the basis of room temperature irradiations.[10,11] Irradiation of **8** gives **9** as a secondary product. A photostationary state is established between **8** and **9**. The ketene (**8**) has been trapped by warming in an argon matrix containing methanol. The product is identified as the known ester (**11**)[11] by infrared and mass spectrometry (ν_{CO} 1730 cm^{-1}; *m/e* 162). The spectra of **8** (2132 cm^{-1}; $\lambda_{max}{}^{2MeTHF}$ 251, 289, 295 nm; Figure 3)[2] and **9** (2040 cm^{-1}; $\lambda_{max}{}^{2MeTHF}$ 520 nm; Figure 3)[2] are quite similar to those of **2** and **3**. It is interesting to note that the absorption maximum for **9** lies to the red from that of **3**. The interconversions of **2** and **3** and of **8** and **9** constitute two novel photochromic systems since **2** and **8** are colorless while **3** and **9** are orange and purple-red, respectively.

Acknowledgment. This research was supported by Grant MPS75-10939 from the National Science Foundation and Grant HD9279 from the National Institute of Child Health and Human Development, U.S. Public Health Service.

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Manganese(II) Gluconate. Redox Model for Photosynthetic Oxygen Evolution

Sir:

In spite of the importance and long-term interest in the oxygen-evolution step of photosystem II in green-plant photosynthesis,[1] there is neither agreement as to the electron-transfer mechanism nor to the manganese oxidation states and their number in the active group. One recent discussion proposes a two-quantum process with the manganese first oxidized from the +2 to the +3 state and then from +3 to the +4 state.[2] In support of this mechanism are studies of the photoactivation process[3] and of the functional sites of manganese within photosystem II.[4] Two earlier studies[5,6] provide a thorough review of the role of manganese and its photoactivation in photosystem II. An alternative four-step mechanism has been proposed[7] for the oxygen-evolution reaction, and has received experimental support from flash photolysis experiments.[8] The latter have led to the formulation of a number of alternative mechanistic models.[9] A recent investigation[10] concludes that there are three manganese atoms per water-oxidizing unit and that the three are equivalent. Almost coincidentally a three-manganese model system has been proposed[11] with a concerted reaction sequence that involves hydroperoxo and peroxo intermediates.

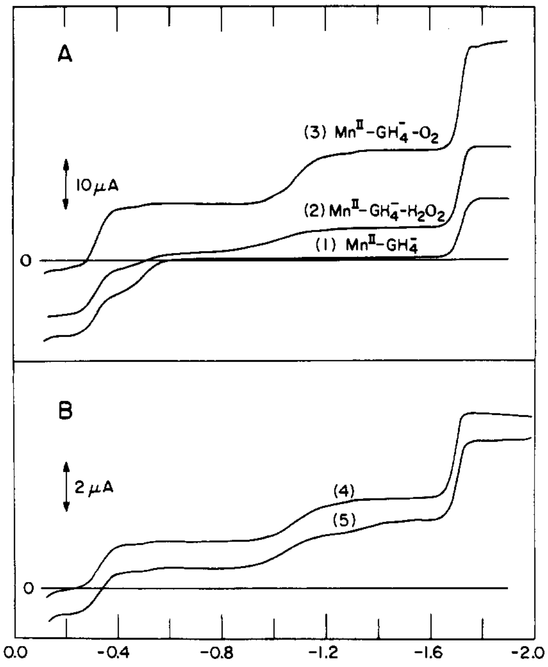
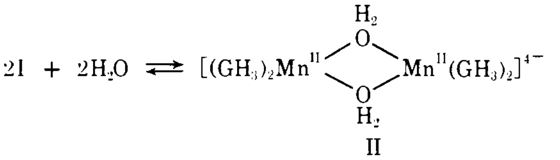


