

Table II. Comparison of Rotational Correlation Times for Some Proteins Determined from Carbonyl Off-Resonance $T_{1\rho}$ Experiments with Other Literature Values

Protein	$\tau_{r,ns}$	
	$T_{1\rho}^{off}$ technique ^a	Other techniques
LY	18	19, ^b 25, ^c 50 ^d
CHY	35	35 ^e
CON A	68	93, ^f 110 ^d
MetHb A	83	47, ^g 61, ^h (84, 130), ⁱ 102 ^d
BSA	105	78, ^b 118, ^j 125 ^k
γ G	338	220, ^j 420 ^d

^a At 25 °C. ^b By NMR ¹³C relaxation at 43 °C. ^c By fluorescence depolarization.¹⁷ ^d By water proton NMR dispersion at 25 °C. ^e By electric birefringence.^{3b} ^f By fluorescence depolarization.¹⁸ ^g By ¹³C NMR relaxation of carbon monoxide hemoglobin at 36 °C. ^h By fluorescence depolarization.¹⁹ ⁱ By dielectric relaxation.²⁰ ^j By dielectric relaxation.²¹ ^k By fluorescence depolarization.²²

rotational motions, however, would require that individual resonances from nuclei on different parts of the protein backbone be observed. Similarly, the investigation of internal motions would require observation of resonances from nuclei on other protein moieties as well as knowledge of the overall tumbling motion of the protein.

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- (4) Abbreviations used are: rf, radiofrequency; NMR, nuclear magnetic resonance; FID, free induction decay; LY, lysozyme; CHY, chymotrypsinogen A; CON A, concanavalin A; Hb, human adult hemoglobin; BSA, bovine serum albumin; γ G, immunoglobulin G.
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Communications to the Editor

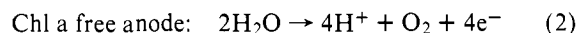
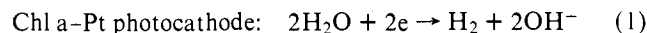
The Primary Water Splitting Light Reaction. Mass Spectrometric Determination of Gaseous Hydrogen and Oxygen Evolution from Water Photolysis by Platinized Chlorophyll a Dihydrate Polycrystals^{1,2}

Sir:

In earlier work we attributed Chl a photogalvanic effects to water splitting reactions that result from illumination of the chlorophyll a dehydrate aggregate $(\text{Chl a} \cdot 2\text{H}_2\text{O})_n$.³ The photooxidation of $(\text{Chl a} \cdot 2\text{H}_2\text{O})_{n \geq 2}$ by water was subsequently observed in ESR experiments.⁴ These observations were corroborated by the finding⁵ that the midpoint reduction potential of $(\text{Chl a} \cdot 2\text{H}_2\text{O})_n$ is 0.92 V, exceeding that, 0.81 V, required for the water oxidation ($\text{O}_2/\text{H}_2\text{O}$) half-reaction at pH 7. The demonstration of water splitting by $(\text{Chl a} \cdot 2\text{H}_2\text{O})_{n \geq 2}$ is of current interest. It has been suggested³ that the water splitting reaction in vivo results directly from the primary light reaction of $(\text{Chl a} \cdot 2\text{H}_2\text{O})_2$. The water splitting question is topical in view of the current search for a direct process for harvesting solar energy to produce gaseous hydrogen for fuel. Considerable attention has been focused on n-type semiconducting photoanodes such as TiO_2 ⁶ and SrTiO_3 .^{7,8} However, these materials operate in the near-ultraviolet wavelength region where the solar radiant energy is low. In contrast, the action

spectrum of the photoreactivity of $(\text{Chl a} \cdot 2\text{H}_2\text{O})_n$ with water spans the visible and far-red wavelength regions.³ In this paper we describe the mass spectrometric determinations of H_2 and O_2 evolution due to water photolysis by platinized $(\text{Chl a} \cdot 2\text{H}_2\text{O})_n$.

