in anodic fluroinations: Koch, V. R.; Miller, L. L.; Clark, D. B.; Fleishman, M.; Joslin, T.; Pletcher, D. *J. Electroanal. Chem.* **1973**, *43*, 318–320.

(3) Peak anodic potential, $E_{p(a)}$, for a 1.0 mM solution of the tetra-*n*-butylammonium (TBA) salt in 0.10 M tetra-*n*-butylammonium perchlorate (TBAP). Geske[4] has noted a concentration dependence of the anodic discharge potential of $NaBPh_4$ in MeCN containing $LiClO_4$.

(4) Geske, D. H. *J. Phys. Chem.* **1959**, *63*, 1062–1070.

(5) Also as the TBA salt in MeCN/0.10 M TBAP at a platinum electrode. No reverse (cathodic) peak is in evidence at scan rates up to 30 V s^{-1}. $TBABBu_4$ was obtained from Alfa-Ventron and purified according to Morrison, G.; Lind, J. E., Jr. *J. Chem. Phys.* **1968**, *49*, 5310–5316. Sources and purification procedures for MeCN and TBAP as well as details of electrochemical instrumentation are summarized in ref 1c.

(6) In MeCN containing 0.10 M TBAP, we have noted extreme *n* values of 1.90 (±0.06) for 80 μM $TBABPh_4$ and 1.06 (±0.04) for 10 mM $TBABPh_4$; cf. ref 4.

(7) Janzen, E. G. *Acc. Chem. Res.* **1971**, *4*, 31–40.

(8) Bard, A. J.; Gilbert, J. C.; Goodin, R. D. *J. Am. Chem. Soc.* **1974**, *96*, 620–621.

(9) Kraeutler, B.; Jaeger, C. D.; Bard, A. J. *J. Am. Chem. Soc.*, **1978**, *100*, 4903–4905.

(10) In MeCN at a platinum electrode, PBN is oxidized and reduced at +1.5 V and −2.4 V, respectively, while the phenyl adduct of PBN is estimated to be electroinactive between +0.7 V and −2.0 V.[8]

(11) The potential of the platinum working electrode in a conventional three-electrode, three-compartment cell was controlled at +0.35 V. Following electrolysis, samples were withdrawn, introduced into flat cells, and deoxygenated again and their ESR spectra were recorded on a Varian E-104 spectrometer.

(12) CPE in the ESR cavity were carried out using a Varian E-256 electrolytic sample cell.

(13) In MeCN/TBAP, NtB is electroinactive between +1.82 and −1.77 V.[14] Spin adducts of NtB provide direct structural information regarding the radical from which the adduct is derived.[15]

(14) McIntire, G. L.; Blount, H. N.; Stronks, H. J.; Shetty, R. V.; Janzen, E. G., unpublished work.

(15) Lagercrantz, C. *J. Phys. Chem.* **1971**, *75*, 3466–3475.

(16) Janzen, E. G.; Blackburn, B. J. *J. Am. Chem. Soc.* **1969**, *91*, 4481–4490.

(17) (a) Merritt, M. V.; Johnson, R. A. *J. Am. Chem. Soc.* **1977**, *99*, 3713–3719. (b) Howard, J. A.; Tait, J. C. *Can. J. Chem.* **1978**, *56*, 176–178.

(18) Yamamoto, Y.; Maruyama, K. *J. Am. Chem. Soc.* **1978**, *100*, 6282–6284.

(19) Note that $E_{p(a)}$ for $TBABPh_4$ is +0.92 V in this medium. At potentials >1.4 V, PBN also undergoes electrooxidation. No radical species were detected by either CPE technique (in situ or external) at $TBABPh_4$ concentrations corresponding to coulometric values of $n \simeq 1$ (10 mM) and $n \simeq 2$ (80 μM).

(20) Janzen, E. G.; Evans, C. A. *J. Am. Chem. Soc.* **1975**, *97*, 205–206.

(21) Such a reaction is reminiscent of and has a formal similarity to the potassium metal reduction of tetraphenylmethane in ether solvents where biphenyl radical anion is detected: Townsend, M. G. *J. Chem. Soc.* **1962**, 51.

