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Electron Spin Resonance Observation of the Photooxidation of Hydrated Chlorophyll a Dimers by Water. In Vitro Photochemical Characterization of Reaction Centers in Photosynthesis

Sir:

In 1953, Levitt proposed that the light reaction in photosynthesis results from the photooxidation of the chlorophyll.[1] In the succeeding years, photoinduced electron spin resonance (ESR) signals were observed in photosynthetic whole cells and chloroplast preparations.[2] A reversible ESR signal, known as signal I, was found to have the free electron g value 2.0025 and a peak-to-peak width of about 7.5 G.[2] In 1971, Norris et al. proposed that the in vivo unpaired electron in signal I was delocalized over two Chl a molecules.[3] These authors postulated that the width of the ESR signal is narrowed by a factor of $\sim 1/\sqrt{n}$ when an unpaired electron is spread over n Chl a molecules. A comparison of the ESR signal width for the monomeric Chl a radical[4] in vitro with that of the P700 in vivo radical shows that the latter is reduced relative to the former by a factor of $\sim 1/\sqrt{2}$.[3] The P700 photoreaction in plant photosynthesis is generally considered[5] to be not directly associated with the water splitting reaction.[5,6] In 1974, Van Gorkum et al. reported[7] a photoinduced ESR signal associated with the water-splitting photoreaction in vivo. In the present communication we describe the first ESR observation of in vitro radical cations of Chl a dimers that are light induced without the introduction of extraneous electron acceptors. We show that these radical cations most probably arise from the photoreactions between water and the dimers of the monohydrate and the dihydrate of Chl a, $(\text{Chl a}\cdot H_2O)_2$ and $(\text{Chl a}\cdot 2H_2O)_2$, which have, respectively, been proposed to be the P700 and the water-splitting reaction centers in plant photosynthesis.[8]

The observed photogalvanic response in Chl a–H_2O cells has been attributed[8] to the photochemical splitting of water by the chlorophyll according to the half-cell reactions (at pH 7)

$$\text{Chl a–Pt photocathode: } 2H_2O + 2e \rightarrow H_2 + 2OH^- \qquad E_0 = -0.42 \text{ V} \quad (1)$$

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

Evidence for reactions 1 and 2 has been derived from the observation of a greatly enhanced P740 $(\text{Chl a}\cdot 2H_2O)_n$ photogalvanic response on introduction of appropriate pH buffers (low pH values at the Chl a half cell and high pH values at the Chl a free half cell). The enhancement effects have been attributed to product disposal of H^+ and OH^- in reactions 1 and 2, respectively. Similar enhancement effects, observed when Fe^{2+}, Ba^{2+}, and Zn^{2+} ions are introduced in the Chl a half cell, are accompanied by the precipitation of the corresponding insoluble hydroxides,[8] providing further positive evidence for the occurrence of reaction 1.

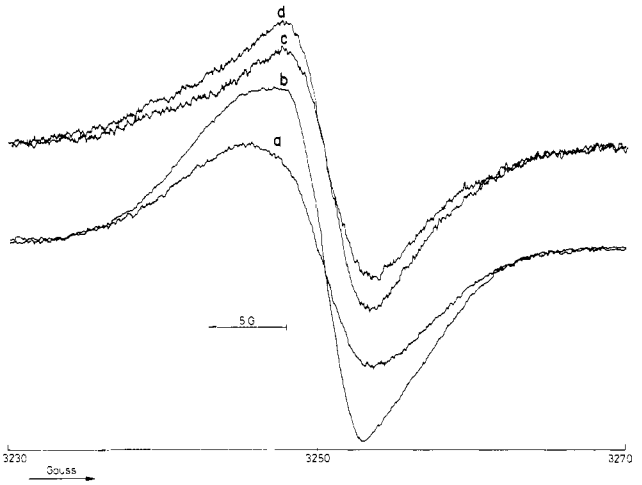

Figure 1. Light-induced ESR spectrum of hydrated Chl a radical cation in dry 1:1 n-pentane and cyclohexane: (a) 10 °C dark spectrum after several cycles of illumination; (b) 10 °C spectrum of sample in a under subsequent illumination by white light; (c) dark spectrum at −140 °C after several cycles of illumination; (d) spectrum of sample in c during illumination at −140 °C. The experimental conditions are given as follows: microwave power, 10 mV; modulation, 6.3 G; gain (a) 3.2×10^3, (b) 4×10^3, (c and d) 6.3×10^3.

