corresponding required change for phase II crystals is about a 5.7% decrease. It is interesting to note for phase I that a 0.025 Å increase (0.25%) in c-axis length was observed at a monomer to polymer conversion of 17%.

Diacetylenes are known which polymerize to high perfection crystals despite similarly large dimensional changes to those required for phase II,[13,14] but these monomers do not have the additional structural constraints imposed by hydrogen bonding. The lower percent conversion for the γ-ray irradiated phase II crystals (17% vs. 70% for phase I after 50 Mrads of ^{60}Co γ-ray irradiation), again a possible consequence of the larger dimensional changes required for polymerization than for phase I, likely contributes to the low degree of order in the monomer-extracted polymer.

Another possible explanation for the difference in reactivity involves a significant difference in the arrangement of side chains. When polymerization occurs, there must be movement of the side chains toward the center of the molecule along the main axis of the side chains. In phase I, the side chain is virtually fully extended (Figure 4a). There would appear to be little hindrance for a cooperative movement of the side chains toward the center with preservation of the hydrogen bonding. The contraction of the molecule in this direction is reflected in the decrease (0.27 Å) in the a-axis length during X-ray irradiation (Table I). In phase II, the molecule adopts a much more "zig-zag" shape with the substituent ethyl groups protruding into a crevice in the adjacent molecules (this direction is normal to the view in Figure 5). Thus there could be more resistance to a cooperative contraction in the direction normal to the polymer direction.

The strong fluorescence observed for the phase I UDD polymer is consistent with the blue-shifted absorption spectra, relative to other polydiacetylenes which do not significantly fluoresce. Eximer emission from phenyl rings is excluded as an origin of this fluorescence, since the monomer and polymer have similar structures (evidenced by the quite similar powder diffraction spectra) and the structure of the phase I monomer indicates little overlap between phenyls. The UDD polymer fluorescence is clearly due to the polymer backbone. Chance[19] and Bhattacharjee et al.[20] have observed strong fluorescence from solutions of soluble polydiacetylenes having blue-shifted absorption spectra, for which a nonplanar backbone is suggested.

The blue-shifted polymer absorption spectra do not reflect a low molecular weight for the phase I polymer, since the mechanical properties in the chain direction indicate a reasonably high molecular weight. Consequently, polymer backbone strain provides the most reasonable explanation for the blue shift. Tensile stress in the polymer chain direction is known to cause large blue shifts in the absorption spectra of other polydiacetylenes.[21] However, the effective stress on the polymer backbone in UDD, provided by minimization of side-group energy, can be much more complicated. Since the mutually reacting diacetylene rods in phase I crystals are nonplanar, retention of this structural feature in the polymer would decrease the effective conjugation, providing a blue-shifted spectra. Patel et al.[22] have suggested that low monomer-to-polymer conversion and blue-shifted absorption spectra result from backbone strain in another polymerizable diacetylene, 2,4-hexadiyne-1,6-bis(m-tolylurethane). In this case, diacetylene rods for mutually reacting molecules (which are related by a glide plane, as for phase I UDD) form an angle of 72°. Additional structural and spectroscopy studies on the polymerized diacetylene crystals are required to further clarify the relationship between polymer electronic structure and backbone configuration.

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Registry No. UDD, 79664-55-4.

Supplementary Material Available: Thermal and positional parameters for phase I after two-site refinement, atomic coordinates and thermal parameters after single-site refinement, bond lengths and angles from single-site refinement, and thermal parameters and structure factors for phase II UDD (62 pp). Ordering information is given on any current masthead page.

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Mechanisms for the Photooxidation of Protoporphyrin IX in Solution[1,2]

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Abstract: Protoporphyrin IX dimethyl ester (**1a**) is photooxidized upon irradiation in aprotic organic solvents in the presence of oxygen to yield a mixture of hydroxyaldehydes (**2** and **3**) (photoprotoporphyrins), monoformylmonovinyldeuteroporphyrins (**4** and **5**), and diformyldeuteroporphyrin (**6**). Studies of the reaction under a variety of conditions show that the major portion of all of these products arises via a singlet oxygen path. The formyl products **4**–**6** can also arise via reaction of the protoporphyrin π cations with superoxide, but this path can be shown to be of only minor importance when only the porphyrin and oxygen are involved in direct irradiation of the porphyrin. Quenching of singlet oxygen by ground-state **1a** occurs with a rate constant $k_p = 8.5 \times 10^5\ M^{-1}\ s^{-1}$; this value is comparable to that measured for other free-base porphyrins but considerably lower than that observed for open-shell metalloporphyrins and for free-base chlorins. The relatively low limiting quantum yield obtained for reaction of **1a** indicates that net physical quenching is the result of most porphyrin–singlet oxygen interactions.