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Photosynthesis of Polyatomic Organic Molecules from Carbon Dioxide and Water by the Photocatalytic Action of Visible-Light-Illuminated Platinized Chlorophyll *a* Dihydrate Polycrystals

Sir:

Sunlight is converted by green plants into the driving force for photosynthesis according to the reaction stoichiometry[1]

$$CO_2 + 2H_2O \xrightarrow[\text{Chl } a]{\text{visible light}} CH_2O + H_2O + O_2 \tag{1}$$

in which water cleavage by the chlorophyll is accompanied by the reduction of carbon dioxide. That water is the source of O_2 evolution in eq 1 was suggested around 1930.[2-5] Experimental support for this suggestion was provided by several workers.[6-8] Recent work in this laboratory demonstrated the Chl *a* water splitting reaction[9,10]

$$2H_2O \xrightarrow[\text{Chl } a]{\text{visible light}} 2H_2 + O_2 \tag{2}$$

using platinized, polycrystalline Chl *a* electrodes. In this communication we report evidence for the photoreduction of CO_2 by H_2O to formic acid by platinized $(\text{Chl } a\cdot 2H_2O)_n$. The reduction is shown to be photocatalyzed by the chlorophyll and may additionally produce formaldehyde.

$$2CO_2 + 2H_2O \xrightarrow[\text{Chl } a]{\text{visible light}} 2H_2CO_2 + O_2 \tag{3}$$

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. Chl *a* was prepared in the usual manner from fresh spinach leaves by chromatographic methods and suspended in *n*-pentane as polycrystalline chlorophyll *a* dihydrate.[11] The Pt black electrode was plated with Chl *a* by suspending the electrode in an aluminum trough filled with 10^{-4} M Chl *a* and subjecting it to a 1000 V cm^{-2} potential under the illumination of a 200-W tungsten lamp. The Chl *a* plated electrode, still under illumination, was platinized again for 15 s at 30 mA in the chloroplatinic acid solution. The platinized $(\text{Chl } a\cdot 2H_2O)_n$ sample was immersed in warm water (40-60 °C) for 2 h and then allowed to equilibrate in the water at room temperature overnight. The electrode was then placed in a cell, fitted with Kel-F valves, containing a mixture of $H_2{}^{16}O$, $D_2{}^{16}O$, and/or $H_2{}^{18}O$. The sample cell containing doubly distilled ^{18}O- and/or D-enriched water was deaerated by purging with Ar gas for 20 min. The water was then saturated with CO_2. Research grade CO_2, purchased from Matheson, was further purified by passing the gas over a red-hot platinum coil to eliminate organic impurities and then through a Pyrex U-tube containing BTS Cu-Mn pellets for oxygen removal.[12] Following CO_2 saturation the cell was closed, and the sample was illuminated with a 1000-W xenon arc lamp. Corning CS 3-69 and water filters were used to eliminate short wavelength (λ <520 nm) and IR photons, respectively. After 30 min of illumination, the gaseous mixture above the aqueous solution was analyzed using a Consolidated Electrodynamics Model 21-110-B mass spectrometer. During the entire procedure the Pt/Chl *a* electrode was not allowed to dry in extended exposure to air.

The effect of CO_2 on the product distribution of the Pt/Chl *a* light reaction is illustrated by the mass spectral results in Figure 1. It is evident that the hydrogen evolution obtained in the absence of CO_2 (Figure 1A) is suppressed in the presence of CO_2 (Figures 1B and 1C). The appearance of $^{16}O^{18}O^+$ (mass 34) and $^{18}O_2{}^+$ (mass 36) lines in the $H_2{}^{18}O$-labeled solution ($^{16}O/^{18}O = 1.82$) establishes that O_2 is liberated from water as the oxidation product.[9,10] The mass 34/36 ratio is 3.2, in agreement with the random scrambling $^{16}O^{18}O/^{18}O_2$ ratio of 3.6 based on the known $^{18}O/^{16}O$ content in the water. (See also ref 9.) There is no evidence for the formation of H_2O_2 on account of the lack of intensity increases at masses 35 ($DH^{16}O_2{}^+$), 37 ($DH^{16}O^{18}O_2{}^+$), 38 ($D_2{}^{16}O^{18}O^+$, $H_2{}^{18}O_2{}^+$), 39 ($HD^{18}O_2{}^+$), or 40 ($D_2{}^{18}O_2{}^+$).

From a comparison of Figures 1B and 1C it is apparent that thermal radiation from the xenon arc lamp produces little effect on the product distribution. Previous work has shown[10] that Pt in water produces H_2 but no O_2 upon heating, and that the concurrent production of H_2 and O_2 occurs only when both light and Chl *a* are present. The observation of O_2 in the presence CO_2 upon illumination in Figures 1B and 1C thus suggests a photochemical pathway involving the chlorophyll. The effects in Figures 1B and 1C are not observed using visible light and a Chl *a* free Pt sample under otherwise identical conditions.

