Acknowledgment. The authors thank Professors T. Saegusa and Y. Ito for their assistance in the NMR measurements and helpful discussion.

References and Notes

(1) T. Zincke, *Justus Liebigs Ann. Chem.*, **330**, 361 (1903); **333**, 296 (1904); **338**, 107 (1905); **341**, 365 (1905).
(2) P. Karrer and H. Keller, *Helv. Chim. Acta.*, **21**, 463 (1938); **21**, 1170 (1938); S. P. Vitler, T. D. Spies, and A. P. Mathews, *J. Biol Chem.*, **125**, 85 (1938).
(3) F. Hamer, "Cyanine Dyes and Related Compounds", Interscience, New York, N.Y., 1964, p 244.
(4) P. Karrer, G. Schwarzenbach, and G. E. Utzinger, *Helv. Chim. Acta.*, **20**, 72 (1937).
(5) H. Lettré, W. Haede, and E. Ruhbaum, *Justus Liebigs Ann. Chem.*, **529**, 123 (1953).
(6) N. Ise, T. Okubo, H. Kitano, and S. Kunugi, *J. Am. Chem. Soc.*, **97**, 2882 (1975).
(7) E. Van, O. Dunghen, J. Nasielski, and P. Van Laer, *Bull. Soc. Chim. Belg.*, **66**, 661 (1957).
(8) R. Oda and S. Mita, *Bull. Chem. Soc. Jpn.*, **36**, 103 (1963).
(9) E. N. Marvell, G. Caple, and I. Shahidi, *J. Am. Chem. Soc.*, **92**, 5641, 5646 (1970).
(10) J. Kavalek and V. Sterba, *Collect. Czech. Chem. Commun.*, **38**, 3506 (1973); J. Kavâlek, J. Polansky, and V. Sterba, *ibid.*, **39**, 1049 (1974).
(11) H. S. Mosher, "Heterocyclic Compounds", Vol. 1, R. C. Elderfield, Ed., Wiley, New York, N.Y., 1950, p 424.
(12) For a convenient review on this subject, see, for example, N. Ise, "Polyelectrolytes and Their Application", E. Selegeny and A. Rembaum, Ed., D. Reidel, Holland, 1975, p 71.
(13) S. Gordon, E. J. Hart, M. S. Matheson, J. Rabani, and J. K. Thomas, *J. Am. Chem. Soc.*, **85**, 1375 (1963); A. Szutka, J. K. Thomas, S. Gordon, and E. J. Hart, *J. Phys. Chem.*, **69**, 289 (1965).
(14) S. Harada and K. Arai, *Makromol. Chem.*, **107**, 78 (1967); Y. Negi, S. Harada and O. Ishizuka, *J. Polym. Sci.*, **5**, 1951 (1967).
(15) T. Okubo and N. Ise, *J. Am. Chem. Soc.*, **95**, 2293 (1973).
(16) N. Ise and Y. Matsuda, *J. Chem. Soc., Faraday Trans. 1*, **69**, 99 (1973).
(17) S. Kunugi and N. Ise, *Z. Phys. Chem.* (*Frankfurt am Main*), **92**, 69 (1974).
(18) T. Okubo and N. Ise, *Proc. R. Soc., London, Ser. A*, **327**, 413 (1972).
(19) G. Manning, *J. Chem. Phys.*, **51**, 924, 934 (1969).
(20) J. N. Brönsted, *Z. Phys. Chem.* (*Leipzig*), **102**, 109 (1922); **115**, 337 (1925).
(21) K. Mita, S. Kunugi, T. Okubo, and N. Ise, *J. Chem. Soc., Faraday Trans. 1*, **71**, 936 (1975).

In Vitro Solar Conversion after the Primary Light Reaction in Photosynthesis. Reversible Photogalvanic Effects of Chlorophyll–Quinhydrone Half-Cell Reactions

Francis K. Fong* and Nicholas Winograd*

Contribution from the Department of Chemistry, Purdue University, West Lafayette, Indiana 47907. *Received October 24, 1975*

Abstract: In this publication, we report the observation of photogalvanic effects arising from chlorophyll a–quinhydrone (Q: H_2Q, 1:1) half-cell reactions. Platinum electrodes have been employed. In the presence of light, a photocurrent is developed as Chl a aggregates presumably undergo a charge-transfer interaction that results in the creation of a p-type semiconductor film. The observed photopotential at the Pt–Chl a electrode is positive. When the light is turned off, the half-cells regress toward the preillumination conditions, and a reverse current is observed. The spectral response of the photogalvanic effect has been determined. It has been found that a distribution of Chl a–H_2O aggregates contribute to the observed photocurrent. The in vitro solar conversion results are discussed in terms of the recently proposed primary light reaction model of photosynthesis.

