

Porphyrin-Sensitized Generation of Singlet Molecular Oxygen: Comparison of Steady-State and Time-Resolved Methods

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Received: January 4, 1995; In Final Form: March 29, 1995[®]

Quantum yields for formation of the triplet excited state and for formation of singlet molecular oxygen have been measured for various porphyrin derivatives in benzene or methanol solution under different concentrations of dissolved O₂. Measurements have been made for both steady-state and pulsed laser excitation, with the resultant singlet molecular oxygen being detected by photooxygenation reactions or time-resolved emission spectroscopy, respectively. In most cases, excellent agreement is observed between the two experimental techniques, allowing accurate determination of the quantum yields. These values may now be used as primary standards for actinometric measurements. For certain tetraphenylporphyrins in highly polarizable solvents, however, the photostationary state method indicated quantum yields for O₂(¹Δ_g) production that were markedly higher than those obtained by laser-induced luminescence. This apparent discrepancy is explained in terms of the formation of a relatively long-lived, nonluminescent encounter complex formed between O₂(¹Δ_g) and ground state sensitizer that can be intercepted by quenchers but not detected by time-resolved emission spectroscopy.

Introduction

Porphyrin derivatives and their metal complexes are well known to be highly effective triplet state photosensitizers^{1–6} and to be capable of producing copious yields of singlet molecular oxygen, O₂(¹Δ_g), under illumination in the presence of oxygen.^{7–17} Such compounds have many important applications in both natural and artificial photosystems and, by appropriate design of the system, can be employed to produce O₂(¹Δ_g) for therapeutic or deleterious purposes.^{18–22} In order to design more efficacious photosystems, it is necessary to be able to establish precise quantum yields for the sensitized production of O₂(¹Δ_g) under operating conditions. In fact, two experimental techniques are commonly employed to detect O₂(¹Δ_g)¹⁷ namely, observation of its characteristic near-infrared luminescence *via* time-resolved emission spectroscopy^{23–28} and steady-state methods that depend on chemical trapping of the product or depletion of the initial oxygen concentration.^{7,29–31} Here, we compare the two techniques with specific reference to the use of porphyrin derivatives as photosensitizers in organic solvents. The primary objective of the study is to establish standard quantum yields for singlet oxygen production, that can be used for actinometric measurements, and to identify any important differences existing between the two techniques. A companion paper³² describes in full detail an advanced procedure for the photostationary state determination of quantum yields for formation of triplet excited states and of O₂(¹Δ_g).

In principle, the two techniques, when utilized properly, are expected to give comparable quantum yields for production of O₂(¹Δ_g). This is not always the case, however, and there are several reports^{17,33} for which the quantum yields differ according to the type of detection method employed. No reasons have been advanced to explain such discrepancies, but we now provide direct experimental evidence that may indicate the origin of these disparate yields. Thus, it is proposed that interaction between certain triplet excited states and oxygen results in intermediate formation of a relatively long-lived complex formed

between ground state sensitizer and O₂(¹Δ_g) that can be intercepted with high concentrations of quencher prior to its dissociation into ground state O₂ or O₂(¹Δ_g). Provided the complex is nonluminescent, at least at the monitoring wavelength, time-resolved emission spectroscopy detects only that fraction of the complex that dissociates to singlet molecular oxygen.

Experimental Section

The various porphyrin derivatives were obtained from Fluka Chemicals or Aldrich Chemicals and were used as received. Chlorophyll a and chlorophyll b were extracted from spinach and purified by column chromatography.^{34,35} Pheophytin a was prepared by demetalation of chlorophyll a and was purified by column chromatography.³⁶ Benzene (Fluka Chemicals) was spectroscopic grade and was used as received. Absorption spectra were recorded with a Kontron Uvikon 930 spectrophotometer.

All laser flash photolysis studies were carried out at the Center for Photochemical Sciences at Bowling Green State University, U.S.A. The excitation source was a frequency-doubled or -tripled Nd:YAG laser (pulse duration 10 ns), for which the pulse intensity was calibrated by reference to the benzophenone actinometer.³⁷ Triplet differential absorption spectra were recorded point-by-point with three individual laser shots being averaged at each wavelength. Decay kinetics were made at fixed wavelength with 50 individual laser shots being averaged and analyzed by computer nonlinear least-squares iteration. Experiments were carried out under an atmosphere of N₂, O₂, or calibrated mixtures thereof. Singlet molecular oxygen was detected after laser excitation by its characteristic luminescence at 1270 nm using a filtered Ge photocell. Emission yields were measured by computer extrapolation of the first-order decay profile to the center of the laser pulse, and the photocell was calibrated by reference to benzophenone in benzene ($\gamma_{\Delta} = 0.29$).³⁸ Yields of singlet oxygen were measured as a function of laser intensity over regions where the yield was directly proportional to the incident photon density. Solutions were

[®] Abstract published in *Advance ACS Abstracts*, May 15, 1995.

