(6) We have observed that the amide ion also participates in a similar gas phase reaction with carbon disulfide to form the thiocyanate ion: $NH_2^- + CS_2 \rightarrow NCS^- + H_2S$.

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Far Red Photogalvanic Splitting of Water by Chlorophyll a Dihydrate. A New Model of Plant Photosynthesis

Sir:

Recently we have studied in detail the properties of P700, the chlorophyll a monohydrate dimer (Chl $a\cdot H_2O)_2$, on the basis of in vitro Chl a-H_2O interactions.[1-4] In this communication, we describe the observation of hitherto unreported Chl a photogalvanic water splitting reactions that result from photoactivation of the C-9 keto-linked chlorophyll a dihydrate aggregate (Chl $a\cdot 2H_2O)_n$.[2a,5]

We made use of the recently developed[6] Chl a photogalvanic cell in the study of Chl a-H_2O photoreactions. The experimental assembly, which has been described previously,[6] consists of two half cells (1) separated by a salt bridge. $LiClO_4$ or KCl was the electrolyte. The Chl a was plated on a Pt electrode from a 10^{-4} M solution in undried 2,2,4-trimethylpentane by a procedure similar to that described by Tang and Albrecht.[7] Film thicknesses corresponding to $\leq 10^{14}$ Chl a molecules cm^{-2} were employed. The content of dissolved oxygen in the cell assembly was controlled in the usual manner.[6] The pH values of the half cells were maintained using citric acid-NaH_2PO_4 buffer solutions in the pH 2-8 range, and NaOH-$NaHCO_3$ at pH >8. Upon illumination of the chlorophyll, a positive photopotential is developed at the Chl a-Pt electrode, generating a flow of electrons that originates from the Chl a free half cell.

$$\mathrm{Pt|Chl\ a{:}H_2O||H_2O|Pt} \qquad (1)$$

The photochemical action spectrum of the freshly prepared Pt-Chl a electrode shows an approximately equal distribution of the observed photocurrent in two bands with maxima at 673 and 740 nm, respectively (see Figure 1A (a) of ref 6b). The latter band is attributed to the dihydrate polymer (Chl $a\cdot 2H_2O)_n$.[2a,d,6b] The 673-nm band has been ascribed to a Gaussian envelope of monomeric and dimeric complexes of chlorophyll a monohydrate.[6b] The photogalvanic action of a rigorously deoxygenated cell is predominantly transient in nature. A large part (~90%) of the observed photogalvanic current decays exponentially (half-life time ~1 s) under steady illumination conditions. The photocurrents recorded in Figure 1 correspond to the initial (*t* 0) readings. When the light is switched off, a reverse photocurrent of the same magnitude is observed. In this case, the observed reversible photogalvanic effects lead to no net photochemical change in the two half cells. These effects appear to be related to the reversible "phototropic" bleaching effect described by Rabinowitch[8] and Livingston.[9]

A minor (~10%) time-independent component in the photogalvanic action is also observed. This component is absent in the dark cycle and signifies an irreversible photoinduced redox reaction between the two half cells due either to unintentional impurities or, in view of the chemical constituents of 1, to the Chl a sensitized half cell reactions

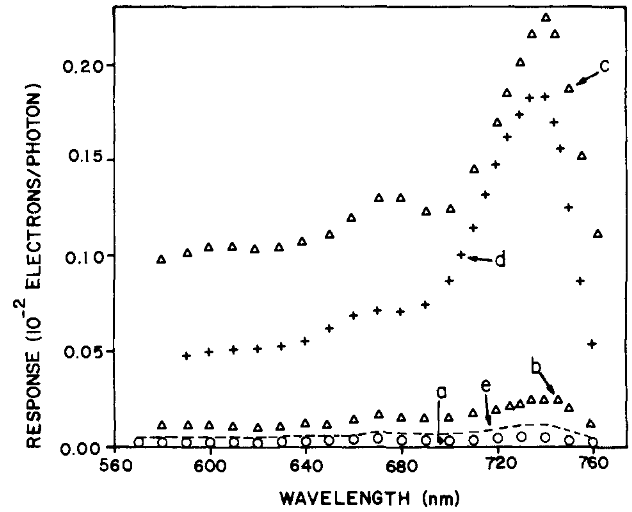


Figure 1. The Fe^{2+} photogalvanic enhancement effect of a freshly prepared Chl a-Pt sample: (a) before Fe^{2+} addition at pH 7, action spectrum consisting of two approximately equal bands at 673 and 740 nm (see Figure 1A (a) of ref 6b for the same spectrum on an expanded scale). (b) at pH 5 in Chl a half cell and pH 7 in Chl a free half cell; (c) at pH 3 in Chl a half cell and pH 7 in Chl a free half cell; (d) after addition of Fe^{2+} (10^{-3} M) in a; (e) at pH 7 in Chl a half cell and pH 11 in Chl a free half cell in the absence of divalent cations. The predominance of the 740-nm band in the enhanced action spectra underscores the critical role of (Chl $a\cdot 2H_2O)_n$ in the water splitting reactions 2 and 3. The action spectra a–e are measured from the initial (*t*0) readings of the photogalvanic response. The corresponding spectra for the irreversible component of the photogalvanic response are lower in intensity by a factor of two to ten, depending on experimental conditions (see text), but are essentially indistinguishable from spectra a–e in spectral distributions.