The splitting of water by the chlorophyll in photogalvanic application³ may be given in terms of the half-reactions:



A Pt foil was platinized by passing a 30-mA current for 10 min through a 7×10^{-2} M chloroplatinic acid solution containing 6×10^{-4} M lead acetate. A layer of polycrystalline chlorophyll, containing 1.5×10^{17} Chl a molecules, was deposited on the platinized electrode surface in the usual manner.^{3,9} The Chl a plated electrode was then platinized again in the same chloroplatinic acid solution by passing the 30-mA current for 15 s. The resulting sample electrode was baked at 60 °C under atmospheric pressure for several hours in order to be rid of any adventitious gaseous occlusion during the platinization procedure.

The action spectrum of the photogalvanic response of the platinized Chl a electrode at pH 7, measured in a cell³ employing as the second half-cell a platinized electrode not

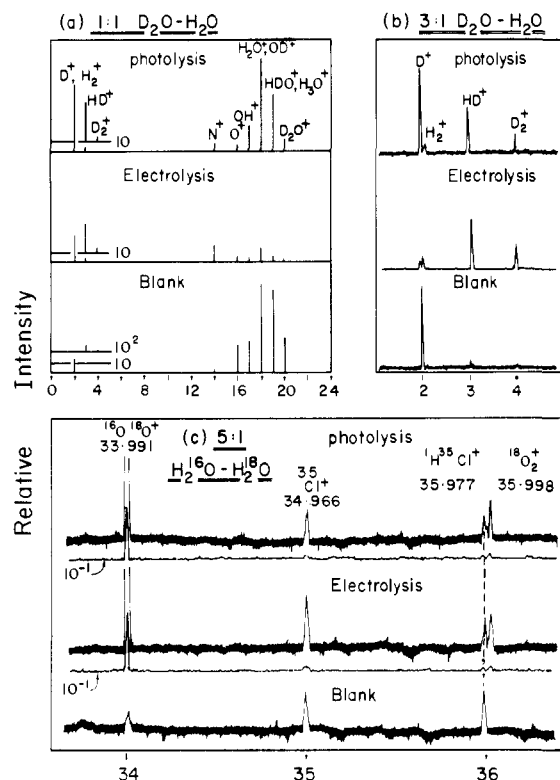


Figure 1. Mass spectrometric analyses of the photolytic and electrolytic products of (a) 1:1 D_2O-H_2O , (b) 3:1 D_2O-H_2O , and (c) 5:1 $H_2^{16}O-H_2^{18}O$. The mass 34 line in the blank run in c is due to the 0.204% natural abundance of ^{18}O . The observed 34:36 mass intensity ratios of ~ 10 for the photolytic and electrolytic runs in c are in agreement with the expected value for 5:1 $H_2^{16}O-H_2^{18}O$. The lines at mass numbers 35 and 36 in c, corresponding to Cl^+ and HCl^+ , respectively, are attributable to the KCl (0.45 M) in the buffered (pH 3) electrolyte solution. The mass spectra in this figure were obtained with the ion source focused at mass 2. The scale about the indicated mass numbers in b has been expanded to allow representation of the spectral resolution at mass 2. The low noise level in the electrolytic run in b is due to the relatively strong signals from passing a 30-mA current for 10 min. The H^+ line at mass 1 is not detected owing to instrumental limitation.

covered with Chl a, shows a 740-nm maximum indicative of the fact that $(Chl\ a \cdot 2H_2O)_n$ ^{10,11} is primarily responsible for the observed photogalvanic effects. Prolonged illumination using the entire output from a 1000-W tungsten halogen lamp led to the observation of gaseous evolution from the Pt-Chl electrode.² In mass spectrometric analyses (Figures 1 and 2) it was ascertained that both H_2 and O_2 were evolved at the Pt-Chl electrode. Air contamination in several early experiments was traced to leakage through the external leads admitted into the sample cell via metal-glass joints for the measurement of photogalvanic currents. These leads were removed in later experiments such as the one summarized in Figure 2. In the following report the "blank" control experiments were carried out without the platinized electrodes under conditions identical with those of the photolytic runs.

