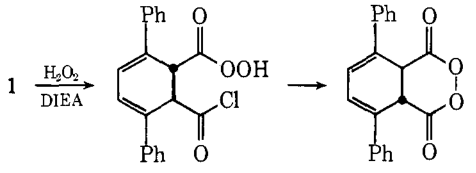
phenyl. The yield of triplet *p*-terphenyl was estimated by comparing the sensitized TBF fluorescence intensity at extrapolated infinite TBF concentration from **1** and from tetramethyldioxetane (TMD) under similar reaction conditions. This analysis indicated that 35 ± 10% of the **1** that is consumed becomes a *p*-terphenyl triplet.[15] Correction of the total yield of excited states for the chemical yield of *p*-terphenyl leads to the conclusion that ca. 60% of the *p*-terphenyl formed in the reaction of **1** is produced in an electronically exicted state. This system, therefore, represents one of the most efficient chemielectronic reactions yet discovered.

The reasonable mechanisms for this chemiluminescent reaction involve at least one intermediate. A reasonable candidate for the intermediate immediately preceding formation of the excited state is the cyclic diacyl peroxide **4**. Rearrangement of **4** to *p*-terphenyl and carbon dioxide is exothermic by ca. 85 kcal/mol.[17] The lowest excited singlet state of *p*-terphenyl is 90 kcal/mol above the ground state.[18] Thus, fragmentation of **4** almost certainly produces sufficient energy to form the observed excited states.[19] This fragmentation may occur by either a stepwise mechanism through a biradical or by a concerted bond cleavage. If concerted, the symmetry "allowed" $2_s + 2_s + 2_s$ path would generate an unlikely trans bond in the central benzene ring of **2**. Alternatively, the "forbidden" $2_s + 2_a + 2_s$ path would be sterically permitted. This path is predicted to lead directly to an electronically excited state of **2**.[21] In any event, the large exothermicity of this rearrangement may be the key factor in promoting the efficient formation of electronically excited states. Further experimental work is aimed at the conclusive identification of the reactive intermediate and elucidation of the mechanism for this interesting chemiluminescent reaction.



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Acknowledgment. The author wishes to thank Professor S. G. Smith for his assistance throughout this work. This work was supported in part by the Office of Naval Research and in part by the donors of the Petroleum Research Fund, administered by the American Chemical Society.