Porphyrins and their metal complexes are among the most widely used sensitizers in photooxidation processes;[3,4] in addition several naturally occurring porphyrins have been implicated as the light absorbing agents in photodynamic action.[5-9] Conse-

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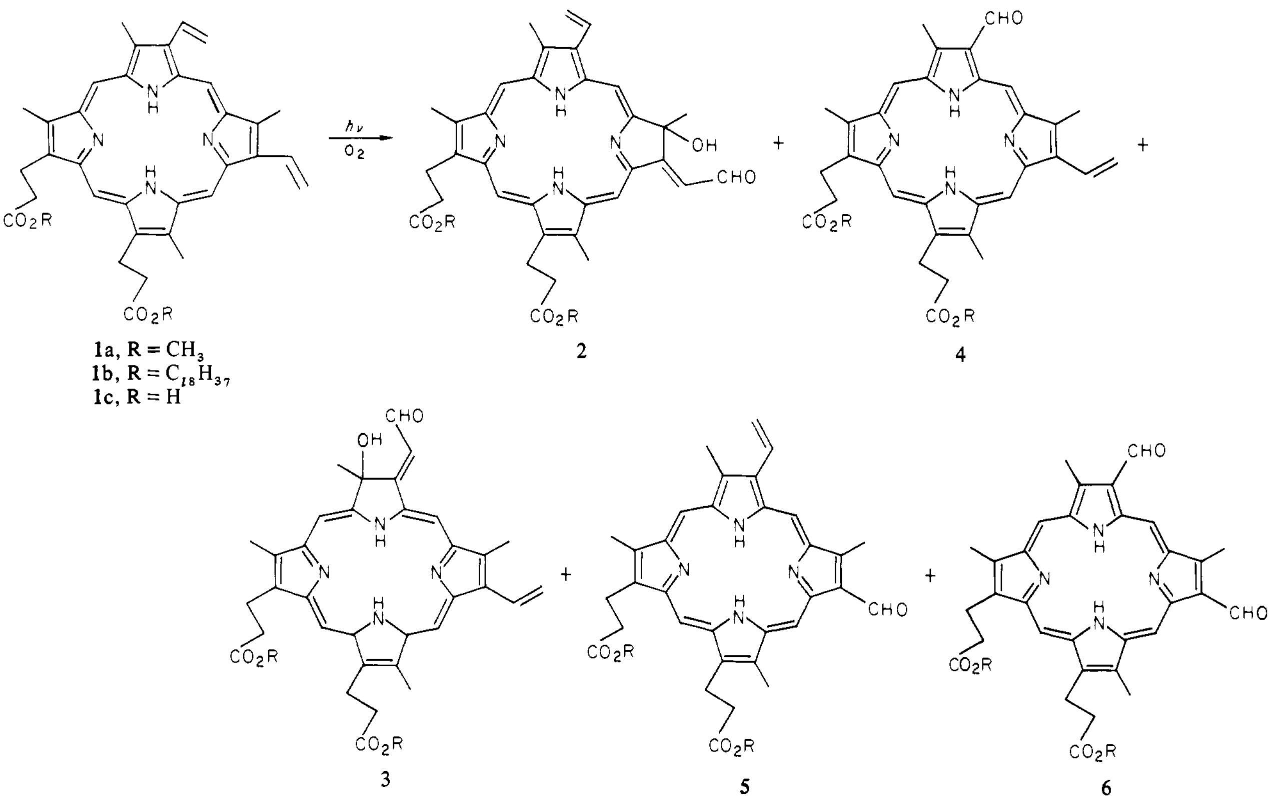

1a, R = CH_3
1b, R = $C_{18}H_{37}$
1c, R = H

2

4

3

5

6

(1)

quently there has been considerable interest in excited-state reactions involving porphyrins and molecular oxygen. One of the most well-studied cases where a porphyrin-sensitized photoreaction is directly implicated in a photobiological process involves the porphyrins; in the genetic disease erythropoietic protoporphyria (EPP) excessive amounts of free-base protoporphyrin IX (**1c**) and its non-heme metal complexes accumulate in red blood cells.[10-16] The disorder is marked by an extreme sensitivity to light in which unsaturated lipids are converted to hydroperoxides whose decomposition culminates in destruction of red blood cell membranes. It has been suggested that sensitization of singlet oxygen by the protoporphyrin triplet is the critical step in the light-sensitive porphyrias.[11]

Protoporphyrin IX itself is photooxygenated in the presence of molecular oxygen; while this reaction has been recognized for some time,[16] the products have only been characterized in more recent studies.[2,17] Inhoffen and co-workers found that the major solution product, the green "photoprotoporphyrin IX" consists of isomeric hydroxyaldehydes **2** and **3**;[17] more recently studies from these laboratories indicated that formyl products **4**–**6** are formed as well (eq 1). While products **2** and **3** predominate when **1a** is irradiated in most organic solvents, it was found that **4**–**6** become the dominant products when **1a** or **1b** are irradiated in aqueous micelles, monolayer films at an air–water interface, or supported multilayer assemblies.[2] While all of the photoproducts could easily be envisioned as arising from singlet oxygen attack on ground-state porphyrin, recent demonstration of photooxygenation reactions occurring by other pathways[18-28] suggests that multiple paths could be involved in this case as well. The wide variation of photooxidation products obtained for **1** in different media together with the question of competition between its role as a sensitizer for photooxidations vs. self-sensitization clearly indicate the need for a detailed mechanistic analysis of these reactions.

