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- (4) While numerous studies have shown inter- and intramolecular heavy-atom enhancement of intersystem crossing for π, π^* states of aromatic hydrocarbons, little or no enhancement has been observed for ketones, particularly when the n, π^* states are the lowest excited states (see, for example, P. J. Wagner, *J. Chem. Phys.*, **45**, 2335 (1966), and D. Kearns and W. Case, *J. Am. Chem. Soc.*, **88**, 5087 (1966)). For β, γ -unsaturated ketones, the lowest singlet excited state is n, π^* , but the triplet excited state is not known. Houk's calculation^{7a} suggests that it has appreciable π, π^* character.
- (5) (a) Details of the synthesis and characterization of all compounds will be given in our full paper to be published later. The 3-halo ketones **2** and **3** were synthesized by oxidation of the corresponding bicyclic alcohol (R. Ratcliffe and R. Rodehorst, *J. Org. Chem.*, **35**, 4000 (1970)). The 1-halo ketones **4** and **5** were obtained by direct irradiation of the corresponding 3-halo ketones. The unsubstituted **1** was obtained by hydrolysis of the Grignard reagent from the ketal of **3**. (b) The rotations of the resolved ketone were $[\phi]_D^{25} = -54.13$ (578 nm), -63.73 (546), -133.70 (436), -309.76 (365) (c 1.03, ether). The optical purity was determined to be 20% from the relative areas of the CF₃ NMR absorptions for the α -methoxy- α -trifluoromethylphenylacetic esters of the resolved alcohol precursor to **3**. This optical purity is somewhat higher than predicted from Berson's study² though comparison of the two is difficult. The absolute configurations are according to Berson.
- (6) Analysis of the crude reaction mixture from irradiation of bromo ketone **3** revealed no buildup of HBr during either the direct or sensitized rearrangements. Furthermore, analysis of the product mixture from **3** showed no formation of **1**, the photoreduction product expected from **3**.
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- (10) The conclusions are not altered if a mechanism invoking an acyl-allyl diradical is employed in this analysis. The quantum yield for diradical formation would be twice that given in Table I (i.e., $\Phi = 0.82$) which is unusually large (see ref 7a and 11). Stereochemical investigations also indicate a stereospecific reaction consistent with a concerted [1,3] acyl migration (R. L. Coffin, R. S. Givens, and R. G. Carlson, *J. Am. Chem. Soc.*, **96**, 7554 (1974)). Complete details of this interesting result will be given in the full paper.
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- (12) Emission of the 440-nm band of acetone (77 K in 1:2 EA) was quenched by adding known concentrations of each of the ketones. The slopes of the linear Stern-Volmer quenching plots were used to obtain the relative quenching efficiencies.
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Anion Radicals of Pheophytin and Chlorophyll a: Their Role in the Primary Charge Separations of Plant Photosynthesis

Sir:

Photosynthesis in algae and green plants functions via two chlorophyll-mediated systems which cooperatively oxidize water (photosystem II, PS II) and reduce carbon dioxide (PS I). PS I utilizes far-red photons ($\lambda \leq 700$ nm) to yield an oxidized chlorophyll pair, P700⁺ (midpoint potential, $E_m \sim +0.4$ to 0.5 V vs. NHE) and a strong reductant, a bound ferredoxin with $E_m \sim -0.54$ to -0.59 V, which is capable of reducing the nicotinamide adenine dinucleotide required to fix CO₂. PS II operates in red light ($\lambda \leq 680$ nm) to generate a second chlorophyll cation (P680⁺) sufficiently electropositive to oxidize water to oxygen ($E_m \geq 0.8$ V) and a weak reductant ($E_m = 0$ to -0.2 V) believed to be a plastoquinone anion radical (see ref 1-8 for reviews).

Table I. Variation of ESR Line Width with Microwave Power

$T, ^\circ\text{C}$	microwave power, mW	Chl a ^{-•}	$\Delta H, \text{G}^a$ deut Chl ^{-•}	Pheo ^{-•}
25	0.01	10.5		10.3
	0.1	10.8		10.5
	1.0	11.5		11.6
	10.0	15.0		15.0
-60 ^b	0.01	11.3		11.3
	0.1	11.6		11.2
	1.0	13.2		13.0
	10.0	17.6		17.2
-140	0.01	12.1	4.8	12.2
	0.1	12.8	5.2	12.5
	1.0	13.5	5.0	13.1
	10.0	13.0	5.3	12.6

^a ΔH = peak to peak line width of the first derivative ESR signal.

^b Near-freezing point.