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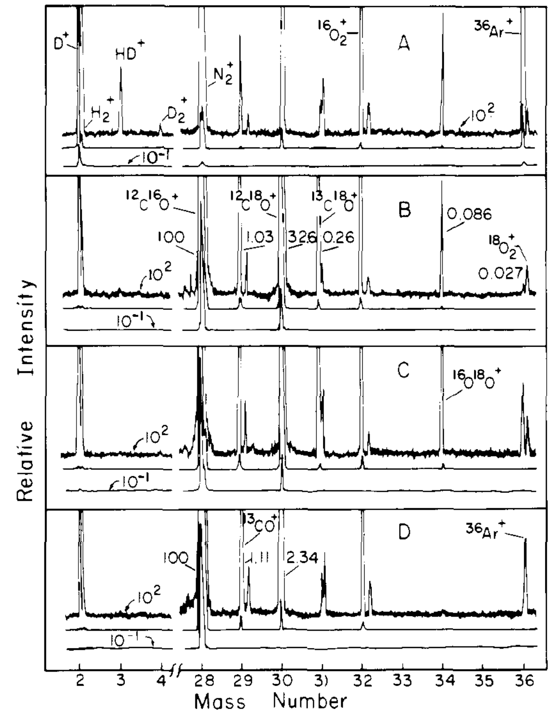

Figure 1. Comparison of the mass spectrometric determination of products from Chl *a* light reaction in Ar-purged H_2O with product analyses using isotope-enriched CO_2-saturated water having 1:1 H/D and 1.82:1 $^{16}O/^{18}O$: (A) platinized (Chl $a\cdot 2H_2O)_n$ in Ar-purged water illuminated for 30 min using red light (see ref 10); (B) platinized (Chl $a\cdot 2H_2O)_n$ in CO_2-saturated water illuminated by light from a 1000-W xenon arc lamp passed through a 2-in. water filter; (C) same conditions as in B except for the elimination of IR radiation from the xenon arc lamp using a 10-in. water filter; (D) CO_2-saturated water illuminated by the white light for 30 min. The intensity ratios of the mass 34 ($^{16}O^{18}O^+$) and 36 ($^{18}O_2^+$) lines in B and C are 3.2 and 3.8, respectively, in fair agreement with the corresponding ratio of 4.2 obtained in A. The predicted ratio from a random scrambling of ^{16}O and ^{18}O derived from water is 3.64. The mass 29 ($^{13}C^{16}O^+$) intensity is found to be ~1% of the mass 28 ($^{12}C^{16}O^+$) intensity consistent with the natural abundance of ^{13}C. The indicated intensity values are relative to a mass 29 signal of unity in Figure 1B-D. The generation of the oxygen lines at masses 34 and 36 is accompanied by growth at masses 30 ($D^{12}C^{16}O^+$, $^{12}C^{18}O^+$) and 31 ($D^{13}C^{16}O^+$, $^{13}C^{18}O^+$), indicative of reduction product fragmentation. A simultaneous loss of the mass 3 (HD^+) and mass 4 (D_2^+) as well as the mass 2 (H_2^+) signal is evident from comparison of A with B and C. The appearance of the $^{36}Ar^+$ line in B-D is the result of the Ar-degassing procedure described in the text.