In this paper we report a study of the photooxidation of protoporphyrin IX dimethyl ester (**1a**) in solution under a wide variety of conditions. The results of this study indicate that even though protoporphyrin can sensitize the production of superoxide ion via electron transfer,[29] virtually all of the photoproducts formed via direct irradiation of **1a** result from singlet oxygen attack on ground-state porphyrin. The results further indicate that despite

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(1) Presented in part at the 181st National Meeting of the American Chemical Society, Atlanta, GA, 1981, Abstracts ORGN-60.

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the occurrence of a self-sensitized photooxidation reaction for **1**, the rate constant for quenching of singlet oxygen by **1** is relatively lower than that obtained for several other porphyrins.

Experimental Section

Materials. Protoporphyrin IX dimethyl ester (**1a**) was synthesized by the method of Grinstein[30] which was modified to use commercial hemin chloride (Aldrich). Photoprotoporphyrin IX dimethyl esters **2** and **3** were synthesized by the method of Inhoffen.[17] Samples of the pure isomers **2** and **3** were kindly provided by Dr. M. Nakashima of the U.S. Army Natick Laboratories. 2,4-Diformyldeuteroporphyrin IX dimethyl ester (**6**) and the isomeric 2-formyl-4-vinyldeuteroporphyrin IX dimethyl ester **4** and 2-vinyl-4-formyldeuteroporphyrin IX dimethyl ester **5** were synthesized by a slight modification of the method of Gaughey.[31,32] All solvents were purified by standard distillation procedures.[33] Cholesterol (Nutritional Biochemicals Corp.) was recrystallized from 95% ethanol. Diazabicyclo[2.2.2]octane (Aldrich) was used as received. Methyl viologen dichloride (Aldrich) was converted to the hexafluorophosphate salt by using ammonium hexafluorophosphate (Alfa). This salt was recrystallized from acetone/water. Methylene Blue (Aldrich) was crystallized from 95% ethanol.

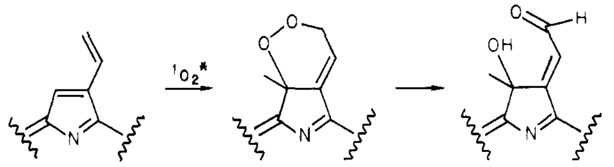
Photochemical Experiments. Irradiations were carried out with a merry-go-round apparatus using a Hanovia 450-W medium-pressure mercury lamp as the light source or in other studies using the Hanovia 97730020 1000-W mercury-xenon arc lamp in a Schoeffel LH151N lamp housing. For the latter source the lamp emission was passed through a Bausch and Lomb Model 3-66-79 high intensity monochromator. For the studies in the merry-go-round apparatus, the 366-nm line was isolated by using 0-52 and 7-37 Corning filters. For studies in the visible the 0-52 or 3-74 Corning filters were employed. Both quantum yields and relative rates were measured in the merry-go-round apparatus using matched cuvettes (100 × 13 mm) (Fisher). For example, in a typical run in which products **2** and **3** were monitored, the growth in absorbance at 670 nm was followed. The starting concentration of **1a** was such that all the light was absorbed and the reaction followed to only 5% conversion of the protoporphyrin. Plots of absorbance at 670 nm vs. time gave straight lines, indicating pseudo-zero-order reaction. The slopes of these plots were measured in different experiments and considered as proportional to the quantum yield. Absolute values of the quantum yield were obtained by using light intensities measured with the potassium ferrioxalate actinometer.

Ultraviolet and visible spectra were recorded on a Perkin-Elmer 576ST spectrophotometer. Fluorescence measurements were carried out by using an Hitachi Perkin-Elmer MPF-2A spectrofluorimeter equipped with a red sensitive Hamamatsu R446 photomultiplier tube. Flash photolysis experiments were conducted on an apparatus previously described.[34,35] Quantitative analysis of the photooxidation products was carried out by using a Perkin-Elmer series I high-pressure liquid chromatograph with a Varian ultraviolet-visible detector. A Whatman Partisil PXS 5/25 or 10/25 column was used with a solvent system of chloroform/hexane (80:20). The products were monitored with the detector set at 420 nm, and the detector was calibrated by using solutions of the photooxidation products synthesized separately as standards.