References and Notes

(1) E. H. White and D. F. Roswell, *Acc. Chem. Res.*, **3**, 54 (1970); K. D. Gundermann, *Fortschr. Chem. Forsch.*, **46**, 61 (1974); N. J. Turro, P. Lechtken, G. B. Schuster, H. C. Steinmetzer, and A. Yekta, *Acc. Chem. Res.*, **7**, 97 (1974).
(2) Prepared from the diacid[3] with thionyl chloride. Anal. ($C_{20}H_{14}O_2Cl_2$) C, H, Cl.
(3) L. E. Fieser and M. J. Haddidian, *J. Am. Chem. Soc.*, **86**, 2392 (1964).
(4) Light was detected with an EMI 9813B photomultiplier by the photon counting technique.
(5) Typical conditions: acid chloride = 2 × 10^{-4}, DIEA = 5 × 10^{-3}, H_2O_2 = 4 × 10^{-3}, perylene = 4 × 10^{-3} M, resulting in an observed pseudo-first-order rate constant at room temperature in air saturated THF of (9.2 ± 0.3) × 10^{-3} s^{-1}.
(6) N. J. Turro, G. B. Schuster, R. G. Bergman, K. J. Shea, and J. H. Davis, *J. Am. Chem. Soc.*, **97**, 4758 (1975).
(7) Any long range component to the energy transfer would result in a shorter calculated lifetime.
(8) C. D. Amata, M. Burton, W. P. Helman, P. K. Ludwig, and S. A. Rodemeyer, *J. Chem. Phys.*, **48**, 2374 (1968); M. Burton, P. Ludwig, and J. T. D'Allessio, *Acta. Phys. Pol.*, **26**, 517 (1964).
(9) Control experiments showed that amine quenching of singlet oxygen did not compete with trapping by TME at the concentrations used: E. A. Ogryzlo and C. W. Tang, *J. Am. Chem. Soc.*, **92**, 5034 (1970); K. Gollnick, *Adv. Photochem.*, **6**, 1 (1968); C. S. Foote, *Acc. Chem. Res.*, **1**, 104 (1968).
(10) T. Wilson, *J. Am. Chem. Soc.*, **88**, 2898 (1966).
(11) M. M. Rauhut, *Acc. Chem. Res.*, **2**, 80 (1969).
(12) P. R. Michael and L. R. Faulkner, *Anal. Chem.*, **48**, 1188 (1976).
(13) R. G. Bennet, R. P. Schwenker, and R. E. Kellog, *J. Chem. Phys.*, **41**, 3040 (1964); R. E. Kellog and R. G. Bennet, *ibid.*, **41**, 3042 (1964); V. L. Ermolaev and E. B. Sveshnikova, *Opt. Spectrosc.* (*USSR*), 17, 321 (1964).
(14) Estimation of the donor lifetime requires an assumed value for the rate constant of energy transfer. Based upon the observed R_0 values for transfer to fluorescein from phenanthrene and 2-acetonaphthone,[13] the rate constant for energy transfer was set equal to 1 × 10^{11} l. mol/s. If energy transfer is slower, the calculated lifetime is longer.
(15) The yield of *p*-terphenyl triplet from this analysis of course depends upon the yield of excited acetone from thermal decomposition of TMD. The literature[16] value of 50% for this quantity was employed.
(16) N. J. Turro and P. Lechtken, *J. Am. Chem. Soc.*, **94**, 2886 (1972).
(17) S. W. Benson, F. R. Cruichshank, D. M. Golden, G. R. Haugen, H. E. O'Neal, A. S. Rodgers, R. Shaw, and R. Walsh, *Chem. Rev.*, **69**, 279 (1969).
(18) I. Berlman, "Handbook of Fluorescence Spectra of Aromatic Molecules", Academic Press, London, 1965.
(19) Another possible energy sufficient intermediate is the diperoxycarboxylic acid. However, bimolecular decomposition of peroxycarboxylic acids has been shown to lead to the acid.[20]
(20) J. F. Goodman, P. Robson, and E. R. Wilson, *Trans. Faraday Soc.*, **58**, 1846 (1962).
(21) R. B. Woodward and R. Hoffmann, "The Conservation of Orbital Symmetry", Academic Press, New York, N.Y., 1970.

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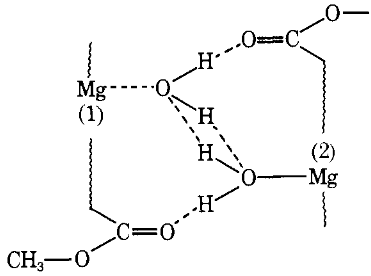
Received July 12, 1976

The Role of Water on the Photoactivity of Chlorophyll a. In Vitro Experimental Characterization of the PSI Light Reaction in Photosynthesis[1]

Sir:

Recent experimental studies in this laboratory have been concerned with the preparation[2] and characterization[3] of the P700 chlorophyll a monohydrate dimer $(\text{Chl a}\cdot H_2O)_2$ after the proposed model for the photosystem I reaction center in plant photosynthesis.[4] It is believed[4] that a singlet-triplet upconversion interaction[5-7] in $(\text{Chl a}\cdot H_2O)_2$ brings about a tautomeric proton shift that results in the creation of a symmetrical charge transfer state[4] (B). The observation[8,9] of positive



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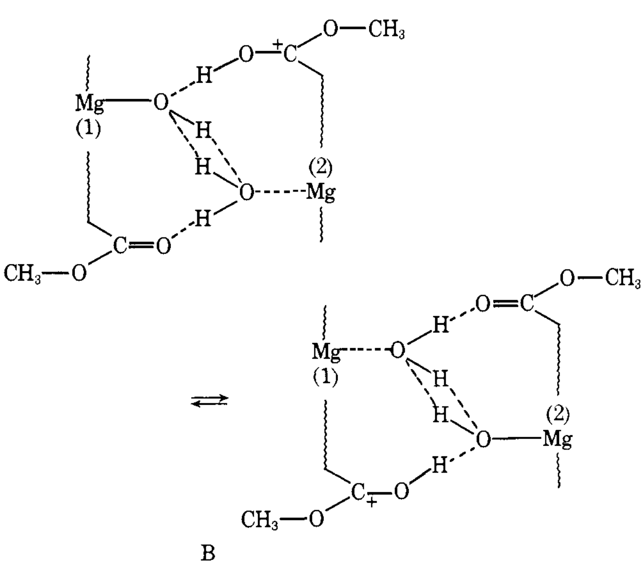