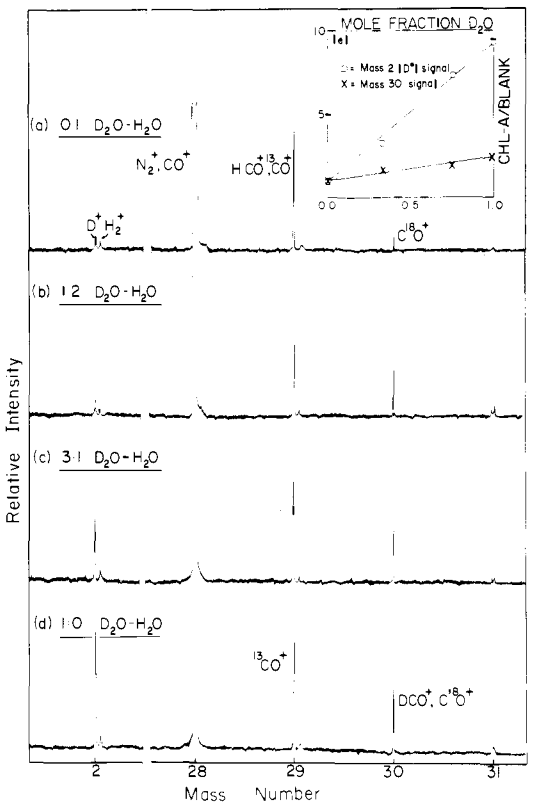

Figure 2. Mass spectral determination of the dependence of product distribution on the mole fraction of D_2O in H_2O. The Pt/Chl *a* sample was subjected to 30 min of illumination with IR and short-wavelength filtered light with CO_2-saturated solutions containing (a) pure $H_2{}^{16}O$; (b) 1:2 $D_2{}^{16}O$-$H_2{}^{16}O$; (c) 3:1 $D_2{}^{16}O$-$H_2{}^{16}O$; and (d) pure $D_2{}^{16}O$. The spectra in the mass 28-31 and mass 2 regions were obtained with the ion source focused at mass 44 and 2, respectively. The mass 29 ($^{13}C^{16}O^+$) signal was observed to be ~1% of the mass 28 ($^{12}C^{16}O^+$) signal consistent with the natural abundance ratio of $^{13}C/^{12}C$. Mass intensities in the 28-31 region were scaled to a constant mass 29 signal. In the mass 2 region the H_2^+ signal was arbitrarily chosen as the reference. The monotonic trend of increasing D^+ and mass 30 ($D^{12}C^{16}O^+$) line intensities with increasing x_D, the mole fraction of D_2O, is evident in Figures 2a-d. In Figure 2e the ratio, Chl *a*/blank, is that of the scaled signal intensity at masses 30 and 2 obtained from the illuminated sample and its corresponding unilluminated blank. The variations of Chl *a*/blank intensity ratios at masses 30 and 2 are linear in x_D.

Figures 1B and 1C also show pronounced increases in signal intensities at masses 30 and 31. The correlative assignment of mass 31 to their ^{13}C analogues is consistent with the observed mass 31/30 intensity ratio of 0.009 ± 0.002. The natural abundance ratio of $^{13}C/^{12}C$ is 0.011. The line at mass 30 is assigned to $^{12}C^{18}O^+$ and/or $D^{12}C^{16}O^+$, $H_2{}^{12}C^{16}O^+$. The $^{12}C^{18}O^+$ fragment arises from the exchange of $^{12}C^{16}O_2$ with $H_2{}^{18}O$ in the ^{18}O-labeled water mixture. The $D^{12}C^{16}O^+$ and $H_2{}^{12}C^{16}O^+$ fragments can conceivably derive from photosynthesized formaldehyde and/or formic acid. Since the mass 30/31 intensity ratio in Figures 1B and 1C approximately mirrors the ^{18}O enrichment, however, the $^{12}C^{18}O^+$ contribution at mass 30 in Figures 1B and 1C appears to be a dominant factor.

The possible generation of CO_2 reduction products is manifested by the variation of the product distribution with x_D, the mole fraction of $D_2{}^{16}O$ in H_2O that is not isotopically enriched in ^{18}O (see Figure 2). Both D^+ and mass 30 intensities evidently increase linearly with x_D (see Figures 2a-d). The observed mass 30/28 intensity ratio of 0.006 in pure D_2O (Figure 2d) corresponds to a total mass 30 line intensity about three times the expected contribution from $^{12}C^{18}O^+$ owing to the natural abundance of ^{18}O (~0.2%). The rise in the mass 30 line with x_D indicates that $D^{12}C^{16}O^+$ is the primary source of contribution to the observed intensity enhancement. Standardized mixtures of DCOOD in 3 mL of CO_2-saturated D_2O were examined by mass spectrometry. Under 1 atm of CO_2, a sample/blank intensity ratio of 5 ± 1 is obtained from the D^+ line from solutions 0.001 and 0.01 M in DCOOD. No significant intensity changes at mass 30 were observed. However, on reduction of the CO_2 pressure by a factor of ~2 in the 0.001 M DCOOD sample and increasing the DCOOD concentration to 0.01 M, we observed a 50-fold increase in the D^+/H_2^+ intensity ratio and a 2-fold increase in the mass 30/29 ratio relative to a blank prepared at 1 atm in CO_2. The simultaneous increases of the D^+ and mass 30 lines thus observed are comparable in magnitude to the corresponding increases observed in Figure 2. This observation suggests that the CO_2 pressure is reduced during the Pt/Chl *a* light reaction, resulting in the $D^{12}C^{16}O^+$ fragment.

The mass spectral analysis in Figure 3 obtained using CO_2-saturated $D_2{}^{16}O$ provides evidence for the photosynthesis of formic acid. Line intensities at masses 2, 30, 46, 47, and 48 increase significantly relative to the blank. The sample signals suggest the presence of deuterated formic acid fragments: $D^{12}C^{16}O_2^+$ (mass 46), $D^{13}C^{16}O_2^+$ (mass 47), $D_2{}^{12}C^{16}O_2^+$