Chemical Generation of Singlet Oxygen. Singlet oxygen was generated chemically by using 9,10-diphenylanthracene peroxide which was synthesized by literature methods[36] except that methylene chloride was used as a solvent instead of carbon disulfide. Protoporphyrin IX dimethyl ester (50 mg) was dissolved in 50 mL of carbon tetrachloride. 9,10-Diphenylanthracene peroxide (350 mg) was added, and the solution was refluxed for 5 days. The solution was then analyzed by HPLC to determine the products formed.

Results and Discussion

The chief products identified up until now in the photooxidation of protoporphyrin IX derivatives (eq 1) can easily be envisioned as arising through familiar photooxidation pathways.[37-42] For example, the hydroxyaldehyde products **2** and **3** probably arise via cycloaddition of oxygen to a diene unit as indicated by eq 2.



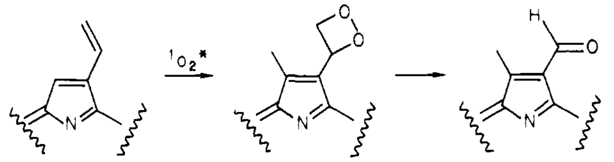
(2)

Table I. Chemical Yields and Product Ratios for Protoporphyrin IX Dimethyl Ester Photooxidation. The Effect of Solvents

solvent	% yield 2 + 3	 4 + 5 + 6	ratio of products^c	% of protoporphyrin 1a reacted
methylene chloride^a	46	1.4	97:3	69
benzene^a	45	4.6	91:9	59
pyridine^a	22	2.2	91:9	59
N,N-dimethylformamide^b	24	3.2	88:12	52
acetonitrile/methylene chloride^b (7:3)	41	4.5	90:10	49

^{a} Merry-go-round apparatus used; source medium-pressure mercury lamp with Corning 3-74 filter. ^{b} Merry-go-round apparatus using 366-nm line of medium-pressure mercury lamp. ^{c} Product ratios were observed to be fairly constant up to ca. 90% conversion of 1a.

The formation of formyl products **4–6** is most conveniently explained as occurring via a dioxetane intermediate as indicated by eq 3. Previous studies have indicated that interaction of excited protoporphyrin with molecular oxygen in solution can give rise to both singlet oxygen formation (eq 4)[40] and electron transfer to generate superoxide (eq 5).[29] The former process is evidently



(3)

$$P^{3*} + O_2 \rightarrow P + {}^1O_2^* \qquad (4)$$

$$P^{3*} + O_2 \rightarrow P^+ + O_2^- \qquad (5)$$

more efficient than the latter; studies by Krasnovsky indicate the efficiency for singlet oxygen formation is 0.77 in CCl_4.[40] In the present study we have verified that products **2–5** are indeed the major products arising from irradiation of protoporphyrin IX dimethyl ester in the presence of molecular oxygen in several solvents. High-pressure liquid chromatography proved to be a useful method for separation of the various products; in fact, it was possible to separate the different monoformyl derivatives as well as the monohydroxyaldehydes (**2** and **3**). However, for most convenient quantitative analysis it proved useful to employ conditions where the isomers were not well separated. Table I summarizes the chemical yields and ratio of groups of products for the photooxidation in several solvents. In most cases, the ratios of the isomeric monooxidation products was within experimental error 1:1. As data in Table I indicate, the total yield of products **2–6** is variable for the different solvents used; however, the ratio of products obtained shows little variation with solvent. Studies of the product rate of distribution as a function of time of irradiation also showed little variation; clearly **2**, **3**, **4**, and **5** are all formed directly from protoporphyrin and do not arise primarily

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Table II. Chemical Yields and Product Ratios for Protoporphyrin IX Dimethyl Ester Photooxidation. The Effect of Quenchers

quencher (concn)[a]	% (2 + 3)	% (4 + 5 + 6)	ratio of products[b]	% of protoporphyrin 1a reacted in 1 h	% of protoporphyrin 1a reacted in 2 h
none	46	1.4	97:3	59	79
DABCO[c] (0.0013 M)	78	6.6	92:8	...	24
DABCO[c] (0.000 25 M)	64	3.8	94:6	...	68
2-propanol (25% v/v)	17	2.7	...	39	...
methanol (25% v/v)	trace	3.3	...	25	
di-*tert*-butyl-4-methylphenol (2.5×10^{-3} M)	5.4	3.3	...	43	...
di-*tert*-butyl-4-methylphenol (5.0×10^{-4} M)	25	1.4		50	

[a] Solvent was methylene chloride. [b] Ratio of (2 + 3):(4 + 5 + 6). [c] 1,4-Diazabicyclo[2.2.2]octane.