B

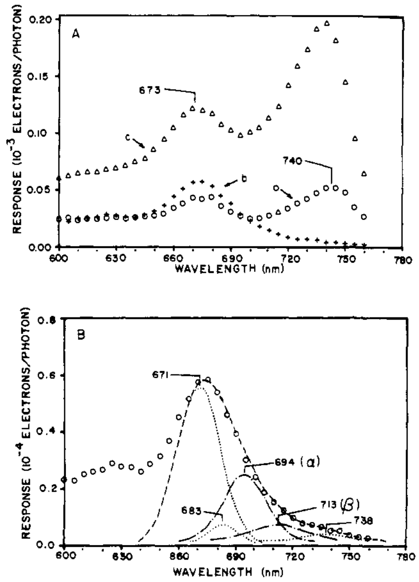


Figure 1. (A) Photogalvanic response action spectrum of a hydrated Chl a film on Pt: (a) freshly prepared sample from an electrode-plating procedure developed by Tang and Albrecht;[11c] (b) sample in (a) heated under vacuum at 80 °C for 24 h; (c) sample in (b) heated in an aqueous solution at 80 °C for 12 h. (B) Computer deconvolution of the spectral response of the vacuum-heated sample. The sequence of observations suggest that the monohydrate complexes (673-nm band) are considerably less photoactive than the dihydrate aggregate (740-nm band) and that the 673-nm band photoactivity becomes enhanced after an acquisition of additional water molecules. See text for detailed discussion.

photopotentials at Chl a electrodes has recently been attributed[9] to the photoactivation of B.

The question of the photoactivity of hydrated chlorophyll has been the subject of numerous investigations in recent decades.[10,11] However, few of the earlier studies have been focused on photochemical properties of specific relevance to the primary light reaction in photosynthesis. In this communication, we report the findings of experiments designed to explore into the origin of the photoactivity of Chl a–H_2O aggregates, with special emphasis on the P700 dimer (Chl a·$H_2O)_2$. The results demonstrate the dramatic enhancement of Chl a photoactivity by water. An important conclusion of our present study is that A by itself is probably not photoactive and that additional water molecules to the two involved in bonding interactions in A are needed for the consummation of the primary photoact.

We make use of the recently developed[9] Chl a photogalvanic cell to determine the action spectrum of Chl a photoactivity under various conditions. The experimental assembly consists of two half cells, a Pt-Chl a electrode immersed in a 0.1 M aqueous solution of $LiClO_4$ and a chlorophyll-free Pt electrode, separated by a glass frit. The details of the cell preparation parallel those described earlier[9] except for a number of refinements, one of which being the employment of a Kiethley current amplifier instead of an IR drop for the photocurrent measurement. 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.[11c]

The photochemical action spectrum of the freshly prepared Pt-Chl a electrode (Figure 1A,a) shows an approximately equal distribution of the observed photocurrent in two bands with maxima at 673 and 740 nm, respectively. The latter band is readily attributable to the presence of the dihydrate polymer (Chl a·$2H_2O)_n$.[2,12,13] After the Pt-Chl a electrode has been heated under vacuum for 80 °C for 24 h, a marked change occurs in the photogalvanic spectral response (see Figure 1A,b). The disappearance of the 740-nm band indicates the partial dehydration of (Chl a·$2H_2O)_n$ to yield monohydrate complexes.[14] The resulting 670-nm band in Figure 1A,b is closely similar to the optical absorption spectrum of a Chl a monohydrate film (on a microscope slide) prepared by the usual vacuum-heat procedure.[14] Bearing in mind the fact that Figure 1A,b has been obtained with the Pt-Chl a electrode in direct contact with water, we deduce that, under ordinary room conditions, the hydrophobic interactions due to the presence of the phytyl chains in Chl a apparently provide an effective nonpolar environment for the existence of an equilibrium mixture of Chl a·H_2O and (Chl a·$H_2O)_2$ in which the integrity of the bonding interactions in A has been kept intact. It has been established that Chl a exists as the monohydrate in a rigorously dried nonpolar medium.[2,12,14]