Introduction

The primary processes of the reversible photochemical reaction involving benzoquinone (Q), hydroquinone (H_2Q), chlorophyll (Chl a), and the Chl a$^+$ cation in different solvent systems has been the subject of numerous investigations.[1-4] The overall reaction may be written

$$2\mathrm{H}^+ + 2(\mathrm{Chl\ a}) + \mathrm{Q} \underset{\text{dark}}{\overset{h\nu}{\rightleftarrows}} 2(\mathrm{Chl\ a}^+) + \mathrm{H_2Q} \qquad (1)$$

in which Chl a and H_2Q act as the electron donor in the light and dark reactions, respectively. In this paper we describe our initial attempt at arriving at reversible photogalvanic action derived from photoelectrochemical interactions between Pt–Chl a and quinhydrone electrodes. The motivation of the present work differs from earlier observations of photoconductive and photoelectrochemical effects of chlorophyll[5-7] and other systems[8-11] in that we shall adopt the rigorous definition of a galvanic cell in which power is derived from spontaneous chemical reaction between two half-cells. The light perturbation should lead to photoelectrochemical effects that may be generically related to the Becquerel effect.[8,9] However, the present results may be of special interest because of the near-infrared photoactivity of Chl a. Most existing photoelectrochemical cells operate in the blue or near-ultraviolet.[10-13]

The proposed photogalvanic cell may be written

$$\underset{\mathrm{A}}{\mathrm{Pt, Chl\ a|Chl\ a^+}}|\mathrm{LiClO_4}||\mathrm{NaOH,\ }\underset{\mathrm{B}}{\mathrm{NaHCO_3|H_2Q|Q, Pt}} \qquad (2)$$

Based on the reversible reactions given in (1), one might expect the Chl a-plated Pt electrode in (2) to develop a negative photopotential due to the photooxidation of Chl a by Q. In the following we report the observed behavior of the Chl a–quinhydrone photoelectrochemical cell. Contrary to our expectations, a positive photopotential has been observed at the Chl a-plated electrode, leading to the somewhat surprising conclusion that Chl a is in fact reduced by the quinhydrone cell under light conditions. It will be shown that this unexpected behavior can be readily accounted for in terms of the p-type semiconductor properties[6] of hydrated Chl a aggregates and of the characteristic photovoltaic behavior of binary compound semiconductors.[14]

Experimental Section

The Chl a was extracted from spinach and purified in the usual manner.[15] The purity of the sample was monitored by the peak positions and the peak ratio of the blue and red absorption bands of Chl a in diethyl ether,[15] cyclic voltametric measurements,[16] liquid

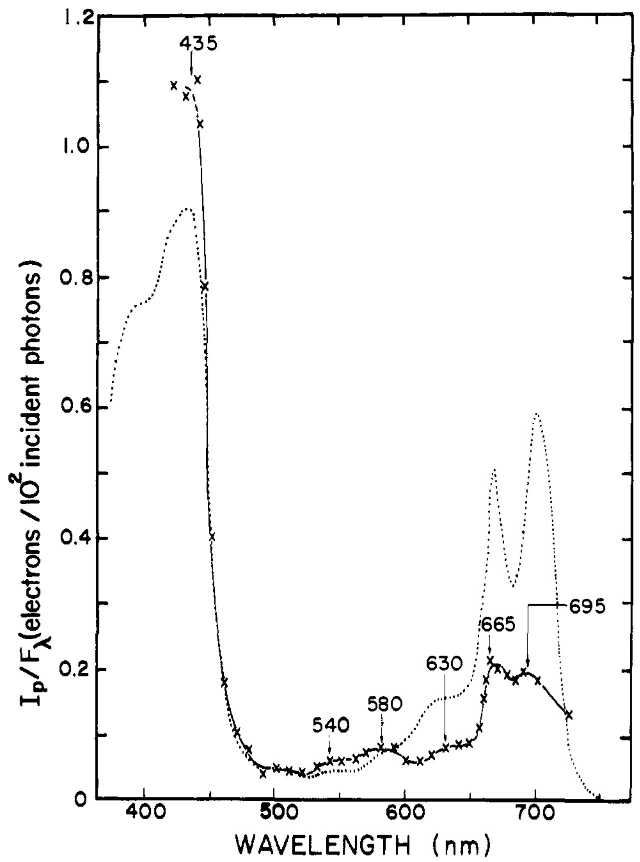

Figure 1. Spectral response of the room-temperature photogalvanic effect (×) of the Chl a/Q system and the 151 K absorption spectrum (····) of a 2×10^{-5} M Chl a solution in methylcyclohexane:*n*-pentane (1:1). The photocurrent I_p was measured across a $R = 2 \times 10^4 \Omega$ resistor. The observed photopotential, given by I_pR, is positive, indicative of a photoreduction current at the Pt-Chl a electrode.

