# Water Photolysis. Part 1. The Photolysis of Co-ordinated Water in $[\{MnL(H_2O)\}_2][ClO_4]_2$ (L = Dianion of Tetradentate $O_2N_2$-Donor Schiff Bases). A Model for the Manganese Site in Photosystem II of Green Plant Photosynthesis†

**Fathy M. Ashmawy**
*Department of Chemistry, Tanta University, Tanta, Egypt*
**Charles A. McAuliffe,* R. V. (Dick) Parish, and Joseph Tames**
*Department of Chemistry, University of Manchester Institute of Science and Technology, Manchester M60 1QD*

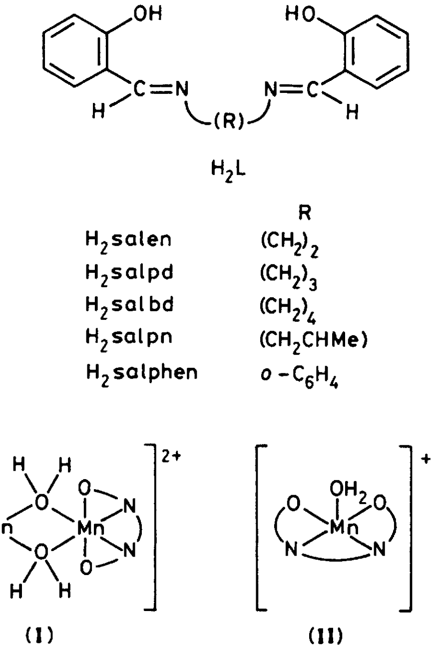
A number of manganese(III) complexes of the type $[\{MnL(H_2O)\}_2]^{2+}$ (L = dianion of $O_2N_2$ tetradentate Schiff base), in aqueous solution, have been shown to liberate dioxygen and reduce *p*-benzoquinone to hydroquinone when irradiated with visible light. The photoactivity is critically dependent on the structure of the ligand, the complex $[\{Mn(salpd)(H_2O)\}_2][ClO_4]_2$ [salpd = propane-1,3-diylbis(salicylideneiminate)] being the most active. All the active complexes exhibit a band at 590 nm in the electronic spectrum, which is absent for the inactive complexes. Amongst the parameters of the photolysis which have been studied are: wavelength of light, temperature, complex and quinone concentrations, ligand structure, pH, and solvent nature. The rate of dioxygen evolution is dependent on the manganese(III) complex (first order) and quinone concentrations (order, 0.5) and the pH of the reaction medium, but is independent of solvent. The water which is photolysed is that bound to the manganese (suggesting that a model for the manganese site of photosystem II of the green plant is represented by these complexes). The energy of activation for $O_2$ evolution in $[\{Mn(salpd)(H_2O)\}_2][ClO_4]_2$ is *ca.* 80 kJ mol$^{-1}$, and the evidence points to homolytic, rather than heterolytic, fission of water. The manganese complex is converted to $[\{Mn(salpd)\}_2O]$ in the photolysis, *i.e.* no oxidation state change of manganese is involved. In addition to *p*-benzoquinone, methylene blue has been shown to be a hydrogen acceptor in this system.

Plant photosynthesis is essentially the catalysed photodecomposition of water; dioxygen is evolved and hydrogen combines with carbon dioxide to produce carbohydrate. There is a great deal of current interest in mimicing this photolysis process, but most systems employ precious metal catalysts.[1] It has been well established that manganese bound to the thylakoid membrane plays an essential and specific role in the dioxygen evolution mechanism of photosystem II;[2,3] manganese-depletion studies have directly implicated this element in dioxygen evolution.[4,5] Thus, model systems have been developed which include manganese.[6,7] In particular, Calvin has presented a justification for this approach in his attempts to decompose water with the di-μ-oxo-bridged complex $[Mn_2O_2(bipy)_4][ClO_4]_3$ (bipy = 2,2′-bipyridine), but initial claims[8] to success with photolytic dioxygen evolution were subsequently withdrawn.[9]

Our own experiments do not involve a μ-oxo-species of inherent great stability, such as that employed by Calvin;[8] rather, we reason that a high-valent manganese complex capable of forming di-μ-hydroxo- or di-μ-oxo-species transiently may more closely mirror the active site of photosystem II. For this reason we have synthesised *ca.* 50 manganese(III) complexes of dianionic tetradentate Schiff-base ligands by a modification of the procedure developed by Boucher and Coe;[10] equation (i).

$$Mn(ClO_4)_2(aq) + H_2L \xrightarrow[NaOH]{[O]} [MnL(H_2O)]ClO_4 \quad (i)$$

All these complexes are novel,[11] with the nearest reported class of compounds being prepared with t-butyl substituted Schiff-base ligands.[12–14] In this paper we report the synthesis, characterisation, and photolysis studies on some of these complexes (Figure 1). A preliminary report has appeared.[15]



| | R |
|---|---|
| $H_2$salen | $(CH_2)_2$ |
| $H_2$salpd | $(CH_2)_3$ |
| $H_2$salbd | $(CH_2)_4$ |
| $H_2$salpn | $(CH_2CHMe)$ |
| $H_2$salphen | $o$-$C_6H_4$ |

(I) (II)

**Figure 1.** Structure of the $[MnL(H_2O)]^+$ complexes

---

† *Non-S.I. unit employed:* B. M. = $0.927 \times 10^{-23}$ A m$^2$.

## Experimental

The ligands $H_2L$ (Figure 1) were prepared by standard methods.