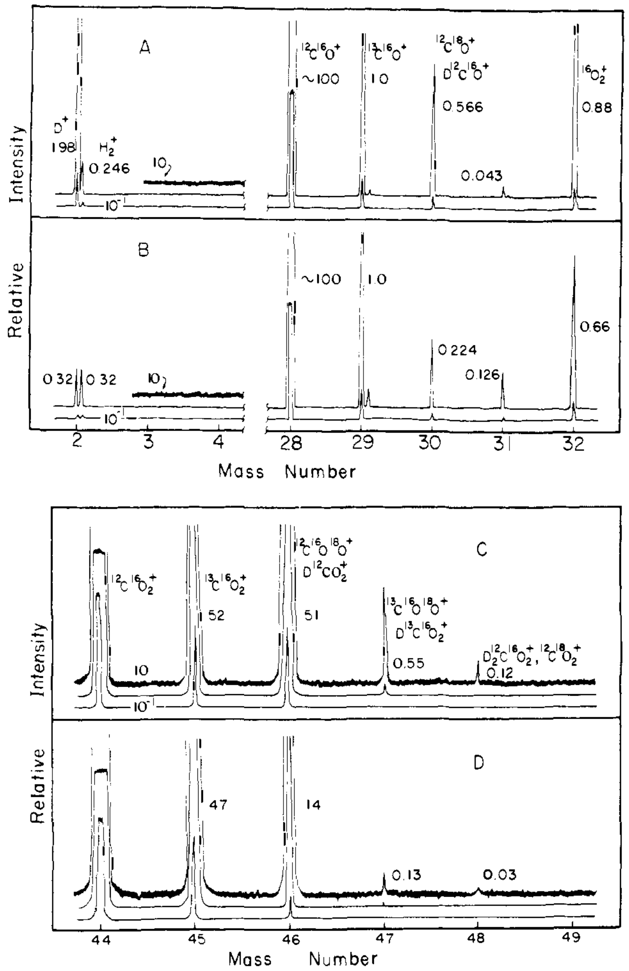

Figure 3. Mass spectrometric analysis of product distribution from an illuminated Pt/Chl *a* sample in CO_2-saturated $D_2{}^{16}O$ using IR and short-wavelength filtered light from a 1000-W xenon arc lamp. Figures 3B and 3D are the blank (unilluminated) signals in the mass regions 2-4, 28-32, and 44-49, respectively. Figures 3A and 3C are the corresponding signals obtained on sample illumination. The indicated line intensities are scaled relative to a mass 29 ($^{13}C^{16}O^+$) line intensity of unity in the mass regions 28-31 and 44-50. The enhancement of the mass 46 line in C is attributed to $D^{12}C^{16}O_2{}^+$.

(mass 48), D^+ (mass 2), and $D^{12}C^{16}O^+$ (mass 30). Significantly, the line intensity at mass 30 exceeds that expected from formic acid alone. The experimental mass spectrum obtained from a CO_2-saturated solution of 0.1 M $H_2{}^{12}C^{16}O_2$ in $H_2{}^{16}O$ gives an $H^{12}C^{16}O^+/H_2{}^{12}C^{16}O_2{}^+$ ratio of 0.05. The observed mass 30/48 ratio in Figure 3 corresponding to the analogous $D^{12}C^{16}O^+/D_2{}^{12}C^{16}O_2{}^+$ ratio is 4.8. Previous studies[13] rule out this large change being due solely to isotope effects in the cracking patterns of HCOOH and DCOOD. This observation and that of the enhanced rise in D^+ compared with $D^{12}C^{16}O^+$ in Figure 2e thus suggest the presence of more than one reduction product: possibly deuterated formaldehyde, formic acid, and methylene glycol.[14]

The total change in line intensities, $\Delta I(k)$, at masses 30 and 46-48 relative to their blank values allows an estimation of the evolved moles of gaseous reduction products, n_g, according to the relation $n_g = \Sigma_k n_{CO_2} \Delta I(k)/I(^{12}C^{16}O_2{}^+)$, where n_{CO_2} is the number of moles of CO_2. The intensity $I(^{12}C^{16}O_2{}^+)$ at mass 44 represents 93-99% of the total mass spectral intensity observed between masses 28 and 50 and is accordingly chosen as the reference signal. $I(^{12}C^{16}O_2{}^+)$ is estimated to be $100 I(^{13}C^{16}O_2{}^+)$. Based on a gas sample volume of 3×10^{-3} L, we have $n_{CO_2} \sim 1.2 \times 10^{-4}$ mol at 1 atm and 298 K. Using the ΔI of masses 30 ($D^{12}C^{16}O^+$), 46 ($D^{12}C^{16}O_2{}^+$), and 48 ($D_2{}^{12}C^{16}O_2{}^+$), we thus obtain $n_g = 9.1 \times 10^{-7}$ mol. The partitioning ratio of number of moles, n_g, of gaseous to that, n_{aq}, of aqueous formic acid is given by $n_g/n_{aq} = 0.47$.[15] Assuming that this ratio holds approximately for the observed photoreduction products, we write $n_p = n_g + n_{aq} \sim 2.76 \times 10^{-6}$ mol for the total number of moles of these products.