chromatographic and x-ray photoelectron spectroscopic determinations.[17] About 3×10^{14} Chl a molecules were deposited on a Pt electrode (~0.2 cm^2 in area) by allowing 2 μl of a 3×10^{-4} M solution of Chl a in butyronitrile to evaporate on one side of the electrode. The Pt-Chl a electrode was then immersed in an 0.1 M aqueous solution of $LiClO_4$. The other half-cell is a Chl a-free Pt electrode immersed in a 5×10^{-3} M aqueous solution of Q:H_2Q (1:1) in a NaOH-$NaHCO_3$ buffer (pH 10.3). The half-cells were separated by a fine glass frit. All sample solutions were rigorously degassed through multiple freeze-pump-thaw cycles. The cell was assembled and sealed under a N_2 atmosphere in a drybox.

The spectral response of the observed photogalvanic effect was measured using a 1000-W tungsten-halogen lamp and a 0.25-m Jarrell-Ash monochromator. The spectral distribution of the incident photon flux (F) in the 400-750-nm wavelength region was determined with a Spectrophysics 401B power meter. The incident source has a maximum F_λ value 1.26×10^{13} photons s^{-1} cm^{-2} at λ 600 nm. The corresponding fluxes at 440 and 750 nm were 1.05 and 3.25×10^{12} photons s^{-1} cm^{-2}, respectively. The measured spectral response of the photocurrent I_p was recorded in terms of the ratio I_p/F_λ.

Experimental Results and Interpretations

At pH 10.3 the quinhydrone electrode has a reversible redox potential −0.12 V vs. SCE.[18,19] In the presence of light, a positive photopotential at the Pt-Chl a electrode is observed. In the range of incident fluxes (~10^{12}–10^{14} photons cm^{-2} s^{-1}), this photopotential appears to be a linear function of light intensity. The sign of the photopotential, indicative of a reduction photocurrent at the Pt-Chl a electrode, rules out the reversible reaction in (1) as the mechanisms underlying the observed photoelectrochemical effects.

Photogalvanic action is generated under light irradiation in the form of an I_pR drop across a resistor R with the photocurrent I_p. The time (τ_p) it takes to develop I_p varies inversely with R ($\tau_p \sim 10$ s, at $R = 2 \times 10^4$ Ω). When the light is switched off, a reverse reaction induces a galvanic current opposite in sign to I_p. The on-off light cycle thus develops an alternating current whose magnitude is proportional to light intensity in the range of incident fluxes employed. The reversible photogalvanic effect described above is observed only when the photon beam is incident on the chlorophyll. This effect is not detected when the (Chl a)-free side of the A electrode is illuminated or when the electrode is illuminated without quinone in the B compartment. The observed action spectrum of the photogalvanic effect is given in Figure 1.

It has been shown[15,20-22] recently that the (room-temperature) red Chl a absorption bands at 665, 678, 695, and 743 nm are attributable to Chl a·H_2O (A665),[15,20,23] (Chl a)$_2$ (A678),[15,20] (Chl a·H_2O)$_2$ (A700),[15,22,24] and (Chl a·$2H_2O$)$_{n\gg1}$ (A743),[15,20,25,26] respectively. XPS studies[17] of the O 1s binding energies of Chl a-H_2O deposits comparable with those employed in the present investigation reveal that the aggregation states of Chl a on a metallic surface are apparently similar to those in a homogeneous nonpolar solution. The I_p contribution from wavelengths to the red of the 665-nm band (see Figure 1) are suggestive of the role played by dimeric and polymeric Chl a-H_2O aggregates. The observation of significant photocurrents in the 700-nm region of the action spectrum is of particular interest because the corresponding absorption band in nonpolar Chl a solutions is only observed at low temperatures due to entropy effects.[15] The restriction of Chl a and H_2O molecules to a two-dimensional space significantly reduces the negative configuration entropy change of the Chl a·H_2O dimerization process and leads to a negative free-energy change that favors the formation of the A700 species. It appears that the above argument may also be applicable to the phenomenological behavior of Chl a molecules in photosynthesis, where it is believed that these molecules are spatially restricted to the interface between protein lipids and lamellae.[27-29] It has recently been proposed[22,30-32] that (Chl a·H_2O)$_2$ is the 700-nm absorbing photosystem I primary molecular unit (P700)[33] in plant photosynthesis. The significant role played by polymeric (A743), as well as dimeric (A700) Chl a-H_2O aggregates in the present case, is reasonable in view of the aqueous electrolyte solution surrounding the Chl a film. The room-temperature formation of a distribution of near-infrared absorbing (in the 700-750-nm wavelength region) aggregates in chlorophyll emulsions and films under excess water conditions has been reported earlier.[34,35]