*Complex Preparation.*—All the manganese(III) Schiff-base complexes were prepared in an identical manner, employing a modified method originally developed by Boucher and Coe.[10] This may be illustrated for $[Mn(salpd)(H_2O)]ClO_4 \cdot 2H_2O$ (**2**). To the ligand $H_2$salpd (14.2 g, 0.05 mol) dissolved in ethanol–methanol (1:1, 200 $cm^3$) was added $Mn(ClO_4)_2 \cdot 6H_2O$ (18.1 g, 0.05 mol) dissolved in ethanol (50 $cm^3$). A dense yellow precipitate formed almost immediately, and the reaction mixture was stirred for 10 min, after which sodium hydroxide solution (5 $cm^3$, 0.05 mol) was added, causing the reaction mixture to darken rapidly. The mixture was stirred in contact with air for 5 d, by which time a deep emerald green solution was obtained. This was reduced in volume (to 20 $cm^3$). Addition of cold diethyl ether (500 $cm^3$) precipitated a deep green solid, which was filtered off, washed with diethyl ether (5 × 20 $cm^3$), and dried *in vacuo*. The complex $[Mn(salpd)(H_2O)]NO_3 \cdot 2H_2O$ (**5**) was similarly prepared using $Mn(NO_3)_2 \cdot 6H_2O$ as the starting material.

*Irradiation Experiments.*—For monitoring, the irradiation was carried out in a colourless glass flask (500 $cm^3$) placed in a thermostatted water-bath. In a typical experiment a solution of $[Mn(salpd)(H_2O)]ClO_4 \cdot 2H_2O$ (**2**) (0.49 g 0.001 mol) and quinone (2.50 g 0.023 mol) in deoxygenated, deionised water was irradiated with light from a 300-W tungsten lamp for 10 h. During the experiment aliquots were withdrawn at appropriate time intervals for u.v. measurements.

*Measurement of Dissolved Dioxygen during Irradiation.*—Quantitative measurements of the amount of dioxygen formed during irradiation were performed using a dissolved-oxygen probe type electrode (Uniprobe, U.K.). In a typical experiment deionised deoxygenated water (400 $cm^3$) was placed in a three-necked flask (500 $cm^3$): one neck contained the oxygen electrode, the middle neck a mechanical stirrer in an oil seal, and the third a Subaseal. The whole flask arrangement was immersed in the thermostatted bath so that the water came up to the base of the necks. Stirring was begun, the complex and quinone were added, and the Subaseal fitted to make the system airtight. Two needles were pushed through the Subaseal, one reaching into the liquid, and a stream of dinitrogen was introduced into the solution for *ca.* 30 min during which time the reading on the oxygen meter fell $<5\%$. Once this was reached the needles were removed and the system was left stirring for 10 min to equilibrate. The oxygen meter reading was recorded and the light then switched on. Further readings were taken at appropriate intervals.

Reproducible results were obtained with this method provided that the temperature of the bath remained constant to within ±0.1 °C and a constant stirring rate was maintained.

*Physical Measurements.*—Infrared spectra were obtained on a Perkin-Elmer 457 spectrophotometer and u.v.–visible spectra on a Cary 210 instrument. Magnetic measurements were carried out at room temperature by the Gouy method. Conductivity measurements were obtained in aqueous solutions employing a Cambridge Instruments conductivity bridge. Mass spectra were obtained on the fast-atom bombardment equipment of the Chemistry Department. Elemental analyses were obtained in the UMIST Microanalytical Laboratory.

## Results and Discussion

The manganese(III) Schiff-base complexes, (**I**), reported here, a few of the more than 50 isolated,[11] are those which show significant photoactivity. All the complexes have the stoicheiometry $[MnL(H_2O)]ClO_4$, Table 1, and in some cases one or more water molecules are associated as water of crystallisation. These could be removed by heating (**CARE!**) the complex *in vacuo* at 100 °C for *ca.* 2 h. The complexes are generally soluble in acetone and somewhat less soluble in water, ethanol, and methanol. They are only sparingly soluble in non-polar solvents.

In general the complexes exhibited very similar i.r. features. This is indirect evidence that the oxidation process used in synthesising the complexes oxidises the metal and not the ligand. The typical bands assigned to Schiff-base ligands[12–14,16] are evident. All show a shift to lower energy of the ligand ν(C=N) band on complexation in the dianionic tetradentate mode,[16] Table 2. In addition, all the complexes exhibit a broad absorption centred *ca.* 3 450 $cm^{-1}$, assigned to a combination of the ν(OH) modes of co-ordinated and lattice water. Other significant absorptions are listed in Table 2.

The structure of the complexes in the solid state is dimeric, (**I**), rather than monomeric, (**II**) (Figure 1). In addition to mass

**Table 1.** Physical properties and analytical data for the manganese(III) complexes

| Complex | Colour | Analysis[a] (%) C | H | N | Cl | Mn | $\mu_{eff.}$[b]/B. M. |
|---|---|---|---|---|---|---|---|
| (**1**) $[Mn(salen)(H_2O)]ClO_4$ | Brown | 43.9 (43.8) | 4.0 (3.7) | 6.3 (6.3) | 8.1 (8.1) | 12.7 (12.5) | 4.7 |
| (**2**) $[Mn(salpd)(H_2O)]ClO_4 \cdot 2H_2O$ | Deep green | 41.9 (41.7) | 4.8 (4.5) | 5.6 (5.7) | 7.7 (7.3) | 11.8 (11.3) | 4.5 |
| (**3**) $[Mn(salbd)(H_2O)]ClO_4$ | Green | 46.7 (46.3) | 4.7 (4.3) | 5.7 (6.0) | 7.0 (7.6) | 12.0 (11.8) | 4.9 |
| (**4**) $[Mn(salpn)(H_2O)]ClO_4$ | Green | 43.9 (45.0) | 4.4 (4.0) | 5.2 (5.7) | 7.9 (7.3) | 12.5 (11.3) | 4.8 |
| (**5**) $[Mn(salpd)(H_2O)]NO_3 \cdot 2H_2O$ | Deep green | 45.6 (45.2) | 5.1 (4.9) | 9.3 (9.3) |  | 12.0 (12.2) |  |
| (**6**) $[\{Mn(salpd)\}_2O]$[c] | Dark brown | 56.5 (56.4) | 5.0 (5.0) | 7.8 (7.7) |  | 15.5 (15.7) | 3.3 |

[a] Calculated values in parentheses. [b] At 295 K. [c] Solid photoproduct.

