The Photolysis of Co-ordinated Water in $[Mn(saltm)(H_2O)]_2(ClO_4)_2$ [saltm = *N,N'*-propylenebis(salicylideneaminato)]

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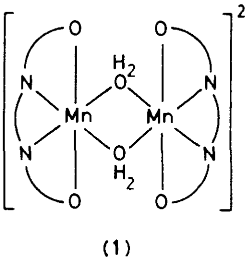
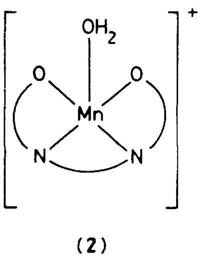
Irradiation with visible light of aqueous solutions of $[Mn(saltm)(H_2O)]_2(ClO_4)_2$ [saltm = *N,N'*-propylenebis(salicylideneaminato)] and quinone results in the evolution of dioxygen and the production of hydroquinone; the manganese product remains in the 3+ oxidation state.

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 mimicking this photolysis process, but most systems employ precious metal catalysts.[1] However, it is well established that manganese plays an essential and specific role in the dioxygen evolution mechanism of photosystem II, PPSII, in green plant photosynthesis,[2—4] and attempts have been made to catalyse the photodecomposition of water by the use of manganese complexes.[5] Calvin[6] has presented a justification for this approach in his attempts to decompose water with the di-μ-oxo bridged complex $[Mn_2O_2(bipyridine)_4](ClO_4)_3$, but initial claims to success with photolytic dioxygen evolution from water[6] were subsequently withdrawn.[7]

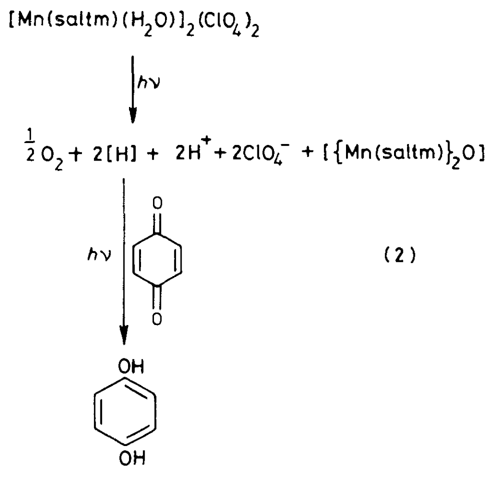


(1)



(2)

Our own experiments do not involve a μ-oxo species of inherently great stability, such as that adopted by Calvin,[6] but rather we reason that a high-valent manganese complex capable of forming di-μ-aquo, di-μ-hydroxy, or di-μ-oxo species transiently may more closely mirror the active site of PPSII. For this reason we have synthesized *ca.* 50 manganese(III) complexes of dianionic tetradentate Schiff's base



(2)

ligands, L, by a modification of the procedure developed by Boucher[8] [reaction (1)].

$$Mn(ClO_4)_2 \cdot (H_2O)_n + H_2L \xrightarrow[NaOH]{[O]} [MnL(H_2O)]ClO_4 \cdot H_2O \quad (1)$$

In the solid state the complexes exhibit an i.r. band at *ca.* 900 cm^{-1}, which has been assigned to bridging water groups,[9] and this, taken with other spectroscopic data,[10] indicates a dimeric structure, (**1**). Molecular weight measurements on acetone solutions indicate a monomeric formula-