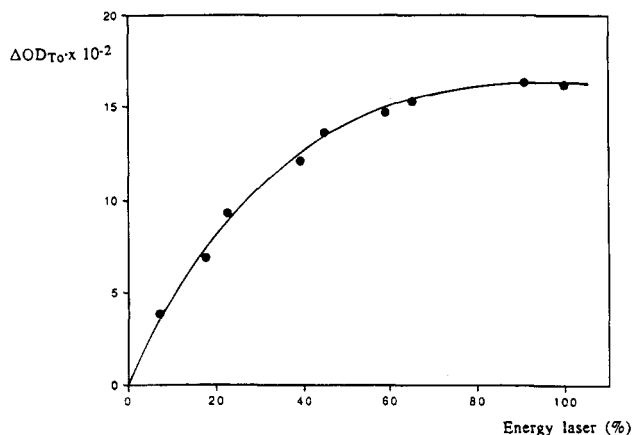


Figure 1. Effect of laser intensity on the initial yield of the triplet state for magnesium tetraphenylporphyrin in benzene solution.

adjusted to possess an absorbance at the excitation wavelength ($\lambda = 355$ or 532 nm) of ca. 0.30.

Triplet excited state quantum yields were measured by reference to benzophenone in benzene solution.³⁷ Differential molar extinction coefficients for the triplet state of each of the porphyrin derivatives were measured by the complete conversion method⁶ in which a high-intensity laser pulse was used to transform a very dilute solution of the chromophore into the metastable state. The achievement of complete conversion was ensured by measuring the transient absorbance as a function of laser intensity. For the triplet quantum yield determinations, optically matched solutions of benzophenone and the chromophore were irradiated with single pulses delivered from the laser. The transient absorbance was measured at an appropriate wavelength as a function of incident laser intensity. All experiments were repeated under an atmosphere of N_2 , air, and/or O_2 . The various quantum yields and differential extinction coefficients were reproducible to within 10%.

The photostationary state method used to measure triplet state quantum yields and quantum yields for production of singlet molecular oxygen has been reported previously^{7,30,31,39} and is described in full detail in a subsequent paper.³² Briefly, tetramethylethylene (0.12 M), a substrate that does not quench the excited triplet state, was used to intercept $O_2(^1\Delta_g)$ prior to its nonradiative deactivation. The consumption of oxygen was measured under steady-state irradiation using a gas microburet. Under such conditions, the rate of consumption of oxygen r_{O_2} is directly proportional to the rate of production of $O_2(^1\Delta_g)$, provided sufficient substrate is used to quantitatively intercept the $O_2(^1\Delta_g)$. The incident light intensity was calibrated by actinometry using methylene blue in methanol as a standard system, for which the quantum yield for production of $O_2(^1\Delta_g)$ was taken^{7,32,39} to be 0.50, allowing determination of the quantum yield for formation of $O_2(^1\Delta_g)$ with unknown systems. Again, the atmosphere was selected to be N_2 , O_2 , or calibrated mixtures thereof. Each experiment was repeated at least 3 times, and the reproducibility was better than 3%.

For chlorophyll a and tetraphenylporphyrin (TPP), quantum yields for formation of the excited triplet state were measured under steady-state illumination using the heavy-atom method^{32,39–42} in the presence of various concentrations of dissolved O_2 . The derived quantum yields were reproducible to within 5%. For the other porphyrin derivatives, the inherent triplet quantum yields were determined by extrapolation of the derived singlet oxygen quantum yields to zero concentration O_2 and assuming that triplet energy transfer to O_2 is quantitative. In this latter case, the experimental reproducibility remained better than 5%.