from interconversion from one another. For the solvents listed in Table I, no other major products could be isolated or identified. Nonetheless, as the data in Table I indicate, the total product yield (corrected for any unreacted protoporphyrin) from **1a** ranges only from 25 to 51% in these solvents. That these products are indeed the primary photooxidation products of **1a** is indicated by the finding that addition of a good singlet oxygen quencher, diazabicyclo[2.2.2]octane (DABCO),[39,43] slows down the rate of formation of these products but simultaneously increases their yield (Table II). Thus, in the presence of 0.0013 M DABCO in CH_2Cl_2, the product ratio is very little changed, but the overall yield of products **2**–**6** is increased to 85%. The relatively lower yields listed in Table I are therefore attributed to subsequent decomposition of the primary photoproducts, presumably by photooxidation, under the reaction conditions. This is not surprising in view of the fact that the products absorb both in the same region as **1a** and also at slightly longer wavelengths. Thus it is virtually impossible to exclude activation of these products by either direct excitation or energy transfer from photoexcited **1a**. In addition there is certainly the possibility that these products may react with activated forms of oxygen generated by **1a**.

As indicated above, the two most likely paths for formation of the photoproducts produced appear to be via singlet oxygen or superoxide intermediates. One possible means of distinguishing the role of the different paths involves the use of selective quenchers. As Table II indicates, DABCO, which is an excellent quencher of singlet oxygen but which does not interact with superoxide ion in aprotic solvents or appear to affect the yield of superoxide produced in porphyrin sensitization of superoxide,[29] sharply decreases the yield of all the photoproducts **2**–**6** in CH_2Cl_2. Similar results were obtained with DABCO in the much more polar solvent *N*,*N*-dimethylformamide. Similar results were also observed with cholesterol as a quencher. Thus it seems clear that all these products arise from singlet oxygen attack on ground-state protoporphyrin. The fact that there is a slight decrease in the ratio of hydroxyaldehyde to formyl products when DABCO is used as a quencher in both CH_2Cl_2 and *N*,*N*-dimethylformamide suggests that a very minor portion of the formyl products may arise from a nonsinglet oxygen path.

It has previously been shown that the peroxide of 9,10-diphenylanthracene will release singlet oxygen on heating.[36] This reaction was used in the present studies in an attempt to verify that singlet oxygen was indeed the precursor for the photooxidation products of **1a**. The use of a tenfold excess of diphenylanthracene peroxide with **1a** (2×10^{-3} M) failed to result in detectable conversion of **1a** to the photoproducts. However, in view of the low overall quantum efficiency for formation of the photooxidation products and the relatively slow rate of reaction of singlet oxygen with **1a** (vide infra), the failure to detect products from thermally generated singlet oxygen is unsurprising. Experiments with methylene blue (which absorbs to the red of protoporphyrin IX and its esters) did result in the generation of the product shown in eq 1 from **1a**; the yields were relatively low in these experiments and it was not possible to precisely determine the product ratios. A persistent problem in obtaining high conversions in the methylene blue experiments is the photodegradation of methylene blue itself under the irradiation conditions.

While the above results seem to indicate that the major path for photooxidation of **1a** in the solvents studied involves reaction of the ground-state protoporphyrin with singlet oxygen, it was of interest to determine whether a small amount of the observed reaction is due to a pathway involving reaction of superoxide with the π cation of **1a**. Experiments using potential quenchers of suuperoxide were relatively inconclusive. For example, methanol, 2-propanol, and other protic solvents will catalyze the dismutation of superoxide;[29,44,45] thus addition of these solvents should inhibit the formation of any protoproducts arising via the superoxide path. As data in Table II indicate, addition of 2-propanol or methanol does indeed change both the rate and the product distribution; however, the major product quenched appears to be the hydroxyaldehyde products **2** and **3** which as shown above, clearly arise via a singlet oxygen path. The inhibition of hydroxyaldehyde probably arises via alcohol trapping of the endoperoxide intermediate with the resultant formation of new products.[46–48] HPLC analysis indicated new products having similar retention times to the hydroxyaldehydes were formed in the presence of hydroxylic solvents. While these products could not be identified, there is literature precedence for interception of endoperoxide by similar reagents.[46–48] The use of di-*tert*-butyl-4-methylphenol (DBMP) as a potential quencher resulted only in a very small decrease in the rate of photooxidation of **1a**. DBMP is an excellent radical scavenger[25] which should efficiently quench superoxide; the small effect observed could be attributed to either quenching of singlet oxygen by DBMP or reaction of DBMP with endoperoxide intermediates en route to the hydroxyaldehydes. Thus while some effects were produced by potential scavengers of superoxide, the interpretation of these effects is not simple and no role of superoxide in the product formation can be clearly ascertained by these studies.