The reduction of the water in reaction presumably results from the photooxidation of the chlorophyll. The oxidation of water in reaction 2 is probably caused by the reduction of the photooxidized chlorophyll to its neutral state. Experimental observations related to the Chl a–H_2O photogalvanic conversion[8] have been made in other laboratories.[9,10] It occurred to us that it would be desirable to attempt a direct detection of the photooxidation of Chl a–H_2O complexes by an ESR determination of the corresponding Chl a radical cations. In particular we hope to delineate further the recently noted[8] differences between the photochemical activities of the monohydrate dimer $(\text{Chl a}\cdot H_2O)_2$ and the dihydrate aggregate $(\text{Chl a}\cdot 2H_2O)_n$.

Chlorophyll monohydrate (Chl a·H_2O) prepared as a solid in the usual manner[11] was dissolved in a 1:1 mixture of n-pentane and cyclohexane that was dried over solid Na and degassed by freeze–thawing under vacuum. The resulting solution ($\sim 10^{-4}$ M in concentration) was encapsulated in a 4-mm-o.d. quartz Spectrosil sample tube under vacuum (5×10^{-6} Torr). The ESR experiments were carried out with a Varian E9 spectrometer equipped with a variable-temperature attachment. The sample was illuminated with white light from a 1000-W tungsten–iodide source. The optical properties of the sample preparation were monitored using a Cary 14 spectrophotometer in the usual manner.[11,12]

The experimental observations are described as follows. (i) The light-induced ESR signal is shown in Figure 1. The g value of this signal is 2.003 ± 0.001. From the decay kinetics observed after the light is turned off (see Figure 2), we note that the ESR signal consists of two components, one transient and the other long lived. (ii) The relative importance of these two components varies with the temperature. At 10 °C the signal decays within 1 s by ~20%. At −140 °C the observed ESR signal is mostly irreversible. (iii) The line shape of the 10 °C

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Table I. Comparison of the Properties of P700 and (Chl a·H_2O)$_2$ and Their Respective Radical Cations[a]

	P700	(Chl a·H_2O)$_2$	P700$^+$	(Chl a·H_2O)$_2^{+\cdot}$
Red maxima of light–dark absorption difference, nm	664, 700 (77 K)[b]			
Red absorption maxima, nm		664, 701 (121 K)[c]		
Fluorescence maximum nm	720 (77 K)[d]	720 (121 K)[c]		
Reduction potential, V			0.43[e]	$\lesssim$0.5[f]
ESR g value			2.0026[b,g]	2.003[h]
ESR line width, G			7.5 (~300 K)[g]	7.5 (283 K)[h]

[a] Additional comparisons between the optical properties of P700 and (Chl a·H_2O)$_2$ have been made by Fong et al.[13] and by Breton.[23] [b] References 23 and 30. [c] F. K. Fong, V. J. Koester, and J. S. Polles, *J. Am. Chem. Soc.*, **98**, 6406 (1976). [d] The attribution of the 77 K 720 nm in vivo fluorescence band, reported by P. Mohanty, B. Z. Braun, Govindjee, and J. P. Thornber, *Plant Cell Physiol.*, **13**, 81 (1972), and by F. Drissler, W. Hägele, D. Schmid, and W. C. Wolf, *Z. Naturforsch., A*, **32**, 88 (1977), to P700 is consistent with the expected Stokes shift in P700 fluorescence. All other observed in vivo fluorescence bands occur at wavelengths shorter than 700 nm. [e] Reference 17. [f] Reference 11. [g] Reference 2 and E. C. Weaver and G. A. Corker in ref 5, p 171. [h] Present work.

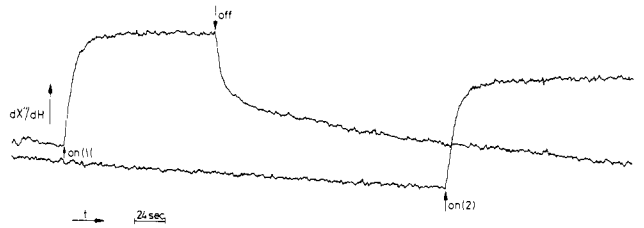

Figure 2. Kinetics of light induction and dark decay of photoinduced hydrated Chl a radical cation in 1:1 *n*-pentane and cyclohexane at 10 °C. Absorption of microwave power was monitored at the low-field first-derivative peak. The microwave power and modulation settings are the same as those given in Figure 1. The gain was 6.3 × 10^3. A preilluminated sample, after having been kept in the dark for 16 min, was illuminated at the first arrow, marked "on (1)". After another period of dark decay, the sample was again illuminated at the second arrow, marked "on (2)". The reproducible kinetic effects were reversible through many light–dark cycles. Complete dark decay of the photoinduced ESR signal took >1 h.