Results

Laser Flash Photolysis Studies. In order to determine quantum yields for formation of the first excited triplet state of the various porphyrin derivatives in deoxygenated benzene solution (γ_{is}) by laser flash photolysis, it is first necessary to measure differential molar extinction coefficients for the transient. These latter values were obtained by the complete conversion method in which an intense laser pulse at 355 or 532 nm was used to totally bleach an extremely dilute solution of the chromophore. The intensity of the laser pulse was increased stepwise until the differential absorbance at an appropriate wavelength reached a plateau (Figure 1). Provided the solution was sufficiently dilute, the concentration of triplet state produced in the laser pulse could be equated to the initial porphyrin concentration and, therefore, the differential molar extinction coefficient ($\Delta\epsilon_T$) at that wavelength could be determined. The derived values are compiled in Table 1 together with the triplet lifetimes (τ_T) recorded under identical conditions. At lower laser intensities, the incident photon density can be measured by reference to benzophenone (excitation at 355 nm)³⁷ or ZnTPP (excitation at 355 or 532 nm),³⁷ enabling the triplet quantum yields to be determined. Again, the derived values are collected in Table 1 and are seen to range from 0.29 for the phthalocyanine to 0.81 for ZnTPP. Where comparison is possible, the derived quantum yields are in good accord with literature data.^{1,4,5,9}

Each of the triplet excited states reacted quantitatively with molecular oxygen and bimolecular quenching rate constants $k_{O_2}^T$, measured for some of the porphyrin derivatives in benzene solution, were found to be ca. $2 \times 10^9 \text{ M}^{-1} \text{ s}^{-1}$. Triplet quantum yields were measured also in air-equilibrated and deoxygenated benzene solution (Table 1). It is seen that the presence of O_2 promotes intersystem-crossing from the first excited singlet state to the triplet manifold for these compounds and, thereby, results in small but significant increases in the triplet yield.

Interaction between these triplet excited states and molecular oxygen results in formation of $O_2(^1\Delta_g)$, as detected by time-resolved emission spectroscopy. Quantum yields for formation of $O_2(^1\Delta_g)$, γ_Δ , following laser excitation were determined by reference to benzophenone in benzene (Figure 2), and the values are collected in Table 1. Again, it is evident that the quantum

TABLE 1: Parameters Derived from Laser Flash Photolysis Studies in Benzene

sensitizer/benzene	λ_T^{\max} , nm	τ_T , μs	$\Delta\epsilon_T$, $10^4 \text{ M}^{-1} \text{ cm}^{-1}$	$k_{O_2}^T$, $10^9 \text{ M}^{-1} \text{ s}^{-1}$	γ_{is}	γ_T air	γ_Δ	
							air	O_2
tetraphenylporphyrin	440	200	6.6	1.8	0.69	0.71	0.56	0.62
zinc tetraphenylporphyrin	470	320	7.3	1.0	0.81	0.81	0.65	0.69
magnesium tetraphenylporphyrin	470	230	6.8	1.0	0.75	0.79	0.62	0.66
protoporphyrin-IX dimethylester	450	320	3.05	2.0	0.68	0.73	0.57	0.62
chlorophyll a	460	200	1.9	2.0	0.52	0.56	0.51	0.59
chlorophyll b	490	120	2.2	1.7	0.57	0.61	0.59	0.66
tetra-tert-butylphthalocyanine	495	150	1.6	1.6	0.29	0.31	0.27	0.33

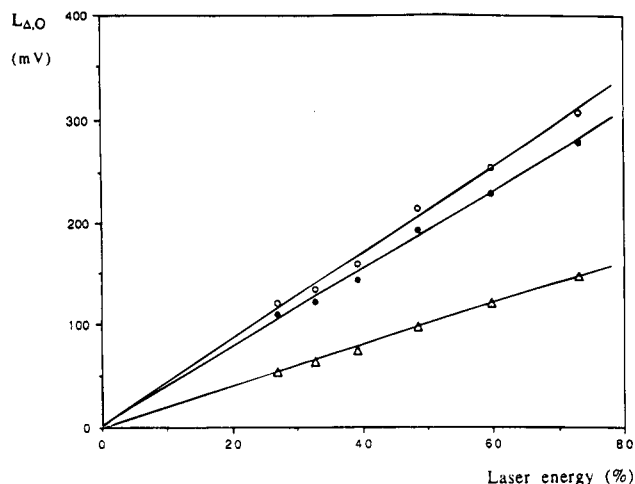


Figure 2. Effect of laser intensity on the initial yield of singlet molecular oxygen measured in benzene solution for (Δ) benzophenone used as primary standard, (\bullet) tetraphenylporphyrin (TPP) in aerated solution, and (\circ) TPP in O_2 -saturated solution.