After the light-induced reaction of a platinized Chl a sample (immersed in a pH 3 citrate-phosphate, KCl containing buffer solution) was allowed to proceed for a given period of time, the gaseous content over the electrolyte solution, on cooling to room temperature, was evacuated directly into the sample chamber of a Consolidated Electrodynamics Corp. 21-110-B mass spectrometer. Mass spectrometric analyses of the light-induced products from various mixtures of $H_2^{16}O$, $D_2^{16}O$, and $H_2^{18}O$ are compared, in Figure 1, with those of electrolyzed samples (30 mA passed for 10 min) containing the corresponding isotopic water mixtures. The results of a light experiment (90-min illumination) using 1:1 D_2O-H_2O are shown

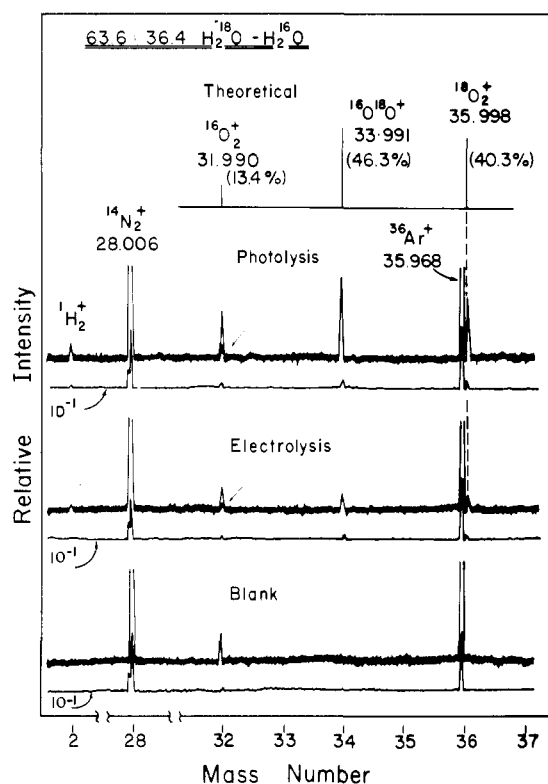


Figure 2. Mass spectrometric study demonstrating the simultaneous generation of molecular hydrogen and oxygen in water photolysis. The light reaction was carried out for 20 min. The control experiment corresponds to the electrolysis of 5×10^{-7} mol of H_2O . The arrows at mass 32 in the photolytic spectrum represents the $^{16}O_2^+$ signal due to water photolysis after correction for air contamination in the sample. After a similar correction in the electrolytic spectrum the isotopic distributions of O_2 obtained in photolysis and electrolysis are seen to be in agreement with the theoretical pattern. The scale about the indicated mass numbers has been expanded by a factor of 3 to facilitate the representation of the line intensities and spectral resolution. The mass spectra in this figure were obtained with the ion source focused at the $^{40}Ar^+$ line.

in Figure 1a. We assume that the observation of the mass 4 (D_2^+) line has resulted from water splitting and use the mass 20 (D_2O^+) line as an internal reference for calibration. We estimate, from a comparison of the relative intensity ratios of lines at masses 20 (D_2O^+) and 4 (D_2^+) observed in the photolytic and electrolytic runs, that water photolysis occurs at a rate of $(9 \times 10^{-6} \text{ mol})/h$, corresponding to a gaseous (H_2 and O_2) evolution rate of 0.3 mL/h. At sufficiently high instrumental resolution, we were able to differentiate the H_2^+ line from the interference at mass 2 due to D_2O fragmentation to D^+ and OD^+ . The determination of the molecular species H_2^+ , HD^+ , and D_2^+ thus made for the photolysis and electrolysis of 3:1 D_2O-H_2O are shown in Figure 1b. The presence of molecular oxygen in the light-induced splitting of water is ascertained by using 5:1 $H_2^{16}O-H_2^{18}O$ (see Figure 1c). The lines at masses 34 ($^{16}O^{18}O^+$) and 36 ($^{18}O_2^+$) observed for the photolytic sample are in agreement with the corresponding lines observed from electrolysis. From statistical considerations the observed 10:1 intensity ratios for the mass 34 ($^{16}O^{18}O^+$) and 36 ($^{18}O_2^+$) lines are compatible with a scrambling of the 5:1 $^{16}O-^{18}O$ atoms in the oxygen evolution process.