reversible signal is distinctly asymmetric. The corresponding long-lived component is nearly symmetrical (see Figure 1a). (iv) The asymmetry becomes more pronounced at lower temperatures. The microwave power saturation behavior of the −140 °C low-field shoulder is indistinguishable from that of the first-derivative peak. The line width of the ESR signal decreases with temperature, being 7.5 and 5.5 G at 10 and −140 °C, respectively (compare spectra a and b with c and d in Figure 1). The 10 °C long-lived component is approximately Gaussian in line shape. At low temperatures, the line shape becomes approximately Lorentzian, suggestive of an increase in the exchange narrowing with decreasing temperature. (v) At 10 °C, the peak-to-peak line width of the transient signal in Figure 1 narrows to 1.3 G 3 to 4 days after the addition of an excess of water. The appearance of the narrow-width ESR signal is accompanied by a diminution of the irreversible ESR component and by the observation of a 743-nm absorbing Chl a aggregate that has been attributed to the formation of the dihydrate polymer (Chl a·$2H_2O$)$_n$.[12]

The observed line widths of the light-induced ESR signal in i suggests the dimeric origin of the Chl a radical cations. The room-temperature peak-to-peak width of ~7.5 G is indistinguishable from that of P700$^+$.[3] The observation in i–iii of two components in the ESR signal with different decay and line shape properties implies the existence of at least two different radical cation species. From observation v we attribute the reversible ESR signal to (Chl a·$2H_2O$)$_2$. It has been established[12] that on addition of an excess amount of water in a rigorously dried nonpolar solution of chlorophyll monohydrate, which presumably exists as an equilibrium mixture of Chl a·H_2O, Chl a·$2H_2O$, Chl a_2, (Chl a·H_2O)$_2$, and (Chl a·$2H_2O$)$_2$, the equilibrium is shifted greatly in favor of the 743-nm absorbing polymer (Chl a·$2H_2O$)$_n$.[12] In $C_{16}H_{34}$ the 743-nm absorbing (Chl a·$2H_2O$)$_n$ gives rise to a reversible light-induced ESR signal having a peak-to-peak width of 0.8 ± 0.2 G.[3]

From observations i and iii–v, we attribute the long-lived ESR component to (Chl a·H_2O)$_2$, which is believed to be the P700 chlorophyll dimer[13] (see comparison of properties of P700 and (Chl a·H_2O)$_2$ in Table I). The g value 2.003 of this component is in agreement with the g value 2.0025 of P700$^+$.[3] The ESR signal of P700$^+$ reportedly has a symmetrical Gaussian line shape.[3] The slight departure from a perfectly symmetrical Gaussian line shape of the ESR signal in Figure 1a may be ascribed to a small admixture of the asymmetrical line shape of the ESR signal of (Chl a·$2H_2O$)$_2^{+\cdot}$. In the monohydrate cation (Chl a·H_2O)$_2^{+\cdot}$, the spin is delocalized over two equivalent Chl a molecules.[13] In (Chl a·$2H_2O$)$_2$ the two Chl a molecules are not equivalent, one being connected to the other through an unsymmetrical C-9 keto C=O···H(H)O···Mg bonding interaction according to the bonding interactions observed in polymeric ethyl chlorophyllide a dihydrate.[14] Accordingly only inequivalent spin delocalization is possible across the two Chl a molecules in (Chl a·$2H_2O$)$_2^{+\cdot}$. This unsymmetrical spin delocalization may account for the observed asymmetry of the ESR line shape, which otherwise may be due to the presence of a broader component with a slightly different g value. A component having a longer life than the narrower and more intense signal attributed to the primary donor "P680" has been found in particles enriched in water-splitting reaction centers.[15]

The interpretations given above are consistent with the conclusion that the dihydrate aggregate (Chl a·$2H_2O$)$_n$ is primarily responsible for the photogalvanic water-splitting reactions.[8] In redox titration experiments, it has been shown[16] that the dihydrate radical cation (Chl a·$2H_2O$)$_{n\geq 2}^{+\cdot}$ is sufficiently strong an oxidant to bring about reaction 2, whereas (Chl a·H_2O)$_2^{+\cdot}$ is not consistent with the earlier observations that the midpoint reduction potentials of the in vitro dimer (Chl a·H_2O)$_2$ and the in vivo P700 are $\lesssim$0.5[11] and 0.43 V,[17] respectively, both falling short of the 0.81 V needed for reaction 2. The present findings thus suggest that, under illumination, both (Chl a·H_2O)$_2$ and (Chl a·$2H_2O$)$_2$ are powerful electron donors that are capable of reducing water according to reaction 1. However, only (Chl a·$2H_2O$)$_2^{+\cdot}$ is regenerated in the neutral state by the water oxidation reaction 2, which accounts for the observation of the two ESR components, one transient and the other long-lived.