Figure 1. Polarograms of manganese in 0.1 *F* lithium gluconate ($LiGH_4$) and 0.3 *F* LiOH. A (1), 5 m*F* $Mn^{II}(GH_4)_2$ (Charles Pfizer Co.), colorless; (2), solution (1) plus 5 m*F* H_2O_2, brown, λ_{max}, 230 nm (ϵ, 8560), 462 (ϵ, 156), 500 (ϵ, 152); (3), solution (1) plus 1 atm of O_2 bubbled for 20 min, "cherry" red, λ_{max}, 273 nm (ϵ, 14300), 387 (ϵ, 2220), 515 (ϵ, 294). The latter solution also can be obtained from solution (1) by electrolysis at −0.2 V vs. SCE or by addition of $K_3Fe(CN)_6$ in a 2-to-1 mole ratio. Solutions are degassed with argon prior to recording their polarograms. B (4), 0.6 m*F* $Mn^{II}(GH_4)_2$ electrolyzed at −0.2 V vs. SCE with a Hg-pool electrode in a sealed cell (oxidation complete in about 30 min); (5), solution (4) after being degassed with argon for 2 hr. Similar results obtained for a 5 m*F* $Mn^{II}(GH_4)_2$ solution, but oxygen removal only 20% complete after 4 hr of argon degassing; 60% complete after 18 hr. Voltage scan-rate, 0.3 V min^{-1}; DME drop time, 4.0 sec. Curves represent the envelope of the maxima of the DME current oscillations, reducing current above zero axis and oxidizing current below. Increasing potentiometric promotion of oxidation to the left and of reduction to the right.

Because the conversion of water to oxygen is a four-electron process that requires two water molecules, the electron transfer mechanism for the photosynthetic manganese group is an intriguing and challenging question. The current belief is that manganese(II) is the oxidation state of the resting system and that it is converted by photooxidants to the +3 and/or +4 state.[10] These unresolved questions have prompted us to seek manganese complexes and solution conditions which result in oxidation-reduction chemistry that mimics that of the water-oxidizing species associated with photosystem II.

The manganese(II) gluconate complex[12] $[Mn^{II}(GH_3)_2]^{2-}$ (I) in basic media represents a system that undergoes oxidation-reduction chemistry which parallels much that is observed for the manganese group in photosystem II. It also represents a system that reversibly binds molecular oxygen. Figure 1A illustrates the polarographic behavior of I, of I in the presence of an equimolar amount of H_2O_2, and of I exposed to O_2 at 1 atm for 20 min prior to degassing with argon. Controlled potential electrolysis of I at −0.2 V vs. SCE results in a two-electron oxidation and a solution that gives curve (4) of Figure 1B. The effect of degassing with argon is indicated by the bottom curve of Figure 1B. Chemical oxidation of I with HgO or $K_3Fe(CN)_6$ yields a polarogram similar to curve (4); the titration stoichiometry is two equivalents per Mn. For the solution conditions of Figure 1, but in the absence of manganese ion, O_2 is reduced in two steps at −0.2 and −1.23 V vs. SCE, and H_2O_2 is reduced at −1.23 V and oxidized at −0.2 V.

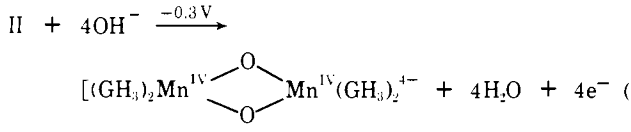
On the basis of the data of Figure 1 and of related electrochemical and spectrophotometric studies, the oxidation–reduction chemistry of I can be summarized by a set of reactions. Polarographic measurements over a range of concentrations and magnetic susceptibility measurements indicate that I probably dimerizes when it is more than 5 m*M*.



(1)

II

Figure 1A indicates that the Mn^{II} complexes are oxidized at −0.55 and at −0.3 V vs. SCE. However, the −0.55 V wave appears to form only a surface film; controlled potential electrolysis at −0.45 V results in negligible oxidation. In contrast, electrolysis at −0.2 V results in a two-electron-per-Mn^{II} oxidation (see curve (4) of Figure 1B).