A mass spectrometric study of the simultaneous generation of H_2 and O_2 from 63.6:36.4 $H_2^{18}O-H_2^{16}O$ in a pH 11 sodium hydroxide-phosphate buffer, in which no KCl was added, is reproduced in Figure 2. The relative line intensities at masses 2 (H_2^+), 34 ($^{16}O^{18}O^+$), and 36 ($^{18}O_2^+$), absent in the blank, are in excellent agreement between the photolytic and electrolytic runs. The experiment was performed under a positive pressure of Ar in order to generate the $^{36}Ar^+$ (0.337% natural

abundance) line, which serves as a useful internal standard in the mass 36 region. The intensity ratio of the lines at masses 28 ($^{14}\text{N}_2^+$) and 32 ($^{16}\text{O}_2^+$) in the blank agrees with that of an air sample. Based on this ratio we correct for the air contamination effect on the line intensity at mass 32 ($^{16}\text{O}_2^+$) of the photolysis sample spectrum. The resulting pattern for the observed isotopic distribution of molecular oxygen is in excellent agreement with the expected pattern (see Figure 2). The photolytic sample was measured after 20 min of illumination. The electrolysis was carried out by passing a 20-mA current for 5 s. Calibrating the line intensities at masses 34 ($^{16}\text{O}^{18}\text{O}^+$) and 36 ($^{18}\text{O}_2^+$) of the photolytic sample against the corresponding intensities of the electrolytic sample, we arrive at a water splitting rate of 10^{-5} mol/h.¹² From the same calibration, using the line intensity at mass 28 (N_2^+) and the known mass intensity ratio of 28 (N_2^+):32 ($^{16}\text{O}_2^+$) for air, we estimate that atmospheric contamination in the photolytic sample amounts to 3×10^{-7} mol of $^{16}\text{O}_2$, approximately an order of magnitude lower than the 2.5×10^{-6} mol of molecular oxygen, occurring variously in the forms of $^{16}\text{O}_2$, $^{16}\text{O}^{18}\text{O}$, and $^{18}\text{O}_2$, produced in 20 min of the light-induced water splitting reaction.

The incident irradiance of photons ("white light") focused on the Pt-Chl a electrode was 1.74 W cm^{-2} . An energy storage efficiency of 0.04%, given by the ratio of the rate of chemical free energy stored (in the form of H_2 and O_2) and the incident irradiance, was thus obtained for the observed rate ($\sim 10^{-5}$ mol/h) of water photolysis employing 10^{17} Chl a molecules. We estimate that <1% of the light was effectively engaged in the photoreaction.¹³ It seems reasonable to suppose that, by increasing the number of Chl a molecules engaged in the photoreaction, it should be possible to enhance the energy storage efficiency by two orders of magnitude.

The enclosure of the sample cell to minimize air contamination precluded direct temperature measurement during the light reaction. Gaseous evolution was evident in bubble formations over the brilliantly blue Chl a coating under illumination. In the absence of Chl a no gaseous bubbling off the platinum was observed under comparable illumination conditions, suggesting that the sample was well below the boiling point of water. In control experiments, we observed that at $T \gtrsim 90^\circ\text{C}$ the platinized $(\text{Chl a} \cdot 2\text{H}_2\text{O})_n$ film visibly disintegrates over a period of several hours. The Chl a purity before and after the light reaction was checked in the usual manner.^{11b} Demetalation of Chl a to pheophytin was observed after light experiments performed under acidic conditions. In corresponding experiments at $\text{pH} \geq 7$ no degradation of the chlorophyll was detected after extended usage of the Pt-Chl a samples.