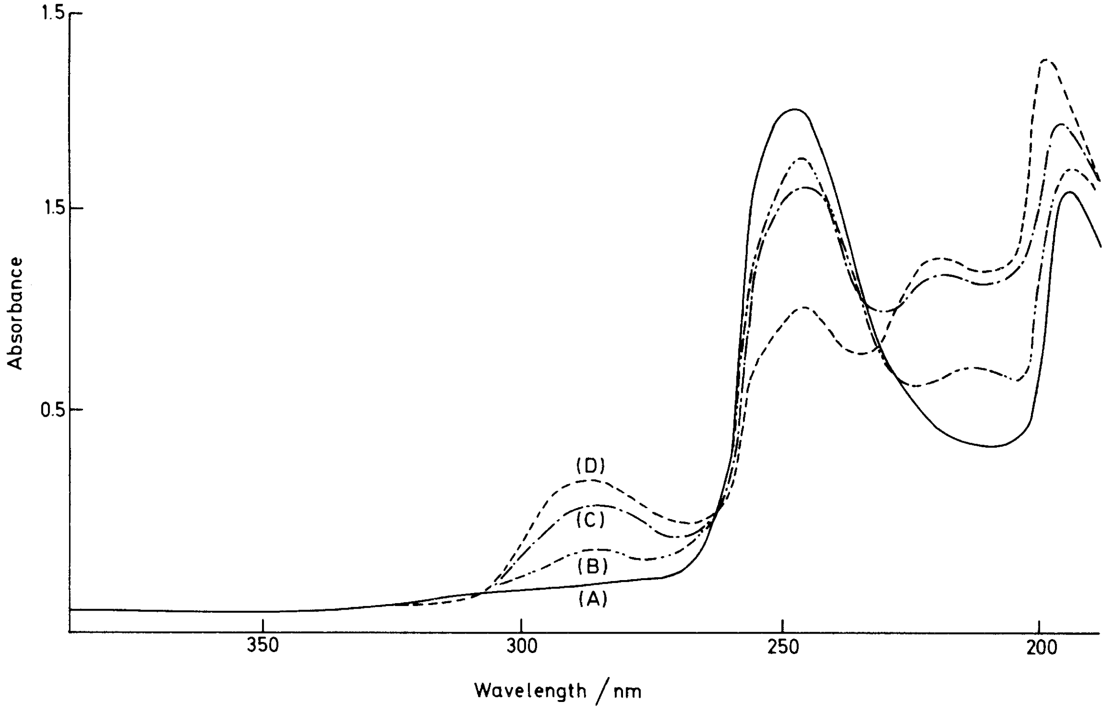


Figure 1. Plot of absorbance *vs.* wavelength of irradiated solutions of [Mn(saltm)H_2O]ClO_4 and quinone. (A) Original solution; (B) after 2 h irradiation; (C) after 4 h irradiation; (D) after 10 h irradiation.

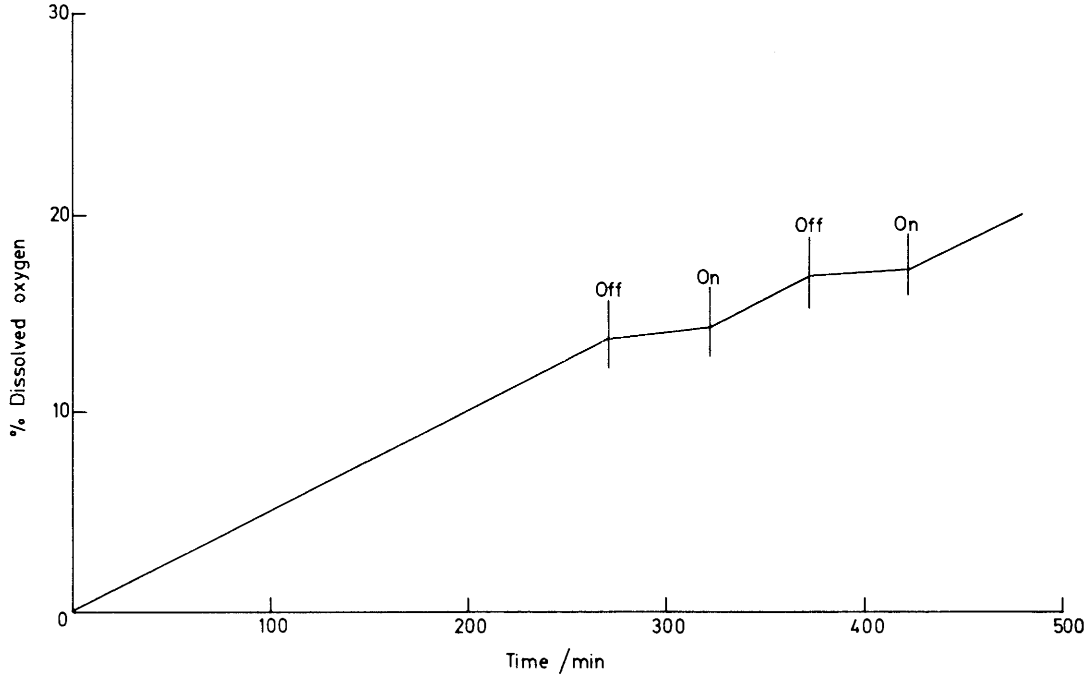


Figure 2. Plot of dissolved O_2 *vs.* time for irradiation of a solution of 2×10^{-2} mol of [Mn(saltm)H_2O]$ClO_4 \cdot 2H_2O$ and 1.0×10^{-1} mol quinone in deoxygenated distilled water (500 cm^3) thermostated at 45 °C (±0.1 °C).