However, recent redox, optical, and magnetic results⁹⁻¹⁷ indicate that additional electron acceptors mediate the transfer of charge from P680 to plastoquinone and from P700 to the iron-sulfur protein. Examination of the emf, ESR, and optical parameters attributed to these short-lived acceptors of PS I and II leads us to suggest that chlorophyll and its free base, pheophytin, act as the primary electron acceptors of PS I and II, respectively. We provide here redox, optical, and paramagnetic characteristics of the anion radicals of chlorophyll (Chl) and pheophytin (Pheo) in vitro to test this hypothesis.

Evidence for anions of Chl and Pheo comes from electrolytic, photolytic, and radiolytic experiments.¹⁸⁻²⁵ Nonetheless, unambiguous spectral characterization of the radicals has been complicated or prevented by the tendency of the anions to add^{26,27} or lose¹⁸ protons in the presence of trace acids or bases. We find that solutions of Pheo^{-•} and Chl^{-•} in dimethylformamide (DMF) which are stable for more than 2 months can be obtained by controlled potential electrolysis if oxygen is rigorously excluded and the solvent has been pretreated on activated molecular sieves followed by contact of the electrolyte and solvent with activated neutral alumina according to the methods described by Bard,²² Borg,²¹ Fajer,²⁸ Parker,²⁹ and co-workers. Electrolysis requires addition of 1 (± 0.1) electron per chlorin molecule to yield the optical spectra of Pheo^{-•} and Chl^{-•} shown in Figure 1. The reactions are reversible: one-electron oxidations of the radicals regenerate better than 90% of the original chlorins. The spectra displayed in Figure 1 do not exhibit any of the optical features associated with protonation of the radical, as in the Krasnovskii product,^{24,26,27} or with the deprotonation at the C-10 position known as the phase test.¹⁸

Electron spin resonance (ESR) and electron nuclear double resonance (ENDOR) spectra of Pheo^{-•} and Chl^{-•} were obtained by generating the radicals electrolytically in ampoules equipped with both ESR sampling tubes and optical cells in order to monitor the electronic spectra immediately before and after the magnetic measurements. Within experimental error, no differences in ESR and ENDOR parameters are detected in samples prepared in deuterated DMF (99.5% *d*₇) even after prolonged standing, again indicating that no significant reactions occur with solvent protons at sites of high spin densities.

The featureless ESR signals obtained from Chl^{-•} and Pheo^{-•} readily saturate with increasing microwave power (Table I) and yield the ENDOR spectra shown in Figure 2. Peaks *a*₁ and *a*₂ display ENDOR features typical of methyl groups in frozen matrices.^{30,31} Self-consistent field molecular orbital calculations³² for free base and metallochlorin anions indicate (Figure 3) that the 1- and 5-methyl groups should exhibit substantial hyperfine splitting constants in a ratio of

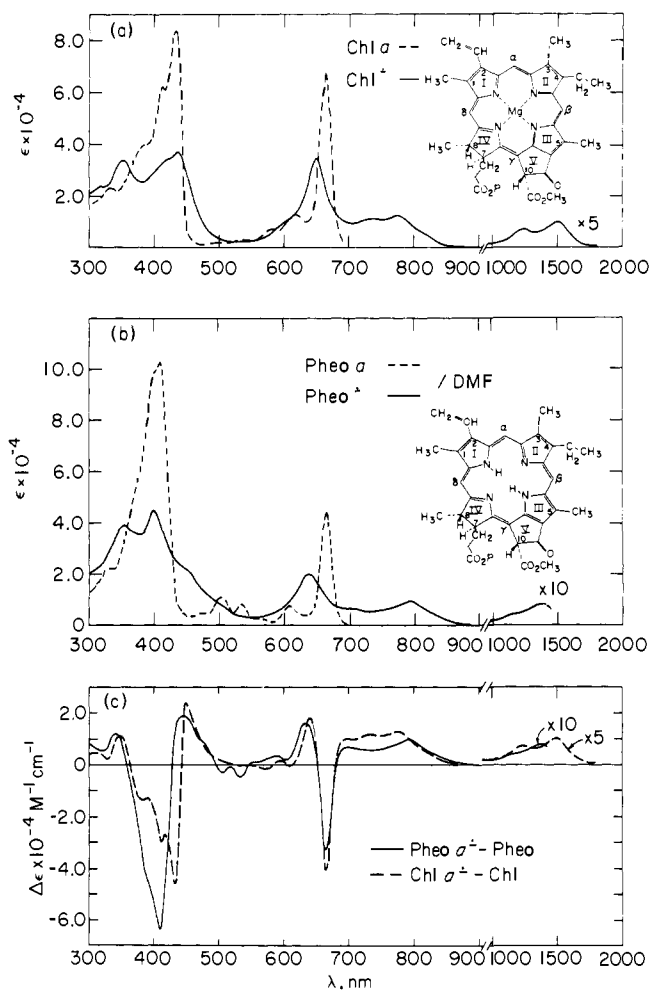


Figure 1. Optical absorption spectra of (a) Chl a, ---, and its anion radical, —; (b) Pheo a, ---, and Pheo⁻, —; and (c) difference spectra (radical minus parent) of Chl, ---, Pheo, —. The anions were generated electro-lytically at a platinum electrode in DMF containing 0.1 M tetrapropylammonium perchlorate.