In view of the observed photoreactivity of $(\text{Chl a} \cdot 2\text{H}_2\text{O})_n$ with water in the absence of Pt,⁴ we believe that the experimental effects described in the present work are attributable, in part at least, to the intrinsic photochemical properties of the chlorophyll. In water splitting work on inorganic semiconductors⁶⁻⁸ the indispensable role⁷ of the platinum black was interpreted in terms of a mechanism that relates properties of the semiconductor with those of the platinum.⁷ However, we have evidence that the platinum itself may be partially responsible for our observations in the UV wavelength region.

The Chl a water splitting reaction *in vivo* provides the sustenance of life on this planet. The photochemical properties of $(\text{Chl a} \cdot 2\text{H}_2\text{O})_{n \geq 2}$ reported here and elsewhere³⁻⁵ suggest possible clues to the origin of this remarkable reaction.

References and Notes

- (1) The work described in this communication was presented in the *In Vitro* Photosynthesis Symposium of the 13th Informal Photochemistry Conference, Clearwater Beach, Fla., Jan 4-7, 1978, and in the *Inorganic Compounds with Unusual Properties. II. Molecular Catalysis and the Conversion, Production, and Storage of Energy* Symposium of the 1978 American

Chemical Society Inorganic Chemistry Meeting, Athens, Ga., Jan 31-Feb 3, 1978.

- (2) A detailed description of a pyrolytic analysis of the water splitting reaction reported here will appear in the Proceedings of the 1978 American Chemical Society Inorganic Chemistry Meeting; see L. Galloway, D. R. Fruge, and F. K. Fong, *Adv. Chem. Ser.*, in press.
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Osmium-Catalyzed Vicinal Oxyamination of Olefins by *N*-Chloro-*N*-argentocarbamates

Sir:

We have previously reported two^{1,2} procedures for the vicinal oxyamination of olefins. One method employs stoichiometric amounts of preformed *tert*-alkyl imido osmium compounds (**1a**).¹ The other method is catalytic in osmium and



1a, R = *tert*-alkyl

1b, R = Ts

1c, R = R'OCO

relies on Chloramine-T (TsNClNa) for the *in situ* regeneration of the imido osmium species **1b**;² this procedure produces vicinal hydroxy *p*-toluenesulfonamides. The relative difficulty of removing sulfonamide protecting groups provided incentive for developing a catalytic method which would place a more easily removed group on the nitrogen. The successful outcome of this search is reported here.

N-Chloro-*N*-argentocarbamates³ are generated *in situ* by reaction of the corresponding *N*-chlorosodiocarbamates (**2**) with silver nitrate in acetonitrile. Addition of the olefin, some water and 1% of osmium tetroxide catalyst to the resulting suspension, affords the vicinal hydroxycarbamates (**3**) in generally good yields (Scheme I and Table I). As revealed in Scheme I the process is very general with respect to the structure of the carbamate.⁴ The *N*-chlorosodiocarbamates (**2a** through **2f**) were prepared from the carbamates according to a convenient method developed by Johnson in the laboratory of Professor Malcolm M. Campbell.⁵ In this way⁵ the *N*-chlorosodiocarbamates **2a**, **2b**, **2c**, and **2d** were prepared and isolated.⁶ However, when isolation of *N*-chlorosodiocarbamates with larger organic groups (e.g., **2e** and **2f**) was attempted, decomposition⁸ sometimes occurred. Fortunately, the crude *N*-chlorosodiocarbamates (i.e., after evaporation of the methanol but before trituration with ether) from the