From molar absorbance measurements the average number of moles of Chl *a* in a Pt/Chl *a* sample is estimated to be 1.2 ($\pm$0.8) $\times 10^{-7}$ mol. Since only one of the two sides of the Pt/Chl *a* sample is exposed to light, $n_{Chl\ a} = 0.6 \times 10^{-7}$ mol of Chl *a* are available for photoinduced reactions. Thus η, the product turnover rate during the 30 min of sample illumination, is estimated by the ratio $\eta = n_p/n_{Chl\ a} \sim 45$. Based on reaction 3 the formation of formic acid involves the transfer of four protons (electrons). Considering the one-electron pathway of the Chl *a* photochemical cycle,[16] we thus arrive at a Chl *a* photocatalytic turnover ratio of $4\eta \sim 180$. This ratio is a rough estimate for three reasons. (1) Several major product fragments, e.g., $^{12}C^{16}O_2{}^+$ (mass 44) and $^{12}C^{16}O^+$ (mass 28), are masked by the intense carbon dioxide signals. (2) The actual amount of Chl *a* available for photoinduced reaction may be less than 6×10^{-8} mol since only a fraction of the electrode surface is illuminated by focused light, and not all the illuminated Chl *a* is uniformly effective on account of uneven contact between the chlorophyll and the platinum. It has been established that Chl *a* photocatalytic effects on water photolysis are dramatically reduced in the absence of Pt.[17] Assuming that only those Chl *a* molecules at the Pt-Chl *a* interface are catalytically effective, we estimate $n_{Chl\ a} \lesssim 10^{-9}$ mol corresponding to a density of 10^{14} molecules cm^{-2} in a monolayer of Chl *a*, in which case we obtain $\eta \sim 10^3$. (3) The estimate in the partitioning of gaseous and aqueous reduction products has not taken into consideration the possible presence of methylene glycol.[14] Using conventional electrolysis results as a calibration, an approximate photochemical yield of 0.8×10^{-6} mol of O_2 is obtained for 30-min sample exposure to visible light (see comparable estimates in ref 9 and 10). This is on the order of but lower than the expected O_2 yield based on the reaction stoichiometry of 3 and the corresponding yield of 2.7×10^{-6} mol of reduction product. Spectrophotometric analyses on sample purity indicate no significant Chl *a* degradation after the light reaction.

The observed enhancement in the D^+ line on CO_2 photoreduction (Figures 1-3) suggests a possible origin for the anomalous D^+ line intensity enhancements observed[9,10] in water photolysis runs in which no CO_2 was intentionally introduced. Atmospheric CO_2 present in deaerated, doubly distilled water is evidenced by the appearance of the CO^+ line at mass 28 in Figure 2 of ref 10 and in Figure 1A. In gas chromatographic work, the rate of O_2 generation was observed over an extended period of time, as the photolytic products were swept out of the photoreaction cell by a continuous flow of He gas. It was observed that the photocatalytic activity of Pt/Chl *a* was maintained for up to 3 h with the heat from IR radiation of the light source filtered by a 10-in. water bath. With unfiltered white light, the sample activity was found to diminish rapidly after 60 min of illumination. Spectrophotometric analyses of the samples thus spent yielded blue (429 nm)/red (663 nm) ratios in the range 1.29-1.36 in diethyl ether. In several cases *no* detectable change in this ratio from the initial value of 1.29 $\pm$ 0.01 for unilluminated, pure Chl *a* in diethyl ether was observed,[18] which suggests that deterioration of the Pt-Chl *a* interface rather than that of the chlorophyll may be responsible for the decay of Pt/Chl *a* photoactivity. This conclusion is closely similar to that drawn from observations on the behavior of platinized $SrTiO_3$ in catalyzing water photolysis using ultraviolet light.[19]

The chlorophyll photoactivity is evidently poisoned by O_2 in both in vivo[20] and in vitro[21] light reactions. It is believed that carotenoids protect triplet excited chlorophyll from oxidation.[22]

In preliminary work we have observed an enhancement of the Chl *a* water photolysis rate on addition of an equimolar amount of β-carotene in the Pt/Chl *a* sample. Independent identification of these products by gas chromatography and microwave spectroscopy are underway. Recently Somorjai et al.[23] described the UV-light-assisted photosynthesis reaction of CO_2 and H_2O adsorbed on $SrTiO_3$ crystals in contact with Pt foils. The visible-light photosynthesis reaction described in this work is relevant to the current interest in solar conversion and energy storage.[24]