$$\text{Chl a-Pt photocathode:}\quad 2H_2O + 2e \rightarrow H_2 + 2OH^- \qquad E_0 = -0.42\ V \qquad (2)$$

$$\text{Chl a free anode:}\quad 2H_2O \rightarrow 4H^+ + O_2 + 4e \qquad (3) \qquad E_0 = -0.81\ V$$

We thus envisage reaction 2 as the electron acceptor in the photooxidation of the chlorophyll. The radical cation of the oxidized chlorophyll is then reduced to the neutral state by the oxidation of water in (3).

To establish the possible implication of reactions 2 and 3 in photogalvanic conversion, we have made the following observations. (i) The photocurrent increases dramatically with decreasing pH of the Chl a half cell (Figures 1a–c). (ii) The photocurrent is also enhanced by the introduction of Fe^{2+} ions in the Chl a half cell (Figure 1d). The observed effect increases with increasing concentration of Fe^{2+}. The steady-state operation of the photogalvanic cell results in the precipitation of $Fe(OH)_2$. Similar enhancement effects are also observed when Ba^{2+}, Ca^{2+}, and Zn^{2+} ions are added in the Chl a cell. (iii) On enhancement of the photogalvanic response in i and ii, the time-independent component of the observed steady-state photocurrent also becomes significantly enhanced, being 50% of the initial (*t* 0) readings in Figures 1c and 1d. (iv) The action spectra in Figure 1 show that the dihydrate polymer (Chl $a\cdot 2H_2O)_n$, corresponding to the 740-nm band,[6b] is primarily responsible for the enhancement effects. The 673-nm band (attributable to monohydrate Chl a complexes[6b]), which is approximately equal in importance to the 740-nm band at pH 7 in the absence of divalent cations such as Fe^{2+}, Ba^{2+}, Ca^{2+}, or Zn^{2+} (see Figure 1a and Figure 1A (a) of ref 6b), becomes relatively unimportant upon addition of the low-pH buffers or divalent cations. (v) An increase in the photocurrent is also observed when the pH of the Chl a free half cell is increased (Figure 1e), although the effect is significantly less pronounced than the corresponding effects in i and ii. (vi) The pH effect

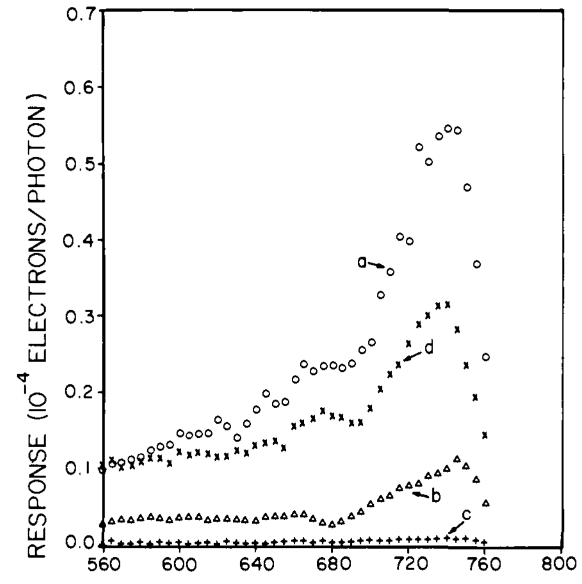


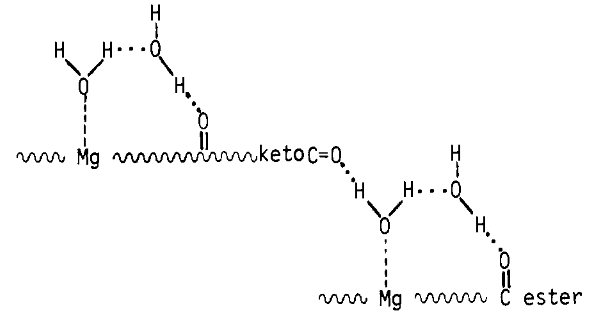
Figure 2. Effects of O_2 quenching of (CHl a·$2H_2O)_n$ light reaction: (a) cell in which both the Chl a plated and Chl a free half cells have been thoroughly degassed; (b) cell from a with the Chl a–Pt half cell bubbled with O_2 for 30 min; (c) cell from a with the Chl a free half cell bubbled with O_2 for 30 min; (d) cell from b or c bubbled with pure Ar gas for 30 min. The Chl a–Pt electrode employed in this experiment was rinsed with *n*-pentane to wash off the monohydrate complexes (corresponding to the 673-nm band in Figure 1 and Figure 1A (a) of ref 6b). The dihydrate film (Chl a·$2H_2O)_n$ is insoluble in *n*-pentane. The action spectra a–d have been measured for the irreversible component of the photogalvanic response. The corresponding spectra for the transient signal, measured at t 0, are 10 times as great in intensity and are the same in spectral distributions in all cases except b. In b the irreversible component is about half that of the initial transient signal height. The distinctly different spectral shape of b suggests a different photochemical pathway for the chlorophyll light reaction in the presence of oxygen.