A somewhat clearer indication of the possible role of superoxide in the photooxidation of **1a** was obtained by carrying out irradiation of **1a** in the presence of the electron acceptor methyl viologen (*N*,*N*′-dimethyl-4,4′-bipyridinium, MV^{2+}). The viologen would be expected to quench excited states of the porphyrin by electron transfer as indicated in eq 6.[49] Subsequent reaction of

$$P^* + MV^{2+} \rightarrow P^+ + MV^+ \tag{6}$$

$$MV^+ + O_2 \rightarrow MV^{2+} + O_2^- \tag{7}$$

$$P^+ + O_2^- \rightarrow \text{products or } P + O_2 \tag{8}$$

reduced viologen to yield superoxide (eq 7) should readily occur as has been demonstrated in previous studies.[50–52] Thus the use

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Table III. Chemical Yields of Products for Protoporphyrin IX Dimethyl Ester Photooxidation. Effect of Methyl Viologen[a]

[methyl viologen][b]	% yield		% of protoporphyrin 1a reacted
	2 + 3	3 + 4	
none	41	4.5	49
0.01 M	6.2[c]	3.7	42

[a] Merry-go-round apparatus; 366-nm irradiation. [b] Solvent is acetonitrile/methylene chloride (7:3). [c] The discrepancy between the amount of 1a reacted and hydroxyaldehyde product formed doubtless reflects some light-induced decomposition of products 2 and 3 at this large an extent conversion. The I^0/I values reported in the text (for 2 and 3) are for experiments involving very low conversion.

of viologen should provide a means of studying reaction between the porphyrin π cation and superoxide (eq 8).

A study of methyl viologen quenching of the fluorescence of **1a** in $CH_3CN/CHCl_3$ (7:3) indicated that the quenching is nearly diffusion controlled ($k_q = 9.0 \times 10^9$ M^{-1} s^{-1}). Flash photolysis of **1a** in the presence of MV^{2+} shows a bleaching of the absorption due to **1a** and a transient absorbance corresponding to the reduced viologen, MV^+. The addition of oxygen results in a decrease in the lifetime of reduced viologen and a slight increase in the lifetime of the bleached porphyrin.

Studies of the products produced from irradiation of **1a** in the presence of MV^{2+} and oxygen indicate that the total rate of photooxidation is substantially retarded by the addition of viologen. A Stern–Volmer plot of methyl viologen quenching of hydroxyaldehyde product formation showns that the viologen must be quenching both the porphyrin singlet and triplet. For example, at 0.01 M methyl viologen the ϕ^0/ϕ for formation of **2** and **3** is 5.45 while the I^0/I for quenching of the fluorescence of **1a** is only 2.17. Table III shows that the yield of hydroxyaldehyde products is dramatically depressed by addition of viologen while the yield of formyl products is relatively little affected. Since an appreciable amount of formyl products **4**–**6** is formed under conditions where most of the porphyrin excited states are quenched by methyl viologen ($\phi^0/\phi = 1.2$), it is possible to conclude that interaction of superoxide with the porphyrin cation leads to selective formation of the formyl products although in relatively low yield.

In summary, the studies with various solvents, quenchers, and sensitizers indicate that in solution the major path for formation of photooxidation products **2**–**6** in the direct irradiation of **1a** in the presence of oxygen involves singlet oxygen attack on the ground state of **1a**. A very small amount of the formyl products **4**–**6** may arise through interaction of superoxide with the porphyrin π cation; however, in all of the solvents studied this is a minor process.

Scheme I

$$P \xrightarrow{h\nu} P^{*1} \xrightarrow{\text{ISC}} P^{*3} \quad \phi = \gamma$$