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References and Notes

(1) H. Levanon and J. R. Norris, *Chem. Rev.*, **78,** 185 (1978).
(2) R. Wurmser, "Oxidations et Reductions", Presses Universitaires de France, Paris, 1930.
(3) K. Shibata, "Carbon and Nitrogen Assimilation", translated by H. Gest and R. K. Togasaki, Japan Science Press, Tokyo, in 1975, 1931.
(4) C. B. Van Niel, *Arch. Mikrobiol.*, **3,** 1 (1931).
(5) C. B. Van Niel, *Cold Spring Harbor Symp. Quant. Biol.*, **3,** 138 (1935).
(6) R. Hill and R. Scarisbrick, *Nature* (*London*), **146,** 61 (1940).
(7) R. Emerson and C. M. Lewis, *Am. J. Botany*, **28,** 789 (1941).
(8) S. Ruben, M. Randall, M. Kamen, and J. Hyde, *J. Am. Chem. Soc.*, **63,** 877 (1941).
(9) F. K. Fong and L. Galloway, *J. Am. Chem. Soc.*, **100,** 3594 (1978).
(10) L. Galloway, D. R. Fruge, G. M. Haley, A. B. Coddington, and F. K. Fong, *J. Am. Chem. Soc.*, **101,** 229 (1979).
(11) J. Brace, F. K. Fong, D. H. Karweik, V. J. Koester, A. Shepard, and N. Winograd, *J. Am. Chem. Soc.*, **100,** 5203 (1978).
(12) The employment of highly purified CO_2 was intended to minimize adventitious effects as well as background contributions to lines at masses 30–32. Results indistinguishable from those shown in Figures 1 and 2 were also obtained with commercial grade CO_2 without further purification.
(13) G. A. Ropp and C. E. Melton, *J. Am. Chem. Soc.*, **80,** 3509 (1958).
(14) The observed magnitude of the mass 46 intensity is notably larger than that of mass 48 (mass 46/48 intensity ratio, 272). An earlier study[13] of pure formic acid cracking patterns reveals that lines at these three masses are approximately equivalent in intensity for DCOOD. Our present mass spectrometric determination obtained from a CO_2-saturated solution of 0.1 M $H_2{}^{12}CO_2$ in $H_2{}^{16}O$ gives a mass 45/46 ratio of 1.1. Manufacturer (Thompson-Packard) specifications indicate no significant ^{18}O enrichment or depletion in D_2O. We have made a mass spectrometric determination of the ^{18}O content in a 1:1 mixture of H_2O–D_2O. The observed mass 22/20 ($D_2{}^{18}O/D_2{}^{16}O$) ratio was observed to be 0.29% in reasonable agreement with the experimentally determined $^{18}O/^{16}O$ ratio of 0.24% based on the relative intensities of $^{16}O_2{}^+$ and $^{16}O^{18}O^+$ lines from an air sample. This ratio is compared with the observed blank mass 46/44 ($^{12}C^{16}O^{18}O^+/^{12}C^{16}O_2{}^+$) ratio of 0.33% in Figure 3D, and is evidently lower than the sample mass 46/44 ratio of 0.98% in Figure 3C. It appears unlikely that the mass 46 line enhancement in Figure 3C is due to a Chl a photocatalyzed ^{18}O enrichment in CO_2 in excess of the ambient $^{18}O/^{16}O$ ratio in view of the concomitant increase in the D^+ line in Figure 2 and the elimination of the hydrogen lines (HD^+ and $D_2{}^+$) in Figures 1B and 1C. No such enrichment is observed in ^{18}O-labeled experiments such as the one corresponding to Figure 1. The pronounced mass 46 line intensity enhancement in Figure 3C is thus attributed to $D^{12}C^{16}O_2{}^+$ and may be indicative of the possible presence of a CO_2 reduction product other than formic acid. It is known that in dilute aqueous solutions ($\lesssim$5%) formaldehyde is largely stabilized as methylene glycol; see J. F. Walker, "Formaldehyde", Reinhold, New York, 1953, pp 49–53, 104–107.
(15) F. Rivenq, *Bull. Soc. Chim. Fr.*, **8,** 1505 (1960).
(16) F. K. Fong, A. J. Hoff, and F. A. Brinkman, *J. Am. Chem. Soc.*, **100,** 619 (1978).
(17) F. K. Fong, L. M. Fetterman, L. Galloway, A. B. Coddington, and D. R. Fruge, *J. Am. Chem. Soc.*, submitted for publication.
(18) This photochemical stability appears to be a property peculiar to (Chl *a*·$2H_2O)_n$, the polycrystalline 743-nm absorbing dihydrate of the chlorophyll.[11] We have determined that the presence of monomeric Chl a in Pt/Chl *a* results in the degradation of Chl a to pheophytin a upon light treatment under otherwise identical conditions.
(19) M. S. Wrighton, P. T. Wolczansdi, and A. B. Ellis, *J. Solid State Chem.*, **22,** 17 (1977).
(20) See, for example, W. Junge In "Photosynthesis I", A. Trebst and M. Avron, Eds., Springer-Verlag, Heidelberg, Germany, 1977, p 70.
(21) L. Galloway, D. R. Fruge, L. M. Fetterman, and F. K. Fong in "The Chemical Conversion and Storage of Solar Energy", R. Bruce King, R. R. Hautala, and C. R. Kutal, Eds., Humana Press, Clifton, N.J., 1979.
(22) M. Griffiths, W. R. Sistrom, G. Cohen-Bazire, and R. Y. Stannier, *Nature* (*London*), **176,** 1211 (1955).
(23) J. C. Hemminger, R. Carr, and G. A. Somorjai, *Chem. Phys. Lett.*, **57,** 100 (1978).
(24) (a) R. J. Marcus, *Science*, **123**, 399 (1965); (b) V. Balzani, L. Moggi, M. F. Manfrin, F. Bolletta, and M. Gleria, *ibid.*, **189,** 852 (1975); (c) D. D. Davis, G. K. King, K. S. Stevenson, E. R. Birnbaum, and J. H. Hageman, *J. Solid State Chem.*, **22,** 63 (1977); (d) C. Creutz and N. Sutin, *Proc. Natl. Acad. U.S.A.*, 7**2,** 2858 (1975); (e) G. Sprintschnik, H. W. Sprintschnik, P. P. Kirsch, and D. G. Whitten, *J. Am. Chem. Soc.*, **98,** 2337 (1976), and **99,** 4947 (1977); (f) K. R. Mann, N. S. Lewis, V. M. Miskowski, D. K. Erwin, G. S. Hammon, and H. B. Gray, *ibid.*, **99,** 5525 (1977); (g) J.-M. Lehn and J.-P. Sauvage, *Nouv. J. Chim.*, **1,** 449 (1977); (h) S. M. Kuznick and E. M. Eyring, *J. Am. Chem. Soc.*, **100,** 6790 (1978).