**Table 2.** Some significant infrared frequencies ($cm^{-1}$) of the manganese(III) complexes (Nujol mull)

| Complex | ν(OH) | ν(CN) | $\nu(ClO_4)$* | $\nu(Mn\text{–}OH_2)$ | ν(MnO) | ν(MnN) |
|---|---|---|---|---|---|---|
| (**1**) $[Mn(salen)(H_2O)]ClO_4$ | 3 430 | 1 618 | 1 160 | 1 280 | 460 | 380 |
| (**2**) $[Mn(salpd)(H_2O)]ClO_4 \cdot 2H_2O$ | 3 410 | 1 620 | 1 130 | 1 275 | 465 | 380 |
| (**3**) $[Mn(salbd)(H_2O)]ClO_4$ | 3 450 | 1 622 | 1 115 | 1 285 | 460 | 385 |
| (**4**) $[Mn(salpn)(H_2O)]ClO_4$ | 3 450 | 1 610 | 1 105 | 1 280 | 460 | 390 |

* Unsplit band.

spectral evidence (see below) the solid-state i.r. spectra exhibit a band at *ca.* 900 cm$^{-1}$, which is assignable to bridging water groups.[17] In all cases the spectra of the perchlorate complexes exhibit broad unsplit absorptions at *ca.* 1 100 and 620 cm$^{-1}$, indicative of unco-ordinated perchlorate groups.[18]

Complexes (**1**)—(**3**) were sufficiently soluble in water to give reproducible electronic spectra; the spectrum of $[\{Mn(salpd)(H_2O)\}_2][ClO_4]_2 \cdot 4H_2O$ (**2**) is shown in Figure 2. The spectra of these complexes are not only similar, Table 3, but are typical of manganese(III) in a pseudo-octahedral $3d^4$ environment. Of particular significance regarding those manganese(III) complexes which exhibit photolysis behaviour, and those which do not, is the presence in the former of a peak at 590 nm, Figure 2. The intensity of this peak varies with the Schiff-base ligand used, with the intensity being greatest for complex (**2**). It is probably significant that this complex, therefore, showed the highest photoactivity in the dioxygen evolution experiments (see below). The identity of this peak is not known; it may be a low-energy ligand-to-Mn charge-transfer band or a transition between the $^5B_{1g}$ and $^5A_{1g}$ states. This peak is, additionally, not present in any of the $[Mn^{III}$(Schiff base)X] complexes (X = halogen or pseudohalogen) synthesised by us,[11] suggesting that the origin of this peak is highly dependent upon the environment of the metal.

The room-temperature magnetic moments of the manganese(III) complexes are listed in Table 1. Only complex $[Mn(salbd)(H_2O)]ClO_4$ (**3**) exhibits a magnetic moment similar to that expected (4.9 B.M.) for high-spin $3d^4$ systems. The other complexes exhibit a lower moment in the ligand order salpn > salen > salpd. This reduction in effective magnetic moment is presumably due to antiferromagnetic coupling of spins within the dimer.[13,19]

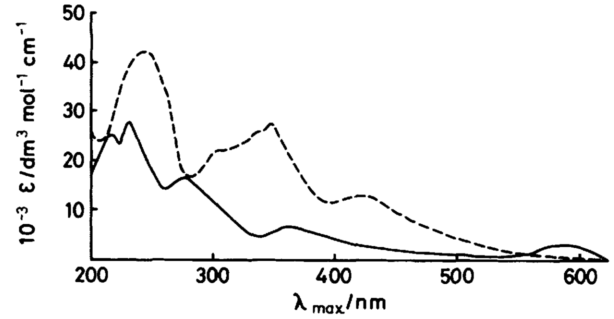


**Figure 2.** U.v.-visible spectra (in water) of $[\{Mn(salpd)(H_2O)\}_2][ClO_4]_2 \cdot 4H_2O$ (**2**) (————) and $[Mn(salphen)(H_2O)]ClO_4$ (— — — —)

**Table 3.** Electronic spectra of the manganese(III) complexes in aqueous solution

| Complex | $\lambda_{max.}$/nm (ε/dm$^3$ mol$^{-1}$ cm$^{-1}$) |
|---|---|
| (**1**) $[Mn(salen)(H_2O)]ClO_4$ | 218 (30 830)<br>236 (35 830)<br>393 (4 500)<br>590 (1 210) |
| (**2**) $[Mn(salpd)(H_2O)]ClO_4 \cdot 2H_2O$ | 219 (24 560)<br>232 (25 200)<br>278 (15 700)<br>369 (5 820)<br>590 (1 670) |
| (**3**) $[Mn(salbd)(H_2O)]ClO_4$ | 221 (24 050)<br>234 (26 600)<br>265 (6 540)<br>590 (1 320) |

At room temperature manganese(III) does not exhibit an e.s.r. spectrum. However, a sample of $[Mn(salpd)(H_2O)]ClO_4 \cdot 2H_2O$ (**2**) does exhibit a very weak e.s.r. pattern, identical to that seen for $[Mn^{II}(salpd)(H_2O)]$.[20] The use of an integrator showed that this pattern represented < 0.02% of the total manganese in the complex but it did suggest the presence of a small quantity of manganese(II) impurity (a fact which was made use of in monitoring the photolysis experiments reported below).