A computer deconvolution of the 670-nm band of the vacuum-heated Chl a action spectrum is given in Figure 1B. We observe that approximately 35% of the observed photocurrent has originated from the α and β exciton components[3] of the P700 monohydrate dimer (Chl a·$H_2O)_2$. Approximately 56% of the area under the 670-nm band appears to be attributable to a Gaussian envelope of inhomogeneously broadened monomeric chlorophyll complexes that possibly act as the light collecting apparatus for the P700 aggregate in analogy to the antenna chlorophylls found in in vivo photosynthesis.[15] The remaining 9% of the 670-nm band has been found to have arisen from two relatively minor components at 683 and 738 nm that are possibly the dimer Chl a_2[12] and polymeric aggregate (Chl a·$2H_2O)_n$.[2,12,13]

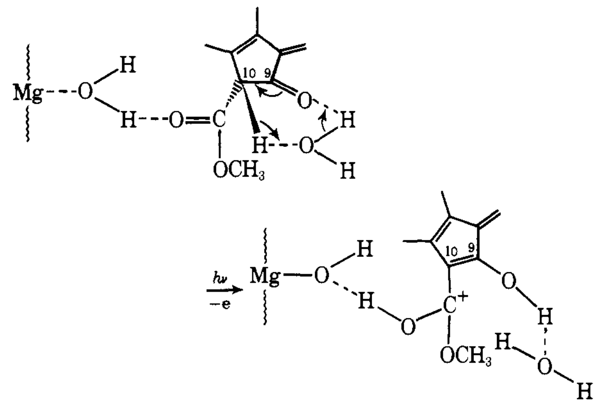
The greatly reduced photoactivity of the vacuum-heated Chl a film is noted by a comparison of Figures 1A,a and b. It is evident that the slight increase in the 670-nm band in Figure 1A,b is not commensurate with the corresponding disappearance of the 740-nm band. It appears that the presence of the two H_2O molecules in A cannot fully account for the photoactivity of A. No signs of photoactivity in rigorously dried nonpolar solutions of chlorophyll monohydrate have been detected in contrast with the well-established light-induced effects[10,11] in the crystalline dihydrate polymer.[2,12,13]

In order to demonstrate the validity of the above deduction, we now immerse the entire photoelectrochemical cell assemply (with the Pt-Chl a electrode submerged in the aqueous $LiClO_4$ electrolyte) in a temperature bath maintained at 80 °C for 12 h. The elevated temperature makes possible a reequilibration of the chlorophyll monohydrate film with the surrounding aqueous environment. The resulting spectral response of the photogalvanic cell is shown in Figure 1A,c. The great enhancement in the observed photocurrent output is accompanied by the dramatic shift of the response function in favor of the 740-nm band. Of interest is the fact that the relatively minor component of chlorophyll monohydrate that has remained after the thermal reequillibration process actually yields more than twice as much photocurrent as the entire output of the vacuum-heated sample (compare Figures 1A,b and c). These observations may be summarized in terms of the hydration equilibria

$$2m\mathrm{Chl\ a{\cdot}H_2O} \rightleftharpoons m(\mathrm{Chl\ a{\cdot}H_2O})_2$$

$$\underset{\substack{-2m\mathrm{H_2O}\\ 80\ ^{\circ}\mathrm{C}}}{\overset{+2m\mathrm{H_2O}}{\rightleftharpoons}} (\mathrm{Chl\ a{\cdot}2H_2O})_{n-2m} \rightleftharpoons m(\mathrm{Chl\ a{\cdot}H_2O})_2{\cdot}2\mathrm{H_2O} \qquad (1)$$

where the two major photoactive components are given on the right side of the equilibria. We have embodied here the concept of a photoactive form of A in assigning two additional H_2O molecules to A. This assignment may be rationalized in view of the expected photoenolization of the cyclopentanone rings in A during the photooxidation of B. The additional waters are presumably needed as the nucleophilic agent that transfers the C-10 hydrogen to the C-9 keto function in the proposed light reaction[16] (eq 2). In in vivo systems, the role played here by the additional waters in the photoenolization of the ring V



(2)

β-keto ester function may possibly be duplicated by an amide or hydroxyl group of the reaction center lipoprotein complex.