TABLE 2: Quantum Yields for Production of Singlet Molecular Oxygen in Air-Equilibrated Methanol

sensitizer	γ_D	
	ss ^a	tr ^b
rose bengal	0.79	0.79
methylene blue ^c	0.50	0.52
phenalene	0.94	0.94
tetrakis(4-sulfonatophenyl)porphyrin	0.69	0.70
hematoporphyrin	0.74	0.75

^a By oxygen consumption methodology in CH_3OH . ^b By time-resolved luminescence spectroscopy in CD_3OD following excitation with a 10-ns laser pulse (see ref 51 for more details). ^c Used as primary standard for quantum yields in methanol (see ref 32).

yields are significantly higher in O_2 -saturated solution than in aerated benzene. This difference is not due to incomplete quenching of the triplet state in air-equilibrated benzene but, instead, is attributed to enhanced triplet state formation in O_2 -saturated solution (Table 1). Comparison of the quantum yields for formation of the triplet state and for production of $O_2(^1\Delta_g)$, at a given concentration of O_2 , shows that formation of singlet oxygen is essentially quantitative for the two types of chlorophyll. Despite its low triplet yield, quenching of the phthalocyanine triplet partitions strongly in favor of singlet oxygen production whereas all the porphyrins give γ_Δ values that are about 80% those of the corresponding γ_T value. Quantum yields for formation of singlet oxygen were also measured in air-equilibrated deuterated methanol using time-resolved luminescence spectroscopy, and the values are given in Table 2.

Steady-State Studies. The corresponding studies were made in order to determine quantum yields for formation of the triplet state and for production of $O_2(^1\Delta_g)$ using the photostationary

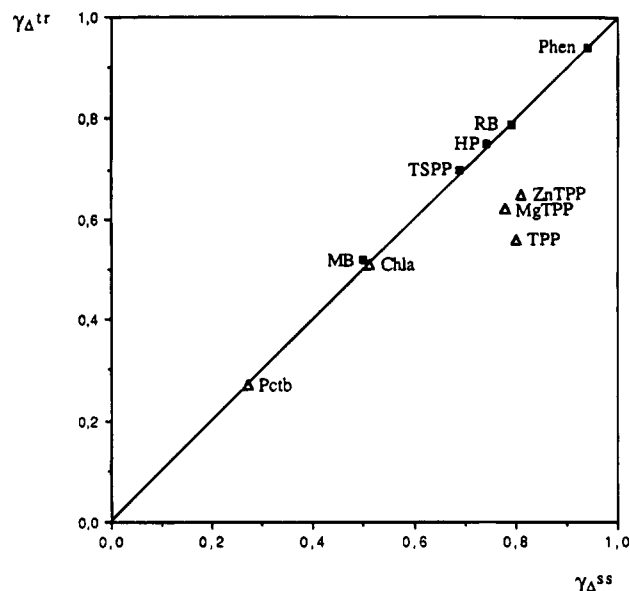


Figure 3. Comparison of the quantum yields for generation of singlet molecular oxygen in air-equilibrated solution measured by time-resolved (tr) and steady-state (ss) methods. Values for MB (methylene blue), TSPP (tetrakis(4-sulfonatophenyl)porphyrin), HP (hematoporphyrin), Phen (phenalene), and RB (rose bengal) were measured in methanol (ss) and deuterated methanol (tr) while those for Pctb (tetra-*tert*-butylphthalocyanine), Chl a (chlorophyll a), TPP (tetraphenylporphyrin) and its derivatives of zinc, ZnTPP, and magnesium, MgTPP, were measured in benzene.

state method. The derived values are collected in Table 3, and again, it is clear that O_2 promotes intersystem-crossing to the triplet manifold. With the noted exception of TPP, there is good agreement between triplet quantum yields measured by the two techniques, regardless of the concentration of dissolved O_2 . For TPP, however, the steady-state method appears to give a significantly higher triplet quantum yield than is apparent from the analogous time-resolved emission studies. The difference might be due to inaccurate determination of the triplet state differential extinction coefficient.