In the absence of a single-crystal *X*-ray structure it is, nonetheless, possible to suggest a dimeric structure, (I), for the complexes in the solid state, both from i.r. data and from antiferromagnetic interactions. Additional evidence comes from fast-atom bombardment mass spectroscopy. Figure 3 shows a typical mass spectrum of one of the complexes studied, complex (**2**). This spectrum shows evidence for the presence of ions of atomic mass 700—740, as expected for the dimer (I) and its fragments in the range 600—740; the monomers (II) have mass equivalent to *ca.* 350.

In acetone, molecular-weight measurements of complexes (**1**)—(**4**) are consistent with the monomeric formulation (**II**). However, conductivity measurements in aqueous solutions at 295 K show that complexes (**1**)—(**3**) exhibit molar conductivity values greater than the values expected for 1:1 electrolytes but below those expected for 1:2 electrolytes, suggesting that there is an equilibrium between monomeric and dimeric formulations [equation (ii)].

$$2[MnL(H_2O)]ClO_4 \rightleftharpoons [\{MnL(H_2O)\}_2][ClO_4]_2 \quad (ii)$$

*Water Photolysis Experiments.*—We recognise that, in attempts to mimic photosystem II, a hydrogen acceptor must also be provided. It is known that quinones of various types, *e.g.* plastoquinone [2,3-dimethyl-5-(3,7,11,15,19,23,27,31,35-nonamethylhexatriaconta-2,6,10,14,18,22,26,30,34-nonaenyl)cyclohexa-2,5-diene-1,4-dione], are involved in binding the hydrogen generated by photosystem II. For our experiments we have employed mainly the water-soluble *p*-benzoquinone and, in

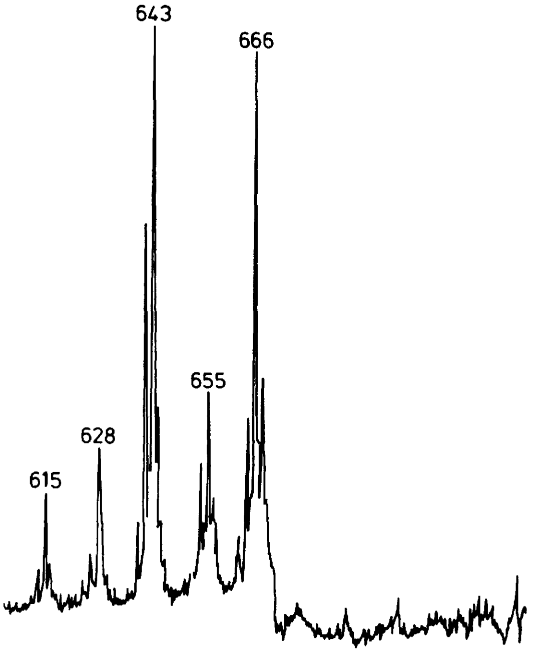


**Figure 3.** Fast-atom bombardment mass spectrum of $[\{Mn(salpd)(H_2O)\}_2][ClO_4]_2 \cdot 4H_2O$ (**2**)

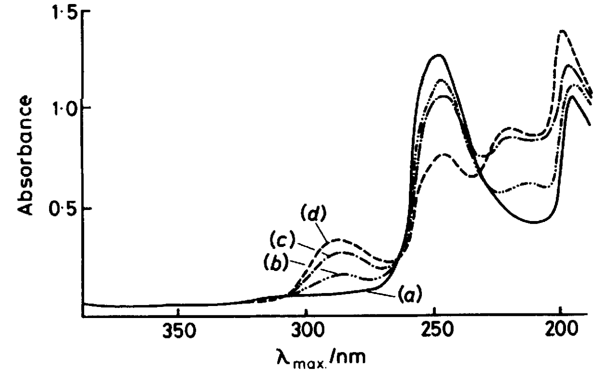


Figure 4. Plot of absorbance *vs.* wavelength of irradiated solutions of $[\{Mn(salpd)(H_2O)\}_2][ClO_4]_2{\cdot}4H_2O$ (2) and quinone: (*a*) original solution; (*b*) after 2 h irradiation, (*c*) after 4 h irradiation, and (*d*) after 10 h irradiation

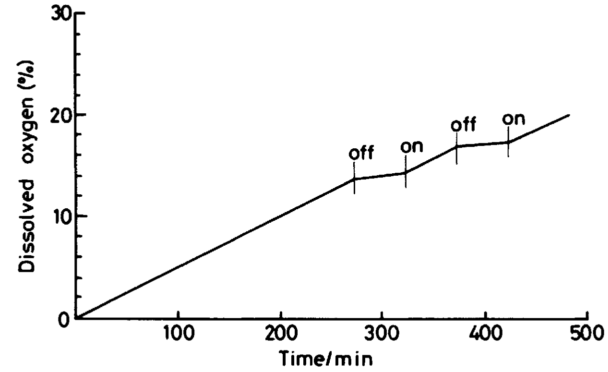


Figure 5. Plot of dissolved $O_2$ *vs.* time for irradiation of a solution of $[\{Mn(salpd)(H_2O)\}_2][ClO]_2{\cdot}4H_2O$ ($4 \times 10^{-2}$ mol) and quinone ($1.0 \times 10^{-1}$ mol) in deoxygenated distilled water (500 $cm^3$), thermostatted at 45 °C (± 0.1 °C)

addition, other hydrogen 'acceptors' such as methyl viologen, benzyl viologen, and methylene blue. Methyl and benzyl viologen [1,1′-dimethyl- and 1,1′-bis(phenylmethyl)-4,4′-bipyridinium dichloride] were inactive, whilst methylene blue showed some activity (though less than that of *p*-benzoquinone).

The course of the water photolysis experiments was followed in two ways. First, it was possible to monitor the electronic spectrum of an aqueous solution of a manganese(III) complex and quinone in order to observe variations when irradiated with visible light. It was seen that the quinone absorption peak at 247 nm decreased, whilst a characteristic hydroquinone peak at 290 nm developed, Figure 4. Secondly, this observation was coupled with quantitative oxygen electrode observations, Figure 5. The concentration of dioxygen in the solution increased linearly during irradiation, Figure 5, but when the light was switched off the evolution of dioxygen into the solution fell sharply; on irradiation once more the dioxygen evolution rate returned to that originally observed. The temperature remained at 45 °C (±0.1 °C) throughout these cycles.

