub>2</sub> formation

| Reactant                        | Supporting solvent | Slope (M <sup>-1/2</sup> )       | Intercept <sup>2</sup> (M) |
|---------------------------------|--------------------|----------------------------------|----------------------------|
| CH <sub>2</sub> Cl <sub>2</sub> | Hexane             | $(4.4 \pm 0.2^a) \times 10^{-4}$ | 0.12                       |
| CHCl <sub>3</sub>               | Hexane             | $(2.9 \pm 0.2) \times 10^{-2}$   | 0.49                       |
| CCl <sub>4</sub>                | Hexane             | 0.20 ± 0.01                      | 0.20                       |

<sup>a</sup>Standard error.

three cases, the linear behaviour is observed but  $\Phi_r$  is negative contrary to the predictions of the Noyes model (rather, the Noyes plots show, unexpectedly [24], intercepts on the positive concentration axis which vary with the nature of CR<sub>2</sub>Cl<sub>2</sub>). The slopes and intercepts are summarized in Table 2. If  $k_s$  were diffusion controlled, its value could be estimated from the modified Debye equation [25] and from knowledge of the viscosity of the solution medium, in the present instance hexane-halocarbon-complex. Unfortunately, the reactive nature of the Os(OEP)[P(OMe)<sub>3</sub>]<sub>2</sub> porphyrin complex, particularly in the presence of CHCl<sub>3</sub> and CCl<sub>4</sub>, precluded determination of the viscosity of the solutions and thus estimation of  $k_s$ . However, it is worth noting that in the reaction of tris(dibenzylthiocarbamato)iron(III) (Fe(DTC)<sub>3</sub>) with similar halocarbons in benzene,  $k_s$  is diffusion controlled ( $1 \times 10^{10} \text{ M}^{-1} \text{ s}^{-1}$ ) and the decreased reactivity in the halocarbons follows CCl<sub>4</sub> > CHCl<sub>3</sub> > CH<sub>2</sub>Cl<sub>2</sub> [23]; this has been attributed to decreased values of  $k_s$  and not to indirect effects of these halocarbons on the constant  $\alpha$  and  $\Gamma$  [24]. It is also remarkable that the intercepts on the concentration axis for the reaction of Fe(DTC)<sub>3</sub> in CHCl<sub>3</sub> and CCl<sub>4</sub> are [24] 0.5 M and 0.2 M respectively, identical with the intercepts found in the present study (cf. Table 2). These were taken by Liu and Zink to represent the minimum [CR<sub>2</sub>Cl<sub>2</sub>] at which the scavenging dynamics represented by the Noyes theory are operative. Once again, the intercept value for CH<sub>2</sub>Cl<sub>2</sub> appears to be anomalous and does not follow the trend of C-Cl bond strengths (see above).

## 5. Conclusions

The Os(OEP)[P(OMe)<sub>3</sub>]<sub>2</sub> complex has a low-lying <sup>3</sup>(dπ,π\*) charge transfer excited state. Excitation at 365 nm (or 405 nm) populates this state which leads to P(OMe)<sub>3</sub> loss. Chlorinated solvents CR<sub>2</sub>Cl<sub>2</sub> react with the resulting five-coordinate Os(OEP)[P(OMe)<sub>3</sub>] intermediate as well as directly with \*Os(OEP)[P(OMe)<sub>3</sub>]<sub>2</sub>. The product (identified in hexane-CH<sub>2</sub>Cl<sub>2</sub> solutions [8]) is Os<sup>IV</sup>(OEP)Cl<sub>2</sub> which undergoes further decomposition in these solvents, particularly in CCl<sub>4</sub>. It is noteworthy that metal-porphyrin

osmium(II) complexes with lowest energy  $^3(\pi, \pi^*)$  excited states are not affected by these chlorinated solvents, at least under our experimental conditions. Of significance is the observation that, while the initial rates and limiting quantum yields of formation of Os(OEP)Cl<sub>2</sub> are dependent on the C—Cl bond strength in the various halocarbons used, values for CH<sub>2</sub>Cl<sub>2</sub> of  $k_{-5}[L]/k_6$  and for the intercept in the Noyes plots appear to be anomalous. The data available at present afford no explanation for this anomaly.

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