We have thus fully specified the role of the ring V β-keto ester group in the photosystem I primary light reaction. The expected[4a] conformation change in B during reaction 2 may provide the mechanism for the energization of the photosynthetic membrane.[17] Experiments are underway to confirm the above interpretations by an NMR spectroscopic determination of the proposed photoenolization process under conditions comparable to those of the present study. We are aware of the fact that our present conclusions appear to be generally consistent with the recognized role of the cyclopentanone ring in the epimerization of Chl a to Chl a′ involving the C-10 hydrogen in protic solvents.[18] We have also begun a parallel series of studies on pyrochlorophyll photoactivity in order to delineate water enhancement effects other than the photoenolization interpretation given above. In pyroChl the C10 carbomethoxy group in Chl a has been replaced by a hydrogen atom, and no photoenolization in ring V is possible.

Acknowledgment. The work reported in this communication was supported by the Alcoa Foundation and the National Science Foundation.

References and Notes

(1) This work was presented by F. K. Fong as part of the Michael Faraday Lecture delivered in the 9th Midwest Theoretical Chemistry Conference held at the Northern Illinois University, DeKalb, Ill., May 21, 1976.
(2) F. K. Fong and V. J. Koester, *Biochim. Biophys. Acta*, **423**, 52 (1976).
(3) (a) F. K. Fong, V. J. Koester, and J. S. Polles, *J. Am. Chem. Soc.*, **98**, 6406 (1976); (b) V. J. Koester and F. K. Fong, *J. Phys. Chem.*, **80**, 2310 (1976).
(4) For a review of recent development, see (a) F. K. Fong, "Theory of Molecular Relaxation: Applications in Chemistry and Biology", Wiley-Interscience, New York, N.Y., 1975, Chapter 9; (b) translated into Japanese by Y. Inoue, *Protein, Nucleic Acid Enzyme*, **21** (9), 701 (1976); (c) *Acc. Chem. Res.* **9**, 433 (1976); (d) "The Primary Light Reaction in Photosynthesis: A Molecular Interpretation", Wiley-Interscience, New York, N.Y., in press.
(5) For related discussions, see R. S. Knox in "Topics in Photosynthesis", Vol. II, J. Barber, Ed., Elsevier, New York, N.Y., in press.
(6) T. S. Rahman and R. S. Knox, *Phys. Status Solidi*, **58**, 715 (1973).
(7) F. K. Fong, *J. Am. Chem. Soc.*, submitted for publication.
(8) V. B. Evstigneev and A. N. Terenin, *Dokl. Akad. Nauk SSSR*, **81**, 223 (1951).
(9) F. K. Fong and N. Winograd, *J. Am. Chem. Soc.*, **98**, 2287 (1976).
(10) (a) E. K. Putseiko in "Elementary Photoprocesses in Molecules", Bertol'd S. Neporent, Ed., Consultants Bureau, New York, N.Y., 1968, p 281; (b) A. N. Terenin, E. Putseiko, and I. Akimor, *Discuss. Faraday Soc.*, **27**, 83 (1959).
(11) (a) C. W. Tang and A. C. Albrecht, *J. Chem. Phys.*, **62**, 2139 (1975); **63**, 953 (1975); (b) C. W. Tang, F. Douglas, and A. C. Albrecht, *J. Phys. Chem.*, **79**, 2823 (1975); (c) C. W. Tang and C. A. Albrecht, *Mol. Cryst. Liq. Cryst.*, **25**, 53 (1974).
(12) (a) F. K. Fong and V. J. Koester, *J. Am. Chem. Soc.*, **97**, 6888 (1975); (b) F. K. Fong, *ibid.*, **97**, 6890 (1975).
(13) A. S. Holt and E. E. Jacobs, *Am. J. Bot.*, **41**, 710 (1954).
(14) N. Winograd, A. Shepard, D. H. Karweik, V. J. Koester, and F. K. Fong, *J. Am. Chem. Soc.*, **98**, 2369 (1976).
(15) See, for example, R. E. Fenna and B. W. Mathews, *Nature (London)*, **258**, 573 (1975). These authors have established that a basic unit of bacterial antenna system in chlorobium *limicola* is a cluster monomeric Chl a–protein complexes.
(16) Reference 4a, p 258.
(17) F. K. Fong, *J. Am. Chem. Soc.*, **98**, 7840 (1976).
(18) H. H. Strain, *J. Agr. Food Chem.*, **2**, 1222 (1954).
(19) Alfred P. Sloan Foundation Fellowship, 1974–1978.