This behaviour, Figure 5, illustrates two important factors: (*a*) the change in potential developed by the oxygen electrode during irradiation is not due to a change in temperature,[8,9] and (*b*) that, on switching off the light, the rate of dioxygen evolution does not fall to zero, but has a small positive value. As completely blacked out solutions do not evolve dioxygen, then it may be assumed that these small residual rates are due to diffuse daylight within the laboratory.

All of the *ca.* 50 complexes[11,20] were evaluated in this way, but only complexes (**1**)—(**5**) were found to be active in the dioxygen evolution experiments, of which the complex $[Mn(salpd)(H_2O)]ClO_4{\cdot}2H_2O$ (**2**), is the most active (the following experiments employed this complex, unless otherwise stated). It is important to mention that no dioxygen evolution was observed when *p*-benzoquinone, methylene blue, or the manganese(III) complexes were separately irradiated.

The overall reaction is given by equation (iii).

The water involved in the photolysis is almost certainly that which is co-ordinated in the complex, since a similar rate and quantity of dioxygen evoluted and hydroquinone produced was observed when the complexes were irradiated in anhydrous ethanol.

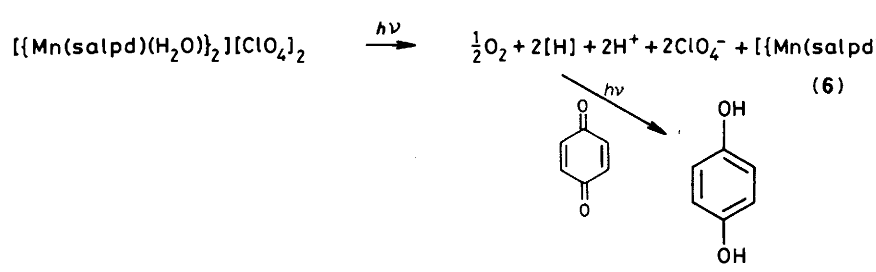
During irradiation a black precipitate was deposited which we identified as $[\{Mn(salpd)\}_2O]$ (**6**), Table 1. This material, $\mu_{eff.}$ = 3.3 B.M., is similar to complexes synthesised by Lewis *et al.*[21] The i.r. spectrum of (**6**) exhibits a sharp peak at 690 $cm^{-1}$ which we tentatively assign to the Mn–O–Mn system; it is at lower energy than that assigned to the corresponding Fe–O–Fe system which occurs at 820 $cm^{-1}$.[22]

We have examined several factors, (*a*)—(*i*), influencing the rate of dioxygen evolution.

(*a*) *Irradiation time.* Prolonged irradiation of quinone and the manganese complexes was examined in order to determine: (*i*) if the reaction rate remained constant, and (*ii*) if more than half a mole of dioxygen per mole of dimer could be evolved. For these reasons solutions were irradiated over a period of 24 h at 60 °C. It was found that $O_2$ evolution continues at a constant rate for 10—12 h, after which the rate soon falls to zero. The total amount of dioxygen evolved was found to be 0.25 mol $O_2$ per mol Mn, as indicated in equation (iii).

(*b*) *Wavelengths of light.* The wavelengths of light which effect this photolysis have been shown to extend throughout the visible region. The greatest activity is shown in the 450—600 nm region. The $O_2$ evolution was observed using irradiation through red (> 560 nm), green (450—600 nm), or blue (300—560 nm) gelatine filters, Figure 6; the dioxygen evolution employing the green filter was virtually identical to that using white light. It is significant that the photoactive complexes have an absorption band at 590 nm, which falls within the transmission field of the green filter.

(*c*) pH. The rate of $O_2$ evolution considerably depended on the pH of the irradiated solutions, with the rate increasing with increasing pH (pH range examined was 4.5—6.9). The results of pH monitoring during the irradiation of each solution are



$$[\{Mn(salpd)(H_2O)\}_2][ClO_4]_2 \xrightarrow{h\nu} \tfrac{1}{2}O_2 + 2[H] + 2H^+ + 2ClO_4^- + [\{Mn(salpd)\}_2O] \quad \text{(iii)}$$

(**6**)

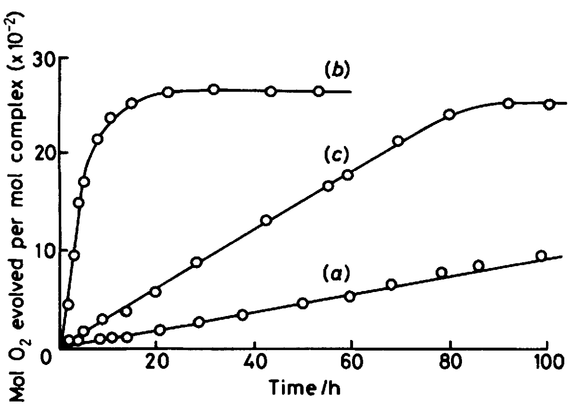


**Figure 6.** Plot of mol of $O_2$ evolved per mol of complex *vs.* time, employing (*a*) red, (*b*) green, or (*c*) blue filters