$$P^{*3} + O_2 \xrightarrow{\alpha k_r} P + {}^1O_2^*$$

$$P^{*3} + O_2 \xrightarrow{(1-\alpha)k_r} P + O_2$$

$$P^{3*} \xrightarrow{k_d^P} P^0$$

$${}^1O_2^* + P \xrightarrow{k_p} (\beta)\text{HA} + (1-\beta)\text{other}$$

$${}^1O_2^* \xrightarrow{k_d^0} O_2 \quad k_d^0 = 1/\tau^0$$

$${}^1O_2^* + Q \xrightarrow{k_q} Q + O_2$$

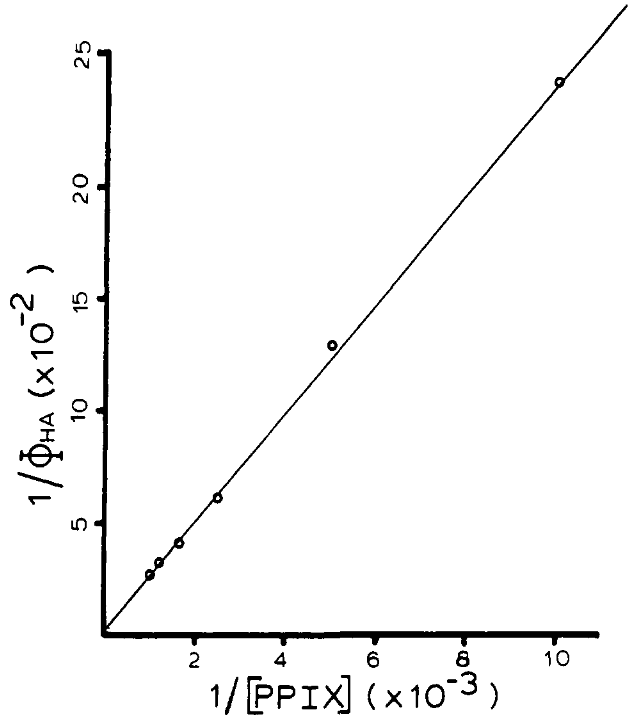

Figure 1. The double reciprocal plot for hydroxyaldehyde quantum efficiency with starting concentration of protoporphyrin IX dimethyl ester.

A quantitative study of the formation of hydroxyaldehyde products in the presence of various singlet oxygen quenchers permits the evaluation of the reaction kinetics for the self-sensitization process with **1a**. The most likely kinetic scheme for the reaction is shown below (Scheme I), where P = **1a** and HA represents products **2** and **3**. According to this scheme the quantum yield of the singlet oxygen products **2** and **3** in the absence of quenchers of P* (other than O_2 or ${}^1O_2^*$ should be given by eq 9a. Since the oxygen concentration was kept constant in

$$\phi_{HA}{}^0 = \gamma\left(\frac{\alpha k_r[O_2]}{k_r[O_2] + k_d{}^P}\right)\left(\frac{\beta k_p[P]}{k_p[P] + k_d{}^0}\right) \qquad (9a)$$

$$\phi_{HA}{}^0 = \gamma\alpha'\left(\frac{\beta k_p[P]}{k_p[P] + k_d{}^0}\right) \qquad (9b)$$

$$\frac{1}{\phi^0} = \frac{1}{\gamma\alpha'\beta}\left(1 + \frac{1}{k_p\tau^0[P]}\right) \qquad (10)$$

$$\phi_{HA} = \gamma\alpha'\left(\frac{\beta k_p[P]}{k_p[P] + k_q[Q] + k_d{}^0}\right) \qquad (11)$$

$$\frac{\phi^0}{\phi} = 1 + \frac{k_q[Q]}{k_p[P] + k_d{}^0} = 1 + \frac{k_q[Q]}{k_p[P] + 1/\tau^0} \qquad (12)$$

these experiments, the second term in 9a can be approximated by the constant α' yielding eq 9b. The reciprocal expression (eq 10) indicates that $1/\phi$ should vary linearly with the inverse of [**1a**]; Figure 1 indicates that a good linear relationship is observed. The intercept/slope ratio should be $k_p\tau^0$ where $\tau^0 = 1/k_d$ and the reciprocal of the intercept gives the limiting quantum yield $\gamma\alpha'\beta$ which equals 0.07 in CH_2Cl_2. Since $\gamma\alpha'$ has been estimated to be 0.77 for **1a**,[40] this indicates $\beta = 0.09$ and thus that approximately 90% of the quenching encounters between ${}^1O_2$ and ground state **1a** lead to physical quenching as opposed to product formation. The value for $k_p\tau^0$ extracted from the plot in Figure 1 is 63 M^{-1}.

The experiments using DABCO or cholesterol as quenchers of the formation of **2** and **3** also provide an independent expression containing k_p and τ^0. Thus the use of eq 9b and 11 leads to the Stern–Volmer relationship (eq 12) which predicts linear plots such as are observed (Figures 2 and 3) for both quenchers. The slopes

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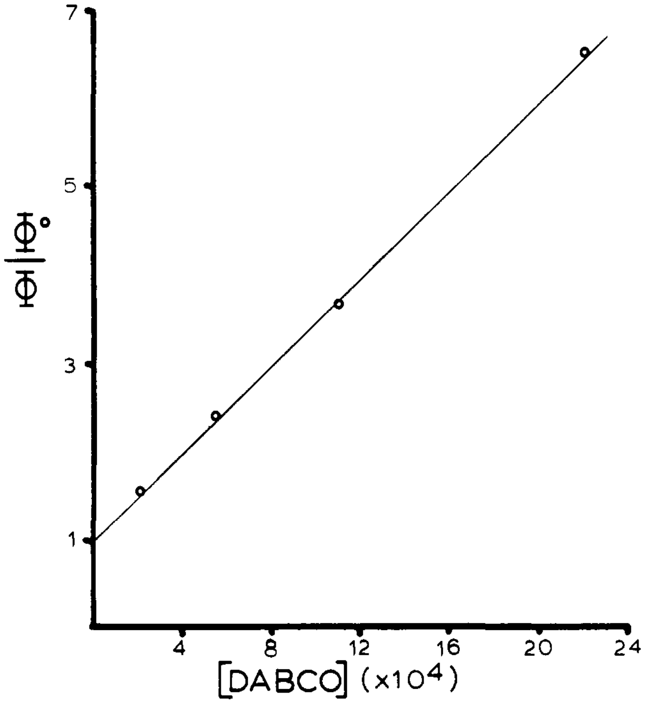