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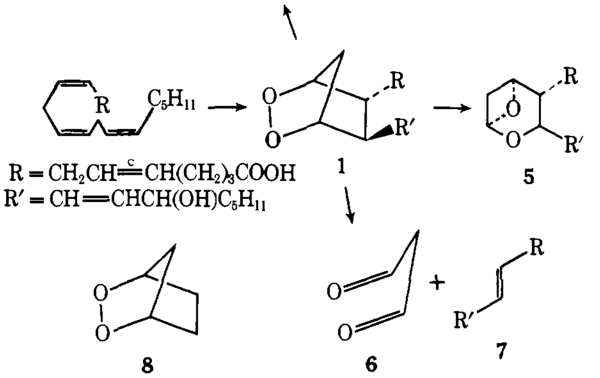
Received April 13, 1976

Synthesis and Thermal Reactivity of Some 2,3-Dioxabicyclo[2.2.1]heptane Models of Prostaglandin Endoperoxides

Sir:

Prostaglandin (PG) endoperoxides[1] (e.g., **1**), the immediate biological precursors of prostaglandins (e.g., **2**, **3**, **4**) and thromboxanes[2] (e.g., **5**), are generally considered to be derivatives of the otherwise unknown 2,3-dioxabicyclo[2.2.1]heptane (**8**) heterobicyclic ring system. Recently, solutions containing PG endoperoxides, PGG_2 and PGH_2, were prepared enzymatically.[3] However, studies of the chemical reactions of these key biomolecules are beclouded by the instability[4] and uncertain purity[5] of samples obtained by bioconversion. We now report: (1) the first nonenzymatic synthesis of bona fide, fully characterized derivatives of the bicyclic ring system **8**, (2) thermal fragmentation of **10**, a derivative of **8**, to a 1,3-dione and olefin, which is reminiscent of the in vitro fragmentation of PG endoperoxides, and (3) thermochemical data for decomposition of this model endoperoxide which show unexpectedly great thermal stability consistent with a homolytic mechanism rather than a concerted electrocyclic fragmentation.

Scheme I



The unsaturated analogue of **8**, 2,3-dioxabicyclo[2.2.1]heptene, and substituted derivatives thereof are readily available, though thermally labile.[6] Thus, the unsaturated peroxide **9** is readily prepared by cycloaddition of singlet oxygen[7] with 1,4-diphenyl-1,3-cyclopentadiene (Scheme II).[8] We now find that diimide[9] selectively reduces the C–C π-bond of **9** to give 1,4-diphenyl-2,3-dioxabicyclo[2.2.1]heptane (**10**).[10] The upfield portion of the ^{1}H NMR spectrum of **10** (Figure 1) in perdeuteriobenzene solution exhibits four multiplets centered at δ 1.90, 2.17, 2.40, and 2.64 which correspond to H_x, H_a, H_n, and H_s, respectively. Geminal coupling J_{xn} = 8 Hz, J_{as} = 10 Hz, and long range W-plan[11] coupling J_{ns} = 2.5 Hz support these assignments. Reduction of **9** with dideuteriodiimide occurs stereospecifically cis-exo to give **11** (Scheme