in v is independent of the Chl a film thickness. However, the dramatic enhancement effects in i and ii are only observed in thin Chl a films ($\lesssim 10^{15}$ Chl a molecules cm^{-2}). (vii) The observed effects in i–vi are quenched by O_2. The effects of O_2 on the (Chl a·$2H_2O)_n$ light reaction are shown in Figure 2.

Observations i–iii and v–vii provide positive evidence for reactions 2 and 3. The precipitation of the highly insoluble ($K_{sp} = 1.65 \times 10^{-14}$) ferrous hydroxide presumably displaces the photocathodic reaction 2 far to the right. The acidic medium provided by the low-pH buffer solutions likewise exerts a favorable influence on (2). We note that effect v may be similarly accounted for in terms of product disposal in reaction 3. The sharp contrast in the extent of the enhancement effects (compare Figures 1c,d and 1e) in i and v has led us to the conclusion that the magnitude of effects i and ii (Figures 1c–d) may be attributable not only to the enhancement of (2), but also to an inhibition of the water oxidation process from occurring in the Chl a half cell. This conclusion seems to be consistent with the observed O_2 quenching effect vii (Figure 2c). The presence of O_2 in the Chl a free half cell is expected to block the forward direction of (3) in the anodic cell compartment of (1). This blockade presumably leads to the consummation of the water photolysis process (i.e., both reactions 2 and 3) within the Chl a half cell, short-circuiting the external flow of electrons in (1).

The O_2 quenching of reaction 1 (Figure 2b) is reminiscent of a similar observation made by Livingston[9] on the phototropic bleaching of Chl a-methanol complexes. This effect may be attributed to Chl a triplet quenching by O_2,[9] which is consistent with the singlet–triplet upconversion mechanism of Chl a light reactions.[1,3c,d] The distinctly different action spectrum of the irreversible photoelectrochemical reaction in the presence of O_2 (Figure 2b) suggests a photochemical pathway, possibly sensitized by the first excited singlet of the chlorophyll, which differs from that of chlorophyll–water light reactions in the absence of O_2.

Observation iv underscores the unique role of (Chl a·$2H_2O)_n$ in reactions 2 and 3. The ability of hydrated chlorophyll to associate via C-9 and C-10 $C{=}O\cdots H(H)O\cdots Mg$ interactions under various conditions[4] suggests the possibility of two different light reactions. It is believed that the onset of photoactivity in the P700 reaction center[4] is accompanied by the photoenolization of (Chl a·$H_2O)_2$.[6b] An examination of the corresponding photoactivation process involving C-9 $C{=}O\cdots H(H)O\cdots Mg$ interactions results in quite a different picture. For example, photoactivation of the charge-transfer state C-9 $C^+{-}OH\cdots(H)O{-}Mg^-$ in (Chl a·$2H_2O)_2$[4], in which the bonding interactions are assumed to be the same as those found in the corresponding 740-nm absorbing polymer (Chl a·$2H_2O)_n$,[2a,5] would result directly in the π delocalization of the positive charge due to the proximity of the C-9 keto group to the chlorin macrocycle. Moreover, it appears that the geometrical arrangement of the bonding interactions in A would preclude the possibility of photoenolization of the ring V cyclopentanone group.



A

The addition of divalent cations or lowering the pH of the aqueous environment affects the photochemical interactions at the Chl a–H_2O interface. The observed photogalvanic response manifests the chemical interactions between the photooxidized chlorophyll and the water in the Chl a free half cell via an external circuit across the two Pt electrodes in 1. The influence of the Chl a film thickness on the enhancement effects in vi thus suggests a cooperation between the photochemical events attending the Chl a–H_2O and Chl a–Pt boundaries.