The bis(chlorophyllide a) ethylene glycol diester polyhydrate,[18] a molecular complex corresponding to the C_2 symmetrical exo C-9 C=O···H(H)O···Mg-linked dimer described by Boxer and Closs,[19] Shipman,[20] Fong,[13] Clarke,[21] and their co-workers is photochemically inactive[22] in the absence of an electron acceptor such as I_2[18] or tetranitromethane.[20] This photochemical inactivity is underscored by the fact that monomeric Chl a in methanolic solutions[29b] and (Chl a·H_2O)$_2$ in nonpolar solutions[11] are oxidized by I_2 in the dark, and that

even demetalated chlorophyll, pheophytin, is photooxidized at 77 K in the presence of tetranitromethane.[31] The present ESR observation[32] of the photooxidation of (Chl a·H_2O)$_2$ and (Chl a·2H_2O)$_2$ by water in the absence of extraneous oxidants thus appears to be of significance in view of the current interest in the in vitro characterization of the primary light reactions in photosynthesis[33] and the in vitro photochemical splitting of water by the chlorophyll.[8]

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Determination of Local Structures of Platinum Uridine Blues and Purples by Extended X-Ray Absorption Fine Structure Spectroscopy

Sir:

A new class of water-soluble "platinum-pyrimidine blues" have been reported to be promising antitumor agents,[1,2] although more recent results suggest otherwise.[3] These compounds, formed when *cis*-[Pt(NH_3)$_2$(H_2O)$_2$]$^{2+}$ and related species are reacted with pyrimidines or their analogues,[1] exhibit interesting colors ranging from purple to blue to green. In fact, the existence of deep blue platinum-amide complexes has been known for a long time.[4] Attempts to crystallize the pyrimidine blues for structural studies have met with little success, presumably because the various preparations represent an admixture of clusters with different degree of oligomerization.[1,4] By far the closest structural model to these complexes is that of *cis*-diammineplatinum α-pyridone blue recently reported by Lippard et al.[5] In an attempt to explore the structural variation of these apparently amorphous compounds, we report here the extended x-ray absorption fine structure (EXAFS) analysis of a purple and a blue compound derived from the reaction of "*cis*-Pt(amine)$_2$(H_2O)$_2^{2+}$" [6] with uridine (UH).

The purple compound was obtained by reacting *cis*-Pt(CPA)$_2$Cl$_2$ (CPA = cyclopropylamine) with uridine. In a typical experiment, 1 mmol of *cis*-Pt(CPA)$_2$Cl$_2$[7] and 1 mmol of uridine are dissolved in 15 mL of water, and the resulting mixture (pH 7.7) is stirred at 40 °C for 24 h, forming a deep purple solution. Addition of large amounts of ethanol or acetone at this point precipitates the water-soluble chloride salt of the purple cation. Alternatively, addition of an aqueous $NaPh_3BCN$ solution to the purple reaction mixture precipitates the water-insoluble [Ph_3BCN]$^-$ salt. The [Ph_3BCN]$^-$ salt can be dissolved in methanol and purified via chromatography on Sephadex LH20-100 using methanol as eluent. Since the EXAFS spectra of these purple compounds are very similar (viz., independent of the nature of the counteranion such as Cl^- or Ph_3BCN^-, and the degree of purification), we will describe herein only the EXAFS spectrum of the purified *cis*-[Pt(CPA)$_2$U](Ph$_3$BCN)$_x$ (**1**, where $x = 1.25 \pm 0.20$).

The blue compound was similarly prepared from *cis*-[Pt(NH_3)$_2$(H_2O)$_2$]$^{2+}$ and uridine. A solution (pH 7.0) of "*cis*-[Pt(NH_3)$_2$(H_2O)$_2$]$^{2+}$ (NO_3)$_2^-$" [6] and uridine (3 mmol each) in 20 mL of water was heated at 38 °C for 48 h to give

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