tion, (**2**), but conductivity measurements in aqueous solution suggest that there is an equilibrium between the monomeric and dimeric formulations. Additionally, fast atom bombardment mass spectrometry shows the presence of ions of atomic mass *ca.* 700—740 a.m.u., expected for the dimer, and its fragments in the 600—740 a.m.u. range; monomers, (**2**), have mass *ca.* 350 a.m.u.[10]

Of the prepared complexes, one shows significantly more photoactivity than the others, *viz.* [Mn(saltm)H_2O]-$ClO_4 \cdot 2H_2O$, $\mu_{eff.} = 4.60\ \mu_B$, where saltm is *N,N'*-propylenebis(salicylideneaminato). When an aqueous solution of this complex and a 10-fold molar excess of quinone (hydrogen acceptor) was subjected to visible light irradiation from a tungsten lamp, the quinone absorption peak at 247 nm decreased, whilst a characteristic hydroquinone peak at 290 nm appeared, Figure 1. This observation was coupled with quantitative oxygen-electrode observations (Figure 2). The concentration of dissolved oxygen increased linearly during irradiation, but when the light was switched off evolution fell sharply; on irradiating 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 illustrates two important factors: (a) the change in the potential developed by the oxygen electrode during irradiation is not due to a change in temperature[6,7] 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, it may be assumed that these small residual rates are due to diffuse daylight within the laboratory.

This overall reaction is thus given by reaction (2) with the hydroquinone product being identified by u.v. spectroscopy and g.c. analysis.† We have, however, been unable to measure the quantum efficiency of this process as yet.

The water involved in the photolysis is almost certainly that which is co-ordinated in the complexes, since a similar rate and quantity of dioxygen evolution and hydroquinone production is observed when the complexes are irradiated in anhydrous ethanol.

We have also shown that it is possible to use a second hydrogen acceptor, methylene blue, in place of quinone. In this case the rate of dioxygen evolution is slower, perhaps due to a back-reaction of the reduced methylene blue with the dioxygen produced. This methylene blue, MB, system is potentially important because Adams and Hall have demonstrated[12] that reduced MB, on interaction with hydrogenase, evolves dihydrogen gas and regenerates MB. Thus, a combination of the [Mn]/H_2O and reduced MB/H_2 systems gives the potential to photolyse water to produce dioxygen and dihydrogen *separately* [equation (3)].

$$2H_2O \xrightarrow[\text{MB, hydrogenase}]{[\text{Mn}],\ h\nu} 2H_2 \uparrow + O_2 \uparrow \qquad (3)$$

The wavelengths of light which activate this photolysis have been shown to extend throughout the visible region, but the greatest activity is shown in the 450—600 nm region. The evolution of dioxygen was observed using irradiation through red, green, or blue gelatine filters, and the O_2 evolution using the green filter was virtually identical to that using white light. The main visible absorption band of the complex at 590 nm falls within the transmission spectrum of the green filter. During irradiation a black precipitate was deposited. We identified this as [{Mn(saltm)}$_2$O] similar to complexes synthesized by Lewis *et al.*[13] Since the oxidation state of the manganese is the same as that in the starting complex, the system offers the hope that we can eventually make the process catalytic, *i.e.* we avoid the necessity of having to regenerate Mn^{III}. We are currently investigating methods of sustaining this reaction.

Finally, we point out that all the available evidence suggests a homolytic rather than heterolytic fission of water. The latter would probably involve an oxidation state change by the manganese. Very careful monitoring of the reaction in a specially designed e.s.r. tube gave no indication of manganese(II) species, showing that there is no oxidation state change from Mn^{III} (e.s.r. inactive) to Mn^{II} (e.s.r. active). Moreover, it also suggests that other radicals formed were short-lived and not detectable by e.s.r. Additional evidence that protons are not formed during photolysis derives from the known fact, now thoroughly confirmed by our experiments, that aqueous protons do not react with quinone to produce hydroquinone. 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. Recently, manganese–quinone complexes have been isolated.[14]

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† We have recently commented on the gross changes in reactivity of these high-valent manganese Schiff base complexes on slight changes in the ligand by isolating [Mn(salen)(CO)]$_2$(ClO_4)$_2$ [salen = *N,N'*-ethylenebis(salicylideneaminato)]. We could not isolate such a complex using the saltm ligand (ref. 11). Of the 50 such complexes investigated here only that of [Mn(saltm)(H_2O)]ClO_4 showed good photolysis behaviour; the analogues of salen and salbutn [salbutn = *N,N'*-butylenebis(salicylideneaminato)] show slight activity, whilst the others are inactive.