The present observation of two different photoreactions of Chl a–H_2O aggregates in vitro coincides with the general belief that plant photosynthesis is powered by two different light reactions of Chl a.[10,11] We have previously associated the monohydrate dimer (Chl a·$H_2O)_2$ with the P700 reaction center in vivo.[1-4] The results described above suggest the possibility that a dimeric aggregate similar to A may be the photoreaction center responsible for the water-splitting reaction in photosynthesis.[12,13] From difference spectral determinations, the absorption maximum of the water splitting reaction Chl a aggregates has been found to occur within the 682–695-nm wavelength region.[14] The large uncertainty in these peak position determinations may be due to the variability in sample preparations.[14] The dihydrate dimer (Chl a·$2H_2O)_2$ has an absorption maximum at 695 nm.[4,15] In A, the two monomeric units observe a C_1 symmetry. In (Chl a·$2H_2O)_2$ one dihydrate monomer acts as a proton donor and the other a proton acceptor through the C-9 keto $C{=}O\cdots H(H)O\cdots Mg$ interaction. This inequality may account for the observed[14b] nonequivalence in the spin delocalization in the photooxidized water-splitting reaction center in vivo.

In the in vivo water-splitting process, oxygen evolution is apparently mediated by manganese ions[16] which presumably eliminate the deleterious oxygen inhibition effects. The photooxidation of the chlorophyll in vivo results in the reduction of water-soluble ferredoxin ($E_0 = -0.42$ V),[17] leading to the reduction of NADP at -0.32 V.[18] The matching of the reduction potential of ferredoxin with that of water in eq 2 may possibly be of significance. If we suppose that the in vivo light reaction directly connects water oxidation with ferredoxin reduction in a single two-quantum photoevent according to the energy upconversion postulate,[1,3c] we arrive at the overall stoichiometry[18a]

$$2H_2O + 4Fd_{ox} + 2ADP + 2P_i \xrightarrow[(Chl\ a\cdot 2H_2O)_2]{h\nu} 4Fd_{red} + 4H^+ + 2ATP + O_2 \quad (4)$$

In eq 4, the transfer of four electrons from H_2O to ferredoxin is accomplished by the expenditure of eight quanta. The reduction of ferredoxin is accompanied[18a] by a concomitant formation of ATP in photophosphorylation. The P700 light reaction is responsible for cyclic photophosphorylation,[19] leading to an additional four quanta/two electrons requirement.[20] The present scheme is consistent with the generally accepted view that oxygen evolution in plant photosynthesis is eight quanta/O_2, and that frequently observed higher-than-eight quanta requirements for the overall process may be attributed to cyclic photophosphorylation.[20] We note that our interpretation is in general agreement with the scheme proposed by Arnon,[20,21] except that Arnon had invoked two separate one-quantum photoevents in the activation of 4, and provides a viable alternate to the "zig-zag" scheme[10,11] of two sequential one-quantum light reactions, in which the NADP reduction occurs off the P700 light reaction and the water-splitting reaction is associated with a second photosystem (PSII) linked to the P700 (PSI) through a dark bridge of charge carriers.[22]

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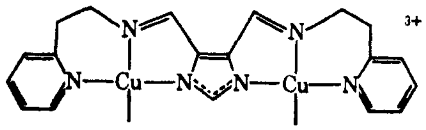
Magnetic Exchange Interactions in Imidazolate Bridged Copper(II) Complexes

Sir:

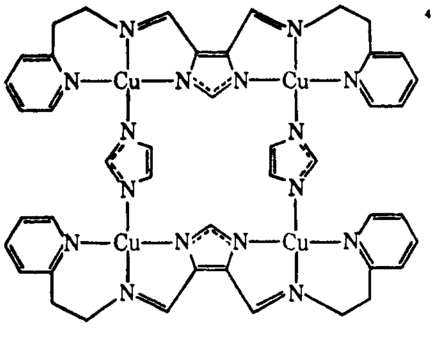
The properties of soluble binuclear imidazolate (im) bridged complexes are of current interest because the active site of the enzyme bovine erythrocyte superoxide dismutase (SOD) is known[1] to have a histidine bridged copper(II)-zinc(II) center in each of two identical subunits. An imidazolate (histidine) bridge has also been proposed[2] to exist between copper and iron in cytochrome *c* oxidase. Oligomeric and polymeric imidazolate bridged metal complexes are quite common in the solid state[3] and have occasionally been identified in solution.[4] Recently we reported[5] the synthesis and characterization of I and II, the first discrete imidazolate bridged transition metal complexes.[6] The existence in aqueous solution of the equilibrium reaction[5] shown in eq 1

$$II + 4H^+ \rightleftharpoons 2I + 2imH_2^+ \quad (1)$$

suggested that it should be possible to prepare binuclear imidazolate bridged complexes with simpler ligands than bpim. Here we describe the synthesis of one such compound, III, as well as an investigation of the temperature dependence of the



Cu_2bpim^{3+}, I



$[Cu_2(bpim)(im)]_2^{4+}$, II