Figure 2. Stern-Volmer plot for quenching of hydroxyaldehyde (**2** + **3**) formation from **1a** as a function of [DABCO].

Table IV. Stern-Volmer Slopes, Quenching Constants, and k_p Values for Protoporphyrin IX Dimethyl Ester Photooxidation with Quenchers

quencher	k_q	Stern-Volmer slope	R	$10^{-5}k_p$, $M^{-1}\ s^{-1}$
DABCO	3.3×10^{7} [a]	2380	0.9997	8.3
cholesterol	6.7×10^{4} [b]	4.86	0.9997	8.6

[a] From ref 43. [b] From ref 53.

of these plots (carried out at constant [**1a**]) are equal to $k_q/[k_p(P) + 1/\tau^0]$ since k_q has been measured independently for each of these quenchers;[43,53] the use of the value for $k_p\tau^0$ obtained above together with the slopes of the Stern-Volmer plots permits an assessment of k_p as indicated in Table IV. The agreement between the values obtained for k_p for the two quenchers whose quenching constants differ by nearly 3 orders of magnitude is remarkable. The lifetime, τ^0, calculated for singlet oxygen from these data is 74 μs which is only slightly shorter than previously reported values (105[39] and 137 μs[54]) in the same solvent.

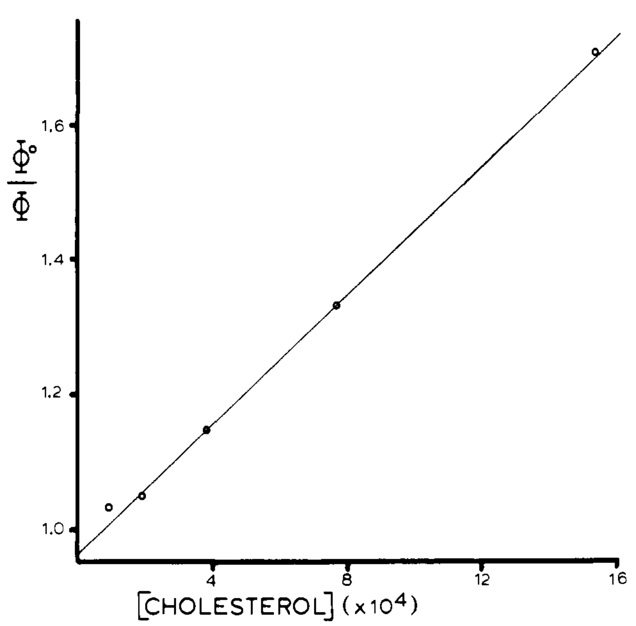

Figure 3. Stern-Volmer plot for quenching of hydroxyaldehyde (**2** + **3**) formation from **1a** as a function of [cholesterol].

The results obtained in the present study indicate that protoporphyrin IX dimethyl ester—despite its potentially reactive vinyl groups—is not an especially effective quencher of singlet oxygen. The values for k_p indicated in Table IV are lower than those reported for several open-shell metal complexes and chlorophyll derivatives (with and without magnesium) by 2–4 orders of magnitude.[40] The present values are in fact very close to those reported for simple porphyrins not containing "extra" double bonds such as mesoporphyrin IX dimethyl ester and tetraphenylporphyrin;[40] even the use of the higher, previously measured value of $\tau^0 = 137$ μs,[54] gives values of k_p substantially below those reported for the bacteriochlorophylls and bacteriochlorins. While the previously reported values for quenching of $^1O_2$ were obtained by using quite different methods,[40] the comparisons indicating a low reactivity for **1a** are clearly valid and serve to underline the role of **1a** as a potent sensitizer for singlet oxygen in biological photooxidations. This point is reinforced by the further observations that formyl derivatives **4**–**6**—which should have even lower quenching constants for $^1O_2$ and thus be even more potent sensitizers—can be formed as minor products in solution but as major products in membrane-like organized media.[2] The role of all four porphyrins as photosensitizers of singlet oxygen (and superoxide) in these media is currently under investigation.

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Registry No. **1a**, 5522-66-7; **2a**, 10200-03-0; **3a**, 79898-86-5; **4a**, 79898-87-6; **5a**, 79898-88-7; **6a**, 15341-25-0.

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