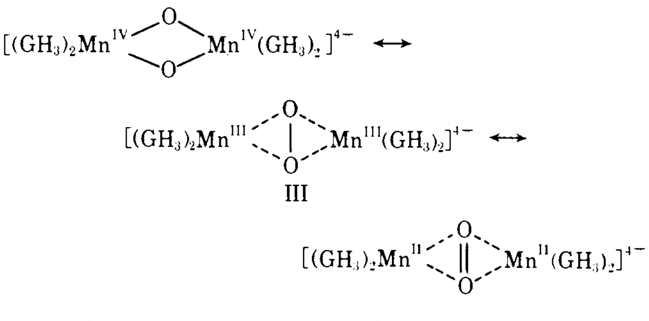
(2)

III

Because of the reversible uptake of O_2 by II and loss by III, as indicated by Figure 1,

$$\text{III} \rightleftharpoons \text{II} + O_2 \tag{3}$$

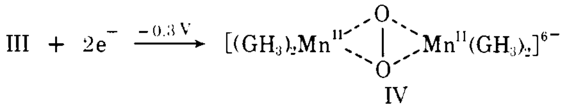
a more delocalized electronic structure for III is likely with some peroxo and oxygen adduct character.



III

An alternative interpretation of Figure 1B (rather than eq 3) is that III slowly oxidizes gluconate by an intramolecular process.[13] Measurements of Ar-purged solutions of III with an oxygen membrane electrode (Beckman Model 1008) indicate O_2 partial pressures below the sensitivity of the instrument. However, neutralization of such solutions with acid results in measurable O_2 partial pressures at pH 12 and a partial pressure of 1 atm at pH 7 (as well as the formation of O_2 bubbles).

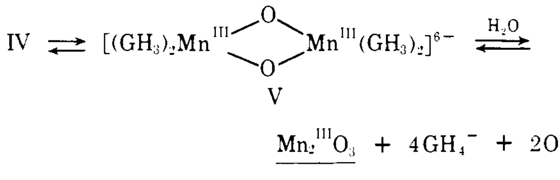
The electrochemistry of III indicates that it is reduced by a one-electron-per-Mn process at −0.3 V to give a system similar to that for curve (2) of Figure 1A (II + H_2O_2)



(4)

IV

Apparently the latter is involved in a hydrolytic equilibrium process



(5)

with IV having a one-electron-per-Mn reduction wave at −1.1 V and V a reduction wave at −0.55 V; both reductions yield II. There is some electrochemical and analytical evidence that III also slowly attacks the medium

$$\text{III} + 3OH^- \longrightarrow \text{IV} + HO_2^- + H_2O \tag{6}$$

Magnetic susceptibility measurements indicate that the manganese oxidation states of II, III, and IV are +2, +4, and +3, respectively.

In summary, chemical or electrochemical oxidation of II at −0.3 V yields III, which, under conditions of low oxygen partial pressures, evolves molecular oxygen plus II. Such a process mimics much of the oxidation–reduction chemistry that has been postulated for the manganese group of photosystem II. The unique feature of this system may be a soluble manganese complex in an aprotic medium. Other solvents and ligands are under investigation to test his proposition.

For the solution conditions of Figure 1 the thermodynamic potential for the four-electron oxidation of water to oxygen is +0.2 V vs. SCE,[14] with the formation of the (O–O) group undoubtedly being the most difficult mechanistic step. In contrast, Figure 1 indicates that in the presence of II water can be oxidized to oxygen at −0.3 V. Conversion of II to III (eq 2) may provide a sterically and kinetically convenient path for water oxidation, and III, as a highly delocalized manganese–oxygen adduct, may be the basis for the observed low-energy path and the means to the pairing of oxygen atoms. The essential role of manganese in the photosynthetic oxygen evolution reaction may be due to the unique oxidation–reduction chemistry and electron delocalization of species similar to III.

The present studies are being extended to other ligands and media to ascertain their effect upon the redox reactions. The kinetics of the several reaction steps that have been outlined are under study, and the solution structures of the various postulated species are being investigated by spectroscopic methods.

Acknowledgment. This work was supported in part by an Intramural Research Grant from the University of California, Riverside, and by the National Science Foundation under Grant No. MPS 73-05204. We are grateful for a Predoctoral Fellowship to M.E.B. from the Catholic University of Chile, and to L. A. Willis for spectrophotometric measurements and T. L. Riechel for magnetic measurements.