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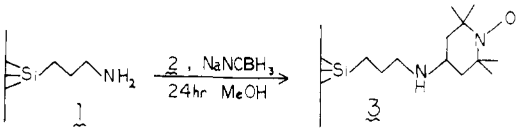
A Method for Determining the Spatial Distribution of Spin-Labeled Organic Ligands Covalently Bound to a Noncrystalline Surface: Dipolar Contribution to Nitroxide EPR Spectrum

Sir:

There is a considerable current interest in the chemistry of organic ligands covalently attached to noncrystalline surfaces. Consequently there is a need for the development of methods for the chemical characterization of these modified surfaces. Where it is necessary to determine merely the composition or structure of the surface-bound ligands, techniques such as Auger, ESCA, EPR, laser Raman, and IR spectroscopy may be useful; however none of these has been used to determine the distribution of ligands on a noncrystalline surface.[1] In addition, with most of these techniques, the bulk substance is not transparent; so application to porous materials is impossible. The design of any experiment in which it is desired to prevent the interaction between ligands covalently bound to an organic polymer or an inorganic surface requires that the ligand distribution be known or assumed.[2] We report here that the contribution from dipolar coupling to the EPR line width from a nitroxide spin-labeled organic ligand, measured under conditions where molecular motion is slow, can give ligand-ligand distances and distributions on a modified silica surface.[3]

Controlled-Pore glass,[4] a commercially available amorphous inorganic support composed of microporous 96% silica, was derivatized with 3-aminopropyl ligands by absorption from degassed aqueous alkaline solutions of freshly hydrolyzed 3-aminopropyltrimethoxysilane followed by drying and curing[5] to yield[6] **1**. Samples of **1** having different surface concentrations[7] of ligand, ρ_{NH_2}, were prepared. It was not possible to bind more organic ligand to the surface than would be required to form one molecular layer; the highest ρ_{NH_2} obtained was 3.9 ± 0.2 nm^{-2}.

Spin labeling of **1** was achieved by reductive alkylation using an excess of 2,2,6,6-tetramethyl-4-oxopiperidine-1-oxyl (**2**) with sodium cyanoborohydride in methanol. The spin-labeled product, **3**, after washing, gave an EPR spectrum characteristic of a partially immobilized nitroxide. Release of mobile nitroxide was seen only under conditions which caused the dissolution of the silica surface itself (e.g., immersion in 0.1 M NaOH); in contrast the Schiff base analogue of **3**, prepared analogously omitting the cyanoborohydride, hydrolyzed readily under mild aqueous conditions liberating mobile nitroxide. From these and other observations, it was established that **3** had the structure shown. That each 3-aminopropyl group was indeed covalently bonded to the surface will be shown below.



The surface density of nitroxides, ρ_{SL}, was determined by EPR double integration. Within the accuracy of determination