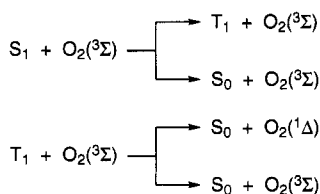
Quantum yields for formation of $O_2(^1\Delta_g)$ were also measured by the steady-state technique for the various sensitizers in benzene or methanol solutions under different concentrations of dissolved oxygen (Tables 2 and 3). With the exception of the tetraphenylporphyrins in benzene solution, there is excellent agreement between γ_Δ values measured by the two techniques, as illustrated in Figure 3. For the three tetraphenylporphyrins, however, the photostationary state method gives γ_Δ values that are markedly higher than those obtained by laser-induced luminescence spectroscopy (Table 1). Whereas the time-resolved technique indicates that quenching of these triplets by O_2 in benzene solution produces $O_2(^1\Delta_g)$ with an efficiency of about 80%, the photostationary state method indicates quantitative formation of $O_2(^1\Delta_g)$. The apparent discrepancy between

TABLE 3: Triplet and Singlet Oxygen Quantum Yields in Benzene Determined by Oxygen Consumption Methodology

sensitizer/benzene	γ_{is}		γ_T				γ_Δ		
			air		O_2		air	N_2/O_2 1/1	O_2
	R_O^a	R_Q^a	R_O	R_Q	R_O	R_Q	R_O	R_O	R_O
tetraphenylporphyrin	0.74	0.72	0.80	0.76	0.89	0.88	0.80	0.85	0.89
zinc tetraphenylporphyrin	0.80		0.81		0.84		0.81	0.83	0.84
magnesium tetraphenylporphyrin	0.74		0.78		0.85	0.86	0.78	0.80	0.85
chlorophyll a	0.47	0.48	0.51	0.51	0.60	0.59	0.51	0.55	0.60
pheophytin a	0.83		0.85			0.89	0.85	0.88	0.90
tetra- <i>tert</i> -butylphthalocyanine	0.23	0.23	0.27	0.27	0.39	0.40	0.27	0.32	0.39

^a See Experimental Section for details. $\{R_O:r_{O_2} = f([O_2]); R_Q:r_{O_2}^Q = f([Q])\}$.

SCHEME 1



the two techniques is well outside the range of the experimental error and is found only for the three tetraphenylporphyrins in benzene solution.

Discussion

Our results may be conveniently discussed in terms of Scheme 1 which indicates our understanding of the mechanism whereby O_2 quenches the excited singlet and triplet states of the porphyrinic chromophores. Here, direct excitation of the porphyrin derivative results in quantitative formation of the corresponding excited singlet state. Intersystem-crossing to the triplet manifold occurs with a probability (γ_{is}) that is less than unity. Both excited singlet and triplet states react with molecular oxygen, the short singlet lifetime requiring significantly higher concentrations of O_2 for efficient quenching. The effect of O_2 on the excited singlet state is to enhance intersystem-crossing to the triplet manifold such that the triplet quantum yield increases with increasing concentration of O_2 (Tables 1 and 3). Indeed, from careful comparison of yields of $O_2(^1\Delta_g)$ at different levels of singlet state quenching, it was concluded that interaction between the excited singlet state of the sensitizer and O_2 results exclusively in catalyzed intersystem-crossing. The resultant triplet state transfers its excitation energy to O_2 , forming $O_2(^1\Delta_g)$ with a certain probability (S_Δ), and thereby returning to the ground state. The quantum yield for production of $O_2(^1\Delta_g)$ depends markedly on the concentration of dissolved O_2 since it is necessary to intercept the triplet state prior to its inherent nonradiative deactivation and, at high concentrations of O_2 , to compete with fluorescence. A variety of secondary reactions follow in which $O_2(^1\Delta_g)$ reacts chemically with the chromophore or with any adventitious substrates to give oxygenated products. For these sensitizers the singlet-triplet energy gap is too small for singlet quenching to give rise to production of $O_2(^1\Delta_g)$ and, consequently, $O_2(^1\Delta_g)$ may be considered to originate exclusively from the triplet state of the sensitizer.

It was observed that both γ_{is} and γ_Δ were independent of chromophore concentration, excitation wavelength, and incident light intensity, at least over modest ranges (Figure 4). As mentioned above, with the exception of TPP and its metal complexes in benzene solution, there is excellent agreement between γ_Δ values derived from time-resolved luminescence spectroscopy and from photostationary state studies (Tables 1–3), as can be seen by examination of Figure 3. For these compounds, comparison of the derived γ_{is} and γ_Δ values indicates that the triplet state reacts quantitatively with O_2 to form $O_2(^1\Delta_g)$ and, therefore, $S_\Delta = 1.0$. This is not the case for the TPP derivatives in benzene solution where $S_\Delta = 0.80$ when the $O_2(^1\Delta_g)$ is detected by time-resolved luminescence spectroscopy (Table 1), even though the triplet state reacts quantitatively with O_2 under the experimental conditions. The photostationary state technique, however, gives S_Δ values close to unity for these compounds under comparable experimental conditions (Table 3).