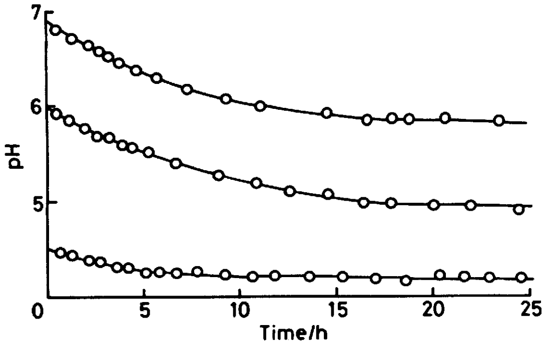


**Figure 7.** Variation of pH of irradiated solutions with time: $[\{Mn(salpd)(H_2O)\}_2][ClO_4]_2 \cdot 4H_2O$ (0.001 mol) and quinone (0.012 mol). Initial pH of solutions is that at zero time

shown in Figure 7. For any solution the pH decreases with irradiation time. This is expected, as hydroquinone is liable to deprotonate in aqueous solution,[23] and perchloric acid is another product, equation (iii). It was not possible to examine the reaction with solutions of pH > 8, as semiquinone is formed under alkaline conditions.[24,25]

(*d*) *Temperature.* The effect of temperature on dioxygen evolution was examined in the range 40—60 °C, Figure 8. The Arrhenius plot of log (rate) *vs.* $T^{-1}$ gives a straight line over the range 40—60 °C, and the activation energy corresponding to the overall reaction is estimated to be 80 kJ $mol^{-1}$.

(*e*) *Manganese*(III) *concentration.* The results are give in Table 4, and a plot of log (rate of $O_2$ evolution) *vs.* log $[Mn^{III}]$ is given in Figure 9, from which it is found that the rate of dioxygen evolution is close to first order with respect to the concentration of the manganese(III) complex.

(*f*) *Ligand structure.* Of all the complexes prepared only complexes (**1**)—(**5**) were found to evolve dioxygen upon irradiation. Thus, for a range of complexes of empirical formula $[MnL(H_2O)]^+$, photoactivity crucially depends on the structure of the ligand and, even within the group of complexes (**1**)—(**5**), quite startling differences are seen for quite small changes in the ligand structures. Figure 10 shows the activity pattern for ligand methylene chain length and dioxygen evolution after irradiation for 2 h.

(*g*) *Effect of* p-*benzoquinone concentration.* Under the same conditions as in Table 4, the rate of oxygen production was found to be approximately 0.5 order with respect to the quinone

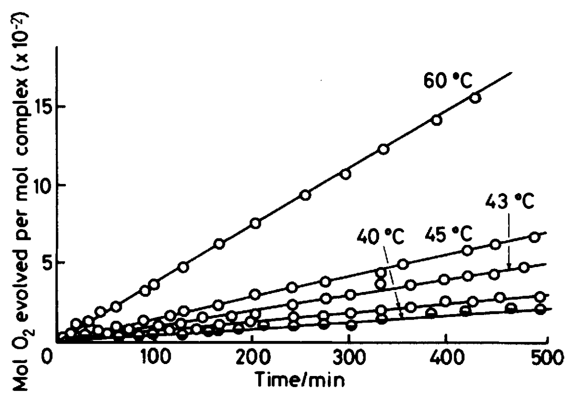


**Figure 8.** Mol of $O_2$ evolved per mol of complex *vs.* time: (O) *p*-benzoquinone, (◒) methylene blue

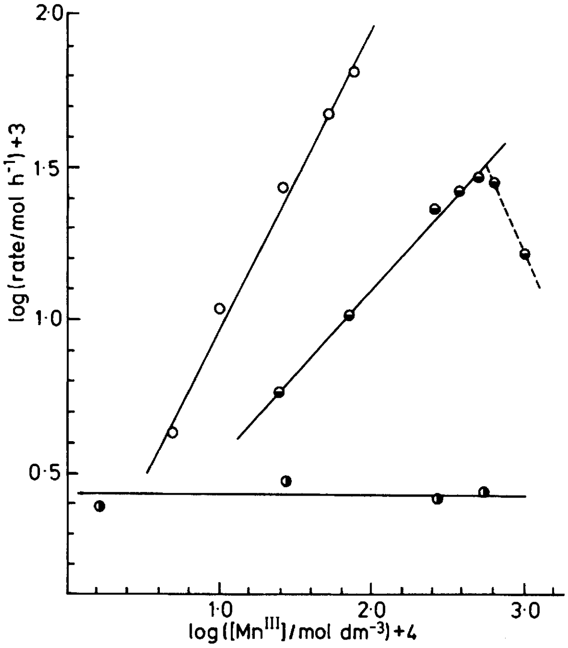


**Figure 9.** Log of rate of $O_2$ evolved *vs.* log of concentration: (O) $[Mn^{III}]$, (◒) [quinone], (◑) [solvent]

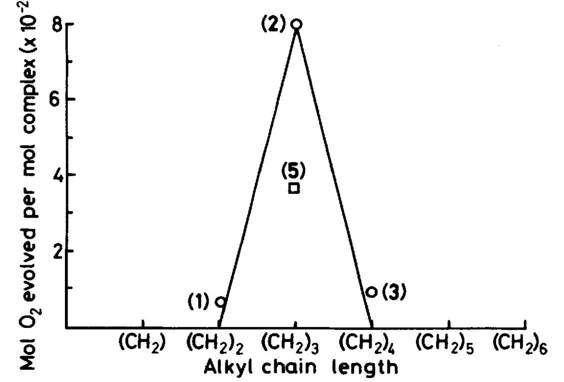


**Figure 10.** Activity pattern for $O_2$ evolution during irradiation. Plot of mol of $O_2$ evolved per mol of complex as a function of the length of the alkyl chain in the ligand: (O) $ClO_4^-$ salts; (☐) $NO_3^-$ salt

**Table 4.** Relative rates of dioxygen evolution by the visible light induced photolysis of the $Mn^{III}$–*p*-benzoquinone system[a]

| $10^3$[Quinone][b]/mol $dm^{-3}$ | $10^3$(Rate of $O_2$ evolution)/mol $h^{-1}$ | $10^3$[$Mn^{III}$][c]/mol $dm^{-3}$ | $10^3$(Rate of $O_2$ evolution)/mol $h^{-1}$ |
|---|---|---|---|
| 2.50 | 4.45 | 0.50 | 3.25 |
| 25.00 | 18.0 | 1.00 | 8.35 |
| 37.50 | 21.0 | 2.50 | 21.0 |
| 50.00 | 23.0 | 5.00 | 37.0 |
| 62.50 | 22.4 | 7.50 | 50.0 |
| 100.00 | 13.0 | | |

[a] Conditions; medium: deoxygenated deionised water (400 $cm^3$); 60 °C; irradiation with a 300-W tungsten lamp for 7 h. [b] In the presence of $[Mn(salpd)(H_2O)]ClO_4 \cdot 2H_2O$ (**2**) (0.001 mol $dm^{-3}$). [c] In the presence of *p*-benzoquinone (0.012 mol $dm^{-3}$).