~1:2. Complementary extended Hückel calculations by Hanson et al.,³³ which specifically treat Chl⁻ and Pheo⁻, yield similar results. Assignment of the large ENDOR splittings a_1 to the 5-methyl groups was verified by examining selectively deuterated anions of methyl pyropheophorbide.³⁴ Deuteration of the 5-methyl group eliminates an ENDOR resonance at 3.7 G and the line width of the ESR signal collapses by an amount consistent with replacement of three protons with splittings $a_H = 3.7$ G by three deuterons with $a_D = 0.57$ G ($a_D/a_H = 0.1535$). The MO calculations cited above also predict large spin densities at the nitrogens of rings II and IV. The decrease in the ESR line width of Chl⁻ on deuteration (Table I) is indeed less than the factor of 4 expected if all contributions to the line width were due solely to protons. The predicted large spin densities on the nitrogens should also cause hyperfine coupling with the Mg atom of Chl⁻ and enrichment of Chl with ²⁵Mg ($I = 5/2$) may prove a useful probe to differentiate Chl⁻ from Pheo⁻ in vivo.³⁵

Substantial evidence exists that monomeric bacteriopheophytin acts as a primary electron acceptor, on a picosecond time scale, in bacterial photosynthesis.³⁶ Extrapolation to algae and green plants suggests that Pheo or Chl may fulfill a similar role. Redox data indicate that a light-induced charge separation into oxidized Chls (P680⁺ or P700⁺) and reduced Pheo is energetically feasible for a single photon event in PS I and II, whereas reduction of Chl is energetically accessible in PS I but less favorable in PS II, if one assumes minimum oxidation potentials of +0.8 V (vs. NHE) for P680 and 0.4 V for P700

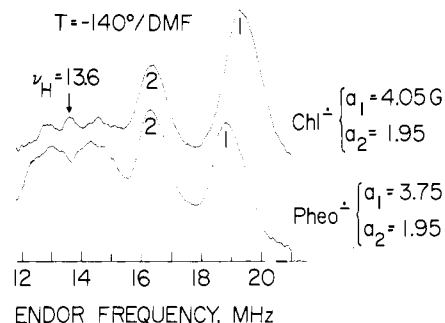


Figure 2. ENDOR spectra of Chl⁻ (top) and Pheo⁻ (bottom) in deuterated DMF at -140 °C. g values are 2.0029 and 2.0030 (± 0.0001), respectively.

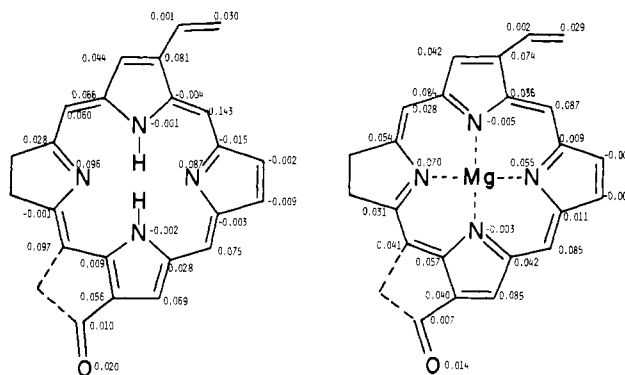
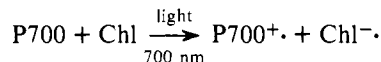
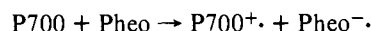


Figure 3. Unpaired spin densities calculated by open shell SCF-MO theory for free base and metallo-chlorin models of Pheo⁻ and Chl⁻.

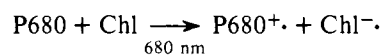
and uses in vitro polarographic $E_{1/2}$ of -0.88 V for Chl and -0.64 V for Pheo (in DMF). In PS I, the reaction



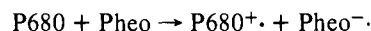
would result in an energy change, ΔE , of ~1.3 V and for



$\Delta E \sim 1$ V. In PS II, for



$\Delta E \sim 1.7$ V and for



$\Delta E \sim 1.4$ V. (Photons of 700 and 680 nm represent energies of 1.77 and 1.82 eV.)