The observed photogalvanic effects can be accounted for in terms of the observed photovoltaic properties of semiconductor binary compounds. It has been established[14] that the photoreaction of an n-type binary compound semiconductor leads to a negative photopotential whereas a p-type semiconductor can only show a positive photopotential. Under illumination the photoactive hydrated Chl a aggregate is presumably excited to a charge-transfer state[30-32] that may be considered to be a binary compound consisting of Chl a$^+$ and Chl a$^-$.[22] While the molecular details remain unclear, we consider the generalized proposal by Williams.[14] The Chl a$^-$ anion may become solvated by the water protons and thus localized at the Chl a-H_2O phase boundary as the bulk of the p-type hydrated Chl a film acquires an excess of positive charge that leads to the observed photoreduction current at the Pt-Chl a electrode. The result is an accumulation of negative charges in cell A during the light cycle, which is apparently responsible for the observed reverse dark current when the light is switched off. The above interpretation appears to provide a reasonable rationalization for the observed effects.

The apparent quantum efficiencies I_p/F_λ (incident) range from about 2.3×10^{-3} in the red wavelength region to about 1.1×10^{-2} in the blue (see Figure 1). However, the actual quantum efficiencies, given by the ratio of electrons released per photon absorbed, are about 2×10^{-1} and 5×10^{-1} in the red- and blue-wavelength regions, respectively. From reflectance measurements, we estimate about 1% of the incident flux was absorbed by the chlorophyll. It appears reasonable to expect that the reflectance loss can be easily remedied by a thicker coat of Chl a on the Pt electrode.

Discussion

The photogalvanic cell described above differs fundamentally from earlier chlorophyll photocells.[5-7] Direct conversion of photons into electricity has been accomplished in the present case. In the work of Tang, Douglas, and Albrecht,[6,7] the observed photocurrents did not result from chemical interactions of the chlorophyll with an electron acceptor. Instead, these authors have demonstrated that the 743-nm absorbing chlorophyll sample, a crystalline aggregate of the Chl a dihydrate,[20] displays photovoltaic effects under proper conditions.[6] In the work of Tributsch and Calvin,[5] the chlorophyll was engaged in photochemistry, but the lack of galvanic separation in their experiments did not allow for spontaneous quantum conversion, and an externally applied voltage was used to induce the observed photocurrents.[5]

The I_p action spectrum given in Figure 1 contrasts with the absorption spectra of Chl a preparations in that the blue-red (435 nm/670 nm) intensity ratio (~4.4) of the I_p spectrum appears to be greatly enhanced over the corresponding peak ratios of Chl a optical absorption. The room-temperature blue/red peak ratios of Chl a absorption are 1.30 and 1.52 in diethyl ether and 1:1 methylcyclohexane and *n*-pentane, respectively.[15] (See, also, the comparison in Figure 1.) The origin of this apparent anomaly is not well understood and deserves more detailed future investigations. The I_p/F_λ determinations in the blue- and red-wavelength regions were encumbered by the weak fluxes of the incident source (see Experimental Section). Extended studies in these laboratories will be concerned with refined techniques for the I_p measurements.

In conclusion, we believe that the results reported above are significant for the following reasons. (i) Preliminary quantum efficiency measurements demonstrate the feasibility of efficient red and near-infrared solar conversion by chlorophyll in vitro. (ii) The above experimental procedure provides a convenient means of investigating Chl a-H_2O aggregates under ordinary room-temperature conditions. Of particular interest is the room-temperature stabilization of the A700 aggregate on surfaces. The A700 is believed[15,22,24] to be the in vitro analogue of the in vivo primary molecular adduct P700.[33] (iii) It appears that the reversible photogalvanic principle based on half-cell Chl a reactions can be generalized to electron-donor systems other than the quinhydrone electrode. The light-induced charge-transfer interaction in the A700 (P700) Chl a monohydrate dimer, considered to be the primary step in the photosynthetic light reaction,[22,30-32] also appears to play a probable role in the primary light reaction in the present photogalvanic system. In photosynthesis Chl a derives its unique function as a photocatalyst from its ability to undergo reversible photooxidation and reduction. Many current investigations have been concerned with the formation of the Chl a radical cation in the primary light reaction.[22] Our present investigation has focused the attention on the electron-accepting properties.