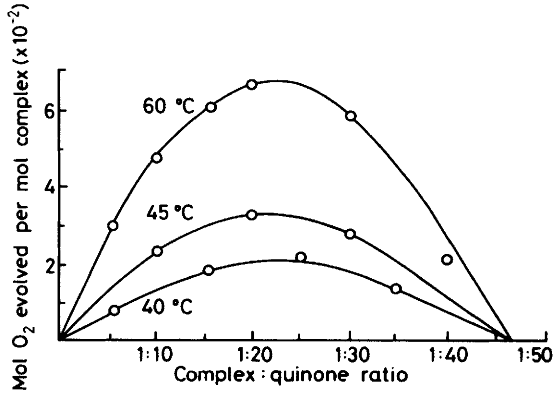


**Figure 11.** Mol of $O_2$ evolved per mol of complex *vs.* complex:quinone ratio at different temperatures

concentration, see Figure 9. As the concentration of the quinone increased (>0.05 mol $dm^{-3}$) the order of the reaction became negative with respect to the quinone concentration. This deviation of the order is not clearly understood, but might be due to the occurrence of some competitive reactions dependent on the concentration of quinone, *i.e.*, the photochemical conversion of *p*-benzoquinone to humic acid[23] and/or the back reaction in equation (iii).

The specific dependence of the rate of oxygen evolution on the concentration of the quinone is clearly illustrated in Figure 11. The rate of oxygen evolution reaches a maximum at the Mn: quinone ratio of 1:20. This ratio is independent of the temperature of the photolysis reaction.

(*h*) *Effect of solvent.* Photolysis experiments were also carried out in which ethanol was added to the reaction medium (deoxygenated deionised water). In all these experiments (from 100% water to 100% ethanol) the rate of $O_2$ evolution upon photolysis remained constant within experimental error, Figure 9, showing that the solvent water does not enter into the photolysis reaction and is not itself photolysed. This suggests that the water being photolysed is the co-ordinated water bound to the manganese metal, as is thought to occur in photosystem II.

(*i*) *E.s.r. experiments.* It was mentioned above that, although $[Mn(salpd)(H_2O)]ClO_4 \cdot 2H_2O$ (**2**) does not exhibit an e.s.r. signal at room temperature, a weak signal arises due to a manganese(II) impurity. Very careful monitoring of the photolysis experiment in a specially designed e.s.r. tube resulted in no change in the e.s.r. signal; in particular there was no increase in the $Mn^{II}$ signal, indicating that there is no reduction of $Mn^{III}$ to $Mn^{II}$ concomitant with the oxidation of oxygen. This experiment also suggests that other radicals formed during irradiation are short-lived and not detectable.

## Conclusions

The results obtained so far indicate that water co-ordinated to high-valent manganese has been successfully photolysed, a process which mimics what is thought to occur in photosystem II in green plant photosynthesis. The dependence of this water dissociation on visible light is illustrated by our 'blacked-out' experiments, Figure 5. We have also shown that the wavelength of the visible light is important, as although photolysis occurs over the whole visible light range, the greatest activity is shown in the 450—600 nm region (green) and decreases in the order green > blue > red light. The photoactive compounds all have a visible absorption band at 590 nm, Figure 2.

The hydrogen evolved in the photolysis can be trapped by *p*-benzoquinone, converting the latter to hydroquinone. We have, as yet, been unable to measure the quantum efficiency of this process.

The use of methylene blue, MB, is potentially more important than *p*-benzoquinone because Adams and Hall[26] have demonstrated that reduced MB, on interaction with hydrogenase, evolves dihydrogen gas and regenerates MB. Thus a combination of the [$Mn^{III}$]–$H_2O$ and reduced MB–$H_2$ systems gives the potential to photolyse water to produce dihydrogen and dioxygen separately [equation (iv)].

$$2H_2O \xrightarrow[\text{MB, hydrogenase}]{Mn^{III},\ h\nu} 2H_2\uparrow + 2O_2\uparrow \qquad \text{(iv)}$$

The kinetic results indicate that the rate of dioxygen evolution is dependent on the concentrations of the manganese(III) complex, the quinone, and the pH of the reaction medium and is independent of the nature of the solvent. Therefore while the rate of dioxygen evolution follows first-order kinetics with respect to [$Mn^{III}$], Figure 9, the half-order dependence on [quinone] indicates that a semiquinone species might be included in the mechanism leading to the formation of hydroquinone and dioxygen.

The temperature dependence of the rate of oxygen evolution in the range 40—60 °C is expressed by equation (v), with an

$$\text{Rate (mol h}^{-1}) = 2.5 \times 10^{12} \exp (E_a/\boldsymbol{RT}) \qquad \text{(v)}$$

apparent activation energy, $E_a/\boldsymbol{RT}$, of 80 kJ $mol^{-1}$ which suggests that the mechanism of dioxygen evolution may involve a chemical step as well as a photochemical step.