Klimov et al. noted¹⁴ that the illumination of a Chl protein of PS II, poised at potentials low enough to reduce the canonical plastoquinone acceptor, yields optical changes attributable to reduction of Pheo. Comparisons of the in vivo spectra with the difference spectra for reduction of Pheo and Chl reported here are shown in Figure 4. The Chl and Pheo changes clearly parallel those observed in vivo but a shift of ~20 nm of the Pheo spectrum yields coincidence with nearly all the peaks of PS II. If, as in bacteria,³⁶ part of the energy of the incident photon is dissipated³⁷ to effect the rapid primary charge separation, then Pheo rather than Chl seems the acceptor of choice by transducing the 1.82 eV of the impinging photon into 1.4 V of chemical energy. With an estimated reduction potential of -0.64 V, Pheo⁻ is easily capable of reducing the next electron acceptor, the plastoquinone,¹⁻⁶ with E_m of 0 to -0.2 V. In PS I, Chl, with an in vitro $E_{1/2}$ of -0.9 V, appears the better choice to reduce the bound ferredoxins,^{3,6,16} which are the next components in the electron transport chain, with reported E_m as high as -0.59 V. Ke et al.^{9,10} have estimated the midpoint

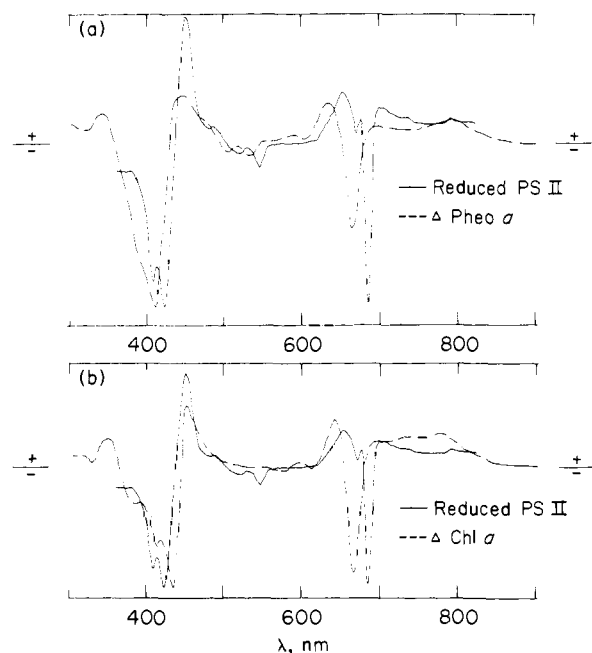


Figure 4. Comparison of the optical changes induced by light in a Chl-protein complex of photosystem II poised at -0.49 V (vs. NHE) as reported by Klimov et al.¹⁴ and the difference spectra obtained on reduction of (a) Pheo and (b) Chl in DMF. Spectra have been normalized at ~ 400 nm.

potential of an intermediate, X, between the ferredoxins and P700 as equal to or greater than -0.73 V. $X^{\cdot-}$ has been detected¹⁶ by ESR only at low temperatures (10 K) where it exhibits $g_z = 1.76$, $g_y = 1.86$, and $g_x = 2.06$, parameters quite distinct from those of $\text{Chl } a^{\cdot-}$. However, major deviations from solution ESR spectra of the anions of bacteriopheophytins and quinones are also observed at comparable temperatures in reduced bacterial systems and arise from magnetic coupling with nearby ferrous ions.^{7,36b,d,e} A similar effect, induced by an interaction of $\text{Chl}^{\cdot-}$ with the iron of the reduced Fe-S protein, could explain the g values of $X^{\cdot-}$.³⁸ Ambient temperature ESR spectra of $X^{\cdot-}$ should conform to those reported here for $\text{Chl}^{\cdot-}$ if our suggestion is correct. Dynamic polarization effects have been elicited^{2,6,12,13} from PS I and are readily ascribed to a radical-radical recombination mechanism³⁹ involving P700^+ and $\text{Chl}^{\cdot-}$.

We have proposed here that the first reduced chemical products of green plant photosynthesis are the anions of pheophytin in PS II and chlorophyll in PS I. Such a mechanism represents a significantly more efficient conversion of incident light into chemical energy than previously assumed and yields strong reductants to drive the biochemistry of both photosystems I and II. We have also described optical and magnetic characteristics of the putative acceptors which should provide the guidelines to further test our suggestion.

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Regiocontrolled Head-to-Tail Coupling of Allylic Boron "Ate" Complexes with Allylic Halides

Sir:

One of the basic unsolved problems of organic synthesis is the lack of selectivity in the Wurtz-type coupling reaction of allylic organometallics with allylic halides.¹ In general, two allylic moieties, one from the allylic organometallics and the other from the organic halides, combine randomly, leading to a mixture of four products (eq 1).² We wish to report that this difficulty, for the first time, can be alleviated by using lithium allylic boron ate complexes, which regioselectively react with allylic halides to produce the head-to-tail 1,5-dienes (eq 2).