Acknowledgments. We are grateful to L. Fetterman, L. Galloway, P. Kissinger, and F. E. Lytle for helpful discussions and technical assistance.

References and Notes

(1) K. Seifert and H. T. Witt, *Naturwissenschaften*, **55**, 222 (1968).
(2) A. K. Chibisor, *Photochem. Photobiol.*, **10**, 331 (1969).
(3) R. A. White and G. Tollin, *Photochem. Photobiol.*, **14**, 15, 43 (1971).
(4) M. Tomkiewicz and M. P. Klein, *Proc. Natl. Acad. Sci. U.S.A.*, **70**, 143 (1973).
(5) H. Tributsch and M. Calvin, *Photochem. Photobiol.*, **14**, 95 (1971).
(6) C. W. Tang and A. C. Albrecht, *J. Chem. Phys.*, **62**, 2139 (1975); **63**, 953 (1975); C. W. Tang, F. Douglas, and A. C. Albrecht, *J. Phys. Chem.*, **79**, 2723 (1975); C. W. Tang and A. C. Albrecht, *Nature*, **254**, 507 (1975).
(7) F. Douglas and A. C. Albrecht, *Chem. Phys. Lett.*, **14**, 150 (1972).
(8) E. Becquerel, *C. R. Acad. Sci.*, **9**, 58, 561, 711 (1839).
(9) T. Kuwana, "Electroanalytical Chemistry", Vol. 1, A. J. Bard, Ed., Marcel Dekker, New York, N.Y., 1966, pp 197–240.
(10) E. Rabinowitch, *J. Chem. Phys.*, **8**, 551 (1940).
(11) E. Rabinowitch, *J. Chem. Phys.*, **8**, 560 (1940).
(12) A. E. Potter and L. H. Thaller, *Sol. Energy*, **3**, 1 (1959).
(13) W. D. K. Clark and J. A. Eckert, *Sol. Energy*, **17**, 147 (1975).
(14) R. Williams, *J. Chem. Phys.*, **32**, 1505 (1960).
(15) F. K. Fong and V. J. Koester, *Biochim. Biophys. Acta*, **423**, 52 (1976).
(16) A. Stanienda, *Z. Phys. Chem.* (*Leipzig*), **229**, 257 (1965).
(17) N. Winograd, A. Shepard, D. H. Karweik, V. J. Koester, and F. K. Fong, *J. Am. Chem. Soc.*, **98**, 2369 (1976).
(18) R. N. Adams, "Electrochemistry at Solid Electrodes", Marcel Dekker, New York, N.Y., p 366.
(19) W. E. Lingren, Ph.D. Thesis, University of Washington, 1962.
(20) F. K. Fong and V. J. Koester, *J. Am. Chem. Soc.*, **97**, 6888 (1975).
(21) F. K. Fong, *J. Am. Chem. Soc.*, **97**, 6890 (1975).
(22) For a review of recent developments, see F. K. Fong, "Theory of Molecular Relaxation: Applications in Chemistry and Biology", Wiley-Interscience, New York, N.Y., 1975, Chapter 9.
(23) R. Livingston, W. F. Watson, and J. McArdle, *J. Am. Chem. Soc.*, **71**, 1542 (1949).
(24) V. J. Koester, L. Galloway, and F. K. Fong, *Naturwissenschaften*, **62**, in press.
(25) A. S. Holt and E. E. Jacobs, *Am. J. Bot.*, **41**, 710 (1954).
(26) C. R. Strouse, *Proc. Natl. Acad. Sci.U.S.A.*, **71**, 325 (1974).
(27) E. Rabinowitch and Govindjee in "Photosynthesis", Wiley, New York, N.Y., 1965, p 98.
(28) J. B. Thomas, K. Minnaert, and P. F. Elbers, *Acta Botan. Neerl.*, **5**, 315 (1956).
(29) J. Wolken in "Photosynthetic Mechanisms of Green Plants", B. Kok and A. T. Jagendorf, Ed., Pub. No. 1145 of NASNRC, 1963, p 575.
(30) F. K. Fong, *J. Theor. Biol.*, **46**, 407 (1974).
(31) F. K. Fong, *Proc. Natl. Acad. Sci. U.S.A.*, **71**, 3692 (1974).
(32) F. K. Fong, *Appl. Phys.*, **6**, 151 (1975).
(33) B. Kok, *Biochim. Biophys. Acta*, **48**, 527 (1961).
(34) G. Sherman and S. F. Wang, *Nature*, **212**, 588 (1966).
(35) G. Sherman and H. Linschitz, *Nature*, **215**, 511 (1967).