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(12) The results of a series of polarographic and controlled potential studies indicate that the formula for the Mn^{II} complex with gluconate ion ($C_6H_{10}O_7^-$, carboxylate derivative of D-glucose) in basic media is

$Mn^{II}(GH_3)_2^{2-}$ with GH_3^{2-} representing the dianion of gluconic acid which results from the removal of the carboxylate proton and one of the secondary alcoholic protons.

(13) A study of the reactivity of III and IV with various organic functional groups is in progress to test this proposition. However, the 60% decrease of III in 2 hr from Ar purging for a 0.6 mF solution in contrast to a 20% decrease in 4 hr for a 5 mF solution indicates that reversible O_2 binding is the dominant process at lower concentrations of III.

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Received June 21, 1975

Preparation of 1,3-Oxazin-6-one. A Potential Precursor to Azacyclobutadiene

Sir:

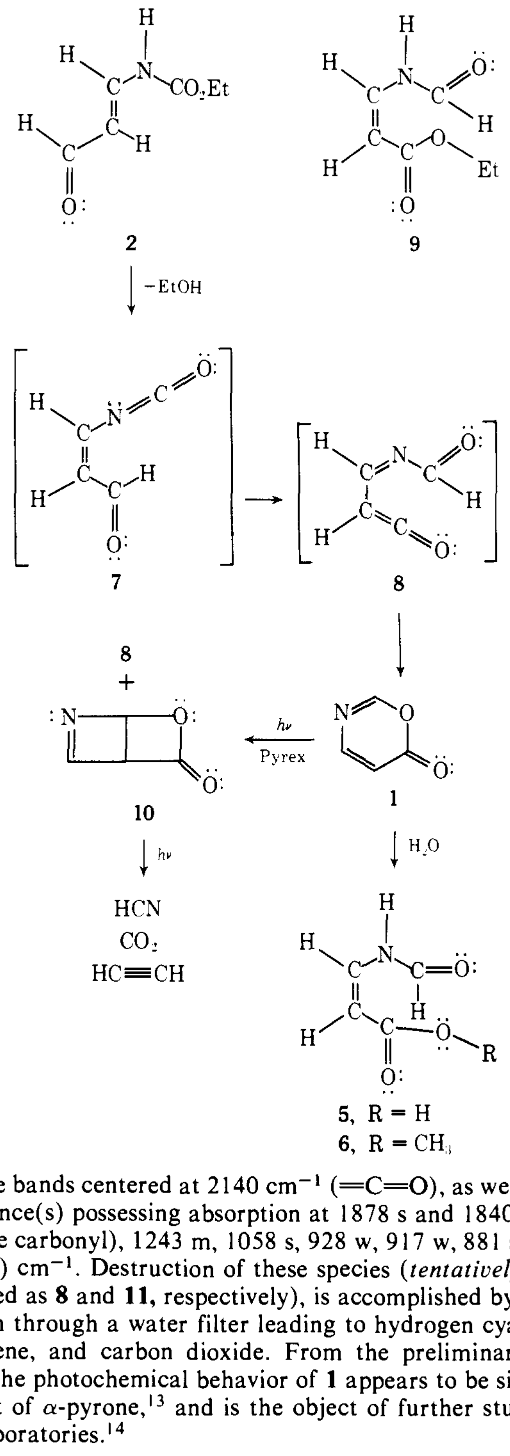
Despite divers reports concerning derivatives of 1,*n*-oxazin-6-ones ("aza-α-pyrones"), in no case has the synthesis of the parent species been realized.[1] These systems (which are potential precursors to the unknown azacyclobutadiene[2,3]) by analogy with the chemistry of α-pyrone,[4] hold the promise of entry to the dihydropyridine manifold. They are also substantial curiosities in and of themselves, because of the presence of imine and ester functionality in a unique cyclic array.