The observed effect of the ligand structure on the rate of oxygen evolution is quite large, see Figure 10. Figure 10 also shows that the dioxygen evolution rate for complex $[Mn(salpd)(H_2O)]ClO_4 \cdot 2H_2O$ (**2**) is approximately twice that of complex $[Mn(salpd)(H_2O)]NO_3 \cdot 2H_2O$ (**5**). The only difference between these two complexes is in the non-co-ordinating anion. The fact that the $NO_3^-$ is a better co-ordinating anion than $ClO_4^-$ may result in a shift in the dimer formation equilibrium of complex (**5**), thus slowing down the overall reaction rate.

Finally it is important to point out that all the available evidence suggests a homolytic rather than heterolytic fission of water. The latter would probably involve a change in oxidation state by the manganese. The results of the e.s.r. monitoring experiments during photolysis show that there is no oxidation state change from $Mn^{III}$ to $Mn^{II}$ and this virtually eliminates $Mn^{II}$ from any proposed mechanism of dioxygen formation. Additionally, initial experiments proved that protons were not the species responsible for forming hydroquinone, and so protons too can be eliminated from any mechanism. The actual state of the hydrogen atoms is not yet known, but it may be that the quinone and the active manganese complex in solution interact in such a way as to allow photolysed homolytic fission of water to occur. It is interesting that of all the so-called hydrogen acceptors used only those with a positive electrode potential were active, *e.g.*, *p*-benzoquinone ($E^0 = +0.699$ V) and methylene blue ($E^0 = +0.11$ V), while the manganese complexes studied have a negative electrode potential.* Recently, manganese–quinone complexes have been isolated.[27]

Since the oxidation state of manganese is the same as that in the starting material, the system offers the hope that we can eventually make the process catalytic, *i.e.*, to avoid the necessity of having to regenerate $Mn^{III}$. We are currently investigating methods of sustaining this reaction.

## Acknowledgements

We are grateful to Professor Sir George Porter for useful discussions and to Professor D. O. Hall for helpful advice and provision of experimental facilities.

---

* Electrode potentials for $[Mn(salpd)(H_2O)]ClO_4{\cdot}2H_2O$:[20] $Mn^0 \longrightarrow Mn^{2+} + 2e^-, E^0 = -1.056$ V; $Mn^{2+} \longrightarrow Mn^{3+} + e^-, E^0 = -1.248$ V; $Mn^{3+} \longrightarrow Mn^{4+} + e^-, E^0 = -0.991$ V.

## References

1 J. Kiwi, K. Kalyanasundrum, and M. Grätzel, *Struct. Bonding* (*Berlin*), 1981, **49**, 37.
2 R. L. Heath, *Int. Rev. Cytol.*, 1973, **34**, 44.
3 G. M. Cheniae, *Ann. Rev. Plant Physiol.*, 1968, **21**, 467.
4 G. M. Cheniae and I. F. Martin, *Biochim. Biophys. Acta*, 1970, **197**, 21.
5 G. M. Cheniae and I. F. Martin, *Plant Physiol.*, 1971, **47**, 568.
6 F. M. Ashmawy, C. A. McAuliffe, and J. Tames, *Inorg. Perspect. Biol. Med.*, 1979, **2**, 211.
7 G. Porter, *Proc. R. Soc. London, Ser. A*, 1978, **362**, 281.
8 M. Calvin, *Science*, 1974, **184**, 375.
9 M. Calvin and S. R. Cooper, *Science*, 1974, **185**, 4148.
10 L. J. Boucher and C. G. Coe, *Inorg. Chem.*, 1975, **14**, 1289.
11 F. M. Ashmawy, C. A. McAuliffe, R. V. Parish, and J. Tames, *Inorg. Chim. Acta*, in the press.
12 L. J. Boucher and M. O. Farrell, *J. Inorg. Nucl. Chem.*, 1973, **35**, 3731.
13 L. J. Boucher, *J. Inorg. Nucl. Chem.*, 1974, **36**, 531.
14 L. J. Boucher, *Inorg. Chem.*, 1976, **15**, 1334.
15 F. M. Ashmawy, C. A. McAuliffe, R. V. Parish, and J. Tames, *J. Chem. Soc., Chem. Commun.*, 1984, 14.
16 J. R. Dilworth, C. A. McAuliffe, and B. J. Sayle, *J. Chem. Soc., Dalton Trans.*, 1977, 849.
17 D. M. Adams, 'Metal-Ligand Vibrations,' Academic Press, New York, 1966, p. 258.
18 S. F. Pavkovic and D. W. Meek, *Inorg. Chem.*, 1965, **4**, 1091.
19 M. Gerloch, J. Lewis, F. E. Mabbs, and A. Richards, *Nature* (*London*), 1966, **212**, 809.
20 J. Tames, Ph.D. Thesis, University of Manchester, 1981.
21 J. Lewis, F. E. Mabbs, and H. Weigold, *J. Chem. Soc. A*, 1968, 1699.
22 J. Lewis, F. E. Mabbs, and A. Richards, *J. Chem. Soc. A*, 1967, 1014.
23 N. M. Atherton, P. A. Cranwell, and A. J. Floyd, *Tetrahedron*, 1967, **23**, 1653.
24 N. K. Bridge and G. Porter, *Proc. R. Soc., London, Ser. A*, 1958, **244**, 259.
25 N. K. Bridge and G. Porter, *Proc. R. Soc., London, Ser. A*, 1958, **244**, 276.
26 M. W. W. Adams and D. O. Hall, personal communication.
27 S. L. Kessel, R. M. Emberson, P. G. Debrunner, and D. N. Hendrickson, *Inorg. Chem.*, 1980, **19**, 1170; M. W. Lynch, D. N. Hendrickson, B. J. Fitzgerald, and C. B. Pierpont, *J. Am. Chem. Soc.*, 1984, **106**, 2041.

*Received* 9*th July* 1984; *Paper* 4/1184