This apparent discrepancy can be rationalized in terms of Scheme 2 if due allowance is made for the intermediate formation of a relatively long-lived complex between $O_2(^1\Delta_g)$

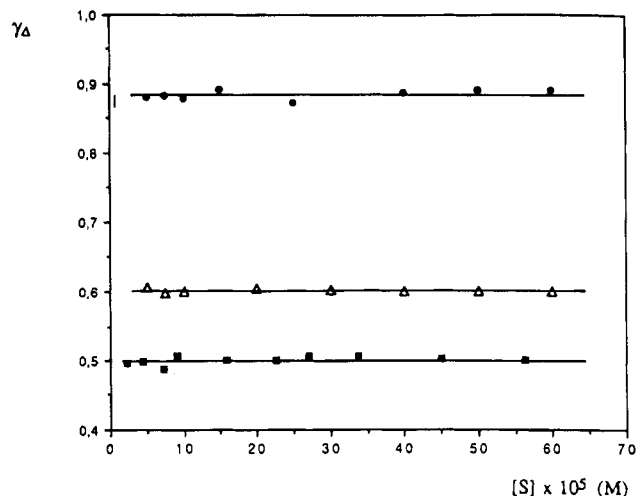
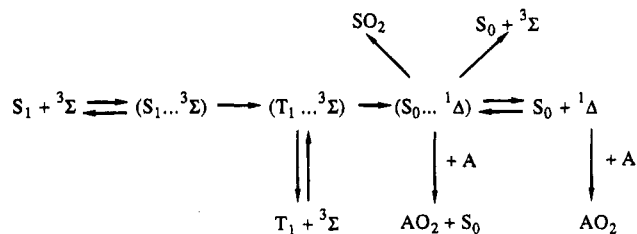


Figure 4. Effect of sensitizer concentration on the quantum yield for formation of singlet molecular oxygen, as measured under steady-state conditions, for (●) tetraphenylporphyrin in benzene, (Δ) chlorophyll a in benzene, and (■) methylene blue in methanol.

SCHEME 2



and the ground state of the sensitizer. This complex may dissociate to give $O_2(^1\Delta_g)$ or O_2 . From the extensive literature pertaining to singlet and triplet state exciplexes,^{43–45} the lifetime of the complex is expected to increase in nonpolar solvents and to be dependent upon the amount of charge-transfer character resident on the complex. Assuming the complex is nonemissive, it will remain undetected by time-resolved luminescence spectroscopy and this technique monitors only that fraction of the complex that dissociates to form $O_2(^1\Delta_g)$. In this case, the lifetime of the complex would need to be less than a few microseconds since the time-resolved luminescence records exhibit no obvious growth of the $O_2(^1\Delta_g)$ signal after the laser pulse that cannot be attributed to diffusional interaction with O_2 . Provided the lifetime of the complex exceeds *ca.* 50 ns or so, it may be intercepted with a high concentration of substrate. If such interaction results in oxygenation of the substrate, as is the case with tetramethylethylene, the photostationary state technique allows (indirect) detection of the complex and, essentially, measures the triplet quantum yield.

Of the sensitizers studied here, only TPP and the corresponding zinc(II) and magnesium(II) derivatives appear to form a long-lived complex that does not dissociate rapidly and quantitatively to form $O_2(^1\Delta_g)$. These studies were made in benzene solution, which may stabilize the complex; we note that TSPP in methanol solution does not form a long-lived complex. Similarly, $S_\Delta = 1$ for chlorophyll a, pheophytin a, and tetra-*tert*-butylphthalocyanine in benzene solution. There is no obvious correlation between triplet energy or redox potential of the sensitizer and stability of the complex. Apparently anomalous behavior has been observed also for certain naphthalene, biphenyl, and fluorene sensitizers in benzene solution where S_Δ values are significantly lower than those in nonbenzenoid media ($S_\Delta = 1$).³⁸ In these latter studies it was suggested that interaction between sensitizer and solvent, but not between

O₂ and solvent, played some role in the overall process. Here, we have proposed a complex between O₂(¹Δ_g) and ground state sensitizer as the important intermediate.