The preparation of 1,3-oxazin-6-one (**1**) has now been achieved via a novel route involving pyrolysis of *trans*-3-ethoxycarbonylaminoprop-2-enal (**2**) (Scheme I). The carbamate **2** was prepared by dropwise addition of ethyl chloroformate (**3**) to a (0°) cooled solution of equivalent amounts (0.05 mol) of β-aminoacrolein[5] (**4**) and triethylamine in 30 ml of acetonitrile. After being stirred at 25° for 10 hr, 50 ml of ether was added to the mixture, which was, in turn, refrigerated overnight, filtered, and concentrated. Purification of the residue by silica gel chromatography (ether-pentane, 1:10) followed by recrystallization from ether-pentane, gave the colorless solid **2**: mp 67-68° (lit.[6] mp 66-67°); 86%; NMR ($CDCl_3$), δ1.34 (3 H, t, *J* = 7.5 Hz), 4.39 (2 H, q, *J* = 7.5 Hz), 5.94 (1 H, dd, *J* = 14.5 Hz, *J* = 8.5 Hz), 7.91 (1 H, dd, *J* = 14.5 Hz, *J* = 12.5 Hz), 9.41 (1 H, br d, *J* = 12.5 Hz), 9.65 ppm (1 H, d, *J* = 8.5 Hz); $\nu_{max}^{CCl_4}$ 3417 m, 1744 s, 1662 m, 1638 vs, and 1140 (s) cm^{-1}. λ_{max}^{ether} 257 nm ($\epsilon \sim 3.6 \times 10^4$); M^+ 143.

When a 9% solution of **2** in benzene was passed through a quartz tube[7] heated to 650°, a 27% yield[8] was attained of a colorless oil, **1**: $\nu_{max}^{CCl_4}$ 1801 m, 1777 s, 1619 s, 1549 m, 1219 s, and 1111 (s) cm^{-1}; NMR (CCl_4), δ 6.38 (1 H, dd, *J* = 7.2 Hz, *J* = 1.8 Hz), 7.78 (1 H, d, *J* = 7.2 Hz), and 8.09 (1 H, br s); M^+ 97; $M^+ - CO$, 69; $M^+ - (CO + HCN)$, 42; λ_{max}^{ether} 262.5 ($\epsilon \sim 10^4$).[9] Compound **1** is very sensitive to moisture and undergoes ready hydrolysis to *cis*-2-(formylamino)acrylic acid (**5**), characterized as its methyl ester **6**: mp 42°; NMR ($CDCl_3$), δ 3.78 (3 H, s), 5.27 (1 H, d, *J* = 9.3 Hz), 7.60 (1 H, dd, *J* = 11.5 Hz, *J* = 9.3 Hz), 8.43 (1 H, br s), and 10.44 (1 H, broad); $\nu_{max}^{CCl_4}$ 3320 m, 1719 m, 1690 s, 1638 s, 1205 (s) cm^{-1}; λ_{max}^{ether} 264 nm ($\epsilon \sim 1.7 \times 10^4$); M^+ 130.

Preliminary studies of the thermal behavior of **2** in chloroform indicate that **2** is labile at even 75°, and gives rise to a mixture whose infrared spectrum shows a band at 2250 cm^{-1}, typical of isocyanate functionality.[11] Possibly this observation provides a clue to the remarkable conversion of **2** to **1** which may be mediated by the β-isocyanatoacrolein (**7**).[10-12]

Scheme I



Irradiation of argon matrix-isolated **1** (M/R ~ 300) with Pyrex-filtered mercury lamp light produces a species with intense bands centered at 2140 cm^{-1} (=C=O), as well as a substance(s) possessing absorption at 1878 s and 1840 s (β-lactone carbonyl), 1243 m, 1058 s, 928 w, 917 w, 881 s, and 870 (s) cm^{-1}. Destruction of these species (*tentatively* formulated as **8** and **11**, respectively), is accomplished by irradiation through a water filter leading to hydrogen cyanide, acetylene, and carbon dioxide. From the preliminary results, the photochemical behavior of **1** appears to be similar to that of α-pyrone,[13] and is the object of further study in our laboratories.[14]

Acknowledgment is made to the donors of the Petroleum Research Fund, administered by the American Chemical Society, and to the National Science Foundation for support of this research. Special thanks are due Mr. Joe Laureni for preliminary experiments on the photochemistry of **1**.

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