Charge-transfer interaction between excited state sensitizer and ground state O₂ has been discussed extensively in the literature.^{46–50} The importance of such effects depends on thermodynamic properties of the sensitizer and on the nature of the solvent. For example, anthracene derivatives have been found to give $S_A = 1$ ⁴⁹ while the more reducing naphthalene derivatives give $S_A < 1$ due to competitive charge-transfer interactions.⁵⁰ Similarly, for the same sensitizer S_A may decrease with increasing solvent polarity. We have shown recently that charge-transfer interactions may be especially significant in water because of the relatively high redox potential for one-electron reduction of O₂ in protic media.⁵¹ Similarly, it has been postulated that an exciplex is formed between O₂(¹Δ_g) and ground state strychnine in toluene solution.⁵² It is our contention that O₂(¹Δ_g) can also react reversibly with ground state sensitizer, both species being present in the solvent cage after completion of the initial energy-transfer process, to form a complex (Scheme 2). This complex retains O₂(¹Δ_g) character and, at least in certain cases, can be trapped by tetramethylethylene. In the absence of a trapping substrate the complex may dissociate to form O₂(¹Δ_g), oxygenated sensitizer, and ground state species (Scheme 2).

At present, too little information exists for us to speculate on the mode of binding or the structure of the complex. We note, however, that the rate of physical quenching of O₂(¹Δ_g) by porphyrin derivatives correlates with the oxidation potential of the macrocycle, as would be expected for intermediate formation of an exciplex.⁵³ Similar correlations have been observed for quenching of O₂(¹Δ_g) with other families of substrates and attributed to involvement of an intermediate possessing considerable charge-transfer character.^{53–59} Indeed, Gorman has proposed that the reaction of O₂(¹Δ_g) with organic substrates proceeds via reversible formation of an exciplex and that, in certain instances, the exciplex might be trapped.⁶⁰ Our findings are consistent with formation of an exciplex between O₂(¹Δ_g) and its parent sensitizer. The same exciplex could be formed by triplet energy transfer within an encounter complex formed between triplet porphyrin and O₂ or by diffusional encounter between ground state sensitizer and O₂(¹Δ_g). That stable complexes, or exciplexes, are formed only with certain sensitizers in benzene suggests to us that (1) benzene plays an intimate role in exciplex stabilization and (2) there are demanding physicochemical properties for the sensitizer. Benzene has often been found to give anomalous lifetimes of exciplexes⁶¹ when compared with other solvents, and in fact, Khalil and Kasha have proposed the existence of a weak complex between benzene and O₂.⁶² The factors controlling the stability of the exciplex, and thereby affecting S_A , remain unknown but may depend markedly on the stereochemistry of the sensitizer.

By careful comparison of steady-state methods, which are capable of high precision,³² and time-resolved techniques, which can be more selective, we have established quantum yields for the photosensitized production of O₂(¹Δ_g) for several porphyrin derivatives. Agreement between the two experimental techniques is excellent for certain sensitizers, and the derived quantum yields can be used now as primary standards by which second generation photosensitizers can be compared. According to the steady-state data (Table 3), which are inherently more precise than the corresponding time-resolved values, interaction between the triplet state of these sensitizers and O₂ results in quantitative generation of O₂(¹Δ_g). That is to say, $S_A = 1$. It is also important to realize that the presence of O₂ promotes

intersystem-crossing to the triplet manifold such that the observed γ_A , but not S_A , depends upon the concentration of O₂ dissolved in the solution. An interesting proposition raised during this investigation is that tetraphenylporphyrins react with O₂(¹Δ_g) in benzene solution to form a relatively long-lived complex that can be trapped chemically. Additional studies are needed to address the exact nature and lifetime of this complex and to ascertain the role, if any, played by benzene in complex stabilization. Such work is in progress in our laboratory.

Acknowledgment. Dr. M. A. J. Rodgers (Center for Photochemical Sciences, Bowling Green State University, USA) and Dr. A. Harriman (Center for Fast Kinetics Research, University of Texas at Austin, USA) are gratefully acknowledged for providing access to the laser flash photolysis and time-resolved emission spectroscopic instrumentation. We also thank Fondation de France for the award of a fellowship to C.W. and Association pour la Recherche sur le Cancer ARC for financial support.

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JP950047K